The Temperature Dependence of the Structure and Dynamics of Solid Benzene

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For my mother, and to the memory of my father.
'Sheets of paper covered with words pile up in archives sadder than cemeteries, because no one ever visits them, not even on All Souls' Day. Culture is perishing in overproduction, in an avalanche of words, in the madness of quantity. That's why one banned book in your former country means infinitely more than the billions of words spewed out by our universities.'

*Milan Kundera*

'One of the things that amazes me,' he said finally, 'is to find that in a University that prides itself on scholarship and research, Porterhouse remains so resolutely a sporting college. I was glancing at the notices just now. No mention of scholarships or academic work. Just the old Rugby lists...'

'And what did you get? A double first was it?' the Dean enquired sweetly.

'A two two,' said Carrington.

'And look where it’s got you,' said the Dean. 'It speaks for itself really. Let’s just say we haven’t succumbed to the American infection yet.'

'The American infection?'

'Doctoratitius.'

*Tom Sharpe*
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Of equal importance are all the people who have distracted me during these three (and a bit) years, and let me vent my aggression by wasting valuable hours on the tennis court or at the pool table, failing abysmally on the cricket pitch, plunging head-first into snowdrifts, or destroying the dreaded Rhody. More peacefully, or maybe not, I would also like to thank all the people who have helped me gain confidence in playing music during my time in Edinburgh, especially John Severn, Jonathan Kinnersley, Gisela Baumer and Sandra Hollingdale - some day the quar-or-so-tet will play again! Finally to the people with whom I have shared flats and houses: thanks for putting up with my untidiness and my moods, and helping me keep warm.
The experiment reported in Chapter 2 was performed with Peter Hatton and Chris Howard. With this exception, the thesis is my own work.
Abstract

This thesis is a study of the structure and dynamics of crystalline benzene across its solid temperature range at ambient pressure, using the techniques of molecular dynamics simulation and neutron powder diffraction.

The simulations cover a wide range of properties, making comparison with the large body of experimental data that is available for benzene. A rescaling of an ab initio potential from the literature is proposed, and this rescaled potential is shown to give structural parameters in good accord with experiment, especially for the temperature dependence. The melting point and elastic compressibilities are determined for the model and it is found that, in the simulations, the crystal can be superheated up to the temperature of an elastic lattice instability. The implementation of a molecular dynamics program on a large array of transputers is described.

The neutron powder diffraction experiment was performed primarily to study the crystal structure close to the melting point, in order to investigate reported premelting phenomena. The results contradict a previous study, but effects are seen that can be explained, using the simulations, as precursors of a form of disordering transition. The simulations predict that the full transition should be observable experimentally by the application of pressure, as this would increase the temperature range over which the solid is stable. Librational spectra are obtained from the simulations, and these indicate an explanation for some experimental results.

Finally, the nature of reorientational motion about the sixfold axis of the molecule is considered. The model is shown to reproduce well the experimentally determined temperature and pressure dependence of the rate. A detailed study of the correlations of reorientation events is made, in a much greater detail than is possible experimentally. Evidence is found for only a very weak local correlation, which is a subject over which there has been considerable debate.
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Wherever possible, SI units are used in this thesis. Where comparison is made with experimental work, however, the appropriate conventional units are used, to ease comparison with the literature, and these are often not strict SI units.

The most important of these units are

- **Length**  
  \[ 1 \, \text{Å} = 10^{-10} \, \text{m} \]

- **Pressure**  
  \[ 1 \, \text{kbar} = 10^8 \, \text{Pa} \]

- **Frequency (for optical spectra)**  
  \[ 1 \, \text{cm}^{-1} = 0.03 \, \text{THz} \]
Chapter 1

Introduction

In many areas of chemistry - theoretical, physical, and synthetic - benzene holds a central position: as a basic building block of the rich field of aromatic organic chemistry, as the prime example of pi-bonding and electron delocalisation, and, of key interest here, in its formation of an archetypal molecular crystal [1].

The most important feature of a molecular crystal, as concerns this thesis, is that the forces binding sets of atoms together, to form molecules, are much stronger than the forces that bind these units to each other to form the crystal. The main forces binding together the crystal are generally rather weak forces, such as van der Waals forces, dipolar interactions and hydrogen bonds, whereas the atoms are bonded to form molecules by much stronger covalent bonds. This difference in the strength of interactions means that molecules can often be approximated to rigid units, as in benzene, nitrogen or methane, for example. Larger molecules can be represented as a chain of rigid units flexibly linked together, as in the case of butane [2] or longer alkanes. Simple geometrical ideas can then be used to gain insight into the structure and dynamics of the crystal, as in the work of Kitaigorodsky[1] in which the structures of crystals were proposed by considering the way that these rigid units could be packed together most efficiently. The rigid molecule approximation is, of course, only appropriate if it is the properties of the crystal that we are interested in, rather than internal properties of the molecule. The range of molecular crystals is as vast as the range of molecules; a few examples of frequently studied compounds are water, ammonia, cyclohexane, sulphur hexafluoride, butane, carbon dioxide, and, here, benzene.

From a theoretical viewpoint molecular crystals are interesting for two main reasons. The first reason is that, as mentioned above, simple geometrical models
can often give insight into the properties of the crystal.

Secondly, there are often rather large amplitude motions present due to the weak bonding between molecules. For example, since the composite units in the crystal are not point-like atoms, the orientational degrees of freedom must be considered. In particular, the molecules often have symmetry axes, so there is the possibility of molecular reorientation occurring in the solid. Such a reorientation consists of a molecule rotating so that it takes up a new orientation which is symmetrically related to the original orientation. In the extreme case, these reorientations can lead to the formation of a special phase for some molecular crystals at high temperatures, characterised by translational order, but with a high degree of orientational disorder. These are termed plastic crystals[3], due to the fact that they creep when subjected to stresses. The orientational disorder may be isotropic, as in the case of nitrogen [3], but is not necessarily so as in the case of sulphur hexafluoride[4]. The plastic phase generally exists between the 'normal' ordered phase and the liquid phase and to a certain extent, plastic crystals can be considered intermediate between these two phases; much of the orientational freedom of a liquid is present, but with the translational order of a solid, and plastic crystals have correspondingly low entropies of fusion. These reorientations are an example of the often highly anharmonic nature of motion in molecular crystals, which makes analytic study difficult. The interactions between molecules can, however, be approximated with a certain degree of accuracy as a sum of central atom-atom interactions between the constituent atoms of the molecules. This makes molecular crystals amenable to study by simulation techniques (q.v.) such as molecular dynamics and Monte Carlo simulation, which are able to cope with arbitrary degrees of anharmonicity. The major problem with these techniques is that they are extremely demanding in terms of computing power.

This thesis is concerned with the study of the structure and dynamics of solid benzene, primarily by computer simulation. The widespread interest in benzene alluded to above has led to the properties of the benzene crystal being the subject of study by many diverse experimental methods, often as a test-bed for new techniques. This provides a large resource of experimental data which is used throughout the thesis to assess the validity of the computational model. The purpose of the simulations was not, however, simply to study the properties of the model per se, but rather to use the model to address some key questions
concerning the properties of solid benzene at a molecular level.

Of greatest antiquity is the question of the nature of the reorientations in benzene about the sixfold axis of the molecule. The first experimental work on this was done in the 1950s [5], yet there remain uncertainties about the details of the motion. Much of the interpretation of the experimental results has rested up to now on the qualitative geometrical model, for instance that molecules might mesh together like gear-wheels to give strongly correlated motion. In the simulations presented here, the effect of thermal motion is explicitly included and this is found to largely invalidate this simple steric argument. A plastic phase has not been found for benzene; the possibility of such a phase forming in which the molecules have reorientational freedom about the sixfold axis has been suggested [6] and is considered in this work.

A second issue is that of premelting [7]. This will be discussed in more detail in Chapter 2, but briefly it is the question of whether it is possible to detect changes in the properties of a solid phase as the melting temperature is approached; such changes have been reported for benzene [8, 9]. The question of premelting is of fundamental importance to a theory of the melting transition, since a first order theory predicts that no such pre-transitional effects should be observable. A neutron powder diffraction experiment has been undertaken to repeat some of the previously reported work, which was felt to have been performed with an unsuitable technique. Coupled with results from the simulations, the diffraction experiment strongly questions the idea of a microscopic premelting effect in benzene.

Whilst these conclusions are slightly negative, in that they refute previous ideas concerning premelting and the idea of strongly cooperative molecular reorientations, the field is not left barren, as a hitherto unreported disordering transition in benzene has been discovered. This transition is manifested most strongly in the simulations, but there is experimental evidence for a partial transition, especially from the work reported in Chapter 2. It is believed that the transition has not been seen fully in experiments to date because it is interrupted by melting in the real solid before the disordering is complete. A proposal is made, however, as to how it might be possible to observe the transition completely experimentally.

An important feature of the present work is that, in comparison with previous simulations of benzene, the behaviour of the model has been studied as a function of temperature. This enables a much wider assessment of the model to be made,
and also allows temperature dependent properties, such as thermal expansivity, to be studied. The ability to make such extensive studies is largely due to the advent of powerful supercomputers, and part of this work involved the implementation of a molecular dynamics program on a large array of transputers.

Organisation of the Thesis

This chapter continues with a consideration of what is known about the structure of solid benzene. There follows a brief introduction to the simulation techniques that are used later, which then leads on to a question of finding a suitable potential function to describe the interaction between two benzene molecules. Finally, previous simulation work for benzene is reviewed.

In Chapter 2, the ideas of premelting are discussed, along with reports of premelting in benzene. The neutron powder diffraction experiment undertaken to study these effects is then reported. This experiment also served to provide more complete structural data for benzene as a function of temperature.

Chapter 3 is devoted to a description of the computational techniques used in the later chapters. The first part of the chapter defines the way in which the simulations were performed, with details of the sample size, potential function, simulation algorithm, and of how the sample was 'prepared'. The second part describes the implementation of the molecular dynamics program on a very large transputer array. This latter part is based on the paper 'Molecular Dynamics of rigid molecules on transputer arrays', by C. J. Craven and G. S. Pawley, which is to appear in Computer Physics Communications (in press).

The main simulation work is covered in Chapter 4, which is concerned with establishing the general features of the behaviour of the model, and assessing the ability of the model to reproduce experimental data for various structural and dynamic properties across the solid temperature range at ambient pressure.

In the concluding two chapters various phenomena are considered in more detail, showing how the simulations can shed light on, often equivocal, experimental results: in Chapter 5, a disordering transition is used to suggest an explanation for some of the features of the experimental data from Chapter 2; finally, the information that the simulations can give about molecular reorientations in solid benzene is considered in Chapter 6.
1.1 Benzene

1.1.1 The Benzene Molecule

Figure 1.1: A schematic diagram of a benzene molecule; in the deuterated compound all hydrogen is replaced by deuterium.

The structure of an isolated benzene molecule is a perfect hexagon of six carbons each with one hydrogen (or deuterium) atom bonded to it (Fig. 1.1). The dashed line in Fig. 1.1 represents the ring-like cloud of electrons that exists above and below the carbon ring as a result of the conjugated pi-bond system. This bonding system makes the ring rigid, and the electron cloud is believed to produce a preferred dimer configuration [10] in which the two molecules are in a T-shaped configuration, rather than 'face-to-face', as this reduces the repulsive interaction between the pi-bonding systems. This fact has important ramifications for the construction of an adequate intermolecular potential function as will be discussed later. The dipole moment of the isolated gas-phase molecule is zero by symmetry, but the molecule has a quadrupole moment [11], which at least partially reflects the presence of the electron system above and below the plane of the ring.

1.1.2 Phase Diagram

The phase diagram of benzene as obtained from calorimetric measurements by Akella and Kennedy [12] is reproduced in Fig. 1.2. Under ambient conditions benzene is liquid. At atmospheric pressure it crystallises at 279.0 K [13] (280.0 K for the deuterated compound) into the phase benzene I. This phase is stable
down to the lowest temperatures studied of 4 K [14], although there has been a phase transition proposed at $\approx 100$ K [15], but this is disputed in Chapter 2. The pressure dependence of the melting temperature has been determined as 26 K/kbar. There are at least two high pressure phases, benzene II and III, and other high pressure phases have also been proposed [15].

1.1.3 Benzene I

The ambient pressure phase, benzene I, is orthorhombic with the space-group $Pbca$. There are four molecules in the unit cell, Fig. 1.3, lying at the origin and face-centres of the cell, arranged in a herringbone pattern. This type of packing is rather typical of crystals of moderately sizes planar molecules [16].

Determinations of the Structure

The structure of benzene I has been studied several times as experimental techniques have developed. As reviewed by Cox[17], the first x-ray diffraction experiments on benzene were made 'out of doors' in 1923 by Broome. In contrast, modern neutron scattering techniques require multi-million pound installations.
Figure 1.3: (a) ‘Ball-and-stick’ structure of the four molecules in the benzene \( \Gamma \) unit cell. (b) The complete unit cell of benzene I. (c) Space-filling representation; the surfaces approximately correspond to the radius of the steep repulsive core of the potential used in the simulations. Note the orientation of the axes in each figure.
The lattice parameters were obtained by Kohzin\cite{18} in 1953 at 78 K and in 1958 the full structure was solved by Cox et al.\cite{19} using single crystal x-ray diffraction at 270 K. Later, Bacon et al.\cite{20} used single crystal neutron diffraction at 138 and 218 K. Recently Jeffrey et al.\cite{21} used single crystal neutron diffraction to study the structure at 15, 53, 80 and 123 K for the deuterated compound $C_6D_6$. High resolution powder diffraction of neutrons (HRPD,\cite{14}) has also been used at 4 K for $C_6D_6$. The lattice parameters from these various sources plotted in Fig. 2.5 of Chapter 2.

The different techniques used, and the study of the deuterated compound in later studies illustrates the development of the various diffraction methods. The first crystallography was done using x-rays, but as neutron sources became available neutron diffraction became the preferred technique, especially for organic compounds, for two reasons.

The first reason is that the form factor for x-rays means that peaks at large scattering angle are attenuated, so that, in comparison, neutron patterns contain much more information in this region, where the intensities are sensitive to the fine details of the crystallographic basis.

Secondly, x-rays are scattered only very weakly by hydrogen (or deuterium), so that only the carbon atoms are ‘visible’. In contrast, neutrons are scattered roughly equally strongly by carbon and hydrogen (or deuterium), allowing the full molecular structure to be studied.

The reason for studying the deuterated compound is that it eliminates the large and undesirable incoherent neutron scattering from hydrogen, which complicates the refinement of the structure from the diffraction pattern. In the absence of hydrogen bonding, the only major difference that deuteration makes is that the mass and moment of inertia of the molecule are changed, and the bond-lengths are fractionally different\cite{21}. Whilst this generally makes little change to the properties of the crystal, apart from proportional changes in the vibration frequencies, in some cases it can make qualitative changes to the phase structure as in cyclohexane\cite{22}. It was to partly to check the effect of deuteration in benzene that the diffraction study in Chapter 2 was made. Deuterated benzene is very readily available, partly because it is a routine solvent in analytical NMR. As the majority of the work that follows is for the deuterated substance, atoms will generally be described as being of deuterium rather than of hydrogen. In fact, in a simulation, if only the mass and moment of inertia of the molecule are changed...
then, since the kinetic energy terms can be factored out of the partition function, 
time averaged properties of the system are unaffected and only the dynamics are 
changed; as in the discussion of vibration frequencies in Chapter 5 for instance. 
Changes in the real crystal structure must then be ascribed to slight changes in 
the molecular structure on deuteration.

Features of the Molecular Packing

The orientations of the four molecules in the unit cell are not identical, being 
related by mirror planes or diads. In Fig. 1.3, molecules I & II are related by a 
diad parallel to \( a \); molecules I & III by a diad parallel to \( b \); and molecules I & IV 
by a diad parallel to \( c \). As the molecule has a centre of symmetry, a mirror plane 
perpendicular to \( a \) is equivalent to a diad parallel to \( a \), and similarly for the other 
axes.

The molecular orientations are, however, similar in that for each molecule the 
plane of the ring is at approximately 45° to the \( a \) and \( c \) axes. For each molecule, 
two of the \( C-D \) bonds lie approximately along the \( b \)-axis; for the labelling of 
atoms in Fig. 1.3(a) these are the \( C_1-D_1 \) bond and the, diametrically opposite, 
\( C_4-D_4 \) bond. The \( C_1-D_1 \) bond lies only 2° out of the \( a-b \) plane and makes an 
angle, at low temperatures, of \( \approx 19° \) with the \( b \)-axis. The molecules I & III are 
approximately parallel, the main difference in orientation being that the 
\( C_1-D_1 \) bond has a component along \(-a\) for I and along \(+a\) for III; similarly for II & IV. 
The planes of I or III type molecules are at approximately 90° to molecules of 
types II or IV.

In the paper of Cox et al.[19] a point was made concerning the packing of the 
molecules which has been much quoted, but which has never been fully justified. 
This is the fact that pairs of molecules of types I & II, (or III & IV), mesh to-
gether like a pair of bevelled cog-wheels: the space-filling representation in Fig. 1.3 
shows this most clearly, examples of the meshing contacts being marked by as-
terisks. The suggestion was made that this meshing could cause reorientations 
of molecules to occur for extended sheets of molecules or, more likely, as a small 
group of molecules. The experimental evidence for this is reviewed in Chapter 
6 along with the results of simulations. The conclusion is that the meshing, al-
though attractive as a concept, does not in fact have a significant effect upon the 
correlations of molecular reorientations.
A final important point is that although the orientations of individual molecules are approximately symmetric with respect to \( a \) and \( c \), the space group operators that build up the crystal structure mean that the \( a \) and \( c \) directions are in fact very different. Within a plane perpendicular to \( a \), the molecules all lie approximately parallel whereas in a plane parallel to \( c \) the molecules form a corrugated sheet of intermeshed molecules. This inequivalence of \( a \) and \( c \) manifests itself strongly in the differences in the thermal expansivity and compressibility of the axes, as will be seen later.

**Distortions of the Molecule in the Crystal**

It was stated at the start of this section that the isolated molecule has a perfectly planar hexagonal structure. As the site symmetry in the crystal is lower than the molecular symmetry, the molecule may be slightly distorted by its crystalline environment. Much of the motivation for previous crystallographic work was, in fact, the determination of the structure of the benzene molecule, and the work of Jeffrey further refined the basic knowledge of the structure from that of Cox \textit{et al.}, showing that the molecule is only very slightly distorted from the perfect hexagonal structure by the influence of neighbouring molecules. The greatest distortion of the bond angles is by less than 1° in one of the 120° angles. The best estimates for the bond lengths in the molecule are from the work of Jeffrey \textit{et al.}, giving \( r_{C-C} = 1.398 \) Å, and \( r_{C-D} = 1.088 \) Å.

### 1.1.4 Benzene II and III

The first high-pressure phase, Benzene II, is found at moderate pressures (~15–20 kbar) and has been well characterised in a single-crystal study by Piermarini \textit{et al.}[23]. The phase has a monoclinic \( P2_1/c \) structure. The transition \( I \rightarrow II \) is extremely sluggish: at 77K and 30 kbar, or 295K and 45 kbar, Ellenson and Nicol[24] did not observe a complete transformation even after ~24h, although at a temperature of between 320 K and 370 K the transformation was complete within about 1h. A possible transformation route proposed by Piermarini \textit{et al.} is that the transformation is of a Martensitic type [25]; that is, a displacive transformation requiring large molecular displacements comparable to the unit cell dimensions. The monoclinic structure can be obtained from the orthorhombic structure by a shear of half a cell dimension in the \( c \) direction of the \( a - c \) plane.
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which bisects the cell. The angle $\gamma$, between the $a$ and $b$ axes also deforms, giving a monoclinic structure. The energy barrier associated with this shear would be large, explaining the low rate of the transformation. The crystal becomes striated during the transformation[23] which is indicative of small portions of the crystal transforming, and therefore shearing, independently.

The phase benzene III, and other high pressure phases that have been proposed[15], have been the subject of little detailed crystallographic work and the structures remain largely unsolved.

1.2 Simulation Techniques

Molecular Dynamics

The main computational technique used in this thesis is the method of molecular dynamics[26]. A portion of the crystal is set up in the computer by specifying the positions and orientations of the molecules at time zero, and the molecules are given random velocities approximately corresponding to the temperature to be studied. The positions and velocities of the molecules are then stepped forward in time using Newton’s laws and a potential function which describes the interactions between molecules. After an equilibration period ‘measurements’ can be made on the system; there are many possible properties that can be studied, from collective quantities such as structural parameters through to individual molecular trajectories. The general motivation for performing molecular dynamics simulations is that they can provide information about a solid in a much greater detail than is often possible experimentally, and can also help to establish models for the interpretation of experimental data. The advantage of molecular dynamics over other more analytic techniques[27] is that it can cope with arbitrary anharmonicity, whereas analytic methods will always fail when the anharmonicity is too great[28].

Some of the main limitations of molecular dynamics simulations are that only very small systems can be studied, of at most ~10000 atoms, and only over very short timescales, typically < 1 ns. This makes it inappropriate for the study of processes that are very slow, such as crystallisation, or that require large samples, such as for the study of defects and their interactions. As computer technology develops, the system sizes and timescales accessible will correspondingly increase.
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However, many orders of magnitude of increase in computing power will be necessary before it is possible to simulate macroscopic samples on even microsecond timescales.

Monte Carlo Simulations

A similar method to molecular dynamics is Monte Carlo simulation\[26\]. In its simplest form this involves calculating thermodynamic configurational averages by picking configurations of the system at random, and weighting the contribution to the thermodynamic average by the Boltzmann probability corresponding to the energy of the configuration. In practice, a slightly more sophisticated method is generally used, where instead of picking configurations completely at random, the system is stepped from one configuration to another similar one, only allowing the step with a probability depending on the energy difference of the two configurations. Whilst Monte Carlo methods have advantages over molecular dynamics in terms of the efficiency of sampling of phase space, they are not suitable for studying dynamics, as even though the system is stepped through similar states, there is no direct connection between this sequence of configurations and the true dynamics of the system.

Zero Temperature Methods

Two semi-analytic methods are available at 0 K which are particularly useful. The first is to calculate the 0 K structure that is predicted by a potential by varying the lattice parameters and molecular orientations, within the constraints of the space group, to minimise the lattice potential energy. This method can be extended to measure elastic properties by the inclusion of a stress-strain energy term in the lattice energy, and then calculating the lattice parameters as a function of applied stress. Secondly, the lattice mode frequencies and eigenvectors can be calculated by the method of lattice dynamics\[29\], which is simply a normal mode analysis of the system making small oscillations about its 0 K structure. The existence of imaginary components in any of the frequencies indicates that the space group assumed for the lattice energy minimisation is not in fact stable. At low temperatures, of course, these classical methods are not strictly valid, as quantum effects become dominant (§ 4.1.1), but at the level of accuracy of much work the problem is not serious. These methods also have a use in establishing
structural, vibrational or elastic properties of a model independently of molecular dynamics simulations: this provides a good test of the correctness of the molecular dynamics program code.

1.3 Intermolecular Potentials for the Benzene-Benzene Interaction

Apart from the restrictions imposed by the available computing power, the major problem that faces the molecular dynamicist is to find a potential function that adequately describes the interaction between the molecules.

General Atom-Atom Potentials

The basic assumption that is made in most work on molecular crystals is that the potential can be described by a sum of pairwise-additive central atom-atom interactions between the atoms of different molecules [1]. A typical functional form is the 12-6 Lennard-Jones potential,

\[ \phi(r) = (a/r)^{12} - (b/r)^6 \]  

(1.1)

where \( r \) is the separation of the two atoms, and \( a \) and \( b \) are the potential parameters. The \((a/r)^{12}\) term represents the short range and rather sharp repulsion caused by overlap of fairly well defined electron orbitals; the \((b/r)^6\) term represents van der Waals attraction which dominates at large distances.

It has often been hoped that it would be possible to find potential parameters that would be transferable between different molecules [30], so that the interactions of complex molecules could be predicted. Attempts are sometimes also made to include many body effects explicitly in simulations but it is generally assumed[11] that in molecular crystals such effects will be small, and that to a sufficient degree of approximation they can be included as modifications to the two-body potential. In the case of polar molecules, it is necessary to include fractional point charges on some atoms in addition to the Lennard-Jones-type interactions.
CHAPTER 1. INTRODUCTION

The Benzene-Benzene Potential

As benzene is the prototypical aromatic molecule, many attempts have been made to obtain a satisfactory benzene-benzene interaction potential, since it may provide potential functions that are suitable for other aromatic molecules. There have been two comprehensive review articles by Bartell et al. [11] and Dzyabchenko [31] on the subject of the many potentials that have been proposed for benzene in the past; only the main conclusions of the reviewers will be highlighted here.

There have generally been two types of model for the interaction of two benzene molecules: the twelve-site models include interactions between all twelve atoms in each benzene molecule; the six-site models attempt to reduce the number of interactions by subsuming the interactions of bonded C-D pairs into a single interaction site, often placed at a position intermediate between the constituent atoms. The obvious motivation for attempting to find a satisfactory six-site model is the four-fold reduction in computation that is obtained compared to the twelve-site models. The conclusion of Bartell et al., however, is that such models can never adequately model the structure of the solid, even if it models the liquid state quite well.

It has been found necessary to include equal and opposite fractional charges on the carbon and hydrogen atoms in order to obtain the correct orientations of molecules in the solid. These charges reproduce the experimental quadrupole moment, but it has been found that a point quadrupole is in itself not adequate. This indicates that the role of the charges is to influence the short range contacts of molecules, as discussed above for the formation of the T-shaped dimer. Bartell et al. claim that at larger distances the effects of these electrostatic effects are reduced by cancellation and polarisation, so that the long range interaction is still the van der Waals term.

The importance of the point charges is one of the reasons why the six-site models can never be successful. The major computational effort in a molecular dynamics program is generally in calculating atomic positions and separations; once the separation of two atoms is calculated the complexity of the interatomic potential function is largely irrelevant. There would therefore be no saving in having six full interaction sites, and a further six purely electrostatic sites, as this would then be effectively a twelve-site model.

The conclusion of Bartell et al. is that the most satisfactory potentials ob-
Table 1.1: Parameters for the benzene-benzene interaction potential of Karistrom et al. [32] Units are kJ/Mol and Å

<table>
<thead>
<tr>
<th>i</th>
<th>( A_i )</th>
<th>( B_i )</th>
<th>( C_i )</th>
<th>( D_i )</th>
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</tbody>
</table>

Obtained so far are those due to Williams and Starr [30], and Karistrom et al. [32]. Williams and Starr used lattice energy minimisation to predict structures at 0 K for a wide range of hydrocarbons. The parameters in their potential function were then refined to give structures closest to experiment. In contrast, Karistrom et al. made an ab initio quantum mechanical calculation of the interaction energy of two benzene molecules in 72 dimer configurations. The results were then fitted to a sum of atom-atom potential functions of the form,

\[
\phi_i(r) = \frac{A_i}{r} + \frac{B_i}{r^4} + \frac{C_i}{r^6} + \frac{D_i}{r^9} + \frac{E_i}{r^{12}}
\]  

(1.2)

where \( i = \text{C-C}, \text{C-H}, \text{H-H} \). The values of \( A_i \) were obtained from the experimentally determined quadrupole moment. The \( B_i \) were constrained so that

\[
36B_{\text{C-C}} + 72B_{\text{C-H}} + 36B_{\text{H-H}} = 0
\]  

(1.3)

and, as it is assumed [11] that the electrostatic effects are screened at large distances, the long range part of the potential is the \( 1/r^6 \) term. The values obtained for the parameters are given in Table 1.1.

Whereas the potential of Williams and Starr was specifically obtained to be transferable between different molecules, the potential of Karistrom et al. is not transferable [11]. The individual atom-atom terms in the Karistrom potential have some strange features, such as that, even excluding electrostatic terms, the long range H-H interaction is repulsive. Therefore the atom-atom interactions cannot be considered as individual interactions, but rather as a suitable interpolation framework for the calculated intermolecular data, and they only have significance as part of the whole group of interactions.

Although it is not transferable, the Karistrom potential represents a considerable step in the process of obtaining better interaction potentials, as it is based
on a largely \textit{ab initio} calculation, rather than by an empirical fit to crystal data. It also predicts molecular orientations and axial ratios in the solid very well, and unlike the potential of Williams and Starr it predicts a T-shaped dimer. It is for these reasons that it is the Karlstrom potential that is exclusively studied in this thesis, although it is slightly modified in Chapter 4. At the level of approximation of the derivation of the potential, the effect of deuteration will be negligible, so that the potential can be justifiably used to simulate the deuterated compound.

**Beyond Atom-Atom Potentials**

A question that is sometimes asked is: can we obtain a description of the benzene-benzene interaction that is not in the form of a sum of central atom-atom potentials? There are two basic motivations for this question.

The first is to try to reduce the computational complexity of a twelve site model that involves calculating 144 interactions between two molecules. Such methods generally involve attempting to replace several interaction sites with a combined ellipsoidal interaction, but so far these attempts have not been shown to give particularly accurate crystal structures\cite{33, 34}, or have been concerned with simulating the liquid\cite{35}.

The second aim is to obtain a potential that more accurately reflects the anisotropy of the electron distribution around bonded atoms. The problem with attempts to find such a potential is that there is a plethora of possible functional forms that could be chosen for the interaction. An attempt to obtain a potential of this type has been made by Yashonath \textit{et al.}\cite{36}, but without great success. The major problem with all the potentials presented in \cite{36} is that in their Monte Carlo simulation at 218 K they do not give the stable phase as orthorhombic: at least one of the interaxial angles is distorted significantly from a right angle in each case. They reported structural parameters for the orthorhombic phase at 0K from energy minimisation, but this may have been constrained to be orthorhombic, or it may simply be only a local minimum. The temperature variation of the cell parameters for their best model BENZ6 is also anomalous, The changes across the range 0 - 218 K being $\delta a = 0.18$, $\delta b = 0.63$ and $\delta c = 0.03$ Å. Making a reasonable classical extrapolation\cite{11} of the data from Chapter 2 to 0 K then experimentally the changes would be $\delta a = 0.09$, $\delta b = 0.20$ and $\delta c = 0.22$ Å. The huge discrepancies between the model and experiment may be due to the artificial
constraints at 0 K, but nevertheless the model seems severely flawed. It will be shown in Chapter 4 that a slightly rescaled Karlstrom potential gives an excellent temperature dependence of the lattice parameters, and so it seems that a sum of central pair potentials still remains the best compromise between the number of variable parameters and adequacy of the model.

### 1.4 Previous Simulations of Benzene

Whilst many potentials have been proposed for benzene, there has been comparatively little simulation work carried out. This is primarily because the computing power required to perform either molecular dynamics or Monte Carlo simulations is very great and the methods are only feasible with modern supercomputers. In contrast, lattice dynamics and lattice energy minimisation make only modest demands on computer resources, and these were the techniques used in the past to assess potentials.

Much of the simulation work has been directed towards simulating the liquid [37, 38, 39, 40, 11, 35]. The only simulations of the solid have been Monte Carlo simulations by Linse et al.[41], and Molecular Dynamics simulations, by Anderson et al.[42], Linse et al.[43] and Yashonath et al. as described above.

Both studies by Linse et al. were carried out at only two temperatures and at enforced experimental densities which correspond to very large negative pressures of \( \approx -10 \) kbar. These two studies were in fact more concerned with the local structure in the liquid than the properties of the solid.

The work of Anderson was made at one temperature for a very small sample of 32 molecules, but is unique in having included the internal degrees of freedom of the molecule. The calculated internal vibration frequencies were found to be in excellent accord with experiment, and were shown to be well separated in frequency from the external (lattice) modes, which supports the use of the rigid-molecule approximation when it is the properties of the benzene lattice that are of interest.

The simulations reported in this thesis test the Karlstrom potential much more thoroughly than any previous potential for benzene has been tested. In particular, the increased computing power available has made it possible to study the structure and dynamics of the model system across a wide range of temperatures. This provides a much more demanding test of the potential than, for instance,
simply determining the 0 K structure, since the complete shape of the potential is probed, rather than just the position and form of its minima. It has also been possible to go beyond simply testing the potential, and use molecular dynamics as a complementary technique to experiment.
Chapter 2

A Neutron Powder Diffraction Study

This chapter reports a neutron powder diffraction experiment to study the structure of the benzene at a range of temperatures. In order to explain the motivations for this study it is first necessary to discuss the idea of premelting.

2.1 Premelting

The term premelting [7] is used to describe any changes in the properties of a crystal that are observed as the melting transition is approached, and that are believed to be causally related to the melting transition. The significance of any such changes is linked to an understanding of the phenomenon of melting [7, 44], about which there are two basic views.

The first considers melting to be a classic first-order phase transition, in which there are two completely distinct phases: one is the high order, low energy and low entropy solid; the other is the disordered, higher energy and higher entropy liquid. At a certain temperature the free energy of the liquid becomes lower than that of the solid and so the solid melts (Fig. 2.1). The crucial idea here is one of thermodynamic stability: the solid is still considered to be mechanically or elastically stable above the melting point, at least for a small region of temperature. In such a view, the solid phase can be said to be 'unaware' of the approach of the melting transition with increasing temperature, so that there should be no corresponding anomalies in any of its properties.

The opposite view was initially put forward by Born [45]. This made the
assertion that one of the properties of a liquid is its lack of resistance to a shear stress, so the melting transition may correspond to an elastic instability of the solid where the shear modulus vanishes. In this theory, the solid is inherently unstable above the melting point, and anomalies would be expected in properties such as the elastic constants or the lattice parameters as the melting transition is approached. Any such anomalies are the so-called 'premelting' effects. There have also been other proposals of the mechanism for the instability being the catastrophic build up of defects [46, 47]; the discussion in this work is restricted to the notion of an intrinsic premelting effect in the lattice, as it is this that can be studied by diffraction experiments.

As recounted by Boyer, Born later retracted the instability theory of melting [48] as no premelting effects were found [49]. It should be pointed out immediately that the experimental study of the bulk properties of a solid near the melting transition is rather difficult because of the effects of impurities. These cause melting to occur across a finite range of temperature, as more impure regions of a solid will melt at a slightly lower temperature than the melting point of the pure solid [50]. This can cause the abrupt changes of, for instance, internal energy and volume to be smeared out over a small temperature range, giving the appearance
of pretransitional effects, and this problem can be very difficult to eliminate.

A fact that has been used in support of the instability theory of melting is that whereas the supercooling of liquids is a commonly observed phenomenon, the superheating of solids has only ever been demonstrated \cite{44} over very short timescales and for rather specially prepared samples. It has been argued that this indicates that the solid is inherently unstable above the melting point, whereas the liquid can be thermodynamically metastable below the melting point. Adherents to the first-order theory counter this argument by claiming that this is a problem of nucleation, not one of stability. In the case of supercooling, a liquid cannot crystallise until a suitable nucleus forms, and this nucleation may not occur until well below the melting point (where the free energy driving force is sufficient). On the other hand, in a solid there are always many defects present in the form of dislocations, vacancies, grain boundaries and surfaces, which can nucleate the melting process \cite{51, 52}. In a simulated solid, the case is rather different as the sample can be free of defects, so that superheating can occur as discussed in Chapter 4.

**Reports of Premelting in Benzene**

Despite a lack of convincing experimental evidence for the instability theory, it is possible that molecular crystals may show melting behaviour different to other types of crystal, as there is the possibility of orientational disorder in the solid \cite{3}, and local orientational order in the liquid \cite{53}.

An x-ray study of the lattice parameters of benzene as a function of temperature close to the melting point was recently reported by Tohji and Murata \cite{8}. They observed large changes in the relative intensities of several diffraction peaks as the melting point was approached, along with a very large expansivity of the c lattice parameter and of the cell-volume. They claimed that the results were qualitatively consistent with a change in the orientations of the molecules within the unit cell that would bring the structure closer to the local structure found in the liquid \cite{53}. This is a direct claim of a premelting effect where the structure of the solid is modified, at least partially, towards that of the liquid.

Further support for a premelting effect in benzene came from recent measurements by Pruzan et al. \cite{9} of the bulk thermal expansivity, $\alpha_V$, of a range of molecular crystals including benzene. The results were claimed to show a power
law divergence of $\alpha_\nu$ in these crystals as a function of pressure on approach to the melting transition. It was argued that the effect of impurities could be separated out in these measurements, leaving an inherent premelting effect, and that the effect would also be expected as a function of temperature.

There has also been a report of the anomalous softening of some Raman modes of benzene close to the melting point [54], although the evidence for this in the literature is somewhat conflicting, as discussed in Chapter 5.

It was partly in an attempt to substantiate the claims of premelting that the present diffraction experiment was undertaken. The intention was to cover the same temperature range as Tohji and Murata, collecting data at intervals of 1–2 K in the 10 K below the melting point.

### 2.2 Experimental

A second motivation for the study was that the molecular dynamics simulations that are presented later in Chapter 4 study the structure of the benzene crystal across a wide temperature range, as predicted by the model potential, and in order to make a critical examination of these results it is necessary to have corresponding experimental data. Prior to the present work a complete coverage of the solid temperature range at ambient pressure was lacking for either the hydrogenated or deuterated compound separately; as reviewed in Chapter 1, data had been obtained at low temperatures ($\leq 123$ K) for $C_6D_6$, and at higher temperatures ($\geq 138$ K) for $C_6H_6$. It was therefore desired to complete the coverage of the solid temperature range for one of these compounds, as whether there will be differences between the $C_6H_6$ and $C_6D_6$ crystal structures cannot be known a priori. Given the advantages of using neutron scattering rather than x-rays as discussed in Chapter 1, and the corresponding desirability of studying deuterated compounds, a neutron diffraction experiment of the deuterated compound was preferable.

#### 2.2.1 Advantages of Using a Powder

As discussed above, there is a general problem with working close to the melting point of a solid which is that even in very pure samples there will inevitably be impurities that cause there to be liquid present several Kelvin below the melting
point. Besides the problems that this can cause for the measurement of bulk properties, it can also make temperature control very difficult. This is because the latent heat needed to melt the solid can produce a thermal lag, so that the temperature stabilises much more slowly than is found further from the melting point. The best way to compensate for this problem is to take the sample completely through the melting transition, as the structure can then be determined right at the melting temperature. The gradual melting will be detectable by the appearance in the diffraction pattern of an increasing background corresponding to the liquid.

A powder sample is therefore much more suitable for this work than a single crystal, as the latter is much more difficult to prepare; a powder sample can be taken through the melting point and readily recrystallised as many times as necessary during the experiment. As will be discussed, problems were encountered with the use of a powder, but these were overcome, and the certainty that the sample was taken right up to the melting point was very important.

Neutron powder diffraction patterns were collected at the Institut Laue Langevin in Grenoble on the powder diffractometer D2B [55]. The sample consisted of 5 ml of deuterated analytical grade benzene contained in a 12mm diameter vanadium sample can, which was first packed with quartz wool in an attempt to prevent the formation of large crystallites. The can was filled with liquid, and cooled as rapidly as possible, at \( \approx 5 \text{ K/minute} \) down to around 5 K, in an attempt to form a good powder. The diffractometer was operated in high-flux mode, with a monitor count of 100000 neutrons at each position of the detector bank which was stepped through 100 \( \times 0.025^\circ \) steps.

### 2.2.2 The Problem of the Formation of Large Crystallites

The first patterns were obtained using a static sample and at temperatures of 5, 200 and 250 K which are well removed from the melting point; reasonable patterns were obtained, although the relative intensities showed small deviations from those predicted from the structure of Jeffrey et al. [21]. Within about 10K of the melting point, however, large changes in intensity were observed, coupled with a splitting of several of the peaks (Fig. 2.2, lower three patterns). Particularly noticeable were the increase in intensity of a peak around 46°, and the splitting
of the (111) peak at $\approx 20^\circ$ (shown in detail to the left of the complete patterns).

In isolation, the large changes in intensity might have been explained by changes in the orientation of the molecules as invoked by Tohji and Murata. The splitting of the peaks, however, is indicative of the problem of the formation of large crystallites within the sample, as illustrated in Fig. 2.3. A crystallite lying in the Bragg reflection condition diffracts at a slightly different apparent $2\theta$ angle depending upon its physical position within the sample. For a fine powder, many crystallites contribute to each peak and so a smooth and symmetric lineshape is obtained. If large crystallites grow in the sample, then only a few crystallites contribute to each peak and the peaks will appear to be split into a corresponding number of fine components. For the geometry of the D2B diffractometer (Fig. 2.3) the maximum peak splitting is $\approx 0.7^\circ$, which is consistent with the splitting seen in Fig. 2.2. The anomalies in the relative intensities of the peaks are also explained, as, for instance, a very large crystallite may happen to lie in the reflection condition for only one peak, making that particular peak very intense.

When a sample is initially cooled, it will supercool by around 20 K, depending on the cooling rate and the purity. This favours the production of a fine powder as increasing numbers of nucleation sites become available as the degree of supercooling is increased. Packing the can with quartz wool also improves the powder quality as the formation of large crystallites is hindered. When the sample is reheated to near the melting point, however, annealing of the small powder crystallites to larger crystallites can occur. The mechanism for this may be related to the enhanced surface diffusion that is observed several Kelvin below the melting point in, for example, methane adsorbed on graphite [56], or it may simply be due to the presence of liquid benzene below the melting point around any impurities.

When the sample can was spun about the $2\theta$ axis, both the splitting effects and the intensity changes were eliminated (Fig. 2.2, upper two patterns). This is because spinning the sample brings many crystallites into the diffraction condition for each peak. The resulting asymmetric lineshape is due to the instrumental resolution function, which is determined by the spectral spread and collimation of the incident neutron beam.
Figure 2.2: The evolution of the diffraction pattern near the melting point. The lower three patterns are for a static sample can. The upper two patterns are for the case where the sample can was rotated about a vertical axis. The plots to the left are expansions of the data between $19^\circ$ and $21^\circ$ in the main figure.
2.2.3 Temperatures Studied

Patterns were obtained at 5, 200 and 250 K with a static sample, and at 105, 260, 270, 272, 274, 275, 276, 277, 278, 279, 280, 281, 282, and 283 K, with the spinning sample. These temperatures were the nominal 'requested' temperatures. For the static patterns, the actual sample temperature was measurable by a thermocouple mounted in the sample holder. A problem arose with the use of the spinning sample holder, in that the sample temperature sensor was faulty and the temperature could not be read by the data-collecting computer. It could, however, be read 'manually' and this was done just before the scans at a requested temperature of 105, 260, 280, and 283 K. The sample temperatures for intermediate temperatures were interpolated.
For large temperature changes the sample was allowed to equilibrate for at least one hour once the requested temperature was obtained. For the smaller temperature changes of one or two Kelvin, the time between the change in temperature and the scan was fifteen minutes, and the duration of the scan was thirty minutes, giving a mean equilibration time of approximately thirty minutes. At the melting point, a background corresponding to the liquid first appeared in the scan at the interpolated temperature of 279.5 K which is in accord with the true melting point of 280.0 K for \( C_6D_6 \). The pattern at the measured temperature of 280.4 K is therefore believed to be at the same actual sample temperature as the previous pattern, right at the melting point of the solid. Following collection of this pattern, data collection continued, and the sample was observed to completely melt.

2.3 Results

The patterns were analysed using the Rietveld refinement program PROFIL [57]. The refined parameters were the lattice parameters, the atomic positions (subject to constraints described below) and isotropic thermal parameters for the carbon and deuterium atoms. The zero error for 2\( \theta \) and the lineshape parameters were fixed on values obtained from a calibration on a sample of powdered nickel. Using \( a_{Ni} = 3.524 \) Å at room temperature [58], the wavelength was determined as 1.593 Å.

The molecular geometry was constrained to be a perfect hexagon, with \( r_{C-C} = 1.39 \) Å, and \( r_{C-D} = 1.08 \) Å. When these constraints were relaxed, distortions resulted which were much larger than those found by Jeffrey et al. This indicated that the quality of the data was not sufficient to allow refinement of the distortion; the patterns contained approximately 100 reflections, in contrast to the single crystal data of Jeffrey et al. where over 900 reflections were observed. Two sample fits are shown in Fig. 2.4, for 105 and 270 K. The range of fitting was 18° < 2\( \theta \) < 130° for 5 and 105 K, and 18° < 2\( \theta \) < 80° for the higher temperatures.

The results are given in Table 2.1. Errors are quoted for the cell parameters as estimated standard deviations from the refinement program. The orientation of the molecule is given in the table as four angles, which over-determine the orientation, but are useful quantities for later discussion. The first three angles,
Figure 2.4: Two example refinements, at (a) 105K, and (b) 270K. The points are the observed data ($I_{obs}$), the solid line is the calculated pattern from the refinement ($I_{calc}$). The lower curve in each figure is the difference, ($I_{obs} - I_{calc}$).
\( \theta_a, \theta_b \text{ and } \theta_c \), are the angles between the normal to the plane of the molecule and the three crystal axes. The angle \( \gamma \) is the angle between the \( C_1-D_1 \) bond and the \( b \)-axis (see § 1.1, and Fig. 1.3). The refinement program gave the errors on \( \theta_a \) and \( \theta_c \) as approximately 0.2°, and for \( \gamma \) and \( \theta_b \) as 0.1°.

For the points at 5, 200 and 250 K, which were obtained without spinning the sample, the lineshape is apparently undistorted, so that the lattice parameters were thought to be reliable. The refined molecular orientations, however, depend upon the intensities of peaks, and the patterns were not found to give reasonable values for the orientational parameters. This is reflected in the values of the intensity R-factor, \( R_P \), which are given in Table 2.1. \( R_P \) is defined as

\[
R_P = \sqrt{\frac{\sum (I_{obs} - I_{calc})^2}{\sum I_{obs}^2}} \times 100
\]

(2.1)

where \( I_{obs} \) are the integrated intensities of the observed data, and \( I_{calc} \) are the corresponding values in the calculated pattern. These values indicate that the fit is significantly worse for the data where the sample was not spinning. The orientational data is therefore only given for the case of the spinning sample.

### 2.4 Discussion

The results are plotted in Figs 2.5, 2.6 and 2.7, along with the literature data. The curves plotted are the smoothest interpolations that could be drawn by eye through the data. The curve for the cell-volume is simply obtained as a product of the curves for \( a \), \( b \), and \( c \).

There is good agreement between the point from this work at 105 K, and the data of Jeffrey et al. This confirms the calibration of the neutron wavelength, which is particularly important as several sets of data are being combined. The data at 5K is not in such good accord, which may indicate that the lattice parameters for temperatures where the sample was not spun may not be as reliable as for temperatures where the sample was spun. There is no systematic difference between the data for the hydrogenated and deuterated compounds, apart from the data of Kohzin which must now be discussed.
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Table 2.1: Structural data from the refinements. $T_{\text{req}}$ is the requested sample temperature and $T_{\text{samp}}$ is the actual sample temperature. Temperatures marked with an asterisk were measured; the remaining values were interpolated (see text). Angles are in degrees.
Figure 2.5: The variation of $a$, $b$, and $c$ with temperature, from this work and from the literature.
Figure 2.6: The variation of the cell volume with temperature, from this work and from the literature.
Figure 2.7: The variation of orientations of the molecules with temperature, from this work and from the literature. The angles are defined in the text.
2.4.1 A Reported Phase-Transition

The temperature dependence of the lattice parameters of benzene are clearly well described by continuous smooth curves, with no evidence for any discontinuities, the major exception to this being the point at 78 K due to Kohzin [18]. This has been used by Thiery and Leger [15] as supporting evidence for a phase transition at a temperature of \( \approx 100 \) K, and it is worthwhile examining their argument.

The equivalent of Fig. 16 of Ref. [15] is replotted in Fig. 2.8, where the authors plotted the crystallographic data for \( C_6H_6 \) at ambient pressure from [19, 20, 18], and room temperature variable pressure data from their own work.

The data was plotted in a rather peculiar way, as cell parameters versus cell volume.
volume. The authors claimed that there is a phase transition at a cell volume of \( \approx 470 \ \text{Å}^3 \), since the data lies on two disjoint lines (for \( a \) and \( b \)). One line is for the point of Kohzin and the high pressure data, and the other is for the data of Cox et al. and Bacon et al. The data of Jeffrey et al. was mentioned, and the fact that it does not confirm the results of Kohzin is attributed to either a different transition temperature for the deuterated substance or to a large hysteresis.

It is not clear that the quality of the data warrants the claim that the data lie on two different lines, but even so this seems to be a fallacious way of presenting the data. The tacit assumption is that, within a single phase \( a(V), b(V) \) and \( c(V) \) are three universal functions independent of whether \( P \) or \( T \) (or both) are varied. A corollary of this is that if the pressure and temperature are changed in such a way as to leave the volume constant, then \( a, b, \) and \( c \) all remain constant also. Whilst such a relationship has been proposed for benzene [59], there is only rather indirect evidence from Raman data. Thus, the fact that the data do not lie on the same lines in Fig. 2.8 is not necessarily evidence of a phase transition at all, since an unjustified comparison of variable temperature and variable pressure data is being made. Furthermore a much more justified comparison is between the data in Fig. 2.8 that is for room temperature, and the extrapolation of the ambient pressure data from the present work to room temperature (in an albeit mythical superheated solid phase). This extrapolated point is shown by the asterisks plotted in the figure. The dashed lines show that the low and high cell volume data at room temperature are quite consistent with the existence of a single phase.

Such an interpretation leaves Kohzin's results in doubt. Since the major discrepancy is that \( a \) is too low and \( b \) is too high, then the error may be caused by correlation of the lattice parameters in the fitting procedure used to extract the lattice parameters. Few details were given in Kohzin's very brief report.

### 2.4.2 Molecular Orientations as a Function of Temperature

The orientational data in Fig. 2.7 also shows good agreement between this work and the literature. The data confirms the observation made by Bacon et al. and Jeffrey et al. that, with increasing temperature, the molecular plane approximately rotates by about 2° around the \( b \)-axis of the crystal, bringing the plane more parallel to the \( c \)-axis. This is presumably correlated with the much greater
expansivity in $c$ than in $a$: the change in angle produces changes in the projection of the molecular diameter onto the $a$ and $c$ axes which is approximately the same as the difference in the overall change in $a$ and $c$ across this temperature range.

The behaviour of $\gamma$ and $\theta_b$ are somewhat peculiar, as they both have very steep slopes near the melting point. This has not been previously noted, and is discussed further below and in greater detail in Chapter 5. The data for $\theta_a$ and $\theta_c$ near the melting point show rather larger scatter than the data for $\gamma$ and $\theta_b$. This is not fully understood, although the errors from the refinement program are larger for $\theta_a$ and $\theta_c$ but not to the same extent as the difference in scatter. Neither could an adequate explanation for the anomalous value of $\theta_b$ at 105 K.

2.4.3 Pretransitional Effects

The Claims of Tohji and Murata

Based on the observation of the intensities of only seven reflections Tohji and Murata [8] proposed several models for a premelting effect over the last 10K prior to melting. None of these models provided quantitative descriptions of the intensity changes that they reported, but their final conclusion was that a rotation about the $b$-axis occurred similar to that described above, but by at least 10° between 265 and 278 K. Our data, which is based upon a complete powder refinement, shows that no such large rotation about the $b$-axis occurs, and neither have we seen the dramatic increase in the $c$ parameter by 0.1Å in a temperature interval of 6 K that they report.

It appears that the results of Tohji and Murata are in fact explainable purely by the formation of large crystallites in the sample. It has been shown in our neutron powder diffraction study that the powder anneals very rapidly near the melting point, and therefore the energy-dispersive technique that they used is totally unsuited for this kind of study:

- The white x-ray beam will induce significant local heating in the sample, which will accelerate the annealing process, and make the temperature control difficult.

- The resolution of the technique is very poor, so that the formation of very sharp, intense lines associated with the formation of large crystallites will not be detected.
It is therefore concluded that the changes in structure claimed by Tohji and Murata were in fact artefacts caused by the formation of large crystallites in their sample. The crystallites would have produced the large changes in the intensities of peaks that they observed, and caused errors in determination of cell parameters by the distortion of peak shape. This underlines the need for care when working close to the melting point with a powder sample.

Remaining Anomalies

Whilst the very large effects reported by Tohji and Murata are believed to be artefacts of their method, there are features of Figs 2.5 and 2.7 that do indicate some change in behaviour above about 230K. The first is the behaviour of $\gamma$ and $\theta_b$ that has been mentioned above, and the second is that slope of the $b$-parameter appears to become anomalously large in the same range. In fact, the slope of the $b$ becomes greater than that of $c$ whereas the opposite is true at lower temperatures. This is strong evidence that the large slope of $b$ that is seen is not due to imperfect temperature control, as this would have an equal effect on the $c$-parameter.

In themselves, these effects are not conclusive evidence of significantly anomalous behaviour. However, it will emerge in Chapters 4 and 5, that it is believed that they are the first indications of a transition in which $\gamma$ drops to zero, but it is a transition that would occur at a higher temperature than the melting point. It should be emphasised here, in order to avoid misunderstanding, that it is not believed that this is a premelting effect as such. The molecular dynamics results are vital in understanding this, so a full discussion must be left until Chapter 5.

There appears to be no significant anomaly in the behaviour of the cell-volume as the melting point is approached which means that there is no evidence in the data for a microscopic explanation for the results of Pruzan et al.

2.5 Conclusions

This work has established a complete description of the variation of the crystal structure of the benzene I phase as a function of temperature right up to the melting point, and it has been shown that the structures of the deuterated and hydrogenated compounds are essentially identical. The variation of all parameters with temperature is smooth, but the angle $\gamma$ and the $b$ parameter have anom-
iously large slopes above about 230 K; this will be the subject of discussion in Chapter 5.

Several claims in the literature have been disputed, namely the existence of a phase transition around 100 K, and of a marked premelting effect. The explanation of the results of Tohji and Murata emphasises the important effect that the formation of large crystallites can have in a powder diffraction experiment near to the melting point. It has been shown, however, that with an appropriate experimental method reliable results can be obtained.
Chapter 3

Computational Details

This chapter is in two parts. The first part gives details of the methods used to perform the simulations that are reported in later chapters. This is not intended to be a full exposition of the various techniques used in a molecular dynamics program, for which references are given, but rather to be in sufficient depth that it should be possible for a future worker to set up equivalent simulations. The choice of the values of various parameters are also discussed, and some quantities that are used in later analysis are introduced. The second part of the chapter describes the implementation of a rather general molecular dynamics program on a large transputer array.

3.1 Details of the Simulation Method

3.1.1 Simulation Algorithm

Representation of Orientations

Molecular orientations were represented by quaternions[60]. A quaternion has four components which can be written

$$q = (q_1, q_2, q_3; q_4)$$

(3.1)

A rotation by an angle $\theta$ in a right handed sense about a normalised vector $r$ is represented by the quaternion,

$$q = (r_1 \sin(\theta/2), r_2 \sin(\theta/2), r_3 \sin(\theta/2); \cos(\theta/2))$$

(3.2)
A quaternion can readily be converted into a rotation matrix. A simple formula exists [60] for combining quaternions, which gives the quaternion $q'$ representing the effect of two successive rotations, $q_1$ followed by $q_2$. This is written

$$q' = q_2 \cdot q_1 \tag{3.3}$$

As quaternion 'multiplication' represents the combination of rotations, it is not commutative except for quaternions representing rotations by small angles.

![Diagram of molecular frame](image)

Figure 3.1: The molecular frame used in the simulations. The numbering of atoms is consistent with the quaternions given in Table 4.1 and the numbering of atoms in Fig. 1.3

The coordinates of the atoms in the molecule are defined in the *molecular* frame, and, at any moment, the *real space* coordinates of the atoms of a particular molecule can be obtained by applying to the molecular frame atomic coordinates the rotation matrix formed from the quaternion for the molecule. Figure 3.1 shows the conventional molecular frame used here and in most of the literature.

**Timestepping Algorithm**

The Beeman timestepping algorithm[61] was used with modifications for the timestepping of quaternions[2]. This algorithm has been found to be satisfactory in the simulation of molecular crystals with rather sharp short range interactions.

A timestep of 0.01 ps was used at all temperatures. This value was chosen because of the criterion that the timestep should be about $1/20$ of the period of the highest frequency mode in the system[62], which for benzene is $\approx 4$ THz.
The best practical test of whether the timestep is short enough is to determine how well the total energy of the system is conserved. The short-term fluctuations were found to be $\sim 0.1\%$, but the drift was very low, by less than $0.001\%$/ps measured during a long run of 100 ps near the melting point. When the timestep was increased to 0.015 ps the drift was found to deteriorate significantly at the higher temperatures studied; no corresponding improvement was found if the timestep was reduced to 0.005 ps, so that the value of 0.01 ps was believed to be near-optimal.

The Parrinello and Rahman scheme[63] was used to maintain constant stress in the sample, this being an extension of the constant pressure method of Anderson[64]. The term 'constant pressure' is often used synonymously with 'constant stress' since we are generally interested in the application of hydrostatic pressure. The critical difference between the true constant stress method and the constant pressure method is that the former allows the cell to distort in shape allowing phase transitions to space-groups of different lattice symmetry.

In the constant stress method, the coordinates of the atoms are stored in reduced units, $s_i$, such that the real space coordinates $r_i$ are given by

$$r_i = h_{ij}s_j$$

where $h$ is the matrix whose columns are the vectors that define the edges of the so-called MD-cell. Periodic boundary conditions are enforced by requiring

$$0 \leq s_i < 1$$

so that if a molecule leaves one side of the cell it re-enters at the other side.

The stress in the sample is calculated via the virial theorem[65]. The $h$-matrix then has dynamics that are governed by an imbalance between the instantaneous stress and the mean (requested) stress, the latter generally being equivalent to a hydrostatic pressure. In this way the cell can expand as the temperature is increased, or contract in response to an applied pressure. Further details of the method, especially as applied to molecular systems, can be found in the paper by Nose and Klein[65]. Following Refson et al.[2] an extra predictor step was inserted in the Beeman algorithm to calculate velocities that are needed to calculate certain extra forces in the Parrinello and Rahman scheme.

In the constant stress algorithm, the size and shape of the cell oscillates about its mean structure (see Chapter 4). The timescale of these fluctuations is determined in the Parrinello and Rahman method implicitly by the elastic moduli of
the sample and, explicitly, by a model parameter, $W$, called the piston-mass. The time-averaged properties of the system are independent of $W[65]$, but in order that the system equilibrates reasonably rapidly the value of $W$ must be chosen carefully. The consensus [64, 65] is that $W$ should be chosen such that the period of oscillations of the cell, $T$, should be roughly equal to the sound crossing time of the cell. From Nose and Klein[65],

$$T \approx 2\pi \sqrt{\frac{W}{3LB}},$$

(3.6)

where $L$ is the typical linear dimension of the MD-cell, and $B$ is the bulk modulus. The sound crossing time, $\tau$ is

$$\tau \approx L \sqrt{\frac{\rho}{B}},$$

(3.7)

where $\rho$ is the density. Equating these two relations gives

$$W \approx \frac{M}{10}$$

(3.8)

where $M$ is the total mass in the MD-cell. The value used in simulations was calculated according to Eqn.(3.8).

3.1.2 Potential Function

The potential used was that due to Karlstrom et al.[32], see Chapter 1, or as slightly modified in Chapter 4. In order to avoid computing interactions that are negligibly small, the potential was truncated with two cutoffs, $R_{\text{inner}}$ and $R_{\text{outer}}$, applied according to the real-space separation, $d$, of the two interacting molecules:

- $d \leq R_{\text{inner}}$
  the full potential function and corresponding force function were used;

- $R_{\text{inner}} < d \leq R_{\text{outer}}$
  A simple centre-centre interaction was used[41], approximating the molecules to point-like particles. The atomic interaction sites were subsumed into two sites, one at the centre of each molecule, and all but the $(1/d)^6$ terms are neglected. The potential function was then

$$\phi(d) = -\frac{36A_{C-C} + 72A_{C-D} + 36A_{D-D}}{d^6}$$

(3.9)

$$= -\frac{A_{\text{comb}}}{d^6}$$

(3.10)
The interaction was neglected, but approximate corrections were made to
the pressure and potential energy to allow for these neglected interactions.
These corrections were calculated by assuming a continuum distribution of
point-like molecules interacting via 3.9, which gives

\[
\phi_{\text{corr}} = \frac{2}{3} \pi \frac{N A_{\text{comb}}}{V R_{\text{outer}}} \\
P_{\text{corr}} = \frac{\phi_{\text{corr}}}{V}
\]

(3.11) (3.12) (3.13)

where \( \frac{N}{V} \) is the number density of molecules in the system

It is possible that the truncations in the force can cause instabilities in the
numerical integration algorithm. This was not believed to be a problem here,
as it was found that the fluctuations of energy were similar in simulations of an
isolated cluster of molecules where no cutoffs were applied.

Initially an inner cut-off of \( R_{\text{inner}} = 10 \text{ Å} \) was tried, and with \( R_{\text{outer}} = R_{\text{inner}} \)
(i.e. no outer shell of pointlike molecules). The value of 10 Å was chosen on the
basis of the figures in [32] and [11], which show that the intermolecular interaction
is very small at this separation. Problems were encountered near the high tem-
perature lattice instability (see Chapter 4), however, as the results were found to
be significantly different to those with \( R_{\text{inner}} = 12 \text{ Å} \). This must reflect in part the
softening of the lattice at these high temperatures, making the effect of the ne-
glected interactions important. In order to be certain that there were no artefacts
induced by the cutoffs, values of \( R_{\text{inner}} = 12 \text{ Å} \) and \( R_{\text{outer}} = 15 \text{ Å} \) were used at all
temperatures. A few trial simulations with \( R_{\text{inner}} = 15 \text{ Å} \) gave identical results;
lattice energy minimisation indicated that no greater cutoff was necessary at 0K,
indeed it indicated that the major influences on the orientations of the molecules
came from the inner two coordination shells of molecules.

With values of \( R_{\text{inner}} = 12 \text{ Å} \), and \( R_{\text{outer}} = 15 \text{ Å} \), approximately fifty molecules
are included within \( R_{\text{inner}} \) and approximately fifty between \( R_{\text{inner}} \) and \( R_{\text{outer}} \). The
latter interactions are much simpler than the interactions for \( d < R_{\text{inner}} \), so that
the computational effort required is largely negligible.
3.1.3 The Sample

The system consisted of 864 molecules of deuterated benzene arranged in a cuboid of $6 \times 6 \times 6$ unit cells of the phase benzene I, except for some simulations mentioned in Chapter 5 where only 256 molecules were used in an attempt to assess finite size effects. The choice of 864 molecules was determined as a balance between having as large a system as possible in order to best approximate an infinite thermodynamic system, and limiting as far as possible the computer time that was required. It was found that with a system of 864 molecules $\sim 250$ ps of simulation time could be simulated in a typical ‘overnight’ run with 131 transputers, which was the computing resource generally available (see § 3.2). This was felt to be a practical timescale, and 864 molecules is certainly larger than any previous simulations that have been run for benzene. Larger simulations of similar molecules have been run, for instance in [28], but in that particular case the sample size was restricted to be large by the nature of the parallel computer architecture that was used.

The temperature fluctuations in a system of $N$ rigid molecules are given approximately by [66]

$$\langle (T - \langle T \rangle)^2 \rangle \sim T^2/2N \quad (3.14)$$

For the system of 864 molecules at 250 K this gives r.m.s. $\delta T \approx 6K$, which is adequate precision for the present work.

The molecule was represented by a rigid perfect hexagon, with $r_{C-C}$ and $r_{C-D}$ bond lengths of 1.395 and 1.084 Å respectively, as used in the derivation of the potential of Karlstrom et al. [32]. Masses of 12 and 2 a.m.u. were used for the C and D atoms.

Periodic Boundary Conditions (PBC) were applied[26], so that the system is considered to be replicated throughout space and therefore has no ‘edges’.

3.1.4 Simulation Procedure

Initialising the Sample

The system was set up initially as a perfectly ordered crystal, with the molecules on lattice sites and with orientations as found by energy minimisation. The h-matrix was set to approximately the value to be expected at 100K, based on
lattice energy minimisation and experimental expansivities. The molecules were given random velocities corresponding roughly to a temperature of 100K. The applied pressure was set to be zero, which is effectively atmospheric pressure for a solid.

The simulation was first run with a very short timestep of 0.001 ps. This procedure was to allow for the fact that the random velocities chosen at the start may bring some molecules unphysically close together; the short timestep allows the system to adjust without the total energy diverging. After 100 timesteps with this short timestep, a timestep of 0.01 ps was used and the sample allowed to equilibrate for at least 50 ps. During this time, velocity rescaling was employed every 1ps. In the velocity rescaling procedure the linear and angular velocities of all the molecules are rescaled by a uniform factor to give a total KE corresponding to the desired temperature. During this primary equilibration phase the MD-cell matrix was monitored to check that the MD-cell stabilised to a mean size about which it made small oscillations (see Chapter 4).

Changing the Temperature of the Sample

Once such an equilibrated 'configuration' had been obtained further simulations could be run. Whenever a new temperature was to be studied a configuration that was the final configuration of a previous simulation at a similar temperature was used as the starting point, in order to accelerate equilibration. Temperature changes were effected by the velocity rescaling method described above.

It was found that following a modest temperature change of ~ 50K, properties of the system such as total energy and cell dimensions achieved stable mean values after about 10 ps. In order to be confident of the equilibration of the system, a standard equilibration time of 20 ps was allowed whenever the temperature was changed. After this period, the velocity rescaling ceased, and the simulation was allowed to run at constant energy, during which time measurements could be made.

The details of the temperatures and pressures at which particular simulations were run, and the way in which measurements were made, are given in appropriate sections of the following chapters.
3.2 Implementation of the Molecular Dynamics Program on a Transputer Array

The molecular dynamics technique is, in general, extremely computationally intensive; an idea of the scale of the computation involved in the present work can be obtained from the following order of magnitude calculation.

In the system described above there are 864 molecules, each interacting with approximately 50 other molecules within \( R_{\text{inner}} \); the interactions outside \( R_{\text{inner}} \) will not be considered here, as their effect on the calculation time is negligible. Each molecule-molecule interaction involves calculating 144 atom-atom interactions, and therefore in one time-step approximately \( 3 \times 10^6 \) atom-atom interactions must be calculated. It was found in this work that the calculation of each atom-atom interaction required approximately 35 floating point operations (flop), so that each timestep approximately \( 10^8 \) flop must be performed. Therefore, a moderately long simulation of 10ps of real time with a timestep of 0.01ps requires approximately \( 10^{11} \) flop. This currently makes molecular dynamics a supercomputer problem, especially if other than very short simulations of small systems are to be made; ‘currently’ because the term supercomputer is a term that only has meaning in relation to current technology.

3.2.1 Parallel Computers

Parallel computers [67] offer a method of obtaining the supercomputing power that is required for molecular dynamics simulations. The basis of such computers is to have several processors work on different parts of a calculation concurrently so that the performance of the computer as a whole is much greater than that of the component processor. The field of parallel computing is both young and rapidly developing, and there have been proposed many, often experimental, computer architectures. In general, the machines can be divided into two broad categories:

- Multiple Instruction Multiple Data (MIMD). In this type of parallel computer each processor runs its own, effectively serial program, independently, and communicates data to other processors as necessary during the calculation. The present work was performed on a transputer array, which is an MIMD machine.
• Single Instruction Multiple Data (SIMD). In an SIMD machine all processors perform the same instructions in lock-step, but each processes its own data. The processors are generally arranged in a regular array, either as a 2D array, or as a higher dimensional hypercube. The Distributed Array Processor (DAP)[67] is an example of an SIMD machine.

There are three main problems with obtaining the optimal efficiency in a parallel program: extra time is spent in communicating the results between processors; time can be wasted whilst processors wait for other processors to finish their calculations (load imbalance); and extra calculation may be necessary to enable the parallel decomposition of the problem.

Molecular dynamics is ideally suited to the use of parallel computers. The problem parallelises very naturally, since at each timestep a very similar calculation must be carried out for all molecules, namely computing the intermolecular forces and updating the positions and velocities of the molecules. It will be shown below that the very large amount of calculation required per timestep renders communication-time almost negligible for the application considered here, and that good load balance can be achieved.

The implementation of molecular dynamics programs on an SIMD machine has been considered by, for instance, Pawley et al. for the DAP[68]. Whilst the DAP is well suited to simulating regular lattices, it is not so suitable for simulating systems with disorder[28]. This is because the positions of the molecules do not then map directly on to the regular array of processors.

An MIMD machine is more flexible than a SIMD machine, since the program running on each processor can be effectively a serial program. Several authors [69, 70, 71] have considered the MIMD implementation of molecular dynamics from a rather abstract point of view, but at the time of writing of the program there were only three other reports of implementations of actual applications of molecular dynamics on transputers [72, 73, 74]. These were all of simple atomic systems, and with the exception of [69] used a small number of transputers, attempting to extrapolate to larger systems.

3.2.2 Transputer Arrays

The transputer arrays that are considered here have the Inmos T800 transputer as the component processor. A brief description of the important features
of the T800 transputer is given below; for more detail the reader is directed elsewhere[75].

On the single chip T800-20, there is

- the CPU which is a 32 bit RISC processor rated at approximately 10 MIPS,
- the FPU which can support 32 and 64 bit floating point arithmetic, with a peak rate of 1.5 MFlops (Million flop per second) for 32-bit arithmetic, and is generally capable of sustaining around 0.6 - 0.8 MFlops in scientific applications,
- four ‘links’, each of which allows bi-directional communication with another processor at a rate of ~1 Mbyte/s; the connections between processors are generally fixed during the running of a single program,
- 4K of on-chip memory with a 50ns access time,
- system hardware such as event interrupts, and timers.

The transputer can access up to 4 Giga-bytes of external memory, which typically has an access time of 200 ns.

There are two features that molecular dynamics simulations can exploit:

(a) the handling of communications by special circuitry on the chip which is separate from the CPU, and

(b) the use of standard techniques to improve the performance of the single-processor program.

Thus under (a), to initialise a communication, the CPU simply loads the appropriate link controller with the start address of a block of memory, and the number of bytes that it is to transfer. After this, the CPU can continue calculation provided that this does not depend upon data that is to be transferred into the processor. Whether this is possible or not depends upon the specific application. The only reduction in speed of calculation (apart from the start-up time) arises because the CPU and the link controller cannot both have access to the memory at the same time. There may thus be times when the CPU requires a memory access and has to wait because the link controller is still accessing memory. The maximum interference of this sort that may occur is one read and
one write operation per 32-bit word of transfer, and as this transfer is generally from external memory this represents a delay of $0.4\mu s$ per word. This is an order of magnitude less than the actual time to transmit the word along the link. The delay per word may however be substantially less than this, because there may be no interference if the CPU is not trying to access memory, but is instead waiting for the FPU to finish a calculation. Thus it is not at all clear that any simple analysis of a particular program can predict the true effect of the communications on efficiency, and it can only be discovered by timings of a practical program. These results are given in § 3.2.6. The relevance of the link speed here is in determining the duration of the communication, because this must be less than the calculation time for the calculation and communication to overlap and the above considerations to be valid. Provided this is the case then the link speed is irrelevant in determining the degradation of the efficiency of the program.

Under (b), the available standard techniques include 'unwinding' sequential loops by explicitly repeating lines of code, using aliases to find the position of an element of an array that is accessed several times, declaring variables locally to reduce the number of bytes required to code instructions, and allocating the fast internal memory efficiently. In a molecular dynamics program, over 90% of the time is generally spent evaluating interatomic forces, so that this short section can be intensively optimised as above to provide maximum performance.

A typical transputer system consists of a host computer to handle file and terminal i/o, along with boards holding the transputers and external memory. The present program was written for the Edinburgh Concurrent Supercomputer (ECS), which is a Meiko Computing Surface with some 400 transputers, each with at least 4 MBytes of memory. The processors are divided into domains, each of which is a single-user virtual Computing Surface. At present, the two largest standard domains contain 132 and 65 processors, and the smaller domains vary in size from 28 to just a single transputer for code development, some of the domains also having fast graphics capabilities. The connection of the links between transputers within a single domain is under the software control of the user prior to the running of a program: a typical connection scheme is shown in Fig. 3.2, this being the one used in the present program.

The ECS is a large multi-user computer, although the individual domains are not shared. The program has however also been run on a much smaller single-user
Figure 3.2: A ring based connection scheme for an array of transputers. The circles represent the processors, and the lines represent the links. Only two of the four available connections are used on each processor, except for the processor connected to the host computer. Such a ring can contain an arbitrary number of transputers.

system hosted by a PC, with only minor modifications caused by differences in the file-handling.

3.2.3 General Design of the Program

The parallel algorithm was developed with the following criteria in mind.

- It would not be designed specifically to simulate the benzene system of the present work.

- It should handle system sizes from a few hundred up to at least ten thousand molecules, and it would be primarily intended to handle simulations of polyatomic molecules, with perhaps 7 (sulphur hexafluoride), 12 (benzene) or even 26 (adamantane) atoms. It is these sorts of systems that really require supercomputer power. It was assumed that a spherical cut-off in the potential would be applied, which makes it a more demanding problem to parallelise than the case without a cut-off.

- If the computational load on each processor is too light, other factors may dominate and the efficiency would be reduced. It was always assumed that the load would be such that the minimum computation time per processor for a timestep would be approximately ~1s, and generally ~5s. This provides a very reasonable rate of simulation of \( \approx 1000 \) timesteps per hour.
for a typical case. The number of processors used can be matched to the system size (or vice versa) in order to achieve this load.

- It should handle both solid and liquid simulations of clusters or of systems with periodic boundary conditions in any of the three dimensions, and should run on a transputer array of arbitrary size. This last point is important if there are various fixed-sized domains on a system like the ECS, or where the maximum spare resources are to be utilised.

- It should assume a maximum of 4 MBytes per processor, but leave sufficient spare memory for the possible implementation of large look-up tables, or for computer systems with perhaps only 2 Mbytes per processor (the memory is often the most expensive part of the system).

In order to gain the generality required, the processors were simply connected in a ring as previously mentioned (Fig. 3.2). A more complex connection topology might be thought more suitable, since a spherical cut-off is used, but as it will be shown that the communication overheads are negligible then the ring configuration is perfectly adequate and preserves simplicity. A simple ring has the advantage that all processors are equivalent (apart from the one connected to the host), and is ideal for problems where the major communication is for each processor to transmit the same data to all the others. It is because we can easily overlap the communication and calculation that a simple uni-directional singly-connected loop was used. Only if the communication duration became more than the calculation time would there be any benefit at all in using either the unused links to boost the ring or a more complex connection topology than the ring.

Each processor runs a calculator process, and the processor connected to the host also runs a controller process in parallel. The controller reads and writes the configurations, the analyses, and the job-control files, distributes data to the calculators, gathers analysis data, and performs certain global calculations. During the main part of each timestep, the controller process is idle, so that all processors can be considered equivalent.
3.2.4 Algorithm

General

The molecular dynamics algorithm that was used has been described previously in this chapter. Since the systems to be studied are large and a cutoff is to be applied, a binning procedure was used similar to that described in [71], in order to eliminate the need to consider all molecule pair separations, as this latter scales as the square of the total number of molecules. In the binning procedure the simulation is divided into parallelepiped bins, of a size such that a molecule can only possibly have interactions with molecules in the same bin or adjacent bins. An alternative would have been to use a neighbour-list, but a binning method is trivial to parallelise, and simpler than the neighbour-list method should it be desired to exchange molecules during run-time between processors to improve load-balancing. The program was written in OCCAM-2[76], using single precision arithmetic.

Parallelisation

The outline of the algorithm is that each processor is responsible for the integration of the motion of a subset of the molecules, after which it broadcasts the new positions to all the other processors so that forces can be calculated. To this extent the algorithm is very similar to those used in [72, 73], however the order of the calculation and communication is rather simpler in the present algorithm.

The N molecules are distributed around the P processors as evenly as possible, N/P not necessarily being integral. The program can function quite adequately if the placement of molecules amongst processors is independent of their spatial position, thus facilitating simulations where, for instance, the molecules diffuse and thus change neighbours. As we shall see, however, the efficiency does improve if bunches of neighbouring molecules are placed on each processor.

In the first stage, each processor calculates the new positions and quaternions of the molecules allocated to it, and updates the binning as necessary, assigning a bin number to each of its molecules. Next, these new positions, quaternions and bin numbers (the 'world-map') are broadcast around the ring. In the first pass, each processor \([q]\) sends its new data to the next processor \([q+1]\) around the ring, whilst in parallel receiving equivalent data from the previous processor \([q-1]\). Next it notes and sends on the data it has just received, whilst receiving
from processor \([q-1]\) the data that originated on processor \([q-2]\). This continues for \(P-1\) passes, by which time all data has passed to every processor.

As explained above, it is generally important in the design of any algorithm for transputers that communication and calculation should be able to proceed in parallel: in the MD context this has been exploited by e.g. [72]. In this algorithm, the ‘world-map’ communication can be performed in parallel with the next stage of the calculation, which is that of ‘same-processor’ interactions (i.e. between molecules on the same processor), as the latter is clearly a calculation which does not depend upon information from other processors. It turns out that the calculation of same-processor interactions is of sufficient duration that only part of it need be done in parallel with the world-map broadcast. The rest can be reserved for calculation in parallel with the communication of forces and torques (see below). The effectiveness of this strategy is demonstrated by the timings in § 3.2.6.

Once the distribution of the world-map is complete, the calculation of interactions between molecules on different processors (‘cross-processor’ interactions) can proceed. The method differs from that of [72], where the world-map broadcast is divided up into a series of ‘pulses’, and the calculation of corresponding cross-processor interactions occurs between these ‘pulses’. This can lead to inefficiency as the processors must remain loosely synchronised at each pulse. All processors will not, however, have an identical computational load in each pulse, giving worse load-balance than in the present method where the only load-imbalance arises from a variation in the total computational load per timestep on each processor.

An important point is that for each cross-processor interaction there are two processors that could do the calculation, and a way must be found to avoid this inefficient double-computation. There are two solutions: either each processor calculates half of the interatomic interactions, of which there are 144 for the interaction of two benzene molecules, or one processor calculates all the interactions. The former gives slightly better load-balancing, whereas the latter is more efficient in terms of reducing computational overheads. In either case a rule must be used to decide which processor does what. In this program the first strategy was used, with the rule that determines which processor calculates which interactions being based upon a comparison of the coordinates of the two molecules involved.
Either of these methods leads to contributions to the forces on any particular molecule being stored on many processors in the ring. A final step must therefore involve the summation of these sub-totals around the ring. In a serial program, provided there is sufficient memory available, the total force on each atom can be accumulated separately, and the net force and torque on each molecule calculated only after all the interactions between all molecules have been calculated. This is efficient on calculation but inefficient on memory usage, and would lead to a large amount of communication around the ring at the force summation stage. In order to gain a balance, the following strategy was used:

(a) Forces are stored for each atom (as described above) only for the molecules that belong to the processor.

(b) To calculate cross-processor interactions, each molecule not belonging to the processor is taken in turn, and a temporary array is accumulated of the atomic forces as this molecule is interacted with all other molecules within the cutoff. The net contribution to the force and torque on this molecule is then calculated and overwrites the values of its position and quaternion as they are no longer required for this timestep.

(c) The net force and torque on the molecules belonging to a processor are only calculated after all the interactions have been calculated.

The torque must therefore be calculated on many processors, as must the atomic positions from the quaternions, and this can be a major source of inefficiency as the number of processors is increased. Both of these local computations are necessary, however, in order to limit the volume of data transfer in a molecular simulation. The symmetry of the molecule can often be used to minimise this extra computation, for instance by reducing the number of vector cross-products required to calculate the torques on two atoms related by inversion symmetry through the centre of mass of the molecule.

As noted, the final stage in the interaction calculation is to return the force and torque sub-totals to their appropriate processors. In [72], it is claimed that such a procedure leads to a large communication overhead, but in the present method the communication cost is identical to that in the broadcast of the world-map, and hence generally negligible. Briefly, each processor[q] sends out a packet of sub-totals (eventually destined for the processor [q-1]) to the next processor.
in the ring\([q+1]\). Similarly it receives a packet from the processor\([q-1]\). The only difference to the broadcast of the world-map is that it then adds on its own appropriate subtotals to this packet before sending it on. After \(P-1\) passes it receives its own accumulated force and torque packet. This communication phase can proceed in parallel with the second part of the calculation of single-processor interactions, as mentioned above.

Finally, quantities such as the stress-tensor, temperatures, potential energy, or correlation functions can be gathered by the controller process. These are calculated as sub-totals on each processor, which are then accumulated into a 'running-total' packet which circulates around the ring. In the constant pressure simulation the controller process can then calculate the new MD-cell matrix and its time derivative; these must be passed back to all the calculator processes so that they can proceed with the final stage of the calculation, the use of the forces and torques to obtain new velocities.

### 3.2.5 Performance

The performance of the program was tested on the benzene system that has been introduced previously. Whilst the large number of interatomic interactions per intermolecular interaction makes this a favourable case in terms of the calculation/communication ratio, we shall see that the communication effects are negligible. The sample sizes that were used, were 864 molecules, as used in the simulations reported in this thesis, and 4224 molecules, in order to demonstrate the performance of the program on a rather larger sample. The program was run on the ECS using a varying number of processors from 1 to 132.

The efficiency as the number of processors is increased, compared to the program running on a single processor, is shown in Fig. 3.3. In both cases, therefore, the program has at least 65% efficiency with 132 processors. This is excellent efficiency for a typical application.

A stringent test of the performance of a molecular dynamics program is to measure its rate of performing floating-point operations based upon the cycle-time for a complete timestep, but only including the arithmetic operations in the innermost loop of the interatomic force calculation (35 in the program). This is plotted in Fig. 3.4. The single processor delivers 0.7 MFlops, and for the 4224 molecule system 132 processors deliver 73 MFlops.
A discussion of the effect of communications and load-imbalance is presented in § 3.2.6. The main real loss of efficiency grows as the proportion of cross-processor interactions increases, because these disrupt the loop structure of the single-processor (serial) program, necessitating extra calculations and addressing of arrays. The extra calculations include those of torques and atomic positions, as mentioned previously, as well as the addition of vectors to implement periodic boundary conditions. The influence of these calculations be seen in the form of the efficiency curves, as the efficiency initially drops rapidly and then levels out somewhat as the proportion of cross-processor interactions approaches 100%. The efficiency can therefore be improved by ensuring that, as far as possible, neighbouring molecules are placed on the same processor as this will reduce the number of cross-processor interactions. This was done for the simulations presented. When, instead, the molecules were assigned to processors with no regard for their spatial location the extra loss of efficiency was similar to that already found. Another reason for attempting to maximise the number of same-processor interactions is that this increases the duration of the calculations which are to
Figure 3.4: The variation of the computational rate as the number of transputers used is increased for fixed sample sizes (see text). The dashed line represents the maximum rate attainable based upon the rate for the program running on a single transputer.

be overlapped with communication thus allowing a smaller number of molecules per processor. The efficiency was also measured for the system of 4224 molecules, but reducing the number of interaction sites to six (everything else remaining unchanged). Performance was poorer than in the twelve site model, but this is understandable as the relative importance of the extra calculation is increased. The load in this system would require around 50 transputers for which the efficiency again approaches 80%.

Timings for molecular dynamics of benzene on a CRAY-XMP are given in [77]. The simulation is of a six-site model, and using the same criteria as above to obtain a computational rate (i.e. assuming 35 Flop per interatomic interaction, and only counting these operations) a rate of around 15 MFlops was obtained from their figures. The calculations in [77] were in 64-bit arithmetic; double-precision arithmetic was found unnecessary in this application, but even with double precision on the transputer the degradation of the computing rate is only about 30% for this work. Notwithstanding this it is clear that for this molecular dynamics application a system of around 50 transputers gives roughly equal performance
to a CRAY-XMP in this application. The rating of 15 MFlops for [77] is not inconsistent with much work done on a single X-MP CPU[78]. In view of the fact that the mean rate given in [78] is 42 MFlops, the program of [77] may well not be optimised.

3.2.6 Communications and Load-balance

It has been argued above that the major loss of efficiency in the program is caused by extra calculation that is required in the parallel algorithm. This section shows from actual measurements that communications have a negligible effect on the performance of the program and that load balance remains good throughout.

Timings of Communications

It must be stressed that these timings are specific to the actual hardware used, which includes the hardware connecting the transputers together. They should therefore be taken as a guide rather than as definite values. The reader is reminded of the typical computational time per timestep of ~5s introduced earlier. There are two main types of communication:

(a) Broadcasts of the 'world map' and gathering of force subtotals

As noted previously, both of these require very similar communications strategies, and in both cases the communication can be efficiently run in parallel with calculation. The relevant timing here is the extra ('stolen') time that the calculation seems to take because of the communication being performed in parallel with it. This can be found by measuring the difference in the time that the calculation takes with the communication run in sequence and then in parallel with it. This was done for both systems and for varying numbers of processors. For the world-map case this gave the stolen time as roughly

\[0.2 \mu s \text{ per word} + 17 \mu s \text{ per packet sent,}\]

the first term being determined by the amount of conflict for memory access as described in the text, and the second term being the start-up time for a communication.

In the program, four packets are required to send the data from one processor to the next (one to say how much data is being sent, and one each for
positions, quaternions, and bin numbers), and each molecule is described by eight words. Selected specific cases give the time as

\[ = 0.0024 \text{ s for 864 molecules on 17 processors (measured)} \]
\[ = 0.010 \text{ s for 864 molecules on 132 processors (measured)} \]
\[ = 0.015 \text{ s for 4224 molecules on 132 processors (measured)} \]
\[ = 0.084 \text{ s for 10000 molecules on 1000 processors (extrapolated)} \]

The start-up time is always significant, except for very large systems, and this could be reduced by a factor of four by fairly simple modifications to the program which would allow the four packets to be reduced to one larger packet. As the times presented above are negligible for our purposes, the program was left in the simpler form.

For the force-gather stage, the stolen time also includes time for subtotals to be added to the running totals. The total time was found to be negligible, being roughly constant with the number of processors (up to \( P=132 \)),

\[ \sim 0.007 \text{ s for 864 molecules} \]
\[ \sim 0.025 \text{ s for 4224 molecules} \]

It remains to show that these communications can be overlapped with calculation. The dominant factor in this case is the link speed, rather than the start-up time. Measurements show this to be \( \sim 5\mu s \) per word, and the actual program gives the duration of communications as

\[ \sim 0.06 \text{ s for 864 molecules} \]
\[ \sim 0.2 \text{ s for 4224 molecules} \]

including both communication phases. It was found that this could always be overlapped with single-processor interaction calculations, for any timestep greater than about one second.

(b) Control broadcasts, and gathering of global data

The control broadcasts allow the controller process to tell the calculator processes what to do next (e.g. do a timestep, send back configurations, etc.), as well as sending out parameters such as the new MD-cell matrix, or temperature rescaling factors. The gathering of global thermodynamic data involves the summation of sub-totals calculated on each processor. A
'grand-total' packet is circulated, which accumulates these sub-totals. Both of these communications are inefficient on a ring, as the processors receive the packets in sequence around the ring, unlike in (a) above, where the processors pass on packets in parallel. The calculation involved in accumulating the grand-totals can also only proceed in sequence. The times involved are very small, however, being found to be

\[ \sim 0.015 \text{ s } + 250 \mu \text{s per processor} \]

\[ \sim 0.05 \text{ s for 132 processors} \]

\[ \sim 0.27 \text{ s for 1000 processors.} \]

This is negligible in practical cases \((P \leq 132)\). For very large numbers of processors, a modification might be necessary in which, for example, spare links are used to send the packets directly to the processor half way around the ring. The circulation can then proceed in two parts, thus halving the time taken, and extra links could be used to reduce the time even more.

In the program as implemented there are moments within each timestep when all the processors are waiting for the controller to perform calculations (e.g. of the new cell matrix) before they can proceed. Timings give the total time for this as \(< \sim 0.004 \text{ s} \) which is again trivial.

Load-balance

The load-balance can be defined as the ratio of the average number of interactions calculated by the processors to of the number of interactions calculated by the most heavily loaded processor. This is plotted in Fig. 3.5: it remains very high throughout at better than 90%.

3.2.7 Extensions to the Algorithm

The program could easily be extended to cope with molecules modelled as flexible chains of rigid units\([2]\), using the method quaternions and constraint dynamics. Apart from the increased complexity of the time-stepping routine (which parallels naturally) the only addition would be that several generalised coordinates would need to be broadcast for each molecule. This would not increase the communication load unduly, especially as the quaternion data could still be sent in one packet with the appropriate use of arrays.
Unlike systolic-loop algorithms [72], the algorithm allows all the molecules to have information about all other molecules simultaneously, facilitating the calculation of many-body forces if necessary.

It seems that the only limitations on the use of the algorithm are:

(a) It is not suitable if the communication overheads dominate the calculation, which might be so with a very short cut-off and/or for very simple molecules/atoms. The timings in § 3.2.6 should allow an estimate of the calculation/communication ratio to be made in specific cases.

(b) It may require too much memory for very large simulations (perhaps many tens of thousands of molecules).

In both of these cases a more strongly geometric spatial decomposition would probably be more suitable.

3.2.8 Conclusions

A relatively simple algorithm for implementing molecular dynamics on an array of transputers has been shown to give very good performance in a practical application. This confirms the suitability of such computers for molecular dynamics, since the timings demonstrate that communications and load-imbalance have a negligible effect on the efficiency of the program. Transputer arrays thus seem to provide a very cost-effective route to the provision of the large amounts of computer resources that molecular dynamics simulations require, enabling the study of larger systems, and on longer time-scales.
Figure 3.5: The variation of the load-balance as the number of transputers is increased for fixed sample sizes
Chapter 4

General Assessment of the Model

In this chapter a study is made of the general features of the molecular dynamics model of benzene that was described in Chapter 3.

In the first part, various extensive quantities, such as the structural parameters and internal energy are calculated across a wide range of temperatures. These results are then used to make a simple rescaling of the potential. Other quantities such as melting point, elastic properties, and thermal vibration amplitudes are then considered to gain further insight into the behaviour of the model.

This rather general study of the model forms a basis for the more detailed discussion of certain features of the model in the two final and concluding chapters.

4.1 Structural Parameters from the Model

The first step in assessing the model was to measure the cell parameters and internal energy for a range of temperatures. Simulations were run as described in Chapter 3, using the original potential of Karlstrom et al., at temperatures from 50 to 430 K.

The upper limit on this temperature range was given by the temperature at which the simulation transformed into the liquid state, this being indicated by a large change in the volume and potential energy, and by the development of large shearing fluctuations of the MD-cell. Such fluctuations are characteristic of a liquid, and were manifested as changes in the off-diagonal terms of the MD-cell matrix, which was set up initially to be diagonal. A simulation at 425 K
remained stable during the longest run attempted of 100 ps, whereas at 430 K the first signs of instability were evident after about 10 ps, and melting was complete within 20 ps. This indicates that the instability is quite sharply defined. 425 K is considerably higher than the true melting point of 280 K, but it will be argued shortly why this instability is believed to be mechanical rather than thermodynamic in nature, and that the true melting point is in fact much closer to the experimental value.

Cell-parameters

The cell parameters can be obtained directly from the lengths of the sides of the MD cell, divided by six for the 864 molecule sample, it being checked that no defects develop in the sample. In a constant stress simulation, the shape of the MD-cell fluctuates even in a solid phase, and the values of the cell parameters must be obtained as time averages over a number of cycles of these oscillations. The fluctuations are thermally driven, and are related to the elastic constants; the greater the stiffness of the solid, the smaller the amplitude and the higher the frequency of the oscillations. In fact, the oscillations can provide a method for measuring the elastic constants of a solid, as described later. The piston-mass also affects the frequency of the oscillations, but not their amplitude[65].

Local density fluctuations occur in real crystals, but in macroscopic samples the overall density fluctuations are negligible; in the relatively small samples used in molecular dynamics, the amplitude of the fluctuations is quite significant. From [79], the mean square strains of the lattice parameters are related to the diagonal terms of the elastic compliance matrix, \( S \) [80]. For the \( a \)-axis

\[
\langle (\delta a)^2 \rangle = \frac{kT}{\Omega} S_{11} \tag{4.1}
\]

where \( \Omega \) is the volume of the MD-cell; similarly for \( b \) and \( c \). For the fluctuations of the volume of the unit-cell, \( V (= \Omega/216) \),

\[
\langle (\delta V)^2 \rangle = \frac{kT}{\Omega B} \tag{4.2}
\]

where \( B \) is the bulk modulus.

The values of the elastic constants of benzene are discussed later; to sufficient accuracy we can use values here of

\[ S_{ii} \approx 3 \times 10^{-10} \text{Pa}^{-1} \]
\[ B \approx 6 \times 10^9 \text{Jm}^{-3} \]

and using \( \Omega \approx 1 \times 10^8 \text{Å}^3 \) for the 864 molecule sample, and \( T \approx 250 \text{K} \), we have,

\[ \text{RMS}(\frac{\delta a}{a}) \approx 0.3\% \quad (4.3) \]

and similarly for \( b \) and \( c \). For the unit-cell volume, \( V \),

\[ \text{RMS}(\frac{\delta V}{V}) \approx 0.2\% \quad (4.4) \]

The volume fluctuations are rather less than would be expected by combining the values for the individual lattice parameters. This is because the oscillations of \( a \), \( b \) and \( c \) are strongly correlated and approximately isochoric, the correlation depending on the (negative) off-diagonal terms of the compliance matrix. The volume is therefore better determined than the individual cell parameters.

The volume fluctuations have a rather shorter period of approximately 2 ps, compared to approximately 8 ps for \( a \), \( b \) and \( c \). The difference in frequencies gives another source of relative inaccuracy in \( a \), \( b \) and \( c \) compared to \( V \), as any time average will be over many less oscillations. In order to study the temperature variation of the cell parameters a precision of \( \approx \pm 0.01 \text{Å}(\approx 0.1\%) \) is necessary, whereas, from above, the peak to peak fluctuations in \( a \), \( b \) and \( c \) are \( \approx 1\% \). A sampling time of 30 ps was used, and the error introduced by the fluctuations was estimated by measuring the oscillations in the cumulative mean as a function of sampling time. This gave the error in \( a \), \( b \) and \( c \) as \( \approx \pm 0.01 \text{Å}(0.1\%) \) and the error in \( V \) was less than \( \approx \pm 0.3 \text{Å}^3 (0.05\%) \).

**Internal Energy**

The internal energy is available directly from the simulation, since the potential energy can be calculated at the same stage as the interatomic force calculations, and the kinetic energy is obtained from the velocities of the molecules.

### 4.1.1 Comparison of the Model with Experiment

**Limitations of the Model**

Before presenting the results and making a comparison with experiment, it is necessary to consider carefully which features of the experimental data the model can be expected to reproduce.
Firstly, molecular dynamics simulations are purely classical, so that quantum effects are not seen, whereas experimentally these effects become dominant at low temperatures. Specifically, quantisation causes temperature dependent quantities, such as expansivities and the heat capacity, to drop to zero at 0 K; corresponding quantities, such as lattice parameters and internal energy, are inflated above the value that a classical extrapolation would predict [81]. These effects can be seen in the form of the experimental lattice parameter curves of Fig. 2.5, which level out at 0 K. Similarly, the heat capacity data of Oliver et al.[13], which is replotted in Fig. 4.1, shows a rapid drop below the classical harmonic value of 6R for rigid non-linear molecules at temperatures below about 100K.

The second point concerns solely the internal energy. At temperatures above about 100 K the experimental heat capacity deviates significantly above the classical harmonic value. There are three main possible reasons for this, there being possible contributions to the energy from defects, internal modes, and anharmonicity. Only anharmonicity will contribute in the simulation, since the sample is too small and simulated over too short a time-scale for defects to develop; and as the molecules are simulated as rigid bodies there can be no energy contained in internal vibrational modes. It is therefore necessary to estimate the contributions from these various sources in the experimental data, before attempting a comparison with data from the model.

The defect concentration in benzene has been studied by Baughman and Turnbull [82]. They concluded that in benzene, even near the melting point, the concentration of vacancies is less than 0.1%, and therefore there would be a negligible contribution to the heat capacity.

The heat capacity due to internal modes can be calculated, assuming that the modes behave as independent harmonic oscillators. The frequencies of the modes are known in the gas phase and are little changed in the solid phase [42]. The relatively high frequencies of the internal modes means that they are strongly quantised at the temperatures considered here. Elementary statistical quantum mechanics gives the heat capacity, \( C \), of a harmonic oscillator of frequency \( f \) as [83],

\[
C = \frac{k F^2 e^F}{(e^F - 1)^2}
\]

(4.5)

where \( F = \frac{hf}{kT} \).

The heat capacity from each mode can be summed, and in Fig. 4.1 the re-
Figure 4.1: The heat capacity of solid benzene. The solid curve is experimental data, $C_{\text{exp}}$, from [13]. The broken curve is the heat capacity in the classical regime with the contribution from internal modes subtracted, $C_{\text{corr}}$ (see text). The data points (+) are for the rescaled potential (see § 4.2). The horizontal line is for $C=6R$ which is the classical harmonic value for a solid composed of rigid nonlinear molecules.
sultant has been subtracted from $C_{\text{exp}}$, to give $C_{\text{corr}}$. As the defect contribution is negligible, then in the classical regime the corrected heat capacity deviates from $6R$ purely due to anharmonicity, and it is $C_{\text{corr}}$ that can be compared with simulation data.

Results

The lattice parameters and internal energy from the molecular dynamics simulations are plotted in Figs 4.2 and 4.3. For the lattice parameters, the interpolation curves from Chapter 2 for the experimental data are also plotted. For the internal energy the experimental curve was obtained by integrating the heat capacity data of Oliver et al. using their value for the sublimation energy at 0 K. The broken curve in Fig. 4.3 is the internal energy corrected for the contributions from internal modes similarly to the heat capacity. Data is also included for 0K obtained from lattice energy minimisation using the same potential and cutoffs.

The general trends in the curves are very satisfactory, bearing in mind the quantum effects in the experimental data below about 100 K. As has been reported[41], however, there are significant discrepancies in the absolute values predicted by the Karlstrom potential: $a$, $b$, and $c$ are too small by $\approx 5\%$; $V$ is low by $\approx 15\%$; the potential is too negative by $\approx 20\%$. Another problem is that the simulation remains in the solid phase up to too high a temperature as mentioned above.

4.2 Rescaling the Potential

In order to improve the accord with experiment, an attempt was made to rescale the potential. The philosophy was to allow only a very simple linear scaling of the energy and length-scale of the interatomic potential, in order that the desirable \textit{ab initio} features of the potential should not be lost.

General Scaling Equations

The internal energy of a simulation can be rescaled by an exact procedure which can be applied after a simulation has been run, effectively by a redefinition of units. Dimensional analysis dictates that if it is wished to scale the energy of a
Figure 4.2: The lattice parameters and unit-cell volume as a function of temperature for the original Karlin model (○), no temperature rescaling applied. The solid curves are the interpolations of the experimental data from Chapter 2.
Figure 4.3: The internal energy as a function of temperature for the original Karlstrom potential, (×) no rescaling applied; (○) same data, with a rescaling to the energy and temperature scales of $\varepsilon = 0.82$ (see text). The solid curve is experimental data from [13]; the broken curve is the experimental data with the contribution from internal modes subtracted (see text).
system by a factor $\epsilon$ such that

$$\phi \rightarrow \epsilon \phi$$

(4.6)

then, if the same values are to be maintained for mass and length, the correct physics is obtained if time intervals are also rescaled so that

$$\delta t \rightarrow \delta t / \sqrt{\epsilon}$$

(4.7)

and therefore frequencies scale as,

$$\nu \rightarrow \nu \sqrt{\epsilon}$$

(4.8)

Temperature must scale as energy, so that

$$T \rightarrow \epsilon T$$

(4.9)

Such a scaling of energy and temperature leaves the statistical mechanics of the system unchanged since the Boltzmann factors in the partition function remain unaltered.

In order to obtain the correct cell-volume, the length-scale of a simulation of a system of atoms could be similarly exactly rescaled by a factor $\mu$, such that

$$\delta r \rightarrow \mu \delta r$$

(4.10)

Constant energy and mass scales would then be maintained by scaling $\delta t$ also by a factor $\mu$.

This gives an implicit rescaling of the potential parameters in a potential of the form

$$\phi = \sum \frac{A_n}{r^n}$$

(4.11)

by a factor $\lambda^n$, i.e.

$$A_n \rightarrow \lambda^n A_n$$

(4.12)

where, in an atomic simulation, $\lambda = \mu$. This does not work exactly for a molecular system, since the molecular size would also be effectively increased by a factor $\lambda$. Instead, we must find a value for $\lambda$ that gives the right scale change, by lattice energy minimisation at 0 K for instance, and then run simulations again to assess the effect of the rescaling of the potential function. These new simulations will also show the effect of the rescaling on the individual lattice parameters.
Rescaling the Benzene Potential

Bartell et al. [11] attempted to rescale the Karlstrom potential by comparing results of lattice energy minimisation with the experimental structure extrapolated to 0 K and approximately corrected for the inflationary effects of zero point motion. As they discuss, the extrapolation and correction scheme is not exact. However, if the comparison is instead made at about 150 K, then these quantum effects become negligible and no such approximate corrections are necessary.

The first part of the length rescaling procedure was to obtain an approximate value for the energy rescaling factor, \( \varepsilon \), so that an approximate temperature scale could be established. A value of \( \varepsilon = 0.82 \) was obtained by finding a value that gave an energy-rescaled simulation curve that was in accord with the experimental curve above 100 K (Fig. 4.3).

Using this value for \( \varepsilon \) to rescale temperature according to Eqn. 4.9 indicated that the cell-volume was too low by \( \approx 55 \text{Å}^3 (13\%) \) at 150 K, which gives \( \mu = 1.04 \). Lattice energy minimisation gave an estimate of \( \lambda = 1.08 \) that would give the correct volume change. The small difference between these two values indicates that the form of the potential is not drastically altered.

A new set of simulations were then run using this length-rescaled potential. The initial configuration was at 100 K. This was heated in sequence to approximate temperatures of 150, 200, 250, 300, 350, 400, 415 and 425 K. In order to check for hysteresis in the temperature dependence, a cooling run was also made, starting from the configuration obtained at 415K, and cooling in sequence through 400, 350, 250, 100 and 50 K.

The internal energy is plotted in Fig. 4.4 with \( \varepsilon = 1 \) and a refined value of \( \varepsilon = 0.78 \). This fully rescaled potential, with \( \varepsilon = 0.78 \) and \( \lambda = 1.08 \), will hereafter be referred to as the 'rescaled potential'.

The sample became liquid in this second set of simulations at the same temperature as the original potential to within less than 5 K. In rescaled temperature units this gives a temperature for the instability, \( T_{\text{instab}} \), as 335 K. All temperatures referred to from this point onwards will be these rescaled temperatures (in Table 4.1 for instance); times and frequencies will be similarly rescaled according to Eqns 4.7 and 4.8. In these rescaled units the standard simulation time for gathering structural data was 34 ps.
Figure 4.4: The internal energy as a function of temperature for the length-rescaled potential: \((x, +)\) no energy or temperature rescaling applied; \((o, \Delta)\) same data, with a rescaling to the energy and temperature scales of \(\epsilon = 0.78\) (see text). Warming sequence \((x, o)\), cooling sequence \((+ , \Delta)\). The solid curve is experimental data from [13]; the broken curve is the experimental data with the contribution from internal modes subtracted (see text).
4.2.1 Results for the Rescaled Potential

The results for the lattice parameters using the rescaled potential are given in Table 4.1, and are plotted in Fig. 4.5. It should be noted that there is no systematic difference between the heating and the cooling data. The cell volume is, of course, now in good agreement with experiment, as this was the parameter upon which the rescaling was based. More importantly, the individual $a$, $b$ and $c$ values are each now approximately correct, the greatest discrepancies being in $b$ and $c$, of $< 2\%$.

The temperature dependence of the lattice parameters, cell volume and lattice energy are all well reproduced, which is a very significant test of the potential as noted in Chapter 1. The heat capacity has been calculated from the internal energy data to give the data in Fig. 4.1; the agreement with $C_{\text{corr}}$ is excellent in the classical regime. The expansivities are compared with experiment in more detail in Chapter 5.

Molecular Orientations

The instantaneous mean orientation of the molecules can be obtained from the mean quaternion. As the four molecules in the unit cell have different mean orientations, the appropriate space-group symmetry operations must be applied to the quaternions before calculating the overall mean. The angles describing the mean orientation of the molecule that were introduced in § 2.3 are given in Table 4.1 and plotted in Fig. 4.6 along with the experimental data from Chapter 2.

The values of the angles at low temperatures compare very well with experiment, being different by at most $2^\circ$. The general trends in the orientations as a function of temperature compare excellently with experiment, although there is a significant feature of the simulation results in the behaviour of $\gamma$, which drops steeply to zero at $\approx 320$ K. The behaviour of $\theta_6$ is closely related to this, because if a diameter of the ring lies along the $b$-axis then the normal to the plane must be perpendicular to $b$. The significance of the behaviour of $\gamma$, and detailed comparison of the experimental and molecular dynamics, will be considered further in Chapter 5; there are other aspects of the molecular dynamics model that must first be examined, as these will bear upon the later discussion.
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Table 4.1: Structural data for the rescaled potential.
Figure 4.5: The lattice parameters and unit-cell volume as a function of temperature for the fully rescaled potential, (o) warming, (A) cooling. The solid curves are the interpolations of the experimental data plotted from Chapter 2.
Figure 4.6: Orientational parameters, in degrees, as defined in the text, as a function of temperature. \((\circ, \Delta)\) Fully rescaled potential, \((\circ)\) warming, \((\Delta)\) cooling. 
\((\times)\) Experimental data from this work and the literature (see Chapter 2).
4.3 Determination of the Melting Point

A vital question for the interpretation of the molecular dynamics results is whether the temperature $T_{\text{instab}}$, at which the sample transformed to a liquid, is in fact the true thermodynamic melting point, $T_m$. For the rescaled potential $T_{3b}$ was found to be 335 K, which is rather higher than the experimental melting point of 280 K for $C_6D_6$. This alone cannot be taken as strong evidence that the transition is not true melting, as it may simply be that the potential predicts the melting point rather inaccurately.

Recently, however, Phillpot et al. [51] demonstrated that a simulation of silicon with three-dimensional periodic boundary conditions (3D-PBC) transformed into the liquid state between 2400 and 2600 K, whereas, in contrast, a free-energy calculation by Broughton and Li [84] for the same model gave the thermodynamic melting point as 1691 ± 20 K. The suggestion was made that with 3D-PBC the crystal is 'too perfect' and that the defects that are necessary to nucleate the melting process are not present. Phillpot et al. believe that the melting process that they did observe with 3D-PBC was melting of a metastable superheated phase nucleated by an elastic, rather than thermodynamic, instability.

By introducing a grain boundary, or making two surfaces by removing the periodic boundary conditions in one direction, Phillpot et al. were able to observe melting initiate at the grain boundary/surface, the liquid region then propagating into the bulk of the crystal. The rate of progression of the interface was measured as a function of temperature for several temperatures above the melting point. This rate was then extrapolated back to zero to give the melting temperature as 1710 ± 50 K which is in good agreement with the results from free energy calculations. Using similar methods, the same workers [52] have also obtained a melting point for copper ($\approx$ 1200 K) in agreement with free energy calculations, whereas they found a 3D-PBC simulation could be superheated by about 300 K.

It was therefore surmised that the true melting point of the benzene model would be rather lower than 335 K. An attempt to determine the melting point was therefore made, using a free surface method, as this is computationally much more simple than a free energy calculation.

It should be pointed out that the reverse procedure of finding the melting point by crystallisation from the melt is expected to be even more problematic due to the long nucleation times required and the ease of supercooling of a liquid.
In rather long simulations, Chokappa and Clancy succeeded in freezing a system of Lennard-Jones particles [85], but with a linked paper [86] on the melting of the solid they showed that there was considerable hysteresis. In a simulation of a cluster of sulphur hexafluoride, Fuchs and Pawley [87] only succeeded in forming a glass on cooling the melt.

4.3.1 Method

The sample was in the form of a slab of pseudo-infinite extent in the plane, achieved by removing the periodic boundary conditions in the crystallographic $b$ direction. This direction was chosen to maximise the slab thickness; whilst the rate of melting may depend upon the plane chosen as the free surface, the extracted melting point should not. In the two periodic directions, the Parrinello and Rahman scheme was employed, and in the third direction the MD-cell size was fixed; in this direction the scaling of the $s_i$ to give $r_i$ (Eqn. 3.4) was then constant and the molecules had normal 'free space' dynamics.

A configuration from previous runs with 3D-PBC that had been equilibrated at 235K was used as the starting point for each of the simulations, which were made at 266, 277, 283, 289 and 296 K. Temperature rescaling was applied every 1 ps in order to allow the latent heat to be supplied. At each temperature, the mean temperature, which was the mean of temperatures measured just before the rescaling procedure, was less than 1 K below the required temperature. This indicates that the melting rate was not significantly limited by the rate of addition of extra energy into the system.

Analysis

The melting process was monitored by calculating the planar structure factor ($PSF$)[51]. The basic idea is to divide the sample slab into planes parallel to the free surface, each containing approximately one layer of molecules, and calculate an order parameter that determines the order within the layer. A suitable order parameter is the component of the 2D spatial Fourier transform for a wavevector that is a reciprocal lattice vector in the plane.

First, $S_i$ is defined for the $i$th plane as

\[
S_i = \frac{1}{N_i} \sqrt{\left( \sum_{j \in i} \cos(k.s_j) \right)^2 + \left( \sum_{j \in i} \sin(k.s_j) \right)^2} \tag{4.13}
\]
where the sum in $j$ is over the $N_j$ molecules in the $i$th plane. Then the planar structure factor, $PSF_i$, for the $i$th layer was defined as,

$$PSF_i = \frac{1}{2} (S_i^{k_1} + S_i^{k_2})$$

(4.14)

where

$$k_1 = (2\pi, 0, 0)$$
$$k_2 = (0, 0, 2\pi)$$

are the $(2,0,0)$ and $(0,0,2)$ reciprocal lattice vectors expressed in reduced coordinates.

The planes were defined as regions of space, rather than by particle indices, to allow for diffusion. The thickness was chosen such that on average planes corresponded to single layers of molecules in the solid. A value of 1 for the $PSF$ indicates a perfect crystal, and as the disorder increases the $PSF$ decreases. It will still have a non-zero value in the liquid as a liquid retains a certain degree of structure, with a fairly well defined nearest neighbour distance.

The $PSF$ is plotted in Fig. 4.7 for a sequence of times during the simulation at 289K. Each plot shows the $PSF$ as a function of distance along the direction normal to the slab. The melting is seen to initiate at the surface and to progress into the bulk:

- in a solid layer, $PSF_i \approx 0.9$
- in a liquid layer, $PSF_i \approx 0.2$

A definition was then proposed that a layer was liquid if $PSF_i < 0.5$ and solid otherwise. The fraction of the solid that had melted could then be approximately calculated, and this is plotted as a function of time in Fig. 4.8 for the five temperatures studied. The steps in the curves are partly artefacts due to the classification of a whole layer as either solid or liquid.

A second quantity used to measure the rate of melting was the rate of change of potential energy, as this monitors the rate of transformation to the higher energy liquid phase. This is not an exact measure, as there are rather uncertain interfacial energies that also influence the potential energy. The potential energy is plotted as a function of time for each temperature in Fig. 4.9, and shows the same general features as Fig. 4.8.
Figure 4.7: A sequence of profiles through the 2D-slab at 289K. For details see text
Figure 4.8: The extent of melting in the sample as a function of time at the five temperatures studied. The left-hand ordinate axis expresses the extent as the fraction that has melted. On the right-hand ordinate axis is shown the corresponding number of molecular planes. For the definition that was used of a melted plane see text.
CHAPTER 4. GENERAL ASSESSMENT OF THE MODEL

Figure 4.9: The potential energy of the sample as a function of time during melting at the five temperatures studied (see text).
CHAPTER 4. GENERAL ASSESSMENT OF THE MODEL

Initially, approximately the first two or three layers melted (see Fig. 4.8), corresponding to approximately one layer on each face of the slab: this rapid melting may simply have been due to the initial disequilibrium when the periodic boundary conditions were removed. Melting then proceeded approximately linearly with time at the four higher temperatures studied. At 296 K, the melting was very rapid. At 277 K, 283 K and 289 K, the melting was slower but it was still possible to melt the whole slab within a reasonable timescale. At these lower rates, it was also possible to observe that the melting rate increased for about the last four layers, which might be expected as the solid layer becomes very thin. As the melting rate appears constant up to this point, it appears that the slab was sufficiently thick for the two melted regions to be considered non-interacting until this final rapid melting stage. This indicates that the sample was large enough to give an accurate melting point.

Evidence that the process observed was true melting, and not a disordering process, was that the 2D MD-cell remained rectangular until the moment that the last few layers melted, and then started to show large shearing fluctuations as expected for the liquid. It may also be that the last four layers melted more rapidly as fluctuations in the MD-cell sheared the thin section of crystal too strongly.

At the lowest temperature studied, 266 K, the melting was only observed to proceed for about one or two layers on each surface, and the fraction that had melted then remained approximately constant during 400 ps. This may represent surface melting[49]. This is a phenomenon which has been proposed, in which, at temperatures close to, but a few Kelvin below, the melting point, a thin liquid-like layer exists on the surface of a solid. This has been reported, for instance, for methane adsorbed on to graphite. Whilst the concept is plausible, given the relatively unbound state of surface molecules, the problems of studying surface melting are formidable: experimentally it is very difficult to ensure that the surface is perfectly clean; and in simulations it is very difficult to ensure equilibration, and that the melted surface is not simply meta-stable. There has been considerable debate on this issue[49], and it will not be pursued here further; as longer simulations were not feasible, the melting rate at 266 K was taken to be zero, and this temperature is therefore a lower bound on the melting point.
Figure 4.10: The rate of melting as a function of temperature. The lines are drawn as guides to the eye.

### 4.3.2 Results

The melting rates were extracted from the linear parts of the curves in Fig. 4.8, as indicated by the dashed lines in the figure, and these rates are plotted in Fig. 4.10. The data are approximately consistent with a linear dependence on $(T - T_m)$ for $T > T_m$, as suggested by Phillpot et al., up to about 290 K beyond which the rate increases much more rapidly. This increase is perhaps related to the approach to the instability temperature. Extrapolation of the rates to zero gives an estimate for the melting point, $T_m$ of 272K ± 5K.

The value of the 272 K for the melting point is very close to the experimental value of 280K. This is remarkable agreement, because the melting point depends upon the relative free energies of the liquid and solid phases, and the free energy depends upon both dynamic and structural properties of the two phases. The
accuracy of the model here adds support to the view that, for many molecular
crystals at high temperatures, the fine details of the potential are not crucial, and
that a well-determined molecular shape plays the most important role.

Volume and Energy Discontinuities at Melting

With this identification of the melting point, the latent heat, $\Delta L$, and volume
discontinuity, $\Delta V$, of the melting transition can be determined for the model. A
liquid 3D-PBC configuration, that had been melted by taking it above $T_{\text{instab}}$, was
cooled to 272 K and after equilibration the internal energy and volume were measured. Along with data that had already been collected for the solid at the
same temperature, this gave

$$\Delta L = 8.5 \text{ kJ/mol}$$
$$\Delta V = 9.3 \text{ cm}^3/\text{mol}$$

which compare well with the experimental values of

$$\Delta L = 9.9 \text{ kJ/mol} \quad [13]$$
$$\Delta V = 10.1 \text{ cm}^3/\text{mol} \quad [88]$$

The variation of the melting temperature with pressure can now be calculated
via the Clausius-Clapeyron Equation[89],

$$\frac{dT_m}{dP} = \frac{T \Delta V}{\Delta L} \quad (4.15)$$

which gives $\frac{dT_m}{dP}$ as 30 K/kbar. This is in good accord with the directly determined
experimental value of 26 K/kbar[12], or 28 K/kbar as determined from the the
experimental values of the latent heat and volume discontinuity.

4.4 The Nature of the High Temperature Instability

If the instability of the 3D-PBC simulation at 335 K is in fact a elastic instability,
rather than true first order melting, then premonitory changes would be expected
in some of the properties of the crystal as the instability temperature,$T_{\text{instab}}$, is
approached.
In Fig. 4.5, the most clear anomaly is the behaviour of the $a$ parameter which rises sharply between 300 K and $T_{\text{instab}}$. It was therefore decided to study some of the elastic properties of the system to see if similar anomalies could be found in the response of the system to pressure.

### 4.4.1 Measurements of Elastic Compressibilities of the Model

The elastic properties that were measured were the compressibilities, which are defined by

$$\beta_x = -\frac{1}{P} \frac{\delta x}{x}$$

where $x = a, b, c$ or $V$, and $\delta x$ is the corresponding change in the parameter when a hydrostatic pressure $P$ is applied.

**Computational Methods**

The compressibilities can be measured directly at 0 K by adding an energy term $PV$ to the lattice energy, and then using lattice energy minimisation to determine the lattice parameters as a function of applied pressure. True harmonic values for the compressibilities can then be obtained by extrapolating the slope of $x(P)$ to zero pressure.

The analogous method is also possible for measuring the compressibilities at finite temperatures using molecular dynamics. As this direct method is computationally rather intensive, requiring several simulations at different pressures for each temperature studied, other methods have been proposed.

The first makes use of the fluctuations of the MD-cell that have been remarked upon previously § 4.1. These fluctuations are thermally driven, and increase as the elastic moduli soften. Parrinello and Rahman[79] and Sprik *et al.*[90] have shown how the correlations between the various components of the fluctuations can be used to extract the full elastic compliance matrix. The major problem with this method is that very long runs are required, of the order of several hundred picoseconds, in order for the values of the compliances to converge.

A second method has been proposed by Ray[91] to improve the convergence, where the elastic moduli are instead obtained from the fluctuations of the internal stress. They conclude, however, that in terms of computational time the direct
method is still comparable. Furthermore, in the orthorhombic case of benzene there is no relation between the non-zero elements of the elastic matrices except from the matrices being symmetric, so that this cannot be used to check the convergence. For these reasons the simpler direct method was used here.

Results

Data was obtained from lattice energy minimisation and from molecular dynamics for the lattice parameters and cell volume at 0, 120, 235 and 315 K at a range of pressures from 0 to 3 kbar. The zero-pressure compressibilities were obtained by extrapolation and are plotted in Fig. 4.11 as a function of $T$.

Again, the behaviour of the $a$ parameter is anomalous at high temperature, with a very large value of the compressibility at 315K. This confirms the view
that this is an elastic instability, and is related to a softening of the crystal in the $a$ direction.

### 4.4.2 Comparison with Experimental Data

At temperatures removed from the instability, the data for the model can be compared with experimental compressibility data to provide further assessment of the model, although the experimental data on the compressibilities for benzene is rather sparse.

There is a value for the bulk modulus from direct PVT measurements, which gives $\beta_v = 1.9 \times 10^{-10} \text{ Pa}^{-1}$ at $250 \text{ K}$: at $235 \text{ K}$ the model gives $2.3 \times 10^{-10} \text{ Pa}^{-1}$ which is in good accord.

The full set of elastic moduli have been measured by Heseltine et al. [92] between 170 and $250 \text{ K}$ by measuring the velocity of ultrasound propagation; the compressibilities derived from the moduli at $240 \text{ K}$ are $\beta_a = 0.7$, $\beta_b = 0.6$, $\beta_c = 0.7 \times 10^{-10} \text{ Pa}^{-1}$. At $235 \text{ K}$ the model gives $\beta_a = 0.9$, $\beta_b = 0.5$, $\beta_c = 0.9 \times 10^{-10} \text{ Pa}^{-1}$, which agree fairly well.

There is a difficulty, however, in obtaining compressibilities from the elastic moduli data. The problem is first that the calculation of a compressibility requires inversion of the measured elastic moduli matrix and the inversion process can greatly magnify errors. Second, the calculation then requires subtracting two off-diagonal terms of the compliance matrix from a diagonal term. As these three terms are of rather similar magnitude the resultant is rather small so that again the error is magnified. Errors were quoted in [92] for the elastic constants, and these were used to calculate errors in the compressibilities by applying the quoted errors to the elastic moduli data in various combinations, and observing the scatter in the resulting compressibilities. This gave estimated errors of up to 50 %.

The crystallographic data under pressure is also rather unsatisfactory. The data of Thiery and Leger was obtained using a very small sample which would be prone to the problems of large crystallite formation (Chapter 2) at the elevated temperatures at which they worked; they report failing to observe one expected reflection, which is indicative of this problem. From the geometry quoted for their sample, the error in the peak positions that the formation of large crystallites would give (Fig. 2.3) can be calculated. As they only observed a few peaks, the
error in the peak positions can be used to give an estimate of the error in their measurements of the lattice parameters as ± 0.2 Å. Their data is therefore of little use in assessing the changes of the lattice parameters, as these would be of a similar magnitude to the errors in the range of pressure that they studied. Furthermore, the data is at two rather large pressures, with zero pressure values extrapolated from variable temperature data, and the variation with pressure is far from linear.

Other crystallographic data does exist from the work of Piermarini et al [23] at 300 K, for a single crystal at an estimated pressure of 0.7 kbar. As noted by Thiery and Leger[15], if the ambient pressure crystallographic data is extrapolated to 300 K and this is used to calculate changes in the cell parameters under pressure in the work of Piermarini, then a value for the bulk modulus that is an order of magnitude too large is obtained. The conclusion must be that the pressure was in fact significantly higher in the sample than they estimated. Using an estimate for the pressure as ≈ 7 kbar to obtain a reasonable value of the volume compressibility, gives values for the axial compressibilities of \( \beta_a = 0.6 \times 10^{-10} \text{Pa}^{-1} \)
\( \beta_b = 0.7 \times 10^{-10} \text{Pa}^{-1} \), and \( \beta_c = 0.9 \times 10^{-10} \text{Pa}^{-1} \). The ratio of these values agrees only approximately with the values of Heseltine et al..

It is therefore rather difficult to make a good critical assessment of the model, as the uncertainty in the experimental values is of the order of 50%. A crystallographic study at a range of pressures would be very useful in this respect.

### 4.5 Amplitudes of Thermal Motion

An important property of the model are the amplitudes of the thermal motions of the molecules. These can be represented by three tensors: the translational vibration tensor, \( T \); the librational tensor, \( L \); and the translational-librational tensor \( S \). See, for example, Willis and Pryor [93]. These tensors are defined as

\[
T_{ij} = u_i u_j \tag{4.17}
\]
\[
L_{ij} = \theta_i \theta_j \tag{4.18}
\]
\[
S_{ij} = u_i \theta_j \tag{4.19}
\]

where \( u \) is the translational displacement of the molecule from its time-averaged position in some suitable set of axes; and \( \theta_i \) is the angle by which the molecule
has been rotated away from its time-averaged orientation about the \( i \)th axis of this frame.

The transformation of \( \mathbf{u}_i \) and \( \theta_i \) under elements of the molecular site symmetry determine restrictions on the number of independent components of \( \mathbf{T} \), \( \mathbf{L} \) and \( \mathbf{S} \). For benzene the site symmetry is \( \bar{I} \), which gives \( S = 0 \) \([93]\) and no restrictions on \( \mathbf{T} \) and \( \mathbf{L} \) (apart from being necessarily symmetric from their definitions). There is a freedom of choice in the orientation of the reference frame used to express \( \mathbf{T} \) and \( \mathbf{L} \). The standard choice for benzene is the molecular reference frame defined in Fig. 3.1

### 4.5.1 Experimental Data

Experimentally, \( \mathbf{T} \) and \( \mathbf{L} \) are generally obtained from x-ray or neutron crystallography. Briefly, \( \mathbf{T} \) and \( \mathbf{L} \) are measured in a diffraction experiment from the intensities of the diffraction peaks. The thermal motion causes a blurring of the atomic positions which, via the Fourier Transform convolution theorem, alters the intensities of the peaks.

In the work of Cox et al.\([19]\) there was insufficient data to determine all the elements of \( \mathbf{T} \) and \( \mathbf{L} \), because of the weak x-ray scattering from hydrogen (or deuterium) atoms. Cox et al. were therefore forced to use similarities between benzene and anthracene (for which \( \mathbf{T} \) and \( \mathbf{L} \) are fully determined) to complete the analysis. Their results are thus somewhat approximate, although the rms-amplitude of angular motion about the six-fold axis was completely determined as 7.9°.

In contrast, in a neutron diffraction experiment the hydrogen or deuterium nuclei scatter neutrons strongly, and the additional data allows complete determination of \( \mathbf{T} \) and \( \mathbf{L} \), provided correction is made for \( C - D \) bond stretching. Jeffrey et al. have obtained \( \mathbf{T} \) and \( \mathbf{L} \) at 15 and 123 K for \( C_6D_6 \), and Bacon et al. obtained values for the rms librational amplitude about the sixfold axis and for the out of plane motion for \( C_6H_6 \) at 138 and 218 K.

An alternative method of measuring the amplitude of thermal motion experimentally is from complete knowledge of the phonon spectrum (including eigenvectors) at a given temperature. The amplitude of each mode can then be calculated from quantum statistical mechanics. More simply, the tensors can be roughly approximated by use of the \( k=0 \) lattice modes, with the assumption that the fre-
quency of each phonon branch is approximately constant[94]. Ito and Shigeoka[95] used Raman data to obtain the diagonal elements of $L$ at 4.2, 77, 195 and 273 K which are in reasonable agreement with the crystallographic data. This technique must be considered very approximate, especially due to the uncertainty of the eigenvectors of the modes, but it at least provides some independent support for the x-ray and neutron values.

The work of Jeffrey et al. showed that the tensors were approximately diagonal in the molecular frame, the off-diagonal terms being at least an order of magnitude smaller than the diagonal terms, indeed the tensors are almost spherical. The experimental data is therefore expressed in Table 4.2 as r.m.s. amplitudes of vibration either along or about the axes of the molecular frame; that is, as the square-roots of the diagonal terms of the tensors.

4.5.2 T and L for the Model

In a molecular dynamics simulation, $L$ can be calculated quite simply by collecting quaternion first and second moments[96].

In a Parinello and Rahman constant stress simulation, $T$ cannot be directly calculated from real space positions, since the effect of oscillations of the cell matrix on the real space positions is not homogeneous. Instead, $T$ must be calculated from fractional coordinates and the result then scaled using the time averaged cell-matrix.

Data from the MD simulations is given in Table 4.2, and plotted in Fig. 4.12, along with experimental data from crystallography. The agreement with experiment is in general good although the molecular dynamics values tend to be rather high for the angular librations, especially for the out of plane motion at high temperature. The crystallographic data at 270K is, however, that of Cox et al. and is therefore somewhat approximate as explained above. The molecular dynamics data indicates that in the model there is rather little difference between the three axes in terms of rotational or translational freedom.

In terms of the reliability of the model and of insight into the rotational freedom in crystalline benzene, the most interesting quantity is the amplitude of librations about the six-fold axis of the molecule. This is because it is found, both experimentally and in the simulations, that the molecules can make distinct jumps between orientations related by the six-fold symmetry of the molecule (see
Table 4.2: Vibrational amplitude data, from this work and from various experimental sources (for details see text). All values are given in the molecular frame.

<table>
<thead>
<tr>
<th>Source</th>
<th>T/K</th>
<th>Axis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>RMS Librational Amplitudes (°)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jeffrey <em>et al.</em></td>
<td></td>
<td></td>
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<tr>
<td>neutron C₆D₆</td>
<td></td>
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</tr>
<tr>
<td>15</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>123</td>
<td>3.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Bacon <em>et al.</em></td>
<td></td>
<td></td>
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<tr>
<td>neutron C₆H₆</td>
<td></td>
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</tr>
<tr>
<td>138</td>
<td>-4.2</td>
<td></td>
</tr>
<tr>
<td>218</td>
<td>-4.2</td>
<td></td>
</tr>
<tr>
<td>Cox <em>et al.</em></td>
<td></td>
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</tr>
<tr>
<td>x-ray C₆H₆</td>
<td></td>
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</tr>
<tr>
<td>270</td>
<td>5.2</td>
<td>5.0</td>
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<tr>
<td>Ito and Shigeoka</td>
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<tr>
<td>Raman C₆H₆/C₆D₆</td>
<td>4</td>
<td>2.6</td>
</tr>
<tr>
<td>77</td>
<td>3.4</td>
<td>2.7</td>
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<tr>
<td>195</td>
<td>5.7</td>
<td>4.2</td>
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<tr>
<td>273</td>
<td>7.9</td>
<td>5.6</td>
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<tr>
<td>This Work</td>
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<tr>
<td>MD</td>
<td>77</td>
<td>3.5</td>
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<td></td>
<td>156</td>
<td>5.4</td>
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<td></td>
<td>272</td>
<td>8.8</td>
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<tr>
<td><strong>RMS Translational Amplitudes (Å)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jeffrey <em>et al.</em></td>
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<td>neutron C₆D₆</td>
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<td>15</td>
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<td>123</td>
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<td>Cox <em>et al.</em></td>
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<td>x-ray C₆H₆</td>
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<td>MD</td>
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<tr>
<td></td>
<td>272</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Figure 4.12: The r.m.s. angular and translational molecular displacements as a function of temperature. All data is expressed in the molecular frame. Large symbols are data from the model; small symbols are from crystallography, for details of sources see text. Axes: (o) $x$, (o) $y$, (□) $z$
Chapter 6) and there is thus the possibility[6] of a continuous transition to a plastic phase, in which the molecules would have more or less total freedom of rotation about the six-fold axis. Experimentally the r.m.s. displacement about the six-fold axis near the melting point is $7.9^\circ$, and the model gives $10^\circ$. Therefore both agree that the molecules are sitting quite deep in the potential well which extends $\pm 30^\circ$ to either side of the equilibrium position. This indicates that the crystal is still fairly far from the possible continuous transition to the plastic phase even at the melting point. This does not exclude the possibility of a first-order transition.

4.6 Benzene II

In Chapter 1, the benzene II phase was described, it being noted that experimentally the transformation from benzene I $\rightarrow$ benzene II is very sluggish. This would suggest that it might be very difficult to observe the transformation in a molecular dynamics simulation. Attempts to observe the transition in the model failed, although at a pressure above about 20 kbar and at temperatures above about 400 K a slight monoclinic distortion did develop. This structure was however very closely related to the orthorhombic structure, and was not the phase benzene II: when referred to a primitive cell, the monoclinic angle of the model structure was $\beta = 130^\circ$, as compared to $110^\circ$ for benzene II, and furthermore the cell parameters did not agree well with those found experimentally. This phase may be similar to one of those found by Dzyabchenko[97] in a search for the global minimum structure of the potential of Williams and Starr; of the five P2$_1$/c structures that he found, four had $\beta \approx 130^\circ$, and only one had the correct monoclinic angle of $108^\circ$. Dzyabchenko showed from lattice energy minimisation calculations this latter structure was the stable one at high pressures at 0 K. In the present work, no transition to the true monoclinic phase was evident even after over 100 ps at 600 K and 50 kbar.

Simulating the True Benzene II Phase

In view of the expected difficulty of observing the transition from phase I $\rightarrow$ II, an alternative strategy is to set up a simulation in the correct structure and verify that it is stable over the timescale available to molecular dynamics. The accuracy
of the lattice parameters given by the model can then be established.

The structure given by Piermarini et al.[23] has \( a = 5.42, b = 5.38, c = 7.53 \) Å, and \( \beta = 110^\circ \). In a Cartesian coordinate system where \( x \) is along \( a \), and \( z \) is along \( b \) (the unique monoclinic axis) their orientational parameters give 
\[
\mathbf{q}_{\text{exp}} = (-0.922, -0.122, -0.287; 0.234)
\]
for the molecule at \((0,0,0)\). The second molecule, related to the first by a diad about \( b \), is at \((0, \frac{1}{2}, \frac{1}{2})\). These values are at 294 K and a quoted pressure of 25 kbar. The pressure is rather uncertain, and based on Bridgman’s work[98] Ellenson and Nicol[24] suggest that the pressure is actually \( \approx 19 \) kbar. The uncertainty is not important, however, as structures given by energy minimisation suggest that such an error in pressure would give an uncertainty in \( a, b \) and \( c \) of < 0.03 Å.

Initially, a lattice energy minimisation was undertaken, to check that the benzene II structure is stable with respect to the orthorhombic structure at 0K and high pressure, and secondly to determine the pressure at which the transition occurs. For pressures between 10 and 20 kbar the minimised lattice energy was obtained for both the orthorhombic and monoclinic structures. The point at which the energy of the structures were equal (including the elastic term) gave the transition as \( 16 \pm 1 \) kbar. Experimental data is only available down to \( \approx 300 \) K(§ 1.2, however the transition is nearly vertical in the \( P \) – \( T \) plane, and an extrapolation gives a transition pressure of \( 19 \pm 3 \) kbar at 0K.

A simulation was run at 300 K and 20 kbar, and the structure was found to be stable over the duration of the simulation of 100 ps. The structural parameters were \( a = 5.31, b = 5.37, c = 7.61 \) Å, \( \beta = 108^\circ \) and 
\[
\mathbf{q}_{\text{MD}} = (-0.938, -0.103, -0.226; 0.232).
\]
\( a, b \) and \( c \) differ from the experimental values by -2%, -0.2% and 1% respectively and \( \beta \) by 2°. The difference in \( \mathbf{q}_{\text{exp}} \) and \( \mathbf{q}_{\text{MD}} \) represents a rotation of the molecule by 8°.

The agreement is clearly excellent, and coupled with the accuracy of the transition pressure gives great added support to the validity of the potential.

### 4.7 Conclusions

This chapter has covered a wide range of properties and it is worthwhile reviewing what has been determined about the model.

It was initially shown how the original potential of Karlstrom et al. could be simply rescaled to give lattice parameters and internal energy that were in very
good accord with experiment across a wide temperature range. This rescaled potential gave at least as good agreement with experiment as the most highly refined potential of Bartell et al., and furthermore the comparison with experiment was made here at temperatures where quantum corrections are no longer necessary. Compared to the many other empirical potentials that have been proposed, this potential has the further attraction of being based upon a theoretical \textit{ab initio} calculation, with only a minor rescaling.

It was found that the solid phase became unstable at 335 K, but it was then shown that this is not the true melting point, but rather a mechanical instability, involving a softening of the crystal in the $a$ direction. By introducing surfaces into the system, the true melting point was determined as 272±5 K, which is very close to the experimental value of 280 K. The latent heat and volume discontinuity were also in very good accord with experiment.

The amplitudes of the thermal motions of the molecules and the elastic compressibilities also compare quite well with experiment, although the experimental data available in both these cases is not completely satisfactory, especially for the compressibilities. Finally it was shown that the first high pressure phase of benzene can also be successfully modelled by the potential, giving excellent values for the structural parameters. It was not, however, possible to simulate the transition, but this is expected to be very sluggish.

In summary, the model has been subjected to far more intensive study than any previous potential for benzene, and it is generally found to behave very satisfactorily. Having completed this assessment stage, we can now move on to use the model to gain understanding of various experimental phenomena in the final two chapters.
Chapter 5

A Transition Near the melting Point

In the preceding chapter, various general aspects of the behaviour of a molecular dynamics model of benzene were studied, in each case making comparisons with experimental data. This was largely with a view to validating this particular model, by taking experimental data and seeing how well it was reproduced by the model. The comparison was generally very satisfactory.

In contrast, this chapter and the following chapter present two examples of the power of molecular dynamics as a complementary technique to experiment: the present chapter demonstrates how the model can rationalise apparently anomalous experimental data; and in Chapter 6 molecular motions are probed in a level of detail inaccessible to experiment.

5.1 The Transition

A Review of Some of the Results of Chapters 2 and 4

It is first necessary to restate briefly some of the results of the previous chapters. In Chapter 2 it was noted that $\gamma$, the angle of the $C_1-D_1$ bond to the $b$-axis, exhibits a steep downward slope as a function of temperature as the melting point is approached. Similarly, the $b$-parameter shows an anomalously large expansivity in a similar temperature range.

Experimentally, $\gamma$ decreases from $\approx 19^\circ$ at low temperatures to $\approx 15^\circ$ at the melting point, yet in the model of Chapter 4 it was possible to observe $\gamma$ decrease
to effectively zero (Fig. 4.6). The upper limit on the temperature range studied in Chapter 4 was given by the temperature of the elastic lattice instability. It was subsequently found, however, that the true thermodynamic melting point of the model, $T_m$ (272 K), is in fact substantially lower than the lattice instability temperature, $T_{\text{instab}}$ (335 K). The simulations above 272 K were therefore of a metastable phase, and at the melting point of the model the angle $\gamma$ is still non-zero, although it has decreased from $\approx 17^\circ$ at low temperatures to $\approx 10^\circ$ at $T_m$.

An interpretation of the experimental results can therefore be made that the decrease in $\gamma$ that is seen experimentally is a precursor of a transition in which $\gamma \to 0$. The transition is not seen fully experimentally because it would occur at a temperature higher than the melting point. Such an effect could appear as a kind of pre-melting effect, but it is in fact apparently unconnected with melting as will be discussed later.

Detailed Comparison of the Orientation Data

Whilst the molecular dynamics results show the same qualitative effects as the experimental data, there are some quantitative differences.

In all four curves in Fig. 4.6 there is a discrepancy of at most 2° between the two curves at low temperatures. This is a very small error in the orientation of the molecular planes and it is not believed that it will affect the temperature dependent behaviour. More importantly, the decrease of $\gamma$ to zero occurs at a slightly lower temperatures in the model than is apparent experimentally. All four curves overlay well if the temperatures of the molecular dynamics results are shifted by 50 K to higher temperatures, and small vertical shifts are made in each model curve in order to overlay the data at low temperatures (Fig. 5.1). The temperature dependence of the orientations from the model are therefore actually in very good quantitative accord with the experimental data, with the proviso that the steep decrease of $\gamma$ occurs at a temperature approximately 50 K lower than that apparent experimentally. We shall see shortly that the temperature, $T_{\gamma \to 0}$, at which $\gamma \to 0$ is rather critically sensitive to the potential parameters.
Figure 5.1: Orientation data from the rescaled potential model shifted to demonstrate agreement of temperature dependence with experimental data. (o) Model data shifted vertically and horizontally as described in text. (x) Experimental data from this work and the literature - see Chapter 2.
CHAPTER 5. A TRANSITION NEAR THE MELTING POINT

Comparison of Expansivities

The rather tentative observation in Chapter 2 concerning the $b$-parameter can now be re-examined, namely that its expansivity increases markedly above about 230 K.

Experimentally, the expansivities of the three lattice parameters, $\alpha_a$, $\alpha_b$, $\alpha_c$, and of the volume, $\alpha_V$, can be obtained from the interpolation curves plotted in Fig. 2.5. It must be recognised that such a procedure is rather inexact, but it should give the broad features of the expansivity as a function of temperature.

Similarly, the expansivities from the molecular dynamics can be calculated by taking differences between pairs of values at adjacent temperatures. Values of temperature that are very close together give a large error in the value of the expansivity, so that the data at 324K in Table 4.1 was excluded from this calculation.

The experimental and molecular dynamics expansivities are plotted in Fig. 5.2; several general observations can be made:

- The experimental results show the quantum drop to zero, below about 100 K, which is of course not observable in molecular dynamics (see § 4.1.1).

- The large rise in $\alpha_a^{MD}$ above about $\approx 300$ K is due to the high temperature instability as discussed in Chapter 4. Anomalous behaviour in this region may partially account for the drop in the $b$-expansivity at the instability temperature.

- Between about 100 K and 200 K, which is at the same time in the classical regime and removed from the $\gamma \to 0$ transition, the expansivities from molecular dynamics agree excellently with experiment.

Of greatest interest here, however, is the rise in $\alpha_b$ near the melting point, this rise being seen in both sets of data. This rise is believed to be associated with the $\gamma \to 0$ transition as discussed further below. It must be emphasised, however, that the experimental evidence for rise in expansivity of the $b$-parameter is not as clear as the drop in $\gamma$ in the orientational data. The molecular dynamics indicates, however, that such a rise in $\alpha_b$ would be expected.
Figure 5.2: The axial and volume expansivities as a function of temperature: comparison of the rescaled model and experiment. (o) Rescaled model, (+) experimental data. For details of calculation of expansivities see text.
5.2 Sensitivity to the Model Parameters

The foregoing discussion has shown how molecular dynamics can be used to provide a model for interpretation of experimental data. A positive advantage of molecular dynamics in this case is the fact that the sample can be maintained in a metastable state above the melting point, which allows the true nature of an effect that would otherwise be interrupted by the melting point to become apparent. This artificially stabilised metastable state was previously encountered as a disadvantage, as it made the determination of the thermodynamic melting point difficult, necessitating the use of a surface to nucleate the melting (§ 4.3). Another apparent defect of the molecular dynamics method can now be exploited, namely the dependence of the results on the model parameters. This enables the relationship to be studied between changes in the lattice parameters and the molecular orientations.

The Original Karlstrom Potential

In Chapter 4, the length-scale of the original potential of Karlstrom et al. was adjusted in order to obtain more accurate cell parameters. This rescaled potential was the one used in subsequent simulations. In simulations made using the original potential the behaviour of \( \gamma \) was found to be rather different (Fig. 5.3). \( \gamma \) does not drop completely to zero with increasing temperature, but does show an initial strong downward curvature, which is this time interrupted by the lattice instability; overlaying the results for the two potentials indicates that the temperature at which \( \gamma \) decreases is about 60 K higher for the original potential than for the length rescaled potential.

In contrast, the instability temperature was found to be little changed at \( \approx 350 \) K, as was the melting point which was determined as 265±10 K. This allows the conclusion that the drop of \( \gamma \) to zero is related neither to the melting transition, nor to the lattice instability. Furthermore, the sensitivity to the model parameters of the temperature at which \( \gamma \) decreases, compared to the relative insensitivity of the melting temperature, also suggests why the melting point is very well determined by the model, whereas there is the discrepancy of \( \approx 50 \) K between \( T_{\gamma \rightarrow 0}^{MD} \) and \( T_{\gamma \rightarrow 0}^{Exp} \).

Somewhat fortuitously, therefore, the sensitivity of \( T_{\gamma \rightarrow 0} \) provides two very similar models in terms of \( T_m \) and \( T_{\text{instab}} \), but in which the behaviour of \( \gamma \) is quite
Figure 5.3: Orientations of the molecules as a function of temperature for the original Karlstrom potential. Temperature rescaling of $\epsilon = 0.82$ applied.
different. A clear picture of the relationship between the lattice parameters and the molecular orientations can now be obtained by comparing the expansivities from the two models (Fig. 5.4):

- The low temperature expansivities are identical in the two models.
- The large rise in $\alpha_a$ as the lattice instability is approached is also little changed.
- The rise in $\alpha_b$ is evident in for both potentials, however it occurs approximately 60 K higher for the original potential than for the rescaled potential. This confirms the view that the excess expansivity and the drop of $\gamma$ to zero are linked.
- The maximum in $\alpha_c$ is shifted in the original potential by about 60K to higher temperature than in the rescaled potential. This therefore appears to be related to the $\gamma \rightarrow 0$ transition.
- Similarly the maximum in $\theta_c$ is shifted by the same amount (it is only apparently just achieved before the lattice instability for the original potential). It would therefore appear that the maximum in $\theta_c$ is also related to the drop of $\gamma \rightarrow 0$; the alternative possibility would be that the behaviour of $\theta_c^{Resc}$ were related to the elastic instability, but this instability is rather similar in both models.
- The connection between the behaviour of $\alpha_c$ and $\theta_c$ at high temperatures is not clear. However, it is plausible that the maximum in $\alpha_c$ corresponds to the point of inflection in $\theta_c$ prior to the maximum: $\alpha_c$ being a temperature derivative.
- The volume expansivities are very similar, except perhaps very close to the lattice instability: this is important for experimental studies, since it means that measurements of the volume expansivity will not be sensitive to $\gamma \rightarrow 0$.

5.3 What is Really Happening?

Having established that in the model a mean quantity such as $\gamma$ behaves as in experiment, molecular dynamics can then be used to look at what is happening
Figure 5.4: The axial and volume expansivities as a function of temperature: comparison of the rescaled model and the original Karlstrom potential. (o) Rescaled model, (+) original Karlstrom model. For details of calculation of expansivities see text.
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at the molecular level.

The Relationship between the Orientations of the Four Molecules in the Unit-Cell

To understand what is happening when $\gamma \to 0$ it is necessary to reconsider the relative molecular orientations within the unit cell. In Fig. 1.3 the molecules I and III are related by a mirror plane perpendicular to $b$, or equivalently a diad parallel to $b$; similarly for molecules II and IV. These two symmetry operations are equivalent because the molecule has a centre of symmetry and the atoms are treated as being indistinguishable.

Molecules I and III do, however, have rather similar orientations: the planes are almost parallel, and the orientations qualitatively differ only in whether the $C_1-D_1$ bond projects towards $+a$ or $-a$. Therefore, if the rather slight distinction between the orientatons of molecules I and III (and therefore II and IV) is lost, then $\gamma$ will drop to zero.

It must be realised that the diad and mirror planes are simply the way that molecules I and III are formally related within the $Pbca$ space-group. The symmetry of the molecule means that there are, however, many more operations that will also relate these two molecules, again treating the atoms as being indistinguishable. The operation that is of particular interest here is a rather small rotation by approximately 35° about the $c$-axis; this is relevant because a rotation by half this angle gives $\gamma \to 0$.

Observing the Transition at a Molecular Level

Figures 5.5(a)-(c) show projections of a unit vector along the $C_1-D_1$ bond onto the $a-c$ plane at temperatures of 160, 270 and 325 K from the warming sequence of Chapter 4. Each figure is a 'snapshot' of a single configuration, with one point for each molecule. Before making the projection the space-group symmetry operations were applied to reduce each of the four molecules in the unit cell to the same mean orientation, so that all $C_1-D_1$ bonds lie to the same side of the $b$-axis. The diagram is best interpreted by imagining that one is looking along the $b$-axis of the crystal. The broken circles on the figures mark the loci of points representing vectors making angles of 10°, 20°, 30° and 40° to the $b$-axis.

In the sequence of plots the crystal can be seen to change from an ordered
Figure 5.5: Plots to show the order of the $C_1-D_1$ bond directions at various temperatures (for details see text). Warming sequence, (a) 160 K (b) 270 K (c) 325 K and then cooling to (d) 80 K. The broken circles are for angles of 10°, 20°, 30° and 40° to the $b$-axis.
to crystal at 160 K, with a mean $C_1-D_1$ bond direction at $\approx 17^\circ$ to $b$; to a state of greater disorder at 270 K, with a mean angle to $b$ that has reduced to $\approx 10^\circ$; and finally at 325K the disorder has increased further to give a mean $C_1-D_1$ bond direction that lies along the $b$-axis. The transition therefore appears to be a disordering one, in which the distinction between the I and III (and II and IV) type molecules is lost.

Fig. 5.5(d) shows a configuration from the cooling sequence of Chapter 4 at 80 K. The cooling sequence started from the configuration of Fig. 5.5(c), so that the orientations have returned to the ordered state from a state of disorder. That a perfect un-twinned crystal was obtained is probably due to a combination of the small size of the system, and of the periodic boundary conditions. In contrast, for an ordering transition in a cluster of sulphur hexafluoride twinned crystals were obtained in simulations of clusters or of rather large systems[87, 99].

A Qualitative Explanation of the Transition

An understanding of the transition can be understood by considering the potential energy function of the crystal.

At 0 K, the precise form of the rotation that takes I $\rightarrow$ III is 34.6$^\circ$ about an axis that makes angles of 86$^\circ$, 90$^\circ$ and 4$^\circ$ with $a$, $b$, and $c$ respectively. The potential energy of the lattice can be calculated as the molecules are rotated about this axis, maintaining the full crystal symmetry, again at 0 K. This is plotted as a function of the rotation angle in Fig. 5.6(a) (solid curve). The two minima correspond to the cases where the molecule I is either in its original orientation, or has been rotated through to the orientation originally corresponding to the molecule III (and II $\rightarrow$ IV); these two cases give identical crystal structures apart from a change of origin. The maximum in the energy is for $\gamma = 0$.

The dashed curve is the equivalent function using as the starting point a structure with lattice parameters obtained from molecular dynamics at 310 K and orientations from energy minimisation for these lattice parameters. It is interesting to note the total failure of lattice statics here. The minima actually become more widely separated, which, without thermal motion, would predict $\gamma$ to increase slightly with increasing temperature.

Fig. 5.6(b) is obtained by rotating only a single molecule and calculating its potential energy, whilst the rest of the lattice is left unchanged. As no second
Figure 5.6: Potential curves. (a) The potential energy of the lattice as all molecules are rotated about the axis described in the text (approximately the c-axis), maintaining the crystal symmetry; the two minima correspond to equivalent crystal structures; the maximum is for $\gamma = 0$. (b) The potential energy of a single molecule as it is rotated about the same axis, the rest of the lattice remaining fixed. Initial structure: solid curves - 0 K structure; broken curves - 310 K lattice parameters and energy minimised quaternions.
minimum is now seen, the process by which $\gamma \to 0$ cannot be interpreted as a disordering of the individual molecules between two orientations in an Ising-type model. This is a model often invoked to explain the formation of certain disordered molecular crystals[3].

The decrease of $\gamma$ to zero can instead be explained in terms of a collective motion where the molecules librate about the axis described above, whilst maintaining the crystal symmetry. The dynamics of this mode are approximately described by the potential well in Fig. 5.6(b), where for the ordered state the crystal sits in one of the two minima that describe equivalent crystal structures. This is only very approximate, especially since it assumes an otherwise undeformed lattice, which is only valid in the harmonic limit. As the amplitude of libration within the well increases, the mean value of $\gamma$ will decrease as the well is strongly harmonic and is much softer towards $\gamma = 0$. Qualitatively, this explains why $\gamma$ starts to decrease.

Taking a rather simple minded approach we could then estimate a characteristic temperature for the well as $\Delta \phi / R$, where $\Delta \phi$ is the height of the barrier separating the two equivalent crystal structures. From Fig. 5.6, $\Delta \phi \approx 1.4$ kJ/mol, which gives $T \approx 170$ K. The barrier is therefore quite small compared to thermal energies at 300 K. This barrier can be compared with the barrier height against motion of individual molecules about the six-fold axis of the molecule (Chapter 6), which is $\approx 14$-17 kJ/mol, which corresponds to a rather high temperature of $\approx 2000$ K.

From Fig. 5.5 we can see that with increasing temperature the thermal disorder eventually becomes so great that the distinction between A and C molecules is lost altogether. When this distinction is lost then so is the notion of the double well potential (or strictly speaking the free-energy double-well), and the mean value of $\gamma$ becomes zero. The reason that $\gamma$ is not precisely zero at the highest temperature in Fig. 4.6 is due to fluctuations in the mean orientation; these can only make $\gamma$ positive from the its definition.

Finite-Size Effects

An attempt was made to assess the effect of the finite size of the system on the transition by performing simulations with a rather smaller sample of 256 molecules. This was to see whether there is a significant difference in the be-
haviour of the system if the number of molecules is reduced by a factor of more than three. The results are shown in Fig. 5.7, along with the data from the 864 molecule sample. There appear to be no systematic differences between the two sets of data, apart from perhaps a small discrepancy in $\theta_e$, and the form and temperature of the $\gamma \to 0$ transition are unaltered. It would therefore seem that the 864 molecule system is sufficiently large not to be greatly affected by finite-size effects.

5.4 Vibrational Spectra

Whilst the above discussion of the motion in the double-well potential is somewhat qualitative, the mode described does correspond to an actual normal mode of the lattice. It is the lowest frequency totally symmetric ($A_{1g}$) Raman mode, and if the model is correct then this mode would be expected to soften markedly as the transition occurs. In fact there have been reports of the softening of this mode, but as will be discussed there are problems with the experimental data. The extraction of the vibrational spectrum from a molecular dynamics simulation will therefore now be considered; this acts as a further test of the model, but it is also possible to demonstrate the softening of this particular mode. The following discussion will only consider librational (rotational) modes: the translational modes can be treated similarly, and will be briefly discussed later.

General Considerations

In the vibrational mode that we are considering, crystallographically equivalent molecules are displaced at each moment by the same amount, and this is therefore a $k=0$ optical lattice mode. Such vibrations are accessible experimentally by Raman and infra-red spectroscopy[100]. The influence of the crystal symmetry on the vibrational modes is discussed in Appendix A, where the standard notation for labelling the various modes is introduced and it is shown that the modes are either purely rotational or purely translational.

As there are four molecules in the unit cell, each with six degrees of freedom, there are 24 $k=0$ modes. The selection rules for optical spectra determine that all the rotational modes are Raman active, whereas the translational modes are
Figure 5.7: Orientation data for the rescaled potential with two different system sizes. (x) 256 molecules, (o) 864 molecules.
either infra-red active or completely forbidden.

5.4.1 Experimental Studies

There have been many experimental studies of the lattice mode region of the benzene Raman spectrum, notably by Fruhling [101], Ito and Shigeoka [95], Bonadeo et al. [102], and Ellenson and Nicol [24]. The most complete assignment of the spectrum was not achieved until the application of pressure allowed Ellenson and Nicol to resolve an accidental degeneracy. Coupled with a polarisation study by Bonadeo et al. and a lattice dynamical calculation, Ellenson and Nicol were able to assign all eleven of the observed peaks. Intensity calculations also allowed them to explain the absence of the twelfth peak.

The available experimental data on the frequencies of the Raman modes at various temperatures is plotted in Fig. 5.8. More extensive temperature dependent studies have been reported by Ghelfenstein and Szwarc [54] and Dumas [103], for three bands at $\approx 60(A_{1g})$, $\approx 80(A_{1g}, B_{2g})$, and $\approx 130(B_{1g}, B_{3g})$ cm$^{-1}$, graphs of the data, and not tabulated values, being presented. The curves of Ghelfenstein and Szwarc are shown in Fig. 5.8. It is claimed that with temperature the frequency of these modes decreases anomalously rapidly as the melting point is approached. The softening of the modes as the melting transition is approached was interpreted by Ghelfenstein and Szwarc as a premelting phenomenon. A rather low value for the lowest frequency $A_{1g}$ mode was also reported by Fruhling [101], but it was disputed by Ito and Shigeoka [95] largely on the grounds that it did not agree with the general trend of the data. The other data of Fruhling does not, however, agree particularly well with that of Ghelfenstein and Szwarc (Fig. 5.8).

The problem with these detailed temperature dependent studies is that the bands become very broad at high temperatures, so that the precise determination of frequencies becomes difficult. The increase in width can be viewed as a form of lifetime broadening; the lifetime of a mode decreases as increasing anharmonicity causes interaction between the modes. The variation of linewidth with temperature has been given by Ghelfenstein [104] for the three bands above. The widths quoted, however, do not agree particularly well with those in spectra presented elsewhere [102, 103], and it is only possible to get a general picture: at low temperature the lines are very sharp (4K, $\approx 1$ cm$^{-1}$, [95]); at around 150 K the widths are $\approx 5$-10 cm$^{-1}$; and near the melting point the widths are $\approx 20$ cm$^{-1}$. It
Figure 5.8: Experimental Raman frequencies as a function of temperature.
must be pointed out that further uncertainty in both the widths and frequencies of peaks is introduced by the fact that none of these bands correspond to a single mode, although the intensity calculations of Ellenson and Nicol[24] indicated that for each band one mode is dominant.

A study of the pressure dependence of the Raman frequencies[59] found a similar decrease of frequencies as the melting pressure is approached from above. The high temperatures at which these spectra were obtained means that they will also be affected by problems of linewidth.

In summary, the experimental evidence concerning the temperature dependence of the Raman frequencies is somewhat conflicting. There is a suspected softening of some of the modes near the melting point[54, 59], but this is backed up by the data of Fruhling only for the lowest frequency band.

5.4.2 Lattice Dynamics

For a particular model, the frequencies of lattice modes can be readily calculated at 0 K using lattice dynamics[29, 83], which amounts to finding the normal modes of the crystal lattice within the harmonic approximation. It is strictly only applicable at 0 K, since the potential expansion is assumed to be made about the minimum energy structure. At non-zero temperatures lattice expansion can be enforced and the harmonic expansion made about the inflated structure; this is the so-called quasi-harmonic approximation. This approximation takes account of the effect on the frequencies of the modification of the potential due to the changes in the crystal structure, but the anharmonicity of the potential, which is implied by the very fact of thermal expansion, is neglected. Some calculations have been performed that do attempt to allow for anharmonicity[27, 105], but all such methods will fail for the very severe anharmonicities often encountered in molecular crystals[28], particularly such as during the $\gamma \rightarrow 0$ transition.

Previously, lattice dynamics was the only method by which the optical spectra of benzene had been studied theoretically. The most recent such calculations were by Ellenson and Nicol[24], Powell and Dolling[106], Sataty and Ron[107], and recently by Filippini and Gramaccioli[108] for low temperatures. The study of Ellenson and Nicol showed the best agreement of frequencies with experiment, and they were also able to verify that the eigenvectors were plausible by calculation of the expected Raman intensities. It should be pointed out that in this, the most
important paper on the assignment of the Raman spectrum, an unconventional choice of molecular axes was used: they followed Bacon and chose the $y$-axis of the molecular frame as the $C1-D1$ bond. This is in contrast to the majority of the crystallographic and vibrational literature and means that the eigenvectors quoted in [24] must be interpreted with care: $x$ and $y$ are interchanged in comparison the convention used here and elsewhere.

A lattice dynamics calculation was carried out for the rescaled potential to give the zero temperature frequencies in Fig. 5.10. As the modes at $k=0$ are either purely translational or purely rotational, the lattice dynamical method is rather simple in this case, consisting of finding the eigenvectors and eigenvalues of a $3\times3$ dynamical matrix[83]. The eigenvectors from this calculation compare fairly well with those found by Ellenson and Nicol, Table 5.1. The comparison of the frequencies is discussed later, as the results of Ellenson and Nicol are for a non-zero temperature structure.

5.4.3 Librational Spectra from Molecular Dynamics

Vibrational spectra can be obtained readily from molecular dynamics simulations, and in contrast to lattice dynamics the full effects of anharmonicity are included. It is possible in principle [105] to calculate the full Raman intensity spectrum, which involves considering the changes of polarisability that the vibrations produce. As the frequencies were of prime interest here, the intensity calculation was not undertaken, and the spectra presented are simple Fourier transforms of various dynamical variables.

Basic Procedure

The $k=0$ rotational spectrum is obtained by recording the instantaneous ensemble-mean quaternions, $q_i(t)$, for each type of molecule in the unit-cell ($i = I, II, III, IV$). The time-average of $q_i(t)$, which will be written $Q_i$, gives the time averaged orientation of the molecules of each type (in fact, the $Q_i$ of the four molecule types will be simply related by the symmetry operations of the space-group). The instantaneous ensemble-means, $q_i(t)$, can then be converted to give instantaneous displacements from the time-averaged orientation,

$$q_i^{disp}(t) = Q^{-1} \ast q_i(t) \quad (5.1)$$
Table 5.1: Eigenvectors for the rotational \( k=0 \) lattice modes, from this work (lattice dynamics at 0 K), and from Ellenson and Nicol (lattice dynamics for 138 K structure). The eigenvectors are expressed in generalised coordinates (see Eqn. 5.3) in the molecular frame as defined in this work, and within each symmetry species are ordered according to increasing frequency.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>This Work</th>
<th>Ellenson &amp; Nicol</th>
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<tbody>
<tr>
<td></td>
<td>( x )</td>
<td>( y )</td>
</tr>
<tr>
<td>( A_{1g} )</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>0.1</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>0.1</td>
<td>-0.9</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( B_{3g} )</td>
<td>0.8</td>
<td>-0.2</td>
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<td></td>
<td>0.5</td>
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<td></td>
<td>0.3</td>
<td>0.9</td>
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where $q_i^{\text{disp}}(t)$ represents the displacement of the molecules in the (mean) molecular frame.

As the librational amplitudes remain small ($\S$ 4.5), the displacement can be described by small rotations $\theta_j$, about the axes of the molecular frame. From Eqn. 3.1.1

$$q_i^{\text{disp}}(t) \approx \left( \frac{\theta_1}{2}, \frac{\theta_2}{2}, \frac{\theta_3}{3}; 1 \right)$$

Suitable generalised coordinates can then be constructed, $x^i$ as

$$x_j^i(t) = \sqrt{I_j} \theta_j^i(t)$$

where $i$ labels the molecule-type; $j$ labels the axis of the molecular frame; and $I_j$ is the moment of inertia of the molecule about the $j$th axis of the molecular frame (in which the inertia tensor is diagonal).

The different symmetry species are separated out by taking appropriate combinations of the time domain data for the four molecule types. For example the $B_1g$ modes are obtained by taking the combination

$$X_{B_1g}(t) = x^I(t) + (2_x \ast x^{II}) - (2_y \ast x^{III}) - (2_z \ast x^{IV})$$

where, for instance, $2_x \ast x^{II}$ represents the displacement coordinates of type-II molecules operated upon by the diad down the x-axis of the crystal. The signs in Eqn. 5.4 are obtained from the character table in Appendix A. This eliminates contributions from other species by the orthogonality of the symmetry species. The other species are obtained by substituting the appropriate signs from the character table.

The frequency spectrum is then obtained as the power-spectrum Fourier transform of $X$. This obtains the $k=0$ mode, since taking the ensemble mean is equivalent to performing the $k=0$ part of a spatial Fourier transform. The $k\neq 0$ modes would be obtained by modifying each term in the mean by a complex phase term.

A spectrum is thus obtained corresponding to each symmetry species. Each spectrum contains three orthogonal modes, each with three Cartesian components. As the peaks corresponding to each mode are generally overlapping it is better to express the spectra in terms of the 0 K eigenvector basis, rather than the original Cartesian basis. In such a basis at 0K each peak is a single component corresponding to the appropriate eigenvector. Provided that the eigenvectors do
not change markedly with temperature then at finite temperatures each peak can be resolved into a single component corresponding to one of the eigenvectors. This procedure was found to be very satisfactory (see below). In general the peaks were found to overlap too much and to be too noisy for the inverse process of obtaining the precise eigenvectors from the spectra at finite temperatures to be satisfactory.

Spectra

Spectra were collected at 40, 120, 200, and 270 K.

The spectra at the lower three temperatures were obtained using the constant stress algorithm for consistency with the rest of the work. This introduces artificial low frequency components into the spectra below 20 cm\(^{-1}\), which correspond to changes in the orientations of the molecules as the MD-cell fluctuates. These peaks are very sharp compared to the true lattice modes peaks, as the oscillations have a large coherence time due to the large inertia of the MD-cell. At 200 K and lower, the peaks due to cell fluctuations were well separated in frequency from the lattice modes. This is an indication that the detailed dynamics of the system should be essentially unaffected by the motion of the MD-cell. At 270 K, the lowest frequency modes softened to such an extent that it was necessary to work at constant volume to eliminate the peaks due to cell fluctuations. Spectra were also obtained with a fixed cell at 200 K, and the positions of the peaks were found to be unaltered within error. This is further evidence that the dynamics of the system are not perturbed by the motion of the MD-cell.

For the spectra at constant stress, the spectra are plotted in two parts: above 20 cm\(^{-1}\) the data has been smoothed with a square window function, because in the raw spectra the peaks are very spiky and this obscures the detail. The spikiness is due to the random nature of the time domain data, and is discussed in [109]. The widths of the window functions were chosen to be the minimum that gave satisfactorily smooth spectra; 3.7 cm\(^{-1}\) at 40 K, 7.3 cm\(^{-1}\) at 120 and 200 K, and 11 cm\(^{-1}\) at 350 K. These widths are depicted on the spectra as vertical bars. As the peaks corresponding to cell fluctuations have a long coherence time they are not affected by the problem of spikiness so the data below 20 cm\(^{-1}\) was not smoothed.

Each set of time domain data consisted of 1000 points at 0.09 ps intervals,
giving a total sampling time of 100 ps. This gives a total frequency range of 184 cm\(^{-1}\) and a digital resolution of 0.37 cm\(^{-1}\). The simulations were made at constant energy.

The method of separating out the separate species is illustrated in Figs 5.9(a)-(c). Fig. 5.9(a) show the spectrum obtained from the coordinates of just one molecule type: all the twelve modes are present, many overlapping, and the result is very difficult to interpret. This is rather similar to an unpolarised Raman spectrum. In Fig. 5.9(b), the four symmetry species have been separated out according to Eqn. 5.4. Each spectrum shows three peaks as expected. In Fig. 5.9(c) the modes within each symmetry species have been separated out by projecting each point in the complex spectrum onto the 0 K eigenvector basis. Each peak is now clearly assigned to a particular mode. The use of the 0 K eigenvector set appears to be adequate in separating out the species right up to the highest temperature studied.
Figure 5.9 (a) Raw $k = 0$ librational power spectrum at 40 K, separated in (b) into the four symmetry species. The colours in these two figures label the spectra for the three Cartesian components of $X$ as introduced in the text: brown - 1, red - 2, blue - 3. (Figure continued on next two pages)
Figure 5.9 (cont.) Power spectra expressed in the 0 K eigenvector basis. (c) 40 K (d) 120 K. Within each species the colours brown, red, blue label the three components in order of increasing frequency at 0 K. The vertical scale is in arbitrary units, but constant for all plots at each temperature.
Figure 5.9 (cont.) (e) 200 K and (f) 270 K, plotted as for (c) and (d).
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Results

The frequencies of the peaks are given in Table 5.2 and plotted in Fig. 5.10 along with the experimental data. The errors are estimated as approximately 1 cm\(^{-1}\) at low temperatures, and 5 cm\(^{-1}\) at the higher temperatures, or slightly more for the rather broad high frequency bands.

For comparison with the experimental data, the values quoted for the model data in Table 5.2 and plotted in Fig. 5.10 have been converted from frequencies for the deuterated compound to frequencies for the hydrogenated compound by multiplying by a factor of 1.10, the square-root of the ratio of the moments of inertia of \( C_6D_6 \) and \( C_6H_6 \). Such a procedure is justified by the experimental observation that the frequencies of the modes are in this ratio for the two compounds[95]. With increasing temperature it became impossible to locate the higher frequency modes, and at 270 K the frequencies of only the two lowest frequency modes could be determined. The data at 0 K is from lattice dynamics. The results of Ellenson and Nicol are also plotted at 138 K and it is clear that the potential used there accounts better for the rotational frequencies. Such a comparison is slightly unfair, however, as their calculation was purely a quasiharmonic lattice dynamics calculation made at the enforced experimental structure, and they actually tried several potentials and chose the results showing best agreement with experiment.

There are, however, clear faults in the present model: the frequency of the lowest frequency \( A_{1u} \) mode is, in particular, rather low even at low temperatures. The discrepancy in the frequency of this mode may correspond to the fact that the \( T_{\gamma=0} \) transition occurs at too low a temperature in the model, which indicates that the barrier in the double well potential is slightly too low: a more steeply curved minimum in the well would give a higher libration frequency. This indicates a feature of the model that should be carefully considered in future modifications to the potential.

The peaks are seen to broaden to an extent similar to that found experimentally, and the temperature dependence of the modes is generally well reproduced. The striking feature is the dramatic softening of the lowest frequency \( A_{1g} \) mode that was predicted above by a consideration of the changes in structure that occur as \( \gamma \) decreases. Spectra obtained at higher temperatures yet were obscured by noise, which may be an indication of the very strong anharmonicity in this disordered phase. The reported softening of this mode experimentally may therefore
Table 5.2: Frequencies of the rotational modes from the model at five temperatures. Frequencies are compensated for deuteration (see text).

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>40</th>
<th>120</th>
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Figure 5.10: Frequencies of the rotational lattice modes: comparison of the model and experiment. (○) Data from the model; (●) Lattice dynamics results of Ellen-son and Nicol; solid lines - guides to the eye through the model data; broken lines - experimental curves from Fig. 5.8
Table 5.3: Frequencies of the infra-red active translational modes. This work at 120 K (MD) compensated for deuteration (see text); from Ellenson and Nicol: experiment at 138 K (Exp$^{E+N}$), calculation (Calc$^{E+N}$).

<table>
<thead>
<tr>
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<th>MD</th>
<th>Exp$^{E+N}$</th>
<th>Calc$^{E+N}$</th>
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<tr>
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<td>67</td>
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<td>$B_{3u}$</td>
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<td>102</td>
<td>99</td>
<td>97</td>
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indeed be related to the $\gamma \rightarrow 0$ phenomenon, rather than to premelting as has been suggested[54]. Further experiments that might be performed to investigate this are discussed below.

### 5.4.4 Translational modes

For the present work, the main interest lies in the rotational modes. For completeness, however, the translational modes should be briefly mentioned. An equivalent procedure to that used above can be applied to gather the translational spectra, by forming appropriate sums of the translational coordinates. Spectra were obtained at 120 K, and the frequencies of the modes can be compared with values quoted in Ellenson and Nicol[24] at 138 K, Table 5.3. The data from the present work are converted to frequencies for the hydrogenated compound, as for the rotational modes. The conversion factor is now the square-root of the masses of the two compounds, 1.04. This ratio is also found for the experimental frequencies[107]. The two models appear to give similarly good account of the translational mode frequencies.
5.5 Pressure Dependence of the Transition

It has been proposed in this chapter that, experimentally, only a precursor to the \( \gamma \to 0 \) transition is observed because, coincidentally, the solid melts before the transition is complete. In general, the application of pressure shifts transitions to higher temperature and there is, therefore, the possibility that the application of pressure may have a greater effect on \( T_m \) than on \( T_{\gamma \to 0} \), so that the solid could be stabilised sufficiently to allow the full transition to be observed experimentally.

Shift of the Transition with Pressure

In order to assess the effect of pressure on the \( \gamma \to 0 \) transition, simulations were carried out at a pressure of 550 MPa (5.5 kbar) and temperatures up to 365 K, giving the variation of orientational parameters as plotted in Fig. 5.11. The transition is shifted to a higher temperature under pressure, as would be expected, and a comparison with Fig. 4.6 shows the transition temperature to be increased by \( \approx 50 \) K.

Shift of the Melting-point with Pressure

The slope of the melting curve in the \( P - T \) plane was determined in § 4.3.2, as 30 K/kbar at zero pressure, in accord with an experimental value of 26 K/kbar. A pressure of 5.5 kbar would therefore be expected to increase the temperature of the transition by \( \approx 140-160 \) K. The experimental \( P - T \) melting curve is slightly curved, so that in fact the application of 5.5 kbar pressure increases the experimental melting point by only \( \approx 110 \) K (Fig. 1.2). In the free surface method of determining the melting point it is not possible to apply pressure in order to determine more accurately the variation of the melting temperature with pressure. In principle it would be possible to start from the melting temperature in the two phases as a point of equal free energy and then calculate free energy changes as the pressure and temperature are varied. Such a calculation would, however, have to be very accurate to detect the curvature, rather than just the average slope of the melting curve.
Figure 5.11: The variation of the orientations of the molecules as a function of temperature at 5.5 kbar pressure.
Comparison

The difference between the shifts, under a pressure of 5.5 kbar, of 50 K in $T_{\gamma \rightarrow 0}^{MD}$ and 110 K in $T_{m}^{exp}$ does therefore provide the possibility that the complete transition could be seen experimentally by the application of pressure: from Fig. 5.1 it appears that the relative shift in $T_{m}^{exp}$ by $\approx 60$ K relative to $T_{\gamma \rightarrow 0}^{exp}$ would be sufficient for the transition to occur completely in the real solid.

In contrast, the elastic lattice instability was found to shift by at least 170 K, so that it appears that this instability actually moves further above the melting point with increasing pressure.

The most suitable technique to detect the transition would be a diffraction experiment. When the transition occurs, the space group of the crystal changes from $Pbca$ to $Abma$ (a setting of $Cmca$). Powder patterns were calculated for two structures (Fig. 5.12) using the PROFIL program with instrumental parameters for the D2B diffractometer as used in Chapter 2. In both cases, the lattice parameters at 325 K from the model were used. In Fig. 5.12(a) orientational parameters from the model at 120 K were used (corresponding to $\gamma \sim 18^\circ$) and in (b) the orientational parameters from the model at 325 K were used ($\gamma = 0$), which is in the high-temperature phase. Peaks for which there are especially clear changes in intensity are marked on the figure. In particular, several peaks disappear in (b), as the lattice becomes $A$-centred, so that peaks with $k+l$ odd are eliminated. Other intensity changes occur, such as the enhancement of the (202) peak. A full refinement of patterns should allow the complete progress of the transition to be followed. Modest pressures of 5 to 10 kbar would be sufficient, and the experiments would have to be made up to temperatures of $\approx 100^\circ$ C; these conditions are technically quite feasible. A Raman spectrum should also show changes, but there would still be the problem of the great width of peaks obscuring the detail at these temperatures.

These proposed experiments would provide an interesting test of the molecular dynamics prediction, and of the interpretation of the data from Chapter 2.

5.6 Conclusions

This chapter has demonstrated how some of the experimental results of Chapter 2 can be understood. In particular it has been shown that a disordering transition
Figure 5.12: Diffraction patterns calculated using structural parameters from the model. (a) Low-temperature phase; (b) High-temperature phase. For details of parameters see text.
occurs in the molecular dynamics in which the distinction between the orientations of some of the molecules in the unit cell is lost. The experimental data appears to show that the same effect would be seen in real benzene were the solid not to melt first. It has also been shown that the application of moderate pressures should make the transition more apparent experimentally.

This transition is interesting in its own right. Equally importantly, however, this chapter has provided an example of how molecular dynamics can rationalise experimental data. Without the idea of the disordered transition, one might be tempted to explain the downward curvature of $\gamma$ that is seen experimentally as a premelting effect. The molecular dynamics shows that such a hypothesis is unnecessary, and that one can explain the experimental data whilst retaining a philosophically appealing first-order theory of melting.
Chapter 6

Molecular Reorientations

The picture of a benzene crystal presented so far has been one of generally an orientationally ordered crystal, the molecules undergoing small angular librations about the mean orientation. Near the melting point these librations have an amplitude of approximately $\pm 10^\circ$ (§ 4.5), and it has been shown in Chapter 5 how this is sufficient to overcome an energy barrier between two equivalent crystalline structures, increasing the symmetry.

In fact, even at temperatures far below the melting point, another type of large amplitude motion is present: occasional reorientations by $60^\circ$ about the hexad axis of the molecule. As this is a symmetry axis of the molecule, the local structure is unchanged following the reorientation event, the motion occurring without any catastrophic effect upon the lattice stability.

The various experimental techniques that have been used to study these reorientational events are discussed below, but as will be seen these can only provide rather limited detail about the nature of the jumps. The questions that molecular dynamics is later used to address are

- Are the jumps discrete events, or does a molecule remain in an excited reorienting state for an extended period?

- If a molecule jumps, are its neighbours more likely to jump, and if so is there a clear steric mechanism for this? In particular, is there evidence for the cog-wheel motion proposed by Cox et al. (§ 1.1.3)? Alternatively, is there an evident local lattice distortion which 'makes room' for a molecule to reorient?
Before pursuing these questions we need to consider what is known experimentally about these reorientation events.

6.1 Experimental Evidence

6.1.1 Basic Principles

The first indication of reorientation events in solid benzene came from the Nuclear Magnetic Resonance (NMR) work of Andrew [5], which showed a rapid decrease in the proton NMR linewidth between 100 and 120 K on warming. Calculations showed that this was consistent with the averaging of inter-protonic interactions by rotations about the hexad axis, the motion being rapid on the NMR timescale. The NMR timescale in this case is defined by the reciprocal of the width of the original unnarrowed line, \( \approx 10\mu s \). The abrupt change in the NMR linewidth is not an indication of a fundamental change of behaviour; it is simply that with increasing temperature the motion becomes rapid on this particular timescale.

Rather than studying the linewidth, the rate has been measured most accurately by determining what is known as the longitudinal proton NMR relaxation time, \( T_1 \). In an NMR experiment, the sample is placed in a strong magnetic field which generates a Zeeman splitting of the nuclear spin states. \( T_1 \) is a measure of how quickly the nuclear spin populations of the two energy levels (in the case of spin-1/2 protons) return to a thermodynamic distribution following a perturbation. A radio-frequency (RF) magnetic field is initially applied which induces transitions between the two levels, the field being applied at the Larmor frequency which corresponds to the splitting of the energy levels expressed in units of \( h \). The Larmor frequency depends upon the strength of the magnetic field used, but is typically \( \sim 100 \) MHz. The relaxation back to a thermal distribution is monitored by measuring the net nuclear magnetic moment as a function of time following the perturbation. This relaxation is effected by random fields acting on the nuclei which induce transitions similarly to the originally applied RF field. The origin of these fields in this case is the dipolar field due to nearby hydrogen nuclei on the same or other molecules. The efficiency of relaxation depends upon the crystal structure and on the rate and geometry of the dynamics: this provides the link between the rotation rate and \( T_1 \), however the analysis is dependent upon a reliable model for the reorientation event. It has generally been found that it is
rather difficult to distinguish between different models as will be described below.

Since the Larmor frequency is typically 100 MHz, the method is only sensitive to rather long time scale fluctuations of the field which is why rapid small angle librations do not contribute significantly to the rate.

6.1.2 Experimental Determinations of the Reorientation Rate

Temperature Dependence

Andrew and Eades[6] were the first workers to measure $T_1$ as a function of temperature and, using a simple model to link $T_1$ to the reorientation rate, they interpreted the results in terms of an Arrhenius rate equation[110],

$$\frac{1}{\tau_c} = \nu_0 e^{-\frac{E_{\text{act}}}{k_B T}}$$ (6.1)

where $\tau_c$ is the mean time between jumps for each molecule; $E_{\text{act}}$ is the activation energy for the process; and $\nu_0$ is a pre-exponential factor that will be discussed later.

The Arrhenius plot was found be be linear over a temperature range of 80-240 K, giving a range of $\tau_c$ of approximately 100 $\mu$s to 100 ps, which is a range spanning six orders of magnitude. The plot was observed to deviate from Arrhenian behaviour over the last 30 K before the melting point, but this effect was not confirmed by subsequent workers. The extracted parameters were $E_{\text{act}} = 15.5$ kJ/mol and $\nu_0 = 9$ THz. The latter is rather approximate as it depends upon the model used to analyse the $T_1$ data.

Later, however, Haeberlen and Maier[111] performed a much more complete calculation relating $T_1$ to $\tau_c$ which became the basis of most later experimental analysis. Their model assumed independent jumps of molecules from one orientation to any of the other five symmetry related orientations. A more plausible model is that molecules can jump only to neighbouring sites. The random jump assumption used by Haeberlen and Maier was introduced to simplify the theory and was not believed to alter the results substantially. This is because a multiple jump would be too rapid to influence the relaxation, so that its effect would be as for a single jump. They found $E_{\text{act}} = 17.6$ kJ/mol, and $\nu_0 = 100$ THz.

Wendt and Noack[112] attempted to extend the theory to improve the theoretical fit to their experimental data. They tried introducing a distribution of
\( \tau_e \), correlations between neighbouring molecules, temperature dependence of the activation energy and used the experimentally determined temperature dependence of the lattice parameters. The improvement of the fit was minimal. Upon introducing the temperature dependent lattice parameters, the term indicating correlation between neighbouring molecules was found to become negligible. All the models gave \( E_{\text{act}} = 17.1 \pm 0.4 \) kJ/mol and \( \nu_0 \approx 60\pm10 \) THz, with a weak temperature dependence of \( E_{\text{act}} \) of \( \approx 0.01 \) kJ/mol/K. Later, Noack[113] et al. used a different NMR measurement, \( T_1 \), and found that the fit of the theory to experiment was rather poor, and that no value for the temperature dependence of \( E_{\text{act}} \) could be extracted. They found \( E_{\text{act}}=18.4\pm0.4 \) kJ/mol, and \( \nu_0 = 170 \pm 50 \) THz.

**Pressure Dependence**

If reorientation requires a local lattice distortion, then it is likely that the rate will be strongly pressure dependent, via an equation of the form[114]

\[
\frac{1}{\tau_e} \propto e^{-\frac{P V_{\text{act}}}{kT}} \tag{6.2}
\]

where \( V_{\text{act}} \) is the activation volume for the process and can be loosely thought of as the local volume change accompanying the distortion.

Experimentally, the pressure dependence has been measured using NMR by Kriger and Obmoin [115] at 300 K and by McGuigan *et al.*[114] at 270 K: the values for \( V_{\text{act}} \) were \( 10.9\pm 0.5 \) and \( 23\pm3 \) Å³/molecule respectively. The discrepancy between these two values is as yet unresolved, but there is a firm conclusion that the dilation of the lattice required is \( \approx 10 - 20 \% \) of the molecular volume, which is quite reasonable considering the packing density in Fig. 1.3.

In this context it should be mentioned that a second type of motion was discovered towards the melting point using \( T_1 \), measurements. The initial suggestion [116] was that the motion was out-of-plane reorientation about the two-fold axes of the molecule, but this was disputed[117] on the grounds that sterically it was too hindered, and a vacancy diffusion process was suggested instead. The activation energy corresponding to this motion was found by McGuigan *et al.* to correspond to \( \approx 100 \% \) of the molecular volume, which is expected for an unrelaxed-vacancy mechanism.
6.1.3 Nature of the Reorientation Event

Recently, Fujara et al.[118] applied a novel NMR spin alignment technique and incoherent quasielastic neutron scattering (IQNS) to this problem. The NMR method allowed distinction between rotational jumps and rotational diffusion, the former being confirmed: such a distinction is not possible in normal $T_1$ measurements. The result that the reorientations are 'jumps' was expected, however, since x-ray diffraction experiments near the melting point[19] had showed the crystal to be orientationally ordered about the sixfold axis. From the IQNS results it was concluded that the reorientations are predominantly 60° jumps, rather than multiple jumps to any of the five available sites.

Arrhenius Rate Equation

We should now turn to the question of the interpretation of the terms in the Arrhenian rate law, Eqn. 6.1, which has been shown to represent accurately the temperature dependence of the reorientation rate.

The simplest interpretation of Eqn. 6.1 is from what can be termed a one-dimensional model in which a reorienting molecule is considered to rotate purely about the sixfold axis (with no out-of-plane motion), the neighbours having fixed positions and orientations. The one dynamic variable in this model is the rotation angle about the sixfold axis. In this model, the molecule sits at the bottom of a potential well which has six minima separated by rotations of 60°. When a molecule undergoes a reorientation it jumps from one well to a neighbouring well, and $E_{act}$ represents the height of the potential barrier that must be overcome.

The molecules are considered to be oscillating about the bottom of the potential well with a frequency $\nu_0$, which determines the rate at which 'attempts' are made to overcome the potential barrier. A factor of two should strictly be included here because two attempts are made per cycle, but at the level of precision of what follows, this factor is irrelevant. The probability of a jump being successful is given by the probability that the molecule has sufficient energy, $E_{act}$, to overcome the barrier. This gives the Boltzmann factor $e^{-E_{act}/RT}$. Eqn. 6.1 then results.

With this picture, there is a problem [119] with the interpretation of $\nu_0$ as the attempt frequency. The value of $\nu_0$ found experimentally is $\approx 100$ THz (apart from the solitary much lower value of [5] of 9 THz). Various estimates for a
physically reasonable attempt frequency can be made by the following methods:

- Assume the frequency can be no greater than the highest frequency rotational lattice mode, which is $\approx 4$ THz;

- use a typical mean thermal angular velocity and calculate the time to rotate $60^\circ$: at 250 K this gives an attempt frequency of $\approx 1$ THz;

- Assume a sinusoidal form for the well, and using the known barrier height calculate a single molecule vibration frequency\[120\]: this gives a frequency of $\approx 2$ THz

It is therefore clear that there is a discrepancy of between one and two orders of magnitude between the experimentally derived attempt frequency, and a plausible physical value. This leads the one-dimensional model to be rejected\[112, 119\].

The alternative model put forward by Boden et al. is that we must instead assume that, when a molecule reorients, the surrounding lattice must become distorted in order to allow the rotation to occur. They term this an 'activated state' model, the activated state being loosely defined as the configuration of molecules when the reorientation has proceeded through approximately $30^\circ$. The term $\nu_0$ in Eqn. 6.1 is then replaced by two terms to give

$$\frac{1}{\tau_c} = \nu'_0 e^{\frac{\Delta S}{k} e^{-\frac{E_{act}}{kT}}}$$

where $\nu'_0$ is again interpreted as an attempt frequency; $E_{act}$ is the typical excess energy of the distorted configuration of molecules that enables the reorientation to take place; $\Delta S$ is the 'entropy of activation'.

An interpretation of $\Delta S$ is via the identification of $W = e^{\Delta S/k}$ as the number of possible 'routes' by which a molecule may reorient. These routes are different configurations of the neighbouring molecules, or activated states.

Using the above estimates for a plausible attempt frequency, $\nu'_0$, of $\approx 2$ THz, and a value of $\nu^{E_{sp}}_0$ of $\approx 100$ THz, and using

$$\nu^{E_{sp}}_0 = W \nu'_0$$

we can estimate $W$ as $\approx 50$.

An exact interpretation of this value is difficult, as the statistical thermodynamical concept of a microstate is not well defined in a system with continuous variables. In other words, how are 'different' configurations to be defined? We can make the following comments however:
• If no neighbours are disturbed, $W=1$, which is the model dismissed above.

• If many neighbours are involved, $W$ will rapidly grow large as the number of possible combinations of motions will grow very rapidly.

We can therefore conclude that several neighbours ($<\approx 10$) are involved in the reorientation process of a single molecule, but this does **not** imply that they too undergo reorientations.

### 6.1.4 Local Correlation

In general, the question of whether the jumps of neighbouring molecules are correlated is rather difficult to address experimentally (see Pethick in [3]). This is because experimental techniques tend to be sensitive to either single molecule properties or to many-body phenomena. The local correlation of reorientations falls between these two extremes.

Fortunately, benzene is one of the few cases where it has been possible to attempt to study the correlation. Using various $C_6H_6/C_6D_6$ mixtures, Anderson[121] was able to separate out intra and intermolecular contributions to the relaxation rate; that is, contributions to the relaxation of a nucleus from interactions with nuclei on the same or different molecules respectively. This is possible because the magnetic interaction between hydrogen and deuterium nuclei is effectively negligible. Therefore as the proportion of $C_6D_6$ is increased the relaxation becomes increasingly that due to interactions between protons on the *same* molecule. Using an approximate calculation, Anderson claimed to show that the jumps of neighbouring molecules were correlated, although the degree of correlation was not precisely defined in the work. The calculations of Haeberlen and Maier[111] showed, however, that the calculation of Anderson was too simplistic, and that no firm conclusion could be reached from his work.

More recently, Gaisin and Enikeev[122] repeated Anderson's experiments in more detail, and concluded that the events of neighbouring molecules are strongly correlated. The problem with their conclusion is that, again, the degree of correlation is not clearly defined. Their theory assumes that when a molecule reorients then all the molecules within the first coordination shell also reorient. This implies that all the neighbours of the molecules in the first coordination shell also reorient, which implies that it is **not** just the molecules within the first shell that...
reorient, and so the assumption is not self-consistent. In their conclusions they comment, however, that 'the concept of correlation of rotation of molecules does not imply that the rotations of all the molecules in a crystal are simultaneous'. They then state that they believe that only small clusters of molecules reorient cooperatively, and thus they are immediately reducing the degree of correlation that they are implying. They conclude by reiterating Cox's suggestion that correlation will only exist within the planes of meshed types I and III molecules (or II and IV) as discussed in Chapter 1. This further reduces the number of correlated neighbours and the effect of this is not considered.

Other Systems

Further insight may be gained by looking at similar molecular crystals. Particularly significant in this respect is the work of Boden et al.\[119\] on $C_6F_6$. This has a different space-group ($P2_1/n$) to that of benzene, but a similar herring-bone packing structure. A crucial difference, however, is that there are two crystallographically different molecules within the unit cell.

There are pairs of molecules in the $C_6F_6$ structure that are meshed in the way envisaged for benzene. Boden et al. point out, however, that these pairs of molecules consist of one molecule of each of the two crystallographic types, and they were able to show that these two types of molecules have markedly different reorientation rates. The difference in rates implies that there can be no strong correlation between the motion of the two different types of molecules, and in particular that there is no strong correlation between the motions of meshed molecules. This casts considerable doubt on the picture of strongly correlated motions in benzene from a cog-wheel mechanism.

There is some evidence for correlated reorientations in plastic crystals. In plastic cyclohexane a comparison of IQNS and light scattering results indicated [123] that the correlation of orientations of extended groups of molecules, which is detected by light scattering, is lost less rapidly than the autocorrelation of single molecules, which is detected by IQNS. This was interpreted to imply locally correlated reorientations.

A similar indication of correlation was found in MD simulations by Pawley[124] of plastic sulphur hexafluoride. In contrast, no such correlations were found in the case of (non-plastic) Naphthalene[28], and it was suggested that this may be
a characteristic difference between plastic and normal molecular crystals.

6.2 Previous Theoretical Studies

Theoretically and computationally, there has been little work in this area for benzene. The effect is inherently highly anharmonic making analytical dynamical theories difficult. Simple calculations have been made [1, 125, 126] to estimate the energy barrier against rotation about the sixfold axis of the molecule. These calculations simply considered the energy of a molecule as it rotates in an otherwise undeformed lattice. These calculations give a rather wide range of barrier heights, from 5 to 20 kJ/mol and also predict the energy barrier to be strongly temperature dependent (via changes in the crystal structure), and this is not found experimentally.

In Andrew's original work, it was noted that the reorientions have a jump-like nature as evidenced by x-ray crystallography, but that this would be consistent with either quantum tunnelling or a thermally induced reorientation across the barrier. Although the temperature dependence of the NMR results indicates the latter, the possibility of quantum tunnelling has been investigated theoretically by Das [127]. The conclusion was that quantum tunnelling will be negligible for benzene because of the large moment of inertia of the molecule.

In the few simulations previously performed for benzene, the reorientations have been little studied, although they were observed in the Monte Carlo study of Yashonath et al.. The rate was not measured, and moreover there is no simple relationship between a number of Monte-Carlo steps and real time.

6.3 The Present Study

Molecular dynamics is ideally suited to the study of single molecule properties, or motions where only local correlations exist: information is available in great detail and local nature of the events means that finite-size effects should not be significant. In the present case, the dynamics are on a suitable timescale for study by molecular dynamics, although this would not be so for studying translational diffusion, for instance, where the motion is much slower [3].

The major problem is to decide how best to analyse the vast amount of information that is available in a molecular dynamics simulation. Rather than
attempt to analyse very complex molecular trajectories, the strategy that was
adopted here was, first, to collect statistical information about a large number
of events over as wide a range of temperatures as possible, and then use statis-
tical/probabilistic analysis to determine the various correlations within the data.
The temperature and pressure dependence of the rate was determined, and then
a brief study was made of the detailed dynamics of a few events.

6.3.1 Event Detection

The method used to detect events was that of Dove and Pawley[128]. The basis of
this method is to calculate the displacement quaternion for each molecule, similarly
to Eqn. 5.1, and to use this to decide if the orientation of the molecule is closer
to a symmetry-related orientation than to the original orientation. If this is the
case then an event is registered.

For the benzene molecule the possible axes of rotation are the sixfold axis
normal to the plane of the molecule, and diad axes in the plane of the molecule.
Reorientation tests were implemented for each of these axes, but no rotations
about the diad axes were ever recorded, except when the crystal was in the process
of melting. This is consistent with the experimental result that out-of-plane
reorientations are not observed.

If, for instance, a +60° reorientation was registered, the coordinates of the
molecule were then rotated by -60°, so that following the reorientation the molecule
had same mean orientation as originally[128]. This rotation by a symmetry ele-
ment does not alter the physics, but is useful because it means that all molecules
remain close to the same orientation of the six equivalent orientations about the
hexad axis. This is vital for calculating a meaningful mean quaternion for in-
stance.

The simulation program was modified to allow the following data to be col-
lected about each event:

- The time of the event.
- Which molecule was involved.
- The sense of the rotation.

Data was collected at 120 K, sampling for 170 ps; 155 K, sampling for 70 ps;
and at 195, 235, 270, 310 and 325 K, sampling for 34ps. The total number of
events observed at each temperature were 1, 56, 269, 1267, 3578, 7537, 9591 respectively. Before using these values to calculate the jump-rate it is necessary to consider the correlations within the data.

6.3.2 Analysis of Auto-Correlation

If the reorientation events of a single molecule are truly independent random events then they can be described by a correlation time $\tau_c$, and Poisson statistics. The independence that is assumed here is that the reorientation events of a single molecule do not influence each other, and also that the events for one molecule are not influenced by those of other molecules. Both of these assumptions will be assessed in what follows.

$\tau_c$ is defined via the statement that the probability per unit time of an event happening is $1/\tau_c$. The key result that follows is that if an arbitrary origin of time is chosen the probability distribution, $P(t)$, for the time $t$ to the next event for a particular molecule is

$$P(t) = \frac{1}{\tau_c} e^{-\frac{t}{\tau_c}}$$  \hspace{1cm} (6.5)

This is equivalent to the theory for the distribution of path-lengths in kinetic gas theory [89].

If the events are indeed uncorrelated then each event can be used as a new origin of time for the observation of the time to the next event. Therefore the intervals between successive events for each molecule, $\delta t$, should form an exponential distribution.

Interevent time distributions were constructed as a sum over the distributions for all the 864 individual molecules for the data at the five higher temperatures (there was insufficient data at the lower temperatures). The data at 310 K is shown in Fig. 6.1, along with the same distribution plotted on a log scale. The latter demonstrates that the distribution is accurately exponential for $\delta t \approx 1$ ps, and that for shorter times there are two peaks in the distribution. The data for a range of other temperatures is shown in Fig. 6.2, plotted on a simple linear vertical scale.

The same features are visible in all cases. The two peaks at low values of $\delta t$ are resolved if the interevent times are separated into two categories, depending on whether the second jump is in the same direction as the first ('forward-forward')
Figure 6.1: Interevent time distributions at 310 K. (a) All types of event; (b) Forward-Forward pairs; (c) Forward-Back pairs. The upper plots are on a linear scale; the lower plots are on a log scale to demonstrate the exponential nature of the distribution.
Figure 6.2: Interevent-time distributions at 195, 235, 270 and 325 K. Linear scales.
pairs), or in the reverse direction ('forward-back' pairs). The two resulting distributions are plotted in Figs 6.1 and 6.2, and show distinct differences:

- **Forward-Forward Pairs.** The distribution has a very low value at short times ($\delta t < 0.2$ ps) and then peaks at around 0.4 ps. The exponential tail dominates beyond $\approx 0.8$ ps. The low value at short times is due to the fact that a molecule must rotate approximately 60° before satisfying the reorientation condition for the second time, and there is thus a minimum time between two events. The peak at $\delta t \approx 0.4$ ps indicates that there is a significant probability that a molecule having reoriented once will retain sufficient energy to reorient for a second time in the same direction. If it is assumed that the activation energy is transformed purely into angular velocity about the hexad axis then the time to rotate 60° can be calculated, assuming an approximately sinusoidal variation of the velocity with rotation angle as it moves through the potential well. This predicts the peak to be at $\delta t \approx 0.5$ Ps which is in excellent accord to that found. The agreement is perhaps surprisingly good, in fact, as it is not clear what fraction of the activation energy will be dissipated amongst the neighbouring molecules. An alternative calculation using the mean thermal angular velocity at 250K gives the time to rotate 60° as $\approx 1.0$ ps. A reorienting molecule will necessarily be more energetic than the mean so that this simpler calculation also gives a reasonable value.

It is not possible to give an exact definition of whether two events are independent, however it seems reasonable from the angular point in the distribution at $\approx 0.8$ps to use this value as the boundary between events that are to be considered independent or multiple. The peak is particularly clearly resolved at lower temperatures where the background rate due to uncorrelated events becomes very low (as uncorrelated events tend to be separated by much longer than 8 ps at these temperatures).

- **Forward-Back Pairs.** The distribution has a sharp peak at $\delta t \approx 0.1$ ps, followed by an exponential tail at longer times. Compared to the case for forward-forward events, the peak is for very low $\delta t$, indicating that it correspond to events where the molecule just reaches the top of the notional energy barrier and registers an event, but then returns to its original orientation, and thus registers a second event. The angular point at $\delta t \approx 0.5$ ps
in the distribution can again be used as an approximate boundary between these forward-back events, and independent successive events occurring in opposite directions. Except at the lowest temperature shown in Fig. 6.2, where there is insufficient data, there is apparently a slight dip in the distribution, following the sharp peak. This must correspond to the random exponential part of the curve dropping to zero at short times as there is a minimum time for a molecule which has descended from the top of the barrier being reactivated over it. This confirms that by assuming that events at $\delta t < 0.5$ ps are all strongly correlated events then very few truly random events will be wrongly included.

In principle, the same bounding value should be used for forward-forward and forward-back events, as there is no distinction between these for independent events. However, as the probabilities involved are so small, the error involved in using a slightly incorrect bounding value is not significant in terms of this semi-quantitative description of the various event probabilities.

6.3.3 Distribution of Multiple Events

The analysis above shows that following an event for a molecule, there is an enhanced probability of another event occurring for the same molecule within a short time. The magnitude of this enhanced probability must now be found, and also it has not yet been determined whether these pairs of correlated events occur as discrete pairs, or as chains of events.

The data was therefore reanalysed to search for chains of correlated events. A chain was deemed to end when the next event for the same molecule occurred later than the bounding times defined above. This next event was then used as the first event of the next chain, and so on.

This analysis indicated that whilst pairs of events occurred predominantly as discrete pairs, there were some longer chains of events: the longest that could be found in the data consisted of nine events. However, these chains often contained several successive forward-back events, which correspond to the molecule staying near to the reorientation condition for a period, and crossing the boundary several times during one true event. As this should not be counted as several events, events which formed the second event of a forward-back pair were not counted in the chain of events; the chain was, however, considered to continue as if the
second event were a valid event. For example if the motion were thus,

![Diagram of valid event in chain]

then three events would be counted in the chain as indicated. Using this procedure, an event sequence where the molecule reaches the top of the energy barrier, and perhaps crosses it several times backwards and forwards, before returning to the same initial well is regarded as a single true event. This is justified since such events must be activated in a very similar way to actual $60^\circ$ reorientations. The effect on the rate is very small in comparison to the range of rates measured.

Analysing the data in this way gave the values in Table 6.1, for the number of chains $n_{\alpha_\nu}(l)$ of each length $l$. Note that a single discrete event is considered to be a chain with $l = 1$.

The predominant motions at each temperature are clearly discrete events or simple pairs of events, but there are a significant number of longer chains. The question that must then be asked is whether the numbers of chains of length $> 2$ are abnormal, or whether they can be adequately described by a simple Markov process. In such a process, the probability of the occurrence of an event that extends a chain is independent of the current length of the chain. This is sometimes said to mean that when a molecule jumps it 'loses its memory' of previous jumps.

If we define

\[ p = \text{The probability of an event being followed by a related event,} \]

\[ = \frac{N_f}{N_{ev}} \]

where

\[ N_{ev} = \text{The total number of events in the sample (using the above criterion for counting an event)} \]

and
Table 6.1: The numbers of chains observed at five different temperatures. For details see text.

<table>
<thead>
<tr>
<th>T = 195 K</th>
<th>(n_{ob}(l))</th>
<th>(n_M(l))</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>222</td>
<td>218</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1</td>
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<td>4</td>
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<tr>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>(n_M(l))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>990</td>
<td>992</td>
</tr>
<tr>
<td>2</td>
<td>91</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
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<td>5</td>
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<tr>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

<table>
<thead>
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<tr>
<td>1</td>
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<td>2546</td>
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<tr>
<td>2</td>
<td>248</td>
<td>275</td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>30</td>
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<tr>
<td>4</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
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<td>2</td>
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<tr>
<td>6</td>
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<td>0</td>
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<tr>
<td>7</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

<table>
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<th>(n_M(l))</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>4795</td>
<td>4744</td>
</tr>
<tr>
<td>2</td>
<td>647</td>
<td>729</td>
</tr>
<tr>
<td>3</td>
<td>132</td>
<td>112</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T = 325 K</th>
<th>(n_{ob}(l))</th>
<th>(n_M(l))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5539</td>
<td>5476</td>
</tr>
<tr>
<td>2</td>
<td>903</td>
<td>1000</td>
</tr>
<tr>
<td>3</td>
<td>196</td>
<td>183</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>33</td>
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<tr>
<td>5</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
CHAPTER 6. MOLECULAR REORIENTATIONS

\( N_f = \) The total number of events that are followed by a related event

then the number of chains of length \( l \) in the Markov model, \( n_M(l) \) is

\[
n_M(l) = N_{ch} p^{(l-1)} (1 - p) \tag{6.6}
\]

where \( N_{ch} \) is the total number of chains observed (including discrete events).

The values for \( p \) and \( n(l) \) are given in Table 6.1.

The agreement of \( n_M \) with \( n_{obs} \) is good. The probability \( p \), of an event being followed by a correlated event remains less than 0.2 across the whole temperature range accessible, which is consistent with the conclusion of Fujara et al. from IQNS that jumps are predominantly single events. They acknowledge that the IQNS technique is not sufficiently discriminating to rule out there being a small proportion of multiple events. \( p \) increases with increasing temperature: if, in a hypothetical case, \( p \) were to reach unity without the crystal melting first, then one could classify the phase as a plastic phase with dynamic disorder about the hexad axis. The value of \( p=0.18 \) at 325 K indicates that the crystal is far from this transition even at more than 50 K above the thermodynamic melting point of the model.

It does appear, though, that long chains do occur slightly more frequently than predicted by a Markov model. The discrepancy is small and must represent the fact that if an event is followed by a correlated event then there is a slightly more violent disruption of the lattice, and that this disruption may remain to enhance slightly the probability of further events in the chain.

6.3.4 Evaluation of \( \tau_e \)

The random reorientation rate can now be determined from the total number of thermally activated events, which is \( N_{ch} \) as the first event in each chain is uncorrelated with a previous event. If the \( N_{ch} \) events occur during an observation period \( T \), and there are \( N \) molecules in the system, then

\[
\tau_e = \frac{N T}{N_{ch}} \tag{6.7}
\]

These values of \( \tau_e \) are given in Table 6.2.

The errors quoted are obtained using an estimate for the error in \( N_{ch} \), of \( \pm 2 \sqrt{N_{ch}} \), which corresponds to 90% confidence limits. Only a very approximate value for the rate could be obtained at 120 K where only one event was observed:
CHAPTER 6. MOLECULAR REORIENTATIONS

Table 6.2: Correlation times from the model at zero pressure.

<table>
<thead>
<tr>
<th>T/K</th>
<th>( \tau_c/\text{ps} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>( 10^5 \left(10^4-10^6\right) )</td>
</tr>
<tr>
<td>155</td>
<td>1050±250</td>
</tr>
<tr>
<td>195</td>
<td>125±15</td>
</tr>
<tr>
<td>235</td>
<td>27±2</td>
</tr>
<tr>
<td>270</td>
<td>10.3±0.5</td>
</tr>
<tr>
<td>310</td>
<td>5.2±0.2</td>
</tr>
<tr>
<td>325</td>
<td>4.4±0.2</td>
</tr>
</tbody>
</table>

the rate was taken to be an order of magnitude estimate only, the lower limit on
the rate being especially uncertain.

Values of \( \nu_0 \) and \( E_{\text{act}} \) in Eqn 6.1 were obtained by fitting a least squares line
to \( \log(\tau_c) \) versus \( 1/T \), excluding the rather uncertain point at 120K. This yielded

\[
E_{\text{act}}^{MD} = 13.7(\pm0.3) \text{ kJ/mol}
\]

\[
\nu_0^{MD} = 39(\pm4) \text{ THz}
\]

This is the solid line plotted in Fig. 6.3. The dashed line is using the parameters
of Haeberlen and Maier[111], \( E_{\text{act}} = 17.6 \text{ kJ/mol} \) and \( \nu= 110 \text{ THz} \), with which
Fujara et al. also found good agreement from IQNS.

Near the melting point, the model gives a value for the rate in good accord
with experiment. The activation energy obtained by the model is, however, \( \approx20\% \)
too low, and therefore the experimental and model rates diverge at lower temper-
atures. It may be significant that \( 20\% \) was approximately the amount by which
the potential energy was reduced in the energy rescaling process. Since the re-
orientation process probes short range interactions it may be that a more careful
rescaling of the potential is necessary, in order to reduce the long range part of
the potential to give the correct binding energy, but leaving the short range part
unaltered.

The value for \( \nu_0 \) is rather low, compared to experiment, although there is a
considerable range of estimates for this from NMR. The important conclusion
remains, however, that the value of \( \nu_0^{MD} \) is at least an order of magnitude greater
than the estimates for the true attempt frequency § 6.1.3. In fact, a value for \( \nu_0 \) of
Figure 6.3: The temperature dependence of the correlation time: Arrhenius plot of $\log_{10}(\tau_c)$ vs. $\frac{1}{T}$ at zero pressure. The solid line is a least-squares fit to the data (see text), and the broken line is from [111]
39 THz gives a period of oscillation that is only approximately five MD-timesteps which is unphysically short. This indicates that, as found experimentally, there is a considerable entropy of activation, or in other words there are several possible local distortions of the lattice that can accompany a reorientation.

From the divergence of the experimental and molecular dynamics Arrhenius fits in Fig. 6.3, it is clear that the small error in the activation energy of $\approx 20\%$ can have a profound effect upon the error in the reorientation rate. Thus at 100 K, the rate is in error by a factor of $\approx 30$. This illustrates two important points

(i) The rate of an activated process is rather critically sensitive to the parameters of the model, due to the exponential term in the Arrhenius rate equation. Therefore, the fact that the rate of such a process measured in molecular dynamics is considerably different from the experimentally measured rate at one particular temperature does not necessarily imply that the molecular dynamics model is particularly poor.

(ii) The corollary to (i) is that the model cannot be expected to predict absolute rates of activated processes with any great accuracy.

It is clear, therefore, that measuring the rate of an activated process as a function of temperature enables a much better evaluation of the model to be made than would be possible from a single rate measurement.

It might be objected that the simulations here are for deuterated benzene, whereas the experimental data is for the hydrogenous compound. Data was collected at 235 K and 310 K, changing the mass and moment of inertia of the molecule to that for $C_6H_6$, giving $1422$ and $7986$ events respectively (uncorrected for correlation). These are both approximately in the ratio 1.1 to the number of events seen for the deuterated compound, which is consistent with the ratio of attempt frequencies that would be expected (c.f. § 5.4.3). This ratio is negligible in terms of the range of reorientation rates measured.

### 6.3.5 Pressure Dependent Behaviour

From studies of the elasticity(§ 4.4.1), reorientation data was also available at a range of pressures at 235 and 315 K. Values of $\tau_e$ were extracted as above, and the resulting values are plotted in Fig. 6.4, as $\log_e(\tau_e/\tau_e^{0\text{bar}})$ vs P/RT. Both plots are linear over the range covered: the range of $\tau_e$ is much smaller than in the variable
Figure 6.4: The pressure dependence of the correlation time: plot as described in text. (□) 235 K, (○) 315 K.

temperature case, but rather similar to that obtained in the experimental studies (§ 6.1.2). The lines drawn in Fig. 6.4 are least squares fits to the data, and the slopes give the activation volume (Eqn. 6.2) \( V_{act} = 21.1 \pm 0.7 \) at 235 K and \( V_{act} = 17.2 \pm 0.5 \) Å³/molecule at 315 K. These are consistent with the two rather different values that have been obtained experimentally of 10.9 and 23 Å³/molecule(§ 6.1.2).

This correct value for the activation volume gives further confirmation that the degree of local disruption occurring in the model is approximately the same as occurs experimentally.
6.3.6 Local Correlation

The question of whether the reorientations of neighbouring molecules are indeed uncorrelated, as has been assumed in the foregoing analysis, can now be examined. As has been discussed in § 6.1.4, this question is not readily accessible experimentally. In principle it should be detectable in MD given that complete data is available of the times of events and the molecules for which they happen.

The problem is not trivial, however, as in the present case there are 864 streams of data, one for each molecule. Ideally, we should like to be able to study the way correlation depends upon the crystallographic relationship of the two reorienting molecules, and also the time scale over which any correlation exists.

The first step to simplify the problem is to reduce the dimensionality, by ignoring the differences between different directions in the crystal, and by picking a particular time $\tau_{test}$ over which the correlation will be assumed to exist. The correlation then becomes simply a function of scalar distance.

The question was then asked whether, within the time $\tau_{test}$ following an event, a molecule that is nearby to the reorienting molecule is more likely to reorient than a more distant molecule.

The precise algorithm used was as follows

(i) Each molecule is assigned coordinates corresponding to its lattice site expressed as $(x/a, y/b, z/c)$, for example $(2,1/2,1/2)$. In terms of these coordinates, each molecule is separated from the other molecules in the sample by a finite set of distances, $R_i$, using a minimum image convention [26].

(ii) The first event within the whole sample is designated the 'trigger' event.

(iii) For each value of $R_i$, the number of molecules at the distance $R_i$ from the central trigger molecule for which an event occurs within $\tau_{test}$ is found, giving $n(R_i)$ (The identification of valid events as made above was used, including the first events in chains).

(vi) Steps (ii) and (iii) are repeated using each event in turn as the trigger molecule, accumulating values of $n(R_i)$.

(v) $n(R_i)$ is then normalised by dividing by the number of molecules that are at a distance $R_i$ from any chosen molecule.
Figure 6.5: Plots of $n(R_i)$ for various values of $\tau_{test}$. From bottom to top, $\tau_{test} = 0.24, 0.8, 2.4, 4.8$, and $9.6$ ps. For details see text.

If the events of neighbouring molecules are independent, then $n(R_i)$ will be randomly distributed about some mean value, but should show no systematic dependence on $R_i$. On the other hand, if the events of neighbouring molecules are strongly correlated with each other, then the value of $n(R_i)$ should be greater than the mean for low values of $R_i$.

Example plots of $n(R_i)/N_{ev}$ are shown for $T = 270$ K in Fig. 6.5. In this figure, five different values of $\tau_{test}$ were used: $0.24, 0.8, 2.4, 4.8$, and $9.6$ ps. It is clear that there is very little dependence of $n(R_i)$ on $R_i$, that is, there is little correlation. For the the middle three plots, however, there is a small but distinct increase in the number of events seen for values of $R_i \leq 1.5$ lattice units. This indicates a weak but definite correlation out to about next-next-nearest neighbours.

For the shortest and longest values of $\tau_{test}$ there is no such clear correlation.
For very small values of $\tau_{\text{test}}$ this simply reflects the fact that correlations will take a finite length of time to propagate. For $\tau_{\text{test}}$ large compared to $\tau_c$, correlations become very difficult to detect, because the extra events induced become swamped by the statistical noise in the number of events that would be expected purely randomly.

Fig. 6.5 gives a good qualitative idea that statistically significant correlations exist, since the increase in the number of events seen for small $R_i$ can be compared visually to the scatter in the values for larger $R_i$. We can attempt to quantify the degree of correlation: this is something that has been lacking in the experimental work to date. The molecular dynamics result may then indicate the feasibility of experiments to detect correlations.

We need to introduce the concept of $N_{\text{exc}}(R_i, \tau_{\text{test}})$, the number of excess events that occur within a time $\tau_{\text{test}}$ of an event for all the molecules at a distance $R_i$ (in reduced units) of the reorienting molecule: the ‘excess’ events are those that occur above the number expected randomly. The value calculated previously for $\tau_c$ cannot be reliably used to calculate the number of random events to be expected, since it involves the assumption that the events of all molecule are in fact uncorrelated. Therefore, a mean uncorrelated value for the number of events to be expected was calculated by using the number of events that occur in the same time $\tau_{\text{test}}$ for molecules that are well separated from the trigger molecule. To define ‘well separated’ we can use Fig. 6.5 and assume that molecules separated by $R_i > 2$ reorient independently.

$N_{\text{exc}}(R_i, \tau_{\text{test}})$ was calculated with a value of $\tau_{\text{test}}$ of 3 ps and the radius $R$ including molecules out to next-nearest neighbours. The value of 3 ps was chosen since it is apparent from Fig. 6.5 that the correlation does not increase significantly between $\tau_{\text{test}} = 2.4$ ps and $\tau_{\text{test}} = 4.8$ ps. At all temperatures, the number of excess events was approximately 0.1 to 0.2, i.e. following an event there is approximately a 20% chance of one of the nearest or next-nearest neighbours also reorienting due to the correlation. This is a very weak correlation, and is completely different to a picture of all the molecules in a small cluster reorienting together.

The analysis was also made including increasing numbers of neighbours, but no clearly statistically significant correlations could be found. Various further possibilities were also considered: that correlations might be stronger between molecules that were meshed; or that the excess correlated events might occur
predominantly following multiple reorientations of a single molecule. The idea for the latter was that these events might be associated with more extreme local disruptions that also favoured the reorientation of a neighbouring molecule. Neither of these connections could be found.

6.3.7 Detailed Dynamics

The technique used up to now in this chapter to study the molecular reorientations has been a statistical one, based on an analysis of a list of times at which events occur. In a molecular dynamics simulation it is also possible to look in much more detail at the dynamics of individual events. In spite of the conclusion drawn above that strong correlations do not exist between the reorientation events of neighbouring molecules, it is worthwhile to look at the details of a few events. This is to see if clear orientational or translational couplings with neighbouring molecules exist, even if they do not entail strong correlations of actual events.

With this purpose, a 'recording' of 10 ps of simulation time was made, noting the orientation and position of every molecule at intervals of 0.1 ps. The sample was at a temperature of 160K. This temperature was chosen so that in the period of 10 ps, several events would be recorded; but, there would be a low probability of two events occurring randomly for neighbouring molecules within a short time of each other, which would otherwise greatly complicate the analysis.

Presentation of Trajectories

The various analyses undertaken were based upon choosing a molecule as a 'central' molecule, and examining the motion of it and of its nearest neighbours. This was done for three central molecules: two cases where the central molecule ('A', 'B') reoriented within the 10 ps window; and one where the molecule ('C') did not reorient, as a control.

The analyses are plotted in Figs 6.6-6.8, for the three different molecules. Three quantities are plotted in each figure:

(a) Angular displacements from the mean orientation.

The angular displacement of each molecule from the mean orientation is separated into two components. One component (solid line) is the rotation
of the molecule about its sixfold axis, and the second (broken line) is the remaining out-of-plane rotation. As the axis for the second motion is not constant, the sign of the rotation is arbitrary and chosen to be positive. The bottom curve is for the central molecule, and the upper twelve curves are for the neighbours related by vectors as marked. The scale for each curve is identical, with the solid horizontal lines marking amplitudes of motion of ± 30°.

(b) Distances to nearest neighbours.

For each molecule the curve gives the distance between the central molecule and the corresponding neighbour in fractional units. There are twelve curves in this case, one for each neighbour, ordered as for (a). The scale is the same for each molecule, the solid lines representing a deviation of ± 10% from the mean separation of $\sqrt{2}/2$.

(c) Potential energy contributions.

There are thirteen curves again here, as for (a). The upper twelve curves represent the potential energy corresponding to the interaction of the central molecule with each of its neighbours. The lowest curve is the sum of the upper twelve curves, and represents the potential energy of the central molecule as a result of all its interactions with its nearest neighbours. The potential energies plotted are the complete bond interaction (rather than one half of it as used to avoid double counting in complete lattice energy calculations). The energy origin for each curve is arbitrary, but each is plotted at the same scale as marked in the figures.

Discussion

Fig. 6.6(a) should be examined first. The central molecule reorients at between 5 and 6 ps from the start of the recording: this is indicated by the sudden step in the in-plane component of the angular displacement from +30° to -30°. The step occurs because the molecule’s coordinates are rotated by -60° in the reorientation testing procedure as mentioned in § 6.3.1. The duration of this reorientation event can be estimated as $\approx 0.8$ ps. This value, and the fact that following the event the amplitude of the motion rapidly returns to the normal non-reorienting value,
Figure 6.6: Molecular trajectory plot for molecule A. For details see text
Figure 6.7: Molecular trajectory plot for molecule B. For details see text.
Figure 6.8: Molecular trajectory plot for molecule C. For details see text.
confirms the conclusions in § 6.3.2 about the auto-correlation of events for single molecules.

The vertical bars marked in all the figures mark the approximate period during which the central molecule reorients. The aim is then to find motions of the neighbouring molecules that are clearly affected during, or slightly before or after, this period. The conclusion from Fig. 6.6(a) is that there is in fact no clearly abnormal orientational motion of any of the neighbouring molecules during this interval.

The reorientation of the neighbour at (-1/2,0,1/2) at 0.8ps is, from the statistical analysis of § 6.3.6, probably independent, as the separation of the two events is ≈5ps which is fairly large compared to the timescale of ≈3 ps over which correlations are believed to develop. Again, the statistical analysis is seen to be plausible from the fact that during the interval between these two events the motion of all the molecules is quite unremarkable, so there seems that there can be no memory of the first event when the event for the central molecule occurs.

In Fig 6.7(a) there is similarly no evidently greater angular disturbance of the neighbours during the reorientation event of the central molecule.

An alternative distortion would be a dilation of the lattice, where the molecules move apart allowing the central molecule to reorient, and this might be seen in the curves in Fig 6.6(b) and Fig 6.7(b). Again, no particularly significant distortions can be seen accompanying the reorientation. The magnitude of any such distortion can however be estimated from the activation volume for the process, with the assumption that each neighbour moves out a similar amount and that the distortion is only significant out to nearest-neighbour contacts. The nearest neighbours are situated approximately on a sphere of volume ≈600Å³, and therefore as \( V_{act} \) is ≈20 Å³/molecule then the radius of the first coordination shell is only expected to increase by ≈ 1%. The assumption of uniform dilation is clearly an over-simplification, but this estimate is adequate to suggest why the lattice distortion is obscured by noise in the trajectory figures.

In Fig. 6.6(c) and Fig. 6.7(c) it can be seen that the potential energy of the molecule during the complete period of observation is greatest during the reorientation process, however the fluctuations of the energy are again significant and the rise in potential energy during the reorientation process is not markedly larger than these fluctuations. The rise is approximately the same magnitude as the activation energy of ≈ 14kJ/mol, although it may be necessary to include fur-
ther interactions to obtain the full value; these interactions might be *between* the neighbours, for instance. A calculation involving these further interactions would be affected by noise even more severely than the data shown. It is interesting to note the ‘blips’ in the potential energy curves for the individual intermolecular interactions, which correspond to hard collisions between molecules. Again, no unusually violent collision is discernible preceding the reorientation events.

Finally, Fig. 6.8 indicates that the overall general motion in Figs 6.6 and 6.7 is qualitatively the same as in the case where the central molecule does not reorient.

**Conclusions**

The indication is, therefore, that molecular reorientation in benzene is not a particularly dramatic event: the reorienting molecule seems simply to happen to find a path to slip past the other molecules. This would explain why no strong correlation of neighbouring events could be seen. These figures also demonstrate how difficult it is to analyse individual molecular trajectories, and that statistical methods are far superior where available. The trajectories do, however, confirm that the statistical results are physically justifiable.

### 6.4 Conclusions

This chapter has illustrated the way in which molecular dynamics can probe phenomena that are very difficult to study experimentally.

In was first demonstrated that the molecular dynamics model of benzene introduced in Chapter 3 reproduces many aspects of the reorientation phenomenon to a good degree of accuracy. The parameters in the Arrhenius rate equation as a function of both temperature and pressure were found to be in good agreement with experiment, and the events were found to occur predominantly as single jumps, rather than chains of events for a single molecule, which is also consistent with experimental findings.

It was then possible to study the local correlations of events, over which the experimental results are somewhat equivocal. It was found in the model that whilst reorientations of neighbouring molecules are generally uncorrelated, there is a small but definite enhanced probability of two neighbouring molecules reorienting. This correlation does not extend far beyond nearest neighbours, and
only represents at most a 20% probability of a reorientation being followed by a correlated reorientation of any of its neighbours.

Detailed trajectories of a reorienting molecule, and of its neighbours, were then analysed, and it was seen that there is no clear evidence of a reorientation mechanism involving strong interaction with the neighbouring molecules. The picture of the reorientations is therefore not one of strongly correlated cogwheel-like meshing of molecules as has been suggested purely on the basis of consideration of the crystal structure. The correlation of neighbouring molecules that does exist is explicable by the idea that the local fluctuation that accompanies a reorientation event will occasionally be sufficient to enable reorientations of two molecules in the same region. The reason why the conjecture of strongly meshed motion is inappropriate is because it neglects the fact that the local arrangement of molecules fluctuates quite strongly due to normal thermal motion, so that ideas of molecular contacts based upon the mean crystal structure are too simplistic.

It is very satisfying to see the way that, by using computer simulation techniques, it has become possible to gain much insight into a rather simple process which was discovered forty years ago, yet for which it was previously impossible to have more than a qualitative, and partially incorrect, theoretical model.
Appendix A

Basic Symmetry Considerations for Vibrational Spectra

In this appendix the results of group-theory as applied to the \( k=0 \) lattice modes are summarised. This also serves to define the labelling of the different symmetry species.

General

As there are four molecules in the unit cell of benzene I, each with six degrees of freedom, there are 24 \( k=0 \) modes. Within the harmonic approximation, each mode belongs to a symmetry species which corresponds to an irreducible representation of the point-group symmetry of the space-group[100]. Within a \( k=0 \) mode all molecules at lattice sites oscillate in phase. The motion of the other molecules in the unit-cell is then determined by the symmetry species.

The \( D_{2h} \) Point Group

The point group of the Pbca space-group is \( D_{2h}(mmm) \), whose character table is
The convention used here for labelling the species is that used generally in the literature. It should be noted that an alternative convention exists, in which the '1' and '3' labels are interchanged (as in [129] for instance).

The practical interpretation of this table in this case is as follows.

The *orientations* of the four molecules in the unit cell are related by elements of $D_{2h}$; for instance molecule II (see Fig. 1.3) is obtained from molecule I by either $2_x$ or $\sigma_z$. These two operations are equivalent because of the inversion symmetry of the molecule.

Suppose that there is a mode of vibration belonging to the symmetry species $B_{3g}$ in which, at an instant of time, molecule I is displaced by a rigid body translation $\tau$, and a small rotation $\theta$. The character table then tells us that, for instance, molecule II is displaced by $-2_x \ast (\tau, \theta)$ or by $-\sigma_z \ast (\tau, \theta)$, either of which must give the same result. $\tau$ is a polar vector, and $\theta$ is an axial vector which have different transformation properties under the action of mirror planes and diads:

\[
2_x \ast \tau = -\sigma_z \ast \tau \\
2_x \ast \theta = \sigma_z \ast \theta
\]

This therefore requires that for a $B_{3g}$ mode $\tau = 0$, so that this is a purely rotational mode. Similarly the $B_{3u}$ modes are purely translational. In general the g(erate) modes (which transform with a positive sign under inversion) are pure rotational modes, and the u(ngerade) modes are pure translational modes.

The rows of the character table are orthogonal, ensuring orthogonality of modes belonging to different symmetry species. Within each symmetry species...
there will be three modes, which will be mutually orthogonal provided the correct generalised displacement coordinates are used (Eqn. 5.3).
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