A GENERAL KINETIC THEORY OF LIQUIDS

THESIS

SUBMITTED BY

HERBERT SYDNEY GREEN
A.R.C.S., B.Sc. (Royal College of Science, University of London)

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A GENERAL KINETIC THEORY OF LIQUIDS

By H.S. Green, A.R.C.S., B.Sc.

Introduction

In the last half-century much attention has been devoted by theoretical physicists to the task of providing an account of the macroscopic properties of matter in terms of its microscopic structure. Indeed, it is clear that the experimental verification of any theory of sub-microscopic phenomena, which by their nature are not susceptible to direct observation, must largely rest on the demonstration that the macroscopic consequences of the microscopic hypotheses are in accord with experience. The field of study thereby exposed has proved very fruitful, not only in explaining otherwise perplexing regularities in the behaviour of matter in bulk, but also as a means of investigating the detailed laws which govern the behaviour of atoms and molecules.

Greatest progress has been made in the development of the theory of gases\(^1\) by Maxwell, Boltzmann, Hilbert, Chapman and Enskog. Due mainly to the work of Born, the theory of crystalline solids\(^2\) is also reasonably complete and comprehensive. An examination of the extensive work on the liquid state of matter, however, reveals that no such comprehensive theory has so
far been evolved in this field. This is largely due to the fact that the molecules in a liquid are near together, and also in a disordered state, so that one may not assume that the density is small, as in gases, or that an orderly lattice structure obtains, as in solids.

Attempts have nevertheless been made to extend both gas-theory and lattice dynamics in an approximative way to apply to the liquid phase. Enskog\(^3\) tried to derive a generalisation of Boltzmann’s equation for multiple encounters between the molecules, but his result was not quite correctly formulated, and contained besides an unknown function which impeded all further development. Moreover, it will appear later that the principal error arising in the application of the theory of gases to liquids is due not to the assumption of 'binary encounters', but to the neglect of certain effects depending on the interaction between the molecules. More successful attempts have been made to modify crystal mechanics so as to apply to liquids; of these, probably the best known is due to Lennard-Jones and Devonshire\(^4\), whose work has the merit of successfully predicting physical constants at temperatures as high as the critical point. The objection to such developments is that the molecules of a liquid do **not** perform
oscillations about fixed lattice positions, a conclusion which is in no way shaken by the evidence of X-ray scattering by liquids, that the molecules have that degree of local order which one would expect of such a close-packed structure.

For the special case of equilibrium, the theory of liquids is much better developed. In statistical mechanics\(^{(5)}\) one has a general method which can be applied to give a formal but exact account of fluid thermodynamics, and the only practical problem remaining is that of making the formal results intelligible, by approximation or otherwise. It is clear that any theory of non-uniform fluids which claims to be rigorous must give results agreeing with those derived from statistical mechanics in this special case of equilibrium; till 1945, when this investigation began, no such theory was available. There already existed, however, a large number of fragmentary theories designed to give an account of various properties of liquids with the aid of special devices or assumptions suited to each particular purpose; one of the most recent is due to Jaffé\(^{(6)}\). Such work is well summarised by Frenkel\(^{(7)}\) in a recent publication; other aspects of progress in the theory of the liquid state have been
summarised by Butler \(^{(7)}\) and by Mott and Gurney \(^{(9)}\).

This literature has no direct bearing on the present theory, and will not be discussed here. The theory to be developed springs from two main sources. The first is the kinetic theory of gases, which culminated in the abortive attempt by Enskog already mentioned to generalise the theory for liquids. More recently the Russian physicist Vlasov \(^{(16)}\) showed that this kind of method can be made to yield definite results provided one is prepared to make somewhat drastic approximations. These approximations can be avoided only by introducing a second idea: that of the 'multiple distribution functions', of which the radial distribution function may be cited as the simplest example. Such functions have been widely used in atomistic theories for some time, with applications to the scattering of X-rays by liquids \(^{(11)}\), and, in a slightly different form, to the Brownian movement \(^{(13)}\). The unassuming but elegant work of Yvon \(^{(13)}\) deserves a special mention in this connection.

Kirkwood \(^{(14)}\) has recently realised the fundamental importance of the multiple distribution functions, and treated special problems by this method. Since the communication of the fundamentals of the present theory for publication \(^{(15)}\), he has also published an
important paper\textsuperscript{(16)} of wider scope, in which, from
the point of view of statistical mechanics and the
Brownian movement, he derives an equation substani-
tially equivalent to (26) in this dissertation.
Although his derivation rests on an unproved
hypothesis, and his method of time-averaging does
not appear correct from the present standpoint, this
paper must be regarded as valuable confirmation of
the fundamentals of the present theory.

The object of this dissertation is to develop
logically a basis from which all the properties of
liquids, at rest and in motion, can be investigated.
As the classical theory can always be obtained by
a limiting process from the quantum theory and has
not the same wide range of validity of the latter,
quantum methods have always been preferred; but
as quantum mechanics is much more difficult
conceptually, the classical foundations are carefully
stated before quantisation. One of the satisfactory
results of the classical theory is, that when 'binary
encounters' are assumed, the theory coalesces with
the classical theory of gases.

In the second chapter, on the equilibrium theory
of fluids, few new results can be expected, and the
main object is to show that all the equilibrium
properties follow rigorously from the foundations
in a way which is both simpler and more satisfactory
than the Darwin-Fowler method in statistical mechanics. The resulting proof of the Boltzmann distribution law embodies no essentially new ideas, but consists of a new synthesis of several detached principles, including the application of ordinary time-dependent perturbation theory to the density matrix of von Neumann\(^{(17)}\) and Dirac\(^{(18)}\), Pauli's modification of the laws of radioactive reactions for the proof of a general H-Theorem\(^{(19)}\), Born's adiabatic principle\(^{(20)}\), and finally a valid application of the method by which Maxwell first tried to establish the Boltzmann law for gases. Afterwards, the equation of state for 'classical' and 'quantum' liquids is obtained, and Mayer's theory of the phenomenon of condensation\(^{(21)}\) discussed in the light of the author's work on this subject\(^{(22)}\).

In the final chapter, an attempt is made to open up a field never before satisfactorily investigated: that of the transport phenomena in liquids. This requires something more than a stereotyped application of the methods devised by Hilbert, Chapman and Enskog, which were tried but found to fail in the case of the multiple distribution functions; a new method of expansion had therefore to be devised. The results make quite clear the reason why the gas formulae for the coefficients of viscosity and thermal conduction fail so lamentably
when applied to liquids; it is because these coefficients consist of two terms, the first of which is due to the thermal motion and decreases with temperature, and the second of which is due to the intermolecular forces and increases rapidly with the density; of these, only the first is determined by gas-theory. No attempt is made here to compare the theory with experiment; this is being done elsewhere, with results which must be considered entirely satisfactory.

Since the theory is quantised, a point of major interest is whether it is capable of explaining the anomalous features exhibited by liquid helium II. On this question, the theory is encouraging: the equation of state, for example, deviates widely from the classical equation, but only at very low temperatures ($\frac{\hbar}{kT} \sim 10^{-11}$ sec.). An initially surprising result is that quantum mechanics requires no modification of the classical equations of motion and energy transfer, but only of their interpretation in terms of atomic events. Another significant result is that the pressure tensor and temperature gradient which enter into the definitions of these quantities bear no direct relation to the pressure and temperature thermodynamically defined, which
no doubt explains why the proportionality laws appear to break down in He II.

The author wishes to acknowledge in this place his profound indebtedness to the supervision of Professor Max Born, who not only contributed most of the ideas which began this theory, but by his continuous advice and encouragement, assisted at every stage of its further development.
Symbolism

The vector and tensor symbolism in this dissertation is based on that devised by Chapman and Milne (1), extended where necessary to \( \alpha \) dimensions. Vectors are once underlined, thus: \( \mathbf{a} \), \( \mathbf{x} \); tensors are twice underlined: \( \mathbf{b} \), \( \mathbf{p} \). \( \mathbf{A} \) denotes the unit tensor, and \( \mathbf{b}^\top \) the transpose of \( \mathbf{b} \). The products of a tensor \( \mathbf{b} \) with a vector \( \mathbf{a} \) (both vectors) are written \( \mathbf{a} \cdot \mathbf{b} \) and \( \mathbf{b} \cdot \mathbf{a} \); the spur product of two tensors \( \mathbf{b} \) and \( \mathbf{b}' \) is written \( \mathbf{b} : \mathbf{b}' \).

Below are listed page numbers where symbols are first introduced.

\( a \) 13, \( a \) 68, \( A \) 40; \( b \) 48, \( b \) 25
\( b \) 48, \( B \) 11; \( c \) 60, \( C \) 60, \( C \) 61, \( C \) 61
\( d \) 62, \( e \) 73, \( E \) 23; \( f \) 14; \( g \) 15, \( g \) 18
\( h \) 16, \( k \) 26, \( H \) 18; \( I \) 52, \( I \) 56; \( k \) 42
\( l \) 54; \( m \) 10, \( n \) 57, \( N \) 13, \( N \) 60, \( N \) 72
\( P \) 11, \( P \) 44, \( P \) 26, \( P \) 54, \( P \) 19; \( q \) 13, \( q \) 57;
\( r \) 22, \( r \) 15, \( R \) 67; \( s \) 47, \( S \) 36
\( t \) 13, \( T \) 41; \( u \) 17, \( U \) 41, \( U \) 65; \( v \) 50
\( V \) 13, \( V \) 33; \( W \) 33, \( W \) 17, \( W \) 34, \( X \) 10
\( y \) 68; \( \Xi \) 21
\( \alpha \) 26; \( \beta \) 40, \( \beta \) 26, \( \beta \) 47; \( \gamma \) 27; \( \zeta \) 20
\( \epsilon \) 68; \( \xi \) 13; \( \eta \) 13, \( \eta \) 52; \( \theta \) 24; \( \kappa \) 64
\( \lambda \) 32, \( \Lambda \) 73, \( \Lambda \) 39; \( \mu \) 71; \( \nu \) 69, \( \nu \) 38
\( \phi \) 18, \( \Phi \) 43; \( \chi \) 27, \( \chi \) 27; \( \psi \) 18
\( \psi \) 32, \( \omega \) 59.
CHAPTER I: THE MOLECULAR DISTRIBUTION FUNCTIONS

1. The Logical and Statistical Basis

In the application of the concept of probability to experience, two quite distinct methods are available. The method usually adopted begins by defining the probability of the occurrence of a given event as that fraction of the entire number of possibilities which satisfies the condition under which the event is deemed to occur. This procedure always leads to certain difficulties in practice. If, as in statistical mechanics, the enumeration of the possibilities is made without direct reference to experience, the identity of the probability so defined with any physical reality cannot be proved, but only tested by experiment. If, however, as in the kinetic theory of gases, the enumeration depends on some hypothetical experiment, the probability is by definition imprecise and liable to vary from experiment to experiment even while the experimental conditions are apparently unchanged.

For example, in gas-theory the number density $n$ of the gas molecules at the point $x$ may be defined in terms of the probability $\frac{n}{dx}$ that the volume element $x, dx$ is occupied by the mass-centre of a molecule. In statistical mechanics this probability is determined by enumeration from an assembly of artificially constructed copies of the macroscopic system, but then the relation to the
物理现实已相当被遮蔽；而在气体的动能理论中，人们在想象中计数分子数
$n\xi_x$ 在体积 $\xi_x$ 周围的数，这是一个介于小的宏观标准和大的
足以包含许多分子的中间值——这是一个定义不明确的过程，它可以给出一个
$n'$ 仅大约等于理想数密度 $n$ 的值。

这些困难可以通过采用更抽象但完全逻辑的方法来避免在当前的展示中。这里
概率被视为一个先验概念：它是公理性的，即可以赋予任何可想象的事件一个数
字来表示事件发生的概率，这个概率与某些与统计概率定律相一致的
定律相符合。因此，如果 $A$ 表示任何事件的发生，$p(A)$ 是该事件发生的概率，
则

$$p(A) = p(A \cdot B) + p(A \cdot \sim B),$$

(1)

$$ (A \supset B) \supset \{p(B) \geq p(A)\},$$

(2)

在逻辑符号中。从这些，两个原则
的原理非常重要的意义对于当前的理论可以
被推导：

...
(1) The probability of $B$, among those events in which $A$ is certain, is given by

$$p_A(B) = \frac{P(A \cdot B)}{P(A)}.$$  

(ii) If $A$ and $B$ are causally connected,

$$P(A) = P(B).$$

It follows immediately from (1) that if $A$ and $B$ are independent, so that $p_A(B) = P(B)$, then $p(A \cdot B) = p(A)p(B)$. The deduction of (ii) from (1) is self-evident when one observes that a causal connection between $A$ and $B$ requires $A \supset B$ and $B \supset A$.

The significance of these principles in the classical theory of fluids will appear as the theory is developed. When the quantum theory is introduced, however, they are found to be quite unnecessary, as quantum mechanics incorporates much of the theory of probability in its foundations; the way in which it is involved is well known and will not be discussed here.

2. Notation and Fundamentals

The fluid whose properties are to be examined
is assumed to consist of \( N \) similar molecules of mass \( m \) confined within a volume \( V \). The configuration of any molecule may be specified by a number \((a)\) of generalised coordinates \( x_1 \ldots x_a \), the first three of which may be chosen to be the coordinates of the mass-centre of the molecule. A molecule is said to occupy a volume element \( dx = dx_1 dx_2 dx_3 \) of real space if its mass-centre \( x \equiv (x_1, x_2, x_3) \) lies within the volume element; similarly the molecule is said to occupy the element \( dx = dx_1 dx_2 \ldots dx_a \) of phase space if its generalised position vector \( \mathbf{x} \equiv (x_1, x_2, \ldots x_a) \) falls within the element. The temporal rate of change \( \dot{x} \) of the 'position vector' \( \mathbf{x} \) is represented by the generalised velocity \( \dot{x} \equiv (\dot{x}_1, \dot{x}_2, \ldots \dot{x}_a) \), and \( \ddot{x} \) by the generalised acceleration \( \ddot{x}_1, \ddot{x}_2, \ldots \), etc.

The probability that at time \( t \) the volume elements \( dx^{(1)}, \ldots dx^{(a)} \) (of phase space, if \( a > 3 \)) are all occupied is denoted by \( n_q(t, x^{(1)}, \ldots x^{(a)}) \). For brevity \( n_q(t, x^{(1)}, \ldots x^{(a)}) \) will often be contracted to \( n_q(t), n_q(x) \), or simply \( n_q \), the variables being sufficiently indicated by the suffix \( q \). If \( a = 3 \), \( n_q \) is the number density of the molecules, and when \( n_q \) is constant, \( n_2/n_1^2 \) is the function referred to in literature as the radial distribution function; if \( a > 3 \), the number density is \( \int dx^{(a-3)} n_1 \frac{\alpha}{\pi} \int dx^{(1)} \). The functions \( n_q \) are connected by the relation
\[ \int_{n_{q+1}} d \mathbf{x}^{(q+1)} = (N-q) n_q \]

This is easily proved with the help of the principle (1) of §1, A now representing the occupation of each of the volume elements \( d \mathbf{x}^{(i)} \ldots d \mathbf{x}^{(q)} \) by molecules, and \( B \) the occupation of \( d \mathbf{x}^{(q+1)} \) by a further molecule. According to (3), the probability of \( B \) when \( A \) is certain is \( \frac{n_{q+1}}{n_q} d \mathbf{x}^{(q+1)} \), and the integral of this expression must be, therefore, the total number of molecules, excluding the \( q \) whose positions are fixed. As the limiting case of (5) when \( q = 0 \), one has

\[ \int n_i d \mathbf{x}^{(i)} = N \]

(5) is also satisfied when \( q = N \), since \( n_{N+1} \) vanishes, by definition.

The probability that at time \( t \) the 'volume' elements \( d \mathbf{x}^{(i)}, \ldots d \mathbf{x}^{(q)} \) are occupied by molecules with 'velocities' \( \mathbf{v}^{(i)}, \ldots \mathbf{v}^{(q)} \) in the elementary ranges \( d \mathbf{v}^{(i)}, \ldots d \mathbf{v}^{(q)} \) respectively is denoted by \( \mathcal{f}_q(t, \mathbf{x}, \mathbf{v}) \ldots \mathcal{f}_q(t, \mathbf{x}^{(q)}, \mathbf{v}^{(q)}; \mathbf{v}^{(q)}) \prod_{i=1}^{a} d \mathbf{x}^{(i)} d \mathbf{v}^{(i)} \); the contracted forms \( \mathcal{f}_q(t, \mathbf{x}, \mathbf{v}) \), \( \mathcal{f}_q(\mathbf{x}, \mathbf{v}) \) or \( \mathcal{f}_q \) will often be used instead of \( \mathcal{f}_q(t, \mathbf{x}^{(i)} \ldots \mathbf{x}^{(q)}, \mathbf{v}^{(i)} \ldots \mathbf{v}^{(q)}) \). If \( a = 3 \), \( \mathcal{f}_q \) coincides with the velocity distribution function of the kinetic theory of gases.
It must be observed that the above definition of $f_\nu$ is only legitimate when one assumes that classical mechanics is adequate for the description of molecular phenomena, since, according to the general principles of quantum mechanics, it is strictly impossible to measure the position and velocity of a molecule simultaneously. The modifications which have to be made to adapt the theory to quantum requirements will be discussed later (\S 6).

The $f_\nu$ satisfy the relation, analogous to (5),

$$\sum \int f_{\nu+1} \, d\mathbf{x}^{(q+1)} \, d\mathbf{\xi}^{(q+1)} = (N-q) \, f_\nu,$$

also, clearly,

$$\sum \int f_\nu \, \prod_{i=1}^{q} d\mathbf{\xi}^{(i)} = n_\nu.$$

Pursuing this method, one may define an acceleration distribution function $g_\nu$ such that

$$g_\nu(t; \mathbf{x}^{(1)}, \ldots, \mathbf{x}^{(q)}; \mathbf{\xi}^{(1)}, \ldots, \mathbf{\xi}^{(q)}; \mathbf{\eta}^{(1)}, \ldots, \mathbf{\eta}^{(q)}; \mathbf{v}^{(1)}, \ldots, \mathbf{v}^{(q)}; \mathbf{\omega}^{(1)}, \ldots, \mathbf{\omega}^{(q)}; \mathbf{\alpha}^{(1)}, \ldots, \mathbf{\alpha}^{(q)}; \mathbf{\beta}^{(1)}, \ldots, \mathbf{\beta}^{(q)}; \mathbf{\gamma}^{(1)}, \ldots, \mathbf{\gamma}^{(q)}).$$

is the probability that at time $t$ the volume elements $d\mathbf{x}^{(i)} \, d\mathbf{\xi}^{(i)}$ are occupied by molecules with velocities $\mathbf{\xi}^{(i)}, \mathbf{\eta}^{(i)}$, and accelerations $\mathbf{\eta}^{(i)}, \mathbf{\omega}^{(i)}$ respectively ($i = 1 \ldots q$). The $g_\nu$ satisfy

$$\sum \sum \sum \sum g_{\nu+1} \, d\mathbf{x}^{(q+1)} \, d\mathbf{\xi}^{(q+1)} \, d\mathbf{\eta}^{(q+1)} = (N-q) \, g_\nu,$$
The definitions and fundamental equations relating to the rate-of-acceleration distribution function \( h_i(t, x, \xi, \eta, \xi) \) etc. are now obvious.

3. **Kinematics and Equations of Continuity**

It is now proposed to make a direct application of the second principle (ii) of § 1 in order to obtain a set of generalised continuity equations describing the motion of the fluid. For this purpose, \( A \) must be interpreted as the occurrence of a molecule at the point \( x \) (and with velocity \( \xi \) ) at time \( t \), and \( B \) as the occurrence of a molecule at \( x - \xi dt \) at time \( t - dt \). These events are clearly causally connected, and the probabilities of their occurrence are therefore equal. Applying the same consideration to a 'cluster' of \( q \) molecules, one has, on summing over all velocities,

\[
\int \int \int \int \int f_q(t - dt, x - \xi dt, \xi) \frac{q}{\int d\xi^i} = n_q(t, x)
\]

Hence, by subtraction from (8),

\[
\int \int \int \int \int \left( \frac{\partial f_q}{\partial t} + \sum_{i=1}^{q} \xi^i \cdot \frac{\partial f_q}{\partial x^i} \right) \frac{q}{\int d\xi^i} = 0
\]

or,

\[
\int \int \int \int \int \left( \frac{\partial f_q}{\partial t} + \sum_{i=1}^{q} \xi^i \cdot \frac{\partial f_q}{\partial x^i} \right) = 0
\]
\[ \frac{\partial \mathbf{u}_q^{(i)}}{\partial t} + \sum_{i=1}^{q} \frac{\partial}{\partial x_{q,i}} \cdot (\mathbf{u}_q \mathbf{u}_q^{(i)}) = 0, \]

where

\[ u_q^{(i)} = \frac{1}{n_q} \int \cdot \sum_{j=1}^{q} f_q \cdot \frac{q}{n_q} \cdot d\xi^{(j)} \]

is the average velocity of the molecule \( (i) \) in the cluster of \( q \) molecules whose positions are known.

When \( \alpha = 3 \), the equation of continuity of ordinary hydrodynamics and the kinetic theory of gases is obtained from (13) simply by putting \( q = 1 \); when \( \alpha > 3 \), the corresponding equation is obtained on integrating over the internal coordinates of the molecules.

The same principle may clearly be employed to show that

\[ \int \cdot \sum_{j=1}^{q} g_1(t-\xi \cdot x - \xi \cdot dt, \xi - \xi \cdot dt, \xi) \frac{q}{n_q} \cdot d\xi^{(i)} = f_q(t, x, \xi), \]

and hence that

\[ \frac{\partial f_q}{\partial t} + \sum_{i=1}^{q} \left( \frac{\partial f_q}{\partial x_{q,i}} \cdot \mathbf{u}_q^{(i)} + \frac{\partial f_q}{\partial \xi} \cdot \mathbf{u}_q^{(i)} \right) = 0, \]

where

\[ \omega_q^{(i)} = \frac{1}{n_q} \int \cdot \sum_{j=1}^{q} g_2 \cdot \frac{q}{n_q} \cdot d\eta^{(i)} \]
is the average acceleration of the molecule (i) in the cluster of q molecules whose positions and velocities are known. The method of derivation of 'continuity equations' for \( \dot{q}_i \) and \( h_i \), analogous to (13) and (16), is now quite obvious.


The mechanical properties of the system of \( N \) molecules are most easily obtained from the Hamiltonian function \( H_N \) for the entire system. One has

\[
H_N = \sum_{i=1}^{N} H^{(i)} + \frac{1}{2} \sum_{i<j}^{N} \phi^{(ij)},
\]

where \( H^{(i)} \) is the Hamiltonian of the molecule (i) in the absence of the others, and \( \phi^{(ij)} = \phi(x^{(i)}, x^{(j)}) \) is the interaction energy between two molecules at \( x^{(i)} \) and \( x^{(j)} \). (It is convenient to adopt the convention \( \phi^{(ii)} = 0 \)). \( H^{(i)} \) is given by

\[
H^{(i)} = \frac{1}{2} \sum_{s=1}^{\alpha} \dot{x}_s^{(i)} \cdot \dot{x}_s^{(i)} + \sum_{s,t=1}^{\alpha} j_x^{(i)}(x^{(i)}) \frac{\partial \phi^{(ij)}}{\partial x_t^{(j)}} x_t^{(j)} x_s^{(i)}
\]

where \( \frac{1}{2} \sum_{s=1}^{\alpha} \dot{x}_s^{(i)} \cdot \dot{x}_s^{(i)} = \frac{1}{2} \sum_{s=1}^{\alpha} j_x^{(i)}(x^{(i)}) \dot{x}_s^{(i)} \dot{x}_s^{(i)} \) represents the kinetic energy, and \( \sum_{s,t=1}^{\alpha} j_x^{(i)}(x^{(i)}) \frac{\partial \phi^{(ij)}}{\partial x_t^{(j)}} x_t^{(j)} x_s^{(i)} \) the potential energy of the molecule due to the external forces as well as to its own internal configuration. The Hamiltonian equations for the entire system, namely

\[
\sum_{s=1}^{\alpha} j_x^{(i)}(x^{(i)}) \frac{\partial \phi^{(ij)}}{\partial x_t^{(j)}} + \frac{1}{2} \sum_{s,t=1}^{\alpha} \frac{\partial \phi^{(ij)}}{\partial x_s^{(i)}} \frac{\partial \phi^{(ij)}}{\partial x_t^{(j)}} x_t^{(j)} x_s^{(i)} + \sum_{j=1}^{N} \frac{\partial \phi^{(ij)}}{\partial x_t^{(i)}} = 0.
\]
may be solved to obtain the (acceleration) \( \eta^{(i)} \) in the form

\[
\eta^{(i)} = g^{(i)-1} \cdot (P^{(i)} - \sum_{j=1}^{N} \frac{\partial \phi^{(i,j)}}{\partial x^{(i)}})
\]

where

\[
P_{r}^{(i)} = -\frac{1}{\epsilon} \sum_{s,t=1}^{a} \left( \frac{\partial g^{(i,s)}}{\partial x^{(i)}_{t}} + \frac{\partial g^{(i,t)}}{\partial x^{(i)}_{s}} - \frac{\partial g^{(i)}}{\partial x^{(i)}_{s}} \right) \xi^{(i)}_{s} \xi^{(i)}_{t} - \frac{\partial x^{(i)}}{\partial x^{(i)}_{r}}
\]

and \( g^{(i)-1} \) is the reciprocal of the tensor \( g^{(i)} \).

When \( a = 3 \), \( g^{(i)} \) reduces to the multiple \( m \) of the unit tensor, and \( P^{(i)} \) to the external force acting on the molecule \( (i) \).

The mean acceleration \( \omega^{(i)} \) of a molecule \( (i) \) in a cluster whose positions and velocities are known is easily obtained, with the help of (21), in the form

\[
\omega^{(i)} = g^{(i)-1} \cdot \left\{ (P^{(i)} - \sum_{j=1}^{3} \frac{\partial g^{(i,j)}}{\partial x^{(i)}}) - \frac{1}{\epsilon_{r}} \int F_{r} \frac{\partial x^{(i)}}{\partial x^{(i)}} d\xi^{(i)} d\xi^{(i)} \right\}
\]

The most obvious way of proving this result is by a further application of the principle (1) of §1 to show that the probability that the volume element \( x^{(q+1)} \), \( d\xi^{(q+1)} \) is occupied by a molecule with velocity \( \xi^{(q+1)} \), \( d\xi^{(q+1)} \) is

\[
\frac{f_{q+1}}{S_{q}} d\xi^{(q+1)} d\xi^{(q+1)}
\]

and it may also be obtained directly from the formula (17) by re-writing it, with the aid of (9), in the form

\[
\omega^{(i)} = \frac{1}{(N-q)!} \int_{v_{q}}^{(3N-24)} \int_{v_{q}}^{(3N-24)} \int_{v_{q}}^{(3N-24)} \int_{v_{q}}^{(3N-24)} \int_{v_{q}}^{(3N-24)} \int_{v_{q}}^{(3N-24)} \int_{v_{q}}^{(3N-24)} \int_{v_{q}}^{(3N-24)}
\]
and substituting

\[ q_N = f_N \sum_{i=1}^{N} \left\{ \frac{1}{2} \psi(r)^i \frac{d}{dx} \left( P^{(i)} - \sum_{j=1}^{N} \frac{d^2}{dx^{(j)}} \right) \right\} \]

where \( \psi \) denotes the Dirac delta-function.

Substituting (23) in (16), one obtains the important equation

\[ \frac{df_r}{dt} + \frac{1}{2} \sum_{i=1}^{N} \left\{ \frac{d^{(i)}}{dx^{(i)}} + \left( P^{(i)} - \frac{1}{2} \frac{d^2}{dx^{(i)}} \right) \frac{d}{dx} \frac{d^{(i-1)}}{dx^{(i-1)}} \right\} \]

\[ = \sum_{i=1}^{N} \int \frac{d^{(i+1)}}{dx^{(i+1)}} \frac{d}{dx} \frac{d^{(i-1)}}{dx^{(i-1)}} \frac{d^2}{dx^2} d\xi^{(i+1)} d\xi^{(i-1)} \]

which may be regarded as an integro-differential equation for the determination of \( f_r \). As, however, it contains \( f_{r+1} \) on the right-hand side, its solution must be effected either by making some approximative assumption concerning the dependence of \( f_{r+1} \) on \( f_r \), or by proceeding to the last equation \( q=N \), where the integral term vanishes, since \( f_{N+1} = 0 \). Of course, the equation is not fully determinate by itself; one may give \( f_N \) any value as a function of the \( x^{(i)} \) and \( \xi^{(i)} \) at an initial time \( t_0 \), subject to the normalising condition

\[ \int \ldots \int f_N \prod_{i=1}^{N} \left\{ d\chi^{(i)} d\xi^{(i)} \right\} = N! \]

and (26) then determines the subsequent variation.

\( q_4 \) may be obtained by integration from (25), but as such integrations can rarely be performed in practice, it is important to obtain the differential
equation which it satisfies and which provides the
best starting point for approximative evaluation.
The derivation of this equation offers no diffi-
culties; from (21) one obtains the 'rate of
acceleration'

$$\xi^{(\nu)} = \frac{1}{z} \sum_{j=1}^{n} \left( \xi^{(j)} \cdot \frac{\partial^{2} \xi^{(j)}}{\partial x^{(j)} \partial y^{(j)}} \right) \cdot \mathcal{I}^{(\nu-1)} \cdot (\mathcal{P}^{(\nu)} - \sum_{k=1}^{N} \frac{\partial \mathcal{F}^{(\nu)}}{\partial x^{(k)}})$$

whose mean value \(Z_{1}^{(\nu)}\) must be substituted in the
equation for \(j_{1}\):

$$\frac{\partial j_{1}}{\partial t} + \sum_{i=1}^{n} \left[ j_{i} \cdot \frac{\partial j_{1}}{\partial x^{(i)}} + \eta_{1} \cdot \frac{\partial j_{1}}{\partial y^{(i)}} + \eta_{2} \cdot \frac{\partial j_{1}}{\partial z^{(i)}} \right] \cdot (j_{1}, Z_{1}^{(\nu)}) = 0$$

5. **Application to Gas-theory**

So far no distinction has been made which
identifies the molecular system under consideration
with a liquid, as opposed to a solid or a gas.
Indeed, it may be claimed for the foregoing that it is
sufficiently general to be applicable to any form of
matter. However, it is important to be able to
differentiate clearly between the three phases, and
their characteristics are therefore now briefly
stated. The solid is distinguished from the fluid
state by the existence of a degree of long-range
order, so that the occurrence of two events A and
B separated by a long distance is not independent,
whereas for a fluid, according to §1, one has
\(p(A \cdot B) = p(A) \cdot p(B)\); thus, for example, in a fluid
when \( |x^{(0)} - x^{(a)}| \) is large, but not in a solid.

The distinction between liquid and gas is in abstract not so clear, and may be said even to disappear above the critical point; it is best understood through the phenomenon of condensation, which will be discussed later. A rough distinction may however be made in the following way. The potential energy \( \phi(x^{(r)}, x^{(j)}) \) between two molecules at \( x^{(r)} \) and \( x^{(j)} \) decreases rapidly with the distance between their mass centres, and (except in the special case of Coulomb forces, applicable to ions) a distance \( r_0 \), which is very small by macroscopic standards, may be specified, beyond which the interaction may without error be assumed to vanish completely. In a liquid, there are many molecules within this distance \( r_0 \) of a given molecule; in a gas, there are usually none, and the probability that there is more than one is very small, except near the point of condensation. The neglect of this small probability is equivalent to the assumption of 'binary encounters' in gas-theory. It will now be shown that when this assumption is made, on substituting \( q = 1 \) in (26) one obtains the Boltzmann equation which is fundamental in the kinetic theory of gases.

For this purpose, one assumes, with Boltzmann,
that the internal structure of the molecules is unimportant, so that $\alpha = 3$; then the right-hand side of (26) reduces, when $q = 1$, to

$$\frac{1}{\pi} \int \frac{2 \phi^{(n)}(x)}{2 \xi^{(n)}} d\xi^{(n)} d\xi^{(l)}.$$  

To transform this into the Boltzmann 'collision integral', an expression for $f_2$ in terms of $f_1$ is first required. Consider, therefore, the motion of two molecules which at time $t$ have positions $x^{(l)}$, $x^{(l)}$ (such that $|x^{(l)} - x^{(l')}| < r_0$) and velocities $\xi^{(l)}$, $\xi^{(l)}$ respectively; and suppose that at time $t_0 < t$, when the molecules were last at a distance $r_0$ from one another, their positions and velocities were $x^{(l)}_0$, $x^{(l)}_0$ and $\xi^{(l)}_0$, $\xi^{(l)}_0$ respectively. During the motion, according to the principle (ii) of §1, the configurational probability

$$f_2(t, x^{(l)}, x^{(l')}, \xi^{(l)}, \xi^{(l')}) d\xi^{(l)} d\xi^{(l')} d\xi^{(l)} d\xi^{(l')}$$

must remain unchanged; also, by Liouville's theorem, the volume in phase space $d\xi^{(l)} d\xi^{(l')} d\xi^{(l)} d\xi^{(l')}$ is unaltered. Hence

(30)  

$$f_2(t, x^{(l)}, x^{(l')}, \xi^{(l)}, \xi^{(l')}) = f_1(t_0, x^{(l)}_0, \xi^{(l)}_0) f_1(t_0, x^{(l')}_0, \xi^{(l')}_0)$$

since, as explained above, molecular events in fluids which occur beyond the range of interaction must be considered independent.

Next one introduces an approximative assumption which is always made in gas-theory, that $t_0$, $x^{(l)}_0$, and $\xi^{(l)}_0$ may be replaced by $t$, $x^{(l)}$, and $\xi^{(l)}$ on the right-hand side of (30). As $r_0$ is so small, the resulting error is of microscopic order; neverthe-
less it is important in explaining why, for example, there are small deviations from the Maxwellian velocity distribution law, which is a rigorous consequence of the Boltzmann equation, in equilibrium conditions.

To calculate \( \bar{\xi}^{(n)} \) and \( \bar{\xi}^{(o)} \) in terms of \( \xi^{(n)} \), \( \xi^{(o)} \), and \( r = x^{(n)} - x^{(o)} \), one may use the Hamiltonian equations of motion

\[
\frac{dx_{ij}}{dt} = \frac{\partial \Phi}{\partial x_{ij}} = -m \frac{\partial \bar{\xi}^{(n)}}{\partial x_{ij}} - m \frac{\partial \bar{\xi}^{(o)}}{\partial x_{ij}}.
\]

The eight functionally independent integrals \( \Theta_k (\Sigma, \bar{\xi}^{(n)}, \bar{\xi}^{(o)}) = \text{const.} \) (\( k = 1 \cdots 8 \)) of these equations just suffice to determine \( r_o, \bar{\xi}^{(n)}_o, \) and \( \bar{\xi}^{(o)}_o \) as the solution of the simultaneous equations

\[
(32) \quad \Theta_k (r_o, \bar{\xi}^{(n)}_o, \bar{\xi}^{(o)}_o) = \Theta_k (\Sigma, \bar{\xi}^{(n)}, \bar{\xi}^{(o)}), \quad |\Sigma| = r_o.
\]

Since, however, all the \( \Theta_k \) satisfy the equation

\[
(33) \quad m \left( \frac{\xi^{(n)} - \xi^{(o)}}{2r} \right) \frac{\partial \Theta_k}{\partial x} = \frac{\partial \Phi}{\partial x} \left( \frac{\partial \Theta_k}{\partial \xi^{(n)}} - \frac{\partial \Theta_k}{\partial \xi^{(o)}} \right),
\]

\( \bar{\xi}^{(n)}_o \) and \( \bar{\xi}^{(o)}_o \), which are now expressed as functions of the \( \Theta_k \), satisfy the same equation, and so does the expression for \( \bar{f}_2 \) obtained from \( (30) \). The integral \( \frac{1}{m} \int \frac{\partial \Phi}{\partial x} \frac{\partial \xi^{(n)}}{\partial x} \xi^{(o)} \) vanishes on account of the integration over \( \xi^{(a)} \) (because there are no
molecules with infinite velocities); hence

\[ \frac{1}{v} \int \frac{3}{2} \frac{\partial \xi}{\partial \xi(i)} \cdot \frac{\partial \xi}{\partial \xi'(i)} \, d\xi(i) d\xi'(i) = \int \int (\xi(i) - \xi'(i)) \cdot \frac{2}{v} \left\{ f_i (\xi(i)) f_i (\xi'(i)) \right\} d\xi(i) d\xi'(i), \]

where the domain of integration over \( \mathbb{R} \) may be limited to the sphere of radius \( r_0 \) surrounding \( x(i) \).

This integration is most conveniently performed by imagining the sphere to be partitioned by elementary tubes parallel to the vector \( \xi(i) - \xi'(i) \); one may then integrate, first over a typical tube specified by the cross-section radius \( b \) (perpendicular from the centre of the sphere), and then over all values of \( b \). At the beginning of the tube, where \( (\xi(i) - \xi'(i)) \cdot \xi < 0 \), the interaction between the molecules is negligible, and \( \xi'(i) \) reduces to \( \xi(i) \) and \( \xi'(i) \) to \( \xi'(i) \); at the end, the values \( \xi'(i) \) and \( \xi'(i) \) of \( \xi(i) \) and \( \xi'(i) \) have to be calculated with the help of (32). Thus the right-hand side of (34) assumes the form

\[ \int \int (\xi(i) - \xi'(i)) \left\{ f_i (\xi(i)) f_i (\xi'(i)) - f_i (\xi(i)) f_i (\xi'(i)) \right\} d\xi(i) d\xi'(i), \]

which is the well-known Boltzmann collision integral.

One is thus assured that all the consequences of the Boltzmann equation in gas-theory can be derived from the present theory when it is assumed that only binary encounters between the molecules are important.
6. **Quantisation of the Theory.**

At this juncture it is necessary to consider carefully how the theory must be modified in order to make it conform with the requirements of quantum mechanics. As is well-known, a formal correspondence between classical and quantum theory can be established by replacing every classical expression \( \alpha_q(t, x_1, \ldots, x_n, \xi_1, \ldots, \xi_n) \) which is a function of positions and velocities by the corresponding operator, represented by the 'matrix' \( \alpha_q(t, x_1, \ldots, x_n, \xi_1, \ldots, \xi_n) \), in the \( x \)-representation. Such a matrix will often be denoted by \( \alpha_q(x, x') \), or simply by \( \alpha_q \). The sum \( (\alpha_q + \beta_q) \) and the product \( (\alpha_q \beta_q) \) of two operators \( \alpha_q \) and \( \beta_q \) are defined by the matrix equations

\[
(\alpha_q + \beta_q)(x, x') = \alpha_q(x, x') + \beta_q(x, x'),
\]

\[
(\alpha_q \beta_q)(x, x') = \int \cdots \int \alpha_q(x, x') \beta_q(x, x') \frac{q}{i} \, dx^{(i)}.\]

The operators corresponding to the position vector \( x^{(i)} \), and the canonical momentum vector \( p^{(i)} = \frac{\partial}{\partial x^{(i)}}, \ldots, \frac{\partial}{\partial x^{(i)}} \) are specified by

\[
x^{(i)}(x, x') = x^{(i)} \frac{q}{i} \int_1 \cdots \int_1 S(x^{(j)} - x^{(j)'}),
\]

\[
p^{(i)}(x, x') = -i \frac{2}{\partial x^{(i)} \int_1} S(x^{(j)} - x^{(j)'}).
\]

With the aid of (35) and (36), the representative of any function of time, coordinates, and momenta can...
be constructed. In particular, one obtains for a function \( \gamma_q(x) \) of coordinates alone,

\[
\gamma_q(x, x') = \gamma_q(x) \sum_{j=1}^q \delta(x^{(j)}) - x'^{(j)}),
\]

and for expressions of the form \((p^q \alpha_q)\) and \((\alpha_q p^q)\),

\[
(p^q \alpha_q)(x, x') = -i \frac{\partial \alpha_q(x, x')}{\partial x^{(i)}},
\]

\[
(\alpha_q p^q)(x, x') = i \frac{\partial \alpha_q(x, x')}{\partial x^{(i)}},
\]

The 'trace' of an operator of the kind \(\alpha_{q+1}\) is denoted by \(\chi_{q+1}(\alpha_{q+1})\), and defined by

\[
\chi_{q+1}(\alpha_{q+1})(x, x') = \int \alpha_{q+1}(x, x') \delta(x^{(q+1)} - x'^{(q+1)}) dx^{(q+1)} dy^{(q+1)}.
\]

except when \(q = 0\), it is an operator of the kind \(\alpha_q\) and must be distinguished from the complete trace, which is a c-number. The complete trace \(X(\alpha_q)\) of \(\alpha_q\) is defined by

\[
X(\alpha_q) = x_1 \left[ x_2 \left[ \cdots x_q(\alpha_q) \right] \right].
\]

\(\chi_{q+1}(\alpha_{q+1})\) is the quantum transcription of the classical expression \(\int \alpha_{q+1}(x, \xi) dx^{(q+1)} d\xi^{(q+1)}\); by comparing this expression with (40), one sees that in quantum theory the operation \(\int d\xi^{(q+1)}\) is replaced by \(\int dx^{(q+1)} \delta(x^{(q+1)} - \xi^{(q+1)})\), i.e., by the substitution of
Suppose that \( \rho_q(x, x') \) is the matrix representative of the operator \( \rho_q \) which corresponds to the velocity distribution function \( f_q(x, \xi) \). To preserve the analogy with the classical theory it is convenient to normalise \( \rho_q \) according to the relation

\[
X_{q+1}^{(q+1)}(\rho_{q+1}) = (N - q)\rho_q,
\]

(41)

Corresponding to (7); whilst the formula (8) now reads

\[
\sum_{q=1}^{q} \int \rho_q \frac{q}{i} \int (x^{(q)} - x') \, dx' = \pi_q,
\]

(42)

or

\[
\rho_q(x, x') = \pi_q(x)
\]

(43)

This is one of the most important properties of the matrix \( \rho_q \), that its diagonal elements are the values of the number density function. It is seen at once that \( \rho_q \) coincides with the 'statistical operator' or 'density matrix' introduced into quantum mechanics by von Neumann\(^{17}\) and Dirac\(^{18}\).

In order to formulate the equation satisfied by \( \rho_q \), it is convenient to begin with \( \rho_N \). Like \( f_N \), this matrix may be given an arbitrary value at time \( t_0 \), subject to the Hermitian condition and the
normalisation

\[(44) \quad \chi(\rho_N) = N! ;\]

its subsequent variation is then determined by the Heisenberg equation

\[(45) \quad \frac{\partial \rho_N}{\partial t} = [H_N, \rho_N] ,\]

where $H_N$ is the Hamiltonian operator constructed from the formula (18), and $[\alpha_i, \beta_i]$, in conformity with Dirac's notation, means simply $-\frac{i}{\hbar}(\alpha_i \beta_i - \beta_i \alpha_i)$. One may define $H_q$ for any value of $q$ by the equation

\[(46) \quad H_q = \sum_{i=1}^{q} H^{(i)} + \sum_{i=1, j=1}^{q} \phi^{(ij)} ,\]

so that, taking the trace of (45), one obtains

\[(47) \quad \frac{\partial \rho_{N-1}}{\partial t} = [H_{N-1}, \rho_{N-1}] + \sum_{i=1}^{N-1} \chi_N \left[ \phi^{(iN)} , \rho_N \right] .\]

The only term of $\chi_N \left[ H^{(n)} , \rho_N \right]$ which does not obviously vanish is $\frac{1}{2m} \left[ \rho^{(n)} , \rho_N \right]$, and when reduced to the form

\[-\frac{1}{2m} \int \frac{\partial^2}{\partial x^{(n)}} \cdot \left( \rho^{(n)} \rho_N + \rho_N \rho^{(n)} \right) dx, dx' S(x^{(n)} - x'^{(n)}) dx^{(n)} dx^{(n)} \]

this obviously vanishes also after transformation to a surface integral. (There are no molecules outside the confines of the volume $V$).

Repeating this procedure indefinitely, and
cancelling the factor \((N-q)!\) which appears, one obtains

\[
\frac{\partial \rho_q}{\partial t} = [H_q, \rho_q] + \sum_{i=1}^{q} \chi_{q+1} \left[ \phi^{(i+1)}, \rho_{q+1} \right],
\]

which is the fundamental equation satisfied by \(\rho_q\).

Now, it is well-known that the classical analogue of the 'Poisson bracket' \([\alpha_q, \beta_q]\) is

\[
\frac{\partial q}{\partial \alpha_q} \cdot \frac{\partial \beta_q}{\partial \alpha_q} - \frac{\partial \alpha_q}{\partial \beta_q} \cdot \frac{\partial \beta_q}{\partial \alpha_q},
\]

and since \(p^{(i)} = \frac{\partial \alpha_q}{\partial \beta_q}\), in the transition to classical mechanics \([H_q, \rho_q]\) becomes

\[
\sum_{i=1}^{q} \left( \frac{\partial \alpha_q}{\partial \beta_q^{(i)}} - \frac{\partial \beta_q}{\partial \alpha_q^{(i)}} \right) \cdot \frac{\partial \beta_q}{\partial \beta_q^{(i)}} + \frac{\partial \alpha_q}{\partial \alpha_q^{(i)}} - \frac{\partial \beta_q}{\partial \alpha_q^{(i)}} \cdot \frac{\partial \alpha_q}{\partial \beta_q^{(i)}}
\]

and \(\chi_{q+1} \left[ \phi^{(i+1)}, \rho_{q+1} \right]\) becomes

\[
\sum \frac{\partial \phi^{(i+1)}}{\partial \beta_q^{(i)}} \cdot \frac{\partial \beta_q^{(i+1)}}{\partial \beta_q^{(i)}}, \frac{\partial \phi^{(i+1)}}{\partial \beta_q^{(i+1)}} \cdot \frac{\partial \beta_q^{(i)}}{\partial \beta_q^{(i+1)}}
\]

so that in the limit \(\hbar \to 0\), (48) goes over into the corresponding classical equation (26). This ensures that in the region of high temperatures, where the energy states are so numerous that they may be replaced without error by a continuous spectrum (thus effectively writing \(\hbar = 0\)), the classical theory developed in previous sections is fully adequate. In the region of very low temperatures, however, the divergences between classical and quantum theory become important, and a quantum treatment is essential. To preserve full generality, therefore, and because the quantum treatment is seldom more difficult than the classical one, the more important developments in the chapters which
follow will be made in the formalism of the present section.
CHAPTER II: THERMODYNAMICS OF FLUIDS.

1. The General Method of Solution.

In order to calculate the density matrix $\rho_N$ from the equation (45), it must first be specified at some initial time $t_0$. For this purpose one first chooses any complete set of independent commuting operators $\chi^{(r)} (r = 1 \ldots N')$, and then specifies the probability $p_N(\omega) = p_N(\chi^{(r)} \ldots \chi^{(n)})$ that at time $t_0$ the fluid is in the state $\ell$ for which the $\chi^{(r)}$ have the simultaneous eigenvalues $\ell^{(r)}$. This represents the maximum of information which can be ascertained experimentally concerning the fluid. Let $\psi_N(\ell, x)$ be the eigenfunction corresponding to the state $\ell$, satisfying the equation

$$\sum_{r=1}^{N'} \chi^{(r)}(x, x') \psi_N(\ell, x') \frac{1}{i} \delta^{(r)}(\chi^{(r)}) = \ell^{(r)} \psi_N(\ell, x),$$

and normalised in such a way that

$$\sum_{r=1}^{N'} \psi_N(\ell, x) \left| \psi_N(\ell, x) \right|^2 \frac{1}{i} \delta^{(r)}(\chi^{(r)}) = N!.$$

Then, at time $t_0$, according to von Neumann and Dirac,

$$\rho_N(x, x') = \sum_{\ell} p_N(\ell) \psi_N(\ell, x) \psi_N^*(\ell, x').$$

One possible set of $\chi$ is that set of operators which commute with the Hamiltonian $H_N$, and are therefore constants of the motion; it is convenient,
however, to choose the $\lambda$ in a slightly different way, as follows. Suppose the fluid is divided into a number of groups containing $q_1, q_2, \ldots, q_\omega$ molecules ($q_1 + q_2 + \ldots + q_\omega = N$), such that the interaction between molecules in different groups is very weak; this may be effected, for example, by imaginary surfaces described in the fluid. Then the $\lambda$ are chosen to be the $\lambda_1, \lambda_2, \ldots, \lambda_\omega$ which commute with $H_{q_1}, H_{q_2}, \ldots, H_{q_\omega}$ respectively. Write

$$H_N = H_{q_1} + H_{q_2} + \ldots + H_{q_\omega} + U,$$

so that $U$ is very small compared with $H_N$. Let $E_1, E_2, \ldots, E_\omega$ be the eigenvalues of $H_{q_1}, H_{q_2}, \ldots, H_{q_\omega}$, and put

$$E_N = E_1 + E_2 + \ldots + E_\omega.$$

Then, in the $l$-representation, (45) reads

$$\frac{\partial \rho_N(l,l')}{\partial t} = (E_N - E_{l'}) \rho_N(l,l') + \sum_{l''} \{U(l,l',l'') \rho_N(l','l'') - \rho_N(l,l'') U(l',l'')\}.$$

Substituting

$$\rho_N(l,l') = e^{-\frac{1}{\hbar}(E_N - E_{l'}) t} \overline{\rho_N(l,l')},$$

$$U(l,l') = e^{-\frac{1}{\hbar}(E_N - E_{l'}) t} \overline{U(l,l')},$$

(54) becomes, in matrix notation,
This equation may be solved by writing

\[ \bar{p}_N = \rho(0) + \rho(1) + \rho(2) + \cdots \]

where \( \rho(0) \) is the value of \( \bar{p}_N \) at time \( t_0 \), given, according to (51), by

\[ \rho(0)(t, t') = \bar{p}_N(t) \delta(t-t') \]

and the \( \rho(u) \) satisfy

\[ \frac{\partial \rho(u)}{\partial t} = \bar{U} \rho(u) - \rho(u) \bar{U}, \quad u = 0, 1, 2, \ldots \]

The probability at any time \( t \geq t_0 \) that the fluid is in the state \( \ell \) is then

\[ \bar{p}_N = \rho(0) + \rho(1) + \rho(2) + \cdots \]

where \( \rho(u)(\ell) = \rho(u)(\ell, \ell) \), so that \( \rho(0) = \bar{p}_N \). If

\[ W = \int_{t_0}^{t} \bar{U} \, dt, \quad \bar{U} = \bar{W}, \]

one obtains from (59)

\[ i\hbar \rho(1) = \bar{W} \rho(0) - \rho(0) \bar{W}, \]
where

\[ w_1 = \frac{1}{3} \int_{t_0}^{t} (\dot{w} w - w \ddot{w}) \, dt, \]  

and similarly, by an easy calculation not reproduced,

\[ -t^2 \mathcal{P}(2) = \frac{1}{6} \left\{ w^3 \rho(0) - 3 w^2 \rho(0) \dot{w} + 3 w \rho(0) \ddot{w} - \rho(0) w^2 \right\} \]

\[ + w \left\{ w_1 \rho(0) - \rho(0) w_1 \right\} \left\{ w_1 \rho(0) - \rho(0) w_1 \right\} \]

\[ + w_2 \rho(0) - \rho(0) w_2, \]

where

\[ w_2 = \frac{1}{3} \int_{t_0}^{t} (\dot{w} \dot{w} - w \dddot{w}) \, dt, \]

Hence

\[ \mathcal{P}(1)(\zeta) = 0 \]

\[ \mathcal{P}(2)(\zeta) = \frac{1}{2} \sum_{\lambda} \left[ \mathcal{U}(\lambda, \zeta) \right] \left\{ \mathcal{P}_n(\zeta') - \mathcal{P}_n(\zeta) \right\} \]

\[ \mathcal{P}(3)(\zeta) = \frac{1}{2} \sum_{\lambda} \left[ \mathcal{U}(\lambda, \zeta) \right] \left\{ \mathcal{P}_n(\zeta') - \mathcal{P}_n(\zeta) \right\} \]

\[ + \frac{1}{2} \sum_{\lambda} \mathcal{U}(\lambda, \zeta) \left\{ \mathcal{P}_n(\zeta') + \mathcal{P}_n(\zeta') \right\} \left\{ \mathcal{P}_n(\zeta') - \mathcal{P}_n(\zeta) \right\} \]

As \( \mathcal{U} \) is small, the series (60) will converge quickly, especially when \( t - t_0 \) is small. Hence, to a sufficiently high order of approximation,

\[ \mathcal{P}_n(\zeta) = \mathcal{P}_n(\zeta) + \frac{1}{4} \sum_{\lambda} \left[ \mathcal{U}(\lambda, \zeta) \right] \left\{ \mathcal{P}_n(\zeta') - \mathcal{P}_n(\zeta) \right\} \]

This equation has a transparent physical significance,
when \(|\psi(l,l')|^2\) is interpreted as the probability of a transition from the state \(l\) to the state \(l'\), or vice versa, in time \(t-t_0\).

2. The \(H\)-Theorem and the Adiabatic Principle

One sees immediately from (68) that a necessary condition for equilibrium at time \(t_0\) is

\[
(w(l,l')=0 \text{ or } p_N(l)=p_N(l'), \text{ all } l \text{ and } l',
\]

in the sense that \(p_N(l)\) and \(p_N(l')\) must be equal for all \(l\) and \(l'\) for which \(w(l,l')\) does not vanish. This condition is also sufficient, as it secures the identical vanishing of \(\rho(i)\), and hence of all the \(\rho(u)\) except \(\rho(o)\). It will now be shown also that, starting from an arbitrary initial state, the fluid must approach a state in which (69) is satisfied.

For this purpose, one defines a quantity \(S_N\) by the equation

\[
S_N = -k \sum_l \frac{P_N(l)}{P_N(l')} \log \frac{P_N(l)}{P_N(l')},
\]

so that, by substitution from (68) and neglect of squares and higher powers of the small quantity \(\psi(l,l')\), one obtains

\[
S_N = -k \sum_l P_N(l) \log P_N(l) + k \sum_{l,l'} \frac{\psi(l,l')}{2} \left\{ \log P_N(l) - P_N(l') \right\} \left[ \log P_N(l) - P_N(l') \right].
\]
Thus \( S_N \) necessarily increases between the times \( t \) and \( t' \), unless (69) is satisfied, when it remains constant; and \( S_N \) will therefore continue to increase while the fluid approaches the equilibrium state, until such a time when \( \rho(2) \) becomes small enough to be comparable with \( \rho(3) \). Then the above argument loses its validity, since \( \delta f(w(l))\delta w(l)\delta w(l') \delta w(l') \) and \( \delta f(w(l))\delta w(l)\delta w(l)\delta w(l) \) are not necessarily positive, and, instead of further approaching the equilibrium state, the fluid is subject to small random fluctuations in the immediate neighbourhood of equilibrium. From this point of view, phenomena like the Brownian movement are readily understood.

Corresponding to (70), one has for one of the groups containing \( q_e \) molecules,

\[
(72) \quad S_e = -k \sum_{l_e} p_e(l_e) \log p_e(l_e),
\]

where \( p_e(l_e) \) is the probability that this group is in the state \( l_e \). Since the groups are virtually independent of one another,

\[
(73) \quad \sum_{l_e} p_e(l_e) = 1
\]

and, substituting this value in (70), and remembering that \( \sum_{l_e} p_e(l_e) = 1 \), one obtains

\[
(74) \quad S_N = \sum_{e=1}^{\omega} S_e.
\]
All these properties of $S_N$ strongly suggest that it is identical with the entropy of the fluid which is defined in classical thermodynamics, but, pending a rigorous proof, no use is made of this presumption.

So far, the way in which the $\rho_\nu$ depend on the time has not been explicitly determined. From (61) and (64) one obtains

$$W(l', l^\prime) = \frac{2}{\gamma_1} \frac{a_V(l', l^\prime)}{l'} e^{\frac{i}{2} \gamma_1 t'} \sin \frac{1}{2} \gamma_1 t'$$

(75) $$\bar{W}(l', l^\prime) = \sum_{l^\prime} \frac{2}{\gamma_1 \nu_2} \frac{a_V(l', l^\prime)}{(\gamma_1 + \nu_2)} e^{\frac{i}{2} (\gamma_1 + \nu_2) t'} \left( \nu_2 \sin \frac{1}{2} \gamma_1 t' \cos \frac{1}{2} \gamma_1 t' - \nu_2 \sin \frac{1}{2} \nu_2 t' \cos \frac{1}{2} \nu_2 t' \right),$$

where $l - \gamma_1 = E_N - E_N'$, $l = E_N - E_N''$, and $t = t - t_0$. Now, all those terms which are periodic in $t'$ and therefore oscillate about a small fixed value do not represent any real change in the fluid, and may be regarded as vanishing. This applies to all terms in $W(l', l^\prime)$ except those for which $\gamma_1 = 0$, and to all terms in $\bar{W}(l', l^\prime)$ except those for which $\gamma_1 + \nu_2 = 0$.

Hence one has effectively

$$W(l', l^\prime) = a_V(l', l^\prime) E_{E_N} E_{E_N'} (t - t_0)$$

(76) $$\bar{W}(l', l^\prime) = a_V \sum_{l^\prime} \frac{a_V(l', l^\prime)}{E_N - E_{N'}} E_{E_N} E_{E_N'} (t - t_0)$$

where $\sum'$ means that terms for which $E_N = E_N'$ are omitted from the summation. The result is, that only those transitions occur which satisfy the principle of conservation of energy. This is the 'adiabatic principle' discovered in quantum theory by Born (20).
the title remains appropriate in the present
application, since the possibility of performing
work on the fluid by moving the external constraints
has not yet been considered. It has been assumed in
the foregoing that the energy levels of the fluid
are discrete, but it is easily verified that the
adiabatic principle holds also for the continuous
spectrum. It is easily seen, further, that the
adiabatic principle holds not only for \( \rho^{(1)} \) and
\( \rho^{(2)} \), but for all the \( \rho^{(\lambda)} \); this extension was
first proved by Born and Fock \(^{(23)}\).

It has been shown that \( \mathcal{U}(l,l') \) is diagonal in
\( E_N \), and the question now arises whether it can be
diagonal in any other combination of the \( \lambda^{(r)} \). To
decide this, let \( \Lambda_N \) be any combination of the \( \lambda^{(r)} \)
such that \( \mathcal{U}(l,l') \) is diagonal in its eigenvalue \( L_N \).
Then \( \Lambda_N \) commutes with \( U \) as well as with the other
\( \lambda \)'s, and therefore also with \( H_N \), according to
\((52)\). As \( U \) is the sum of a number of arbitrarily
selected terms \( \phi^{(i)} \), \( \Lambda_N \) must commute with the
\( \phi^{(i)} \) individually. The only constants of the motion,
however, which commute with the potential energy,
are the momentum and angular momentum. Hence one has

\[
\Lambda_N = \sum_{i=1}^{N} \Lambda^{(i)} = \sum_{\varepsilon=1}^{\tilde{N}} \Lambda_{\varepsilon} \quad \text{and} \quad L_N = \sum_{i=1}^{N} L^{(i)} = \sum_{\varepsilon=1}^{\tilde{N}} L_{\varepsilon}
\]

where \( \Lambda^{(i)} \) represents either \( p^{(i)} \), or one component
and the square of \( x^{(i)} \) or \( p^{(i)} \). It thus appears that \( \mathcal{U} \)
can be diagonal only in those constants of the motion which are also "summational invariants".

3. The Equilibrium Distribution Law

It is now possible to determine the equilibrium form assumed by $p_{N}$ from the condition for equilibrium (69). It follows from this condition that $p_{N}(l)$ must have the same value for all those states which can be connected by a chain of transitions not forbidden by the vanishing of the matrix elements of $W$; but that for states, such as different energy or momentum states, which cannot be so connected, $p_{N}(l)$ will have different values. Thus, in equilibrium,

$$p_{N}(l) = p(E_{N}, L_{N}), \tag{78}$$

and, according to (73),

$$p(E_{N}, L_{N}) = \frac{\tilde{W}}{e=1} p_{e}(l_{e}) \tag{79}$$

where $E_{N}$ is given in terms of the $E_{e}$ by (53), and $L_{N}$ in terms of the $L_{e}$ by (77). It follows rigorously from this that the dependence of $p_{N}$ and $p_{e}$ on $E_{N}$ and $E_{e}$ is given by

$$\log p_{N}(E_{N}) = \beta (A_{N} - E_{N}), \tag{80}$$

$$\log p_{e}(E_{e}) = \beta (A_{e} - E_{e})$$
where $\beta$ is a constant and $A_N = \sum_{e=1}^{w} A_e$. $A_N$ is in general a linear combination of the $L_N$, but for simplicity it is assumed here that the mean momentum and angular momentum of the fluid both vanish, in which case $A_N$ is a constant, determined by the condition $\sum_{l} p_N(l) = 1$ in the form

$$e^{-\beta A_N} = \sum_{l} e^{-\beta E_N}. \tag{81}$$

To determine $\beta$, one employs a well-known argument, stated concisely by Schrödinger $^{(24)}$. An external agency is permitted to do work on the fluid by moving the external constraints; the effect of this is to change the eigenvalues $E_N$ of the energy of the fluid. In a small change $dE_N$ of the $E_N$, the work done on the fluid is $\sum_{l} p_N(l) dE_N$; the corresponding change in the internal energy $U_N$, given by

$$U_N = \sum_{l} p_N(l) E_N, \tag{82}$$

exceeds this by

$$\sum_{l} dP_N(l) E_N = \sum_{l} e^{\beta(A_N-E_N)} d\left[\beta(A_N-E_N)\right] E_N = -\sum_{l} e^{\beta(A_N-E_N)} (A_N-E_N) d\left[\beta(A_N-E_N)\right], \tag{83}$$

and this must be $TdS_N$, where $T$ is the thermodynamic temperature and $S_N$ the entropy. The
reciprocal of the integrating factor $\beta$ of the right-hand side of (83) must therefore be a multiple $k$ of $T$, ($\beta^{-1} = kT$), and the entropy $S_N$ must be

$$-\frac{k}{\beta} \frac{1}{T} (A_N - E_N) \ell \beta (A_N - E_N)$$

apart from an unimportant constant. This justifies the interpretation of the quantity defined in (70) as the entropy. Finally, the free energy $A_N = U_N - T S_N$ is given, apart from an unimportant constant, by the equation (81).

The equilibrium expression for $\rho_N$ may be written down at once with the aid of (51), (78) and (80); it is

$$\rho_N = \ell \beta (A_N - H_N)$$

in operational form, since one may now consider the fluid as a whole, and put $\gamma = 0$. ($q_1 = N; q_2 = \ldots = q_m = 0$).

Taking the complete trace of (85), one finds

$$N! \ell^{-\beta A_N} = X (\ell^{-\beta H_N}),$$

which is equivalent to (81); also, by repeated application of (41), one obtains

$$(N - q)! \ell^{-\beta A_N} \rho_q = X_{q+1} \left[ X_{q+2} \ldots X_N (\ell^{-\beta H_N})^q \right]$$
In this way, all the equilibrium properties of the fluid are in principle determined.

The transition to classical, as opposed to quantum theory, is easily made. (85) and (86) may immediately be transcribed in the form

$$f_N = e^{\beta (H_N - H)}$$

(88) $$N! e^{-\beta A_N} = \int \cdots \int e^{-\beta H_N} \frac{1}{n_1! \cdots n_N!} d\mathbf{x}(1) d\mathbf{x}(2)$$

where \( H_N \) is now interpreted as a function of positions and velocities. Integration over the velocities is readily performed, and, corresponding to \( \alpha \) degrees of freedom, one has

(89) $$N! e^{-\beta A_N} = \left( \frac{2\pi kT}{m_1 \cdots m_\alpha} \right)^{\frac{\alpha}{2}} \int \cdots \int e^{-\beta \Phi} \frac{1}{n_1! \cdots n_N!} d\mathbf{x}(1)$$

where \( m_1 \cdots m_\alpha \) are the masses involved, and \( \Phi \) is the total potential energy of the fluid in a given configuration; also

(90) $$e^f = \frac{(m_1 \cdots m_\alpha)^{\frac{\alpha}{2}}}{(2\pi kT)^{\frac{\alpha}{2}}} n_x e^{-\beta \sum_i \frac{1}{2} \mathbf{v}_i^2}$$

When this expression is substituted in (26), one obtains the equation

(91) $$\frac{\partial n_4}{\partial x^{(4)}} + \frac{n_4}{kT} \left( \frac{\partial \mathbf{x}^{(4)}}{\partial x^{(4)}} - \sum_j \frac{2 \mathbf{p}^{(j)})}{n_j} \right) + \int \frac{n_{4+1}}{kT} \frac{\partial \mathbf{p}^{(4+1)}}{\partial x^{(4+1)}} d\mathbf{x}^{(4+1)} = 0,$$
which is very useful for determining the approximate equilibrium value of \( n_1 \) for small values of \( q \), when the procedure of integrating the known value of \( n_N \) is impracticable.

4. The Equation of State for Fluids.

The pressure \( p^o \) in a fluid in equilibrium is defined thermodynamically by the equation \( p^o = -\frac{\partial A_N}{\partial V} \), and may now be calculated with the help of the formula (86), which, on writing \( x = \sqrt[3]{\frac{j}{j}} \), assumes the form

\[
N! \, e^{-\frac{\beta A_N}{j}} = \sqrt{N} \int (\frac{n}{n}) \int e^{-\frac{\beta \Delta_i}{j}} \left( \sqrt{\frac{j}{j}}, \sqrt{\frac{j}{j}} \right) \frac{N}{j} \, dy^n,
\]

so that

\[
N! \, e^{-\frac{\beta A_N}{j}} p = \sqrt{\frac{N}{N!}} e^{-\frac{\beta A_N}{j}} + \frac{1}{3} \int (\frac{n}{n}) \int \left( \frac{N}{x}, \frac{N}{2} \right) \frac{2}{x} \left( e^{-\frac{\beta \Delta_i}{j}} (x, x) \right) \frac{N}{j} \, dx^n.
\]

For simplicity, it is assumed in this section that \( \alpha = 3 \), and that \( \psi' \) vanishes. By symmetry, each term in the summation in the integrand of (93) has the same value, so that this equation may be rewritten, according to (43) and (87), in the form

\[
\beta p^o = n_1 + \frac{1}{\varepsilon (n-1) \int (\frac{x}{x}) \frac{2}{x} (x, x) + \varepsilon (\frac{x}{x}) \frac{2}{x} (x, x) n_2 (x, x) \, dx \, dx \, dx \, dx \]

\[
= n_1 + \frac{1}{\varepsilon (n-1) \int r n_2 (r) \, dx \, dx},
\]

since \( n_2 \) is in equilibrium a function of \( r = |x^{(n)} - x^{(n)}| \) only. If in (94) one substitutes the classical expression, for \( \frac{\partial n_2}{\partial x^{(n)}} \) given by (91), one obtains the
more useful formula

$$p^o = n_k kT - \frac{1}{e} \int r n_2(r) \phi(r) \, dr$$

which is the equation of state, expressed in terms of $n_2(r)$, itself a function of density and temperature.

This form is valid only within the limits of the classical theory; to obtain the corresponding quantum formula, it is necessary to proceed as follows. One has

$$\left\langle \sum_{i=1}^{N} \frac{\partial}{\partial x_i} \right. \left[ \gamma(x') e^{-\frac{\beta H_n(x,x')}{\hbar}} \right] = \frac{1}{\hbar} \sum_{i=1}^{N} \left[ \phi^{(i)}(x) e^{-\frac{\beta H_n}{\hbar} - \frac{\beta H_n}{\hbar}} \phi^{(i)}(x) \right]$$

in the interior of the fluid. (When $x'$ is near the surface, the identity fails, as may be seen by integration over all space, when the right-hand side vanishes.) The right-hand side of (96) may be evaluated with the aid of the lemma that, if $\sigma$ and $\tau$ are any two operators, and $f(\tau)$ any power series in $\tau$, then

$$\sigma f(\tau) - f(\tau)\sigma = \sigma f^{(1)}(\tau) \frac{\sigma_1}{1!} + \sigma f^{(2)}(\tau) \frac{\sigma_2}{2!} + \sigma f^{(3)}(\tau) \frac{\sigma_3}{3!} + \cdots
$$

$$= \frac{\sigma_1}{1!} f^{(1)}(\tau) - \frac{\sigma_2}{2!} f^{(2)}(\tau) + \frac{\sigma_3}{3!} f^{(3)}(\tau) - \cdots$$

$$= \frac{1}{1!} \left( \{\sigma_1, f^{(1)}(\tau) \} + \frac{1}{3!} \{\sigma_3, f^{(3)}(\tau) \} + \cdots \right)$$

$$- \frac{1}{\hbar} \left\{ \left[ \frac{1}{2} \{\sigma_1, f^{(1)}(\tau) \} + \frac{1}{4!} \{\sigma_4, f^{(4)}(\tau) \} + \cdots \right] \right\}$$

where $\sigma_1 = \sigma \tau - \tau \sigma$, $\sigma_{k+1} = \sigma_k \tau - \tau \sigma_k$ ($k = 1, 2, \cdots$), and
\( \{ \alpha_3, \beta_3 \} \) represents \( \frac{1}{2} (\alpha_4 \beta_4 + \beta_4 \alpha_4) \). This lemma is easily proved by induction for \( f(\tau) = \tau^n \), after which the generalisation is obvious. Substituting 
\( \sigma = \sum_{i=1}^{N} \psi^{(i)}(x) \), \( \tau = H_N \), and \( f(\tau) = e^{-\beta \tau} \), one obtains for the right-hand side of (96) the expression
\[
-\frac{1}{h} \left[ \frac{\beta}{1!} \left\{ \psi^{(1)}(x) e^{-\beta H_N x} + \frac{\beta^2}{2!} \left\{ \psi^{(2)}(x) e^{-\beta H_N x} + \cdots \right\} + \frac{1}{2} \sum_{i=1}^{N} \sigma_i e^{-\beta H_N x} + \frac{\beta^4}{4!} \left\{ \psi^{(4)}(x) e^{-\beta H_N x} + \cdots \right\} \right] \right.
\]
where
\[
(98) \quad \sigma_i = \frac{1}{\pi} \sum_{j=1}^{N} \left\{ i \tilde{x} \psi^{(j-1)2} - \frac{1}{2} \sum_{j=1}^{N} \gamma^{(j)} \phi^{(j)} \right\}, \text{ etc.}
\]
Substituting in (93) (this is now permissible, since the commutator in (96) has been evaluated), and using the property \( X(\alpha N \beta N) = X(\beta N \alpha N) \), one obtains
\[
(99) \quad N! \beta e^{-\beta a_0} \rho^0 = \frac{1}{3!} \sum_{j=1}^{N} \left\{ \alpha^{(j)} \right\} \left\{ \frac{\beta^2}{1!} \left\{ \psi^{(2)}(x) e^{-\beta H_N x} + \cdots \right\} + \frac{\beta^4}{4!} \left\{ \psi^{(4)}(x) e^{-\beta H_N x} + \cdots \right\} \right\} \left( \alpha, x \right)^{\frac{N-2}{2}} dx^2
\]
and hence
\[
(100) \quad \rho^0 = \rho^0 + \frac{\frac{1}{3!} \beta^2}{\beta^2} p_3^0 + \frac{(\beta \beta)^4}{5!} p_5^0 + \cdots
\]
where
\[
(101) \quad \frac{3}{2} N \kappa T = \frac{1}{2} \sum_{j=1}^{N} \left\{ \frac{1}{2} \tilde{x} \psi^{(j)} \right\}, \text{ etc.}
\]
The classical equation of state (95) is obtained from (100) by writing \( \kappa = 0 \), since in classical
theory $T$ and $T_f$ are equal. In quantum theory, however, this is not so, and the terms involving $p_3^*$, $p_5^*$, etc. in (100) obviously become more and more important at low temperatures. Thus it may be expected that the equation of state of a liquid near absolute zero will show quite a different character from that of liquids at ordinary temperatures.

5. The Phenomenon of Condensation

In recent years much effort has been devoted to the study of the process of condensation from the gas to the liquid through the exact development of the equation of state as a power series in the density, thus:

\[(102) \quad p^* = n_1 kT \left( 1 - \sum_{s=1}^{\infty} \frac{s}{s+1} \beta_s n_1^s \right),\]

so that the quantities $-\frac{s \beta_s}{s+1}$ are the so-called virial coefficients. This development, first made by Ursell, was shown by Mayer to diverge at a certain density for each temperature, which he associated with the point of condensation. His work, improved by Born and Fuchs, and given a quantum generalisation by Kahn, has since become the centre of considerable confusion and controversy. By solving the equation (91) with $q = 2$ and substituting the value of $n_2$ so obtained in (95), the author has succeeded in obtaining an equation of state which can be developed in the form (102)
but has a meaning also in the region in which \((102)\) diverges. In this way it is possible to elucidate the nature of the singularity and gain a clear understanding of previous work on this subject; the conclusions reached may be stated briefly in the following way.

With any finite values of \(N\) and \(V\), it is clear that the value of \(A_N/N\) given by \((89)\) is \(O(1)\), remaining finite as \(N \to \infty\); for, even if \(F\) is given its minimum value \(F_0 = N\phi_0\) in the integrand, \(A_N\) is \(O(N)\). Hence one sees that

\[
(103) \quad A_N = NkT^2 \left[ \log \left( \frac{\beta_T^N}{(\pi T)^{\frac{\beta_T^N}{2}}} \right) - \sum_{S=1}^{\infty} \frac{\beta_T^S \phi_1^S}{S + 1} \right]
\]

for high but finite densities must be illusory. This illusion is created by the assumption that all the \(\beta_T^S\) are independent of \(\phi_1\), whereas it is clear from their definition as integrals over the volume \(V\) that the density is involved when \(s = O(N)\), though the error entailed in extending the integration to the whole of space is negligible for small \(s\). Kahn (in his dissertation\(^{27}\), Ch. 3, \(\S 6\)) is the victim of a similar illusion when he interprets the second branch of the isotherm which he has found as the isobar commonly supposed to connect the vapour and the liquid; his error arises from assuming that all
the $\beta_s$ are constants, and it is not hard to see that the second branch is not an isobar but corresponds to the liquid state.

In fact, the isobaric 'line of condensation' on the isotherm in the $p-V$ diagram has no fundamental significance, but represents merely mixtures of the liquid and the gas, which have densities represented by the left and right end-points of the isobar respectively. Such mixtures cannot appear in the theory of a single phase, where the density is assumed to be the same everywhere; therefore one need not expect to obtain an isobaric part of the isotherm, though states of supersaturation of the vapour and superheating of the liquid ought to appear. The isotherm thus obtained will not be very different from the original conception of van der Waals, except that in the limit $N \to \infty$, the apparent divergence of the series (102) will be marked as a branch point at the minimum of the curve, from which spring two branches associated with the liquid and the gas respectively.

The distinction between the liquid and gas is roughly marked by the relative values of the two terms on the right-hand side of (95). For the gas, the second term is negligible in comparison with the first; for the liquid, the second term, increasing roughly as the square of the density, becomes of paramount importance.
CHAPTER III: THEORY OF NON-UNIFORM FLUIDS


From the fundamental equation (48), the laws of hydrodynamics will now be deduced with the full generality of quantum mechanics. For simplicity it will be assumed that the internal degrees of freedom of the molecules are unimportant, so that one may take \( \alpha = 3 \), throughout the present chapter.

With the notation \( \{ \alpha \beta \} = \frac{1}{2} (\alpha \beta \beta \alpha \), one may first define the mean velocity \( \gamma_q^{(i)} \) of a molecule (i) in a cluster of \( q \) molecules with known positions by the equation

\[
(104) \quad \gamma_q^{(i)}(x) = \mathfrak{P}_q \sum_j \gamma^{(j)}(x, x_j).
\]

Since the expression \( \{ \alpha \beta \} \) corresponds to the simple product \( \alpha \beta \) in classical theory, and \( \alpha_q(x, x) \) to the integral \( \int (x) \int \alpha_q \bar{\imath}_{\alpha_q} d^3 x \), this definition is fully equivalent to the classical definition expressed by (14). Similarly one defines the generalised 'temperature' \( T_q^{(i)} \) of a molecule, in a cluster of molecules whose positions are known, by

\[
(105) \quad T_q^{(i)}(x) = \mathfrak{P}_q \sum_j \gamma^{(j)}(x, x_j).
\]

where

\[
(106) \quad \gamma^{(i)}(x, x') = \mathfrak{P}^{(i)}(x, x') - \gamma^{(i)}(x) \delta(x - x').
\]
is the particular velocity of \( i \) relative to the average motion. In classical theory (105) goes over into the form

\[ 3m n_q k T_i^{(i)} = \oint \int \frac{\nu_i^{(i)} - \nu_i^{(i)\prime}}{1} d\bar{x}^{(i)} \]

where \( \nu_i^{(i)} = \bar{x}^{(i)\prime} - \nu_i^{(i)} \); thus \( T_i = T_i^{(i)} \) is the same as the temperature defined in classical theory. In quantum theory, \( T_i \) is not the thermodynamic temperature, but coincides with the 'dynamic' temperature, already defined in (101) for the special case of equilibrium, when it has the same value throughout the fluid.

Since

\[ (\rho^{(2)} - \rho_i^{(1)})^{(2)}(x, x') = \oint \oint (\rho_i^{(1)} + \rho_i^{(2)})^{(2)}(\rho_i^{(1)} + \rho_i^{(2)})^{(2)}(x, x') \]

\[ = - \oint \oint \left( \frac{\partial}{\partial x^i} + \frac{\partial}{\partial x'^i} \right) (\rho_i^{(1)} + \rho_i^{(2)})^{(2)}(x, x') \]

(48) may be written in the form

\[ \oint \oint \left( \frac{\partial}{\partial x^i} + \frac{\partial}{\partial x'^i} \right) \rho_i^{(1)}(x, x') + \sum_{i=1}^{2} \left( \frac{\partial}{\partial x^i} + \frac{\partial}{\partial x'^i} \right) \rho_i^{(2)}(x, x') \]

\[ + \sum_{i=1}^{2} \oint \oint (\phi^{(1)} - \phi^{(2)}) \rho_{i+1}^{(2)}(x, x') d\bar{x}^{(i)\prime} d\bar{x}^{(i+1)\prime} \]

On putting \( x = x' \) in this equation, all terms on the right-hand side vanish, leaving

\[ \frac{\partial n_i^{(1)}}{\partial t} + \sum_{i=1}^{2} \frac{\partial}{\partial x^i} \rho_i^{(1)} \cdot (n_i^{(1)} u_i^{(1)}) = 0 \]
This is formally the same as the equation of continuity (13), the only difference being in the definition of $w_j^i$ and $n_i$ in terms of the atomic data.

Let $I_q$ be any function of time and the coordinates $x^{(i)}$, ..., $x^{(q)}$. Then it follows from (110) that

$$\frac{\partial}{\partial t} (n_i I_q) = n_i \frac{\partial}{\partial t} I_q - \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \left( n_i I_q w_j^i \right)$$

(111)

where $\frac{d}{dt}$ represents the operator $\frac{\partial}{\partial t} + \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}}$.

Now, by multiplying half the sum, one obtains

$$\dot{P} (x) = \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \left( \phi^{(j)} y_j^l \right) \rho_j (x, x')$$

(112)

Again writing $x = x'$, one is left with

$$\frac{\partial}{\partial t} (n_i \rho_j) = \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \left( n_i \rho_j \right) \rho_j^i (x, x')$$

(113)

where

$$\frac{\partial}{\partial t} (n_i \rho_j) = - \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \left( \frac{n_i \rho_j}{n_i} \right)$$

(114)
The same equation can be obtained by multiplying the classical equation (26) by \( \xi^{(\nu)} \) and integrating over all the velocities, except that \( \frac{1}{\hbar} \int \mathcal{H} \rho \mathcal{F}^{(j)}\mathcal{F}^{(n)}(\xi, \kappa) \) is replaced by its classical analogue \( \int \mathcal{H} \rho \mathcal{F}^{(j)}\mathcal{F}^{(n)}(\xi, \kappa) \). Thus the equation of motion, like the equation of continuity, differs in quantum theory from the classical equation only in the definition of the quantities which appear, in terms of the atomic data.

At first it may appear strange that quantum mechanics requires no modification of the equations of motion and continuity, and indeed, this result is in strong contradiction to the work of Landau\(^{(29)}\), who developed a quantum hydrodynamics in which the hydrodynamical equations themselves have an operational form. Reflection shows, however, that Landau's equations can have no physical significance: the macroscopic, visible changes in a fluid give no indication of the existence of quantum phenomena, and must be described by the same equations in classical and quantum theory. This is true even for liquid helium II, where the apparently abnormal viscosity, thermal conductivity, etc. in no way conflict with the macroscopic description of matter, although they cause one to suspect that quantum phenomena are responsible. It is readily seen that the present theory greatly favours such an hypothesis, as the evaluation of \( n_\xi \), \( q_\xi^{(n)} \), \( T_\xi^{(n)} \), etc. is quite different in the classical and quantum formalisms.
so that quantum complications are to be expected at very low temperatures.

By using the formula (111), with \( v_i^{(i)} \) substituted for \( I_i \), (113) may be rewritten in the form

\[
\frac{m}{\alpha} \frac{d}{dt} \chi_i^{(i)} + \sum_{j=1}^{q} \frac{\alpha}{2x_j} \cdot k_i^{(i)} = m \chi_i^{(i)}
\]

where

\[
k_i^{(i)} = m \sum p_i v_i^{(j)} v_{-i}^{(i)} f(x, x)
\]

Further, on writing

\[
P_i^{(i)} = k_i^{(i)} + l_i^{(i)}
\]

where \( l_i^{(i)} \) is defined by the equation

\[
\sum_{j=1}^{q} \frac{\alpha}{2x_j} \cdot l_i^{(i)} = n_x \sum_{j=1}^{q} \frac{\partial v_i^{(i)}}{\partial x_j} + \int n_{x_{q+1}} \frac{\partial v_i^{(i)}}{\partial x_{q+1}} d x
\]

(115) assumes the form

\[
\frac{m}{\alpha} \frac{d}{dt} \chi_i^{(i)} + \sum_{j=1}^{q} \frac{\alpha}{2x_j} \cdot P_i^{(i)} = n \cdot \frac{\partial v_i^{(i)}}{\partial x_j} + \int \frac{\partial v_i^{(i)}}{\partial x_{q+1}} d x
\]

This is to be regarded as the generalisation for molecular clusters of the equation of motion of ordinary hydrodynamics, to which it reduces when \( q = 1 \). It is clear that the pressure tensor \( P_i^{(i)} \) consists of two parts \( k_i^{(i)} \) and \( l_i^{(i)} \), of which the
first is due to the thermal motion of the molecules, and the second to the intermolecular forces. Only the kinetic part \( k^{(ij)}_q \) of \( \mathcal{P}^{(ij)}_q \) is found in the kinetic theory of gases, and the validity of the theory rests on the circumstance that the potential part \( \mathcal{L}^{(ij)}_q \), which is roughly proportional to the square of the density, is small; in liquids, however, far from being small, the term \( \mathcal{L}^{(ij)}_q \) is the dominant one in the complete expression.

To obtain the equation of energy transport, take half the sum of the scalar products of equation (112) with \( \mathcal{P}^{(i)} \), and afterwards write \( x = x' \). The result is

\[
\frac{2}{\alpha_t} \left( 3 \nu \mathcal{L}^{(ij)}_q + m \mathcal{N}^{(ij)}_q \right) + \frac{1}{2 \mathcal{N}^{(ij)}_q} \sum_{j=1}^{q} \left( \mathcal{P}^{(i)}_q \mathcal{P}^{(ij)}_q \mathcal{P}^{(ij)}_q \right) (x, x)
\]

(120)

since \( \left\{ \left( \mathcal{P}^{(i)}_q \right) \cdot \mathcal{P}^{(ij)}_q \right\} (x, x) = m \left( 3 \nu \mathcal{L}^{(ij)}_q + m \mathcal{N}^{(ij)}_q \right) \).

With the help of equations (111) and (115), (120) is now transformed to

\[
\frac{2}{\alpha_t} \nu \mathcal{L}^{(ij)}_q + m \mathcal{N}^{(ij)}_q \sum_{j=1}^{q} \left( \mathcal{P}^{(i)}_q \mathcal{P}^{(ij)}_q \mathcal{P}^{(ij)}_q \right) (x, x)
\]

(121)

\[
\nu \mathcal{L}^{(ij)}_q \mathcal{N}^{(ij)}_q - \nu \mathcal{N}^{(ij)}_q \sum_{j=1}^{q} \left( \mathcal{P}^{(i)}_q \mathcal{P}^{(ij)}_q \mathcal{P}^{(ij)}_q \right) (x, x)
\]

and then, with the aid of (116), to the form

\[
\frac{2}{\alpha_t} \nu \mathcal{L}^{(ij)}_q \mathcal{N}^{(ij)}_q + m \mathcal{N}^{(ij)}_q \sum_{j=1}^{q} \left( \mathcal{P}^{(i)}_q \mathcal{P}^{(ij)}_q \mathcal{P}^{(ij)}_q \right) (x, x)
\]

(122)

\[
\mathcal{P}^{(i)}_q \mathcal{P}^{(ij)}_q \mathcal{P}^{(ij)}_q - \nu \mathcal{N}^{(ij)}_q \sum_{j=1}^{q} \left( \mathcal{P}^{(i)}_q \mathcal{P}^{(ij)}_q \mathcal{P}^{(ij)}_q \right) (x, x)
\]
where

\[
\mathfrak{m}^{(ji)}_q = \mathfrak{m}^{(ji)}_q \mathfrak{F}_q \mathfrak{F}_q^{(ji)} \mathfrak{F}_q^{(j)} \mathfrak{F}_q^{(i)} (x, x).
\]

An equation formally identical with (122) may be obtained from the classical equation (26) by multiplying by \( \sqrt{(\mathfrak{m})^2} \), integrating over all velocities, and then transforming in the same way as above.

(122) is not yet, however, the equation of energy transport, as it refers only to the thermal energy of motion \( \frac{1}{2} k T_i^{(ji)} \). To obtain a similar equation for the potential energy, it must first be localised by sharing the potential energy \( \phi^{(ji)} \) equally between the two molecules \((i)\) and \((j)\). Then, substituting the energy of one molecule

\[
\Gamma_{ji} = \frac{1}{2} \sum_{j=1}^{N} \phi^{(ji)} + \frac{1}{2} \int \phi^{(ji)} \frac{m^{(ji)}_q}{m^{(ji)}_p} dx^{(i+1)}
\]

in the formula (111), one obtains

\[
\frac{\partial \mathfrak{F}_q^{(ji)}}{\partial t} = \frac{3}{2} \sum_{j=1}^{N} \phi^{(ji)} + \frac{1}{2} \int \phi^{(ji)} \frac{m^{(ji)}_q}{m^{(ji)}_p} dx^{(i+1)} \cdot \left( \mathfrak{F}_q^{(ji)} \right).
\]

Transforming this equation with the help of (110) leads to

\[
\frac{\partial \mathfrak{F}_q^{(ji)}}{\partial t} = -\frac{1}{2} \sum_{j=1}^{N} \left( \frac{\partial \phi^{(ji)}}{\partial x} \cdot \frac{\partial \phi^{(ji)}}{\partial x} + \frac{1}{2} \int \phi^{(ji)} \frac{m^{(ji)}_q}{m^{(ji)}_p} \frac{m^{(ji)}_q}{m^{(ji)}_p} dx^{(i+1)} \right)
\]

(125)
which may be rewritten in the form

$$n_i \frac{\partial \bar{u}_i^{(j)}}{\partial t} + \sum_{j=1}^{q} \frac{2}{2\pi q} \cdot n_i \bar{u}_i^{(j)} = \int \Phi_{i+1} (\bar{u}_i^{(j)} - \bar{u}_i^{(i)}) \, d\bar{x}^{(j+1)} \tag{127}$$

where $n_i^{(j)}$ is defined as the solution of the equation

$$\sum_{j=1}^{q} \frac{2}{2\pi q} \cdot n_i^{(j)} = \sum_{j=1}^{q} \frac{2}{2\pi q} \cdot n_i^{(j)} \cdot \int \Phi_{i+1} (\bar{u}_i^{(j)} - \bar{u}_i^{(i)}) \, d\bar{x}^{(j+1)} \tag{128}$$

Then, on adding (122) and (127), one obtains finally

$$n_i \frac{\partial \bar{u}_i^{(j)}}{\partial t} + \sum_{j=1}^{q} \frac{2}{2\pi q} \cdot n_i \bar{u}_i^{(j)} + \left( \frac{2}{2\pi q} \cdot u_i^{(i)} \right) \cdot n_i = 0 \tag{129}$$

where

$$U_i^{(j)} = \frac{3}{2} kT_i^{(j)} + \bar{U}_i^{(j)} \tag{130}$$

and

$$q_i^{(j)} = m_i^{(j)} + n_i \tag{131}$$

To interpret the equation (129) correctly, it must be compared with

$$\frac{1}{2} m_i \frac{\partial u_i^{(j)}}{\partial t} + \frac{q_i}{\gamma} \cdot \sum_{j=1}^{q} \frac{2}{2\pi q} \cdot \bar{u}_i^{(j)} \cdot P_i^{(j)} = n_i \bar{u}_i^{(i)} \cdot P_i^{(i)} \tag{132}$$

which is the equation satisfied by the 'visible' energy $\frac{1}{2} m_i u_i^{(j)^2}$, obtained by multiplying (119)
with \( u_q^{(i)} \). The terms \( \frac{q}{2} \left( \frac{\partial^2 v_j^{(i)}}{\partial q_j} \right) \cdot \nabla_j \) and \( \nabla_j \left( \frac{\partial A_j^{(i)}}{\partial q_j} \right) \) from (129) and (132) together represent the work done per unit time and volume on molecules outside the cluster of \( q \) molecules, and it follows that for energy balance \( q^{(i)}_j \) must be interpreted as a generalised energy flux, reducing to the ordinary energy flux when \( q = 1 \). (129) is therefore the equation of energy transport in the usual form, and it is apparent that the energy flux, like the pressure tensor, consists of two parts, due to the thermal motion and the intermolecular forces respectively. Of these, only the first in equation (131) is obtained in gas-theory, but it may be anticipated that the second, 'potential' part is preponderant in liquids.

2. The General Method of Expansion.

It has already been observed that the equation (48) possesses a great variety of solutions, corresponding to the very diverse forms which may be ascribed to the density matrix \( \rho \) at an initial time \( t_0 \). In attempting a general solution of practical value, however, it must be recognised that the majority of these solutions can occur only under highly abnormal conditions, the probability of which is extremely small, and that non-uniform fluids occur in nature almost invariably as a result of some disturbance of a state of equilibrium. In assessing the physical condition of a fluid
experimentally, the only independent quantities which one measures are the density, temperature, macroscopic velocity and external force throughout the fluid, and if these are uniform, the fluid is assumed to be in equilibrium.

Instead of specifying \( n_i^{(i)}, T_i^{(i)}, u_i^{(i)}, \) and \( P^{(i)} \) throughout the fluid, one may, at least for quite a large volume, specify these quantities, together with their space gradients \( \frac{\partial n_i}{\partial x}, \frac{\partial^2 n_i}{\partial x^2}, \frac{\partial^3 n_i}{\partial x^3}, \ldots \quad \frac{\partial T_i}{\partial x}, \ldots \) at a single point, most conveniently chosen to be the centre of gravity of the cluster of \( q \) molecules which is always considered. Also, it is necessary to specify all except the force only at some initial time \( t \), as the rates of change \( \frac{\partial n_i}{\partial t}, \frac{\partial T_i}{\partial t}, \ldots \) of the others are given by the hydrodynamical equations of the previous section.

Accordingly it will be assumed that

\[
(133) \quad \rho_i(x,x') = P_q(x, x', \omega_k, \frac{\partial \omega_k}{\partial x}, \frac{\partial^2 \omega_k}{\partial x^2}, \ldots)
\]

where the \( \omega_k (k = 1 \ldots 8) \) represent the values \( n_i, T_i, u_i \) and \( P \) assumed by \( n_i^{(i)}, T_i^{(i)}, u_i^{(i)}, \) and \( P^{(i)} \) at some point \( x_4 \) in the part of the fluid considered, and that the variation of \( \rho_i \) with \( t \) and \( x_4 \) is accounted for by the variation of the \( \omega_k \) and their space derivatives. For purposes of symmetry, \( x_4 \) is most conveniently chosen to be the mean centre of the points \( x_i' \) and \( x_i'' \), thus:
(134) \[ x_1 = \frac{1}{2^4} \sum_{i=1}^{2^4} (x^{\infty})^i \]

The difference between \( \rho \) and \( \rho' \) is, that while \( \rho \) is explicitly a function of the independent variables \( x^n, x'^n \) and \( t \), \( \rho' \) is explicitly a function of \( x'^n, x'^{n'} \), \( \omega_k, \frac{\partial \omega_k}{\partial x_i} \), ... , and only implicitly a function of \( t \) and \( x_1 \). It follows that

\[ \frac{\partial \rho}{\partial t} = \sum_k \left( \frac{\partial \rho}{\partial \omega_k} \frac{\partial \omega_k}{\partial t} + \frac{\partial \rho}{\partial \frac{\partial \omega_k}{\partial x_i}} \frac{\partial^2 \omega_k}{\partial x_i \partial t} + \ldots \right) \]

(135) \[ \frac{\partial \rho'}{\partial x^n} = \frac{\partial \rho}{\partial x^n} + \frac{1}{2^4} \sum_k \left( \frac{\partial \rho}{\partial \omega_k} \frac{\partial \omega_k}{\partial x_i} + \frac{\partial \rho}{\partial \frac{\partial \omega_k}{\partial x_i}} \frac{\partial^2 \omega_k}{\partial x_i \partial x_i} + \ldots \right) \]

From the definitions of \( n_1, u_1, T_1, P_1, q_1, q_1', \) etc., it follows that they also may be expressed in terms of the \( \omega_k \) and their space derivatives; for example, by putting \( x' = x^{n'} \) in (133) one obtains \( n_1 = N_1(x, \omega_k, \frac{\partial \omega_k}{\partial x_i}, \ldots) \), and, more generally, if \( c_1 \) represents any of the quantities enumerated,

(136) \[ c_1 = C_1(x, \omega_k, \frac{\partial \omega_k}{\partial x_i}, \ldots) \]

the large letter always replacing the small to denote explicit dependence on the \( \omega_k, \frac{\partial \omega_k}{\partial x_i}, \ldots \).

Corresponding to (135), one has

\[ \frac{\partial c_1}{\partial t} = \sum_k \left( \frac{\partial c_1}{\partial \omega_k} \frac{\partial \omega_k}{\partial t} + \frac{\partial c_1}{\partial \frac{\partial \omega_k}{\partial x_i}} \frac{\partial^2 \omega_k}{\partial x_i \partial t} + \ldots \right) \]

(137) \[ \frac{\partial c_1}{\partial x_i} = \frac{\partial c_1}{\partial x_i} + \frac{1}{2^4} \sum_k \left( \frac{\partial c_1}{\partial \omega_k} \frac{\partial \omega_k}{\partial x_i} + \frac{\partial c_1}{\partial \frac{\partial \omega_k}{\partial x_i}} \frac{\partial^2 \omega_k}{\partial x_i \partial x_i} + \ldots \right). \]
In a displacement of the centre of gravity
\[ x_l = \frac{1}{2} \sum_{i=1}^{9} x_i^{(n)} \], \( C_l \) is altered only on account of the variation in the \( \omega_q \); hence

\[ \sum_{i=1}^{9} \frac{\partial C_l}{\partial x_i^{(n)}} = 0 \]  

(138)

The form of (137) suggests the utility of an expansion of all variables in powers of \( \frac{\partial \omega_k}{\partial x}, \frac{\partial^2 \omega_k}{\partial x^2}, \ldots, \) in the form

\[ C_l = C_l^0 + C_l^1 + C_l^2 + \ldots \]

where

\[ C_l^0 = C_l^{(0)}(x, \omega_k), \]
\[ C_l^1 = \sum_k \frac{\partial \omega_k}{\partial x} \cdot C_l^{(1)}(x, \omega_k), \]
\[ C_l^2 = \sum_{k, l} \frac{\partial^2 \omega_k}{\partial x^2} \cdot C_l^{(2)}(x, \omega_k), \]

(139)

and, quite generally, \( C^{(r)} \) consists of terms involving just \( r \) derivatives of the \( \omega_k \). With the help of (137), space and time derivatives are easily expanded in the same way, the \( \frac{\partial \omega_k}{\partial t} \) being given by the

hydrodynamical equations

\[ \frac{\partial n_1}{\partial t} = - \frac{2}{\partial x_1} \cdot (n_1 u_1), \]
\[ \frac{\partial u_1}{\partial t} = - u_1 \cdot \frac{2}{\partial x_1} u_1 - \frac{1}{m n_1} \frac{2}{\partial x_2}, \]
\[ + \frac{1}{m n_1} \frac{2}{\partial x_1} P_1 \]

(140)

Care is necessary in the expansion of integrals like \( \int \frac{\partial n_1}{\partial x^{(n+1)}} \cdot C_{l+1} \cdot dx^{(n+1)} \) to take account of the fact that the values of \( \omega_k, \frac{\partial \omega_k}{\partial x}, \ldots \) appearing in
\[ C_{q+1} \] are initially those at the centre of gravity
\[ x_{q+1} = \frac{1}{q+1} \sum_{i=1}^{q+1} x^{(i)} \]

of \( q+1 \) molecules, whereas the expansion procedure refers always to values at the point \( x_q \). Thus, in expansion, \( C_{q+1} \) must first be replaced by

\[ C_{q+1} + d \cdot \frac{\partial C_{q+1}}{\partial x_q} + \frac{1}{2} \left( d \cdot d \right) \cdot \frac{\partial^2 C_{q+1}}{\partial x_q^2} \]

where the displacement \( d \) of the centre of gravity is

\[ d = x_{q+1} - x_q = \frac{1}{q+1} \sum_{i=1}^{q+1} (x^{(q+1)} - x^{(i)}) \]

and \( \frac{\partial}{\partial x_q} \) has the significance

\[ \sum_{k} \left\{ \frac{\partial \omega_k}{\partial x_q} \frac{\partial}{\partial \omega_k} + \frac{\partial^2 \omega_k}{\partial x_q^2} \cdot \frac{\partial}{\partial (\frac{\partial \omega_k}{\partial x_q})} + \ldots \right\} \]

Hence

\[ \oint \frac{\partial \Phi^{(q+1)}}{\partial x_q} C_{q+1} \, dx^{(q+1)} = \oint \frac{\partial \Phi^{(q+1)}}{\partial x_q} \left( C_{q+1} + d \cdot \frac{\partial C_{q+1}}{\partial x_q} + \ldots \right) \, dx^{(q+1)} \]

When \( \rho^{(i)}_q \), \( \rho^{(i)}_q' \), \( \rho^{(i)}_q'' \), \ldots are known, it is easy to calculate the \( c^0 \), \( c' \), \( c'' \), \ldots explicitly; for example,

\[ n^{(0)}(x) = \rho^{(0)}_q(x, x) \]
\[ n^{(1)}(x) = \rho^{(1)}_q(x, x) \]

\[ u^{(i)}_q(x) = \frac{1}{m^{(i)}_q(x)} \left[ \frac{\partial \rho^{(i)}_q}{\partial x} \right] dx(x, x) \]
\[ v^{(i)}_q(x) = \frac{1}{m^{(i)}_q(x)} \left[ \frac{\partial \rho^{(i)}_q}{\partial t} \right] dx(x, x) \]

\[ u^{(i)}_q(x) = -u^{(i)}_q' \]
\[ T_{q_i}^{(i)}(x) = \frac{m}{3 kn_3(x)} \{ \Sigma p_i \psi_4^{(i)} \} \varphi_4^{(i)}(x, x); \]

\[ \begin{aligned} k_4^{(ij)}(x) &= m \{ \Sigma \varphi_4^{(i)} \} \varphi_4^{(j)}(x, x), \\
k_4^{(ij)}(x) &= m \{ \Sigma \varphi_4^{(i)} \} \varphi_4^{(j)}(x, x); \end{aligned} \]

\[ m_{4,ij}^{(i)}(x) = \frac{1}{3} m \{ \Sigma \varphi_4^{(i)} \} \varphi_4^{(j)}(x, x). \]

3. The Zero-Order Solution and Condensation

To determine \( \rho_4^0 \), one requires to observe only that it may be obtained from \( \rho_4 \) simply by writing

\[ \frac{\partial \omega_k}{\partial x_4} = \frac{\partial \omega_k}{\partial x_4} = \ldots = 0, \]

which is the same as postulating a state of equilibrium in which the density, temperature, etc., have uniformly the values assumed at \( x_4 \). What is needed, therefore, is that equilibrium solution which makes

\[ X_i(\rho_4, \varphi_4^{(i)}) = 0; \]

\[ X_i(\rho_4, \varphi_4^{(i)}) = 3 m^{-1} N k T_i. \]

To satisfy the first of these conditions, one need only replace \( p_i^{(i)} \) by \( p_i^{(i)} - \frac{1}{m} \omega_i \) in the solution of
Ch. 2, §3; the second condition may then be regarded as giving the relation between $T_i$ and the thermodynamic temperature $T$. In classical theory, $T_i$ and $T$ are identical, but in quantum theory, to satisfy the uncertainty principle, $T_i$, which is proportional to the mean square momentum, must remain finite as $T$ tends to zero, and at low temperatures $T$ must be regarded as a function of $T_i$ and $\eta_i$, given implicitly by (149).

In principle, the $c$ are now all determinate with the help of (143) - (148). It is, however, clear from considerations of symmetry alone that $k_1^{(n)}(x_0)$ and $m_1^{(n)}(x_0)$ must remain unchanged on reversing the sign of $\nu_1^{(0)}$ in the formulae (146) and (147), so that

$$\begin{align*}
k_1^{(n)} &= n_1 k T_i \frac{1}{2}, \\
m_1^{(n)} &= 0,
\end{align*}$$

(150)

where $\frac{1}{2}$ denotes the unit tensor. Also, $n_1 = n_1$, $\nu_1^{(i)} = \nu_1$, and $T_1^{(i)} = T_1$, so that $n_1 = \nu_1^{(i)} = T_1^{(i)} = 0$ and $n_1^{(i)} = \nu_1^{(i)} = T_1^{(i)} = 0$, etc. In quantum theory, the remaining zero-order expressions derived from (143) - (148) cannot be much simplified, but on making the transition to the classical theory by replacing $\rho_1^{(0)}$ by $\mathcal{F}_2^{(0)} = n_1 \left( \frac{2\pi k T_i}{m} \right)^{\frac{3}{2}} \exp\left\{ -\frac{1}{2} k T_i (x_0 - \mu_1)^2 \right\}$ and $\int dx^{(0)} \mathcal{S}(x^{(0)} - x^{(0)})$ by $\int dx^{(1)}$, one obtains

$$\begin{align*}
\nu_1^{(i)} &= \nu_1, \\
\nu_1^{(i)} &= \nu_1^{(i)} = \xi^{(i)} - \mu_1, \\
T_1^{(i)} &= T_1, \\
\eta_1^{(i)} &= n_1 k T_i \frac{1}{2}, \\
\eta_1^{(i)} &= 0.
\end{align*}$$

(151)
At present, however, it is desirable to adhere to the quantum theory, and (151) will not be used.

It now follows from (137) and (140) that

\[ (\frac{\partial c}{\partial t}) = \frac{1}{m} \cdot \frac{2c^*}{\partial x} - \frac{1}{3} \left( \frac{\partial^2}{\partial x^2} \right) c_1 (\gamma - 1) + \frac{2}{3} \left( \frac{\partial^2}{\partial x^2} \right) c_2 + \frac{2}{3} \left( \frac{\partial^2}{\partial x^2} \right) c_3 \]

and

\[ \left( \frac{\partial c}{\partial t} \right)' = \frac{1}{m} \cdot \frac{2c^*}{\partial x} - \frac{1}{3} \left( \frac{\partial^2}{\partial x^2} \right) c_1 (\gamma - 1) + \frac{2}{3} \left( \frac{\partial^2}{\partial x^2} \right) c_2 + \frac{2}{3} \left( \frac{\partial^2}{\partial x^2} \right) c_3 \]

In the particular cases \( c_1 = n_1, \, n_2, \, T^{(1)} \), these formulae may be compared with those obtained directly from the hydrodynamical equations, with the help of (137) and (138); for example,

\[ (\frac{\partial n_1}{\partial t}) = - \sum_{i=1}^{2} \frac{2}{\partial x} \cdot (n_1 U_i'') \]

\[ (\frac{\partial n_2}{\partial t}) = - \sum_{i=1}^{2} \frac{2}{\partial x} \cdot (n_2 U_i'') - \frac{1}{3} \cdot \frac{2}{\partial x} \cdot (\sum_{i=1}^{2} n_i U_i'') \]

It is obvious that \( N_2 \) cannot depend on the particular inertial system of reference, and is therefore independent of \( U_2 \) and \( P^{(1)} = P \). Further comparison of (152) and (154) yields

\[ \frac{3}{2} \left( \frac{\partial c}{\partial x} \right) = \sum_{i=1}^{2} \frac{2}{\partial x} \cdot (n_1 U_i'') = \sum_{i=1}^{2} \frac{2}{\partial x} \cdot (U_i^{(0)} - U_i) \cdot \frac{2}{\partial x} \cdot \frac{N_2}{N_1} \]
The form of $U_2^{(1)}$ can be decided on general
grounds: it must be linear in $\gamma$, can contain in
addition only $r = x^{(0)} - x^{(1)}$, $\gamma$, and $T_1$, and, besides
(156), must satisfy $\int N_2 \frac{\partial U_2^{(1)}}{\partial r} \, dr = (N-1) \gamma$; hence
one may write

$$(157) \quad U_2^{(1)} = U_2^{(0)} = \gamma + \Theta (\gamma \cdot \gamma - \frac{1}{3} \gamma^2 \gamma),$$

where $\Theta$ contains only $\gamma$, $\gamma$, and $T_1$. $U_2^{(1)}$ is
obtained from $U_2^{(0)}$ by substituting $-\gamma$ for $\gamma$
(interchange of $x^{(0)}$ and $x^{(1)}$). For all $q$, the
right-hand side of (156) now vanishes, because the
integrand is an odd function of $r$; thus one
obtains, as might be expected, $\frac{\partial \gamma}{\partial t} = 0$, in the
zero-order, equilibrium, approximation. This
follows even more easily in the classical theory,
valid at high temperatures, where $\Theta = 0$.

Next, comparing (153) and (155), one finds,
when $q = 2$,

$$(158) \quad \frac{2}{\alpha_1} \left( N_2 (U_2^{(0)} - U_2^{(1)})' - \frac{1}{3} \frac{\partial N_2^{(0)}}{\partial T} \right) \int N_2 (U_2^{(0)} - U_2^{(1)})' \, \frac{\partial \gamma}{\partial t} \, dr$$

since $N_2$ and $U_2^{(1)} - U_2^{(0)}$ contain $x^{(0)}$ and $x^{(1)}$ explicitly
only in the combination $r = x^{(0)} - x^{(1)}$. This equation
may be regarded as an integral equation to determine
the non-rotational part of $\int N_2 (U_2^{(0)} - U_2^{(1)})' \, dr$; the
solution is
(159) \[ N_z \left( \frac{d_j}{d_{\phi}} - j_{\phi}^{(n)} \right)^2 = \frac{r}{1} \int_0^1 \left[ R + \frac{\int R \, d\phi}{3} + \frac{\int N_{\phi}^2}{\phi} \right] R^2 \, d\phi + \frac{2}{3} \frac{\phi}{T_1} \]

where \( R \), standing for the right-hand side of (158), reduces in classical theory to \( \left( \frac{3}{2} N_2^0 \frac{d_j}{d_{\phi}} - N_2^0 + \frac{2}{3} T_1 \frac{2 N_{\phi}^0}{\phi} \frac{d_j}{d_{\phi}} \right) \), and \( \phi \) satisfies \( \frac{2}{2T_1} \phi = 0 \).

A noteworthy feature of (159) is the divergence of the right-hand side when

(160) \[ \frac{2}{N_{\phi}^0 \frac{d_j}{d_{\phi}}} \int R^2 \, d\phi = -3k \]

namely, when the internal energy is changing at a certain rate with temperature. On approaching this point, the average velocity of two molecules relative to one another becomes infinite at any separation; this means that the condition of the fluid, even when in equilibrium, is highly unstable for small perturbations. One can hardly fail to associate such a condition with condensation, or rather that extremely unstable state which arises from superheating the liquid as far as possible above the boiling point. In normal condensation, the region in which (160) is satisfied will be by-passed in the process of a very rapid transition from one density to another.

4. Viscosity and Thermal Conduction in Fluids

Although the exact determination of quantities such as \( \rho_j', \ h_j', (n_\phi^2)^', \) etc. from the general
equations is a difficult matter, their form may be deduced quite easily from elementary considerations. For example, \( \rho_i = \rho_i'(x^{(0)}, x^{(0)}; \omega_k; \frac{\partial \omega_k}{\partial x}) \), as well as being linear and homogeneous in the \( \frac{\partial \omega_k}{\partial x} \), can contain \( x^{(0)} \) and \( x^{(0)}' \) only in the combination \( y = y^{(0)} - x^{(0)} \), the variation with \( \epsilon_i = \left( \frac{\partial \omega_k}{\partial x} x^{(0)} \right) \) being contained in the \( \omega_k \).

For brevity, the notation

\[
\begin{align*}
\alpha &= \frac{\partial \omega_k}{\partial x}, \quad \alpha^+ = \frac{\partial \omega_k}{\partial \omega_k}, \quad b = \frac{\partial \omega_k}{\partial x}, \quad b^+ = \frac{\partial \omega_k}{\partial x}; \\
(161) \quad \beta &= \frac{1}{2} \left( \frac{\partial \omega_k}{\partial x} + \frac{\partial \omega_k}{\partial \omega_k} \right) - \frac{2}{3} \frac{\partial \omega_k}{\partial x} \cdot \left( \frac{\partial \omega_k}{\partial x} \right), \\
\beta^+ &= \frac{1}{2} \left( \frac{\partial \omega_k}{\partial x} + \frac{\partial \omega_k}{\partial \omega_k} \right) - \frac{2}{3} \frac{\partial \omega_k}{\partial x} \cdot \left( \frac{\partial \omega_k}{\partial x} \right)
\end{align*}
\]

is introduced. \( \rho_i' \) can contain, besides the \( \alpha \)'s and \( b \)'s, only \( n_1, \, T_1 \), and \( y \), and satisfies

\[
\begin{align*}
\left[ \rho_i' \right]_{y=0} &= \rho_i' = 0, \\
\left[ \frac{\partial \omega_k}{\partial x} \right]_{y=0} &= (n_1, T) = 0, \\
\text{and} \quad \left[ \frac{\partial \omega_k}{\partial x} (n_1, T) \right]_{y=0} &= 3 \pi k(n_1, T) = 0 \text{ identically};
\end{align*}
\]

hence it must have the form

\[
(162) \quad \rho_i' = \epsilon_1 y \cdot \alpha + \epsilon_2 \cdot a^+ + \epsilon_2 y \cdot b \cdot y + \epsilon_2 y \cdot b^+ y,
\]

where \( \epsilon_1, \, \epsilon_2^+ \), \( \epsilon_2 \), and \( \epsilon_2^+ \) contain only \( n_1, \, T_1 \), and \( y = |y| \). If \( \epsilon_1 \) and \( \epsilon_2 \) are expanded as power series in \( y \), one must have \( \epsilon_1(y) = \epsilon_1'(0) \frac{y^2}{2} + \epsilon_1''(0) \frac{y^4}{3!} + \ldots \) and \( \epsilon_2(y) = \epsilon_2'(0) \frac{y^2}{2} + \epsilon_2''(0) \frac{y^4}{3!} + \ldots \). When \( \rho_i' \) (and \( \rho_i \)) are transformed to the momentum representation, they become diagonal, containing a factor \( S \left( \frac{\partial \omega_k}{\partial x} x^{(0)} \right) \) - the momentum states are discrete, as long as the volume \( V \) is finite.
\( N_2' \) is linear in the \( a \)'s and \( b \)'s; can contain besides only \( n_1, \bar{n}_1, \) and \( r = x^{(i)} - x^{(j)}; \) it is unaltered on replacing \( r \) by \(-r\) (interchange of \( x^{(i)} \) and \( x^{(j)} \)); and satisfies \( \int N_2' \, dx = (N-1)N_2' = c; \) hence it must have the form

\[
(163) \quad N_2' = \nu \cdot b \cdot r + \nu^+ \cdot b^+ \cdot r,
\]

where \( \nu \) and \( \nu^+ \) contain only \( n_1, \bar{n}_1, \) and \( r = |r| \).

\( N_2'(y^{(i)}_2 + y^{(j)}_2) \) is linear in the \( a \)'s and \( b \)'s; can contain besides only \( n_1, \bar{n}_1, \) and \( r \); it is unaltered on replacing \( r \) by \(-r\); and satisfies \( \int N_2'(y^{(i)}_2 + y^{(j)}_2) \, dx = 2(N-1)U_1 = 0; \) hence

\[
(164) \quad N_2'(y^{(i)}_2 + y^{(j)}_2) = \kappa (a \cdot r \cdot r - \frac{1}{3} \tau a) + \kappa^+(a^+ \cdot r \cdot r - \frac{1}{3} \tau a^+) \]

where \( \kappa \) and \( \kappa^+ \) contain only \( n_1, \bar{n}_1, \) and \( r \).

Finally, \( N_2'(y^{(i)}_2 - y^{(j)}_2) \) is linear in the \( a \)'s and \( b \)'s; can contain besides only \( n_1, \bar{n}_1, \) and \( r \); changes sign on replacing \( r \) by \(-r\); and satisfies \( \int N_2'(y^{(i)}_2 - y^{(j)}_2) \, dx = 0; \) hence

\[
(165) \quad N_2'(y^{(i)}_2 - y^{(j)}_2) = \upsilon \cdot b \cdot r + \upsilon_2 \cdot b \cdot r + \overline{\upsilon} \cdot r^2 \cdot b \cdot r + \upsilon^+ \cdot b^+ \cdot r + \upsilon^+_2 \cdot b^+ \cdot r + \overline{\upsilon}^+ \cdot r^2 \cdot b^+ \cdot r,
\]

where \( \upsilon, \upsilon_2, \overline{\upsilon}, \upsilon^+, \upsilon^+_2, \) and \( \overline{\upsilon}^+ \) are functions of \( n_1, \bar{n}_1, \) and \( r \), largely determined by equation (159).
It is now possible to calculate the coefficients of viscosity and thermal conduction in terms of the quantities already defined. According to (118), the part \( \frac{1}{x} \) of the pressure tensor due to the intermolecular forces is given by

\[
\frac{2}{2x^2} \cdot \frac{1}{x_1} = - \int n_2 \frac{\partial \phi}{\partial r} \, dx^{(2)}.
\]

Expanding both sides of this equation in accordance with (137) and (142) respectively, one obtains

\[
\frac{2}{2x_1} \cdot \frac{1}{x_1} = - \frac{2}{2x_1} \cdot \int \frac{2}{2x} N_2 \frac{\partial \phi}{\partial r} \, dr,
\]

\[
\frac{2}{2x_1} \cdot \frac{1}{x_1'} = - \frac{2}{2x_1} \cdot \int \frac{2}{2x} N_2' \frac{\partial \phi}{\partial r} \, dr,
\]

\[
\frac{2}{2x_1} \cdot \frac{1}{x_1''} = - \frac{2}{2x_1} \cdot \int \frac{2}{2x} N_2'' \frac{\partial \phi}{\partial r} \, dr - \frac{1}{6} \frac{3^2}{2x_1^2} \int \frac{2}{2x} N_2' \frac{\partial \phi}{\partial r} \, dr
\]

etc. Integrating these equations with the help of the boundary condition \( \frac{1}{x_1} \to 0 \) as \( n_1 \to 0 \), one has

\[
\frac{1}{x_1} = - \frac{1}{2} \int r N_2 \frac{\partial \phi}{\partial r} \, dr = - \frac{1}{6} \int \frac{2}{2x} N_2' (\phi (r)) \, dx
\]

and

\[
\frac{1}{x_1'} = - \frac{1}{2} \int r N_2' \frac{\partial \phi}{\partial r} \, dr
\]

\[
= - \frac{1}{6} \int r^2 (\nu b + \nu b^+) \phi (r) \, dr,
\]

\[
\frac{1}{x_1''} = \frac{1}{x_1'} + \ldots
\]
with the help of \((163)\). The corresponding expressions for \(k_i^o\) and \(k_i'\) are obtained from \((146)\); as already obtained in \((150)\), \(k_i^o = n_i kT_i\), whilst

\[
k_i' = \left[ -\frac{k^2}{\kappa} \frac{\partial}{\partial y} P_i' \right]_{y=0} = -\frac{2k^2}{\kappa} (\epsilon_i b + \epsilon_i^+ b^+).
\]

The zero-order (equilibrium) formula for the pressure tensor, namely

\[
P_{\xi_1}^o = \left( \mu kT_i - \frac{1}{e} \int r \nabla^2 \phi(r) \phi(r) \, dr \right) \Xi
\]

may be compared with the expression for the thermodynamic pressure given by \((100)\); it is seen that the classical equivalence breaks down at low temperatures. The first-order correction to the pressure tensor,

\[
P_{\xi_1}' = -\left\{ \frac{2k^2}{\kappa} (\epsilon_i b + \epsilon_i^+ b^+) + \frac{1}{15} \int r^3 (\nu b + \nu^+ b^+) \phi(r) \, dr \right\}
\]
gives the coefficient of viscosity \(\mu\), which is defined by the equation

\[
P_{\xi_1}' = -2\mu b^\Xi
\]
on the understanding that \(b^\Xi = 0\). Clearly,

\[
\mu = \frac{2k^2 \epsilon_i (\nu)}{\kappa} + \frac{1}{15} \int r^3 \nu(r) \phi(r) \, dr,
\]
showing that viscosity in fluids is due to two causes, the thermal motion of the molecules, and the mutual forces between the molecules. Of these, only the first is considered in the kinetic theory of gases; this is justified by the circumstance that the second, which is roughly proportional to the square of the density, is small. In liquids, however, the second, 'potential' term in (176), far from being small, is the dominant one in the entire expression. The temperature dependence \( \mu = A e^{-q/T} \) suggested by de Guzman \(^{29}\) and established by Andrade \(^{30}\) for many liquids, is a direct consequence of the proportionality of \( \nu(r) \) to \( N_2^0(r) \), which contains the Boltzmann factor \( e^{-\phi(r)/kT} \).

The coefficient of thermal conduction may be investigated in a somewhat similar way. According to (128), the 'potential' part \( n_1 \) of the thermal flux vector is given by

\[
(177) \quad \frac{\partial}{\partial x} \cdot n_1 = \frac{2}{2\pi} \cdot \int_{\frac{1}{2}}^{\frac{1}{2}} n_2 \frac{1}{\alpha} (u_2^{(1)} - u_1) dx^{(2)} - \frac{1}{2} \int n_2 \frac{2}{\alpha} \cdot (u_2^{(1)} + u_2^{(0)} - 2u_1) dx^{(1)}
\]

so that, on expansion in the usual way and omission of obviously vanishing terms,

\[
(178) \quad \frac{\partial}{\partial x} \cdot n_1 = -\frac{1}{2} \frac{2}{2\pi} \cdot \int_{\frac{1}{2}}^{\frac{1}{2}} \{N_2 (u_2^{(1)} + u_2^{(0)} - 2u_1)\}^2 \frac{2}{\alpha} dx^{(1)},
\]

and, on integration,
In classical theory, where \( \varphi_2^{(\alpha)} = \varphi_2^{(\alpha')} = \varphi_1 \), this reduces, by virtue of (164), to

\[
\begin{align*}
\hat{\mathbf{n}}_1 &= -\frac{1}{18} \int (\kappa_\alpha + \kappa^{+} a^{+}) \phi'(r) r^3 dr
\end{align*}
\]

For the 'kinetic' term \( \hat{\mathbf{n}}_1 \) of the thermal flux, one finds from (147)

\[
\begin{align*}
\hat{\mathbf{n}}_1 &= \left[ - \left( \frac{n^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{3k_\alpha}{2} \right) \phi'(r) r^2 \right] \frac{\partial \phi_1}{\partial y} y = 0
\end{align*}
\]

\[
\begin{align*}
&= - \frac{3k_\alpha^2}{4m^2} (\phi_1'' a + \phi_1^{+-} a^{+})
\end{align*}
\]

where the double prime indicates the second derivative.

The thermal conductivity \( \lambda \) is defined by the equation

\[
\begin{align*}
\hat{\mathbf{n}}_1 &= -\lambda \frac{\partial \phi_1}{\partial x_1}
\end{align*}
\]

on the understanding that \( \phi_1' \) is the same everywhere, so that \( \frac{\partial \phi_1'}{\partial x_1} \), or \( a^+ = e a \), where

\[
\begin{align*}
\phi_1' &= \frac{1}{1 - \frac{1}{6m_1 kT_1} \int \frac{\partial N_1}{\partial T_1} \phi'(r) r^2 dr}
\end{align*}
\]

Hence, classically and at high temperatures,

\[
\lambda = \frac{3k_\alpha^2}{4m^2} (\phi_1'' + e e_1^{+} + \phi_1^{+-}) + \frac{1}{18} \int (\kappa + e^2 k^+) \phi'(r) r^3 dr.
\]
For gases, the second term, which is roughly proportional to the square of the density, may be neglected, but for liquids it becomes of overriding importance.

In quantum liquids, the situation is more complex, and one has, instead of (180),

\[
\begin{align*}
\sigma_i &= -\frac{3}{4\pi} \int \Re e \omega \cdot (\nu_1 + \nu_2 + \nu_3 + \nu_4 + \nu_5 + \nu_6) \phi(r) dr \\
&\quad - \frac{1}{8} \int (\kappa a + \kappa a^+) \phi(r) r^2 dr,
\end{align*}
\]

according to (157). Thus the simple law (182) ceases to hold, and there is no thermal conductivity in the ordinary sense. This provides the key to the anomalies found experimentally in liquid helium near absolute zero. As has already been noted, \(T_i\) is equal to \(T\) at high temperatures, but remains finite as \(T\) tends to zero; it follows that \(a\), which is the gradient of \(T_i\), must be very small or vanish near absolute zero, even where there are substantial variations in the thermodynamic temperature. Thus only the first term in (185) is important at very low temperatures, and one reaches the surprising conclusion that energy transport is there governed by the motion of the fluid.

5. Conclusion

In one sense, the kinetic theory of liquids is now complete, since an account has been given of all those properties of fluids at rest and in motion
which are independent of foreign influences, such as material surfaces. It would be idle to pretend, however, that even a small part of the field has been exhausted; on the contrary, if this work has merit, it consists mainly in that it provides a basis for further study. In particular, liquid mixtures, plasticity, propagation of wave disturbances, and surface phenomena have been given no attention at all. Apart from these, many interesting questions concerning normal and superfluid liquids have been set aside because they involve much detail, and no numerical calculations have been made for comparison with experiment.

This does not imply that the theory lacks experimental verification. It has been seen that the theory provides a qualitative explanation of many phenomena which have hitherto been only imperfectly understood. Quite apart from this, the theory makes contact in many places with the kinetic theory of gases and statistical mechanics, which do not lack experimental confirmation. The main ground for supposing that the theory is correct, however, is that not a single approximation, simplification, or assumption has been made the validity of which has not been abundantly confirmed in many other fields.
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