STUDIES OF CRITICAL DYNAMICS AND INTERFACES

AT STRUCTURAL PHASE TRANSITIONS

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DECLARATION

This thesis has been composed and written entirely by myself. The original research work described herein was conducted largely by myself. Where the work involved collaboration with others due acknowledgement is made of this, and in each case a substantial contribution was made by the author.
"Zeus, whose will has marked for man
The sole way where wisdom lies;
Ordered one eternal plan:
*Man must suffer to be wise.*"

[Aeschylus, Agamemnon]
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This work contains studies of four problems of current interest with a particular emphasis on the interpretation of scattering experiments. The spectral functions for one-phonon and two-phonon scattering above $T_c$ are studied for the van Hove and Time-Dependent Ginzburg-Landau models and the ratio of the characteristic widths of these functions is shown to be a universal quantity. The results of neutron, and Raman scattering experiments reported by previous authors on $\text{SrTiO}_3$ and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ are discussed in the context of these calculations. Critical dynamics below $T_c$ have been studied for $\text{SrTiO}_3$ by a programme of high-resolution neutron and Raman scattering experiments. Differences between the results of the two techniques are noted which may arise from two-phonon and interference terms in the Raman tensor. The low-frequency neutron scattering (below 0.2THz) is shown to be inconsistent with the accepted soft phonon interpretation and it is suggested that the one-phonon spectral function should be interpreted as consisting of a broad central peak superimposed on the propagating soft phonons.

A discrete lattice model of an incommensurate system exhibiting a lock-in phase transition is considered. It is shown that while the description of the incommensurate ground state in terms of a soliton lattice close to lock-in, and as an incommensurate plane wave close to the high temperature phase, which emerges from studies of continuum models is relevant to the discrete lattice model, the discommensurations in the phase profile experience a pinning force due to the lattice. The effects of this pinning force are shown to result in possible changes to the phase diagram including the appearance of a 'devil's staircase' of commensurate-commensurate transitions terminated by an unpinning transition. The effect on the electronic properties and of
soliton 'roughening' are also considered.

Finally, a theory is developed for the scattering of neutrons or X-rays by static ferroelectric domain walls. Experiments are reported and their results analysed in terms of this model and an existing continuum model. It is shown that the walls are sufficiently narrow to invalidate the continuum approximation upon which much recent work has been based.
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CHAPTER I

STRUCTURAL PHASE TRANSITIONS

51.1 Introduction

Structural Phase Transitions have been the subject of intensive experimental and theoretical study for many years, particularly in the last two decades. The work in this thesis covers a range of problems all related to structural phase transitions (SPTs) or to materials which undergo SPTs with a particular emphasis on the scattering properties of each of the phenomena under investigation. The material is grouped into introductory and descriptive chapters in such a manner as to eliminate the need for unnecessary repetition, while keeping the work entirely self-contained. The introductory chapters review the background which is an essential basis for the understanding of the current field of SPTs. The remainder of this chapter serves to explain the historical development of the study of phase transitions allowing the problems considered in Chapters 3 to 6 to be placed in perspective, and also to define the notation and terminology used throughout the work. The second chapter reviews the standard techniques which have been utilised in the work, either explicitly or implicitly. As this material is not original it is convenient to collect it all in one chapter, leaving the remaining chapters free to concentrate exclusively on the particular details of the problems under consideration without making continual references to this widely publicised material. In Chapters 3 to 6, the original research work which I have undertaken is described. In each of these chapters one problem is discussed. The problems are set in context with the previous state of knowledge or belief, and where possible appropriate conclusions are drawn.
Traditionally, the theoretical study of many-body problems involving effectively an infinite number of particles, has required certain approximations to make the theory tractable. It is only in the simplest approximation, the harmonic approximation, that the lattice dynamics and statistical mechanics of a model crystal can be solved exactly enabling one to calculate the quantities of experimental interest, such as the characteristic frequencies of vibration and the specific heat, from the microscopic details of the model. Interest in SPTs has been stimulated by the fact that the existence of a phase transition, in other words a change of structure, is possible only for an anharmonic crystal. The study of phase transitions may therefore be seen as an attempt to deduce the more important features associated with anharmonic (or non-linear) systems. In this general context, SPTs represent relatively simple and convenient systems for both theoretical and experimental study, the results of which transcend the boundaries of the apparently very restricted field of study.

Since SPTs can occur only in strongly anharmonic solids, the experimental and theoretical study of materials undergoing phase transitions involves the measurement and calculation of quantities which are not directly accessible by means of exact calculation from first principles. Rather than attempting to model the behaviour of anharmonic solids by using microscopic models and treating these by exact statistical mechanics, solid state theorists have turned to what may be termed semi-phenomenological models to which a variety of approximation schemes may be applied. The test of these methods by comparison with experimental results and with the few exactly soluble special cases of the models used provides 'a posteriori' justification for the approximations which have been made. Abandoning truly microscopic models for pragmatic reasons brings the advantage that the essential similarity between the effects associated with SPTs
and the corresponding effects associated with many other cooperative phenomena become more readily apparent. This similarity has led to the realisation that the critical behaviour of any system may depend to only a very limited extent on the microscopic details of the interactions between its component parts, a realisation which has given important insight into the most useful manner in which to classify and study the multifarious, and apparently widely different phase transitions encountered in condensed matter physics. A similar concept, the development of order in complex systems independent of the local configurations has formed the basis of the recently developed field of synergetics (Haken, 1978; Langer, 1980) which may be viewed as a natural extension of the semi-phenomenological methodology to problems beyond the realm of physics.

The experimental technique which has been largely responsible for the interest in SPTs is neutron scattering. Elastic neutron scattering experiments, in which beams of neutrons are diffracted by a crystal lattice without a change of energy, have been carried out since around 1948 and have proved invaluable in determining the structures of materials undergoing phase transitions, especially when light atoms such as hydrogen are of importance (Bacon and Pease, 1953). The major breakthrough experimentally and the technique which is used extensively in the experiments described in Chapters 4 and 6 of this work, was the development of inelastic neutron scattering techniques in which the energy transfer of the neutron beam is analysed, providing information concerning the dynamics of the scattering crystal (Brockhouse, 1961, Als Nielsen, 1976). The explosion of interest in the last twenty years can be largely attributed to the availability of these powerful experimental tools and the interesting and unexpected results which they have produced.
The four problems considered in Chapters 3 to 6 fall conveniently into two categories, but in all of them a major motivating factor in their study has been the attempt to interpret the results of scattering experiments. A second factor common to most of this work has been an attempt to critically and where possibly quantifiably appraise the approximations conventionally used in both the experimental analysis and the theoretical development of SPTs.

Chapters 3 and 4 are both concerned with the interpretation of inelastic neutron and light scattering studies of a 'conventional' phase transition (a term whose meaning will become apparent later in this chapter). Standard techniques are used to discuss the relationship between the apparently conflicting results obtained from the two techniques and the various approximations commonly made in analyses of such experiments are considered.

Chapters 5 and 6 examine problems in which the commonly used continuum approximation may not be valid. In these problems, the simplifying assumption that microscopic details may be ignored, essential to the synergetic approach of the renormalisation group studies (Fisher, 1974) is inapplicable due to the appearance of low-dimensional or localised structures. In Chapter 5 the concept of incommensurate phases is introduced and the critical dynamics are studied using a perturbation technique which leans heavily on recent ideas in nonlinear wave (soliton) theory. The phase transitions exhibited by the model are much more diverse than the 'conventional' transition studied in Chapters 3 and 4 but wherever possible the similarities to previous work are exploited. Finally in Chapter 6 the techniques of neutron and X-ray scattering are shown to be useful for the study of ferroelectric domain walls, and the results of experiments are discussed which show that the narrow width of these walls may require that a truly
microscopic model of these crystals will be an essential prerequisite for a complete understanding of their properties, and it is suggested that the relevance of recent applications of soliton theory to such domain walls is questionable.

§1.2 The Elements of a Prototypic Phase Transition

1.2.1 The order parameter

The concept of the development of order at a phase transition comes from the study of magnetic phase transitions where a lattice of ferromagnetic spins in a high temperature paramagnetic phase may intuitively be thought of as disordered, while on lowering the temperature below the critical temperature, \( T_c \), the spins become 'ordered' by pointing preferentially in one direction. One hallmark of a phase transition is usually the appearance below a critical temperature of long range order by which it is implied that the microscopic configuration of the system at one point bears a definite relation to the configuration at an infinite (in principle) distance from this point, a relationship which was not present in the high-temperature, or disordered, phase. The order parameter is chosen to be a macroscopic observable, such as the magnetisation density, which characterises the development of this long-range order. It has the value zero in the high temperature phase and typically increases as the temperature is lowered until the system is notionally completely ordered at absolute zero.

In most phase transitions, the occurrence of a critical point reflects the fact that a symmetry of the system which was present above the critical temperature is no longer present below \( T_c \). This phenomenon of spontaneous symmetry breaking can be used to define an order parameter as the amplitude of any property of the system which has the lower
symmetry of the ordered phase and is thus identically zero above $T_c$ where it is forbidden by symmetry. The notion of symmetry and symmetry breaking are of particular interest in the field of structural phase transitions since the study of crystalline solids provides examples of many symmetry elements not encountered in the more traditional fields of interest for critical phenomena such as liquid-gas and liquid helium critical points.

Throughout much of the study of phase transitions it is convenient to work with a reduced, dimensionless temperature $t$ defined by

$$t = \frac{(T_c - T)}{T_c} \quad (1.1)$$

Experiments on a wide variety of systems have shown that close to a phase transition the order parameter, $P$, grows according to an algebraic power law and in this regime, it is usually represented as

$$P = P_0 t^\beta \quad (1.2)$$

where $P_0$ is a constant amplitude, and $\beta$ is a critical exponent. (The use of the letter $\beta$ for the order parameter exponent is conventional as are the assignments of other critical indices to be used in this work.)

1.2.2 The susceptibility

Originally, many phase transitions, particularly structural phase transitions, were identified by the observation of divergences in the response functions of the system. The order parameter susceptibility, generally denoted as $\chi$, is one such divergent response function, the name susceptibility again arising in magnetic systems. If the thermodynamic conjugate to the order parameter is a field $E$, then the isothermal, zero-field susceptibility is a measure of the
response of the system to an application of this field, and is defined by

\[ \chi = \frac{\partial P}{\partial E} \bigg|_{E=0} \]  

(1.3)

In the critical region close to \( T_c \), experiments have shown that \( \chi \) diverges algebraically, and it is conventionally represented as

\[ \chi = C_\pm |t|^{-\gamma} \]  

(1.4)

where the signs + and − refer to \( T > T_c \) and \( T < T_c \) respectively. In the case of uniaxial ferroelectrics such as \( \text{Pb}_5\text{Ge}_3\text{O}_{11} \) and \( \text{LiNbO}_3 \), the order parameter is the electric polarisation and the conjugate field is the internal electric field. In other cases such as the anti-ferro-distortive transition in \( \text{SrTiO}_3 \), there is no macroscopic field which can be applied to the system in order to measure a susceptibility directly, nevertheless the concept of a susceptibility which diverges strongly at the phase transition remains useful in almost all cases. When considering dynamic phenomena the susceptibility, or dynamic response function, is the analogous response to an alternating field with a frequency \( \omega \), and wave vector \( \mathbf{k} \),

\[ G(k, \omega) = \frac{\partial P(k, \omega)}{\partial E(k, \omega)} \bigg|_{E=0} \]  

(1.5)

1.2.3 Critical exponents

The prominence given in work on critical phenomena to the calculation and measurement of critical exponents arises from two causes. The more obvious reason for concentrating on the asymptotic behaviour of a system, rather than describing its behaviour by an equation of state, is the difficulty in calculating, and in observing a system over many orders of magnitude of reduced temperature. The more fundamental reason is, however,
that experiments on widely different systems appeared initially to give the same values for $\beta$ and $\gamma$, and the earliest applications of Landau theory (section 1.2.4) predicted that whereas outside the critical region, each type of system would require its own equation of state, in the critical region the same exponents $\beta$ and $\gamma$ would govern the critical behaviour of all systems. Simple theories suggest that critical exponents ought to be given by simple rational numbers, but evidence from magnetic, structural and liquid-gas transitions suggests that this intuitively appealing idea is incorrect. (See Stanley, 1971). Further exponents have been introduced to describe the singularities in other thermodynamic functions and those relevant to this work are enumerated below.

The specific heat appears to diverge at some transitions, but much more weakly than the susceptibility, while at other transitions it displays only a cusp-like behaviour or a discontinuity. The singular part of the specific heat is written

$$C = A \pm |t|^{-\alpha}.$$  

The other exponents which we shall need refer to the behaviour of certain correlation functions. Firstly, we introduce the notation

$$\langle \hat{O} \rangle \equiv \text{Tr}\{\exp(-\beta \hat{H})\hat{O}\}/\text{Tr}\{\exp(-\beta \hat{H})\}$$  

where $\beta = 1/k_B T$

and $\hat{H}$ is the Hamiltonian operator for the system, $\langle \hat{O} \rangle$ denotes the thermal expectation value for the operator $\hat{O}$ using classical Maxwell Boltzmann statistics. (Throughout most of this work the use of classical statistics will be adhered to, only at low temperatures are explicitly quantum effects important in cooperative phenomena.) We define the order parameter correlation function as
\[ \Gamma(x) = \langle P(0), P(x) \rangle - \langle P(0) \rangle \langle P(x) \rangle . \] (1.8)

At a critical point, for large \( x \), \( \Gamma \) is assumed to be of the form
\[ \Gamma(x) \sim x^{-(d-2+\eta)} \] (1.9)
where \( d \) is the dimensionality of the system, and \( \eta \) is defined in this way to ensure that it is small. In classical theories such as Landau theory, \( \eta = 0 \). For \( T \neq T_c \), the correlation function decays exponentially with a characteristic length, or correlation length, \( \xi \), which diverges at \( T_c \) so that
\[ \Gamma(x) \sim \exp(-x/\xi) \] (1.10)
\[ \xi \sim t^{-\nu} \]

These quantities all refer to time-independent, equilibrium properties of the system. Much of this work is concerned with dynamics, for which one extra exponent is required. It is assumed that the Fourier Transform of the order parameter correlation function, \( \Gamma(k, \omega) \), can be described by a characteristic frequency \( \omega_p \), which depends upon the wavevector \( k \) in the usual power law form, so that the dynamical exponent \( z \) is defined by
\[ \omega_p \sim k^z \] (1.11)

1.2.4 Landau Theory

The first attempt to produce a general theory of phase transitions and critical phenomena was due to Landau (1937). The approach which he adopted was phenomenological and based on established thermodynamic principles. Landau's theory, together with the earlier van der Waals (1873) theory of the liquid-gas transition and the Weiss (1907) molecular
field theory of ferromagnetism, are frequently grouped together nowadays as the 'classical' theories of phase transitions because they lead to the same values of critical exponents, and make fundamentally the same assumptions. Although in many cases the predictions of Landau theory disagree with experimental results, the modern theories of critical phenomena and phase transitions rely heavily on similar principles to such an extent that the construction of a Landau theory for any system is still a necessary first step in the application of more sophisticated techniques.

The systems first, and most conveniently discussed by Landau theory, are those with a scalar order parameter. The assumption made by Landau was that close to $T_c$, the 'free energy' of the system could be represented as a power series in the order parameter, $P$. In this connection the free energy would be the magnetic Gibbs function in the case of a magnetic transition, or the Helmholtz potential for a structural transition. The number of terms which appear is restricted by stability requirements. The stable value for $P$ is given by minimising the free energy, $F(P)$, in the form

$$F(P) = F_0 + \frac{1}{2}AP^2 + \frac{1}{4}BP^4 + O(P^6) . \quad (1.12)$$

To ensure that a transition occurs, it is sufficient to assert that the coefficient $A$ changes sign at $T_c$, while to ensure stability, the coefficient $B$ must be strictly positive. Writing

$$A = \frac{a(T - T_c)}{T_c} = -a t \quad (1.13)$$

we obtain the Landau critical exponents $\beta = \frac{1}{2}$ and $\gamma = 1$. Also by calculating the amplitudes $C_+$ and $C_-$ of the susceptibility, we obtain the result $C_+/C_- = 2$. Since all the system-specific phenomenological constants in the free energy expansion have dropped out, these predictions are expected to apply to all phase transitions for which the
form of the free energy in eqn. (1.11) is appropriate. The concept that exponents and amplitude ratios are identical for all systems with a qualitatively similar free energy expansion, is known as universality, and the systems which share the same set of universal quantities are said to form a universality class. Even within Landau theory complete universality is not predicted, but the failure of this phenomenological approach to predict the correct values for critical exponents makes it more expedient to delay further discussion of universality to section 2.1.5, where it can be considered within the more fundamental picture of the renormalisation group.

The connection between the classical theories of phase transitions, is their assumption of spatial homogeneity which allows them to neglect all the long-wavelength fluctuations in the system. It is this neglect which causes the discrepancies between theory and experiment in the cases alluded to in 1.2.1 where, for example, $\beta \approx 0.31$ (Fisher, 1967). For certain universality classes, Landau theory gives an accurate description of the critical behaviour due to effects such as long range dipolar forces which inhibit the critical fluctuations. In the case of uniaxial ferroelectrics, Landau theory appears to give a correct description of the critical regime, a fact which stimulated much of the interest in the soft mode concept of section 1.3.2 (see however §3.5).

§1.3 Additional Aspects of Structural Phase Transitions

1.3.1 The microscopic lattice dynamical approach

The general observations of §1.2 concerned almost exclusively the macroscopic quantities of interest in a system undergoing a phase transition. The phenomenological approach of Landau theory to cooperative phenomena has achieved remarkable success despite its ignoring any
microscopic consideration of the detailed nature of the system. Historically this was a necessary approach, because before the availability of high-resolution crystallography the microscopic details of many phase transitions were unknown. The modern theories of phase transitions are based on a semi-microscopic description in which an effective Hamiltonian is constructed containing the minimum information necessary to model the behaviour of the system. Having constructed the Hamiltonian it is then treated by classical statistical mechanics to solve, in principle, the problems of interest.

We now consider the model which will be used as a basis for the whole of chapters 3 and 5 of this work. We consider a crystal in which a structural phase transition takes place, which may conveniently and without loss of generality, be thought of as a ferroelectric transition.

It is appropriate to use initially the notation of lattice dynamics due to Born and Huang (1954). Each atom in the crystal is described by a position vector

\[ \mathbf{r}(\ell, \kappa) = \mathbf{R}(\ell, \kappa) + \mathbf{u}(\ell, \kappa) \]  

(1.14)

where \( \ell \) is an index specifying the unit cell in which the atom is located, \( \kappa \) is an index which runs over the atoms in the unit cell, \( \mathbf{R}(\ell, \kappa) \) is the equilibrium position of the atom in the high temperature phase, and \( \mathbf{u}(\ell, \kappa) \) represents the additional displacement in the low temperature phase and that due to the thermal fluctuations.

It is usually more useful to consider the Fourier transform of the displacement field \( \mathbf{u}(\mathbf{r}) \), as it is the Fourier components of \( \mathbf{u} \) which are probed by scattering experiments. We therefore define

\[ \mathbf{\hat{u}}_{\ell\kappa}(\mathbf{r}, t) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q(\mathbf{k}, \omega) \exp \left( i \mathbf{k} \cdot \mathbf{R}(\ell, \kappa) - \omega t \right) d\omega ~ d\mathbf{k} \]  

(1.15)
where $Q(\hat{k}_j, \omega)$ is the normal mode amplitude of a mode with wave vector $\hat{k}$ and branch number $j$, and $\hat{e}(\hat{k}_j, \ell \kappa)$ is the corresponding eigenvector. This substitution converts the harmonic part of the Hamiltonian into the diagonal expression.

$$\mathcal{H}([Q]) = \sum_{kj} \frac{1}{2} \omega^2(\hat{k}) Q(\hat{k}_j) Q(-\hat{k}_j) + \gamma ([\dot{Q}])$$

where $\gamma ([\dot{Q}])$ represents the kinetic energy.

In the harmonic lattice this diagonal Hamiltonian causes the linear equations of motion for the normal mode coordinates to separate, and the static and dynamic properties may be calculated exactly. The importance of the harmonic lattice is that almost the only satisfactory treatments of anharmonic lattices rely on perturbation methods developed to perturb about the harmonic normal modes, or phonons.

In the anharmonic lattice, the transformation to normal mode coordinates no longer diagonalises the Hamiltonian and the equations of motion for the normal mode amplitudes contain mode coupling terms. If the anharmonicity is not too strong the phonon remains a useful concept and the lattice potential energy may be written as a series of multi-phonon terms. The kinetic energy remains diagonal, and as the partition function separates into a kinetic and a potential energy part, for the effective Hamiltonian of the system we consider only the potential energy in the Landau-Ginzburg form

$$\mathcal{H}([Q]) = \sum_{k} \frac{1}{2} \omega^2(\hat{k}) Q(\hat{k}) Q(-\hat{k}) + \frac{1}{N} \sum_{k_1 k_2 k_3} v_3(k_1, k_2, k_3)$$

$$\times Q(\hat{k}_{k_1}) Q(\hat{k}_{k_2}) Q(\hat{k}_{k_3}) \Delta(\hat{k}_1 + \hat{k}_2 + \hat{k}_3)$$

$$+ \frac{1}{N^2} \sum_{k_1 k_2 k_3 k_4} v_4(k_1, k_2, k_3, k_4) Q(\hat{k}_1) Q(\hat{k}_2)$$

$$\times Q(\hat{k}_3) Q(\hat{k}_4) \Delta(\hat{k}_1 + \hat{k}_2 + \hat{k}_3 + \hat{k}_4)$$

(1.17)
where
\[ \Delta(\mathbf{k}) = \begin{cases} N & \text{if } \mathbf{k} \text{ is a reciprocal lattice vector} \\ 0 & \text{otherwise.} \end{cases} \]

In principle the normal modes \((i_t, j)\) corresponding to all phonon branches should be retained but for most purposes it is sufficient to retain only the lowest lying phonon branch in the effective Hamiltonian as the low energy modes dominate the critical behaviour.

By analogy with the phenomenological theory of phase transitions we define an order parameter and free energy. The order parameter is the expectation value for the amplitude of the normal mode with wave vector \(\mathbf{k}_s\) where \(\mathbf{k}_s = 0\) for a ferroelectric, \(\mathbf{k}_s\) is a zone boundary mode for an antiferroelectric, and \(\mathbf{k}_s\) is some general vector for an incommensurate transition. To make the order parameter independent of crystal size a factor of \(N^{-\frac{1}{2}}\) is introduced so that
\[ P = N^{-\frac{1}{2}} \langle Q(\mathbf{k}_s) \rangle . \] (1.18)

The free energy is defined by a partition function \(Z\) as
\[ F = -k_B T \ln Z \] (1.19)

where
\[ Z = \int \exp \left[ -\mathcal{H}(\{Q\})/k_B T \right] . \] (1.20)

In principle the study of the model defined above requires no more than the evaluation of the functional integral defined in (1.20), but except for the harmonic case where the calculation involves only Gaussian integrals, it is necessary to resort to approximation schemes to evaluate the integral.

The simplest such scheme involves the consideration of only the ground state of the effective Hamiltonian, in which case by including
only the normal mode amplitudes corresponding to the order parameter one regains the Landau theory. By making the Hartree approximation in the four-phonon term, that only contributions with two of the Q's corresponding to the order parameter will be significant, we obtain the classical theory including wave-vector dependent quantities, from which we obtain the exponent values of \( \nu = 0.5 \) and \( \eta = 0 \). This latter approach is generally known as Landau-Ginzburg theory because of its similarity to the Landau-Ginzburg theory of superconductivity.

More satisfactory schemes for considering this integral are considered in Chapter 2 as they would be out of place in this general introductory section.

The parameters of \( \chi(Q) \) are not directly measurable by experiment, however, in a weakly anharmonic crystal the normal mode frequency \( \omega(k) \) corresponds closely to the energy at which a peak occurs in the scattering intensity measured in neutron or light scattering experiments at wave vector transfer \( \vec{k} \), while the magnitude of the anharmonic terms which cause a damping of the normal modes, may be estimated from the width, in energy, of the peak.

1.3.2 Soft modes

The similar role of the constant \( A \) in Landau theory, and the harmonic normal mode frequency \( \omega^2(k_s) \) in the Landau-Ginzburg theory led Anderson (1960) and Cochran (1960) to postulate that at a ferroelectric SPT there will be one phonon branch with an anomalously temperature dependent dispersion relation having a minimum frequency at \( \vec{k}_s \) which they termed a soft mode. Below the transition temperature the harmonic frequency of this mode becomes imaginary and the crystal becomes unstable against this vibration which condenses.
At temperatures close to $T_c$ the dispersion relation of the soft mode branch is generally represented by the first two terms in a Taylor expansion, which may be written, for the simplest, isotropic case,

$$\omega^2(k) = \omega^2(k_s) + c|k - k_s|^2$$

(1.21)

where

$$\omega^2(k_s) = a(T - T_o)$$

$a$ and $c$ are constants, and $T_o$ is a mean field transition temperature. For a real material the dispersion surface around $k_s$ will not be isotropic. This requires the replacement of the $(k - k_s)^2$ term by a tensor term in which the elements may be determined by measurements along several principal symmetry directions and symmetry considerations.

Soft modes have been observed at many SPTs, including for example SrTiO$_3$ (Cowley, 1962) and Pb$_5$Ge$_3$O$_{11}$ (Ryan and Hisano, 1973).

1.3.3 Classification of structural phase transitions

Structural phase transitions occur in a variety of systems, but there are two essential characteristics which are invariably of interest and which serve to define the method of theoretical treatment and the types of phenomena encountered.

The most obvious distinction between phase transitions is the development of the order parameter at $T_c$. In 1.2.1 the order parameter was said to develop according to a power law close to $T_c$ which implies that $P$ goes continuously to zero at the transition. This behaviour occurs at all critical points, and transitions where this occurs are referred to as continuous transitions. In many SPTs the crystal structure changes abruptly at the transition temperature so that there is a jump discontinuity in the order parameter and usually a latent heat.
These transitions, which include for example, that in KH$_2$PO$_4$, are known collectively as first order transitions, as there is a singularity in the first derivative of the Gibbs function at $T_c$. At first order transitions the soft mode concept may, or may not be appropriate, but the appearance of true critical behaviour is pre-empted by the sudden onset of long range order. Because of this lack of critical behaviour, weakly first order transitions are usually better described by Landau theory than their continuous counterparts.

A second division is the classification of phase transitions as displacive or order-disorder. The transition described in 1.3.1 is of the displacive type, so-called because the atoms were assumed to sit on one high-symmetry site above $T_c$, and to have a small displacement, $\langle u(\kappa) \rangle$, below $T_c$. In a typical order-disorder transition such as that in NaNO$_2$ (Hishano and Motegi, 1967) the atoms which move at $T_c$ are not situated on high-symmetry sites above $T_c$, but are randomly distributed over two or more symmetrically placed sites. The spontaneous symmetry breaking at $T_c$ involves the preferential ordering of these atoms onto one of the sites. In this type of transition the displacements are not small, and so the $n$-phonon terms to many orders in the Landau-Ginzburg Hamiltonian are large, consequently it is not a useful description of the system. The solution of this difficulty lies in the use of a pseudospin representation which is beyond the scope of this work, but it is appropriate to mention here that the Landau-Ginzburg approach may be applied to the pseudo spin representation formally reducing the calculation of critical properties for an order-disorder transition to the same problem mathematically as that for a displacive transition. The frequency of the 'hopping' soft mode may be much lower than typical phonon frequencies, necessitating the use of different experimental techniques to those appropriate to the
displacive systems discussed here. The distinction between order-disorder and displacive systems is not always clear, for the materials KD$_2$PO$_4$ and LiNbO$_3$ (Ch. 6) it is not clear to which category the transitions belong, if indeed it is useful to assign them to either category.

1.3.4 Symmetry and Critical Dimensionality

Within the Landau theory presented in 1.2.4, the simplest possible phase transition was represented by a single order parameter $P$, which for a ferroelectric represents the spontaneous polarisation. For a real material such as BaTiO$_3$, for example, which has cubic symmetry, there are three equivalent directions in which the polarisation can lie and therefore the order parameter becomes a set of three parameters, $P_1$, $P_2$ and $P_3$. In this case these three components form a real-space vector but in general an order parameter may have $n$ components which may not all have such a direct interpretation. The appropriate Landau free energy expansion must now contain all combinations of $P_1$, $P_2$ and $P_3$ which are invariant under the point group symmetry elements of the crystal. In the case of BaTiO$_3$, Devonshire (1949) was able to obtain the sequence of first order transitions rhombohedral + orthorhombic + tetragonal + cubic with a simple theory of this type. More generally the soft mode will, if $\vec{k_S} \neq \vec{0}$, comprise a set of symmetry-related vectors, usually called the star of the soft mode, which will dictate the terms involving interactions between critical modes appearing in the effective Hamiltonian and hence in the Landau free energy. This relation between symmetry and the form of the free energy results in a direct connection between the symmetry of a crystal and the critical behaviour associated with it, or in the language of modern critical phenomena, the symmetry is one of the factors determining the universality class.
Another symmetry dependent effect is the anisotropy which characterises the dispersion relation of a non-cubic material. In particular, the uniaxial ferroelectrics such as Pb$_3$Ge$_3$O$_{11}$ and LiNbO$_3$ have long-range dipolar interactions which cause the dispersion, or inverse susceptibility, to be of the form

$$\omega^2(k) = G^{-1}(k) = \omega^2(0) + ck^2 + g\left(\frac{z}{k}\right)^2 .$$  \hfill (1.22)

It can be seen that at $T_c$, $G(k)$ diverges as $k \to 0$ only if $k$ lies in the $x,y$ plane, hence critical fluctuations are confined to this plane, being strongly inhibited in directions along the $z$-axis by the long-range forces. This reduction in the volume of critical fluctuations reduces their effect on the critical behaviour to the extent that Landau theory predicts the correct behaviour for uniaxial ferroelectrics apart from logarithmic corrections. Again it is possible to be more general, and rather than examining the volume of critical fluctuations it is appropriate to use the volume of correlations in real space. Generally this can be written, for a d-dimensional system, as

$$\Omega = \xi^{d+m}$$  \hfill (1.23)

where for an isotropic system, $m = 0$. For the uniaxial system the correlations along the $z$-axis are superdiverging and scale as $\xi^2$, hence $m = 1$. An argument due to Als-Nielsen and Birgeneau (1977), based on the Ginzburg criterion that for Landau theory to be valid, the order parameter fluctuations must be much less in magnitude than the value of the order parameter for any $T < T_c$, shows that there exists a critical value of $d_c$, called the upper critical dimensionality, and given by

$$d_c = (\gamma + 2\beta)/\nu - m$$  \hfill (1.24)
above which Landau theory should be valid close to $T_C$. For the uniaxial ferroelectrics $d_C = 3$ and so the experiments are conducted on a system at its upper critical dimensionality. Isotropic systems have $d_C = 4$, therefore fluctuation effects should dominate the observed critical behaviour in three dimensions.

The systems which can be modelled by the effective Hamiltonian (1.17) fall into three classes. For those at, or above, their upper critical dimensionality we expect classical behaviour as the fluctuations have negligible weight even near $T_C$. The uniaxial ferroelectrics $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and $\text{LiNbO}_3$ considered in this work are both members of this category of system. For systems which are below the upper critical dimensionality for their universality class, and thus in what is termed the weakly fluctuating regime typified in this work by $\text{SrTiO}_3$ for which $d_C = 4$, the onset of long-range order is non-classical as described in detail in the next chapter. Finally a second critical dimensionality, the lower critical dimensionality or $d^*$, exists, below which fluctuations are of sufficient magnitude to prevent the occurrence of any long-range order. Although this strongly fluctuating region is of limited relevance to this work it is appropriate to mention it here as for pure systems $d^*$ is typically two, which implies that the strictly two-dimensional surface monolayer systems referred to in Chapter 5 are not strictly crystalline and so application of general $d$-dimensional results in these cases must be made with caution.

§1.4 Summary of Chapter 1

In this chapter a review of the current state of research into structural phase transitions and critical phenomena was presented in order to provide a background against which the remainder of this work could be set in context. The concluding sections served to
define a certain amount of standard notation and conventional terms which have become part of the language of this field of study. The descriptive chapters of this work contain some more specialised introductory material, the inclusion of which would have made this brief review needlessly unwieldy and obscured the unity of the fundamental physics underlying the whole field of phase transitions, summarised by the concept of universality classes which are determined only by symmetries and the range of microscopic interactions in a manner to be described in 2.1.5. A comprehensive review of current research in SPTs is given in Cowley (1980).
CHAPTER 2

TECHNIQUES USED IN THE STUDY OF PHASE TRANSITIONS

§2.1 Modern Theory of Critical Phenomena

2.1.1 The field theoretic approach to condensed matter

It was remarked in 1.3.1 that in principle the study of the Landau-Ginzburg model for critical phenomena required the evaluation of the functional integral of equation (1.20) for the partition function. This is not at the present time a feasible method of approach to the problem, but the formulation of statistical mechanics in terms of such a functional integral is of value because it brings out the similarity between statistical mechanics and relativistic quantum field theory. By making an analogy between the effective Hamiltonian of statistical mechanics, and the Lagrangian density (or action) of a field, the techniques used in the successful study of quantum electrodynamics can be directly utilised for condensed matter problems. Two major differences between relativistic quantum field theory and statistical mechanics are the replacement of temperature by imaginary time, a replacement which was first pointed out in a more basic development of many-body anharmonic perturbation theory by Matsubara (1955), and the occurrence in the momentum integrals of a natural high-momentum cut off due to the finite lattice spacing. The field theory problem has complete isotropic symmetry and so results based on it will ignore the symmetry elements of the lattice. The principal extension required in adapting the field theory approach to the discussion of critical phenomena at SPTs is the inclusion of terms of the correct symmetry in the effective Hamiltonian. The soft mode frequency is included in the theory as a phonon 'mass' which changes sign at the phase transition. As explained in the next section,
below the critical dimensionality this results in divergences in the conventional Feynman graph perturbation theory used in field theory, which are the principal reason for the employment of the sophisticated apparatus of the renormalisation group, but which also reflect the divergences in actual physical observables at a critical point which lie at the heart of the universality encountered at phase transitions.

2.1.2 Anharmonic perturbation theory

The initial development of many-body theory beyond the harmonic system which is exactly soluble, was concentrated into schemes for calculating the properties of weakly anharmonic systems by treating the low-order multi-phonon terms in the Hamiltonian as perturbations of the harmonic problem which are in some sense small. In the case of electrodynamics the natural expansion parameter is the fine structure constant \( \alpha = \frac{1}{137} \), but for an anharmonic solid the appropriate parameter from equation (1.17) is \( v_4/k_B T \). The direct expansion of quantities in terms of this parameter may be expected to work well at high temperature where the anharmonicity is small because the coupling constant is small, but for studies of phase transitions, the justification for high temperature series expansion results is not rigorous and the accuracy which quantum electrodynamics provides is not to be expected. Nevertheless in the spirit of the early approach, it is worthwhile to sketch the perturbation method as it is still a central technique for theoretical studies, albeit because since the advent of the renormalisation group, the ad hoc assumption upon which it is based has been put on a somewhat firmer footing.

The starting point for the perturbation series is the harmonic Hamiltonian in units of \( k_B T \).
\[ \mathcal{H}(\{Q\}) = \sum_{\vec{k}} \frac{1}{2} \omega^2(\vec{k}) Q(\vec{k}) Q(-\vec{k}). \] (2.1)

From the prescription for calculating expectation values (eqn. (1.7)) the harmonic one-phonon Greens function, or propagator, is

\[ G_0(\vec{k}) = \langle Q(\vec{k}) : Q(-\vec{k}) \rangle_0 = \frac{1}{\omega^2(\vec{k})} \] (2.2)

where the subscript \( o \) is used to denote that these results apply to the harmonic approximation.

The expectation values of all other quantities involving products of normal mode amplitudes vanish unless the expression factorises into pairs of amplitudes corresponding to opposite wave vectors as in \( 2.2 \).

The anharmonic perturbation is incorporated into the Hamiltonian as an extra multi-phonon 'vertex' so that

\[ \mathcal{H} = \mathcal{H}_o + \mathcal{H}_I \] (2.3)

where

\[ \mathcal{H}_I = \frac{U_o}{N^2} \sum_{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4} Q(\vec{k}_1) Q(\vec{k}_2) Q(\vec{k}_3) Q(\vec{k}_4) \Delta(\vec{k}_1 + \vec{k}_2 + \vec{k}_3 + \vec{k}_4) \]

which is the same expression as the last term in (1.17) except that as a simplification the wave vector dependence of \( U_o \) has been neglected.

The exponential in the numerator of (1.7) can now be expanded so that we obtain

\[ \langle \hat{O} \rangle = \langle \hat{O} \rangle_0 - \langle \mathcal{H}_I \rangle_0 + \frac{1}{2} \langle \mathcal{H}_I^2 \rangle_0 \] (2.4)

which can be represented elegantly in diagrammatic form as in Fig. 2.1. Because in the harmonic model the normal modes are uncoupled, expectation values of operators involving products of normal
Figure 2.1: Diagrammatic representation of the perturbation series.

(a) The dot represents an interaction vertex $U_0$, the four legs represent phonon amplitudes $Q(\mathbf{k})$. Pairwise contraction of amplitudes is represented by joining the legs with lines representing the harmonic propagator $\omega^{-2}(k)$.

(b) Low order terms in the expansion of the anharmonic Greens function, $\langle Q(\mathbf{k})Q(-\mathbf{k}) \rangle$. 
modes are evaluated by taking all pairwise contractions of the normal
mode amplitudes, \( Q(\vec{k}) \).

From this discussion it is not obvious that the anharmonic per-
turbation approach must fail at a critical point, or that the spatial
dimensionality of the system is a feature of major importance. To see
this we take a typical term in our Feynman graph expansion, depicted
in Fig. 2.2, which arises in the expansion for the one-phonon Greens
function, \( G(\vec{k}) \). Disregarding the external "legs" the contribution
from this graph is

\[
\delta G(\vec{k}) \propto 12 U_0 \left( \frac{a}{2\pi} \right)^d \int \frac{d^d k_1 \{(r + k_1^2)^{-1} - k_1^{-2}\}}{|\vec{k}|<\Lambda} \tag{2.5}
\]

where the sum over modes has been replaced by an integral over a spherical
Brillouin zone, and the frequency of the soft mode branch has been written
in the form \( \omega^2(\vec{k}) = r + k^2 \) with the units chosen to simplify the
notation. Carrying out the angular integral will, because of the sym-
metry, lead to only the inclusion of an extra dimensionality-dependent
constant

\[
K_d = 2^{1-d} \pi^{-d/2} \Gamma(|d|) \tag{2.6}
\]

so that in the limit \( r \to 0 \) the value of the graph becomes

\[
\delta G(k) \propto 12 U_0 r \left( \frac{a}{2\pi} \right)^d K_d \int_0^A k^{d-1} dk.k^{-4} = \int dk.k^{d-3} \tag{2.7}
\]

which diverges if \( d \leq 4 \), the critical dimensionality. It is easily shown
(see Wallace, 1976) that the higher order diagrams exhibit similar
divergences by the same approach of counting the powers of \( k \) appearing
in the numerator and denominator. This establishes clearly the claim
of 1.3.4 that the critical region exhibits mean-field behaviour for
\( d > d_c \) as the effect of the small number of long wavelength modes
Figure 2.2: The lowest order anharmonic contribution to the one-phonon Greens function.

The contribution from this graph has a factor of $U_0$ from the vertex, a factor of 12 from the number of ways of pairing the phonon amplitudes, and a summation over wave-vector dependent propagators from the loop.
at the Brillouin zone centre is overcome by the much larger number of non-critical modes with non-infinitesimal values of $k$. Below $d_c$ the small proportion of zone centre critical modes are able to completely dominate the thermal expectation values causing divergences without parallels in mean field theory. The renormalisation group operation reduces the number of critical degrees of freedom in a systematic manner for which the motivation arose expressly from these dimensionality dependences, so as to eliminate these divergences from the integrals which arise, in a sense mapping a system which is intractable owing to its closeness to criticality, onto a system for which the standard technique described above is applicable.

2.1.3 The static renormalisation group

The literature over the last ten years has abounded in reviews of the renormalisation group (RG) as formulated originally by Wilson (1971) in its application to critical phenomena. Such aspects of the theory as are of particular relevance to SPTs are extensively discussed by Bruce (1976, 1980) and so only the salient points which are required for an appreciation of this work are mentioned here.

The starting point for the renormalisation group treatment of any semi-microscopic model is a Hamiltonian of the form given in equation (2.3) which, in this connection, is generally referred to as a Landau-Ginzburg-Wilson (or LGW) Hamiltonian to emphasize the fact that the wave vector summations are assumed to run over only critical or near-critical modes to a wave vector cut off $\Lambda$ which is arbitrary. The origin of reciprocal space is chosen to be at the soft mode wave vector by a change of coordinates if necessary. The RG transformation consists of taking a partial trace over the least critical
modes in the functional integral of equation (1.20). The effects of
this partial trace are twofold. Firstly as these modes are well-
behaved even at $T_c$, they will give rise to a contribution to the
partition function which is regular at $T_c$ and slowly varying with
the temperature. This term is generally neglected as it does not
influence the critical properties which are determined by the singular
parts of $Z$ associated with the critical modes. Secondly, where the
modes involved in this partial trace interact explicitly with the more
critical modes, they contribute a renormalisation of the coupling con-
stants $r$ and $U_0$. The RG transformation is completed by a rescaling
of the wave vector lengths so that the effective Hamiltonian containing
the remaining modes is again defined over a sphere in reciprocal space
of radius $\Lambda$. There is a certain freedom of choice in this rescaling
operation and it is convenient to ensure that the energy scale is
always chosen to keep the coefficient of $k^2$ in the dispersion relation
equal to unity. Carrying out this renormalisation group operation for
all modes such that $\Lambda/b < |k| < \Lambda$ generates a new Hamiltonian, $\mathcal{H}(b)$
which depends upon the scale factor $b$, through the dependence on $b$
of the renormalised values of $r(b)$ and $U(b)$. This Hamiltonian des-
cribes a system with a (dimensionless) correlation length $\xi(b)$ which
is related to the correlation length of the initial system by the relation

$$\xi(b) = \xi/b .$$

In this light the transformation which is schematically represented by
the Wilson equation

$$\mathcal{R}_b \mathcal{H} = \mathcal{H}^*$$

maps a system defined by the original effective Hamiltonian $\mathcal{H}$ onto a
system further from criticality with a shorter correlation length. By repeated application of $R_b$, either the system must eventually reach a sufficiently non-critical state that conventional perturbation theory as described above will be sufficient to treat the remaining problem, or else the system will reach a Hamiltonian for which

$$R_b H^* = H^*$$

(2.10)

It can be seen from (2.8) that this can only be satisfied if $\xi$ is infinite or zero. The case with $\xi = 0$ corresponds once again to the mean field regime of a system far from criticality, whereas the physically interesting case $\xi \rightarrow \infty$ corresponds to a system exactly at its critical point where $\Gamma(x)$ displays power law, rather than exponential decay. The actual calculations involving RG transformations are generally intractable unless the operator $R_b$ is linear in the sense that a vector of Hamiltonian parameters, or 'fields', $\mu = (r, U_0, \ldots)$ is related to the transformed parameters by the matrix equation

$$R_b \mu = \bar{\mu}(b)$$

(2.11)

$$\bar{\mu} = (r(b) - r^*, U_0(b) - U_0^*, \ldots)$$

In this notation, the condition for criticality expressed in (2.10) is that the vector $\mu$ in parameter space must flow to some fixed point, $\mu^* = (r^*, U_0^*, \ldots)$.

The renormalisation group hypothesis proposes that all critical properties of the system are defined by its fixed point Hamiltonian, and that specifying the universality class to which a system belongs is equivalent to specifying the fixed point to which the system Hamiltonian flows at criticality.

As an example, the LGW Hamiltonian corresponding to equations
(2.3) has two fixed points with respectively

\[ \mu_1 = (0, 0) \], the Gaussian fixed point

\[ \mu_2 = \left( \frac{(d-4)A^2}{6}, \frac{4-d}{36K_{dA}} \right) \], the Ising fixed point.  \((2.12)\)

The Ising fixed point is stable only for \( d < 4 \). The change in critical behaviour at \( d_c \) can therefore be interpreted in RG parlance as a change in the fixed point Hamiltonian structure from the anharmonic \( \mathcal{H}_A \) with Ising fixed point parameters, to the harmonic decoupled Hamiltonian with \( r^* = U^* = 0 \).

2.1.4 Small parameter expansions in the renormalisation group

It is a regrettable fact that the elaborate approach to critical phenomena of the renormalisation group is still greatly restricted in its applicability by the impossibility of carrying out even the partial trace in the functional integral except by using a conventional perturbation theory and expanding in terms of some small parameter. The approach adopted has been to obtain a model for which the critical behaviour is well-established, and then to expand in some small parameter away from this model. For example, the LGW Hamiltonian is known to define a system with classical exponents for \( d > d_c = 4 \). For systems of practical interest it is necessary to extend the known result to three dimensions, and this is done by solving the four-dimensional problem and expanding the corrections to it as a power series in the small parameter \( \varepsilon = d_c - d \) (Wilson, 1972). In this way the parameter \( U_0 \) of the conventional perturbation theory is effectively replaced by the dimensionality difference. \( \varepsilon \). This parameter is small only close to \( d_c \) and for results in three dimensions it is not clear that the perturbation
series in $\epsilon$ will be convergent, and it is also not clear that the low-order terms of the series available will give accurate estimates of the appropriate universal quantities (see Wilson, 1972). Despite this lack of a rigorous basis the $\epsilon$ expansion has been enthusiastically applied to many situations which provide a posteriori justification for the somewhat cavalier assumptions made, by the excellent agreement with both the available experimental evidence and with the best results of other theoretical approaches, high and low temperature series, exact solutions, and numerical simulation, as reviewed by Wilson and Kogut (1974) and Fisher (1974).

In addition to the spatial dimensionality $d$, a second essential qualitative feature which entered into the discussion on Landau theory was the dimensionality of the order parameter, $n$. The isotropic LGW Hamiltonian (2.3) requires only slight modification to describe systems of general $n$, and in this case the fixed point parameters, and the exponents all become $n$-dependent. In particular the constant $U^*$ is of order $1/n$. This has enabled a systematic expansion of quantities in powers of $\frac{1}{n}$, with a zeroth order theory which corresponds to the exactly soluble ($n = \infty$) spherical model of Berlin and Kac (1952), to be used for the calculation of universal quantities in arbitrary dimensions (Ma, 1973a, 1973b, 1976a).

Explicit use of both the $\epsilon$ expansion and the $\frac{1}{n}$ expansion is made in Chapter 3.

2.1.5 Scaling theory and universality

Scaling theories of phase transitions were originally introduced as a 'phenomenological guess' as to the behaviour near criticality of thermodynamic properties. By making the assumption that properties, such as the free energy are homogeneous functions of the 'scaling fields'
such as \( t \), certain relations between the critical exponents can be derived as equalities where rigorous phenomenological arguments without the scaling hypothesis can deduce only inequalities (see Stanley, 1971, Kadanoff, 1971).

The renormalisation group has put the static scaling hypothesis on a firmer footing. Close to the fixed point the scaling fields are identified with the eigenvectors of the RG matrix. Due to the iterative (or subgroup) property of the RG

\[
R_{b_1}R_{b_2} = R_{b_1 \cdot b_2}
\]

(2.13)

the eigenvalues \( \lambda_i \) of the matrix can be expressed in the form

\[
\lambda_i(b) = b^{\lambda_i}
\]

(2.14)

hence any quantity which close to \( T_c \) depends on the parameters of \( \mu \) such as, for example, the correlation length, will be expressible from (2.8) and (2.14) as

\[
\xi(r, U_0, \ldots) \equiv b^{\lambda_1} r, b^{\lambda_2} U_0, \ldots)
\]

(2.15)

which is just the condition that \( \xi \) is a homogeneous function of the scaling fields. The importance of the scaling forms of the properties of interest is two-fold. From a practical point of view, numerical estimates for exponents are obtained by matching expressions such as (2.15), against the expected scaling forms written in terms of the indices \( \beta, \gamma, \nu, \) etc. and obtaining the thermodynamic exponents in terms of the eigenvalues \( \{\lambda_i\} \). From a more fundamental point of view, the form of the eigenvalues and eigenvectors of the RG at its fixed point provide a systematic prescription for considering the effects of
perturbations appropriate to real solids and not included in the over-
simplified LGW Hamiltonian, (2.3). In 2.1.3 it was remarked that only
Hamiltonians already precisely at $T_c$ will flow to a fixed point in
parameter space other than a trivial one with $\xi = 0$. This considera-
tion implies that at least one of the eigenvalues $\lambda_j$ of the linearised
transformation matrix must be positive in which case the temperature
may be identified with the scaling field $\mu_j$ so that a small perturba-
tion away from $\mu_j^*$ will be amplified by the application of $R_b$. In
the same way a field conjugate to the order parameter which contributes
a term

$$H_{E_-} = E(-k_s)Q(k_s)$$

(2.16)

to the Hamiltonian, must have a positive eigenvalue as the critical point
is unstable against application of such a field for which the system has
infinite susceptibility. These scaling fields are said to be relevant
because they are not transformed away by the RG transformation. In contrast
scaling fields which have a negative eigenvalue will vanish under successive
application of $R_b$. Scaling fields which are transformed away in
this manner are termed irrelevant because they do not influence the
behaviour observed over the long length scales which correspond to the
large values of $b$. The universality class of a Hamiltonian is there-
fore completely determined by the form of the relevant scaling fields.
For structural transitions, the various extra terms which may be in-
corporated into a realistic Hamiltonian have been examined to deter-
mine which types of perturbation give rise to relevant scaling fields
which may change the universality class of a transition (Bruce, 1976).
2.1.6 The application of the renormalisation group to dynamics

A major similarity between the study of dynamic (time-varying) critical phenomena and that of static (time-averaged) critical phenomena, is the relationship between the theory of van Hove (1954b) and the renormalisation group formulation of Halperin, Hohenberg and Ma (1972, 1974, 1976) which parallels the relationship between Landau theory and the static renormalisation group described in the preceding sections. In the van Hove theory, the effective Hamiltonian of the harmonic model is used to describe a system with a kinetic coefficient $\Gamma$ defined by the relation

$$\Gamma^{-1} = i \frac{\partial G(k, \omega)}{\partial \omega} \bigg|_{\omega=0}$$

(2.17)

which is assumed to be a constant. This theory may be seen as the dynamic analogue of the classical theories of equilibrium properties and as it predicts that long wavelength fluctuations will decay with a relaxation time

$$\tau_k = \xi^2 (1 + \xi^2 k^2)^{-1}$$

(2.18)

it suggests the notion of a dynamic scaling hypothesis (Ferrel et al., 1967, Halperin and Hohenberg, 1967) which fulfils the same role as the static scaling hypothesis, namely that

$$\tau_k = \xi^z f(k\xi)$$

(2.19)

where the scaling function $f$ and the exponent $z$ are universal. This hypothesis allows the dynamic exponent $z$, which has the value 2 in the classical theory, to be related to the static exponents. In particular, it suggests (see Ma, 1976b) the relation $z = 2 - \eta$.

The divergence of the relaxation time at $T_c$ due to the divergence
of $\xi$ in (2.19) is generally referred to as critical slowing down and is to be expected at all continuous SPTs. In 1.2.3 a brief mention was made of a characteristic frequency for the order parameter susceptibility. This may be identified in the van Hove theory with either the relaxation time defined above or with the softening frequency of the soft mode. In practice, for a system with a propagating soft mode these identifications do not appear to be equivalent (see Chapter 3).

The study of dynamic critical phenomena has closely paralleled the recent developments in the theory of equilibrium static phenomena. Initial attempts to apply graphical perturbation theory to condensed matter studies (Cowley, 1963; Maradudin & Fein, 1962) by calculating exactly all inter-mode interactions, prove intractable when applied to the analysis of problems exhibiting critical divergences similar to those encountered in the static perturbation series mentioned in 2.1.2. The solution to this problem has been to focus attention on the behaviour only of the long-wavelength order parameter modes and the conserved fields which couple strongly to them, in order to turn the deterministic problem of solving the complete set of equations of motion for the system into a stochastic problem in which the effects of couplings to the non-critical modes are represented by random (Gaussian) noise terms in the equations of motion for the critical modes. This approximate treatment of the hard modes is qualitatively similar to the underlying assumptions of the kinetic Ising models (Glauber, 1963) in which a lattice of spins is assumed to interact with a hypothetical thermal reservoir which causes random 'spin-flip' transitions, a concept which lends itself to computer simulation by Monte Carlo methods (Schneider et al., 1972), and which has been used directly by various authors as the basis for an alternative, real space formulation of the dynamic renormalisation group (Mazenko, 1979; Suzuki, 1979).
which utilises coarse-graining procedures developed originally for the real space static RG by Migdal (1975) and by Kadanoff (1976).

In the RG formulation of Halperin, Hohenberg and Ma (1974) the system is represented by the LGW Hamiltonian which would describe its equilibrium universality class, and by an equation of motion of the Liouville type for each relevant field, including both terms to ensure the correct relaxation to the equilibrium configuration, and possibly additional mode coupling terms to simulate the interaction between the conserved fields and the order parameter. The universality class of a system is now defined not only by the terms appearing in the Hamiltonian, as in the static case, but also by the form of the interaction terms in the equation of motion and by the conservation laws which are applicable. The concept of an upper critical dimensionality is still found to apply although this is now defined by the form of the equation of motion and conservation laws as well as by the Hamiltonian and so it need not be the same as the upper critical dimensionality in the sense in which this was defined in 1.3.4. For example, the addition of Larmor precession terms in the $n = 3$ model (Heisenberg model) of a magnet raises the value of $d_c$ for dynamics to 6 compared to the static value of 4 (Gunton, 1979). Above this critical dimensionality, the conventional (van Hove) critical dynamics apply, hence for systems such as the structural phase transitions represented by the model of Chapter 3, where the upper critical dimensionality remains at $d = 4$, a Feynman graph expansion in $\varepsilon = 4 - d$ dimensions may be used to calculate deviations from the van Hove theory.

The initial work on dynamic renormalisation group was restricted to the verification of the dynamic scaling hypothesis, and the calculation of the dynamic exponent $z$ in cases for which the scaling hypothesis is
correct. In this work the method is used to establish the characteristic frequencies of the correlation functions observed in neutron and light scattering experiments.

2.2 Alternative Approaches to Non-linear Dynamical Problems

2.2.1 Direct calculations of strongly anharmonic behaviour

The study of anharmonic systems by perturbation theory outlined in the previous section depends on the smallness of the coupling constants, such as $U_0$, from which it is inferred that the anharmonic terms result only in a renormalisation of the harmonic phonon frequencies and the kinetic coefficients which corresponds to the introduction of finite phonon lifetimes. In the renormalisation group studies where $U_0$ is of order $\epsilon$ the use of weakly anharmonic perturbation theory is rigorously justifiable provided one is working close to the critical dimensionality and close to $T_c$. The $\epsilon$ expansion calculations performed in this work are for systems with $d_c = 4$, for which the successful application of the $\epsilon$ expansion in the calculation of static properties indicates that extrapolations to $\epsilon = 1$ may be made with some confidence, however the use of expansions in $6 - \epsilon$ dimensions (Ma and Mazenko, 1975) cannot be expected to give quantitative results in three dimensions. For systems where the anharmonic coupling constants are not small, studies of non-linear wave equations (Zabusky & Kruskal, 1965, Bocchieri et al., 1970) suggest that a new type of dynamics which is characteristic of non-linear systems will occur.

Instead of the thermal energy being classically distributed amongst quasi-harmonic phonon modes, localised excitations or solitons appear. These are stable structures which, due to their localised nature, are specifically excluded by the principle of the RG approach of (2.1)
which treats only the long-wavelength, or hydrodynamic, modes of the system. The natural framework for the description of these localised structures is a real space formulation, however the coarse-graining procedure of the real space RG also eliminates the unique solitonic properties of these excitations from the fixed point properties of the system.

A more plausible treatment of the statistical mechanics of a real anharmonic system is to obtain the eigenstates of a real space Hamiltonian and to carry out exact statistical mechanics. This approach was adopted by Scalapine et al. (1972) and by Krumhansl and Schrieffer (1975). The transfer integral method used by these authors to calculate the partition function has proved practical only in one dimension and in a continuum approximation. Despite the lack of long range order at finite temperature in any model in only one spatial dimension, the results which these authors obtained for the $\phi^4$ model, the real space equivalent of the model defined in 1.3.1, give a useful guide to the qualitative features which may be expected in a more realistic model.

These studies which attempt to treat both the localised non-linear solitonic modes, and extended phonon-like modes, have the great restriction that the enumeration of non-linear modes is strictly possible only for integrable Hamiltonian systems (see review by Scott et al., 1973). In these systems the normal modes interact to produce only asymptotic phase shifts, and hence the partition function can be factorised into a phonon part and a soliton part, each of which can be treated independently (Bishop, 1978). This suggests that it will be necessary to ascribe the singular behaviour of the thermodynamic functions at a phase transition to one or the other parts of the partition function, i.e. to either solitonic and explicitly non-linear effects which may be viewed in a crystal as the occurrence of interfacial structures, or to
the anharmonic phonon part of the partition function which is most clearly indicated in the case of a soft mode transition. The soft soliton concept, wherein the creation energy for a soliton vanishes at a phase transition, rather than the frequency of a phonon, has been considered as a mechanism for certain incommensurate transitions (Bak & Emery, 1976 and this work Chapter 5) and also for one-dimensional melting (Axe & Emery, 1978). Similar topological defects or vortices have formed the basis for a theory of two-dimensional phase transitions (Kosterlitz and Thouless, 1972; Halperin and Nelson, 1978).

In comparison with the well-established treatment of linear systems by Fourier transformation, the study of non-linear systems has been greatly hampered by the absence of any general technique for their solution. The attention of researchers has therefore been drawn to an intensive study of the few equations for which exact solutions may be obtained by a variety of special techniques. Typical of these equations is the sine-Gordon equation introduced in Chapter 5. For these (one-dimensional) equations, a complete set of soliton solutions can be generated iteratively by Bäcklund transformation techniques (Bullough & Dodds, 1978; Hirota, 1973), and these were introduced into non-linear field theories by Perring and Skyrme (1962) but attracted little attention. An outburst of activity followed the discovery of the inverse scattering transform technique (Gardner et al., 1967) in which non-linear equations are solved by a succession of linear transformations, but the application of this technique is still too specialised to enable it to be applied to any but a few special cases.

Faced with this severe restriction, but guided by numerical studies of similar equations, the subject of non-linear wave equations has entered the realm of experimental mathematics in which the solitonic
behaviour calculable for the simplest systems is assumed to hold true for large classes of system, whether these can be shown to be completely integrable or not. With this assumption the corresponding physical models may be studied by linearising for small fluctuations about the non-linear solutions, an approach which is exploited in Chapter 5 and discussed by Newell (1978).

2.2.2 Numerical studies

This section is necessarily brief as the work presented in this work does not rely to any extent on the contents of the recent numerical studies of phase transitions and non-linear systems, although it is instructive to make comparisons in many instances.

The previous section referred to numerical studies of non-linear equations. This form of study has an extensive literature in its own right as a branch of applied mathematics and in general the results obtained are of marginal relevance to SPT models except in the suggestion that there is a 'universalism' in non-linear wave theory which may justify the restriction of dynamic studies to the simplest non-linear wave equations in the same way that the universalism of the renormalisation group allows the restriction of attention to the simplest Hamiltonians (Bishop, 1978).

Outside the main stream of this approach to strictly mathematical equation-solving, two extensively applied numerical techniques have been applied in works which are of direct relevance to SPTs in general and to this work in particular. The molecular dynamics technique, in which classical equations of motion are iteratively solved for a lattice model has been applied to the calculation of dynamical structure factors for the one and two-component, real space versions of
the model of §2.1 by Schneider and Stoll in one to four dimensions and by Aubry in one dimension. The approach of Schneider and Stoll is of particular interest as, to compensate for the simplifications which they had introduced into their model, they added a phenomenological noise field, hence studying in practice the same problem as that which is defined in the renormalisation group approach and described in §3.2 (see Schneider and Stoll, 1973, 1976, 1978 and Aubry, 1975, 1976).

The Monte Carlo technique is particularly suited to the investigation of the properties of discrete spin magnetic models, or the corresponding pseudo-spin order-disorder transition models, which are in the same universality class as the displacive systems considered by Schneider and Stoll, but which have qualitatively different dynamics. This technique has been used by Bak and von Boehm (1978) and by Selke and Fisher (1979) to study the equilibrium behaviour of a class of anisotropic next-nearest neighbour Ising models which may be used as a microscopic model to derive the semi-phenomenological model used in Chapter 5. The Monte Carlo technique has also been used in dynamical studies of phase transitions where it is particularly suited to discussion of the kinetic Ising model. Notable work here has been done by Schneider et al. (1972) who gave a detailed consideration of dynamic scaling in extending the exact one-dimensional work of Glauber to two dimensions.

The advantage of these numerical methods is that for low-dimensional systems where the $\epsilon$ expansions are at their least reliable, and where short-range fluctuations and domain wall, or soliton effects are most prevalent, they are capable of yielding exact results except very close to $T_c$ when the correlation length becomes comparable with the finite size of the lattice. The $\epsilon$ expansions may therefore be seen as an interpolation between the known classical behaviour at high dimensionality,
and the numerical results which should be of high accuracy in two
dimensions.

§2.3 Experimental Studies of Phase Transitions

§2.3.1 Diffraction techniques used for phase transition studies

It was mentioned in the introduction that the great interest in phase
transitions exhibited over the last twenty years or so was greatly stimu-
lated by the availability of high flux reactors with their associated
neutron spectrometers and diffractometers. Neutrons have been of con-
siderable value to crystallographers interested in changes in the micro-
scopic structure of materials such as KDP where the phase transition
mechanism is intimately concerned with the position of hydrogen-bonding
protons which exhibit a strongly first-order, order-disorder tran-
sition. There are many hydrogen-bonded ferroelectrics in which the
positions of light atoms are of crucial importance, which means that
X-ray structural determinations, for which the atomic structure factors
are proportional to the atomic number, give less accurate information
than neutron diffraction studies where scattering lengths for light
and heavy atoms are of comparable magnitude. Neutron diffractometers
which are used for structural studies measure only the elastic scattering
from single-crystal or powder samples. The neutron scattering experi-
ments described in this work were all performed on a neutron triple-axis
spectrometer (TAS).

Unlike the diffractometer, the TAS uses monochromating crystals for
energy analysis of both incident and scattered beams. This allows the
experimenter to determine both the wave-vector and frequency transfer
to the scattered neutrons from which it is possible to determine, as
described in the next section, the dynamic scattering function $S(k, \omega)$,
which is closely related to the Fourier transform of the correlation function $\Gamma(r, t)$ defined in 1.2.3.

The peak neutron flux from a thermal nuclear reactor occurs for neutrons with wave-vectors and energies comparable to normal phonon wave vectors and energies, hence it is possible to measure $S(\mathbf{k}, \omega)$ over the whole Brillouin zone of a crystal. This represents a major advantage over the complementary light scattering techniques of Raman and Brillouin scattering in which, due to the very short wave-vectors of the visible light used in comparison to phonon wave-vectors, it is possible only to measure $S(\mathbf{k}, \omega)$ only in the vicinity of the origin of reciprocal space. Although X-rays have wave-vectors comparable to phonon wave-vectors, their use in the study of dynamic phenomena is restricted by their high energies which makes it possible to measure only the integrated intensity

$$S(\mathbf{k}) = \int_{-\infty}^{\infty} d\omega \ S(\mathbf{k}, \omega) \quad (2.20)$$

due to the negligibly small, in comparison, energy changes incurred by the X-rays in a normal phonon scattering event.

2.3.2 The dynamic structure factor $S(\mathbf{k}, \omega)$

The intensity of neutrons scattered with a given wave-vector $\mathbf{k}_o$ and frequency transfer $\omega_o$ per unit incident flux, is defined in terms of the differential cross-section

$$\frac{\partial^2 \sigma(\mathbf{k}, \omega)}{\partial \mathbf{k} \partial \omega} \bigg|_{\mathbf{k}_o \omega_o} = \frac{k_f}{k_i} S(\mathbf{k}_o \omega_o) \quad (2.21)$$

where $\mathbf{k}_i$ is the incident wave-vector, $\mathbf{k}_f$ is the scattered wave-vector,
and \( S(\mathbf{k}_o,\omega) \) is variously called the van Hove scattering function or dynamic structure factor. The observed intensity, \( I(\mathbf{k}_o,\omega) \) is given by the convolution of the differential cross section with the resolution function \( R(\mathbf{k} - \mathbf{k}_o, \omega - \omega_o) \) for the spectrometer, in the form

\[
I(\mathbf{k}_o,\omega) = \int \int d^3k d\omega \ R(\mathbf{k} - \mathbf{k}_o, \omega - \omega_o) \ \frac{\partial^2 \sigma(\mathbf{k},\omega)}{\partial k \partial \omega} .
\tag{2.22}
\]

In the majority of experiments, the quantity of interest is the van Hove scattering function. If the instrumental resolution is good, in the sense that \( R(\mathbf{k} - \mathbf{k}_o, \omega - \omega_o) \) is sharply peaked in a region where \( \frac{\partial^2 \sigma}{\partial k \partial \omega} \) is approximately planar, the instrumental resolution may be taken to be a delta function in which case

\[
I(\mathbf{k}_o,\omega) = \frac{k_f}{k_i} S(\mathbf{k}_o,\omega) .
\tag{2.23}
\]

For triple-axis experiments in which this approximation is not adequate, the form of the resolution function as well as the form of the van Hove function in the four-dimensional \((\mathbf{k}, \omega)\) space must be specified in order to carry out numerically the convolution in (2.22) before comparing the theoretically obtained form of \( S(\mathbf{k},\omega) \) with the experimental results. This point is extensively discussed in Chapter 4, where it is shown that the results of neutron scattering experiments analysed without sufficient resolution corrections can be highly misleading.

Neutron scattering experiments are usually accomplished, not by counting for a set time at each point, but by inserting a monitor counter of low efficiency in the incident beam and then counting for a given number of monitor counts to compensate automatically for any variation in reactor flux. The monitors used generally have an efficiency proportional to the inverse of the incident wave vector, so that in a 'constant \( k_f \) scan', the factor \( k_f/k_i \) can be ignored.
and the measured intensity is proportional to the dynamic structure factor, \( S(\mathbf{k}, \omega) \).

The importance of the dynamic structure factor derives from its connection with the microscopic correlation functions which are the usual point of contact between theoretical and experimental studies. The scattering function may be written in the form (van Hove, 1954a)

\[
S(\mathbf{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt F(\mathbf{k} \cdot t) F(-\mathbf{k}, 0) \exp(i\omega t) \tag{2.24}
\]

where \( F \) is an operator which represents the probability of scattering from a state with wave vector \( \mathbf{k}_i \) to one with wavevector \( \mathbf{k}_f \) where \( \mathbf{k} = \mathbf{k}_f - \mathbf{k}_i \). For neutron scattering this operator is conveniently represented in terms of a scattering length, \( b \), for each type of nucleus as

\[
F(\mathbf{k} \cdot t) = \sum_{\mathbf{\ell} \mathbf{K}} b_{\mathbf{\ell} \mathbf{K}} \exp[i\mathbf{k} \cdot \mathbf{r}(\mathbf{\ell} \mathbf{K}, t)] \tag{2.25}
\]

If the \( k \)th sites in all unit cells are populated by one species of nucleus, \( b_{\mathbf{\ell} \mathbf{K}} \) will be independent of \( \mathbf{\ell} \) and \( F(\mathbf{k} \cdot t) \) will give rise to only coherent scattering. Since real materials usually contain a mixture of isotopes, each of which has a different scattering length, the coherent scattering must be described by using an average value of \( b_{\mathbf{\ell} \mathbf{K}} \). The additional scattering which arises from the variation of \( b_{\mathbf{\ell} \mathbf{K}} \) with \( \mathbf{\ell} \) causes incoherent scattering, a background of intensity which is almost independent of wave-vector and occurs predominantly for zero energy transfer. This incoherent scattering, which is approximately independent of temperature, must be subtracted from measurements of \( S(\mathbf{k}, \omega) \).

By expanding \( r(\mathbf{\ell} \mathbf{K} t) \) in the normal mode coordinates \( Q(\mathbf{\ell}) \), the dynamic structure factor may be written as the sum of a static (Bragg)
term $S^0(k, 0)$, and a series of multi-phonon terms of which the simplest are the Bragg term

$$S^0(k, \omega) = N|F^0(k)|^2 \delta(\omega) \Delta(k) \quad (2.26)$$

and the one-phonon term

$$S^1(k, \omega) = \sum_{\vec{k}'j j'} F(\vec{k}, \vec{k}'j) F(-\vec{k}, -\vec{k}'j') \zeta(\vec{k}'j j', \omega) \Delta(k + \vec{k}') \quad (2.27)$$

where $\zeta(\vec{k}'j j', \omega)$ is the displacement-displacement correlation function

$$\zeta(\vec{k}'j j', \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega <Q(\vec{k}'jt)Q(-\vec{k}'j'0)> \exp i\omega t \quad (2.28)$$

This correlation function may be calculated from a microscopic model either directly as is done in Chapter 3, or by using the fluctuation-dissipation theorem result that

$$\zeta(\vec{k}'j j', \omega) = \frac{\hbar}{\pi}(n(\omega) + 1) \text{Im} G(\vec{k}'j j', \omega) \quad (2.29)$$

where $G(\vec{k}'j j', \omega)$ is the linear response function, or susceptibility. In the analysis of experimental results it is customary to disregard inter-branch interactions and to approximate the response function by that of a damped harmonic oscillator.

$$G(\vec{k}, \omega) = \left[\omega^2(\vec{k}) - \omega^2 - i\omega \Gamma(\vec{k})\right]^{-1} \quad (2.30)$$

where $\omega^2(\vec{k})$ and $\Gamma(\vec{k})$ contain adjustable parameters.

The coefficients $F(\vec{k}, \vec{k}'j)$ appearing in equation (2.2) are usually treated in the first instances as wave-vector, frequency, and temperature-independent constants in which case the dynamic structure factor is simply proportional to the microscopic displacement-displacement correlation function. In particular, during Chapter 3 where the scattering functions of interest are those for $\vec{k} = \vec{k}'_s$ the soft mode
wavevector, $S(\mathbf{k}, \omega)$ will be used in the sense of meaning the one phonon correlation function and the (directly proportional) scattering function.

2.3.3 **Quasielastic scattering**

Elastic scattering of neutrons by a crystal refers to both the Bragg coherent scattering which produces sharp peaks in $S(\mathbf{k}, \omega)$ at $\omega = 0$ and $\mathbf{k} = \mathbf{I}$, a reciprocal lattice vector, and to the incoherent background scattering due to the isotopic inhomogeneity of a crystal which produces a constant background at $\omega = 0$ for all $\mathbf{k}$. The scattering due to these processes is not in any way time-dependent and should therefore have a width in frequency which is determined by the instrumental resolution. In this work the term quasielastic is used to describe the scattering at low frequency transfer by any other process which is not, in principle, restricted to producing perfectly elastic scattering, but which may produce scattering centred on zero frequency transfer. There are two types of phenomena which give rise to these effects, soft modes and interfaces, in addition to the small inelastic, incoherent background.

The scattering due to normal modes in a harmonic crystal produces delta-function peaks at $\omega = \pm \omega(\mathbf{k})$. In a weakly anharmonic crystal, these peaks shift slightly in frequency and become broadened so that the spectral lines are described approximately by the damped harmonic oscillator expression of equations (2.27) to (2.30). Close to a phase transition where, in mean field theory at least, $\omega(\mathbf{k}_s)$ vanishes, the soft mode response must eventually become overdamped, i.e.

$$\omega^2(\mathbf{k}_s) < \Gamma(\mathbf{k}_s) \quad (2.31)$$

in which case the dynamic structure factor for this mode will become a
single peak centred on zero frequency, but with a finite width, except possibly at \( T_c \), due to the non-zero values of \( \omega(\vec{k}_s) \) and \( \Gamma(\vec{k}_s) \).

In the case of \( \text{SrTiO}_3 \) the soft modes are overdamped only for a range of around ten degrees to either side of \( T_c \) whereas for the isomorphous \( \text{KMnF}_3 \) the soft mode at the 186K transition is overdamped for a wide temperature range (Shapiro et al., 1972), and in \( \text{KD}_2\text{PO}_4 \), coupling between the soft mode and the acoustic modes just above \( T_c \) produces strong and highly anisotropic critical quasi-elastic scattering (Hosea, 1980, see also Chapter 6).

Quasi-elastic scattering is also produced by low-dimensional structures such as domain walls. If these features are truly static then the scattering from them takes the form of lines of elastic scattering perpendicular to the walls (Chapter 6). If the walls are not static but are able to move either close to a phase transition where dynamic domain wall peaks may occur (Cowley et al., 1976) or else under the influence of a field, this scattering may assume some measureable width in frequency. Ferroelectric domain walls such as those discussed in Chapter 6 are believed to be strongly pinned to the lattice and so any scattering from them may be expected under circumstances other than those described above, to be effectively elastic. With interfaces which are not expected to be strongly pinned, or even not pinned at all such as the discommensurations or solitons of Chapter 5, the quasi-elastic scattering may take the form of an extra Goldstone mode branch in the excitation spectrum, in other words a mode for which \( \omega = 0 \) for \( k = 0 \). This will show up as genuine quasi-elastic scattering for small \( \vec{k} \) and as an oscillatory mode for larger \( \vec{k} \) (Aubry, 1976). Scattering of this form has been reported in magnetic systems (Steiner, 1978) and interpreted in terms of a soliton model of Villain (1979) and Mikeska (1978) although this interpretation has recently been challenged (Reiter, 1981).
§2.3.4 Other experimental techniques

Although the main content of this work refers to the calculation of one-phonon or two-phonon terms in the van Hove function with express mention of the application to inelastic neutron scattering, there are several references to resonance techniques, and extensive discussion of light scattering in Chapters 3 and 4. Both of these techniques measure only the frequency dependence and not the wavevector dependence of $S(k, \omega)$ or in the case of light scattering, in some instances, of an analogous two-phonon correlation tensor.

Electron paramagnetic resonance (EPR) and nuclear quadrupole resonance (NQR) have both been used for the measurement of dynamic susceptibilities. Since the resonant impurity atoms sample only a local field the susceptibilities measured are local rather than macroscopic quantities. If the line-width of the resonance line is $\Gamma(\omega)$ where $\omega$ is the resonant frequency, then according to Blinc (1971)

$$\Gamma(\omega) = \frac{1}{N} \sum_{\k} |A_1(\k)|^2 \zeta(\k, \omega)$$

(2.32)

where $\zeta(\k, \omega)$ is the usual one-phonon correlation function as in eq. (2.28), and $A_1(\k)$ is a coefficient in the expansion of the local field in normal mode coordinates. This technique has been used for measuring line widths of the very narrow central peak scattering observed at certain displacive phase transitions and discussed in Chapter 3, but the wave vector summation in eq. (2.32) causes some difficulty in interpreting the data and some functional form has to be assumed for $\zeta(\k, \omega)$.

The other experimental technique of major relevance to this work is the study of soft modes by Raman scattering. Since the wave vectors for visible light are of the order of only $10^{-3}$ Å$^{-1}$, all light
scattering experiments measure effectively the $\mathbf{k} = 0$ response of the crystal. The scattering cross-section may be derived in an analogous manner to the derivation of the neutron scattering cross-section (eq. (2.27)) except that for light scattering the operator $F(\mathbf{k} t)$ is replaced by the polarisability tensor $P_{\alpha\beta}(\mathbf{k} j)$ which is then expanded as a power series in the normal mode coordinates. For systems in which a direct coupling between the light and the $(\mathbf{k} j)$ phonons is not symmetry forbidden, the one-phonon Raman intensity is given by the Raman tensor element

$$\Gamma^{(1)}_{\alpha\beta\gamma\delta}(\mathbf{k} j j' \omega) = P_{\alpha\beta}(\mathbf{k} j) P_{\gamma\delta}(\mathbf{k} j') \zeta(\mathbf{k} j j' \omega) . \quad (2.33)$$

In the temperature range above a structural phase transition, one phonon Raman scattering is often forbidden by symmetry, and in this case the two phonon scattering caused by coupling of the light to pairs of phonons, effectively to the phonon density, will be important both above $T_c$ where it is the lowest order of scattering permitted, and also in the critical region below $T_c$ where the one-phonon polarisability goes to zero as the order parameter, i.e. in mean field theory

$$P^2_{\alpha\beta}(\mathbf{k}_s) \sim P^2_0 (T_c - T) \quad (2.34)$$

so that for $T < T_c$ the one and two-phonon scattering intensities may be of comparable magnitude. The two-phonon scattering intensity may conveniently be expressed as

$$\Gamma^{(2)}_{\alpha\beta\gamma\delta}(\mathbf{k} \omega) = P^{(2)}_{\alpha\beta}(\mathbf{k}) P^{(2)}_{\gamma\delta}(\mathbf{k}) \Gamma(\mathbf{k} \omega) \quad (2.35)$$

where $\Gamma(\mathbf{k} \omega)$ is the two-phonon spectral function, the analogue of the one-phonon van Hove function. A detailed discussion of the form of $\Gamma(\mathbf{k} \omega)$ is more appropriately left until Chapter 3, but for completeness the definition is given here as
\[
\Gamma(\mathbf{k}, \omega) = \frac{1}{2\pi} \sum_{\mathbf{k}_1, \mathbf{k}_2} \int dt <\mathbf{Q}(\mathbf{k}_1, t)\mathbf{Q}(\mathbf{k}_1, t)\mathbf{Q}(\mathbf{k}_2, 0)\mathbf{Q}(-\mathbf{k}_2, 0)> \exp i\omega t
\]

(2.36)

For convenience, all phonon branch indices have been suppressed in equations (2.35) and (2.36) and the normal mode amplitudes are all assumed to be of the dominant soft mode branch.
CHAPTER 3

CRITICAL SCATTERING ABOVE $T_c$

3.1 The Central Peak Problem

3.1.1 Introduction, critical scattering observations above $T_c$

Some initial investigations into the dynamic structure factor of crystals undergoing structural phase transitions agreed well with the soft mode concept of Cochran and Anderson. (For reviews of this work see Scott, 1974; and Shirane, 1974). A phonon branch could be located in these materials which decreased in frequency, becoming overdamped as the transition temperature was approached. For materials such as KNbO$_3$ which undergo first order phase transitions the softening of the phonon is incomplete (Currat et al., 1974; Nunes et al., 1971), and the low energy scattering close to $T_c$ originates only from the soft mode and the acoustic phonons.

In materials which undergo continuous phase transitions, the critical region is generally characterised by intense low-frequency, or quasi-elastic, scattering. When the low-frequency scattering occurring at continuous SPTs in the isomorphous KMnF$_3$ and SrTiO$_3$ compounds was examined (Riste et al., 1971; Shapiro et al., 1972), it was found that the neutron scattering intensity, and hence the van Hove structure factor, displays characteristic behaviour in two different frequency regimes.

In the case of SrTiO$_3$ the structure factor above $T_c$ contains a well-defined propagating soft mode which decreases in frequency as the transition is approached, but which may not have a vanishing frequency...
at $T_c$. The width of the phonon also decreases as $T_c$ is approached attaining a limiting value of around $10^{11}$ Hz. In addition to this soft phonon mode, the van Hove function is found to show a large amount of quasi-elastic scattering at the $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ superlattice point. The discovery of this critical scattering, which persists for a temperature range of approximately 50 degrees above $T_c$, was almost coincident with the discovery that the order parameter exponent in SrTiO$_3$ had the value $\frac{1}{3}$ (Müller and Berlinger, 1971), a value characteristic of short range critical behaviour, rather than the value of $\frac{1}{2}$ which was previously expected from mean field theory. The quasi-elastic scattering is concentrated in a narrow peak centred in zero energy transfer, with a width below the resolution limit for neutron spectroscopy. In the original experiments carried out by the conventional triple axis technique, the resolution limit was of the order of 0.8 meV full width at half maximum, but subsequent measurements with a back-scattering technique (Töpler et al., 1977) showed that the width of the central peak is less than 0.08 meV, corresponding to a frequency of $\omega \sim 10^7$ Hz.

The SrTiO$_3$ central peak, being the first to be discovered, has remained the most intensively studied, not only by inelastic neutron scattering (Riste et al., 1971; Shapiro et al., 1972; Töpler et al., 1977; Currat et al., 1978; Hastings et al., 1978) but also by EPR (v. Waldkirch et al., 1972; Müller et al., 1974, Reiter et al., 1979). This technique has also been unable to resolve a width for the central peak, but has reduced the upper bound on its width to 0.6 MHz.

Other cubic perovskites, notably K$\text{MnF}_3$ and LaAlO$_3$ also undergo anti-ferroelectric transitions with an R point soft mode (Gesi et al., 1972; Kjems et al., 1973). In both of these materials the soft mode is overdamped throughout the critical region, and the central peak appears as an extra, very sharp peak on top of the much wider phonon peak.
As in the case of SrTiO$_3$, neutron-scattering experiments in KMnF$_3$ (Shapiro et al., 1972) were unable to resolve the width of the peak, but critical ultrasonic absorption measurements (Hatta et al., 1974) have suggested a width of $2 \times 10^7$ Hz at $T = T_c$, while Mössbauer experiments give an upper limit to the width of only $2.5 \times 10^6$Hz (Hanisch and Drosg, 1976).

Materials which undergo ferroelectric transitions can also give rise to central peaks as was first shown by Cowley et al. (1976) for Pb$_5$Ge$_3$O$_{11}$. In this case Brillouin scattering experiments placed an upper limit for the central peak width at $8 \times 10^7$ Hz (Fleury and Lyons, 1976). Unlike the perovskite central peaks, however, the peak in Pb$_5$Ge$_3$O$_{11}$ was not concentrated at a single point in reciprocal space, but gave rise to lines of scattering at wavevectors $(\zeta, \zeta, \xi)$. Cowley et al. ascribed this scattering to domain wall effects due to its similarity to scattering from static domain walls which persists down to temperatures well below $T_c$ where critical scattering would not be observed in any case, and where measurements on the perovskites with R point instabilities could not be made due to the presence of a genuinely elastic Bragg peak at the superlattice point in the ordered phase.

The interest shown in the central peak phenomenon centred around the possibility of ascribing the origin of the scattering to various types of non-linear phonon coupling or truly non-linear excitation. A major controversy was whether the central peak arises from intrinsic effects, i.e. those which would be present in a pure sample of perfect crystal, or from extrinsic effects, due to the presence of impurities or crystal defects which are not present in an ideal sample.
3.1.2 Proposed origins of the central peak

The extremely narrow frequency width of the central peaks observed by neutron and EPR studies suggests that their origin lies in a coupling between the order parameter, and some unspecified degree of freedom capable of exhibiting long time-scale behaviour. An attempt was originally made by Schwabl (1972) to describe the van Hove function by the phenomenological form

\[ S(k, \omega) = \frac{n(\omega)+1}{\pi \omega} \int \frac{1}{\omega_0^2(k,T) + \omega^2 - i\omega [\Gamma_0 + \Gamma(\omega,T)]} \]

where \( n(\omega) \) is the phonon occupation number and \( \Gamma(\omega,T) \) is assumed to be given by the form

\[ \Gamma(\omega,T) = \frac{\delta^2(T)}{\gamma - i\omega} \]

The assumption underlying this approximation is that the order parameter couples to some relaxational degree of freedom which has a response given by the Debye oscillator form in eq. (3.2), which involves the characteristic decay time \( \gamma^{-1} \). Experiments on SPTs mentioned in the last section concentrated upon extracting from the data, values for the parameters \( \delta^2(T) \) and \( \gamma \) which represent respectively the spectral weight of the central peak and its width.

In a similar vein, theoretical explanations concentrated initially on deriving a contribution to the soft mode self energy of the form given in (3.2) by considering coupling of the soft phonon to slowly-relaxing, intrinsic degrees of freedom. In this conceptually straightforward approach, coupling to phonon density fluctuations (Cowley, 1970; Coombs and Cowley, 1973), acoustic modes (Silberglitt, 1972; Enz, 1972) and heat diffusion or second sound (Feder, 1971; Wehner and Klein, 1972)
were all investigated but found to be unable to explain the extreme narrowness of the central peak. A second suggestion for the central peak origin was made by Kruhnsn and Schrieffer (1975) and by Aubry (1975). From studies of a one-dimensional Ising model they showed that domain wall, or soliton, formation at low temperatures could give rise to quasi-elastic scattering. The connection between these models and the $n = 3, d = 3$ perovskite system is not clear. The one-dimensional Ising model is at its lower critical dimensionality and therefore does not undergo a phase transition at finite temperature. The domain wall excitations are, in this system, point-like structures which cost only finite energies and are thus always present for $T > 0$. In three dimensions the analogous domain wall structures are planar and thus cost macroscopic energies which will make their formation highly unlikely except in substances such as ferroelectrics where it is energetically favourable to form a domain structure to minimise the macroscopic field, so that although this is suspected to be the mechanism giving rise to the central peak in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ which is observed for a range of wavevectors close to the reciprocal lattice points, it does not seem to be a suitable explanation for the scattering at the superlattice point in $\text{SrTiO}_3$, however the studies of Feder (1971), Murata (1975) and Bruce (1978) which interpret the long time scale dynamics of the central peak in terms of clusters of precursor order above $T_c$, imply the existence of some form of domain boundaries.

The alternative explanation of the central peak origin as arising from a coupling between the order parameter, and slowly-relaxing defects made by Axe et al. (1974) and by Folk and Schwabl (1974) was developed by Halperin and Varma (1976) who, by a mean field argument, suggested that the presence of an impurity with a relaxation time of the order of $1/\gamma$ would induce the narrow central peak in the one-phonon scattering.
The final source of information on the van Hove function is the numerical studies by molecular dynamics carried out by Aubry (1975, 1976) in 1 dimension and by Schneider and Stoll (1976, 1978) in 2, 3 and 4 dimensions. These studies produced central peaks from pure 'crystals' which are, in common with the anharmonic phonon-coupling studies, of a width comparable to the soft phonon. The addition of some slowly-relaxing defects to the computer model had the effect of considerably narrowing the central peak (Schneider and Stoll, 1977).

The picture which emerged from this intensive study was that the central peak was caused by the formation of clusters of precursor order which are in some way controlled by the presence of slowly relaxing defects. This viewpoint was partly supported by the experimental evidence (Currat et al., 1978) which indicated that the central peak amplitude, \( \delta^2(T) \), is sample-dependent at temperatures above \( T_c + 5K \), but has a common value closer to \( T_c \).

3.1.3 Light scattering experiments

Scattering experiments at phase transitions generally fall into one of two classes. In the neutron scattering experiments discussed so far, the radiation couples linearly to the order parameter and so the scattered intensity is proportional to the one-phonon correlation function. In light scattering experiments it is frequently the case that the light will not couple linearly to the order parameter in the high-symmetry phase. This is due to the symmetry of the soft mode rendering it Raman inactive, and in the cases such as the perovskites mentioned in 3.1.1, where the soft mode occurs at the Brillouin zone boundary in the high temperature phase, the infinitesimal wave vector transfer
available in a light scattering experiment always prevents a linear coupling to the near-critical modes. The light then couples quadratically to the order parameter, and the intensity of the scattering is proportional to a two-phonon correlation function $\Gamma(\vec{k}, \omega)$ to be defined precisely later (eqns. (3.15) to (3.18)). Early light scattering studies by Steigmeier et al. (1973), indicated the presence of critical quasi-elastic scattering (or critical opalescence) in SrTiO$_3$, and this was investigated by Lyons and Fleury (1977) using an iodine filter to absorb elastically scattered light, which would cut out any scattering as narrow in frequency as the central peaks observed in the neutron scattering experiments. In the off-diagonal spectrum they observed a weakly divergent peak with a width at $T_c$ of $2 \times 10^{10}$ Hz which was visible for only a range of approximately 5K on either side of $T_c$. The appearance of a third time scale in the dynamics of the system was quite unexpected, however it was clear that there was a need for a theoretical study of the form, and particularly of the width of the one- and two-phonon scattering functions $S(\vec{k} = \vec{k}_s, \omega)$ and $\Gamma(\vec{k} = \vec{0}, \omega)$, in order to establish whether or not the dynamic light-scattering peak can be identified with either of the features in the one-phonon spectrum. This analysis is carried out in the next section where the widths of the one- and two-phonon spectral functions are shown to form a universal ratio, but firstly it is appropriate to review the properties of the correlation functions which may be deduced from scaling theory.

3.1.4 General observations on the one- and two-phonon correlation functions

For the purposes of comparing one- and two-phonon central peak widths a complete study of the spectral functions $S(\vec{k}, \omega)$ and $\Gamma(\vec{k}, \omega)$
is required. These correlation functions can be calculated exactly, only from a consideration of a microscopic model, and this is accomplished in §3.2. An essential pre-requisite for the calculations is a knowledge of the general form of the spectral functions close to criticality. In the same way that static critical phenomena have been characterised by scaling theories, application of the dynamic scaling hypothesis to the order parameter susceptibility, termed restricted scaling by Hohenberg and Halperin (1977), allows the behaviour of the one-phonon scattering to be deduced. Writing the one-phonon dynamic response in the scaling form

\[ G^{-1}(t, \mathbf{k}, \omega) = t^{-\gamma} G^{-1}(k/t^{\gamma}, \omega/t^{z\nu}) \]  

(3.3)

and making the approximation that quantum effects can be ignored, so that \( h(n(\omega) + 1) \approx k_B T/\omega \), it follows immediately from eqns. (2.27) and (2.29) that

\[ S(t, \mathbf{k}, \omega) = t^{-\gamma-z\nu} S(k/t^{\gamma}, \omega/t^{z\nu}) \]  

(3.4)

This shows that the integrated intensity should have a strong divergence characterised by the exponent, \( \gamma \), of the static susceptibility. The width, \( \omega^{(1)} \) of the one phonon critical scattering, to be defined precisely in 3.2.1, can be given by the expression \( \omega^{(1)}(t) = \Omega^{(1)} t^{z\nu} \) which exhibits critical slowing down, or narrowing as predicted by the conventional theory of lattice dynamics (van Hove, 1954b). The scaling approach gives no information concerning the shape function \( \tilde{S} \) apart from specifying the manner in which the variables entering it must be combined, nor does it give a value for the non-universal amplitude \( \tilde{\Omega}^{(1)} \).

The position is similar, although more complicated, when considering
the two-phonon scattering. In this case there are two qualitatively different types of scattering to be considered, as it has been shown by Murata (1976a) that the Raman tensor for cubic symmetry has only two linearly independent components. The origin of these two types of two-phonon correlations can be traced to the thermodynamic and non-thermodynamic fluctuations. Thermodynamic fluctuations correspond to changes in the phonon density arising from local fluctuations in the temperature which preserve the symmetry of the lattice. Non-thermodynamic fluctuations represent fluctuations of lower symmetry which cannot be conveniently represented by some macroscopic thermodynamic variable.

In the critical region we shall demonstrate that the non-thermodynamic component of the Raman tensor will dominate experiments on all systems with n > 1. The correlation functions $\Gamma_T$ and $\Gamma_{NT}$ corresponding to thermodynamic and non-thermodynamic fluctuations respectively, are also defined in 3.2.1. The scaling forms for these correlation functions are given by Hohenberg and Halperin (1977) to be

$$\Gamma_T(t, k, \omega) \sim t^{-a-2\nu} \Gamma_T(k/t^\nu, \omega/t^{2\nu})$$

(3.5)

and

$$\Gamma_{NT}(t, k, \omega) \sim t^{-\gamma-2\nu} \Gamma_{NT}(k/t^\nu, \omega/t^{2\nu})$$

(3.6)

where

$$\gamma = 2\phi + \alpha - 2$$

(3.7)

and $\phi$ is the crossover exponent characterising the instability of the fixed point against a uniaxial perturbation, introduced by Riedel and Wegner (1969, 1970). From these expressions it can be seen that both types of two-phonon scattering will have a width given by the expression

$$\omega_T^{(2)} \sim \Omega_T^{(2)} t^{2\nu}$$

(3.8)

$$\omega_{NT}^{(2)} \sim \Omega_{NT}^{(2)} t^{2\nu}$$
which will exhibit critical slowing down governed by the same exponent as the one-phonon width. The two-phonon spectral functions will, however, display different critical divergences in their integrated intensities. The thermodynamic fluctuations will display the same critical behaviour as the specific heat which diverges in three dimensions only for the case with \( n = 1 \) (Fisher, 1967). The intensity due to the non-thermodynamic fluctuations, which are not present in an \( n = 1 \) system, will always diverge at \( T_c \) with an exponent \( \bar{\gamma} \) which is considerably smaller than the exponent \( \gamma \) governing the behaviour of the one-phonon correlation function.

§3.2 Model Calculations of Spectral Functions

3.2.1 The models

For the calculation of the spectral functions \( S(\mathbf{k}, \omega) \) and \( \Gamma(\mathbf{k}, \omega) \) we turn in the spirit of the universality hypothesis to the simplest models exhibiting the minimum essential qualitative features, which may then serve as a basis for extending the analysis to include relevant perturbations. The appropriate model for a system close to its upper critical dimensionality is the time-dependent Ginzburg-Landau (TDGL) model introduced in 2.1.6. The equilibrium properties of this model are defined by the partition function

\[
Z = \int \exp \left[ -\mathcal{H}_o \{ \mathbf{Q} \} \right] \{ \mathbf{Q} \}
\]

where \( \mathcal{H}_o \) is the effective Hamiltonian of the LGW model defined in 1.3.1 which, for general values of \( n \) may be written in the form

\[
\mathcal{H}_o = \frac{1}{2} \sum_{\alpha=1}^{n} \omega^2(\mathbf{k})Q_\alpha(\mathbf{k})Q_\alpha(-\mathbf{k}) + \frac{U_0}{N} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \sum_{\alpha,\beta=1}^{n} Q_\alpha(\mathbf{k}_1)Q_\alpha(\mathbf{k}_2) \\
\times Q_\beta(\mathbf{k}_3)Q_\beta(\mathbf{k}_4) \delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4,0} \quad (3.10)
\]
with \( N \) the system volume and \( \delta \) a Kronecker function. Without loss of generality we define the origin of reciprocal space to coincide with the soft mode wavevector. From studies of the static properties (see Wilson and Kogut, 1974) it is known that for \( d \geq 4 \), the fixed point value of \( U_0 \) is zero, for which the Hamiltonian reduces to the quasi-harmonic approximation of van Hove, the conventional theory.

Sufficiently close to \( T_c \), the linear response of the critical fluctuations in the order parameter is known to be overdamped. This is certainly so for the case of primary interest, SrTiO\(_3\), throughout the temperature region in which the two-phonon dynamic central peak is observed. In this regime, it is appropriate to model the time evolution of the critical modes by the relaxational Langevin equation of motion introduced by Halperin et al. (1972)

\[
\frac{\partial Q_{\alpha}(\mathbf{k}, t)}{\partial t} = -\frac{1}{\gamma_0} \frac{\partial H}{\partial Q_{\alpha}(-\mathbf{k}, t)} + \zeta_{\alpha}(\mathbf{k}, t) .
\]

(3.11)

where \( \gamma_0 \) is a damping constant which we assume to be independent of temperature and wave vector, and \( \zeta_{\alpha}(\mathbf{k}, t) \) is a Gaussian white noise source. These terms simulate the effect of non-critical fluctuations on the time evolution of the near-critical modes. The amplitude of the noise term representing thermal perturbations away from equilibrium is related to the magnitude of the damping constant \( \gamma_0 \) which determines the time scale of the relaxation to equilibrium by the Einstein relation or fluctuation-dissipation theorem (see, e.g., Ma, 1976)

\[
<\zeta_{\alpha}(\mathbf{k}, t)\zeta_{\beta}(\mathbf{k}', t')> = \frac{2}{\gamma_0} \delta_{\alpha, \beta} \delta_{\mathbf{k}, -\mathbf{k}'} \delta(t-t').
\]

(3.12)

The phenomenological form of the kinetic equation may be shown to arise naturally by renormalisation group transformation of a plausible microscopic model of a system corresponding to the LGW Hamiltonian without
the inclusion of artificial damping terms (Hohenberg & Halperin, 1977) and to this extent the TDGL model may be justifiably deemed to be the correct description in both the microscopic and semi-microscopic approach.

The one-phonon spectral function, \( S(\vec{k}, \omega) \) is defined in the general case by

\[
2\pi \delta(\omega + \omega') \delta_{\vec{k}, -\vec{k}'} S(\vec{k}, \omega) = \langle Q_{\alpha}(\vec{k}, \omega) Q_{\beta}(\vec{k}', \omega') \rangle. \tag{3.13}
\]

This correlation function is, in perturbation theory, more simply calculated from the one-phonon response function, or propagator \( G(\vec{k}, \omega) \), by means of the fluctuation-dissipation theorem result

\[
S(\vec{k}, \omega) = \frac{2}{\omega} \text{Im} G(\vec{k}, \omega). \tag{3.14}
\]

The two-phonon correlation function, \( \Gamma(\vec{k}, \omega) \) has two components which may be defined by the relations

\[
2\pi \delta(\omega + \omega') \delta_{\vec{k}, -\vec{k}'} \Gamma_{T}(\vec{k}, \omega) = \langle \psi_{T}(\vec{k}, \omega) \psi_{T}(\vec{k}', \omega') \rangle_{c} \tag{3.15}
\]

and

\[
2\pi \delta(\omega + \omega') \delta_{\vec{k}, -\vec{k}'} \Gamma_{NT}(\vec{k}, \omega) = \langle \psi_{NT}(\vec{k}, \omega) \psi_{NT}(\vec{k}', \omega') \rangle_{c} \tag{3.16}
\]

where the subscripts \( T \) and \( NT \) again refer to the thermodynamic and non-thermodynamic fluctuations respectively and \( c \) denotes the corrected part of the thermal average. The thermodynamic fluctuations are described by the particular combination of order parameter components which possess the overall symmetry of the Hamiltonian, effectively the energy density

\[
\psi_{T}(\vec{k}, t) = \frac{1}{\sqrt{N}} \sum_{\vec{k}', \alpha=1}^{\Sigma} Q_{\alpha}(\vec{k}', t) Q_{\alpha}(\vec{k}', t) \tag{3.17}
\]
while the non-thermodynamic fluctuations are represented, for the $n > 1$ case, by the anti-symmetrised form

$$
\psi_{NT}(\vec{k},t) = \frac{1}{\sqrt{N}} \sum_{\vec{k}'} \left\{ Q_\alpha(\vec{k}',t)Q_\alpha(-\vec{k}'-\vec{k},t) - \frac{1}{n-1} \sum_{\beta \neq \alpha} Q_\beta(\vec{k}',t)Q_\beta(-\vec{k}'-\vec{k},t) \right\} .
$$

(3.18)

The frequency widths of the spectral functions $S(\vec{k} = 0, \omega)$ and $\Gamma(\vec{k} = 0, \omega)$ may be defined in a number of essentially equivalent ways (see, e.g. Hohenberg & Halperin, 1977). In the following section on the van Hove theory where the spectral functions are directly calculable, and for any spectral function which is known to exhibit a single (central) peak, it is most intuitively obvious to define the width $\omega(1)$ by the full width at half maximum of the spectral function. For calculational purposes in 3.2.3, it proves more convenient to define the width of the spectral function as the ratio of frequency-integrated spectral weight to the zero-frequency peak height, in which case we can define the widths to be

$$
\omega(1) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{S(\vec{k} = 0, \omega)}{S(\vec{k} = 0, \omega = 0)}
$$

and

$$
\omega_T = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\Gamma(\vec{k} = 0, \omega)}{\Gamma(\vec{k} = 0, \omega = 0)}
$$

(3.19)

(3.20)
3.2.2 The van Hove model calculation

The calculation of quantities in the modern theory of critical phenomena by expanding in the small parameter \( \varepsilon = d_c - d \), relies upon the possibility of calculating exactly the quantity of interest in the classical limit as \( d \to d_c \) or equivalently, when non-linear phonon coupling can be ignored and the probability distribution defined by the effective Hamiltonian is Gaussian. In this approximation the normal modes become independent and the correlation functions may be determined without recourse to any further approximations, (van Hove, 1954b).

(a) The one-phonon spectral function

In the van Hove approximation, the normal mode amplitudes have a correlation function given by

\[
\langle Q_\alpha(\mathbf{k}, t)Q_\beta(-\mathbf{k}, 0) \rangle = g(\mathbf{k}, t)
\]

\[
= \delta_{\alpha\beta} g(\mathbf{k}) \exp(-|t|/\tau(\mathbf{k})) \quad (3.21)
\]

where

\[
\delta(\mathbf{k}) = \omega^2(\mathbf{k}) = a(T-T_o) + ck^2
\]

and

\[
\tau^{-1}(\mathbf{k}) = \omega^2(\mathbf{k}) \gamma_o^{-1}
\]

where \( a \) and \( c \) are constants, and by suitable choice of energy scales we may set \( c \) equal to unity. The one-phonon spectral function for critical scattering is now given by the Fourier transform of this

\[
S(\mathbf{k} = 0, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ g(\mathbf{k} = 0, t) \exp(i\omega t)
\]

\[
= \frac{g(0)}{\pi} \frac{\tau(0)}{1 + (\omega \tau(0))^2} \quad (3.22)
\]
The spectrum consists of a single Lorentzian with a net (integrated) intensity given by \( g(0) \) which diverges as \((T - T_0)^{-1}\). This is in accordance with the scaling result eq. (3.4) and the mean field value for the susceptibility exponent \( \gamma = 1 \). The important feature for comparison with the two-phonon scattering is the width \( \omega^{(1)} \) which exhibits critical slowing down, and is given by

\[
\omega^{(1)} = \tau(0)^{-1} = a \gamma_0^{-1} (T - T_0)
\]

where the amplitude \( \gamma^{(1)} \) is non-universal as it retains the two system-specific constants \( a \) and \( \gamma_0 \), but the exponent (unity) is, in agreement with the predictions of mean field theory and the dynamic scaling hypothesis.

(b) The two-phonon spectral function

In the quasi harmonic Hamiltonian of the van Hove model, there is no coupling permitted between the different components of the order parameter. Because of this the two types of fluctuation, referred to as thermodynamic and non-thermodynamic in the previous section, give rise to only one form of two-phonon scattering function, the diagonal term

\[
\Gamma_D(\vec{k} = 0, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, \varepsilon \langle Q_\alpha(\vec{k}_2, t) Q_\alpha(-\vec{k}_1, t) Q_\alpha(\vec{k}_2, 0) Q_\alpha(-\vec{k}_2, 0) \rangle_c \times \exp i\omega t
\]

which due to the lack of mode-mode coupling, decouples to give

\[
\Gamma_D(\vec{k} = 0, \omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} dt \, \varepsilon \, g^2(\vec{k}_1, t) \exp i\omega t
\]
The behaviour of the integrated intensity is established by carrying out the integration over $\omega$ and then converting the summation over $k^+$ in eqn. (3.24) to an integral over a spherical Brillouin zone of radius $A$, which gives

$$I \propto \frac{d}{r_o^2 - 2} \int_{A^2/r_o}^{\infty} \frac{k^{d-1}dk}{(1 + k^2)^2}$$

(3.25)

where $r_o = a(T - T_0)$. Since the wave vector cutoff in the integral $A^2/r_o$ goes to infinity close to $T_C^2$, and for $d < 4$ the integral is convergent in this limit, this expansion gives the exponent for the divergence of the intensity as $\frac{1}{2}(4 - d)$ which demonstrates the dimensionality-dependence of critical exponents even in the simple model, and which emphasises the importance of the critical dimensionality $d_c = 4$ above which the two-phonon correlation function does not diverge. This corresponds to the fact that the thermodynamic fluctuations are expected to show the behaviour of the specific heat which does not diverge at $T_C$ in mean field theory which holds in the classical regime beyond four dimensions.

The spectral functions obtained from this model are shown in Fig. 3.1 and the widths and exponents are tabulated in Table 3.1. The spectral functions are listed in Appendix 1.

The width exponent $\chi$ defined by the relation

$$\omega^{(2)} = \Omega^{(2)} r^\chi$$

(3.26)

is seen to have the universal value unity irrespective of the system dimensionality. The two-phonon spectral function is a single peak centred on zero energy but with considerable weight in the high-frequency tail. The width of the two-phonon scattering is larger than that of the one-
Figure 3.1: Spectral functions for the van Hove model.

The spectral functions calculated for the van Hove model and listed in Appendix 1 are shown, normalised to unity at zero frequency. The frequency is measured in units of the one-phonon width, $\Omega = \frac{2\Gamma_0}{\gamma_0} \omega$ (see Appendix 1).

(a) The one-phonon spectral function $S(\tilde{k}_g, \omega)$

(b) The two-phonon spectral function $\Gamma(0, \omega)$ for the two-dimensional model.

(c) The two-phonon spectral function $\Gamma(0, \omega)$ for the three-dimensional model.
TABLE 1: The numerical values of the exponents characterising the two-phonon intensity divergence, \( \alpha \), and the critical narrowing, \( x \), together with the ratio of one- and two-phonon widths (f.w.h.m.) for the van Hove model.

<table>
<thead>
<tr>
<th>( d )</th>
<th>( \alpha )</th>
<th>( x )</th>
<th>( \omega_{\frac{1}{2}}^{(1)}/\omega_{\frac{1}{2}}^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>1</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{1}{4} )</td>
<td>1</td>
<td>0.22</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0.31</td>
</tr>
</tbody>
</table>
phonon scattering to which it is related by at most one order of magnitude.

We now return to the TDGL model to establish systematically the deviations from this oversimplified behaviour.

3.2.3 The time-dependent Ginzburg-Landau calculation

In the simplified van Hove model an exact calculation of the spectral functions was possible. In order to determine the frequency-integrated and zero-frequency spectral functions for the full TDGL model it is necessary to use perturbation expansion techniques. As these methods are sufficiently well described elsewhere (see e.g. Ma, 1976b) only an outline of the calculations will be given here.

The method employed, although not explicitly employing the renormalisation group formalism, rests heavily on the known RG behaviour of the TDGL model. We assume that the correlation functions which we require have the scaling forms suggested in 3.1.4, and then by expanding the correlation functions as power series in $\epsilon = d_v - d$, and matching the powers of reduced temperature appearing in the low-order terms in the expansion, we extract the values of the associated exponent and amplitude.

For the evaluation of certain expressions which arise in the perturbation theory it is convenient to introduce a smooth cut-off to the wave vector integrals by writing the phonon frequency in the form

$$\omega^2(k) = r_0 + k^2 + k^4$$

(3.27)

instead of the form used in eq. (1.21). To prevent spurious divergences in the perturbation series at the mean field transition temperature $T_0$ instead of the true transition temperature $T_c$, we carry out the usual 'mass renormalisation' (Wilson, 1972) of the theory by
replacing the frequency $\omega(k)$ by the renormalised frequency $\tilde{\omega}(k)$, and adding to the Hamiltonian the counter term

$$\Delta \mathcal{H}(\{Q\}) = \frac{1}{2} \sum_k \sum_{\alpha=1}^n \left[ \omega^2(k) - \tilde{\omega}^2(k) \right] Q_\alpha(k) Q_\alpha(-k)$$

which is treated as an additional perturbation. The equation of motion may now be written

$$Q_\alpha(k,\omega) = Q_\alpha^0(k,\omega) - G_\alpha(k,\omega) \left( \sum_{\alpha=1}^n \sum_{\beta=1}^n \int_0^\infty \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} Q_\alpha(k_1,\omega_1) Q_\beta(k_2,\omega_2) \right)$$

$$\times Q_\beta(k-k_1-k_2,\omega - \omega_1 - \omega_2)$$

$$\quad (3.29)$$

where

$$Q_\alpha^0(k,\omega) \equiv \gamma_{\alpha} G_\alpha(k,\omega)$$

$$G^{-1}_\alpha(k,\omega) \equiv \omega^2(k) - i\gamma_{\alpha}\omega.$$  

$$Q_\alpha^0(k,\omega) \quad \text{and} \quad G_\alpha^0(k,\omega) \quad \text{are respectively the normal mode amplitude and the linear response functions of the quasi harmonic model. The renormalised frequencies, } \tilde{\omega}^2(k) \quad \text{are chosen to fulfill the requirement that }$$

$$\tilde{\omega}^{-2}(k=0) \quad \text{is equal to the exact long-wavelength static susceptibility, so that}$$

$$G^{-1}(k=0,\omega=0) = \frac{\omega^2(k=0)}{r}.$$  

$$\quad (3.30)$$

The one-phonon self energy, $\Sigma(k,\omega)$, defined by the relation

$$G^{-1}(k,\omega) = G^{-1}_\alpha(k,\omega) + \Sigma(k,\omega)$$

$$\quad (3.31)$$

must then satisfy the self-consistency relation

$$\Sigma(k=0,\omega=0) = 0.$$  

$$\quad (3.32)$$
From this condition the inverse susceptibility $\chi$ is related to the temperature and hence to the unrenormalised frequency $\omega_0$—which is now removed from the theory by subtracting out from the perturbation theory graphs the $\Sigma(k=0, \omega=0)$ part of any self-energy insertion as described in Wallace (1976).

The perturbation series for this model is generated by iteratively solving the equation of motion (3.29) to obtain expressions for $Q(k, \omega)$ in powers of the coupling constant $U_0$, and the Langevin noise sources $\zeta$. The desired correlation functions are obtained by substituting the expressions for $Q(k, \omega)$ into the defining equations (3.13) to (3.18) and then taking thermal averages by substituting from equation (3.29c) for all pairwise contractions of the noise sources. Summations in reciprocal space are replaced by integrations which are evaluated in $\epsilon = 4 - d$ dimensions. This procedure ultimately leads to expressions for $S(k, \omega)$ and $\Gamma(k, \omega)$ in the form of a double power series in $U_0$ and $\ln \chi$. To ensure that the series exponentiates to give the correct scaling behaviour we set the coupling constant $U_0$ equal to the special value $U_{oc}$ which eliminates the leading corrections to scaling, or 'slow transients' as described by Wilson (1972) and also in the context of this model by Halperin et al. (1974). For the soft cut-off implied by our choice of dispersion relation (eqn. (3.27)) the value of $U_{oc}$ is known from static renormalisation group studies to be (e.g. Wallace, 1976)

$$U = Kd U_{oc} = \frac{\epsilon}{4(n+8)} (1 - \frac{n^2 - 2n - 20}{2(n + 8)^2} \epsilon) + O(\epsilon^3) \quad (3.33)$$

where $Kd$ is the usual constant arising from the angular integrals (eq. (2.6)).

The ratio of width amplitudes $\Omega^{(1)}/\Omega^{(2)}$ is, as we shall see, of order $\epsilon$. In order to calculate this to second order in $\epsilon$ each of the
Figure 3.2: Diagrammatic representation of processes contributing to the two-phonon spectral function.

Diagrams (a) to (e) show the contributions to $\Gamma(\vec{k}, \omega)$. Diagram (f) shows the leading contribution to the one-phonon self energy $\Sigma(\vec{k}, \omega)$. The directed lines are associated with the unperturbed propagator $G_0(\vec{k}, \omega)$, the lines carrying noise vertices (open circles) are associated with the unperturbed correlation functions $S_0(\vec{k}, \omega)$. 
width amplitudes must be calculated to two orders in $\varepsilon$.

The one-phonon spectral function is most easily calculated by a direct
determination of $\Sigma(\mathbf{k}, \omega)$ and the use of eqns. (3.14) and (3.31), but
since the first wave-vector dependent contribution to $\Sigma(\mathbf{k}, \omega)$ is of order
$\varepsilon^2$, and the width amplitude of the one-phonon scattering, $\Omega^{(1)}$, is of order
unity, the one-phonon scattering function $S(\mathbf{k}, \omega)$ is required only in the
zeroth order, a simple repetition of the problem for the uncoupled model.

The calculation of two-phonon functions is considerably more com-
plicated as the widths $\Omega^{(2)}_T$ and $\Omega^{(2)}_{NT}$ are both of order $\frac{1}{\varepsilon}$ due to
the logarithmic divergences of the integrated intensities in four
dimensions. Because of the absence of a term independent of $\varepsilon$, it is
necessary to retain in the calculation of the two-phonon correlation
functions, all of the one- and two-vertex graphs which are generated
by the perturbation expansions. The graphical representation of these
terms are depicted in Fig. 3.2. Fig. 3.2a represents the zeroth order
spectral function of the unperturbed system, the calculation of which is
straightforward. The internal frequency integration may be carried out
by contour integration reducing the expression to wave vector summa-
tions similar to those encountered in static calculations. The
one- and two-vertex processes shown in Fig. 3.2b and c are also
straightforward to evaluate for the $\mathbf{k} = 0$ spectral functions, both
for their zero frequency (dynamic) contributions, and for their
frequency-integrated (static) contributions. The evaluation of con-
tributions from the final two sets of diagrams 3.2d and 3.2e is more
difficult. The static expressions have been evaluated to the appro-
priate accuracy, that is ignoring terms of less than order $\ln r$, by
Nickel (1974) and are tabulated in Wallace (1976). The dynamic cal-
culation is most expediently achieved to the same accuracy by expressing
the contributions in terms of the leading wave-vector and frequency-dependent contribution to the self energy \( \Sigma^{(2)}(\mathbf{k}, \omega) \), depicted in Fig. 3.2(f), and its derivatives with respect to the mass, \( r \) and the external frequency, \( \omega \). The terms arising from these expressions of the form \( \frac{\partial \Sigma}{\partial r} \) or \( \frac{\partial^2 \Sigma}{\partial r^2} \) are then deduced from the known homogeneity properties of the self energy by making use of the dynamic scaling relation

\[
G^{-1}(r, \mathbf{k}, \omega) = r^{\frac{z}{d}} \left( \frac{k^2}{r^{2z/y}}, \frac{\omega}{r^{2z/y}} \right) \tag{3.34}
\]

where the dynamic critical exponent \( z \) is known from the renormalisation group study of Halperin et al. (1974) to be

\[
z = 2 + c \eta \tag{3.35}
\]

with \( c \) a constant of order 1 (for \( d = 4 \), \( c = 0.726 \)) and \( \eta = 2 - \gamma/v \) is of order \( \epsilon^2 \).

### 3.2.4 Results for the TDGL model

a) The one-phonon spectral function

In this section the results of the calculations outlined in 3.2.3 are briefly summarised.

The self-consistency condition given by equation (3.32) may be solved to give the usual result relating the inverse susceptibility \( r \) to the reduced temperature \( t \) in the form

\[
r = C_0 t^\gamma \tag{3.36}
\]

where \( C_0 \) is a non-universal parameter. The one-phonon spectral function is given to the desired order by the Lorentzian function
The relevant properties of the one-phonon correlation function may now be written simply as

\[
\frac{1}{2\pi} \int dw \ S(k=0, \omega) = C_0^{-1} [ 1 + O(\epsilon^2) ] \ t^{-\gamma} \tag{3.38}
\]

and

\[
S(k=0, \omega=0) = 2\gamma_0 C_0^{-1} \omega^2 \ [ 1 + O(\epsilon^2) ] \ t^{-\gamma} \tag{3.39}
\]

The characteristic width of the one-phonon correlation function follows from eqn. (3.19) as

\[
\omega^{(1)} = (C_0^{z\nu}/2\gamma_0) [ 1 + O(\epsilon^2) ] t^{z\nu} \tag{3.40}
\]

which is consistent with the form expected from the definition following eq. (3.4) with

\[
\Omega^{(1)} = C_0^{z\nu}/2\gamma_0 [ 1 + O(\epsilon^2) ] \tag{3.41}
\]

but the exponent, unlike the classical value of unity obtained for \( x \) in the van Hove model, now takes the non-classical value

\[
z\nu = 1 + \frac{n+2}{2(n+8)} \epsilon \tag{3.42}
\]

b) The two-phonon spectral function

The divergent contributions to the frequency-integrated correlation function, and to the zero frequency peak \( \Gamma (k=0, \omega=0) \) from all the diagrams up to order \( \epsilon^2 \) are given in Table 2. By applying the usual power matching techniques we find that the integrated intensities have the form, for the thermodynamic fluctuations

\[
\frac{1}{2\pi} \int_{-\infty}^{\infty} dw \ \Gamma_T (k=0, \omega=0) = \frac{nKd}{\epsilon} C_0^{-\alpha/\gamma} \left[ \frac{2(n+8)}{4-n} \right] \ t^{-\alpha} + \text{const.} \tag{3.43}
\]
and for the non-thermodynamic fluctuations

\[
\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \Gamma_{NT}(k=0, \omega=0) = \frac{nKd}{\epsilon(n-1)} C_0^{-\gamma/\gamma} \left[ \frac{2(n+8)}{n+4} - \frac{n^2 + 10n - 44}{(n+8)(n+4)} \epsilon + O(\epsilon^2) \right] t^{-\gamma} + \text{const.}
\]

where \( \alpha \) is the specific heat exponent

\[
\alpha = \frac{4-n}{2(n+8)} \epsilon - \frac{(n+2)^2(n+8)}{4(n+8)^3} \epsilon^2 + O(\epsilon^3)
\]

and \( \gamma \) is the analogous exponent governing the divergence of thermodynamic coordinates defined in eq. (3.7). These results are consistent with the expectations from general scaling arguments discussed in Bruce and Cowley (1980) and 3.1.4.

The zero frequency spectral functions were also found to exponentiate correctly to pure power laws in the critical region, the forms which are obtained are

\[
\Gamma_T(k=0, \omega=0) = \frac{nKd\gamma_0}{2} C_0^{-\alpha+\gamma_\nu}/\gamma \left[ 1 + \frac{3n}{2(n+8)} \epsilon + O(\epsilon^2) \right] \times t^{-\alpha+2\gamma_\nu}
\]

and

\[
\Gamma_{NT}(k=0, \omega=0) = \frac{nKd\gamma_0}{2(n-1)} C_0^{-\gamma_\nu+\gamma_\nu}/\gamma \left[ 1 + \frac{n}{2(n+8)} \epsilon + O(\epsilon^2) \right] \times t^{-\gamma_\nu+2\gamma_\nu}.
\]

As with the frequency-integrated spectral functions, the values of the exponents obtained agree in both cases with the predictions of general scaling arguments. By combining equations (3.43) to (3.47) using the definition of characteristic width given in eq. (3.20), we obtain the characteristic widths of the two-phonon spectral functions in the form

\[
\omega_T^{(2)} = \Omega_T^{(2)} t^{z\nu}
\]

\[
\omega_{NT}^{(2)} = \Omega_{NT}^{(2)} t^{z\nu}
\]

(3.48)
<table>
<thead>
<tr>
<th>Diagram</th>
<th>Combinatorial Factor</th>
<th>Integration factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>zero-frequency</td>
</tr>
<tr>
<td>T</td>
<td>NT</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>$2n$</td>
<td>$\frac{2n}{n-1}$</td>
</tr>
<tr>
<td>b</td>
<td>$8n(n+2)$</td>
<td>$\frac{16n}{n-1}$</td>
</tr>
<tr>
<td>c</td>
<td>$32n(n+2)^2$</td>
<td>$\frac{128n}{n-1}$</td>
</tr>
<tr>
<td>d</td>
<td>$192n(n+2)$</td>
<td>$\frac{64n(n+6)}{n-1}$</td>
</tr>
<tr>
<td>e</td>
<td>$128n(n+2)$</td>
<td>$\frac{128n(n+2)}{n-1}$</td>
</tr>
</tbody>
</table>

TABLE 2: Terms contributing to the perturbation expansions of the zero-frequency and integrated two-phonon correlation functions $\Gamma_T$ and $\Gamma_{NT}$. The contribution made by each of the diagrams (a) to (e) in Fig. 3.2 is given by the product of the appropriate (T or NT) combinatorial factor and the appropriate (zero-frequency or frequency-integrated) integration factor.
with
\[
\Omega_T^{(2)} = \frac{4C_0 z^{\nu/\gamma}}{\gamma_0} \frac{(n+8)}{(n+4)} \left( 1 + \frac{(n+2)(13n+44) \varepsilon}{(n+8)^2(4-n)} + O(\varepsilon^2) \right)
\]  
and
\[
\Omega_{NT}^{(2)} = \frac{4C_0 z^{\nu/\gamma}}{\gamma_0} \frac{(n+8)}{(n+4)} \left( 1 + \frac{(22-n)(n+4) \varepsilon}{(n+8)^2} + O(\varepsilon^2) \right)
\]  

These widths, like the one-phonon width \( \Omega^{(1)} \) given in eqn. (3.41) are non-universal, depending explicitly upon the system-specific parameters, \( C_0 \) which determines the width of the critical region, and \( \gamma_0 \) which determines the time-scale of the order parameter relaxation.

c) The amplitude ratio \( \Omega^{(1)}/\Omega^{(2)} \)

Although the three amplitudes defined by equations (3.41), (3.49) and (3.50) are non-universal they each depend on the system parameters in the same manner, and therefore the ratio of any two amplitudes will form a universal quantity. The two ratios which are of experimental relevance are the ratios
\[
\frac{\Omega^{(1)}}{\Omega_T^{(2)}} = \frac{\alpha}{4\gamma}
\]  
and
\[
\frac{\Omega^{(1)}}{\Omega_{NT}^{(2)}} = \frac{\gamma}{4\gamma}
\]

which may be expressed in terms of the static exponents \( \alpha, \gamma \) and \( \tilde{\gamma} \) in the manner indicated. These last expressions involving only the static exponents are rigorously proved only to order \( \varepsilon^2 \) by this calculation although it is tempting to speculate that the equality may hold for all orders. However, this can only be checked under rather
special circumstances, as is the case for the spherical model discussed in 3.4.2.

The numerical values of the amplitude ratios and critical exponents for systems of experimental interest, are displayed in Table 3.

§3.3 Discussion

It is appropriate at this point, having obtained the results for the TDGL model of the simplest structural phase transition, to discuss the relevance to, and the implications for experiment of these results, before considering in the succeeding sections of this chapter the extensions of the model to incorporate the additional features of real systems.

The calculations of §3.2 extend the previous studies of the TDGL model (Halperin et al., 1972, 1974, 1976; Murata, 1976b, Brezin and de Dominicis, 1975) which have concentrated largely on the determination of the dynamic exponent $z$, and the verification of the dynamic scaling hypothesis. A similar study by Murata (1976b) showed that the amplitudes characterising the manner in which the widths of the correlation functions $S(k, \omega)$ and $\Gamma(k, \omega)$ depend on $k$ at $t = 0$ also form a universal ratio which is of order $\varepsilon$, but unlike the case studied here these amplitudes are not directly accessible to experiment.

As remarked in §3.1 the two-phonon scattering, or Raman tensor has the two linearly independent components which were calculated in the previous section. It can be shown that there is no light scattering experimental geometry which will sample only one of these two components, and therefore the correlations with the strongest critical divergence will dominate any scattering experiment. With the exception of the scalar ($n = 1$) case, where the non-thermodynamic fluctuation coordinate
<table>
<thead>
<tr>
<th></th>
<th>n = 1</th>
<th>n = 2</th>
<th>n = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exponent</strong></td>
<td>$\alpha = 0.125^{(a)}$</td>
<td>$\gamma = 0.300$</td>
<td>$\gamma = 0.340$</td>
</tr>
<tr>
<td><strong>Amplitude</strong></td>
<td>$\frac{\Omega^{(1)}}{\Omega^{(2)}} = 0.025^{(b)}$</td>
<td>$\frac{\Omega^{(1)}}{\Omega^{(2)}} = 0.060$</td>
<td>$\frac{\Omega^{(1)}}{\Omega^{(2)}} = 0.067$</td>
</tr>
<tr>
<td><strong>Ratio</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 3:** The numerical values of the exponent characterising the two-phonon intensity divergence, and of the one- and two-phonon widths, in three dimensions. The result (a) is taken from series expansions (see e.g. Stanley, 1971); the result (b) exploits series values for $\alpha$ and $\gamma$ together with the $\epsilon$-expansion result (3.52); the remaining numbers follow directly from the second-order $\epsilon$ expansions reported in the text with $\epsilon = 1$. 
\( \gamma_{NT} \) vanishes identically, the non-thermodynamic correlation function \( \Gamma_{NT}(k=0, \omega) \) will always display a stronger divergence than the thermodynamic correlation function \( \Gamma_T(k=0, \omega) \). For the \( n = 2 \) and \( n = 3 \) cases the two phonon critical scattering should diverge with an exponent \( \gamma \) which is large in comparison with typical specific heat exponents, but this divergence will be much weaker than the divergence of the one-phonon quasielastic scattering which is characterised by the exponent \( \gamma \). In the \( n = 1 \) case, the two-phonon critical scattering will display the much weaker singularity of the specific heat. In all cases it is possible to assert that the occurrence of divergent quasi-elastic scattering in the one-phonon correlation function implies the existence of a divergent component in the two-phonon scattering, the width of which is related to the width of the one-phonon scattering by a universal amplitude ratio, \( \Omega^{(1)}/\Omega^{(2)} \), which in all cases implies that the two-phonon scattering should be wider by approximately an order of magnitude than the associated one-phonon scattering.

In applying these results to the experimental observations for \( \text{SrTiO}_3 \), it is apparent that the three time-scales noted in \( \S 3.1 \) cannot be related by the above ratios. This indicates that the dynamic central peak observed in the Raman scattering experiment of Lyons and Fleury (1977) is not the two-phonon analogue of either of the features observed in the neutron scattering experiments. The reason for this discrepancy between the theory and the experimental results is not readily apparent but it may arise from either the interpretation of the experimental results, or from the simplifications embodied in the TDGL model.

In the analysis of the experimental results, the scattering from the soft mode observed in the neutron scattering experiments is the only feature whose origin is not open to question. As the width of the peak observed in the light scattering experiments is considerably less than
that of the soft mode, there must be some doubt as to whether its origin
is intrinsic, however the existence of a corresponding feature in the
one-phonon scattering with a width implied by the ratio \( \Omega^{(1)}/\Omega^{(2)} \) of
the order of \( 10^9 \text{Hz} \) is not incompatible with the results of the neutron
studies as such a feature would be obscured by the strong, probably
defect-controlled central peak. Some support for the existence of such
an intrinsic feature may be drawn from the sample-independence of the
central peak amplitude \( \delta^2_0(T) \) close to \( T_c \) (Currat et al. 1978) which
indicates that close to \( T_c \), intrinsic effects dominate the low-energy
scattering. In view of the dubious origin of the light-scattering peak
it is not certain that it represents a genuine two-phonon scattering
process, therefore its origins may lie in the persistence into the
high temperature phase of one of the processes properly described in
the next chapter, which are symmetry-forbidden above \( T_c \), but which
were suggested by, for example, Feder (1971), to be capable of causing
central peaks by one-phonon processes, due to the symmetry-breaking
effect of short-range order close to, but above, \( T_c \).

The development of the model in §3.2 rested upon certain assumptions
which have the effect of restricting the applicability of the results to
a considerable extent. The experimental results have been discussed at
this stage in the development of this topic on the assumption that the under-
lying simplifications do not change the universality class of the model
and invalidate the above comparison. In the remaining sections of this
chapter the possible extensions and modifications to the TDGL model will
be discussed, and, where possible, their effects will be shown to be at
least asymptotically irrelevant at \( T_c \). It will be seen that only in
the special case where \( n = 1 \) are the results of this section liable
to be seriously affected by the lack of explicit incorporation of defects,
conservation laws, or anisotropy in the model.
§3.4 Extensions to the TDGL Model

3.4.1 The sharp cut-off formulation; a test for universality

In the development of the LGW models for equilibrium critical phenomena, the evaluation of Feynman graphs arising in the perturbation expansions beyond first order is a complicated and specialised task. Two quite different procedures have been used to remove the ultra-violet divergences which would arise if the momentum-space integrals encountered in the perturbation series were not restricted by some high-momentum cut-off. In the problem of statistical mechanics on a lattice, there is a natural cut-off wave-vector, the Brillouin zone boundary, and in the more straightforward form of regularisation this natural cut-off is reflected in the restriction of wave-vector summations to run over only wave-vectors of magnitude less than some final value, $A$. This is the procedure which was described in 2.1.2 when perturbation theory in its reciprocal space formalism was described. The procedure adopted for convenience in 3.2.2 was, instead of introducing a cut-off at finite $\vec{k}$, when converting reciprocal space summations to integrations, an extra $k_n^2$ term was included in the one-phonon propagator, the so-called smooth cut-off approach, which has the effect of gradually reducing the importance of the non-critical modes. Although the two types of model lead to different contributions from the perturbation series diagrams, the cut-off procedure adopted is of importance only as a calculational device and it cannot therefore alter the universality class of the model. It is a useful check on the universality of a quantity such as the amplitude ratios, $\Omega^{(1)}/\Omega^{(2)}$ that they are not affected by the cut-off procedure.

In the sharp cut-off case, the frequency of the soft mode is given by

$$\omega^2(\vec{k}) = r_o + k^2$$

and in evaluating the wave-vector summations implied by (3.29) we make the
substitution

\[ \frac{1}{N} \sum_{k} \rightarrow (\frac{a}{2\pi})^{d} \int_{|k|<\Lambda} d^{d}k \]  

(3.54)

The calculations outlined in 3.2.3 were repeated for this altered model. The differences obtained for the non-universal quantities may be illustrated by the behaviour of the zero-frequency two-phonon spectral functions which are found to have the forms

\[ r^{T}(k=0, \omega=0) = \frac{nKd\gamma_{0}}{2} c_{0}^{-(\alpha+z\nu)/\gamma} \left[ 1 - \frac{4-n}{2(n+8)} \varepsilon + O(\varepsilon^2) \right] t^{-(\alpha+z\nu)} \]  

(3.55)

\[ r^{NT}(k=0, \omega=0) = \frac{nKd\gamma_{0}}{2(n-1)} c_{0}^{-(\gamma+z\nu)/\gamma} \left[ 1 - \frac{n+4}{2(n+8)} \varepsilon + O(\varepsilon^2) \right] t^{-(\gamma+z\nu)} \]  

(3.56)

which may be compared to the same quantities arising in the smooth cut-off model given by eqns. (3.46) and (3.47). Similar alterations are to be found in the expressions for the integrated intensities and these produce an overall cancellation with the differences noted above, so that one finds that the widths are given by equations (3.41), (3.49) and (3.50) and the values of the amplitude ratios ((3.51) and (3.52)) are unaffected.

3.4.2 Higher order terms: The spherical model limit

The Feynman graph expansion technique used in §3.2 has found widespread application in physics, particularly in recent years as a vehicle for constructing \( \varepsilon \) expansions. It is ironic that the renormalisation group apparatus which was developed to avoid the necessity of summing a perturbation series which was known to be divergent in the critical regime,
depends for its realisation in three dimensions upon the summation of another series, namely the $\varepsilon$ expansion, which is widely believed to be asymptotic (Wilson, 1972). Whether or not the $\varepsilon$ expansions give a convergent series for the case $\varepsilon = 1$ which is of predominant interest, it cannot be denied that the low-order truncation of the series utilised in all calculations gives at best a very crude method of extrapolating to three dimensions. The folklore of $\varepsilon$-expansion techniques suggests, basing its case largely on the success of the initial calculations of critical exponents to order $\varepsilon^2$ (see, e.g. Wilson & Kogut, 1974), that terms of order $\varepsilon^3$ and higher do not improve the results of such extrapolations, although it cannot suggest a basis for this assumption. An alternative to the $\varepsilon$ expansion, introduced by Brezin and Wallace (1973) and by Ma (1973a,b), is the expansion of quantities as a power series in $\frac{1}{n}$. This technique exploits the fact that the coupling constant $U_0$ in the TDGL model is known to have a fixed point value of order $\frac{1}{n}$ which reduces to 0 in the limit as $n \rightarrow \infty$. In this limit, the perturbation series is exactly summable to infinite orders, and the integrals involved may be evaluated exactly in $d$ dimensions so that, at least in the $n \sim \infty$ limit, there are no unknown dimensionality-dependent factors.

The use of the $\frac{1}{n}$ expansion in practice to calculate critical exponents has been disappointing, therefore it was felt to be useful to compare the $n \sim \infty$ limit with the results of the $\varepsilon$ expansion calculation but not to repeat the calculation for small values of $n$.

In the $n \rightarrow \infty$ limit, it is known that the specific heat does not diverge for the isotopic LGW model (see, e.g. Fisher, 1974). In this regime it is therefore necessary only to consider the behaviour of the non-thermodynamic fluctuations.

The one-phonon scattering is again required only in the zeroth order approximation, described in 3.2.2.
The frequency-integrated (static) spectral function for the non-thermodynamic fluctuations is given by

\[
\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \Gamma_{NT}(k=0, \omega) = NJ r^{-\varepsilon/2}
\] (3.57)

where

\[
J = \frac{1}{2} K_d \pi (\frac{d}{2} - 1) \csc(\frac{d}{2} - 1)
\]

and the zero-frequency spectral function is given by

\[
\Gamma_{NT}^{(2)}(k=0, \omega=0) = \frac{NeK_Y_0}{2} r^{-1-\varepsilon/2}
\] (3.58)

for which the width ratios may be calculated as

\[
\Omega_{NT}^{(1)} / \Omega_{NT}^{(2)} = \frac{\varepsilon}{8} + O(\frac{1}{n})
\] (3.59)

which agrees with the result of the \( \varepsilon \) expansion in the limit \( n \to \infty \).

This calculation does not show, of course, that terms of under \( \varepsilon^3 \) are not important at realistic values of \( n \), but it does show that any such terms must be of order \( \frac{1}{n} \) at least. As the actual expansion parameter, the four phonon coupling constant is of the form \( \frac{1}{n+8} \) rather than \( \frac{1}{n} \) (see Suzuki, 1973), this offers at least some justification for the assumption that their effect will be small, and it shows that the result

\[
\Omega_{NT}^{(1)} / \Omega_{NT}^{(2)} = \frac{\gamma}{4Y}
\] (3.60)

is valid to all orders in \( \varepsilon \) at least for the case \( n \to \infty \).

3.4.3 Extra terms in the Hamiltonian \( H_0 \)

On the introduction of the LGW Hamiltonian it was stressed that it is the simplest effective Hamiltonian with the necessary features to simulate the behaviour of a system undergoing a structural phase transition. The isotropy in the \( n \)-component of order parameter space, the
wave-vector independence of the coupling constant $U_0$, and the neglect of interaction terms higher than fourth order are all essentially unphysical and it is in principle necessary to consider the effect of each of these, if only to establish their irrelevance in the sense of 2.1.5.

From the renormalisation group studies of Halperin et al. (1974, 1976), it is known that although the parameter space of the LGW Hamiltonian has to be enlarged to include the kinetic coefficient $\gamma_0$ in a study of the dynamic properties, the RG recursion relations for static and dynamic parameters decouple, implying that a fixed point for the static RG will remain a fixed point for the dynamic RG. Its stability with respect to perturbations in the LGW Hamiltonian can therefore be discussed purely in terms of the well understood static renormalisation group studies of these perturbations.

Of the perturbations mentioned above which are all, in principle, present in the case of a perovskite, the most important perturbations, and the most difficult to evaluate exactly are those of cubic symmetry. These arise from terms in the Hamiltonian of the form

$$\Delta H_v = v \sum_{\alpha=1}^{n} \sum_{k} Q_{\alpha}(\mathbf{k}_1)Q_{\alpha}(\mathbf{k}_2)Q_{\alpha}(\mathbf{k}_3)Q_{\alpha}(-\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3)$$

(3.61)

and from anisotropic terms in the dispersion relation which lead to a term in the Hamiltonian of the form

$$\Delta H_f = f \sum_{\alpha=1}^{n} \sum_{k} k^2 \mathbf{Q}_\alpha(\mathbf{k})Q_{\alpha}(-\mathbf{k})$$

(3.62)

The former of these perturbations is, in renormalisation group language, irrelevant for $n < 3.13$ (see Cowley and Bruce, 1973; Aharony, 1973a; and Ketley and Wallace, 1973) and its neglect in our calculation is
justifiable as the fixed point value of $v$ to which we should have to
set the coupling constant to obtain the pure scaling behaviour is zero.
The latter perturbation is also irrelevant, but only very weakly irre-
levant, and it has been suggested (Bruce, 1974; Natterman and Trimper
1976) that effects due to perturbations of this type will be observable
through much of the critical region. The calculation of these effects
in the static critical behaviour has been performed (to $O(\varepsilon)$) by
Natterman and Trimper, who show that the inclusion of these
anisotropic terms leads to critical exponents corresponding to the iso-
tropic exponents obtained for a slightly larger (non-integral) value of
$n$. As these effects are small, and as the quantity $\Omega_{NT}^{(2)}$ shows no
pathological behaviour for $n \lesssim 4$ it seems reasonable to assume that
these perturbations may also be neglected. In the case of $KMnF_3$ it
has been suggested that this cubic perturbation is responsible for the
transition being first order, in which case presumably, their neglect
can no longer be justified.

The other perturbations mentioned above can be more quickly dis-
missed. It is established that the next higher-order phonon-phonon
coupling constant to become relevant in the LGW model is the six-phonon
term, which is a relevant perturbation only for $d < 3$. It is also
possible to show that any wave-vector dependent component which appears
in the coupling constant $U_0$ will be irrelevant for $d \geq 3$ or even
less depending on its symmetry (see e.g. Ma, 1976b).

It should finally be commented that these perturbations which become
marginal at $d = 3$ may introduce logarithmic corrections to the critical
behaviour but these will be experimentally unobservable.
3.4.4 The role of defects

In the analysis of the TDGL model pursued in previous sections, the order parameter dynamics have been assumed to be controlled by the equation of motion (3.11), which features only a single time scale set by the kinetic coefficient \( \gamma_0 \). The role of defects, impurities and dislocations, is built into the theory only through their contribution to the relaxation processes affecting the order parameter fluctuations, thus although the van Hove function has structure in two different frequency regimes corresponding to the central peak and to the soft phonon, the TDGL model is capable of reproducing only one of these features. In applying the results of the calculation to both the ratio of the width of the central peak, and that of the soft phonon to the width of the light scattering peak, we have implicitly assumed that the two processes contributing over different frequency ranges can be treated independently. While it is consistent with the underlying assumptions of the Langevin formalism, that the 'fast' processes can be absorbed into the stochastic variables, to treat the very narrow (slow) central peak without explicit consideration of the effect of the faster overdamped phonon processes, it is not always the case that the presence of a slow central peak process cannot influence the critical properties of a much faster phonon process.

The early suggestions (Folk and Schwabl, 1974; Axe, 1974) that the central peak in SrTiO₃ is controlled by slowly-relaxing defects is strongly supported by the experiments of Hastings et al. (1978) who showed, using samples of hydrogen-reduced SrTiO₃, that the central peak intensity varied with the defect concentration. In order to assess the effect on the order parameter dynamics of slowly relaxing defects we note that if the defects have a relaxation time set by the central peak
width, as suggested by the theory of Halperin and Varma (1976), then this will be at least four orders of magnitude slower than the relaxation times of the intrinsic fluctuations, set by the width of the soft mode. The difference between these time-scales is sufficient to allow the defects to be treated as static perturbations over the period of several phonon lifetimes, for which we must consider the phonon dynamics.

The Halperin and Varma (HV) model in which the defects are coupled to the square of the order parameter has been studied by static RG methods by Lubensky (1975) and by Khmelnitsky (1975). In these studies the defects are simulated by a random field which takes the place of the harmonic frequency, $r_0$, in the effective Hamiltonian. The above authors conclude that for models for which the specific heat does not diverge ($n > 1$ in $d = 3$), the fixed point of the pure system remains stable against the perturbation of the defect field, thus the static critical properties are unaffected by the presence of static (or quenched) defects (see e.g. Ma, 1976b). From the decoupling of the recursion relations for static and dynamic quantities in the pure model (Halperin et al., 1974) we may infer that the dynamical critical properties will be similarly unaffected. For the $n = 1$ model, the defect field represents a relevant perturbation driving the fixed point of the pure system to an alternative 'random' system fixed point with $U_0^*$ of order $\sqrt{c}$, at which the specific heat does not diverge. It may be that in this case the slowly relaxing HV defects should not be regarded as a static perturbation since the manner in which they are introduced into the effective Hamiltonian represents their effect as a local temperature variation, and the removal by the defects of the specific heat divergence is not expected to be repeated in a system where
the configuration of the defects can remain in thermal equilibrium. The dynamical RG has not been applied to an explicit calculation for the random-field TDGL model although the graphical perturbation theory has been developed and studied within a simple approximation by Ma and Rudnick (1978) for the relaxational model, and by Hertz and Klemm (1978, 1980) in 6-ε dimensions for a spin glass with Larmor precession terms in the equation of motion.

The calculation of critical properties for the n = 1 system with short range interactions and a random defect field will not be pursued here. As the critical soft phonon response of the SrTiO₃ (n = 3, d = 3) model is unaffected by the HV defect field we consider instead, in the next section, the similar problem of coupling the order parameter field to a conserved energy density. The problem involving relaxing HV defects requires a similar coupling to a non-conserved field.

3.4.5 Coupling to an auxiliary conserved field

In 2.1.6 where the idea of dynamical universality classes was introduced it was remarked that the static universality classes characterised by a particular choice of effective Hamiltonian, were subdivided into smaller dynamic universality classes according to the conservation laws which are obeyed and the coupling terms appearing in the kinetic equations. The single-field TDGL model with a non-conserved order parameter upon which the analysis of §3.2 was based is appropriate for the case of a structural phase transition where the relaxation time of the thermal reservoir of hard modes represented in the kinetic equations by the Langevin noise, is infinitesimal compared to the relaxation time of the order parameter fluctuations.
It was shown by Bausch and Halperin (1978) in a study of a microscopic model undergoing a displacive SPT, that this restriction can be overcome by adding the energy of the modes eliminated in the RG transformation to an energy density field. The relaxation time of the energy density field is determined by a second kinetic coefficient. In this section it will be shown that coupling to a slowly-relaxing conserved field which may be taken to represent the energy density or thermal reservoir, does not alter the critical behaviour described in §3.2 and §3.3 in any case for which the specific heat remains finite at the phase transitions. In the case of the three-dimensional scalar model it is known that coupling to a thermal diffusion mode alters the value of the dynamical exponent, $z$, but we find that it does not alter the ratio $\Omega^{(1)}/\Omega^{(2)}$, at least to first order in $\varepsilon$.

The effective Hamiltonian for this coupled system can be expressed in terms of the LGW Hamiltonian $\mathcal{H}_o$ as given by eqn. (3.10), plus a perturbation involving the energy density field $\rho(\mathbf{x},t)$ of the form

$$\mathcal{H}_\rho(\{Q\},\{\rho\}) = \frac{1}{2} \sum_{\mathbf{k}} \rho(\mathbf{k})\rho(-\mathbf{k}) + \frac{g_o}{\sqrt{N}} \sum_{\mathbf{k}_1,\mathbf{k}_2} \rho(\mathbf{k}_1)Q(\mathbf{k}_2)Q(-\mathbf{k}_1,-\mathbf{k}_2)$$  

(3.63)

To generate the perturbation theory for this extended model, a second Langevin noise source, $\eta(\mathbf{k},t)$, is introduced to represent interactions between the thermal diffusion modes, while conservation of the energy field is ensured by writing the kinetic coefficient in the form $DV^2$, where $V$ is the real space gradient operator. The equation of motion for the energy field can now be written

$$\frac{\partial \rho(\mathbf{k},t)}{\partial t} = -Dk^2 \frac{\partial \mathcal{H}(\{Q\},\{\rho\})}{\partial \rho(-\mathbf{k},t)} + \eta(\mathbf{k},t)$$  

(3.64)
The equilibrium critical behaviour of the system is unaffected by the additional field, as by a simple change of variables the $\rho$ coordinates may be integrated out of the partition function (1.20) leaving an effective Hamiltonian of the LGW form (3.10) but with a renormalised coupling constant

$$U'_0 = U_0 - g_0^{2/2},$$

(3.65)

thus the perturbation cannot change the static universality class.

The dynamic behaviour depends upon the fixed point ratio of the kinetic coefficients $D$ and $\gamma_0^{-1}$ which determine the relaxation rates for the order parameter and thermal diffusion modes. As in the case of the TDGL model with no conserved fields, we adopt the fixed point values for $D$, $\gamma_0$ and $g_0$ from the renormalisation group studies (Halperin et al., 1974).

In those cases for which the specific heat remains finite at the transition, the only stable fixed point is the decoupled fixed point with $g^* = 0$ (Ma, 1976b). This may be interpreted as signifying that the non-divergent fluctuations in the energy density are too weak to influence the strongly-divergent fluctuations in the order parameter.

The fixed point value for the kinetic coefficient, $D^*$, is in this case given by $D^* \to \infty$ and so the thermal conductivity is effectively infinite, which justifies a posteriori the assumption made in setting up the TDGL model in §3.2, that interactions with a heat bath of effectively infinite thermal conductivity are sufficient to represent the hard modes.

The scalar model can be seen to flow under the RG transformation to a different fixed point for which the parameters of interest are given by the expressions (Ma, 1976b)
\[ z = 2 + \frac{\alpha}{\nu} \]
\[ g_0 = \frac{2\alpha}{n\nu k_0} \]  
\[ D = \frac{1}{\nu_0} \left( \frac{2}{n} - 1 \right)^{-1} \]  

(3.66)

In this case the coupling terms between the energy density and the order parameter introduce frequency-dependent terms of order \( \varepsilon \) into the soft mode self-energy \( \Sigma(\vec{k}, \omega) \), so that the form of the one-phonon scattering, while still Lorentzian, now has a different half-width. The extra \( \varepsilon \)-dependent terms can be shown, however, to arise solely from the change in the dynamical exponent \( z \), so that there are no corrections to \( \Omega^{(1)} \) of order \( \varepsilon \). Similarly the two-phonon spectral width involves changes due only to the change in the exponent \( z \), and the ratio of the two amplitudes, calculated to \( O(\varepsilon) \), is given again by

\[ \frac{\Omega^{(1)}(n=1)}{\Omega^{(2)}(n=1)} = \frac{\varepsilon}{24} = \frac{\alpha}{4\nu} \]  

(3.67)

It is appropriate at this point to make a final remark. There exists, for the coupled field model, a fixed point which is stable for \( 2 < n < 4 \) which corresponds to a regime for which the energy density kinetic coefficient has the fixed point value \( D^* = 0 \). It has not been possible to show rigorously that this fixed point is unstable with respect to the \( g^* = 0 \) decoupled fixed point because the calculations have been carried out only to order \( \varepsilon \). It is possible, although it disagrees with the intuitive argument given above, that this fixed point may be stable for the three-dimensional case. If this is the case it would correspond to a regime in which the relaxation processes associated with the thermal diffusion modes are slow on the time-scale of the order parameter relaxation processes. This would explain the appearance of a second intrinsic time-scale in the dynamics of the TDGL model which, like the time scale implied by the
width of the two-phonon dynamic central peak will be slow in comparison
with that set by the overdamped soft mode width.

§3.5 The Uniaxial Ferroelectric

3.5.1 The uniaxial problem

The most important class of structural phase transitions for which
the analysis of sections 3.3 and 3.4 is not relevant is the case of a
uniaxial ferroelectric. For the uniaxial system with long-range
dipolar forces the Coulomb anomaly in the dispersion relation restricts
the volume of critical fluctuations in reciprocal space, strongly sup-
pressing the fluctuations with wave-vectors parallel to the \( c \) axis.
The reduction in the dimensionality of the volume of critical fluctua-
tions causes a corresponding reduction in the value of the upper critical
dimensionality, \( d_c \), to three dimensions, causing the momentum space
integrals in the perturbation theory of these systems to give rise to
logarithmically divergent terms rather than the algebraically diver-
gen terms characteristic of the critical behaviour in the fluctuation
dominated regime below \( d_c \).

Despite the difference in the critical dimensionality, the observed
critical scattering in the uniaxial ferroelectric \( \text{Pb}_5\text{Ge}_3\text{O}_{11} \) shows
many features in common with the scattering from perovskites discussed
earlier. \( \text{Pb}_5\text{Ge}_3\text{O}_{11} \) exhibits a continuous, displacive SPT which is
well described by the soft mode framework. The soft mode in this
material is overdamped for a range of up to 50K below the transition
temperature of 451K (Hosea et al., 1979) and for a considerable range
of temperatures above \( T_c \). (Cowley and Satija, 1981). The one-phonon
spectral function measured by neutron scattering shows a critical
narrowing, attaining a limiting width of approximately 0.15 THz at the
transition temperature. The ferroelectric soft mode is, like the soft mode in SrTiO$_3$, Raman active only in the low-temperature phase. Close to the transition temperature, by using the same iodine filter technique as in the SrTiO$_3$ experiments, Fleury and Lyons (1976, 1978) have observed a very weakly critical central component in the two-phonon Raman spectrum which is observable for a temperature range of only around seven degrees above and below the transition temperature. This dynamic, two-phonon central peak has a width which decreases with the approach to the transition attaining a limiting width of around $8 \times 10^9$ Hz. The finite widths of these features at the transition are probably largely due to a smearing of the transition temperature of around 1K due to sample inhomogeneity, therefore a measurement of the saturated width effectively represents a measurement of the width at a temperature close to $T_c$.

In complete disagreement with the results of Fleury and Lyons, in a Raman scattering experiment to measure the one-phonon Raman scattering, Hosea et al. (1979) found that the overdamped wing of the soft mode persisted well into the high-temperature phase where the distortion-induced one-phonon Raman scattering ought to merge smoothly into the two-phonon scattering as discussed in Chapter 4. The width of the overdamped central peak observed in these experiments was found to be approximately $1.2 \times 10^{11}$ Hz, much too large to be observable in the iodine filter experiments. In view of the possibly extrinsic nature of the very narrow central peak obtained by the iodine filter experiments on SrTiO$_3$, it is quite likely that the anomalously narrow central peak of Fleury and Lyons is again due to defects and that the quasi-elastic scattering observed by Hosea et al. corresponds to genuine
two-phonon order parameter scattering.

In order to determine the expected behaviour of the scattering widths, we repeat the analysis of §3.2 using a modified technique.

3.5.2 The TDGL model at \( d_c \)

The uniaxial ferroelectric in three dimensions is an example of an \( n = 1 \) system exactly at its upper critical dimensionality. By exploiting this fact, it has been shown (Larkin and Khmelnitsky, 1969; Aharony, 1973b) that near \( T_c \) the critical properties of an Ising system with long-range dipolar forces in three dimensions, will be the same as the critical properties of an Ising system with conventional short-range forces at its upper critical dimensionality, \( d_c = 4 \). By utilising this correspondence the critical dynamics of the uniaxial ferroelectric can be studied by a consideration of the TDGL model of §3.2 in four dimensions.

Although the same model is required for the calculation of uniaxial properties an application of the Feynman graph \( \epsilon \) expansion and power matching techniques which were used for the previous calculation is no longer appropriate. The reason for this lies in the behaviour of the coupling constant \( U_0 \) in four dimensions. The renormalisation group shows that \( U_0 \) is a marginal parameter so that although the only fixed point value for \( U_0 \) is given by \( U^* = 0 \), the approach to the value under iterative RG transformations is necessarily slow. This slow transient behaviour is the origin of the logarithmic corrections to mean field behaviour. In this instance, there is no longer the possibility of setting \( U_0 \) to a special value to eliminate the logarithmic corrections as these are now the leading divergent terms, and setting the coupling constant \( U_0 \) equal to its fixed point value would reduce the problem to the van Hove model without anharmonicity.
Rather than choosing a particular value for $U_0$, we carry out the calculations in the weak-coupling limit by requiring that $U_0$ be a small, but otherwise unspecified parameter, which must not appear in any of universal quantities which we calculate.

The one-phonon correlation function is again required only to zeroth order in the weak-coupling limit so that the form of the function is the Lorentzian expressed in eq. (3.37), and the width is given by

$$
\omega^{(1)} = (C \gamma^2 / 2U_0) \left[ 1 + O(U^2) \right] \gamma^2
$$

(3.65)

where $U = K_4 U_0$, and the exponents take their mean field values

$$
\gamma = \nu = 1.
$$

(3.66)

The behaviour of the two-phonon correlation requires a variation of the straightforward power matching technique utilised earlier. The scalar model requires only the calculation of the thermodynamic correlation function, $\Gamma_T(k, \omega)$ for which the integrated intensity shows the singular behaviour of the specific heat. The form of the specific heat in the uniaxial dipolar model was shown by Larkin and Khmelnitsky (1969) to be given by

$$
C = A_0 + A_1 \left[ 1 + A_2 \ln U \right] \gamma.
$$

(3.67)

By matching this expression against the leading terms in the perturbation expansion which are equivalent to those listed in Table 3.2 with $\varepsilon$ set to zero, and using terms of order up to $U^2 \ln^3 r$, it is possible to extract unambiguously the values of $A_1$, $A_2$, and $\gamma$, so that apart from an additive constant term, which we do not require, the integrated intensity takes the form
The zero-frequency spectral function, \( \Gamma_T(k=0, \omega=0) \), may be assumed to show similar logarithmic corrections to its classical behaviour. In this case the classical behaviour suggests that \( \Gamma_T(k=0, \omega=0) \) ought to diverge as \( 1/t \), and so guided by these two expectations we match the expressions for the leading order perturbation terms to an expression of the form

\[
\Gamma_T(k=0, \omega=0) = \frac{\kappa}{A_1^2} \left[ 1 + \frac{A_2}{t} \right] \ln t \gamma. \tag{3.69}
\]

In this case the constants \( \kappa, A_1, A_2 \) and \( \gamma \) can be found from leading terms of up to order \( \bar{U}^2 \ln^2 r/r \) yielding an expression for the zero frequency spectral function as

\[
\Gamma_T(k=0, \omega=0) = \frac{K_4 \gamma_0}{2C_0 t} (1 - 18U \ln C_0 t)^{-2/3} \tag{3.70}
\]

plus an additive constant. Now from the definition in eq. (3.20) we find the width of the two-phonon scattering to be

\[
\omega(2) = \frac{C_0 t}{3\bar{U}\gamma_0} \left[ 1 - 18U \ln C_0 t \right] \tag{3.71}
\]

The first term is the expected mean field behaviour which is evidently non-universal, involving the system parameters \( C_0 \) and \( \gamma_0 \) and the coupling constant \( U_0 \). For temperatures sufficiently close to the transition temperature, the logarithmic correction term will dominate the critical narrowing, and in this term it can be seen that the coupling constant \( \bar{U} \) cancels out, as it must do if our matching technique is correct.

The amplitude ratio calculated from equations (3.65) and (3.71)
now, instead of yielding a unique universal number, gives in the limit as $U \to 0$,

$$\frac{\omega^{(1)}}{\omega^{(2)}} = \frac{-1}{12 \ln t} \quad (3.72)$$

where the prefactor of $\ln t$ is a universal number.

3.5.3 Discussion

The results of the TDGL model calculation in four dimensions imply that for the uniaxial ferroelectric, as for the isotropic Heisenberg or Ising systems, the one-phonon characteristic frequency should be smaller than the two-phonon characteristic frequency. The width ratio $\frac{\omega^{(1)}}{\omega^{(2)}}$ is no longer a constant but is instead of the form of a universal constant multiplying a logarithmically divergent quantity. This is consistent with the $\epsilon \to 0$ limit of the isotropic TDGL model for $d < 4$ considered in §3.3 where the ratio is shown to be of order $\epsilon$. A comparison of this result with the experimental values quoted in 3.5.1 supports the hypothesis mentioned there, that the anomalously narrow central peak observed by Lyons and Fleury (1976, 1978) is not connected with the two-phonon scattering from the order parameter fluctuation. The results of a recent neutron scattering study by Cowley and Satija (1981) suggest that the ratio of the one-phonon width to the light-scattering determined width of Hosea et al. (1979) is approximately a ratio of one to three over a range of temperatures from $T_C$ to $T_C + 20$. In view of the fact that the widths observed in these two experiments both decrease rapidly as $T_C$ is approached from above, but in neither case does the experimentally determined width actually go to zero, the experiments are probably unable, due to the effects of instrument resolution, non-critical low frequency scattering and sample
inhomogeneity, to give a good quantitative measurement of this ratio.

For the three-dimensional $^4$ model with dipolar interactions there is no equivalent computer simulation work with which to compare the results of this section. However, Schneider and Stoll (1978b) have analysed the four-dimensional Ising model corresponding to the TDGL model studied here. They found two features in the dynamic correlation function, a softening, ultimately overdamped phonon, and a quasi-elastic central peak whose origin they ascribed to the occurrence of domain walls. In the Pb$_5$Ge$_3$O$_{11}$ experiments it is possible that the narrow central peak of Fleury and Lyons may be identified with this domain wall scattering rather than with a defect mechanism but there is no proof that this is the case.
$\S 4.1$ The Critical Region Below $T_c$

4.1.1 Introduction

The critical region below $T_c$ at a conventional SPT displays features which are qualitatively different from the region above $T_c$, the most notable of which is the appearance of a non-zero, symmetry breaking order parameter. The phenomena in the region below $T_c$ are not conceptually more difficult to study than the critical dynamics above $T_c$. However, for systems with multi-component order parameters the dynamic response and correlation functions for longitudinal and transverse components of the order parameter have different forms which may lead to different behaviour as the transition temperature is approached. In SrTiO$_3$ the soft mode corresponds to rotations of oxygen octahedra about one of the cubic axes. In the cubic phase it is triply degenerate and has a symmetry conventionally denoted $F_{2u}$ (Fleury et al., 1968). Below $T_c$ it splits into a doubly degenerate branch of transverse fluctuations of $E_g$ symmetry, and a non-degenerate branch of longitudinal fluctuations with $A_{1g}$ symmetry. The change in symmetry which causes the lifting of the degeneracy of the soft mode, also causes multi-phonon interactions, which were forbidden in the high-temperature phase, to be allowed in the reduced symmetry below $T_c$. A short discussion of this point, most conveniently given in terms of perturbation theory, is delayed until the next section.

In Raman scattering experiments conducted below $T_c$ the distortion associated with the static component of the order parameter allows a direct coupling between light and the one-phonon response.
The coupling is proportional to the amplitude of the static distortion \(\langle Q(\mathbf{k}_s) \rangle\), which implies that far below \(T_c\), outside the critical region both Raman and neutron scattering techniques may be used to measure the one-phonon response. On entering the critical region, the Raman scattering experiments will cease to be dominated by the one-phonon term in the Raman tensor which will contain contributions of comparable magnitude arising from higher order processes, until at \(T_c\), the distortion-induced processes vanish with the order parameter and the light scattering evolves smoothly into the characteristic two-phonon spectrum of the high-temperature phase.

In this chapter the implications of the above assumption that neutron scattering measures the one-phonon soft mode spectrum, and that Raman scattering measures a sum of higher-order processes are explored. It is shown that while some differences may be detected between the results of the two techniques, the simple one-phonon interpretation of neutron scattering experiments does not account for the observed critical scattering.

4.1.2 Correlation functions below \(T_c\)

Perturbation expansions are of limited usefulness in the study of critical dynamics below \(T_c\) at a SPT as the techniques outlined in Chapter 3 become cumbersome to use due to the large number of terms which contribute even at low orders to the perturbation series, and because the problems of divergences of the series are more acute below \(T_c\) than above, requiring that the perturbation series be summed to infinite orders. The main utility of graphical perturbation theory may be that it remains a convenient method of depicting physical processes.

It is convenient to define the \(1\) axis of the order parameter space by the \(c\) axis of the tetragonal phase, and to redefine
the normal mode coordinate \( Q_1(k_s) \) by subtracting its static expectation value \( Q_0 \). In Fig. 4.1a the first two terms of the two-phonon correlation function, \( \Gamma(k,\omega) \) familiar from Chapter 3 are shown. Replacing two of the normal mode operators by the static part of the order parameter leads to the diagrams of Fig. 4.1b. The first of these is the distortion-induced one-phonon term since the scattering to which it gives rise is \( Q_0^2 S(k-k_s,\omega) \). The second term is known as the 'interference term' as it results from an interference between one- and two-phonon processes mediated by the effective three-phonon interaction which is symmetry-forbidden above \( T_c \). Since \( Q_0^2 \) is of order \( 1/U_0 \), the one-phonon term will be large at low temperatures. The interference term is of order 1, equivalent to the zeroth order two-phonon term to which it may be comparable in magnitude (for numerical estimates, see Reid, 1971).

A dynamic perturbation theory can be constructed for the LGW model below \( T_c \) (Ma and Mazenko, 1976) based on the relaxational equations of motion given in §3.2, leading to a graphical expansion with terms corresponding to those in Fig. 4.1 with the addition of propagator arrows and noise vertices, analogous to those of Chapter 3. The most important difficulty in applying the LGW formalism to the case of SPTs with a non-zero order parameter, is that the isotropic symmetry in the order-parameter space implied by the LGW model is not an acceptable approximation. The propagator corresponding to transverse fluctuations of the order parameter has a 'mass' which is non-zero only in the presence of a symmetry breaking field. These massless (or gapless) transverse modes are the Goldstone modes corresponding to the continuous rotational symmetry of the LGW Hamiltonian of eqn. (3.10), and they lead to divergences in the perturbation series at all temperatures below \( T_c \) which dominate the
Figure 4.1: The correlation functions probed by Raman scattering below $T_c$.

(a) The zeroth and first-order contributions to the two-phonon spectral function. The static (frequency-integrated) graphs are shown, dynamic graphs carry noise vertices and propagator arrows as shown in Fig. 3.2.

(b) The correlation functions resulting from the replacement of pairs of normal mode amplitudes by the static order parameter $Q_0$ (represented by the dotted lines). The two terms shown depict the distortion-induced one-phonon and one-two-phonon interference scattering.
correlation functions of both longitudinal and transverse fluctuations to such an extent that several authors, following Patashinskii and Pokrovskii (1973) have studied the LGW model below $T_C$ with the length of the order parameter held fixed, and the critical behaviour determined by the transverse fluctuations. (For a review, see Szepfalussy (1979)). In order to model the dynamical behaviour below $T_C$ of SrTiO$_3$, (or any SPT) where the frequencies of transverse and longitudinal fluctuations (E and A modes) are comparable, a symmetry breaking term must be introduced into the Hamiltonian to remove the Goldstone modes. In practice, the proliferation of low-order diagrams encountered for even the isotropic model restricts any calculation by the methods used in Chapter 3 to only the physically inaccessible cases with $n \to \infty$ (Mazenko, 1976; Mazenko et al., 1978) or $d \lesssim 4$ (Schäfer, 1978). In the Ising model, to which the above remarks about transverse fluctuations do not apply, it has been shown that for a system which allows a direct coupling between the soft mode and pairs of phonons of equal and opposite wave-vector and frequency, effectively the phonon density, there will be a coupling to the heat diffusion mode if the specific heat diverges at $T_C$ (see Bruce and Cowley, 1980; Coombs and Cowley, 1973, Wehner and Klein, 1972). In this case, as in Chapter 3, it is necessary to consider the dynamics of an order parameter coupled to a conserved energy density field which causes a further proliferation of low order diagrams. Because of the divergences introduced by the phonon density fluctuations it is in principle necessary to sum the perturbation series to infinite orders, as discussed originally by Klein and Wehner, 1968, 1969).

These technical difficulties are sufficient to prevent the calculation of the critical dynamics of the LGW models by series expansion methods at the present time. A more serious objection to this method
of calculation comes from the ambiguous results of scattering experiments (see below) which suggest that the relaxational equation of motion corresponding to the limit of a heavily overdamped soft mode may give a very poor description of the dynamics if the soft mode saturates close to $T_c$ at a fairly high ($\sim 0.2\text{THz}$) frequency.

An alternative to the sophisticated approach of the $\epsilon$ expansion calculations which fail in all but the $n \to \infty$ or $d \to 4$ limits due to their complexity, and which in any case give a reasonable description of only the asymptotic behaviour as $T$ tends to $T_c$, is to calculate approximately the one- and two-phonon spectral functions in a low order perturbation theory which will be valid only well below $T_c$, and to determine the range of its validity by noting the temperature at which the approximations upon which the calculation is based appear to break down. This approach was used by Yacoby et al. (1978) in their analysis of the Raman scattering from Pb$_5$Ge$_3$O$_{11}$ where, by approximating the response of a phonon as

$$G^0(\mathbf{k}, \omega) = \left[\omega^2(\mathbf{k}) - \omega^2 \right] - i\gamma_0 \omega^{-1}$$

for an underdamped mode, and

$$G^0(\mathbf{k}, \omega) = \omega^{-2}(\mathbf{k}) \left[1 + i\omega \tau_D \right]^{-1}$$

for an overdamped mode with a Debye relaxation time $\tau_D$, they were able to make quantitative estimates of the relative magnitudes of the one-phonon, two-phonon, and interference terms. This approach would be expected to work well for a uniaxial ferroelectric such as Pb$_5$Ge$_3$O$_{11}$ since the critical region for a uniaxial ferroelectric is expected to cover a small temperature range (see Stauffer, 1978) due to the weak (logarithmic) singularities induced by the fluctuations. Calculations of the self-energy contributions arising from phonon density fluctuations have also been made for SrTiO$_3$ by Cowley and Bruce (1973).
but these cannot be expected to describe the critical region well in this $n = 3, d = 3$ system. However, they are of interest as they show that even 30K below the transition temperature the E mode self-energy contribution amounts to some 10% of the total quasi-harmonic frequency squared, above which the mean field approximation must be considered doubtful.

In view of the lack of an adequate theory of the critical region appropriate to the case of SPTs, experimental studies of the critical dynamics are of particular interest.

4.1.3 Experimental studies of $\text{SrTiO}_3$ and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ below $T_C$.

The Raman scattering below $T_C$ in both $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and $\text{SrTiO}_3$ has been the subject of a number of studies which have generally assumed that the one-phonon term dominates the scattering to such an extent that the scattering may be fitted by a damped oscillator response with the frequency and damping treated as variable parameters. The latter is expected to be only weakly temperature dependent (Pytte, 1970) while the former is expected to go to zero as $T$ approaches $T_C$, though it has been suggested that coupling to an acoustic mode causes the soft mode frequency to saturate at a non-zero value (Cowley et al., 1969; Bell and Rupprecht, 1963).

Raman scattering studies of the low temperature phase soft mode of $\text{SrTiO}_3$ were originally carried out by Fleury et al. (1968) who identified the soft modes of A and E symmetry, and subsequently by Worlock and Olsen (1971), Steigmeier and Auwerset (1973) and Yacoby et al. (1976), the latter two concentrating on the A mode only. Although the results of these studies are consistent below the critical region the descriptions of the limiting behaviour at the transition
temperature are equivocal. In the work by Steigmeier and Auderset, the A mode was parametrised by the classical oscillator response to within 3K of the transition, showing that the square of the soft mode frequency followed the square of the order parameter and the damping increased only weakly with temperature even in the critical region where the order parameter displays non-classical critical behaviour. In contrast to this, the experiments of Yacoby et al. suggest that as $T \to T_c$, the A mode frequency may saturate at the limiting frequency of the high temperature soft mode deduced from the neutron scattering data of Shapiro et al. (1972). The E mode has received less attention experimentally, possibly because being at a lower frequency it is more affected by the low frequency elastic or quasi-elastic scattering (Steigmeier; Auderset & Harbeke, 1973) and it is possible to describe it by an underdamped oscillator response only at temperatures well below $T_c$. Fleury et al. (1968) suggested that the frequencies of both modes vanishes as $t^n$ with $n = 0.31$ in contrast to Worlock and Olsen (1971) who concluded that a better fit to both modes could be obtained by taking $n = \frac{1}{4}$. In view of the suggestion by Yacoby et al. (1978) that two-phonon and interference terms may give rise to misleading frequencies and widths in this type of one-phonon analysis of Raman scattering measurements, it is necessary to look for differences between the results of Raman scattering experiments and neutron scattering experiments. An early comparison between the two types of experiment was given in the work by Worlock and Olsen (1971). In comparing the frequencies obtained by their Raman scattering measurements with the neutron scattering results of Shirane and Yamada (1969) they obtained excellent agreement for the A mode frequency, but found that the neutron-determined E mode frequencies were systematically up to 50% higher at all temperatures.
In a similar neutron scattering experiment, Cowley et al. (1969) obtained E mode frequencies systematically higher than those measured by Fleury et al. (1968) and concluded that the soft mode frequency did not go to zero at $T_c$.

In $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ a broadly similar situation exists. The earliest measurements by Burns and Scott (1972) and by Ryan and Hisano (1973) showed that the soft mode becomes overdamped about 50 degrees below the transition temperature of 450K, but below this temperature it can be described by a damped oscillator with a frequency proportional to $(T_c - T)^{\frac{1}{2}}$. In a subsequent study, Hosea et al. (1979) showed that above $T_c - 80$K the soft mode is not well described by the damped oscillator form due to the presence of additional low-frequency scattering which is not evident in the neutron scattering experiment of Cowley et al. (1976), although in the latter it may well have been masked by the intense quasi-elastic scattering from domain walls (see Chapter 6). The model calculations by Yacoby et al. (1978) suggest that the appreciable contributions from the one-two-phonon interference terms and the genuine two-phonon scattering may be able to explain this discrepancy, but in the absence of an accurate determination of the one-phonon lineshape it is not conclusive that the discrepancies originate in higher order scattering processes.

In order to elucidate further the contributions made to the Raman scattering by the two-phonon and interference terms a programme of experiments was undertaken utilising the above-mentioned materials. High resolution neutron scattering studies were made to determine the one-phonon spectral function accurately, and in the case of $\text{SrTiO}_3$ a complete set of Raman scattering data was obtained for comparison.

In a neutron scattering experiment performed by the author on a crystal of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ it was found that difficulties in separating the
low energy acoustic mode contribution from the spectrum prevented an accurate determination of the low energy line shape in the energy range (<10 cm\(^{-1}\)) where Hosea et al. (1979) observed a quasi-elastic peak. Because of space limitations, this work is not discussed here, however, in a subsequent experiment, Cowley and Satija (1981) have studied the evolution of the soft mode scattering at higher energies. The description of the one-phonon spectrum which emerges from a consensus of these studies, consisting of a soft phonon whose frequency does not go to zero at \(T_c\), and a narrow, critical quasi-elastic component of undetermined origin is strikingly similar to the behaviour deduced from the experiments on SrTiO\(_3\) discussed in this work.

§4.2 Experimental Study of SrTiO\(_3\)

4.2.1 Neutron scattering experiments

A preliminary experiment to measure the line shape of the soft mode both above and below \(T_c\) was performed by R.A. Cowley (1979) using the high flux reactor at Risö. This experiment studied only the \(E\) mode over a temperature range from 80K to the transition at 102K, and the degenerate soft mode up to a temperature of 50K above \(T_c\). The results of this experiment, in which the scattering data was fitted to a classical damped oscillator spectral function (eqns. 2.27 to 2.30) with no resolution corrections, suggested that the soft mode frequency, \(\omega(k_s)\), decreases as \(T \rightarrow T_c\) from above \(T_c\). Below the transition temperature, the frequency displayed an unexpected maximum at a temperature of \(T_c - 10K\), which is indicated in Fig. 4.4a. The phonon damping constant and amplitude, both expected to be constant in the simplest theory, displayed broad maxima several degrees below \(T_c\). Because this experiment was not analysed in sufficient detail it is not possible to assign
the anomalous behaviour of these parameters unambiguously to one origin, however it is interesting to note that this behaviour suggested that even the one-phonon spectral function measured by neutron scattering is not adequately described by a damped harmonic oscillator in the temperature range from $T_C - 15K$ to $T_C + 5K$.

In order to establish clearly the form of the one-phonon spectral function an experiment was performed by the author at the Institut Laue-Langevin in Grenoble, using the triple axis spectrometer IN12. The sample of SrTiO$_3$ was a clear boule in the form of a cylinder with a volume of approximately 6 cm$^3$. It was mounted in a displex crystal with a (1, 3, 0) axis vertical, and all observations were made at the $\left(\frac{3}{2}, \frac{1}{2}, \frac{1}{2}\right)$ superlattice point. Monochromation and analysis of the neutrons was performed by pyrolytic graphite (0, 0, 2) reflections, which with the collimation used of 30' Soller slit collimators throughout the instrument, gave an energy resolution, estimated from the width of a vanadium scan, of 0.025 THz. All scans were performed in the 'constant $k_F$' mode under conditions of neutron energy loss. Contamination by neutrons with wavelengths of a fraction of the primary wavelength of 4Å was removed by a nitrogen-cooled Beryllium filter mounted before the analyser. Because of the large scattering angles involved, the instrument could not be used in the conventional 'W' configuration which gives the optimal resolution (see, e.g., Peckham, 1967) but was operated with the sense of scattering at the sample reversed which would cause some loss of focussing. This was not felt to be a serious restriction as the major limitation on the observations was due to the vertical resolution of the spectrometer.

Energy scans at the superlattice point were made at a range of temperatures from 15K to 112K. The majority of these were made in the temperature range, from $T_C - 20$ to $T_C + 6$, where the preliminary
experiment had given unexpected behaviour for the quasi-harmonic frequency and damping of the E mode. The scans at the lower temperatures were performed to enable a check to be made of the consistency of the neutron and Raman scattering results in the mean-field regime. The highest temperature investigated extended the results into the regime where the preliminary experiment had indicated that the quasi-harmonic parameters are well behaved. Typical examples of the energy scans at several representative temperatures are shown in Fig. 4.2. The maximum energy transfer available did not permit observations of the A mode at the lowest temperatures.

Scans at room temperature over the same energy range were made to determine the background scattering due to incoherent scattering and fast neutrons. The transition temperature was measured by monitoring the intensity of the (0, 0, 1) Bragg peak while heating and cooling the sample through $T_c$. The relief of extinction below the transition temperature due to the formation of domains corresponding to the rotation of the oxygen octahedra about different axes leads to a variation in intensity of the Bragg peaks proportional to the square of the order parameter. This gives a sharper indication of the transition temperature than direct observations of the superlattice point intensity which merges smoothly into the critical scattering at $T_c$. The transition temperature measured in this way was found to be $T_c = 102.4 \pm 0.1K$.

4.2.2 The Raman scattering experiment

For comparison with the neutron scattering data, a Raman scattering experiment was performed to collect spectra for the A and E modes below $T_c$ at the same temperatures used in the neutron experiment. The crystal used for the Raman experiment was a slice with a volume of
Figure 4.2: Energy scans at the \((\frac{3}{2}, \frac{1}{2}, \frac{1}{2})\) superlattice point.

Neutron scattering data at six representative temperatures below \(T_c\) and at two temperatures above \(T_c\). The solid curves show the results of a fit to the uncoupled oscillator model described in 4.2.3.

Temperatures:

- (a) 15.2K
- (b) 71.8K
- (c) 86.5K
- (d) 94.2K
- (e) 98.5K
- (f) 102.4K
- (g) 104.4K
- (h) 111.6K
50 mm$^3$ cut from the same boule as the sample used for the neutron experiments to prevent any problems from arising due to sample dependence. The instrument resolution was 0.5 cm$^{-1}$. From measurements at 15K it was ascertained that the edge of the elastic scattering from the laser line occurred sharply at an energy of 4 cm$^{-1}$. An estimate of the effect of laser heating of the sample was made by monitoring the A mode frequency for different laser powers, and all temperature settings were then adjusted (by 0.6K) to account for this. The data points were collected with a spacing of 0.5 cm$^{-1}$ (0.015 THz), using 200m W of laser light from the 576 nm Argon line. With the small crystal used for the Raman experiment of which only a small fraction was illuminated by the laser, it was necessary to make all of the measurements below $T_c$ without allowing the crystal to pass through the transition since changes in the intensity of the soft modes attributed to domain effects were noticeable.

Unlike the neutron scattering experiments where the radiation couples simultaneously to the A and E modes, in a Raman experiment, analysis of the polarisation of the incident and scattered light allows a separation of the SrTiO$_3$ spectrum into a diagonal (A mode) and an off-diagonal (E mode) spectrum (a discussion of the selection rules is given by Taylor and Murray, 1979).

Typical spectra obtained are shown in Fig. 4.3. The edge of the laser line is shown clearly in the 15K scans to be sharply cut off at 4 cm$^{-1}$. At temperatures of 72K and above, where the A and E modes are clearly underdamped, there is a large amount of quasi-elastic scattering extending to energies of perhaps 12 cm$^{-1}$ close to $T_c$. This quasi-elastic component was briefly remarked on by Worlock and Olsen (1971) who concluded that it showed no critical properties at $T_c$ but could not be accounted for by Rayleigh or Brillouin (acoustic mode).
Figure 4.3: Raman spectra of the A and E modes.

The diagonal A mode spectrum (open circles) and the off-diagonal E mode spectrum (crosses). Temperatures are the same as the corresponding elements (a to e) of Fig. 4.2. In (b) and (c) the A mode intensity is halved for clarity. Energies are quoted in cm$^{-1}$ as this is normal practice for Raman scattering, for practical purposes $10 \text{ cm}^{-1} \approx 0.3 \text{ THz}$. 
scattering. The presence of this strong quasi-elastic scattering makes it difficult to study the shape of the E mode line in detail. A second feature which causes some complication in the analysis is the presence in both spectra of a contribution due to the 'ferroelectric' soft mode. This mode, which should not be Raman active in a perfect crystal, was studied by Fleury and Worlock (1968) by electric field induced Raman spectroscopy. Its frequency was shown to decrease with temperature throughout the temperature range covered in this experiment. The presence of this scattering is almost certainly due to symmetry breaking defects permitting a linear coupling between the light and the ferroelectric mode. In the off-diagonal spectrum it appears, not as a resonant line, but as the low frequency edge of the broad two-phonon background scattering, and the presence of this broad, temperature-dependent edge to the background over an energy range coincident with the A mode phonon for intermediate temperatures imposes some restriction on the accuracy with which the line can be fitted below 90K. A further weak contribution to the off-diagonal spectrum was observed at energies just below 50 cm$^{-1}$. This has been identified with a defect mode by Taylor and Murray (1979). In the preliminary data analysis the effect of these background features is minimised by fitting the phonon profiles over a narrow energy range assuming the background to be constant. In the more detailed investigation at temperatures near $T_c$, the ferroelectric and defect mode scattering occurred at a sufficiently high energy to be of no importance.

4.2.3 Preliminary data analysis

The analysis of the data obtained in the above experiments has been carried out in three stages. The first two stages constitute the preliminary analysis described in this section, which highlights the danger of misinterpretation which is inherent in the traditional analyses of
scattering experiments with only rudimentary resolution corrections. The conclusions reached concerning the treatment of the phonon amplitudes are a necessary justification for the procedure adopted in 4.2.4. The analysis was performed with the specific intention of extracting from the data the best description in terms of damped oscillator modes, and of examining any systematic deviations from the oscillator model such as were suggested by the preliminary experiment.

(a) The uncoupled mode model

Initially, the neutron data was fitted to a spectral function in which the A and E modes below $T_c$, and the degenerate soft mode above $T_c$, were represented by the damped harmonic oscillator spectral functions

$$S_j(\omega) = A_j(n(\omega) + 1) \frac{\gamma_j \omega}{(\omega_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2}$$

(4.3)

where $n(\omega)$ is the Bose occupation number, $n(\omega) = \left[\exp(\hbar \omega/k_B T) - 1\right]^{-1}$, and $A_j$, $\omega_j$ and $\gamma_j$ are the amplitude, frequency and damping constants of mode $j$ ($j \equiv A$ or $E$ below $T_c$, $F$ above $T_c$). All three parameters for each mode were allowed to vary in the fitting. The spectral function was assumed to consist of the sum of the two contributions from the soft modes (one above $T_c$) plus a temperature-independent background determined from room temperature measurements. At the lowest temperatures there is a weak peak at an energy below the E mode energy (Fig. 4.2a). This was initially thought to arise from some spurious effect and so it was approximated by a constant Gaussian peak to prevent it from affecting the fitting (but see 4.2.4). The total $S(\omega)$ obtained from these contributions was convoluted with a one-dimensional Gaussian energy resolution function as mentioned in 2.3.2.
Least squares fits were carried out at all temperatures for this uncoupled oscillator model, the solid curves in Fig. 4.2 show the best fit obtained. Several points are immediately apparent. The A mode is very much weaker in intensity than the E mode to the extent that for temperatures above 87K the two modes are not resolved and the actual shape of the A mode line clearly cannot be determined. In previous experiments (Shirane and Yamada, 1969; Cowley, 1979) the A mode was ignored above 80K. In this study it has been assumed that the A mode is adequately represented by the oscillator form, 4.3, at all temperatures, and that any systematic differences between the observed and calculated intensities arises from the E mode line shape or possibly from other processes. The intensity difference between the A and E modes is in reasonable agreement with the effects of domain population, structure factors and Bose factors. The overall quality of the fits is good, except paradoxically at low temperatures where the simple approximations leading to the oscillator form for the one-phonon spectral function ought to be most reliable. From the lowest temperature scans it can be ascertained that for energy transfers larger than 0.06 THz, the high resolution obtained by using long wavelength (4Å) neutrons prevents any contamination due to the tail of the \( \frac{3}{2}, \frac{1}{2}, \frac{1}{2} \) superlattice peak or due to the acoustic modes which may be seen close to the Bragg peak below \( T_c \). All of the fitting described in this section was performed for energy transfers greater than 0.08 THz.

The parameters obtained for the uncoupled oscillator model are shown in Fig. 4.4. The frequencies for both modes appear to behave well below \( T_c \) although the three modes should approach a common value at \( T_c \). The limiting frequency attained by the E mode is 0.23 THz, at \( T \approx T_c \). It is the behaviour of the other parameters which shows that the uncoupled oscillator model is inadequate. There
Figure 4.4: Parameters for the uncoupled oscillator model.

The frequencies, widths and amplitudes obtained by fitting the neutron scattering data to the uncoupled oscillator model. A mode parameters are denoted by circles, E mode parameters by triangles. The transition temperature ($T_c = 102.4$K) is marked and the frequency and width of the F mode above $T_c$ are shown by filled circles.

The frequencies obtained in the preliminary model are marked by the dashed line. As these frequencies agree well with the E mode and F mode results well away from $T_c$, it is probable that the unexpected variation over a range of 15K below $T_c$ arises from the neglect of the A mode in the preliminary experiment analysis.

Spectral functions corresponding to these parameters are compared with the data in Fig. 4.2.
\( N = 0.5 \)

\( \omega / \text{THz} \)

\( \nu / \text{THz} \)

\( A \)

\( T / \text{K} \)
is little reason to believe that the damping constants, $\gamma_A$ and $\gamma_E$ should show any sudden variation with temperature. The soft mode amplitudes $A_A$ and $A_E$ should be temperature-independent constants depending on only the inelastic structure factors ($F(K_s)$ in 2.25), the experimental geometry and the ratio of domain populations. A marked temperature dependence of either of these parameters shows that the assumptions underlying the oscillator model are invalid, even though the calculated curve appears to give a good fit to the scattering data. It is clear that for temperatures above 90K the model is unable to assign the observed intensity correctly to the A and E modes. It is surprising that the aggregate amplitude, $A_A + A_E$, behaves almost as expected, remaining constant to within 10% of its value at 72K.

The Raman scattering measurements were also fitted to the spectral functions of eqn. (4.3). Since the A and E modes were observed in different spectra there was no problem in separating the scattering. No 'leak-through' due to depolarising effects was observable in any of the spectra. The assumption of a constant background had little effect on the parameters obtained below 90K but above this temperature attempts to fit the E mode from 6 cm$^{-1}$ to 25 cm$^{-1}$ led to unrealistic behaviour for the parameters, which was probably due more to the tail of the quasi-elastic scattering than to the actual shape of the E line.

Values of the parameters obtained for the Raman scattering in this uncoupled oscillator model are discussed below where they are compared to the neutron scattering parameters resulting from the coupled model.

(b) The coupled oscillator model.

The unphysical variation of the mode amplitudes $A_A$ and $A_E$ above 90K implies that in the temperature range where the two modes are not resolved, some constraint must be placed upon the fitting parameters. Since the mode amplitudes are expected to be independent of temperature
and since the aggregate amplitude as noted above is approximately constant, the neutron scattering data was re-fitted to a five parameter model in which an overall amplitude was used as a fitting parameter and the ratio $A_A/A_E$ was fixed. In the presence of an equal distribution of domains of each of the three orientations, the value of this ratio is $\frac{1}{3}$. It was found that quality of fit to the data was much improved if the ratio was taken to be 0.43.

This simple modification to the model produced fits to the data which were almost indistinguishable from the original model, but for which the parameters (shown in Fig. 4.5) have a much more reasonable behaviour. The frequencies obtained are relatively little changed by the linking of amplitudes but the damping constants (or widths) now increase smoothly as $T_c$ is approached. The overall amplitude shows a slight increase with $T$. Also shown in Fig. 4.5 for comparison, are the values determined for the frequencies and damping constants obtained from the Raman scattering measurements.

None of the neutron-determined parameters disagree substantially with the results of Shirane and Yamada (1969), and indeed the low-temperature frequencies agree almost exactly with their work so that the coupled oscillator model appears to give a good description of the scattering throughout the temperature region where the single-mode fitting to the preliminary experiment indicated anomalous behaviour. There are several important points which show that the results of the analysis are not consistent with the assumptions of the simple oscillator model.

Firstly, the frequencies obtained for the A and E modes do not go to zero at $T_c$ although the expectation that $\omega_j$ should go to zero led previous authors to conclude that their measurements could be extrapolated to zero at the transition temperature. It is surprising
Figure 4.5: Parameters for the coupled model and the Raman model.

Frequencies and widths for the A mode (circles) and E mode (triangles). The coupled model parameters from the neutron scattering experiment are denoted by filled points. Parameters obtained by fitting the Raman spectra are shown by open points.

Parameters for the F mode are shown above $T_c$ for comparison.
that if the soft mode frequencies do saturate at $T_c$, the A and E modes do not appear to attain the same limiting frequency even though they become degenerate above $T_c$, and in any case they do not saturate at the limiting frequency of the high temperature mode deduced by Shapiro et al. (1972) to be $0.13 \pm 0.03$ THz.

Secondly, the large differences between the values deduced for $\omega_E$ from the neutron data and from the Raman data cannot be attributed entirely to the interference and two-phonon terms in the Raman scattering at temperatures well below $T_c$.

Thirdly, the model cannot explain why the oscillator gives such a poor representation of the observed line shape at low temperatures. This may be explained either by instrumental resolution effects or by a genuine microscopic dynamical effect, but in either case the implications for the higher temperatures must be considered to be serious.

4.2.4 The soft mode spectral functions

The preliminary analysis of the neutron scattering experiment has been described at some length in order to explain the procedure to be adopted in this section for fitting the data to an extended model, to indicate criteria by which it may be ascertained that such a model describes correctly the structure of the one-phonon spectral function, and to provide a plausible basis for the explanation of the differences between the interpretation of the scattering given here and the conclusions of previous authors.

The only obvious failure of the classical oscillator model described above is the failure to give a good description of the shape of the E mode spectral line at low temperatures. In this regime the approximation that the anharmonic contributions to the quasi-harmonic frequency and damping are small and frequency-independent ought to have
more justification than in the critical region where the oscillator models appear to give a good fit to the data. It was possible to differentiate between the uncoupled and coupled models in the last section not by examining the quality of the fits in the high temperature region where the models gave rise to different parameters, but by examining the behaviour of the fitted parameters themselves. In attempting to account adequately for the low temperature line shape the criteria by which we must judge the new model would appear to be that it must describe the low temperature line shape accurately without the introduction of further variable parameters, and that it must remove the discrepancies between the neutron and Raman scattering measurements in this temperature range, while at higher temperatures it must produce a set of parameters which have a plausible temperature dependence.

Apart from the assumption of simple oscillator functions to describe the soft phonons, the major simplification inherent in the preliminary analysis is the use of only a one-dimensional resolution correction. The resolution function of a triple axis spectrometer was introduced briefly in 2.3.2. However a detailed discussion of its form and usage have been delayed until this section because of the unique importance of instrumental resolution in the interpretation of this experiment. The form of the resolution function, $R(k - k_0, \omega - \omega_0)$, was examined by Cooper and Nathans (1967), who used Gaussian functions to approximate the mosaic spreads of monochromator and analyser crystals and the transmission of Soller slit collimators, and who showed that in this approximation the resolution function could be represented by a four-dimensional Gaussian. The Gaussian widths of this function were determined by scanning through the $(3/2, 1/2, 1/2)$ Bragg point in the $(3, 1, 0)$ and $(0, 0, 1)$ directions,
to obtain the in-plane wave-vector resolution, rocking the crystal on
its goniometer arcs to determine the vertical or \((1, \frac{3}{2}, 0)\), width, and
measuring at the \((\frac{3}{2}, \frac{1}{2}, \frac{1}{2})\) point the width in energy of the incoherent
scattering from a vanadium sample. Denoting by \(\Delta\) the full width at
half maximum of the intensity, the values obtained were
\[
\begin{align*}
\Delta k_{310} & = 0.018 \ \text{Å}^{-1} \\
\Delta k_{001} & = 0.022 \ \text{Å}^{-1} \\
\Delta k_{130} & = 0.15 \ \text{Å}^{-1} \\
\Delta \omega & = 0.025 \ \text{THz}.
\end{align*}
\]

It can be seen that the vertical resolution, \(\Delta k_{130}\), is much poorer than
the in-plane resolution, corresponding to an angular deviation for the
scattering vector of approximately 2°.

In order to carry out the convolution required by eqn. (2.22) it is
necessary to specify the form of \(S(\vec{k}, \omega)\) for all values of \(\vec{k}\) and
\(\omega\) in the neighbourhood of \(\vec{k}_s\). We make the logical assumption that
the scattering due to mode \(j\) is given by the oscillator expression
of eqn. (4.3) with \(\omega_j^2\) replaced by \(\omega_j^2(\vec{k})\). The dispersion surface
of SrTiO\(_3\) close to \(\vec{k}_s\) is highly anisotropic being relatively flat
along directions parallel to \((1, 0, 0)\) and steeply sloped away from this
direction. The soft mode has three components and there are three types
of domain in the low temperature phase, giving a total of nine possible
modes below \(T_c\). The structure factors for those corresponding to
rotations of the oxygen octahedra about the \(x\) axis are zero at the
\((\frac{3}{2}, \frac{1}{2}, \frac{1}{2})\) lattice point, but the dispersion surfaces for the others are
shown in the \(k_{130} - \omega\) plane together with a schematic resolution ellipse
drawn to scale (Fig. 4.6). The parameters for the dispersion surface
have been calculated from measurements by Stirling (1972), in the form
of eqn. (1.21) with the coefficient \(c = 27(\text{THz})^2\) for rotations
The dispersion relations for the A and E modes along the direction with $\mathbf{k}$ vertical, i.e. the $(1, 3, 0)$ direction. The A and E modes are both split for $\mathbf{k} \neq \mathbf{k}_g$ into two branches corresponding to rotations of the oxygen octahedra about the y and z axes. Dispersion relation parameters were obtained from the study of Stirling (1972).

A schematic resolution ellipse is drawn to scale below the dispersion curves.
about the y axis, and \( c = 207(\text{THz} \, \AA)^2 \) for rotations about the z axis. As the widths of the resolution function in the horizontal plane are less than one seventh of the vertical resolution, it can be seen from Fig. 4.6 that to a good approximation the dispersion surface will be flat within the resolution limits. We are therefore able to account for spectrometer resolution adequately by considering only a two-dimensional convolution in the \( k_{130} - \omega \) plane. A step size of 0.008 \( \AA^{-1} \) was used for the numerical wave-vector integration, smaller meshes being used to check that truncation errors were unimportant. Least squares fits at temperatures below 80K showed no variation of the amplitude \( A_E \), and so for the remainder of the fitting, the amplitude \( A_E \) was fixed at the value obtained at low temperatures and \( A_A \) was fixed at one half of this value, the ratio corresponding to equal domain populations. Above \( T_C \), \( A_F \) was set to be equal to \( A_E + A_A \).

The results of a fit to the data at 15K are shown in Fig. 4.7a, where the dashed line shows the actual form of \( S(k, \omega) \) before resolution corrections. The shape of the spectral line, including the high-energy tail, are seen to be very well described, and the width of the calculated phonon line much reduced by the procedure. It is possible to describe the line shape in this way at temperatures below 90K where the E mode becomes overdamped, but it is noticeable that above 80K there is a certain amount of low energy scattering, below 0.2 THz which is not accounted for by the resolution-corrected oscillator shape. Above 90K the resolution-corrected oscillator fits gave larger values for \( \chi^2 \), the statistical error, due almost entirely to marked discrepancies in the low energy scattering.

As the source of the extra low energy intensity could not be explained, and as the origin of the weak scattering observed below 82K at around 0.17 THz could not be traced to any of the spurious
Figure 4.7: A comparison of the neutron data with the resolution-corrected model spectral functions.

The data points obtained in the neutron experiment and shown in Fig. 4.2 are repeated. The solid curves are the fitted spectral functions composed of two resolution-corrected oscillator functions to represent the A and E modes, a constant Gaussian peak to represent the low-energy feature shown clearly in (a), and a fixed background.

The bare oscillator functions, $S_A(k_s, \omega)$ and $S_E(k_s, \omega)$, are shown by dashed lines, with an arbitrary normalisation adopted for clarity.

The temperatures correspond to those of Fig. 4.2 (a to h).
processes known to affect triple axis measurements (such as high order reflections from monochromator and analyser) it was felt that the intensity due to the soft modes could be unambiguously determined and fitted, only above 0.2 THz. An extrapolation of the oscillator line shape to lower energies was then used to subtract the theoretical spectral function from the data.

For consistency, the Raman spectra were re-fitted over the same energy range.

The parameters obtained from these fits are shown in Fig. 4.8. We focus attention primarily on the E mode for which the neutron parameters are most reliable. At low temperatures the agreement between the parameters is excellent. At higher temperatures the Raman frequency is systematically higher than the neutron frequency, to the extent that the Raman data cannot be fitted with the frequency fixed at the neutron-determined value for temperatures above 90K.

This data analysis answers several of the key questions posed in 4.2. The E mode frequency clearly does not decrease to zero at $T_c$. In fact $\omega_E^2$ is within the accuracy of the data, proportional to $108 - T$ and the value at $T_c$ (102.4K) is $\omega_E = 0.17 \pm 0.02$ THz. The high temperature F mode appears to reach the same frequency at $T_c$, while the A mode remains at a higher frequency ($\omega_A = 0.36 \pm 0.02$ THz) the difference between the two frequencies, $\omega_E$ and $\omega_A$ at $T_c$, is more than one can attribute to experimental error or to an artefact of the fitting process. The difference in frequencies, as obtained in the preliminary analysis between the Raman and neutron data which repeated the discrepancies obtained in the results of previous studies Cowley et al., 1969; Shirane and Yamada, 1969; Worlock and Olsen, 1971) all of which obtained higher values for the neutron determined frequencies, has been shown to be caused entirely by resolution effects.
Figure 4.8: The soft mode frequencies and widths.

Frequencies and widths obtained from the resolution-corrected oscillator model are shown together with the results of fits over the same frequency range to the Raman data.

(a) E mode. Open triangles show the Raman parameters. Filled triangles show the neutron parameters. The F mode parameters above $T_c$ are shown by filled squares.

(b) A mode. Open circles show the Raman points. Filled circles show the neutron parameters. The F mode points are plotted again for comparison.
There is a systematic difference between the two experiments above 82K with the Raman scattering giving rise to higher frequencies which cannot be explained by spurious effects due to the quasi-elastic background, to temperature differences between the two experiments, or to sample dependence. We have not endeavoured to show that the difference in frequencies, and the anomalous behaviour of the Raman determined width above 94K are due to interference terms as suggested by Yacoby et al. (1978) because the behaviour of the low energy intensity observed in the neutron scattering experiment casts considerable doubt on the accuracy with which even the one-phonon spectral function can be interpreted purely in terms of the soft modes.

To conclude this section, we show in diagrammatic form the evolution of the spectral function of the E mode deduced from the analysis of the neutron scattering experiment which may be compared to the actual data obtained from the Raman experiment, showing the gradual softening of the mode, becoming overdamped above 92K.

4.2.5 Low energy structure in $S(k, \omega)$

Having ascertained that the neutron scattering data above 0.2 THz (6.7 cm$^{-1}$) can be accurately described by the soft mode model at all temperatures, but that close to $T_c$ there is considerable additional low energy scattering which cannot be accounted for by the simple model considered above, the nature of this extra intensity can be most clearly determined by extrapolating the calculated soft mode scattering beyond the range of fitting, to 0.08 THz (2.7 cm$^{-1}$), and subtracting this from the observed neutron scattering. The results of this subtraction are shown in Fig. 4.10. The additional scattering close to $T_c$ has the form of a quasi-elastic peak whose intensity diverges strongly at $T_c$. 
Figure 4.9: The evolution with temperature of $S_{E}(\mathbf{k}, \omega)$.

The soft mode spectral function $S_{E}(\mathbf{k}, \omega)$ determined from the neutron scattering data, showing that the transition from overdamped to underdamped response occurs at about 94K, or $T_{c} - 8$. The curves are marked by the approximate temperature.
Figure 4.10 The central peak.

The central peak intensity, obtained by subtracting the oscillator model spectral functions extrapolated into the low-energy regime below 0.2 THz, is shown for temperatures below $T_c$ in (a) and above $T_c$ in (b). The curves are marked with the approximate temperature.
The width of this peak is difficult to estimate accurately as the zero energy peak height would appear to be considerably above the value of the intensity at 0.08THz, and the effects of instrumental resolution cannot be reliably estimated as we have no guide to the extent in reciprocal space of the critical scattering. However, the peak width is not resolution limited and appears to narrow as $T \to T_c$. In the scan at 72K the contribution to this extra intensity appears to come largely from the weak feature in the spectrum at 0.17 THz (5.7 cm$^{-1}$) which is clearly visible as a sharp, but not resolution limited peak at 37K and 15K (Fig. 4.2a). It is conceivable that this feature which is weakly temperature dependent at low temperatures is the remnant of the low frequency critical scattering. Above $T_c$, the critical, quasi-elastic component vanishes more rapidly with temperature leaving no underdamped remnant.

The interpretation of these quite unexpected findings must remain somewhat speculative since it is not clear that the separation of the spectral function into a phonon part and a central part is a better procedure than assuming the existence of a more complex form for the $E$ mode self-energy as suggested in §3.1 and used by Hosea et al. (1979) to give 'merely a phenomenological description of the data' for $\text{Pb}_5\text{Ge}_3\text{O}_{11}$. The only clue to the origin of the scattering comes from the Raman scattering data. In the off-diagonal ($E$ mode) spectrum, extrapolating the fitted curve to lower energy showed that, in contrast to the neutron experiments, the intensity at low energy is somewhat less than predicted. For the diagonal spectrum, extrapolation to low energies showed that an excess of intensity at low energy is observed. These results suggest that the critical quasi-elastic peak does not arise simply from the change in shape of the $E$ mode, but rather from an independent process.
§4.3 Conclusion

These experiments have shown that the description of the one-phonon spectral function by a soft mode model in which the two modes are parametrised by the damped oscillator form, is not adequate to account for the intensity observed after accounting correctly for the experimental resolution. The soft mode model was shown to describe the scattering beyond 0.20 THz accurately and analysis of the neutron and Raman results in this energy range revealed slight differences which may be attributed to higher order scattering processes contributing to the Raman tensor, the discrepancies mentioned in §4.1 having been shown to arise merely from resolution effects.

Of considerably greater importance is the appearance of the quasi-elastic critical scattering which may become underdamped at low temperatures. This quasi-elastic peak was obscured in the earlier studies (Cowley et al., 1969; Shirane and Yamada, 1969) by the lower resolution employed. The width of this feature (∼0.1 THz) is similar to the widths predicted for the central peaks due to heat diffusion or acoustic mode coupling reviewed in §3.1, implying that the critical scattering predicted by theory and by computer simulation, but previously identified with the anomalously narrow (defect-controlled) central peak above $T_c$, should be identified instead with this new feature.

As a footnote, it is appropriate to note that in the study of the high temperature critical scattering, Shapiro et al. (1972) probably masked the existence of the 'broad' central peak by attempting to fit the very narrow (defect) central peak with a width of 0.005 THz, and by using incorrect dispersion relation parameters for their resolution corrections. It may be assumed that the difference in the limiting frequencies attained by the $F$ mode between this work and theirs arises from this incorrect resolution correction.
CHAPTER 5

DISCRETE LATTICE EFFECTS IN INCOMMENSURATE SYSTEMS

§5.1 Incommensurate Structural Phase Transitions

5.1.1 Introduction to incommensurate systems

In the discussion of phase transitions pursued so far in this thesis, the concept of a soft mode has figured prominently, not only in the ferroelectric crystals for which the suggestion of Cochran (1960) and Anderson (1960) was originally made, but also for the discussion of microscopic models in general. The soft mode wave-vector \( \hat{k}_s \) has been taken to be either at the Brillouin zone centre in the high temperature phase, as in \( \text{Pb}_2\text{Ge}_3\text{O}_{11} \), or at the Brillouin zone boundary as in \( \text{SrTiO}_3 \), in which case the transition involves a doubling of the unit cell. The occurrence of a large number of transitions to which one of these descriptions can conveniently be applied has led to the extensive study of models whose behaviour, while by no means trivial, is at least quite well understood. There exist, however, systems to which the above-mentioned description is not applicable. For some of them the soft mode concept still applies and experimentalists have measured a phonon branch which softens at a transition temperature, but the mode may have a wave-vector occurring at a general point in the Brillouin zone, not at a point of high symmetry like the zone centre or \( R \) point (zone corner). All such systems may be conveniently classified into one of two categories. If the soft mode wave-vector may be expressed in the form,

\[
\hat{k} = \frac{\hat{r}}{p}
\]

(5.1)

where \( \hat{r} \) is a reciprocal lattice vector, and \( p \) is an integer, then the ordered phase is said to be commensurate. In this type of transition
the unit cell dimension of the low temperature phase is some integer multiple of the unit cell dimension of the high temperature phase. In the alternative classification, the ordered phase is said to be incommensurate. In this type of phase, the distortion due to the order parameter has a periodicity which is unrelated to the periodicity of the high-temperature phase lattice; hence, if the definition is strictly applied, the truly incommensurate phase posses no translational symmetry and is therefore not strictly crystalline. In practice the definition of commensurability is applied only in the sense that \( p \) must be a small number (i.e. \( p \ll 10 \)) otherwise the phase is termed incommensurate as it is not possible to distinguish between true incommensurability and high order commensurability by crystallographic measurements. The behaviour of commensurate and incommensurate systems is not always amenable to treatment by the standard methods developed for the simpler ferro distortive and anti-ferro distortive systems. Transitions to incommensurate phases may occur for three-dimensional pure systems such as the insulators \( \text{BaMnF}_4 \) (Cox et al., 1979) and \( \text{K}_2\text{SeO}_4 \) (Iizumi et al., 1977), but a large number are known to occur in low-dimensional systems and in mixed crystals.

A feature common to many of the systems which exhibit transitions to incommensurate phases, is the occurrence of one or more additional transitions at lower temperatures. The most common of these sequences of transitions is that the crystal distorts on cooling to first an incommensurate phase, and on cooling further, to a commensurate phase below a temperature known as the lock-in temperature, where the name, the lock-in transition, derives from the concept that the distortion has become 'locked' or pinned to the lattice. This sequence of two transitions is clearly displayed by the \( \text{K}_2\text{SeO}_4 \) system which distorts at a temperature of 128K to an incommensurate phase described by the
condensation of a soft mode of wave-vector $\vec{k}_s = (0.31, 0, 0)$ in reduced units. This system has a lock-in transition to a commensurate phase with $p = 3$, corresponding to a soft wave-vector of $(1/3, 0, 0)$, at a temperature of 92K (Iizumi et al., 1977). The model developed in §5.2 is chosen to represent a complete universality class, but because of this sequence of transitions and phases, as well as the established relevance of the soft mode description, $K_2SeO_4$ may be thought of as the prototype system for the model.

The genesis of the soft mode at a general value in $K_2SeO_4$ appears to lie in some type of anharmonic phonon coupling which is not clearly understood (but see Haque and Hardy, 1980). The mechanism responsible for producing incommensurability in many low-dimensional conductors is well understood. In these materials, electron-phonon couplings between electron states with wave-vectors at the Fermi level, $\vec{k}_F$, and phonons with wave-vector $2\vec{k}_F$ can produce a sharp minimum, or Kohn anomaly (Kohn, 1959), in the phonon dispersion. In extreme cases, this anomaly is sufficient to drive a transition (Peierls, 1955) to a phase which may be described by the formation of a charge density wave (CDW), or equivalently in the adiabatic approximation by a mass density wave or order parameter of amplitude $\langle Q(\vec{k}_s) \rangle$. The origin of the soft mode wave-vector in the electronic structure of the material at an incommensurate CDW transition shows clearly that the origin of the incommensurability lies in the presence of competing interactions, and hence frustration. Briefly, the high temperature phase is stabilised by interactions, principally between near neighbour atoms, which determine the lattice spacing. In this regime the electron-phonon interaction may be said to be frustrated as the as the crystal does not distort to promote the electron-phonon coupling. In the incommensurate phase, however, the balance between the two effects changes and the electron-phonon
coupling is strong enough to dictate the periodicity. Finally, at still lower temperatures the occurrence of a lock-in transition indicates that the lattice is now stabilised by some Umklapp process which is capable, at least partially, of frustrating the incommensurate-favouring process. The effects of these competing interactions can be seen in the case of the organic charge transfer salt TTF-TCNQ (tetrathiofulvalene tetracyanoquinodimethane) which is a one-dimensional conductor. This material has a sequence of three phase transitions. The high temperature phase first distorts to allow a Peierls transition in one set of chains at 54K, a second transition at 47K then involves a competition between the ordering on the second set of chains favoured by the ordering on the first set, and the natural inclination of the second set of chains to order with a different periodicity. This competition produces an incommensurate phase between 38 and 47K in which the wave-vector of the distortion is strongly temperature dependent, before at 38K a lock-in transition occurs at which the transverse periodicity becomes commensurate due to Umklapp terms with $p = 4$, although the ordering along the chains remains incommensurate (Bak and Emery, 1976).

In the case of $K_2SeO_4$, mentioned above, it has been suggested that competition between Coulomb and short range forces produces the instability at $\vec{k_s} \sim 0.3a^*$ (Haque and Hardy, 1980).

In other systems the origin of the competing forces is more readily apparent than in the cases above. Incommensurate and commensurate phases of sorts occur in adsorbed monolayers which have recently been extensively studied (McTague, 1979; Villain, 1979; Pokrovskii and Talapov, 1979). Here the competition arises between the natural spacing of the adsorbed atoms which typically interact through Lennard Jones potentials, and the underlying substrate lattice spacing, usually of exfoliated graphite. A similar type of transition is exhibited by the
crystal Hg$_{3-\delta}$AsF$_6$ (Hastings et al., 1977) where chains of mercury atoms form an essentially one-dimensional structure which, at low temperatures 'freezes' and locks in to the underlying lattice of the AsF$_6$ units. A final set of systems of considerable interest are the transition metal chalcogenides which form both two-dimensional (dichalcogenide) and one-dimensional (trichalcogenide) metals. In Nb$_x$V$_{1-x}$O$_2$ (Comes et al., 1974), the wave-vector of the incommensurate phase depends upon the concentration of niobium in the sample, the low temperature phase being commensurate for NbO$_2$ with $p = 4$ (Pynn and Axe, 1976) and ferrodistor- tive for VO$_2$ (Marezio et al., 1974). We shall see later that being able to vary the soft mode wave-vector in this way may have important experimental consequences. Other two-dimensional metals (e.g. NbSe$_2$, TaS$_2$) have more than one stable structure at room temperature differing in the chalcogen layer stacking sequence, and exhibit a variety of CDW tran- sitions (for a review, see Friend and Jerome, 1979). The one-dimensional compounds have both commensurate (TaSe$_3$ - Sambongi et al., 1977; Tsutsumi et al., 1978) and incommensurate (NbSe$_3$ - Meerschaut and Rouxel, 1975) CDW phases and have received considerable attention due to their unique non-linear conductivity (Ong and Monceau, 1977; Fleming and Grimes, 1979; Thompson et al., 1981).

5.1.2 Landau and renormalisation group theory of static initial behaviour

For convenience, in the discussion of this and subsequent sections, we restrict consideration to a system which undergoes transitions from a high-temperature (H) phase to an incommensurate (I) phase, and at a lower temperature, to a commensurate (C) phase. The transition temperatures will be represented by $T_C$ for the H-I transition, and $T_L$ for the I-C or lock-in transition.

The first step in understanding any phase transition is normally to
consider the appropriate Landau theory and in the case of the H-I transition this proves to be most instructive. For simplicity we restrict discussion to a system where the star of the soft mode contains only the two wave-vectors \( \pm \mathbf{k}_s \) as this simplest case of an H-I transition forms the basis of the model developed in §5.2. The normal mode amplitudes are related by the condition that \( u(\mathbf{k},\mathbf{\kappa}) \) must always be real, which forces the relation

\[
Q(\mathbf{k},\mathbf{j}) = Q^*(-\mathbf{k},\mathbf{j}) \quad (5.2)
\]

For an order parameter corresponding to a zone centre or zone boundary soft mode, this condition ensures that \( Q(\mathbf{k}_s) \) is real, and so the Landau theory for the simplest case may be formulated for a single-component order parameter as was described in 1.2.4. When \( \mathbf{k}_s \) is a general wave-vector the order parameter is complex and so the Landau theory requires the use of a two-component parameter which may conveniently be written

\[
Q(\mathbf{k}_s) = \frac{1}{\sqrt{2}} A \exp i\phi. \quad (5.3)
\]

The Landau free energy, written in terms of the wave-vector conserving symmetry invariants forbids terms of the form \( Q^n(\mathbf{k}_s) \) due to the incommensurability of \( \mathbf{k}_s \), and so may be written in the form, making use of (5.2)

\[
F = F_0 + r_0 Q(\mathbf{k}_s)Q(-\mathbf{k}_s) + U_o Q^2(\mathbf{k}_s)Q^2(-\mathbf{k}_s) \quad (5.4)
\]

\[
= F_0 + \frac{1}{2} r_0 A^2 + \frac{1}{4} U_o A^4.
\]

This expression is identical to the corresponding free energy in the simple scalar order parameter case, and it shows that in this naive argument the free energy depends only upon the amplitude \( A \), of the order parameter, and not on the phase, \( \phi \). Not surprisingly the Landau
result represents an oversimplification and in a renormalisation group study of the H-I transition it can be shown (Cowley & Bruce, 1978) that the static critical behaviour at this continuous transition should be given by the $n = 2$ component Heisenberg model (often referred to as the X-Y model). In certain cases these H-I transitions can be first order. Landau theory predicts that this should be so whenever the lattice type is such that cubic invariants are allowed in the free energy expansion. In practice, measurements in the dichalogen systems, e.g. TaSe$_2$ (Moncton et al., 1975), do not show this to be the case and in the remainder of this chapter, first order H-I transitions will not be considered. RG study of this point has been inconclusive but strongly suggests that all systems which allow cubic anharmonic coupling between critical modes will produce first order H-I transitions. Where the transitions are continuous, the Landau and RG approaches give a suitable framework for discussing the phenomenology of the H-I transitions because, as will be demonstrated in §5.2 for the discrete lattice model, and as is well known from the continuum model and from experimental studies, the incommensurate phase close to the H-I transition is well described by the appearance of only a single ordering Fourier coordinate. In this regime the Landau assumption that only a single coordinate need be considered has some justification, and the RG remains a suitable method of considering the effects of critical fluctuations close to this wave-vector. The critical region above the H-I transition is therefore not qualitatively different from the critical region above a 'conventional' phase transition and the singular quantities display power law behaviour with critical exponents well known from studies of the X-Y model.

The behaviour of the system close to the lock-in transition differs considerably from the above picture. In neutron scattering experiments on, for example, 2H-TaSe$_2$ (Moncton et al., 1975), not only a single
satellite peak corresponding to the wave-vector \( \hat{k}_s \), but a set of peaks corresponding to all harmonics of this wave-vector appear with considerable intensity as \( T_c \) is approached from above. This suggests that the distortion of lowest energy no longer corresponds to a single Fourier component ordering, but to some configuration which consists of a mass (or charge) density wave with a wave-vector close to the lock-in wave-vector modulated by a long-wavelength distortion. This was first suggested by Moncton et al. (1975) who performed an approximate treatment by allowing the distortion to consist of two Fourier components where the relative amplitudes were obtained by minimising a phenomenological free energy. This suggestion was improved by McMillan again considering specifically the \((p = 3)\) CDW transition in the layered transition metal dichalcogenides (McMillan, 1975, 1976). McMillan pointed out that due to the absence of phase-dependent terms in the simple Landau theory, any long-wavelength modulation of the phase \( \phi \), in equation (3.3), would cost much less energy than a corresponding modulation of the amplitude \( A \), and adopted the 'phase-only modulation' ansatz, that the amplitude of the order parameter is independent of position while allowing the phase to be a position-dependent function \( \phi(\vec{x}) \). This ansatz allows the phenomenological free energy to be expressed in terms of the function \( \phi \) and its derivatives. McMillan then expanded \( \phi \) as a Fourier series and minimised the free energy by optimising the amplitudes of the first 20 terms numerically. In effect this approach generates a Landau theory of some twenty order parameters. In practice the transition cannot be described in terms of a conventional Landau order parameter which is non zero below the transition temperature and zero above it. The form obtained for the phase function \( \phi(\vec{x}) \) shows, close to \( T_L \) regions of commensurate ordering with \( \phi(\vec{x}) \) approximately constant.
separated by sharp steps or discommensurations, where the phase angle evolves rapidly through an angle of $2\pi/3$ (Fig. 5.1). The lock-in transition can be conveniently represented as a defect melting transition in which the discommensurations are defects which appear in the commensurate mass or charge density wave. The localised discommensurations or defects of McMillan's theory were recognised as being highly suggestive of the solitary waves in non-linear fields which were attracting much interest. Bak and Emery (1976) applied a more elegant treatment to a model of the lock-in transition in TTF-TCNQ and showed that for this model, the ground state of the phase function was given by a solution of the time-independent sine-Gordon equation which is known to exhibit an infinite number of exact n-soliton solutions. In this picture the order parameter of the transition is the 'soft soliton' density, the creation energy of a soliton being positive in the low temperature phase excludes solitons from the ground state, but the soliton creation energy passes through zero at the lock-in transition and is negative in the I phase where there is a finite soliton density. Although the nature of the order parameter, the soliton density, is unusual being non-zero only above the transition temperature, the concept is similar to the theory of melting in two dimensions (Kosterlitz & Thouless, 1972; Halperin and Nelson, 1978) where the order parameter for the transition is a finite density of vortices and vortex pairs which have a creation energy which goes to zero at the melting point. The discommensuration 'melting' is unusual in that the vortex creation energy goes to zero at a melting transition due to entropy effects, whereas the discommensuration or soliton energy goes to zero in the Landau theory because of the competing interactions. Although the transition is continuous the soliton density close to the transition displays, in mean field theory, a logarithmic dependence on $T - T_c$ rather than the power laws familiar
Figure 5.1 Phase profile of the continuum multi-soliton ground state.

The regions where $\phi(z)$ changes rapidly by $2\pi/p$ are the discommensurations or solitons. Between these discommensurations are regions of commensurate crystal.
from more usual phase transitions.

There is a conflict with experiment implied by the last statement, as the lock-in transition in 2HTaSe$_2$ has been found to exhibit a thermal hysteresis (Barmatz et al., 1975) which shows that the transition is first order. The measurements of Barmatz et al. (1975) also indicate that the Young's modulus has an anomalous frequency dependence which they attribute to the existence of an unspecified 'slow loss mechanism'. A weak hysteresis in the resistivity was reported by the same authors, although the difference in resistivity between the heating and cooling behaviour was only about 1%. Thermal hysteresis effects are also observed in the three-dimensional compound $\{\text{N(CH}_3)_4\}_2 \text{ZnCl}_4$ (tetramethylammonium tetrachlorozincate) which has a structure very similar to K$_2$SeO$_4$ but in this case the transition is from an incommensurate phase with $k_s = 0.42C^*$ to a commensurate phase with $k_s = \frac{2}{5} C^*$ (Mashiyama and Tanisaki, 1980; Tanisaki and Mashiyama, 1980).

The microscopic details of the systems mentioned so far in this chapter are generally quite complex, but one particularly simple idealised system has attracted much theoretical attention, and serves as an excellent illustration of the effects of competing interactions. This model sometimes called the anisotropic next nearest neighbour Ising, or ANNNI model, envisages a lattice of magnetic spins interacting with nearest neighbours with a ferromagnetic exchange interaction $J_1$, and interacting along one axis only with next nearest neighbours with an antiferromagnetic exchange interaction $J_2$. Using a low-temperature series expansion, Fisher and Selke (1980) have shown that for $J_2 < \frac{1}{3}J_1$ the ordered phase is ferromagnetic, but for $J_2 > \frac{1}{3}J_1$ the model exhibits, in the low temperature series approximation an infinite sequence of commensurate phases with wave-vectors $\pi j/(2j+1)a$ ($j = 1, 2, \ldots$). This type of behaviour, where an infinite sequence
of first order transitions between neighbouring commensurate phases occurs, has been given the picturesque name of the 'devil's staircase' by Aubry (1978) who found a similar sequence of transitions in a simple model appropriate to adsorbed monolayers and introduced originally by Frank and van der Merwe (1949). Studies of magnetic models by mean field theory (Bak and van Boehm, 1978) and by Monte Carlo simulation (Selke and Fisher, 1979) have shown that these very simple models give rise to a rich variety of commensurate, and possibly incommensurate phases. Bak and van Boehm identified the devil's staircase of nine commensurate phases which they found in their mean field model with the six phases observed experimentally (Höcher et al., 1978) in the magnetic system CeSb.

A final model which deserves to be mentioned is a 2D microscopic dual lattice model of two interpenetrating ionic sublattices with the same lattice constant in one direction but with differing natural periodicities in the perpendicular direction. This model was considered by Theodorou and Rice (1978). Although they considered a discrete lattice model, all of their calculations were performed by taking a continuum limit in which their model becomes similar to the Frank and van der Merwe (FVDM) model as studied by Ying (1971).

The major point of disagreement between all these theoretical approaches to what is basically the same question, is whether sequences of commensurate phases (devil's stairs) which appear in the discrete spin models and in the discrete FVDM model separated by first order transitions, or incommensurate phases consisting of lattices of solitons or discommensurations causing a genuinely incommensurate structure, are to be expected in real systems.
5.1.3 The phason mode problem

In the preceding section it was shown that in a simple Landau theory of the incommensurate phase, the free energy depends only upon the amplitude, $A$, of the order parameter, and not upon the phase, $\phi$. The continuous symmetry of the free energy under 'rotations' in $\phi$ is the condition from which Goldstone's theorem predicts that there should be a zero-frequency, or gapless, mode of excitation at $k = 0$ reflecting the broken continuous symmetry (see, e.g. Wagner, 1966).

For the regime close to the H-I transition, where the ground state of the system is well-described by only a single Fourier component distortion, the incommensurate plane wave (IPW) limit, it can be shown that in a refined Landau theory where the effects of spatial fluctuations are taken into account (Bruce & Cowley, 1978), the Goldstone mode persists, and that the fluctuations corresponding to this mode consist in the zero wave-vector limit, of a uniform translation of the phase profile. This Goldstone mode of the IPW system was termed a phason originally by Overhauser (1971). In the same theory one finds a second branch of excitations corresponding to fluctuations in the amplitude of the order parameter, which exhibits a soft mode type of behaviour going to zero frequency in the $k = 0$ limit, as the H-I transition temperature is approached from below.

When one considers the regime in which the incommensurate phase displays the effects of higher order harmonics or discommensurations, which for convenience may be referred to as the multi-soliton regime, the quasi-harmonic approach mentioned above is no longer appropriate. Bruce and Cowley (1978) treated the multi-soliton lattice in their continuum formulation by a tight-binding approximation, and were able to show that the excitation spectrum of the phase modes contains a
gapless branch corresponding to the acoustic modes of the soliton lattice, which in the zero wave-vector limit again corresponds to a uniform displacement of the phase profile. They also found that a second branch ought to exist which corresponds to fluctuations of the phase in the inter-soliton commensurate regions of the system. This branch has a finite frequency gap at the lock-in transition, and it merges smoothly into the expected phase fluctuations of the commensurate phase.

From this analysis, it can be claimed that the Goldstone mode, or gapless phason mode, should be observed throughout the incommensurate phase.

In the two-lattice model of Theodorou and Rice (1978) the excitation spectrum can be calculated exactly in the continuum approximation (Sutherland, 1973). As in the more general continuum model referred to above, the excitation spectrum contains a gapless branch throughout the incommensurate phase. Again there are two branches in the spectrum. Theodorou and Rice ascribe the gapless branch to the 'collective modes of the lattice dislocations' and the upper branch to 'renormalised phonons'.

The dynamic structure factor of the incommensurate phase can be shown to include components from the phason modes which should make the gapless branch directly visible with neutron and light scattering. Experimentally the search for phason modes has failed to locate the expected gapless branches, except in those cases where no lock-in transition occurs and hence the IPW limit appears to describe the structure throughout the incommensurate phase. A phonon-like excitation of this type has been observed in biphenyl by Cailleau et al. (1980), and some anomalous Brillouin scattering in BaMnF₄ has been tentatively ascribed to effects due to phasons (Lockwood et al., 1981).
The two major causes of conflict between theory and experiment which this work sets out to resolve are the questions of firstly, whether the lock-in transition can be described in a real lattice by the continuous defect melting transition of McMillan (1975, 1976), and secondly, whether we can explain the dynamics of the system adequately, accounting for the failure to observe phason modes in systems which undergo lock-in transitions, and the existence of the 'slow loss mechanism' of Barmatz et al. (1975). The inspiration for this study came from the speculation by Bruce et al. (1978) and by Aubry (1978) that in a discrete lattice there could be a pinning effect which would tend to lock the discommensurations to the lattice in the same way that a dislocation in a crystal experiences a Peierls potential due to the discreteness of the system. In section 5.3.4 it will be shown that this discrete lattice pinning force may in fact dominate the behaviour of the system throughout the multi-soliton regime.

§5.2  The Discrete Lattice Model

5.2.1  The model Hamiltonian

The fundamental assumption underlying the theory outlined in this and subsequent sections is that the soft mode picture of displacive structural phase transitions which has been highly successful in describing zone centre or zone boundary soft mode transitions from a phenomenological point of view, can be equally well applied to a system with a soft mode at a general wave-vector $\vec{k}_s$. The origin of this soft mode lies, of course, in the competing microscopic interactions and may result from anharmonic phonon interactions or from electron-phonon interactions producing a Kohn anomaly in the CDW transitions. In the spirit of a Landau-Ginzburg theory the electronic effects as well as
those due to hard phonon modes appear in the effective Hamiltonian
only through their effect on the phenomenological coupling constants.
Initially we consider a quasi-one-dimensional model in which it is
assumed that the displacement field in the crystal, \( u(\mathbf{r}) \), is inde-
dependent of the \( x \) and \( y \) directions, and we ignore the effects of
fluctuations. Both of these approximations will be considered in
some detail in a subsequent section. For temperatures below a critical
(lock-in) temperature, \( T_L \), the distortion is assumed to lock in to
a commensurate wave-vector which may be written \( \mathbf{r}/p \) where \( \mathbf{r} \) is a
reciprocal lattice vector in the \( z \) direction, and \( p \) is an integer
which would typically be 3, 4 or 5 for systems of current experimental
interest. The incommensurate soft-mode wave-vector \( \mathbf{k}_s \) may be assumed to
lie close to \( \mathbf{r}/p \) and so the critical modes in the Hamiltonian will
appear in the harmonic two-phonon term, the leading anharmonic (four-
phonor) term, and a \( p \)-phonon Umklapp term. The effective Hamiltonian
may be written

\[
\mathcal{H}([Q]) = \mathcal{H}_A + \mathcal{H}_p
\]

(5.5)

where \( \mathcal{H}_A \) is the familiar anharmonic phonon Hamiltonian

\[
\mathcal{H}_A = \frac{1}{2N} \sum_{\mathbf{k}} \omega^2(Q(\mathbf{k})Q(-\mathbf{k})

+ \frac{1}{N^4} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} U_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4) \times

Q(\mathbf{k}_1)Q(\mathbf{k}_2)Q(\mathbf{k}_3)

\times Q(\mathbf{k}_4)\Delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4)
\]

(5.6)

and \( \mathcal{H}_p \) is the \( p \)-phonon Umklapp Hamiltonian which is responsible for
the stabilisation of the commensurate phase,
\[ \mathcal{H}_p = \frac{1}{N^p} \sum_{\vec{k}_1, \ldots, \vec{k}_p} U_p(\vec{k}_1, \ldots, \vec{k}_p) Q(\vec{k}_1) \cdots Q(\vec{k}_p) \Delta(\vec{k}_1 + \cdots + \vec{k}_p + \vec{\tau}) \]  

(5.7)

In these expressions \( \Delta \) is the wave-vector conservation constraint introduced in section 1.3, and for convenience the normal mode amplitudes, \( Q(\vec{k}) \), differ from the definition of (1.15) by a factor of \( \sqrt{N} \). The dispersion relation in the vicinity of the soft mode wave-vector is assumed to be of the form

\[ \omega^2(\vec{k}) = r_0 + |\vec{k} - \vec{k}_s|^2 \]  

(5.8)

with \( r_0 = T - T_0 \), where \( T_0 \) is a mean field transition temperature. In this Landau theory neglecting fluctuations, \( T_0 \) is the H-I transition temperature for the continuum limit of the above model.

The Hamiltonian \( \mathcal{H}_A \) will favour the incommensurate plane wave structure for \( T < T_c \) while the Umklapp terms in \( \mathcal{H}_p \) will favour the locked-in commensurate phase. In order to convert the effective Hamiltonian of eqn. (5.5) to a direct space representation we introduce coordinates \( A_\ell \) and \( \phi_\ell \) such that the displacement field in the \( \ell \)th unit cell due to the distortion in the low-temperature (I or C) phases may be written

\[ u_\ell = \sqrt{2} A_\ell \cos[(\vec{r}/p) \cdot \vec{R}_\ell + \phi_\ell] \]  

(5.9)

where \( R_\ell \) is the position vector of the cell, and we introduce the wave-vector \( \vec{\delta}_0 \) such that

\[ \vec{k}_s = \vec{\tau}/p + \vec{\delta}_0 \]  

(5.10)

In our one-dimensional treatment we assume that \( \vec{\tau} \) and \( \vec{\delta}_0 \) both lie in the \( z \) axis direction. We also assume that the wave-vector dependence of the coupling constants \( U_4 \) and \( U_p \) is irrelevant, in which case we
can define two new coupling constants,

\[
U_0 = \frac{3}{2} U_4 \left( \frac{\pi}{p}, -\frac{\pi}{p}, \frac{\pi}{p}, -\frac{\pi}{p} \right)
\]

\[
v_p = U_4 \left( \frac{\pi}{p}, ..., \frac{\pi}{p} \right) / 2 - 1 + p / 2.
\]

By substituting from equations (5.8) to (5.11) and (1.15) into the expressions (5.6) and (5.7) we obtain the direct space form of the effective Hamiltonian for our model,

\[
\mathcal{H}([A_\ell, \phi_\ell]) = \sum_\ell \left( \frac{1}{2} \left( r_0 + \delta^2 \right) A_{\ell}^2 + \frac{1}{2c^2} \left[ A_{\ell+1}^2 + A_{\ell}^2 - \frac{2A_{\ell+1}A_{\ell} \cos(\phi_{\ell+1} - \phi_{\ell}) - \delta_0}{c} A_{\ell+1}A_{\ell} \sin(\phi_{\ell+1} - \phi_{\ell}) \right] \right) + v_p A_\ell^p \cos \phi_\ell + U_0 A_\ell^4
\]

where \( c \) is the unit cell dimension in the \( z \) direction.

In the continuum models which correspond to the above model, it has been necessary to introduce some assumption relating to the behaviour of the amplitude \( A(z) \). The original choice of Moncton et al. (1975) was to force an equal distortion of phase and amplitude, but this seems unrealistic as the energy required to create a long-wavelength distortion of the phase profile is expected to be very much lower than that required to produce an amplitude modulation.

The alternative ansatz due to McMillan assumes that \( A(z) \) is independent of \( z \). The assumption is physically plausible, and furthermore it has been shown by Nakanishi and Shiba (1978) and by Jackson et al. (1978), that allowing amplitude modulation in addition to phase modulation results in only a slight change in the lock-in transition temperature and the quantitative behaviour of the system.

By adopting the phase-only modulation ansatz, and by making the
final substitutions, the Hamiltonian may be written

$$\mathcal{H}(p, \delta_o) = \mathcal{H}_C + \Delta \mathcal{H} \tag{5.13}$$

where

$$\mathcal{H}_C = N \left[ (r_o + \delta_o^2)A^2 + U_o A^4 - vA^2 \right] \tag{5.14a}$$

$$\Delta \mathcal{H} = \frac{A^2}{c^2} \sum_{\ell} \left( 1 - \cos(\phi_{\ell+1} - \phi_{\ell}) - D \sin(\phi_{\ell+1} - \phi_{\ell}) \right) - \frac{W}{p} \left[ \cos(p\phi_{\ell}) - 1 \right] \tag{5.14b}$$

$$D = \frac{c}{p} \delta_o$$

$$W = p vc^2 = -pc^2 \nu p A^{D-2}.$$

The notation has been chosen to emphasise that $\mathcal{H}_C$ is the effective Hamiltonian of the commensurate phase which has $\phi_{\ell} = 0$ for all values of $\ell$. In order to consider the lock-in transition, the Hamiltonian $\mathcal{H}_C$ may be expected to represent a contribution to the free energy which will vary smoothly through the transition, and therefore it is sufficient to consider only the behaviour of the term $\Delta \mathcal{H}$. The only temperature dependence in the original Hamiltonian of eq. (5.5) is contained in the parameter $r_o$, the square of the incommensurate soft mode frequency. In the commensurate phase, the amplitude, $A$, depends upon $r_o$, and through this temperature dependence, a temperature dependence is introduced into the coupling constant, $W$, of the lock-in term in $\Delta \mathcal{H}$. In the incommensurate phase, $A$ is again determined by $r_o$, and provided that the energy of the phase modulation term $\Delta \mathcal{H}$ is small compared to $\mathcal{H}_C$, $A$, and hence $W$, will decrease monotonically as temperature increases throughout the incommensurate phase, becoming zero at $T_c$. A study of the temperature dependence of the system is therefore equivalent to studying the behaviour of the ground state of $\Delta \mathcal{H}$ for different values of $W$. 


5.2.2 The general character of the phase function $\phi$

In the study of the continuum models analogous to that described above, the ground state of the Hamiltonian can be determined analytically by deriving the Euler-Lagrange equation for $\phi$ which yields a second order differential equation which may be solved by standard techniques. For the discrete lattice model a similar procedure may be applied, but in this case the condition for obtaining an extremum of $\Delta H$ which results from minimising (5.13) with respect to an arbitrary $\phi_m$, is given by the second-order non-linear difference equation

$$\sin(\phi_m - \phi_{m-1}) - \sin(\phi_{m+1} - \phi_m) = D[\cos(\phi_m - \phi_{m-1}) - \cos(\phi_{m+1} - \phi_m)] + W \sin p \phi_m \quad (5.15)$$

Given the present state of knowledge of solution of non-linear difference equations it is unlikely that the solutions to (5.15) can be written in a closed form. This equation may be rearranged to give a three-term recursion relation from which the solution for $\{\phi_k\}$ can be constructed numerically once two initial starting points have been specified. The ground state can then be obtained by varying the initial conditions slowly. In Figure 5.2 several typical ground states obtained in this manner for the model with $p = 3$ are shown for various values of $W$.

It can be seen that for small values of $W$ the phase varies approximately linearly with distance, this is the condition for an IPW distortion. Increasing $W$, which is equivalent to reducing the temperature, reduces the average slope of the phase profile and causes the appearance of harmonics of the effective wave-vector until for large values of $W$, close to the lock-in transition, the phase profile shows short regions of commensurate structure separated by sharp
Figure 5.2: Ground states of the discrete lattice model.

Ground states of $\{\phi_i\}$ obtained numerically for the case $p = 3, D = 0.4$ which has $W_L \approx 0.2911$.

$\circ W \approx 0; \quad x \ W = 0.2000; \quad \bullet \ W = 0.2906.$
domain walls or discommensurations. These two types of solution correspond qualitatively to the expected behaviour since the order parameter for the lock-in transition in the continuum theory of Bak and Emery (1976) is the soliton density, whereas for the I-H transition the order parameter is the amplitude of the distortion with wave-vector $\mathbf{k}_s$ which corresponds to a phase angle for the $\ell$th cell of

$$\phi_\ell = \ell D .$$

### 5.2.3 Behaviour close to the high-temperature phase

The I-H transition occurs when the energy given by eq. (5.13) becomes zero. In a case where this transition is continuous in the sense that $A$ goes continuously to zero as the transition temperature is approached from below, the transition may be expected to occur for $W \to 0$. In this limit eq. (5.15) is satisfied by a solution of the form

$$\phi_\ell = \alpha \ell D .$$

The value of $\alpha$ which minimises the energy of the plane-wave solution may be calculated from eq. (5.14) to be

$$\alpha = \tan^{-1} D/D \approx 1 - D^2/3 .$$

(5.17)

This corresponds to a wave-vector for the distortion of

$$k = \tau/p + \delta_o (1 - c^2 \delta_o^2 /3).$$

(5.18)

The energy for this IPW distortion is given by

$$E_\text{I} = N \left[ r^* A^2 + U_o A^4 \right]$$

(5.19)
with

\[ \frac{1}{4} r^* = \frac{1}{4} r_o + \left( \frac{1}{2} - \alpha - \frac{a^2}{2} \right) \delta_o^2 + \left( \frac{a^4}{24} \right) (4/\alpha - 1) c^2 \delta_o^4 \]

\[ \approx \frac{1}{4} r_o + \frac{1}{8} c^2 \delta_o^4. \tag{5.20} \]

Treating this result by mean field theory gives a continuous transition when \( r^* = 0 \) from the high-temperature to the IPW phase. The effect of the discrete lattice has been to lower the transition temperature by the amount \( \frac{1}{4} c^2 \delta_o^4 \). Since the Umklapp terms do not appear in equation (5.19) this result is independent of \( p \).

By writing \( \mathcal{H}_c \) in the form

\[ \mathcal{H}_c = N \left[ \frac{1}{2} (r_o + \delta_o^2) A^2 + U_o A^4 - |v_p|^2 A^p \right] \tag{5.21} \]

the direct commensurate to high temperature (C-H) phase transition is seen to be continuous for \( p = 4 \) at a temperature given by \( r_o = -\delta_o^2 \).

In this case there will always be an IPW state between the commensurate and disordered (high temperature) states in the phase diagram. For other values of \( p \) the C-H transition may be first order, in which case the condition for the IPW phase to be stable is that

\[ v < \frac{1}{4} \delta_o^2 - \frac{c^2}{8} \delta_o^4 \tag{5.22} \]

for some temperature below \( T_c \). For values of \( p \) greater than 4 additional higher-order terms should in principle be included in the effective Hamiltonian to stabilise the commensurate phase and these terms will determine \( A \) and hence \( v \). These terms have not been included in this work because they do not contribute to \( \Delta \mathcal{H} \), but it is implied throughout this chapter that condition (5.22) is satisfied, otherwise the IPW phase will be pre-empted by the first
order C-H transition. In practice, since $v$ is proportional to $A^{p-2}$, the above condition is always likely to be satisfied for the larger values of $p$.

Close to the I-H transition the order parameter, $A$, is given by the mean field expression

$$A^2 = -\frac{r^*}{4U_o}$$

As the corrections to $k_0$, $r_0$ and $A$ are all of order $\delta_0$, they are evidently small and so it is reasonable to conclude that the continuum model gives an adequate description of the phase diagram close to $T_c$.

5.2.4 Behaviour in the multi-soliton regime

From Fig. 5.2 it can be seen that a non-zero value of $W$ will cause a distortion of the IPW. This is only a slight modulation for small values of $W$, but gives rise to the formation of a sharply stepped profile as $W$ increases. For values of $W$ greater than a critical value $W_L$, which depends on $p$ and $D$, it is no longer possible to generate solutions to equation (5.15) which correspond to a negative value of the energy $\Delta \mathcal{H}$. This corresponds to the critical temperature, $T_L$, for the lock-in transition.

One feature of the recursively obtained solutions close to the lock-in phase boundary is the fact that it is possible for two solutions to have a very similar appearance, in the sense that each consists of an array of equally spaced discommensurations with the same spacing in each solution, and yet to have a significant difference in energy. This is because the energy of a discommensuration is dependent on its position relative to the underlying lattice. There is evidently an
interaction between the discommensurations and the lattice which makes it energetically favourable for the discommensurations to be centred on a unique location within the unit cell. This behaviour was investigated by assuming a form for the ground state.

The continuum limit of the Hamiltonian obtained by the phase-only modulation ansatz is

$$\Delta H_{\text{con}} = \frac{A^2}{c^2} \int \text{d}z \left[ \left( \frac{\partial \phi}{\partial z} - \phi_0 \right)^2 - v (\cos \phi - 1) \right].$$

(5.24)

The Euler-Lagrange equation for an extremum in $\Delta H_{\text{con}}$ is, as observed by Bak and Emery (1976), the time-independent sine-Gordon equation

$$\frac{\partial^2 \phi(z)}{\partial z^2} = v \sin p \phi(z).$$

(5.25)

This equation is known to have an infinite family of multi-soliton solutions (Hirota, 1973) of which the simplest is the single-soliton function

$$\Theta(z) = \frac{4}{p} \tan^{-1} \exp(p v^2 z).$$

(5.26)

In Fig.5.3 several of these continuum soliton functions are compared with the numerically obtained exact solutions of (5.15). It can be seen that the soliton gives a surprisingly good fit even in the case where the soliton width is only a few lattice spacings.

Exploiting this close agreement, the distortion of a sine-Gordon soliton in a discrete lattice was studied by a variational method. In this the initial phases of the linear chain model were set to the continuum soliton values, and then the forces in each unit cell were calculated and the phases were changed to balance these forces. For a wide range of values of $p$, $D$ and $W$ the continuum solitons were found to be in excellent approximation to the ground state, the phases
changing by only the order of 5% when the soliton was allowed to distort.

Figure 5.4 shows the results of a typical calculation with \( p \) equal to 4 and \( W \) approximately its lock-in value. It can be seen that the soliton has distorted in such a way as to increase the phase separation between the central unit cells and thus to make the discommensuration slightly narrower. Since discrete lattice effects are likely to be most pronounced for narrow discommensurations, this shows that a calculation made using the sine-Gordon profile will slightly underestimate the discrete lattice effects. The difference between the sine-Gordon soliton energy, and the variationally distorted soliton energy is negligible except close to the value of \( W \) where the energy changes sign. The ground state of the incommensurate phase may therefore be studied by using the sine-Gordon solitons as they will certainly give a qualitatively correct description of the ground state close to the lock-in transition.

§5.3 The Lock-in Transition

5.3.1 The multi-soliton ground state

In Chapter 2 where a brief review of non-linear wave equations was given, solitons were introduced as localised solutions to these equations with very restrictive properties, for example, their stability properties in soliton-soliton collisions. There has been a tendency amongst physicists to apply the term soliton to almost any localised solution of a non-linear equation largely due to the difficulty of establishing rigorously the existence of the infinite number of conservation laws required to define an integrable system. Such rigorously defined solitons as the sine-Gordon system shows, may exist in discrete systems of difference equations, but the description of the ground state in the vicinity of the lock-in transition as a multi-soliton ground state
Figure 5.4: The distortion of a continuum model soliton

The distortion of a soliton by a discrete lattice for $p = 4, D = 0.5, W = 0.64 \approx W_L$.
The full curve shows the sine-Gordon soliton, the full circles show the variationally obtained phases.
is intended to imply only that it consists of a lattice of discommen-
surations, the wider question of whether these localised solutions of
eq. (5.15) display true soliton properties, is for practical purposes
irrelevant as will shortly become apparent. For this reason, and for
these stated at the end of the previous section, it is consistent to
approximate the ground state of our discrete lattice model, not by
the true multi-soliton states of the sine-Gordon model but by the
simpler linear superposition

$$\phi_z(b) = \sum_m \Theta(\xi c - mb - z_0)$$

(5.27)

where $\Theta(z)$ is given by (5.26). This function represents a lattice
of sine-Gordon solitons, linearly superposed, and separated by a
contant lattice spacing $b$. Most of the numerical calculations were
performed using a 100 cell chain; longer chains were used to check
for any finite size effects. Soliton spacings of between 5 and 1000
lattice spacings were investigated for different values of $p, \delta_o$
and $W$. The equilibrium configuration was determined by the minimum
in the energy function

$$E(b) = \left(\frac{c^2}{NA^2}\right)\Delta (\{|\phi_z(b)|\})$$

(5.28)

In all of the results which follow it may be assumed that the
value of $z_0$, the phase profile 'sliding' coordinate, has been chosen
to minimise the energy $E(b)$, except where it is explicitly stated to
the contrary.

5.3.2 Soliton energies and the phase diagram

At the lock-in boundary the soliton lattice spacing $b$ may be
expected to be large and therefore the critical value, $W_L$, of the parameter


W, will occur where the single-soliton creation energy changes sign. For a continuum sine-Gordon field the single-soliton creation energy is given by

\[ E = 8Wp^{3/2} - 2\pi D/p \quad (5.29) \]

In Fig. 5.5(a) this prediction is compared with the energies obtained numerically for the case \( p = 4, D = 0.5 \). The results show that over the relevant range of \( W \) there is an approximately constant discrepancy between the two energies, with the continuum energy being somewhat higher than the actual energy. This leads to a change in the value of \( W_L \) of approximately 5% in the case shown. The effect of this change on the phase diagram is shown in Fig. 5.5(b). The value of \( T_L \) is reduced in all cases. For the larger values of \( p \) and \( D \) which correspond to the narrower solitons the effect can be considerable. The phase diagrams are plotted against \( cv^{1/2} \) rather than \( W \) to allow a comparison with the continuum theory which, for all values of \( p \), gives

\[ v_L = \frac{1}{16} \pi^2 D^2/c^2 \quad (5.30) \]

The line at which the IPW becomes stable compared with the commensurate phase is also shown in Figure 5.5(b). For small \( D \) this is given by

\[ v_{IPW} = (\frac{1}{4} D^2 - \frac{1}{8} D^4)/c^2 \quad (5.31) \]

Since for any non-zero value of \( D \), \( v_{IPW} < v_L \) the lock-in transition in this model will always proceed via a multi-soliton phase rather than by a direct first-order commensurate to IPW transition.

Also shown on the phase diagram of Figure 5.5(b) are the horizontal lines which the phase boundary must approach for large values of
Figure 5.5: Soliton energies and the phase diagram.

(a) Single soliton energies in the multi-soliton region, \( p = 4, D = 0.5 \). The full curve shows the continuum energy, the full circles show numerically computed values for the discrete lattice.

(b) Phase boundaries for the incommensurate (I)-commensurate (C) lock-in transition with \( p = 3 \) (dotted curve), \( 4 \) (chain curve), and \( 8 \) (dashed curve). The straight line which the numerically obtained boundaries approach for small \( D \) is the continuum model result. The horizontal lines show the sharp soliton limits for \( p = 4 \) and \( 8 \). The full curve above the lock-in boundary shows the value of \( v \) at which the IPW becomes stable with respect to the commensurate phase.
v. These can be calculated by recognising that the limit of large \(v\) corresponds to the sharp soliton limit where \(\phi\) is given by

\[
\phi_L = \frac{(2\pi/p)H(\ell c - z_0)}
\]

(5.32)

where \(H\) is the Heaviside step function

\[
H(z) = \begin{cases} 
1 & z \geq 0 \\
0 & z < 0 
\end{cases}
\]

In this limit the stability criterion is given by

\[
D > \frac{1 - \cos 2\pi/p}{\sin 2\pi/p} 
\]

(5.33)

For larger values of \(D\) any lock-in transition will lock in to a phase with \(\phi_L\) given by

\[
\phi_L = \frac{2\pi \ell/p}{2}\]

(5.34)

thus the wave-vector of what may be called a super-commensurate distortion is given by

\[
k_s = \frac{2\pi}{p} 
\]

(5.35)

This criterion sets an upper limit on \(D\) for a given value of \(p\) for which the following theory is valid. In the model which we have considered the soft mode wave-vector has been assumed to be independent of temperature. The temperature dependence of the system's behaviour is therefore given by a fixed value of \(D\) on the phase diagram. In the model of Bak and Emery (1976), the wave-vector was temperature dependent, and for a typical real system we might reasonably expect a variation in \(k_s\) as is seen above \(T_c\) in \(K_2SeO_4\). The only change which this may be expected to induce in the behaviour is to widen either the IPW or multi-soliton regions of the phase diagram. If \(D(T)\)
is a convex function of $v(T)$, the commensurate phase will be stable for small values of $v$, but as the system cools it may undergo a transition to an incommensurate or even a super-commensurate phase. The relevance of this super-commensurate limit may be understood by the observation that a single effect which produces a soft mode at one wave-vector, $k_s$, may be responsible for both inducing a continuous lock-in transition to a phase with a commensurate ordering of periodicity $p$ close to the soft mode $k_s$, or a strongly first order lock-in transition to a commensurate phase of a different periodicity. It is possible that the $\{\text{N(H}_3\text{)}_4\}_2\text{ZnCl}_4$ system which exhibits a lock-in transition with $p = 3$ at $1^\circ\text{C}$ and a strongly first order lock in at around $7^\circ\text{C}$ (on heating only) to a commensurate phase with $k_z = 0.4 \, \text{c}^*$ may be showing behaviour of this type. (Mashiyama and Tanisaki, 1980). Unfortunately this remains only a speculation until the $\{\text{N(CH}_3\text{)}_4\}_2\text{ZnCl}_4$ system can be studied by inelastic neutron scattering to investigate the possible occurrence of a soft mode.

5.3.3 The equilibrium soliton density

The equilibrium density of solitons in the ground state was obtained for different values of $W$ close to $W_L$ from the position of the minimum in the $E(n)$ versus $n$ curve, where $n$ is the density of solitons. Figure 5.6 shows the form of this function close to $T_L$ for $p = 4$, $D = 0.5$. Slightly below $T_L$ the minimum is well defined and the equilibrium density may be determined with confidence. For temperatures close to the lock-in temperature the curve is virtually flat for $n$ less than 0.03 and within the accuracy with which the calculations were carried out it was not possible to demonstrate any inter-soliton interaction for lower densities. This does not prove
Figure 5.6: The multi-soliton energy density.

The energy density $E(n)$ is shown for a range of soliton density $n$, for $T < T_L$ (A), $T = T_L$ (B) and $T > T_L$ (C). The equilibrium density is given by the position of the minimum.
that the transition is first order, but it strongly suggests that experimentally the transitions will appear first order as the region of W for smaller values of n will be vanishingly small. Since the multi-soliton state can be characterised by an effective wave-vector \( \vec{k} \) given by

\[
\vec{k} = (2\pi/p)n
\]  

(5.36)

if n appears to vanish discontinuously at \( T_L \), the observed 'order parameter', the ordering wave-vector, will appear to change discontinuously from \( k = \tau/p + \vec{k} \) to \( k = \tau/p \). Similar behaviour was observed for other values of p and D.

In a continuum sine-Gordon field two solitons have a mutual interaction energy which decreases exponentially at distances much greater than the soliton width leading to a multi-soliton energy of the form

\[
E(b) = (8v^{1/4}/pb)\left[1 + 4 \exp(-pv^{1/4}b)\right] - (2\pi/pb)\delta_0.
\]  

(5.37)

With an energy of this form the soliton density close to \( T_L \) is given by

\[
n \propto -1/n(T - T_L)
\]  

(5.38)

Figure 5.7(a) shows the equilibrium soliton density for the case \( p = 4, D = 0.5 \). The extreme steepness of the slope close to \( T_C \) is obvious, and this is the feature which may well be interpreted in an experiment as discontinuous. The full curve is a best fit to a function of the form given in equation (5.38) with the proportionality constant extracted from the logarithmic plot of Figure 5.7(c). Similar data are displayed for the case \( p=3, D = 0.4 \) to emphasise the similarity in behaviour in a case where the broader solitons make the inter-soliton interaction appreciable for lower densities.
Figure 5.7: The equilibrium soliton density.

(a) Soliton density close to $W_L$ for $p = 4$, $D = 0.5$. The full circles show numerically obtained values, the full curve shows a function of the form given in eqn. 5.38. The pinning energy exceeds the soliton creation energy for $W > 0.598$.

(b) Soliton density close to $W_L$ for $p = 3$, $D = 0.4$. The vertical lines indicate the region for which the pinning energy exceeds the soliton creation energy.

(c) Soliton density versus $-1/(n(W_L - W))$ for low soliton densities, with $p = 4$ (full circles) and $p = 3$ (crosses).
For an IPW with \( k_s = \frac{\pi}{p} + 6.9 \), the effective soliton spacing is given by

\[
\beta_{IPW} = \frac{2\pi}{p\delta_o}.
\] (5.39)

Decreasing \( W \) from \( W_L \), the soliton spacing rapidly decreases, following approximately a \( \ln(T - T_L) \) law, until \( \beta/c \) reaches the nearest integral value to \( \beta_{IPW}/c \). For smaller values of \( W \) the solitons retain this spacing and as their width increases they merge into an approximately plane wave as \( W \) approaches zero. Because, as explained in the next section, \( \beta \) is always expected to be an integral number of unit cells, the multi-soliton phase cannot be expected to change continuously into the IPW, hence some essential feature of the incommensurate state is noticeably missing from this analysis. This point will be fully discussed in §5.4.

### 5.3.4 The soliton-lattice pinning energy

The original motivation for studying the discrete lattice came largely from the conviction that for narrow solitons, that is solitons with a width of only several unit cells, there would be a contribution to the soliton energy which depended upon the position of the soliton in relation to the underlying lattice. To investigate this possibility, the energy of a single soliton, \( \Theta(z - z_o) \) close to the lock-in boundary was calculated for different values of \( z_o \). The results for a typical case are shown in Fig. 5.8. In every case which was examined, the minimum energy was found to correspond to the soliton being centred midway between two lattice points. This is qualitatively simple to understand as the commensurability pinning potential \( v(\cos p\phi - 1) \), will cause the value \( \phi_x = \pi/p \) to be a high-energy
Figure 5.8: The soliton-lattice interaction potential.

The energy of a soliton centred at different positions within the unit cell. The horizontal line shows the continuum theory energy, $p = 4$, $D = 0.5$, $W = 0.643 \sim W_L$. 
position, and so the lattice will always distort to exclude such high-energy positions in its ground state. The difference between the maximum and minimum energies in Fig. 5.8 represents a pinning energy which will tend to restrict the inter-soliton spacing to integral values of $b/c$. Close to $T_C$ the soliton energy is dominated by the pinning energy hence the ground state may be expected to show pronounced discrete lattice effects. For the case shown, which has $p = 4$, the pinning energy is considerably greater than the inter-soliton interaction energy for inter-soliton spacings of as little as 8 unit cells, and it is greater than the total soliton energy for the temperature interval shown in Fig. 5.7(a). Because of the rapidity with which the soliton density rises for $W < W_L$ the pinning energy ought to dominate the behaviour of the system throughout the multi-soliton regime.

Two effects are immediately apparent in this strongly-pinned soliton picture. The more immediate effect is that the continuous variation of soliton density $n$ and hence of the order parameter $\bar{k}$, must now be replaced by a series of first-order, or discontinuous changes. The phase corresponding to a soliton lattice with a soliton spacing of $b$, equal to an integral number of unit cells will not be truly incommensurate, but will be commensurate with a long repeat distance. The variation of $\bar{k}$ with temperature will now take the form of a sequence of weakly first-order transitions between an infinite set of phases in which $b/c$ takes every integral value. In an extreme case where the pinning energy is sufficiently strong to prevent the movement of solitons due to thermal fluctuations, etc. to establish the minimum-energy ground state, it is possible that a condensation of solitons on random (minimum-energy) lattice sites will occur, in which case the phase will be neither incommensurate in the normal sense meaning that it shows some well-defined periodicity, nor commensurate,
but instead it will be inhomogeneous. If the pinning energy is comparable to thermal energies the 'devil's staircase' of Aubry (1978) and Bak and Boehm (1978) will result. The second effect of the pinning potential is relevant primarily to CDW systems. In these systems the phase solitons can be associated with a localised electron state which will contribute to the conductivity if the solitons are free to move. If the solitons are pinned by the lattice with a small pinning force the electrical conductivity in the multi-soliton regime might be expected to exhibit a hopping conductivity mode with an anomalously small activation energy. This would offer an explanation of the 'slow loss mechanism' required to account for the properties of 2H-TaSe₂, (Barmatz et al., 1975). The observability of pinning effects in the electronic properties of a system is discussed in some detail in 5.5.1.

The comments made above are relevant not only to the case with p = 4 which was chosen to illustrate the argument, similar comments could be made for p = 3 and for p ≥ 5, although for the case with p = 3, the broader solitons show a considerably weaker pinning energy (the range of for which the pinning energy exceeds the creation energy is shown in Figure 5.7(b)).

5.3.5 An energy gap in the phason spectrum

In the continuum model (Bruce and Cowley, 1978) the excitation spectrum of the phase function φ(z) for a single-soliton state may be calculated by a method due originally to Zittartz (1967). In this method the phase is written

\[ \phi(z) = \phi_0(z) + \delta\phi(z) \]

(5.39)

where \( \phi_0(z) \) is the ground state of a static single soliton, and the
configurational energy (5.24) is expanded to second order in the fluctuation \( \delta \phi(z) \). By incorporating a kinetic energy term in the Hamiltonian and assuming an oscillating solution of frequency \( \omega \), the problem is reduced to solving the linear Schrödinger-like equation

\[
\frac{\partial^2}{\partial z^2} \delta \phi(z) + a^2 \cos \phi_0(z) \delta \phi(z) = \omega^2 \delta \phi(z)
\]

(5.40)

where \( a = pv^{\frac{1}{2}} \). When the explicit form of \( \phi_0(z) \) is inserted into eq. (5.40), the equation becomes one for which the solutions are known (Landau and Lifschitz, 1959) to consist of one solution with a zero eigenvalue which represents a uniform translation of the soliton, and a continuum of wave-like solitons whose amplitude is reduced in the region of the soliton. In order to treat the multi-soliton ground state, the 'potential' term in (5.40) must be replaced by some approximate form to render the equation tractable. Applying a tight-binding approximation in which the solitons are considered to be well separated and interacting with only their nearest neighbours, the excitation spectrum for the M soliton lattice is calculated by expanding the fluctuations \( \delta \phi(z) \) in terms of Bloch functions of the single soliton excitations. In effect the non-linear Hamiltonian has been treated by linearising the fluctuations about an exact ground state and keeping only the lowest terms in the fluctuations. The zero frequency local mode of the single soliton gives rise to a branch of the excitation spectrum extending over a Brillouin zone determined by the soliton lattice spacing \( b \). These fluctuations correspond to the longitudinal acoustic branch of the soliton lattice. The energy of the zero wave-vector excitation is expected to be zero from the translational symmetry of the Hamiltonian 5.24. The wave-like modes of the single soliton problem corresponding to extended fluctuations in the regions of
commensurate ordering away from the solitons, correspond in this analysis to a branch of excitations with a dispersion relation of the form

\[ \omega^2(k) = \alpha^2 + k^2 \quad . \] (5.41)

This branch of excitations merges smoothly into the excitations of the commensurate phase at \( T_L \).

The zero wave-vector excitations in the discrete lattice model were investigated by assuming that, as in the continuum case, the lowest energy fluctuations will represent a uniform translational motion of the solitons.

The phase function may now be written

\[ \phi_\ell = \sum_m \theta(\delta c - mb - z_{\text{min}} - z_0) \quad . \] (5.42)

where \( z_{\text{min}} \) is now the position of lowest energy, and \( z_0 \), the fluctuation amplitude is assumed to be small.

The effective Hamiltonian (eqn. 5.5) which we have considered while discussing the ground state properties of the system contains only potential energy terms, since the contribution to the free energy of the kinetic energy terms in the Hamiltonian does not influence the properties of the ground state. For a study of the dynamic properties the kinetic energy must be included. This may be written

\[ J(Q) = \frac{1}{N} \sum_k \dot{Q}(k)\dot{Q}(-k) \quad . \] (5.43)

By applying the same transformation to the direct space coordinates as we used for the potential energy, the extra term in the Hamiltonian becomes

\[ J = \sum_\ell \frac{1}{2} A_\ell^2 \phi_\ell^2 \quad . \] (5.44)
The assumption that the lowest energy mode involves only a uniform translation of the phase profile reduces the problem to one involving only the single variable, \( z_0 \), the soliton lattice sliding coordinate. Both the kinetic energy \( \mathcal{J} \), and the potential energy \( \mathcal{V} \), must therefore be expressed in terms of \( z_0 \). For the kinetic energy, substituting the appropriate expression for \( \phi_z \) from equation (5.27), for small values of \( z_0 \), we may write

\[
\mathcal{J}(z_0) = \frac{1}{2} m^* z_0^2 \tag{5.45}
\]

where \( m^* \) is a soliton effective mass given by

\[
m^* = A^2 \left[ \frac{\partial^2 \phi_z}{\partial z^2} \right]_{z_{\text{min}}} \tag{5.46}
\]

The potential energy cannot be expressed in a simple analytic form, but for small values of \( z_0 \), it is reasonable to expand \( \mathcal{V} \) about the minimum-energy position in the form

\[
\mathcal{V}(z_0) = \mathcal{V}_0 + \frac{1}{2} \mathcal{V}''(z_0) z_0^2 + O(z_0^4) \tag{5.47}
\]

For the case of well-separated solitons, both the effective mass \( m^* \) and the constants in the potential energy are simply proportional to the number of solitons. The expressions for \( \mathcal{J} \) and \( \mathcal{V} \) can be combined to give the equation of motion for \( z_0 \)

\[
\ddot{z}_0 = -\omega_G^2 z_0 + O(z_0^3) \tag{5.48}
\]

showing that the coordinate \( z_0 \), and hence the soliton lattice, executes approximately simple harmonic motion with a frequency \( \omega_G \), a phason mode gap frequency, where

\[
\omega_G^2 = \mathcal{V}''(z_{\text{min}})/m^* \tag{5.49}
\]
The quantities $V''(z_{min})$ and $m^*$ have to be calculated numerically. In Fig. 5.9a they are shown for the case $p = 4, D = 0.5$. As the solitons become sharper the effective mass decreases because fewer atoms actually move as the soliton moves, reducing the number of non-zero terms in (5.46). As the Umklapp coupling constant $W$ increases, the curvature $V''(z_{min})$ increases and hence $\omega_G$ increases. Figure 5.9b shows the dependence of $\omega_G$ on $W$ for the case $p = 4, D = .5$ and compares it with the continuum prediction for the frequency gap associated with the phase fluctuations in the inter-soliton commensurate regions. Close to the lock-in transition at $W_L$ the frequency gap for the phason modes is approximately half of the gap predicted for the commensurate fluctuations, $\alpha$, shown by the broken line. Because of the approximations which have been necessary in deriving this frequency it should be borne in mind that the use of continuum solitons will have systematically underestimated the effects of soliton pinning, and so it may be that the frequency gaps associated with phason and commensurate fluctuations will be approximately equal even for the low values of $p$ which are of relevance to current experiments. For the larger values of $p$, it can be seen from Fig. 9c that the phason gap frequency near the lock-in transition is at least comparable with the commensurate fluctuation gap. The appearance of the phason gap due to soliton pinning could make experimental separation of the two branches difficult, which would explain the failure of the search for phason modes.

The behaviour of $\omega_G$ for small values of $W$, where $\omega_G$ approaches zero is interesting since as $W$ tends to zero the stable configuration should be the IPW for which the frequency gap must disappear. In Fig. 9b it can be seen that for values of $\alpha$ less than 0.65, the phason gap $\omega_G$ is vanishingly small. The parameter $\alpha$ as well as representing the commensurate frequency gap is proportional
Figure 5.9: Soliton mass, force constant and phason gap frequency.

(a) Effective mass $m^*$ (broken curve) and force constant $\mathcal{V}''(z_{\text{min}})$ (full curve) in units of $A^2/c^2$ for $p = 4$, $D = 0.5$.

(b) Phason gap frequency $\omega_G$ (full curve) and commensurate fluctuation gap frequency $\alpha$ (broken curve).

(c) $\alpha$ (broken curve) and $\omega_G$ (full circles) for different values of $p$ with $W$ set to the continuum $W_L = (\pi D/4)^{1/2}$ and $D = 0.5$. 
to the inverse width of a soliton, and the limiting value $a \approx 0.65$
is equivalent to a soliton width of approximately 12 unit cells. This
may be interpreted as the minimum soliton width for which the continuum
theories should be applied uncritically.

The difference in temperature dependence which is exhibited in Fig.
9b by the energy gap in the phason and commensurate fluctuation spectra
may provide a means of distinguishing the two types of fluctuation as the
phason contribution may appear to soften at a temperature below $T_c$, the
I-H transition temperature, because although, according to the ground state
calculation, the frequency $\omega_G$ does not become zero for finite values of
$W$, the very small values of $\omega_G$ in the region close to $T_c$ would pre-
sumably be interpreted as zero due to the finite resolution available
experimentally. It will be shown in the next section, however, that the
ground state calculation is unreliable in the region where $\omega_G$ is small
and that in fact phason modes may be characterised by an abrupt dis-
appearance of the associated frequency gap at an unpinning transition
temperature between $T_c$ and $T_L$, therefore the predictions of Fig. 9b
for the region with small $W$ must be interpreted with caution.

5.4 The Effects of Fluctuations

5.4.1 Fluctuation effects near the I-H transition

The model which has formed the basis of sections 5.2 and 5.3 has been
quasi-one-dimensional in the sense that although only one spatial dimen-
sion has been explicitly considered, this was a consequence of the
elementary observation that the symmetry of our system will restrict
the ground state to a configuration in which there will be no variation
of $A$ or $\phi$ in a direction perpendicular to the $z$ axis. Since the examples
of systems exhibiting incommensurate phases mentioned in §5.1 include
many low-dimensional systems, the critical behaviour which we expect to observe will be in the fluctuation-dominated regime in which we expect corrections to mean-field analysis to arise when fluctuations are taken into account.

In the mean-field study, the H-I transition was adequately described by the condensation of a single Fourier component at the transition temperature, and the techniques and results which were obtained in the discrete lattice model were shown to be essentially unchanged from the continuum model which itself was reduced to a simple Landau theory. In the same way that the selection of appropriate coordinates transformed the mean-field problem into a standard Landau-like theory of ferroelectricity, the application of a suitable coordinate transformation converts the LGW Hamiltonian of equation (5.5) into the much-studied isotropic two-component Heisenberg, or X-Y, model provided that the Umklapp terms are not included. Since the I-H transition is not in a first approximation influenced by the Umklapp terms because they have disappeared from the effective Hamiltonian of equation (5.21), it may be concluded that in the discrete lattice model, the critical behaviour close to \( T_c \) will be that of the X-Y model.

There is some experimental evidence to support this conjecture in the case of the transition at 128K in \( K_2\text{SeO}_4 \). In a neutron-scattering experiment to measure the order parameter experiment \( \beta \), Iizumi et al. (1977) obtained a value of 0.40 ± 0.05. The best available prediction from series expansion methods (Pfeuty et al., 1974, Gerber and Fisher, 1975) give \( \beta(n=2) \approx 0.35 \), which lies just within the experimental limits. These agree with dielectric constant measurements which give \( 2\beta = 0.7 \) (Shiozaki et al., 1977) and \( 2\beta = 0.76 \pm 0.1 \) (Unruh et al., 1979). These experiments show that fluctuation effects are significant
since our mean-field approach gives the classical value of $\beta = 0.5$, however it can hardly be taken as a convincing demonstration that the behaviour is that of the $n = 2$ model rather than the $n = 1$, Ising model which one might naively expect. In a subsequent neutron scattering experiment, Majkrzak et al. (1980) obtained a value of $2\beta = 0.75 \pm 0.05$ for the exponent characterising the growth of the primary order parameter, and a value of $2\beta = 1.57 \pm 0.07$ for the experiment characterising the growth of intensity below $T_c$ of the secondary Bragg satellite at $k_{26} = (\frac{1}{3} + 2\delta_0) c^*$, which is again in fairly good agreement with the X-Y model prediction of $1.69$. Critical exponent measurements for Rb$_2$ZnCl$_4$ give $\beta = 0.37 \pm 0.03$ (Gesi and Iizumi, 1980) and $\alpha = -0.026 \pm 0.002$ (Lopez-Echarri et al., 1980) again indicating X-Y model critical behaviour at the H-I transition.

For two-dimensional systems, there are global theorems due to Mermin and Wagner (1966) and Hohenberg (1967) which show that the isotropic two-dimensional X-Y model does not have a phase with long range order at finite temperature. At any non-zero temperature the Goldstone spin waves or phonons corresponding to transverse fluctuations of the order parameter destroy the long range order showing that two dimensions is the lower critical dimensionality for the X-Y model. This result can be demonstrated by constructing a low-temperature renormalisation group equation for the isotropic $n$-component, $d$-dimensional LGW model (see e.g. Young, 1979) from which the fixed point value of the critical temperature is given by

$$T^* = \frac{d - 2}{n - 2}.$$

From this equation one can see that there is a fixed point for $d = 3$ although for $n = 2$ this occurs at a temperature above the low temperature
regime for which this model holds and an extra term must be included in the RG equation to yield a finite value of $T^*$. In the two-dimensional X-Y model, there is a phase transition of a rather unusual nature as argued by Berezinskii (1971) and Kosterlitz & Thouless (1972). They point out that although there is no long-range order at any temperature above absolute zero, the decay of order parameter correlations is algebraic rather than exponential up to a certain temperature, the Kosterlitz-Thouless transition temperature, where the short range order is overcome by a melting process involving the spontaneous creation and unbinding of vortex pairs. The existence of a second type of transition occurring at a still higher temperature involving the creation of disclinations was postulated by Halperin and Nelson (1978) as the reason for the change in the decay of angular correlations from algebraic above the Kosterlitz-Thouless transition temperature to exponential at high temperature. The two dimensional incommensurate phases observed in the transition metal dichalcogenides $\text{Tas}_2$ and $\text{NbSe}_2$ (Moncton et al., 1975) and in adsorbed monolayers of $\text{H}_2$, $\text{D}_2$ and Ar on exfoliated graphoil (McTague, 1979) do not appear to be the ephemeral short range ordered phases of the X-Y model but genuinely long-range ordered structures. This would appear to conflict with the above arguments relating their critical behaviour to the X-Y model.

The most immediate suggestion as to how to resolve this conflict is to assume that since the two-dimensional systems mentioned do not have the simplest possible star for their soft mode wave vectors, but have instead a 'triple-$\vec{k}$' structure in which the soft mode can take any of the six directions allowed by the hexagonal lattice symmetry, the model may be oversimplified in neglecting coupling between modes located at different pairs of soft mode vectors.
In fact this concept is not capable of explaining the discrepancy. The appropriate triple-\vec{k} Hamiltonian can be treated by RG methods (Sak., 1974, Aharony, 1976), showing that the cross-coupling terms, which couple critical fluctuations close to one of the soft mode wave-vectors, \vec{k}_1, with critical modes close to another of the soft mode wave-vectors \vec{k}_2 (\neq -\vec{k}_1) lead to scaling fields which evolve under the operation of the RG with a scaling component

$$\lambda = \alpha(n = 2)/\nu(n = 2)$$

Since the specific heat exponent for the XY model is negative in two and three dimensions (Fisher, 1974) the critical behaviour associated with any of the triple-\vec{k} systems will be described by decoupled models of the type discussed in §5.2 and §5.3.

The necessary conclusion is that the solution to this conflict must come from a simplification inherent within the one-dimensional model. It was shown in §5.3 that there is a pinning energy for any modulated phase which will tend to produce a devil's staircase of commensurate phases close to the lock-in transition, and it was assumed that close to the high temperature phase, this devil's staircase can evolve smoothly into the incommensurate plane wave of §5.2.3. In fact for temperatures below \(T_c\), there will still be a small pinning energy which may be thought of as arising from the Umklapp terms which are neglected by the derivation of the X-Y model. This pinning energy will break the continuous symmetry in \(\phi\) implied by the X-Y model causing a uniaxial perturbation. According to RG folklore, (see, e.g. Ma, 1976b) this uniaxial perturbation is relevant with a scaling exponent \(y_T = 1.36\) for \(n = 2, d = 2\) to second order in \(\epsilon\), and this will cause a crossover from the isotropic X-Y behaviour to the well-understood Ising behaviour of the Onsager model (Onsager, 1946; Fisher and Pfeuty, 1972).
From this brief analysis we conclude that the behaviour at the I-H transition can be described within the existing framework of RG studies of the LGW model, but that there is an essential difference between the three-dimensional case where the behaviour is of the X-Y model type and the IFW description of the incommensurate phase is appropriate, and the two-dimensional case where the existence of an ordered phase requires the retention of the Umklapp terms which cause the pinning effect, in which case the phase is not truly incommensurate and the critical behaviour is that of the two-dimensional Ising model.

Unfortunately the experimental systems in which these two-dimensional transitions occur have certain flaws which make it difficult to test this prediction. Three-dimensional crossover effects in the layered systems such as TaSe₂ may obscure the genuinely two-dimensional critical behaviour. For the adsorbed monolayer systems, the transition to a high temperature phase is a melting transition to a fluid, which appears, for sub-monolayer coverage, to be first order. However, for a solid at the registered filling, Horn et al. (1978) interpreted their X-ray data on a series of monolayer films of Krypton on graphite, as indicating a continuous transition with order parameter exponent \( \beta \approx 0.08 \). This is reasonably close to the 2D Ising value of \( \beta = 0.125 \).

5.4.2 Fluctuation effects in the multi-soliton regime

Close to the lock-in transition, where the order parameter is more usefully considered to be the soliton density than the amplitude of an incommensurate plane wave, the renormalisation group methods used to describe fluctuation effects at the I-H transition are no longer appropriate, since the system is dominated by pinning effects which arise from high-order Umklapp processes which are required to have a negligible
effect in the RG formulation. The quasi-one-dimensional model again obscures the fundamental importance of the system dimensionality which, as with the behaviour close to $T_c$, may produce a marked difference between the behaviour in two and three dimensions when fluctuations are taken into account. The usual result that a truly one-dimensional system cannot support a phase with long-range order still holds even though the solitons which form the ground state are fundamentally the same as the kinks which destroy the long range order in a one-dimensional Ising model.

In §5.3 we concluded that the ground state close to $T_L$ would consist of an array of 'flat' domain walls, where by 'flat' is meant that the phase angle, $\phi$, does not vary in the $x$ and $y$ directions. The Umklapp terms in the effective Hamiltonian, $v(1 - \cos 4\phi)$, will break the rotational symmetry in $\phi$ causing the critical behaviour in both 2 and 3 dimensions to be that of the Ising model rather than the X-Y model. It was first conjectured by Burton and Cabrera (1949) that any interface such as the solitons considered here would undergo a so-called roughening transition at a finite temperature. Ideally below the roughening temperature the surface would be approximately flat as we have assumed our one-dimensional solitons to be, whereas above the roughening temperature the increase in entropy for an irregular wall will outweigh the extra energy involved in its construction, and the surfaces formed will themselves display only short range ordering in the sense that if the position of the surface is defined as $z(x)$, then the correlation function

$$G(x) = \langle(z(x) - z(0))^2\rangle \quad (5.51)$$

diverges as $x$ tends to infinity. The roughening temperature for an Ising system of $d$ dimensions is given in the simplest (Burton et al.,
1951) theory—by the bulk transition temperature for an Ising system of d-1 dimensions. In more realistic models (v. Reijsen, 1975; Weeks et al., 1973) it has been suggested that the transition temperature for the three-dimensional model is higher than this simplest theory would suggest, and that the transition temperature, $T_R$, is dependent only upon the coupling constant perpendicular to the wall. It will be shown in 5.5.3 that for three-dimensional systems such as $K_2SeO_4$ it is reasonable to suppose that the material is well below the soliton roughening temperature. Based on this assumption, the dominant fluctuations of the multi-soliton state are treated in 5.4.3 by a simple perturbation theory.

For a system with only two spatial dimensions, the domain walls are necessarily one-dimensional structures. The roughening transition studies indicate that the roughening 'transition', like the 1-dimensional Ising bulk transition, should be at zero temperature, and that above this transition the correlation function of the interface position will have the form for large $x$,

$$G(x) = \ln x.$$ (5.52)

Clearly under such circumstances the approximation that $\phi(\tau)$ is independent of one spatial direction is unrealistic. To put the problem in perspective it is appropriate to note that the logarithmic divergence expected does not preclude the development of effectively long-range order on the graphite surfaces where surface defects limit the maximum range of correlations to typically a distance of approximately 120 Å (McTague, 1979) in the experiments mentioned in this work, although very recently surfaces of several thousand Angstroms have become available. In the layered materials we note that three-dimensional effects may help to induce long-range transverse correlations. Provided that the transverse correlation length is much
greater than one unit cell width the two-dimensional system may exhibit the type of behaviour which will be discussed in succeeding sections explicitly for a three-dimensional model.

5.4.3 The three-dimensional Hamiltonian

The effective Hamiltonian introduced in §5.2.1 was considered for only one dimension in §5.2 and §5.3 but the form is unchanged from that given in eq. (5.5) when \( \mathbf{k} \) is allowed to be a d-dimensional vector, provided that the star of the soft mode contains only the two wave-vectors at \( \pm \mathbf{k}_s \) on the z axis. It is convenient at this point to allow the dispersion relation to be anisotropic by writing it in the form

\[
\omega^2(\mathbf{k}) = \omega_0 + J_{\perp} \mathbf{k}^2 + J_z (k_z - k_s)^2
\]  

(5.53)

where \( \mathbf{k} \) is the transverse component of the wave-vector \( \mathbf{k} \). Transforming the Hamiltonian by the same procedure as in §5.2 yields an expression analogous to eqn. (5.13) with all energies expressed in units of \( J_z \),

\[
\mathcal{H}(p, \delta_s) = \mathcal{H}_c + \Delta \mathcal{H} + \mathcal{H}_\perp.
\]  

(5.54)

The first term in this expression is still the Landau-like energy of the commensurate ground state given by eq. (5.14(a)). The second term is the familiar function of the phase variables given by eq. (5.14(b)) except that now the summation over \( \ell \) must be replaced by a summation over three spatial indices. The extra term, \( \mathcal{H}_\perp \) is given by

\[
\mathcal{H}_\perp = \frac{J A^2}{2a^2} \sum_{jk\ell} \left[ 2 - \cos(\phi_{j+1,k,\ell} - \phi_j,k,\ell) - \cos(\phi_{j,k+1,\ell} - \phi_j,k,\ell) \right]
\]  

(5.55)
where \( a \) is the lattice spacing in the transverse direction and \( J = J_\perp /J_z \).

Since the expectation value is always positive except for the pseudo-one-dimensional case where \( \phi_{j,k,l} \) depends only on \( l \), the extra terms do not affect the ground state.

At finite temperatures it is necessary to take into account the effect of fluctuations in the transverse profile, and in order to do this, it is convenient to introduce a continuum model in which the Hamiltonian incorporates a term to take account of the pinning effect.

The continuum analogue of (5.54) is

\[
\mathcal{H} = \mathcal{H}_c + \frac{A^2}{ca^2} \int d^3r \left\{ \frac{1}{2} \left( \frac{\partial \phi}{\partial z} - \delta_{0} \right)^2 - v(\cos \phi - 1) \right. \\
+ \left. \frac{J}{2} \left[ \left( \frac{\partial \phi}{\partial x} \right)^2 + \left( \frac{\partial \phi}{\partial y} \right)^2 \right] \right\}.
\]

In the spirit of the approach suggested by the assumption that the partition function will factorise into a phonon part and an essentially non-linear part as described by Bishop (1978), we consider only the fluctuations in \( \phi \) corresponding to small deviations from the single, or multi-soliton ground state. Considering for the time being only the single soliton ground state we can write the low-energy fluctuations in the form

\[
\phi(\mathbf{r}) = \phi_0(z - z_0) + \phi_1(\mathbf{r})
\]

where \( \phi_0 \) is the ground state phase function and \( \phi_1 \) is a small perturbation. The continuum Hamiltonian of (5.57) has as its lowest energy excitation the Goldstone mode reflecting the continuous translational symmetry which is broken by the choice of \( z_0 \) for the soliton position (Bruce and Cowley, 1978). Following the procedure adopted by
Bak and van Boehm (1980) it is assumed that the lowest energy fluctuations are simple bends in an otherwise rigid soliton, in which case for a single soliton state, $\phi_1(r)$ is proportional to the derivative $\partial \phi_0(r)/\partial z$ and so the phase function may be written (see Wallace, 1980)

$$\phi(r) = \phi_0(x,y,z - \theta(x,y))$$

(5.59)

where $\theta(x,y)$ is the displacement of the soliton from its ground state position. The condition that $T < T_R$ ensures that $\theta$ is small, and therefore we may regard $\theta(x,y)$ as equivalent to the sliding coordinate $z_0$ in the calculation of $\omega_0$ in 5.3.5. To incorporate the effects of a discrete lattice into this continuum model we add a term proportional to $\theta^2$ into the fluctuation Hamiltonian $\mathcal{H}_\perp$,

$$\mathcal{H}_\perp = \frac{1}{ca^2} \int d^3r \left[ \frac{\partial \theta}{\partial x} \frac{\partial \theta}{\partial y} \right] + \frac{c}{2L} \nu'(z_0) \theta^2$$

(5.60)

where the mass of the phase field $\nu''(z_0)$ is obtained numerically.

If the ground state consists of well-separated solitons we may neglect the exponentially small inter-soliton interaction, in which case the fluctuation energy density becomes

$$\frac{C}{L} \mathcal{H}_\perp = \frac{1}{a^2} \int dx \ dy E_0 \left[ \left( \frac{\partial \theta}{\partial x} \right)^2 + \left( \frac{\partial \theta}{\partial y} \right)^2 + \left( \frac{\pi \Omega}{2} \right)^2 \theta^2 \right]$$

(5.61)

where

$$E_0 = 2v^{1/2} JA^2/pb$$

(5.62)

and

$$\Omega^2 = ca^2 \nu''(z_{\text{min}}) / 4\pi^2 v^{1/2} JA^2$$

(5.63)

Introducing $\theta(k)$, the Fourier transform of $\theta(x,y)$, $\mathcal{H}_\perp$ can be rewritten in the form
\[
\frac{C}{L} \mathcal{H} = \frac{a^2}{\pi^3} \int_{0}^{\pi/a} d^2k \ E(k) \delta^2(k) \quad (5.64)
\]

where
\[
E(k) = E_0 \left[ |k|^2 + (\pi \Omega/a)^2 \right] . \quad (5.65)
\]

In this representation \( E(k) \) is the energy of a phonon mode as discussed by Bak and van Boehm (1980).

5.4.4 The effect of entropy terms in the free energy

In the ground state calculations of §5.2 and §5.3 we examined the properties of the model by considering only the internal energy given by the effective Hamiltonian rather than the free energy which was introduced in 1.2.4 and 1.3.1. In order to calculate the free energy for the model incorporating the \( \theta \) fluctuations we return to the definition of the free energy in terms of a partition function and instead of assuming that the functional integral is dominated only by the extremum of \( \mathcal{H} \), the general state approximation, we assume that the partition function is dominated by that part which corresponds to the linearised fluctuation about the ground state described above. The free energy of the multi-soliton lattice is then given by the expression.

\[
F = -T \ln \text{Tr} \exp(-\mathcal{H}/T)
\]

\[
= E_{gs} - T \frac{a^2}{\pi^3} \int d^2k \ \ln \int d\delta(k) \exp \left[ -E(k) \delta^2(k)/T \right] \quad (5.66)
\]

where \( T \) is the absolute temperature in units of \( J_z/k_B \), \( E_{gs} \) is the ground state energy, and all energies are again measured in units of \( J_z \). The result for a single soliton is

\[
F = E_{gs} + \frac{1}{2} T \ln \left[ (2vJ^2 A^2 c/\pi Ta^2) \gamma(f(\Omega)) \right] \quad (5.67)
\]
where \( g = \frac{\pi^2}{e} \) and \( f(\omega) = \omega^2(1 + \frac{1}{\omega^2})^{1+\frac{1}{2}} \). The factor \( g \) is a geometrical constant arising from the choice of a Brillouin zone for the phason wavevectors which is circular in the transverse direction. The factor \( f(\omega) \) arises from the soliton pinning and reduces to unity for zero pinning energy. The fluctuation term in equation (5.67) may become negative for high temperatures. Because the scale of \( T \) is determined by \( J_z \), which was arbitrarily set to be unity in §5.2 the sign of this term at \( T_L \) will depend upon the system to which the theory is applied. The pinning energy factor, \( f(\omega) \), has the effect of increasing the temperature at which the fluctuation free energy becomes negative, thus the discrete lattice effects tend to stabilise the commensurate phase by increasing \( T_L \). Choosing for convenience \( J = a^2/c^2 \) we find that for \( D = 0.5, \ p = 4, \) the factor \( f(\omega) \) has the value 1.58 at \( T_L \). This value increases quite rapidly with \( p \) so that, for example, with \( p = 6, \) we find that \( f(\omega_L) = 3.19. \) For systems with highly anisotropic dispersion where \( J < a^2/c^2 \) the values of \( f(\omega_L) \) will be large. This will occur particularly for the incommensurate transitions driven by a Kohn anomaly in the dispersion of a low-dimensional conductor where the dispersion surface slopes very steeply in directions perpendicular to the Fermi surface, i.e. along the \( c \) axis in our model.

The full free energy density for the multi-soliton state, neglecting the exponentially small inter-soliton repulsion, is

\[
F = \langle c/L \rangle H_c + \Delta F
\]

where

\[
\Delta F = A^2(8v_{1}^{1/2} - \frac{2\pi}{pb} \delta_{0}) + \frac{Tc}{2b} \ln \left( \frac{2A^2 v_{1}^{1/2} J_c^2}{\pi Da^2} \right) + \frac{Tc}{2} \ln f(\omega)
\]

The three terms in this expression for the free energy represent, in a sense, the different levels of approximation employed. The first term
gives the ground state creation energy for the soliton lattice, which changes sign at the mean-field lock-in temperature. The second term represents the contribution to the free energy from the continuum-like fluctuations of the solitons. For a range of temperatures close to $T_L$ this term will have the form of a slowly varying function of the absolute temperature. Over the narrow temperature range for which the multi-soliton phase exists, it may be expected to contribute only an additive constant to the free energy. This additive constant will change $v_L$ and hence $T_L$ but, since the logarithmic dependence of the soliton density in $T - T_L$ arises from the exponential repulsion between solitons, this will not be affected by the fluctuations. In the case considered by Bak and van Boehm (1980) of the ANNNI model with an incommensurate phase, the continuum fluctuations are found to reduce $T_L$. By noting that the energy required to create a soliton-anti-soliton pair is $\eta = 16A v^4 / pc$ we can see that the temperature at which the free energy contribution from the continuum soliton fluctuations becomes negative, is $T = \eta / 8$. This suggests that our treatment of fluctuations around a single soliton ground state does indeed capture all of the relevant fluctuations, as the lowest-energy non-linear excitations which we have not considered are the so-called breathers (Steiner, 1979) and unbound soliton-anti-soliton pairs which require an energy of $\eta$ to create, while the single soliton fluctuations will reduce the transition temperature from its mean field value whenever this is above $\eta / 8$. The third term represents the discrete lattice pinning effect. It is positive for all temperatures and may be interpreted as increasing $T_L$ and favouring commensurability by suppressing the Goldstone phason fluctuations.

We may conclude that apart from the change in $T_L$ resulting from
the additive and approximately constant terms in the free energy, the
results and conclusions of section 5.3 may be expected to remain
qualitatively correct.

Two hypotheses relating to fluctuations of marginal relevance to
this work require a brief consideration in view of the last statement.
It has been shown that the application of renormalisation group methods
to the one-dimensional quantum and two-dimensional classical models
(Pokrovski and Talapov, 1978, 1979) and to the $2+\epsilon$ - dimensional model
(Natterman, 1980a, b) with a Hamiltonian similar to 5.24 in which
temperature dependence is introduced through a variation of $\delta_0$ rather
than $W$ with $T$, leads to the generation of a $k^3$ term in the free
energy from which it is apparent that $k$ varies as $(\delta - \delta_c)^{1/2}$ and
hence as $(T - T_L)^{1/2}$ rather than as $|2n(T - T_L)|$. As the temperature
dependence is introduced in a different manner in these models, and
as the soliton effects are incorporated into the RG in a rather
artificial manner, this result is not directly relevant to our model
and does not invalidate the conclusion reached in the last paragraph,
however it does suggest that a variation of $\delta_0$ in a real system may
be of some qualitative and not merely quantitative importance. It has
also been pointed out (Bak and Fukuyama, 1980) that quantum zero-point
fluctuations may destroy the devil's staircase in the FVDM model at
low temperatures. This effect is of little importance here as none of
the lock-in transitions discussed in this work occur at sufficiently
low temperatures. However, there is some evidence from dielectric
measurements that 2H-NbSe$_3$ may have such a transition below 5K, in
which case quantum fluctuations may be of importance.
5.4.5 The floating soliton phase and unpinning transition

There is one important difference between the multi-soliton phase and the IPW state which prevents the incommensurate phase from evolving smoothly from the single-soliton limit to the IPW limit. In the single soliton limit it was shown in §5.3 that there is an energy gap in the phason mode spectrum which decreases monotonically as $W$ decreases, whereas in the IPW limit a zero-frequency sliding mode is possible. Although, as it is shown in Fig. 5.9(b), the gap frequency, $\omega_g$, is close to zero for a range of $W$, the gap never vanishes for a finite $W$. At some point in this region the pinning energy, which decreases to zero as the H-I transition is approached, is small enough to be overcome by thermal fluctuations and the solitons become unpinned. For higher temperatures the solitons are able to move freely through the lattice and the soliton lattice spacing, $b$, is no longer restricted to integer multiples of the unit cell dimension. In this regime the phase is truly incommensurate and the gapless sliding mode may be expected.

To investigate this transition an extra term has to be introduced into the free energy to represent the average potential energy gained by a soliton moving freely through the lattice. By defining a dimensionless energy, in the notation of 5.3.5, by

$$\varepsilon = \frac{1}{2} \int_A \varepsilon \left( \frac{1}{c} \int_{z_c}^{(k+1)c} V'(z_o)dz_o - V_o \right)$$

(5.69)

the free energies of the pinned, and unpinned, or floating soliton phases may be written

$$F_p = F_0 + \frac{(T_c/2b)}{\ln f(\Omega)}$$

(5.70)

and
\[ F_u = F_o + \frac{(A/c)^2 \varepsilon c}{b} \]  

(5.71)

The stable configuration of the system will be determined by the lower of these two free energies. The solitons will be pinned for temperatures satisfying the condition

\[ T < (A/c)^2 \frac{2\varepsilon}{\ln f(\Omega)} \]  

(5.72)

The function \( 2\varepsilon/\ln f(\Omega) \) is shown in Fig. 5.10 for the typical case \( p = 4, D = 0.5 \). Since it decreases monotonically to zero as \( T \) approaches \( T_c \), the solitons will always be unpinned at some temperature below \( T_c \). Whether or not the solitons are pinned at \( T_L \) depends on the value of \( T_c \) and the overall scale of the Hamiltonian which is defined by the sharpness of the minimum in the dispersion relation, \( J_z \).

These constants must be chosen to fit a particular system. It is useful to define an unpinning temperature \( T_u \) by the expression

\[ T_u = 2(\frac{A_L}{c})^2 \frac{\varepsilon L}{\ln f(\Omega_L)} \]  

(5.73)

This is the temperature at which the solitons at the lock-in boundary become unpinned. It is determined by the model parameters \( p, \delta_o, J \) and \( J_z \). The lock-in temperature, \( T_L \), depends upon \( p, \delta_o \) and \( J_z \), and also on \( T_o \), the mean-field, I-H transition temperature. For the case \( T_u < T_L \) the phase profile will be unpinned and most of the discrete lattice effects will be obscured by the motion of the solitons throughout the incommensurate phase which will evolve smoothly from the single-soliton limit at the continuous lock-in transition, into the IPW phase close to the continuous I-H transition. If, however, \( T_u > T_L \), the solitons will be pinned close to the lock-in phase boundary and at some intermediate temperature between \( T_L \) and \( T_c \) there will be a phase
Figure 5.10: The function $2\varepsilon/\ln f(\Omega)$.

The numerically determined values of the function $2\varepsilon/\ln f(\Omega)$ for the model with $p = 4$, $D = 0.5$. 
transition characterised by the abrupt disappearance of the energy gap in the phason spectrum. In this case the incommensurate phase will evolve from the first-order lock-in transition by means of a devil's staircase of first-order transitions at which the soliton density changes discontinuously. This line of first order transitions will be terminated by the unpinning transition, above which temperature the phase will evolve smoothly into the IPW.

§5.5 Secondary Effects of Soliton Pinning

5.5.1 Electronic properties of CDW systems

The observation of a soliton unpinning transition described above is complicated by the lack of a macroscopically observable order parameter. In the conventional language of phase transitions the vanishing frequency of the phason mode $\omega_c$, may be interpreted as a divergent susceptibility $\chi_{ph} = \omega_c^{-2}$. The order parameter of the transition may be defined on a microscopic level as the expected deviation of a soliton from its equilibrium position, $\langle \theta(x,t) \rangle$, which is zero in the pinned phase and non-zero if the soliton is unpinned, however this definition is not useful as the quantity $\langle \theta(x,t) \rangle$ is not macroscopically observable. The most direct method of establishing the existence of an unpinning transition would thus appear to be by observing the softening of a phason mode at some temperature in the incommensurate phase.

The difficulty of establishing the limiting frequencies attained by softening phonons at even a 'conventional' phase transition has already been discussed in Chapter 4. In the SrTiO$_3$ transition discussed there the phonon frequency of the soft mode approached its limiting value more gradually than the phason model frequency approaches zero in Fig. (5.9b). It is further shown in Chapter 6 of this work, that static planar
domain boundaries give rise to quasi-elastic scattering, and this may cause considerable problems in a scattering experiment which endeavours to study very low energy response. A better method of observing the unpinning transition, and a potentially important role for the soliton pinning effect occurs in the CDW systems such as TTF-TCNQ and the transition metal chalcogenides, due to the possibility of collective conductivity.

The problem of the behaviour of the low-temperature conductivity of a one-dimensional metal was studied independently by Peierls (1955) and by Fröhlich (1954). Peierls conjectured that at low temperatures the structure would distort, forming a CDW to promote an electron-phonon coupling between electrons at the Fermi surface and phonons with a wave-vector equal to twice the Fermi wave-vector. This CDW, he argued, would lower the energy of the system by creating an energy gap at the Fermi surface which would cause the system to be insulating at \( T = 0 \), and semi-conducting rather than metallic at low temperatures. Fröhlich proposed a different solution. If the mass density wave of the lattice is accompanied by a periodic modulation in the macroscopic conduction electron density, \( n \), of the form \( n(z) = n_o + \delta n(z) \) where \( n_o \) is the uniform density of the metallic state and \( \delta n(z) \) is given by

\[
\delta n(z) = n_o A \cos(k_z z + \phi)
\] (5.74)

then a variation of \( \phi \) translates the entire CDW condensate uniformly and so represents a net electrical current flow. Fröhlich argued that for a translationally invariant system (the continuum approximation in a slightly different form) the condensate may be set in uniform motion. Fröhlich proposed this as a mechanism for superconductivity.

Experimentally it is found that the one-dimensional conductors are
semi-conducting at low temperature (see e.g. Friend, 1978), a fact which has been interpreted by invoking several pinning mechanisms for the condensate (Lee et al., 1974; Okabe and Fukuyama, 1976; Fukuyama and Lee, 1978).

In the model described in this chapter the low-temperature behaviour of the CDW will be determined by the commensurability pinning energy. Two conduction processes have been investigated for the continuum model, both of which are relevant also to the discrete model, these envisage conduction by a uniform translation of the rigid condensate, and conduction by a gas of thermally excited solitons.

The rigid CDW model was investigated by Bishop (1979). Using a Langevin equation including the commensurability pinning potential $v(1 - \cos\phi)$, and a phenomenological damping term, Bishop showed that the exact transport results of Abegaokar and Halperin (1969) for an unpinned CDW could be extended to include the non-linear commensurability pinning by means of the approximate Fokker-Planck treatment of Trullinger et al. (1978), except at low temperatures where soliton diffusion is important, a conclusion which is supported by the numerical studies of Bocchieri et al. (1970) of the F.P.U. problem (Fermi et al., 1955) which showed that soliton diffusion is important in the $\phi^4$ model only at low temperatures. In the high temperature regime where the rigid CDW transport is expected, Bishop found that the conductivity is ohmic for small fields. The calculation is applicable without any modification to the discrete lattice model, for which it suggests that the conductivity should be proportional to $A^2(T)$, and therefore only weakly temperature dependent in the C phase provided that the temperature is sufficiently high, that is, according to Bishop (1979)
In the soliton gas model it is proposed that the mechanism of collective conduction is by thermally excited solitons. Although the above discussion suggests that soliton diffusion is important only at 'low temperatures', experimental results (see 5.6.2) suggest that in some systems this mechanism may be dominant throughout the C phase. The role of soliton anti-soliton pairs was investigated by Pietronero et al. (1975) and by Rice et al. (1976). The latter were able to show that the conductivity will have a single-particle component with an activation energy equal to one half of the Peierls electron energy gap, and a collective Fröhlich mode conductivity due to the soliton pairs, which they termed \( \phi \) particles, of the form

\[
\sigma_\phi = \frac{\tau_0}{2m} \exp\left(-\frac{\eta}{2k_B T}\right)
\]  

(5.76)

where \( e^* \) is the effective charge of a soliton and \( \tau_\phi \) is its lifetime. If the activation energy \( \eta \) is less than the electron energy gap, the Fröhlich mode will be the dominant current carrier in the commensurate phase. In the continuum approximation this conductivity is also ohmic for low fields. In applying the \( \phi \) particle description to the discrete lattice model it must be noted that the solitons and anti-solitons will be pinned below \( T_u \) and thus the collective conductivity due to them will be of the thermally activated 'hopping' type for low fields, and therefore non-ohmic as discussed below for the I phase solitons. For large fields and higher temperatures the discrete lattice and commensurability pinning will be overcome and the \( \phi \) particle dynamics may be discussed in a linear approximation (Lee et al., 1974).
In the incommensurate phase the commensurability pinning effect will continue to prevent a uniform translatory mode of the condensate, but in the continuum model there will be no restriction on the motion of the solitons, and so the solitons which are now a part of the ground state will become the major current carriers. If the solitons are unpinned and the continuum dynamics are applicable (Bruce and Cowley, 1978; Theodorou and Rice, 1978; Trullinger et al., 1978) then the Goldstone sliding mode of the phase solitons will give a collective conductivity which will no longer be of the thermally activated form given in eqn. (5.76), but will now be proportional to the equilibrium soliton density, \( k \sim \ln (T - T_L) \).

An array of pinned solitons will exhibit qualitatively different behaviour. Starting from the equation of motion discussed in 5.3.6 for a pinned soliton, we may add an extra term to represent the force on a charged CDW soliton with an effective charge \( e^* \), due to an applied electric field \( E(\omega) \), so that from (5.48)

\[
\dot{z}_o = \frac{e^*}{m} E - \frac{\omega^2}{\omega_G^2} z_o .
\]  

(5.77)

The conductivity for low values of the field \( E \) for an array of solitons with a lattice spacing \( b \) is now given by

\[
\sigma(\omega) = \frac{e^{*2}(-i\omega)}{b m \omega_G^2 \left[ \omega_G^2 - \omega^2 \right]} .
\]

(5.78)

and the static dielectric constant \( \varepsilon_s \), by

\[
\varepsilon_s = \frac{e^{*2}}{b m \omega_G^2} .
\]

(5.79)

The significance of the soliton pinning is most apparent at low frequencies where the pinned solitons cannot follow the frequency of the
field so that at zero frequency there is no D.C. conductivity in contrast to the unpinned soliton case where the Fröhlich conductivity is infinite for the pure system. The above formulae predict that at the unpinning transition, where $\omega_c$ vanishes, the static dielectric constant will diverge, and the D.C. conductivity will exhibit an anomaly, the single particle semi-conductor behaviour of the pinned phase being supplemented in the unpinned phase by a Fröhlich mode.

At higher fields the weak soliton pinning close to the unpinning transition will permit a further collective conduction mechanism. The solitons of the ground state will be able to move under the influence of the field by 'hopping' from one unit cell to the next. The conductivity will now be proportional to the product of the number of solitons and the rate of soliton hopping. The problem of hopping conductivity by electrons in a medium containing a number of localised but loosely bound states has been one of the standard problems of semiconductor physics which has attracted a considerable degree of attention in recent times (for reviews see Bottger, 1976; Ambegaokar et al., 1973). The soliton hopping may be viewed as a thermally activated, classical process, and the hopping rate may be calculated approximately If the discrete pinning is weak ($\epsilon \ll k_B T$) and the interactions between the solitons and phonons may be adequately represented by a random noise in the equation of motion (5.77), then a study of the associated Fokker-Planck equation (von Kampen, 1978) gives the hopping rate as

$$z_0 = \frac{\beta \tilde{\epsilon}}{(k_B T)^2} \exp(-\tilde{\epsilon}/k_B T) \quad (5.80)$$

where $\beta$ is a Langevin damping constant, and $\tilde{\epsilon}$ is the barrier energy

$$\tilde{\epsilon} = 2\epsilon - \frac{1}{2} e^* E \quad (5.81)$$
where $\varepsilon$ is the pinning energy defined by eqn. (5.69). The exponential (Arrhenius) factor does not depend on the approximations made in the derivation of eqn. (5.80), and will dominate the conductivity (see e.g. Mott, 1969). The form of the prefactor is less reliable, a low-temperature approximation due to Wiener and Sanders (1964) suggests that it should be simply proportional to the 'attempt frequency' $\omega_G$ (see Sokoloff and Widom, 1978). The points of major importance in eqns. (5.80) and (5.81) are the predictions that the conductivity has a thermally activated form with an activation energy, $\hat{\varepsilon}$, well below the Peierls energy gap for single particle conductivity, and that there is a critical field $E_c = 4\varepsilon / ce^*$ at which the discrete pinning will be overcome and the low frequency conductivity will become ohmic, proportional to the soliton density.

In the truly incommensurate phase where the solitons are unpinned the Fröhlich conductivity will be adequately described by the continuum models, except that as discussed in the next section, the presence of defects will break the translational symmetry and limit the conductivity. Finally, in the IPW limit the rigid-condensate model of Bishop (1979) may be applicable with the commensurability potential interpreted as a weak defect pinning potential.

In concluding, it is useful to summarise these results for the conductivity of the quasi one-dimensional model. In the commensurate phase, the conductivity may be dominated by a single-particle component due to electrons excited across the Peierls energy gap, a collective component due to excited soliton - anti-soliton pairs with a lower activation energy $\eta/2$, or a collective component due to a uniform CDW translation with only a weak temperature dependence. In the pinned, multi-soliton, $I$ phase the low frequency, low field conductivity will be controlled by an activation energy related to the
pinning energy $\varepsilon$ which will be smaller than the activation energy of the C phase soliton component. In contrast to the C phase, the conductivity will be non-ohmic for fields below a critical field which will unpin the solitons. The high-frequency conductivity in the I phase will show no anomalous features, although the resonance at $\omega = \omega_G$ may be detectable by microwave or infra-red absorption. Finally in the unpinned phase, the conductivity at all frequencies should be ohmic, and proportional to either the soliton density in the multi-soliton regime, or to the IPW amplitude close to $T_c$.

5.5.2 The role of defects

The description of the incommensurate phase in terms of an array of phase solitons which may or may not be pinned to the underlying lattice, rests on the assumption that in the pure system which the model of §5.3 describes, although the continuous translational symmetry for the phase profile in the continuum approximation has been broken by the lattice, there remains the original translational symmetry of the lattice which provides a one-dimensional array of 'soliton sites', each of which is identical. The presence of a defect in the lattice, whether in the form of a dislocation or an impurity, will alter the energy of a soliton centred on, or close to, the defect.

Studies of the one-dimensional sine-Gordon chain coupled to a random field to represent the existence of defects have been performed by Fukuyama (1978) and by Nakanishi (1979). The former showed that the strength of the coupling to the defect field is of crucial importance. If the coupling is sufficiently strong the phase profile will be determined by the defect field rather than by the commensurability pinning or incommensurate-favouring terms in the Hamiltonian. In this defect-dominated regime the phase profile is more accurately described
as a charge density glass (CDG) than as a charge density wave (CDW) and the author speculated on the possibility of producing a sharp CDG-CDW transition. The CDG state is characterised by a lack of long-range order which in the model considered in this work is equivalent to a random distribution of solitons. Nakanishi showed by numerically minimizing a Ginzburg-Landau type free energy, that in the presence of impurity sites which lower the energy of a soliton, the soliton density does not go sharply to zero as depicted in Fig. 5.7 for the pure material, but instead has a long 'tail' which reflects the stability of the solitons centred on impurity sites for a range of temperatures below $T_L$. This temperature region below $T_L$ where some solitons are present may be identified with the CDG state of Fukuyama.

The presence of localised defects, such as impurities, in a two or three-dimensional model will not lead to the CDG state described above, provided that the almost-planar soliton picture used in §5.4 is valid. In this case the pinning energy caused by a single defect will be infinitesimal compared to the elastic, Umklapp, and discrete-lattice pinning energies which, although possibly smaller than the impurity potential energy at the impurity site, will nevertheless dominate the soliton energy as they are proportional to the area of the soliton. When one considers the large surface area of a soliton in a homogeneously defected lattice, the impurity pinning energy, when averaged over the surface of the soliton, will merely contribute a constant energy per soliton, and a constant pinning energy. We may therefore assert that the only change in the description presented of our pure system in the presence of dilute defects, is a small renormalisation of the soliton creation and pinning energies.

There are two caveats which must be considered before dismissing
the role of defects, both of which may be of importance in special cases. These concern the effect of random defects (disorder) on the asymptotic critical behaviour at the H-I transition, and the effect of ionised impurities on the electronic properties of CDW systems.

The critical behaviour of the pseudo-one-dimensional continuum model at the I-H transition is expected to be that of the d-dimensional X-Y model. It has already been shown that discrete lattice pinning effects may cause a cross-over to Ising behaviour, and indeed must do so in the two-dimensional systems. In the critical region near $T_c$ where the ground state is an IPW we may use the results of RG analysis in the same manner as they were utilised to study defects in 3.4.4. Unlike the HV defects in SrTiO$_3$ which occupy high-symmetry sites in the lattice and thus couple only to the modulus squared of the order parameter (diagonal disorder) which represent a relevant perturbation only when the specific heat diverges (Ma, 1976b), the defects in the incommensurate lattice couple to the phase, $\phi$, of the order parameter and so induce 'off-diagonal' disorder. An argument due to Harris (1974), and based on scaling arguments of Kadanoff (1966) applied to dilute systems, predicts that systems such as the X-Y model, for which the specific heat exponent is negative, will exhibit sharp transitions in the presence of random disorder. However RG study of a model with off-diagonal disorder by Aharony (1975) showed that the pure system fixed point is unstable with respect to such a perturbation. This led Aharony to conclude that the transition may be 'smeared' over a small temperature range, obscuring the expected critical behaviour of the pure X-Y model. This effect is likely to be of importance in the study of mixed systems such as Nb$_x$V$_{1-x}$O$_2$.

The second caveat refers to the conductivity and Fermi wave-vector
of CDW systems in the presence of ionised impurities which may act as
electron donors or acceptors if present in small densities, and which
may induce electron localisation (Anderson, 1958) at higher densities.
Both of these mechanisms are capable of inducing a single-particle
conductivity with a thermal activation energy below the Peierls
energy gap. Although these will be unaffected by the lock-in transition,
they may obscure the pure-sample behaviour. Particularly complete
studies have been made of the effect of doping the layered dichalcogenides with a small number of impurities, showing that in 1T-TaS$_2$
the addition of a small amount of Ti impurities is sufficient to keep
the system semi-metallic in the C phase (Di Salvo et al., 1975;
Di Salvo and Graebner, 1977), and a study of Nb$_{1-x}$V$_x$Se$_2$ (Bayard and
Sienko, 1976) showed a similar change in low temperature properties
with $x = 0.005$. If the electron density contributed by the ionised
defects is large enough to change the Fermi wave-vector by several
per cent it is quite possible that the existence of a lock-in
transition will depend upon the defect concentration.

A final role for defects was speculated on by Lee and Rice (1979)
who suggested that defects might serve as Frank-Read sources for the
nucleation of solitons in the same way that Frank and Read (1950)
proposed for the nucleation of dislocations. In the discrete lattice
model this remains possible although it is not necessary to invoke
any nucleation mechanism for the spontaneous creation of solitons in
groups of $p$.

5.5.3 Soliton roughening

As a final point in the theoretical study of the incommensurate
system model it is appropriate to introduce another type of phase
transition, the roughening transition. The concept of the roughening
transition arose in crystal growth studies (Burton and Cabrera, 1949; Burton et al., 1951) where it was postulated that crystal surfaces would grow either rough in the sense that the surface width would be infinite, or smooth, in which case the surface would be effectively flat. In recent years considerable interest has arisen in the physics of interfaces as it has been suggested that roughening transitions may be expected at any interface (for a review see Weeks, 1979). The concept of a planar soliton which has been used to describe the finite-temperature effects is justified provided the temperature is less than the soliton roughening temperature, $T_R$.

For a soliton in the three-dimensional model, two forms of distortion must be considered. Firstly, very long wavelength ripples of the soliton surface may build up so that over large distances the soliton position has wandered a large distance from its centre at $x = y = 0$. This is the mechanism which causes unpinning of the soliton when the long-distance wandering is of the order of only one lattice constant, and therefore the unpinning transition temperature must be less than the roughening temperature $T_R$ if the soliton roughening proceeds by this mechanism.

Secondly, if the discrete lattice pinning effect is sufficiently strong that the soliton is restricted to lie at its minimum-energy position in each unit cell, then the only alternative mechanism by which it may be roughened is the appearance of 'kinks' in the profile where the centre of the soliton changes from the $l$th row of unit cells in the $n$th column, say to the $(l+1)$th row in the $(n+1)$th column, as depicted in Fig. 5.11. This type of distortion of the soliton costs only the elastic energy which arises from bending the soliton, but does not cost any energy from the pinning term in $\mathcal{U}$ or from the $x$-$y$ independent $\Delta \mathcal{U}$ terms. If we assume that the solitons are narrow,
Figure 5.11: The roughening process for a strongly pinned soliton

The central part of the diagram shows the $x - z$ plane of the lattice, the squares representing unit cells. The centre of the soliton is marked by the heavy line. The abrupt change in its position is schematic as the phase variables are associated with the unit cell centres. The top and bottom figures show the phase profile for sections parallel to the $z$ axis. The bend in the soliton costs elastic energy but costs no energy from the pinning potential.
and that only kinks corresponding to a single lattice spacing are important, the summation over $k$ in the Hamiltonian may be performed, projecting out of the full Hamiltonian the part associated with kinks in the soliton profile

$$\mathcal{H}_R = \sum_{h,k} J \left( \frac{A^2}{a^2} \right) \left( 1 - \cos \left( \frac{2\pi}{p} \right) \right) \left\{ \delta_{z, h, k} z_{h+1, k} - \delta_{z, h, k} z_{h, k+1} \right\}$$

(5.82)

where $z_{h, k}$ is now the position of the soliton centre in the $(h, k)$th column of unit cells. For the purpose of estimating the roughening temperature $T_R$, this Hamiltonian can be conveniently written in the form of a $d - 1$ dimensional Ising model,

$$\mathcal{H}_R = \sum_{n, n} J_{\text{IS}} \sigma_i \sigma_j + \text{const.}$$

(5.83)

where the pseudo-spin variable $\sigma$ takes the value $+1$ if $z_{h, k}$ is odd, and $-1$ if $z_{h, k}$ is even, the summation runs over nearest neighbour pairs $(i, j)$, and the exchange constant is given by

$$J_{\text{IS}} = \frac{1}{4} J \left( \frac{A}{a} \right)^2 \left( 1 - \cos \left( \frac{2\pi}{p} \right) \right).$$

(5.84)

In this form, the roughening transition model is generally referred to as the Solid-on-Solid (S.O.S.) model (see Weeks, 1979).

The roughening transition temperature is now given by the exact solution of the Ising model so that for the $d = 3$ case where the roughening Hamiltonian $\mathcal{H}_R$ is that for the two-dimensional Ising model, the appropriate result is

$$T_R = \frac{2.27 J_{\text{IS}}}{k_B}$$

$$= \frac{1.14 (A/a)^2 (1 - \cos(2\pi/p)) J}{k_B}. \quad (5.85)$$
More realistic roughening models allowing for multiple steps lead to similar or slightly larger values of the numerical factor, for example Zittartz (1978) obtained $k_B T_R/J_{IS} = 2.56$ theoretically and Shugard et al. (1978) obtained Monte Carlo estimates of 2.48 and 2.92 for models in which the energy is linear and quadratic respectively in the height difference.

In this single-soliton picture, the neglect of inter-soliton interactions which will tend to oppose the roughening, establishes a lower bound to the roughening temperature. Utilising the expression for $T_u$, the characteristic unpinning temperature for the soliton defined by (5.73), we can write

$$T_R = 1.14 J \frac{a^2}{\sigma^2} \left( \ln(\Omega)/2\varepsilon_L \right) (1 - \cos \frac{2\pi}{p}) T_u. \quad (5.86)$$

Substituting into this expression the values obtained for the case $D = .5$, $p = 4$, we obtain the estimate $T_R \approx 40 T_u$ for the case with $J = \frac{a^2}{c^2}$. Qualitatively the result expressed in (5.86) is not difficult to understand. For larger values of $p$, the lattice pinning energy, which prevents a gradual deformation of the solitons, but which does not prevent the development of the localised, large amplitude kinks studied above, will cause the solitons to be pinned at quite high temperatures, while the elastic energy associated with the kinks, proportional to $\left( 1 - \cos \frac{2\pi}{p} \right)$ will be relatively small. Therefore for large values of $p$ these two characteristic energies may be comparable, in which case the solitons will roughen at $T_R$ rather than remaining planar but unpinned. The smaller values of $p$ which correspond to the systems of current experimental interest, will have phase solitons in the ground state which are constrained by their elastic energy to be planar and which will remain approximately planar in the unpinned phase.
§5.6 Summary and Conclusions to Chapter 5

5.6.1 Theoretical considerations

In the field of structurally incommensurate systems the continuum approximation, upon which much of the contemporary work in condensed matter systems is based, met its ultimate test. The assumption of continuous translational symmetry for the phase profile of the incommensurate order parameter has, as a necessary consequence, the appearance of the Goldstone modes, predicted by the theories of Bruce and Cowley (1978) and of Theodorou and Rice (1978), but not observed experimentally. It is apparent from the results of §5.3 and §5.4 that at the I-H transition, where the order parameter may be represented by a single Fourier component of the displacement field, the continuum approximation, including the renormalisation group formalism may be applied. An important caveat in this regime is that a discrete-lattice pinning term which causes even an extremely small dependence of the Hamiltonian on the phase angle, $\phi$, will represent a relevant perturbation in the RG sense which will be of practical significance in applying the theory to a two-dimensional system, where without this perturbation the long-range incommensurate ordering would not develop at finite temperatures.

The important new features of incommensurate systems which have been discovered in the course of this work are mainly encountered in the region of the phase diagram for which the continuum approximation is least realistic, where the order parameter of the incommensurate phase is no longer homogeneous in real space, but is distorted to form localised discommensurations or solitons. The localised nature of the solitons renders the coarse graining procedure of the RG inapplicable. The system has therefore been studied in an approximate, linearised framework by perturbing around the continuum ground state...
solutions. The qualitative behaviour of the system has been shown to depend upon the characteristic temperature $T_u$. For systems which have $T_u$ less than the lock-in temperature $T_L$, the continuum approximation retains its validity and the system has only two phase transitions, the C-I transition at $T_L$, and the I-H transition at $T_c$. The lock-in transition in this case is continuous, although we have not considered the effect of coupling the phase to a strain field which, in the continuum model, may cause the I-C transition to be first order (Bruce et al., 1978; Natterman and Trimper, 1981) although this is disputed by Bak, (1978) and by Dvorak and Ishibashi (1978). The dynamics of the continuum model have been exhaustively studied by other authors, in a tight-binding approximation (Bruce and Cowley, 1978) which is most relevant at low temperatures, in a Fokker-Planck approach (Trullinger et al., 1978; Guyer and Miller, 1978) using a Smoluchowski diffusion equation which gives a somewhat different result which may be of relevance to the transport properties of the solitons especially at high temperature, and in the presence of defects (Paul, 1979). For these systems where $T_u$ is higher than the lock-in temperature, the lock-in transition is only one of a series of first order transitions in which the system evolves through a 'devil's staircase' of commensurate phases until at the unpinning transition the true incommensurability is restored and the continuum treatments of the system are again applicable. In the pinned phase the frequency gap of the phason mode has been calculated by a variational technique analogous to the tight-binding approximation of Bruce and Cowley. Utilising the numerical estimates for the pinning frequency $\omega_0$, the properties of the pinned soliton phase have been investigated yielding expressions for the electronic properties of the model and the soliton roughening temperature which may
be used to give semi-quantitative estimates for these properties in real systems as well as providing a posteriori justification for the planar soliton approach adopted throughout this chapter.

5.6.2 Experimental considerations

The primary difficulty in applying the theory as it stands to the real systems such as K₂SeO₄ or TTF-TCNQ for which it is most appropriate in a directly quantitative manner is the paucity of experimental data which leaves a determination of the constants such as Jₚ and m* subject to large errors. Existing experimental data is insufficient to establish unequivocally the occurrence of an unpinning transition as the key experiments on the most promising systems, to be summarised below, have not yet been performed. However, the following general observations on the current state of agreement with experiment may be made.

The serious conflict between theory and the experimental search for phason modes in materials which exhibit lock-in transitions is simply explained by the discrete lattice pinning effect. The failure to observe phason branches indicates that in none of the systems examined so far have the solitons been unpinned in the temperature range of the experimental work. This is not too surprising as the 'obvious' temperature at which one would perform an experiment would be close to Tₗ if the continuum picture were to be believed, since at this temperature the amplitude A and hence the structure factor will be maximised. The conclusions reached in this work suggest that at this temperature the solitons are most likely to be pinned, and by looking for a softening phason mode close to Tₖ the chances of seeing an unpinning transition are maximised. Further indirect support for the general argument that a phase profile may be pinned comes from the electronic properties
of the organic charge transfer salts, in particular TTF-TCNQ, and from the transition metal chalcogenides in both two-dimensional (e.g. TaS$_2$, TaSe$_2$) and one-dimensional (e.g. NbSe$_3$, TaSe$_3$) forms. At atmospheric pressure, TTF-TCNQ undergoes a transition to a phase with $\mathbf{k}_s = (0.5, 0.29, 0)$ at 53K and to a phase with $\mathbf{k}_s = (0.25, 0.29, 0)$ at 38K. Between 38K and 49K the wave-vector $\mathbf{k}_s$ is incommensurate in both the $a$ and $b$ directions. At high pressure ($\sim$19 kbar) the sequence of transitions is replaced by a single transition to a phase in which the charge transfer causes a lock-in to a 3b-commensurate (i.e. $\mathbf{k}_s = (k_x, \frac{1}{3}, 0)$) phase. The complexity of the 1 bar sequence of transitions is obviously rather far removed from our simple model. However, although the wave-vector in the $b$ direction is apparently incommensurate ($2k_F^* = 0.29$, it is apparent that the IPW description of the phase is inappropriate due to the appearance of strong scattering at harmonics of this wave-vector, especially at $4k_F^*$ (Yamada and Takatera, 1977; Nakanishi et al., 1977). This $4k_F^*$ scattering has not been adequately explained, although several explanations have been proposed from multiple CDWs (Emery, 1976) to 'spin waves' (Torrance, 1977) but it is presumably indicative of some coupling to the Umklapp terms which ultimately bring about the $p = 3$ lock-in transition along the $b$ axis at high pressure. The conductivity measured along the $b$ axis shows that in the incommensurate region TTF-TCNQ is semi-conducting (Friend, 1978). The Fröhlich mode is presumably either absent, or else pinned to the lattice and therefore having the thermally activated form indicated in eqn. (5.80). The successive phase transitions produce changes in the slope of the conductivity versus temperature curve at the various phase transitions which would not be expected to affect single-particle mechanisms showing that the latter hypothesis is to be expected. In contrast to this behaviour, the selenium analogue TSF-TCNQ
which does not show the $4k_F$ scattering and in which the IPW description is presumably appropriate, shows an almost constant conductivity from above 50K to below 30K. This suggests that for this compound, for which the charge transfer (and hence Fermi wave-vector) is different from that of TTF-TCNQ, but other details are similar, may have an unpinned Fröhlich mode conductivity in this temperature region (see Friend, 1978; Heeger, 1979). More convincing evidence for the existence of a Fröhlich mode in TTF-TCNQ comes from the studies of TTF-TCNQ, just above the $p = 3$ lock-in transition where the conductivity displays a marked drop in the region of 19kbar (Andrieux et al., 1979). This indicates that the CDW is pinned by the commensurate locking terms even in the temperature region where the phase is still incommensurate, a fact which strongly suggests that the formation of a locally-commensurate phase, or soliton lattice, with a high order commensurability has occurred.

Further evidence in support of the existence of pinned discommensurations, or solitons, comes from studies of the transition metal chalcogenides. In NbSe$_3$, the niobium atoms are arranged in long chains, and Shubnikov-de Haas measurements (Fleming and Coleman, 1977; Monceau, 1977) show that the Fermi surface is cylindrical, suggesting that approximately one-dimensional behaviour may be expected, although below 7K the material becomes superconducting unlike the 'one-dimensional metals' above, indicating that the behaviour is really three-dimensional. NbSe$_3$ shows two incommensurate CDW phases each of which has $k_3^*$ close to $c^*/4$. Below each of the transitions, at $T_{c_1} = 145$K and $T_{c_2} = 59$K, large resistive anomalies occur. (Ong and Monceau, 1977) which have been shown to arise from intrinsic effects by studies of doped material (Ong, 1979; Ong et al., 1979). These anomalies are inconsistent with single-particle conduction mechanics and show that the transport in the incommensurate phases is largely due
to a collective Fröhlich component. There are three major features of interest which provide strong evidence in support of a pinned soliton picture of the incommensurate phase. Firstly, it was shown by Ong and Monceau (1977) that the conductivity anomalies are only evident in D.C. measurements, the hopping regime of 5.5.1, and not at high frequency. This implies that the carrier density has not been changed by the transition, but that some of the carriers (\(\sim 20\%\)) are localised in CDW phase and able to contribute to the conductivity only at high frequency. Secondly, Ong and Monceau (1977) showed that NbSe\(_3\) has a strong absorption mode in the CDW phase at microwave frequencies (9.3GHz) which may be identified with the resonance predicted by 5.78 for \(\omega = \omega_C\). Thirdly, more recent measurements of the non-ohmic D.C. conductivity (Fleming and Grimes, 1979; Monceau et al., 1980) have shown that the non-ohmic conductivity is observed only above a critical electric field of approximately 4.4mV/cm in accordance with the expectation expressed in 5.5.1 that the D.C. conductivity of the condensate will change from a 'hopping' to a 'sliding' mode at a critical field. A recent study of the conductivity of the similar TaSe\(_3\) (Thompson et al., 1981) found a similar D.C. resistive anomaly and critical field non-ohmic conductivity although the only known ordered phase in TaSe\(_3\) is believed on the basis of diffraction experiments (Sambongi et al., 1977; Tsutsumi et al., 1978), to be commensurate with \(k_s = \frac{1}{4}\). Thompson et al. also report that the dielectric constant is low above \(T_c\) and 'extremely high and frequency dependent in the CDW state' and that there is no critical field effect at high frequency, as we would expect for a pinned soliton conductor.

The layered dichalcogenides such as TaS\(_2\) are expected to show two-dimensional behaviour. In these materials the metal ions occupy layers separated by two layers of chalcogen atoms. Several polytopes are known to be stable at room temperature, these are designated 1T,
2H and 4Hb, depending on the stacking sequence of chalcogen layers. Since the low temperature properties of 1T-TaS₂ which is a semiconductor are markedly different from those of 2H-TaS₂ which remains a rather low-conductivity metal down to helium temperatures, these systems are rather poor approximations to the hypothetical two-dimensional metal (see Fazekas and Tosatti, 1979), nevertheless both the 1T and 2H polytypes provide a variety of CDW transitions. 1T-TaSe₂ and 2H-TaSe₂ both have a single incommensurate phase and a lock-in transition to a low temperature C phase (Scruby et al., 1975; Moncton et al., 1975). X-ray photo-emission measurements on 1T-TaSe₂ by Hughes and Pollak (1976a) in the commensurate phase showed that the Ta atoms occupied sites of two different types leading to a twin peak for the transition between the atomic \(4f^{5/2}\) and \(4f^{7/2}\) levels. The twin peaks are resolvable over a temperature range of 30K above the lock-in transition which occurs at 200K, indicating that the phase remains locally commensurate in this temperature range although the superlattice points no longer occur at the \(p = 3\) superlattice positions. If this conclusion is valid for the 2H-TaSe₂ system the slow loss mechanism which Barmatz et al. (1975) noted was more characteristic of 'diffusion, dislocation or domain-wall motion' than of electronic relaxation mechanisms, may be identified with the hopping motion of the weakly pinned solitons suggested by §5.5. The only system which appears to offer some direct evidence for an unpinning transition is 1T-TaS₂, which has three CDW phases denoted by Williams et al. (1974). \(T_1\), \(T_2\) and \(T_3\). The \(T_3\) phase is commensurate, the CDW forming a \(\sqrt{13} \times \sqrt{13}\) superlattice. The \(T_2\) phase is described as 'nearly commensurate' by Williams et al. (1974) while the \(T_1\) phase is incommensurate, with \(\frac{5}{3} \vec{s}\) rotated by approximately 12° from the \(\sqrt{13}\) superlattice vector \(\vec{\tau}\) and aligned parallel to the hexagonal axes of the high temperature lattice. The \(T_3\) to \(T_2\) (C-I) transition occurs below
250K and shows a large thermal hysteresis as one would expect for a pinned phase profile. The $T_2$ to $T_1$ transition occurs at 350K without observable thermal hysteresis, but showing an abrupt increase in the conductivity on heating. Fazekas and Tosatti (1979) present conductivity data showing that in the $T_2$ phase the conductivity increases monotonically by a factor of about 4 over the range 250 to 350K but they do not examine the temperature dependence to ascertain whether it shows a thermally activated or power law behaviour. It is tempting to suggest that the $T_2$ phase is a pinned multi-soliton phase where pinning of the solitons to the lattice maintains the alignment of the ordering wave-vector in the direction required by the $\sqrt{13}$ superlattice, and that above the unpinning ($T_2 \rightarrow T_1$) transition the direction of the ordering wave-vector is determined solely by the position of the Kohn anomaly minimum which causes the rotation of $\sim 12^\circ$. Some evidence in support of this hypothesis is provided by studies of the $T_2$ and $T_3$ phases in the presence of defects (Fazekas and Tosatti, 1979; Tosatti and Fazekas, 1976) which show that the $T_2$ phase is stabilised at low temperatures by a small concentration of impurities and from the results of X-ray photo-emission measurements (Wartheim et al., 1975; Hughes and Pollak, 1976b) which were interpreted by Fazekas and Tosatti (1980) as indicating the presence of electron localisation at the impurities, causing discommensurations in a locally commensurate CDW, equivalent in the adiabatic approximation to the existence of the charge density glass state of Fukuyama (1978). Fazekas and Tosatti (1980) also conclude that the decrease in resistivity with increasing impurity concentrations coupled with the known carrier density (Tanuma et al., 1978), imply that the dominant current carrier in the $T_2$ phase is a collective, Fröhlich mode. This requires that the change in conductivity at the $T_2 - T_1$ transition be attributed to an unpinning of the
condensate rather than to a single-particle, Anderson localisation. Since this appears to be a case where $k_s$ and $\tau$ are not parallel, the pseudo one-dimensional model cannot be used to describe the alignment of $k$, but otherwise the transition appears to have qualitatively the expected features of the unpinning transition of 5.4.5. Further experimental work will be necessary to look for the pinning frequency $\omega_c$, by microwave absorption measurements, or by NMR techniques (see Blinc et al., 1980, and Zumer and Blinc, 1981), and to look for a soft mode at $k_s$ by light or neutron scattering, to provide conclusive tests of this conjecture.

With the exception of the 1T-TaS$_2$ system, the above remarks indicate only that the soliton picture of incommensurate systems with lock-in transitions is consistent with experiment, and that the solitons, if they exist, must be pinned to the lattice. The systems for which data is available are not good candidates for the observation of unpinning transitions as the I-H transitions in $p = 3$ systems such as TTF-TCNQ under pressure and TaSe$_2$, may be first order. In these cases it is not necessary, although it is possible for the unpinning transition to take place between $T_L$ and $T_c$. Experiments are however suggested by the theory which may be able to give a direct test of the predictions. The primary requirement would appear to be a system with a $p = 4$ H-I transition and a first order lock-in transition. Since lock-in transitions can be produced under pressure in TTF-TCNQ and in KCP when the Fermi wave-vector may become sufficiently close to a commensurate value, it is reasonable to suppose that from the large number of charge transfer salts, one will be able by suitable doping or application of pressure to create a half-field TCNQ band which will allow lock-in transitions at $\frac{1}{2}b^*$. In this case, the continuous I-H transition would guarantee the presence of an unpinned
phase profile close to $T_c$ while the fact that the $p = 3$ profile is pinned above lock-in in TTF-TCNQ suggests that the $p = 4$ profile in the hypothetical case above might be expected to be pinned at $T_L$. If such a system can be found, the full range of discrete lattice effects should be observable. Finally, in view of the similarity in electronic properties of incommensurate NbSe$_3$ and commensurate TaSe$_3$, it is quite possible that NbSe$_3$ may exhibit a $p = 4$ commensurate phase under pressure, or that closer examination of TaSe$_3$ may reveal an incommensurate phase. Either of these possibilities, or the provision of mixed Nb$_x$Ta$_{1-x}$Se$_3$ crystals, would provide an excellent testing ground for the theory.

All of the above-mentioned commensurate phases correspond to fairly low values of $p$. It will be of considerable interest to produce by doping or pressure, or to discover pure systems with lock-in transitions to C phases with higher values of $p$. 
CHAPTER 6

STUDIES OF DOMAIN WALLS IN FERROELECTRIC CRYSTALS

§6.1 Introduction

The domain structures of ferroelectrics have attracted considerable interest because of the important role which they play in determining the macroscopic properties of these materials, however little work has been done experimentally to investigate the detailed structure and dynamics of the domain walls because of the difficulty of observing them directly. Despite the lack of experimental evidence, several theoretical studies of simple model systems have recently focused attention on domain walls as candidates for the observation of non-linear excitations or solitons, roughening transitions, and central peaks.

The first of these studies was undertaken by Krumhansl and Schrieffer (1975) who analysed the statistical mechanics of a one-dimensional continuum, $\phi^4$ model using the transfer integral function developed by Scalapino et al. (1972). Krumhansl and Schrieffer showed that the solitons of the $\phi^4$ field, which correspond to domain walls if the model is used to describe a ferroelectric material, could lead to a characteristic quasi-elastic peak in the dynamic structure factor $S(\mathbf{k}, \omega)$, and that close to the transition temperature ($T = 0$ in the 1-dimensional case) the solitons represent an important part of the excitation spectrum. This approach was extended by Bishop et al. (1978) who extended the analysis of the classical model to a quantum-mechanical model, and by Sarker (1980) who examined the behaviour of solitons in a more general model incorporating long range forces. A mean-field theory of the statics and
dynamics of the $\phi^4$ model solitons or domain walls, was carried out by Collins et al. (1979) by using a Langevin equation technique, again leading to a quasi-elastic component in the structure factor related to the stochastic motion of the domain walls.

These theories are all based on the continuum approximation and so are applicable to the domain walls which occur in real ferroelectrics only if the widths of the domain walls are large on the scale of the lattice constant. This problem, although considerably more straightforward than the phase soliton problem of Chapter 5, contains the same essential elements, namely that a continuum approximation which is very successful in describing, for example, the broad Bloch walls which occur in Heisenberg magnets, must in ferroelectrics be applied to a situation where the walls are much narrower, and consequently the calculations of soliton dynamics which assume continuous translational symmetry may be inapplicable to the ferroelectric domain walls in real systems where discrete lattice pinning effects will be important if the walls are narrow enough.

Recent developments in the theory of surfaces, referred to in 5.5.2, suggest that at some temperature below the bulk transition temperature a surface such as a ferroelectric domain wall should undergo a roughening transition. In the soliton problem it was shown that roughening transitions are unlikely to be observed as the weak pinning mechanisms responsible for the sequence of transitions will be overcome at temperatures well below $T_R$. For narrow domain walls in ferroelectrics we might expect that the pinning forces due to the lattice will be considerably stronger, so that the domain walls represent surfaces which may undergo a roughening transition at some temperature in the ferroelectric phase. This possibility is again closely related to the width of the domain wall and the importance
of the continuum approximation and discrete lattice pinning forces. If the walls are broad enough for the continuum approximation to be valid then there is no transition and the interface width diverges at all temperatures. When discrete lattice effects are taken into account, as they must be for narrow walls it has been shown by Dobrushin, (1972) and by van Beijeren (1975) that the three-dimensional Ising model, which may be used to represent a uniaxial ferroelectric, has a smooth interface at low temperatures, which may roughen at a temperature below $T_c$ which is closely related to the transition temperature of the corresponding 2-dimensional Ising model (see Wallace, 1980, and refs. therein.)

Several estimates have been made of the thickness of domain walls in ferroelectric materials but the results have varied considerably. By assuming that the $90^\circ$ domain walls in tetragonal BaTiO$_3$ were directly visible with electron microscopy, Little (1955) estimated their thickness as $4,000 \, \AA$, however this assumption is almost certainly unrealistic. A phenomenological theory by Zhirnov (1958) predicted a domain wall width of between $50 \, \AA$ and $100 \, \AA$ for the $90^\circ$ BaTiO$_3$ wall and a width of between $5 \, \AA$ and $20 \, \AA$ for the $180^\circ$ wall in the same substance. Similar work by Merz (1954), again based on a continuum approximation, suggested that domain wall widths would be of the order of ten unit cells. These results are in poor agreement with a microscopic calculation of Kinase and Takahashi (1957) who concluded that the wall thickness is 'practically zero' for the $180^\circ$ BaTiO$_3$ wall. In the case of the uniaxial ferroelectric KH$_2$PO$_4$ which has a simpler domain structure, estimates of the domain wall thickness are more nearly in agreement ranging from one to several unit cells. These estimates and other properties of ferroelectric domain walls were discussed by Zheludev (1971).

The first direct measurement of the width of a ferroelectric domain
wall was performed by Cowley et al. (1976). In a neutron scattering experiment on the uniaxial ferroelectric \( \text{Pb}_5\text{Ge}_3\text{O}_{11} \), they found lines of quasi-elastic scattering in a direction perpendicular to the \( 180^\circ \) domain walls from which they were able to deduce a domain wall width of between 10 Å and 15 Å. Some quasi-elastic scattering which may have a similar origin was also observed in orthorhombic \( \text{K NbO}_3 \) and briefly commented on by Currat et al. (1974). Qualitatively similar scattering was also observed by Axe and Samuelson (1978) in an experiment on \( \text{LiTaO}_3 \), a uniaxial ferroelectric which undergoes a weakly first order transition at 910K (Abrahams et al., 1973).

In section 6.2 a simple model of a ferroelectric domain wall in a discrete lattice is introduced and the scattering to which it gives rise is calculated. The model is applicable to a wide range of materials and shows that as a general rule, all domain structures ought to give rise to lines of quasi-elastic scattering in directions perpendicular to the domain walls. The wave-vector dependence of the scattering is shown to be closely related to the width of the domain walls. The implications of roughening of the domain walls is discussed and it is shown that the surface roughening leads to a Debye-Waller-like factor for the domain wall scattering which will cause the sharply defined lines of scattering to become diffuse at the roughening transition.

Neutron scattering experiments in the uniaxial ferroelectrics \( \text{LiNbO}_3 \) and deuterated KDP(DKDP) and the \( n = 3 \) systems \( \text{BaTiO}_3 \) and \( \text{K NbO}_3 \) are then discussed with reference to both the continuum structure factors of Cowley et al. (1976) and the discrete lattice calculations presented here in §6.2.
6.2 The Scattering from Domain Walls

6.2.1 The infinitely sharp domain wall

In a discrete lattice where the domain wall pinning effects are large, the domain walls may be approximated by making the assumption that the crystal consists of two domains each having a perfect lattice, joined together at the wall in such a manner as to leave the unit cells undistorted. The model of a wall in this limit which we shall consider is based on the configuration which is believed to arise in KDP. The paraelectric phase of this material has a tetragonal lattice, and below the Curie point at 122K, the lattice becomes orthorhombic with a polarisation directed along the c axis, and with the a and b crystallographic axes rotated by 45° relative to the tetragonal unit cell. For the purposes of this calculation it is convenient to describe the crystal in the ferroelectric phase by the monoclinic unit cells shown in Fig. 6.1a which correspond to the primitive tetragonal unit cells of the paraelectric phase. The order parameter of the transition is proportional to the deformation angle ψ which is zero above the transition temperature, and approximately 34° well below T_C. The two types of unit cell shown in Fig. 6.1a have opposite polarisations directed out of the plane of the diagram. Similar domain walls occur in the ferroelectric phase parallel to the y axis.

The same model may be applied to the domain walls which are formed in both the orthorhombic and the tetragonal phases of BaTiO_3 or KNbO_3. At high temperature BaTiO_3 has the cubic perovskite structure. Below 0°C the structure has orthorhombic symmetry with the axes of the orthorhombic unit cell rotated by 45° from the axes of the primitive unit cell in the high temperature phase. Again it is more convenient to use the primitive unit cells of Fig. 6.1a to describe the system in the orthorhombic phase. The polarisation is in this case
Figure 6.1: The infinitely sharp domain wall models.

(a) The KDP model of a (1,0,0) wall.

(b) The (1,1,0) wall of BaTiO$_3$. The monoclinic unit cells used in the text are depicted by bold lines. It is possible to use the KDP model for this case by considering the non-primitive cells shown by dashed lines with an appropriate structure factor.

Domain 1 has $y > 0$ : Domain 2 has $y < 0$. 
directed along the elongated diagonal of the monoclinic unit cells. The
domain wall shown in Fig. 6.1a, which is a (1, 0, 0) plane in the
pseudo-cubic coordinates, corresponds to a 90° wall. The angle ψ
is in this case about 36°. Between 0°C and +120°C, BaTiO₃ has a tetra-
gonal structure with the polarisation directed along the c axis which
may correspond to any of the three (1, 0, 0) directions of the high
temperature phase. The 180° walls in this phase are (1, 0, 0) planes
and as no distortion of the lattice occurs at these walls, they cor-
respond to the KDP model with a = b' and ψ = 0. The polarisation
is out of the plane of the diagram. The 90° walls in this system
correspond to (1, 1, 0) planes in the high temperature structure.
They can be represented by the model described above with the lattice
parameters chosen to be a = $\sqrt{2}$ b and ψ = 45° as shown in Fig.
6.1b. This choice of parameters also allows the model to describe
the 60° and 180° walls in the orthorhombic phase which both correspond
to (1, 1, 0) planes, the 180° walls in this phase, which involve no
lattice distortion, have a = $\sqrt{2}$ b and ψ = 45°. As these walls
cost less energy to create than the 60° walls which involve a dis-
tortion of the lattice, it is probable that the 180° walls will be
present in sufficient numbers to obscure any effects due to the 60°
walls.

A final special case of the model is appropriate to describe the
180° domain walls which occur in crystals such as Pb₅Ge₃O₁₁ and
LiNbO₃. These materials have hexagonal lattices with three and six
formula units per hexagonal unit cell respectively (Iwata et al.,
1973; Abrahams et al., 1966). In the same way that the 180° domain
walls may be represented by the model of Fig. 6.1b, the hexagonal
lattice with 180° domain walls may be represented by choosing ψ = 30°
and a = b, to represent the walls if these are (1, 0, 0) planes, or by
choosing $\psi = 60^\circ$, and $a = \sqrt{3} \, b$ if the walls are (1,1,0) planes.

The scattering from a crystal is in general directly proportional to its volume. The scattering from a single domain wall may be expected to be proportional to its area, thus the scattering from the domain wall in the model of Fig. 6.1 may be calculated by obtaining the total scattering intensity for the crystal and then separating out the part proportional to the cross-sectional area. To facilitate the separation of scattering, also proportional to the cross-sectional area, from the exterior surfaces, the boundaries of the model crystal are chosen to be in directions which are not parallel to the domain wall.

The calculation of the structure factor for the crystal is presented in some detail in the enclosed paper "Scattering properties of ferroelectric domain walls" and so only brief details of the results will be given here.

It is assumed that a unit cell in domain $j$ scatters the incident beam of neutrons or X-rays with an amplitude $f_j(\mathbf{k})$ where $\mathbf{k}$ is the wave-vector transfer, $\mathbf{k} = \frac{2\pi}{b} (\xi, \eta, \zeta)$. The overall scattering amplitude for the crystal is defined to be

$$A(\mathbf{k}) = \sum_j \sum_{\mathbf{R}} f_j(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R})$$  \hspace{1cm} (6.1)

where the sum over $j$ represents a sum over the two domains, and the sum over $\mathbf{R}$ runs over the unit cells in the $j$th domain. The amplitude for scattering from the domain walls, $A_w(\mathbf{k})$ is extracted from the above expression by taking the term proportional to the domain wall area. This scattering is confined to narrow ridges in $\mathbf{k}$-space extending from the Bragg points in directions perpendicular to the $x-z$ plane, or in other words perpendicular to the plane of the domain wall.

In order to simplify the expressions obtained for $A_w(\mathbf{k})$ it is
convenient to rewrite the unit cell structure factor in the form

\[
\begin{align*}
    f_1(\mathbf{k}) &= f^0(\mathbf{k}) + i f^1(\mathbf{k}) \\
    f_2(\mathbf{k}) &= f^0(\mathbf{k}) - i f^1(\mathbf{k})
\end{align*}
\] (6.2)

where \( f^0(\mathbf{k}) \) is the symmetric part of the structure factor, approximately given by the structure factor of the high temperature phase, and \( f^1(\mathbf{k}) \) is the anti-symmetric part of the structure factor caused by the opposite displacements of the atoms in the two domains, and may be expected to be approximately proportional to the inelastic structure factor of the ferroelectric mode above \( T_c \). The advantage of making this substitution is that the domain wall scattering amplitude, \( A_w(\mathbf{k}) \), consists of two components, one proportional to the Bragg structure factor \( f^0(\mathbf{k}) \) which is identically zero for a domain wall where no lattice distortion is caused, and a second component proportional to the 'one-phonon' structure factor \( f^1(\mathbf{k}) \) which may be expected to be small compared to the Bragg term, at least for \( \mathbf{k} \) close to a reciprocal lattice vector. The intensities \( I_w(\mathbf{k}) \) which correspond to the experimentally observable convolution of the scattering with a sharp but finite resolution function are calculated for the domain walls which involve a lattice distortion by assuming that the Bragg term dominates the scattering, while for the cases where no lattice distortion is caused, the only scattering comes from the 'one phonon' term which is calculated exactly.

For the KDP model, retaining only terms proportional to \( f^0(\mathbf{k}) \) we find that the intensity is given, for a crystal of \( N^3 \) unit cells, by
The two factors in the denominator have zeroes corresponding to the different Bragg points of the two domains. The direction in reciprocal space for which this intensity is observable is shown in Fig. 6.2a. In Fig. 6.2b the form of $I_W(k)\overline{k}$ is shown, neglecting the wavevector dependence of $f(k)\overline{k}$ and with the value of $\psi$ chosen to be 0.05.

In the special cases mentioned earlier where $\psi$ takes the values 0, 30, 45, or 60°, the intensity is proportional to the 'one-phonon' structure factor. For the case with $a = b$ and $\psi = 0$ corresponding to the 180° walls in the tetragonal phase of the perovskites the intensity is

$$I_W(k) = N^2 |f^1(k)\overline{k}|^2 \frac{\cos^2[\pi n \cos \psi] \sin^2[\pi f \sin \psi]}{\sin^2(\pi n \cos \psi + \xi \sin \psi) \sin^2(\pi n \cos \psi - \xi \sin \psi)}$$

(6.3)

The Bragg peaks are no longer split as the two domains have the same lattice, but otherwise the form of the scattering is similar to that shown in Fig. 6.2b, decreasing as $1/k^2$ close to the reciprocal lattice point.

Similar expressions are obtained for the two hexagonal domain walls,

$$I_W(k) = N^2 |f^1(k)\overline{k}|^2 / \sin^2(\sqrt{3}/2 \pi n)$$

(6.5a)

for the (1,0,0) walls, and

$$I_W(k) = N^2 |f^1(k)\overline{k}|^2 / \sin^2(\pi n)$$

(6.5b)

for the (1,1,0) walls.

In the model with a general value for $\psi$, the domain wall intensity is proportional to the distortion angle squared. In those cases with $\psi$ fixed at a special value, the intensity is proportional to $|f^1(k)\overline{k}|^2$ which is proportional to the ferroelectric displacements, i.e. the order
Figure 6.2: Scattering ridges from the model domain wall.

(a) The reciprocal lattice for the model of Fig. (6.1a). The Bragg points (●) are split into separate components from each of the two domains. Bold lines are used to depict the ridges of domain wall scattering.

(b) $I_W(\vec{k})$ in arbitrary units where $\vec{k} = \frac{2\pi}{b}(2,\eta,0)$. The parameter values used here are $a = b$, $\psi = 0.05$. In the units chosen the Bragg peaks, denoted by arrows, have intensities of $10^6$. 
parameter, squared. In all cases the intensity close to a continuous transition, such as occurs in Pb$_5$Ge$_3$O$_{11}$, will vary as

\[ I_w(\vec{r}) \propto (T_c - T)^{2\beta} \quad (6.6) \]

where for a uniaxial ferroelectric, the order parameter exponent \( \beta \) will have the classical value 0.5.

6.2.2 Domain walls of finite width

The assumption which underlies the model of 6.2.1, that the domain wall is infinitely sharp and contains no distorted unit cells, is not expected to be realistic in many materials. There are two ways in which the model may usefully be extended to give a more realistic description of a domain wall. It is possible to simulate the effect of the domain wall having a width extending over several unit cells, as assumed in the continuum theories, by inserting a narrow domain of distorted cells between the two domains with the perfect bulk crystal structure. The simplest model of this type is shown in Fig. 6.3. In contrast to the infinitely sharp wall model which contained no parameters other than an overall amplitude and the unit cell dimensions of the bulk material, the finite wall model contains the extra parameters, \( W \), the width of the wall in unit cells, and \( b_3 \), the lattice parameter of the distorted cells in the direction perpendicular to the wall.

An alternative extension to the model may be made to cover the realistic case of a domain wall which is not perfectly flat. In this case the width of the wall is equivalent to the degree of roughness caused at low temperatures by crystal imperfections, and at higher temperatures by entropy effects. An exaggerated form of the rough wall
Figure 6.3: The model of a broad domain wall.

The simplest extension of the KDP model of Figure (6.1a) to the case of a wall with a width of two unit cells. The rectangular unit cells of the wall are assumed to have the high temperature structure.
Figure 6.4: The model of a rough domain wall.

The model used for the rough domain wall calculation which represents the $180^\circ$ walls in BaTiO$_3$. The + and - signs represent up and down polarisation. The position of the wall is marked by the bold line.
model is shown in Fig. 6.4. The effective width of the wall due to roughening is represented by an additional variable parameter.

As full details of these calculations are given in the accompanying paper, again only an outline of the results will be given here.

In the case of the three-domain model, the scattered intensity cannot be reduced to an elegant form such as that given in eq. (6.3) for the sharp wall, unless the lattice constant $b_3$ of the wall cells is equal to $b_3 \cos \psi$, the spacing of unit cells in domains 1 and 2 in the $y$ direction. It is instructive to examine first the simplest case which displays the essential differences from the sharp wall model. For this special case, which corresponds to the $180^\circ$ wall in tetragonal BaTiO$_3$, we have $\psi = 0$ and assume for simplicity that $b_3 = b$, as deduced by Kinase and Takahashi (1957) from their microscopic model. Making the plausible assumption that $f_3(\kvec)$ is given by the high-temperature phase structure factor $f^0(\kvec)$ we find that the scattered intensity is given by

$$I_w(\kvec) = N^2 |f^1(\kvec)|^2 \frac{\cos^2(\pi \eta \eta)}{\sin^2(\pi \eta)} \quad (6.7)$$

The form of this intensity is similar to that obtained for the infinitely sharp wall close to the Bragg points, but it differs from the latter by the modulating cosine factor which contains the information regarding the width of the wall.

In a general case where $\phi_3$ is not simply related to $b$ and the angle $\psi$ is non-zero, the intensities obtained show a behaviour qualitatively similar to the above example. The intensity consists of a broad wing on either side of the twin Bragg peaks which is modulated by an oscillatory term which depends upon the width of the walls. Several examples of the intensity obtained for the KDP model...
for different values of $W$ are shown in Fig. 6.5, where the structure factors have been assumed to be equal and independent of $\vec{k}$ and the parameters $b_3$ and $\psi$ have been assigned realistic values. In all of the cases studied it was apparent that the width, $W$ controlled the positions of the maxima of intensity, while the parameter $b_3$ controlled the sharpness of the minima which were most pronounced when $b_3 \sim b$.

The rough wall model has been studied in two approximations, the first corresponding to low temperatures where the walls are assumed to be static, and the second, which is applicable at high temperatures and makes use of a continuum approximation. The position of the centre of the domain wall is represented by a coordinate $\theta(x, z)$ which gives the displacement of the wall parallel to the $y$-axis. At low temperatures the position of the wall is determined by random factors such as the presence of defects, and so as the intensity observed by a scattering experiment involves a summation over an ensemble of a macroscopically large number of walls, we may take $\theta(x, z)$ to be a stochastic variable whose probability density function we approximate by a Gaussian distribution

$$P(\theta) = \sqrt{\frac{2\lambda^2}{\pi}} \exp(-\frac{\theta^2}{\lambda^2})$$

where $\lambda$ is the effective wall width.

Taking a configurational average over this distribution we find the effective amplitude for scattering by the domain wall to be

$$<A_W(\vec{k}, \lambda) > = \exp \left[ -\frac{1}{2}(bk_y \lambda)^2 \right] A_{W}^{0}(\vec{k})$$

(6.9)

where $A_{W}^{0}(\vec{k})$ is the amplitude scattered by a flat domain wall. The effect of the wall roughness is contained in the exponential Debye-Waller-like factor. This exponential factor will be unimportant close
Figure 6.5: Scattering intensities predicted from the broad wall model.

The intensity $I_w(k)$ in arbitrary units for the model with a finite width, for $k = \frac{2\pi}{b} (2, \eta, 0)$. The curves shown are for $W = 2$ (dashed curve), $W = 4$ (dotted curve) and $W = 6$ (solid curve). The amplitudes of the scattering have, in each case, been chosen to aid comparability. The parameters used were appropriate to DKDP, $\psi = .0104$, $a = b = 7.45\AA$. The value of $b_3$ was arbitrarily set to 7.60.
to the $[h, 0, \ell]$ Bragg points where the intensity varies as $1/\sin (\frac{1}{2} k_y)$, but it will modify the scattering for larger values of $k_y$.

At higher temperatures the walls may undergo a roughening transition (Lajzercowitz, 1980) where the correlation function $\langle (\theta(x,z) - \theta(0,0))^2 \rangle$ diverges for large $x$ or $z$. The effect of allowing the effective width $\lambda$ to diverge is to completely suppress the infinitely narrow ridge of scattering discussed above. Since as the temperature approaches the roughening temperature the values of $\theta(x,z)$ cease to be independently distributed the above approximation may not be used.

Above the roughening temperature the effect of long-wavelength fluctuations of $\theta$ must be taken into account. In this case it is essential to calculate the intensity due to a single domain wall before averaging over the distribution of domain walls, and that the probability distribution for the position of the wall centre is governed by a Hamiltonian modelling the interactions between neighbouring cells, rather than the independent site distribution of equation (6.8). Short wavelength fluctuations will again lead to an effective Debye-Waller factor similar to that caused by the stochastic variation considered above. The roughening transition is characterised by the growth of long-wavelength fluctuations and restricting our attention to those we evaluate the correlation functions in the continuum limit. The result of this calculation can be expressed in the form

$$\langle I_W(k) \rangle = I_W^{(0)}(k) \times \frac{1}{4N} \sum_{m=1}^{N} \Sigma \left( m^2 + p^2 \right)^{-\mu} \exp i(mak_x + pck_z)$$

$$\mu = \frac{k_n T}{2J} (bk_y)^2$$
The effect of the long wavelength fluctuations can be seen without evaluating the summations in (6.10). The scattering intensity is concentrated into ridges perpendicular to the domain wall but these now have a width in the transverse direction proportional, not to $N^{-1}$ as was the case for the flat wall, but to the number of non-zero terms in the summation in (6.10). This implies that the ridge of scattering will have a width which increases more rapidly than $k_y$ for small values of $k_y$.

The observation of a non-zero width of the ridges of scattering observed above $T_c$ in the transverse wave-vector direction in the experiments on Pb$_2$Ge$_3$O$_{11}$ by Cowley et al. (1976) and in DKDP (see section 6.3) suggests that the occurrence of a roughening transition in the ferroelectric phase would be experimentally observable by measuring the transverse width of the ridges of intensity.

6.2.4 Domain wall structure factors from continuum approximations

Before discussing the experimental results it is appropriate here to review briefly the results of continuum studies of domain walls corresponding to the $\phi^4$ solitons which were referred to in the introduction to this chapter.

Krumhansl and Schrieffer (1975) showed that for the one-dimensional $\phi^4$ model the important domain wall or soliton solutions correspond to a displacement field of the form

$$u(x,t) = u_0 \tanh[(x - vt)/d]$$

(6.12)

where $u_0$ is a constant, $v$ is the soliton velocity and $d$ is a relativistic width. They showed that within a simple phenomenological framework in which the domain walls were assumed to have a random
parameter \( d \) which they measured to be approximately 10 to 15 Å leads to a reversal of the polarisation over a distance of two or three unit cells, showing that the walls are probably too narrow in this substance for the continuum approximation to be reliable. The programme of experiments reported in the following section was undertaken to establish generally which of the approaches, discrete model or continuum approximation, should be used to describe ferroelectric domain walls.

§6.3 Experimental Studies of Ferroelectric Domain Walls

6.3.1 \( 180^\circ \) Walls in LiNbO\(_3\)

In the experiment by Axe and Samuelson (1978) the scattering which was briefly observed in LiTaO\(_3\) was qualitatively very similar to the scattering observed in the Pb\(_5\)Ge\(_3\)O\(_{11}\) experiment of Cowley et al. (1976). Narrow ridges of scattering were observed perpendicular to the \( c \) axis. The intensity of these ridges decreases as temperature increases except for a range of temperature close to \( T_c \) in which there is a sharp increase, also observed in the Pb\(_5\)Ge\(_3\)O\(_{11}\) experiment. This behaviour is what one would expect from a displacive system where the structure factor is proportional to \( u_o^2 \) or \( |f'(\mathbf{k})|^2 \) in the continuum or discrete models respectively, and this quantity varies as \( (T_c - T)^{2B} \). LiNbO\(_3\) is isomorphous to LiTaO\(_3\), both having hexagonal lattices with 6 formula units per cell (Abrahams, 1966, 1973). However, although the transition in LiTaO\(_3\) is believed to be a displacive ordering of the Lithium atom along the \( c \)-axis, it has been suggested (Chowdhury and Peckham, 1978) that the transition in LiNbO\(_3\) is of the order-disorder type, again involving predominantly the movement of only the Lithium ions. In other respects the LiNbO\(_3\) system gave the simplest case for domain wall formation since, like Pb\(_5\)Ge\(_3\)O\(_{11}\), it is a uniaxial ferroelectric.
with only two types of domain and therefore only one type of domain wall at which the polarisation direction is reversed.

The experiment was performed using the PLUTO triple axis spectrometer at the Atomic Energy Research Establishment, Harwell. The sample of LiNbO$_3$ was in the form of a cylinder with a length of 5 cm and a diameter of 2.5 cm. The c-axis was inclined at an angle of 20° to the axis of the cylinder. The sample was mounted with a (1,1,0) axis vertical. All measurements were made in the (h o l) plane. The best possible wave-vector resolution was obtained by using 20' collimation throughout the instrument and by using the longest wavelength of incident neutrons at which the desired reciprocal lattice vectors could be reached. Higher order contamination of the incident neutron beam was removed by a polycrystalline graphite filter which required that the incident energy used be 14.8 meV, which corresponds to a wavelength of 2.35Å. For both the monochromator and analyser, the (0 0 2) planes of pyrolytic graphite were used.

Ridges of scattering in the (ξ o ξ) direction were observed at the (0,0,6) lattice point. Scans through these ridges in both the 'constant E' and 'constant k' mode were performed, and the ridges were found to be resolution limited in width in both energy and k$_z$. The steep slope of the intensity against k$_x$ curves displayed in Fig. 6.6a for a range of temperatures is in qualitative agreement with the predictions of either the continuum and discrete models and it was necessary to carry out fitting of the data to the appropriate expressions (6.5a or 6.14) to obtain a useful comparison. It is immediately apparent from the lack of any marked change in the scattering intensity with temperature that the behaviour of the displacive systems Pb$_5$Ge$_3$O$_{11}$ and LiTaO$_3$, where the scattering decreased as the temperature increased, is not repeated by LiNbO$_3$. This may be taken as evidence
in support of the hypothesis that the transition is of an order-disorder nature, and is not displacive, although owing to the high transition temperature of LiNbO$_3$ ($T_c = 1210^\circ$C) and equipment limitations it was not possible to make measurements close to $T_c$.

(a) The continuum model analysis

Initially, to determine whether or not the continuum description of the domain walls was consistent with the observations, the observed scattering was fitted to the form given in eq. (6.14). The domain wall width parameter, $d$, the amplitude of the scattering, $A$, and the background intensity were all allowed to vary in the least squares fitting. No resolution corrections were felt to be necessary in view of the high resolution employed in the experiment and the approximate nature of the theory. Values of the parameters obtained are listed in Table 4. As an example of the results of this procedure, the experimental data at 400$^\circ$C is shown in Fig. 6.6b together with the best continuum model fit. The extremely rapid variation of $S(k)$ for the smaller values of $k_x$ caused the alignment of the crystal to be of particular importance, a slight error in $k_x$ causing a considerable change in $A$. It is quite possible that the large variations in $A$ above 300$^\circ$C may be largely ascribed to the effects of quite small positioning errors. The decrease of $A$ and $d$ at the lower temperatures ($T < 300K$) is accompanied by a worsening of the quality of the fits obtained. As these parameters are highly correlated in the fitting procedure, the change in the parameter values indicate that the model is less able to describe the data at these temperatures and the errors in the values of $A$ and $d$ are of the order of 100%.

Between the temperatures of 400$^\circ$C and 750$^\circ$C there is no detectable change in the domain wall width parameter $d$. The average value obtained
<table>
<thead>
<tr>
<th>T/K</th>
<th>A</th>
<th>d/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>123</td>
<td>289</td>
<td>1.66</td>
</tr>
<tr>
<td>200</td>
<td>143</td>
<td>1.15</td>
</tr>
<tr>
<td>300</td>
<td>600</td>
<td>2.13</td>
</tr>
<tr>
<td>400</td>
<td>1103</td>
<td>2.88</td>
</tr>
<tr>
<td>500</td>
<td>969</td>
<td>2.73</td>
</tr>
<tr>
<td>600</td>
<td>1170</td>
<td>3.06</td>
</tr>
<tr>
<td>750</td>
<td>697</td>
<td>2.75</td>
</tr>
</tbody>
</table>

**TABLE 4:** Continuum model parameters for the domain walls obtained by a least-squares fit of the intensity given by eqn. (6.14) to the data at seven temperatures, T.
is 2.96Å which implies a complete polarisation reversal within a distance of approximately 10 Å. The lattice parameter of LiNbO₃ is 5.15 Å which corresponds to a spacing of the planes of Li atoms 4.46Å apart in the direction perpendicular to the domain wall. The results obtained by the continuum model are inconsistent with the approximation that the polarisation changes gradually as the above result suggests that the Li displacements are reversed in neighbouring unit cells.

(b) The discrete model analysis

The similarity of the functional forms quoted in (6.5a) and (6.14) suggests that for small values of d the two expressions will be different to distinguish experimentally. If the scattering is assumed to be accurately described by the discrete lattice expression (6.5a), then fitting to a 1/sinh²(πd/2k) for small values of the argument ought to give a value of d = 1.43 Å. Since the values obtained for d are a factor of two greater than this at the high temperatures, it is possible to conclude immediately that the infinitely sharp wall model will not be sufficient to describe the observed scattering above 300°C, however the low values obtained for d below 300°C suggests that in this region of temperature it may be possible to apply (6.5a) directly.

Combining the analysis of the slightly roughened domain wall with the infinitely sharp wall formula for the hexagonal lattice, we obtain the form for the discrete model scattering as

\[ I_w(k) = A \exp(-2(\pi \lambda k_x)^2)/\sin^2(\pi k_x) \]  

(6.15)

where \( k_x \) is measured in the appropriate reduced units.

At 123°C it is apparent from the continuum model analysis that the scattering will be adequately described without assuming that the walls are rough, and so in Fig. 6.7 the experimental data is compared
Figure 6.7: The perfect wall model at 123°C.

A comparison of the experimental points with the discrete wall model. The background has been set to the measured value away from the ridge (450 counts) and the amplitude chosen to be 200.
with the form of eq. (6.15) with the constant $\lambda$ set to zero and suitable values chosen (not fitted) for the amplitude and background. The agreement between the theory and experiment is surprisingly close when one considers the approximations which have been made.

At the higher temperatures, 400°C to 700°C, the larger width obtained in (a) suggests that the domain walls have a finite width. Assuming that the effective width comes from a slight roughening of the walls which corresponds to the centre of the wall moving by only about one lattice spacing, the width $\lambda$ of the Gaussian probability distribution must be set equal to 1. By estimating the background from the intensity away from the ridge, the amplitude is again the only free parameter. In Fig. 6.8 the experimental data at 400°C is compared with the form of (6.15) with the amplitude, $A$, chosen to give a good agreement. For higher temperatures the constancy of the parameters obtained in (a) indicates that the same model can be used up to 750°C.

To conclude this section, it is appropriate to summarise the result described above. The domain walls observed in LiNbO$_3$ have been shown to be narrow to the extent that their width is comparable to a single unit cell width and that the continuum approximation cannot be expected to give an adequate description of their properties. Below a temperature of 300°C the walls are well described by the model of an ideal, infinitely sharp wall, whereas above this temperature the walls do show a detectable width which may be due to a slight roughening. There is no evidence for either the occurrence of a roughening transition or any dynamic features associated with the domain walls as the widths of the scattering ridges were unresolvable at all temperatures.
Figure 6.8: The slightly roughened wall model at 400°C.

A comparison of the experimental points with the discrete wall model with $\lambda = 1$. The amplitude and background have been set to 280 and 500 respectively.
6.3.2 180° domain walls in D.K.D.P.

(a) The preliminary experiment

A preliminary neutron scattering experiment to measure the width of domain walls in KDP was carried out, again using the PLUTO triple axis spectrometer at Harwell. This experiment was performed on a sample of deuterated KDP (DKDP) rather than natural KDP to reduce the intense incoherent quasi-elastic background scattering obtained from hydrogen-rich materials. This experiment is described in some detail in the accompanying paper. It was not possible to use the same experimental configuration as was used for the LiNbO₃ experiment due to the fact that the split Bragg peaks in the low temperature phase of DKDP give rise to satellite Bragg peaks from multiple scattering processes which, using the 14.8 meV neutrons, effectively obscure the ridges of quasi-elastic scattering close to the Bragg points. This problem was avoided by using neutrons with an incident energy of 7.0 meV which ensured that no multiple scattering of the primary wavelength was possible. Higher order contamination was removed by using a germanium analyser and a pyrolytic graphite filter. The low energy neutrons provided better wave-vector resolution than was possible in the previous experiment, but prevented observations from being made at reciprocal lattice points further from the origin than (2,2,0) which has a fairly small structure factor, hence the quality of the data was unavoidably impaired by the low intensities. The intensity was slightly improved at some cost in wavevector resolution by the use of a focussing monochromator.

Ridges of quasi-elastic scattering were observed in the predicted directions close to the (2,2,0) lattice point at a temperature of 100K. This scattering can be inferred to correspond to the ferroelectric domain
Figure 6.9: The ridge of scattering in DKDP from the preliminary experiment.

The intensity of the ridge observed at ($\xi, 2, 0$). The solid line shows the best fit to the data with $b_3 = 7.39$ (b = 7.45) and $W = 2$. The dashed line shows the tail of the Bragg peak at $\xi = 1.981$ determined from measurements of the (2,2,0) reflection in the high temperature phase.
walls as measurements of the intensity in the ridge directions at $T_c + 28K$ showed that the ridges did not remain in the paraelectric phase.

The experimental data was fitted to the infinitely sharp wall model of eq. (6.3), and to the intensity calculated for the 'three-domain' model of Fig. 6.3 (see eq. (16) of Bruce, 1981), making resolution corrections to the calculated scattering. It is apparent that the maximum width of the domain walls consistent with the experimental data, is two unit cells. The best fitting curve, obtained by fixing the background and the width, $W$, and treating the amplitude and the domain wall lattice constant $b_3$ as variable parameters is shown, together with the experimentally measured ridge intensity, in Fig. 6.9.

(b) **Subsequent experiments on DKDP**

After the preliminary experiment on DKDP had demonstrated the correctness in general terms of the calculations of §6.2, the experiment was repeated under improved conditions using the H-5 triple axis spectrometer at Brookhaven National Laboratory, New York. This spectrometer offered several advantages over the equipment used for the preliminary experiment and the experimental configuration was changed to exploit these. The capability of the H-5 spectrometer to make measurements at larger scattering angles than were obtainable with the PLUTO instrument meant that neutrons with an incident energy of 5 meV could be used to make observations at the (2,2,0) Bragg point. At this energy, contamination due to higher order reflections from the monochromator was eliminated by a nitrogen cooled beryllium filter mounted before the monochromator, allowing the use of a pyrolytic graphite monochromator and analyser. The sample was in the form of a cuboid with a volume of approximately 4 cm$^3$. It was mounted with the $c$ axis vertical in a nitrogen cryostat which allowed temperatures to be set to within 0.1K and to be held
constant to within 0.01K. Measurements of the quasi-elastic ridges of scattering were made at six temperatures below $T_c$ and at several temperatures above $T_c$, which was measured to be 220.7 ± 0.1K.

At the lowest temperature the ridges of scattering were observed up to a wave-vector transfer of 0.4 reciprocal lattice units, the results are shown in Fig. 6.10. The most significant feature of the scattering is the asymmetry displayed close to the Bragg peaks, which indicates that the structure factor $f_1^1(k)$ is not negligible close to the (2,2,0) reflection. For this reason, rather than using the approximate form for the domain wall scattering given in eq. (6.3) and the corresponding expressions for $W \neq 0$, the exact structure factors $f_j^1(k)$ were used in the least squares fitting. The reciprocal lattice indices used in this section are all referred to the reciprocal lattice shown in Fig. 6.2a. It is conventional crystallographic practice to define a monoclinic unit cell with $\gamma > 90^\circ$ in which case the reflection at which measurements were made must be regarded as a (2,2,0) reflection for domain 2, and as a (2,2,0) reflection for domain 1. The structures of the two unit cells are related by a $\overline{4}$ reflection axis. Structure factors for domains 1 and 2 were calculated by taking the values of the fractional atomic coordinates from Nakano et al. (1974) and Kennedy (1977) obtained at 211K, and the value of the distortion angle $\psi$ from measurements made during the experiment. For fitting to a three-domain, wide wall model, the domain wall cells were assumed to have the high temperature structure for which the structure factor was calculated from the data of Nelmes et al. (1981) at 227K. Least squares fits to the data were carried out for values of $W$ from 0 to 6 at all temperatures. Models with $W \geq 2$ were unable to account satisfactorily for the scattering, predicting a more rapid decrease of intensity close to the Bragg peaks. The results of fits with $W = 1$ and $W = 0$ are shown
in Fig. 6.10. The characteristic asymmetrical shape of the calculated scattering arises from the large \( f_1(k) \) terms causing constructive interference with the \( f_0(k) \) terms for \( \eta < 2 \) and destructive interference for \( \eta > 2 \). The downward turn in the \( W = 0 \) curve at \( \eta = 2.05 \) is a result of cancellations between two large terms and even small inaccuracies in the data used for the calculation of \( f(k) \) could remove this feature. The overall shape of the sharp wall scattering is not able to give a good fit to the wings on both sides of the Bragg peaks from which we may conclude that the domain walls have a finite width. The model with \( W = 1 \) gives an excellent fit to the 78K data, however the reciprocal lattice parameter of the distorted cells, \( b_3 = 7.77 \pm .03 \, \text{Å} \), represents a change of almost 5% in the lattice parameter which is disconcertingly large. Measurements at a temperature of 165K are also depicted in Fig. 6.10a. It can be seen that no change has taken place over this temperature range.

For temperatures close to, but below \( T_c \), the collimation of the spectrometer was changed from 20-20-20-40' slits to four 20' slits, in order to improve the wave-vector resolution and to improve the signal to background ratio. The high resolution obtained allowed the data to be fitted directly without resolution corrections.

The effect of increasing the temperature can be seen in the data shown in Fig. 6.11. In Fig. 6.11a, the ridge of scattering is shown at four temperatures on a logarithmic scale. The intensity can be seen to decrease with increasing temperature so that, whereas the ridge at 78K is clearly visible above background at \( \eta = 1.6 \), at 220K the ridge is barely visible at \( \eta = 1.8 \). In Fig. 6.11b, the central part of the ridge is shown on a linear scale to emphasise the changes taking place.

Fitting the scattering to the discrete models with two variable parameters, an overall amplitude \( A \), and the lattice constant \( b_3 \), produced the unexpected result that while the amplitude decreases more
Figure 6.10: The domain wall scattering in DKDP at low temperatures.

The intensity of the \((2, \eta, 0)\) domain wall scattering ridge at 78K and 165K. The solid curve shows the fit to the discrete wall model with \(b_3 = 7.77 \text{ Å}\) and \(W = 1\), the dashed curve shows the prediction of the infinitely sharp \((W=0)\) wall model.
Figure 6.11: The domain wall scattering in DKDP close to $T_c$.

(a) The intensity of the $(2, \eta, 0)$ ridge observed for a range of temperatures up to $T_c$. The spectra are shown on logarithmic scales offset by 1 unit from each other for clarity, the scale is correct for the observations at 78K.

Temperatures: $\circ$ 78K; $\times$ 200K; $\Delta$ 215K; $\cdot$ 220K.

(b) The intensities of the central part of the ridge close to $T_c$. The points are shown on a linear scale to emphasise the changes in intensity and joined by straight lines as a guide to the eye.

Temperatures: $\times$ 200K; $\bullet$ 210K; $\Delta$ 215K; $+$ 217K; $\square$ 220K.

(c) The discrete model fits for $W = 1$.

$\times$ $T = 200K$, $b_3 = 7.16 \ \text{Å}$.

$\square$ $T = 220K$, $b_3 = 7.03 \ \text{Å}$. 
rapidly than $|\psi|^2$, the constant $b_3$ remains at a value of $b_3 = 7.09 \pm 0.08 \text{ Å}$. The results of these fits are shown in Fig. 6.11.

The change in the value of $b_3$ between the low temperature value where $b_3$ is greater than the undistorted value ($b = 7.44 \text{ Å}$) seems to reflect a change in the properties of the wall at some temperature between 165 and 200K. The large changes occurring in $b_3$ seem unphysical, indicating that although the model gives an excellent qualitative agreement with the observed scattering, at least one of the underlying approximations, most probably the somewhat cavalier assumption that the cells of the wall could be adequately represented by the high temperature structure, is insufficient to give an exact description of the wall.

It was found empirically that over the range 200K to 220K the amplitude could be represented adequately by the form $A = A_0 t^x$ with $x = 0.25 \pm 0.02$. Over the same range $\psi^2 \sim t^{-1/8}$ showing that the decrease in intensity is not as predicted in §6.2 proportional to the decrease in order parameter squared. Since no marked temperature dependence was noted for the weaker ridges at the (2,0,0) lattice point it is quite likely that the decrease is due to the effective Debye-Waller factor of eqn. (6.9), indicating that the walls become less perfect as $T \to T_c$. The decrease in intensity may also be attributed partly to a reduction in the wall density.

(c) The 'central peak' above $T_c$

Above the transition temperature ridges of scattering persisted, although decreasing rapidly with temperature, up to a temperature of around 300K. In the high temperature phase the Bragg peaks are no longer split into components from individual domains, therefore the ridges of scattering do not originate from regions of the low temperature, orthorhombic structure with a higher value of $T_c$, but from some
short-range ordering (or clusters) in the tetragonal crystal phase. In Fig. 6.12 the ridge of scattering is shown together with the broad critical scattering observed by Skalyo et al. (1970) and Hosea (1980) which results from coupled acoustic and ferroelectric fluctuations, (Cowley et al., 1971; Cowley, 1976). Energy scans show that the ridge has a width below the resolution limit (0.02 THz FWHM), whereas the critical scattering has a width in energy which is just resolvable. Transverse wave-vector scans (Fig. 6.12b) show that for wave-vectors \((2, 2-\eta, 0)\) the ridge has a finite transverse width for \(\eta \geq 0.03\). It is difficult to extract an accurate value for the width due to the effects of instrumental resolution, for \(\eta = 0.03\) the width is about the resolvable limit of 0.005, whereas for \(\eta = 0.10\) the width is about 0.03.

Previous measurements of the critical scattering in DKDP carried out with considerably lower resolution to measure the integrated intensity of the critical fluctuations at \(T_c + 5\)K have been unable to separate the ridge due to the cluster walls from the broad critical scattering. Hosea (1980) noted that the intensity in the directions of the ridges was systematically higher than predicted by the coupled mode theory, a discrepancy which is explained by the extra intensity from the cluster walls.

The concept of clusters of short-range order above \(T_c\) with approximately planar walls giving rise to elastic, or at least quasi-static scattering explains some curious light scattering results in KDP referred to by Muller (1979) as "the Disappearing Central Peak". Lagakos and Cummins (1974) found a critical central peak in KDP by Brillouin scattering which was narrower than their instrumental resolution of \(10^9\) Hz. This feature was studied further by Durvasula and Gammon (1977) who concluded that it originated from a static feature, and by Courtens (1977, 1978) who found that the central peak in the paraelectric phase could be removed by annealing the crystal for 18 hrs.
The domain wall and critical scattering above $T_c$.

(a) Transverse scans across the ridge at $\eta = 1.95$. The critical scattering from the coupled ferroelectric and acoustic fluctuations appears as the broad peak while the narrow domain wall scattering ridge can be easily identified by its narrow width and its temperature dependence.

Temperatures: $\circ$ 220.8K
$\times$ 225.8K

(b) Transverse scans across the ridge at 220.8K showing the finite width away from the Bragg peak. A resolution-limited transverse scan at 200K with $\eta = 1.95$ is shown by the solid curve with the peak height rescaled by a factor of 0.31 for comparison.

$\Delta$ $\eta = 1.97$
$\times$ $\eta = 1.95$
$\circ$ $\eta = 1.90$
at 413K. This implies that in KDP the clusters of short-range order are not regions of precursor ordering forming on the approach to \( T_c \), but are regions of crystal which remain partly ordered only on heating from the low temperature phase, i.e. showing a large thermal hysteresis. In the experiment on DKDP we were unable to remove the scattering ridges by thermal annealing at 350K, although the ridges were not visible above 300K they reappeared on cooling.

In order to improve the domain wall model, to deduce the structure of distorted cells, and to examine the origin of the temperature dependence of the intensity, studies of the domain wall scattering at reciprocal lattice points with larger Miller indices will be required. Because of the multiple scattering problem referred to in (a), this will be possible only using small samples and X-ray radiation. Domain wall scattering in DKDP has been observed by X rays and a full programme of experiments has commenced (Bleif, 1981).

6.3.3 Experiments involving \( \text{KNBO}_3 \) and \( \text{BaTiO}_3 \)

In addition to the experiments on uniaxial systems described above, experiments have also been performed on the cubic perovskites, \( \text{KNBO}_3 \) and \( \text{BaTiO}_3 \).

An experiment using a 1 cm\(^3\) sample of \( \text{KNBO}_3 \) was carried out on the PLUTO triple axis spectrometer with an incident energy of 14.8 meV and 20\(^\circ\) collimation throughout the instrument. Strong quasi-elastic scattering in the (1,0,0) direction was observed in the tetragonal phase close to the (0,2,0) and (0,3,0) points which may originate from 180\(^\circ\) domain walls. Fitting the continuum model of eqn. (6.14) to the ridge of intensity at \((\xi, 2, 0)\) for \( 0 < \xi < .2 \) at a temperature of 410K \((T_c = 20K)\) gave a reasonable fit for a domain wall width parameter \( d = 9.7 \text{ Å} \), approximately two lattice spacings. The interpretation of this scattering as originating from domain walls is not conclusive as
the scattering persists to temperatures over 200K above the cubic-tetragonal transition temperature. The experiment did not look for scattering from the 90° domain walls, or from the domain walls in the orthorhombic phase in which Currat et al. (1974) reported a strong ridge of quasi-elastic scattering.

A similar experiment, carried out using a 6 cm³ sample of BaTiO₃ and the H-5 spectrometer with 20-10-10-20' collimation found no evidence for 180° domain walls in the tetragonal phase. There is an extremely weak ridge of scattering close to the (2,2,0) reciprocal lattice point in the (I,1,0) direction, which was observed to a reduced wave-vector of 0.1 from the Bragg peak which may be due to 90° walls.

The dramatic difference in the intensities of the ridges observed in the isomorphous materials is not understood. Although the domains formed in the BaTiO₃ sample appeared to be quite large when the sample was viewed through a polarising microscope which would explain the weakness of the domain wall scattering in the material, the domain wall interpretation of the strong quasi-elastic scattering in KNbO₃ requires a very small domain size, perhaps less than 100 Å. It is hoped that a programme of X ray experiments will be able to resolve this paradox.
CHAPTER 7

"LABOR OMNIA VINCIT"

It would be superfluous in this final chapter to recapitulate the detailed conclusions, interspersed throughout the text, which summarise the scientific contributions of this work. There is, however, one theme which recurs at many points in the text although it is seldom explicitly stated, which I wish to highlight here. The study of critical dynamics and that of interfaces at structural phase transitions is greatly restricted by the limitations of experimental measurements, so that many of the experiments which may be conducted in these fields do not allow a unique theoretical interpretation. This is most strikingly evidenced by the fact that both critical and domain wall scattering are cited in the literature as explanations for the same observations. In such circumstances, where theoretical interpretations do not suggest an 'Experimentum Crucis' by which they can be tested, an intimate interplay between theoretical and experimental studies is of paramount importance.

It is only by considering a synthesis of the results of all of the available experimental techniques that one may confidently identify the physical processes underlying these difficult fields of study avoiding the pitfalls of misinterpretation which are prevalent when considering isolated experiments. The major role of theoretical studies must include not only the interpretation of existing observations but also the provision of experimentally verifiable predictions which may serve to guide the course of experimental studies.

For this reason it is to be hoped that the unanswered questions raised in this thesis where the necessity for, and direction of further work is indicated, will ultimately prove not the least valuable
contribution which it contains. By such direction of effort we may hope to minimise the labour which will be required to complete our understanding of the topics discussed in this work. While our compendium of experimental information is still incomplete, we must, while recognising the limitations on our theories, avoid the temptation to adopt the attitude of mind summarised by the admonition with which Plato prefaced the first "scientific" work and which might have been framed with critical dynamics in mind:-

"Don't therefore be surprised, Socrates, if on many matters concerning the whole world of change we are unable in every respect and on every occasion to render consistent and accurate account. You must be satisfied if our account is as likely as any."

(Timaeus: 29)
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APPENDIX 1: Spectral Functions for the van Hove Model

It is convenient to measure all frequencies in units of the one-phonon spectral function full width at half maximum intensity. Thus we define the frequency variable as

\[ \Omega = \frac{2r_0}{\gamma_0} \omega . \]

With this substitution the one-phonon spectral function is

\[ S(k = 0, \omega) = \frac{\gamma_0}{\pi r_0^2} \frac{1}{1 + (2\Omega)^2} . \]

The two-phonon spectral function, \( \Gamma(k = 0, \omega) \) can be evaluated exactly in both 2 and 3 dimensions. Introducing a sharp wave-vector cutoff at \( \Lambda \), and defining \( \lambda^2 = \Lambda^2 c / r_0 \) we find

\[ \Gamma_{2D}(k = 0, \omega) = \frac{\gamma_0}{2c r_0^2 \Omega^2} \left[ \ln(1 + \lambda^2) - \frac{1}{2} \ln\left(\frac{(1+\lambda^2)^2 + \Omega^2}{1 + \Omega^2}\right) \right] \]

and

\[ \Gamma_{3D}(k = 0, \omega) = \frac{2\pi \gamma_0}{(c r_0)^{3/2} \Omega^2} \ln \left| \frac{\lambda^2 + 2\Lambda \lambda + 2B^2 - 1}{\lambda^2 - 2\Lambda \lambda - 2B^2 + 1} \right| \]

\[ + B\left\{ \tan^{-1}\left(\frac{\Lambda + A}{B}\right) + \tan^{-1}\left(\frac{\Lambda - A}{B}\right) - \tan^{-1}(\lambda) \right\} \]

where \( \Lambda^2(\Omega) = \frac{1}{2}(\sqrt{1 + \Omega^2} - 1) \)

and \( B^2(\Omega) = \frac{1}{2}(\sqrt{1 + \Omega^2} + 1) \).

In each case we have suppressed a factor of \( (\frac{a}{2\pi})^d \) in \( \Gamma \). As \( T \to T_0 \) the dimensionless cut-off wave-vector \( \lambda \) tends to infinity and the expressions above assume their asymptotic form which is independent of \( \lambda \). The three-dimensional spectral function of Fig. 3.1 was calculated with \( \lambda = 10^5 \).
APPENDIX 2: PUBLICATIONS

Discrete lattice effects in incommensurate systems;


The theory of two-phonon critical scattering; with A.D. Bruce;


Scattering properties of ferroelectric domain walls;


The work of §3.5 is to be published as an appendix to the paper by
Cowley and Satija (1981). It is intended to publish details of the
experiments on SrTiO$_3$ (Chapter 4) and DKDP (Chapter 6) separately.
Discrete lattice effects in incommensurate systems

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Abstract. The behaviour of systems which exhibit both commensurate and incommensurate phases is studied for a discrete lattice model. Close to the lock-in transition the incommensurate phase is shown to be well described by a soliton theory in which the solitons may be pinned to the lattice. This pinning effect leads to a ‘devil's staircase’ type of behaviour and causes an energy gap in the phason spectrum. It is also shown that an entropy-driven unpinning transition may take place dividing the incommensurate phase into a region in which the soliton density changes discontinuously and the phase is not strictly incommensurate, and a region in which the soliton density changes continuously and the phase is strictly commensurate.

1. Introduction

During the last few years there has been considerable interest in systems which undergo phase transitions to form structures with a periodicity which is incommensurate with the underlying lattice. Examples of such systems are the insulators BaMnF$\textsubscript{4}$ (Cox et al 1979) and K$\textsubscript{2}$SeO$\textsubscript{4}$ (Iizumi et al 1977), and various low-dimensional metals such as the charge-density wave (CDW) transitions in layered transition metal dichalcogenides (Moncton et al 1975, Wilson et al 1975) and one-dimensional metals (reviewed by Berlinsky 1979).

Similar transitions may be induced in other systems such as adsorbed monolayers on graphoil (Kjems et al 1974), and in the mixed VO$_2$/NbO$_2$ system (Comès et al 1974) where the incommensurate wavevector depends on the relative concentrations. Another interesting system which displays almost one-dimensional behaviour of this kind is Hg$_{3-x}$AsF$_6$ (Hastings et al 1977), in which chains of mercury atoms form a structure which is incommensurate with the underlying AsF$_6$ structure.

Many, but not all, of these systems exhibit a sequence of phase transitions in which, as the system is cooled from the high-temperature phase, it first distorts at a temperature $T_c$ to produce an incommensurate phase, and at a lower temperature $T_L$ the wavevector of the distortion locks in to a commensurate value. In the case of the structural phase transitions the transition from an undistorted to incommensurate phase at $T_c$ may be described as an instability of the crystal against a soft normal mode (Cowley and Bruce 1978) with the appropriate incommensurate wavevector. The lock-in transition at $T_L$ may be described as the instability of the commensurate phase against the formation of discommensurations or phase solitons as described by McMillan (1976) or by Bak and Emery (1976). These theories are reviewed by Bruce et al (1978). They were developed
using a continuum model to describe the properties of the normal modes with wave-vectors close to the commensurate wavevector.

Similar theories have been developed for an Ising spin model with competing interactions, and these too are able to discuss the occurrence of phase transitions from a paramagnetic phase to ones with a spatial variation of the magnetic moment incommensurate with the underlying lattice and lock-in transitions to phases with a commensurate magnetisation variation (Bak and von Boehm 1978, Selke and Fischer 1979).

One aspect of all theories based on a continuum model is that the excitation spectrum of the incommensurate phase has a gapless phase mode, called a phason by Overhauser (1971). This mode is the Goldstone mode of the broken continuous phase symmetry of the incommensurate phase.

Careful experimental investigation of the excitation spectra of many of the structurally incommensurate phases has failed to reveal the existence of this mode, except possibly in biphenyl (Cailleau et al 1980) which does not exhibit a lock-in transition; consequently the present work was commenced to investigate the role of discrete lattice effects on the phase transitions and excitations of incommensurate phases.

A different approach to this problem has been developed by Aubry (1978) who suggested that the wavevector will lock in to all commensurate wavevectors. In this case the wavevector of the distortion will not vary continuously but will be described by the so-called devil's staircase. Similar behaviour was found by Bak and von Boehm (1978) in spin models using a mean-field theory. More recently Bak and von Boehm (1980) have suggested that when finite-temperature effects are included there is lock-in only to the commensurate wavevectors with four and six times the underlying lattice periodicity.

In §§2 and 3 of this paper the calculations for a discrete lattice system are followed in the same manner as for the continuum model used in the above papers by Bruce and Cowley. The discrete lattice is shown to cause the distortion in the incommensurate phase to be both modulated and pinned to the lattice, preventing a truly incommensurate state from arising and causing the appearance of a gap in the phason spectrum. The calculations of §§2 and 3 are essentially one dimensional and at \( T = 0 \), but in §4 the changes required to account for finite temperature and three-dimensionality are discussed by means of a modified continuum theory. These changes are shown to lead to the occurrence of an unpinning transition for the phase solitons characterised by a change in the excitation spectrum.

2. An analytic treatment of the model

The fundamental assumption underlying the theory is that the soft-mode picture of structural phase transitions which has been highly successful in describing zone-centre or zone-boundary transitions from a phenomenological point of view, can be equally well applied to a system with a soft mode at a general wavevector \( q \). The origin of this soft mode lies of course in the microscopic interactions and may result from anharmonic phonon interactions, or from electron–phonon interactions producing a Kohn anomaly in the CDW transitions.

2.1. The model Hamiltonian

Initially we consider a quasi-one-dimensional model in which it is assumed that the dis-
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Placement field in the crystal, \( u(r) \), is independent of the \( x \) and \( y \) directions, and we ignore the effects of fluctuations. Both of these approximations will be considered in §4. For low temperatures the distortion locks in to a commensurate wavevector which may be written \( \tau/p \) where \( \tau \) is a reciprocal-lattice vector and \( p \) is an integer. The incommensurate soft-mode wavevector \( q_s \) may be assumed to be close to \( \tau/p \) and so the critical modes in the Hamiltonian will appear in the usual two- and four-phonon anharmonic terms, and in a \( p \)-phonon Umklapp term. The Hamiltonian may be written

\[
\mathcal{H}([Q]) = \mathcal{H}_A + \mathcal{H}_p
\]

where \( \mathcal{H}_A \) is the anharmonic phonon Hamiltonian

\[
\mathcal{H}_A = \frac{1}{2N} \sum_q \omega^2(q) Q(q) Q(-q) + \frac{1}{N^4} \sum_{q_1,q_2,q_3,q_4} u_4(q_1, q_2, q_3, q_4) \\
\times Q(q_1) Q(q_2) Q(q_3) Q(q_4) \Delta(q_1 + q_2 + q_3 + q_4)
\]

and \( \mathcal{H}_p \) is the \( p \)-phonon Umklapp Hamiltonian

\[
\mathcal{H}_p = \frac{1}{N^p} \sum_{q_1, \ldots, q_p} u_p(q_1, \ldots, q_p) Q(q_1) \ldots Q(q_p) \Delta(q_1 + \ldots + q_p + \tau).
\]

In these expressions, \( \Delta \) is a wavevector conservation constraint such that

\[
\Delta(q) = \begin{cases} 
N & \text{if } q = 0 \\
0 & \text{if } q \neq 0.
\end{cases}
\]

The dispersion relation in the vicinity of the soft-mode wavevector is assumed to be of the form

\[
\omega^2(q) = r_0 + |q - q_s|^2
\]

with \( r_0 \propto T - T_0 \), where \( T_0 \) is a mean-field transition temperature.

The Hamiltonian \( \mathcal{H}_p \) will favour the incommensurate plane wave (ipw) structure for \( T < T_c \) while the Umklapp terms in \( \mathcal{H}_s \) favour the locked-in commensurate phase. In order to convert the Hamiltonian of equation (1) to a direct space representation we write the displacement of an atom in the \( l \)th unit cell from its high-temperature equilibrium position, \( R_l \), as

\[
u_i = \sqrt{2A_i \cos[(\tau/p) \cdot R_l + \phi_i]},
\]

and introduce the wavevector \( \delta_0 \) such that

\[
q_s = \tau/p + \delta_0.
\]

In our one-dimensional treatment we assume that \( \tau \) and \( \delta_0 \) both lie in the \( z \) axis direction. Now by following the procedure outlined by Bruce et al (1978) the Hamiltonian (1) may be re-written as

\[
\mathcal{H}([A, \phi]) = \sum_l \left( \frac{1}{2}(r_0 + \delta_0^2) A_l^2 + \frac{1}{2c^2} [A_{l+1}^2 + A_l^2 - 2A_{l+1} A_l \cos(\phi_{l+1} - \phi_l)] \right) \\
- \frac{\delta_0}{c} A_{l+1} A_l \sin(\phi_{l+1} - \phi_l) + v_p A_l^p \cos p\phi_l + u_0 A_l^4
\]

(4)
where

\[ u_0 = \frac{\sqrt{2}}{2} u_c \left( 1 - \frac{1}{p}, \frac{p}{p}, \frac{1}{p} \right), \]

\[ v_p = u_p \left( 1 - \frac{1}{p}, \frac{p}{p}, \frac{1}{p} \right) \]

and \( c \) is the unit cell dimension in the \( z \) direction.

It is convenient to introduce the widely accepted phase-only modulation ansatz which assumes that \( A_l \) is constant for all \( l \) since from studies of the continuum model (Nakanishi and Shiba 1978) the amplitude modulation produces only slight changes in the transition temperatures and quantitative behaviour of the system, but no change in the qualitative behaviour.

By making two final substitutions the Hamiltonian may be written

\[ \mathcal{H}(p, \phi) = \mathcal{H}_c + \Delta \mathcal{H} \]

where

\[ \mathcal{H}_c = \frac{1}{2} \left[ \frac{1}{2} (r_0 + \delta_0^2) A^2 + u_0 A^4 - v A^2 \right] \]

and

\[ \Delta \mathcal{H} = \frac{A^2}{c^2} \sum \left[ \sin(\phi_{l+1} - \phi_l) - \left( \cos(\phi_{l+1} - \phi_l) - \frac{w}{p} \left[ \cos(p \phi_l) - 1 \right] \right) \right] \]

with \( D = c \delta_0 \) and \( w = p v c^2 = -p c^2 v A^p \). The notation is chosen to emphasise that \( \mathcal{H}_c \) is the energy of the commensurate phase where \( \phi = 0 \), and therefore consideration of the stability of the incommensurate or modulated phases requires only the consideration of \( \Delta \mathcal{H} \). The only temperature dependence in the original Hamiltonian of equation (1) is contained in the parameter \( r_0 \), the incommensurate phonon self-energy. In the commensurate phase \( A \) depends on \( r_0 \), and through this temperature dependence a temperature dependence is introduced into the coupling constant \( w \) in \( \Delta \mathcal{H} \). Studying the temperature dependence of the system is therefore reduced to studying the behaviour of \( \Delta \mathcal{H} \) for different values of \( w \).

2.2. The general character of the phase function \( \phi_l \)

In the study of continuum models the ground state of a Hamiltonian can be determined analytically, but in the case of the function (5) the problem of determining the ground state is much more difficult. Minimising (5) with respect to an arbitrary \( \phi_k \) gives the condition for an extremum in \( \Delta \mathcal{H} \) as

\[ \sin(\phi_k - \phi_{k-1}) - \sin(\phi_{k+1} - \phi_k) = D \left[ \cos(\phi_k - \phi_{k-1}) - \cos(\phi_{k+1} - \phi_k) \right] + w \sin p \phi_k. \]

This equation may be rearranged to give a three-term recursion relation from which the solution for \( \{ \phi_l \} \) can be constructed numerically once two initial starting points have been specified. The ground state can then be found by varying these conditions slowly. Typical solutions are shown in figure 1 for different values of \( w \).

It can be seen that for small values of \( w \) the phase varies approximately linearly with distance, the condition for an IPW distortion. Increasing \( w \) reduces the average slope of the phase function and causes the appearance of harmonics of the effective wavevector until for large values of \( w \) the phase profile shows short regions of commensurate structure separated by domain walls or, as McMillan termed them, discommensurations.
These discommensurations correspond to the sine–Gordon solitons obtained in the continuum theory (Bak and Emery 1976). The two types of solution, multiple discommensuration or plane wave, correspond qualitatively to the expected behaviour since the order parameter for the lock-in transition in the continuum theory is the soliton density, whereas for the incommensurate to high-temperature (I–H) phase transition the order parameter is the amplitude of the distortion with wavevector $q_s$ which corresponds to a phase of

$$\phi_I = lD.$$ 

2.3. Behaviour close to the high-temperature phase

The I–H transition occurs when the energy given by equation (5) becomes zero. In a case where this transition is continuous in the sense that $A$ goes continuously to zero as $T \to T_c^-$ the transition may be expected to occur for $w \to 0$. In this limit equation (6) is satisfied by a solution of the form

$$\phi_I = \alpha lD.$$ 

The value of $\alpha$ which minimises the energy of the plane-wave solution may be calculated from equation (5) to be

$$\alpha = \tan^{-1} D/D \approx 1 - D^2/3.$$ 

This corresponds to a wavevector for the distortion of

$$q = \tau/p + \delta_0(1 - c^2\delta_0^2/3).$$ 

(7)
The energy for this IPW distortion is given by

$$E_1 = N[\frac{1}{2}r^*A^2 + u_0 A^4]\quad (8a)$$

with

$$\frac{1}{2}r^* = \frac{1}{2}r_0 + (\frac{1}{2} - \alpha - \alpha^2 / 2) \delta_0^2 + (\alpha^4 / 24)(4/\alpha - 1)c^2 \delta_0^4$$

$$\approx \frac{1}{2}r_0 + \frac{1}{8}c^2 \delta_0^4.\quad (8b)$$

Treating this result by mean-field theory gives a continuous transition when \(r^* = 0\) from the high-temperature to the IPW phase. The effect of the discrete lattice has been to lower the transition temperature by the amount \(\frac{1}{8}c^2 \delta_0^4\). Since the Umklapp terms do not appear in equation (8a) this result is independent of \(p\).

By writing \(\mathcal{H}_c\) in the form

$$\mathcal{H}_c = N[\frac{1}{2}(r_0 + \delta_0^2)A^2 + u_0 A^4 - |v_p| A^p]\quad (9)$$

the direct commensurate to high-temperature phase (C–H) transition is seen to be continuous for \(p = 4\) at a temperature given by \(r_0 = -\delta_0^2\). In this case there will always be an IPW state between the commensurate and disordered states on the phase diagram. For other values of \(p\) the C–H transition may be first order in which case the condition for the IPW phase to be stable is that

$$v < \frac{1}{2} \delta_0^2 - (c^2 / 8) \delta_0^4\quad (10)$$

for some temperature below \(T_c\). When \(p > 4\) additional higher-order terms should in principle be included in equations (5) and (9) to stabilise the commensurate phase and these terms will determine \(A\) and hence \(v\). These terms have not been included in this paper because they do not contribute to \(\Delta \mathcal{H}\) but it is implied throughout this paper that condition (10) is satisfied, otherwise the IPW phase will be pre-empted by the C–H transition.

Close to the I–H transition the order parameter \(A\) is given by

$$A^2 = -r^*/4u_0.$$ As the corrections to \(q, r_0\) and \(A\) are all of order \(\delta_0^2\) they are evidently small and so it is reasonable to conclude that the continuum model gives an adequate description of the phase diagram close to \(T_c\).

2.4. Behaviour in the multi-soliton regime

From figure 1 it can be seen that a non-zero value of \(w\) will cause a distortion of the IPW. This is only a slight modulation for small \(w\) but gives rise to the formation of a sharply stepped profile as \(w\) increases. For values of \(w\) greater than a critical value \(w_L\) which depends on \(p\) and \(D\) it is no longer possible to generate solutions to equation (6) with a negative value for \(\Delta \mathcal{H}\). This corresponds to the critical temperature \(T_L\) for the lock-in transition. One feature of the recursively obtained solutions close to the phase boundary was the fact that it was possible for two solutions to have a very similar appearance, in the sense that each contained the same spacing between domain walls, and yet to have a significant difference in energy. This is because the energy of a domain wall is very dependent on its position because of the interaction between it and the underlying lattice which makes it energetically favourable for the domain walls to be centred on a unique location within the unit cell. This behaviour was investigated by assuming a form for the ground state.
According to the continuum theory (Bak and Emery 1976), the continuum Hamiltonian analogous to equation (5b) is

$$\Delta \mathcal{H} = \frac{A^2}{c} \int dz \left[ \left( \frac{\partial \phi}{\partial z} - \delta_0 \right)^2 - \nu(\cos p \phi - 1) \right]$$

(11)

and has minimum-energy solutions which are solutions of the time-independent sine-Gordon equation. The simplest of these solutions is the soliton function

$$\Theta(z) = \frac{4}{p} \tan^{-1} \exp(\nu^{1/2} z),$$

(12)

In figure 2 several of these functions are compared with the numerically obtained exact solutions of equation (6). It can be seen that the soliton gives a surprisingly good fit even in the case where the soliton width is only a few lattice spacings.

Exploiting this close agreement, the distortion of a sine–Gordon soliton in a discrete lattice was studied by a variational method. For a wide range of values of $w$ the continuum solitons were found to be an excellent approximation to the ground state, the phases changing by only the order of 5% when the soliton was allowed to distort. Figure 3 shows the result of such a calculation. It can be seen that the soliton has distorted in such a way as to increase the phase separation of the central atoms and thus to make the soliton slightly narrower. Since discrete lattice effects are likely to be most pronounced for narrow solitons this shows that a calculation made using the sine–Gordon profile instead of a true ground state will slightly underestimate the discrete lattice effects. The difference between the sine–Gordon soliton energy and the variationally distorted soliton energy was negligible except close to the value of $w$ where the energy changed sign. The ground state may therefore be studied using sine–Gordon solitons as they will certainly give a qualitatively correct description of the ground state near the lock-in transition.
3. The multi-soliton ground state

For the reasons stated in the last section, the ground state of the model in the region close to the lock-in phase boundary was approximated by the expression

\[ \phi_L(b) = \sum_m \Theta(ic - mb - z_0) \quad (13) \]

where \( \Theta(z) \) is given by (12). This function represents a lattice of sine–Gordon solitons, linearly superposed, and separated by a constant lattice spacing \( b \). Most of the numerical calculations were performed using a 100 cell chain; longer chains were used to check for any finite-size effects. Soliton spacings of between 5 and 1000 lattice spacings were investigated for different values of \( p, \omega_0 \) and \( w \). The equilibrium configuration was determined by the minimum in the energy function

\[ E(b) = \left( c^2/NA^2 \right) \Delta \mathcal{H}(\{ \phi_L(b) \}). \]

In all the results which follow it may be assumed that the value of \( z_0 \), the phase profile 'sliding' coordinate, has been chosen to minimise \( E(b) \), except where it is explicitly stated to the contrary.

3.1. Soliton energies and the phase diagram

At the lock-in boundary the soliton lattice spacing \( b \) may be expected to be large and therefore the critical value of \( \omega_0 \), of the parameter \( \omega_0 \), will occur where the single-soliton creation energy changes sign. For a continuum sine–Gordon field the single-soliton energy is given by

\[ E = 8w^{1/2}p^{-3/2} - 2\pi D/p. \quad (14) \]
Figure 4. (a) Single soliton energies in the multi-soliton region, $p = 4$, $D = 0.5$. The full curve shows the continuum energy, the full circles show numerically computed values for the discrete lattice.

(b) Phase boundaries for the incommensurate (I)–commensurate (C) lock-in transition with $p = 3$ (dotted curve), 4 (chain curve), and 8 (broken curve). The straight line which the numerically obtained boundaries approach for small $D$ is the continuum model result. The horizontal lines show the sharp soliton limits for $p = 4$ and 8. The full curve above the lock-in boundary shows the value of $v$ at which the IPW becomes stable with respect to the commensurate phase.

In figure 4(a) this prediction is compared with the energies obtained numerically for the case $p = 4$, $D = 0.5$. The results show that over the relevant range of $w$ there is an approximately constant discrepancy between the two energies, with the predicted energy being somewhat higher than the actual energy. This leads to a change in the value of $w_L$ of approximately 5% in the case shown. The effect of this change on the phase diagram is shown in figure 4(b) as a function of $w$ and $D$. The value of $T_L$ is usually reduced, especially for the larger values of $p$ and $D$ which correspond to the narrower solitons. The phase diagrams are plotted against $cv^{1/2}$ rather than $w$ because they can be compared with the continuum theory which, for all values of $p$, gives

$$v_L = \frac{1}{16} \pi^2 D^2/c^2.$$ 

The line at which the IPW becomes stable compared with the commensurate phase is also shown in figure 4(b). For small $D$ this is given by

$$v_{IPW} = (\frac{1}{2} D^2 - \frac{1}{8} D^4)/c^2.$$ 

Since for any non-zero value of $D$, $v_{IPW} < v_L$ the lock-in transition in this model will
always proceed via a multi-soliton phase rather than by a direct first-order commensurate to \text{IPW} transition.

Also shown on figure 4(b) are the horizontal lines which the phase boundary must approach for large values of \( v \). These can be calculated by recognising that the limit of large \( v \) corresponds to the sharp soliton limit where \( \phi \) is given by

\[ \phi_i = (2\pi/p) H(lc - z_0) \]

where \( H \) is the Heaviside step function. In this limit the stability criterion is given by

\[ D > (1 - \cos 2\pi/p)/\sin 2\pi/p \] (15)

and so for larger values of \( D \) any lock-in transition will lock in to a phase with \( \phi \) given by

\[ \phi_i = 2\pi l/p \]

thus the wavevector of what may be called a super-commensurate distortion is given by

\[ q_s = 2\tau/p. \]

This criterion sets an upper limit on \( D \) for a given value of \( p \) for which the following theory is valid. In the model considered in this paper \( D \) is independent of temperature and so thus the wavevector of what may be called a super-commensurate distortion is given by the model used by Bak and Emery (1976), the wavevector \( D \) was temperature dependent. The only change which this may be expected to induce in the behaviour is to widen either the IPW or multi-soliton regions provided that \( D(T) \) is not a convex function of \( v^{1/2}(T) \) in which case the commensurate phase will be stable for small \( v^{1/2} \) but as the system cools it may undergo a transition to an incommensurate or even a super-commensurate phase.

3.2. The equilibrium soliton density

The equilibrium density of solitons was obtained for different values of \( w \) close to \( w_L \) from the position of the minimum in the \( E(n) \) versus \( n \) curve, where \( n \) is the density of solitons. Figure 5 shows the form of this function close to \( T_L \) for \( p = 4, D = 0.5 \). Slightly below \( T_L \) the minimum is well defined and the equilibrium density may be determined with confidence. For \( T \approx T_L \) the curve is virtually flat for \( n < 0.03 \) and within the accuracy with which the calculations were carried out it was not possible to demonstrate any inter-soliton interaction for lower densities. This does not prove that the transition is first order, but it strongly suggests that experimentally the transitions may appear first order as the region of \( w \) for small values of \( n \) will be vanishingly small. Since the multi-soliton state can be characterised by an effective wavevector \( \bar{q} = (2\pi/p)n \), if \( n \) appears to change discontinuously at \( T_L \) the observed order parameter, the effective wavevector, will appear to change discontinuously from \( q = \tau/p + \bar{q} \) to \( q = \tau/p \). Similar behaviour was observed for other values of \( p \) and \( D \).

In a continuum sine–Gordon field two solitons have a mutual interaction energy which decreases exponentially at distances much greater than the soliton width leading to a multi-soliton energy of the form

\[ E(b) = (8v^{1/2}/pb) [1 + 4 \exp(-pv^{1/2}b)] - (2\pi/pb) \delta_0. \] (16)

With an energy of this form the soliton density close to \( T_L \) should be given by

\[ n \sim -1/\ln(T - T_L). \] (17)
Figure 5. Energy density for different soliton densities, $n$, for $T \leq T_L$ (A), $T = T_L$ (B) and $T \geq T_L$ (C).

Figure 6. (a) Soliton density close to WL for $p = 4$, $D = 0.5$. The full circles show numerically obtained values, the full curve shows a curve of the form given in equation (17). The pinning energy exceeds the soliton creation energy for $w > 0.598$.

(b) Soliton density close to $w_L$ for $D = 0.4$, $p = 3$. The vertical lines indicate the region for which the pinning energy exceeds the soliton creation energy.

(c) Soliton density versus $-1/\ln(w_L - w)$ for low soliton densities, with $p = 4$ (full circles) and $p = 3$ (crosses).
Figure 6(a) shows the density of solitons for the case \( p = 4, D = 0.5 \) where the steepness of the slope close to \( T_L \) is obvious. The full curve is the best fit to a function of the form given in equation (17) with the proportionality constant extracted from the logarithmic plot of figure 6(c). Similar data are displayed for the case \( p = 3, D = 0.4 \) to emphasise the similarity in behaviour in a case where the broader solitons made the inter-soliton interaction appreciable for lower densities.

For an IPW with \( q_s = \tau/p + \delta_0 \), the effective soliton spacing is given by

\[
b_{IPW} = 2\pi/p\delta_0.
\]

Decreasing \( w \) from \( w_L \) the soliton spacing rapidly reached the nearest integral value to \( b_{IPW} \), and thereafter remained constant, the width of the solitons increasing to merge into the IPW as \( w \to 0 \). Because, as explained in the next section, \( b \) is expected to be an integral number of unit cells, the multi-soliton phase cannot be expected to change continuously into the IPW. This point is fully discussed in §4.

### 3.3. The pinning energy

The original motivation for studying the discrete lattice came largely from the conviction that for narrow solitons, i.e. solitons with a width of only several unit cells, there would be a contribution to the soliton energy which depended on the position of the soliton relative to the underlying lattice. To investigate this the energy of a single soliton \( \Theta(z - z_0) \) close to the lock-in phase boundary was calculated for various values of \( z_0 \).

The results for a typical case are shown in figure 7. In every case studied the results were similar to those shown in figure 7, the minimum energy being obtained for the soliton centred midway between two atoms. This is qualitatively simple to understand as the commensurability pinning potential, \( v(\cos p\phi - 1) \), will cause the value \( \phi l = \pi/p \) to be a high-energy position for an atom and so the lattice will always distort to exclude such high-energy positions in its ground state. The difference between the maximum and
minimum energies in figure 7 represents a pinning energy which will restrict the inter-
soliton spacing to integral values of b/c. A multi-soliton phase with b/c integral will not
be truly incommensurate. For temperatures well above the lock-in temperature the
pinning energy is small compared with the total soliton energy and therefore the dis-
crete lattice may be expected to have a limited effect on the equilibrium configuration.
Close to \( T_L \) the soliton energy is dominated by the pinning energy, hence the ground state
may be expected to show pronounced discrete lattice effects. In particular, instead of
changing continuously the soliton density will change by a sequence of first-order transi-
tions between configurations in which b/c takes every integral value. Throughout the
temperature region shown in figure 6(a) the pinning energy is greater than the total
creation energy for a soliton, and because of the rapidity with which the soliton density
rises for \( W < W_L \) the pinning energy ought to dominate behaviour throughout the region
of well separated solitons.

Similar comments could be made for the case \( p = 3 \), although in this case the pinning
energies were considerably smaller (the range of \( w \) for which the pinning energy exceeds
the creation energy is shown in figure 6(b), and for \( p \geq 5 \).

3.4. An energy gap in the phason spectrum

In the continuum model (Bruce and Cowley 1978), the excitation spectrum of the
phase function was calculated by a tight-binding approximation. In the multi-soliton
region it was shown to consist of two branches. The lower-lying branch corresponds to a
simple translational motion of the solitons analogous to acoustic modes in a soliton
lattice. The frequency of this Goldstone or phason branch is proportional to \( |k| \) giving
the traditional gapless mode corresponding to broken symmetry. The second branch
of the spectrum characterises fluctuations in the commensurate regions between the
solitons and it merges smoothly into the excitations of the commensurate phase at \( T_L \).
The frequency of such fluctuations is given by the dispersion relation

\[
\omega^2(k) = \alpha^2 + k^2, \quad \alpha = pu^{1/2}.
\]

The \( k = 0 \) excitations in the discrete lattice model were investigated by assuming
that as in the continuum case, the lowest-energy fluctuations will represent a uniform
translation of the solitons.

The phase function may now be written

\[
\phi_i = \sum_m \Theta(ic - mb - z_{\text{min}} - z_0)
\]

where \( z_{\text{min}} \) is the position of lowest energy and \( z_0 \), the fluctuation amplitude, is assumed
to be small.

The Hamiltonian (1) considered so far contains only potential energy terms. Although
there is also a kinetic energy contribution this does not influence the ground state cal-
culation. For a study of the dynamic properties we include the kinetic energy, which in
the notation of equation (1) may be written

\[
\mathcal{F}([Q]) = \frac{1}{N} \sum_q \dot{Q}(q) \dot{Q}(-q). \tag{19}
\]

and by the same reciprocal to direct space transformation as used for the potential
energy, the extra term in the Hamiltonian of equation (5) becomes

\[
\mathcal{F} = \sum_i \frac{1}{2} A_i^2 \dot{\phi}_i^2.
\]
The assumption that the phase profile moves uniformly reduces the problem to one involving only a single variable, and so both $\mathcal{F}$ and $V$ must be expressed as functions of $z_0$. It is not possible to give a simple analytic form for $V(z_0)$ but from figure 7, for small values of $z_0$, it should be reasonable to expand $V$ about $z_{\text{min}}$ in the form

$$V(z_0) = V_0 + \frac{1}{2} V''(z_{\text{min}}) z_0^2 + O(z_0^4).$$  

(20)

Similarly $\mathcal{F}$ can be written for small $z_0$ as

$$\mathcal{F}(z_0) = \frac{1}{2} m^* z_0^2$$

(21a)

where $m^*$ is a soliton effective mass given by

$$m^* = A^2 \sum_i \left( \frac{\partial \phi_i}{\partial z_0} \right)^2_{z_{\text{min}}}.$$  

(21b)

Equations 20 and 21 show that the coordinate $z_0$ executes simple harmonic motion with a frequency $\omega_G$, a phason mode gap frequency, where

$$\omega_G^2 = V''(z_{\text{min}})/m^*.$$  

(22)

The quantities $V''$ and $m^*$ have to be calculated numerically and in figure 8(a) they are shown for the case $p = 4, D = 0.5$. As the solitons become sharper, the effective mass decreases because fewer atoms actually move as the soliton moves reducing the number of non-zero terms in (21b). As the Umklapp coupling constant $w$ increases, the curvature of $V(z_0)$ increases and hence $\omega_G$ increases. Figure 8(b) shows the dependence of $\omega_G$ on $w$ for the case $p = 4, D = 0.5$ and compares it with the continuum prediction for the inter-soliton commensurate fluctuations. Close to $w_L$, the phason gap frequency is approximately one half of the gap in the commensurate fluctuations, $\alpha$, shown by the broken line. The appearance of the phason gap could make experimental separation of the two branches difficult, which would explain the failure of the search for phason modes.

Figure 8. (a) Effective mass (broken curve) and $V''(Z_{\text{min}})$ (full curve) for $p = 4, D = 0.5$ in units of $A^2/c^2$.

(b) Phason gap frequency $\omega_G$ (full curve) and commensurate fluctuation gap frequency $\alpha$ (broken curve).

(c) $\alpha$ (broken curve) and $\omega_G$ (full circles) for different values of $p$ with $w$ set to the continuum $w_L = (\pi D/4)^{1/2}$ and $D = 0.5$. 
In this connection it is important to bear in mind the remarks of §2.4 which suggest that the effects of the soliton pinning are probably underestimated.

The behaviour of $\omega_o$ for small values of $w$ where $\omega_o$ approaches zero is interesting since as $w \to 0$ the stable configuration should be the IPW for which the energy gap must disappear. The parameter $\alpha$, as well as representing the commensurate frequency gap, is proportional to the inverse width of a soliton. For $\alpha$ below 0.65, the gap frequency is very small. This corresponds to a width of approximately 12 unit cells and thus this may be interpreted as the minimum soliton width for which continuum theories should be applied uncritically. Figure 8(c) shows the values of $\omega_o$ and $\alpha$ at the continuum lock-in temperature for different values of $p$. For large values of $p$ the two gap frequencies are of similar magnitude and it is possible for $\omega_o$ to exceed $\alpha$.

4. The effects of fluctuations

The theory and results presented in §§2 and 3 are for a quasi-one-dimensional system in the sense that no account has been taken of variations in $A$ or $\phi$ in transverse directions, although the existence of non-zero transition temperatures and long-range ordered structures requires the system to have more than one dimension. For a real three-dimensional system it is plausible to regard the solitons as surfaces which should have a roughening temperature $T_R$ (Weeks et al 1973) below which the solitons will be approximately planar. In this case the theory of §§2 and 3 will be valid provided $T < T_R$. With such a proviso the ground state will consist of an array of flat, pinned solitons.

4.1. The three-dimensional Hamiltonian

Although the Hamiltonian of (1a)-(1c) was considered for only one dimension in §2, the form is unchanged when $q$ is allowed to be an $n$-dimensional vector provided that the star of the soft mode contains only the two wavevectors at $\pm q_s$ on the $z$ axis. It is convenient at this stage to allow the dispersion relation to be anisotropic by writing it in the form

$$\omega^2(q) = r_0 + J_1 q_1^2 + J_z (q_z - q_o)^2 \quad (23)$$

where $q_1$ is the transverse component of the wavevector $q$. Transforming the Hamiltonian by the same procedure as in §2 yields an expression analogous to (5), with all energies expressed in units of $J_z$

$$\mathcal{H} = \mathcal{H}_c + \Delta \mathcal{H} + \mathcal{H}_\perp \quad (24a)$$

where the sum in $\Delta \mathcal{H}$ is over the three spatial indices, and the extra $\mathcal{H}_\perp$ is given by

$$\mathcal{H}_\perp = \frac{J_A^2}{2a^2} \sum_{jkl} [2 - \cos(\phi_{j+1,k,l} - \phi_{j,k,l}) - \cos(\phi_{j,k+1,l} - \phi_{j,k,l})]. \quad (24b)$$

$a$ is the lattice spacing in the transverse direction, and $J = J_1/J_z$.

Since the expectation value of $\mathcal{H}_\perp$ is always positive except for the planar case where $\phi$ depends only on $z$, the extra terms do not affect the ground state. At finite temperatures the effect of fluctuations in the transverse profile must be taken into account. To do so it is convenient to introduce a continuum model in which the Hamiltonian is suitably
modified to take account of the pinning effect. The continuum analogue of (24b) is
\[ \mathcal{H} = \mathcal{H}_c + \frac{A^2}{c a^2} \int d^3 r \left\{ \frac{1}{2} \left( \frac{\partial \phi}{\partial z} - \delta_0 \right)^2 - v(\cos p\phi - 1) + \frac{J}{2} \left( \frac{\partial \phi}{\partial x} + \frac{\partial \phi}{\partial y} \right)^2 \right\}. \] (25)

Following the procedure of Bak and von Boehm (1980) it is assumed that the lowest-energy fluctuations are simple bends in an otherwise rigid solution, in which case for a single-soliton state
\[ \phi(x, y, z) \rightarrow \phi(x, y, z - \theta(x, y)). \] (26)

where \( \theta \) is the displacement of the soliton from its ground state position. The condition that \( T < T_R \) requires that \( \theta \) is small, and therefore \( \theta \) is equivalent to \( \zeta_0 \) in the calculation of \( \omega_G \) (equations 20–22). The discrete lattice pinning effect may be incorporated into (25) by adding a term proportional to \( \theta^2 \) into \( \mathcal{H}_\perp \) so that the energy associated with the phase fluctuations becomes
\[ \mathcal{H}_\perp = \frac{1}{ca^2} \int d^3 r \left\{ \frac{JA^2}{2} \left[ \left( \frac{\partial \theta}{\partial x} \right)^2 + \left( \frac{\partial \theta}{\partial y} \right)^2 + \theta^2 \right] + \frac{c}{2L} V''(z_{\min}) \theta^2 \right\}. \] (27)

If the ground state consist of well separated solitons the fluctuation energy density becomes
\[ \frac{c}{L} \mathcal{H}_\perp = \frac{1}{a^3} \int dx \, dy \, E_0 \left[ \left( \frac{\partial \theta}{\partial x} \right)^2 + \left( \frac{\partial \theta}{\partial y} \right)^2 + \left( \frac{\pi \Omega}{2} \right)^2 \theta^2 \right] \] (28)

where
\[ E_0 = 2v^{1/2}JA^2/pb \quad \text{and} \quad \Omega^2 = ca^2 pV''(z_{\min})/4\pi^2 v^{1/2}JA^2. \]

Introducing \( \theta(q) \), the Fourier transform of \( \theta(x, y) \), \( \mathcal{H}_\perp \) can be rewritten in the form
\[ \frac{c}{L} \mathcal{H}_\perp = \frac{a^2}{\pi^3} \int_0^{\pi/a} d^2 q \, E(q) \theta^2(q) \] (29)

where \( E(q) = E_0[q^2 + (\pi \Omega/a)^2] \). In this representation \( E(q) \) is the energy of a phason mode as discussed by Bak and von Boehm.

4.2. The effect of entropy terms in the free energy

The free energy for a soliton can be calculated from the expression
\[ F = -T \ln \text{Tr} \exp(-\mathcal{H}/T) \]
\[ = E_{GS} - T \frac{a^2}{\pi^3} \int_0^{\pi/a} d^2 q \ln \int d\theta(q) \exp[-E(q) \theta^2(q)/T] \]
(30)

where \( T \) is the absolute temperature in units of \( J_s/k_B \) and \( E_{GS} \) is the ground state energy. The result for a single soliton is
\[ F = E_{GS} + \frac{1}{2} T \ln \left[ (2v^{1/2}JA^2c/\pi pTa^2) k f(\Omega) \right] \]
(31)

where \( k = \pi^2/e \) and \( f(\Omega) = \Omega^2(1 + 1/\Omega^2)^{1+\Omega^2} \). The factor \( k \) is purely a geometrical constant arising from the choice of a Brillouin zone for the phason wavevectors which was circular in the transverse direction. The factor \( f(\Omega) \) arises from the soliton pinning and reduces to unity for zero pinning energy. The fluctuation term in equation (31) may
become negative for high temperatures. Since the scale of \( T \) is determined by \( J_z \) which was arbitrarily set to be unity in equation (2), the sign of this term at \( T_L \) will depend on the system to which the theory is applied. The pinning energy factor has the effect of increasing the temperature at which the fluctuation free energy becomes negative, thus the discrete lattice effects tend to stabilise the commensurate phase by increasing \( T_L \). Choosing for convenience \( J = a^2/c^2 \) we find that for \( D = 0.5 \), \( p = 4 \) the factor \( f(\Omega) \) has the value 1.58 at \( T_L \) and this increases to 3.19 for \( p = 6 \). For systems with highly anisotropic dispersion (\( J \approx a^2/c^2 \)) the values of \( f(\Omega) \) will be large.

The full free energy density for the multi-soliton state, neglecting the exponential inter soliton repulsion is

\[
F = (c/L) \mathcal{H}_c + \Delta F
\]

where

\[
\Delta F = A^2 \left( \frac{8v^{1/2}}{pb} - \frac{2\pi}{pb} \delta_0 \right) + \frac{T_c}{2b} \ln \left( \frac{2A^2v^{1/2}Jc\kappa}{\pi pTa^2} \right) + \frac{T_c}{2b} \ln f(\Omega). \tag{32}
\]

The second term in \( \Delta F \) has the form of a slowly varying function of the absolute temperature and over the narrow temperature range for which the multi-soliton state exists it may be expected to contribute only an additive constant to the free energy. This will change \( v_L \) and hence \( T_L \) but, since the logarithmic dependence of the soliton density on \( T - T_L \) arises from the exponential repulsion between solitons, this will not be affected by the fluctuations. We conclude that apart from this change in \( v_L \) the results and conclusions of §3 may be expected to remain qualitatively correct.

4.3. The floating soliton phase and unpinning transition

There is one important difference between the multi-soliton phase and the IPW state which prevents the incommensurate phase from evolving smoothly from the single-soliton limit to the IPW limit. In the single-soliton limit we concluded that there is an energy gap in the phason mode which decreases monotonically as \( \omega \) decreases, whereas in the IPW limit a zero-frequency sliding mode is possible. Although, as is shown in figure 8(b), the gap frequency \( \omega_G \) is close to zero for a range of \( \omega \), the gap never vanishes for a finite \( \omega \). At some point in this region the pinning energy is small enough to be overcome by thermal fluctuations and the solitons become unpinned. For higher temperatures the solitons are able to move freely through the lattice and the soliton lattice spacing \( b \) is no longer restricted to integral multiples of the unit cell dimension. In this regime the phase is truly incommensurate and the gapless sliding mode may be expected.

To investigate this transition an extra term has to be introduced into the free energy to represent the average potential energy gained by a soliton moving freely through the lattice. By defining, in the notation of §3.4

\[
\epsilon = \left( \frac{c}{A} \right)^2 \left( \frac{1}{c} \int_{\kappa}^{(\kappa+1)\kappa} V(z_0) \, dz_0 - V_0 \right)
\]

the free energies of the pinned and unpinned, or floating soliton phases may be written

\[
F_p = F_0 + \left( T_c/2b \right) \ln f(\Omega)
\]

and

\[
F_u = F_0 + \left( A/c \right)^2 \epsilon c/b.
\]
The stable configuration of the system will be determined by the lower of these two free energies. The solitons will be pinned for temperatures satisfying the condition

\[ T < (A/c)^2 \frac{2\varepsilon}{\ln f(\Omega)}. \]

The function \( 2\varepsilon/\ln f(\Omega) \) is shown in figure 9 for the typical case \( p = 4, D = 0.5 \). Since it decreases monotonically to zero as \( T \) tends to \( T_c \) the solitons will always be unpinned at some temperature below \( T_c \). Whether or not the solitons are pinned at \( T_L \) depends on the value of \( T_c \) and the overall scale of the Hamiltonian which is determined by the sharpness of the minimum in the dispersion relation. These constants must be chosen to fit a particular system. It is possible to define an unpinning temperature \( T_u \) by

\[ T_u = 2(A_L/c)^2 \varepsilon_L/\ln f(\Omega_L). \]

This is the temperature for which solitons at the lock-in boundary become unpinned and is a constant for any given set of model parameters. For the case \( T_u < T_L \) the phase profile will be unpinned and most of the discrete lattice effects will be obscured by the motion of the solitons throughout the incommensurate phase. If, however \( T_u > T_L \), the solitons will be pinned close to the lock-in phase boundary and at some intermediate temperature between \( T_L \) and \( T_c \) there ought to be a phase transition characterised by the abrupt disappearance of the energy gap in the phason spectrum.

In the case of \( CDW \) transitions the solitons correspond to the \( \phi \) particles which were shown (Rice et al 1976) to be capable of carrying current and in this case an unpinning transition would lead to an abrupt change in the electrical properties.

5. Conclusion

The sequence of phase transitions from commensurate to high-temperature has been shown to be well described by the continuum theories in many respects, by calculations on a discrete model. The description in terms of solitons remains valid even when the soliton width is only several unit cells, a common occurrence with domain walls in Ising systems. It was shown in §3 that the main effect of the lattice is to produce a pinning energy which will lock the solitons into a commensurate super-lattice causing a sequence of first-order transitions between different soliton spacings close to the lock-in boundary, giving a behaviour similar to the ‘devil’s staircase’. This may explain,
for example, the first-order lock-in transition observed in \( \{N(CH_3)_4\}_2ZnCl_4 \) (Mashiyama and Tanisaki 1980) which shows marked temperature hysteresis as would be expected for an assembly of strongly pinned solitons. It was demonstrated that the soliton pinning leads to a gap in the phason spectrum which may make the experimental identification of phason modes impossible.

In §4 it was shown that the differences between the continuum and discrete models depend crucially on the entropy of fluctuations which can overcome the pinning energy and restore the truly incommensurate phase. This was shown to enable an extra phase transition to take place whenever the lock-in temperature is below a characteristic temperature. At this unpinning transition the excitation spectrum, and in some cases the conductivity, change discontinuously and the equilibrium structure becomes incommensurate with a large unit cell determined by the soliton spacing.

It would be interesting to determine the overall scale factors for the Hamiltonian of real systems to establish \( T_u \) so that a search for the above-mentioned behaviour may be made. This requires accurate measurements of the dispersion relations at \( T_u \), data which are not yet available in many cases.

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The theory of two-phonon critical scattering

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Abstract. The two-phonon critical scattering occurring near a structural phase transition is studied within the framework of a time-dependent Landau—Ginzburg model. It is established that the width of the critical low-frequency scattering appearing in the two-phonon spectrum (accessible to light-scattering experiments) and the width of the critical scattering in the one-phonon spectrum (accessible to neutron-scattering experiments) form a universal ratio, which is calculated to second order in \( \varepsilon = 4 - d \). Implications for scattering experiments on structural phase transitions are discussed.

1. Introduction

Perhaps the most familiar hallmark of the critical region occurring near a phase transition is the strong low-frequency scattering of incident radiation by fluctuations in the ordering coordinates. This phenomenon is characteristic of continuous phase transitions of all kinds; the range of systems to which the results of this paper are relevant is correspondingly wide. Nevertheless, in formulating the problem we have addressed, it is helpful to use the language appropriate to the particular class of phase changes—structural phase transitions—where the experimental motivation for our study is most compelling. In this context the local ordering coordinate is the displacement of an atom, or group of atoms, with respect to some high-symmetry configuration; the order parameter is then the thermal average of a particular Fourier component \( Q_\alpha(q_s) \) \( (\alpha = 1, \ldots, n) \) of the associated \( n \)-component displacement field. The critical scattering then generally falls into one or other of two categories.

If the radiation couples linearly to the local ordering coordinate (as is typically the case in a neutron-scattering experiment) the scattering at frequency transfer \( \omega \) (and wavevector transfer \( K = q_s \) ) is directly proportional to the 'one-phonon' correlation function (or spectral function) \( S(\omega) \) of the soft coordinates. The total (frequency-integrated) scattering intensity has a strong critical divergence (controlled by the exponent \( y \) of the static order parameter susceptibility). The width \( \omega^{(1)} \) of the spectral range over which the intensity is distributed vanishes critically, according to the power law

\[
\omega^{(1)} = \Omega^{(1)} t^v
\]

(1a)

where \( t \equiv (T - T_c)/T_c \), \( v \) is the correlation-length exponent, \( \zeta \) the basic dynamic critical exponent and \( \Omega^{(1)} \) a 'non-universal' (system-specific) amplitude.

If the radiation couples quadratically to the local ordering coordinate (as in many
light-scattering experiments), the scattering at frequency transfer $\omega$ (and wavevector transfer $K \approx 0$) is directly proportional to a 'two-phonon' correlation function $\Gamma(\omega)$. The integrated intensity should then display a relatively weak divergence (to be defined more precisely in the following section) and the spectrum is again expected to exhibit critical narrowing, with a width $\omega^{(2)}$ satisfying

$$\omega^{(2)} = \Omega^{(2)} t^z$$

where $\Omega^{(2)}$ is a further non-universal amplitude.

Theoretically, these assertions are well grounded in the dynamic scaling hypothesis and the dynamic renormalisation group method (cf. the review by Hohenberg and Halperin 1977). Experimentally, however, they remain largely untested, at least in the structural phase transition context where the basic time scale of the critical slowing-down (effectively set by the frequency $\omega^{(1)}$) has often proved difficult to establish, even approximately. This problem has proved most intriguingly acute in the case of the Brillouin-zone boundary ($q_s = R$) instabilities exhibited by many perovskites (SrTiO$_3$ in particular), whose dynamic critical behaviour has attracted much attention in recent years (cf. the review by Bruce and Cowley 1980).

In the vicinity of such phase transitions the one-phonon correlation function has been shown to have significant structure in two distinct frequency regimes: an indeterminately-narrow central peak (with a width $\lesssim 10^7$ Hz in the case of SrTiO$_3$) and a broader feature attributable to a softening phonon (attaining a limiting width $\sim 10^{11}$ Hz close to $T_c$ in SrTiO$_3$).

The interpretation of these results remains a matter of some controversy (Bruce and Cowley 1980). It is possible that the additional narrow central component is a consequence of defect-induced precursor order, and that the intrinsic slowing-down process is represented only in the (defect-limited) softening of the phonon feature. It is conceivable (though it seems unlikely) that the additional central peak is an intrinsic phenomenon, and that the rate of critical slowing down is, in fact, manifested in its uncertain width. A third possibility (Lyons and Fleury 1977) is that the narrow central peak is a defect-induced (or, at least, defect-controlled) phenomenon but that there is a further (intrinsic?) time scale manifested in additional low-frequency structure, masked (in the neutron-scattering experiments) by the strong defect-induced central peak.

This suggestion was motivated by light-scattering studies of SrTiO$_3$ (Lyons and Fleury 1977) revealing a weakly-critical central component with a width $\omega^{(2)} \sim 10^{10}$ Hz in the immediate vicinity of the critical point. However, to substantiate the inference, and to synthesise the various strands of experimental data in a satisfactory way, it is clearly necessary to establish precisely what relationships exist between the one-phonon and two-phonon correlation functions, probed in the different experiments. This is the purpose of the work presented here.

We will show that although the amplitudes $\Omega^{(1)}$ and $\Omega^{(2)}$ are different, and non-universal, their ratio is universal (i.e. like critical exponents, a constant specific to each universality class: cf. Bruce 1980). We present results of calculations of this amplitude ratio to second order in $\epsilon = 4 - d$, where $d$ is the dimension of space. The calculations have been carried out within the framework of the time-dependent Landau–Ginzburg–Wilson (LGW) model, to be introduced in §2.1, where the correlation functions $S(\omega)$ and $\Gamma(\omega)$ are also explicitly defined. The calculations, which employ the now-standard techniques described, for example, by Ma (1976), are outlined in §2.2, and the results presented in §2.3. In §3 we review the implications and limitations of our study.
2. Theory

2.1. Terminology

The equilibrium properties of the LGW model are defined by the partition function (see e.g. Ma 1976, Bruce 1980)

\[ Z = \int \exp[-\mathcal{H}_0(\{Q\})] \quad (2) \]

where the effective Hamiltonian \( \mathcal{H}_0 \) may be written in the form

\[ \mathcal{H}_0 = \frac{1}{2} \sum_k \sum_{\alpha=1}^{n} \omega^2(k) Q_\alpha(k) Q_{\alpha(-k)} + \frac{\mu_0}{V} \sum_{k_1 k_2 k_3 k_4 \alpha, \beta=1}^{n} Q_\alpha(k_1) Q_\beta(k_4) \delta_{k_1+k_2+k_3+k_4,0} \quad (3) \]

with \( V \) the system volume and \( \delta_{k,0} \) a Kronecker function. Without loss of generality we choose to work in a representation in which the critical wavevector \( q_c \) defines the origin of reciprocal space. With suitable scale normalisation, the partially renormalised 'soft-mode' frequency, \( \omega(k) \) may then be taken to have the form

\[ \omega^2(k) = a(T - T_0) + k^2 + k^4 \quad (4) \]

where \( T_0 \) is a Landau approximation to the true transition temperature \( T_c \).

Sufficiently close to \( T_c \), the spectral weight of the soft fluctuations will lie predominantly in an overdamped (central) component: in this regime it is reasonable to model the dynamic behaviour of the system described by equation (3) by the kinetic equation (Halperin et al 1974, Ma 1976).

\[ \frac{\partial Q_\alpha(k,t)}{\partial t} = -\frac{1}{\gamma_0} \frac{\partial \mathcal{H}}{\partial Q_\alpha(-k,t)} + \zeta_\alpha(k,t) \quad (5) \]

where the damping constant \( \gamma_0 \) and the white noise \( \zeta \) simulate the effects which non-critical fluctuations have on the time evolution of the near-critical modes. They are interrelated by the fluctuation-dissipation theorem:

\[ \langle \zeta_\alpha(k,t) \zeta_\beta(k',t') \rangle = \frac{2}{\gamma_0} \delta_{\alpha\beta} \delta_{k,-k'} \delta(t-t') \quad (6) \]

Despite the numerous simplifying assumptions implicit in the defining equations (2) through (6) this TDGL model is expected to capture correctly the universal features of the critical behaviour in a wide range of systems. We defer discussion of the models' limitations to § 3.

The one-phonon correlation function \( S(k\omega) \) is defined by

\[ 2\pi \delta(\omega + \omega') \delta_{k,-k} \delta_{\alpha\beta} S(k\omega) = \langle Q_\alpha(k\omega) Q_\beta(k'\omega') \rangle \quad (7) \]

where

\[ Q_\alpha(k\omega) = \int_{-\infty}^{\infty} dt \ e^{i\omega t} Q_\alpha(k,t) \quad (8) \]

This correlation function satisfies the fluctuation–dissipation relation

\[ S(k\omega) = \langle 2/\omega \rangle \text{Im} G(k\omega) \quad (9) \]

where \( G(k\omega) \) is the one-phonon propagator. The latter function describes the linear
response of the coordinate $Q_a(k \omega)$,

$$\langle Q_a(k \omega) \rangle = G(k \omega) E_a(k \omega)$$

(10)

to the space- and time-dependent perturbation

$$\Delta \mathcal{H}_E(\{Q\}) = - \sum_k Q_a(k t) E_a(-k t).$$

(11)

The two-phonon correlation function is actually a fourth rank tensor. For a system with the isotropy presupposed in equation (3) this tensor has two linear-independent components (Murata 1976b, Bruce and Cowley 1980) defined by

$$2\pi \delta(\omega + \omega') \delta_{k,-k'} \Gamma_T(k \omega) = \langle \psi_T(k \omega) \psi_T(k' \omega') \rangle_c$$

(12a)

and

$$2\pi \delta(\omega + \omega') \delta_{k,-k} \Gamma_{NT}(k \omega) = \langle \psi_{NT}(k \omega) \psi_{NT}(k' \omega') \rangle_c$$

(12b)

where

$$\psi_T(k t) = \frac{1}{\sqrt{V}} \sum_{k'} \sum_{a=1}^{n} Q_a(k' t) Q_a(-k' - k t)$$

(13a)

and

$$\psi_{NT}(k t) = \frac{1}{\sqrt{V}} \sum_{k'} \{Q_a(k' t) Q_a(-k' - k t)$$

$$- \frac{1}{n - 1} \sum_{\beta \neq a} Q_\beta(k' t) Q_\beta(-k' - k t)$$

(13b)

while $\langle \ldots \rangle_c$ denotes the connected thermal average. The function $\Gamma_T$ is the spectral density of fluctuations in the 'thermodynamic' coordinates $\psi_T$ (effectively the energy density); $\Gamma_{NT}$ is the spectral density of fluctuations in the 'non-thermodynamic' coordinates $\psi_{NT}$. The different underlying symmetry of the two correlation functions is reflected in their differing critical singularities. Both functions are studied in the following sections, although we shall see that it is the behaviour of $\Gamma_{NT}$ that is likely to dominate most experiments.

The frequency widths of the spectral functions (12a) and (12b) may be characterised in a number of essentially equivalent ways (see e.g. Hohenberg and Halperin 1977). For calculational purposes it is most convenient to identify the spectral 'width' with the ratio of the frequency-integrated spectral weight, to the zero-frequency spectral height. Thus, specifically, we define

$$\omega^{(1)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{S(k = 0, \omega)}{S(k = 0, \omega = 0)}$$

(14a)

and

$$\omega_{NT}^{(2)} = \omega^{(2)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\Gamma(k = 0, \omega)}{\Gamma(k = 0, \omega = 0)} \begin{cases} \Gamma = \Gamma_T \\ \Gamma = \Gamma_{NT} \end{cases}$$

(14b)

2.2. Calculation

The determination of the zero-frequency and frequency-integrated correlation functions, which together define the characteristic frequencies of interest, employs perturbation
The theory of two-phonon critical scattering

expansion techniques which are now well established. Accordingly we describe the calculations in outline only.

The usual mass renormalisation needed to make the perturbation theory tractable is accomplished by replacing the frequency \( \omega(k) \) (equation 3) with its renormalised counterpart \( \tilde{\omega}(k) \), and adding to the Hamiltonian the appropriate counter term

\[
\Delta \mathcal{H}^{\text{ct}}(\{Q\}) = \frac{1}{2} \sum_{k} \sum_{a} \left[ \omega^2(k) - \tilde{\omega}^2(k) \right] Q_a(k) Q_a(-k)
\]

which is itself treated as a perturbation. The equation of motion (5) may then be recast in the form

\[
Q_x(k,\omega) = Q_x^0(k,\omega) - G_0(k,\omega) \left( \left[ \omega^2(k) - \tilde{\omega}^2(k) \right] Q_a(k) + 4u_v \frac{1}{V} \sum_{k_1, k_2} \sum_{\beta=1}^n \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} Q_2(k_1,\omega_1) Q_2^* (k_2,\omega_2) Q_2^\beta (k - k_1 - k_2, \omega - \omega_1 - \omega_2) \right)
\]

where

\[
Q_x^0(k,\omega) \equiv \gamma_0 G_0(k,\omega) \tilde{\zeta}_x(k,\omega)
\]

while

\[
G_0^{-1}(k,\omega) \equiv \tilde{\omega}^2(k) - i\gamma_0 \omega
\]

is the one-phonon propagator of the unperturbed system. The corresponding zeroth-order approximation to the one-phonon correlation function follows from equation (9) as

\[
S_0(k,\omega) = 2\gamma_0 / (\tilde{\omega}^4(k) + \omega^2\gamma_0^2).
\]

The renormalised frequencies \( \tilde{\omega}(k) \) are chosen such that \( \tilde{\omega}^2(k = 0) \) gives the exact long-wavelength static susceptibility:

\[
G^{-1}(k = 0, \omega = 0) = \tilde{\omega}^2(k = 0) \equiv r.
\]

The one-phonon self-energy function \( \Sigma(k,\omega) \), defined by

\[
G^{-1}(k,\omega) = G_0^{-1}(k,\omega) + \Sigma(k,\omega)
\]

must then satisfy the self-consistency relation

\[
\Sigma(k = 0, \omega = 0) = 0
\]

a condition which, in effect, relates the inverse susceptibility \( r \) to the temperature \( T \).

The equation of motion (16) is iterated to yield a hierarchy of equations relating the mode amplitudes to the amplitudes of the Langevin noise source. Substituting the resulting expressions into the defining equations (7) and (12), and performing the thermal averages according to the prescription (6) one obtains the required systematic expansions for the correlation functions in powers of the coupling constant. To expose the pure scaling behaviour of the critical region the coupling constant must be set to the special value \( u_0 \) which eliminates the leading corrections to scaling (Wilson 1972, Halperin et al 1972). For the soft \( (k^4) \) cut-off implied by our choice of dispersion (equation 4) one finds (see e.g. Wallace 1976)

\[
\bar{u}_c = K_d u_0 c = \frac{\epsilon}{4(n + 8)} \left( 1 - \frac{n^2 - 2n - 20}{2(n + 8)^2} \epsilon \right) + O(\epsilon^3)
\]
where $K_d$ is the usual constant arising from angular integrations. Finally, summations over reciprocal space are replaced by integrals, which are evaluated in $d = 4 - \epsilon$ dimensions to yield power series in $\epsilon \ln r$, from which amplitudes and exponents can be determined by the usual matching techniques.

It transpires that the amplitude ratios $\Omega^{(1)}/\Omega^{(2)}$, of primary interest, are of order $\epsilon$. To calculate these quantities to second order in $\epsilon$ one requires the behaviour of the one-phonon correlation function to be determined to order $\epsilon$, and the behaviour of the two-phonon correlation functions to order $\epsilon^2$. The former task is trivial since the leading contribution to the one-phonon self-energy $\Sigma(k \omega)$ is $O(\epsilon^2)$, and may be neglected in this part of the calculation. The latter task is less readily accomplished. The processes which have to be considered are represented diagrammatically in figure 1(a)–(e). The contributions which these processes make to the frequency-integrated (equal time) correlation functions may be determined from the results derived by B G Nickel (1974 unpublished results), and tabulated by Wallace (1976). Of the contributions to the zero-frequency correlation functions, those made by processes (a), (b) and (c) are straightforward to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Diagrammatic representation of processes contributing to the two-phonon correlation functions ((a)–(e)) and to the one-phonon self-energy (f). The directed lines are associated with the unperturbed propagator $G_0$; the lines carrying noise vertices (open circles) are associated with the unperturbed correlation function $S_0$. (See Ma (1976) for a clear exposition of the diagrammatic method.)}
\end{figure}
evaluate. Those arising from processes (d) and (e) may be determined most expeditiously by exploiting the fact that they may be expressed in terms of the leading contribution (figure 1f) to the one-phonon self-energy, and its derivatives with respect to the mass \( r \), and external frequency \( \omega \). The relevant integrals may then be evaluated, with the requisite logarithmic accuracy, by invoking the homogeneity properties of the self-energy, implied by the dynamic scaling relation

\[
G^{-1}(r k, \omega) = r \tilde{G}^{-1}(k^2/r^2, \omega/r^2) \tag{24}
\]

where the dynamic critical exponent \( z \) is of the form (Halperin et al 1972)

\[
z = 2 + c \eta
\]

with \( c \) a constant of order 1 and \( \eta = 2 - \gamma/\nu \) of order \( \epsilon^2 \).

2.3. Results

We now summarise the results of the calculations outlined in the preceding section.

The self-consistency condition (22) may be solved in the usual way to give

\[
r = C_0 t^\tau \tag{26}
\]

where \( C_0 \) is a non-universal parameter.

To the requisite order the relevant properties of the one-phonon correlation function may then be written simply as

\[
\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, S(k = 0, \omega) = C_0^{-1}[1 + O(\epsilon^2)] t^{-\gamma} \tag{27a}
\]

and

\[
S(k = 0, \omega = 0) = 2\gamma_0 C_0^{-1 - \gamma/\nu}[1 + O(\epsilon^2)] t^{-\gamma - \nu} \tag{27b}
\]

The characteristic width of the one-phonon correlation function then follows from equation (14a) as

\[
\omega^{(1)} = (C_0^{\nu/\gamma}/2\gamma_0) [1 + O(\epsilon^2)] t^{\gamma} \tag{28}
\]

which is consistent with equation (1a), with the identification

\[
\Omega^{(1)} = (C_0^{\nu/\gamma}/2\gamma_0) [1 + O(\epsilon^2)]. \tag{29}
\]

Applying power-matching techniques to the perturbation expansions for the two-phonon correlation functions compiled in table 1 one finds, firstly, that the equal-time (frequency-integrated) functions have critical singularities of the form

\[
\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, \Gamma_1(k = 0, \omega = 0) = \frac{nK_d}{\epsilon} C_0^{-\nu/\gamma} \left( \frac{2(n + 8)}{4 - n} \right.
\]

\[
- \frac{-3n^3 + 14n^2 + 236n + 176}{(n + 8)(4 - n)^2} \epsilon + O(\epsilon^2) \left) t^{-\alpha} + \text{constant} \right. \tag{30a}
\]

and

\[
\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, \Gamma_{NT}(k = 0, \omega = 0) = \frac{nK_d}{\epsilon(n - 1)} C_0^{-\nu/\gamma} \left( \frac{2(n + 8)}{n + 4} \right.
\]

\[
- \frac{n^2 + 10n - 44}{(n + 8)(n + 4)} \epsilon + O(\epsilon^2) \left) t^{-\gamma} + \text{constant} \right. \tag{30b}
\]
Table 1. Terms contributing to the perturbation expansions of the zero-frequency and frequency-integrated two-phonon correlation function $\Gamma_T$ and $\Gamma_{NT}$. The contribution made by each of the diagrams ((a) through (e) in figure 1) is given by the product of the appropriate (T or NT) combinatorial factor and the appropriate (zero-frequency or frequency-integrated) integration factor.

<table>
<thead>
<tr>
<th>Diagram</th>
<th>Combinatorial factor</th>
<th>Zero frequency</th>
<th>Integration factor</th>
<th>Frequency integrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>$2n$</td>
<td>$\frac{2n}{n-1}$</td>
<td>$(K_d y_0/4r) \left[ 1 - \frac{3}{8} \epsilon + \left(1 - \frac{11}{8} \epsilon^2 + \frac{3}{16} \epsilon^3 \right) \ln r + \frac{3}{8} \epsilon^2 \ln^2 r \right]$</td>
<td>$-\frac{1}{8} K_d \left[ 2 + \left(1 - \frac{11}{8} \epsilon^2 + \frac{3}{16} \epsilon^3 \right) \ln r + \left(1 - \frac{11}{8} \epsilon^2 + \frac{3}{16} \epsilon^3 \right) \ln^2 r \right]$</td>
</tr>
<tr>
<td>(b)</td>
<td>$8(n+2)$</td>
<td>$\frac{16n}{n-1}$</td>
<td>$(\bar{u}K_d y_0/4r) \left[ 2 + (1 - 2 \epsilon) \ln r - \frac{3}{2} \epsilon \ln^2 r \right]$</td>
<td>$-\frac{1}{8} \bar{u} K_d \left[ 4 + (4 - 2 \epsilon) \ln r + (1 - 2 \epsilon) \ln^2 r - \frac{3}{2} \epsilon \ln^3 r \right]$</td>
</tr>
<tr>
<td>(c)</td>
<td>$32(n+2)^2$</td>
<td>$\frac{128n}{n-1}$</td>
<td>$(3\bar{u}^2 K_d y_0/4r) \left( \ln r + \frac{1}{2} \ln^2 r \right)$</td>
<td>$-\frac{1}{8} \bar{u}^2 K_d \left[ \ln^3 r + 6 \ln^2 r + 12 \ln r \right]$</td>
</tr>
<tr>
<td>(d)</td>
<td>$192(n+2)$</td>
<td>$\frac{64n(n+6)}{n-1}$</td>
<td>$(\bar{u}^2 K_d y_0/16r) \left( 2 \ln r + \ln^2 r \right)$</td>
<td>$-\frac{1}{8} \bar{u}^2 K_d \left[ \frac{1}{3} \ln^3 r + \ln^2 r - (4 + \pi^2 - 10 \lambda) \ln r \right]$</td>
</tr>
<tr>
<td>(e)</td>
<td>$128(n+2)$</td>
<td>$\frac{128n(n+2)}{n-1}$</td>
<td>$(\bar{u}^2 K_d y_0/64r) \left( 1 - \epsilon \right) \ln r$</td>
<td>$-\frac{1}{8} \bar{u}^2 K_d \left[ \frac{1}{4} \ln^2 r + (1 - \frac{1}{3} \pi^2) \ln r \right]$</td>
</tr>
</tbody>
</table>
where \( \alpha \) is the specific heat exponent,

\[
\alpha = \frac{4-n}{2(n+8)} \epsilon - \frac{(n+2)^2(n+28)}{4(n+8)^3} \epsilon^2 + O(\epsilon^3)
\]

(31a)

and \( \tilde{\gamma} \) is given by

\[
\tilde{\gamma} = \frac{n+4}{2(n+8)} \epsilon + \frac{(n-2)(n^2+18n+56)}{4(n+8)^3} \epsilon^2 + O(\epsilon^3)
\]

\[
= 2\phi + \alpha - 2
\]

(31b)

where \( \phi \) is the crossover exponent for a uniaxial perturbation. These results are consistent with expectations based on general scaling arguments (Bruce 1980, Bruce and Cowley 1980).

The perturbation expansions for the zero-frequency correlation functions are consistent with pure power laws of the form

\[
\Gamma_T(k = 0, \omega = 0) = \frac{nK^2\gamma_0}{2} C_0^{-\frac{\alpha + zv}{\gamma}} \left( 1 + \frac{3n}{2(n+8)} \epsilon + O(\epsilon^2) \right) t^{-\frac{\alpha + zv}{\gamma}}
\]

(32a)

and

\[
\Gamma_{NT}(k = 0, \omega = 0) = \frac{nK^2\gamma_0}{2(n-1)} C_0^{-\frac{\eta + zv}{\gamma}} \left( 1 - \frac{n}{2(n+8)} \epsilon + O(\epsilon^2) \right) t^{-\frac{\eta + zv}{\gamma}}
\]

(32b)

Combining equations (14b), (30) and (32) one obtains the results

\[
\Omega^{(2)}_T = \Omega^{(2)}_T \tau^{zv}
\]

(33a)

\[
\Omega^{(2)}_{NT} = \Omega^{(2)}_{NT} \tau^{zv}
\]

(33b)

where

\[
\Omega^{(2)}_T = \frac{4C_0^{zv/\gamma}}{\gamma_0} \left( \frac{n + 8}{4 - n} \epsilon \left( 1 + \frac{(n+2)(13n+44)}{(n+8)^2(4-n)} \epsilon + O(\epsilon^2) \right) \right)
\]

(34a)

and

\[
\Omega^{(2)}_{NT} = \frac{4C_0^{zv/\gamma}}{\gamma_0} \left( \frac{n + 8}{n + 4} \epsilon \left( 1 + \frac{(22-n)}{(n+8)^2} \epsilon + O(\epsilon^2) \right) \right)
\]

(34b)

The three amplitudes defined by equations (29) and (34a, b) are clearly non-universal, depending explicitly upon the system-specific parameters \( \gamma_0 \) and \( C_0 \). In contrast the amplitude ratios

\[
\frac{\Omega^{(1)}}{\Omega^{(2)}_T} = \frac{1}{4} \left[ \frac{4-n}{2(n+8)} \epsilon - \frac{(n+2)(13n+44)}{2(n+8)^3} \epsilon^2 + O(\epsilon^3) \right] = \frac{\alpha}{4\tilde{\gamma}}
\]

(35a)

and

\[
\frac{\Omega^{(1)}}{\Omega^{(2)}_{NT}} = \frac{1}{4} \left[ \frac{n+4}{2(n+8)} \epsilon - \frac{(22-n)(n+4)}{2(n+8)^3} \epsilon^2 + O(\epsilon^3) \right] = \frac{\tilde{\gamma}}{4\tilde{\gamma}}
\]

(35b)

are independent of these parameters and may in fact be expressed (to the order of our calculation) in terms of the critical exponents, in the manner indicated. They are also independent of the form of cut-off employed in the calculation—a result we have checked by repeating the analysis we have described, using a sharp cut-off. Accordingly we con-
Table 2. The numerical values of the exponent characterising the two-phonon intensity divergence, and of the ratio of two-phonon and one-phonon widths, in three dimensions. The result \(\alpha\) is taken from series expansions (see e.g. Stanley 1971); the result \(\tilde{\gamma}\) exploits series values for \(\epsilon\) and \(\gamma\) together with the \(\epsilon\)-expansion result (35a); the remaining numbers follow directly from the second-order \(\epsilon\) expansions reported in the text, with \(\epsilon = 1\).

<table>
<thead>
<tr>
<th>(n)</th>
<th>(\alpha)</th>
<th>(\tilde{\gamma})</th>
<th>(\Omega^{(1)}/\Omega^{(2)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(0.125^{(a)})</td>
<td>(0.300)</td>
<td>(0.025^{(b)})</td>
</tr>
<tr>
<td>2</td>
<td>(0.340)</td>
<td>(0.060)</td>
<td>(0.067)</td>
</tr>
</tbody>
</table>

3. Discussion

In this concluding section we set the calculations described above in the context of the work of other authors, assess the key assumptions implicit in the analysis, and discuss the implications of our results for experimental studies of structural phase transitions.

The behaviour of the TDGL model has been the subject of numerous studies (Halperin et al 1972, 1974, 1976; Murata 1976a, b) designed to establish the universal characteristics of its critical dynamics. Our results for the exponents characterising the critical singularities of the two-phonon correlation functions (equations 30, 32) are not new: they are implicit in Murata’s (1976b) study of ultrasonic attenuation, and indeed follow immediately from a synthesis of scaling arguments and studies of the one-phonon correlation function. Our principal results, for the amplitude ratios \(\Omega^{(1)}/\Omega^{(2)}\) (equations 35a, b) are new. Halperin et al (1976) observe that the ratio \(\Gamma T(k \omega)/\Gamma T(0)\) is \(O(\epsilon)\), but present no explicit calculations. Murata (1976a) calculates the ratio of analogous amplitudes characterising the manner in which the widths of the correlation functions \(S(k \omega)\) and \(F T(k \omega)\) depend upon \(k\) (at \(t = 0\)) rather than on \(t\) (at \(k = 0\)); this amplitude ratio, like those reported here, is \(O(\epsilon)\).

The calculations we have reported rest on three key, and potentially limiting, assumptions.

Firstly the model Hamiltonian (3) presupposes an isotropy in the \(n\)-component order parameter space that is not generally physically realistic. The existence of perturbations of cubic symmetry in the order parameter interaction term is unlikely to lead to results significantly different from those reported here (cf. Murata 1976b); the effects of cubic symmetry-breaking perturbations in the soft-mode dispersion, however, are harder to assess at present.

Our second major assumption is that the effects of energy conservation on the critical dynamics can be neglected. For the \(n > 1\)-component models, whose specific heat remains finite at the phase transition \((\alpha < 0)\) this assumption is formally justifiable: the coupling of the order parameter to the energy density is asymptotically negligible in these circumstances (Halperin et al 1974, 1976). For the \(n = 1\)-component (scalar) model, however, the neglect of energy conservation is acceptable only in the temperature regime in which the characteristic thermal diffusion frequency \(D \kappa^2\) \((D\) is the thermal diffusion constant, \(\kappa\) the inverse correlation length) is large compared with the characteristic...
order parameter frequency $\omega^{(1)}$ (Halperin et al 1974). Closer to criticality, where this criterion is not satisfied, the critical slowing down is controlled by the coupling to the thermal diffusion mode. The behaviour in this regime is much less tractable to graphical analysis. Nevertheless we have established that energy-conservation effects (incorporated in the manner described by Halperin et al (1974)) do not change the ratio $\Omega^{(1)}/\Omega^{(2)}$ to leading order in $\epsilon$.

The third, and potentially most serious limitation of our analysis is that it presupposes ideal crystal dynamics: we have made no attempt to incorporate the effects of crystal imperfections which may in fact control the critical slowing down in real systems, and promote quasi-elastic scattering in both one- and two-phonon spectra (see e.g. Bruce and Cowley 1980). Thus the results we have derived are trustworthy only as long as the weight of the scattering associated with any defect-induced distortions is small compared with the scattering associated with intrinsic order parameter fluctuations.

With these caveats in mind we turn, finally, to assess the implications which our results have for scattering experiments.

As remarked in our introductory section, Raman scattering experiments on structural phase transitions frequently probe the two-phonon rather than the one-phonon correlation function: indeed this is the case above the critical point of all structural transitions except those for which the ordering coordinate is (or is linearly coupled to) a strain. The particular linear combination of two-phonon correlation functions $\Gamma_T$ and $\Gamma_{NT}$ actually probed in a given experiment depends upon the scattering geometry. However one may show that there is no configuration from which the component $\Gamma_{NT}$ is absent. Since $\Gamma_{NT}$ is more strongly singular than $\Gamma_T$ its critical behaviour should dominate the cases $n = 2$ and $n = 3$: the two-phonon scattering intensity should then diverge with an exponent $\tilde{\gamma}$ (cf. table 2) larger than typical specific heat exponents, but considerably smaller than the corresponding exponent $\gamma$ characterising the divergence of one-phonon scattering intensities. In the case $n = 1$, however, the contributions of $\Gamma_{NT}$ vanish identically, and the two-phonon scattering intensity will have the singular behaviour of the specific heat.

It is, however, the results for the amplitude ratio $\Omega^{(1)}/\Omega^{(2)}$ that we wish to highlight. These results, summarised in table 2, suggest that the appearance of critical quasi-elastic scattering in a two-phonon spectrum is likely to imply the existence of a corresponding central component in the one-phonon spectrum, that is narrower by roughly one order of magnitude. The dynamic central peak reported by Lyons and Fleury (1977), in a light-scattering study of SrTiO$_3$, would, on this view, be indicative of a feature in the one-phonon spectrum with a width (near criticality) of the order of $10^9$ Hz.

Two final comments are now in order. Firstly we note that the width of this predicted feature is small on the scale of the soft-phonon width: its intrinsic status is therefore questionable, but not demonstrably undermined. Secondly we remark that the existence of such a feature is not incompatible with the neutron-scattering studies of SrTiO$_3$ performed to date (Shapiro et al 1972, Töpler et al 1977), which would not readily distinguish such a feature against the background of narrower scattering that certainly exists.

Acknowledgments

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Scattering Properties of Ferroelectric Domain Walls

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Abstract
Ferroelectric domain walls have recently been considered as candidates for the occurrence of non-linear (soliton) excitations and roughening transitions. It is shown that by means of X-ray or neutron scattering experiments the domain walls may be observed directly and their width may be measured. It is also shown that the occurrence of a roughening transition would be observable by these techniques, and the roughening mechanism is suggested as an explanation of existing experimental results for Pb$_5$Ge$_3$O$_{11}$.

In the concluding section a neutron scattering study of the domain walls in deuterated KH$_2$PO$_4$ is described. The domain walls in this system are shown to have a width of around two unit cells. This result implies that the continuum approximation used to describe non-linear excitations in systems with domain walls is not applicable to KH$_2$PO$_4$, and quite probably to many other systems.

1. Introduction
The domain structures of ferroelectrics have attracted considerable interest because of the important role which they play in determining the macroscopic properties of these materials, however little work has been done to investigate the detailed structure and dynamics of the domain walls because of the difficulty of observing them directly. Despite the absence of experimental evidence, several theoretical studies of simple model systems have suggested that ferroelectric domain walls might represent an interesting case of observable non-linear excitations, or solitons (Krumhansl and Schrieffer 1975, Bishop et al. 1976, 1977, Collins et al. 1979 and Lajzerowicz and Niez 1978). These theoretical studies are based on the continuum approximation and so are applicable to the domain walls which occur in real ferroelectrics only if the widths of the domain walls are large on the scale of the lattice constant. We shall see in Section 3 that this condition is likely to fail in real systems.

Recent developments in the theory of surfaces suggest that at some temperature below the bulk transition temperature a surface such as a ferroelectric domain wall should undergo a roughening transition, at which the width of the surface diverges (for a review see Weeks 1979). In the crystal growth problem where roughening transitions were originally postulated (Burton and Cabrera 1949, Burton et al. 1951) it is not possible to alter the conditions of growth to bring about a transition experimentally, crystals will either grow with rough surfaces or with smooth surfaces depending upon whether the melting temperature is above or below the roughening temperature. In ferroelectrics, the domain
walls represent surfaces which may undergo a genuine roughening transition at some temperature in the ferroelectric phase (Lajzerowicz 1980). This possibility is closely related to the width of the ferroelectric domain walls. If these are broad enough for the continuum approximation to be valid, then there is no roughening transition and the interface width diverges at all temperatures. When discrete lattice effects are taken into account, as they must be for narrow walls, it has been shown (Dobrushin 1972, van Beijeren 1977) that the three dimensional Ising model has a smooth interface at low temperatures which may roughen at a temperature below \( T_c \) (See Wallace 1980 and refs. therein).

Several estimates have been made of the thickness of domain walls in ferroelectric materials, but the results have varied considerably. By assuming that the 90° domain walls in tetragonal BaTiO₃ were directly visible with electron microscopy, Little (1955) estimated their thickness as 4,000Å, however this assumption is almost certainly unrealistic. A phenomenological theory by Zhimov (1958) predicted a domain wall width of between 50Å and 100Å for the 90° BaTiO₃ wall, and a width of between 5Å and 20Å for the 180° wall in the same substance. This result is in poor agreement with a microscopic calculation of Kinase and Takahashi (1957) who concluded that the wall thickness is "practically zero". In the case of the uniaxial ferroelectric KH₂PO₄ (KDP) which has a simpler domain structure, estimates of the domain wall thickness are more nearly in agreement ranging from one, to several unit cells. These estimates, and other properties of ferroelectric domain walls were discussed by Zheludev 1971.

The first direct measurement of the width of a ferroelectric domain wall was performed by Cowley et al. (1976). In a neutron scattering experiment on the uniaxial ferroelectric Pb₅Ge₃O₁₁, they found lines of quasi-elastic scattering in a direction perpendicular to the 180° domain walls from which they were able to deduce a domain wall width of between 10Å and 15Å. Similar quasi-elastic scattering may be observed in the uniaxial ferroelectric LiNbO₃ indicating an even narrower width for the domain walls in this system (Bruce 1981), and in the isomorphous LiTaO₃ (Axe and Samuelson 1978). Some quasi-elastic scattering which may have a similar origin was also observed in orthorhombic KNbO₃ and briefly commented on by Currat et al. (1973).

In section 2, a simple model of a ferroelectric domain wall is introduced and the scattering to which it gives rise is calculated. The model is applicable to a wide range of materials, and the results of this section show that as a general rule, all domain structures ought to give rise to lines of quasi-elastic scattering in directions perpendicular to the domain walls. The wave vector dependence of these lines of scattering is shown to be closely related to the width of the domain walls. The implications of roughening of the domain walls is discussed in Section 2.6 where it is shown that the surface roughening leads to a Debye-Waller-like factor for the domain wall scattering which will cause the sharply defined lines of scattering to become diffuse at the roughening transition.

In the concluding section the results of a neutron scattering
experiment on a sample of deuterated KDP (DKDP) are reported. The scattering is shown to be consistent with the results of the model calculation, and to show that the width of the domain walls in this material is about two unit cells.

2. The scattering from a domain wall

2.1 The infinitely sharp wall

The model of a domain wall which we shall consider in this section is based on the configuration which is believed to arise in KDP. The high-temperature, paraelectric phase of this material has a tetragonal lattice, with unit cell parameters $a = 7.45\text{Å}$ and $c = 6.96\text{Å}$ at room temperature. There are four formula units in the primitive unit cell (Bacon and Pease 1953). On cooling below the Curie point ($T_C = 122\text{ K}$) the structure of KDP has orthorhombic symmetry with axes in the $x$-$y$ plane rotated by $45^\circ$ relative to the crystallographic axes in the paraelectric phase. The spontaneous polarisation is along the $c$ axis. For the purposes of this calculation it is more convenient to describe the crystal in the ferroelectric phase by the monoclinic unit cells shown in figure (1a) which correspond to the primitive, tetragonal unit cells of the paraelectric phase. The order parameter of the transition is proportional to the deformation angle $\psi$, which is zero above the transition temperature, and approximately $34^\circ$ well below $T_C$. The two types of unit cell shown in figure (1a) have opposite polarisations directed out of the plane of the diagram. Although only the domain wall parallel to the $x$ axis, shown in fig. (1a) will be considered in this section, in KDP the situation is complicated by the existence of similar domain walls parallel to the $y$ axis of the high temperature phase.

The same model may be applied to the domain walls which are found in both the orthorhombic and the tetragonal phases of $\text{BaTiO}_3$ or $\text{KNbO}_3$. At high temperature $\text{BaTiO}_3$ has the cubic perovskite structure. Below $0^\circ\text{C}$ the structure has orthorhombic symmetry.
with the axes of the orthorhombic unit cell rotated by 45° from the
axes of the primitive unit cell in the high temperature phase.
Again it is more convenient to use the primitive unit cells of
fig. (1a) to describe the system in the orthorhombic phase. The
polarisation is in this case directed along the elongated
diagonal of the monoclinic unit cells. The domain wall shown in
fig. (1a), which is a (1,0,0) plane in the pseudo-cubic
coordinates, corresponds to a 90° wall. The angle Ψ in this
case about 36°. Between 0°C and +120°C, BaTiO₃ has a tetragonal
structure with the polarisation directed along the c axis which
may correspond to any of the three (1,0,0) directions of the
high temperature phase. The 180° walls in this phase are (1,0,0)
planes, and as no distortion of the lattice occurs at these walls,
they correspond to the KDP model of fig. (1a) with a = b and Ψ = 0.
The polarisation is out of the plane of the diagram. The 90° walls
in this system correspond to (1,1,0) planes in the high temperature
structure. They can be represented by the model described above
with the lattice parameters chosen to be a = √2 b and Ψ = 45° as
shown in fig. (1b). This choice of parameters also allows the model
to describe the 60° and 180° walls in the orthorhombic phase which
both correspond to (1,1,0) planes, the 180° walls which involve no
lattice distortion have a = √2 b and Ψ = 45°. As these walls
cost less energy to create than the 60° walls which involve a
distortion of the lattice, it is probable that the 180° walls will
be present in sufficient numbers to obscure any effects due to the 60° walls.

A final special case of the model is appropriate to describe
the 180° domain walls which occur in crystals such as Pb₅Ge₃O₁₁
and LiNbO₃. These materials have hexagonal lattices with three and
six formula units per hexagonal unit cell respectively (Iwata et al. 1973,
Abrahams et al. 1966). In the same way that the (1,1,0) domain
walls may be represented by the model of fig. (1b), the hexagonal
lattice with 180° domain walls may be represented by choosing
Ψ = 30°, and a = b, to represent the walls if these are (1,0,0)
planes, or by choosing Ψ = 60°, and a = √3 b if the walls are (1,1,0) planes.

The scattering from a crystal is in general directly proportional
to its volume. The scattering from a domain wall may be expected to be
proportional to its area. To facilitate the separation of scattering,
also proportional to the cross-sectional area of the crystal, from
the exterior surfaces, the boundaries of the model crystal are chosen
to be in directions which are not parallel to the domain wall.

If a unit cell in domain j scatters the incident beam of
neutrons or X-rays with an amplitude f(j)(K) where K is the wave-vector
transfer, the structure factor for the crystal is given by

\[ A(K) = \sum_j f_j(K) \exp(i\mathbf{K} \cdot \mathbf{R}) \]

(1)

where the sum over j represents a sum over the two domains, and the
sum over R runs over the unit cells in the jth domain.

Assuming that the domain walls are sharp as shown in fig. (1),
the position vector \( \mathbf{R} \), for the centre of a unit cell in the jth domain,
may be written

\[ \mathbf{R} = m \mathbf{a}_j + n \mathbf{b}_j + p \mathbf{c}_j + \mathbf{t}_j \]

where m, n, and p are integers, \( \mathbf{a}_j, \mathbf{b}_j \) and \( \mathbf{c}_j \) are the primitive lattice
vectors of domain j, and \( \mathbf{t}_j = \frac{1}{2}(\mathbf{a}_j + \mathbf{b}_j + \mathbf{c}_j) \). The structure factor
may now be written

\[ A(\mathbf{K}) = \sum_{j,n,p} f_j(\mathbf{K}) t_j(\mathbf{K}) \chi^m \gamma^p \]  

(2)

where

\[ X(\mathbf{K}) = \exp(2\pi i a f / b) \]
\[ Y_1(\mathbf{K}) = \exp(2\pi i (m \sin \psi + n \cos \psi)) \]
\[ Y_2(\mathbf{K}) = \exp(2\pi i (m \sin \psi - n \cos \psi)) \]
\[ Z(\mathbf{K}) = \exp(2\pi i c / b) \]
\[ t_j(\mathbf{K}) = \exp(i \mathbf{K} \cdot \mathbf{r}_j) \]

and

\[ \mathbf{K} = \frac{2\pi}{b}(x, n, \zeta) \]

The limits for the summations over m, n and p are determined by the crystal boundaries. It is convenient to allow m and p to run from 0 to \(N - 1\), and to allow n to run from 0 to \(N - 1 - m\). This defines an approximately cubic crystal of \(N^3\) cells for the case of fig. (1b), and a kite-shaped prism for the model of fig. (1a). This allows us to identify the scattering due to these surfaces without requiring that the crystal be of infinite extent.

The contribution to the structure factor from domain \(j\) is given by

\[ A_j(\mathbf{K}) = f_j(\mathbf{K}) t_j(\mathbf{K}) \left[ \frac{1 - X^N}{(1 - X)(1 - Y_j)} \right] \frac{\gamma^N}{1 - Y_j} Y_j^N \]

(3)

When \(X = Y_j = Z = 1\) we get Bragg scattering from the domain with \(A_j(\mathbf{K})\) proportional to \(N^3\), the volume of the crystal. Scattering from the domain wall we would expect to be proportional to the wall area, \(N^2\). This term may be extracted from the expression in (4) by allowing \(X\) and \(Z\) to be equal to 1, but requiring that \(Y_j \neq 1\), when we obtain

\[ A_j(\mathbf{K}) = N^2 \sum_j f_j(\mathbf{K}) t_j(\mathbf{K}) \left[ \frac{1 - 1}{1 - Y_j} + O(\frac{1}{N}) \right] \]

(4)

The condition \(X(\mathbf{K}) = Z(\mathbf{K}) = 1\) shows that this scattering will form lines in reciprocal space, extending from the Bragg points in directions perpendicular to the \(x - z\) plane, or in other words perpendicular to the plane of the domain wall. The second term in equation (4) is the surface scattering referred to above.

The form of this term depends on the boundaries chosen for the crystal, but in the direction perpendicular to the domain wall its amplitude is only of order \(N\) and hence negligible in comparison with the domain wall scattering which has an amplitude given by

\[ A_w(\mathbf{K}) = N^2 \sum_j f_j(\mathbf{K}) t_j(\mathbf{K}) \left[ \frac{1 - 1}{1 - Y_j} + O(\frac{1}{N}) \right] \]

(5)

The intensity of the scattering is given by the modulus squared of the scattering amplitude \(A_w(\mathbf{K})\)

\[ I_w(\mathbf{K}) = |A_w(\mathbf{K})|^2 \]

(6)

This intensity forms a set of sharply peaked ridges in the direction shown in fig. (2a), perpendicular to the domain wall. Since the amplitude \(A_w(\mathbf{K})\) is proportional to \(N^2\), the peak intensity
where $b_K$ is the scattering length of the $i$th atom in the unit cell multiplied by its Debye-Waller factor, and the position of the atoms has been written

$$ u^j_k = u^0_k + u^{ij}_k $$

so that $u^0_j$ is the position of the atom in the high temperature phase, and $u^{ij}_k$ is the (small) static displacement below $T_c$ for an atom in domain $j$. To calculate the intensity for those domain walls which cause only a distortion of the crystal (i.e. $\psi$ is not equal to $0^\circ$, $30^\circ$, $45^\circ$ or $60^\circ$) it is sufficient to approximate $f_i(\vec{k})$ by the high-temperature part $f^0_i(\vec{k})$, and this is done in Section 2.2.

For domain walls such as those observed in Pb$_5$Ge$_3$O$_{11}$ and LiNbO$_3$ where no such distortion is caused, the second term in equation (8) must be retained, but the expression for the intensity is greatly simplified by setting $\psi = 0^\circ$, $30^\circ$, $45^\circ$ or $60^\circ$.

2.2 The intensity for the KDP model

To calculate the domain wall scattering from KDP we use the model of fig. (1a) with $a \times b$ and $\psi = 34^\circ$. Since the displacements in the low temperature phase, $u^0_j$, are in opposite senses in the two domains, the structure factors defined by equation (8) can be written in the form

$$ f_j(\vec{k}) = f^0_j(\vec{k}) + i f^1_j(\vec{k}) $$

and

$$ f_j(\vec{k}) = f^0_j(\vec{k}) - i f^1_j(\vec{k}) . $$

The appropriate expressions for $t_1(\vec{k})$ and $t_2(\vec{k})$ from equations (2) and (3), are given by

$$ t_j(\vec{k}) = Y_j(\vec{k}) . $$

Substituting these expressions into equation (5) we find that the integrated intensity observed in an experiment for a real crystal ($N^3 \approx 10^{23}$) is therefore proportional to $N^2$ and can be written as

$$ I(\vec{k}) = N^2 \left[ \frac{t_1(\vec{k}) t_1(\vec{k})}{1-Y_1(\vec{k})} + \frac{t_2(\vec{k}) t_2(\vec{k})}{1-Y_2(\vec{k})} \right] $$

by discarding an overall constant of $(2\pi)^2/\alpha \varepsilon$.

Before evaluating $I(\vec{k})$ it is useful to make certain simplifying assumptions which will correspond to the different types of domain wall mentioned above and in the introduction. The structure factor of a single unit cell, $f_j(\vec{k})$ can be written in the form

$$ f_j(\vec{k}) = \sum_k b_k \exp(i\vec{k} \cdot \vec{r}_k) $$

$$ = \sum_k b_k \exp(i\vec{k} \cdot \vec{r}_k^0) \left[ 1 + i\vec{k} \cdot \vec{u}_k^0 + 0(\vec{u}_k^0)^2 \right] $$

$$ = f^0_j(\vec{k}) + i f^1_j(\vec{k}) $$

where $b_k$ is the scattering length of the $k$th atom in the unit cell multiplied by its Debye-Waller factor, and the position of the atoms has been written

$$ u^j_k = u^0_k + u^{ij}_k $$

respectively, which imply that the widths in these directions are

$$ \delta_k = \frac{2\pi}{Na} , \ \delta_k = \frac{2\pi}{Nc} . $$

The integrated intensity observed in an experiment for a real crystal ($N^3 \approx 10^{23}$) is therefore proportional to $N^2$ and can be written as

$$ I(\vec{k}) = N^2 \left[ \frac{t_1(\vec{k}) t_1(\vec{k})}{1-Y_1(\vec{k})} + \frac{t_2(\vec{k}) t_2(\vec{k})}{1-Y_2(\vec{k})} \right] $$

by discarding an overall constant of $(2\pi)^2/\alpha \varepsilon$.
The intensity corresponding to (11) is given by
\[ I_\psi(K) = \frac{N^2 |f^0(K)\cos\eta \cos\varphi|}{(1-Y_1(K))(1-Y_2(K))} \times \sin[\pi \xi \sin \varphi] + f_1^\top(K) \sin[\pi \cos \varphi \cos[\pi \xi \sin \varphi]] \]

where \( \xi \) and \( \eta \) are defined after equation (2), and we have discarded a phase factor of unit modulus. The two terms in the above expression have a similar form close to the Bragg peaks where the scattering amplitude is dominated by the behaviour of the common term outside the brackets. Since \( f_1^\top(K) \) is proportional to \( \mathcal{U}_K^1 \) which is a small quantity we may assume that \( |f_1^\top(K)| \ll |f^0(K)| \) and, as a first approximation, neglect the second term in equation (10). In making this approximation it must be borne in mind that \( f^0(K) \) appears in equation (10) multiplied by a small quantity, \( \sin[\pi \xi \sin \varphi] \approx \pi \xi \varphi \), whereas \( f_1^\top(K) \) is multiplied by \( \sin[\pi \cos \varphi \cos[\pi \xi \sin \varphi]] \). \( \sin[\pi \xi \sin \varphi] \) will be of the same order of magnitude close to the Bragg peak as \( \pi \xi \varphi \) so the approximation will be adequate in this region. If domain wall scattering is observable near the Brillouin zone boundary (\( \eta = \frac{3}{2} \)) the second term in equation (10) may not be negligible and must therefore be retained.

If we retain only the first term in equation (10) we find that the corresponding observable intensity, \( I_\psi(\hat{K}) \) is

\[ I_\psi(\hat{K}) = N^2 |f(\hat{K})|^2 \frac{\cos^2[\pi \cos \varphi \cos[\pi \xi \sin \varphi]]}{\sin^2[\pi \cos \varphi \cos[\pi \xi \sin \varphi]]} \times \sin[\pi \cos \varphi \cos[\pi \xi \sin \varphi]] \]

The direction in reciprocal space for which this intensity is observable is shown in fig. (2a). In figure (2b) the form of \( I_\psi(\hat{K}) \) is shown, neglecting the wave vector dependence of \( f(\hat{K}) \) and with the value of \( \varphi \) chosen to be 0.05 to exaggerate the form for clarity.

The domain walls which have been observed experimentally do not correspond to the model described in section 2.2. From equation (10) it is immediately apparent that the domain wall intensity proportional to \( |f^0(\hat{K})|^2 \) vanishes if \( \psi \) is equal to zero, whereas the 180 degree walls observed in \( \text{Pb}_5\text{Ge}_3\text{O}_{11} \) and other substances correspond to this type of distortionless limit. The approximation made in the previous section, that \( |f_1^\top(K)| \ll |f^0(K)| \) is clearly no longer useful. If the crystal has inversion symmetry in the high temperature phase, then in the ferroelectric phase the unit cell structure factors must satisfy

\[ f_1^\top(K) = f_2^\top(K) \]

at least at a 180° wall. The real part of \( f_1^\top(K) \) may now be subsumed into the 'Bragg' term \( f^0(K) \) so that the structure factor for the two domains may again be written in the form given in equation (9).

The scattering amplitude for the walls, \( A_\psi(\hat{K}) \) is now given by the limit as \( \psi \) tends to zero of the expression in equation (10). The first term vanishes and the remaining term which was discarded in 2.2 may now be written

\[ A_\psi(\hat{K}) = \frac{2N^2 f_1^\top(\hat{K})}{(1-Y_1(\hat{K}))} \]

where the last step again involves discarding an unimportant phase factor, and using the relations

\[ t_1^\top(\hat{K}) = t_2^\top(\hat{K}) = \tau_1^\top(\hat{K}) \]

The intensity corresponding to (11) is given by

\[ I_\psi(\hat{K}) = N^2 |f(\hat{K})|^2 / \sin^2[\pi \xi] \]

This form of the scattering intensity should be appropriate to describe the scattering for \( 180^\circ \) walls in \( \text{Pb}_5\text{Ge}_3\text{O}_{11} \).
no longer split in the low temperature phase, but the domain wall scattering is qualitatively the same as in the KDP model consisting of wings on the sides of the Bragg peaks which decrease rapidly with increasing $k_y$.

Finally in this section we can repeat this analysis for the hexagonal models. The scattering proportional to $f^0(\vec{k})$ again vanishes since there is no distortion of the lattice at these walls. If we again represent $f_3^j(\vec{k})$ by the form given in equation (9) and note that in this case when the scattering condition $X(\vec{k}) = 1$ is satisfied we have $Y_1(\vec{k}) = Y_2^*(\vec{k})$, the intensity scattered by the domain walls can be shown to be

$$I_w(\vec{k}) = N^2 |f^1(\vec{k})|^2 / \sin^2 \left( \frac{k_y a}{2} \right)$$  \hspace{1cm} (14a)

for the $(1,0,0)$ walls, and

$$I_w(\vec{k}) = N^2 |f^1(\vec{k})|^2 / \sin^2 \left( \frac{k_y a}{2} \right)$$  \hspace{1cm} (14b)

for the $(1,1,0)$ walls, close to the $(0,0,K)$ reflections.

In the KDP model the domain wall intensity is proportional to the intensity of the Bragg peak multiplied by the distortion $\phi^2$. In this section the domain wall intensity is proportional to $|f^1(\vec{k})|^2$ which is proportional to the square of the order parameter. If $\phi$ is proportional to the order parameter the intensity close to a continuous transition in both cases varies as

$$I_w(\vec{k}) = (T_c - T)^{28}$$

where for a uniaxial ferroelectric, the order parameter exponent $\delta$ has its classical value 0.5.

### 2.4 Domain walls of finite width

The assumption which underlies the model of section 2.1, that the domain wall was infinitely sharp and contained no distorted unit cells, is not expected to be realistic in many substances. The simplest model which incorporates a wall of finite width is shown in fig.(3), the domain wall is represented by a narrow domain, domain 3, of distorted cells with scattering amplitude $f_3^j(\vec{k})$. In contrast to the infinitely sharp wall model which contained no parameters other than an overall amplitude and the unit cell dimensions of the bulk material, the finite wall model contains the extra parameters $w$, the width of the domain wall in unit cells, and $b_3$, the lattice parameter of the distorted cells in the direction perpendicular to the wall. The lattice parameters of the distorted cells in the plane of the wall are equal to the lattice parameters of the bulk material.

Choosing the origin of the coordinate system at the centre of the wall to keep the problem symmetrical, the insertion of the wall of $w$ unit cells changes the phase factors $t_j^k(\vec{k})$ which now become

$$t_1^k(\vec{k}) = \exp i (\vec{k} \cdot \vec{r}_j - \frac{w}{2} \vec{k} \cdot \vec{b}_3)$$

$$t_3^k(\vec{k}) = \exp i \left( \frac{1}{2} k_y x + \frac{1}{2} k_x z \right)$$  \hspace{1cm} (15)

The sequence of steps leading to equation (6) is now repeated, the only change required is that the summation over $j$ in equation (3) now runs over all the 'domains', and that in the wall (domain 3)
Scattering with an amplitude proportional to \( N^2 \) is again given when the condition \( X(\vec{k}) = Z(\vec{k}) = 1 \) is satisfied. We now find that when this condition is satisfied the scattering amplitude is given by

\[
A_{\omega}(\vec{k}) = N^2 f_1(\vec{k}) t_1(\vec{k}) + f_2(\vec{k}) t_2(\vec{k}) \frac{1 - Y_1(\vec{k})}{1 - Y_2(\vec{k})} f_3(\vec{k}) \sin\left(\frac{\pi b_3 n}{b}\right) \sin\left(\frac{\pi n}{b}\right) + \sin\left(\frac{\pi n}{b}\right) \]

(16)

where \( Y_1(\vec{k}) \) and \( Y_2(\vec{k}) \) are as defined in equation (3).

If the lattice parameter, \( b_3 \), of the distorted cells, is not equal to \( b \cos \phi \), the spacing of planes of cells in the \( y \) direction, the expression for \( A_{\omega}(\vec{k}) \) given in equation (16), cannot be reduced to an elegant form by making the approximation which led to equations (11) and (13).

It is instructive to examine the simplest case of the finite wall which corresponds to the 180° wall in tetragonal BaTiO\(_3\). For this special case we have \( \phi = 0 \) and we assume for simplicity that \( b_3 = b \), as deduced by Kinase and Takahashi (1957).

Substituting from equation (9) the expressions previously used for \( f_j(\vec{k}) \) and making the plausible assumption that

\[
f_3(\vec{k}) = f^0(\vec{k}) \]

(17)

we find that the scattering amplitude has the form

\[
A_{\omega}(\vec{k}) = N^2 f^0(\vec{k}) \frac{\cos(\omega n)}{\sin(\frac{\pi n}{b})} \]

(18)

and the intensity \( I_{\omega}(\vec{k}) \) is given by

\[
I_{\omega}(\vec{k}) = N^2 |f^0(\vec{k})|^2 \frac{\cos^2(\omega n)}{\sin^2(\frac{\pi n}{b})} \]

(19)

The form of this intensity is similar to the form of the intensity obtained from the infinitely sharp wall close to the Bragg points, but it differs from the latter by the modulating cosine factor, which contains the information regarding the width of the wall.

In a general case where \( b_3 \) is not simply related to \( b \), and the angle \( \psi \) is non-zero the intensities obtained from the amplitude given by equation (16) show a behaviour qualitatively similar to the above example. The intensity consists of a broad wing on either side of the twin Bragg peaks which is modulated by one oscillatory term which depends upon the width \( \omega \) of the walls.

Several examples of the intensity obtained in the KRP model for different values of \( \omega \), are shown in fig. (4), where the structure factors have been assumed to be equal and independent of \( \omega \), and the parameters \( b_3 \) and \( \psi \) have been assigned realistic values. It is appropriate to stress that the oscillations shown by these curves arise partly from the cells in the domain wall itself which contribute the third term in equation (16), and partly from an interference effect between the contributions from the bulk crystal of domains 1 and 2. The first of these is possibly spurious as it may result from Fourier transforming an object with sharp boundaries, and so it may not be observable in real systems where the polarisation changes gradually. The latter effect, however, is real, in the sense that it would not be eliminated by choosing a model with the form of "rounded-off" boundaries which we would expect to arise in real systems.
The analysis in this form is directly relevant to the case of KDP and any similar material where the walls are (1, 0, 0) planes and $\psi = 0$. To extend the analysis to walls which form (1, 1, 0) planes such as the 90° BaTiO$_3$ walls depicted in fig. (lb), it is most convenient to use the non-primitive, monoclinic unit cell to define the lattice and to modify the structure factor $f_j(K)$ accordingly.

2.5 The intensity for a set of domain walls

Throughout the discussion of section 2.1 to section 2.4 it has always been assumed that the intensity due to a single wall would be observed experimentally. In practice this is not a realistic consideration. Since the intensity scattered by a single domain wall is proportional to $N^2$ while the scattering due to other processes such as Bragg scattering, thermal diffuse scattering and incoherent scattering, is proportional to $N^3$, the volume of the system, the intensity due to a single wall would almost certainly be too weak to observe experimentally. This implies that before domain wall scattering is likely to be observed the crystal must contain a large number of domain walls, and we must therefore consider interference effects between these arrays of walls.

The domain patterns which are observed experimentally in ferroelectrics such as KDP (Toshev 1963) consist predominantly of parallel "stripes" of domains of alternating polarity as indicated in fig.(5). The domain walls separating the stripes are of two types which we may conveniently term positive and negative. The calculation of section 2.2 corresponds to a positive domain wall. The scattering amplitude for a negative domain wall in the sharp wall approximation $\Lambda_w^-(K)$, is given by

$$\Lambda_w^-(K) = -\Lambda_w^+(K)$$

where $\Lambda_w^+(K)$ is the amplitude for a positive wall calculated from equation(10) or (12). This result is only approximately true in the more general case (equation 16), however it is not crucial to the argument.

The positions of the centres of the positive and negative domain walls bordering the pth domain may be written $y_p^+$ and $y_p^-$ respectively. The scattering amplitude for the two walls is then

$$A_p(K) = \Lambda_w^+(K) [\exp(iK_y y_p^+) - \exp(iK_y y_p^-)]$$

To obtain the amplitude for the crystal we sum this expression over all pairs, $p$. The intensity for the crystal is now given by

$$I_w(K) = \frac{(4\pi^2)}{acN^2} \Lambda_w^+(K) \Lambda_w^-(K) \times \sum_{pq} \{[\exp(iK_y y_p^+)-\exp(iK_y y_q^-)][\exp(-iK_y y_p^-)-\exp(-iK_y y_q^+)]\}$$

(20)

If the domains in the crystal have a width which is sufficiently random, and the wave vector $K_y$ is greater than the inverse width of the domains, the cross terms in equation (20) of the form

$$\sum_{pq} \exp iK_y(y_p^2 - y_q^2)$$

will be vanishingly small due to the randomness of the arguments. The same remark applies to the terms for $q = p$ unless both terms involve $y_p^-$ or both involve $y_p^+$ in which case they contribute a factor of unity. The average domain size in both KDP and BaTiO$_3$ is around...
10^{-4}$ cm. In both of these materials interference effects between domain walls, which can occur only when $k_y^{-1}$ is comparable to the average domain width, will be restricted to the experimentally inaccessible region very close to the Bragg peaks. Throughout the remainder of the Brillouin zone, the intensity will be given by a simple superposition of the single-wall intensities so that if the average domain width is $\xi$, the domain wall scattering intensity due to the $N/I$ walls is

$$I_{\text{TOTAL}}(\vec{k}) = \frac{N}{\xi} I_{\text{w}}(\vec{k})$$

In the examples BaTiO$_3$ and KDP, this suggests that the domain wall scattering intensity may be a factor of $10^5$ weaker than the Bragg scattering.

2.6 The scattering from rough walls

Domain walls in real crystals are never expected to be perfectly flat as the models considered so far would suggest. A more realistic domain wall is shown in fig. (6). Although the infinitely sharp wall picture has been used, the wall now has a finite width due to the wandering of its centre which may be caused by static imperfections such as defects or growth strains. If the energy of a step is sufficiently small the domain walls, even in a perfect crystal, will wander due to entropy effects, which may lead to a roughening transition, where the width of the wall diverges if the free energy of a step vanishes at a temperature $T_R$, below the bulk transition temperature $T_c$. In fig. (6) the wall shown is of the type, such as the 180$^\circ$ wall in tetragonal BaTiO$_3$, which involves no lattice distortion, and only this situation will be explicitly considered in this section since the stresses involved in creating a step in a wall in a case for which $\psi$ is not equal to zero will presumably cause the energy of a step to be considerably higher than in the $\psi = 0$ case. We would therefore expect the general conclusions which follow for the $\psi = 0$ case to extend to the more general $\psi \neq 0$ case with the premise that if $\psi \neq 0$, the widths should be narrower than in the case considered, and a roughening transition is not to be expected since this would require the creation of dislocations.

The wall shown in fig. (6) may be represented by defining a coordinate, $0(m,p)$, to be the position in the $y$ direction of the wall centre, in units of $b$. Repeating the steps of the calculation in section 2.1, the summations over $n$ must now be carried out for $n \neq 0(m,p)$ in domain 1, and for $n \neq -0(m,p)$ in domain 2. Summing over $n$ and retaining only the domain wall scattering terms in the amplitude we obtain

$$A_w(\vec{k}) = \frac{f_1(\vec{k})}{1-Y_1} \sum_{m,n} 0(m,p) x^m z^n$$

with $X$, $Y_1$ and $Z$ defined by equation (3), where we have used equation (9) for $f_1(\vec{k})$. Since a scattering experiment observes a macroscopic number of walls, we can treat $0(m,p)$ as a random variable which must be averaged over all possible domain wall configurations, i.e. all possible values of the set $0(m,p)$, to obtain the observed scattering. It is useful to treat separately the two cases, (a), $T \ll T_R$ which corresponds to nearly smooth walls, and (b), $T \geq T_R$ where the walls are broad on the scale of the lattice constant and some
continuum approximations can be made.

Case (a) $T \ll T_R$

When the temperature is well below the roughening temperature the steps in the domain wall profile are caused by random effects such as the presence of local strains which affect domain nucleation on cooling through $T_c$. It is reasonable in this regime to assume that the domain wall centre, $\{\Theta(m,p)\}$, can be treated as a set of random variables constrained by a probability distribution which for convenience we take to be Gaussian,

$$P(\Theta_m) = \sqrt{\frac{2\pi}{2\lambda^2}} \exp\left(-\frac{1}{2} \frac{\Theta^2}{\lambda^2}\right)$$  \hspace{1cm} (22)

where $P$ is the probability density, and $\lambda$ is the effective wall width. For a Gaussian distribution we can make the substitution

$$\exp\left[ibK_y \Theta(m,p)\right] \approx \exp\left(-\frac{1}{2}bK_y^2 \Theta^2(m,p)\right)$$ \hspace{1cm} (23)

where the angular brackets denote the configurational average. With this substitution the effective amplitude becomes

$$<A_w(\mathbf{K})> = \exp\left[-\frac{1}{2}(bK_y)^2 \langle \Theta^2(m,p)\rangle\right]$$ \hspace{1cm} (24)

in which $A_w(\mathbf{K})$ denotes the amplitude scattered by a flat domain wall. The effect of the roughness is contained in the exponential factor which is analogous to a Debye-Waller factor for the surface $\{\Theta(m,p)\}$. This exponential factor will be unimportant close to the $[h,0,0]$ Bragg points where the intensity varies as $1/\sin^2(\frac{1}{2}bK_y)$, but it may cause the scattering further out in the Brillouin zone to be strongly suppressed, and scattering at general $[h,k,l]$ values to be unobservable for large values of $k$.

As the temperature approaches the roughening temperature, the values of $\Theta(m,p)$ cease to be independently distributed and the above analysis is not sufficient, and close to $T_R$ the scattering may be better described by the following approximation which is strictly valid only above $T_R$.

Case (b) $T \gg T_R$

Taking the roughening transition as the temperature at which the effective width $\lambda$ of the domain wall diverges, the above calculation implies that the domain wall scattering component proportional to $N^2$ in the scattering amplitude disappears as the temperature approaches $T_R$. This behaviour is oversimplified due to the neglect of correlations between the position of the wall in one row of unit cells, and the position in nearby rows. When these cooperative effects are important it is necessary to take the configurational average of the intensity rather than the amplitude since it is intensities which are additive as explained in section 2.5.

In this case we have to evaluate the effective intensity

$$<I_w(\mathbf{K})> = \frac{|f^1(\mathbf{K})|^2}{2\sin^2(\frac{1}{2}bK_y)} \frac{\Sigma_{m,m'} \exp\left[ibK_y \Theta(m,p) - \Theta(m',p')\right]}{mm'} \times z^{m-n} z^{p-p'}$$ \hspace{1cm} (25)

where instead of the previous stochastic average, we must now use a thermal average with the probability weighting for different
configurations specified by a Hamiltonian $\mathcal{H}(\theta(m,p))$. To make contact with the literature on surface roughening transitions (see Weeks 1979) we assume that the discrete Gaussian model Hamiltonian may be used to obtain the thermal averages. The Hamiltonian for this model is given by

$$\mathcal{H}^{DG}(\theta(m,p)) = \sum_{i} \left[ \mathcal{J}(\theta_i - \theta_{i+1})^2 \right]$$

where $\mathcal{J}$ is a phenomenological constant representing the step energy and the sum over $i$ runs over all nearest neighbour pairs.

If the energy of a wall segment is due to short range forces, the energy of a step ought to be proportional to $|\theta_i - \theta_{i+1}|$ and not $(\theta_i - \theta_{i+1})^2$, however as the two interactions lead to critical behaviour of the same universality class, the correlation functions obtained should have the correct form. The quadratic interaction by understanding the effect of multiple steps, leads to a slightly higher value of $T_R$ for a given $\mathcal{J}$ than the linear interaction (Shugard et al. 1978). This shows that multiple steps are of little importance close to $T_R$.

The fluctuations of the wall position can be thought of as consisting of two types. Short wavelength fluctuations will lead to an effective Debye-Waller factor similar to that caused by the stochastic variation considered in case (a). The roughening transition is characterised by the growth of long-wavelength fluctuations, for which we can evaluate the thermal average in equation (25) in the continuum approximation.

Because the Hamiltonian is Gaussian in the step heights we can make the replacement

$$\langle \exp[iKb(\theta(m,p)-\theta(m',p'))] \rangle \approx \exp[-\frac{1}{2} K^2 b^2 \langle (\theta(m,p)-\theta(m',p'))^2 \rangle]$$

and on the assumption that the sum in equation (25) is dominated by terms for which $p \approx pm$ and $p' \approx pm$ we obtain the expression for the intensity

$$I(K) = \frac{N^2}{2} \frac{f^2(\xi)}{2\sin^2(\frac{1}{2}bK y)} = \frac{N^2}{2} \frac{f^2(\xi)}{2\sin^2(\frac{1}{2}bK y)} \sum_{n,m} (m^2 + p^2)^{-\mu} x^{m^2 n^2}$$

where

$$\mu = \frac{K^2 T}{2 J} \left( bK y \right)^2$$

and the lattice sums have been allowed to go to infinity. It is appropriate to emphasize that the effective intensity $I^*_r(K)$ is defined by equation (6) and to obtain the experimentally observed, $I^*_r(K)$, we should integrate this over a small but finite volume. The effect of the long wavelength fluctuations can be seen without evaluating the summations in (29). The peak intensities at $X = Z = 1$ are now proportional to $N^2$ instead of $N$ as they are in equation (6).

The scattering intensity is still concentrated in ridges perpendicular to the domain wall but these now have a width in the transverse direction proportional, not to $N^{-1}$ but to the number of appreciably non-zero terms in the summation in (29). For example if only terms with $s^{-1}$ greater than $1/f$ are retained then the transverse width of the scattering will be given approximately by

$$\delta X = \frac{2 \pi f^{-1/\mu}}{a}.$$
Since $k_B T_R = 2.45J$ (Weeks, 1979) we obtain

$$\delta k_x = \frac{2\pi}{a} e^{-1/(b\chi)^2}$$

The scattering near \((h0l)\) Bragg points will remain concentrated in a narrow ridge with a transverse width which is equal to zero at the Bragg peak and which increases as \(k_y\) increases. In the experiment on Pb$_2$Ge$_3$O$_{11}$, Cowley et al (1976) found that the domain wall scattering persisted above \(T_c\). This feature they attributed to the existence of metastable or 'dynamic' domains. In the temperature region above \(T_c\) they found that the width close to the \((004)\) reflection was limited by the instrumental resolution, but that it increased approximately as \(k^2\) over the short range of wave vector for which they were able to make measurements. Although this cannot be regarded as evidence for a roughening transition as the width was measurable only above the ferroelectric transition temperature, the wave vector dependence of the width of the scattering is in agreement with the qualitative predictions of the above theory which suggests that the walls may have become roughened at \(T_c\). This suggests that the occurrence of a roughening transition would be observable by measuring the transverse width of the ridges of intensity.

It must be borne in mind that for an array of domain walls arranged as in fig. (5) the surface roughening can never be complete as the walls cannot cross. The effect described above will, however, be effectively unchanged in the event of such an incomplete roughening in which the interface width becomes comparable with the average domain width, since this is wide enough for eqn.(28) to remain a good approximation.

2.7 Summary of Section 2

In this section we have calculated the scattering intensity from a simple model of a ferroelectric domain wall.

For all domain walls which involve a distortion of the lattice, it was shown that the domain wall scattering takes the form of broad wings on the sides of the Bragg peaks with an intensity proportional to the square of the Bragg part of the structure factor, \(f^0(\vec{k})\).

Domain walls which involve no distortion of the lattice were shown to give rise to qualitatively similar scattering, except that the intensity is in this case proportional to the square of the 'one-phonon' part of the structure factor \(f^1(\vec{k})\).

The effect of the width of the domain wall was considered in two models. In section 2.4 it was shown that a flat wall in which the polarisation changes direction over an extended region, will give rise to scattering with an intensity which is modulated by an oscillatory factor which should be experimentally observable. In section 2.6 it was shown that if the wall has a finite width due to a wandering of the position of its centre, this will cause the scattering intensity to be reduced by an effective Debye-Waller factor. Finally, it was shown that if the wall undergoes a roughening transition, the ridges of intensity have a finite width which will cause little change in the intensity close to the \((h0l)\) Bragg peaks, but may render the width of the scattering experimentally measurable.
3. Observation of domain wall scattering in D.K.D.P.

A preliminary neutron scattering experiment was recently performed using a sample of deuterated KDP (DKDP) to measure the domain wall width using the results obtained in section 2. The experiment was carried out on the PLUTO triple-axis spectrometer at the Atomic Energy Research Establishment, Harwell. The sample of DKDP was in the form of a cuboid with a volume of approximately 2cm³, this was mounted with the c axis vertical. To obtain the best possible wave vector resolution, Soller slit collimators with a width of 20° of arc were used throughout the instrument.

Particular care was taken to eliminate multiple Bragg scattering which causes the appearance of a number of satellite peaks around the primary, split Bragg peaks in the ferroelectric phase. An incident energy of 7 meV was used to prevent possible multiple scattering of the primary wavelength, \( \lambda \). Contamination by neutrons of wavelength \( \lambda/2 \) was removed by using (111) planes of a germanium crystal to provide energy analysis, and higher order contamination was removed by a polycrystalline graphite filter. Observations were made around the (2,0,0) and (2,2,0) reciprocal lattice points, at a temperature of 100 K, well below the ferroelectric transition temperature which was measured for this crystal to be 222.3 K in a previous study (Hosea 1980), and at 250 K, above the transition.

The reciprocal lattice of DKDP close to the origin is shown schematically in fig. (7), in which the positions of the expected lines of domain wall scattering are shown. Close to the (2,2,0) lattice point, narrow ridges of scattering were observed in both the (\( \xi,2,0 \)) and the (\( 2,\eta,0 \)) directions. The intensities of the ridges with \( \xi \) or \( \eta \) less than 2 is greater than the intensity of the ridges with \( \xi \) or \( \eta \) greater than 2 by a factor of about 3.3 This can be largely attributed to a difference in the structure factor \( f_0(\mathbf{K}) \) since the Bragg peaks at (1.981,2,0) and at (2.019,2,0) differ by a factor of 3.12. The possibility cannot be ruled out that the 'one-phonon' part of the structure factor \( f^1(\mathbf{K}) \) was not sufficiently small to prevent the terms in the structure factor which were discarded in sections 2.2 and 2.4 from causing an interference effect since these terms change sign traversing the Bragg peak (see equation 10). The bulk of the experimental work was restricted to studying the ridge of scattering in the (\( \xi,2,0 \)) direction as this was least affected by the tails of the Bragg peaks.

The widths of the ridges of scattering in both energy and wavevector are within the resolution limit of the instrument, which had full widths at half maximum of 0.15 meV and 0.007\( a^* \) respectively, where \( a^*=0.0844 \AA^{-1} \) is the reciprocal unit cell dimension in the (hk0) plane. Scans across the ridge for several values of \( K_x \) are shown in fig. (8).

The intensity measured along the ridge is shown in fig. (9). The dashed line in this figure shows the tail of the Bragg peak at (1.981,2,0). This was estimated by measuring the shape of the single (2,2,0) Bragg peak in the high-temperature phase, which amounted to measuring the instrumental resolution, and then recalcing this to match the height and centre of the observed (1.981,2,0) peak at 100 K. The solid line in fig. (g) shows the result of a least squares fit to the data of an intensity calculated from the expression for the amplitude of a wall of width \( w \) given in equation (16), convoluted with a one-dimensional Gaussian resolution function. The data fitting was carried out by fixing the background...
at a level of 50 counts, the average value obtained for $k_y$ equal to
1.98 or 2.02, and treating $b_3$ and the overall amplitude as variable
parameters. The Bragg structure factor $f_0(\bar{k})$ was assumed to be
constant for the small range of wave vector for which the scattering
was observed. A comparison of the observed intensity with the predicted
intensities shown in figure (4) suggests that as no oscillatory behaviour
was observed in the intensity out to one fifth of the way across
the reciprocal unit cell, the maximum domain wall width is four
unit cells. Least squares fits for values of w from 0 to six were
carried out in the manner described above, the results for a
width of two unit cells being significantly better than those for
other widths. In view of the approximations made, namely the
neglect of the wavevector dependence of the structure factors
$f_j(\bar{k})$, and the assumption that the domain wall consists of three
well-defined regions with sharp boundaries and identical structure
factors instead of a region of deformed cells in which the
polarisation changes gradually, the agreement between theory and
experiment is surprisingly good.

Some qualitatively similar scattering was observed near the
$(2,0,0)$ Bragg point in the $(2,n,0)$ direction but this was not
examined in any detail.

4. Conclusions

In the introductory section it was explained that recent
theoretical studies of ferroelectric domain walls are of relevance
to the domain walls which arise in real systems only in those cases
where the width of the domain walls is large enough to apply a
continuum approximation. Although this is certainly the case for
the magnetic domain walls (Bloch walls) which arise in Heisenberg
systems, estimates of the widths of ferroelectric walls based
upon microscopic theories (Kinase and Takahashi 1957) and
experimental evidence (Cowley et al. 1976) indicate that this
approximation is in general unrealistic for ferroelectric domain
walls.

It was shown in section 2 that for a large number of ferroelectrics
the width of the domain walls is directly measurable by
neutron scattering techniques, although few such measurements have
been performed. The occurrence of roughening transitions in
ferroelectric domain walls has been considered, and the possibilities
of detecting the occurrence of such a transition by observing
either the width of the ridges of scattering, or the effective
Debye-Waller factor, were noted. In all ferroelectrics where the
domain walls cause a distortion of the lattice it was argued that
the domain walls would remain almost flat at all temperatures below
the Curie point due to the stresses which accompany the formation
of a step in the domain wall profile.

In section 3 the results of relevant parts of the theory were
applied to a preliminary neutron scattering experiment on DKDP. The
width of two unit cells which was deduced for the wall in DKDP is certainly too narrow to expect that continuum approximations could be usefully applied to their study. The measured width of walls in PbGeO₃ (Cowley et al. 1976) is also close to the lower limit for which continuum approximations are reasonable. These two experiments suggest that it will be necessary to establish whether the broader walls expected on phenomenological grounds actually exist, or whether in agreement with the microscopic model of Kinase and Takahashi (1957) the domain walls in all ferroelectrics will be of the order of one unit cell thick. If this proves to be the case then ferroelectric domain walls cannot be a candidate for the observation of (continuum) non-linear excitations as recent authors have suggested. Instead it would seem more appropriate to consider the theory of domain walls from a microscopic point of view. It is to be hoped that the availability of a technique for the study of domain walls will stimulate the development of such microscopic methods.

For the future, further experiments are planned to study the temperature and electric field dependence of domain wall scattering, and to look for the existence of the wider domain walls predicted by phenomenological theories (Zhirmov 1958).

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Figure Captions

Fig.(1a) The model for a domain wall in KDP. The polarisation
is directed out of the plane of the diagram, domain 1
(y > 0) has a polarisation directed up, domain 2
(y < 0) has a polarisation directed down.

Fig.(1b) The (1,1,0) domain wall in tetragonal BaTiO₃. The
rectangles represent the tetragonal unit cells. The
monoclinic primitive unit cells with \( \psi = 45^\circ \) and
a = \( \sqrt{2}b \) are depicted in bold lines at the origin. The
dashed lines show the non-primitive monoclinic unit
cells which may be used to describe the system. It is
necessary to use these cells if the finite width model
of section 2.4 is to be applied.

Fig.(2a) The reciprocal lattice for the model of fig.(1a). The
Bragg points (+) are split into separate components
from each of the two domains. Bold lines are used to
depict the ridges of domain wall scattering corresponding
to the condition \( X(\mathbf{K}) = 1 \).

Fig.(2b) \( I_w(\mathbf{K}) \) in arbitrary units where \( \mathbf{K} = \frac{2\pi}{b}(2,n,0) \). The parameter
values used are a = b, \( \psi = -0.05 \). In the units chosen, the
Bragg peaks, denoted by arrows, have intensities of \( 10^6 \).

Fig.(3) The model for a domain wall with a width of two unit cells.

Fig.(4) \( I_w(\mathbf{K}) \) in arbitrary units for the model with a finite width
for \( \mathbf{K} = \frac{2\pi}{b}(2,n,0) \). The curves shown are for \( w = 2 \), dashed
line; \( w = 4 \), dotted line; and \( w = 6 \), solid line. The
amplitudes of the scattering have in each case been chosen to
aid comparability. The parameters used were appropriate to DKDP, $\psi = 0.0104$, $a = b = 7.45$. The value of $b_3$ was arbitrarily set to 7.60.

Fig. (5) The domain structure of KDP. There are two types of wall, positive (a) and negative (b). These alternate to produce the 'ladder' of random width domains (c), see Toshev 1963.

Fig. (6) The model used for a 'rough' domain wall. The + and - signs denote the direction of polarisation. The wall is depicted by the bold line.

Fig. (7) The $(h,k,0)$ plane of DKDP. Only the allowed reflections are shown. The ridges of scattering predicted are shown in bold lines. The splitting of the Bragg peaks has been greatly exaggerated for clarity.

Fig. (8) Neutron scattering scans in wavevector (a) and energy (b) across the ridge of quasielastic scattering at $(\xi,2,0)$. The spacing between points is in each case approximately the resolution width of the instrument. The scattering is seen to be concentrated about the $(\xi,2,0)$ direction with an unresolvable width.

Fig. (9) The intensity of the $(\xi,2,0)$ ridge. The solid line shows the best fit to the data with $b_3 = 7.39$ ($b = 7.45$) and $w = 2$. The dashed line shows the tail of the Bragg peak at $\xi = 1.981$ determined from measurements of the $(2,2,0)$ reflection in the high temperature phase.
Figure 4.

Figure 5.

Figure 6.
Figure 7.