A GENERAL KINETIC THEORY OF LIQUIDS

THESIS

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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 devel-
opment 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 <u>not</u> 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[8] 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[10] 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[12]. 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[16] of wider scope, in which, from
the point of view of statistical mechanics and the
Brownian movement, he derives an equation substan-
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 trnsport 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 $(\hbar/kT \sim 10^{-11}$ 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 a dimensions. Vectors are once underlined, thus: $\underline{a}$, $\underline{x}$; tensors are twice underlined: $\underline{\underline{b}}$, $\underline{\underline{p}}$. $\underline{\underline{1}}$ denotes the unit tensor, and $\overline{\underline{\underline{b}}}$ the transpose of $\underline{\underline{b}}$. The products of a tensor $\underline{\underline{b}}$ with a vector $\underline{a}$ (both vectors) are written $\underline{a}\cdot\underline{\underline{b}}$ and $\underline{\underline{b}}\cdot\underline{a}$; the spur product of two tensors $\underline{\underline{b}}$ and $\underline{\underline{b}}'$ is written $\underline{\underline{b}}:\underline{\underline{b}}'$. Below are listed page numbers where symbols are first introduced.

a 13 , $\underline{a}$ 68 , A 11 , A_N 40 ; b 68 , $\underline{b}$ 25

$\underline{\underline{b}}$ 68 , B 11 ; c 60 , C 60 , $\underline{C}$ 61 , $\underline{\underline{C}}$ 61 ;

$\underline{d}$ 62 , e 73 , E 33 ; f 14 ; g 15 , $\underline{g}$ 18 ;

h 16 , $\hbar$ 26 , H 18 ; I 52 , $I^{(1)}$ 56 ; k 42 ,

$\underline{\underline{k}}$ 54 ; l 32 , $\underline{l}$ 54 , L 39 , $\underline{\underline{L}}$ 70 ; m 13 ,

$\underline{m}$ 56 ; n 10 , $\underline{n}$ 57 , N 13 , N_q 60 , $\underline{N}$ 72 ;

P 11 , $P°$ 44 , $\underline{\underline{P}}$ 26 , $\underline{\underline{P}}$ 54 , $\underline{P}\cdot$ 19 ; q 13 ,

$\underline{q}$ 57 ; r 22 , $\underline{r}$ 15 , R 67 ; s 47 , S 36 ;

t 13 , T 41 ; $\underline{u}$ 17 , U 41 , $\underline{U}$ 65 ; $\underline{v}$ 50 ,

V 13 , $\mathcal{V}$ 33 ; w 33 , $\underline{w}$ 17 , $\mathcal{W}$ 34 , $\underline{x}$ 10 ;

$\underline{y}$ 68 ; $\underline{z}$ 21 .

α 26 ; β 40 , β_q 26 , β_s 47 ; γ 27 ; δ 20 ;

ϵ 68 ; $\underline{\Sigma}$ 13 ; η 13 , η_l 52 ; θ 24 ; κ 69 ;

λ 32 , $\hat{\lambda}$ 73 , Λ 39 ; μ 71 ; ν 69 , ν_i 38 ;

$\underline{\xi}$ 13 ; ϖ 66 ; ρ 28 , P 54 ; σ 45 , τ 45 ;

υ 69 ; ϕ 18 , $\underline{\Phi}$ 43 ; χ 27 , X 27 ; $\dagger$ 18 ,

$\dagger_N$ 32 , ω 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 $\underline{x}$ may be defined
in terms of the probability $n d\underline{x}$ that the volume
element $\underline{x}$, $d\underline{x}$ 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

physical reality is quite obscured; whilst in the
kinetic theory of gases one counts in imagination the
number $n'\delta_x$ of molecules in a volume δ_x surrounding
$\underline{x}$ which is small by macroscopic standards, yet large
enough to contain many molecules. - an ill-defined
procedure which can give a value n' only approx-
imately equal to the ideal number density n .

These difficulties can be avoided by the more
abstract but entirely logical method adopted in the
present exposition. Here probability is treated as
an a priori concept: it is axiomatic that one can
attach to any conceivable event a number signifying
the probability of the occurrence of the event,
which conforms with certain laws coinciding with the
laws of statistical probability. Thus, if A
represents the occurrence of any event, and $p(A)$
the probability of the occurrence of the event, one
has

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

(2) $\qquad (A \supset B) \supset \{p(B) \geqslant p(A)\},$

in the symbolism of logic. From these, two principles
of fundamental importance for the present theory may
be deduced:

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

$$(3) \qquad p_A(B) = p(A \cdot B)/p(A).$$

(ii) If A and B are causally connected,

$$(4) \qquad p(A) = p(B).$$

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 (2) 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 $x_1 \cdots x_a$, the first
three of which may be chosen to be the coordinates of the
the mass-centre of the molecule. A molecule is said
to occupy a volume element $d\underline{x} = dx_1 dx_2 dx_3$ of real space
if its mass-centre $\underline{x} \equiv (x_1, x_2, x_3)$ lies within the volume
element; similarly the molecule is said to occupy
the element $d\underline{x} = dx_1 dx_2 \cdots dx_a$ of phase space if its
generalised position vector $\underline{x} \equiv (x_1, x_2, \cdots x_a)$ falls
within the element. The temporal rate of change $\dot{\underline{x}}$
of the 'position vector' $\underline{x}$ is represented by the
generalised velocity $\underline{\xi} \equiv (\xi_1, \xi_2, \cdots \xi_a)$, and $\dot{\underline{\xi}}$ by the
generalised acceleration $\underline{\eta}$, $\dot{\underline{\eta}}$ by $\underline{\zeta}$, etc.

The probability that at time t the volume
elements $d\underline{x}^{(1)}$, $d\underline{x}^{(2)}$, ... $d\underline{x}^{(q)}$ (of phase space,
if $a > 3$) are all occupied is denoted by
$n_q(t, \underline{x}^{(1)}, \cdots, \underline{x}^{(q)}) \prod_{i=1}^{q} d\underline{x}^{(i)}$;   for brevity $n_q(t, \underline{x}^{(1)}, \cdots, \underline{x}^{(q)})$
will often be contracted to $n_q(t, \underline{x})$, $n_q(\underline{x})$, or
simply n_q , the variables being sufficiently
indicated by the suffix q . If $a = 3$, n_1 is the
number density of the molecules, and when n_1 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 $\int^{(a-3)} \cdots \int n_1 \prod_{r=4}^{a} dx_r^{(1)}$.
The functions n_q are connected by the relation

(5) $$\int n_{q+1}\, d\underline{x}^{(q+1)} = (N-q)\, n_q$$

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

(6) $$\int n_1\, d\underline{x}^{(1)} = N$$

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

The probability that at time t the 'volume'
elements $d\underline{x}^{(1)}, \ldots d\underline{x}^{(q)}$ are occupied by molecules
with 'velocities' $\underline{\xi}^{(1)}, \ldots \underline{\xi}^{(q)}$ in the elementary
ranges $d\underline{\xi}^{(1)}, \ldots d\underline{\xi}^{(q)}$ respectively is denoted by
$f_q(t, \underline{x}^{(1)}, \ldots \underline{x}^{(q)}, \underline{\xi}^{(1)}, \ldots \underline{\xi}^{(q)}) \prod_{i=1}^{q} d\underline{x}^{(i)} d\underline{\xi}^{(i)}$; the contracted forms
$f_q(t, \underline{x}, \underline{\xi})$, $f_q(\underline{x}, \underline{\xi})$ or f_q will often be used
instead of $f_q(t, \underline{x}^{(1)}, \ldots \underline{x}^{(q)}, \underline{\xi}^{(1)}, \ldots \underline{\xi}^{(q)})$. If $a=3$, f_1
coincides with the velocity distribution function of
the kinetic theory of gases.

It must be observed that the above definition of f_q 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 (§6).

The f_q satisfy the relation, analogous to (5),

$$(7) \qquad \iint f_{q+1} \, d\underline{x}^{(q+1)} d\underline{\xi}^{(q+1)} = (N-q) f_q \; ;$$

also, clearly,

$$(8) \qquad \int \overset{(q)}{\cdots} \int f_q \prod_{i=1}^{q} d\underline{\xi}^{(i)} = n_q \; .$$

Pursuing this method, one may define an acceleration distribution function g_q such that $g_q(t, \underline{x}^{(i)}, \cdots \underline{x}^{(q)}, \underline{\xi}^{(i)}, \cdots \underline{\xi}^{(q)}, \underline{\eta}^{(i)}, \cdots \underline{\eta}^{(q)}) \prod_{i=1}^{q} d\underline{x}^{(i)} d\underline{\xi}^{(i)} d\underline{\eta}^{(i)}$ is the proabability that at time t the volume elements $\underline{x}^{(i)}$, $d\underline{x}^{(i)}$ are occupied by molecules with velocities $\underline{\xi}^{(i)}$, $d\underline{\xi}^{(i)}$ and accelerations $\underline{\eta}^{(i)}$, $d\underline{\eta}^{(i)}$ respectively ($i = 1 \cdots q$). The g_q satisfy

$$(9) \qquad \iiint g_{q+1} \, d\underline{x}^{(q+1)} d\underline{\xi}^{(q+1)} d\underline{\eta}^{(q+1)} = (N-q) g_q ,$$

and

$$(10) \qquad \int \overset{(q)}{\cdots} \int g_q \prod_{i=1}^{q} d\underline{\eta}^{(i)} = f_q .$$

The definitions and fundamental equations relating to the rate-of-acceleration distribution function $h_q(t, \underline{x}, \underline{\xi}, \underline{\eta}, \underline{\zeta})$ etc. are now obvious.

3. Kinematics and Equations of Continuity

It is now proposed to make a direct application of the second principle (11) 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 $\underline{x}$ (and with velocity $\underline{\xi}$) at time t , and B as the occurrence of a molecule at $\underline{x} - \underline{\xi} dt$ 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,

$$(11) \qquad \int \overset{(q)}{\cdots} \int f_q(t-dt, \underline{x} - \underline{\xi} dt, \underline{\xi}) \prod_{i=1}^{q} d\underline{\xi}^{(i)} = n_q(t, \underline{x})$$

Hence, by subtraction from (8),

$$(12) \qquad \int \overset{(q)}{\cdots} \int \left(\frac{\partial f_q}{\partial t} + \sum_{i=1}^{q} \underline{\xi}^{(i)} \cdot \frac{\partial f_q}{\partial \underline{x}^{(i)}} \right) \prod_{j=1}^{q} d\underline{\xi}^{(j)} = 0 ,$$

or,

$$(13) \quad \frac{\partial n_q}{\partial t} + \sum_{i=1}^{q} \frac{\partial}{\partial x^{(i)}} \cdot \left(n_q \, \underline{u}_q^{(i)} \right) = 0 ,$$

where

$$(14) \quad \underline{u}_q^{(i)} = \frac{1}{n_q} \int \cdots^{(q)} \int f_q \, \underline{\xi}^{(i)} \prod_{j=1}^{q} d\underline{\xi}^{(j)}$$

is the average velocity of the molecule (i) in the cluster of q molecules whose positions are known. When $a = 3$, the equation of continuity of ordinary hydrodynamics and the kinetic theory of gases is obtained from (13) simply by putting $q = 1$; when $a > 3$, the corresponding equation is obtained on integrating over the internal coordinates of the molecules.

The same principle may clearly be employed to show that

$$(15) \quad \int \cdots^{(q)} \int g_q \left(t - dt, \, \underline{x} - \underline{\xi} \, dt, \, \underline{\xi} - \eta \, dt, \, q \right) \prod_{i=1}^{q} d\eta^{(i)} = f_q (t, \underline{x}, \underline{\xi}) ,$$

and hence that

$$(16) \quad \frac{\partial f_q}{\partial t} + \sum_{i=1}^{q} \left\{ \underline{\xi}^{(i)} \cdot \frac{\partial f_q}{\partial x^{(i)}} + \frac{\partial}{\partial \underline{\xi}^{(i)}} \cdot \left(f_q \, \underline{w}_q^{(i)} \right) \right\} = 0 ,$$

where

$$(17) \quad \underline{w}_q^{(i)} = \frac{1}{f_q} \int \cdots^{(q)} \int g_q \, \eta^{(i)} \prod_{j=1}^{q} d\eta^{(i)}$$

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 g_q and h_q, analogous to
(13) and (16), is now quite obvious.

4. **Mechanics and Equations of Motion.**

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

$$(18) \qquad H_N = \sum_{i=1}^{N} H^{(i)} + \frac{1}{2} \sum_{i,j=1}^{N} \phi^{(ij)},$$

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 $\underline{x}^{(i)}$ and
$\underline{x}^{(j)}$. (It is convenient to adopt the convention
$\phi^{(ii)} = 0$). $H^{(i)}$ is given by

$$(19) \qquad H^{(i)} = \frac{1}{2} \underline{\xi}^{(i)} \cdot \underline{\underline{g}}^{(i)} \cdot \underline{\xi}^{(i)} + \psi^{(i)}$$

where $\frac{1}{2} \underline{\xi}^{(i)} \cdot \underline{\underline{g}}^{(i)} \cdot \underline{\xi}^{(i)} = \frac{1}{2} \sum_{r,s=1}^{a} g_{rs}^{(i)}(\underline{x}^{(i)}) \xi_r^{(i)} \xi_s^{(i)}$ represents the
kinetic energy, and $\psi^{(i)} = \psi(x^{(i)})$ 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

$$(20) \sum_{s=1}^{a} g_{rs}^{(i)} \eta_s^{(i)} + \frac{1}{2} \sum_{s,t=1}^{a} \left(\frac{\partial g_{rs}^{(i)}}{\partial x_t^{(i)}} + \frac{\partial g_{rt}^{(i)}}{\partial x_s^{(i)}} - \frac{\partial g_{st}^{(i)}}{\partial x_r^{(i)}} \right) \xi_s^{(i)} \xi_t^{(i)} + \frac{\partial \psi^{(i)}}{\partial x_r^{(i)}} + \sum_{j=1}^{N} \frac{\partial \phi^{(ij)}}{\partial x_r^{(i)}} = 0,$$

may be solved to obtain the 'acceleration' $\eta^{(i)}$ in the form

$$(21) \qquad \eta^{(i)} = \underline{\underline{g}}^{(i)-1} \cdot \left(\underline{P}^{(i)} - \sum_{j=1}^{N} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} \right)$$

where

$$(22) \qquad P_r^{(i)} = -\frac{1}{2} \sum_{s,t=1}^{a} \left(\frac{\partial g_{rs}^{(i)}}{\partial x_t^{(i)}} + \frac{\partial g_{rt}^{(i)}}{\partial x_s^{(i)}} - \frac{\partial g_{st}^{(i)}}{\partial x_r^{(i)}} \right) \xi_s^{(i)} \xi_t^{(i)} - \frac{\partial \psi^{(i)}}{\partial x_r^{(i)}} \,,$$

and $\underline{\underline{g}}^{(i)-1}$ is the reciprocal of the tensor $\underline{\underline{g}}^{(i)}$. When $a = 3$, $\underline{\underline{g}}^{(i)}$ reduces to the multiple m of the unit tensor, and $\underline{P}^{(i)}$ to the external force acting on the molecule (i).

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

$$(23) \qquad \underline{w}_q^{(i)} = \underline{\underline{g}}^{(i)-1} \cdot \left\{ \left(\underline{P}^{(i)} - \sum_{j=1}^{q} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} \right) - \frac{1}{f_q} \iint f_{q+1} \frac{\partial \phi^{(i,q+1)}}{\partial \underline{x}^{(i)}} d\underline{x}^{(q+1)} d\underline{\xi}^{(q+1)} \right\}.$$

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 $\underline{x}^{(q+1)}$, $d\underline{x}^{(q+1)}$ is occupied by a molecule with velocity $\underline{\xi}^{(q+1)}$, $d\underline{\xi}^{(q+1)}$ is $\frac{f_{q+1}}{f_q} d\underline{x}^{(q+1)} d\underline{\xi}^{(q+1)}$. (23) may also be obtained directly from the formula (17) by re-writing it, with the aid of (9), in the form

$$(24) \qquad \underline{w}_q^{(i)} = \frac{1}{(N-q)! f_q} \int \overset{(3N-2q)}{\cdots} \int g_N \, \eta^{(i)} \prod_{j=1}^{N} d\underline{\eta}^{(j)} \prod_{k=q+1}^{N} d\underline{\xi}^{(k)} d\underline{x}^{(k)}$$

and substituting

$$(25) \qquad g_N = f_N \prod_{i=1}^{N} \delta \left\{ \underline{\eta}^{(i)} - \underline{g}^{(i)-1} \cdot \left(\underline{P}^{(i)} - \sum_{j=1}^{N} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} \right) \right\}$$

where δ denotes the Dirac delta-function.

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

$$(26) \qquad \frac{\partial f_q}{\partial t} + \sum_{i=1}^{q} \left\{ \underline{\xi}^{(i)} \cdot \frac{\partial f_q}{\partial \underline{x}^{(i)}} + \left(\underline{P}^{(i)} - \sum_{j=1}^{q} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} \right) \cdot \underline{g}^{(i)-1} \cdot \frac{\partial f_q}{\partial \underline{\xi}^{(i)}} \right\}$$
$$= \sum_{i=1}^{q} \iint \frac{\partial \phi^{(i,q+1)}}{\partial \underline{x}^{(i)}} \cdot \underline{g}^{(i)-1} \cdot \frac{\partial f_{q+1}}{\partial \underline{\not{x}}^{(i)}} \, d\underline{x}^{(q+1)} d\underline{\xi}^{(q+1)},$$

which may be regarded as an integro-differential equation for the determination of f_q . As, however, it contains f_{q+1} on the right-hand side, its solution must be effected either by making some approximative assumption concerning the dependence of f_{q+1} on f_q , 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 $\underline{x}^{(i)}$ and $\underline{\xi}^{(i)}$ at an initial time t_0 , subject to the normalising condition

$$(27) \qquad \int \overset{(2N)}{\cdots} \int f_N \prod_{i=1}^{N} d\underline{x}^{(i)} d\underline{\xi}^{(i)} = N! \, ,$$

and (26) then determines the subsequent variation.

g_q 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'

$$(28) \qquad \underline{\zeta}^{(i)} = \sum_{j=1}^{N} \left(\underline{\xi}^{(j)} \cdot \frac{\partial}{\partial \underline{x}^{(j)}} + \underline{\eta}^{(j)} \cdot \frac{\partial}{\partial \underline{x}^{(j)}} \right) \cdot \underline{g}^{(i)-1} \cdot \left(\underline{P}^{(i)} - \sum_{k=1}^{N} \frac{\partial \phi^{(ik)}}{\partial \underline{x}^{(i)}} \right)$$

whose mean value $\underline{z}_q^{(i)}$ must be substituted in the equation for g_q :

$$(29) \qquad \frac{\partial g_q}{\partial t} + \sum_{i=1}^{q} \left\{ \underline{\xi}^{(i)} \cdot \frac{\partial g_q}{\partial \underline{x}^{(i)}} + \underline{\eta}^{(i)} \cdot \frac{\partial g_q}{\partial \underline{\xi}^{(i)}} + \frac{\partial}{\partial \underline{\eta}^{(i)}} \cdot \left(g_q \, \underline{z}_q^{(i)} \right) \right\} = 0$$

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 $p(A \cdot B) = p(A) \, p(B)$; thus, for example, in a fluid

$$f_2\left(\underline{x}^{(1)}, \underline{x}^{(2)}\right) = f_1\left(\underline{x}^{(1)}\right) f_1\left(\underline{x}^{(2)}\right)$$ when $|\underline{x}^{(2)} - \underline{x}^{(1)}|$ 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 $\phi\left(\underline{x}^{(i)}, \underline{x}^{(j)}\right)$ between two molecules at $\underline{x}^{(i)}$ and $\underline{x}^{(j)}$ 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

$$\frac{1}{m} \iint \frac{\partial \phi^{(12)}}{\partial \underline{x}^{(1)}} \cdot \frac{\partial f_2}{\partial \underline{\xi}^{(1)}} \, d\underline{x}^{(2)} d\underline{\xi}^{(2)}$$

. 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 $\underline{x}^{(1)}$, $\underline{x}^{(2)}$ (such that $|\underline{x}^{(2)} - \underline{x}^{(1)}| < r_0$)
and velocities $\underline{\xi}^{(1)}$, $\underline{\xi}^{(2)}$ 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 $\underline{x}_0^{(1)}$, $\underline{x}_0^{(2)}$ and $\underline{\xi}_0^{(1)}$, $\underline{\xi}_0^{(2)}$ respect-
ively. During the motion, according to the principle
(ii) of §1, the configurational probability
$f_2(t, \underline{x}^{(1)}, \underline{x}^{(2)}, \underline{\xi}^{(1)}, \underline{\xi}^{(2)}) \, d\underline{x}^{(1)} d\underline{x}^{(2)} d\underline{\xi}^{(1)} d\underline{\xi}^{(2)}$ must remain unchanged;
also, by Liouville's theorem, the volume in phase
space $d\underline{x}^{(1)} d\underline{x}^{(2)} d\underline{\xi}^{(1)} d\underline{\xi}^{(2)}$ is unaltered. Hence

(30)

$$(30) \quad f_2(t, \underline{x}^{(1)}, \underline{x}^{(2)}, \underline{\xi}^{(1)}, \underline{\xi}^{(2)}) = f_1(t_0, \underline{x}_0^{(1)}, \underline{\xi}_0^{(1)}) f_1(t_0, \underline{x}_0^{(2)}, \underline{\xi}_0^{(2)})$$

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 , $\underline{x}_0^{(1)}$,
and $\underline{x}_0^{(2)}$ may be replaced by t , $\underline{x}^{(1)}$, and $\underline{x}^{(2)}$ 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 $\underline{\xi}_0^{(1)}$ and $\underline{\xi}_0^{(2)}$ in terms of $\underline{\xi}^{(1)}$, $\underline{\xi}^{(2)}$, and $\underline{r} = \underline{x}^{(2)} - \underline{x}^{(1)}$, one may use the Hamiltonian equations of motion

$$(31) \qquad \frac{d\underline{r}}{\left(\underline{\xi}^{(2)} - \underline{\xi}^{(1)}\right)} = m\, d\underline{\xi}^{(1)} \bigg/ \frac{\partial \phi}{\partial \underline{r}} = -\, m\, d\underline{\xi}^{(2)} \bigg/ \frac{\partial \phi}{\partial \underline{r}}.$$

The eight functionally independent integrals $\Theta_k\left(\underline{r}, \underline{\xi}^{(1)}, \underline{\xi}^{(2)}\right) = \text{const.}$ $(k = 1 \cdots 8)$ of these equations just suffice to determine $\underline{r}_0$, $\underline{\xi}_0^{(1)}$, and $\underline{\xi}_0^{(2)}$ as the solution of the simultaneous equations

$$(32) \qquad \Theta_k\left(\underline{r}_0, \underline{\xi}_0^{(1)}, \underline{\xi}_0^{(2)}\right) = \Theta_k\left(\underline{r}, \underline{\xi}^{(1)}, \underline{\xi}^{(2)}\right), \quad |\underline{r}_0| = r_0.$$

Since, however, all the Θ_k satisfy the equation

$$(33) \qquad m\left(\underline{\xi}^{(2)} - \underline{\xi}^{(1)}\right) \cdot \frac{\partial \Theta_k}{\partial \underline{r}} = \frac{\partial \phi}{\partial \underline{r}} \cdot \left(\frac{\partial \Theta_k}{\partial \underline{\xi}^{(2)}} - \frac{\partial \Theta_k}{\partial \underline{\xi}^{(1)}}\right),$$

$\underline{\xi}_0^{(1)}$ and $\underline{\xi}_0^{(2)}$, which are now expressed as functions of the Θ_k, satisfy the same equation, and so does the expression for f_2 obtained from (30). The integral $\frac{1}{m} \iint \frac{\partial \phi}{\partial \underline{r}} \cdot \frac{\partial f_2}{\partial \underline{\xi}^{(1)}}\, d\underline{x}^{(2)} d\underline{\xi}^{(2)}$ vanishes on account of the integration over $\underline{\xi}^{(2)}$ (because there are no

molecules with infinite velocities); hence

(34) $\quad \frac{1}{m} \iint \frac{\partial \phi}{\partial \underline{x}^{(1)}} \cdot \frac{\partial f_2}{\partial \underline{\xi}^{(1)}} d\underline{x}^{(2)} d\underline{\xi}^{(2)} = \iint (\underline{\xi}^{(2)} - \underline{\xi}^{(1)}) \cdot \frac{\partial}{\partial \underline{r}} \{ f_1(\underline{\xi}_o^{(1)}) f_1(\underline{\xi}_o^{(2)}) \} d\underline{r} d\underline{\xi}^{(2)},$

where the domain of integration over $\underline{r}$ may be
limitied to the sphere of radius r_o surrounding $\underline{x}^{(1)}$.

This integration is most conveniently performed
by imagining the sphere to be partitioned by
elementary tubes parallel to the vector $\underline{\xi}^{(2)} - \underline{\xi}^{(1)}$; one
may then integrate, first over a typical tube
specified by the cross-section radius $\underline{b}$ (perpend-
icular from the centre of the sphere), and then over
all values of $\underline{b}$. At the beginning of the tube,
where $(\underline{\xi}^{(2)} - \underline{\xi}^{(1)}) \cdot \underline{r} < 0$, the interaction between the
molecules is negligible, and $\underline{\xi}_o^{(1)}$ reduces to $\underline{\xi}^{(1)}$ and
$\underline{\xi}_o^{(2)}$ to $\underline{\xi}^{(2)}$; at the end, the values $\underline{\xi}^{(1)\prime}$ and $\underline{\xi}^{(2)\prime}$
of $\underline{\xi}_o^{(1)}$ and $\underline{\xi}_o^{(2)}$ have to be calculated with the help
of (32). Thus the right-hand side of (34) assumes
the form

$\iint |\underline{\xi}^{(2)} - \underline{\xi}^{(1)}| \{ f_1(\underline{\xi}^{(1)\prime}) f_1(\underline{\xi}^{(2)\prime}) - f_1(\underline{\xi}^{(1)}) f_1(\underline{\xi}^{(2)}) \} d\underline{b} \, d\underline{\xi}^{(2)},$

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.

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be constructed.   In particular, one obtains for a function $\gamma_q(\underline{x})$ of coodinates alone,

$$(37) \qquad \gamma_q(\underline{x}, \underline{x}') = \gamma_q(\underline{x}) \prod_{j=1}^{q} \delta(\underline{x}^{(j)} - \underline{x}^{(j)'}),$$

and for expressions of the form $(p^{(i)}\alpha_q)$ and $(\alpha_q p^{(i)})$,

$$(38) \qquad (\underline{p}^{(i)}\alpha_q)(\underline{x}, \underline{x}') = -i\hbar \frac{\partial \alpha_q(\underline{x}, \underline{x}')}{\partial x^{(i)}},$$

$$(\alpha_q p^{(i)})(\underline{x}, \underline{x}') = i\hbar \frac{\partial \alpha_q(\underline{x}, \underline{x}')}{\partial x^{(i)'}}.$$

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

$$(39) \qquad \chi_{q+1}(\alpha_{q+1})(\underline{x}, \underline{x}') = \iint \alpha_{q+1}(\underline{x}, \underline{x}') \delta(x^{(q+1)} - \underline{x}^{(q+1)'}) d\underline{x}^{(q+1)} d\underline{x}^{(q+1)'};$$

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

$$(40) \qquad \chi(\alpha_q) = \chi_1 \left[\chi_2 \left\{ \cdots \chi_q(\alpha_q) \right\} \right].$$

$\chi_{q+1}(\alpha_{q+1})$ is the quantum transcription of the classical expression $\iint \alpha_{q+1}(\underline{x}, \underline{\xi}) d\underline{x}^{(q+1)} d\underline{\xi}^{(q+1)}$; by comparing this expression with (40), one sees that in quantum theory the operation $\int d\underline{\xi}^{(q+1)}$ is replaced by $\int d\underline{x}^{(q+1)'} \delta(\underline{x}^{(q+1)} - \underline{x}^{(q+1)'})$, i.e., by the substitution of

$\underline{x}^{(q+1)}$ for $\underline{x}^{(q+1)\prime}$.

Suppose that $\rho_q(\underline{x}, \underline{x}')$ is the matrix representative of the operator ρ_q which corresponds to the velocity distribution function $f_q(\underline{x}, \underline{\xi})$. To preserve the analogy with the classical theory it is convenient to normalise ρ_q according to the relation

$$(41) \qquad \chi_{q+1}(\rho_{q+1}) = (N-q)\rho_q ,$$

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

$$(42) \qquad \int \overset{(q)}{\cdots} \int \rho_q \prod_{i=1}^{q} \delta(\underline{x}^{(i)} - \underline{x}^{(i)\prime}) \, d\underline{x}^{(i)\prime} = n_q ,$$

or

$$(43) \qquad \rho_q(\underline{x}, \underline{x}) = n_q(\underline{x})$$

This is one of the most important properties of the matrix ρ_q, that its diagonal elements are the values of the number density function. It is seen at once that ρ_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 ρ_q, it is convenient to begin with ρ_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) $\qquad X(\rho_N) = N!$;

its subsequent variation is then determined by the Heisenberg equation

(45) $\qquad \dfrac{\partial \rho_N}{\partial t} = [H_N, \rho_N]$,

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

(46) $\qquad H_q = \sum_{i=1}^{q} H^{(i)} + \frac{1}{2}\sum_{i,j=1}^{q} \phi^{(i:j)}$,

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

(47) $\dfrac{\partial \rho_{N-1}}{\partial t} = [H_{N-1}, \rho_{N-1}] + \sum_{i=1}^{N-1} \chi_N [\phi^{(i:N)}, \rho_N]$

The only term of $\chi_N[H^{(N)}, \rho_N]$ which does not obviously vanish is $\frac{1}{2m}[p^{(N)2}, \rho_N]$, and when reduced to the form $-\frac{1}{2m}\int \frac{\partial}{\partial x}(N) \cdot \int (p^{(N)}\rho_N + \rho_N p^{(N)})(x, x') \delta(x^{(N)} - x^{(N)'}) dx^{(N)'} dx^{(N)}$ this obviously vanishes also after transformation to a surface integral. (There are <u>no</u> molecules outside the confines of the volume V).

Repeating this procedure indefinitely, and

cancelling the factor $(N-q)!$ which appears, one obtains

$$(48) \quad \frac{\partial \rho_q}{\partial t} = [H_q, \rho_q] + \sum_{i=1}^{q} \chi_{q+1} [\phi^{(i:q+1)}, \rho_{q+1}],$$

which is the fundamental equation satisfied by ρ_q. Now, it is well-known that the classical analogue of the 'Poisson bracket' $[\alpha_q, \beta_q]$ is

$$\sum_{i=1}^{q} \left(\frac{\partial \alpha_q}{\partial x^{(i)}} \cdot \frac{\partial \beta_q}{\partial p^{(i)}} - \frac{\partial \alpha_q}{\partial p^{(i)}} \cdot \frac{\partial \beta_q}{\partial x^{(i)}} \right),$$

and since $p^{(i)} = g^{(i)} \cdot \xi^{(i)}$, in the transition to classical mechanics $[H_q, \rho_q]$ becomes

$$\sum_{i=1}^{q} \left\{ \left(\sum_{j=1}^{q} \frac{\partial \phi^{(ij)}}{\partial x^{(i)}} - p^{(i)} \right) \cdot g^{(i)-1} \cdot \frac{\partial f_q}{\partial \xi^{(i)}} - \xi^{(i)} \cdot \frac{\partial f_q}{\partial x^{(i)}} \right\},$$

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

$$\iint \frac{\partial \phi^{(i:q+1)}}{\partial x^{(i)}} \cdot g^{(i)-1} \cdot \frac{\partial f_{q+1}}{\partial \xi^{(i)}} \, dx^{(q+1)} d\xi^{(q+1)}$$

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 ρ_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 $\lambda^{(r)}$ ($r = 1 \cdots N'$), and then specifies the probability $p_N(l) = p_N(l^{(1)} \cdots l^{(N')})$ that at time t_0 the fluid is in the state l for which the $\lambda^{(r)}$ have the simultaneous eigenvalues $l^{(r)}$. This represents the maximum of information which can be ascertained experimentally concerning the fluid. Let $\psi_N(l, \underline{x})$ be the eigenfunction corresponding to the state l, satisfying the equation

$$(49) \quad \int \cdots^{(N)} \int \lambda^{(r)}(\underline{x}, \underline{x}') \psi_N(l, \underline{x}') \prod_{i=1}^{N} d\underline{x}^{(i)\prime} = l^{(r)} \psi_N(l, \underline{x}),$$

and normalised in such a way that

$$(50) \quad \int \cdots^{(N)} \int |\psi_N(l, \underline{x})|^2 \prod_{i=1}^{N} d\underline{x}^{(i)} = N! \ .$$

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

$$(51) \quad \rho_N(\underline{x}, \underline{x}') = \sum_l p_N(l) \psi_N(l, \underline{x}) \psi_N^*(l, \underline{x}').$$

One possible set of λ 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 λ in a slightly different way, as follows. Suppose the fluid is divided into a number of groups containing $q_1, q_2, \cdots q_w$ molecules ($q_1 + q_2 + \cdots + q_w = N$), 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 λ are chosen to be the $\lambda_1, \lambda_2, \cdots \lambda_w$ which commute with $H_{q_1}, H_{q_2}, \cdots H_{q_w}$ respectively. Write

$$(52) \qquad H_N = H_{q_1} + H_{q_2} + \cdots + H_{q_w} + \mathcal{V},$$

so that $\mathcal{V}$ is very small compared with H_N. Let $E_1, E_2, \cdots E_w$ be the eigenvalues of $H_{q_1}, H_{q_2}, \cdots H_{q_w}$, and put

$$(53) \qquad E_N = E_1 + E_2 + \cdots + E_w .$$

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

$$(54) \qquad i\hbar \frac{\partial \rho_N(\ell, \ell')}{\partial t} = (E_N - E_N') \rho_N(\ell, \ell') + \sum_{\ell''} \left\{ \mathcal{V}(\ell, \ell'') \rho_N(\ell'', \ell') - \rho_N(\ell, \ell'') \mathcal{V}(\ell'', \ell') \right\}$$

Substituting

$$\rho_N(\ell, \ell') = e^{-\frac{i}{\hbar}(E_N - E_N')t} \, \overline{\rho}_N(\ell, \ell'),$$

$$(55) \qquad \mathcal{V}(\ell, \ell') = e^{-\frac{i}{\hbar}(E_N - E_N')t} \, \overline{\mathcal{V}}(\ell, \ell'),$$

(54) becomes, in matrix notation,

$$(56) \qquad i\hbar \frac{\partial \overline{\rho_N}}{\partial t} = \overline{\mathcal{V} \overline{\rho_N}} - \overline{\rho_N} \overline{\mathcal{V}}.$$

This equation may be solved by writing

$$(57) \qquad \overline{\rho_N} = \rho(0) + \rho(1) + \rho(2) + \cdots,$$

where $\rho(0)$ is the value of $\overline{\rho_N}$ at time t_0 , given, according to (51), by

$$(58) \qquad \rho(0)(l, l') = p_N(l)\, \delta_{ll'}$$

and the $\rho(u)$ satisfy

$$(59) \qquad i\hbar \frac{\partial \rho(u+1)}{\partial t} = \overline{\mathcal{V} \rho(u)} - \rho(u)\overline{\mathcal{V}}, \quad u = 0, 1, 2, \cdots$$

The probability at any time $t \geqslant t_0$ that the fluid is in the state l is then

$$(60) \qquad \overline{p_N} = p(0) + p(1) + p(2) + \cdots,$$

where $p(u)(l) = \rho(u)(l, l)$, so that $p(0) = p_N$. If

$$(61) \qquad \mathcal{W} = \int_{t_0}^{t} \mathcal{V}\, dt, \qquad \overline{\mathcal{V}} = \dot{\mathcal{W}},$$

one obtains from (59)

$$(62) \qquad i\hbar\, \rho(1) = \mathcal{W}\rho(0) - \rho(0)\mathcal{W},$$

$$(63) \quad -\hbar^2 \rho(2) = \int_{t_0}^{t} \{ \dot{w} w \rho(0) - \dot{w} \rho(0) w - w \rho(0) \dot{w} + \rho(0) w \dot{w} \} \, dt$$
$$= \tfrac{1}{2} \{ w^2 \rho(0) - 2w \rho(0) w + \rho(0) w^2 \} + w_1 \rho(0) - \rho(0) w_1 ,$$

where

$$(64) \qquad w_1 = \tfrac{1}{2} \int_{t_0}^{t} (\dot{w} w - w \dot{w}) \, dt ,$$

and similarly, by an easy calculation not reproduced,

$$(65) \quad \begin{aligned} - \hbar^3 \rho(3) &= \tfrac{1}{6} \{ w^3 \rho(0) - 3 w^2 \rho(0) w + 3 w \rho(0) w^2 - \rho(0) w^3 \} \\ &\quad + w \{ w_1 \rho(0) - \rho(0) w_1 \} - \{ w_1 \rho(0) - \rho(0) w_1 \} w \\ &\quad + w_2 \rho(0) - \rho(0) w_2 , \end{aligned}$$

where

$$(66) \qquad w_2 = \tfrac{1}{3} \int_{t_0}^{t} (\dot{w}_1 w - w \dot{w}_1) \, dt .$$

Hence

$$(67) \quad \begin{aligned} \rho(1)(l) &= 0 \\ \rho(2)(l) &= \frac{1}{\hbar^2} \sum_{l'} | w(l, l') |^2 \{ p_N(l') - p_N(l) \} \\ \rho(3)(l) &= \frac{1}{2\hbar^3} \sum_{l', l''} \mathcal{G} \{ w(l, l') w(l', l'') w(l'', l) \} \{ p_N(l'') - p_N(l') \} \\ &\quad + \frac{1}{\hbar^3} \sum_{l'} \mathcal{G} \{ w(l, l') w_1(l', l) + w_1(l, l') w(l', l) \} \{ p_N(l') - p_N(l) \} \end{aligned}$$

As ν is small, the series (60) will converge quickly, especially when $t - t_0$ is small. Hence, to a sufficiently high order of approximation,

$$(68) \qquad \overline{p_N}(l) = p_N(l) + \frac{1}{\hbar^2} \sum_{l'} | w(l, l') |^2 \{ p_N(l') - p_N(l) \} .$$

This equation has a transparent physical significance,

when $|w(l,l')|^2$ is interpreted as the probability of a
transition from the state l to the state l', or
vice versa, in time $t-t_o$.

2. The H-Theorem and the Adiabatic Principle

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

$$(69) \qquad w(l,l')=0 \quad \text{or} \quad p_N(l)=p_N(l'), \quad \text{all } l \text{ and } l',$$

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 $\rho(1)$, and hence of all the
$\rho(u)$ except $\rho(0)$. 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

$$(70) \qquad S_N = -k \sum_l \overline{p_N}(l) \log \overline{p_N}(l),$$

so that, by substitution from (68) and neglect of
squares and higher powers of the small quantity
$|w(l,l')|^2$, one obtains

$$S_N = -k \sum_l p_N(l) \log p_N(l) + \frac{k}{\hbar^2} \sum_{l,l'} |w(l,l')|^2 \{p_N(l)-p_N(l')\}\{1+\log p_N(l)\}$$

$$(71)$$

$$= -k \sum_l p_N(l) \log p_N(l) + \frac{k}{2\hbar^2} \sum_{l,l'} |w(l,l')|^2 \{p_N(l)-p_N(l')\} \log\left\{\frac{p_N(l)}{p_N(l')}\right\}.$$

Thus S_N necessarily increases between the times t_o 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 $p(2)$ becomes small enough to be comparable with $p(3)$. Then the above argument loses its validity, since $\mathcal{I}\{w(l,l')w(l',l'')w(l'',l)\}$ and $\mathcal{I}\{w(l,l')w_i(l',l)+w_i(l,l')w(l',l)\}$ 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,

$$(72) \qquad S_e = -k \sum_{l_e} p_e(l_e) \log p_e(l_e),$$

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,

$$(73) \qquad \overline{p}_N(l) = \prod_{e=1}^{w} p_e(l_e),$$

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

$$(74) \qquad S_N = \sum_{e=1}^{w} S_e .$$

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 $\rho(u)$ depend on the time has not been explicitly determined. From (61) and (64) one obtains

$$w(l,l') = \frac{2\,\mathcal{V}(l,l')}{\nu_1}\, e^{\frac{1}{2}i\nu_1 t'} \sin\tfrac{1}{2}\nu_1 t',$$

(75)
$$w_1(l,l'') = \sum_{l'} \frac{2\,\mathcal{V}(l,l')\mathcal{V}(l',l'')}{\nu_1\nu_2\,(\nu_1+\nu_2)}\, e^{\frac{1}{2}i(\nu_1+\nu_2)t'}\left(\nu_2 \sin\tfrac{1}{2}\nu_1 t' \cos\tfrac{1}{2}\nu_2 t' - \nu_1 \sin\tfrac{1}{2}\nu_2 t' \cos\tfrac{1}{2}\nu_1 t'\right),$$

where $\hbar\nu_1 = E_N - E_N'$, $\hbar\nu_2 = E_N' - E_N''$, 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 $w(l,l')$ except those for which $\nu_1 = 0$, and to all terms in $w_1(l,l'')$ except those for which $\nu_1 + \nu_2 = 0$. Hence one has effectively

$$w(l,l') = \mathcal{V}(l,l')\,\delta_{E_N E_N'}\,(t-t_0)$$

(76)
$$w_1(l,l'') = \frac{i}{\hbar}\sum_{l'}{}' \frac{\mathcal{V}(l,l')\mathcal{V}(l',l'')}{E_N - E_N'}\,\delta_{E_N E_N''}\,(t-t_0)$$

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 $\rho(u)$; this extension was
first proved by Born and Fock [23].

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

$$(77) \quad \Lambda_N = \sum_{i=1}^{N} \Lambda^{(i)} = \sum_{e=1}^{\widetilde{w}} \Lambda_e ; \quad L_N = \sum_{i=1}^{N} L^{(i)} = \sum_{e=1}^{w} L_e$$

where $\Lambda^{(i)}$ represents either $p^{(i)}$, or one component
and the square of $\underline{x}^{(i)} \wedge p^{(i)}$. It thus appears that W

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 ρ_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,

$$(78) \qquad p_N(l) = p(E_N, L_N),$$

and, according to (73),

$$(79) \qquad p(E_N, L_N) = \prod_{e=1}^{w} p_e(l_e)$$

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

$$(80) \qquad \begin{aligned} \log p_N(E_N) &= \beta(A_N - E_N), \\ \log p_e(E_e) &= \beta(A_e - E_e), \end{aligned}$$

where β is a constant and $A_N = \sum\limits_{e=1}^{w} A_e$. 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 $\sum\limits_{\ell} P_N(\ell) = 1$ in the form

$$(81) \qquad e^{-\beta A_N} = \sum_{\ell} e^{-\beta E_N}$$

To determine β , 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 $\sum\limits_{\ell} P_N(\ell) dE_N$; the corresponding change in the internal energy U_N , given by

$$(82) \qquad U_N = \sum_{\ell} P_N(\ell) E_N ,$$

exceeds this by

$$(83) \qquad \begin{aligned} \sum_{\ell} dP_N(\ell) E_N &= \sum_{\ell} e^{\beta(A_N - E_N)} d\{\beta(A_N - E_N)\} E_N \\ &= -\sum_{\ell} e^{\beta(A_N - E_N)} (A_N - E_N) d\{\beta(A_N - E_N)\}, \end{aligned}$$

and this must be $T dS_N$, where T is the thermo-dynamic temperature and S_N the entropy. The

reciprocal of the integrating factor β 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

$$(84) \qquad -k\beta \sum_{i} (A_N - E_N) e^{\beta(A_N - E_N)}$$

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

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

$$(85) \qquad \rho_N = e^{\beta(A_N - H_N)}$$

in operational form, since one may now consider the
fluid as a whole, and put $\vartheta = 0$. ($q_1 = N; q_2 = \cdots = q_w = 0$).
Taking the complete trace of (85), one finds

$$(86) \qquad N! \, e^{-\beta A_N} = X(e^{-\beta H_N}),$$

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

$$(87) \qquad (N-q)! \, e^{-\beta A_N} \rho_q = X_{q+1} [X_{q+2} \{ \cdots X_N (e^{-\beta H_N}) \}].$$

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

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

$$(88) \qquad N! \, e^{-\beta A_N} = \int^{(2N)} \cdots \int e^{-\beta H_N} \prod_{i=1}^{N} dx^{(i)} d\xi^{(i)}$$

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

$$(89) \qquad N! \, e^{-\beta A_N} = \frac{(2\pi kT)^{\frac{Na}{2}}}{(m_1 \cdots m_a)^{\frac{N}{2}}} \int^{(N)} \cdots \int e^{-\beta \Phi} \prod_{i=1}^{N} dx^{(i)}$$

where $m_1 \cdots m_a$ are the masses involved, and Φ is the total potential energy of the fluid in a given configuration; also

$$(90) \qquad f_q = \frac{(m_1 \cdots m_a)^{\frac{q}{2}}}{(2\pi kT)^{\frac{qa}{2}}} n_q \, e^{-\beta \sum_{i=1}^{q} \frac{1}{2} \xi^{(i)} \cdot \underline{g}^{(i)} \cdot \xi^{(i)}} \quad .$$

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

$$(91) \qquad \frac{\partial n_q}{\partial x^{(i)}} + \frac{n_q}{kT} \left(\frac{\partial \psi^{(i)}}{\partial x^{(i)}} + \sum_{j=1}^{q} \frac{\partial \phi^{(ij)}}{\partial x^{(i)}} \right) + \int \frac{n_{q+1}}{kT} \frac{\partial \phi^{(i,q+1)}}{\partial x^{(i)}} dx^{(q+1)} = 0,$$

which is very useful for determining the approximate
equilibrium value of n_q 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 $p°$ in a fluid in equilibrium is
defined thermodynamically by the equation $p° = -\frac{\partial A_N}{\partial V}$,
and may now be calculated with the help of the
formula (86), which, on writing $\underline{x} = V^{\frac{1}{3}} \underline{y}$, assumes
the form

$$(92) \quad N! \, e^{-\beta A_N} = V^N \int \cdots^{(N)} \int e^{-\beta W_N}(V^{\frac{1}{3}}\underline{y}, V^{\frac{1}{3}}\underline{y}) \prod_{i=1}^{N} d\underline{y}^{(i)},$$

so that

$$(93) \quad N! \beta e^{-\beta A_N} p° = \frac{N}{V} N! \, e^{-\beta A_N} + \frac{1}{3V}\int\cdots^{(N)}\int \sum_{i=1}^{N} \underline{x}^{(i)} \cdot \frac{\partial}{\partial \underline{x}^{(i)}} \{ e^{-\beta W_N}(\underline{x}, \underline{x})\} \prod_{j=1}^{N} d\underline{x}^{(j)}.$$

For simplicity, it is assumed in this section that
$a = 3$, and that $\psi^{(i)}$ 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

$$(94) \quad \beta p° = n_1 + \frac{1}{6V(N-1)} \iint \left(\underline{x}^{(1)} \cdot \frac{\partial}{\partial \underline{x}^{(1)}} + \underline{x}^{(2)} \cdot \frac{\partial}{\partial \underline{x}^{(2)}} \right) n_2(\underline{x}^{(1)}, \underline{x}^{(2)}) \, d\underline{x}^{(1)} d\underline{x}^{(2)}$$

$$= n_1 + \frac{1}{6(N-1)} \int r \, n_2'(r) \, d\underline{x}^{(2)}$$

since n_2 is in equilibrium a function of $r = |\underline{x}^{(2)} - \underline{x}^{(1)}|$
only. If in (94) one substitutes the classical
expression for $\frac{\partial n_2}{\partial \underline{x}^{(i)}}$, given by (91), one obtains the

more useful formula

(95) $$p^o = n_1 kT - \frac{1}{6} \int r \, n_2(r) \, \phi'(r) \, dr$$

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

(96) $$\sum_{i=1}^{N} \frac{\partial}{\partial \underline{x}^{(i)}} \cdot \left[\underline{x}^{(i)} \{ e^{-\beta H_N}(\underline{x},\underline{x}) \} \right] = \frac{\iota}{\hbar} \sum_{i=1}^{N} \left(\underline{p}^{(i)} \underline{x}^{(i)} e^{-\beta H_N} - e^{-\beta H_N} \underline{p}^{(i)} \underline{x}^{(i)} \right)(\underline{x},\underline{x})$$

in the interior of the fluid. (When $\underline{x}^{(i)}$ 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 σ and τ are any two operators, and $f(\tau)$ any power series in τ , then

(97) $$\begin{aligned}\sigma f(\tau) - f(\tau)\sigma &= f'(\tau)\frac{\sigma_1}{1!} + f''(\tau)\frac{\sigma_2}{2!} + f'''(\tau)\frac{\sigma_3}{3!} + \cdots \\ &= \frac{\sigma_1}{1!} f'(\tau) - \frac{\sigma_2}{2!} f''(\tau) + \frac{\sigma_3}{3!} f'''(\tau) - \cdots \\ &= \frac{1}{1!} \{\sigma_1, f'(\tau)\} + \frac{1}{3!}\{\sigma_3, f'''(\tau)\} + \cdots \\ &\quad - \frac{1}{2}\, \mathrm{ch}\left\{ \frac{1}{2!}[\sigma_2, f''(\tau)] + \frac{1}{4!}[\sigma_4, f^{(iv)}(\tau)] + \cdots \right\}\end{aligned}$$

where $\sigma_1 = \sigma\tau - \tau\sigma$, $\sigma_{k+1} = \sigma_k \tau - \tau \sigma_k$ $(k=1, 2, \cdots)$, and

$\{\alpha_4, \beta_4\}$ represents $\frac{1}{2}(\alpha_4\beta_4 + \beta_4\alpha_4)$. This lemma is easily proved by induction for $f(\tau) = \tau^h$, after which the generalisation is obvious. Substituting $\sigma = \sum_{i=1}^{N} p^{(i)} \cdot \underline{x}^{(i)}$, $\tau = H_N$, and $f(\tau) = e^{-\beta\tau}$, one obtains for the right-hand side of (96) the expression

$$-\frac{\iota}{\hbar}\left[\frac{\beta}{1!}\{\sigma_1, e^{-\beta H_N}\} + \frac{\beta^3}{3!}\{\sigma_3, e^{-\beta H_N}\} + \cdots\right] + \frac{1}{2}\left\{\frac{\beta^2}{2!}[\sigma_2, e^{-\beta H_N}] + \frac{\beta^4}{4!}[\sigma_4, e^{-\beta H_N}] + \cdots\right\},$$

where

$$(98) \qquad \sigma_1 = \iota\hbar \sum_{i=1}^{N} \left\{\frac{1}{m} p^{(i)2} - \frac{1}{2}\sum_{j=1}^{N} r^{(ij)} \phi'^{(ij)}\right\}, \text{ etc.}$$

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

$$(99) \; N! \beta e^{-\beta A_N} P^{\circ} = \frac{1}{3V} \int^{(N)} \cdots \int \left(-\frac{\iota}{\hbar}\right)\left\{\left(\frac{\beta\sigma_1}{1!} + \frac{\beta^3\sigma_3}{3!} + \cdots\right), e^{-\beta H_N}\right\}(x, x) \prod_{j=1}^{N} d\underline{x}^{(j)}$$

and hence

$$(100) \qquad p^{\circ} = p_1^{\circ} + \frac{(\hbar\beta)^2}{3!} P_3^{\circ} + \frac{(\hbar\beta)^4}{5!} P_5^{\circ} + \cdots ,$$

where

$$(101) \qquad \begin{aligned} p_1^{\circ} &= n_1 kT_1 - \frac{1}{6}\int r n_2(r) \phi'(r) \, d\underline{r}, \\ \frac{3}{2}NkT_1 &= X_1\left(\frac{1}{2m} p^{(i)2} p_1\right), \text{ etc.} \end{aligned}$$

The classical equation of state (95) is obtained from (100) by writing $\hbar = 0$, since in classical

theory T and T_1 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:

$$(102) \qquad p^\circ = n_1 k T \left(1 - \sum_{s=1}^{\infty} \frac{s}{s+1} \beta_s n_1^s \right),$$

so that the quantities $-\dfrac{s\beta_s}{s+1}$ are the so-called virial coefficients. This development, first made by Ursell [25], 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 [26], and given a quantum generalisation by Kahn [27], 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 [22] 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 $\mathcal{E}$ is given its minimum value $\mathcal{E}_0 = N\phi_0$ in the
integrand, A_N is $O(N)$. Hence one sees that
the divergence of

$$(103) \qquad A_N = NkT \left\{ \log(n_1 T^{-\frac{3}{2}}) - \sum_{s=1}^{\infty} \frac{\beta_s \, n_1^{\,s}}{s+1} \right\}$$

for high but finite densities must be illusory.
This illusion is created by the assumption that all
the β_s are independent of n_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, §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 β_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 $N \rightarrow \infty$, 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

1. Hydrodynamics.

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 $a = 3$, throughout the present chapter.

With the notation $\{\alpha_q \beta_q\} = \frac{1}{2}(\alpha_q \beta_q + \beta_q \alpha_q)$, one may first define the mean velocity $\underline{u}_q^{(i)}$ of a molecule (i) in a cluster of q molecules with known positions by the equation

$$(104) \qquad m n_q \, \underline{u}_q^{(i)}(\underline{x}) = \{\rho_q \, p^{(i)}\}(\underline{x},\underline{x}) \ .$$

Since the expression $\{\alpha_q \beta_q\}$ corresponds to the simple product $\alpha_q \beta_q$ in classical theory, and $\alpha_q(\underline{x},\underline{x})$ to the integral $\int^{(q)} \int \alpha_q \prod_{i=1}^{q} d\underline{\xi}^{(i)}$, 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

$$(105) \qquad 3 m n_q \, k T_q^{(i)}(\underline{x}) = \{\{\rho_q \, \underline{v}_q^{(i)}\} \cdot \underline{v}_q^{(i)}\}(\underline{x},\underline{x}),$$

where

$$(106) \qquad \underline{v}_q^{(i)}(\underline{x},\underline{x}') = \frac{1}{m} p^{(i)}(\underline{x},\underline{x}') - \underline{u}_q^{(i)}(\underline{x}) \, \delta(\underline{x} - \underline{x}')$$

is the particular velocity of (i) relative to the average motion. In classical theory (105) goes over into the form

$$(107) \qquad 3mn_q kT_q^{(i)} = \int \cdots^{(q)}\!\int f_q \, v_q^{(i)\,2} \prod_{j=1}^{q} d\underline{\xi}^{(j)},$$

where $\underline{v}_q^{(i)} = \underline{\xi}^{(i)} - \underline{u}_q^{(i)}$; thus $T_1 = T_1^{(i)}$ is the same as the temperature defined in classical theory. In quantum theory, T_1 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

$$(p^{(i)\,2} p_q - p_q |p^{(i)\,2})(\underline{x},\underline{x}') = \{ p^{(i)} \cdot (p^{(i)} p_q + p_q p^{(i)}) - (p^{(i)} p_q + p_q p^{(i)}) \cdot p^{(i)} \}(\underline{x},\underline{x}')$$

$$(108) \qquad = -i\hbar \left(\frac{\partial}{\partial x^{(i)}} + \frac{\partial}{\partial x^{(i)\prime}} \right) \cdot (p^{(i)} p_q + p_q p^{(i)})(\underline{x},\underline{x}'),$$

(48) may be written in the form

$$i\hbar \frac{\partial}{\partial t} p_q(\underline{x},\underline{x}') + \frac{i\hbar}{m} \sum_{i=1}^{q} \left(\frac{\partial}{\partial x^{(i)}} + \frac{\partial}{\partial x^{(i)\prime}} \right) \cdot \{ p_q p^{(i)} \}(\underline{x},\underline{x}')$$

$$= \frac{1}{2} \sum_{i,j=1}^{q} (\phi^{(ij)} - \phi^{(ij)\prime}) p_q(\underline{x},\underline{x}') + \sum_{i=1}^{q} (\psi^{(i)} - \psi^{(i)\prime}) p_q(\underline{x},\underline{x}')$$

$$(109) \qquad + \sum_{i=1}^{q} \iint (\phi^{(i\,q+1)} - \phi^{(i\,q+1)\prime}) p_{q+1}(\underline{x},\underline{x}') \,\delta(\underline{x}^{(q+1)} - \underline{x}^{(q+1)\prime}) \, d\underline{x}^{(q+1)} d\underline{x}^{(q+1)\prime}.$$

On putting $\underline{x} = \underline{x}'$ in this equation, all terms on the right-hand side vanish, leaving

$$(110) \qquad \frac{\partial n_q}{\partial t} + \sum_{i=1}^{q} \frac{\partial}{\partial x^{(i)}} \cdot (n_q \underline{u}_q^{(i)}) = 0 .$$

This is formally the same as the equation of
continuity (13), the only difference being in the
definition of $\underline{u}_q^{(i)}$ and n_q in terms of the atomic data.

Let I_q be any function of time and the
coordinates $\underline{x}^{(1)}, \cdots \underline{x}^{(q)}$. Then it follows from (110)
that

$$(111) \quad \frac{\partial}{\partial t}(n_q I_q) = n_q \frac{\partial I_q}{\partial t} - I_q \sum_{i=1}^{q} \frac{\partial}{\partial \underline{x}^{(i)}} \cdot (n_q \underline{u}_q^{(i)})$$

$$= n_q \frac{dI_q}{dt} - \sum_{i=1}^{q} \frac{\partial}{\partial \underline{x}^{(i)}} \cdot (n_q I_q \underline{u}_q^{(i)}),$$

where $\frac{d}{dt}$ represents the operator $\frac{\partial}{\partial t} + \sum_{i=1}^{q} \underline{u}_q^{(i)} \cdot \frac{\partial}{\partial \underline{x}^{(i)}}$.

Now, by multiplying (109) before and after by
$\underline{P}^{(i)}$, and taking half the sum, one obtains

$$(112) \quad i\hbar \frac{\partial}{\partial t}\{\rho_q P^{(i)}\}(\underline{x},\underline{x}') + \frac{i\hbar}{m}\sum_{j=1}^{q}\left(\frac{\partial}{\partial \underline{x}^{(j)}} + \frac{\partial}{\partial \underline{x}^{(j)}{}'}\right) \cdot \{\{\rho_q P^{(j)}\}P^{(i)}\}(\underline{x},\underline{x}')$$

$$= \frac{1}{2}\sum_{j,k=1}^{q}(\phi^{(jk)} - \phi^{(jk)'})\{\rho_q P^{(i)}\}(\underline{x},\underline{x}') - \frac{i\hbar}{2}\sum_{j=1}^{q}\left(\frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} + \frac{\partial \phi^{(ij)'}}{\partial \underline{x}^{(i)}{}'}\right)\rho_q(\underline{x},\underline{x}')$$

$$+ \sum_{j=1}^{q}(\psi^{(j)} - \psi^{(j)'})\{\rho_q P^{(i)}\}(\underline{x},\underline{x}') + \frac{i\hbar}{2}(P^{(i)} + P^{(i)'})\rho_q(\underline{x},\underline{x}')$$

$$+ \sum_{j=1}^{q}\iint(\phi^{(jq+1)} - \phi^{(jq+1)'})\{\rho_{q+1}P^{(i)}\}(\underline{x},\underline{x}')\delta(\underline{x}^{(q+2)} - \underline{x}^{(q+1)'})d\underline{x}^{(q+1)}d\underline{x}^{(q+1)'}$$

$$- \frac{i\hbar}{2}\iint\left(\frac{\partial \phi^{(iq+1)}}{\partial \underline{x}^{(i)}} + \frac{\partial \phi^{(iq+1)'}}{\partial \underline{x}^{(i)}{}'}\right)\rho_{q+1}(\underline{x},\underline{x}')\delta(\underline{x}^{(q+1)} - \underline{x}^{(q+1)'})d\underline{x}^{(q+1)}d\underline{x}^{(q+1)'}.$$

Again writing $\underline{x} = \underline{x}'$, one is left with

$$(113) \quad \frac{\partial}{\partial t}(n_q \underline{u}_q^{(i)}) + \frac{1}{m^2}\sum_{j=1}^{q}\frac{\partial}{\partial \underline{x}^{(j)}} \cdot \{\{\rho_q P^{(j)}\}P^{(i)}\}(\underline{x},\underline{x}) = n_q \underline{\eta}_q^{(i)}$$

where

$$(114) \quad m\underline{\eta}_q^{(i)} = -\sum_{j=1}^{q}\frac{\partial \phi^{(j)}}{\partial \underline{x}^{(i)}} + \underline{P}^{(i)} - \int\frac{\partial \phi^{(iq+1)}}{\partial \underline{x}^{(i)}}\frac{n_{q+1}}{n_q}d\underline{x}^{(q+1)}$$

The same equation can be obtained by multiplying
the classical equation (26) by $\xi^{(i)}$ and integrating
over all the velocities, except that $\frac{1}{m^2}\{\{p_4 p^{(j)}\} p^{(i)}\}(x,x)$
is replaced by its classical analogue $\int\ldots\int f_4\,\xi^{(j)}\,\xi^{(i)}\prod_{k=1}^{q}d\xi^{(k)}$.
Thus the equation of motion, like the equation of
continuity, differs in quantum theory from the
classical equation only in the definition of the
quantites 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[28], 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_q , $\underline{u}_q^{(i)}$, $T_q^{(i)}$, 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 $\underline{u}_q^{(i)}$ substituted for $\underline{I}_q$, (113) may be rewritten in the form

$$(115) \qquad mn_q \frac{d}{dt} u_q^{(i)} + \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \cdot \underline{\underline{k}}_q^{(ji)} = mn_q \eta_q^{(i)},$$

where

$$(116) \qquad \underline{\underline{k}}_q^{(ji)} = m \left\{ \left\{ \rho_q \underline{v}_q^{(j)} \right\} \underline{v}_q^{(i)} \right\} (\underline{x}, \underline{x})$$

Further, on writing

$$(117) \qquad \underline{\underline{p}}_q^{(ij)} = \underline{\underline{k}}_q^{(ij)} + \underline{\underline{l}}_q^{(ij)},$$

where $\underline{\underline{l}}_q^{(ij)}$ is defined by the equation

$$(118) \qquad \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \cdot \underline{\underline{l}}_q^{(ji)} = n_q \sum_{j=1}^{q} \frac{\partial \phi^{(ij)}}{\partial x^{(i)}} + \int n_{q+1} \frac{\partial \phi^{(i,q+1)}}{\partial x^{(i)}} d\underline{x}^{(q+1)},$$

(115) assumes the form

$$(119) \qquad mn_q \frac{d}{dt} u_q^{(i)} + \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \cdot \underline{\underline{p}}_q^{(ji)} = n_q \underline{P}^{(i)}$$

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 $\underline{\underline{p}}_q^{(ij)}$ consists of two parts $\underline{\underline{k}}_q^{(ij)}$ and $\underline{\underline{l}}_q^{(ij)}$, of which the

first is due to the thermal motion of the molecules, and the second to the intermolecular forces. Only the kinetic part $\underline{\underline{k}}_q^{(ij)}$ of $\underline{\underline{p}}_q^{(ij)}$ is found in the kinetic theory of gases, and the validity of the theory rests on the circumstance that the potential part $\underline{\underline{l}}_q^{(ij)}$, which is roughly proportional to the square of the density, is small; in liquids, however, far from being small, the term $\underline{\underline{l}}_q^{(ij)}$ 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 $\underline{p}^{(i)}$, and afterwards write $\underline{x} = \underline{x}'$. The result is

(120)
$$\frac{\partial}{\partial t}\left(3n_q k T_q^{(i)} + mn_q \underline{u}_q^{(i)2}\right) + \frac{1}{m^3}\sum_{j=1}^{q}\frac{\partial}{\partial x^{(j)}}\cdot\left\{\left\{\left\{\rho_q \underline{p}^{(ij)}\right\}\underline{p}^{(i)}\right\}\cdot\underline{p}^{(i)}\right\}(\underline{x},\underline{x})$$
$$= -2\sum_{j=1}^{q}n_q\frac{\partial\phi^{(ij)}}{\partial x^{(i)}}\cdot\underline{u}_q^{(i)} + 2n_q\underline{p}^{(i)}\cdot\underline{u}_q^{(i)} - 2\int n_{q+1}\frac{\partial\phi^{(iq+1)}}{\partial x^{(i)}}\cdot\underline{u}_{q+1}^{(i)}d\underline{x}^{(q+1)},$$

since $\left\{\left\{\rho_q \underline{p}^{(i)}\right\}\cdot\underline{p}^{(i)}\right\}(\underline{x},\underline{x}) = m\left(3n_q k T_q^{(i)} + mn_q \underline{u}_q^{(i)2}\right)$.
With the help of equations (111) and (115), (120) is now transformed to

(121)
$$\frac{3}{2}n_q k\frac{dT_q^{(i)}}{dt} + \frac{1}{2m}\sum_{j=1}^{q}\frac{\partial}{\partial x^{(j)}}\cdot\left\{\left\{\left\{\rho_q \underline{v}_q^{(j)}\right\}\underline{p}^{(i)}\right\}\cdot\underline{p}^{(i)}\right\}(\underline{x},\underline{x})$$
$$= \underline{u}_q^{(i)}\cdot\sum_{j=1}^{q}\frac{\partial}{\partial x^{(j)}}\cdot\underline{\underline{k}}_q^{(ji)} - \int n_{q+1}\frac{\partial\phi^{(iq+1)}}{\partial x^{(i)}}\cdot\left(\underline{u}_{q+1}^{(i)} - \underline{u}_q^{(i)}\right)d\underline{x}^{(q+1)},$$

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

(122)
$$\frac{3}{2}n_q k\frac{dT_q^{(i)}}{dt} + \sum_{j=1}^{q}\left\{\frac{\partial}{\partial x^{(j)}}\cdot\underline{m}_q^{(ji)} + \left(\underline{\underline{k}}_q^{(ij)}\cdot\frac{\partial}{\partial x^{(j)}}\right)\cdot\underline{u}_q^{(i)}\right\}$$
$$= -\int n_{q+1}\frac{\partial\phi^{(iq+1)}}{\partial x^{(i)}}\cdot\left(\underline{u}_{q+1}^{(i)} - \underline{u}_q^{(i)}\right)d\underline{x}^{(q+1)},$$

where

(123) $\underline{m}_q^{(ji)} = m\{\{\{\rho_q \underline{v}_q^{(j)}\} \underline{v}_q^{(i)}\} \cdot \underline{v}_q^{(i)}\} (\underline{x}, \underline{x}).$

An equation formally identical with (122) may be obtained from the classical equation (26) by multiplying by $\underline{\xi}^{(i)2}$, 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 $\frac{3}{2} k T_q^{(i)}$. To obtain a similar equation for the potential energy, it must first be localised by sharing the potential energy $\phi^{(ij)}$ equally between the two molecules (i) and (j). Then, substituting the energy of one molecule

(124) $T_q^{(i)} = \frac{1}{2} \sum_{j=1}^{q} \phi^{(ij)} + \frac{1}{2} \int \phi^{(iq+1)} \frac{n_{q+1}}{n_q} d\underline{x}^{(q+1)}$

in the formula (111), one obtains

(125) $n_q \frac{dT_q^{(i)}}{dt} = \frac{\partial}{\partial t} \{\frac{1}{2} n_q \sum_{j=1}^{q} \phi^{(ij)} + \frac{1}{2} \int n_{q+1} \phi^{(iq+1)} d\underline{x}^{(q+1)}\} + \sum_{j=1}^{q} \frac{\partial}{\partial \underline{x}^{(j)}} \cdot (n_q T_q^{(i)} \underline{u}_q^{(j)}).$

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

(126) $n_q \frac{dT_q^{(i)}}{dt} + \sum_{j=1}^{q} \frac{\partial}{\partial \underline{x}^{(j)}} \cdot \{\frac{1}{2} \int n_{q+1} \phi^{(iq+1)} (\underline{u}_{q+1}^{(j)} - \underline{u}_q^{(j)}) d\underline{x}^{(q+1)}\}$

$= -\frac{1}{2} n_q \sum_{j=1}^{q} (\underline{u}_q^{(j)} - \underline{u}_q^{(i)}) \cdot \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} - \frac{1}{2} \int n_{q+1} (\underline{u}_{q+1}^{(q+1)} - \underline{u}_{q+1}^{(i)}) \cdot \frac{\partial \phi^{(iq+1)}}{\partial \underline{x}^{(i)}} d\underline{x}^{(q+1)},$

which may be rewritten in the form

$$(127) \qquad n_q \frac{d \underline{I}_q^{(i)}}{dt} + \sum_{j=1}^{q} \frac{\partial}{\partial \underline{x}^{(j)}} \cdot \underline{n}_q^{(ji)} = \int n_{q+1} \frac{\partial \phi^{(i,q+1)}}{\partial \underline{x}^{(i)}} \cdot (\underline{u}_{q+1}^{(i)} - \underline{u}_q^{(i)}) d \underline{x}^{(q+1)},$$

where $\underline{n}_q^{(ji)}$ is defined as the solution of the equation

$$(128) \qquad \begin{aligned} \sum_{j=1}^{q} \frac{\partial}{\partial \underline{x}^{(j)}} \cdot \underline{n}_q^{(ji)} &= \sum_{j=1}^{q} \frac{\partial}{\partial \underline{x}^{(j)}} \cdot \left\{ \frac{1}{2} \int n_{q+1} \, \phi^{(i,q+1)} (\underline{u}_{q+1}^{(j)} - \underline{u}_q^{(j)}) \, d\underline{x}^{(q+1)} \right\} \\ &\quad + \frac{1}{2} n_q \sum_{j=1}^{q} (\underline{u}_q^{(j)} - \underline{u}_q^{(i)}) + \frac{1}{2} \int n_{q+1} (\underline{u}_{q+1}^{(q+1)} + \underline{u}_{q+1}^{(i)} - 2\underline{u}_q^{(i)}) \cdot \frac{\partial \phi^{(i,q+1)}}{\partial \underline{x}^{(i)}} d\underline{x}^{(q+1)}. \end{aligned}$$

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

$$(129) \qquad n_q \frac{d \underline{U}_q^{(i)}}{dt} + \sum_{j=1}^{q} \left\{ \frac{\partial}{\partial \underline{x}^{(j)}} \cdot \underline{q}_q^{(ji)} + \left(\underline{\underline{k}}_q^{(ij)} \cdot \frac{\partial}{\partial \underline{x}^{(j)}} \right) \cdot \underline{u}_q^{(i)} \right\} = 0,$$

where

$$(130) \qquad U_q^{(i)} = \frac{3}{2} k T_q^{(i)} + I_q^{(i)}$$

and

$$(131) \qquad \underline{q}_q^{(ij)} = \underline{m}_q^{(ij)} + \underline{n}_q^{(ij)}.$$

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

$$(132) \qquad \frac{1}{2} m n_q \frac{d}{dt} \underline{u}_q^{(i)2} + \underline{u}_q^{(i)} \cdot \sum_{j=1}^{q} \frac{\partial}{\partial \underline{x}^{(j)}} \cdot \underline{\underline{P}}_q^{(ji)} = n_q \underline{u}_q^{(i)} \cdot \underline{P}^{(i)},$$

which is the equation satisfied by the 'visible' energy $\frac{1}{2} m \underline{u}_q^{(i)2}$, obtained by multiplying (119)

with $\underline{u}_q^{(i)}$. The terms $\sum_{j=1}^{q} (\underline{k}_q^{(ij)} \cdot \frac{\partial}{\partial x^{(j)}}) \cdot \underline{u}_q^{(i)}$ and $\underline{u}_q^{(i)} \cdot \sum_{j=1}^{q} \frac{\partial}{\partial x^{(j)}} \cdot \underline{P}_q^{(ji)}$ 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 $q_q^{(ji)}$ 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 ρ_N 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 $n_1^{(i)}$, $T_1^{(i)}$, $\underline{u}_1^{(i)}$, and $\underline{P}^{(i)}$
throughout the fluid, one may, at least for quite a
large volume, specify these quantities, together with
their space gradients $\frac{\partial n_1}{\partial x}$, $\frac{\partial^2 n_1}{\partial x \partial x}$, $\frac{\partial^3 n_1}{\partial x \partial x \partial x}$, $\ldots$
$\frac{\partial T_1}{\partial x}$, $\ldots$ 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_0 , as the rates of change
$\frac{\partial n_1}{\partial t}$, $\frac{\partial T_1}{\partial t}$, $\ldots$ of the others are given by the
hydrodynamical equations of the previous section.

Accordingly it will be assumed that

$$(133) \qquad \rho_q(\underline{x},\underline{x}') = P_q\left(\underline{x},\underline{x}', \omega_k, \frac{\partial \omega_k}{\partial x_q}, \frac{\partial^2 \omega_k}{\partial x_q \partial x_q}, \ldots\right)$$

where the ω_k ($k = 1 \cdots 8$) represent the values
n_1 , T_1 , $\underline{u}_1$ and $\underline{P}$ assumed by $n_1^{(i)}$, $T_1^{(i)}$, $\underline{u}_1^{(i)}$ and
$\underline{P}^{(i)}$ at some point $\underline{x}_q$ in the part of the fluid
considered, and that the variation of ρ_q with t
and $\underline{x}_q$ is accounted for by the variation of the ω_k
and their space derivatives. For purposes of
symmetry, $\underline{x}_q$ is most conveniently chosen to be
the mean centre of the points $\underline{x}^{(i)}$ and $\underline{x}^{(iv)}$, thus:

$$(134) \qquad \underline{x}_q = \frac{1}{2q} \sum_{i=1}^{q} \left(\underline{x}^{(i)} + \underline{x}^{(i)\prime} \right)$$

The difference between ρ_q and P_q is, that while ρ_q is explicitly a function of the independent variables $\underline{x}^{(i)}$, $\underline{x}^{(i)\prime}$ and t, P_q is explicitly a function of $\underline{x}^{(i)}$, $\underline{x}^{(i)\prime}$, ω_k, $\frac{\partial \omega_k}{\partial x_q}$, ... , and only implicitly a function of t and $\underline{x}_q$. It follows that

$$(135) \quad \begin{aligned} \frac{\partial \rho_q}{\partial t} &= \sum_k \left\{ \frac{\partial P_q}{\partial \omega_k} \frac{\partial \omega_k}{\partial t} + \frac{\partial P_q}{\partial \left(\frac{\partial \omega_k}{\partial x_q} \right)} \cdot \frac{\partial^2 \omega_k}{\partial x_q \partial t} + \cdots \right\} \\ \frac{\partial \rho_q}{\partial \underline{x}^{(i)}} &= \frac{\partial P_q}{\partial x^{(i)}} + \frac{1}{2q} \sum_k \left\{ \frac{\partial P_q}{\partial \omega_k} \frac{\partial \omega_k}{\partial x_q} + \frac{\partial P_q}{\partial \left(\frac{\partial \omega_k}{\partial x_q} \right)} \cdot \frac{\partial^2 \omega_k}{\partial x_q \partial x_q} + \cdots \right\} \end{aligned}$$

From the definitions of n_q, $\underline{u}_q^{(i)}$, $T_q^{(i)}$, $P_{=q}^{(ij)}$, $\underline{q}_q^{(ij)}$, etc., it follows that they also may be expressed in terms of the ω_k and their space derivatives; for example, by putting $\underline{x}^{(i)} = \underline{x}^{(i)\prime}$ in (133) one obtains $n_q = N_q \left(\underline{x}, \omega_k, \frac{\partial \omega_k}{\partial x_q}, \cdots \right)$, and, more generally, if c_q represents any of the quantities enumerated,

$$(136) \qquad c_q = C_q \left(\underline{x}, \omega_k, \frac{\partial \omega_k}{\partial x_q}, \cdots \right)$$

the large letter always replacing the small to denote explicit dependence on the ω_k, $\frac{\partial \omega_k}{\partial x_q}$, ... Corresponding to (135), one has

$$(137) \quad \begin{aligned} \frac{\partial c_q}{\partial t} &= \sum_k \left\{ \frac{\partial C_q}{\partial \omega_k} \frac{\partial \omega_k}{\partial t} + \frac{\partial C_q}{\partial \left(\frac{\partial \omega_k}{\partial x_q} \right)} \cdot \frac{\partial^2 \omega_k}{\partial x_q \partial t} + \cdots \right\} \\ \frac{\partial c_q}{\partial \underline{x}^{(i)}} &= \frac{\partial C_q}{\partial x^{(i)}} + \frac{1}{q} \sum_k \left\{ \frac{\partial C_q}{\partial \omega_k} \frac{\partial \omega_k}{\partial x_q} + \frac{\partial C_q}{\partial \left(\frac{\partial \omega_k}{\partial x_q} \right)} \cdot \frac{\partial^2 \omega_k}{\partial x_q \partial x_q} + \cdots \right\} . \end{aligned}$$

In a displacement of the centre of gravity

$$\underline{x}_q = \frac{1}{q} \sum_{i=1}^{q} \underline{x}^{(i)} \, , \quad C_q \text{ is altered only on account of}$$

the variation in the ω_q ; hence

$$(138) \qquad \sum_{i=1}^{q} \frac{\partial C_q}{\partial x^{(i)}} = 0$$

The form of (137) suggests the utility of an expansion of all variables in powers of $\frac{\partial \omega_k}{\partial x_q}$, $\frac{\partial^2 \omega_k}{\partial x_q \partial x_q}$, ... , in the form $c_q = c_q^o + c_q' + c_q'' + \cdots$, where

$$(139) \qquad
\begin{aligned}
c_q^o &= C^o(\underline{x}, \omega_k), \\
c_q' &= \sum_k \frac{\partial \omega_k}{\partial x_q} \cdot \underline{C}_k'(\underline{x}, \omega_k), \\
c_q'' &= \sum_k \frac{\partial^2 \omega_k}{\partial x_q \partial x_q} : \underline{C}_k''(\underline{x}, \omega_k) + \sum_{k,\ell} \left(\frac{\partial \omega_k}{\partial x_q} \frac{\partial \omega_\ell}{\partial x_q} \right) : \underline{C}_{k\ell}''(\underline{x}, \omega_k),
\end{aligned}$$

and, quite generally, $c^{(r)}$ consists of terms involving just r derivatives of the ω_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

$$(140) \qquad
\begin{aligned}
\frac{\partial n_1}{\partial t} &= - \frac{\partial}{\partial x_q} \cdot (n_1 \underline{u}_1), \\
\frac{\partial}{\partial t} \underline{u}_1 &= - \underline{u}_1 \cdot \frac{\partial}{\partial x_q} \underline{u}_1 - \frac{1}{m n_1} \frac{\partial}{\partial x_q} \cdot \underline{P}_1 + \frac{1}{m} \underline{P}, \\
\frac{3}{2} n_1 k \frac{\partial T_1}{\partial t} &= - \frac{3}{2} n_1 k \underline{u}_1 \cdot \frac{\partial T_1}{\partial x_q} - \frac{\partial}{\partial x_q} \cdot \underline{m}_1 - \left(\underline{k}_1 \cdot \frac{\partial}{\partial x_q} \right) \cdot \underline{u}_1 - \int \frac{\partial \phi}{\partial x^{(1)}} \cdot (\underline{u}_2^{(1)} - \underline{u}_1) n_2 d\underline{x}^{(2)}.
\end{aligned}$$

Care is necessary in the expansion of integrals like $\int \frac{\partial \phi^{(i, q+1)}}{\partial x^{(i)}} c_{q+1} d\underline{x}^{(q+1)}$ to take account of the fact that the values of ω_k, $\frac{\partial \omega_k}{\partial x_{q+1}}$, ... appearing in

C_{q+1} are initially those at the centre of gravity

$$\underline{x}_{q+1} = \frac{1}{q+1} \sum_{i=1}^{q+1} \underline{x}^{(i)}$$ of $q+1$ molecules, whereas

the expansion procedure refers always to values at the
point $\underline{x}_q$. Thus, in expansion, C_{q+1} must first be
replaced by

$$C_{q+1} + \underline{d} \cdot \frac{\partial C_{q+1}}{\partial \underline{x}_q} + \frac{1}{2} (\underline{d}\,\underline{d}) : \frac{\partial C_{q+1}}{\partial \underline{x}_q \partial \underline{x}_q}$$

where the displacement $\underline{d}$ of the centre of gravity is

$$(141) \qquad \underline{d} = \underline{x}_{q+1} - \underline{x}_q = \frac{1}{q(q+1)} \sum_{i=1}^{q} \left(\underline{x}^{(q+1)} - \underline{x}^{(i)} \right),$$

and $\frac{\partial}{\partial \underline{x}_q}$ has the significance

$$\sum_k \left\{ \frac{\partial \omega_k}{\partial \underline{x}_q} \frac{\partial}{\partial \omega_k} + \frac{\partial^2 \omega_k}{\partial \underline{x}_q \partial \underline{x}_q} \cdot \frac{\partial}{\partial \left(\frac{\partial \omega_k}{\partial \underline{x}_q} \right)} + \cdots \right\}$$

Hence

$$(142) \qquad \int \frac{\partial \phi^{(i; q+1)}}{\partial \underline{x}^{(i)}} C_{q+1} \, d\underline{x}^{(q+1)} = \int \frac{\partial \phi^{(i; q+1)}}{\partial \underline{x}^{(i)}} \left\{ C_{q+1} + \underline{d} \cdot \frac{\partial C_{q+1}}{\partial \underline{x}_q} + \cdots \right\} d\underline{x}^{(q+1)}.$$

When ρ_q° , ρ_q' , ρ_q'' , ... are known, it is
easy to calculate the c° , c' , c'' , ...
explicitly; for example,

$$(143) \qquad \begin{aligned} n_q^{\circ}(\underline{x}) &= \rho_q^{\circ}(\underline{x}, \underline{x}), \\ n_q'(\underline{x}) &= \rho_q'(\underline{x}, \underline{x}) ; \end{aligned}$$

$$(144) \qquad \begin{aligned} \underline{u}_q^{(i)0}(\underline{x}) &= \frac{1}{m\, n_q^{\circ}(\underline{x})} \{ \rho_q^{\circ} \, \underline{p}^{(i)} \}(\underline{x}, \underline{x}), & \underline{v}_q^{(i)0} &= \frac{1}{m} \underline{p}^{(i)} - \underline{u}_q^{(i)0}, \\ \underline{u}_q^{(i)'}(\underline{x}) &= \frac{1}{n_q^{\circ}(\underline{x})} \{ \rho_q' \, \underline{v}_q^{(i)0} \}(\underline{x}, \underline{x}), & \underline{v}_q^{(i)'} &= - \underline{u}_q^{(i)'} ; \end{aligned}$$

$$(145) \quad T_q^{(i)0}(\underline{x}) = \frac{m}{3kn_q^o(\underline{x})} \{\{\rho_q^o \, \underline{v}_q^{(i)0}\} \cdot \underline{v}_q^{(i)0}\} (\underline{x},\underline{x}),$$

$$T_q^{(i)'}(\underline{x}) = \frac{m}{3kn_q^o(\underline{x})} \big[\{\{\rho_q' \, \underline{v}_q^{(i)0}\} \underline{v}_q^{(i)0}\} - \frac{3kT_q^{(i)0}}{m} \rho_q'\big](\underline{x},\underline{x});$$

$$(146) \quad \underline{\underline{k}}_q^{(ij)0}(\underline{x}) = m \{\{\{\rho_q^o \, \underline{v}_q^{(i)0}\} \, \underline{v}_q^{(j)0}\}(\underline{x},\underline{x}),$$

$$\underline{\underline{k}}_q^{(ij)'}(\underline{x}) = m \{\{\{\rho_q' \, \underline{v}_q^{(i)0}\} \, \underline{v}_q^{(j)0}\}(\underline{x},\underline{x});$$

$$(147) \quad \underline{m}_q^{(ij)0}(\underline{x}) = \tfrac{1}{2} m \{\{\{\{\rho_q^o \, \underline{v}_q^{(i)0}\} \, \underline{v}_q^{(j)0}\} \cdot \underline{v}_q^{(j)0}\}(\underline{x},\underline{x})$$

$$\underline{m}_q^{(ij)'}(\underline{x}) = \tfrac{1}{2} m \big[\{\{\{\rho_q' \, \underline{v}_q^{(i)0}\} \, \underline{v}_q^{(j)0}\} \cdot \underline{v}_q^{(j)0}\} - \frac{(3+2\delta_{ij})kT_q^{(i)0}}{m}\{\rho_q' \, \underline{v}_q^{(i)0}\}\big](\underline{x},\underline{x});$$

$$(148) \quad m\eta_q^{(i)0} = -\sum_{j=1}^{q} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} - \int \frac{\partial \phi^{(i:q+1)}}{\partial \underline{x}^{(i)}} \frac{N_{q+1}^o}{N_q^o} d\underline{x}^{(q+1)} + \underline{P},$$

$$m\eta_q^{(i)'} = -\int \frac{\partial \phi^{(i:q+1)}}{\partial \underline{x}^{(i)}} \Big(\frac{N_{q+1}}{N_q}\Big)' d\underline{x}^{(q+1)} - \frac{1}{N_q^o} \int \frac{\partial \phi^{(i:q+1)}}{\partial \underline{x}^{(i)}} \underline{d} \cdot \frac{\partial N_{q+1}^o}{\partial \underline{x}_q} d\underline{x}^{(q+1)}$$
$$+ (\underline{x}^{(i)} - \underline{x}_q) \cdot \frac{\partial}{\partial \underline{x}_q} \underline{P}.$$

3. The Zero-Order Solution and Condensation

To determine ρ_q^o, one requires to observe only
that it may be obtained from ρ_q simply by writing
$\frac{\partial \omega_k}{\partial x_q} = \frac{\partial^2 \omega_k}{\partial x_q \partial x_q} = \cdots = 0$, which is the same as
postulating a state of equilibrium in which the
density, temperature, etc., have uniformly the
values assumed at $\underline{x}_q$. What is needed, therefore,
is that equilibrium solution which makes

$$(149) \quad \begin{aligned} X_1 (\rho, \underline{v}_1^{(i)}) &= 0, \\ X_1 (\rho, \underline{v}_1^{(i)2}) &= 3m^{-1} NkT_1 . \end{aligned}$$

To satisfy the first of these conditions, one need
only replace $\underline{p}^{(i)}$ by $\underline{p}^{(i)} - \frac{1}{m}\underline{u}_i$ in the solution of

Ch. 2, §3; the second condition may then be regarded as giving the relation between T_1 and the thermodynamic temperature T. In classical theory, T_1 and T are identical, but in quantum theory, to satisfy the uncertainty principle, T_1, 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_1 and n_1, given implicitly by (149).

In principle, the c^0 are now all determinate with the help of (143) – (148). It is, however, clear from considerations of symmetry alone that $\underline{\underline{k}}_1^{(11)0}(\underline{x}^{(1)})$ and $\underline{\underline{m}}_1^{(11)0}(\underline{x}^{(1)})$ must remain unchanged on reversing the sign of $\underline{v}_1^{(1)0}$ in the formulae (146) and (147), so that

$$(150) \quad \begin{aligned} \underline{\underline{k}}_1^{(11)0} &= n_1 k T_1 \, \underline{\underline{1}} \, , \\ \underline{\underline{m}}_1^{(11)0} &= 0 \, , \end{aligned}$$

where $\underline{\underline{1}}$ denotes the unit tensor. Also, $n_1^0 = n_1$, $\underline{u}_1^{(1)0} = \underline{u}_1$, and $T_1^{(1)0} = T_1$, so that $n_1' = \underline{u}_1^{(1)'} = T_1^{(1)'} = 0$ and $n_1'' = \underline{u}_1^{(1)''} = T_1^{(1)''} = 0$, 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 ρ_q^0 by $f_q^0 = n_q^0 \left(\frac{2\pi k T}{m} \right)^{\frac{3}{2}} \exp\left\{ -\frac{1}{2} m \sum_{i=1}^{q} (\underline{\xi}^{(i)} - \underline{u}_1)^2 \right\}$ and $\int d\underline{x}^{(i)\prime} \, \delta(\underline{x}^{(i)} - \underline{x}^{(i)\prime})$ by $\int d\underline{\xi}^{(i)}$, one obtains

$$\begin{aligned} \underline{u}_q^{(i)0} &= \underline{u}_1 \, ; \quad \underline{v}_q^{(i)0} = \underline{v}_1^{(i)} = \underline{\xi}^{(i)} - \underline{u}_1 \, ; \\ (151) \quad T_q^{(i)0} &= T_1 \, ; \quad \underline{\underline{k}}_q^{(ij)0} = n_q^0 k T_1 \delta_{ij} \, \underline{\underline{1}} \, ; \quad \underline{\underline{m}}_q^{(ij)0} = 0 \, . \end{aligned}$$

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

$$(152)\quad \left(\frac{\partial c_q}{\partial t}\right)^o = \frac{1}{m}\,\underline{P}\cdot\frac{\partial C_q^o}{\partial u_1} - \frac{2}{3km_1}\int\frac{\partial\phi}{\partial x^{(1)}}\cdot(\underline{U}_2^{(1)o}-\underline{u}_1)N_2^o\,d\underline{x}^{(2)}\frac{\partial C_q}{\partial T_1} + \underline{\dot{P}}\cdot\frac{\partial C_q^o}{\partial P}$$

and

$$(153)\quad \left(\frac{\partial c_q}{\partial t}\right)' = \frac{1}{m}\,\underline{P}\cdot\frac{\partial C_q'}{\partial u_1} - \frac{2}{3km_1}\int\frac{\partial\phi}{\partial x^{(1)}}\cdot(\underline{U}_2^{(1)o}-\underline{u}_1)N_2^o\,d\underline{x}^{(2)}\frac{\chi_q'}{\partial T_1} + \underline{\dot{P}}\cdot\frac{\partial C_q'}{\partial P}$$
$$-\frac{\partial}{\partial x_q}\cdot(n_1\underline{u}_1)\frac{\partial C_q^o}{m_1} - \left(\underline{u}_1\cdot\frac{\partial}{\partial x_q}\underline{u}_1 + \frac{1}{mn_1}\frac{\partial}{\partial x_q}\cdot\underline{P}_1\right)\cdot\frac{\partial C_q^o}{\partial u_1}$$
$$-\left[\underline{u}_1\cdot\frac{\partial T_1}{\partial x_q} + \frac{2}{3}T_1\frac{\partial}{\partial x_q}\cdot\underline{u}_1 + \frac{2}{3km_1}\int\frac{\partial\phi}{\partial x^{(1)}}\cdot\{(\underline{U}_2^{(1)o}-\underline{u}_1)N_2' + \underline{U}_2^{(1)'}N_2^o\}\,d\underline{x}^{(2)}\right]\frac{\partial C_q^o}{\partial T_1}.$$

In the particular cases $c_q = n_q,\ \underline{u}_q^{(i)},\ T_q^{(i)}$, these formulae may be compared with those obtained directly from the hydrodynamical equations, with the help of (137) and (138); for example,

$$(154)\quad \left(\frac{m_q}{\partial t}\right)^o = -\sum_{i=1}^q \frac{\partial}{\partial x^{(i)}}\cdot(N_q\underline{U}_q^{(i)})^o\ ;$$

$$(155)\quad \left(\frac{m_q}{\partial t}\right)' = -\sum_{i=1}^q \frac{\partial}{\partial x^{(i)}}\cdot(N_q\underline{U}_q^{(i)})' - \frac{1}{q}\frac{\partial}{\partial x_q}\cdot\left(\sum_{i=1}^q N_q\underline{U}_q^{(i)}\right)^o.$$

It is obvious that N_q cannot depend on the particular inertial system of reference, and is therefore independent of $\underline{u}_1$ and $\underline{P}^{(i)o}=\underline{P}$. Further comparison of (152) and (154) yields

$$(156)\quad \frac{3}{2}kn_1\sum_{i=1}^q \frac{\partial}{\partial x^{(i)}}\cdot(N_q\underline{U}_q^{(i)})^o = \int\frac{\partial\phi}{\partial x^{(1)}}\cdot(\underline{U}_2^{(1)o}-\underline{u}_1)N_2^o\,d\underline{x}^{(2)}\frac{\partial N_q^o}{\partial T_1}.$$

The form of $\underline{U}_2^{(1)o}$ can be decided on general grounds: it must be linear in $\underline{u}_1$, can contain in addition only $\underline{r} = \underline{x}^{(2)} - \underline{x}^{(1)}$, n_1, and T_1, and, besides (156), must satisfy $\int N_2^o \, \underline{U}_2^{(1)o} d\underline{r} = (N-1) n_1 \underline{u}_1$; hence one may write

$$(157) \qquad \underline{U}_2^{(1)o} = \underline{U}_2^{(2)o} = \underline{u}_1 + \varpi \left(\underline{u}_1 \cdot \underline{r} \; \underline{r} - \tfrac{1}{3} r^2 \underline{u}_1 \right),$$

where ϖ contains only r, n_1, and T_1. $\underline{U}_2^{(2)o}$ is obtained from $\underline{U}_2^{(1)o}$ by substituting $-\underline{r}$ for $\underline{r}$ (interchange of $\underline{x}^{(1)}$ and $\underline{x}^{(2)}$). For all q, the right-hand side of (156) now vanishes, because the integrand is an odd function of $\underline{r}$; thus one obtains, as might be expected, $\frac{\partial n_q}{\partial t} = 0$, in the zero-order, equilibrium, approximation. This follows even more easily in the classical theory, valid at high temperatures, where $\varpi = 0$.

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

$$(158) \quad
\begin{aligned}
&\frac{\partial}{\partial \underline{r}} \cdot \left\{ N_2 \left(\underline{U}_2^{(2)} - \underline{U}_2^{(1)} \right) \right\}' - \frac{1}{3k n_1} \frac{\partial N_2^o}{\partial T_1} \int \left\{ N_2 \left(\underline{U}_2^{(2)} - \underline{U}_2^{(1)} \right) \right\}' \cdot \frac{\partial \phi}{\partial \underline{r}} \, d\underline{r} \\
&= \frac{\partial}{\partial \underline{x}_2} \cdot (n_1 \underline{u}_1) \frac{\partial N_2^o}{\partial n_1} - \left(\underline{u}_1 \cdot \frac{\partial T_1}{\partial \underline{x}_2} + \tfrac{2}{3} T_1 \frac{\partial}{\partial \underline{x}_2} \cdot \underline{u}_1 \right) \frac{\partial N_2^o}{\partial T_1} - \tfrac{1}{2} \frac{\partial}{\partial \underline{x}_2} \cdot \left\{ N_2 \left(\underline{U}_2^{(1)} + \underline{U}_2^{(2)} \right) \right\}^o,
\end{aligned}$$

since N_2 and $\underline{U}_2^{(2)} - \underline{U}_2^{(1)}$ contain $\underline{x}^{(1)}$ and $\underline{x}^{(2)}$ explicitly only in the combination $\underline{r} = \underline{x}^{(2)} - \underline{x}^{(1)}$. This equation may be regarded as an integral equation to determine the non-rotational part of $\left\{ N_2 \left(\underline{U}_2^{(2)} - \underline{U}_2^{(1)} \right) \right\}'$; the solution is

$$(159) \quad \left\{N_2\left(\underline{v}_2^{(2)}-\underline{v}_2^{(1)}\right)\right\}' = r/r^3 \int_0^r \left\{R(r)-\frac{\int R\phi\, d\underline{r}}{3kn_1+\int\frac{\partial N_2^0}{\partial T_1}\phi\, d\underline{r}}\,\frac{\partial N_2^0(r)}{\partial T_1}\right\}r^2\,dr + \underline{v}$$

where R , standing for the right-hand side of (158),
reduces in classical theory to $\left(m\frac{\partial N_2^0}{\partial n_1}-N_2^0+\frac{2}{3}T_1\frac{\partial N_2^0}{\partial T_1}\right)\frac{\partial}{\partial x_2}\cdot\underline{u}_1$,
and $\underline{v}$ satisfies $\frac{\partial}{\partial r}\cdot\underline{v}=0$.

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

$$(160) \quad \frac{\partial}{\partial T_1}\int\frac{N_2^0}{n_1}\phi\, d\underline{r} = -3k$$

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 super-
heating 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 ρ_1', n_2', $(n_2\underline{u}_2^{(1)})'$, etc. from the general

equations is a difficult matter, their form may be deduced quite easily from elementary considerations. For example, $P_i' = P_i'\left(\underline{x}^{(1)}, \underline{x}^{(1)\prime}, \omega_k, \frac{\partial \omega_k}{\partial x_i}\right)$, as well as being linear and homogeneous in the $\frac{\partial \omega_k}{\partial x_i}$, can contain $\underline{x}^{(1)}$ and $\underline{x}^{(1)\prime}$ only in the combination $\underline{y} = \underline{x}^{(1)\prime} - \underline{x}^{(1)}$, the variation with $\underline{x}_i = \frac{1}{2}(\underline{x}^{(1)} + \underline{x}^{(1)\prime})$ being contained in the ω_k.

For brevity, the notation

$$\underline{a} = \frac{\partial T_1}{\partial x_q}, \quad \underline{a}^+ = \frac{\partial n_1}{\partial x_q}; \quad b = \frac{\partial}{\partial x_q} \cdot \underline{u}_1, \quad b^+ = \frac{\partial}{\partial x_q} \cdot \underline{P};$$

(161)
$$\underline{\underline{b}} = \frac{1}{2}\left(\frac{\partial}{\partial x_q} \underline{u}_1 + \overline{\frac{\partial}{\partial x_q} \underline{u}_1} - \frac{2}{3}\frac{\partial}{\partial x_q} \cdot \underline{u}_1 \underline{\underline{1}}\right),$$

$$\underline{\underline{b}}^+ = \frac{1}{2}\left(\frac{\partial}{\partial x_q} \underline{P} + \overline{\frac{\partial}{\partial x_q} \underline{P}} - \frac{2}{3}\frac{\partial}{\partial x_q} \cdot \underline{P}\, \underline{\underline{1}}\right)$$

is introduced. P_i' can contain, besides the a's and b's, only n_1, T_1, and $\underline{y}$, and satisfies $[P_i']_{y=0} = n_i' = 0$, $\left[\frac{i\hbar}{m}\frac{\partial P_i'}{\partial y}\right]_{y=0} = (n_1 u_1)' = 0$ and $\left[\left(\frac{i\hbar}{m}\frac{\partial}{\partial y} - \underline{u}_1\right)^2 P_i'\right]_{y=0} = 3mk(n_1 T_1)' = 0$ identically; hence it must have the form

(162)
$$P_i' = \iota \epsilon_1 \underline{y} \cdot \underline{a} + \iota \epsilon_1^+ \underline{y} \cdot \underline{a}^+ + \epsilon_2 \underline{y} \cdot \underline{\underline{b}} \cdot \underline{y} + \epsilon_2^+ \underline{y} \cdot \underline{\underline{b}}^+ \cdot \underline{y},$$

where ϵ_1, ϵ_1^+, ϵ_2, and ϵ_2^+ contain only n_1, T_1, and $y = |\underline{y}|$. If ϵ_1 and ϵ_2 are expanded as power series in y, one must have $\epsilon_1(y) = \epsilon_1''(0)\frac{y^2}{2!} + \epsilon_1'''(0)\frac{y^3}{3!} + \cdots$ and $\epsilon_2(y) = \epsilon_2(0) + \epsilon_2'(0)\frac{y}{1!} + \cdots$. When P_i' (and P_i^0) are transformed to the momentum representation, they become diagonal, containing a factor $\delta(\underline{p}^{(1)}, \underline{p}^{(1)\prime})$ — 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, T_1, and $\underline{r} = \underline{x}^{(2)} - \underline{x}^{(1)}$; it is unaltered on replacing $\underline{r}$ by $-\underline{r}$ (interchange of $\underline{x}^{(1)}$ and $\underline{x}^{(2)}$); and satisfies $\int N_2' d\underline{r} = (N-1)N_1' = c$; hence it must have the form

$$(163) \qquad N_2' = \nu\, \underline{r} \cdot \underline{\underline{b}} \cdot \underline{r} + \nu^+ \underline{r} \cdot \underline{\underline{b}}^+ \cdot \underline{r},$$

where ν and ν^+ contain only n_1, T_1, and $r = |\underline{r}|$.

$N_2^o(\underline{u}_2^{(1)\prime} + \underline{u}_2^{(2)\prime})$ is linear in the a's and b's; can contain besides only n_1, T_1, and $\underline{r}$; it is unaltered on replacing $\underline{r}$ by $-\underline{r}$; and satisfies $\int N_2^o(\underline{u}_2^{(1)\prime} + \underline{u}_2^{(2)\prime}) d\underline{r} = 2(N-1)\underline{u}_1' = 0$; hence

$$(164) \qquad N_2^o(\underline{u}_2^{(1)\prime} + \underline{u}_2^{(2)\prime}) = \kappa(\underline{a} \cdot \underline{r}\,\underline{r} - \tfrac{1}{3}r^2\underline{a}) + \kappa^+(\underline{a}^+ \cdot \underline{r}\,\underline{r} - \tfrac{1}{3}r^2\underline{a}^+),$$

where κ and κ^+ contain only n_1, T_1, and r.

Finally, $N_2^o(\underline{u}_2^{(2)\prime} - \underline{u}_2^{(1)\prime})$ is linear in the a's and b's; can contain besides only n_1, T_1, and $\underline{r}$; changes sign on replacing $\underline{r}$ by $-\underline{r}$, and satisfies $\int N_2^o(\underline{u}_2^{(2)\prime} - \underline{u}_2^{(1)\prime}) d\underline{r} = 0$; hence

$$(165) \qquad \begin{aligned} N_2^o(\underline{u}_2^{(2)\prime} - \underline{u}_2^{(1)\prime}) &= \upsilon_o b\underline{r} + \upsilon_2\, \underline{r} \cdot \underline{\underline{b}} \cdot \underline{r}\,\underline{r} + \overline{\upsilon_2}\, r^2 \underline{\underline{b}} \cdot \underline{r} \\ &\quad + \upsilon_o^+ b^+\underline{r} + \upsilon_2^+ \underline{r} \cdot \underline{\underline{b}}^+ \cdot \underline{r}\,\underline{r} + \overline{\upsilon_2}^+ r^2 \underline{\underline{b}} \cdot \underline{r} \end{aligned}$$

where υ_o, υ_2, $\overline{\upsilon_2}$, υ_o^+, υ_2^+, and $\overline{\upsilon_2}^+$ are functions of n_1, T_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 $\underline{\underline{l}}_1$ of the pressure tensor due to the inter-molecular forces is given by

$$(166) \qquad \frac{\partial}{\partial \underline{x}^{(1)}} \cdot \underline{\underline{l}}_1 = - \int n_2 \frac{\partial \phi}{\partial r} \, d\underline{x}^{(2)} .$$

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

$$(167) \qquad \frac{\partial}{\partial \underline{x}_1} \cdot \underline{\underline{l}}_1^\circ = - \frac{\partial}{\partial \underline{x}_1} \cdot \int \tfrac{1}{2} \underline{r} \, N_2^\circ \frac{\partial \phi}{\partial r} \, d\underline{r} ,$$

$$(168) \qquad \frac{\partial}{\partial \underline{x}_1} \cdot \underline{\underline{l}}_1' = - \frac{\partial}{\partial \underline{x}_1} \cdot \int \tfrac{1}{2} \underline{r} \, N_2' \frac{\partial \phi}{\partial r} \, d\underline{r} ,$$

$$(169) \quad \frac{\partial}{\partial \underline{x}_1} \cdot \underline{\underline{l}}_1'' = - \frac{\partial}{\partial \underline{x}_1} \cdot \int \tfrac{1}{2} \underline{r} \, N_2'' \frac{\partial \phi}{\partial r} \, d\underline{r} - \tfrac{1}{6} \frac{\partial^3}{\partial x_1 \partial x_1 \partial x_1} : \int \tfrac{1}{8} \underline{r}\,\underline{r}\,\underline{r} \, N_2^\circ \frac{\partial \phi}{\partial r} d\underline{r}$$

etc. Integrating these equations with the help of the boundary condition $\underline{\underline{l}}_1 \to 0$ as $n_1 \to 0$, one has

$$(170) \qquad \underline{\underline{l}}_1^\circ = -\tfrac{1}{2} \int \underline{r} \, N_2^\circ \frac{\partial \phi}{\partial r} d\underline{r} = -\tfrac{1}{6} \int r \, N_2^\circ(r) \phi'(r) \, d\underline{r} \; \underline{\underline{1}}$$

and

$$(171) \qquad \begin{aligned} \underline{\underline{l}}_1' &= -\tfrac{1}{2} \int \underline{r} \, N_2' \frac{\partial \phi}{\partial r} \, d\underline{r} \\ &= -\tfrac{1}{15} \int r^3 \left(\nu \underline{\underline{b}} + \nu^+ \underline{\underline{b}}^+ \right) \phi'(r) \, d\underline{r} , \end{aligned}$$

with the help of (163). The corresponding expressions
for $\underline{\underline{k}}_1^o$ and $\underline{\underline{k}}_1'$ are obtained from (146); as already
obtained in (150), $\underline{\underline{k}}_1^o = n_1 k T_1 \underline{\underline{1}}$, whilst

$$(172) \qquad \underline{\underline{k}}_1' = \left[-\frac{\hbar^2}{m} \frac{\partial^2}{\partial y \, \partial y} P_1' \right]_{y=0}$$

$$= -\frac{2\hbar^2}{m} \left(\epsilon_2 \underline{\underline{b}} + \epsilon_2^+ \underline{\underline{b}}^+ \right).$$

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

$$(173) \qquad \underline{\underline{P}}_1^o = \left(n_1 k T_1 - \tfrac{1}{6} \int r \, N_2^o(r) \phi'(r) d\underline{r} \right) \underline{\underline{1}} \quad .$$

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

$$(174) \qquad \underline{\underline{P}}_1' = -\left\{ \frac{2\hbar^2}{m} \left(\epsilon_2 \underline{\underline{b}} + \epsilon_2^+ \underline{\underline{b}}^+ \right) + \tfrac{1}{15} \int r^3 \left(\nu \underline{\underline{b}} + \nu^+ \underline{\underline{b}}^+ \right) \phi'(r) d\underline{r} \right\}$$

gives the coefficient of viscosity μ, which is
defined by the equation

$$(175) \qquad \underline{\underline{P}}_1' = -2\mu \underline{\underline{b}}$$

on the understanding that $\underline{\underline{b}}^+ = 0$. Clearly,

$$(176) \qquad \mu = \frac{2\hbar^2 \epsilon_2(0)}{m} + \tfrac{1}{15} \int r^3 \nu(r) \phi'(r) d\underline{r},$$

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 $\mu = A e^{-c/T}$ 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 $\underline{n}_1$ of the thermal flux vector is given by

$$(177) \quad \frac{\partial}{\partial \underline{x}^{(1)}} \cdot \underline{n}_1 = \frac{\partial}{\partial \underline{x}^{(1)}} \cdot \int \frac{1}{2} n_2 \phi (\underline{u}_2^{(1)} - \underline{u}_1) d\underline{x}^{(2)}$$
$$- \frac{1}{2} \int n_2 \frac{\partial \phi}{\partial r} \cdot (\underline{u}_2^{(1)} + \underline{u}_2^{(2)} - 2\underline{u}_1) d\underline{x}^{(2)}$$

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

$$(178) \quad \frac{\partial}{\partial \underline{x}_1} \cdot \underline{N}_1' = -\frac{1}{2} \frac{\partial}{\partial \underline{x}_1} \cdot \int \frac{1}{2} \underline{r} \{ N_2 (\underline{u}_2^{(1)} + \underline{u}_2^{(2)} - 2\underline{u}_1) \}' \cdot \frac{\partial \phi}{\partial r} d\underline{r},$$

and, on integration,

(179)
$$\underline{n}_1' = -\tfrac{1}{4}\int \underline{r}\, N_2'(\underline{v}_2^{(1)0}+\underline{v}_2^{(2)0}-2\underline{u}_1)\cdot\frac{\partial\phi}{\partial\underline{r}}\, d\underline{r}$$
$$-\tfrac{1}{4}\int \underline{r}\, N_2^0(\underline{v}_2^{(1)\prime}+\underline{v}_2^{(2)\prime})\cdot\frac{\partial\phi}{\partial\underline{r}}\, d\underline{r}$$

In classical theory, where $\underline{v}_2^{(1)0}=\underline{v}_2^{(2)0}=\underline{u}_1$, this reduces, by virtue of (164), to

(180)
$$\underline{n}_1' = -\tfrac{1}{18}\int (\kappa\underline{a} + \kappa^+\underline{a}^+)\,\phi'(r)\,r^3 dr$$

For the 'kinetic' term $\underline{m}_1'$ of the thermal flux, one finds from (147)

(181)
$$\underline{m}_1' = \left[-\left(\tfrac{\hbar^2}{2m}\tfrac{\partial^2}{\partial\underline{y}\cdot\partial\underline{y}} + \tfrac{5kT_1}{2}\right)\left(-\tfrac{\hbar}{m}\tfrac{\partial P_1'}{\partial\underline{y}}\right)\right]_{\underline{y}=0}$$
$$= -\tfrac{5\hbar^3}{4m^2}\left(\epsilon_1''\,\underline{a} + \epsilon_1^{+\prime\prime}\,\underline{a}^+\right)$$

where the double prime indicates the second derivative.

The thermal conductivity λ is defined by the equation

(182)
$$\underline{q}_1' = -\lambda\underline{a}$$

on the understanding that $\underline{P}_1^0$ is the same everywhere, so that $\frac{\partial P_1^0}{\partial x_1}$, or $\underline{a}^+ = e\underline{a}$, where

(183)
$$e = -\frac{n_1}{T_1}\;\frac{1 - \tfrac{1}{6n_1 kT_1}\int T_1\tfrac{\partial N_2^0}{\partial T_1}\phi'(r)\,r\,dr}{1 - \tfrac{1}{6n_1 kT_1}\int n_1\tfrac{\partial N_2^0}{\partial n_1}\phi'(r)\,r\,dr}\;.$$

Hence, classically and at high temperatures,

(184)
$$\lambda = \tfrac{5\hbar^3}{4m^2}(\epsilon_1'' + e\epsilon_1^{+\prime}) + \tfrac{1}{18}\int (\kappa + e\kappa^+)\phi'(r)\,r^3 dr .$$

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),

$$(185) \quad \underline{n}_1' = -\tfrac{2}{45} \int r^5 \varpi \, \underline{u}_1 \cdot (\nu \underline{b} + \nu^+ \underline{b}^+) \phi'(r) \, d\underline{r}$$
$$-\tfrac{1}{18} \int (\kappa \underline{a} + \kappa^+ \underline{a}^+) \phi'(r) \, r^3 \, d\underline{r} \, ,$$

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
tends to zero; it follows that $\underline{a}$, 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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