

A GENERAL KINETIC THEORY
OF LIQUIDS

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BY

M. BORN, F.R.S.

AND

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PREFACE

The six articles collected in this little volume have appeared during the last two years in the *Proceedings of the Royal Society*. The demand for reprints was so great that our store was exhausted even before they could be distributed in the usual way with the publications of our Department. We are grateful to the Royal Society for permission to publish them again in the form of a book. As this was produced by photolithography, we had to abstain from alterations and have therefore added an appendix containing short notes, additions and corrections.

Five of the papers carry the common title 'A General Kinetic Theory of Liquids'. One, however (the fifth in order), is of a more general character, dealing with the kinetic foundations of thermodynamics in general; we wrote it when we found that the rigorous development of quantum statistics given in the previous paper (part IV) could not be completed without carefully preparing the ground.

We are aware that these six papers contain only a very general outline of the statistical theory of condensed matter and that a great amount of work remains to be done in applying it to more complicated systems. A beginning of this task has been made by some of our pupils; three of their papers have been submitted to the Royal Society for publication. Among possible generalizations, we have already examined the theory of multi-atomic liquids where the interactions are not central forces; this is formally very simple, though difficult to apply. Other extensions which appear to merit attention are the rigorous development of the 'relaxation' theory of liquids, by determining solutions which are periodic in time; the investigation of the solid state and of melting from the standpoint of the kinetic theory; a detailed study of quantum liquids, etc. Until all this has been accomplished, a comprehensive treatise on the kinetic theory of condensed matter would be premature. We hope that this little volume may be useful as a preliminary introduction.

M. B.
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EDINBURGH
30 December 1948

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A general kinetic theory of liquids

I. The molecular distribution functions

By M. BORN, F.R.S. AND H. S. GREEN

A general kinetic theory of liquids

I. The molecular distribution functions

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This paper outlines a general theory whose object is to provide a basis from which all the equilibrium and dynamical properties of liquids can be investigated.

A set of multiform distribution functions is defined, and the generalized continuity equations satisfied by these functions are derived. By introducing the equations of motion, a set of relations is obtained from which the distribution functions may be determined. It is shown that Boltzmann's equation in the kinetic theory of gases follows as a particular case, and that, in equilibrium conditions, the theory gives results consistent with statistical mechanics. An integral equation for the radial distribution function is obtained which is the natural generalization of one obtained by Kirkwood for 'rigid spherical molecules'. Finally, it is indicated how the theory may be applied to solve both equilibrium and dynamical problems of the liquid state.

1. INTRODUCTION

It has been said that there exists no general theory of liquids because it is impossible to utilize the simplifying conditions either of the kinetic theory of gases (Chapman & Cowling 1939) where the density is small, or of the theory of solids (Born 1923) where a high degree of spatial order may be assumed. Yet a mathematical formulation of the problem should be possible, without making such an assumption, since only the general laws of mechanics and statistics are involved; though the solution itself may be extremely difficult.

In the following we shall give a set of equations which describe not only the equilibrium of a statistical assembly of molecules—this could be done equally well by the methods of statistical mechanics—but also the dynamical properties. Our method consists of the introduction of not a single distribution function, as in the kinetic theory of gases, but a complete set of such functions for singlets, doublets, triplets, etc., of molecules in the assembly, and depending not only on position and velocity, but also on higher derivatives with respect to the time.

The latter are eliminated with the help of the equations of motion. The only previous publications known to us where this device is employed are due to A. Vlasov (1945), but his work can be regarded only as in the right direction, as it is rendered unconvincing by the introduction of certain arbitrary approximations at an early stage. The idea of multiple distribution functions is also not entirely new; for example, the investigation of the scattering of X-rays by liquids has led to the introduction of the so-called radial distribution function, which is a special case of our second-order distribution functions. In the theory of the Brownian motion, another kind of multiform distribution function, representing the correlation of events at different times, has also been introduced quite recently (Ming Chen Wang & Uhlenbeck 1945).

In the present first part, we give only the definitions and fundamental equations of the theory, but we indicate how Boltzmann's gas theory follows as a special case, and how Kirkwood's derivation of the radial distribution function for 'rigid spherical molecules' (Kirkwood & Boggs 1942) can be generalized for an arbitrary potential between the molecules. A more detailed investigation of the integral equation obtained by this latter method will be left to Part II of this series. The equilibrium solution which results may then be made the foundation of a theory of viscosity, thermal conduction, self-diffusion, etc., for the liquid state.

2. NOTATION

We consider an assembly of N molecules confined within a volume V . We specify the position of the r th molecule by the vector $\mathbf{x}^{(r)}$, its velocity by $\xi^{(r)}$, its acceleration by $\eta^{(r)}$, its rate of acceleration by $\zeta^{(r)}$, etc.

We denote by $n_h(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \dots, \mathbf{x}^{(h)}) \prod_{i=1}^h d\mathbf{x}^{(i)}$ the probability that h distinct molecules, which for convenience we number $1, 2, \dots, h$, occupy volume elements $d\mathbf{x}^{(1)}, d\mathbf{x}^{(2)}, \dots, d\mathbf{x}^{(h)}$, located at $\mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \dots, \mathbf{x}^{(h)}$, respectively at time t . We shall often abbreviate $n_h(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \dots, \mathbf{x}^{(h)})$ to $n_h(t, \mathbf{x})$, or even to n_h , the variables being sufficiently indicated by the suffix. In our notation, n_1 is simply the number density, and n_2/n_1^2 the radial distribution function of the molecular assembly in isotropic conditions.

Similarly, we denote by $f_h(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \dots, \mathbf{x}^{(h)}, \xi^{(1)}, \xi^{(2)}, \dots, \xi^{(h)}) \prod_{i=1}^h d\mathbf{x}^{(i)} d\xi^{(i)}$ the probability that h distinct molecules, with their velocities in the ranges $\xi^{(i)}, d\xi^{(i)}$, $i = 1, 2, \dots, h$, occupy the volume elements $d\mathbf{x}^{(i)}$, $i = 1, 2, \dots, h$, at time t . Then f_h is the velocity distribution function commonly employed in the kinetic theory of gases. The f_h satisfy

$$\int \dots \int f_h(t, \mathbf{x}, \xi) \prod_{i=1}^h d\xi^{(i)} = n_h(t, \mathbf{x}). \quad (2.1)$$

In the same way an acceleration distribution function $g_h(t, \mathbf{x}, \xi, \eta)$ may be defined satisfying

$$\int \dots \int g_h(t, \mathbf{x}, \xi, \eta) \prod_{i=1}^h d\eta^{(i)} = f_h(t, \mathbf{x}, \xi), \quad (2.2)$$

and, further, a rate-of-acceleration distribution function satisfying an analogous equation, etc.

There exist also formulae connecting distribution functions of the same kind, but with different values of h ; it is obvious, for example, from the definitions, that

$$\int n_{h+1}(t, \mathbf{x}) d\mathbf{x}^{(h+1)} = (N - h) n_h(t, \mathbf{x}), \quad (2.3)$$

$$\iint f_{h+1}(t, \mathbf{x}, \xi) d\mathbf{x}^{(h+1)} d\xi^{(h+1)} = (N - h) f_h(t, \mathbf{x}, \xi), \quad (2.4)$$

and similar relations must hold between the g_h 's and higher distribution functions.

3. THE EQUATIONS OF CONTINUITY

The equations of continuity are derived from the requirement that the probability of any molecule occupying the volume element $\mathbf{x}^{(i)}, d\mathbf{x}^{(i)}$ at time t must be the limit of the sum, over all values of $\xi^{(i)}$, of the probability of the same molecule having velocity $\xi^{(i)}$, and position $\mathbf{x}^{(i)} - \xi^{(i)}\delta t$, at time $t - \delta t$. Thus

$$\int \dots \int f_h(t - \delta t, \mathbf{x} - \xi \delta t, \xi) \prod_{i=1}^h d\xi^{(i)} = n_h(t, \mathbf{x}). \quad (3 \cdot 1)$$

Subtracting from equation (2·1), we obtain

$$\int \dots \int \left(\frac{\partial f_h}{\partial t} + \sum_{i=1}^h \frac{\partial f_h}{\partial \mathbf{x}^{(i)}} \xi^{(i)} \right) \prod_{i=1}^h d\xi^{(i)} = 0, \quad (3 \cdot 2)$$

or

$$\frac{\partial n_h}{\partial t} + \sum_{i=1}^h \frac{\partial}{\partial \mathbf{x}^{(i)}} (n_h \overline{\xi^{(i)}}) = 0, \quad (3 \cdot 3)$$

where

$$\overline{\xi^{(i)}} = \frac{1}{n_h} \int \dots \int f_h \xi^{(i)} \prod_{i=1}^h d\xi^{(i)} \quad (3 \cdot 4)$$

is the average velocity of the i th molecule in a group of h molecules whose positions are specified. For $h = 1$, (3·3) is the ordinary equation of continuity for a statistical assembly.

By precisely similar reasoning, we obtain for f_h ,

$$\frac{\partial f_h}{\partial t} + \sum_{i=1}^h \frac{\partial f_h}{\partial \mathbf{x}^{(i)}} \xi^{(i)} + \sum_{i=1}^h \frac{\partial}{\partial \xi^{(i)}} (f_h \overline{\eta^{(i)}}) = 0, \quad (3 \cdot 5)$$

where

$$\overline{\eta^{(i)}} = \frac{1}{f_h} \int \dots \int g_h \eta^{(i)} \prod_{i=1}^h d\eta^{(i)} \quad (3 \cdot 6)$$

is the mean acceleration of the i th molecule in a group of h molecules with given positions and velocities, the positions and velocities of the other molecules remaining unspecified.

Plainly g_h and the distribution functions for higher accelerations will all satisfy equations similar to (3·3) and (3·5).

4. THE EQUATIONS OF MOTION

Let Φ denote the potential energy of the entire assembly; we shall suppose, for convenience, that it can be expressed in the form

$$\Phi = \frac{1}{2} \sum_{r,s=1}^N \phi^{(rs)}, \quad (4 \cdot 1)$$

where $\phi^{(rs)} = \phi(\mathbf{x}^{(r)}, \mathbf{x}^{(s)})$ is the mutual potential energy of two molecules at $\mathbf{x}^{(r)}$ and $\mathbf{x}^{(s)}$. When the intermolecular forces are central forces, $\phi^{(rs)}$ will depend only on

the distance $|x^{(s)} - x^{(r)}|$ between two molecules. In the sequel we assume this, and that the molecules are all alike; but there is always an easy generalization in case these conditions are not fulfilled.

The acceleration of a molecule at $x^{(r)}$ is given by

$$\eta^{(r)} = -\frac{1}{m} \sum_{s=1}^N \frac{\partial \phi^{(rs)}}{\partial x^{(r)}} \quad (4.2)$$

in the absence of external forces, where m is the common mass of the molecules. Also

$$\zeta^{(r)} = -\frac{1}{m} \sum_{s,t=1}^N \left(\xi^{(t)} \frac{\partial}{\partial x^{(t)}} \right) \frac{\partial \phi^{(rs)}}{\partial x^{(r)}}. \quad (4.3)$$

Hence we find the following expression for the mean acceleration $\bar{\eta}^{(i)}$, alternative to (3.6):

$$\bar{\eta}^{(i)} = -\frac{1}{m} \sum_{j=1}^h \frac{\partial \phi^{(ij)}}{\partial x^{(i)}} - \frac{1}{mf_h} \int \int \frac{\partial \phi^{(i,h+1)}}{\partial x^{(i)}} f_{h+1} dx^{(h+1)} d\xi^{(h+1)}. \quad (4.4)$$

When we substitute this expression in (3.5), we obtain

$$\frac{\partial f_h}{\partial t} + \sum_{i=1}^h \frac{\partial f_h}{\partial x^{(i)}} \xi^{(i)} = \frac{1}{m} \sum_{i,j=1}^h \frac{\partial f_h}{\partial \xi^{(i)}} \frac{\partial \phi^{(ij)}}{\partial x^{(i)}} + \frac{1}{m} \int \int \sum_{i=1}^h \frac{\partial \phi^{(i,h+1)}}{\partial x^{(i)}} \frac{\partial f_{h+1}}{\partial \xi^{(i)}} dx^{(h+1)} d\xi^{(h+1)}. \quad (4.5)$$

By making use of (4.3) and similar formulae, equations similar to (4.5) are easily derived for g_h and the higher acceleration distribution functions.

The equations (4.5) for $h = 1, 2, \dots, N$ constitute a set of differential equations to determine the f_h , all except the last of which involve the solution of the next equation. The solution of these equations may therefore be effected either by commencing at the last equation and working backwards, or by using an approximate expression for f_{h+1} in terms of f_h . One such approximation results from the assumption that only binary encounters between the molecules need be considered, and the consequences of this assumption are examined in Appendix I, where it is shown that the equation (4.5) then reduces to the familiar Boltzmann equation of the kinetic theory of gases. Plainly a valid theory of the liquid state can never be founded on this particular basis, but there exists an alternative approximation which can be employed with far greater confidence. This is

$$f_3 = \frac{f_2^{(23)} f_2^{(31)} f_2^{(12)}}{f_1^{(1)} f_1^{(2)} f_1^{(3)}}, \quad (4.6)$$

expressing that the relative probability $\frac{f_3}{f_1^{(3)} f_2^{(12)}}$ of the occurrence of a molecule $x^{(3)}$, $\xi^{(3)}$ in conjunction with two others should be the product of the relative probabilities $\frac{f_2^{(31)}}{f_1^{(3)} f_1^{(1)}}$ and $\frac{f_2^{(12)}}{f_1^{(3)} f_1^{(2)}}$ of the occurrence of the same molecule in conjunction with each of the others separately.

5. THE EQUATIONS OF EQUILIBRIUM

From the fundamental equations (4.5) for the f_h , we now endeavour to find the equilibrium solution by substituting $\frac{\partial f_h}{\partial t} = 0$. It is known from statistical mechanics that the solution must be of the form

$$f_h = n_h \left(\frac{m}{2\pi kT} \right)^{\frac{3h}{2}} \exp \left\{ -\frac{m}{2kT} \sum_{i=1}^h \xi^{(i)2} \right\}. \quad (5.1)$$

By trial we find that (5.1) does in fact satisfy (4.5), provided

$$\frac{\partial n_h}{\partial \mathbf{x}^{(i)}} + \sum_{j=1}^h \frac{n_h}{kT} \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} + \int \frac{n_{h+1}}{kT} \frac{\partial \phi^{(i,h+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(h+1)} = 0. \quad (5.2)$$

When $h = N$, the integrand of (5.2) vanishes, and the residual equation can be integrated, with the result

$$Qn_N = \exp(-\Phi/kT), \quad (5.3)$$

where Q is a constant of integration. This formula embodies a well-known result of statistical mechanics. By repeated use of (2.3) we find

$$Q = \frac{1}{N!} \int \dots \int e^{-\Phi/kT} \prod_{i=1}^N d\mathbf{x}^{(i)}, \quad (5.4)$$

so that Q is simply the phase integral which is the starting point of many investigations in statistical thermodynamics. From (5.3) we obtain also

$$Qn_h = \frac{1}{(N-h)!} \int \dots \int e^{-\Phi/kT} \prod_{i=h+1}^N d\mathbf{x}^{(i)}, \quad (5.5)$$

which completes the formal solution.

The evaluation of the integrals (5.4) and (5.5) is, however, so complicated for any but the simplest forms of potential that it seems preferable, for practical purposes, to make immediate use of (5.2) when h is small, in conjunction with some relation such as (4.6), which now reduces to

$$n_2^3 n_3 = n_2^{(12)} n_2^{(23)} n_2^{(31)}. \quad (5.6)$$

This is equivalent to the 'superposition approximation' which has been examined and used by Kirkwood & Boggs (1942). When (5.6) is substituted in equation (5.2), we find, after some analysis, which is given in Appendix II, that

$$\log \frac{n_2(r)}{n_1^2} + \frac{\phi(r)}{kT} = \frac{\pi}{n_1^3} \int_0^\infty \int_{-s}^s (s^2 - t^2) \frac{t+r}{r} \{n_2(t+r) - n_1^2\} dt n_2(s) \frac{\phi'(s)}{kT} ds_2, \quad (5.7)$$

where $n_2(r)$ and $\phi(r)$ depend only on the distance r between the two molecules. This is the generalization for an arbitrary potential of an equation obtained by Kirkwood & Boggs (1942), to which it reduces in the case of 'rigid spherical molecules'. It is capable of giving solutions which agree well with the experimental data obtained from the study of X-ray scattering by monatomic liquids.

Once $n_2(r)$ has been determined, all the equilibrium properties of the assembly follow, for, the internal energy E is given by*

$$E = \frac{1}{2} \left\{ \sum_{r,s=1}^N \phi^{(rs)} + m \sum_{r=1}^N \xi^{(r)2} \right\} = \frac{1}{2} V \int_0^\infty n_2(r) \phi(r) 4\pi r^2 dr + \frac{3}{2} N k T, \quad (5.8)$$

and the free energy A by $\frac{\partial}{\partial T} \left(\frac{A}{T} \right) = - \frac{E}{T^2}$, (5.9)

together with a suitable limiting condition, such as that provided by the third law of thermodynamics. It is well known that all equilibrium properties can be derived from A , when expressed as a function of n_1 and the temperature T .

6. THE DYNAMICAL EQUATIONS

It has been seen how it is possible to obtain the equilibrium solution of the equations

$$\frac{\partial f_1^{(r)}}{\partial t} + \frac{\partial f_1^{(r)}}{\partial \mathbf{x}^{(r)}} \xi^{(r)} + \frac{\partial f_1^{(r)}}{\partial \xi^{(r)}} \mathbf{F}^{(r)} = \iint \frac{\partial f_2^{(rs)}}{\partial \xi^{(r)}} \frac{\partial \phi^{(rs)}}{\partial \mathbf{x}^{(s)}} d\mathbf{x}^{(s)} d\xi^{(s)}, \quad (6.1)$$

$$\begin{aligned} \frac{\partial f_2^{(rs)}}{\partial t} + \frac{\partial f_2^{(rs)}}{\partial \mathbf{x}^{(r)}} \xi^{(r)} + \frac{\partial f_2^{(rs)}}{\partial \mathbf{x}^{(s)}} \xi^{(s)} + \frac{\partial f_2^{(rs)}}{\partial \xi^{(r)}} \left(\mathbf{F}^{(r)} - \frac{\partial \phi^{(rs)}}{\partial \mathbf{x}^{(r)}} \right) + \frac{\partial f_2^{(rs)}}{\partial \xi^{(s)}} \left(\mathbf{F}^{(s)} - \frac{\partial \phi^{(rs)}}{\partial \mathbf{x}^{(s)}} \right) \\ = \iint \left(\frac{\partial f_3^{(rst)}}{\partial \xi^{(r)}} \frac{\partial \phi^{(rt)}}{\partial \mathbf{x}^{(r)}} + \frac{\partial f_3^{(rst)}}{\partial \xi^{(s)}} \frac{\partial \phi^{(st)}}{\partial \mathbf{x}^{(s)}} \right) d\mathbf{x}^{(t)} d\xi^{(t)}, \end{aligned} \quad (6.2)$$

with the aid of (4.6). It will be noticed that an additional term has been introduced into these equations to meet with the possibility of an external force $\mathbf{F}^{(r)}$ which is a function of the position $\mathbf{x}^{(r)}$.

To obtain the most general solution which does not differ greatly from the equilibrium solution, we replace

$$f_1^{(r)} \text{ by } f_1^{(r)}(1 + u_1^{(r)}), \quad f_2^{(rs)} \text{ by } f_2^{(rs)}(1 + u_2^{(rs)}), \quad (6.3)$$

so that $f_1^{(r)}$ and $f_2^{(rs)}$ now refer to the equilibrium solution, and neglect terms quadratic in the $u_1^{(r)}$ and $u_2^{(rs)}$. This procedure gives

$$\frac{\partial u_1^{(r)}}{\partial t} + \frac{\partial u_1^{(r)}}{\partial \mathbf{x}^{(r)}} \xi^{(r)} + \frac{\partial u_1^{(r)}}{\partial \xi^{(r)}} \mathbf{F}^{(r)} = \frac{1}{f_1^{(r)}} \frac{\partial}{\partial \xi^{(r)}} \iint f_2^{(rs)} u_2^{(rs)} \frac{\partial \phi^{(rs)}}{\partial \mathbf{x}^{(r)}} d\mathbf{x}^{(s)} d\xi^{(s)}, \quad (6.4)$$

$$\begin{aligned} \frac{\partial u_2^{(rs)}}{\partial t} + \frac{\partial u_2^{(rs)}}{\partial \mathbf{x}^{(r)}} \xi^{(r)} + \frac{\partial u_2^{(rs)}}{\partial \mathbf{x}^{(s)}} \xi^{(s)} + \frac{\partial u_2^{(rs)}}{\partial \xi^{(r)}} \mathbf{D}^{(rs)} + \frac{\partial u_2^{(rs)}}{\partial \xi^{(s)}} \mathbf{D}^{(rs)} \\ = \frac{1}{f_2^{(rs)}} \frac{\partial}{\partial \xi^{(s)}} \iint f_3^{(rst)} (u_2^{(rt)} + u_2^{(st)} - u_1^{(r)} - u_1^{(s)} - u_1^{(t)}) \frac{\partial \phi}{\partial \mathbf{x}^{(r)}} d\mathbf{x}^{(t)} d\xi^{(t)} \\ + \frac{1}{f_2^{(rs)}} \frac{\partial}{\partial \xi^{(s)}} \iint f_3^{(rst)} (u_2^{(st)} + u_2^{(rt)} - u_1^{(s)} - u_1^{(r)} - u_1^{(t)}) \frac{\partial \phi}{\partial \mathbf{x}^{(s)}} d\mathbf{x}^{(t)} d\xi^{(t)}, \end{aligned} \quad (6.5)$$

where $-\mathbf{D}^{(rs)} = \frac{\partial \phi^{(rs)}}{\partial \mathbf{x}^{(r)}} + \iint f_3^{(rst)} \frac{\partial \phi^{(rt)}}{\partial \mathbf{x}^{(r)}} d\mathbf{x}^{(t)} d\xi^{(t)} - \mathbf{F}^{(r)}$. (6.6)

* Additional terms would, of course, be required if the molecules had internal degrees of freedom.

Equations (6.4) and (6.5) constitute a pair of simultaneous linear integro-differential equations for the determination of $u_1^{(r)}$ and $u_2^{(rs)}$. Once solved with the appropriate boundary conditions, the dynamical properties of the assembly may be investigated in the usual way.

7. APPENDIX I

We shall prove here that when $\hbar = 1$, our equation (4.5) reduces to Boltzmann's equation, in the case when only binary encounters need be considered. First it is necessary to obtain an expression for $f_2(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \xi^{(1)}, \xi^{(2)})$.

Examine the orbits of two molecules which at time t have positions $\mathbf{x}^{(1)}, \mathbf{x}^{(2)}$, and velocities $\xi^{(1)}, \xi^{(2)}$, and consider motion relative to the mass-centre of the two molecules, which must be in one plane. Let $\lambda^{(1)}, \lambda^{(2)}$ be their velocities before the encounter, and $\mu^{(1)}, \mu^{(2)}$ their velocities after the encounter. Write $\mathbf{r} = \mathbf{x}^{(2)} - \mathbf{x}^{(1)}$, $\rho = \xi^{(2)} - \xi^{(1)}$, and denote by \mathbf{k} the vector joining the intersections of the initial and final asymptotes to the orbits of the two molecules.

Now, as the molecules move along their respective orbits, the configurational probability $f_2(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \xi^{(1)}, \xi^{(2)}) d\mathbf{x}^{(1)} d\mathbf{x}^{(2)} d\xi^{(1)} d\xi^{(2)}$ must remain unchanged; also the 'volume' in phase space, $d\mathbf{x}^{(1)} d\mathbf{x}^{(2)} d\xi^{(1)} d\xi^{(2)}$, is unaltered, by Liouville's theorem. Hence

$$f_2(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \xi^{(1)}, \xi^{(2)}) = f_1(\lambda^{(1)}) f_1(\lambda^{(2)}), \quad (7.1)$$

where $\lambda^{(1)}$ and $\lambda^{(2)}$ are given in terms of $\xi^{(1)}, \xi^{(2)}, \mathbf{r}$ and \mathbf{k} by the conservation equations

$$\left. \begin{aligned} \lambda^{(1)} + \lambda^{(2)} &= \xi^{(1)} + \xi^{(2)}, \\ \mathbf{k} \times (\lambda^{(2)} - \lambda^{(1)}) &= \mathbf{r} \times (\xi^{(2)} - \xi^{(1)}), \\ \lambda^{(1)2} + \lambda^{(2)2} &= \xi^{(1)2} + \xi^{(2)2} + \frac{2\phi(r)}{m}. \end{aligned} \right\} \quad (7.2)$$

Hence, by some easy vector algebra,

$$\mathbf{k}^2(\lambda^{(2)} - \lambda^{(1)}) = \pm \left\{ \mathbf{k}^2\rho^2 + \frac{4\mathbf{k}^2\phi(r)}{m} + (\mathbf{r} \cdot \rho)^2 - \mathbf{r}^2\rho^2 \right\}^{\frac{1}{2}} \mathbf{k} + (\mathbf{k} \cdot \mathbf{r})\rho - (\mathbf{k} \cdot \rho)\mathbf{r}. \quad (7.3)$$

The ambiguity in sign is due to the fact that $\mu^{(1)}, \mu^{(2)}$ also satisfy the equations (7.2). Hence from (7.3), when \mathbf{k} is fixed,

$$\left(\mathbf{r} \frac{\partial}{\partial \rho} \right) (\lambda^{(2)} - \lambda^{(1)}) \frac{2\phi'(r)}{mr} = \left(\rho \frac{\partial}{\partial \mathbf{r}} \right) (\lambda^{(2)} - \lambda^{(1)}). \quad (7.4)$$

It is now possible to evaluate the right-hand side of (4.5), which, with $\hbar = 1$, becomes

$$\begin{aligned} \frac{1}{m} \iint \frac{\partial f_2}{\partial \xi^{(1)}} \frac{\partial \phi}{\partial \mathbf{x}^{(1)}} d\mathbf{x}^{(2)} d\xi^{(2)} &= \frac{1}{m} \iint \left(\frac{\partial f_2}{\partial \xi^{(1)}} - \frac{\partial f_2}{\partial \xi^{(2)}} \right) \frac{\partial \phi}{\partial \mathbf{x}^{(1)}} d\mathbf{x}^{(2)} d\xi^{(2)} \\ &= \iint \frac{\phi'(r)}{mr} \left(\mathbf{r} \frac{\partial}{\partial \rho} \right) (\lambda^{(2)} - \lambda^{(1)}) \left\{ f_1(\lambda^{(1)}) \frac{\partial f_1(\lambda^{(2)})}{\partial \lambda^{(2)}} - f_1(\lambda^{(2)}) \frac{\partial f_1(\lambda^{(1)})}{\partial \lambda^{(1)}} \right\} d\mathbf{x}^{(2)} d\xi^{(2)}. \end{aligned} \quad (7.5)$$

Along a trajectory, where \mathbf{k} is constant, the integrand reduces to

$$\left(\rho \frac{\partial}{\partial \mathbf{r}} \right) \{ f_1(\lambda^{(1)}) f_1(\lambda^{(2)}) \},$$

because of (7.4) and the relations $\frac{\partial}{\partial \mathbf{r}} \lambda^{(2)} = - \frac{\partial}{\partial \mathbf{r}} \lambda^{(1)} = \frac{1}{2} \frac{\partial}{\partial \mathbf{r}} (\lambda^{(2)} - \lambda^{(1)})$, which follow immediately from (7.2). The integration over $\mathbf{x}^{(2)}$ is now performed by integrating first along a trajectory, and then over all values of $\mathbf{b} = \mathbf{k} \times \rho / \rho$. It is easily seen that the entire available space is covered just once in this way. The result is

$$\iint \{ f_1(\mu^{(1)}) f_1(\mu^{(2)}) - f_1(\xi^{(1)}) f_1(\xi^{(2)}) \} \rho d\mathbf{b} d\xi^{(2)}, \quad (7.6)$$

in complete agreement with Boltzmann's well-known formula.

8. APPENDIX II .

We give here the derivation of the integral equation (5.7) from equation (5.2) with $h = 2$, and (5.6) inserted, namely,

$$\frac{\partial n_2^{(12)}}{\partial \mathbf{x}^{(2)}} + \frac{n_2^{(12)}}{kT} \frac{\partial \phi^{(12)}}{\partial \mathbf{x}^{(2)}} = \frac{n_2^{(12)}}{n_1^3 kT} \int n_2^{(23)} n_2^{(31)} \frac{\partial \phi^{(23)}}{\partial \mathbf{x}^{(3)}} d\mathbf{x}^{(3)}. \quad (8.1)$$

Writing $\mathbf{r} = \mathbf{x}^{(2)} - \mathbf{x}^{(1)}$, $\mathbf{s} = \mathbf{x}^{(3)} - \mathbf{x}^{(2)}$, $\mathbf{t} = \mathbf{x}^{(3)} - \mathbf{x}^{(1)}$, and $\mathbf{r} \cdot \mathbf{s} = rs \cos \theta$; then, after scalar multiplication by \mathbf{r} ,

$$n'_2(r) + n_2(r) \frac{\phi'(r)}{kT} = \frac{2\pi n_2(r)}{n_1^3} \int_0^\infty \int_0^\pi n_2(s) n_2(t) \frac{\phi'(s)}{kT} s^2 \sin \theta \cos \theta d\theta ds, \quad (8.2)$$

where $t = (r^2 + s^2 + 2rs \cos \theta)^{1/2}$, or

$$\frac{d}{dr} \left\{ \log n_2(r) + \frac{\phi(r)}{kT} \right\} = \frac{\pi}{n_1^3 r^2} \int_0^\infty \int_{|r-s|}^{|r+s|} n_2(t) t(t^2 - r^2 - s^2) dt n_2(s) \frac{\phi'(s)}{kT} ds. \quad (8.3)$$

We define $n_2(r)$ and $\phi(r)$ for negative r by the equations $n_2(r) = n_2(-r)$ and $\phi(r) = \phi(-r)$; it is then found that it is possible to integrate the right-hand side of (8.3) by parts, giving

$$\log n_2(r) + \frac{\phi(r)}{kT} = \frac{\pi}{n_1^3} \int_0^\infty \int_{-s}^s (s^2 - t^2) \frac{t+r}{r} n_2(t+r) dt n_2(s) \frac{\phi'(s)}{kT} ds + a, \quad (8.4)$$

where the constant of integration a is fixed by $n_2(r) \rightarrow n_1^2$ as $r \rightarrow \infty$. Thus

$$\log n_1^2 = \frac{\pi}{n_1^3} \int_0^\infty \int_{-s}^s (s^2 - t^2) \frac{t+r}{r} n_1^2 dt n_2(s) \frac{\phi'(s)}{kT} ds + a, \quad (8.5)$$

and, by subtraction from (8.4), (5.7) follows.

9. CONCLUSION

We have described a set of molecular distribution functions adequate for the formulation of the fundamental equations of a kinetic theory of liquids. From these equations we have shown that Boltzmann's theory of gases and some of the results of statistical mechanics can be obtained as special cases. We have indicated how our equations can be solved and applied to the solution of both static and dynamic problems concerning liquids.

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A general kinetic theory of liquids.

II. Equilibrium properties.

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The object of this paper is to expand and develop the equilibrium theory outlined in the first part of this series, within the framework of a general kinetic theory of fluids.

The entropy of the fluid is first defined in such a way that agreement with the definition of statistical mechanics is obtained in equilibrium conditions. It is then found possible, provided care is taken to avoid certain well-known fallacies in the application of statistics to mechanical systems, to prove that the quantity defined will in general increase with time towards a certain maximum. The equilibrium solution of the fundamental equations is thereby derived without any appeal to statistical mechanics. At the same time a direct proof is offered of certain general formulae in statistical thermodynamics.

The second half of the paper is devoted to a more detailed study of the equilibrium state by a method proposed in part I of the series. It is shown that the liquid state is distinguished from the gaseous state by the existence of real roots of a certain transcendental equation. Approximate but tractable expressions are found for all the virial coefficients in the gaseous phase. An equation of state is derived with two branches, which are identified with the gaseous and liquid states respectively.

1. INTRODUCTION

In part I of this series (Born & Green 1946), Professor Max Born and the author gave a general survey of a theory designed to describe both equilibrium and dynamical properties of liquids. A brief treatment of the equilibrium state was included, sufficient to show that results consistent with the application of statistical mechanics could be obtained. There were, however, two important gaps in our outline, which it is the purpose of the present paper to fill.

In the first place, we found it necessary to appeal to statistical mechanics in order to prove that the Maxwellian distribution of velocities in a molecular assembly was a *unique* consequence of our equilibrium theory, though we were afterwards able to show that by assuming this, the complete statistical mechanical solution could be obtained. It is obviously desirable, however, to make an exposition of this kind independent, as far as possible, of external theories, even though their subject-matter may overlap to a certain extent with our own. The first part of this paper is therefore devoted to a generalization of the famous Boltzmann *H*-theorem (Chapman & Cowling 1939), which enables us to establish our treatment of the equilibrium properties on an independent basis. At the same time a direct proof is offered of certain general formulae of statistical thermodynamics.

Secondly, although the object of this series is specifically to provide a theory of the liquid state, in part I no indication was given of the role played by this particular phase in our theory. Indeed, in its present form, it is equally applicable to the gaseous phase, and, apart from modifications probably of a quantum-mechanical

nature, to the solid state as well. It just happens that there are already theories which adequately describe these other states. However, some explanation of the phenomenon of condensation, and the distinction between the gaseous and liquid states, is plainly required, and this it is the endeavour of the second part of the present paper to give.

A theory of condensation, based on statistical mechanics, has already been elaborated by Mayer and others (Mayer 1937; Born & Fuchs 1938; Kahn 1938), who showed that condensation is associated with the divergence of the series obtained by expanding the normalized phase integral in powers of the density. The nature of this singularity, and of the continuation beyond, has, however, so far remained somewhat obscure. The investigation which follows indicates that the singularity is, in fact, a branch point, from which spring two branches associated with the gaseous and liquid states respectively.* With the aid of an approximate solution of an integral equation derived in part I, it has been found possible to derive equations of state for both phases, and any other equilibrium properties which may be required. This part of the work offers many opportunities for numerical comparison with experiment, but it has not seemed worth while to specialize in this way at present; on account of the approximation involved, qualitative rather than exact quantitative agreement may be expected. However, the equilibrium theory now seems sufficiently well established to enable us to proceed to the more interesting dynamical properties, some of which Professor Born and the author hope to treat in the third part of this series.

2. PRELIMINARY

A fundamental theorem in the kinetic theory of gases, due to Boltzmann, shows that a certain quantity H , closely connected with the entropy S , cannot, on the average, increase, but must tend to a fixed minimum, associated with the equilibrium state. Both the definition of H , and the proof of the so-called H -theorem, must, however, be generalized to apply to the liquid phase.

The appropriate definition is suggested by known results of statistical mechanics, in the following way. In equilibrium, the free energy A of an assembly of N molecules is known to be given by

$$e^{-A/kT} = \frac{1}{N!} \int \dots \int e^{-W/kT} \prod_{i=1}^N d\mathbf{x}^{(i)} d\boldsymbol{\xi}^{(i)}, \quad (2.1)$$

where

$$W = \frac{1}{2}m \sum_{i=1}^N \boldsymbol{\xi}^{(i)2} + \Phi, \quad (2.2)$$

in the notation of part I. An independent proof of this result, based on the exact formula for n_2 , will be found in the appendix. Note here that (2.2) implies that the molecules possess no internal degrees of freedom, a simplification which will be made throughout the present paper.

* The liquid phase is distinguished from the gaseous phase by the existence of real roots of a certain transcendental equation. In this respect the theory resembles a theory of condensation proposed by Kaplan & Dresden (1944). In spite of its attractive simplicity, however, the latter remains extremely speculative.

It was found in part I that, for equilibrium,

$$Qf_N = e^{-W/kT}, \quad (2.3)$$

where

$$Q = \frac{1}{N!} \int^{(2N)} \cdots \int e^{-W/kT} \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)}, \quad (2.4)$$

so that

$$\begin{aligned} -\frac{A}{kT} &= \log Q \\ &= \frac{1}{N!} \int^{(2N)} \cdots \int f_N \log Q \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)} \\ &= -\frac{1}{N!} \int^{(2N)} \cdots \int \left(\frac{W}{kT} + \log f_N \right) f_N \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)}. \end{aligned} \quad (2.5)$$

The entropy is

$$S = \frac{E - A}{T}, \quad (2.6)$$

where

$$E = \frac{1}{N!} \int^{(2N)} \cdots \int W f_N \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)} \quad (2.7)$$

is the internal energy. Hence, in equilibrium,

$$S = -\frac{k}{N!} \int^{(2N)} \cdots \int f_N \log f_N \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)}. \quad (2.8)$$

(2.8) will be adopted as the definition of the entropy, even when equilibrium conditions do not exist, and the proof of the H -theorem will then consist of showing that

$$H = \int^{(2N)} \cdots \int f_N \log f_N \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)} \quad (2.9)$$

cannot increase.

According to (4.5) of part I, the equation satisfied by f_N is

$$\frac{\partial f_N}{\partial t} + \sum_{i=1}^N \frac{\partial f_N}{\partial \mathbf{x}^{(i)}} \xi^{(i)} = \frac{1}{m} \sum \frac{\partial f_N}{\partial \xi^{(i)}} \frac{\partial \Phi}{\partial \mathbf{x}^{(i)}}, \quad (2.10)$$

if f_{N+1} is assumed to vanish. The 'auxiliary equations' for the integration of (2.10),

$$\frac{dt}{1} = d\mathbf{x}^{(i)}/\xi^{(i)} = -m d\xi^{(i)} / \left(\frac{\partial \Phi}{\partial \mathbf{x}^{(i)}} \right) \quad (2.11)$$

are identical with Lagrange's equations for the motion of the system. They yield $6N$ functionally independent integrals of the form

$$I_r(t, \mathbf{x}^{(1)}, \dots, \mathbf{x}^{(N)}, \xi^{(1)}, \dots, \xi^{(N)}) = C_r, \quad r = 1, \dots, 6N,$$

which, when solved for $\mathbf{x}^{(i)}$ and $\xi^{(i)}$, provide a detailed description of the motion in terms of the time t and the parameters C_r which are specified by the initial

conditions. f_N is thereby determined as an arbitrary function of the $6N$ variables L_r , which include the total energy W , the total momentum M , and the total angular momentum A of the system. This solution is, however, much too general for the present purpose, which requires the form assumed by f_N when the system has been left for some time, and has arrived at a 'normal' state. Also, the idea of statistical interaction has disappeared from the equations, which, as one might expect, leads to the paradoxical result $\partial H/\partial t = 0$ even when statistical equilibrium has not been reached.

Therefore, instead of (2.10) the equation

$$\frac{\partial f_N}{\partial t} + \sum_{i=1}^N \frac{\partial f_N}{\partial \mathbf{x}^{(i)}} \xi^{(i)} = \frac{1}{m} \sum_{i=1}^N \frac{\partial f_N}{\partial \xi^{(i)}} \frac{\partial \Phi}{\partial \mathbf{x}^{(i)}} + \frac{1}{m} \iint \sum_{i=1}^N \frac{\partial f_{N+1}}{\partial \xi^{(i)}} \frac{\partial \phi^{(iN+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(N+1)} d\xi^{(N+1)} \quad (2.12)$$

will be considered, which has the effect of providing an external system (to be imagined as the vapour with which the liquid is in contact, for example) with similar distribution properties, and with which the given system may statistically interact. Also, to make the treatment as general as possible, the possibility of a conservative field of force $-\partial\Psi/\partial\mathbf{x}$ acting on the molecules is contemplated, which requires only the replacement of Φ by $\Phi' = \Phi + \sum_{i=1}^N \Psi(\mathbf{x}^{(i)})$ in (2.12). This innovation has the advantage that the boundary of the fluid may be represented by a wall where $\Psi \rightarrow \infty$; of course, at the wall, f_N and surface integrals involving f_N must vanish, otherwise the total potential energy of the fluid would diverge.

3. THE GENERALIZED H -THEOREM

Now proceed to calculate the rate of change with time of the quantity H defined in (2.9). Thus

$$\begin{aligned} \frac{\partial H}{\partial t} &= \int \cdots \int (1 + \log f_N) \frac{\partial f_N}{\partial t} \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)} \\ &= \frac{1}{m} \int \cdots \int (1 + \log f_N) \sum_{i=1}^N \frac{\partial f_{N+1}}{\partial \xi^{(i)}} \frac{\partial \phi^{(iN+1)}}{\partial \mathbf{x}^{(i)}} \prod_{j=1}^{N+1} d\mathbf{x}^{(j)} d\xi^{(j)}, \end{aligned} \quad (3.1)$$

since

$$\int \cdots \int \xi^{(i)} \frac{\partial}{\partial \mathbf{x}^{(i)}} (f_N \log f_N) \prod_{j=1}^N d\mathbf{x}^{(j)} d\xi^{(j)}$$

and

$$\int \cdots \int \frac{\partial \Phi}{\partial \mathbf{x}^{(i)}} \frac{\partial}{\partial \xi^{(i)}} (f_N \log f_N) \prod_{j=1}^N d\mathbf{x}^{(j)} d\xi^{(j)}$$

both vanish on transformation to surface integrals. f_N and f_{N+1} are symmetrical functions of their positions and velocities, so all terms under the summation in (3.1) contribute the same value, and hence

$$\frac{\partial H}{\partial t} = \frac{N}{m} \int \cdots \int (1 + \log f_N) \frac{\partial f_{N+1}}{\partial \xi^{(1)}} \frac{\partial \phi^{(1N+1)}}{\partial \mathbf{x}^{(1)}} \prod_{i=1}^N d\mathbf{x}^{(i)} d\xi^{(i)}. \quad (3.2)$$

The analysis which follows is a generalization of that in appendix I to part I of this series, with which it should be compared. Write

$$\left. \begin{aligned} \mathbf{x} &= \frac{1}{2}(\mathbf{x}^{(1)} + \mathbf{x}^{(N+1)}), & \mathbf{r} &= \mathbf{x}^{(N+1)} - \mathbf{x}^{(1)}, \\ \xi &= \frac{1}{2}(\xi^{(1)} + \xi^{(N+1)}), & \rho &= \xi^{(N+1)} - \xi^{(1)}, \end{aligned} \right\} \quad (3.3)$$

$$\mathbf{m} = 2m\xi, \quad \mathbf{a} = \frac{1}{2}m\mathbf{r} \times \boldsymbol{\rho}, \quad w = \frac{1}{4}m\rho^2 + \phi(r). \quad (3.4)$$

By solving the equations (3.4) ξ and ρ can be expressed, and therefore $\xi^{(1)}$ and $\xi^{(N+1)}$, in terms of \mathbf{m} , \mathbf{a} , w and \mathbf{r}^* . A function \bar{f}_{N+1} can then be defined by

$$f_{N+1} = \bar{f}_{N+1}(t, \mathbf{x}^{(1)}, \dots, \mathbf{x}^{(N+1)}, \xi^{(2)}, \dots, \xi^{(N)}, \mathbf{m}, \mathbf{a}, w), \quad (3.5)$$

and it is easily verified that

$$\frac{1}{m} \left(\frac{\partial f_{N+1}}{\partial \xi^{(1)}} - \frac{\partial f_{N+1}}{\partial \xi^{(N+1)}} \right) \frac{\partial \phi}{\partial \mathbf{x}^{(1)}} = \frac{\partial \bar{f}_{N+1}}{\partial w} \rho \frac{\partial \phi}{\partial \mathbf{r}} = \rho \left(\frac{\partial f_{N+1}}{\partial \mathbf{x}^{(N+1)}} - \frac{\partial \bar{f}_{N+1}}{\partial \mathbf{x}^{(N+1)}} \right). \quad (3.6)$$

On substituting $\frac{1}{m} \frac{\partial f_{N+1}}{\partial \xi^{(1)}} \frac{\partial \phi}{\partial \mathbf{x}^{(1)}}$ from (3.6) into (3.2) the only term which does not vanish is found to be

$$-N \int^{(2N+2)} \dots \int (1 + \log f_N) \rho \frac{\partial \bar{f}_{N+1}}{\partial \mathbf{x}^{(N+1)}} \prod_{i=1}^{N+1} d\mathbf{x}^{(i)} d\xi^{(i)}.$$

Now, \mathbf{m} , \mathbf{a} and w may be regarded as geometrical parameters specifying the trajectories which would be followed by the molecules numbered (1) and ($N+1$) if no other molecules were present. Thus, if the $\mathbf{x}^{(N+1)}$ domain be imagined as partitioned by tubes formed by the trajectories of ($N+1$) relative to (1), it is seen that the integration over $\mathbf{x}^{(N+1)}$ may be performed, as in appendix I to part I, first along the typical trajectory, where \mathbf{m} , \mathbf{a} and w are constant, and then over all values of the cross-section radius \mathbf{b} . At each end of the trajectory the interaction vanishes, and f_{N+1} factorizes into $f_1^{(N+1)} f_N$. Since the sphere around $\mathbf{x}^{(1)}$ in which ϕ is effectively different from zero is of microscopic dimensions, it need not be supposed that $\mathbf{x}^{(N+1)}$ differs macroscopically from either $\mathbf{x}^{(1)}$ or \mathbf{x} , or that the time differs from t , at the ends of the trajectories. The initial velocities $\xi^{(1)}$ and $\xi^{(N+1)}$ must, however, be determined from the actual, final velocities by the equations, following from (3.4)

$$\left. \begin{aligned} m(\xi^{(1)} + \xi^{(N+1)}) &= m(\xi^{(1)} + \xi^{(N+1)}), \\ m(\mathbf{x}^{(1)} \times \xi^{(1)} + \mathbf{x}^{(N+1)} \times \xi^{(N+1)}) &= m(\mathbf{x}^{(1)} \times \xi^{(1)} + \mathbf{x}^{(N+1)} \times \xi^{(N+1)}), \\ \frac{1}{2}m(\xi^{(1)2} + \xi^{(N+1)2}) &= \frac{1}{2}m(\xi^{(1)2} + \xi^{(N+1)2}). \end{aligned} \right\} \quad (3.7)$$

After the integration, (3.2) becomes

$$\frac{\partial H}{\partial t} = -N \int^{(2N+2)} \dots \int (1 + \log f_N) (f_N f_1^{(N+1)} - f'_N f_1^{(N+1)}) \rho d\mathbf{b} d\mathbf{x} \prod_{i=2}^N d\mathbf{x}^{(i)} \prod_{j=1}^{N+1} d\xi^{(j)}. \quad (3.8)$$

* Only two components of \mathbf{a} are strictly required for this transformation, but for symmetry this fact is ignored.

Now denote by F_N the function obtained from f_N by replacing the variables $\mathbf{x}^{(i)}$ and $\xi^{(i)}$ by $\mathbf{x}^{(i+N)}$ and $\xi^{(i+N)}$ respectively, and rewrite (3.8), using (2.4) of part I, in the form

$$\frac{\partial H}{\partial t} = -\frac{N}{(N-1)!} \int^{(4N)} \cdots \int (1 + \log f_N) (f_N F_N - f'_N F'_N) \rho d\mathbf{b} d\mathbf{x} \prod_{i=2, N+2}^{N, 2N} d\mathbf{x}^{(i)} \prod_{j=1}^{2N} d\xi^{(j)}. \quad (3.9)$$

By a series of transformations familiar in the proof of the H -theorem for gases, one obtains finally

$$\frac{\partial H}{\partial t} = -\frac{N}{4(N-1)!} \int^{(4N)} \cdots \int \log \left(\frac{f_N F_N}{f'_N F'_N} \right) (f_N F_N - f'_N F'_N) \rho d\mathbf{b} d\mathbf{x} \prod_{i=2, N+2}^{N, 2N} d\mathbf{x}^{(i)} \prod_{j=1}^{2N} d\xi^{(j)}. \quad (3.10)$$

which makes it clear that $\partial H/\partial t$ is essentially negative or zero.

4. THE EXACT EQUILIBRIUM SOLUTION

It is inferred from the calculations of the last section that it is a condition of equilibrium that the entropy should have attained its maximum value, for which

$$\log f_N + \log F_N = \log f'_N + \log F'_N, \quad (4.1)$$

where

$$\left. \begin{aligned} F_N &= f_N(\mathbf{x}^{(N+1)}, \dots, \mathbf{x}^{(2N)}, \xi^{(N+1)}, \dots, \xi^{(2N)}), \\ f'_N &= f_N(\mathbf{x}^{(1)}, \dots, \mathbf{x}^{(N)}, \xi^{(1)'}, \xi^{(2)'}, \dots, \xi^{(N)'}) \\ F'_N &= F_N(\mathbf{x}^{(N+1)}, \dots, \mathbf{x}^{(2N)}, \xi^{(N+1)'}, \xi^{(N+2)'}, \dots, \xi^{(2N)'}) \end{aligned} \right\} \quad (4.2)$$

and equations (3.7) are satisfied. Owing to the symmetry between the variables, one obtains from (4.1) by a succession of $N-1$ arbitrary transformations of the type (3.7),

$$\log f_N + \log F_N = \log f''_N + \log F''_N, \quad (4.3)$$

where

$$\left. \begin{aligned} f''_N &= f_N(\mathbf{x}^{(1)}, \dots, \mathbf{x}^{(N)}, \xi^{(1)'}, \dots, \xi^{(N)'}) \\ F''_N &= f_N(\mathbf{x}^{(N+1)}, \dots, \mathbf{x}^{(2N)}, \xi^{(N+1)'}, \dots, \xi^{(2N)'}) \end{aligned} \right\} \quad (4.4)$$

and the only restrictions on the variables are

$$\left. \begin{aligned} \sum_{i=1}^{2N} \xi^{(i)} &= \sum_{i=1}^{2N} \xi^{(i)'}, \\ \sum_{i=1}^{2N} \mathbf{x}^{(i)} \times \xi^{(i)} &= \sum_{i=1}^{2N} \mathbf{x}^{(i)} \times \xi^{(i)'}, \\ \sum_{i=1}^{2N} \xi^{(i)2} &= \sum_{i=1}^{2N} \xi^{(i)'2}. \end{aligned} \right\} \quad (4.5)$$

It follows that

$$\log f_N = C + mc \sum_{i=1}^N \xi^{(i)} + mc' \sum_{i=1}^N \mathbf{x}^{(i)} \times \xi^{(i)} + \frac{1}{2} m C' \sum_{i=1}^N \xi^{(i)2}, \quad (4.6)$$

where C , c , c' and C' may be functions of the $\mathbf{x}^{(i)}$.

To determine these functions, substitute in (2.12), modified for equilibrium conditions. Then

$$\frac{\partial f_N}{\partial t} + \sum_{i=1}^N \overline{\xi^{(i)}} \frac{\partial f_N}{\partial \mathbf{x}^{(i)}}$$

vanishes; the statistical term

$$\frac{1}{m} \int \int \sum_{i=1}^N \frac{\partial f_N}{\partial \xi^{(i)}} \frac{\partial \phi^{(iN+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(N+1)} d\xi^{(N+1)}$$

can be reduced to terms of the form

$$-\frac{1}{(N-1)!} \int \cdots \int (f_N F_N - f'_N F'_N) \rho d\mathbf{b} \prod_{i=N+2}^{2N} d\mathbf{x}^{(i)} \prod_{j=N+1}^{2N} d\xi^{(j)}$$

by analysis similar to that of the last section, and also vanishes. (2.12) therefore reduces to

$$\sum_{i=1}^N \frac{\partial f_N}{\partial \mathbf{x}^{(i)}} (\xi^{(i)} - \bar{\xi}^{(i)}) = \frac{1}{m} \sum_{i=1}^N \frac{\partial f_N}{\partial \xi^{(i)}} \frac{\partial \Phi}{\partial \mathbf{x}^{(i)}}, \quad (4.7)$$

and then, on substitution from (4.6),

$$\left. \begin{aligned} \frac{\partial C'}{\partial \mathbf{x}^{(i)}} &= 0, \\ \frac{\partial}{\partial \mathbf{x}^{(i)}} (\mathbf{c} + \mathbf{c}' \times \mathbf{x}^{(j)}) + \frac{\partial}{\partial \mathbf{x}^{(j)}} (\mathbf{c} + \mathbf{c}' \times \mathbf{x}^{(i)}) &= 0, \\ \frac{\partial C}{\partial \mathbf{x}^{(i)}} &= C' \frac{\partial \Phi'}{\partial \mathbf{x}^{(i)}} + m \sum_{j=1}^N \bar{\xi}^{(j)} \cdot \frac{\partial}{\partial \mathbf{x}^{(j)}} (\mathbf{c} + \mathbf{c}' \times \mathbf{x}^{(i)}), \\ \sum_{i=1}^N (\mathbf{c} + \mathbf{c}' \times \mathbf{x}^{(i)}) \frac{\partial \Phi'}{\partial \mathbf{x}^{(i)}} + \sum_{i=1}^N \bar{\xi}^{(i)} \frac{\partial C}{\partial \mathbf{x}^{(i)}} &= 0. \end{aligned} \right\} \quad (4.8)$$

The first and second of these equations show that C' , \mathbf{c} and \mathbf{c}' are all constants; C' is found to be given by $-1/kT$, when the temperature T is defined by

$$\frac{3}{2}kT = \frac{1}{2N!} \int \cdots \int f_N \sum_{i=1}^N (\xi^{(i)} - \bar{\xi}^{(i)})^2 \prod_{j=1}^N d\mathbf{x}^{(j)} d\xi^{(j)}. \quad (4.9)$$

Also, by calculation, it is found that $\bar{\xi}^{(i)} = kT(\mathbf{c} + \mathbf{c}' \times \mathbf{x}^{(i)})$, so that \mathbf{c} and \mathbf{c}' find simple interpretations as multiples of the velocity and angular velocity respectively; the fluid, if in motion, must behave macroscopically like a rigid body. The third of equations (4.8), taking account of the second, requires that

$$C = C' \left(\Phi' + \frac{1}{2}m \sum_{i=1}^N \bar{\xi}^{(i)2} \right) + C'',$$

where C'' is a pure constant; and the last reduces to $\sum_{i,j=1}^N \bar{\xi}^{(i)} \cdot \frac{\partial}{\partial \mathbf{x}^{(i)}} \bar{\xi}^{(j)2} = 0$, showing

only that the visible kinetic energy $\frac{1}{2}m \sum_{j=1}^N \bar{\xi}^{(j)2}$ is conserved.

The most general form for f_N when there are no changes in the entropy has thus been obtained.

5. THE SOLUTION OF THE INTEGRAL EQUATION

Now proceed to examine the equilibrium state in detail by the method proposed in § 5 of part I, namely, by the solution of the integral equation for $n_2(r)$:

$$\log \frac{n_2(r)}{n_1^2} + \frac{\phi(r)}{kT} = \frac{\pi}{n_1^3} \int_0^\infty \int_{-s}^s (s^2 - t^2) \frac{t+r}{r} \{n_2(t+r) - n_1^2\} dt n_2(s) \frac{\phi'(s)}{kT} ds. \quad (5.1)$$

First linearize the equation by writing

$$n_2(r) = n_1^2 e^{-\phi(r)/kT} \{1 + f(r)\}, \quad (5.2)$$

and neglecting squares and higher powers of $f(r)$. This procedure will be justified if the right-hand side of (5.1) is not too large; hence

$$\begin{aligned} rf(r) &= -\pi n_1 \int_0^\infty \int_{-s}^s (s^2 - t^2) (t+r) f(t+r) \{1 + \alpha(t+r)\} dt \alpha'(s) \{1 + f(s)\} ds \\ &\quad - \pi n_1 \int_0^\infty \int_{-s}^s (s^2 - t^2) (t+r) \alpha(t+r) dt \alpha'(s) \{1 + f(s)\} ds, \end{aligned} \quad (5.3)$$

where

$$\alpha(r) = e^{-\phi(r)/kT} - 1. \quad (5.4)$$

Now observe that $\alpha(r)$ and $\alpha'(r)$ are both negligible except for small r , so that, when multiplied by these factors, $f(r)$ may be replaced by $\epsilon - 1$, its average value in the neighbourhood of the origin. Then, after integration by parts,

$$rf(r) = 2\pi n_1 \int_0^\infty \int_{-s}^s (t+r) \{f(t+r) + \epsilon \alpha(t+r)\} dt \epsilon \alpha(s) s ds. \quad (5.5)$$

This equation can be solved by Fourier transforms; writing

$$\left. \begin{aligned} rg(r) &= \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} sf(s) \sin(rs) ds, \\ r\beta(r) &= \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} s\alpha(s) \sin(rs) ds, \end{aligned} \right\} \quad (5.6)$$

then (5.5) becomes

$$\lambda g(r) = \{g(r) + \epsilon \beta(r)\} \epsilon \beta(r), \quad (5.7)$$

where $\lambda^{-1} = (2\pi)^{\frac{1}{2}} n_1$, so that

$$rf(r) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \frac{\epsilon^2 s \beta(s)^2 \sin(rs) ds}{\lambda - \epsilon \beta(s)}. \quad (5.8)$$

It will be supposed that there is an analytic function $\beta(z)$ which reduces to $\beta(r)$ when $z = r$ is real. The most general solution of (5.5) is then given by (5.8), where the path of integration may follow any course from negative to positive infinity in the complex plane. This is most easily seen by remarking that if $f(r)$ is a solution, so is $f(r) + \frac{A_k}{r} \sin(rz_k)$, where z_k is any root of the transcendental equation

$$\beta(z) = \lambda/\epsilon; \quad (5.9)$$

the additional term may, however, be obtained from (5.8) by deforming the path of integration to enclose the singular point z_k . It will be seen in the next section,

however, that the precise path of integration is determined by the boundary condition

$$f(r) = O(r^{-3}) \quad \text{as} \quad r \rightarrow \infty, \quad (5.10)$$

which follows from the requirement that $\int (n_2^{(12)} - n_1^2) d\mathbf{x}^{(2)}$ should converge. (Strictly, one should write $f(r) = O(r^{-(3+\delta)})$, $\delta > 0$, but owing to the approximate nature of (5.2), this refinement is not compulsory.)

6. THERMODYNAMICAL EXPRESSIONS

It is now possible to calculate explicitly the internal energy E , given by

$$E = \frac{1}{2}V \int_0^\infty n_2(r) \phi(r) 4\pi r^2 dr + \frac{3}{2}NkT, \quad (6.1)$$

and the pressure p from

$$p = n_1 kT - \frac{1}{6} \int_0^\infty n_2(r) \phi'(r) r 4\pi r^2 dr. \quad (6.2)$$

These formulae are known, but a comprehensive derivation is included in the appendix. Then, from (5.2) and (5.8),

$$E = \frac{NkT^2}{2\lambda} \left[\frac{\partial}{\partial T} \{ \beta(0) \} + \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \frac{\epsilon^2 \beta(s)^2 \frac{\partial \{\beta(s)\}}{\partial T} s^2 ds}{\lambda - \epsilon \beta(s)} \right] + \frac{3}{2}NkT, \quad (6.3)$$

and

$$p = n_1 kT \left\{ 1 + \frac{n_1 I}{6(2\pi)^{\frac{1}{2}} \lambda} \right\}, \quad (6.4)$$

where

$$\begin{aligned} I &= \int_{-\infty}^{\infty} \alpha'(r) \{ 1 + f(r) \} r^3 dr \\ &= - \int_{-\infty}^{\infty} \alpha(r) [3\{1+f(r)\} + rf'(r)] r^2 dr \\ &= - 3(2\pi)^{\frac{1}{2}} \beta(0) - \int_{-\infty}^{\infty} \frac{\epsilon^2 \beta(s)^2 \{3\beta(s) + s\beta'(s)\} s^2 ds}{\lambda - \epsilon \beta(s)} \\ &= - 3(2\pi)^{\frac{1}{2}} \beta(0) - \int_{-\infty}^{\infty} \left[-\frac{1}{2}\epsilon \beta(s)^2 + \frac{\lambda^2 \beta(s)}{\lambda - \epsilon \beta(s)} + \frac{\lambda^2}{\epsilon} \log \left| 1 - \frac{\epsilon}{\lambda} \beta(s) \right| \right] s^2 ds. \end{aligned} \quad (6.5)$$

Combining (6.3) and (6.4), it is confirmed that the equation

$$d\left(\frac{A}{T}\right) = -\frac{E}{T^2} dT - \frac{p dV}{T} \quad (6.6)$$

is integrable, yielding for the free energy

$$\begin{aligned} A &= \frac{NkT}{2\lambda} \left[-\beta(0) + \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \left[\frac{1}{2}\epsilon \beta(s)^2 + \lambda \beta(s) + \frac{\lambda^2}{\epsilon} \log \left| 1 - \frac{\epsilon}{\lambda} \beta(s) \right| \right] s^2 ds \right. \\ &\quad \left. - \frac{3}{2}NkT \log T + NkT \log n_1 \right] \end{aligned} \quad (6.7)$$

apart from an insignificant multiple of T .

Explicit formulae for all the important thermodynamical functions have thus been obtained, except that the path of integration, which is the same in (5.8), (6.3), (6.5) and (6.7), is so far undetermined. To apply the boundary condition use is made of the well-known lemma

$$\lim_{r \rightarrow \infty} \int_{-\infty}^{\infty} \frac{\psi(s)}{s} \sin(rs) ds = \lim_{t \rightarrow 0} \pi \psi(t). \quad (6.8)$$

It is necessary also to discuss the dependence of $\alpha(r)$ and $\beta(r)$ on the temperature. Since $\phi(r)$ is negative for all large r , in this range $\alpha(r)$ will become increasingly positive as the temperature decreases. It follows that $\beta(r)$ will behave in the same way when r is small. Referring to (5.9), it is necessary to distinguish between two cases. For sufficiently low densities and high temperatures, λ/e exceeds the upper bound of $\beta(r)$, and (5.9) has no real roots; the path of integration may then be taken along the real axis, since (5.10) is thereby satisfied. In the region of higher densities and lower temperatures, however, (5.9) will have a pair of equal and opposite real roots (since $\beta(z)$ is an even function of z), and in this case the path of integration must be taken just above both singularities on the real axis. On such a path,

$$\int_{-\infty}^{\infty} \frac{s\psi(s) \sin(rs) ds}{s^2 - s_0^2} = \int_{-\infty}^{\infty} \frac{s\{\psi(s) - \psi(s_0)\} \sin(rs) ds}{s^2 - s_0^2},$$

so that the singularities in the integrand do not affect the behaviour of the integral for large r .

The possibility that *the two cases described above correspond to the gaseous and liquid phases respectively* has already been expressed, and in the following sections convincing evidence will be given to confirm this view.

7. DEVELOPMENT FOR THE GASEOUS PHASE

The expressions found in the last section for the thermodynamical functions are quite general, but not very informative to the physical intuition, or convenient for numerical evaluation. Certain developments in series of the general expressions will therefore be considered. In the region of low densities and high temperatures $\left| \frac{e\beta(s)}{\lambda} \right| < 1$ for all real s , and it is permissible to develop the infinite integrals in powers of the density. Hence

$$A = -NkT \left\{ \frac{\beta(0)}{2\lambda} + \sum_{\nu=2}^{\infty} \frac{e^{\nu}}{2(2\pi)^{\frac{1}{2}} \lambda^{\nu}} \int_{-\infty}^{\infty} \frac{\beta(s)^{\nu+1} s^2 ds}{\nu+1} \right\} - \frac{3}{2} NkT \log T + NkT \log n_1 \quad (7.1)$$

and $p = n_1 kT \left\{ 1 - \frac{\beta(0)}{2\lambda} - \sum_{\nu=2}^{\infty} \frac{\nu e^{\nu}}{2(2\pi)^{\frac{1}{2}} \lambda^{\nu}} \int_{-\infty}^{\infty} \frac{\beta(s)^{\nu+1} s^2 ds}{\nu+1} \right\}, \quad (7.2)$

which is the equation of state.

Under the same conditions, however, Mayer (1937) has obtained an exact development quite analogous to (7.1) by evaluation of the integral expression in (2.1). A concise and perfected exposition of the method has been given by Born & Fuchs (1938); the result obtained is

$$A = -NkT \sum_{\nu=1}^{\infty} \frac{\beta_{\nu} n_{\nu}^{\nu}}{\nu+1} - \frac{3}{2} NkT \log T + NkT \log n_1, \quad (7.3)$$

where the first β_{ν} are given by

$$\left. \begin{aligned} \beta_1 &= \int_0^{\infty} \alpha(r) 4\pi r^2 dr, \\ \beta_2 &= \frac{1}{2} \iint \alpha^{(12)} \alpha^{(23)} \alpha^{(31)} d\mathbf{x}^{(2)} d\mathbf{x}^{(3)}, \\ \alpha^{(rs)} &= \alpha(|\mathbf{x}^{(s)} - \mathbf{x}^{(r)}|), \end{aligned} \right\} \quad (7.4)$$

or

$$\left. \begin{aligned} \beta_1 &= (2\pi)^{\frac{1}{2}} \beta(0), \\ \beta_2 &= \frac{1}{2}(2\pi)^{\frac{1}{2}} \int_0^{\infty} \beta(y)^3 4\pi y^3 dy, \\ \alpha^{(rs)} &= \frac{1}{(2\pi)^{\frac{1}{2}}} \int e^{iy(\mathbf{x}^{(s)} - \mathbf{x}^{(r)})} \beta(y) dy. \end{aligned} \right\} \quad (7.5)$$

Comparing (7.1) and (7.3), it is found that

$$\beta_{\nu} = \frac{1}{2} \epsilon^{\nu} (2\pi)^{\frac{1}{2}(3\nu-1)} \int_{-\infty}^{\infty} \beta(s)^{\nu+1} s^2 ds. \quad (7.6)$$

Substituting $\nu = 2$ in (7.6), agreement is obtained with the value of β_2 given by (7.5), provided $\epsilon = 1$; the remaining β_{ν} given by (7.6) are approximate, but far more tractable expressions for the viral coefficients than those obtained by Mayer's combinational method.

Mayer found that the equation of state derived from (7.3) will not describe the liquid phase, for the simple reason that the infinite series becomes divergent on approaching the point of condensation. Precisely the same thing happens to the present series (7.1) when the transcendental equation (5.9) first has a real root, and the provisional hypothesis advanced at the end of the last section is therefore confirmed.

It is important to notice, however, that the solution of the equation (5.9) will not necessarily yield the boiling-point as a function of density, but rather the highest temperature to which the liquid can be superheated without boiling. The boiling-point must be determined by the usual thermodynamical method of considering the equilibrium between the two phases.*

* The authors of this series believe that the view of Kahn (1938) on this matter is incorrect, and will give detailed reasons later.

8. DEVELOPMENT FOR THE LIQUID PHASE

It has been seen that the power series (7.1) can describe only the gaseous phase, and that another form of expansion is required to adapt the formulae of § 6 for the liquid as well as the gas. For this purpose it is convenient to consider the complex roots z_u ($u = 1, 2, 3, \text{etc.}$) of (5.9) in the upper half of the z -plane. Assume that $\beta(z) \rightarrow 0$ as $|z| \rightarrow \infty$, uniformly with respect to $\arg z$, in this region; by the theory of residues, the following expansion is then obtained from (5.8):

$$r\{f(r) + \epsilon\alpha(r)\} = -(2\pi)^{\frac{1}{2}} \sum_u \frac{z_u e^{iz_u}}{\beta'(z_u)}, \quad (8.1)$$

where, according to (5.6),

$$z_u \beta'(z_u) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \cos(rz_u) \alpha(s) s^2 ds - \lambda/\epsilon, \quad (8.2)$$

$$\text{so that } -z_u \beta'(z_u) kT^2 \frac{\partial z_u}{\partial T} = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \sin(rz_u) e^{-\phi(s)/kT} \phi(s) s ds. \quad (8.3)$$

Now use (8.1) to calculate E afresh from (6.1), and obtain

$$E = \frac{NkT^2}{2\lambda} \left[\frac{\partial}{\partial T} \left\{ \beta(0) - \frac{\epsilon}{2(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \beta(s)^2 s^2 ds \right\} + (2\pi)^{\frac{1}{2}} i \frac{\lambda^2}{\epsilon} \sum_u z_u^2 \frac{\partial z_u}{\partial T} \right] + \frac{3}{2} NkT. \quad (8.4)$$

The equation of state, obtained similarly from (6.2), is

$$p = n_1 kT \left[1 - \frac{\beta(0)}{2\lambda} + \frac{\epsilon}{4(2\pi)^{\frac{1}{2}} \lambda} \int_{-\infty}^{\infty} \beta(r)^2 r^2 dr + \frac{(2\pi)^{\frac{1}{2}} i \lambda}{2\epsilon} \sum_u \left(\frac{\lambda z_u^2}{\epsilon \beta'(z_u)} + \frac{z_u^3}{3} \right) \right]. \quad (8.5)$$

Since

$$\beta'(z_u) \frac{\partial z_u}{\partial V} = \frac{\lambda n_1}{\epsilon N}, \quad (8.6)$$

the equation (6.6) is again integrable, and

$$A = -\frac{NkT}{2\lambda} \left\{ \beta(0) - \frac{\epsilon}{2(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \beta(r)^2 r^2 dr + \frac{(2\pi)^{\frac{1}{2}} i \lambda^2}{3\epsilon} \sum_u z_u^3 \right\} - \frac{3}{2} NkT \log T + NkT \log n_1. \quad (8.7)$$

The formulae of this section hold equally for the liquid and the gas. The difference arises from the fact that in the case of the liquid there are two real roots which are not included in the u -summation; when the temperature is raised beyond the boiling-point these roots migrate in opposite directions into the complex plane, and the one above the real axis is now included in the u -summation. Thus there is a real discontinuity in the radial distribution function and all the thermodynamic functions at the point of condensation—a consequence of the theory which is confirmed by experience. However, the discontinuity in the radial distribution function corresponds only to a transfer from one branch of the general solution of the integral equation to another; the point of condensation is therefore a kind of branch point.

An approximate classical theory of the solid state appears to result in the following way. When the boundary condition (5.10), which can be correct only for liquids, is omitted, the possibility of a periodic term $\frac{Ak}{r} \sin rz_k$ in the expression for $n_2(r)$, where z_k is the real root of (5.9), is not excluded. Such periodicity at large distances from a given lattice point is characteristic of the solid state. This may provide confirmation of the idea of Vlasov mentioned in the introduction to the first paper of this series.

9. APPENDIX

Here a proof of the formula (2.1) for the free energy will be given. First show that the quantity there defined satisfies the differential equation (6.6), or the equivalent partial differential equations

$$\frac{\partial}{\partial T} \left(\frac{A}{T} \right) = -\frac{E}{T^2}; \quad \frac{\partial}{\partial V} \left(\frac{A}{T} \right) = -\frac{p}{T}, \quad (9.1)$$

where E and p are defined by (6.1) and (6.2) respectively. Use is made of the formula

$$Q_1 n_2 = \frac{1}{(N-2)!} \int^{(N-2)} \cdots \int e^{-\Phi/kT} \prod_{i=3}^N d\mathbf{x}^{(i)}, \quad (9.2)$$

where

$$\begin{aligned} Q_1 &= \frac{1}{N!} \int^{(N)} \cdots \int e^{-\Phi/kT} \prod_{i=1}^N d\mathbf{x}^{(i)} \\ &= \left(\frac{2\pi kT}{m} \right)^{-\frac{1}{2}(3N)} e^{-A/kT}. \end{aligned} \quad (9.3)$$

The first of the equations (9.1) follows immediately on differentiating (9.3); to obtain the second, write $\mathbf{x}^{(i)} = l\theta^{(i)}$, where $l^3 = V$; then

$$\left. \begin{aligned} Q_1 &= \frac{l^{3N}}{N!} \int_{-\frac{1}{2}}^{\frac{1}{2}(3N)} \cdots \int_{-\frac{1}{2}}^{\frac{1}{2}} e^{-\Phi/kT} \prod_{i=1}^N d\theta_1^{(i)} d\theta_2^{(i)} d\theta_3^{(i)}, \\ \Phi &= \frac{1}{2} \sum_{i,j=1}^N \phi \{ l | \theta^{(j)} - \theta^{(i)} | \}, \end{aligned} \right\} \quad (9.4)$$

so that

$$\frac{\partial Q_1}{\partial l} = \frac{3NQ_1}{l} - \frac{l^{3N}}{2(N-2)!} \int_{-\frac{1}{2}}^{\frac{1}{2}(3N)} \cdots \int_{-\frac{1}{2}}^{\frac{1}{2}} e^{-\Phi/kT} \frac{\phi' \{ l | \theta^{(2)} - \theta^{(1)} | \}}{kT} | \theta^{(2)} - \theta^{(1)} | \prod_{i=1}^N d\theta_1^{(i)} d\theta_2^{(i)} d\theta_3^{(i)} \quad (9.5)$$

and

$$\frac{\partial Q_1}{\partial V} = \frac{1}{3l^2} \frac{\partial Q_1}{\partial l}$$

$$= n_1 Q_1 - \frac{1}{6} Q_1 \int n_2(r) \frac{\phi'(r)}{kT} r dr. \quad (9.6)$$

This leads immediately to the second of equations (9.1).

It remains to be shown that the quantities E and p as defined correspond to the internal energy and pressure as observed experimentally. That this is so in the case of the internal energy follows easily on calculating the mean value of the Hamiltonian energy W . The evaluation of the pressure requires rather more attention; in order to make the discussion as general as possible, equilibrium conditions will not be assumed, and the pressure tensor in the fluid will be evaluated in the first instance. (The analysis which follows is borrowed from part III on dynamical properties, now in preparation by Professor M. Born and the author.)

Multiply the equation

$$\frac{\partial f_1}{\partial t} + \xi^{(1)} \frac{\partial f_1}{\partial \mathbf{x}^{(1)}} = \frac{1}{m} \iint \frac{\partial \phi}{\partial \mathbf{x}^{(1)}} \frac{\partial f_2}{\partial \xi^{(1)}} d\mathbf{x}^{(2)} d\xi^{(2)}, \quad (9.7)$$

which is satisfied by f_1 in the absence of external forces, by $m\xi^{(1)}$, and integrate over $\xi^{(1)}$, obtaining

$$\begin{aligned} \frac{\partial}{\partial t} \left\{ \int m \xi_\alpha^{(1)} f_1 d\xi^{(1)} \right\} + \sum_{\beta=1}^3 \frac{\partial}{\partial x_\beta^{(1)}} \left\{ \int m \xi_\alpha^{(1)} \xi_\beta^{(1)} f_1 d\xi^{(1)} \right\} \\ = \sum_{\beta=1}^3 \iiint \frac{\partial \phi}{\partial x_\beta^{(1)}} \frac{\partial f_2}{\partial \xi_\beta^{(1)}} \xi_\alpha^{(1)} d\mathbf{x}^{(2)} d\xi^{(2)} d\xi^{(1)} \\ = - \int \frac{\partial \phi}{\partial x_\alpha^{(1)}} n_2 d\mathbf{x}^{(2)}. \end{aligned} \quad (9.8)$$

To simplify further the right-hand side, note that, although macroscopically uniform conditions are not yet assumed, within the microscopic sphere around $\mathbf{x}^{(2)}$, where $\partial\phi/\partial\mathbf{x}^{(1)}$ is effectively different from zero, n_2 may be represented as a function of $r = |\mathbf{x}^{(2)} - \mathbf{x}^{(1)}|$, and writing

$$\nu(\mathbf{x}^{(2)}, r) = \int_{\infty}^r n_2(\mathbf{x}^{(2)}, r') \phi'(r') dr', \quad (9.9)$$

then (9.8) becomes

$$\frac{\partial}{\partial t} (mn_1 \xi_\alpha^{(1)}) + \sum_{\beta=1}^3 \frac{\partial}{\partial x_\beta^{(1)}} \left\{ \int m \xi_\alpha^{(1)} \xi_\beta^{(1)} f_1 d\xi^{(1)} + \int \nu d\mathbf{x}^{(2)} \delta_{\alpha\beta} \right\} = 0. \quad (9.10)$$

Further, since $\frac{\partial}{\partial t} (n_1 \xi_\alpha^{(1)}) = n_1 \frac{d\xi_\alpha^{(1)}}{dt} - \sum_{\beta=1}^3 \frac{\partial}{\partial x_\beta^{(1)}} (n_1 \overline{\xi_\alpha^{(1)} \xi_\beta^{(1)}})$, (9.10) reduces to

$$mn_1 \frac{d\xi_\alpha^{(1)}}{dt} + \sum_{\beta=1}^3 \frac{\partial p_{\alpha\beta}}{\partial x_\beta^{(1)}} = 0, \quad (9.12)$$

where $p_{\alpha\beta} = m \int (\xi_\alpha^{(1)} \xi_\beta^{(1)} - \overline{\xi_\alpha^{(1)} \xi_\beta^{(1)}}) f_1 d\xi^{(1)} + \int \nu d\mathbf{x}^{(2)} \delta_{\alpha\beta} + \pi_{\alpha\beta}$, (9.13)

and $\pi_{\alpha\beta}$ is any tensor which satisfies $\sum_{\beta=1}^3 \frac{\partial \pi_{\alpha\beta}}{\partial x_{\beta}^{(1)}} = 0$. $\pi_{\alpha\beta}$ must be determined by conditions at the boundary of the fluid, where the part of $p_{\alpha\beta}$ due to the molecular forces, namely,

$$\int \nu(\mathbf{x}^{(1)} + \mathbf{r}, r) d\mathbf{r} \delta_{\alpha\beta} + \pi_{\alpha\beta},$$

must vanish. (The interaction between the walls and the fluid is neglected.)

In uniform conditions, $\nu(\mathbf{x}^{(2)}, r)$ depends only on r , and $\pi_{\alpha\beta}$ is a constant tensor, given by

$$\pi_{\alpha\beta} = -\frac{1}{2} \int_0^\infty \nu(r) 4\pi r^2 dr \delta_{\alpha\beta}, \quad (9.14)$$

since \mathbf{r} ranges only over a hemisphere at the boundary. The hydrostatic pressure in equilibrium conditions is therefore given by

$$\begin{aligned} p &= \frac{1}{3} \int \xi^{(1)2} f_1 d\xi^{(1)} + \frac{1}{2} \int_0^\infty \nu(r) 4\pi r^2 dr \\ &= n_1 kT - \frac{1}{6} \int_0^\infty n_2(r) \phi'(r) r 4\pi r^2 dr, \end{aligned} \quad (9.15)$$

in agreement with the value found previously by differentiating the phase integral.

The author wishes to express here his grateful appreciation of numerous helpful discussions with Professor Born in the course of this work. He is also indebted to Dr R. Fürth for some useful comments.

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A general kinetic theory of liquids

III. Dynamical properties

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The theory of liquids formulated in part I and applied to the equilibrium state in part II is here extended to liquids in motion. The connexion between the macroscopic and microscopic properties is revealed by the derivation of a set of generalized hydrodynamical equations, of which the fundamental equations of hydrodynamics are a special case; the more general equations describe the mean motion of clusters of molecules in the fluid. It is shown that the pressure tensor and energy-flux vector in a fluid consist of two parts, due to the thermal motion of the molecules and the intermolecular forces respectively, of which only the first is found in the kinetic theory of gases, but of which the second is dominant for the liquid state.

A method is evolved for the study of those 'normal' non-uniform states which relate to actual monatomic fluids in motion. It becomes apparent, as in the case of equilibrium, that there is a region of temperature and density where analytical singularities arise, closely associated with the process of condensation.

Rigorous expressions for the coefficients of viscosity and thermal conduction are then derived which apply equally to the liquid and the gas. They consist of two parts due to the thermal motion and molecular forces respectively, of which the first is dominant for the gas, and the second for the liquid. By approximating to the rigorous formula, an expression for the viscosity of liquids is obtained, comparable with certain other formulae, previously proposed on quasi-empirical grounds, and giving good agreement with experiment.

An integro-differential equation is derived for the determination of the distribution functions relating to the non-uniform state. A full discussion is given of the simplest case, and the velocity distribution in non-uniform liquids and gases examined.

1. INTRODUCTION

In the first paper of this series (Born & Green 1946), we have explained a general method for dealing with an assembly of equal particles not in equilibrium; in the second (Green 1947), the special case of equilibrium has been treated, and it has been shown that even here, where the new method is completely equivalent to statistical mechanics, it is more powerful in obtaining explicit results. In the present paper, a moving fluid will be treated in more detail, and not only the thermo-mechanical

equations of motion, but also rigorous expressions for the coefficients of viscosity and thermal conduction will be given. The latter will be simplified for comparison with expressions found in the literature (which, however, can be regarded only as dimensional formulae). In this way theoretical justification for certain empirical formulae will be found, of the type first mentioned by de Guzman (1913) and studied in detail by Andrade (1934), which are known to give excellent agreement with experiment.

Concerning the method of approximation, it has been found that the method developed by Hilbert (1912), Enskog (1911, 1917) and Chapman (1912, 1916), fails for the multiple distribution functions ($h > 1$). A new one has therefore been devised, based on an expansion with respect to the space gradients of the equilibrium parameters (density, mean velocity and temperature).

One feature of the results has to be mentioned particularly, namely, the appearance of condensation as a singularity not only in the equilibrium equations, but also in the expressions for the dynamical constants. We wish to stress the point that we differ fundamentally from the ideas about condensation held by many modern writers, and clearly formulated by Kahn (1938) in his well-known dissertation, namely, that the horizontal part of the isotherm in the p - v diagram ($p = \text{const.}$), representing the co-existence of liquid and gas, is contained in the general thermodynamical expressions. In fact, the co-existence of the two phases means only that there are two values of v for the same p ; the straight line connecting these points has no meaning unless a parameter strange to the theory of one phase is introduced, e.g. the mass ratio of the two phases. We believe that Kahn's derivation of this line $p = \text{const.}$ is based on a misconception of the situation; for he assumes the virial coefficients (β_n) to be constants, whereas they depend on the volume for high values of n . Kahn's results have really a different meaning: he has found the liquid branch of the isotherm without noticing it.

In this paper no attempt will be made to obtain exact numerical values for physical constants, as this will require extended and tedious calculations. Apart from these, we hope to generalize the theory in the following different directions. The first and most obvious step is the introduction of internal degrees of freedom of the particles (molecules); this is probably closely connected with giving up the assumption of central forces. Then mixtures of two or more kinds of particles have to be considered in order to obtain the laws of ordinary and thermal diffusion; the latter (Soret effect) will be of special interest, as no satisfactory theory for liquids seems to exist. Also our theory gives, as shown in part II, clear indications of the appearance of the solid state; we hope that it will lead to a better understanding of the present lattice dynamics and its limits, in particular to a theory of melting and plasticity.

The most important generalization envisaged is the introduction of quantum mechanics. For there are known several examples of quantum 'liquids': helium II (superfluidity), the substance of nuclei (droplet model), and perhaps electrons in metals (superconductivity). It is, of course, hopeless to try to understand the

abnormal viscosity in liquid helium if one has no theory of viscosity in normal liquids. This gap has now been closed, and we wish to extend our theory of viscosity to quantum liquids.

The tensor notation used in this paper is that devised by Chapman & Milne (see Chapman & Cowling 1939, chapter 1). Vectors are represented in clarendon type (\mathbf{a}), and cartesian tensors in sans serif type (\mathbf{w}). The transpose of a tensor \mathbf{w} is $\overline{\mathbf{w}}$; its products with a vector \mathbf{a} (both vectors) are denoted by $\mathbf{w} \cdot \mathbf{a}$ and $\mathbf{a} \cdot \mathbf{w}$; the spur product with a second tensor \mathbf{w}' (a scalar), by $\mathbf{w} : \mathbf{w}'$, etc.

2. HYDRODYNAMICS

The fundamental equation of the theory [(4.5) of part I] may be written in the form

$$\begin{aligned} \frac{\partial f_h}{\partial t} + \sum_{i=1}^h \left(\xi^{(i)} \cdot \frac{\partial f_h}{\partial \mathbf{x}^{(i)}} + \eta_h^{(i)} \cdot \frac{\partial f_h}{\partial \xi^{(i)}} \right) \\ = \frac{1}{m} \sum_{i=1}^h \iint \left(\frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial}{\partial \xi^{(i)}} \right) \left(f_{h+1} - \frac{f_h f_1^{(h+1)} n_{h+1}}{n_h n_1^{(h+1)}} \right) d\mathbf{x}^{(h+1)} d\xi^{(h+1)}, \quad (2.1) \end{aligned}$$

where

$$m\eta_h^{(i)} = - \sum_{j=1}^h \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} - \int \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \frac{n_{h+1}}{n_h} d\mathbf{x}^{(h+1)} + \mathbf{P}^{(i)}, \quad (2.2)$$

so that, while $\mathbf{P}^{(i)} = \mathbf{P}(t, \mathbf{x}^{(i)})$ is the *external* force acting on a molecule at $\mathbf{x}^{(i)}$ at time t , $m\eta_h^{(i)}$ includes the average force due to the presence of the other molecules, the positions of the first h of which are assumed to be known.

In this section, the generalized hydrodynamical equations referring to such a cluster of h molecules will be derived from (2.1). By integrating this equation over the velocities $\xi^{(1)} \dots \xi^{(h)}$,

$$\frac{\partial n_h}{\partial t} + \sum_{i=1}^h \frac{\partial}{\partial \mathbf{x}^{(i)}} \cdot (n_h \mathbf{u}_h^{(i)}) = 0 \quad (2.3)$$

is obtained, where

$$n_h \mathbf{u}_h^{(i)} = \int \dots \int f_h \xi^{(i)} \prod_{j=1}^h d\xi^{(j)}. \quad (2.4)$$

(2.3) and (2.4) were obtained previously, as (3.3) and (3.4) of part I, where (2.3) was interpreted as the generalized equation of continuity.

Let I be any function of the time t and the co-ordinates $\mathbf{x}^{(1)} \dots \mathbf{x}^{(h)}$. Then it follows from (2.3) that

$$\frac{\partial}{\partial t} (n_h I) = n_h \frac{dI}{dt} - \sum_{i=1}^h \frac{\partial}{\partial \mathbf{x}^{(i)}} \cdot (n_h I \mathbf{u}_h^{(i)}), \quad (2.5)$$

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

Next, after multiplying (2.1) by $\xi^{(i)}$ and integrating over all the velocities,

$$\frac{\partial}{\partial t} (n_h \mathbf{u}_h^{(i)}) + \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \left(\int \dots \int f_h \xi^{(j)} \xi^{(i)} \prod_{k=1}^h d\xi^{(k)} \right) = n_h \dot{\eta}_h^{(i)} \quad (2.6)$$

is obtained, since the right-hand side of (2.1) is seen to contribute nothing, after an integration by parts over $\xi^{(i)}$. On applying (2.5), (2.6) becomes

$$mn_h \frac{d}{dt} \mathbf{u}_h^{(i)} + \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{k}_h^{(ji)} = mn_h \eta_h^{(i)}, \quad (2.7)$$

where

$$\mathbf{k}_h^{(ij)} = m \int \dots \int f_h \mathbf{v}_h^{(i)} \mathbf{v}_h^{(j)} \prod_{k=1}^h d\xi^{(k)}, \quad (2.8)$$

and

$$\mathbf{v}_h^{(i)} = \xi^{(i)} - \mathbf{u}_h^{(i)}. \quad (2.9)$$

Further, on writing

$$\mathbf{p}_h^{(ij)} = \mathbf{k}_h^{(ij)} + \mathbf{l}_h^{(ij)}, \quad (2.10)$$

where $\mathbf{l}_h^{(ij)}$ is defined by the equation

$$\sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{l}_h^{(ji)} = n_h \sum_{j=1}^h \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} + \int n_{h+1} \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(h+1)}, \quad (2.11)$$

$$(2.7) \text{ assumes the form } mn_h \frac{d}{dt} \mathbf{u}_h^{(i)} + \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{p}_h^{(ji)} = n_h \mathbf{P}^{(i)}. \quad (2.12)$$

This is the generalization of the equation of motion of ordinary hydrodynamics, to which it reduces when $h = 1$. It is clear that the pressure tensor $\mathbf{p}_h^{(ij)}$ consists of two parts $\mathbf{k}_h^{(ij)}$ and $\mathbf{l}_h^{(ij)}$, of which the first is due to the thermal motion of the molecules, and the second to the intermolecular forces. It is customary to neglect this latter part in the kinetic theory of gases, but in liquids, far from being negligible, it is clearly the dominant part.

When (2.1) is multiplied by $\frac{1}{2}\xi^{(i)2}$ and integrated over all the velocities, the resulting equation is

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\frac{3k}{2m} n_h T_h^{(i)} + \frac{1}{2} n_h \mathbf{u}_h^{(i)2} \right) + \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \left(\int \dots \int f_h \xi^{(j)} \frac{1}{2} \xi^{(i)2} \prod_{k=1}^h d\xi^{(k)} \right) \\ &= n_h \mathbf{u}_h^{(i)} \cdot \eta_h^{(i)} - \frac{1}{m} \int n_{h+1} \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot (\mathbf{u}_{h+1}^{(i)} - \mathbf{u}_h^{(i)}) d\mathbf{x}^{(h+1)}, \end{aligned} \quad (2.13)$$

where

$$\frac{3k}{2m} n_h T_h^{(i)} = \int \dots \int f_h \frac{1}{2} \mathbf{v}_h^{(i)2} \prod_{j=1}^h d\xi^{(j)}, \quad (2.14)$$

defining a generalized temperature $T_h^{(i)}$, which reduces to the ordinary temperature $T_1^{(i)}$ at the point $\mathbf{x}^{(i)}$ when $h = 1$. Equation (2.13) is first transformed by means of (2.5) and (2.12), with the result

$$\begin{aligned} & \frac{3k}{2m} n_h \frac{dT_h^{(i)}}{dt} + \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \left(\int \dots \int f_h \mathbf{v}_h^{(j)} \frac{1}{2} \xi^{(i)2} \prod_{k=1}^h d\xi^{(k)} \right) \\ &= \frac{1}{m} \mathbf{u}_h^{(i)} \cdot \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{k}_h^{(ji)} - \frac{1}{m} \int n_{h+1} \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot (\mathbf{u}_{h+1}^{(i)} - \mathbf{u}_h^{(i)}) d\mathbf{x}^{(h+1)}, \end{aligned} \quad (2.15)$$

Finally, by using (2.8), the following is obtained:

$$\frac{3}{2}k n_h \frac{dT_h^{(i)}}{dt} + \sum_{j=1}^h \left\{ \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{m}_h^{(ij)} + \left(\mathbf{k}_h^{(ij)} \cdot \frac{\partial}{\partial \mathbf{x}^{(j)}} \right) \cdot \mathbf{u}_h^{(i)} \right\} = - \int n_{h+1} \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot (\mathbf{u}_{h+1}^{(i)} - \mathbf{u}_h^{(i)}) d\mathbf{x}^{(h+1)}, \quad (2.16)$$

where

$$\mathbf{m}_h^{(ij)} = m \int \dots \int f_h v_h^{(i)} \frac{1}{2} v^{(j)2} \prod_{k=1}^h d\mathbf{x}^{(k)}. \quad (2.17)$$

(2.16) is not yet the energy equation, as it refers only to the thermal energy of motion $\frac{3}{2}k T_h^{(i)}$. The corresponding equation for the potential energy is derived by writing

$$I_h^{(i)} = \frac{1}{2} \sum_{j=1}^h \phi^{(ij)} + \frac{1}{2} \int \frac{n_{h+1}}{n_h} \phi^{(ih+1)} d\mathbf{x}^{(h+1)} \quad (2.18)$$

for I in (2.5); note that a factor $\frac{1}{2}$ must be inserted in localizing the potential energy, to show that the energy is shared by the two molecules concerned; otherwise an incorrect expression for the internal energy would result from integrating over the whole fluid. It is found that

$$n_h \frac{dI_h^{(i)}}{dt} = \frac{\partial}{\partial t} \left\{ \frac{1}{2} n_h \sum_{j=1}^h \phi^{(ij)} + \frac{1}{2} \int n_{h+1} \phi^{(ih+1)} d\mathbf{x}^{(h+1)} \right\} + \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot (n_h I_h^{(i)} \mathbf{u}_h^{(j)}), \quad (2.19)$$

and so, with the aid of (2.3),

$$\begin{aligned} n_h \frac{dI_h^{(i)}}{dt} &+ \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \left\{ \frac{1}{2} \int n_{h+1} \phi^{(ih+1)} (\mathbf{u}_{h+1}^{(j)} - \mathbf{u}_h^{(j)}) d\mathbf{x}^{(h+1)} \right\} \\ &= -\frac{1}{2} n_h \sum_{j=1}^h (\mathbf{u}_h^{(j)} - \mathbf{u}_h^{(i)}) \cdot \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} - \frac{1}{2} \int n_{h+1} (\mathbf{u}_{h+1}^{(h+1)} - \mathbf{u}_{h+1}^{(i)}) \cdot \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(h+1)}. \end{aligned} \quad (2.20)$$

This may be written in the form

$$n_h \frac{dI_h^{(i)}}{dt} + \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{n}_h^{(ji)} = \int n_{h+1} \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot (\mathbf{u}_{h+1}^{(i)} - \mathbf{u}_h^{(i)}) d\mathbf{x}^{(h+1)}, \quad (2.21)$$

$$\begin{aligned} \text{where } \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{n}_h^{(ji)} &= \sum_{j=1}^h \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \left\{ \frac{1}{2} \int n_{h+1} \phi^{(ih+1)} (\mathbf{u}_{h+1}^{(j)} - \mathbf{u}_h^{(j)}) d\mathbf{x}^{(h+1)} \right\} \\ &+ \frac{1}{2} n_h \sum_{j=1}^h (\mathbf{u}_h^{(j)} - \mathbf{u}_h^{(i)}) \cdot \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} + \frac{1}{2} \int n_{h+1} (\mathbf{u}_{h+1}^{(h+1)} + \mathbf{u}_{h+1}^{(i)} - 2\mathbf{u}_h^{(i)}) \cdot \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(h+1)}. \end{aligned} \quad (2.22)$$

Then, on adding (2.16) and (2.22), the following composite equation results:

$$n_h \frac{dE_h^{(i)}}{dt} + \sum_{j=1}^h \left\{ \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{q}_h^{(ji)} + \left(\mathbf{k}_h^{(ij)} \cdot \frac{\partial}{\partial \mathbf{x}^{(j)}} \right) \cdot \mathbf{u}_h^{(i)} \right\} = 0, \quad (2.23)$$

where

$$E_h^{(i)} = \frac{3}{2} k T_h^{(i)} + I_h^{(i)}, \quad (2.24)$$

and

$$\mathbf{q}_h^{(ji)} = \mathbf{m}_h^{(ij)} + \mathbf{n}_h^{(ji)}. \quad (2.25)$$

(2.23) may now be regarded as the generalization of the equation of energy transport, and it is seen that the energy flux $\mathbf{q}_h^{(ij)}$, like the pressure tensor, must be regarded as having two parts, due to the thermal motion and the molecular forces respectively.

3. THE GENERAL EXPANSION PROCEDURE

It was pointed out in § 2 of part II that the integro-differential equation (2.1) possesses solutions much more general than those which, apart from minute random deviations, describe the condition of actual fluids; the latter we call ‘normal’ solutions.

A normal solution is determined completely when the density n_1 , the mean velocity \mathbf{u}_1 , the temperature T_1 , and the external force \mathbf{P} , are known throughout the fluid; it is sufficient to know the first three of these at a given time t , since the hydrodynamical equations (2.3), (2.6) and (2.13) for $h = 1$ determine their subsequent variation. The more general solutions are distinguished from the normal solutions in that they may depend on the time t directly, as well as indirectly through the density, velocity, and temperature; also they may depend on the co-ordinates explicitly in a more general way than we expect of the normal solutions, namely, as a symmetrical function of the relative co-ordinates of the h molecules. As only the normal solutions of (2.1) are required for the present purpose, we postulate

$$f_h = F_h \left(\mathbf{x}^{(i)}, \xi^{(i)}, \lambda_k, \frac{\partial \lambda_k}{\partial \mathbf{x}}, \frac{\partial^2 \lambda_k}{\partial \mathbf{x} \partial \mathbf{x}}, \dots \right), \quad (3.1)$$

where the $\mathbf{x}^{(i)}$ occur only symmetrically in the combinations $\mathbf{r}^{(ij)} = \mathbf{x}^{(j)} - \mathbf{x}^{(i)}$, and the λ_k ($k = 1, \dots, 8$) represent the values n , \mathbf{u} , T and \mathbf{P} of the density, velocity, temperature, and force respectively at the *mean centre* $\mathbf{x} = \frac{1}{h} \sum_{i=1}^h \mathbf{x}^{(i)}$ of the molecules. From the definitions of n_h , $\mathbf{u}_h^{(i)}$, $T_h^{(i)}$, $\mathbf{v}_h^{(i)}$, $\mathbf{p}_h^{(ij)}$, $\mathbf{q}_h^{(ij)}$, etc., it then follows that all these quantities will be functions of the same kind as F_h ; for example,

$$n_h = N_h \left(\mathbf{x}^{(i)}, \xi^{(i)}, \lambda_k, \frac{\partial \lambda_k}{\partial \mathbf{x}}, \dots \right),$$

where again the $\mathbf{x}^{(i)}$ occur only in the combinations $\mathbf{r}^{(ij)}$, so that $\sum_{i=1}^h \frac{\partial N_h}{\partial \mathbf{x}^{(i)}} = 0$. More generally, if c represents any of the quantities enumerated,

$$c = C \left(\mathbf{x}^{(i)}, \xi^{(i)}, \lambda_k, \frac{\partial \lambda_k}{\partial \mathbf{x}}, \frac{\partial^2 \lambda_k}{\partial \mathbf{x} \partial \mathbf{x}}, \dots \right), \quad (3.2)$$

the small letter always being replaced by the corresponding large letter to denote explicit dependence on the λ_k .

It is now supposed that C is expanded in powers of $\frac{\partial \lambda_k}{\partial \mathbf{x}}, \frac{\partial^2 \lambda_k}{\partial \mathbf{x} \partial \mathbf{x}}, \dots$, so that

$$c = c^0 + c' + c'' + \dots, \quad (3.3)$$

where $c^0 = C^0(\mathbf{x}^{(i)}, \xi^{(i)}, \lambda_k),$

$$\left. \begin{aligned} c' &= \sum_k \frac{\partial \lambda_k}{\partial \mathbf{x}} \cdot C'_k(\mathbf{x}^{(i)}, \xi^{(i)}, \lambda_k), \\ c'' &= \sum_k \frac{\partial^2 \lambda_k}{\partial \mathbf{x} \partial \mathbf{x}} : C''_k(\mathbf{x}^{(i)}, \xi^{(i)}, \lambda_k) + \sum_{k,l} \left(\frac{\partial \lambda_k}{\partial \mathbf{x}} \frac{\partial \lambda_l}{\partial \mathbf{x}} \right) : C''_{kl}(\mathbf{x}^{(i)}, \xi^{(i)}, \lambda_k), \end{aligned} \right\} \quad (3.4)$$

and, in general, $c^{(r)}$ involves only r derivatives of the λ_k .

From the hydrodynamical equations (2.3), (2.12) and (2.16) with $h = 1$, it follows that

$$\begin{aligned} \frac{\partial c^0}{\partial t} &= \sum_k \frac{\partial C^0}{\partial \lambda_k} \frac{\partial \lambda_k}{\partial t} \\ &= - \frac{\partial C^0}{\partial n} \left\{ \frac{\partial}{\partial \mathbf{x}} \cdot (n \mathbf{u}) \right\} - \frac{\partial C^0}{\partial \mathbf{u}} \cdot \left(\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{x}} \mathbf{u} + \frac{1}{mn} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p} - \frac{1}{m} \mathbf{P} \right) \\ &\quad - \frac{\partial C^0}{\partial T} \left\{ \mathbf{u} \cdot \frac{\partial T}{\partial \mathbf{x}} + \frac{2}{3kn} \left(\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{m} + \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} + \int \frac{\partial \phi}{\partial \mathbf{x}^{(1)}} \cdot (\mathbf{u}_2^{(1)} - \mathbf{u}) n_2 d\mathbf{x}^{(2)} \right) \right\} + \frac{\partial C^0}{\partial \mathbf{P}} \cdot \frac{\partial}{\partial t} \mathbf{P}. \end{aligned} \quad (3.5)$$

Also $\frac{\partial c'}{\partial t} = \sum_k \frac{\partial C'}{\partial \lambda_k} \frac{\partial \lambda_k}{\partial t} + \sum_k C'_k \cdot \frac{\partial}{\partial \mathbf{x}} \frac{\partial \lambda_k}{\partial t}, \quad (3.6)$

whilst $\frac{\partial c^0}{\partial \mathbf{x}^{(i)}} = \frac{\partial C^0}{\partial \mathbf{x}^{(i)}} + \frac{1}{h} \sum_k \frac{\partial \lambda_k}{\partial \mathbf{x}} \frac{\partial C^0}{\partial \lambda_k}, \quad (3.7)$

and $\frac{\partial c'}{\partial \mathbf{x}^{(i)}} = \frac{\partial C'}{\partial \mathbf{x}^{(i)}} + \frac{1}{h} \sum_k \frac{\partial \lambda_k}{\partial \mathbf{x}} \frac{\partial C'}{\partial \lambda_k} + \frac{1}{h} \sum_k C'_k \cdot \frac{\partial}{\partial \mathbf{x}} \frac{\partial \lambda_k}{\partial \mathbf{x}}. \quad (3.8)$

It must be noted that in calculating integrals like $\int \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} c_{h+1} d\mathbf{x}^{(h+1)}$, where c_{h+1} is a function differing from $c = c_h$ only in containing $h+1$ instead of h co-ordinates and velocities, account must be taken of the shift of the mean centre from

$$\mathbf{x}_{h+1} = \frac{1}{h+1} \sum_{i=1}^{h+1} \mathbf{x}^{(i)} \quad \text{to} \quad \mathbf{x} = \mathbf{x}_h = \frac{1}{h} \sum_{i=1}^h \mathbf{x}^{(i)}.$$

Thus c_{h+1} must be replaced by

$$c_{h+1} + \sum_k \frac{\partial c_{h+1}}{\partial \lambda_k} \frac{\partial \lambda_k}{\partial \mathbf{x}} \cdot (\mathbf{x}_{h+1} - \mathbf{x}) + \dots$$

when $\lambda_k(\mathbf{x}_{h+1})$ is replaced by $\lambda_k(\mathbf{x})$; the actual displacement \mathbf{d} of the mean centre is

$$\mathbf{d} = \mathbf{x}_{h+1} - \mathbf{x} = \frac{1}{h(h+1)} \sum_{i=1}^h (\mathbf{x}^{(h+1)} - \mathbf{x}^{(i)}). \quad (3.9)$$

Hence

$$\int \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} c_{h+1} d\mathbf{x}^{(h+1)} \rightarrow \int \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \left\{ c_{h+1} + \mathbf{d} \cdot \frac{\partial c_{h+1}}{\partial \mathbf{x}} + \frac{1}{2} (\mathbf{d} \mathbf{d}) : \frac{\partial^2 c_{h+1}}{\partial \mathbf{x} \partial \mathbf{x}} + \dots \right\} d\mathbf{x}^{(h+1)}, \quad (3.10)$$

where $\frac{\partial}{\partial \mathbf{x}}$ signifies $\sum_k \frac{\partial \lambda_k}{\partial \mathbf{x}} \frac{\partial}{\partial \lambda_k} + \sum_k \frac{\partial^2 \lambda_k}{\partial \mathbf{x} \partial \mathbf{x}} \cdot \frac{\partial}{\partial \left(\frac{\partial \lambda_k}{\partial \mathbf{x}} \right)} + \dots$

When f_h^0, f'_h, \dots are known, it is easy to calculate c^0, c', \dots explicitly; for example,

$$\left. \begin{aligned} n_h^0 &= \int \cdots \int_{\xi}^{(h)} f_h^0 \prod_i d\xi^{(i)}, \\ n'_h &= \int \cdots \int_{\xi}^{(h)} f'_h \prod_i d\xi^{(i)}, \end{aligned} \right\} \quad (3.11)$$

$$\left. \begin{aligned} \mathbf{u}_h^{(i)0} &= \int \cdots \int_{\xi}^{(h)} \frac{f_h^0}{n_h^0} \xi^{(i)} \prod_j d\xi^{(j)}, \quad \mathbf{v}_h^{(i)0} = \xi^{(i)} - \mathbf{u}_h^{(i)0}, \\ \mathbf{u}_h^{(i)'} &= \int \cdots \int_{\xi}^{(h)} \frac{f'_h}{n_h^0} \mathbf{v}_h^{(i)0} \prod_j d\xi^{(j)}, \quad \mathbf{v}_h^{(i)'} = -\mathbf{u}_h^{(i)'}, \end{aligned} \right\} \quad (3.12)$$

$$\left. \begin{aligned} T_h^{(i)0} &= \frac{2m}{3k} \int \cdots \int_{\xi}^{(h)} \frac{f_h^0}{n_h^0} \frac{1}{2} \mathbf{v}_h^{(i)02} \prod_j d\xi^{(j)}, \\ T_h^{(i)'} &= \frac{2m}{3k} \int \cdots \int_{\xi}^{(h)} \frac{f'_h}{n_h^0} \left(\frac{1}{2} \mathbf{v}_h^{(i)02} - \frac{3k}{2m} T_h^{(i)0} \right) \prod_j d\xi^{(j)}, \end{aligned} \right\} \quad (3.13)$$

$$\left. \begin{aligned} \mathbf{k}_h^{(ij)0} &= m \int \cdots \int_{\xi}^{(h)} f_h^0 \mathbf{v}_h^{(i)0} \mathbf{v}_h^{(j)0} \prod_k d\xi^{(k)}, \\ \mathbf{k}_h^{(ij)'} &= m \int \cdots \int_{\xi}^{(h)} f'_h \mathbf{v}_h^{(i)0} \mathbf{v}_h^{(j)0} \prod_k d\xi^{(k)}, \end{aligned} \right\} \quad (3.14)$$

$$\left. \begin{aligned} \mathbf{m}_h^{(ij)0} &= m \int \cdots \int_{\xi}^{(h)} f_h^0 \mathbf{v}_h^{(i)0} \frac{1}{2} \mathbf{v}_h^{(j)02} \prod_k d\xi^{(k)}, \\ \mathbf{m}_h^{(ij)'} &= m \int \cdots \int_{\xi}^{(h)} f'_h \mathbf{v}_h^{(i)0} \left\{ \frac{1}{2} \mathbf{v}_h^{(j)02} - (\frac{3}{2} + \delta_{ij}) \frac{k}{m} T_h^{(j)0} \right\} \prod_k d\xi^{(k)}, \end{aligned} \right\} \quad (3.15)$$

$$\left. \begin{aligned} m\eta_h^{(i)0} &= - \sum_j \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} - \int \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \frac{n_{h+1}^0}{n_h^0} d\mathbf{x}^{(h+1)} + \mathbf{P}, \\ m\eta_h^{(i)'} &= - \int \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \left(\frac{n_{h+1}}{n_h} \right)' d\mathbf{x}^{(h+1)} - \frac{1}{n_h^0} \int \mathbf{d} \cdot \sum_k \frac{\partial \lambda_k}{\partial \mathbf{x}} \frac{\partial N_{h+1}^0}{\partial \lambda_k} \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(h+1)} \\ &\quad + (\mathbf{x}^{(i)} - \mathbf{x}) \cdot \frac{\partial}{\partial \mathbf{x}} \mathbf{P}. \end{aligned} \right\} \quad (3.16)$$

One further remark may be made concerning the dependence of F_h on \mathbf{u} : it is clear, on physical grounds, that the distribution of velocities among the molecules of a fluid about the mean \mathbf{u} is independent of any translational motion of the fluid as a whole. Hence F_h will contain \mathbf{u} only in the combinations $\mathbf{v}^{(i)} = \xi^{(i)} - \mathbf{u}$, and in the derivatives $\frac{\partial}{\partial \mathbf{x}} \mathbf{u}$, $\frac{\partial^2}{\partial \mathbf{x} \partial \mathbf{x}} \mathbf{u}$, etc.; so that

$$\frac{\partial F_h}{\partial \mathbf{u}} + \sum_{i=1}^h \frac{\partial F_h}{\partial \xi^{(i)}} = 0. \quad (3.17)$$

By integration over the velocities it follows also that

$$\frac{\partial N_h}{\partial \mathbf{u}} = 0. \quad (3.18)$$

The equation to determine F_h^0 is easily derived from (2.1); it follows from (3.5) that $\left(\frac{\partial f_h}{\partial t}\right)^0 = \frac{1}{m} \mathbf{P} \cdot \frac{\partial F_h^0}{\partial \mathbf{u}}$, so

$$\sum_{i=1}^h \left(m \xi^{(i)} \cdot \frac{\partial F_h^0}{\partial \mathbf{x}^{(i)}} - \sum_{j=1}^h \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial F_h^0}{\partial \xi^{(j)}} \right) = \sum_{i=1}^h \int \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial F_{h+1}^0}{\partial \xi^{(i)}} d\mathbf{x}^{(h+1)} d\xi^{(h+1)}. \quad (3.19)$$

It is unnecessary to solve this equation, however, as it has been obtained from (2.1) by writing $\partial \lambda_k / \partial \mathbf{x} = 0$, i.e. by postulating equilibrium conditions, and the solution of (3.19) must therefore coincide with the known equilibrium solution of (2.1):

$$F_h^0 = N_h^0 \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left(- \frac{m}{2kT} \sum_{i=1}^h \mathbf{v}^{(i)2} \right). \quad (3.20)$$

Here, in accordance with (3.18), N_h^0 does not contain \mathbf{u} , though it is, in general, a function of n and T as well as the relative co-ordinates. Substitution of (3.20) in (3.11) to (3.15) now leads to $n_1^0 = n$, and

$$\left. \begin{aligned} \mathbf{u}_h^{(i)0} &= \mathbf{u}, & \mathbf{v}_h^{(i)0} &= \mathbf{v}^{(i)} = \xi^{(i)} - \mathbf{u}, \\ T_h^{(i)0} &= T, & \mathbf{k}_h^{(ij)0} &= N_h^0 k T \delta_{ij} \mathbf{1}, & \mathbf{m}_h^{(ij)0} &= 0; \end{aligned} \right\} \quad (3.21)$$

it follows from these that $n'_1, T'_1, \mathbf{u}'_1, n''_1, T''_1, \mathbf{u}''_1$, etc., must all vanish.

From (3.5) it is found that

$$\left(\frac{\partial n_h}{\partial t} \right)^0 = 0, \quad \left(\frac{\partial}{\partial t} \mathbf{u}_h^{(i)} \right)^0 = \frac{1}{m} \mathbf{P}, \quad \left(\frac{\partial T_h^{(i)}}{\partial t} \right)^0 = 0, \quad (3.22)$$

and

$$\left(\frac{\partial n_h}{\partial t} \right)' = - \frac{\partial N_h^0}{\partial n} \left\{ \frac{\partial}{\partial \mathbf{x}} \cdot (n \mathbf{u}) \right\} - \frac{\partial N_h^0}{\partial T} \left\{ \mathbf{u} \cdot \frac{\partial T}{\partial \mathbf{x}} + \frac{2}{3} T \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} + \frac{2}{3k} \int \frac{\partial \phi}{\partial \mathbf{x}^{(1)}} \cdot \mathbf{u}_2^{(1)'} n_2^0 d\mathbf{x}^{(2)} \right\}. \quad (3.23)$$

These expressions can also be calculated from the hydrodynamical equations (2.3), (2.6) and (2.16), which give

$$\left(\frac{\partial n_h}{\partial t} \right)^0 = 0, \quad \left(\frac{\partial}{\partial t} \mathbf{u}_h^{(i)} \right)^0 = \frac{1}{m} \left(- \frac{kT}{N_h^0} \frac{\partial N_h^0}{\partial \mathbf{x}^{(i)}} + \eta_h^{(i)0} \right), \quad \left(\frac{\partial T_h^{(i)}}{\partial t} \right)^0 = 0, \quad (3.24)$$

and $\left(\frac{\partial n_h}{\partial t} \right)' = - \left\{ N_h^0 \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} + \frac{\partial N_h^0}{\partial n} \mathbf{u} \cdot \frac{\partial n}{\partial \mathbf{x}} + \frac{\partial N_h^0}{\partial T} \mathbf{u} \cdot \frac{\partial T}{\partial \mathbf{x}} + \sum_{i=1}^h \frac{\partial}{\partial \mathbf{x}^{(i)}} \cdot (N_h^0 \mathbf{u}_h^{(i)'}) \right\}, \quad (3.25)$

since $\sum_{i=1}^h \frac{\partial N_h^0}{\partial \mathbf{x}^{(i)}}$ vanishes.

Comparison of the second of equations (3.22) and (3.24), with reference to (3.16), leads to

$$\frac{kT}{N_h^0} \frac{\partial N_h^0}{\partial \mathbf{x}^{(i)}} + \sum_{j=1}^h \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} + \int \frac{N_{h+1}^0}{N_h^0} \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(h+1)} = 0, \quad (3.26)$$

which agrees precisely with the equation, first found in part I, for determining the equilibrium value of n_h , thus confirming our adoption of the equilibrium form of f_h for F_h^0 . Note that the external force $\mathbf{P}(\mathbf{x}^{(i)})$ does not influence the 'zero' approximation in any explicit way; this could be foreseen from the fact that the constant force $\mathbf{P}(\mathbf{x})$ accelerates all the molecules in the same way, and can therefore influence only the density distribution, which has been assumed to be given.

The following equation is found by comparing (3.23) and (3.25); and writing $h = 2$ and $\mathbf{r} = \mathbf{x}^{(2)} - \mathbf{x}^{(1)}$:

$$\begin{aligned}\frac{\partial}{\partial \mathbf{r}} \cdot \{N_2^0 (\mathbf{U}_2^{(2)\prime} - \mathbf{U}_2^{(1)\prime})\} &= \left(n \frac{\partial N_2^0}{\partial n} - N_2^0 + \frac{2}{3} T \frac{\partial N_2^0}{\partial T} \right) \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} \\ &\quad + \frac{1}{3kn} \frac{\partial N_2^0}{\partial T} \int \frac{\partial \phi}{\partial \mathbf{r}} \cdot (\mathbf{U}_2^{(2)\prime} - \mathbf{U}_2^{(1)\prime}) N_2^0 d\mathbf{r}. \end{aligned} \quad (3.27)$$

This may be regarded as an integro-differential equation for the (partial) determination of $\mathbf{U}_2^{(2)\prime} - \mathbf{U}_2^{(1)\prime}$. Multiplication by $\phi(r)$ and integration over \mathbf{r} gives

$$\int \frac{\partial \phi}{\partial \mathbf{r}} \cdot (\mathbf{U}_2^{(2)\prime} - \mathbf{U}_2^{(1)\prime}) N_2^0 d\mathbf{r} = nkT\sigma \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u}, \quad (3.28)$$

$$\text{where } nkT\sigma = - \frac{\int \left(n \frac{\partial N_2^0}{\partial n} - N_2^0 + \frac{2}{3} T \frac{\partial N_2^0}{\partial T} \right) \phi d\mathbf{r}}{1 + \frac{1}{3kn} \int \frac{\partial N_2^0}{\partial T} \phi d\mathbf{r}}, \quad (3.29)$$

$$\text{so that } N_2^0 (\mathbf{U}_2^{(2)\prime} - \mathbf{U}_2^{(1)\prime}) = \frac{\mathbf{r}}{r^3} \int_0^r \left\{ n \frac{\partial N_2^0}{\partial n} - N_2^0 + \frac{1}{3}(\sigma + 2) T \frac{\partial N_2^0}{\partial T} \right\} r^2 dr \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} + \mathbf{v}, \quad (3.30)$$

provided $\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v} = 0$. It will appear later how \mathbf{v} can be determined from other sources.

At present we wish to draw attention to the failure of the above solution when

$$\frac{\partial}{\partial T} \int \frac{N_2^0}{n} \phi d\mathbf{r} = -3k, \quad (3.31)$$

i.e. when the internal energy of the fluid is changing at a certain rate with temperature. On approaching this point, the average relative velocity of two molecules at a given separation tends to infinity, unless $\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} = 0$; this means that the condition of the fluid, even in equilibrium, is highly unstable for small changes in the volume. One can hardly fail to associate such a condition with condensation, or rather the limit of superheating above the boiling point, and we therefore regard (3.31) as the exact analogue of the 'condition for condensation' found in part II.

4. VISCOSITY AND THERMAL CONDUCTION IN LIQUIDS

Before proceeding to calculate the viscosity and thermal conduction coefficients, the form of F'_1 , N'_2 and $N_2^0 (\mathbf{U}_2^{(1)\prime} + \mathbf{U}_2^{(2)\prime})$ which can be determined qualitatively from quite general considerations, is required. Write

$$\left. \begin{aligned} \mathbf{a} &= \frac{\partial T}{\partial \mathbf{x}}, \quad \mathbf{a}' = \frac{\partial n}{\partial \mathbf{x}}, \\ \mathbf{b} &= \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u}, \quad \mathbf{b}' = \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{P}, \\ \mathbf{b} &= \frac{1}{2} \left(\frac{\partial}{\partial \mathbf{x}} \mathbf{u} + \overline{\frac{\partial}{\partial \mathbf{x}} \mathbf{u}} \right) - \frac{1}{3} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} \mathbf{1}, \\ \mathbf{b}' &= \frac{1}{2} \left(\frac{\partial}{\partial \mathbf{x}} \mathbf{P} + \overline{\frac{\partial}{\partial \mathbf{x}} \mathbf{P}} \right) - \frac{1}{3} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{P} \mathbf{1}. \end{aligned} \right\} \quad (4.1)$$

Now F'_1 is linear in the a 's and b 's, can contain besides only n , T and v , and satisfies $\int F'_1 dv = N'_1 = 0$; hence it is of the form

$$F'_1 = \varphi_1 v \cdot a + \varphi'_1 v \cdot a' + \varphi_2 v \cdot b \cdot v + \varphi'_2 v \cdot b' \cdot v, \quad (4.2)$$

where φ_1 , φ'_1 , φ_2 and φ'_2 contain only n , T and v .

N'_2 is linear in the a 's and b 's, can contain besides only n , T and r , it is unaltered on replacing r by $-r$ (interchange of $x^{(1)}$ and $x^{(2)}$), and satisfies $\int N'_2 dr = (N - 1) N'_1 = 0$; hence it is of the form

$$N'_2 = \nu r \cdot b \cdot r + \nu' r \cdot b' \cdot r, \quad (4.3)$$

where ν and ν' are functions of n , T and r only.

$N''_2(U_2^{(1)'} + U_2^{(2)'})$ is linear in the a 's and b 's, can contain besides only n , T and r , is unaltered on replacing r by $-r$, and satisfies

$$\int N''_2(U_2^{(1)'} + U_2^{(2)'}) dr = 2n(N - 1) u'_1 = 0;$$

hence it is of the form

$$N''_2(U_2^{(1)'} + U_2^{(2)'}) = \tau(r \cdot ar - \frac{1}{3}r^2 a) + \tau'(r \cdot a'r - \frac{1}{3}r^2 a'), \quad (4.4)$$

where τ and τ' are functions of n , T and r only. The form of other functions involving the a 's and b 's may be determined in a similar way, but here it is necessary to note only that N''_2 and N'''_2 , like N'_2 , must be even functions of r .

Now turn to the equation (2.11), which, with $h = 1$, determines the part I of the pressure tensor due to the molecular forces, namely,

$$\frac{\partial}{\partial x} \cdot I = - \int n_2 \frac{\partial \phi}{\partial r} dx^{(2)}. \quad (4.5)$$

When each side of this equation is expanded in the way shown in (3.3) and (3.10) (substituting n_2 for c_{h+1} in the latter), the following are obtained:

$$\frac{\partial}{\partial x} \cdot I^0 = - \frac{\partial}{\partial x} \cdot \int \frac{1}{2} r N''_2 \frac{\partial \phi}{\partial r} dr, \quad (4.6)$$

$$\frac{\partial}{\partial x} \cdot I' = - \frac{\partial}{\partial x} \cdot \int \frac{1}{2} r N'_2 \frac{\partial \phi}{\partial r} dr, \quad (4.7)$$

$$\frac{\partial}{\partial x} \cdot I'' = - \frac{\partial}{\partial x} \cdot \int \frac{1}{2} r N'''_2 \frac{\partial \phi}{\partial r} dr - \frac{1}{6} \frac{\partial^3}{\partial x \partial x \partial x} : \int \frac{1}{2} r \frac{1}{2} r \frac{1}{2} r N''_2 \frac{\partial \phi}{\partial r} dr. \quad (4.8)$$

The other terms on the right-hand side vanish when account is taken of the fact, noted above, that N'_2 , N''_2 and N'''_2 are even functions of r . Then, on integrating (4.6),

$$\begin{aligned} I^0 &= - \frac{1}{2} \int N''_2 r \frac{\partial \phi}{\partial r} dr \\ &= - \frac{1}{6} \int N''_2 \phi'(r) r dr I, \end{aligned} \quad (4.9)$$

in agreement with the formula found previously for the part of the pressure tensor due to the molecular forces in equilibrium. The constant of integration has been rejected to ensure $l^0 \rightarrow 0$ as $n \rightarrow 0$.

In the same way, from (4.7),

$$\begin{aligned} l' &= -\frac{1}{2} \int N'_2 \mathbf{r} \frac{\partial \phi}{\partial \mathbf{r}} d\mathbf{r} \\ &= -\frac{1}{15} \int (\nu \mathbf{b} + \nu' \mathbf{b}') \phi'(r) r^3 dr, \end{aligned} \quad (4.10)$$

on substitution from (4.3). Similar formulae for l'' , etc., may be obtained from (4.8), etc. To obtain the corresponding expression for k' , substitute (4.2) in (3.14); it is found that

$$k' = \frac{2}{15} m \int (\varphi_2 \mathbf{b} + \varphi'_2 \mathbf{b}') v^4 dv. \quad (4.11)$$

Now the viscosity coefficient μ is defined by the equation

$$p' = -2\mu b, \quad (4.12)$$

on the understanding that $b' = 0$. Hence

$$\mu = \frac{1}{30} \int \nu(r) \phi'(r) r^3 dr - \frac{1}{15} m \int \varphi_2(v) v^4 dv. \quad (4.13)$$

In the kinetic theory of gases, no account is taken of the first term in (4.13), due to the molecular forces; the second term is found to be small and to decrease with the temperature. In liquids, however, the viscosity is much larger, and increases with decreasing temperature; it is therefore reasonable to conclude that the first term of (4.13), far from being negligible for the liquid state, is the dominant one in the complete expression. This conclusion is supported by the observation that it is roughly proportional to the square of the density, and so becomes very many times larger in the process of condensation.

To calculate the coefficient of thermal conduction, it is necessary to obtain first the energy flux vector \mathbf{q}' . From (2.22) it is found that

$$\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{n}' = -\frac{1}{2} \frac{\partial}{\partial \mathbf{x}} \cdot \int \frac{1}{2} \mathbf{r} \frac{\partial \phi}{\partial \mathbf{r}} \cdot (\mathbf{U}_2^{(1)\prime} + \mathbf{U}_2^{(2)\prime}) N_2^0 d\mathbf{r}, \quad (4.14)$$

and, on integration,

$$\begin{aligned} \mathbf{n}' &= -\frac{1}{4} \int \mathbf{r} \frac{\partial \phi}{\partial \mathbf{r}} \cdot (\mathbf{U}_2^{(1)\prime} + \mathbf{U}_2^{(2)\prime}) N_2^0 d\mathbf{r} \\ &= -\frac{1}{18} \int (\tau \mathbf{a} + \tau' \mathbf{a}') \phi'(r) r^3 dr, \end{aligned} \quad (4.15)$$

when substitution is made from (4.4). Also, from (3.15),

$$\mathbf{m}' = \frac{1}{6} \int (\varphi_1 \mathbf{a} + \varphi'_1 \mathbf{a}') \left(v^2 - \frac{5kT}{m} \right) v^2 dv. \quad (4.16)$$

Now, the thermal conductivity coefficient λ is defined by

$$\mathbf{q}' = -\lambda \mathbf{a}, \quad (4.17)$$

on the understanding that $\partial p / \partial x = 0$, $p = k^0 + l^0$, so that, according to (3.21) and (4.9),

$$\mathbf{a}' = \kappa \mathbf{a},$$

$$\kappa = -\frac{n}{T} \frac{\frac{1}{6nkT} \int T \frac{\partial N_2^0}{\partial T} \phi'(r) r dr}{1 - \frac{1}{6nkT} \int n \frac{\partial N_2^0}{\partial n} \phi'(r) r dr}. \quad (4.18)$$

$$\text{Hence } \lambda = \frac{1}{18} \int (\tau + \kappa \tau') \phi'(r) r^3 dr - \frac{1}{6} \int (\varphi_1 + \kappa \varphi'_1) \left(v^2 - \frac{5kT}{m} \right) v^2 dv, \quad (4.19)$$

where, again, the second part is dominant for the gaseous state, but the first term, which does not appear in the theory of gases, becomes of major importance for the liquid state.

5. PRELIMINARY DISCUSSION OF THE COEFFICIENTS OF VISCOSITY AND THERMAL CONDUCTION

The complete content of the formulae (4.13) and (4.19) can be discussed only after a rigorous determination of the deformation of the radial distribution function by the motion of the fluid. However, this requires the solution of a complicated integro-differential equation, to be developed in the next section, which is a considerable task. It therefore seems desirable to derive simple approximations to the exact laws, for comparison with experiment.

It will be assumed that the second term, due to the thermal motion, in each of the formulae (4.13) and (4.19), can be completely neglected for the liquid state.

$\nu r \cdot b \cdot r$, which is the second approximation to the radial distribution function in non-equilibrium conditions, must clearly be proportional to the first approximation $N_2^0(r)$, which gives the density dependence. Hence*

$$\nu = \alpha_1 N_2^0(r), \quad (5.1)$$

where α_1 is a factor of dimensions $[l^{-2}t]$ involving only r and kT/m ; accordingly

$$\alpha_1 \sim \frac{1}{r} \left(\frac{m}{kT} \right)^{\frac{1}{2}}. \quad (5.2)$$

Substituting (5.1) in (4.13),

$$\mu \sim \frac{1}{30} \left(\frac{m}{kT} \right)^{\frac{1}{2}} \int N_2^0 \phi'(r) r^2 dr. \quad (5.3)$$

The factor N_2^0 in the integrand of (5.3) rises from zero to a sharp maximum at the distance r_1 of the nearest neighbours from a given molecule. When account is taken

* A closer study shows that the details of the following calculation require amendment; but the result (5.11) is still unaffected.

of the second factor $\phi'(r)r^4$, this maximum is only slightly displaced, and the integrand is almost zero elsewhere. Hence the integral may be evaluated by the method of 'steepest descent', with the result

$$\mu \sim \frac{2\pi}{15} \left(\frac{m}{kT} \right)^{\frac{1}{2}} N_2^0(r_1) \phi'(r_1) r_1^4 \left(\frac{\pi}{\beta} \right)^{\frac{1}{2}}, \quad (5.4)$$

where $\beta = \left[\frac{d^2}{dr^2} \{ \log N_2^0(r) + \log \phi'(r) + 4 \log r \} \right]_{r=r_1}. \quad (5.5)$

For the further simplification of (5.4), $N_2^0(r)$ may be replaced by its first approximation $n^2 e^{-\phi(r)/kT}$, and, in (5.5), since r_1 is known to lie beyond the potential minimum in the attractive part of the field, it may be assumed that

$$\phi(r) = -\gamma r^{-6}. \quad (5.6)$$

Then $\beta = \frac{42\gamma}{kTr_1^8} + \frac{3}{r_1^2} = -\frac{42}{r_1^2} \{ \phi(r_1) - \frac{1}{14} \}, \quad (5.7)$

where the second term is generally negligible in comparison with the first. Thus

$$\mu \sim \frac{2\pi}{105} (42\pi m\gamma)^{\frac{1}{2}} n^2 r_1 e^{-\phi(r_1)/kT}. \quad (5.8)$$

In order to compare (5.8) with corresponding formulae involving the frequency ν_0 of vibration of the molecules about the equilibrium point r_0 in the molecular field, one may take

$$\phi(r) = -\gamma r^{-6} \{ 1 - \frac{1}{2}(r_0 r^{-1})^6 \}, \quad (5.9)$$

according to Lennard-Jones (1924); then ν_0 is given by

$$4\pi^2 m \nu_0^2 = \phi''(r_0) = 36\gamma r_0^{-8}. \quad (5.10)$$

Substituting for γ from (5.10) into (5.8), and taking $n = 2^{-\frac{1}{3}} r_1^{-3}$ (as for a face-centred cubic structure), it is found finally that

$$\mu \sim \frac{\pi^2}{315} (42\pi)^{\frac{1}{2}} \left(\frac{r_0}{r_1} \right)^5 \frac{m \nu_0}{r_0} e^{-\phi(r_1)/kT}. \quad (5.11)$$

Formulae of this type have been suggested before. Andrade (1934) regards viscosity as produced by the transfer of the momentum of molecular vibrations from one 'layer' to a neighbouring one, and obtains, for the melting-point, $\mu \sim m \nu_1 / r_1$, where ν_1 is Lindemann's frequency. One recognizes this factor in our formula, but with constant ν_0 referring to the diatomic molecule; the actual dependence on volume is given by the factor $(r_0/r_1)^5 = (v_0/v_1)^{\frac{5}{3}}$. In fact, Andrade's derivation seems to us an ingenious dimensional consideration, which, however, fails to give the correct dependence on volume since dimensionless factors (powers of v_0/v_1) cannot be found in this way. Andrade also finds the exponential factor, but gives no theoretical explanation except that it ought to be of the form of a Boltzmann factor.

A different formula for the coefficient of viscosity has been given by Fürth (1941). It is based on his theory of 'holes'; the liquid is regarded as a continuum containing small bubbles, the size and apparent mass of which depend on the surface tension.

As these bubbles transfer energy and momentum from one layer to another, the coefficient of viscosity can be expressed in terms of the surface tension. Fürth's formula contains an exponential factor of the same type as ours; the remaining factor cannot be compared with ours because of the entirely different assumptions made. But Fürth has shown that his formula is practically identical with Andrade's because of some empirical relations between the constants involved; and similar considerations can be applied by coupling Fürth's formula with our own, or that of Ewell & Eyring (1937) with our own.

The thermal conductivity may be discussed in a similar way, starting from the rigorous equation (4·19), and omitting the second term as unimportant for the liquid. If one writes

$$\tau = \epsilon N_h^0, \quad (5·12)$$

it follows from simple dimensional considerations that

$$\epsilon \sim \frac{k}{m r} \left(\frac{m}{kT} \right)^{\frac{1}{2}}. \quad (5·13)$$

It is now seen by substitution in (4·19) that the thermal conductivity consists of two terms, the first of which is proportional to the viscosity, and the second of which depends on the coefficient of expansion, through the parameter κ . Owing to the complication of this second term, it is more difficult to derive a simple formula of general applicability for the thermal conductivity, the complete discussion of which is therefore deferred until a rigorous treatment can be given.

6. THE INTEGRAL EQUATION FOR F'_h

The equation for the determination of f'_h will now be derived from (2·1) in accordance with the general expansion procedure outlined in § 3. The expression for $\left(\frac{\partial f_h}{\partial t} \right)' = \left(\frac{\partial f_h^0}{\partial t} \right)' + \left(\frac{\partial f'_h}{\partial t} \right)'$ is found to be

$$\begin{aligned} \left(\frac{\partial f_h}{\partial t} \right)' &= - \frac{f_h^0}{n_h^0} \frac{\partial N_h^0}{\partial n} \left\{ \frac{\partial}{\partial \mathbf{x}} \cdot (n\mathbf{u}) \right\} - \frac{m f_h^0}{kT} \left(\sum_i \mathbf{v}^{(i)} \right) \cdot \left\{ \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{x}} \mathbf{u} + \frac{1}{mn} \frac{\partial p^0}{\partial \mathbf{x}} \right\} \\ &\quad - \frac{f_h^0}{T} \left\{ \frac{T}{n_h^0} \frac{\partial N_h^0}{\partial T} + \frac{m}{2kT} \left(\sum_i v^{(i)2} \right) - \frac{3h}{2} \right\} \left\{ \mathbf{u} \cdot \frac{\partial T}{\partial \mathbf{x}} + \frac{2T}{3} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} + \frac{\sigma T}{3} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} \right\} \\ &\quad + \frac{1}{m} \mathbf{P} \cdot \frac{\partial F'_h}{\partial \mathbf{u}}, \end{aligned} \quad (6·1)$$

by substituting f_h for c , and picking out the 'first-order' terms in (3·5) and (3·6). Also, from (3·7) and (3·8),

$$\begin{aligned} \left(\sum_i \xi^{(i)} \cdot \frac{\partial f_h}{\partial \mathbf{x}^{(i)}} \right)' &= \left\{ \frac{1}{h} \left(\sum_i \mathbf{v}^{(i)} \right) + \mathbf{u} \right\} \cdot \left[\frac{f_h^0}{n_h^0} \frac{\partial N_h^0}{\partial n} \frac{\partial n}{\partial \mathbf{x}} + \frac{m f_h^0}{kT} \left(\sum_i \mathbf{v}^{(i)} \right) \cdot \overline{\frac{\partial}{\partial \mathbf{x}}} \mathbf{u} \right. \\ &\quad \left. + \frac{f_h^0}{T} \left\{ \frac{T}{n_h^0} \frac{\partial N_h^0}{\partial T} + \frac{m}{2kT} \left(\sum_i v^{(i)2} \right) - \frac{3h}{2} \right\} \frac{\partial T}{\partial \mathbf{x}} \right] + \sum_i \mathbf{v}^{(i)} \frac{\partial F'_h}{\partial \mathbf{x}^{(i)}}, \end{aligned} \quad (6·2)$$

and

$$\left(\frac{1}{m} \sum_i \left(\mathbf{P}^{(i)} - \sum_j \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} \right) \cdot \frac{\partial f_h^0}{\partial \xi^{(i)}} \right)' = - \frac{f_h^0}{kT} \sum_i \mathbf{v}^{(i)} \cdot \left((\mathbf{x}^{(i)} - \mathbf{x}) \cdot \frac{\partial}{\partial \mathbf{x}} \mathbf{P} \right) + \frac{1}{m} \sum_i \left(\mathbf{P} - \sum_j \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} \right) \cdot \frac{\partial F'_h}{\partial \xi^{(i)}}. \quad (6.3)$$

(2.1) therefore yields the following equation:

$$\begin{aligned} & - \left[\frac{n}{n_h^0} \frac{\partial N_h^0}{\partial n} + \frac{\sigma + 2}{3} \left\{ \frac{\partial N_h^0}{\partial T} \frac{T}{n_h^0} + \frac{m}{2kT} \left(\sum_i v^{(i)2} \right) - \frac{3h}{2} \right\} - \frac{m}{3hkT} \left(\sum_i \mathbf{v}^{(i)} \right)^2 \right] f_h^0 b \\ & - \frac{1}{3kT} \sum_i \mathbf{v}^{(i)} \cdot (\mathbf{x}^{(i)} - \mathbf{x}) f_h^0 b' + \left(\frac{\partial N_h^0}{\partial T} \frac{T}{hn_h^0} - \frac{1}{nk} \frac{\partial p^0}{\partial T} + \frac{m}{2hkT} \left(\sum_i v^{(i)2} \right) - \frac{3h}{2} \right) \frac{f_h^0}{T} \left(\sum_i \mathbf{v}^{(i)} \right) \cdot \mathbf{a} \\ & + \left(\frac{n}{hn_h^0} \frac{\partial N_h^0}{\partial n} - \frac{1}{kT} \frac{\partial p^0}{\partial n} \right) \frac{f_h^0}{n} \left(\sum_i \mathbf{v}^{(i)} \right) \cdot \mathbf{a}' + \frac{mf_h^0}{hkT} \left(\sum_i \mathbf{v}^{(i)} \right) \cdot \mathbf{b} \cdot \left(\sum_i \mathbf{v}^{(i)} \right) - \frac{f_h^0}{kT} \sum_i \mathbf{v}^{(i)} \cdot \mathbf{b}' \cdot (\mathbf{x}^{(i)} - \mathbf{x}) \\ & - \frac{f_h^0}{2kT} \left\{ \sum_i (\mathbf{x}^{(i)} - \mathbf{x}) \times \mathbf{v}^{(i)} \right\} \cdot \frac{\partial}{\partial \mathbf{x}} \times \mathbf{P} + \sum_i \left(\mathbf{v}^{(i)} \cdot \frac{\partial F'_h}{\partial \mathbf{x}^{(i)}} - \frac{1}{m} \sum_j \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial F'_h}{\partial \xi^{(i)}} \right) \\ & = \frac{1}{m} \iint \sum_i \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial F'_{h+1}}{\partial \xi^{(i)}} d\mathbf{x}^{(h+1)} d\xi^{(h+1)} \\ & + \frac{1}{mh(h+1)} \iint \sum_i (\mathbf{x}^{(h+1)} - \mathbf{x}^{(j)}) \cdot \frac{\partial}{\partial \mathbf{x}} \sum_i \frac{\partial \phi^{(ih+1)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial F'_{h+1}}{\partial \xi^{(i)}} d\mathbf{x}^{(h+1)} d\xi^{(h+1)}. \quad (6.4) \end{aligned}$$

As an indication of the general method, this equation will now be discussed for the simplest case $h = 1$, when it reduces to

$$-\frac{1}{3}\sigma \left(\frac{mv^2}{2kT} - \frac{3}{2} \right) f_1^0 b + \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) \frac{f_1^0}{T} \mathbf{v} \cdot \mathbf{a} + \frac{mf_1^0}{kT} \mathbf{v} \cdot \mathbf{b} \cdot \mathbf{v} = -\frac{1}{m} \iint \frac{\partial \phi}{\partial \mathbf{r}} \cdot \frac{\partial f'_2}{\partial \mathbf{v}^{(1)}} d\mathbf{r} d\mathbf{v}^{(2)}. \quad (6.5)$$

The last term on the right-hand side of (6.4) cancels with the terms involving the pressure on the left-hand side. Apart from a term involving σb , (6.5) is an exact analogue of the corresponding equation in the theory of gases. It is convenient to define the function

$$e = \int f'_2 d\mathbf{v}^{(2)}, \quad (6.6)$$

which must be of the form

$$e = e_0 b + e_{1r} r \mathbf{v} \cdot \mathbf{a} + e_{1v} r \mathbf{v} \cdot \mathbf{a} + e_{2r} v^2 \mathbf{r} \cdot \mathbf{b} \cdot \mathbf{r} + e_{2m} r v \mathbf{r} \cdot \mathbf{b} \cdot \mathbf{v} + e_{2v} r^2 \mathbf{v} \cdot \mathbf{b} \cdot \mathbf{v}. \quad (6.7)$$

Terms involving b' , a' and b' may possibly occur, but if they do, (6.5) can clearly provide little information concerning them, because they do not occur on the left-hand side.

A number of conditions must be satisfied by e ; for example, since

$$\begin{aligned} \iint f'_2 d\mathbf{x}^{(2)} d\xi^{(2)} &= (N-1) f'_1, \\ -f'_1 &= \int (e - n_1 f'_1) d\mathbf{r}. \end{aligned} \quad (6.8)$$

Also

$$n'_2 = \int e d\mathbf{v}, \quad (6.9)$$

$$n_2^0 u_2^{(1)\prime} = \int e v d\mathbf{v}. \quad (6.10)$$

In (6.7), e_0 , e_{1r} , e_{1v} , e_{2r} , e_{2m} and e_{2v} are all functions of r , v and z , where

$$rvz = \mathbf{r} \cdot \mathbf{v}; \quad (6.11)$$

it is convenient to expand them with respect to z in Legendre polynomials, thus:

$$e_k = \sum_l e_k^{(l)} P_l(z), \quad (6.12)$$

where the $e_k^{(l)}$ involve r and v only.

Now substitute from (4.2) and (6.7) into (6.8), making use of integration formulae which will be found in the appendix (§ 7); comparing coefficients of b , a and b respectively, it appears that

$$\left. \begin{aligned} \int e_0^{(0)} d\mathbf{r} &= 0, \\ \int (\frac{1}{3}e_{1r}^{(1)} r + e_{1v}^{(0)} r - n_1 \varphi_1) d\mathbf{r} &= -\varphi_1, \\ \int (\frac{1}{5}e_{2r}^{(2)} r^2 + \frac{1}{3}e_{2m}^{(1)} r^2 + e_{2v}^{(0)} r^2 - n_1 \varphi_2) d\mathbf{r} &= -\varphi_2. \end{aligned} \right\} \quad (6.13)$$

Similarly, from (6.9) and (4.3),

$$\left. \begin{aligned} \int e_0^{(0)} dv &= 0, \\ \int (e_{1r}^{(0)} + \frac{1}{3}e_{1v}^{(1)}) v d\mathbf{v} &= 0, \\ \int (e_{2r}^{(0)} + \frac{1}{3}e_{2m}^{(1)} + \frac{1}{5}e_{2v}^{(2)}) v^2 d\mathbf{v} &= v. \end{aligned} \right\} \quad (6.14)$$

To treat (6.10) in the same way, an expression for $N_2^0(\mathbf{U}_2^{(2)\prime} - \mathbf{U}_2^{(1)\prime})$ is required, to combine with (4.4). It must be an odd function of \mathbf{r} , and is accordingly of the form

$$N_2^0(\mathbf{U}_2^{(2)\prime} - \mathbf{U}_2^{(1)\prime}) = v_0 b \mathbf{r} + v_2 \mathbf{r} \cdot \mathbf{b} \cdot \mathbf{r} \mathbf{r} + \bar{v}_2 r^2 \mathbf{b} \cdot \mathbf{r}, \quad (6.15)$$

where v_0 , v_2 and \bar{v}_2 are functions of n , T and r only. It now follows from (6.10) that

$$\left. \begin{aligned} \int \frac{1}{3}e_0^{(1)} v d\mathbf{v} &= -\frac{1}{2}r v_0, \\ \int (\frac{1}{3}e_{1r}^{(1)} + \frac{1}{5}e_{1v}^{(2)}) v^2 d\mathbf{v} &= \frac{1}{2}r \tau, \\ \int (\frac{1}{3}e_{1v}^{(0)} - \frac{1}{15}e_{1v}^{(2)}) v^2 d\mathbf{v} &= \frac{1}{2}r \tau, \\ \int (\frac{1}{3}e_{2r}^{(1)} + \frac{1}{5}e_{2m}^{(2)} + \frac{1}{7}e_{2v}^{(3)}) v^3 d\mathbf{v} &= -\frac{1}{2}r v_2, \\ \int (\frac{1}{3}e_{2m}^{(0)} + \frac{2}{15}e_{2v}^{(1)} - \frac{1}{15}e_{2m}^{(2)} - \frac{2}{35}e_{2v}^{(3)}) v^3 d\mathbf{v} &= -\frac{1}{2}r \bar{v}_2. \end{aligned} \right\} \quad (6.16)$$

According to (3.30),

$$v_0 = r^{-3} \int_0^r \left(n \frac{\partial N_2^0}{\partial n} - N_2^0 + \frac{\sigma+2}{3} T \frac{\partial N_2^0}{\partial T} \right) r^2 dr, \quad (6.17)$$

and

$$\frac{\partial}{\partial \mathbf{r}} \cdot (v_2 \mathbf{r} \cdot \mathbf{b} \cdot \mathbf{r} \mathbf{r} + \bar{v}_2 r^2 \mathbf{b} \cdot \mathbf{r}) = 0, \quad (6.18)$$

so that

$$\frac{d}{dr} (r^5 v_2) + r^3 \frac{d}{dr} (r^2 \bar{v}_2) = 0. \quad (6.19)$$

Now the integral equation separates into the following three:

$$\frac{\partial}{\partial \mathbf{v}} \cdot \int \frac{\partial \phi}{\partial \mathbf{r}} e_0 d\mathbf{r} = \frac{m\sigma}{3} \left(\frac{mv^2}{2kT} - \frac{3}{2} \right) f_1^0, \quad (6.20)$$

$$\frac{\partial}{\partial \mathbf{v}} \cdot \int \frac{\partial \phi}{\partial \mathbf{r}} (e_{1r} v \mathbf{r} + e_{1v} r \mathbf{v}) d\mathbf{r} = - \frac{mf_1^0}{T} \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) \mathbf{v}, \quad (6.21)$$

$$\begin{aligned} \frac{\partial}{\partial \mathbf{v}} \cdot \int \frac{\partial \phi}{\partial \mathbf{r}} \{ e_{2r} v^2 (\mathbf{r} \mathbf{r} - \frac{1}{3} \mathbf{r}^2 \mathbf{1}) + e_{2m} r v (\frac{1}{2} \mathbf{r} \mathbf{v} + \frac{1}{2} \mathbf{v} \mathbf{r} - \frac{1}{3} \mathbf{r} \cdot \mathbf{v} \mathbf{1}) + e_{2v} r^2 (\mathbf{v} \mathbf{v} - \frac{1}{3} v^2 \mathbf{1}) \} d\mathbf{r} \\ = - \frac{m^2 f_1^0}{kT} (\mathbf{v} \mathbf{v} - \frac{1}{3} v^2 \mathbf{1}). \end{aligned} \quad (6.22)$$

Since $\frac{\partial}{\partial \mathbf{v}} \cdot (v^{-3} \mathbf{v}) = 0$, the integral of (6.20) is

$$\int \phi'(r) e_0^{(1)} d\mathbf{r} = \frac{m\sigma}{v^2} \int_{\infty}^v v^2 \left(\frac{mv^2}{2kT} - \frac{3}{2} \right) f_1^0 dv. \quad (6.23)$$

Also, since $\frac{\partial}{\partial \mathbf{v}} \cdot \{ v^{-5} (\mathbf{v} \mathbf{v} - \frac{1}{3} v^2 \mathbf{1}) \} = 0$, it follows from (6.21) that

$$\int \phi'(r) (\frac{1}{3} e_{1v}^{(1)} + \frac{1}{5} e_{1r}^{(2)}) r d\mathbf{r} = - \frac{3m}{2T v^4} \int_{\infty}^v v^4 \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) f_1^0 dv. \quad (6.24)$$

Finally, since $\sum_{\alpha} \frac{\partial}{\partial v_{\alpha}} [v^{-7} \{ v_{\alpha} v_{\beta} v_r - \frac{1}{6} v^2 (v_{\alpha} \delta_{\beta r} + v_{\beta} \delta_{\gamma \alpha} + v_r \delta_{\alpha \beta}) \}] = 0$,

one obtains from (6.22)

$$\int \phi'(r) (\frac{1}{3} e_{2v}^{(1)} + \frac{1}{5} e_{2m}^{(2)} + \frac{1}{7} e_{2r}^{(3)}) r^2 d\mathbf{r} = - \frac{5m^2}{3kT v^6} \int_{\infty}^v v^6 f_1^0 dv. \quad (6.25)$$

These relations do not suffice to determine the function e completely without other assumptions; however, if one assumes, as seems reasonable, e_0 , e_1 and e_2 each involve the velocity as a simple factor (self-consistent field), it follows from (6.23) to (6.25) that

$$\left. \begin{aligned} e_0 &\sim \frac{1}{v^2} \int_{\infty}^v v^2 \left(\frac{mv^2}{2kT} - \frac{3}{2} \right) f_1^0 dv, \\ e_1 &\sim \frac{1}{v^4} \int_{\infty}^v v^4 \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) f_1^0 dv, \\ e_2 &\sim \frac{1}{v^6} \int_{\infty}^v v^6 f_1^0 dv. \end{aligned} \right\} \quad (6.26)$$

Then the velocity dependence of e is determined by (6.4) with $h = 1$ in terms of incomplete gamma-functions; to obtain the dependence on r , it will be necessary to proceed to the equation $h = 2$, using the 'Kirkwood' approximation [(4.6) of part I] for f_3 in terms of f_2 . When e has been determined, v and r are given by (6.14) and (6.16) respectively, and the coefficients of viscosity and thermal conduction may be accurately calculated.

7. APPENDIX

Here are derived some formulae of integration which are required in § 6. The following properties of Legendre polynomials are involved:

$$\frac{1}{2} \int_{-1}^1 P_m(z) P_n(z) dz = \frac{\delta_{mn}}{2m+1}, \quad (7.1)$$

and

$$\left. \begin{aligned} P_0(z) &= 1, \\ P_1(z) &= z, \\ P_2(z) &= \frac{1}{2}(3z^2 - 1), \\ P_3(z) &= \frac{1}{2}z(5z^2 - 3). \end{aligned} \right\} \quad (7.2)$$

It follows immediately that

$$\begin{aligned} \int e_k dr &= \int_0^\infty \frac{1}{2} \int_{-1}^1 P_0(z) \sum_l e_k^{(l)} P_l(z) dz \cdot 4\pi r^2 dr \\ &= \int e_k^{(0)} dr, \end{aligned} \quad (7.3)$$

and

$$\begin{aligned} \int e_k r dr &= v^{-1} v \int e_k r z dr \\ &= v^{-1} v \int_0^\infty \frac{1}{2} \int_{-1}^1 P_1(z) \sum_l e_k^{(l)} P_l(z) dz r \cdot 4\pi r^2 dr \\ &= \frac{1}{3} v^{-1} v \int e_k^{(1)} r dr. \end{aligned} \quad (7.4)$$

Next, it is seen that

$$\begin{aligned} \int e_k r r dr &= \int e_k (rr - \frac{1}{3}r^2 1) dr + \frac{1}{3} \int e_k r^2 dr 1 \\ &= v^{-2} (vv - \frac{1}{3}v^2 1) \int e_k \frac{1}{2}(3z^2 - 1) r^2 dr + \frac{1}{3} \int e_k r^2 dr 1 \\ &= \frac{1}{5} v^{-2} (vv - \frac{1}{3}v^2 1) \int e_k^{(2)} r^2 dr + \frac{1}{3} 1 \int e_k^{(0)} r^2 dr. \end{aligned} \quad (7.5)$$

In a similar way,

$$\begin{aligned} \int e_k r_\alpha r_\beta r_\gamma dr &= \int e_k \{r_\alpha r_\beta r_\gamma - \frac{1}{5}r^2(r_\alpha \delta_{\beta\gamma} + r_\beta \delta_{\gamma\alpha} + r_\gamma \delta_{\alpha\beta})\} dr \\ &\quad + \frac{1}{5} \int e_k r^2(r_\alpha \delta_{\beta\gamma} + r_\beta \delta_{\gamma\alpha} + r_\gamma \delta_{\alpha\beta}) dr \\ &= v^{-3} \{v_\alpha v_\beta v_\gamma - \frac{1}{5}v^2(v_\alpha \delta_{\beta\gamma} + v_\beta \delta_{\gamma\alpha} + v_\gamma \delta_{\alpha\beta})\} \int e_k \frac{1}{2}(5z^3 - 3z) r^3 dr \\ &\quad + \frac{1}{5} v^{-1} (v_\alpha \delta_{\beta\gamma} + v_\beta \delta_{\gamma\alpha} + v_\gamma \delta_{\alpha\beta}) \int e_k z r^3 dr \\ &= \frac{1}{7} v^{-3} \{v_\alpha v_\beta v_\gamma - \frac{1}{5}v^2(v_\alpha \delta_{\beta\gamma} + v_\beta \delta_{\gamma\alpha} + v_\gamma \delta_{\alpha\beta})\} \int e_k^{(3)} r^3 dr \\ &\quad + \frac{1}{15} v^{-1} (v_\alpha \delta_{\beta\gamma} + v_\beta \delta_{\gamma\alpha} + v_\gamma \delta_{\alpha\beta}) \int e_k^{(1)} r^3 dr. \end{aligned} \quad (7.6)$$

It is obvious that the formulae of this section remain valid when r and v are interchanged.

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A general kinetic theory of liquids
IV. Quantum mechanics of fluids

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A general kinetic theory of liquids IV. Quantum mechanics of fluids

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In this paper the classical theory of liquids developed in the first three parts of this series is translated into the quantum formalism. After the fundamental equations have been reformulated, it is shown that in the classical limit $\hbar = 0$, they go over into the corresponding classical equations. A quantized proof of the Boltzmann distribution law is given which is simpler and more direct than that of the Darwin-Fowler method. Then the equation of state is derived in a form which exhibits clearly the deviations from the classical law at very low temperatures.

An approximate method of solution of the fundamental equations is developed in a form suitable for practical application. Finally, the quantum equations of motion and energy transport are obtained, and it is shown that they are formally identical with the classical 'hydrodynamical equations'. This enables a discussion of the viscosity and thermal conductivity of quantum liquids to be given which exposes clearly the alternative explanations of the abnormal properties of liquid He II.

I. INTRODUCTION

In the first three parts of this series the theory of liquids was treated with the help of classical mechanics. In the present paper we propose to apply instead quantum mechanics. This is necessary because there are physical phenomena which indicate quantum effects, namely, the superfluidity of He II, and the superconductivity of certain metals; further, it seems very likely that atomic nuclei must be treated as

* I have signed this paper, as it is part of the programme with which we started this series. My contribution consists of some general suggestions, such as the use of the density matrix as the proper tool, and many critical remarks. The work itself is due to Mr Green.—M. BORN.

droplets of a very dense liquid consisting of neutrons and protons. Superfluidity is the simplest case, in so far as only one kind of particle is involved; the main phenomenon consists in an abnormally small viscosity. We shall develop the theory in this paper far enough to be able to discuss the possible explanations of this effect. Superconductivity is more involved, as it presents a diffusion problem concerning two kinds of particles, the mobile electrons and the almost fixed ions. The rigorous theory of diffusion in liquids is complicated; the classical treatment is now in preparation. The case of diffusing electrons is still more difficult, as the Coulomb forces between them and the ions do not have a short range. Therefore we have to postpone this problem.

The main result of the present paper is that the hydrodynamico-thermal equations are not changed by the introduction of quantum mechanics, but only their interpretation in terms of microscopic phenomena and therefore the values of the physical constants in terms of atomic data. This result is at variance with the only previous attempt to develop a quantum hydrodynamics, namely that made by Landau (1941). Landau transcribes the hydrodynamical equations themselves into operator equations; the meaning of these is obscure, and Landau himself does not make any real application of them, apart from a very general contention that the vortex motion is quantized (in 'rotons'), and has therefore discrete lowest states of rotation. Landau's results concerning the behaviour of He II have nothing to do with his general quantum theory of fluids, but are based on the idea of rotons and some other independent assumptions. We do not think that he has solved the problem of superfluidity. We believe, on the other hand, that our paper contains the correct basis for an explanation, and we shall discuss the different possibilities, while postponing the solution itself to the following publication.

2. THE QUANTUM FORMALISM

According to the general principles of quantum mechanics, it is impossible to measure simultaneously the position and velocity of a molecule; so that the classical theory of the early parts of this series is invalidated by the assumption that it is possible to define a function $f_q(t, \mathbf{x}^{(1)} \dots \mathbf{x}^{(q)}, \xi^{(1)} \dots \xi^{(q)})$, which determines the probability of a group of molecules having simultaneous positions and velocities. Thus the theory of parts I to III must be re-examined in the light of quantum theory to ascertain its range of validity.

The transition from classical to quantum theory is effected by replacing every function $\alpha_q(t, \mathbf{x}^{(1)} \dots \mathbf{x}^{(q)}, \xi^{(1)} \dots \xi^{(q)})$ of co-ordinates and velocities by a corresponding operator represented by the 'matrix' $\alpha_q(t, \mathbf{x}^{(1)} \dots \mathbf{x}^{(q)}, \mathbf{x}^{(1)\prime} \dots \mathbf{x}^{(q)\prime})$, often abbreviated to $\alpha_q(\mathbf{x}, \mathbf{x}')$ or α_q . The sum $(\alpha_q + \beta_q)$ and the product $\alpha_q \beta_q$ of two operators α_q and β_q are operators defined by the matrix equations

$$\left. \begin{aligned} (\alpha_q + \beta_q)(\mathbf{x}, \mathbf{x}') &= \alpha_q(\mathbf{x}, \mathbf{x}') + \beta_q(\mathbf{x}, \mathbf{x}'), \\ \alpha_q \beta_q(\mathbf{x}, \mathbf{x}') &= \int \dots \int \alpha_q(\mathbf{x}, \mathbf{x}'') \beta_q(\mathbf{x}'', \mathbf{x}') \prod_{i=1}^q d\mathbf{x}^{(i)}. \end{aligned} \right\} \quad (2.1)$$

The operators corresponding to the position vector $\mathbf{x}^{(i)}$ and the momentum vector $\mathbf{p}^{(i)} = m\boldsymbol{\xi}^{(i)}$ of the molecule (i) are represented by the matrices

$$\left. \begin{aligned} \mathbf{x}^{(i)}(\mathbf{x}, \mathbf{x}') &= \mathbf{x}^{(i)} \prod_{j=1}^q \delta(\mathbf{x}^{(j)} - \mathbf{x}^{(j)\prime}), \\ \mathbf{p}^{(i)}(\mathbf{x}, \mathbf{x}') &= -i\hbar \frac{\partial}{\partial \mathbf{x}^{(i)}} \prod_{j=1}^q \delta(\mathbf{x}^{(j)} - \mathbf{x}^{(j)\prime}). \end{aligned} \right\} \quad (2.2)$$

With the aid of (2.1) the operator $\alpha_q(\mathbf{x}, \mathbf{x}')$ corresponding to any function $\alpha_q(\mathbf{x}, \boldsymbol{\xi})$ of the positions and velocities of the molecules can be constructed. As special cases, one has for a function $\gamma_q(\mathbf{x})$ of positions alone,

$$\left. \begin{aligned} \gamma_q(\mathbf{x}, \mathbf{x}') &= \gamma_q(\mathbf{x}) \prod_{j=1}^q \delta(\mathbf{x}^{(j)} - \mathbf{x}^{(j)\prime}), \\ (\mathbf{p}^{(i)}\gamma_q)(\mathbf{x}, \mathbf{x}') &= -i\hbar \frac{\partial \gamma_q(\mathbf{x})}{\partial \mathbf{x}^{(i)}} \prod_{j=1}^q \delta(\mathbf{x}^{(j)} - \mathbf{x}^{(j)\prime}). \end{aligned} \right\} \quad (2.3)$$

The trace of an operator α_q will be denoted by $\chi_q(\alpha_q)$, and is defined by

$$\chi_q(\alpha_q) = \iint \alpha_q(\mathbf{x}, \mathbf{x}') \delta(\mathbf{x}^{(q)} - \mathbf{x}^{(q)\prime}) d\mathbf{x}^{(q)} d\mathbf{x}^{(q)\prime}; \quad (2.4)$$

for $q > 1$ it is an operator of the type α_{q-1} , and must be distinguished from the 'complete trace' $X(\alpha_q)$, defined by

$$X(\alpha_q) = \chi_1[\chi_2[\dots \chi_q(\alpha_q)]], \quad (2.5)$$

which is a *c*-number. $\chi_q(\alpha_q)$ is the quantum analogue of the classical expression $\iint \alpha_q(\mathbf{x}, \boldsymbol{\xi}) d\mathbf{x}^{(q)} d\boldsymbol{\xi}^{(q)}$; by comparison with (2.4) it is seen that the classical operation $\int d\boldsymbol{\xi}^{(q)}$ is replaced by $\int d\mathbf{x}^{(q)\prime} \delta(\mathbf{x}^{(q)} - \mathbf{x}^{(q)\prime})$ in the quantum theory.

It is clear from what has been said that the classical distribution function $f_q(\mathbf{x}, \boldsymbol{\xi})$ is replaced by an Hermitian matrix operator $\rho_q(\mathbf{x}, \mathbf{x}')$. ρ_q is normalized according to the relation

$$\chi_{q+1}(\rho_{q+1}) = (N-q)\rho_q, \quad (2.6)$$

which corresponds to $\iint f_{q+1} d\mathbf{x}^{(q+1)} d\boldsymbol{\xi}^{(q+1)} = (N-q)f_q$

[(2.4) of part I] in the classical theory. The formula

$$\int^{(q)} \dots \int f_q \prod_{i=1}^q d\boldsymbol{\xi}^{(i)} = n_q$$

[(2.1) of part I] now reads

$$\int^{(q)} \dots \int \rho_q \prod_{i=1}^q \delta(\mathbf{x}^{(i)} - \mathbf{x}^{(i)\prime}) d\mathbf{x}^{(i)\prime} = n_q, \quad (2.7)$$

or

$$\rho_q(\mathbf{x}, \mathbf{x}') = n_q(\mathbf{x}),$$

expressing the important property of the matrix $\rho_q(\mathbf{x}, \mathbf{x}')$, that its diagonal element is the number-density function. It will now be clear that ρ_q is the density matrix introduced into quantum mechanics by von Neumann (1932) and Dirac (1935), the equilibrium properties of which have been carefully examined by Husimi (1940).

To formulate the equation satisfied by ρ_q , consider first the operator ρ_N . Like f_N , this may be given an arbitrary initial value, subject only to the normalizing condition and the Hermitian property; its subsequent variation is then given by the Heisenberg equation

$$\frac{\partial \rho_N}{\partial t} = [W_N, \rho_N], \quad (2.8)$$

where W_N is the Hamiltonian operator for the system of N molecules, and, in conformity with Dirac's notation, $[\alpha, \beta]$ means simply $-\imath(\alpha\beta - \beta\alpha)/\hbar$. The Hamiltonian W_q for a system of q molecules is given by

$$W_q = \frac{1}{2m} \sum_{i=1}^q \mathbf{p}^{(i)2} + \frac{1}{2} \sum_{i,j=1}^q \phi^{(ij)} + \sum_{i=1}^q \psi^{(i)}, \quad (2.9)$$

where $\psi^{(i)}$ is the potential energy at $\mathbf{x}^{(i)}$ due to the external forces, which are assumed to constitute a conservative system, so that $\mathbf{P}^{(i)} = -\partial\psi^{(i)}/\partial\mathbf{x}^{(i)}$.

Taking the trace of (2.8), one obtains

$$\frac{\partial \rho_{N-1}}{\partial t} = [W_{N-1}, \rho_{N-1}] + \sum_{i=1}^N \chi_N [\phi^{(iN)}, \rho_N], \quad (2.10)$$

since $\chi_N[\mathbf{p}^{(N)2}, \rho_N]$ is reducible to

$$-\int \frac{\partial}{\partial \mathbf{x}^{(N)}} \int (\mathbf{p}^{(N)} \rho_N + \rho_N \mathbf{p}^{(N)}) (\mathbf{x}, \mathbf{x}') \delta(\mathbf{x}^{(N)} - \mathbf{x}'^{(N)}) d\mathbf{x}'^{(N)} d\mathbf{x}^{(N)},$$

which in turn may be transformed to a vanishing surface integral. Repeating this operation indefinitely, and cancelling the factor $(N-q)!$ which appears, one obtains

$$\frac{\partial \rho_q}{\partial t} = [W_q, \rho_q] + \sum_{i=1}^q \chi_{q+1} [\phi^{(iq+1)}, \rho_{q+1}]. \quad (2.11)$$

Now, the well-known classical analogue of $[\alpha_q, \beta_q]$ is the 'Poisson bracket'

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

so that $[W_q, \rho_q]$ becomes

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

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

$$\frac{1}{m} \int \int \frac{\partial \phi^{(iq+1)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial f_{q+1}}{\partial \xi^{(i)}} d\mathbf{x}^{(q+1)} d\xi^{(q+1)}$$

in the transition to classical theory. Thus (2.11) goes over into the classical form

$$\frac{\partial f_q}{\partial t} + \sum_{i=1}^q \left\{ \xi^{(i)} \cdot \frac{\partial f_q}{\partial \mathbf{x}^{(i)}} + \frac{1}{m} \left(\mathbf{P}^{(i)} - \sum_{j=1}^q \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} \right) \frac{\partial f_q}{\partial \xi^{(i)}} \right\} = \frac{1}{m} \int \int \frac{\partial \phi^{(iq+1)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial f_{q+1}}{\partial \xi^{(i)}} d\mathbf{x}^{(q+1)} d\xi^{(q+1)}$$

in the limit $\hbar \rightarrow 0$, and it may be inferred that in the region of high temperatures, where the number of energy states is so large that one may substitute a continuous spectrum without error (thus effectively writing $\hbar = 0$), the classical theory will not give rise to any appreciable error.

3. THEORY OF THERMODYNAMIC EQUILIBRIUM

In order to calculate the density matrix ρ_N by means of the equation (2.8), it must first be specified at an initial time t_0 . For this purpose it is necessary to choose any commuting set of operators $\lambda^{(r)}$ ($r = 1, \dots, 3N$), and to specify the probability $a_N(l) = a_N(l^{(1)} \dots l^{(3N)})$ that at time t_0 the molecular assembly is in the state l in which the $\lambda^{(r)}$ have the simultaneous eigenvalues $l^{(r)}$. Let $\psi_N(l, \mathbf{x})$ be the corresponding normalized eigenfunction, satisfying

$$\lambda^{(r)}\psi_N(l, \mathbf{x}) = l^{(r)}\psi_N(l, \mathbf{x}). \quad (3.1)$$

Then at time t_0 , ρ_N is given by (cf. Dirac 1935)

$$\rho_N = N! \sum_l a_N(l) \psi_N(l, \mathbf{x}) \psi_N^*(l, \mathbf{x}'). \quad (3.2)$$

One possible set of λ is that set of independent operators which commute with the Hamiltonian energy W_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 parts containing q_1, q_2, \dots, q_w molecules ($q_1 + q_2 + \dots + q_w = N$) in such a way that the interaction between molecules in different parts is very weak; then the λ are chosen to be the $\lambda_1, \lambda_2, \dots, \lambda_w$ which commute with $W_{q_1}, W_{q_2}, \dots, W_{q_w}$ respectively. Write

$$W_N = W_{q_1} + W_{q_2} + \dots + W_{q_w} + V \quad (3.3)$$

so that V is very small. Let E_N be the eigenvalue of $W_{q_1} + W_{q_2} + \dots + W_{q_w}$, which is a function of the λ . Then, in the l -representation, (2.8) reads

$$i\hbar \frac{\partial \rho_N}{\partial t}(l, l') = (E_N - E'_N) \rho_N(l, l') + \sum_r \{V(l, l'') \rho_N(l'', l') - \rho_N(l, l'') V(l'', l')\}, \quad (3.4)$$

where, according to (3.2), at time t_0 ,

$$\rho_N(l, l') = a_N(l) \delta_{ll'}. \quad (3.5)$$

The condition for the equilibrium between the various parts of the fluid is expressed by the vanishing of the last term in (3.4), or

$$V(l, l') \{a_N(l') - a_N(l)\} = 0. \quad (3.6)$$

It is not difficult to show further that starting from any initial state the fluid will approach asymptotically a state in which (3.6) is satisfied, apart from small random fluctuations; a detailed discussion of the H -theorem, of which this is a special case, is being given by the authors elsewhere.

(3.6) means that in equilibrium $a_N(l)$ will have the same value for all states l between which transitions are not forbidden by the vanishing of the matrix elements $V(l, l')$.

In general, however, the only transitions thus forbidden will be those from one energy state to another, which violate the principle of conservation of energy. Thus, in equilibrium,

$$a_N(l) = a(E_N), \quad (3.7)$$

though in certain circumstances, namely, when motion in a certain direction or rotation about a given axis is entirely uninhibited, the momentum and angular momentum must be included among the 'absolute' constants of the motion, and $a_N(l)$ will depend also on these.

Now let $a_{q_1}(l_1)$ be the probability that the first group of q_1 molecules is in the eigenstate l_1 at time t_0 , etc. Then, since the different groups are virtually independent of one another,

$$a(E_N) = a_{q_1}(l_1) a_{q_2}(l_2) \dots a_{q_w}(l_w); \quad (3.8)$$

also

$$E_N = E_1 + E_2 + \dots + E_w \quad (3.9)$$

where E_1, E_2, \dots are the eigenvalues of W_{q_1}, W_{q_2}, \dots and depend only on the l_1, l_2, \dots respectively. It follows rigorously from (3.8) and (3.9) that

$$\left. \begin{aligned} a(E_N) &= e^{-(\alpha + \beta E_N)}, \\ a_{q_1}(E_1) &= e^{-(\alpha_1 + \beta E_1)}, \text{ etc.,} \end{aligned} \right\} \quad (3.10)$$

where $\alpha = \alpha_1 + \alpha_2 + \dots + \alpha_w$. As is well known, (3.10) summarizes the whole of statistical thermodynamics. It is unnecessary to give here the argument, stated concisely by Schrödinger (1946), by which β is identified with $(kT)^{-1}$, where T is the thermodynamic temperature, and the entropy expressed in the form

$$S = -k \sum_l a_N(l) \log a_N(l) = -\frac{k}{N!} X(\rho_N \log \rho_N). \quad (3.11)$$

The internal energy U is given by

$$U = \sum_l a_N(l) E_N = \frac{1}{N!} X(\rho_N W_N), \quad (3.12)$$

and the free energy $A = U - TS$ by

$$e^{-A/kT} = \frac{1}{N!} \sum_l e^{-E_N/kT} = \frac{1}{N!} X(e^{-W_N/kT}). \quad (3.13)$$

The constant α in (3.10) is determined by the condition $\sum_l a_N(l) = 1$ in the form $e^\alpha = N! e^{-A/kT}$, and it follows that ρ_N may be expressed in the operator form

$$\rho_N = e^{(A-W_N)/kT}. \quad (3.14)$$

Using (2.6), one obtains

$$(N-q)! \rho_q = \chi_{q+1}[\chi_{q+2}\{\dots \chi_N(e^{(A-W_N)/kT})\}]. \quad (3.15)$$

To calculate the thermodynamic pressure p from (3.13) with the aid of the formula $p = -\partial A/\partial V$, it is convenient to assume that $\psi^{(i)}$ vanishes. Writing $\sigma_N = e^{-W_N/kT}$, and $\mathbf{x}^{(i)} = b\theta^{(i)}$, where $b^3 = V$, one has

$$X(\sigma_N) = b^{3N} \int \dots \int \sigma_N(b\theta, b\theta) \prod_{i=1}^N d\theta^{(i)}, \quad (3.16)$$

so that $\frac{1}{3b^2} \frac{\partial X(\sigma_N)}{\partial b} = \frac{N}{V} X(\sigma_N) + \frac{1}{3V} \int \cdots \int_{i=1}^{(N)} \sum_{j=1}^N \mathbf{x}^{(i)} \cdot \frac{\partial}{\partial \mathbf{x}^{(i)}} \sigma_N(\mathbf{x}, \mathbf{x}) \prod_{j=1}^N d\mathbf{x}^{(j)},$

or $\frac{\partial X(\sigma_N)}{\partial V} = \frac{1}{3V} \int \cdots \int_{i=1}^{(N)} \sum_{j=1}^N \frac{\partial}{\partial \mathbf{x}^{(i)}} \{\mathbf{x}^{(i)} \sigma_N(\mathbf{x}, \mathbf{x})\} \prod_{j=1}^N d\mathbf{x}^{(j)}. \quad (3 \cdot 17)$

This expression can be simplified in two ways. First, writing (3·13) in the form $N! e^{-A/kT} = X(\sigma_N)$, and making use of (3·14) and (2·6), one obtains

$$\begin{aligned} p &= \frac{kTe^{A/kT}}{N!} \frac{\partial X(\sigma_N)}{\partial V} \\ &= n_1 kT + \frac{kT}{6V(N-1)} \iint \left(\mathbf{x}^{(1)} \cdot \frac{\partial}{\partial \mathbf{x}^{(1)}} + \mathbf{x}^{(2)} \cdot \frac{\partial}{\partial \mathbf{x}^{(2)}} \right) \rho_2(\mathbf{x}, \mathbf{x}) d\mathbf{x}^{(1)} d\mathbf{x}^{(2)} \\ &= n_1 kT + \frac{kT}{6V(N-1)} \iint r n'_2(r) d\mathbf{x}^{(1)} d\mathbf{x}^{(2)}, \end{aligned} \quad (3 \cdot 18)$$

where $\mathbf{r} = \mathbf{x}^{(2)} - \mathbf{x}^{(1)}$. Because of the classical equation

$$\frac{\partial n_2}{\partial \mathbf{x}^{(i)}} + \frac{n_2}{kT} \frac{\partial \phi}{\partial \mathbf{x}^{(i)}} + \int \frac{n_3}{kT} \frac{\partial \phi^{(i)3}}{\partial \mathbf{x}^{(i)}} d\mathbf{x}^{(3)} = 0,$$

this reduces classically to the formula

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

Next, the integrand of (3·17) may be written in the form

$$\frac{i}{\hbar} \sum_{i=1}^N (\mathbf{P}^{(i)} \cdot \mathbf{x}^{(i)} \sigma_N - \sigma_N \mathbf{P}^{(i)} \cdot \mathbf{x}^{(i)}) (\mathbf{x}, \mathbf{x});$$

to evaluate this expression one may make use of the lemma that if μ and ν are any two operators, and $f(\nu)$ is any power series in ν , then

$$\begin{aligned} \mu f(\nu) - f(\nu) \mu &= f'(\nu) \frac{\mu_1}{1!} + f''(\nu) \frac{\mu_2}{2!} + f'''(\nu) \frac{\mu_3}{3!} + \dots \\ &= \frac{\mu_1}{1!} f'(\nu) - \frac{\mu_2}{2!} f''(\nu) + \frac{\mu_3}{3!} f'''(\nu) + \dots \\ &= \frac{1}{1!} \{\mu_1 f'(\nu)\} + \frac{1}{3!} \{\mu_3 f'''(\nu)\} + \dots - \frac{1}{2!} \left\{ \frac{1}{2!} [\mu_2, f''(\nu)] + \frac{1}{4!} [\mu_4, f^{(iv)}(\nu)] + \dots \right\}, \end{aligned} \quad (3 \cdot 19)$$

where $\{\alpha\beta\}$ stands for $\frac{1}{2}(\alpha\beta + \beta\alpha)$, $\mu_1 = \mu\nu - \nu\mu$ and $\mu_{k+1} = \mu_k\nu - \nu\mu_k$ ($k = 1, 2, \dots$). This is easily proved by induction for $f(\nu) = \nu^n$, after which the generalization is trivial. Putting $\nu = W_N$, $\mu = \sum_{i=1}^N \mathbf{P}^{(i)} \cdot \mathbf{x}^{(i)}$, and $f(\nu) = e^{-\nu/kT} = \sigma_N$, one obtains, for the integrand in (3·17), the expression

$$-\frac{i}{\hbar} \left[\frac{(kT)^{-1}}{1!} \{\mu_1 \sigma_N\} + \frac{(kT)^{-3}}{3!} \{\mu_3 \sigma_N\} + \dots \right] + \frac{1}{2} \left\{ \frac{(kT)^{-2}}{2!} [\mu_2, \sigma_N] + \frac{(kT)^{-4}}{4!} [\mu_4, \sigma_N] + \dots \right\}.$$

The terms involving μ_{2k} vanish on insertion in (3.16), but terms in μ_{2k-1} survive, giving a power series in $(\hbar/kT)^2$, effectively, for the pressure. Since

$$\mu_1 = \hbar \sum_{i=1}^N \left(\frac{1}{m} \mathbf{p}^{(i)2} - \frac{1}{2} \sum_{j=1}^N r^{(ij)} \phi'^{(ij)} \right), \quad (3.20)$$

the first term alone gives

$$p_1 = n_1 k T_1 - \frac{1}{6} \int n_2(r) r \phi'(r) dr, \quad (3.21)$$

$$\text{where } T_1 \text{ is defined by } \frac{3}{2} N k T_1 = \chi_1 \left(\frac{1}{2m} \mathbf{p}^{(1)2} \rho_1 \right) \quad (3.22)$$

in terms of the mean kinetic energy of the molecules. This T_1 is in quantum theory quite distinct from the thermodynamic temperature T which appears in (3.18). Quite apart from this, the neglect of squares and higher powers of \hbar/kT shows that (3.21) is only an approximation valid for high temperatures.

In view of this deviation from the classical formula which occurs under quantum conditions at low temperatures, it is worth noting the physical meaning of the thermodynamic pressure, namely the force per unit area on the wall of the vessel as measured, for example, by the work done on a movable piston. It does not follow in quantum mechanics that this will be the same as the diagonal elements p_1 of the pressure tensor \mathbf{p}_1 which appears in the equation of motion

$$mn_1 \frac{d}{dt} \mathbf{u}_1 + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p}_1 = 0$$

and it will be seen from the calculations of § 5 that the two quantities are indeed different, inasmuch as p_1 is given *exactly* by the equation (3.21) in equilibrium. Thus in quantum mechanical fluids the situation is that both pressure and temperature may be defined either thermodynamically or in terms of dynamical properties, but the definitions will not be equivalent. In problems where equilibrium obtains, the thermodynamic definitions have the obvious advantage of describing what is actually measured; but in non-equilibrium problems the dynamical quantities may play an important role. Thus in the process of thermal conduction, the energy flux is proportional to the gradient of the 'dynamical' temperature, and it is the pressure tensor, as defined in § 5, which plays an important part in the phenomenon of viscosity. These considerations may help to elucidate some of the puzzling properties of liquid He II.

4. THE BEHAVIOUR OF MOLECULAR CLUSTERS

The exact equilibrium theory of the previous section is quite unsuited to the practical investigation of the properties of condensed systems. For this purpose the study of the density matrices of small clusters of molecules is quite sufficient, since all macroscopic quantities can be obtained in terms of ρ_1 and ρ_2 . In this section

the equation (2.11) will therefore be examined with small values of q ; it may be written in the form

$$i\hbar \frac{\partial \rho_q}{\partial t} = W_q \rho_q - \rho_q W_q + V_q \rho_q - \rho_q V_q^\dagger, \quad (4.1)$$

where

$$V_q = \sum_{i=1}^q \chi_{q+1}(\phi^{(i_{q+1})} \rho_{q+1}) \rho_q^{-1}, \quad (4.2)$$

and V_q^\dagger denotes the Hermitian conjugate, which is generally different from V_q , though both quantities correspond classically to the average potential energy of the cluster of q molecules due to the other molecules. As in § 3, one may take an l -representation in which W_q is diagonal with eigenvalue E_q , when, after writing

$$\left. \begin{aligned} \rho_q(l, l') &= \bar{\rho}_q(l, l') e^{i(E_q - E_{q'}^*) t/\hbar}, \\ V_q(l, l') &= \bar{V}_q(l, l') e^{i(E_q - E_{q'}^*) t/\hbar}, \end{aligned} \right\} \quad (4.3)$$

(4.1) takes the form

$$i\hbar \frac{\partial \bar{\rho}_q}{\partial t} = \bar{V}_q \bar{\rho}_q - \bar{\rho}_q \bar{V}_q^\dagger. \quad (4.4)$$

If $t - t_0$ is small, this equation may be solved by writing

$$\bar{\rho}_q = \rho(0) + \rho(1) + \rho(2) + \dots, \quad (4.5)$$

where $\rho(0)$ is the value at time t_0 , so that

$$i\hbar \frac{\partial}{\partial t} \rho(s+1) = \bar{V}_q \rho(s) - \rho(s) \bar{V}_q^\dagger. \quad (4.6)$$

If $a(l)$ is the probability of finding the cluster of q molecules in the state l at time t_0 , one may take $\rho(0) = a(l) \delta_{ll'}$; also, if

$$U = \int_{t_0}^t \bar{V}_q dt; \quad \bar{V}_q = \dot{U}, \quad (4.7)$$

one finds

$$\left. \begin{aligned} i\hbar \rho(1) &= U \rho(0) - \rho(0) U^\dagger, \\ -\hbar^2 \rho(2) &= \int_{t_0}^t (\dot{U} U \rho(0) + \rho(0) U^\dagger \dot{U}^\dagger) dt - U \rho(0) U^\dagger. \end{aligned} \right\} \quad (4.8)$$

Taking the diagonal elements of these equations, it becomes clear that the probability $p_{ll'}$ of a transition from the state l' to the state l in the small time $t - t_0$ is $\frac{1}{\hbar^2} |U(l, l')|^2$, but that this is generally different from $p_{ll'}$, since V_q is not Hermitian.

The condition for equilibrium is now

$$a(l) P_l = \sum_{l'} a(l') p_{ll'}, \quad (4.9)$$

where

$$P_l = \sum_{l'} \int_{t_0}^t \{ \dot{U}(l, l') U(l'l) + U^\dagger(l, l') \dot{U}^\dagger(l'l) \} dt. \quad (4.10)$$

Whether one has equilibrium or not, if there is to be no increase in the sum of the probabilities of the occupation of all states, one must have

$$\sum a(l) P_l = \sum_{ll'} a(l') p_{ll'}, \quad (4.11)$$

and it follows from this, since the $a(l)$ are arbitrary, that

$$P_l = \sum_r p_{lr}. \quad (4.12)$$

(4.9), together with the normalizing condition $\sum_l a(l) = 1$, suffices to determine the equilibrium values of the $a(l)$ when V_q is regarded as known. The calculation of V_q , however, requires a knowledge of $\rho_{q+1}\rho_q^{-1}$, and although certain properties of this matrix are known, for example,

$$\chi_{q+1}(\rho_{q+1}\rho_q^{-1}) = N - q, \quad (4.13)$$

its exact evaluation is as difficult as that of ρ_q . As in the classical theory, therefore, it is necessary to make some approximative assumption to render the problem in a tractable form. Probably the simplest assumption to make is that V_q is approximately Hermitian, which amounts to replacing the field of the other molecules by a corresponding conservative field imposed from outside; this procedure is similar to Hartree's method of the self-consistent field. Then, as was seen in §3, the precise form of V_q is unimportant, and only its vanishing elements must be known. In equilibrium, these will include those which represent transitions from one energy state to another; and we find that this condition, together with (4.13), makes the problem quite determinate.

5. QUANTUM HYDRODYNAMICS

From the fundamental equation (2.11), the hydrodynamical equations will now be derived in a manner corresponding to the classical theory of part III. For this purpose, the quantum definitions of the number density function n_q , the mean velocity $\mathbf{u}_q^{(i)}$, and the generalized temperature $T_q^{(i)}$, relating to a cluster of molecules whose positions are known, are first required. The definitions ought to conform to the condition that in passing from classical to quantum theory, the operation $\int d\mathbf{x}^{(i)}$ becomes $\int d\mathbf{x}^{(i)} \delta(\mathbf{x}^{(i)} - \mathbf{x}^{(i)})$, and a product $\alpha\beta$ is replaced by $\{\alpha\beta\} = \frac{1}{2}(\alpha\beta + \beta\alpha)$, which is Hermitian when α and β are Hermitian. Then, in agreement with (2.7), $n_q(\mathbf{x}) = \rho_q(\mathbf{x}, \mathbf{x})$, and

$$mn_q \mathbf{u}_q^{(i)}(\mathbf{x}) = \{\rho_q \mathbf{p}^{(i)}\}(\mathbf{x}, \mathbf{x}), \quad (5.1)$$

whilst

$$3mn_q k T_q^{(i)}(\mathbf{x}) = \{\{\rho_q \mathbf{v}_q^{(i)}\} \cdot \mathbf{v}_q^{(i)}\}, \quad (5.2)$$

where $\mathbf{v}_q^{(i)}$ is defined by

$$\mathbf{v}_q^{(i)}(\mathbf{x}, \mathbf{x}') = \frac{1}{m} \mathbf{p}^{(i)}(\mathbf{x}, \mathbf{x}') - \mathbf{u}_q^{(i)}(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}'). \quad (5.3)$$

$$\begin{aligned} \text{Since } (\mathbf{p}^{(i)2} \rho_q - \rho_q \mathbf{p}^{(i)2})(\mathbf{x}, \mathbf{x}') &= -\hbar^2 \left(\frac{\partial^2}{\partial \mathbf{x}^{(i)2}} - \frac{\partial^2}{\partial \mathbf{x}^{(i)'2}} \right) \rho_q(\mathbf{x}, \mathbf{x}') \\ &= -i\hbar \left(\frac{\partial}{\partial \mathbf{x}^{(i)}} + \frac{\partial}{\partial \mathbf{x}^{(i)'}} \right) \cdot (\mathbf{p}^{(i)} \rho_q + \rho_q \mathbf{p}^{(i)})(\mathbf{x}, \mathbf{x}'), \end{aligned} \quad (5.4)$$

one may write (2.11) in the form

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \rho_q(\mathbf{x}, \mathbf{x}') &+ \frac{i\hbar}{m} \sum_{i=1}^q \left(\frac{\partial}{\partial \mathbf{x}^{(i)}} + \frac{\partial}{\partial \mathbf{x}^{(i)'}} \right) \cdot \{\rho_q \mathbf{p}^{(i)}\}(\mathbf{x}, \mathbf{x}') \\ &= \frac{1}{2} \sum_{i,j=1}^q (\phi^{(ij)} - \phi^{(ij)'}) \rho_q(\mathbf{x}, \mathbf{x}') + \sum_{i=1}^q (\psi^{(i)} - \psi^{(i)'}) \rho_q(\mathbf{x}, \mathbf{x}') \\ &\quad + \sum_{i=1}^q \int \int (\phi^{(iq+1)} - \phi^{(iq+1)'}) \rho_{q+1}(\mathbf{x}, \mathbf{x}') \delta(\mathbf{x}^{(q+1)} - \mathbf{x}^{(q+1)'}) d\mathbf{x}^{(q+1)} d\mathbf{x}^{(q+1)'} \quad (5.5) \end{aligned}$$

On writing $\mathbf{x} = \mathbf{x}'$ in this equation, all terms on the right-hand side vanish, and one has

$$\frac{\partial n_q}{\partial t} + \sum_{i=1}^q \frac{\partial}{\partial \mathbf{x}^{(i)}} \cdot (n_q \mathbf{u}_q^{(i)}) = 0, \quad (5.6)$$

which is the quantum expression of the equation of continuity, and its generalization for $q > 1$.

Next, multiplying (5.4) before and after by $\mathbf{p}^{(i)}$, and taking half the sum, one obtains

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \{\rho_q \mathbf{p}^{(i)}\}(\mathbf{x}, \mathbf{x}') &+ \frac{i\hbar}{m} \sum_{j=1}^q \left(\frac{\partial}{\partial \mathbf{x}^{(j)}} + \frac{\partial}{\partial \mathbf{x}^{(j)'}} \right) \cdot \{\{\rho_q \mathbf{p}^{(j)}\} \mathbf{p}^{(i)}\}(\mathbf{x}, \mathbf{x}') \\ &= \frac{1}{2} \sum_{j,k=1}^q (\phi^{(jk)} - \phi^{(jk)'}) \{\rho_q \mathbf{p}^{(k)}\}(\mathbf{x}, \mathbf{x}') - \frac{i\hbar}{2} \sum_{j=1}^q \left(\frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} + \frac{\partial \phi^{(ij)'}}{\partial \mathbf{x}^{(i)'}} \right) \rho_q(\mathbf{x}, \mathbf{x}') \\ &\quad + \sum_{j=1}^q (\psi^{(j)} - \psi^{(j)'}) \{\rho_q \mathbf{p}^{(j)}\}(\mathbf{x}, \mathbf{x}') + \frac{i\hbar}{2} (\mathbf{p}^{(i)} + \mathbf{p}^{(i)'}) \rho_q(\mathbf{x}, \mathbf{x}') \\ &\quad + \sum_{j=1}^q \int \int (\phi^{(jq+1)} - \phi^{(jq+1)'}) \{\rho_{q+1} \mathbf{p}^{(j)}\}(\mathbf{x}, \mathbf{x}') \delta(\mathbf{x}^{(q+1)} - \mathbf{x}^{(q+1)'}) d\mathbf{x}^{(q+1)} d\mathbf{x}^{(q+1)'} \\ &\quad - \frac{i\hbar}{2} \int \int \left(\frac{\partial \phi^{(iq+1)}}{\partial \mathbf{x}^{(i)}} + \frac{\partial \phi^{(iq+1)'}}{\partial \mathbf{x}^{(i)'}} \right) \rho_{q+1}(\mathbf{x}, \mathbf{x}') \delta(\mathbf{x}^{(q+1)} - \mathbf{x}^{(q+1)'}) d\mathbf{x}^{(q+1)} d\mathbf{x}^{(q+1)'} \quad (5.7) \end{aligned}$$

Again writing $\mathbf{x} = \mathbf{x}'$, one has

$$\frac{\partial}{\partial t} (n_q \mathbf{u}_q^{(i)}) + \sum_{j=1}^q \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \{\{\rho_q \mathbf{p}^{(j)}\} \mathbf{p}^{(i)}\}(\mathbf{x}, \mathbf{x}') = n_q \eta_q^{(i)}, \quad (5.8)$$

where $m\eta_q^{(i)} = - \sum_{j=1}^q \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} + \mathbf{p}^{(i)} - \int \frac{\partial \phi^{(iq+1)}}{\partial \mathbf{x}^{(i)}} \frac{n_{q+1}}{n_q} d\mathbf{x}^{(q+1)}. \quad (5.9)$

As in the case of the corresponding classical equation [(2.6) of part III], (5.8) is easily transformed to

$$mn_q \frac{d}{dt} \mathbf{u}_q^{(i)} + \sum_{j=1}^q \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{k}_q^{(ji)} = mn_q \eta_q^{(i)}, \quad (5.10)$$

where $\frac{d}{dt}$ means $\frac{\partial}{\partial t} + \sum_{i=1}^q \mathbf{u}_q^{(i)} \cdot \frac{\partial}{\partial \mathbf{x}^{(i)}}$, and

$$\mathbf{k}_q^{(ji)} = m \{\{\rho_q \mathbf{v}_q^{(j)}\} \mathbf{v}_q^{(i)}\}(\mathbf{x}, \mathbf{x}). \quad (5.11)$$

Equation (5.10) is the quantum equation of motion, differing only from the classical equation by the definition in atomistic terms of those quantities which classically involve the velocities.

To obtain the corresponding equation for $T_q^{(i)}$, take the scalar product of (5.6) with $\mathbf{p}^{(i)}$ before and after, and half the sum of the resulting expressions, afterwards putting $\mathbf{x} = \mathbf{x}'$. The result is

$$\begin{aligned} \frac{\partial}{\partial t} (3n_q k T_q^{(i)} + mn_q \mathbf{u}_q^{(i)2}) + \frac{1}{m^2} \sum_{j=1}^q \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \{\{\rho_q \mathbf{p}^{(j)}\} p^{(i)}\} (\mathbf{x}, \mathbf{x}') \\ = -2 \sum_{j=1}^q n_q \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{u}_q^{(i)} + 2n_q \mathbf{p}^{(i)} \cdot \mathbf{u}_q^{(i)} - 2 \int n_{q+1} \frac{\partial \phi^{(iq+1)}}{\partial \mathbf{x}^{(i)}} \cdot \mathbf{u}_{q+1}^{(i)} d\mathbf{x}^{(q+1)}. \quad (5.12) \end{aligned}$$

This is also readily transformed to

$$\begin{aligned} \frac{3}{2} n_q k \frac{dT_q^{(i)}}{dt} + \sum_{j=1}^q \left\{ \frac{\partial}{\partial \mathbf{x}^{(j)}} \cdot \mathbf{m}_q^{(j)} + \left(\mathbf{k}_q^{(ji)} \cdot \frac{\partial}{\partial \mathbf{x}^{(j)}} \right) \cdot \mathbf{u}_q^{(i)} \right\} \\ = - \int n_{q+1} \frac{\partial \phi^{(iq+1)}}{\partial \mathbf{x}^{(i)}} \cdot (\mathbf{u}_{q+1}^{(i)} - \mathbf{u}_q^{(i)}) d\mathbf{x}^{(q+1)}, \quad (5.13) \end{aligned}$$

where

$$\mathbf{m}_q^{(ji)} = \frac{1}{2} m \{\{\rho_q \mathbf{v}_q^{(j)}\} \mathbf{v}_q^{(i)}\} (\mathbf{x}, \mathbf{x}). \quad (5.14)$$

(5.13) differs from the classical equation of energy transport only in the atomistic definition of quantities which classically involve the velocities.

At first it is rather surprising to find that quantum mechanics involves no change of the equations of continuity, motion, and energy transport from those obtained through the classical theory, but reflexion shows that this must be so: the macroscopic, visible changes of a fluid in motion give no indication of the existence of quantum phenomena. This is true even in the case of liquid He II, where the abnormal viscosity, thermal conductivity, etc., in no way conflict with the macroscopic description of matter, though they lead one to suspect that quantum phenomena are responsible. This may indeed be the case, since the evaluation of n_q , $\mathbf{u}_q^{(i)}$, $T_q^{(i)}$, etc., from the atomistic standpoint is quite different in the quantum formalism from the classical procedure, and one therefore expects quantum complications at low temperatures.

6. DISCUSSION

The fact that we have been able, in the last section, to derive hydrodynamical equations, identical in form with those resulting from the classical theory of part III, has far-reaching consequences. One conclusion which may be drawn immediately is that the theory of viscosity and thermal conductivity developed from these hydrodynamical equations in part III can be taken over into the quantum theory unchanged, provided one interprets the classical temperature and pressure as the 'dynamical' temperature and pressure of quantum theory. The formulae for the pressure tensor and thermal flux are unaltered, and so, therefore, are those for the coefficients of viscosity and thermal conduction. This enables us without further analysis to examine the possible causes of the abnormal values found experimentally for these constants in liquid He II.

First consider the expression for the viscosity, namely

$$\mu = \frac{1}{30} \int v(r) \phi'(r) r^3 dr - \frac{1}{15} m \int \phi_2(v) v^4 dv, \quad (6.1)$$

where $\phi_2(v) v \cdot b \cdot v$ is the distortion of the velocity (momentum) distribution function by the motion, and $v(r) r \cdot b \cdot r$ the corresponding distortion of the radial distribution function, b representing the symmetrical non-divergent part of the velocity gradient tensor. It is clear that an abnormally small value of μ can arise at low temperatures from three main causes. In the first place, it is possible that the second, or 'kinetic' term, which is usually positive but entirely negligible for the liquid phase, by becoming negative and of appreciable magnitude, might annul the first, or 'potential' term, which usually has a considerable positive value. This has to be considered because under quantum conditions there is no longer any obvious reason why $\phi_2(v)$ should be negative; but in view of the entirely different nature of the two terms, the likelihood of their cancelling in this way over any substantial range of temperature is small enough to be dismissed.

We therefore turn to the alternative hypothesis, that both terms appearing in (6.1) are very small for He II. That the kinetic term should be small is quite acceptable: there is no positive reason to suppose that the ordinary formula of the kinetic theory of gases does not describe its behaviour quite well, even down to the lowest temperatures. The potential term, which contains the force on one molecule due to others at distance r in the integrand, may almost vanish for two distinct reasons. In the first place, the function $v(r)$ may almost vanish around the minimum of potential between the two molecules. In principle, this can be decided on theoretical grounds; one of the authors has undertaken the calculation of $v(r)$ for the helium atom, and his results so far appear to confirm this hypothesis in a remarkable way. It should, however, be possible to decide this point also experimentally by the study of the scattering of X-rays by He II; the experiments of Keesom & Taconis (1938) and Reekie (1940) indicate that the assumption is correct; yet it is desirable that this important experimental determination of the structure of He II should be effected with the highest possible accuracy.

A third and obvious way of accounting for the smallness of the potential term in (6.1) is by supposing that the interaction between the molecules represented by the potential function $\phi(r)$ breaks down at low temperatures. This question is beyond the scope of the methods developed in our theory of liquids, and must, if it appears to be useful, be treated by the investigation of the means of interaction between the elementary particles.

It appears that nearly all the properties of He II can be explained in terms of its low viscosity. For example, the apparently high thermal conductivity is caused by the transference of energy by the visible motion of the liquid, and the true thermal conductivity is thereby completely masked. For this reason we believe that our formula for the thermal conductivity corresponding to (6.1) has no great interest in the application to He II. The driving force for the convection currents transporting

heat is, as was pointed out at the end of § 3, not the hydrostatic pressure, but the dynamical pressure, which differs from it at low temperatures. From this standpoint, some strange features of the behaviour of He II become less puzzling. These questions, and the problem of the discontinuity between the normal and superfluid states, may be discussed in a subsequent paper.

Some previous attempts to explain the abnormal properties of He II have been based on the application of Bose-Einstein statistics to the molecular assembly; these are not successful because they omit to take into consideration the interaction between the molecules. It is worth examining, however, how far the present theory is in accord with the new statistics. For Bose-Einstein statistics the density matrices ρ_q are unchanged for any permutation of either the $x^{(1)}, x^{(2)}, \dots$ or the $x^{(1)!}, x^{(2)!}, \dots$ while for Fermi-Dirac statistics ρ_q changes sign for odd permutations of either of these two sets. In both events ρ_q remains unaltered if both the $x^{(1)}, x^{(2)}, \dots$ and the $x^{(1)!}, x^{(2)!}, \dots$ are subjected to the same permutation. The general conclusion seems to be that Bose-Einstein statistics do not play a very important part, even at low temperatures, in determining the properties of a fluid; this conclusion was reached also by Kahn (1938). Much more important than this effect of 'second quantization' is that of the low temperatures themselves on the occupation of the lowest energy states not forbidden by the exclusion principle.

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The kinetic basis of thermodynamics

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In this paper the thermodynamical properties of any system whatsoever are deduced from quantum mechanics. Two fundamental irreversible processes are considered: the conversion of other forms of energy into heat, and the flow of heat from one temperature to another. By the proof of a generalized H -theorem, it is shown that in each case the entropy, correctly defined, must increase, and the system tend towards a state of equilibrium.

A simple but rigorous proof of Boltzmann's law is given from which the thermodynamics of reversible processes may be inferred. An appendix includes the exact solution of the most general time-dependent perturbation problem of quantum mechanics.

1. INTRODUCTION

There are three principal ways of establishing the laws of thermodynamics. The first is the classical way of Clausius and Kelvin, brought to logical perfection by Carathéodory (1909), where no use is made of atomistics, and the fundamental laws are derived from simple principles which express very general experiences. The second way is that of statistical mechanics, which operates with virtual assemblies, and derives their thermo-mechanical properties in statistical equilibrium by applying the laws of probability. This method is worked out in a mathematically satisfactory way for both classical and quantum mechanics (cf. the elegant presentation in Schrödinger's little book *Statistical Thermodynamics*, or in the voluminous work by Fowler & Guggenheim (1939)), but the physical foundations of this procedure are obscure. It is assumed that the observable properties of the system considered are the same as the average properties of a virtual assembly of equal but unconnected systems. The only justification of this hypothesis is that it gives useful results. Einstein (1902, 1903), in his classical papers on statistical mechanics, was aware of

this difficulty and based his theory on the consideration of a single system, taking averages over time. He showed by a plausible argument that this 'time assembly' (*Zeitgesammtheit*) is equivalent to a special kind of virtual assembly, called a micro-canonical or ergodic assembly (Gibbs 1901), and this again can be shown to be equivalent to Gibbs's canonical assembly. A rigorous proof of this so-called ergodic theorem was later given by Birkhoff (1931) and von Neumann (1932a) for classical mechanics. No corresponding theorem has been formulated for quantum mechanics. Apart from this objection against the logical foundations of statistical mechanics, it has the disadvantage of saying nothing about the way in which statistical equilibrium is reached.

The third way of treating thermodynamics is that of kinetic theory, which deals with atomistic systems in motion, and regards equilibrium as a special case. The central point of this theory is the so-called H -theorem, first formulated and proved by Boltzmann for ideal gases. It expresses the irreversibility of thermal processes, and shows that the quantity H , which is essentially identical with the negative entropy, always decreases in time, until equilibrium is reached. It has been proved for dense (non-ideal) gases by Enskog (1922), and by ourselves (1946, 1947) for any condensed system, under the assumption that the laws of classical mechanics hold; this restricts the validity to the domain of high temperatures. For complete generality, one has to apply quantum mechanics; there are a few attempts to extend the H -theorem to these conditions, the most notable one by Pauli (1928). He divides the problem into two parts. In the first part, the laws for the temporal change of the number of particles in a given quantum state are formally established in analogy to the equations of radioactive reactions, assuming the existence of certain transition probabilities. In the second part, the essential properties of these probabilities are derived from quantum mechanics. This procedure is not satisfactory, as it appears to use two different sets of assumptions; quantum mechanics, which combines the mechanical and statistical laws in a single formalism, should alone be sufficient to derive the H -theorem for any system under proper conditions.

We shall show in the following that this is in fact the case. Our attention was drawn to this problem when we tried to extend our kinetic theory of liquids (1946, 1947), or rather of dense matter, to quantum systems. The natural formalism in dealing with this problem consists in the use of the statistical operator, or, in the co-ordinate representation, the density matrix of von Neumann (1932b) and Dirac (1935), the equilibrium properties of which have been studied by Kôdi Husimi (1940). This method is very well suited to the derivation of the H -theorem, and we find that the resulting kinetic theory leads to the laws of thermodynamics in a way which is both simpler and more convincing than statistical mechanics, since it does not involve any enumeration of states, but is derived directly from the laws of quantum mechanics.

The problem will be attacked in two stages, corresponding to the two main types of irreversible process: transformation of other forms of energy into heat, and conduction of heat.

The first type of process is that studied by Joule's experiments, where the work done in bringing a thermally isolated system from one state to another is measured by mechanical or electrical devices. Joule showed that this adiabatic work is independent of the way it is applied, which proves the first law of thermodynamics. Carathéodory has further shown that one needs only to add the observation that the system cannot return from its final to the initial state in order to prove the existence of entropy and absolute temperature, and the second law of thermodynamics. Our theoretical model for Joule's experiment consists of a quantum-mechanical system, subject to an external perturbation which may or may not depend on the time. It is possible to represent in this way any cyclic process which communicates energy to the system, for example, the stirring of a fluid or the oscillations of a piston, as long as the size of the stirring wheel and the displacements of the piston are not too large. The behaviour of the system is described in terms of the constants of the motion of the unperturbed system. A complete solution of the perturbation problem is given (in the first appendix), and it is shown that, if the external potential is independent of the time, the energy is conserved. This verifies that the model corresponds to the thermally isolated system of Joule. Previous work (Born & Fock 1928) has shown that this adiabatic, or rather quasi-static, behaviour holds also for the sufficiently slow variation of any external force. One can now give an atomistic definition of the entropy S in agreement with the known applications to gases and liquids and holding not only in equilibrium, and thereby prove that S always increases in time. If the time-dependent perturbation ceases, starting from any initial state, a state of equilibrium is reached in which the density, given by the diagonal elements of the density matrix, is constant for a state of given energy.

The second type of irreversible process relates to completely isolated systems, where no external work is done. The experimental fact is that if the system consists of initially isolated parts with given entropies which are then brought into energy contact, the parts tend to a state of complete mutual equilibrium such that the total entropy in the final state is greater than in the initial state. At the same time there is a tendency for the redistribution of energy, due to the transfer or conduction of heat. Now, a completely isolated system is and remains in a definite quantum state, and from this standpoint nothing can ever happen in it; it would not even be susceptible to observation. One has, therefore, to adapt the definitions to these circumstances in a way corresponding exactly to the experimental arrangement. In order to observe a change in the system at all, one has to assume that it consists of several parts in given quantum states which are loosely coupled. This interaction can be treated as a perturbation in the same way as before, with the only difference that the properties of the system are expressed in terms of the constants of the motion of the partial systems, and not of the whole.

The definition of the entropy S is readily modified in a corresponding manner; it can then be shown that S always increases, and that a final state is reached in which each single system and the whole system as well have an energy distribution given by Boltzmann's law. This follows essentially from the fact that for loosely

coupled systems the energies are additive, whilst the eigenfunctions, and hence the density matrices, are multiplicative; no enumeration of 'complexions', as made in statistical mechanics, is necessary. This result can be easily generalized for the case where slowly varying external forces are acting which shift the energy levels, and the whole formalism of thermodynamics follows immediately.

2. QUANTUM-MECHANICAL FOUNDATIONS

Consider the most general system whose state at any time t can be specified by the values of a set of generalized co-ordinates q_α ($\alpha = 1, \dots, n$) and whose Hamiltonian is $\mathfrak{H}(p_\alpha, q_\alpha)$, where p_α is the canonical momentum corresponding to q_α . In the q -representation, the representatives $Q_\alpha(q, q')$ and $P_\alpha(q, q')$ of the operators Q_α and P_α , which replace q_α and p_α in quantum mechanics, are given by

$$\left. \begin{aligned} Q_\alpha(q, q') &= q_\alpha \prod_\beta \delta(q_\beta - q'_\beta), \\ P_\alpha(q, q') &= -i\hbar \frac{\partial}{\partial q_\alpha} \prod_\beta \delta(q_\beta - q'_\beta). \end{aligned} \right\} \quad (2.1)$$

With the aid of the addition and multiplication rules

$$\left. \begin{aligned} (A + B)(q, q') &= A(q, q') + B(q, q'), \\ (AB)(q, q') &= \int A(q, q'') B(q'', q') dq'', \end{aligned} \right\} \quad (2.2)$$

the representatives of all functions of Q_α and P_α , including the Hamiltonian \mathfrak{H} , may be constructed. For a function $f(Q_\alpha)$ of the co-ordinates alone, one has

$$\left. \begin{aligned} f(Q_\alpha)(q, q') &= f(q_\alpha) \prod_\beta \delta(q_\beta - q'_\beta), \\ \{P_\beta f(Q_\alpha)\}(q, q') &= -i\hbar \frac{\partial f(q_\alpha)}{\partial q_\beta} \prod_\gamma \delta(q_\gamma - q'_\gamma). \end{aligned} \right\} \quad (2.3)$$

The possibility that the system under consideration has spin co-ordinates is not excluded in this formalism. If particles with spin are present, the elements $\mathfrak{H}(q, q')$ of the 'matrix' representative of \mathfrak{H} will themselves be matrices. In order to avoid an unnecessarily complicated notation, the spin indices are not shown explicitly, and can be omitted from further consideration on the understanding that all products of quantities which normally have spin components are to be interpreted as matrix products with summation over the spin index.

It is always possible to find a set of independent quantities A_α ($\alpha = 1, \dots, n'$) such that

$$A_\alpha \mathfrak{H} = \mathfrak{H} A_\alpha, \quad A_\alpha A_\beta = A_\beta A_\alpha; \quad (2.4)$$

they are the constants of the motion. They may include the internal energy, and the momentum and angular momentum of a mechanical system; \mathfrak{H} can always be expressed in terms of them and together they furnish a complete basis for matrix

representation. Let $\psi(\lambda, q)$ be the normalized eigenfunction for which the A_α have the simultaneous eigenvalues λ_α , so that

$$\int A_\alpha(q, q') \psi(\lambda, q') dq' = \lambda_\alpha \psi(\lambda, q), \quad (2.5)$$

and let $a_0(\lambda)$ be the probability that at an initial time t_0 these eigenvalues are realized. Then the 'density matrix' ρ may be defined at time t_0 by the equation

$$\rho_0(q, q') = \sum_{\lambda} a_0(\lambda) \psi(\lambda, q) \psi^*(\lambda, q'), \quad (2.6)$$

and subsequently by Heisenberg's 'equation of change'

$$i\hbar \frac{\partial \rho}{\partial t} = \mathfrak{H}\rho - \rho \mathfrak{H}, \quad (2.7)$$

if there is no interaction with any external system. In the event of such interaction, (2.7) must be replaced by

$$i\hbar \frac{\partial \rho}{\partial t} = (\mathfrak{H} + \mathfrak{B})\rho - \rho(\mathfrak{H} + \mathfrak{B}), \quad (2.8)$$

where \mathfrak{B} is the interaction energy, which is not necessarily small. \mathfrak{B} depends on the co-ordinates of the system under consideration, and may or may not vary in time. It must not depend explicitly on the co-ordinates of the particles of the external environment, whose motion is unknown, but only on macroscopic parameters which may be considered as given functions of time. This is a mathematical description of the physical situation where, for example, the system is enclosed by *adiabatic* walls; for, if the walls could transmit heat, the perturbation \mathfrak{B} would depend on the unpredictable motion of its constituent molecules. The walls may, however, make any small movements in time. One has only to represent the wall by a steep slope of finite height of the potential energy; the perturbed eigenfunction corresponding to a small displacement of the wall can then still be expanded in terms of the unperturbed eigenfunctions. Small oscillations of a piston, stirring by means of a paddle, and in general any small cyclic process can be represented in the same way. Changes of a more general nature are also not excluded, but necessitate the incorporation of part of the environment into the system considered.

The equation (2.8) is most conveniently solved by transforming to the λ -representation. Expanding ρ and \mathfrak{B} in terms of the orthonormal functions $\psi(\lambda, q)$, thus:

$$\left. \begin{aligned} \rho(q, q') &= \sum_{\lambda, \lambda'} \rho(\lambda, \lambda') \psi(\lambda, q) \psi^*(\lambda', q'), \\ \mathfrak{B}(q, q') &= \sum_{\lambda, \lambda'} \mathfrak{B}(\lambda, \lambda') \psi(\lambda, q) \psi^*(\lambda', q'), \end{aligned} \right\} \quad (2.9)$$

one obtains†

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \rho(\lambda, \lambda') &= \mathfrak{H}(\lambda) \rho(\lambda, \lambda') + \sum_{\lambda''} \mathfrak{B}(\lambda, \lambda'') \rho(\lambda'', \lambda') \\ &\quad - \rho(\lambda, \lambda') \mathfrak{H}(\lambda') - \sum_{\lambda''} \rho(\lambda, \lambda'') \mathfrak{B}(\lambda'', \lambda'), \end{aligned} \quad (2.10)$$

† The same symbol \mathfrak{H} is used to denote both the Hamiltonian and its eigenvalue.

and writing $\rho(\lambda, \lambda') = \bar{\rho}(\lambda, \lambda') \exp\left[-\frac{i}{\hbar}(\mathfrak{H} - \mathfrak{H}') (t - t_0)\right]$, $\mathfrak{B}(\lambda, \lambda') = \bar{\mathfrak{B}}(\lambda, \lambda') \exp\left[-\frac{i}{\hbar}(\mathfrak{H} - \mathfrak{H}') (t - t_0)\right]$,

$$\left. \begin{aligned} & \mathfrak{B}(\lambda, \lambda') = \bar{\mathfrak{B}}(\lambda, \lambda') \exp\left[-\frac{i}{\hbar}(\mathfrak{H} - \mathfrak{H}') (t - t_0)\right], \\ & \text{it follows, in matrix notation, that} \end{aligned} \right\} \quad (2.11)$$

$$i\hbar \frac{\partial \bar{\rho}}{\partial t} = \bar{\mathfrak{B}}\bar{\rho} - \bar{\rho}\bar{\mathfrak{B}}. \quad (2.12)$$

This equation is usually solved by a perturbation method, in which, however, the calculation of successive terms becomes more and more difficult. For this reason, an exact solution has been obtained by one of us (H.S.G.) which will be presented in the appendix 1. From this solution it is easy to write down an approximation with any desired degree of accuracy. Let

$$\left. \begin{aligned} u &= -\frac{i}{\hbar} \int_{t_0}^t \bar{\mathfrak{B}} dt, \quad i\hbar \dot{u} = \bar{\mathfrak{B}}; \\ \dot{u}_{22} &= \dot{u}u - u\dot{u}, \quad \dot{u}_{23} = \dot{u}_{22}u - u\dot{u}_{22}, \\ \dot{u}_{24} &= \dot{u}_{23}u - u\dot{u}_{23}, \quad \dot{u}_{34} = \frac{1}{4}(\dot{u}_{22}u_{22} - u_{22}\dot{u}_{22}), \end{aligned} \right\} \quad (2.13)$$

where all the u 's vanish at time t_0 ; then one has the expansion

$$\bar{\rho} = \rho_0 + \rho_1 + \rho_2 + \dots, \quad (2.14)$$

where $\rho_1 = u\rho_0 - \rho_0u$,

$$\left. \begin{aligned} \rho_2 &= \frac{1}{2}(u^2\rho_0 - 2u\rho_0u + \rho_0u^2) + \frac{1}{2}(u_{22}\rho_0 - \rho_0u_{22}), \\ \rho_3 &= \frac{1}{6}(u^3\rho_0 - 3u^2\rho_0u + 3u\rho_0u^2 - \rho_0u^3) \\ &\quad + \frac{1}{2}\{u(u_{22}\rho_0 - \rho_0u_{22}) - (u_{22}\rho_0 - \rho_0u_{22})u\} + \frac{1}{3}(u_{23}\rho_0 - \rho_0u_{23}), \end{aligned} \right\} \quad (2.15)$$

etc. To obtain the corresponding expansion $a = a_0 + a_1 + a_2 + \dots$ of $a(\lambda)$, which is the probability of finding the system in the state λ at time t_0 , one simply writes $\lambda = \lambda'$ in the above; then $a_1 = 0$ and

$$a_2(\lambda) = \sum_{\lambda'} u(\lambda, \lambda') u(\lambda', \lambda) \{a_0(\lambda) - a_0(\lambda')\}. \quad (2.16)$$

Since \mathfrak{B} is Hermitian, and u is anti-Hermitian, $p(\lambda, \lambda') = -u(\lambda, \lambda') u(\lambda', \lambda)$ is a real positive quantity, which, in view of the relation

$$a(\lambda) = a_0(\lambda) + \sum_{\lambda'} p(\lambda, \lambda') \{a_0(\lambda') - a_0(\lambda)\} \quad (2.17)$$

(correct to the second order), must be interpreted as the probability of a transition from the state λ to the state λ' , or vice versa, in time $t - t_0$.

For small \mathfrak{B} or $t - t_0$, it may be expected that (2.17) will provide a sufficiently exact description of the changes occurring in the system. When a_2 is small, however, it may happen that a_3 becomes important; its value, according to (2.15), is

$$a_3(\lambda) = \sum_{\lambda, \lambda''} p_1(\lambda, \lambda', \lambda'') \{a_0(\lambda'') - a_0(\lambda')\} + \sum_{\lambda'} p_2(\lambda, \lambda') \{a_0(\lambda') - a_0(\lambda)\}, \quad (2.18)$$

where $\left. \begin{aligned} p_1(\lambda, \lambda', \lambda'') &= \frac{1}{2}\Re\{u(\lambda, \lambda') u(\lambda', \lambda'') u(\lambda'', \lambda)\}, \\ p_2(\lambda, \lambda') &= \frac{1}{2}\Re\{u(\lambda, \lambda') u_{22}(\lambda', \lambda) + u_{22}(\lambda, \lambda') u(\lambda', \lambda)\}. \end{aligned} \right\} \quad (2.19)$

3. CONSERVATION OF ENERGY

In the special but important case where \mathfrak{B} does not vary with the time, it is possible to calculate u , u_{22} , etc., explicitly and so to reveal the time dependence of a_2 , a_3 , etc.

For convenience one writes $t' = t - t_0$, $\hbar\omega = \mathfrak{H} - \mathfrak{H}'$, $\hbar\omega' = \mathfrak{H}' - \mathfrak{H}''$, and abbreviates $e^{i\omega t}$ to e , $e^{i\omega' t}$ to e' , so that, according to (2.11) and (2.13),

$$\left. \begin{aligned} i\hbar\dot{u} &= \mathfrak{B}e, \\ i\hbar\dot{u} &= \mathfrak{B} \frac{e-1}{i\omega}, \end{aligned} \right\} \quad (3.1)$$

and, by integration of $\dot{u}_{22} = \dot{u}u - u\dot{u}$,

$$\hbar^2 u_{22}(\lambda, \lambda'') = \sum_{\lambda'} \frac{\mathfrak{B}(\lambda, \lambda') \mathfrak{B}(\lambda', \lambda'')}{\omega\omega'(\omega+\omega')} \{ \omega(e+1)(e'-1) - \omega'(e'+1)(e-1) \}. \quad (3.2)$$

It is clear that most of the elements of u and u_{22} , etc., consist of terms which are constant or periodic in the time; these terms must be rejected on the ground that they do not represent continuous and permanent transitions from one state to another. When this is done, only those terms for which energy is conserved survive, thus:

$$\left. \begin{aligned} i\hbar\dot{u} &= \mathfrak{B}t'\delta_{\mathfrak{H}\mathfrak{H}'}, \\ \hbar^2 u_{22}(\lambda, \lambda'') &= 2 \sum_{\lambda'} \frac{\mathfrak{B}(\lambda, \lambda') \mathfrak{B}(\lambda', \lambda'')}{\omega'} t'\delta_{\mathfrak{H}\mathfrak{H}''}. \end{aligned} \right\} \quad (3.3)$$

It is easily verified that the same is true for all the u 's defined previously. As a result,

$$p(\lambda, \lambda') = \frac{1}{\hbar^2} |\mathfrak{B}(\lambda, \lambda')|^2 t'^2 \delta_{\mathfrak{H}\mathfrak{H}'}, \quad (3.4)$$

and
$$\left. \begin{aligned} p_1(\lambda, \lambda', \lambda'') &= -\frac{1}{2\hbar^3} \Im\{\mathfrak{B}(\lambda, \lambda') \mathfrak{B}(\lambda', \lambda'') \mathfrak{B}(\lambda'', \lambda)\} t'^3 \delta_{\mathfrak{H}\mathfrak{H}'\mathfrak{H}''}, \\ p_2(\lambda, \lambda') &= -\frac{1}{\hbar^3} \sum_{\lambda'} \Re\left\{ \mathfrak{B}(\lambda, \lambda') \sum_{\lambda''} \frac{\mathfrak{B}(\lambda', \lambda'') \mathfrak{B}(\lambda'', \lambda)}{\omega'} + \sum_{\lambda''} \frac{\mathfrak{B}(\lambda, \lambda'') \mathfrak{B}(\lambda'', \lambda')}{\omega'} \mathfrak{B}(\lambda', \lambda) \right\}. \end{aligned} \right\} \quad (3.5)$$

It has been assumed here that the energy levels form a discrete series; but in practice they are generally continuous, and the summation $\sum_{\mathfrak{H}'}$ has to be interpreted as an integration. Then one finds that the principle of conservation of energy remains valid, although the time dependence of the u 's is different:

$$p(\lambda, \lambda') = \frac{2\pi}{\hbar} |\mathfrak{B}(\lambda, \lambda')|^2 t' \delta_{\mathfrak{H}\mathfrak{H}'} \quad (3.6)$$

and
$$p_1(\lambda, \lambda', \lambda'') = -\frac{2\pi^2}{\hbar} \Im\{\mathfrak{B}(\lambda, \lambda') \mathfrak{B}(\lambda', \lambda'') \mathfrak{B}(\lambda'', \lambda)\} t' \delta_{\mathfrak{H}\mathfrak{H}'\mathfrak{H}''}, \quad (3.7)$$

whilst, as is shown in the second appendix, $p_2(\lambda, \lambda')$ effectively vanishes. It has been proved by one of the authors (Born 1926) that this principle of conservation of

energy can be generalized for systems which are subject to slowly varying external forces, where it becomes the 'adiabatic principle', in the terminology of Ehrenfest, though the term quasi-static would be more appropriate. Although in these circumstances the energy is not conserved, it can be proved that no quantum transitions between different energy states take place: the general proof of this theorem for any approximation has been given by Born & Fock (1928). Their result will be required subsequently for application to systems under the action of quasi-static external forces. When \mathfrak{B} varies rapidly with the time, it is clear on physical grounds alone that the theorem can no longer hold: the system absorbs energy, which is generally converted into heat. In mathematical language, the u 's are no longer diagonal in \mathfrak{H} , so that transitions from one energy state to another may occur. This, however, does not exclude the exceptional possibility that, owing to the physical nature of the perturbation \mathfrak{B} , such jumps cannot occur; in such cases \mathfrak{B} itself is diagonal in \mathfrak{H} , so that the u 's are also diagonal, quite independently of the 'adiabatic principle'.

4. THE GENERAL H -THEOREM

So far, no restriction has been put on the state of the system, characterized by the values of the $a(\lambda)$. Defining a quantity \mathfrak{S} by the equation

$$\left. \begin{aligned} \mathfrak{S} &= -\frac{k}{\mathfrak{A}} \sum_{\lambda} a(\lambda) \log a(\lambda), \\ \mathfrak{A} &= \sum_{\lambda} a(\lambda) = \sum_{\lambda} a_0(\lambda), \end{aligned} \right\} \quad (4.1)$$

one finds, on substitution from (2.17) and neglecting squares and higher powers of the small quantity $p(\lambda, \lambda')$,

$$\left. \begin{aligned} \mathfrak{S} &= -\frac{k}{\mathfrak{A}} \sum_{\lambda} a_0(\lambda) \log a_0(\lambda) + \frac{k}{\mathfrak{A}} \sum_{\lambda, \lambda'} p(\lambda, \lambda') \{1 + \log a_0(\lambda)\} \{a_0(\lambda) - a_0(\lambda')\}, \\ &= -\frac{k}{\mathfrak{A}} \sum_{\lambda} a_0(\lambda) \log a_0(\lambda) + \frac{k}{2\mathfrak{A}} \sum_{\lambda, \lambda'} p(\lambda, \lambda') \log \left(\frac{a_0(\lambda)}{a_0(\lambda')} \right) \{a_0(\lambda) - a_0(\lambda')\}. \end{aligned} \right\} \quad (4.2)$$

If (3.6) is introduced, one has further

$$\frac{\mathfrak{S} - \mathfrak{S}_0}{t - t_0} = \frac{2\pi k}{2\hbar \mathfrak{A}} \sum_{\lambda, \lambda'} |\mathfrak{B}(\lambda, \lambda')|^2 \delta_{\mathfrak{H}\mathfrak{H}'} \log \left(\frac{a_0(\lambda)}{a_0(\lambda')} \right) \{a_0(\lambda) - a_0(\lambda')\}. \quad (4.3)$$

In any case, \mathfrak{S} increases with time, and must continue to do so until

$$a(\lambda) = a(\lambda') \quad \text{for all } \lambda, \lambda' \text{ for which } u(\lambda, \lambda') \neq 0. \quad (4.4)$$

This is the condition for equilibrium, which could have been deduced immediately from (2.12); but only now can it be seen that, whatever the initial state, the effect of the perturbation is to cause the system to approach asymptotically a state in which (4.4) is satisfied.

It has been assumed in the above that the remainder $\rho_3 + \rho_4 + \dots$ of the series (2.14) may be completely neglected; although these terms are very small under the

conditions postulated, they have an effect when equilibrium has almost been reached. It is clear, from (2.18), that the condition for equilibrium (4.4) suffices to make a_3 vanish. However, since $p_1(\lambda, \lambda', \lambda'')$ and $p_2(\lambda, \lambda')$ are not necessarily positive, when a_2 has decreased to be of the same order as a_3 , the convergence on the equilibrium state will not necessarily proceed further, and the result will be continuous random fluctuations in the neighbourhood of equilibrium. This is in accord with experience; and it is clear that a new approach to the theory of phenomena such as the Brownian movement and the 'shot effect' can be made from this point of view.

One might conclude immediately from the calculations of this section that \mathfrak{S} must be identified with the entropy of the system. It should be noticed, however, that if the system is imagined to be isolated from the rest of the world, \mathfrak{B} vanishes, and there is no change in \mathfrak{S} , whatever the initial state of the system. This is necessarily so, since in the absence of external perturbations, the system must remain in the same quantum state, and any quantity defined solely in terms of the quantum state cannot be altered. It is true that it is physically impossible to isolate a system from all other objects, and that if it were possible, the system would be unobservable; yet one would expect that even in such conditions, the internal interactions would lead to an increase in the entropy of the system. In the next section it will be shown how to define a function which in this respect conforms more closely to the conception of macroscopic thermodynamics.

5. MODIFICATION FOR COMPOSITE SYSTEMS

It will now be supposed that one has to do with a system Σ consisting of a number of subsystems $\Sigma^{(i)}$ ($i = 1, \dots, j$) in interaction with one another. There is no formal difference whether the system so far considered is identified with Σ or one of the $\Sigma^{(i)}$. Let $H^{(i)}$ be the Hamiltonians of the individual subsystems, omitting the interaction energies of one with another. Write $H = \sum_{i=1}^j H^{(i)}$, and let V be the total interaction energy, so that

$$\mathfrak{H} = H + V. \quad (5.1)$$

If there is a perturbation energy arising from influences external to Σ , this is included in V ; it is subject to the same restrictions as were mentioned in § 2, to ensure the thermal isolation of the system. Substituting (5.1) in (2.7), one obtains

$$i\hbar \frac{\partial \rho}{\partial t} = (H + V)\rho - \rho(H + V), \quad (5.2)$$

which is formally the same as (2.8). The commuting quantities which commute also with H are now simply the constants of the motion $A^{(i)}$ of all the uncoupled systems; also $a(\lambda^{(1)} \dots \lambda^{(j)}) = \rho(\lambda^{(1)} \dots \lambda^{(j)}, \lambda^{(1)} \dots \lambda^{(j)})$, or briefly

$$a(\lambda^{(i)}) = \rho(\lambda^{(i)}, \lambda^{(i)}), \quad (5.3)$$

the $\lambda^{(i)}$ -representation now becoming fundamental. Corresponding to (4.1), one has

$$S = -\frac{k}{A} \left(\sum_{i=1}^j \sum_{\lambda^{(i)}} \right) a(\lambda^{(i)}) \log a(\lambda^{(i)}), \quad (5.4)$$

and it now follows, by an argument at every step identical with that employed in §§ 2 to 4, that S must increase until a state is reached for which the analogue of (4.4) is satisfied. Energy is conserved as long as V is not too large and does not depend explicitly on the time.

Now, making the explicit assumption that the interaction is small, one has

$$a(\lambda^{(i)}) = \prod_{i=1}^j a^{(i)}(\lambda^{(i)}), \quad (5.5)$$

where $a^{(i)}(\lambda^{(i)})$ is the probability that $\Sigma^{(i)}$ is in the state $\lambda^{(i)}$. If one writes

$$S^{(i)} = -\frac{k}{A^{(i)}} \sum_{\lambda^{(i)}} a^{(i)}(\lambda^{(i)}) \log a^{(i)}(\lambda^{(i)}), \quad A^{(i)} = \sum_{\lambda^{(i)}} a^{(i)}(\lambda^{(i)}), \quad (5.6)$$

then, since $A = \prod_{i=1}^j A^{(i)}$, it follows that

$$\left. \begin{aligned} S &= -\frac{k}{A} \left(\sum_{i=1}^j \sum_{\lambda^{(i)}} \right) \frac{A}{A^{(i)}} a^{(i)}(\lambda^{(i)}) \log a^{(i)}(\lambda^{(i)}) \\ &= \sum_{i=1}^j S^{(i)}. \end{aligned} \right\} \quad (5.7)$$

Thus the entropy is additive for weakly coupled systems; the same can no longer be proved, however, for cases of strong interaction.

In the limiting case of vanishing interaction, the quantities S and \mathfrak{S} coalesce; but in general the interaction will cause an increase in S whilst \mathfrak{S} remains constant. This was discussed in the introduction, but can be illustrated in a different way, by an example from the kinetic theory of gases. Consider a system of gas molecules distributed uniformly between perfectly reflecting walls, with a velocity distribution differing from the natural equilibrium distribution. On account of the interaction between the molecules, S will generally increase, and the distribution will approach more closely the equilibrium distribution. Imagine now, however, that there is no interaction between the molecules; then the velocity of each molecule remains unchanged, S is constant, and the velocity distribution is unaltered. \mathfrak{S} remains constant, whether the molecules interact or not.

If the system considered is not a gas with small interactions between its molecules, but a liquid or solid, then this whole system can be identified with one of the $\Sigma^{(i)}$, the rest being surrounding bodies, which constitute a 'temperature bath', in the language of ordinary thermodynamics, assumed to be in energy contact with the system considered. This point of view is similar to that taken by Schrödinger (1946) in his exposition of statistical thermodynamics, except that our temperature bath may be a real environment, and not a fictitious one consisting of copies of the original system.

6. THE EQUILIBRIA OF LOOSELY COUPLED SYSTEMS

The condition for the equilibrium of the most general type of system, namely $a(\lambda) = a(\lambda')$ for all λ, λ' for which $u(\lambda, \lambda') \neq 0$, must now be examined in greater detail. There will be among the A_α ($\alpha = 1, \dots, n'$) a set of operators M_α ($\alpha = 1, \dots, m$) which commute not only with H but also with V ; they are those constants of the motion which are not changed by the perturbation V . The number m of these 'absolute' constants of the motion is in general much smaller than that (n') of the A . The matrix $u(\lambda, \lambda')$ is reducible, being diagonal in the eigenvalues μ of the M ; the numerical degeneracy for the eigenvalue μ is denoted by $n(\mu)$. Then, in equilibrium, the $a(\lambda)$ must have the same value for all states λ which have the same μ . Thus one may write $a(\lambda_1 \dots \lambda_{n'}) = a(\mu_1 \dots \mu_m)$, or briefly

$$a(\lambda) = a(\mu). \quad (6.1)$$

It has already been seen that under adiabatic conditions, and in the absence of work performed by moving the constraints of the system, the energy H is one of the μ . By virtue of the 'adiabatic principle' of Born & Fock already referred to, H is also included when quasi-static forces are acting. There may well be other quantities μ , however. For example, in a system which has an axis of symmetry in real space, the angular momentum about this axis will be included, and a system which is free to move in a given direction will have the momentum in this direction among the residual constants of the motion μ . Under non-adiabatic conditions, H will not be included, and quite a different variable may play the same role.

Substituting (6.1) in (2.6), one finds for the density matrix in equilibrium the expression

$$\rho(q, q') = \sum_{\mu} n(\mu) a(\mu) \psi(\mu, q) \psi^*(\mu, q'), \quad (6.2)$$

where $n(\mu)$ is the degeneracy of the state μ ; this factor arises through the renormalization of the ψ -functions after performing the summation $\sum_{\lambda(\mu)} \psi(\lambda, q) \psi^*(\lambda, q')$ over all those λ 's which correspond to the same μ . This reduction has been found possible by consideration of the external constraints of the system; it will now be shown that the form of the function $a(\mu)$ is determined by the internal constitution of the system.

Suppose the original system Σ consists of a number of subsystems $\Sigma^{(i)}$, all in *weak* energy contact with one another; then (5.5) is satisfied, and in equilibrium takes the form

$$a(\mu) = \prod_{i=1}^j a^{(i)}(\lambda^{(i)}). \quad (6.3)$$

Now the μ may always be expressed in terms of the $\lambda^{(i)}$, thus:

$$\mu = \mu(\lambda^{(i)}) \quad (6.4)$$

and the equations (6.3) and (6.4) suffice to determine a and $a^{(i)}$ as far as is possible without knowing the initial state of Σ from which the state of equilibrium evolved.

As a special case, consider a system subject only to the condition that its energy remains constant; then the μ reduce to the single variable H . As the subsystems are

in energy contact with one another, the $H^{(i)}$ are not included among the μ , but (6.4) takes the form

$$\mu = H = \sum_{i=1}^j H^{(i)}. \quad (6.5)$$

Substituting (6.5) in (6.3), and solving the resulting functional equation by the well-known method used by Maxwell in his attempt to prove the classical velocity distribution law in gases, one finds

$$\left. \begin{aligned} \log a(H) &= \beta(A - H), & a(H) &= e^{\beta(A-H)}, \\ \log a^{(i)}(H^{(i)}) &= \beta(A^{(i)} - H^{(i)}), & a^{(i)}(H^{(i)}) &= e^{\beta(A^{(i)}-H^{(i)})}, \end{aligned} \right\} \quad (6.6)$$

where β , A and the $A^{(i)}$ are constants, and $A = \sum_{i=1}^j A^{(i)}$.

Maxwell's argument was not rigorous, because it is impossible to imagine 'weak energy contact' between different degrees of freedom of the same molecule, but the present derivation is quite free from this defect. Thus the fundamental Boltzmann law of statistical mechanics has been derived in a way which is not only perfectly rigorous, but is simpler and more fundamental than the usual method.

The subsequent development of statistical thermodynamics from (6.6) is well known (cf. Schrödinger 1946), and will only be summarized here.

The constant A is determined from (6.6) with the aid of the normalizing condition $\sum_{\lambda} a(H) = 1$:

$$e^{-\beta A} = \sum_{\lambda} e^{-\beta H}, \quad (6.7)$$

whilst the internal energy U is given by

$$U = \sum_{\lambda} a(H) H. \quad (6.8)$$

Consider now the external work done in moving the external constraints of the system Σ . This process might be regarded as included among the irreversible changes discussed in earlier sections, but if effected very slowly may be treated specifically as a reversible change in virtue of the 'adiabatic' theorem, quoted in § 3, and represented by a variation of the eigenvalues of the unperturbed system. The increase in U when external work is done on the system, by moving the external constraints and consequently changing the eigenvalues λ by the small quantities $d\lambda$, is

$$dU = \sum_{\lambda} \{H da(H) + a(H) dH\}, \quad (6.9)$$

and this exceeds the work done $\sum_{\lambda} a(H) dH$ by the amount

$$\left. \begin{aligned} T dS &= \sum_{\lambda} H da(H) \\ &= - \sum_{\lambda} (A - H) e^{\beta(A-H)} d\{\beta(A-H)\}. \end{aligned} \right\} \quad (6.10)$$

The additional term $-A \sum_{\lambda} e^{\beta(A-H)} d\{\beta(A-H)\}$ vanishes, according to (6.7). In order that dS should be a perfect differential, one must have $1/T = k\beta$, where k is a pure constant, and

$$S = -k \sum_{\lambda} \beta(A - H) e^{\beta(A-H)}, \quad (6.11)$$

apart from an unimportant constant. It thus appears that the whole of thermodynamics is contained in (6.6).

However, this must be regarded as a special case even among equilibrium phenomena, in view of the general nature of the equations (6.3) and (6.4). The possibility of treating the 'dynamic equilibria' of systems under conditions more general than that of constant energy, in which other variables play the part of constants of the motion, may prove to be of considerable interest.

7. APPENDIX I. BY H. S. GREEN

Here the exact solution of the equation

$$i\hbar \frac{\partial \bar{\rho}}{\partial t} = \bar{\mathfrak{B}}\bar{\rho} - \bar{\rho}\bar{\mathfrak{B}} \quad (7.1)$$

is derived. If one writes $\bar{\mathfrak{B}} = \dot{u}$, where $u = 0$ at time t_0 , and substitutes

$$\left. \begin{aligned} \bar{\rho} &= \sigma \rho_0 \tau, & \dot{\sigma} &= \dot{u} \sigma, & \dot{\tau} &= -\tau \dot{u}, \\ \sigma &= \tau = 1, & \text{when } t &= t_0, \end{aligned} \right\} \quad (7.2)$$

one sees that (7.1) is satisfied, and that ρ_0 is the value of $\bar{\rho}$ at time t_0 , given by

$$\rho_0(\lambda, \lambda') = \alpha_0(\lambda) \delta_{\lambda \lambda'}, \quad (7.3)$$

according to (2.6). It is now necessary to solve only the equations $\dot{\sigma} = \dot{u} \sigma$ and $\dot{\tau} = -\tau \dot{u}$. One requires the lemma in quantum algebra to the effect that if $f(u)$ is any power series in u , and v any operator, then

$$\left. \begin{aligned} vf(u) &= f(u) v + f'(u) \frac{v_1}{1!} + f''(u) \frac{v_2}{2!} + \dots, \\ f(u)v &= vf(u) - \frac{v_1}{1!} f'(u) + \frac{v_2}{2!} f''(u) - \dots, \end{aligned} \right\} \quad (7.4)$$

where $v_1 = vu - uv$ and $v_{k+1} = v_k u - uv_k$, $k = 1, 2, 3$, etc.

In particular, if v is the Hamiltonian operator, one obtains

$$\frac{d}{dt} f(u) = \frac{\dot{u}}{1!} f'(u) - \frac{\dot{u}_{22}}{2!} f''(u) + \frac{\dot{u}_{23}}{3!} f'''(u) - \dots, \quad (7.5)$$

where $\dot{u}_{22} = \dot{u}u - u\dot{u}$ and $\dot{u}_{2,k+1} = \dot{u}_{2,k}u - u\dot{u}_{2,k}$ ($k = 2, 3, 4$, etc.).

Hence, if one writes $\sigma = e^u \sigma_2$ (7.6)

one obtains, using (7.4) for the transposition of each term,

$$\left. \begin{aligned} \dot{\sigma} &= \left(\frac{\dot{u}}{1!} - \frac{\dot{u}_{22}}{2!} + \frac{\dot{u}_{23}}{3!} - \dots \right) e^u \sigma_2 + e^u \dot{\sigma}_2 \\ &= \dot{u}e^u \sigma_2 - e^u \left\{ \frac{1}{2!} \left(\dot{u}_{22} + \frac{1}{1!} \dot{u}_{23} + \frac{1}{2!} \dot{u}_{24} + \dots \right) - \frac{1}{3!} \left(\dot{u}_{23} + \frac{1}{1!} \dot{u}_{24} + \dots \right) \right. \\ &\quad \left. + \frac{1}{4!} (\dot{u}_{24} + \dots) - \dots \right\} \sigma_2 + e^u \dot{\sigma}_2 \\ &= \dot{u}\sigma + e^u (-\dot{u}_2 \sigma_2 + \dot{\sigma}_2), \end{aligned} \right\} \quad (7.7)$$

where

$$\dot{u}_2 = \frac{1}{2!} \dot{u}_{22} + \frac{2}{3!} \dot{u}_{23} + \frac{3}{4!} \dot{u}_{24} + \dots, \quad (7.8)$$

so that the equation $\dot{\sigma} = \dot{u}\sigma$ is reduced to

$$\dot{\sigma}_2 = \dot{u}_2 \sigma_2. \quad (7.9)$$

For the complete specification of u_2 , it is necessary to add the condition $u_2 = 0$ at time t_0 .

Again, writing $\sigma_2 = e^{u_2} \sigma_3$, one obtains

$$\dot{\sigma}_3 = \dot{u}_3 \sigma_3, \quad (7.10)$$

where

$$\dot{u}_3 = \frac{1}{2!} \dot{u}_{34} + \frac{2}{3!} \dot{u}_{36} + \frac{3}{4!} \dot{u}_{38} + \dots, \quad (7.11)$$

and $\dot{u}_{34} = \dot{u}_2 u_2 - u_2 \dot{u}_2$, $\dot{u}_{36} = \dot{u}_{34} u_2 - u_2 \dot{u}_{34}$, etc. The suffix l in u_{kl} has been chosen to indicate the power of \mathfrak{B} which is involved in the expression; clearly $u_k = O(\mathfrak{B}^{2k-1})$, and decreases very rapidly with k when \mathfrak{B} or $t - t_0$ is small. One obtains finally

$$\sigma = e^u e^{u_2} e^{u_3} \dots \quad (7.12)$$

as the exact solution of the equation $\dot{\sigma} = \dot{u}\sigma$, the boundary condition being satisfied as u , u_2 , u_3 , etc., vanish at time t_0 . Similarly one obtains

$$\tau = \dots e^{-u_3} e^{-u_2} e^{-u}, \quad (7.13)$$

so that

$$\bar{\rho} = e^u e^{u_2} e^{u_3} \dots \rho_0 \dots e^{-u_3} e^{-u_2} e^{-u}. \quad (7.14)$$

Expanding all the exponentials in power series, and separating terms of the same order, one obtains the expansion

$$\bar{\rho} = \rho_0 + \rho_1 + \rho_2 + \dots, \quad (7.15)$$

where

$$\left. \begin{aligned} \rho_1 &= u\rho_0 - \rho_0 u, \\ \rho_2 &= \frac{1}{2}(u^2\rho_0 - 2u\rho_0 u + \rho_0 u^2) + \frac{1}{2}(u_{22}\rho_0 - \rho_0 u_{22}), \\ \rho_3 &= \frac{1}{6}(u^3\rho_0 - 3u^2\rho_0 u + 3u\rho_0 u^2 - \rho_0 u^3) \\ &\quad + \frac{1}{2}\{(u_{22}\rho_0 - \rho_0 u_{22}) - (u_{22}\rho_0 - \rho_0 u_{22})u\} + \frac{1}{3}(u_{23}\rho_0 - \rho_0 u_{23}), \\ \rho_4 &= \frac{1}{24}(u^4\rho_0 - 4u^3\rho_0 u + 6u^2\rho_0 u^2 - 4u\rho_0 u^3 + \rho_0 u^4) \\ &\quad + \frac{1}{4}\{(u^2(u_{22}\rho_0 - \rho_0 u_{22}) - 2u(u_{22}\rho_0 - \rho_0 u_{22})u + (u_{22}\rho_0 - \rho_0 u_{22})u^2) \\ &\quad + \frac{1}{3}\{(u(u_{23}\rho_0 - \rho_0 u_{23}) - (u_{23}\rho_0 - \rho_0 u_{23})u\} + \frac{1}{8}(u_{22}^2\rho_0 - 2u_{22}\rho_0 u_{22} + \rho_0 u_{22}^2) \\ &\quad + \frac{1}{8}(u_{24}\rho_0 - \rho_0 u_{24}) + \frac{1}{2}(u_{34}\rho_0 - \rho_0 u_{34}), \end{aligned} \right\} \quad (7.16)$$

etc. This series can be obtained with much greater difficulty by ordinary time-dependent perturbation theory.

8. APPENDIX 2. BY H. S. GREEN

Here is given a formal proof of the statement in the text that $p_2(\lambda, \lambda')$ effectively vanishes in the continuous spectrum. For brevity one writes

$$\left. \begin{aligned} \alpha &= \omega + \omega' = (\tilde{\mathfrak{H}} - \tilde{\mathfrak{H}}'')/\hbar, \\ \beta &= \omega' - \omega = (2\tilde{\mathfrak{H}}' - \tilde{\mathfrak{H}} - \tilde{\mathfrak{H}}'')/\hbar, \\ F(\tilde{\mathfrak{H}}, \alpha, \beta) &= \mathcal{B}(\tilde{\mathfrak{H}}, \tilde{\mathfrak{H}}') \mathcal{B}(\tilde{\mathfrak{H}}', \tilde{\mathfrak{H}}'') \mathcal{B}(\tilde{\mathfrak{H}}'', \tilde{\mathfrak{H}}). \end{aligned} \right\} \quad (8.1)$$

Then

$$e^{-\frac{i}{\hbar}(\omega+\omega')t'} u_{22}(\tilde{\mathfrak{H}}, \tilde{\mathfrak{H}}'') = \frac{1}{\hbar^2} \int \frac{\mathcal{B}(\tilde{\mathfrak{H}}, \tilde{\mathfrak{H}}') \mathcal{B}(\tilde{\mathfrak{H}}', \tilde{\mathfrak{H}}'')}{\frac{1}{4}\alpha(\alpha^2 - \beta^2)} 2i(\alpha \sin \frac{1}{2}\beta t' - \beta \sin \frac{1}{2}\alpha t') \frac{1}{2}\hbar d\beta, \quad (8.2)$$

and

$$e^{\frac{i}{\hbar}(\omega+\omega')t'} u(\tilde{\mathfrak{H}}'', \tilde{\mathfrak{H}}) = \frac{1}{i\hbar} \frac{\mathcal{B}(\tilde{\mathfrak{H}}'', \tilde{\mathfrak{H}})}{\alpha} 2 \sin \frac{1}{2}\alpha t'. \quad (8.3)$$

Hence

$$\left. \begin{aligned} \int u_{22}(\tilde{\mathfrak{H}}, \tilde{\mathfrak{H}}'') u(\tilde{\mathfrak{H}}'', \tilde{\mathfrak{H}}) d\tilde{\mathfrak{H}}'' &= \frac{8}{\hbar} \iint \frac{F(\tilde{\mathfrak{H}}, \alpha, \beta)}{\alpha^2(\alpha^2 - \beta^2)} (\beta \sin \frac{1}{2}\alpha t' - \alpha \sin \frac{1}{2}\beta t') \sin \frac{1}{2}\alpha t' d\beta d\alpha \\ &= \frac{8}{\hbar} \iint F\left(\tilde{\mathfrak{H}}, \frac{2\alpha}{t'}, \frac{2\beta}{t'}\right) \frac{\frac{1}{2}t'(\beta \sin \alpha - \alpha \sin \beta)}{\alpha^2(\alpha^2 - \beta^2)} \sin \alpha d\beta d\alpha \\ &= \frac{8}{\hbar} F_\beta(\tilde{\mathfrak{H}}, 0, 0) \iint \frac{\beta \sin \alpha (\beta \sin \alpha - \alpha \sin \beta)}{\alpha^2 - \beta^2} d\beta d\alpha \end{aligned} \right\} \quad (8.4)$$

for large t' , which does not increase with t' and may therefore be ignored.

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A general kinetic theory of liquids

V. Liquid He II

By H. S. GREEN

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This paper fulfils the programme announced in part IV of the series by examining the detailed application of the general quantum theory of fluids to liquid He II. It is shown that although the classical laws of hydrodynamics and thermodynamics are formally obeyed by the quantum liquid, important divergences arise in the manner of their interpretation. Without introducing any assumption other than the validity of the general laws of quantum mechanics, it is possible to explain qualitatively and quantitatively the well-known properties of liquid helium, including the thermodynamic discontinuity, the thermomechanical effect, the transfer effect, and the presence of thermal waves in the liquid. The connexion with earlier theories is traced, and it is shown that although they are in agreement with the theory here proposed in certain respects, their fundamental concepts are in need of considerable revision. The theory can be applied with slight changes to the phenomenon of superconductivity.

1. INTRODUCTION

The classical theory of liquids developed in the first three papers of this series (Born & Green 1946; Green 1947; Born & Green 1947a) and the quantization effected in the subsequent paper (Born & Green 1947b) led to a conception of the nature of viscous and thermal conductive processes in liquids which the authors hoped would be of assistance in the understanding not only of normal liquids, but also of the ‘quantum liquids’ of which liquid He II is the simplest example. (The electrons in certain metals at low temperatures may be cited as a second example.)

Many distinguished contributions have been made to the experimental evidence relating to the phenomena which are studied in this paper. Among them, those of Kapitza (1941b) on the thermomechanical effect, and of Daunt & Mendelssohn (1939) on the related transfer effect appear to be of special importance, as they

demonstrate most clearly the existence of a special kind of reversible process which can occur in thin layers of the liquid. Other non-equilibrium phenomena are readily interpreted as manifestations of the same type of reversible process, adulterated in many instances by the simultaneous operation of irreversible effects. The remarkable feature exhibited by all these experiments is the apparent failure in He II of two well-established physical laws: the law of thermal conduction, which requires the heat flow to be proportional to the temperature gradient, and the law of viscosity, which requires the velocity gradient to be proportional to the non-hydrostatic pressure forces.

No satisfactory explanation has yet been given of these phenomena. They lie outside the province of ordinary reversible thermodynamics, which requires for its validity that changes of any kind should occur with infinite slowness. Further, no account can be expected of the anomalous viscosity and thermal conduction in He II without prior understanding of the corresponding processes in ordinary liquids. In spite of these handicaps, several attempts have been made to elucidate certain aspects of the problem, of which the best known are due to London (1938, 1939), Tisza (1938, 1940, 1947), and Landau (1941, 1944). The first two of these authors endeavoured to connect superfluidity with the 'condensation' which occurs in a gas of non-interacting Bose particles at a temperature not far from the λ -point. They were not able, however, to take adequate account of the interaction between the helium molecules; moreover, it seemed improbable that Bose-Einstein statistics could be of crucial importance for the existence of superfluidity, since entirely analogous phenomena were known to occur in superconductors, where the electrons obey Fermi-Dirac statistics. Landau, while retaining the idea of London and Tisza that He II could be regarded as a mixture of two phases of which only one could participate in the superfluid motion, eliminated these objections by introducing a new description of the superfluid as a liquid devoid of 'rotons', rather vaguely defined as states of quantized vortex motion. The theoretical foundations of Landau's work were very insubstantial; nevertheless, his theory was in close relation to the experimental evidence, and justified itself by predicting the existence of two kinds of wave propagation for He II and therefore two velocities of 'sound'.

The present paper reveals that the limited successes of the earlier theories are derived principally from the two-phase conception of the quantum liquid; yet it appears clearly that this is an over-simplification of the real situation, which demands a different physical interpretation. In fact, the classical laws of mechanics and thermodynamics hold only in a modified form, in which the difference π between the thermodynamic and 'kinetic' pressures plays an important part. While many details remain to be investigated, the author believes that all the properties of He II can be explained by the theory developed below in a way not only satisfactory to the physical intuition, but requiring no assumption other than the accepted laws of quantum mechanics. Incidentally, the properties of a quantum liquid are derived in their most general form, which can easily be applied to the electrons in a metal and the phenomenon of superconductivity; one requires only to replace the ordinary pressure tensor by the electromagnetic stress tensor, and to represent the almost stationary metallic ions by a conservative field of force.

2. HE II IN EQUILIBRIUM

Since the radial distribution function plays an important part in determining the properties of both classical and quantum liquids, it is desirable, as a preliminary step, to ascertain the general properties of this function in liquid helium at very low temperatures where the usual methods of statistical mechanics (cf. de Boer & Michels 1939) cannot be applied. The method here adopted was indicated in § 4 of part IV, where it was shown that the density matrix $\rho_2(\mathbf{x}, \mathbf{x}')$ relating to a pair of particles may be expanded in the form

$$\rho_2(\mathbf{x}, \mathbf{x}') = \sum_{\lambda} a(\lambda) \psi_2(\lambda, \mathbf{x}) \psi_2^*(\lambda, \mathbf{x}'), \quad (2.1)$$

where $a(\lambda)$ is the probability of finding a pair of molecules in the unperturbed eigenstate λ , characterized by the eigenfunction $\psi_2(\lambda, \mathbf{x})$ which is the solution of the equation

$$\left\{ \frac{1}{2m} (\mathbf{P}^{(1)2} + \mathbf{P}^{(2)2}) + \phi(r) \right\} \psi_2(\lambda, \mathbf{x}) = E' \psi_2(\lambda, \mathbf{x}). \quad (2.2)$$

The λ comprise the quantities $\mathbf{p} = \mathbf{p}^{(1)} + \mathbf{p}^{(2)}$, m_3 , where $\mathbf{m} = \frac{1}{2}\mathbf{r} \times (\mathbf{p}^{(2)} - \mathbf{p}^{(1)})$, l , satisfying $l(l+1)\hbar^2 = \mathbf{m}^2$, and $E = \frac{1}{4m}(\mathbf{p}^{(2)} - \mathbf{p}^{(1)})^2 + \phi(r) = E' - \frac{1}{4m}\mathbf{p}^2$. Then

$$\psi_2(\lambda, \mathbf{x}) = e^{i\mathbf{p} \cdot \mathbf{x}/\hbar} Y_l(\theta, \phi) r^{-1} \psi(r), \quad (2.3)$$

where Y_l is a spherical harmonic of order l , and $\psi(r)$ satisfies

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{m}{\hbar^2} \{E - \phi(r)\} \right] \psi(r) = 0. \quad (2.4)$$

The radial distribution function is derived from $\rho_2(\mathbf{x}, \mathbf{x}')$ simply by putting $\mathbf{x} = \mathbf{x}'$, so that

$$n_2(\mathbf{x}) = \sum_{\lambda} a(\lambda) |\psi_2(\lambda, \mathbf{x})|^2. \quad (2.5)$$

As was shown in part IV, if the perturbation energy V_2 experienced by the given pair of molecules on account of the other molecules in the liquid is assumed to be Hermitian, the $a(\lambda)$ occurring in (2.1) and (2.5) will have the same value in equilibrium for all states λ between which transitions are not forbidden by the vanishing of the matrix elements of V_2 . Now the effect of the other molecules, reflected in the form of the matrix V_2 , is to make n_2 tend to a constant value c , equal to r_1^2 in the infinite fluid, when r is large. Thus

$$n_2(\mathbf{x}) \rightarrow c \quad \text{as} \quad r \rightarrow \infty. \quad (2.6)$$

Subject only to this condition, one will have, in equilibrium,

$$a(\lambda) = e^{-E/\hbar T}. \quad (2.7)$$

From this it is apparent that the behaviour of each individual term $a(E) |\psi_2(E, \mathbf{x})|^2$ in the expansion (2.5) depends strongly on E at low temperatures, and, as a result, near absolute zero, one may write

$$n_2(\mathbf{x}) = c |\psi_2(E_0, \mathbf{x})|^2, \quad (2.8)$$

where E_0 is the lowest fully occupied energy level. Now, for $E_0 < 0$ or $E_0 > 0$, $r^{-1}\psi(r)$ tends to zero or infinity for large r , so that the boundary condition (2.6) is violated. Hence $E_0 = 0$, and in the normal condition all molecule-pairs are in the state of zero energy at absolute zero.

This result does not affect the possibility of a limited occupation of the negative energy states. (In the instance of helium, on account of the weakness of the attraction between the molecules, it is unlikely that there are more than one.) In particular, near the walls at the boundary of the fluid, the condition (2.6) no longer holds, and one may substitute the ordinary Schrödinger boundary condition, which is satisfied only in the negative energy states. Hence one is led to predict the existence of liquid helium in an abnormal, negative energy state near the walls of the containing vessel; this is confirmed in the exact treatment of non-uniform conditions developed in the following sections.

To determine $n_2(r)$ for the normal state, one need only solve (2.4) for positive values of E ; the Lennard-Jones formula for $\phi(r)$ is chosen because of the hardness of the repulsive term vr^{-12} , which allows one to consider only the attractive term $-\mu r^{-6}$, provided that the part of the wave function corresponding to distances below the potential minimum is subsequently ignored. With the further substitutions $\chi = r^{-\frac{1}{2}}\psi$ and $t = r^{-2}$, (2.4) reduces to

$$\frac{d^2\chi}{dt^2} + \left\{ \frac{mE}{4\hbar^2 t^3} - \left(\frac{l}{2} - \frac{1}{4} \right) \left(\frac{l}{2} + \frac{3}{4} \right) t^{-2} + \frac{m\mu}{4\hbar^2} \right\} \chi = 0. \quad (2.9)$$

When $E = 0$, this equation has the solution

$$\chi = t^{\frac{1}{2}} J_{(\frac{l}{2}-\frac{1}{2})}(\beta t), \quad \beta = \left(\frac{m\mu}{4\hbar^2} \right)^{\frac{1}{4}}, \quad (2.10)$$

from which it is clear that only the value $l = 0$ is consistent with the boundary conditions. The form of the radial distribution function obtained from the solution (2.10) is shown in figure 1, and is very different from that characteristic of classical liquids, having a minimum instead of the usual maximum near the minimum of $\phi(r)$. The variation of $n_2(r)$ with temperature can be taken into account by making use of the solution of (2.9) with positive values of E , which is obviously obtained by writing $t - (2mE/3\hbar^2)$ for t in (2.10), when E is small, and making use of the formula

$$n_2(r) = r^{-2} \int_0^\infty e^{-E/kT} |\psi_2(E, r)|^2 dE. \quad (2.11)$$

The resulting curve, within its range of validity, does not differ significantly from the curve shown in figure 1.

It is clear from (2.9) that the form of the radial distribution function will undergo a considerable modification when energies of the order of $2\hbar^2/mr_1^2$ ($r_1 = 3 \text{ \AA}$) are excited, due to contributions from the states $l = 2, 4, \text{ etc.}$ This corresponds to a temperature of $2\hbar^2/mkr_1 \sim 2^\circ \text{K}$, near the λ -point. It is known that the effect of the higher angular momentum states is to contribute to the normal maxima of the radial distribution function, so that one is led to expect that the unusual features of liquid helium will disappear above 2°K . These plausibility considerations are confirmed

by the more precise calculations of the next section, but they are of interest here because they tend to confirm the suggestion of Landau (1941) that the unusual features of He II are associated with a deficiency of 'rotons', or quantized rotational states.

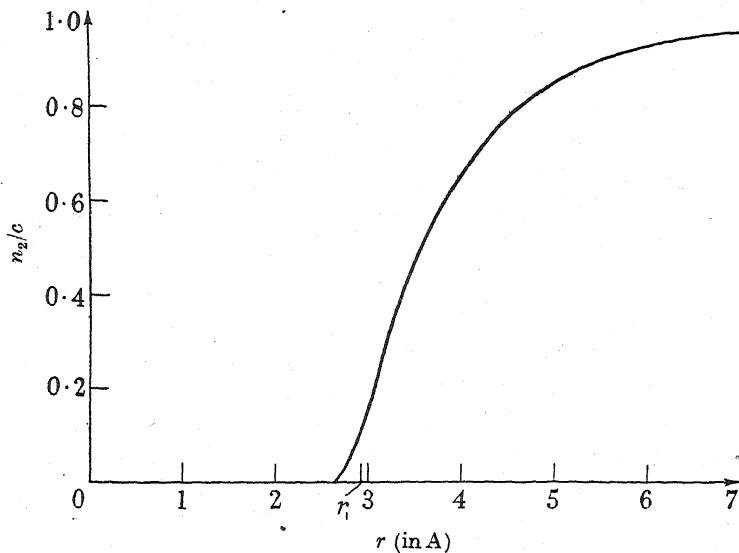


FIGURE 1. Radial distribution function for liquid helium in the normal state near absolute zero. Distance of potential maximum $r_1 = 2.93 \text{ \AA}$.

3. THERMOMECHANICS OF HE II

In part IV certain definite conclusions were reached concerning the similarities and differences which may be expected between an ordinary liquid and the 'quantum' modification which must occur, in the absence of solidification, at low temperatures. These conclusions may be briefly summarized as follows.

$$\text{The equation of motion } mn \frac{d}{dt} \mathbf{u} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p}_1 = n \mathbf{F}, \quad (3.1)$$

$$\text{and the law of viscosity } \mathbf{p}'_1 = -2\mu \underbrace{\frac{\partial}{\partial \mathbf{x}} \mathbf{u}}_{(3.2)}$$

for the non-hydrostatic part of the pressure tensor, remain formally correct, but the 'kinetic' pressure tensor \mathbf{p}_1 differs, even in equilibrium, from the thermodynamic pressure tensor \mathbf{p} which is directly measurable. Similarly, the equation of energy transfer

$$n \frac{dU}{dt} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{q} + \mathbf{k}_1 : \left(\frac{\partial}{\partial \mathbf{x}} \mathbf{u} \right) = 0 \quad (3.3)$$

and the law of thermal conduction

$$\mathbf{q} = -\lambda \frac{\partial T_1}{\partial \mathbf{x}}, \quad (3.4)$$

where nkT_1 is the diagonal element of the thermal part \mathbf{k}_1 of the kinetic pressure tensor, require no modification, but the 'kinetic' temperature T_1 differs from the thermodynamic temperature T .

Part of the remaining task is therefore the examination of the connexion between the kinetic and thermodynamic quantities. In equilibrium one has, according to § 3 of part IV,

$$p = p_1 + p_3 + p_5 + \dots, \quad (3.5)$$

where

$$p_j = \frac{kT}{3\hbar VN!} X \left(\frac{\rho_N \mu_j}{j!(kT)^j} \right) \quad (3.6)$$

and

$$\mu_{j+1} = \mu_j W_N - W_N \mu_j, \quad \mu_1 = \hbar \sum_{i=1}^N \left\{ \frac{\mathbf{p}^{(i)2}}{m} - \frac{1}{2} \sum_{j=1}^N r^{(ij)} \phi'^{(ij)} \right\}, \quad (3.7)$$

so that

$$\left. \begin{aligned} \mu_2 &= \frac{\hbar^2}{m} \sum_{i,j=1}^N \left\{ \mathbf{p}^{(ij)}, \frac{\partial \psi^{(ij)}}{\partial \mathbf{x}^{(i)}} \right\}, \quad \psi^{(ij)} = \phi^{(ij)} + \frac{1}{2} r^{(ij)} \phi'^{(ij)}, \quad \mathbf{p}^{(ij)} = \mathbf{p}^{(i)} - \mathbf{p}^{(j)}, \\ \mu_3 &= \frac{i\hbar^3}{m^2} \sum_{i,j=1}^N \left\{ \mathbf{p}^{(ij)} \cdot \left(\mathbf{p}^{(ij)}, \frac{\partial^2 \psi^{(ij)}}{\partial \mathbf{x}^{(i)} \partial \mathbf{x}^{(j)}} \right) \right\} - \frac{2i\hbar^3}{m} \sum_{i,j,k=1}^N \frac{\partial \phi^{(ij)}}{\partial \mathbf{x}^{(i)}} \cdot \frac{\partial \psi^{(ik)}}{\partial \mathbf{x}^{(i)}}. \end{aligned} \right\} \quad (3.8)$$

Hence

$$p_3 = \frac{1}{6m} \left(\frac{\hbar}{kT} \right)^2 \left\{ \int n_2 kT_2 \left(\frac{2}{3} \psi'' + \frac{4}{3r} \psi' \right) d\mathbf{r} - 2 \int \int n_3 \frac{\phi'(r)}{r} \frac{\psi'(s)}{s} \mathbf{r} \cdot \mathbf{s} dr ds \right\}. \quad (3.9)$$

One can now estimate roughly the critical temperature, which will be identified provisionally with the λ -point in liquid helium, below which the quantum correction $p_3 + p_5 + \dots$ becomes comparable with p_1 , given by

$$p_1 = nkT_1 - \frac{1}{6} \int n_2 \phi'(r) r dr. \quad (3.10)$$

This is done by substituting the approximation T_1 for T_2 in the first term of (3.9), and by applying a Kirkwood-like approximation to the second term in this equation, which then reduces to

$$p_3 = \frac{1}{6m} \left(\frac{\hbar}{kT} \right)^2 \left\{ nkT_1 \int \frac{n_2}{n} \left(\frac{2}{3} \psi'' + \frac{4}{3r} \psi' \right) d\mathbf{r} - \int n_2 \phi'(r) r dr \int \frac{n_2}{n} \psi'(s) s^{-1} ds \right\}. \quad (3.11)$$

Both the integrals involving ψ in (3.11) have values of the magnitude of

$$-2r_1^{-2} \int \frac{n_2}{n} \phi'(r) r dr,$$

so that p_3 becomes of the same order as p_1 at a temperature given by

$$(kT)^2 \sim \frac{\hbar^2}{3mr_1^2} \int \frac{n_2}{n} \phi'(r) r dr, \quad (3.12)$$

where r_1 is the maximum of the integrand. Using (3.10),

$$T = T_0 \left(1 - \frac{p_1}{nkT_1} \right), \quad (3.13)$$

where $T_0 = 2\hbar^2/mkr_1^2 \sim 2^\circ \text{K}$ for helium, with $r_1 = 3 \text{\AA}$.

The formula (3.13) gives the λ -point, together with its variation with pressure, sufficiently well, considering the roughness of the estimation, to support the expectation that a rigorous evaluation of the series (3.5) will yield complete information

concerning the thermodynamic discontinuity at the λ -point, the sharpness of the transition being due to the cumulative effect of the higher terms in the infinite series. For the present, write

$$p_1 - p = \pi, \quad (3.14)$$

so that π almost vanishes above the λ -point and becomes positive just below it, as may be seen from the fact that p_3 is negative. It will be found shortly that values of π can be inferred from a variety of experimental determinations; at the saturation vapour pressure (cf. figure 2), it increases to a maximum at 1.5°K , and becomes zero again at absolute zero.

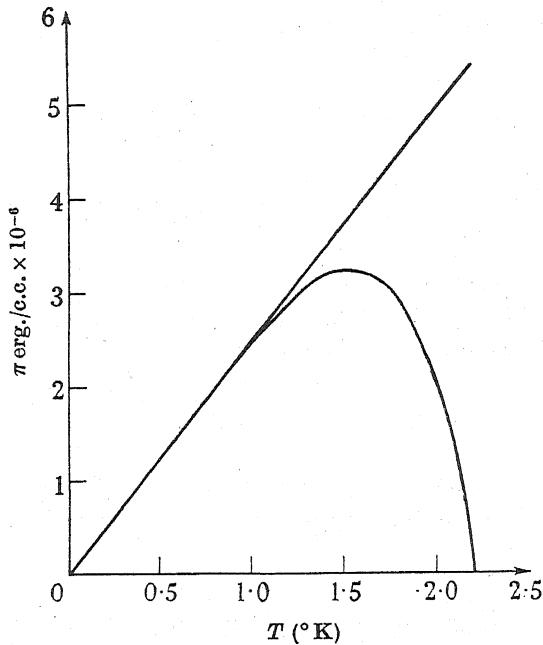


FIGURE 2. π as a function of temperature at the saturation vapour pressure. Upper curve: ground state. Lower curve: normal state. The difference between the two curves is the quantity $nR/nTS/m$ measured by Kapitza (1941*b*, figure 5).

Equation (3.1) may be written in the form

$$mn \frac{du}{dt} + \frac{\partial p}{\partial x} = -\frac{\partial \pi}{\partial x} - \frac{\partial}{\partial x} \cdot p'_1 + nF, \quad (3.15)$$

which shows that differences in π , such as may occur in the presence of a temperature gradient, will have the effect of obscuring the viscosity and simulating the action of external forces on the liquid; this already secures a qualitative understanding of the thermomechanical phenomena observed in He II.

The thermodynamic pressure tensor p has as yet been given no strict definition applicable to non-uniform conditions. It is now defined by the property that, if dS is a surface element moving with the liquid, the work done in an elementary displacement dx of dS should be $dx \cdot p \cdot dS$. This definition evidently coincides with that available in equilibrium conditions, as the negative derivative of the free energy

with respect to volume. Consider now a small volume moving with the liquid; the equation of conservation of energy within this volume is

$$\int n \frac{d}{dt} (\frac{1}{2} m u^2 + U) d\mathbf{x} = \int n \frac{dQ}{dt} d\mathbf{x} - \int \mathbf{u} \cdot \mathbf{p} \cdot d\mathbf{S}, \quad (3.16)$$

where dQ/dt is the rate of absorption of heat energy per molecule, and the external force is omitted from consideration. dQ is not, of course, a perfect differential. From this equation one obtains

$$\frac{1}{2} mn \frac{d}{dt} (u^2) + n \frac{dU}{dt} = n \frac{dQ}{dt} - \frac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{p} \cdot \mathbf{u}), \quad (3.17)$$

which may be regarded as the definition of the thermodynamic pressure tensor \mathbf{p} in symbolic language. The corresponding equation for the energy of the macroscopic motion, obtained by multiplying (3.1) by \mathbf{u} , is

$$\frac{1}{2} mn \frac{d}{dt} (u^2) + \mathbf{u} \cdot \left(\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p}_1 \right) = 0 \quad (3.18)$$

since \mathbf{F} vanishes. Subtracting from (3.17), one obtains

$$n \frac{dQ}{dt} = n \frac{dU}{dt} + \mathbf{p} : \left(\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} \right) + \mathbf{u} \cdot \left\{ \frac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{p} - \mathbf{p}_1) \right\}, \quad (3.19)$$

or, by virtue of (3.14) and the equation of continuity,

$$n \frac{dQ}{dt} = n \frac{dU}{dt} + np \frac{d}{dt} \left(\frac{1}{n} \right) - \mathbf{u} \cdot \frac{\partial \pi}{\partial \mathbf{x}} \quad (3.20)$$

on the assumption that the viscosity may be neglected; the conditions of validity of this hypothesis will be examined in § 5.

To complete the present account of non-uniform thermodynamics, it is necessary to add only the definition of the thermodynamic temperature T by means of the equation

$$\frac{dQ}{dt} = T \frac{dS}{dt}, \quad (3.21)$$

where S is the entropy per molecule, regarded as a space function of the three independent variables n , T and π . (3.21) is the customary formulation of the second law of thermodynamics, which, as was shown in part IV, goes over unchanged into the quantum theory: the necessity for this is, of course, obvious from the physical point of view. On the other hand, it is clear from (3.20) that the first law of thermodynamics does not hold in its usual sense for a quantum liquid; this does not imply any violation of the law of conservation of energy, which is actually implicit in its derivation, but is symptomatic of the existence of a curious interconnexion between the thermal energy and the energy of macroscopic motion.

4. THE ELEMENTARY THERMAL PROCESSES IN HE II

It is now expedient to consider the application of the general theory of the previous section to the three simple processes in fluids which are of special physical significance.

Consider first the quasi-static process in which a transition is made from one uniform state to another by the infinitely slow variation of an external parameter l . Such ideal conditions never occur naturally, but are of special importance inasmuch as they are the only kind to which ordinary reversible thermodynamics is strictly applicable. As the number density is a function of l only, the equation of continuity leads to

$$n'(l) \frac{dl}{dt} + n(l) \frac{\partial}{\partial x} \cdot u = 0, \quad u = u_0 - x \frac{n'(l) dl}{n(l) dt}, \quad (4.1)$$

assuming that the motion is in the x -direction. As $(dl/dt)^2$ and d^2l/dt^2 are completely negligible, the equation of motion (3.1) shows merely that p_1 and hence π are uniform. Thus (3.20) reduces to

$$dQ = dU + pd\left(\frac{1}{n}\right), \quad (4.2)$$

which is the ordinary law of thermodynamics.

When, however, steady processes, which are of frequent physical occurrence, are considered, one has $u \cdot \frac{\partial \pi}{\partial x} = \frac{dp}{dt}$, so that (3.20) takes the form

$$dQ = dU + pd\left(\frac{1}{n}\right) - \frac{1}{n} d\pi \quad (4.3)$$

on multiplication by the time-differential. Part of any thermal energy communicated is absorbed by the macroscopic motion, as may be seen from (3.18), which leads to

$$d\left(\frac{1}{2}mu^2\right) + \frac{1}{n} dp = -\frac{1}{n} d\pi. \quad (4.4)$$

The equation (4.3) may be written in the form

$$TdS = d\left(U - \frac{\pi}{n}\right) + p_1 d\left(\frac{1}{n}\right), \quad (4.5)$$

showing that the flowing helium behaves thermodynamically as if its internal energy were $U - \pi/n$, and the pressure were the kinetic pressure. The anomalous internal energy $-\pi/n$ gives rise to an anomalous specific heat additional to the normal specific heat, the additional energy supplied being converted into energy of motion. The motion may be visible, as in the transfer effect and in the flow through capillaries, or may take the form of closed currents analogous to the persistent currents in superconductors. It will be seen that such motion generally occurs only near the boundary walls containing the fluid, and takes another form inside the liquid. One may further rewrite (4.5) in the form

$$d\Phi = \frac{1}{n} dp_1 - SdT, \quad (4.6)$$

where $\Phi = U + p/n - TS$ is the thermodynamic potential per molecule. For simultaneous mechanical and thermal equilibrium, one has $d\Phi = 0$, since $dp_1 = dT = 0$, and in a purely thermomechanical process, $d\Phi = 0$, so that

$$\frac{dp_1}{dT} = nS. \quad (4.7)$$

A third type of process, again of major physical interest, is that of wave propagation. There the number density may be taken to be a function of $t - v^{-1}\mathbf{k} \cdot \mathbf{x}$ only, so that

$$v \frac{\partial n}{\partial \mathbf{x}} + \mathbf{k} \frac{\partial n}{\partial t} = 0, \quad (4.8)$$

where \mathbf{k} is a unit vector in the direction of propagation, and v is the velocity of propagation. More complex types of wave disturbance may be obtained by the superposition of elementary waves of this type. From the substitution of (4.8) into the equation of continuity it follows that

$$\frac{\partial}{\partial \mathbf{x}} \cdot (n\mathbf{u} - nv\mathbf{k}) = 0, \quad \mathbf{u} = v \left(1 - \frac{n_0}{n}\right) \mathbf{k}, \quad (4.9)$$

where n_0 is a constant equal to the density at any place where the motion associated with the wave vanishes. Also

$$\left. \begin{aligned} n \frac{\partial \mathbf{u}}{\partial t} &= v \frac{n_0}{n} \frac{\partial n}{\partial t} \mathbf{k} = -v^2 \frac{n_0}{n} \frac{\partial n}{\partial \mathbf{x}}, \\ n\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{x}} \mathbf{u} &= v^2 \frac{n_0}{n} \left(1 - \frac{n_0}{n}\right) \frac{\partial n}{\partial \mathbf{x}} = v^2 \frac{n_0}{n} \frac{\partial n}{\partial \mathbf{x}} + v^2 n_0^2 \frac{\partial}{\partial \mathbf{x}} \left(\frac{1}{n}\right), \end{aligned} \right\} \quad (4.10)$$

so that the equation of motion leads to

$$\frac{\partial}{\partial \mathbf{x}} \left(m v^2 \frac{n_0^2}{n} + p_1 \right) = 0, \quad m v^2 \frac{n_0^2}{n} + p_1 = c, \quad \text{a constant.} \quad (4.11)$$

Differentiating with respect to the density, one obtains

$$v^2 = \frac{1}{m} \frac{n^2}{n_0^2} \frac{dp_1}{dn}. \quad (4.12)$$

This is the ordinary formula for the velocity of sound if the propagation process is adiabatic, a condition which is obviously satisfied if the disturbance is purely mechanical, but not in thermal processes where the additional variable π comes into play. It is on the latter type of wave propagation that interest is now mainly centred.

For any thermodynamical variable, such as U , one has

$$\frac{\partial U}{\partial t} = -v\mathbf{k} \cdot \frac{\partial U}{\partial \mathbf{x}} = \frac{n}{n_0 - n} \mathbf{u} \cdot \frac{\partial U}{\partial \mathbf{x}} = \frac{n}{n_0} \frac{dU}{dt}, \quad (4.13)$$

so that, for wave propagation, (3.20) leads to the law

$$dQ = dU + pd \left(\frac{1}{n} \right) - \frac{n_0 - n}{n_0 n} d\pi \quad (4.14)$$

or $TdS = d \left(U + \frac{\pi}{n_0} - \frac{\pi}{n} \right) + p_1 d \left(\frac{1}{n} \right). \quad (4.15)$

The anomalous specific heat is in this instance $\frac{d}{dT} \left(\frac{\pi}{n_0} - \frac{\pi}{n} \right)$, which is much smaller than that found for steady motion if the difference $n_0 - n$ is small. The effect of

superposing a large number of waves with different directions, shapes and amplitudes, however, is to reduce the density considerably. This is evident from (4.9), on the understanding that the macroscopic velocity is in the opposite direction to the wave vector when the latter is identified with the direction of flow of heat. It thus appears that nearly all the anomalous specific heat in He II is accounted for by the presence of thermal waves, which are also responsible for the sudden decrease of the density below the λ -point.

To clarify the picture presented by the thermal waves, consider the effect of the transmission of a pulse of length l along a tube of cross-section σ , containing the liquid initially in its ground state, at rest. If, during the passage of the pulse, the value of π is reduced from ϖ to $\varpi - \Delta\pi$, it is clear from (4.14) that the heat transmitted is $(1 - n/n_0)l\sigma\Delta\pi$, neglecting the small contribution $pd(1/n)$. From (4.9), on the other hand, one sees that the volume $uv^{-1}l\sigma = (n_0/n - 1)l\sigma$ is transferred in the opposite direction. The whole process may occur isothermally and without variation of the pressure. This was found experimentally by Kapitza (1941*b*), who also measured the ratio $R = \Delta\pi/mn$ of the heat to the mass transfer. From (4.14), which for waves of small amplitude should be rewritten in the form

$$TdS = dU + (p + \Delta\pi)d\left(\frac{1}{n}\right), \quad (4.16)$$

one obtains further

$$R = \frac{T}{mn} \frac{dS}{d(1/n)}. \quad (4.17)$$

This formula is exact. The approximate formula $mR = TS$ which has been found empirically follows from the integral

$$TS = U + \frac{p + \Delta\pi}{n} + TS' \quad (4.18)$$

of (4.16) if one observes that nearly all the entropy is associated with the thermal wave, and hence $TS - \Delta\pi/n$ is very small.

Kapitza's measurements allow one to infer the variation with temperature of π for the normal state of the liquid, on the presumption that

$$\Delta\pi = nTS, \quad \varpi = nTS_0, \quad \pi = nT(S - S_0), \quad (4.19)$$

where S_0 is the maximum entropy associated with the thermal waves. The resulting curve is shown in figure 2, together with the linear curve for the ground state. From the point of view of London, Tisza, and Landau, an artificial separation of liquid helium can be made into a 'superfluid' and a 'normal' component; this could be expressed in terms of the present theory by writing $\pi = \varpi(n_s/n)$ and $\Delta\pi = \varpi(n_n/n)$, where n_s and n_n are the superfluid and normal densities respectively. This analogy between the theories suggests that the difference may be merely one of interpretation; physically absurd conclusions, however, result from the two-fluid conception, quite apart from its lack of theoretical justification, and it must therefore be discarded in favour of the more fundamental outlook.

The existence of the thermal waves in liquid helium in bulk was demonstrated experimentally by Peshkov (1944, 1946), who succeeded in evoking a train of

waves with weak thermomechanical properties by passing an alternating current through an electrical heater immersed in the liquid, and measured the velocity of propagation by a resonance method. The conditions for the propagation of these waves, which may be inferred from (4.6) and (4.15), are

$$d\Phi = 0 \quad \text{and} \quad d\pi = 0; \quad (4.20)$$

it follows that $\frac{dp_1}{dT} = nS, \quad \frac{d}{dn}\{n(S - S_0)\} = 0,$ (4.21)

if one neglects the small variation of temperature with density, and that the velocity of propagation of the waves is given by

$$mv^2 = \frac{dp_1}{dn} = S(S_0 - S) \frac{dT}{dS}. \quad (4.22)$$

Tisza (1947) has shown that excellent numerical agreement with the experimentally observed velocity of 'second sound' can be obtained from this formula, using Kapitza's measurements of S . His method of derivation of this formula, on the basis of the two-fluid theory, is, however, complex, and open to objection from the present point of view.

5. VISCOSITY AND THERMAL CONDUCTION IN HE II

It has been supposed in the foregoing that there are certain processes, other than quasi-static processes, in quantum liquids, for which the effect of viscosity can be neglected. From equation (3.2) it follows that viscosity is mainly due to the existence of the non-diagonal elements of the potential pressure l_1 , defined by

$$\frac{\partial}{\partial \mathbf{x}^{(1)}} \cdot l_1 = - \int \frac{\phi'(r)}{r} \mathbf{r} n_2(\mathbf{r}, \mathbf{x}) d\mathbf{x}^{(2)}, \quad (5.1)$$

where $\mathbf{r} = \mathbf{x}^{(2)} - \dot{\mathbf{x}}^{(1)}$ and $\mathbf{x} = \frac{1}{2}(\mathbf{x}^{(1)} + \mathbf{x}^{(2)})$. The validity of the classical expansion in powers of the space gradients of density, temperature, and velocity is made rather dubious by the presence of waves and large velocities; fortunately, however, the equation (5.1) can be solved exactly by the operational methods of quantum mechanics. Since

$$e^{\frac{i}{\hbar} \mathbf{p}^{(1)} \cdot \mathbf{r}/\hbar} n_2(\mathbf{r}, \mathbf{x}^{(1)}) = n_2(\mathbf{r}, \mathbf{x}^{(1)} + \frac{1}{2}\mathbf{r}) = n_2(\mathbf{r}, \mathbf{x}), \quad (5.2)$$

the equation reduces to

$$\frac{i}{\hbar} \mathbf{p}^{(1)} \cdot l_1 = - \int \frac{\phi'(r)}{r} \mathbf{r} e^{\frac{i}{\hbar} \mathbf{p}^{(1)} \cdot \mathbf{r}/\hbar} n_2(\mathbf{r}, \mathbf{x}^{(1)}) d\mathbf{r}. \quad (5.3)$$

Also, because $n_2(\mathbf{r}, \mathbf{x}) = n_2(-\mathbf{r}, \mathbf{x})$, the coefficient $(i/\hbar) \mathbf{p}^{(1)}$ can be cancelled from this equation, leaving

$$l_1 = - \frac{1}{2} \int \frac{\phi'(r)}{r} \mathbf{r} \mathbf{r} \frac{\sin(\frac{1}{2} \mathbf{p}^{(1)} \cdot \mathbf{r}/\hbar)}{\frac{1}{2} \mathbf{p}^{(1)} \cdot \mathbf{r}/\hbar} n_2(\mathbf{r}, \mathbf{x}^{(1)}) d\mathbf{r}. \quad (5.4)$$

This leads to the classical approximation formulae if the ordinary expansion procedure is followed. One infers that the viscosity will vanish completely in the liquid bulk only if $n_2(\mathbf{r}, \mathbf{x}^{(1)})$ is independent of $\mathbf{x}^{(1)}$; on the other hand, since n_2 is abnormally

small in He II near the potential minimum, the viscosity will also be small, though finite. The experimental evidence available on the damping of mechanical motion in the liquid supports this conclusion. Also, as effectively uniform conditions are associated with the thermal waves investigated in the previous section, these waves will be quite undamped. The reversible processes in capillaries and narrow slits are accounted for entirely in terms of such waves, and viscosity need therefore be taken into account only to the extent to which these processes are often adulterated by the simultaneous operation of ordinary irreversible processes.

It is of interest to re-examine the derivation of Poiseuille's formula for the steady flow of a quantum liquid in a capillary. If r is the radial and x the axial co-ordinate, one has from (3.1) and (3.2)

$$\frac{dp_1}{dx} + \frac{1}{r} \frac{d}{dr}(rp_{xr}) = 0, \quad p_{xr} = -\mu \frac{du_x}{dr} = -\frac{r}{2} \frac{dp_1}{dx}, \quad (5.5)$$

where p_{xr} is the non-diagonal element of the pressure tensor, showing that the rate of decrease of velocity from the centre to the circumference is diminished in the ratio dp_1/dp , compared with the classical theory, and actually vanishes if p_1 is constant along the tube. In general, the slip between the walls and the fluid will be only partial, and the integral of (5.5) is

$$u_x = \frac{1}{4\mu} \left(-\frac{dp_1}{dx} \right) (a_1^2 - r^2), \quad (5.6)$$

where the constant of integration a_1 becomes infinite only in the limit $dp_1/dx \rightarrow 0$, when u_x must tend to the constant value $-v(1 - n_0/n)$. Indeed, in Kapitza's experiments (1941a) on the jet phenomenon produced by heating the liquid in a capillary sealed at one end, it is necessary to suppose that a_1 is less than the radius a of the capillary, as may be seen from the expression $\frac{\pi a^4}{8\mu} \left(-\frac{dp_1}{dx} \right) \left(\frac{2a_1^2}{a^2} - 1 \right)$ for the volume flow across the cross-section, which must almost vanish for a sealed capillary. These experiments were proved to be strongly irreversible, consistent with the large viscous forces required on theoretical grounds.

The laws of viscosity and thermal conduction, expressed in the form of (3.2) and (3.4) respectively, are not very useful because they contain reference to the 'kinetic' temperature and pressure alone. To formulate approximate laws with reference to the corresponding thermodynamic quantities, one is guided by the requirement that \mathbf{q} and \mathbf{p}' should be linear in the space derivatives of T and \mathbf{u} , and must accordingly have the form

$$\mathbf{q} = -\lambda' \frac{\partial T}{\partial \mathbf{x}} + 2\kappa \mathbf{u} \cdot \left(\overbrace{\frac{\partial}{\partial \mathbf{x}}}^{} \mathbf{u} \right), \quad \mathbf{p}' = -2\mu' \frac{\partial}{\partial \mathbf{x}} \mathbf{u} + \frac{2\theta}{u^2} \overbrace{\frac{\partial T}{\partial \mathbf{x}}}^{} \mathbf{u}. \quad (5.7)$$

The second term in each of these equations does not appear in the classical theory, for the reason that there, \mathbf{u} may not occur explicitly, but they are not excluded and are indeed required by the quantum theory, where thermal and dynamical quantities are inseparably linked. The quantity κ may be called 'the coefficient of thermal mobility', and θ 'the modulus of thermal stress'.

For the complete discussion of irreversible phenomena, it is necessary to have the general solution of the equation (3.1) in steady conditions, when, together with the equation of continuity, it reduces to

$$mn\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{x}} \mathbf{u} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p}_1, \quad \frac{\partial}{\partial \mathbf{x}} \cdot (n\mathbf{u}) = 0. \quad (5.8)$$

This pair of equations is integrable, with the solution

$$mn\mathbf{u}\mathbf{u} + \mathbf{p}_1 = \frac{\partial}{\partial \mathbf{x}} \times \mathbf{s}, \quad (5.9)$$

where \mathbf{s} is an arbitrary tensor, fixed by the boundary conditions, or

$$mn\mathbf{u}\mathbf{u} + \mathbf{p}_1^0 = \frac{\partial}{\partial \mathbf{x}} \times \mathbf{s}^0, \quad \mathbf{p}'_1 = \frac{\partial}{\partial \mathbf{x}} \times \mathbf{s}'. \quad (5.10)$$

The first of these equations can be satisfied by substituting for \mathbf{s}^0 an antisymmetrical tensor defined by $(s_{yz}^0, s_{zx}^0, s_{xy}^0) = \mathbf{t} \cdot \mathbf{x}$ ($t_{xy} = t_{yx}$, etc.) if the left-hand side is uniform, or otherwise by a more complicated integral expression. Then one has

$$mn\mathbf{u}\mathbf{u} + \mathbf{p}_1^0 = tr(\mathbf{t}) \mathbf{1} - \mathbf{t}. \quad (5.11)$$

Now suppose the flow is in a slit bounded by two planes separated by a very small distance d and normal to the z -axis. Then k_{1zz} , which represents the mean square momentum in the z -direction, must, according to Heisenberg's uncertainty principle, be of order $(\hbar d^{-1})^2$. The relevance of this conclusion has been pointed out by Daunt & Mendelsohn (1946). Writing

$$p_{1zz}^0 = p_1 + \gamma(\hbar d^{-1})^2, \quad (5.12)$$

so that p_1 is the hydrostatic pressure in the infinite liquid, from (5.11) it follows, since $u_z = 0$, that

$$p_1 + \gamma(\hbar d^{-1})^2 = tr(\mathbf{t}) - t_{zz}. \quad (5.13)$$

This shows that \mathbf{t} has a part of order d^{-2} , so that

$$\mathbf{t} = \mathbf{t}^0 + (\hbar d^{-1})^2 \mathbf{t}', \quad \gamma = t'_{xx} + t'_{yy}. \quad (5.14)$$

It is then clear from the equations

$$mn u_x^2 + p_1 = tr(\mathbf{t}) - t_{xx}, \quad mn u_y^2 + p_1 = tr(\mathbf{t}) - t_{yy}, \quad (5.15)$$

that when d is very small, u_x and u_y are of order d^{-1} , being given, sufficiently nearly, by

$$(mn)^{\frac{1}{2}} u_x d = \hbar(t'_{yy} + t'_{zz})^{\frac{1}{2}}, \quad (mn)^{\frac{1}{2}} u_y d = \hbar(t'_{xx} + t'_{zz})^{\frac{1}{2}}. \quad (5.16)$$

The tensor \mathbf{t} is determined by the boundary conditions, effectively the conditions beyond the end of the slit. This confirms the conclusion reached previously, that the volume flow through capillaries and narrow slits includes a component depending not on the width of the channel, but only on the thermal transfer between the two ends. There may, however, exist an independent component corresponding to the behaviour of normal liquids.

The same conclusions apply to the behaviour of the thin films associated with the transfer phenomenon, where the distance d is determined naturally instead of by

physical constraints. The method of initial formation of these films is rather complex, involving thermal fluctuations within the liquid and perhaps also evaporation and condensation from the vapour. Once formed, however, the mechanism responsible for their perpetuation is precisely the same as that involved in the superfluid motion through capillaries and narrow slits.

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NOTES

(1) Part I, § 7, p. 8.

The derivation of Boltzmann's collision integral given in the text is not quite rigorous, and does not make clear the fundamental assumptions inherent in gas-theory. An alternative derivation follows, which, though substantially equivalent to that of § 7, is completely rigorous.

It is assumed that the potential energy $\phi(r)$ between two molecules decreases rapidly with the distance between them, and is completely negligible for $r \geq r_0$, where r_0 is very small by macroscopic standards. If two molecules, moving only under their mutual interaction, have positions $\mathbf{x}^{(1)}, \mathbf{x}^{(2)}$ such that $|\mathbf{x}^{(1)} - \mathbf{x}^{(2)}| < r_0$, and velocities $\xi^{(1)}, \xi^{(2)}$ at time t , let their positions and velocities at the time $t_0 < t$ when they were previously at distance r_0 apart be $\mathbf{x}_0^{(1)}, \mathbf{x}_0^{(2)}$ and $\xi_0^{(1)}, \xi_0^{(2)}$ respectively. Then (7.1) of the text, which expresses the postulate of binary encounters, is strictly

$$f_2(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \xi^{(1)}, \xi^{(2)}) = f_1(t_0, \mathbf{x}_0^{(1)}, \xi_0^{(1)}) f_1(t_0, \mathbf{x}_0^{(2)}, \xi_0^{(2)}), \quad (\text{N. 1})$$

where $|\mathbf{x}_0^{(1)} - \mathbf{x}_0^{(2)}| = r_0$. It is necessary to introduce at this point an approximation which is also made implicitly in the usual derivation of Boltzmann's equation: $t_0, \mathbf{x}_0^{(1)}$ and $\mathbf{x}_0^{(2)}$ are replaced by $t, \mathbf{x}^{(1)}$, and $\mathbf{x}^{(1)}$ (not $\mathbf{x}^{(2)}$) respectively on the right-hand side of (N. 1), so that

$$f_2(t, \mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \xi^{(1)}, \xi^{(2)}) = f_1(t, \mathbf{x}^{(1)}, \xi_0^{(1)}) f_1(t, \mathbf{x}^{(1)}, \xi_0^{(2)}). \quad (\text{N. 2})$$

At $t - t_0$, $\mathbf{x}^{(1)} - \mathbf{x}_0^{(1)}$, and $\mathbf{x}^{(1)} - \mathbf{x}_0^{(2)}$ are all obviously very small by macroscopic standards, it may be expected that the error so introduced is also small; nevertheless the fact that the approximation is necessary shows that Boltzmann's equation is not quite exact even when the postulate of binary encounters is made. The exact magnitude of the necessary correction will be given in Note (6).

It is next necessary to express $\xi_0^{(1)}$ and $\xi_0^{(2)}$ in terms of $\xi^{(1)}, \xi^{(2)}$ and \mathbf{r} . This is done by solving completely the equations of motion

$$\frac{d\mathbf{r}}{\xi^{(2)} - \xi^{(1)}} = \frac{m d\xi^{(1)}}{\partial \phi} = \frac{m d\xi^{(2)}}{-\frac{\partial \phi}{\partial \mathbf{r}}} \quad (= dt) \quad (\text{N. 3})$$

of the two molecules, which have eight independent integrals

$$F_k(\mathbf{r}, \xi^{(1)}, \xi^{(2)}) = \text{const.} = F_k(\mathbf{r}_0, \xi_0^{(1)}, \xi_0^{(2)}) \quad (k = 1, \dots, 8) \quad (\text{N. 4})$$

satisfying the differential equation

$$(\xi^{(2)} - \xi^{(1)}) \cdot \frac{\partial F}{\partial \mathbf{r}} = \frac{1}{m} \frac{\partial \phi}{\partial \mathbf{r}} \cdot \left(\frac{\partial F}{\partial \xi^{(2)}} - \frac{\partial F}{\partial \xi^{(1)}} \right) \quad (\text{N. 5})$$

and including those written down in (7.2) of the text. These eight equations (N. 4), together with the extra relation $|\mathbf{r}_0| = r_0$ can be solved to express $\xi_0^{(1)}, \xi_0^{(2)}$ and \mathbf{r}_0 in terms of the F_k and r_0 . From this it is clear that $\xi_0^{(1)}$ and $\xi_0^{(2)}$ must satisfy the equation (N. 5), and if one writes

$$f_1(t, \mathbf{x}^{(1)}, \xi_0^{(1)}) f'_1(t, \mathbf{x}^{(1)}, \xi_0^{(2)}) = f'_2(t, \mathbf{x}^{(1)}, \mathbf{r}, \xi^{(1)}, \xi^{(2)}), \quad (\text{N. 6})$$

f_2 will also satisfy the same equation. Hence

$$\begin{aligned} \frac{1}{m} \iint \frac{\partial \phi}{\partial \mathbf{x}^{(1)}} \cdot \frac{\partial f_2}{\partial \xi^{(1)}} d\mathbf{x}^{(2)} d\xi^{(2)} &= -\frac{1}{m} \iint \frac{\partial \phi}{\partial \mathbf{r}} \cdot \left(\frac{\partial f'_2}{\partial \xi^{(1)}} - \frac{\partial f'_2}{\partial \xi^{(2)}} \right) d\mathbf{x}^{(2)} d\xi^{(2)} \\ &= \iint (\xi^{(2)} - \xi^{(1)}) \cdot \frac{\partial f'_2}{\partial \mathbf{r}} d\mathbf{x}^{(2)} d\xi^{(2)}, \end{aligned} \quad (\text{N. 7})$$

where it is clear from the left-hand side that the integration over $\mathbf{x}^{(2)}$ may be limited to a sphere of radius r_0 surrounding the point $\mathbf{x}^{(1)}$. The integral on the right-hand side can be partially evaluated by dividing this sphere into elementary tubes parallel to the vector $\xi^{(2)} - \xi^{(1)}$. If $d\mathbf{b}$ is the cross-section of such a tube, one has

$$(\xi^{(2)} - \xi^{(1)}) \cdot \int \frac{\partial f'_2}{\partial \mathbf{r}} d\mathbf{x}^{(2)} = |\xi^{(2)} - \xi^{(1)}| \int [f'_2] d\mathbf{b}, \quad (\text{N. 8})$$

where $[f'_2]$ is the difference between the values at the upper and lower ends of the tube. At the lower end, where $\mathbf{r} \cdot (\xi^{(2)} - \xi^{(1)}) < 0$, $\xi_0^{(1)} = \xi^{(1)}$ and $\xi_0^{(2)} = \xi^{(2)}$, so

$$f'_2 = f_1(\xi^{(1)}) f_1(\xi^{(2)});$$

at the upper end, $\xi_0^{(1)}$ and $\xi_0^{(2)}$ are the velocities 'after the encounter', which can be calculated from the equations (N. 4).

(2) Part II, § 5, p. 18.

When this section was written, the validity of the various approximations made in the derivation of the integral equation (5.5) was not properly discussed. There are essentially three:

(a) The Kirkwood 'superposition' approximation made already in (5.7) of part I, and implicit in (5.1). This has been discussed and shown to involve little error by Dr A. E. Rodriguez in a paper called part VI of the present series in the *Proceedings of the Royal Society* (vol. 196, p. 73).

(b) The linearization approximation. This is considerably improved by writing instead of (5.2)

$$n_2(r) = n_1^2 \exp \{-\phi(r)/kT + f(r)\},$$

which leads equally well to (5.3). This approximation has also been discussed by Rodriguez (*loc. cit.*), and shown to involve negligible error.

(c) The replacement of $f(s)$ by an average value $\epsilon - 1$ in (5.3). This is obviously satisfactory for the first line of (5.3), but not so satisfactory in the second line, where it has the effect in subsequent developments of giving the liquid too high a density. This and the previous approximation have been eliminated by Dr A. G. McLellan in a paper not yet published. Solving the equation (5.1) directly by another method, he finds a liquid density which agrees almost exactly with observed values.

(3) Part II, § 8, p. 22.

Some of the integrals in this section on examination prove to be divergent, and the correctness of (8.5) and (8.7) is therefore questionable. It has to be remembered that in the right-hand side

$$-(2\pi)^{\frac{1}{2}} \frac{\lambda^2}{\epsilon} \sum_u \frac{z_u e^{irz_u}}{\beta'(z_u)}$$

of equation (8·1) r may not assume negative values, and must be replaced by $-r$ when r is negative. The result is that it is not so easy to obtain compact formulae for p and A , but the question must be treated by the method elaborated by Dr Rodriguez (*loc. cit.*).

(4) Part III, § 4, p. 39.

The second integral on the right-hand side of (4·19) can be slightly simplified by the omission of the term $\frac{5kT}{m}$, since

$$\int \varphi_1 v^2 d\mathbf{v} = \int \varphi'_1 v^2 d\mathbf{v} = 0.$$

This follows from the vanishing of \mathbf{u}'_1 and r'_1 , because, when $\mathbf{b} = \mathbf{b}' = 0$, one obtains from (4·2)

$$\begin{aligned} \frac{1}{3} \int (\varphi_1 \mathbf{a} + \varphi'_1 \mathbf{a}') v^2 d\mathbf{v} &= \int (\varphi_1 \mathbf{v} \cdot \mathbf{a} + \varphi'_1 \mathbf{v} \cdot \mathbf{a}') \mathbf{v} d\mathbf{v} \\ &= \int F'_1(\xi^{(1)} - \mathbf{u}_1) d\xi^{(1)} \\ &= n_1 \mathbf{u}'_1 - n'_1 \mathbf{u}_1 = 0. \end{aligned}$$

The gradients \mathbf{a} and \mathbf{a}' are arbitrary, so their coefficients in the expression on the left-hand side must vanish identically.

(5) Part III, § 5, p. 39.

There is an error in this calculation, namely that the sign of β in the equation (5·5) is incorrect. This makes the factor $\left(\frac{\pi}{\beta}\right)^{\frac{1}{2}}$ in (5·4), representing the 'spread' of the curve $N^0(r)\phi'(r)r^4$ about its maximum, imaginary. However, as the spread can only change the result (5·11) by a constant factor, this is not an important source of error. The origin of the difficulty lies in the fact that for many liquids the function $N_2^0(r)\phi'(r)r^4$ has a narrow but deep negative minimum in the repulsive part of the molecular field; this probably accounts for the deviations from the Andrade formula which have been observed in many organic liquids as well as mercury. Under such circumstances no simple analytic formula can be found for the viscosity over the whole range, and it is necessary to compute it by numerical integration from the formula (5·3).

(6) Part III, § 6, p. 42.

The equation (6·5) has some terms missing on the left-hand side, which arise from the incomplete cancellation of the second term on the right-hand side of (6·4) with terms involving the pressure on the left. The corrected equation is

$$\begin{aligned} -\frac{2}{3} \left(\frac{\sigma}{2} + \frac{l^0}{n_1 kT} \right) \left(\frac{mv^2}{2kT} - \frac{3}{2} \right) + \frac{p}{n_1 kT} \left\{ \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) k\mathbf{v} \cdot \mathbf{a} + mv \cdot \mathbf{b} \cdot \mathbf{v} \right\} \frac{f_1^0}{kT} \\ = -\frac{1}{m} \iint \frac{\partial \phi}{\partial \mathbf{r}} \cdot \frac{\partial f'_2}{\partial \mathbf{v}^{(1)}} d\mathbf{r} d\mathbf{v}^{(2)}. \end{aligned}$$

For a gas in which only binary encounters need be considered, the right-hand side of this equation can be transformed into a collision integral in the way explained in Note (1), except that no approximation need now be employed, as f'_2 is formally

independent of time and the position of the mean centre of the two molecules. Hence one sees that the viscosities and thermal conductivities computed from Boltzmann's equation should be multiplied by $\frac{p}{n_1 kT}$ to obtain accurately the 'kinetic' part depending on the thermal motion. The 'potential' term depending on the molecular forces could also be calculated accurately without great difficulty from f'_2 , expressed in terms of f'_1 with the help of the formula (N. 2) of Note (1). In this way a rigorous theory of dense gases can be obtained depending only on the postulate of binary encounters.

It even seems to be possible to extend this method to liquids. Naturally the postulate of binary encounters cannot be maintained there, and the velocities $\xi_0^{(1)}$ and $\xi_0^{(2)}$ in (N. 2) have to be calculated for a *mean* trajectory described under the *average* force between two molecules in the presence of many others. This force is the gradient not of $\phi(r)$, but of $\phi^*(r) = -kT \log N_2^0(r)$. One cannot, therefore, complete the transformation of the collision integral into Boltzmann's form; however, the fundamental integral equation for f'_1 becomes closed, and therefore soluble, after the substitution of (N. 2).

(7) Thermodynamics, § 2, p. 69.

The restriction that the time difference should be small can be removed from the formula (2.17) and the entropy theorem of § 4 (p. 71). For let $U = e^{u_1} e^{u_2} e^{u_3} \dots$ be the unitary operator evaluated in § 7, so that $\bar{\rho} = U \rho_0 U^{-1}$. The diagonal term of this matrix equation is then

$$a(\lambda) = \sum_{\lambda'} U(\lambda, \lambda') a_0(\lambda') U^{-1}(\lambda', \lambda)$$

but as U is unitary, $U^{-1}(\lambda', \lambda) = U^*(\lambda, \lambda')$ and one has

$$a(\lambda) = \sum_{\lambda'} |U(\lambda, \lambda')|^2 a_0(\lambda'), \quad \sum_{\lambda'} |U(\lambda, \lambda')|^2 = 1.$$

Hence (2.17) is satisfied with $p(\lambda, \lambda') = |U(\lambda, \lambda')|^2$ quite generally. Defining \mathfrak{S} by (4.1), one has further

$$\begin{aligned} \mathfrak{S} - \mathfrak{S}_0 &= -\frac{k}{\mathfrak{A}} \sum_{\lambda} \{a(\lambda) \log a(\lambda) - a_0(\lambda) \log a_0(\lambda)\} \\ &= \frac{k}{\mathfrak{A}} \sum_{\lambda} [\{a_0(\lambda) - a(\lambda)\} \log a_0(\lambda) - a(\lambda) \log \{a(\lambda)/a_0(\lambda)\}]. \end{aligned}$$

$$\begin{aligned} \text{Now } \sum_{\lambda} \{a_0(\lambda) - a(\lambda)\} \log a_0(\lambda) &= \sum_{\lambda \lambda'} p(\lambda, \lambda') \{a_0(\lambda) - a_0(\lambda')\} \log a_0(\lambda) \\ &= \frac{1}{2} \sum_{\lambda \lambda'} p(\lambda, \lambda') \{a_0(\lambda) - a_0(\lambda')\} \log \frac{a_0(\lambda)}{a_0(\lambda')} \geq 0 \end{aligned}$$

$$\begin{aligned} \text{and } -\sum_{\lambda} a(\lambda) \log \frac{a(\lambda)}{a_0(\lambda)} &\geq \sum_{\lambda} a(\lambda) \left\{ \frac{a(\lambda)}{a_0(\lambda)} - 1 \right\} \\ &= \sum_{\lambda} \left[\{a(\lambda) - a_0(\lambda)\} + \frac{\{a(\lambda) - a_0(\lambda)\}^2}{a_0(\lambda)} \right] \geq 0, \end{aligned}$$

since $\sum_{\lambda} a(\lambda) = \sum_{\lambda} a_0(\lambda)$. Hence $\mathfrak{S} - \mathfrak{S}_0 \geq 0$ for all time.