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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) · P.O. B. 586 · MIRAMARE · STRADA COSTIERA 11 · TELEPHONES: 224281/2/3-4/5-6
CABLE: CENTRATOM · TELEX 460392-I

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DESCRIPTION OF THE LIQUID STATE
(Lectures III & IV)

G.H.A. COLE
Department of Physics
University of Hull
England

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LECTURE 3

STATISTICAL THEORIES OF LIQUIDS: EQUILIBRIUM

Once it is recognised that the liquid is composed of atoms and molecules the question arises of the relationship between the observed macroscopic bulk properties of the liquid and the collective properties of the enormous numbers of atoms and molecules in simultaneous interaction. The statistical theory of liquids has been developed in an attempt to answer this question. We shall be primarily (though not entirely) concerned with classical liquids in planetary science and so will concentrate on classical statistical theory.

The enormous number of particles involved has led to the use of statistical methods in classical physics as an expedient; the use of statistical methods in quantum physics is, of course, a matter of principle.

It must be recognised immediately that the development and general application of the statistical theory to real liquids is far less complete than for the macroscopic theory considered in the last lecture. The reason is partly mathematical but the central difficulty is largely associated with the physics involved. The essential stumbling block of the statistical theory is that of accounting for the simultaneous motion of a very large number of interacting particles. Progress has been most pronounced where the interaction is in a special sense weak (the dilute gas) or has a simplifying periodicity (crystalline solids).

The subject has a vast literature with a variety of approaches. We select here a particular approach which is based on the rigorous

arguments of statistical mechanics and which also can be expected to be appropriate for application to a simple liquid.

3.1. Fluctuations of Physical Quantities

The known fluctuations in the magnitudes of measured macroscopic physical quantities give evidence for the atomic constitution of matter.

3.1.1. A small volume: the fluid point.

A volume V of matter of mass M and macroscopic mass density contains $N = M/A m_p$ atoms where each atom contains A nucleons each of mass m_p . The number n of atoms per unit volume is $n = N/V = \rho/A m_p$. A small volume dV contains $dn = (\rho/A m_p) dV$ atoms. This number decreases with the size of the volume but remains extremely large even for the smallest macroscopic volumes. As an example if $\rho = 10^3 \text{ kg m}^{-3}$ (typical of much of condensed matter) and $A = 30$ (typical of the constituents of silicates) then, with $m_p = 1.6 \times 10^{-27} \text{ kg}$, $n = 2 \times 10^{28}$ atoms per cubic metre. For the macroscopic insignificant volume (essentially a point) of linear dimension 10^{-6} m (cubic micron) $dn = 10^9$ and the collective effect of so large a number of atoms will be indistinguishable in the mean from that of the whole. This is the resolution at the atomic level of the concept of the macroscopic fluid point.

3.1.2. Thermodynamic fluctuations.

The number of atoms in a given fixed volume of matter will change with time and the change will be larger the larger the atomic motion (that is the higher the temperature). A knowledge of the fluctuations in the macroscopic properties of a small volume allows an estimate to be made of the degree of random atomic agitation.

The fluctuations can be expressed either in terms of the

changing number (with the time) of atoms in a small volume of fixed size or alternatively as the changing volume occupied by a chosen number of atoms. In terms of thermodynamics it is necessary to account for fluctuations in the volume V , pressure P , temperature T or entropy S characterising the small volume.

Thermodynamics associates such rearrangements with the expenditure of energy in the form of work. If R is the minimum work necessary to produce a given fluctuation in the small volume the probability w that this fluctuation will occur is written

$$R = -kT \ln w \quad (1)$$

for the temperature T , k being the Boltzmann constant.

From the 1st and 2nd laws of thermodynamics the minimum energy R for a fluctuation is related to the internal energy U , entropy and pressure by

$$R = \Delta U - T \Delta S + P \Delta V. \quad (2)$$

But $U = U(S, V)$ so, for small fluctuations

$$2R = [\Delta S \cdot \Delta T - \Delta P \cdot \Delta V]. \quad (3)$$

Two separate cases must be recognised - one with S and P as independent variables and the other with T and V as independent variables.

3.1.2.1. S and P as independent variables.

In this case $T = T(S, P)$ and $V = V(S, P)$ and

$$\begin{aligned} \Delta V &= -V \chi_S \Delta P + (\partial V / \partial P)_S \Delta S \\ \Delta T &= (T/C_P) \Delta S + (\partial T / \partial P)_S \Delta P. \end{aligned} \quad (4)$$

Here $\chi_S = - (1/V)(\partial V / \partial P)_S$ is the adiabatic compressibility (the inverse is the adiabatic bulk modulus K_S) and C_P is the specific heat capacity at constant pressure. We have also used the thermodynamic relation $(\partial V / \partial S)_P = (\partial T / \partial P)_S$. The minimum work R is obtained by

substituting (4) into (3) to obtain

$$2R = [(T/C_P)(\Delta S)^2 + V \chi_S (\Delta P)^2]. \quad (5)$$

The probability for the occurrence of the fluctuation then follows by inserting (5) into (1) to give a Gaussian distribution for the two statistically independent variables. This can be used to find the mean square deviations for entropy and pressure in the form

$$\begin{aligned} \langle (\Delta S)^2 \rangle &= kC_P \\ \langle (\Delta P)^2 \rangle &= kT/V \chi_S. \end{aligned} \quad (6)$$

Apparently the mean square fluctuation of the entropy is proportional to the specific heat at constant pressure while the mean square fluctuation of the pressure is proportional to the adiabatic bulk modulus.

3.1.2.2. T and V as independent variables.

The same arguments can be applied again to obtain the expression for the minimum work for a fluctuation

$$2R = [(C_V/T)(\Delta T)^2 + V \chi_T (\Delta V)^2] \quad (7)$$

in place of (5) with C_V the specific heat capacity at constant volume and χ_T is the isothermal compressibility. The mean square deviations for the temperature and volume are then found to be

$$\begin{aligned} \langle (\Delta T)^2 \rangle &= kT^2/C_V \\ \langle (\Delta V)^2 \rangle &= kT/V \chi_T. \end{aligned} \quad (8)$$

The mean square deviation of the temperature fluctuation is proportional to the specific heat capacity at constant volume while the mean square deviation for the volume fluctuation is proportional to the isothermal bulk modulus K_T .

These formulae allow us to get some preliminary indication of the level of thermal motion in a liquid. The compressibilities (and so their bulk moduli) of liquids are very similar: they all lie between

10^8 and 10^{10} N m^{-2} with the majority being about 10^9 N m^{-2} . The compressibility (both isothermal and adiabatic) increases on melting. This implies a similarity between the pressure fluctuations and the volume fluctuations throughout the liquid range and that these fluctuations are larger than for a solid. Again, C_p decreases on melting while C_v increases consistent with an increasing entropy and an increasing temperature fluctuation on melting. These factors suggest a greater atomic motion in a liquid than in a solid. Similar arguments lead to the conclusion that the atomic freedom in a gas is greater than in a liquid. The atomic arrangement is the crucial difference between the three states of matter.

3.2. Energy and the Macroscopic States of Matter

The state of any volume of macroscopic matter is represented by a collection of N atoms contained within a volume V . The number of atoms (particles) per unit volume $n = N/V$. The total energy E of the system is the sum of a kinetic part (describing the particle motion) and a potential part (describing the interparticle force, assumed represented by a potential function $\Psi(1,2,3,...N)$;

$$E = \sum p_j^2/2m + \Psi(1,2,3,...N). \quad (9)$$

The three idealised states of matter reflect the three possible results of the comparison between the kinetic and potential energies.

3.2.1. Kinetic energy \gg potential energy.

The total kinetic energy is greater than the total potential energy when the particle number density is small and the average distance between the particles is large. Each particle is outside the range of interaction with neighbours most of the time, travelling in a straight line between collisions. Expressed another way, the time τ_c for a collision is very small compared with the time τ_f between

collisions.

Momentum and energy are exchanged between particles during a collision and it is through this interaction that the gas reaches a state of thermodynamic equilibrium. If L is the mean distance between particles and σ the radius of each particle, the number density n is related to the close-packed density n_c by $n = n_c(\sigma/L)^3$ for $L \gg \sigma$. As an example, for $L \sim 10^{-8} \text{ m}$, $n \sim 10^{-3} n_c$ which is typical of many laboratory situations. The freedom of the particles is consistent with a low mean density and high compressibility (low bulk modulus).

The full theory was developed by Boltzmann following the earlier work by Maxwell. Each collision is supposed to involve a representative pair of particles, the simultaneous interaction between three or more particles being too rare an event to take into account. Each particle enters the collision with a random velocity and after the collision moves to infinity without further collisions. Each collision is characterised by a large change of particle momentum $\Delta p \gg 1$. On this basis the distribution of velocities is determined by solving a non-linear integro-differential equation first enunciated by Boltzmann. The solution of this equation for a realistic potential has proved the major mathematical problem of the theory.

The situation is somewhat different for a plasma immersed in a magnetic field. Here the interaction between the (now charged) particles is through the electromagnetic field independently of the particle collisions. It is, then, possible for the plasma to reach thermodynamic equilibrium through the action of the electromagnetic field alone, without collisions, the system forming a collisionless plasma.

3.2.2. Potential energy \gg kinetic energy.

The other extreme of highest density, when the particles are sufficiently close together because the potential energy dominates the kinetic energy, is found in solids. There may be "clumps" of particles but all the particles can be involved simultaneously and so form a lattice structure throughout the material. Then the collective energy is such that the outer electrons are shared between all the atoms forming at most lightly interacting electron gas throughout the volume. The close packing of the particles accounts for the high mass density and low compressibility (high bulk modulus). The free electron gas accounts for the high electrical conductivity.

The ions forming the lattice are free to vibrate about the equilibrium positions (which formally mark the lattice sites) but some diffusive movement is possible. The development of these ideas requires the use of quantum mechanics but the general form of the model is clear.

3.2.3. Kinetic energy \sim potential energy.

The intermediate case is the model for the liquid. The atoms are closely bound together but not so closely as to form a spatial lattice structure. They are free to move but only in a restricted volume or cell and remain in the vicinity of a particular equilibrium position for considerable periods of time. The particle motion is random within the cell around a 'lattice' site but the lattice sites are not fixed. Particle diffusion is therefore easier than in a solid. There is only limited resistance to reorientation of neighbouring atoms and here the material behaves as a fluid.

That the atoms are constrained together accounts for the mass density comparable to that for a solid, and for the low

compressibility. Because the conditions are not dissimilar from one liquid to another the compressibility (and so the bulk modulus) is similar for all liquids. It is possible for free electrons to engulf the liquid ions and liquid metals are possible under particular circumstances.

This general model shows how a liquid will have some properties similar to a solid (where the potential energy dominates) but others where instead the kinetic energy dominates) similar to a gas. From a theoretical point of view the comparable importance of the kinetic and potential energies presents considerable mathematical difficulties for a calculation of macroscopic properties particularly when associated with a realistic interparticle potential function. The physics is a cure for a liquid in equilibrium and the problems are entirely mathematical. For a liquid not in equilibrium the physics itself is still open to some doubt. Because the overwhelming number of liquids met with in planetary problems are classical we shall concentrate on the classical theory.

Computer simulation of liquid problems has developed as an important aspect of the study of liquids over the last two decades. This approach has confirmed the general ideas outlined above but has not so far made a significant contribution to the specification of the model for a liquid.

3. General Formulation: The Liouville Equation

The state of a system of particles in classical mechanics is defined by specifying the phase (both the momentum \underline{p} of each particle and its location \underline{r} in space). The large number of particles involved with even the smallest volume of macroscopic matter makes it unavoidable to appeal to statistical arguments.

3.3.1. Phase and Configuration Distribution Functions.

Suppose a macroscopic volume V contains N particles. The probability $f^{(N)}$ that at the time t a representative particle (suppose particle j) will be found to have the phase $\underline{p}_j, \underline{r}_j$ within the small phase volume $d\underline{p}_j d\underline{r}_j$ is written

$$f^{(N)}(\underline{p}^{(N)}, \underline{r}^{(N)}, t) d\underline{p}^{(N)} d\underline{r}^{(N)} \quad (10)$$

where

$$\begin{aligned} \underline{p}^{(N)} &= p_1 p_2 p_3 \dots p_N \\ \underline{r}^{(N)} &= r_1 r_2 r_3 \dots r_N \\ d\underline{p}^{(N)} &= dp_1 dp_2 dp_3 \dots dp_N \\ d\underline{r}^{(N)} &= dr_1 dr_2 dr_3 \dots dr_N \end{aligned} \quad (11)$$

This the maximum information that can be available to describe the phase of the system of particles.

Unwanted phase information can be integrated away to provide reduced distribution functions. Thus, for a sub-group of n ($< N$) atoms the phase is described by the n -th order phase distribution function

$$f^{(n)}(\underline{p}^{(n)}, \underline{r}^{(n)}, t) = \int \dots \int f^{(N)}(\underline{p}^{(N)}, \underline{r}^{(N)}, t) d\underline{p}^{(N-n)} d\underline{r}^{(N-n)} \quad (12)$$

using an obvious notation.

The phase distribution is finally reduced to a configuration distribution $n^{(N)}$ by integrating over all the momenta; for the n -th order distribution

$$n^{(n)}(\underline{r}^{(n)}, t) = \int \dots \int f^{(N)}(\underline{p}^{(N)}, \underline{r}^{(N)}, t) d\underline{p}^{(N)} d\underline{r}^{(N-n)}. \quad (13)$$

These distributions provide the basic descriptive tools for the calculation of liquid properties.

3.3.2. The Liouville Equation.

The relation between the distribution functions and the properties of the atoms, which is the heart of the statistical theory, is derived by making an appeal to the general equation of balance (7)

of Lecture 2 but now in phase space. For this we set $q = f^{(N)}$, $\underline{J} = \dot{\underline{p}} f^{(N)} + \dot{\underline{r}} f^{(N)}$ and, because probability is conserved, $\dot{\Phi} = 0$. Then

$$\text{div } \underline{J} = \sum_{j=1}^N \left\{ \dot{\underline{r}}_j \cdot \frac{\partial f^{(N)}}{\partial \underline{r}_j} + \dot{\underline{p}}_j \cdot \frac{\partial f^{(N)}}{\partial \underline{p}_j} \right\}$$

and (2.7) takes the form

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{j=1}^N \left\{ \frac{\dot{\underline{p}}_j}{m} \cdot \frac{\partial f^{(N)}}{\partial \underline{r}_j} + \dot{\underline{p}}_j \cdot \frac{\partial f^{(N)}}{\partial \underline{p}_j} \right\} \quad (14)$$

because $\dot{\underline{r}}_j = \underline{p}_j/m$ where m is the mass of each particle.

According to Newton's second law of motion

$$\dot{\underline{p}}_j = \underline{F}_j = - \frac{\partial \Psi(1,2,\dots,N)}{\partial \underline{r}_j} \quad (14a)$$

where $\Psi(1,2,3,\dots,N)$ is the total potential energy of atomic interaction. Then (14) reduces to

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{j=1}^N \left\{ \frac{\underline{p}_j}{m} \cdot \frac{\partial f^{(N)}}{\partial \underline{r}_j} + \frac{\partial \Psi}{\partial \underline{r}_j} \cdot \frac{\partial f^{(N)}}{\partial \underline{p}_j} \right\} \quad (15)$$

which is the Liouville equation.

Reduced forms of this equation are obtained by integrating over unwanted phase variables. The utility of this depends entirely on the form of the interaction potential. As an example, for a dilute gas interest is with the movement of single atoms with pair collisions and the singlet distribution $f^{(1)}$ is a sufficient specification. In this case the Liouville equation is rearranged to form the Boltzmann equation. An analogous reduction is possible for simple liquids where

the distribution of pairs of atoms in space is a sufficient specification of the structure (see Serction 3.4)

3.3.3. A Formal Solution.

The Liouville equation is written in operator form by introducing the Hermitian Liouville operator

$$\hat{L} = -i \sum_{j=1}^N \left\{ \frac{\hat{p}_j}{m} \cdot \frac{\partial}{\partial \mathbf{r}_j} + \mathbf{F}_j \cdot \frac{\partial}{\partial \mathbf{p}_j} \right\} \quad (16)$$

Then (15) becomes alternatively

$$i \frac{\partial f^{(N)}}{\partial t} = -\hat{L} f^{(N)}. \quad (17)$$

This is of a similar mathematical form to the Schrödinger equation of wave mechanics.

(17) has the formal solution

$$f^{(N)}(t) = \exp \{-i \hat{L} t\} f^{(N)}(0). \quad (18)$$

If the interparticle forces are specified this expression can be evaluated and has the form of a Bromwich integral. In practice this has no other the formal interest because the integral cannot be directly evaluated.

THERMODYNAMIC EQUILIBRIUM

3.4. Arrangement of Atoms in Space

Experimental studies of the diffraction of X-rays and thermal neutrons by bulk liquids can be interpreted in terms of a radial distribution function $g^{(2)}(r)$ specifying the distance of neighbours from a chosen atom as the centre.

Explicitly, the number dn of atoms in a shell of thickness dr and radius r about any atom as centre is written

$$dn = 4\pi r^2 g^{(2)}(r) dr n \quad (19)$$

and $g^{(2)}(r)$ is open to experimental determination. For the N atoms contained within the volume V

$$N = 4\pi \int_0^\infty n g^{(2)}(r) r^2 dr.$$

Angular dependencies can be introduced into $g(r)$ to form a pair distribution $g^{(2)}$ which is related to the general configurational pair distribution by

$$n^{(2)}(1,2) = n^2 g^{(2)}(1,2). \quad (20)$$

In terms of the potential of the force

$$n^2 g^{(2)}(1,2) = [1/(N-2)!] \iint \exp\{-\Phi(1,2,3,\dots,N)/kT\} d\mathbf{r}_3 \dots d\mathbf{r}_N \quad (21)$$

For the n -th order distribution

$$n^n g^{(n)}(1,2,3,\dots,n) = [1/(N-n)!] \iint \exp\{-\Phi(1,2,3,\dots,N)/kT\} d\mathbf{r}_{n+1} \dots d\mathbf{r}_N \quad (22)$$

so that

$$g^{(2)}(1,2) = [n/(N-n)!] \int_V g^{(3)}(1,2,3) d\mathbf{r}_3. \quad (23)$$

It will be realised that the factor $n/[(N-n)!] \rightarrow 1/V$ for $n \ll N$. These are general relations we will need later.

For a lattice arrangement of atoms, as in a crystal, $g(r)$ will be a distribution of delta functions. For a liquid the corresponding pattern is a series of diffuse rings corresponding to nearest, next nearest, and so on, neighbours. Generally, the number of nearest neighbours is fewer than 12.

The radial distribution is related to the molecular motion in the liquid through the concept of the potential $\Phi(r)$ of the mean

pair force in the presence of the remaining atoms. We write

$$\bar{\Phi}(r) = -kT \ln g^{(2)}(r) \quad (24)$$

and assume the gradient of this potential to determine the force on the pair in the presence of neighbours. This formula is extended in an obvious way to include the interaction between more than two particles.

The difference between the potentials of the mean and actual pair forces can be used to define a new useful function $y(r)$ of the pair separation distance r . Thus

$$\exp\{-[\Psi(r) - \bar{\Phi}(r)]/kT\} = g^{(2)}(r) \exp\{\Psi(r)/kT\} = y(r). \quad (25)$$

This function will prove useful later.

3.5. Formal link with Thermodynamics

The micro- and macro- worlds are linked by identifying the free energy of Helmholtz F (macroscopic quantity) with the normalised partition function Z (microscopic quantity, normalising the n -th order phase distribution function). Explicitly

$$F(V, T, N) = -kT \ln Z(V, T, N), \quad (26)$$

where

$$Z(V, T, N) = \Lambda^{3N} Z_r(V, T, N) \quad (27)$$

$$\Lambda^2 = h^2/2mkT$$

$$Z_r = 1/N! \int \exp\{-(1,2,3,\dots,N)/kT\} d\mathbf{r}^N.$$

is called the thermal wavelength.

Once Z_r is known as function of volume, temperature and number of particles the free energy can be calculated.

3.5.1. Various Formulae of Thermodynamics.

From the macroscopic point of view

$$F = U - TS + \mu N \quad (28)$$

where U is the internal energy, S the entropy and the chemical potential. Also

$$TdS = dU + PdV + \mu dN. \quad (29)$$

Various formulae follow immediately. Thus

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}, \quad S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}, \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}$$

$$U = F - T\left.\frac{\partial F}{\partial T}\right|_{V,N} = -T^2\left.\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right|_{V,N}$$

$$F = -kT \ln Z_r(N) + NkT \left(\ln N + \frac{3}{2} \ln \Lambda - 1\right) \quad (30)$$

$$H_e = -T^2\left.\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right|_V - V\left.\frac{\partial F}{\partial V}\right|_T,$$

where H_e is the enthalpy or total heat. Also

$$C_v = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_V \quad (31)$$

$$C_p = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_P + T\left(\frac{\partial^2 F}{\partial T \partial V}\right)\left.\frac{\partial V}{\partial T}\right|_P$$

Various coefficients also follow immediately. If Ψ_e is the isothermal enthalpy pressure coefficient, μ_T the Joule-Thomson coefficient,

the isothermal compressibility and c_s the speed of sound we have

$$\varphi_F = V + T \left(\frac{\partial^2 F}{\partial V \partial T} \right) \left(\frac{\partial^2 F}{\partial V^2} \right)^{-1}$$

$$\mu_T = T \left\{ \left(\frac{\partial^2 F}{\partial V \partial T} \right) + V \frac{\partial^2 F}{\partial V^2} \right\} / T \left\{ \frac{\partial^2 F}{\partial V^2} \frac{\partial^2 F}{\partial T^2} - \left(\frac{\partial^2 F}{\partial V \partial T} \right)^2 \right\} \quad (32)$$

$$K = V \left(\frac{\partial^2 F}{\partial V^2} \right)^{-1}$$

$$c_s^2 = V^2 \left\{ \frac{\partial^2 F}{\partial V^2} \frac{\partial^2 F}{\partial T^2} - \left(\frac{\partial^2 F}{\partial V \partial T} \right)^2 \right\} \left(\frac{\partial^2 F}{\partial T^2} \right)^{-1}$$

Finally, the Gibbs free energy G is given by

$$G = F + PV = F - V \left. \frac{\partial F}{\partial V} \right|_{T,N} = -V^2 \frac{\partial}{\partial V} (F/V). \quad (33)$$

These various formulae lead to various other thermodynamic relations such as

$$\frac{\partial}{\partial V} \left(\frac{U}{T^2} \right) \Big|_T = \frac{\partial}{\partial T} \left(\frac{P}{T} \right) \Big|_V \quad (34)$$

which can act as checks of consistency of calculations.

It is seen that once the configurational partition function has been evaluated and $F(V, T, N)$ determined all the thermodynamic functions can be calculated directly from the formulae of the theory. The central problem is the evaluation of Z_T .

The problem is simplest for a dilute gas with pair interaction forces when the integration becomes

$$Z_T = \left[\int \exp\{-\psi(r)/kT\} d\mathbf{r} \right]^N \quad (35)$$

for spherical atoms. The problem is also tractable for a crystalline solid where the potential function has the symmetry of the crystal

lattice. No special assumptions can be used for evaluating the configurational partition function for a liquid.

3.5.2. Thermodynamics and the Pair Distribution.

For a simple liquid with pair interaction forces

$$\Psi(1,2,3,\dots,N) = \sum_{i,j} \psi(i,j) \quad (36)$$

we can introduce the pair distribution. Thus we find for the internal energy u per unit volume ($= U/V$)

$$u = 3nkT/2 + (n^2/2) \int g^{(2)}(r) \psi(r) d\mathbf{r}. \quad (37)$$

The pressure P is given by

$$P = nkT - (n^2/6) \int g^{(2)}(r) (\mathbf{r} \cdot \text{grad } \psi(r)) d\mathbf{r}. \quad (38)$$

The fluid compressibility is found in the form

$$k_B T \frac{\partial n}{\partial P} \Big|_T = 1 + n \int_0^\infty h(r) d\mathbf{r} \quad (39)$$

where $h(r) = [g^{(2)}(r) - 1]$ is called the total correlation function. It is used to define a direct correlation function $c(r)$ according to the Ornstein-Zernicke relation

$$h(1,2) = c(1,2) + n \int c(2,3) h(1,3) d\mathbf{r}. \quad (40)$$

Integrating this expression over the separation distance between particles 1 and 2 and using the compressibility formula gives

$$\frac{1}{k_B T} \frac{\partial P}{\partial n} \Big|_{T,N} = 1 - 4\pi n \int_0^\infty c(r) r^2 dr \quad (41)$$

which is closely related to the expression for the liquid bulk modulus.

It is often expedient to introduce a reduced coupling between the particles: for reduced coupling of the particle 1 we write

$$\Psi(1,2,\dots,N) = \xi \sum_{i>2}^N \psi(1,i) + \sum_{i,j>2}^N \psi(i,j) \quad (42)$$

where ξ is a coupling parameter that can take any value between 0 and

1. Then the chemical potential can be calculated from

$$\mu = \ln(n\Lambda^3) + \frac{n}{k_B T} \int_0^\infty d\xi \int_0^\infty \psi(r) g^{(1)}(r, \xi) dr. \quad (43)$$

These various formulae can be extended to include others so the full thermodynamics of the liquid can be calculated once the pair distribution function is known. This now becomes the central problem of the theory.

3.6. Determination of the Pair Distribution

The expression (21) for the pair distribution cannot be evaluated directly due to the very large number of particles involved. The modified form (23) can be used only if $g^{(3)}$ is known but this is not so. Progress can be made either by rearranging the theory of by introducing an approximation, or perhaps both.

3.6.1. Kirkwood Superposition Approximation.

The most elementary approximation is to accept the basic pair nature of the interaction between three atoms as a method of deducing a closure approximation. Regarding the mean potential of the force for a triplet of particles to be the sum of the pair potentials of the constituent pairs we write

$$\Phi(1,2,3) = \Phi(1,2) + \Phi(2,3) + \Phi(1,3).$$

In terms of the distribution functions

$$g_K^{(3)}(1,2,3) = g^{(2)}(1,2)g^{(2)}(1,3)g^{(2)}(2,3) \quad (44)$$

which is the famous Kirkwood superposition approximation. The insertion of (44) into (23) provides a statement which is false so

(44) is not a suitable closure expression as it stands.

The exact triplet function can be written

$$g^{(3)}(1,2,3) = g_K^{(3)}s^{(3)}(1,2,3) \quad (45)$$

where $s^{(3)}$ is a correcting triplet correlation. The Kirkwood approximation amounts to setting $s^{(3)} = 1$. We shall return to this point later.

3.6.2. The BGYKB Equation.

The Kirkwood closure approximation has been used with the actual separation of a pair of particles but it may be more acceptable in equations concerned with the effects of changes in the pair separation. The association can then be made to the mean potential of the force acting on each particle of the pair. Such an equation is obtained by differentiating (21) with respect to the pair separation distance r . The result is

$$\frac{\partial g^{(1)}(r)}{\partial r} + \frac{1}{k_B T} \frac{\partial \psi(r)}{\partial r} g^{(1)}(r) = -\frac{n}{k_B T} \int_V \frac{\partial \psi(r_{12})}{\partial r_{12}} g^{(1)} d\mathbf{r}_2 \quad (46)$$

an equation given independently by Born and Green, Yvon, Kirkwood and Bogoliubov some 40 years ago. The boundary condition $g^{(2)}(1,2) \rightarrow 1$ as $r_{12} \rightarrow \infty$ applies. The equation may be extended to involve the triplet distribution $g^{(3)}(1,2,3)$ but the quadruplet distribution $g^{(4)}(1,2,3,4)$ is also involved. The basic equation can be extended further to include also the triplet force interaction $\phi(1,2,3)$ and the form is then

$$\begin{aligned} \frac{\partial g^{(1)}(r)}{\partial r} + \frac{1}{k_B T} \frac{\partial \psi(r)}{\partial r} g^{(1)}(r) \\ = -\frac{n}{k_B T} \int_V g^{(3)}(1,2,3) \frac{\partial}{\partial r_{12}} \{ \psi(r_{12}) + \phi(1,2,3) \} d\mathbf{r}_2 \end{aligned} \quad (47)$$

$$-\frac{n^2}{k_B T} \int_V g^{(4)}(1,2,3,4) \frac{\partial}{\partial r_{13}} \phi(1,3,4) dr_3 dr_4$$

$$-\frac{n^3}{k_B T} \int_V g^{(5)}(1,2,3,4,5) \frac{\partial}{\partial r_{13}} \phi(3,4,5) dr_3 dr_4 dr_5.$$

The use of the triplet force potential leads to the introduction of further lower order distribution functions.

The association with the mean force follows immediately from (46). The first term on the lefthand side is the mean force on the particle pair while the second term is the force due to the direct interatomic interaction. The right hand side of the equation describes the indirect force on the pair due to interaction with the remaining particles of the system, taking particle 3 as representative.

3.6.3. Second Order Equation.

The second derivative of a function is a measure of the deviation about the local mean. This is also associated with change in the mean force with changing separation distance. A second order equation follows by differentiating (46) again with respect to the separation distance. The result as derived by Cole is

$$\frac{\partial^2 g^{(2)}(1,2)}{\partial r_{12}^2} + A(1,2) \frac{\partial g^{(2)}(1,2)}{\partial r_{12}} + B(1,2) g^{(2)}(1,2) = D(1,2)$$

$$A(1,2) = \frac{2}{k_B T} \frac{\partial \psi(1,2)}{\partial r_{12}} \quad (48)$$

$$B(1,2) = \frac{1}{k_B T} \frac{\partial^2 \psi(1,2)}{\partial r_{12}^2} + \left(\frac{1}{k_B T} \right)^2 \left(\frac{\partial \psi(1,2)}{\partial r_{12}} \right)^2$$

$$D(1,2) = -n/k_B T \int dr_3 \left[\left\{ \frac{\partial^2 \psi(1,3)}{\partial r_{12}^2} - \left(\frac{\partial \psi(1,3)}{\partial r_{12}} \right)^2 \right\} g^{(3)}(1,2,3) \right. \\ \left. - n \int \frac{\partial \psi(1,3)}{\partial r_{12}} \frac{\partial \psi(1,4)}{\partial r_{12}} g^{(4)}(1,2,3,4) dr_4 \right]$$

Here $g^{(4)}$ is involved as well as $g^{(3)}$. This equation is reduced to one involving only $g^{(2)}$ by invoking a closure approximation.

3.6.4. Dependence on Density and Temperature.

The dependence of $g^{(2)}$ on the number density n is described by the exact equation involving $g^{(2)}$ but not higher order correlations such as $g^{(3)}$ (very rare in the theory!) first given by Schofield.

$$\frac{\partial}{\partial n} \ln g^{(2)}(1,2) = \frac{\int [g^{(3)}(1,2,3)/g^{(2)}(1,2) - 1] dr_3 - 2 \int h(r) dr}{1 + n \int h(r) dr} \quad (49)$$

This is not so for the temperature dependence where once again the higher order distributions are involved. Explicitly

$$k_B T^2 \frac{\partial g^{(2)}}{\partial T} = \left[\sum_{i=1}^2 \left\{ \sum_{j>i} \psi(i,j) g^{(2)} + n \int g^{(3)}(i,2,3) \psi(i,3) dr_3 \right\} \right. \\ \left. + \frac{n^2}{2} \int \left\{ g^{(4)} - g^{(2)} g^{(2)}(3,4) \right\} dr_3 dr_4 \right] \\ - \frac{\partial}{\partial n} (n^2 g^{(2)}) \left[\int g^{(2)}(r) \psi(r) dr \right. \\ \left. + \frac{n}{2} \int \left\{ g^{(3)}(1,2,3) - g^{(2)}(1,2) \right\} \psi(1,2) dr_2 dr_3 \right].$$

3.7. Closure Procedures

The possibility of constructing explicit expressions for $S^{(n)}(1,2,3,\dots,n)$ has been explored and formulae obtained. One method is using the approach of functional differentiation has been used by Cole. As an example for the triplet correlation to the first order in the number density, and with $f(r) = \exp\{-\psi(r)/kT\} - 1$

$$S^{(3)}(1,2,3) = 1 + n \int f(1,4) y(1,4) T_1(2,3,4) dr_4 \quad (50)$$

where

$$T_1 = [g^{(3)}(1,2,3)/g^{(2)}(2,3)] - g^{(2)}(2,4) - g^{(2)}(3,4) + 1$$

$g^{(3)}$ appears in this expression and an obvious iterative procedure

is appropriate in which the Kirkwood form $s^{(3)} = 1$ is first inserted and then continually corrected.

To the second order of the density it is found that

$$s^{(3)}(1,2,3) = 1 + n \int f(1,4)y(1,4)T_1(2,3,4)d\mathbf{r}_4 + n^2 \int f(1,4)f(1,5)y(1,4)y(1,5)T_2(2,3,4,5)d\mathbf{r}_4 d\mathbf{r}_5 \quad (51)$$

where

$$T_2 = \frac{1}{2} \frac{g^{(4)}(2,3,4,5)}{g^{(2)}(2,3)} - \frac{g^{(2)}(2,3,4)g^{(2)}(2,5)}{g^{(2)}(2,3)} - \frac{g^{(2)}(2,3,4)g^{(2)}(3,5)}{g^{(2)}(2,3)} - \frac{g^{(2)}(2,3,4)g^{(2)}(4,5)}{g^{(2)}(2,3)} - \frac{1}{2}g^{(2)}(2,4,5) + 2 \frac{g^{(2)}(2,3,4)}{g^{(2)}(2,3)} + g^{(2)}(2,5)g^{(2)}(2,4) + g^{(2)}(3,5)g^{(2)}(2,4) + g^{(2)}(4,5)g^{(2)}(2,4) + g^{(2)}(3,4)g^{(2)}(4,5) + g^{(2)}(3,4)g^{(2)}(3,5) - 2g^{(2)}(2,4) - 2g^{(2)}(3,5) - \frac{1}{2}g^{(2)}(4,5) + 1.$$

The function $g^{(4)}$ appears now and this can be found by an analogous expansion in powers of n . Then

$$s^{(4)} = 1 + n \int f(1,5)T_3(1,2,3,4,5)\exp\{\psi(1,5)/kT\}d\mathbf{r}_5 \quad (52)$$

with

$$T_3 = \frac{g^{(3)}(1,2,5)g^{(3)}(1,3,5)\Theta_3}{g^{(2)}(1,2)g^{(2)}(1,3)g^{(2)}(4,5)g^{(2)}(2,5)g^{(2)}(3,5)}$$

and

$$\Theta_3 = \frac{g^{(4)}(2,3,4,5)}{g^{(2)}(2,3,4)} - \frac{g^{(2)}(2,3,5)}{g^{(2)}(2,3)} - \frac{g^{(2)}(3,4,5)}{g^{(2)}(3,4)} - \frac{g^{(2)}(2,4,5)}{g^{(2)}(2,4)} + g^{(2)}(4,5) + g^{(2)}(3,5) + g^{(2)}(2,5) - 1.$$

These are complicated and cumbersome formulae and well exemplify the difficulties of applying the theory to even the simplest liquids.

Tests of the formulae at liquid densities have not been applied but tests have been applied for a gas of low density. The approach involves the calculation of the virial coefficients and the formulae are able to provide exact expressions for these coefficients. The summation to liquid densities is not possible.

3.8. Other Theories

The BGYKB equation (46) and using the Kirkwood superposition approximation has been shown by Rushbrooke to be integrable in the form

$$\ln\{y(r)\} = n \int_V c(2,3)h(1,3)d\mathbf{r}_3, \quad (53)$$

where

$$c(r) = (1/kT) \int_0^\infty ds g^{(2)}(s) d\psi(s)/ds.$$

Give $g^{(2)}(s)$ its asymptotic form unity: the integral can be evaluated to give

$$c(r) = h(r) - \ln\{y(r)\}. \quad (54)$$

Inserting this into the left hand side of (53) gives the Ornstein-Zernicke relation (40). This allows us to interpret $c(r)$ as the direct correlation function introduced through (40).

If (54) is introduced in to the right hand side of (53) we obtain the equation for $g^{(2)}$

$$\ln\{y(1,2)\} = n \int [h(2,3) - \ln\{y(2,3)\}]h(1,3)d\mathbf{r}_3 \quad (55)$$

which is the original form of the hypernetted chain equation.

Alternatively, if $\ln y(r) \approx y(r) - 1$ and

$$c(r) = f(r)y(r) \quad (56)$$

Inserting (54) into the right hand side of (53) gives instead the equation

$$\ln\{y(r)\} = f(1,2)y(1,2) + nh(2,3)f(1,3)y(1,3)dr_3 \quad (57)$$

which is the Percus - Yevick equation in its original form.

The Percus - Yevick and hypernetted chain approximations were originally introduced as methods of summing the diagrams for atomic interactions and so apply strictly to a dilute gas and not a liquid. The deductions given here are different and could be regarded as applying to liquid densities. The equations have been developed to include higher powers in the number density than the first (particularly by Verlet) and in our formulation can be associated with improved statements of the superposition (closure) approximation. There is little point setting the various possibilities down here without a thorough going comparison between the predictions of the theory and experimental data, but such a comparison has not so far been carried out.

3.9. An Inside-Out Approach

In applying the equation we have derived so far it has been assumed that the interparticle force potential is specified and the calculation is aimed at calculating $g^{(2)}$. The radial distribution function is accessible to experimental determination and then the formulae are available for the deduction of the pair potential function itself. This approach has been pioneered by March with an interesting comparison between the pair functions for argon and sodium. There could well be considerable scope in the future for such an approach to our problem.

3.10. Accounting For Atomic Movements

The arguments developed so far have not been concerned

explicitly with atomic motion and it is often convenient to consider this explicitly. Various arguments have been developed for this purpose and we consider these now.

3.10.1. Van Hove Correlation Function.

This is a generalised configurational distribution function written $G(\underline{r}, t)$. It is proportional to the probability of finding an atom at \underline{r}_2 at time t_2 given that an atom (which may be the same one but not necessarily so) as at \underline{r}_1 at time t_1 .

Let $f(p_2, \underline{r}_2, t_2; p_1, \underline{r}_1, t_1)$ be the probability of finding a molecule with phase (p_2, \underline{r}_2) at time t_2 given that a molecule had the phase (p_1, \underline{r}_1) at time t_1 . The corresponding configurational distribution is found by averaging over the momenta

$$G(\underline{r}, t) = \iint f(p_2, \underline{r}_2, t_2; p_1, \underline{r}_1, t_1) dp_2 dp_1 \quad (58)$$

where $\underline{r} = \underline{r}_2 - \underline{r}_1$ and $t = t_2 - t_1$. G has the dimensions of $1/V$ and is normalised to become equal to the average particle density n for the total system. This means $G(\underline{r}, t) \rightarrow n$ as $\underline{r} \rightarrow \infty$. The same limit is supposed to apply for an indefinitely large time interval when the two events become statistically independent. The alternative limit $t \rightarrow 0$ refers to conditions at two points at essentially the same time.

3.10.2. The Function $S(k)$.

The radial distribution is determined experimentally by processes which involve the transfer of momentum (photon or neutron) between the scattered "radiation" field and the atoms. For neutrons energy is transferred as well. If $I(k)$ is the intensity of the radiation of wave length λ scattered through the half angle θ , with $k = (4\pi/\lambda)\sin\theta$, and I_0 is the intensity of the incident radiation, the scattering function $S(k)$ is defined by

$$S(k) = I(k)/I_0 - 1. \quad (59)$$

Both $I(k)$ and I_0 are measures experimentally for a range of k to determine $S(k)$. The Fourier transform of $S(k)$ gives $g^{(2)}$ according to

$$g^{(2)}(r) = 1 + (1/8\pi^2 n) \int (S(k) - 1) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{k}. \quad (60)$$

Other information is available when $S(k)$ is known; thus the isothermal compressibility is given by

$$K_T = S(0)/nk_B T$$

where k_B is the Boltzmann constant.

For the scattering of thermal neutrons the energy transfer must also be accounted for. If $\mathbf{K} = \mathbf{k}_0 - \mathbf{k}$ is the change of wave number of the neutrons during a collision and the angular frequency $\omega = h/4\pi m(k_0^2 - k^2)$, the scattering function is defined by

$$S(\mathbf{K}, \omega) = 1/2 \iint \{G(\mathbf{r}, t) - n\} \exp[i(\mathbf{K} \cdot \mathbf{r} - \omega t)] d\mathbf{r} dt$$

with G being the van Hove function met with before. The radial distribution is obtained again by Fourier inverting this expression and time averaging the result.

The full range of $S(\mathbf{K}, \omega)$ has three distinctive component parts:

- i. the hydrodynamic limit. If L is the characteristic length of a molecular interaction lasting the time τ then $KL \ll 1$ and $\omega\tau \ll 1$. This is the situation in ordinary hydrodynamics where the atomic sub-structure is ignored.
- ii. very high frequencies. This is the alternative limit and $\omega\tau \gg 1$ for all K . The response of the liquid to all forces is virtually instantaneous and the static average of quantities is the appropriate description of the liquid structure.
- iii. between the two limits. This involves wavelengths in the range 10^{-11} to 10^{-9} m and frequencies in the range 10^{11} to 10^{13} s. These ranges are difficult to deal with theoretically but are well covered by the experimental studies of thermal neutron scattering.

LECTURE 4

STATISTICAL THEORIES OF LIQUID NON-EQUILIBRIUM

The arguments of the last lecture apply for a liquid in thermodynamic equilibrium and must be extended to include the various non-equilibrium conditions. The essential point now is that dissipative processes must be accounted for and conditions are not those of thermodynamic equilibrium.

4.1. The Atomic Distributions

The dynamic processes in a simple liquid are associated with thermally excited fluctuations of the local number of molecules. The most significant macroscopic properties of the liquid are proportional to the mean number of molecules which interact to form the average collective effect and this means that the number of molecules in any volume is of central importance for the calculation of physical properties. It was seen in the last lecture that the number of molecules in any volume as a function of the time is represented by the scattering function $S(\mathbf{k}, \omega)$ and so is open to experimental measurement.

The specification of the thermal motion of the molecules is made through the van Hove function. Let δn be the correlation function between two events with two separate components; first that the i -th molecule is situated at the point $\mathbf{r}_1 - \mathbf{r}_2$ at time $t = 0$, irrespective of whether or not there is a molecule located at the point \mathbf{r}_2 and second that the j -th molecule will be located at the point \mathbf{r}_2 at time $t = \tau$, irrespective of whether there is then a molecule located at the point $\mathbf{r}_1 - \mathbf{r}_2$. Although we distinguish between the i -th and j -th

molecules, we will allow the possibility of them in fact being the same molecule that has moved the distance $\underline{r}_1 - \underline{r}_2$ during the time τ . Then δn is expressed in the form

$$\delta(\underline{r} - \underline{r}_1(0)) \cdot \delta(\underline{r}_2 - \underline{r}_1(\tau)). \quad (4.1)$$

Extending this expression to cover all pairs of molecules and all possible locations for the vector \underline{r}_2 we obtain the van Hove function in the form

$$G(\underline{r}, \tau) = 1/N \sum_{i,j} \delta(\underline{r} + \underline{r}_i - \underline{r}_j) \quad (4.2)$$

account having been taken of the commutativity in classical physics.

The particle number density is then given by the expression

$$n(\underline{r}, \tau) = \sum_j \delta(\underline{r} - \underline{r}_j(\tau)) \quad (4.3)$$

so that (4.2) is transformed into the ensemble average

$$nG(\underline{r}, \tau) = \langle n(0,0)n(\underline{r}, \tau) \rangle. \quad (4.4)$$

After a large time interval the two particles are statistically independent so $G \rightarrow n$ as $\tau \rightarrow \infty$.

There are, then, two contributions to G , distinguished by whether $i = j$ or not. If $i = j$ we consider one molecule and consider the probability that it will move from \underline{r}_1 to \underline{r}_2 during the time τ . This is the self-correlation function written $G_s(\underline{r}, \tau)$. The second contribution is the distinct correlation and involves the two molecules 1 and 2, written $G_d(\underline{r}, \tau)$. We can therefore write

$$G(\underline{r}, \tau) = G_s(\underline{r}, \tau) + G_d(\underline{r}, \tau). \quad (4.5)$$

There are the limiting forms

$$G_s(\underline{r}, 0) = \delta(\underline{r}) \quad G_d(\underline{r}, 0) = ng^{(2)}(\underline{r}). \quad (4.6)$$

In this way they relate the dynamic correlations to the static singlet and pair correlation functions.

The calculation of the thermal fluctuations in a liquid are expressed in terms of the calculation of the structure factor S .

4.2. Irreversibility

It is assumed that the same molecular properties control the movement to equilibrium as control the equilibrium property itself. The equations of motion of individual molecules are reversible - the Hamiltonian energy function is not explicitly dependent on the time and is quadratic in the momenta. The collective properties of the molecules show the irreversible move to equilibrium which is a different behaviour. There is the problem of reconciling these two features of the collection of molecules. This apparent paradox took some time to resolve but the resolution has given insight into the process of irreversibility.

4.2.1. Recurrence of Initial Phases.

It was shown long ago by Poincaré that a conservative dynamical system composed of many particles, where the energy is independent of the time and the force on each particle depends only on the relative configuration, any given initial phase (momentum and position) must recur to an arbitrary specified degree of accuracy an indefinitely large number of times. The trajectories representing the particles have a quasi-periodic form so that any initial phase will recur if we are willing, or able, to wait for it. The Poincaré period τ_p is the time taken for the initial phase to reappear, and the cycle is the Poincaré cycle. The initial phase determines the later phase because the phase trajectories do not cross (equations of motion) and the phase volume is constant (incompressible phase fluid - Liouville theorem).

Boltzmann estimated the magnitude of the recurrence time for an abnormal initial state of a dilute gas and found it to be many orders greater than the age of the Universe. Although the system is strictly

practical terms this initial state will never recur in any experiment. The system shows macroscopic irreversibility even though the underlying molecular dynamics are strictly reversible. The same conclusion has been reached by many subsequent authors considering a range of actual or idealised systems. These ideas of irreversibility are closely related to fluctuation phenomena. There is a limit to the magnitude possible for a fluctuation which is to recur in the sense of those considered in the last lecture. The entire movement to equilibrium can, indeed, be regarded as a gigantic fluctuation of the system with a recurrence time of enormous magnitude. The question does arise of what such a fluctuation might involve if once it started and of the effects of non-Gaussian phenomena in this connection.

4.2.2. Probability After-Effects.

The general study of the molecular aspects of macroscopic fluctuations was started by von Smoluchowski in the so-called theory of after effects. The analysis is based on the theory of the Brownian movement elaborated by Einstein some time before; the experimental verification was given by Perrin. To see the general form of the results consider a small volume V_1 of a system of volume V ($\gg V_1$) containing colloidal particles and count the number of colloidal particles in V_1 on successive occasions for the same time interval t_1 . During this time interval the colloidal particles will have undergone Brownian motion, and at the end of the interval some particles initially inside will have moved out and some initially outside will have moved in. Many questions can be asked but two are relevant now: what is the mean life t_L of a particular state?; how long must we wait before some chosen initial number of particles $N(t_0)$ (which is

the initial state) will recur (time of recurrence t_r)?

Answers were given by Smoluchowski by using probability arguments and the analysis can be extended to continuous variables. Suppose N is the number of particles observed in V_1 on a particular occasion and $\langle N \rangle$ is the mean number averaged over many observations. Then it is found that whereas t_L is proportional to $(N + \langle N \rangle)^{-1}$, t_r involves N through an exponential factor. Smoluchowski showed that calculated data are astonishing. Consider oxygen gas with $\langle N \rangle = 3 \times 10^9$ and $T = 3 \times 10^2 \text{ K}$. the initial state is chosen so that the mean molecular concentration in V_1 (supposed a sphere with radius R) differs from the mean by 1%. For $R = 10^{-7} \text{ m}$, $t_r \sim 10^{-11} \text{ s}$; again for $R = 2.5 \times 10^{-7} \text{ m}$, $t_r \sim 1 \text{ s}$; for $R = 3 \times 10^{-7} \text{ m}$, $t_r \sim 10^6 \text{ s}$; while for $R = 5 \times 10^{-7} \text{ m}$, t_r has the astonishing magnitude of 10^{68} s . This is orders of magnitude greater than the age of the Universe.

These arguments, referring to a gas, have a wider application and can be generalised to apply to condensed states of matter. It is in this way that the reversibility of the dynamics of molecular motion is made fully compatible with the observed irreversible behaviour of macroscopic matter.

4.3. Entropy S .

The problem of identifying the expression for the generalised entropy is a difficult one.

4.3.1. The H-function.

Thermodynamically the equilibrium state is one of maximum entropy for a given energy. For a state not in equilibrium the entropy increases to a maximum value. Maximum entropy corresponds to a minimum of the Helmholtz free energy. For equilibrium the entropy is conventionally defined by

$$S = -k_B \int f_0^{(N)} \log f_0^{(N)} dp^N dr^N$$

$$= -k_B \langle \log f_0^{(N)} | f_0^{(N)} \rangle$$

where $f_0^{(N)}$ is the canonical distribution and the brackets are a short hand way of writing the integration. The corresponding integral involving the non-equilibrium distribution $f^{(N)}$ was called by Boltzmann the H-function and this does not increase as it must if it is to be identified with the entropy.

4.3.2. Course-graining of phase space.

The phase fluid is incompressible so the movement of the system to equilibrium cannot involve the rearrangement of phase points between contiguous small volumes of phase. To obtain a uniform distribution of phase points corresponding to equilibrium the alternative is to limit the fineness with which phase space can be viewed and so form a uniform mosaic in the mean rather than a true uniform distribution. This is fully compatible with the quantum ideas associated with the Heisenberg principle. The initially non-uniform system must lose information (or have a bad memory!) in order to reach equilibrium and a course-graining in phase is a way of achieving this. This was the original (non-quantum) idea of Ehrenfest: Kirkwood altered went to the next stage of realising that measurements take a finite (though perhaps very small) time interval so there should also be some course-graining over the time as well. The course-grained distribution in time (said to be a time smoothing) is then defined by

$$\bar{f}^{(N)}(t) = \frac{1}{\tau} \int_0^\tau f(t+s) ds$$

$$\bar{f}^{(N)}(r^N) \delta p^N \delta r^N = \int \bar{f}^{(N)}(p^{(N)}) dp^{(N)}$$

where τ is a time microscopically large (in comparison with the typical time for particle interactions) but macroscopically very small. It turns out that the precise magnitude of τ is not critical.

4.3.3. Statistical Particle Interactions.

The approach advocated by Kirkwood involves the definition of the autocorrelation of the force on a representative particle. If $\underline{F}(t)$ is the force on a chosen particle at time t and $\underline{F}(t+s)$ is the corresponding force on the same particle at time $t+s$, we form the autocorrelation function for the force according to

$$\underline{E}(s,t) = \langle \underline{F}(t) \cdot \underline{F}(t+s) \rangle_{N-1}$$

where the integration is over all the remaining $N-1$ particles.

For an equilibrium system $\underline{E}(s,t)$ has a mean value characteristic of the system. For a non-equilibrium system it is assumed that $\underline{E}(s,t) = 0$ for $s > \tau$. This means that for times larger than τ mentioned above the force on the particle is uncorrelated in time. It is this break of correlation that introduces the feature of non-equilibrium into the analysis of the theory. It plays the same role for the continuous interaction that the hypothesis of molecular chaos plays in the theory of the dilute gas.

4.4. Molecular Fluxes.

It is assumed that the equations of macroscopic hydrodynamics treated in lecture 2, and involving the balance of mass, momentum and energy, are related to corresponding expressions for the fluxes of these quantities at the microscopic level. We can develop the arguments either by supposing the movement to equilibrium is a unique event or is part of a general fluctuation.

4.4.1. General Expressions for the Fluxes.

A macroscopic observable $Q(t)$ referring to the time t is regarded as a collective flux of the microscopic variable $Q^{(N)}$ being a function of the total phase but not the time. In particular we calculate the observed (macroscopic) flux from

$$Q(t) = \langle Q | f^{(N)} \rangle = \int \int Q(\Gamma^{(N)}) f^{(N)}(\Gamma^{(N)}, t) d\Gamma^{(N)}. \quad (1)$$

For equilibrium $f^{(N)}$ will have the canonical form and Q will be a thermodynamical function.

For non-equilibrium we are concerned with the change of Q with time

$$\langle Q | f^{(N)} \rangle = \int \int d\Gamma^{(N)} Q(\Gamma^{(N)}) \partial f^{(N)} / \partial t.$$

The integration is to be performed by using the Liouville equation and in operator form this gives

$$\langle Q | f^{(N)} \rangle = \int \int Q(\Gamma^{(N)}) (-i\tilde{L}) \exp\{-i\tilde{L}t\} d\Gamma^{(N)}$$

where \tilde{L} is the Liouville operator. For the mass flux, for particles of mass m

$$Q = m \sum_j \delta(\underline{x} - \underline{r}_j);$$

for the momentum flux

$$Q = \sum_j p_j \delta(\underline{x} - \underline{r}_j);$$

and for the energy flux

$$Q = \sum_j (p_j^2/2m) \delta(\underline{x} - \underline{r}_j) + 1/2 \sum_{j,k} \psi(j,k) \delta(\underline{x} - \underline{r}_j).$$

The energy flux is seen to involve the actual pair interaction force potential. The use of these expressions for the fluxes allow the macroscopic expressions of balance to be recovered. In particular expressions for the transport coefficients can be identified.

The expressions for the fluxes derived this way define the macroscopic fluxes only to an additive term of vanishing divergence: this is appropriate for use in the expressions of balance derived in Lecture 2.

4.4.2. Response to External Forces.

The maintenance of a given non-equilibrium condition involves the expenditure of external work. The liquid will show a characteristic response to external systems when mechanical forces are

applied to it. To avoid unnecessary complications it is usual to suppose the external forces to be applied instantaneously.

The Hamiltonian (energy) of the liquid is supposed to be of two parts: one is the contribution without the external forces; and the other is the contribution arising from the forces themselves. The total phase distribution will be associated with a phase current flow: if a force F_A of type A gives rise to a flux J_B of type B a linear response to the force of frequency ω is expressed in the form

$$J_B(\omega) = L_{AB}(\omega) F_A(\omega)$$

where L_{AB} is a transport coefficient for the flux B in response to the force A. For a periodic driving force $F_A(\omega) = F_A \exp\{-i\omega t\}$ the formula

$$L_{AB}(\omega) = (1/Vk_B T) \int_0^\infty \langle J_B(t) J_A(s-t) \rangle \exp\{-i\omega t\} ds$$

was obtained by Mori as the classical form of a more general quantum expression. The upper integration limit is made indefinitely large on the assumption that the time s is greater than the correlation time for the fluxes. The static coefficient $L_{AB}(0)$ is obtained by setting $\omega = 0$.

If the flux is written as the time derivative of some quantity a , so that $J = da/dt = \dot{a}$, L_{ij} takes the form

$$L_{ij} = c \langle a_i(s) a_j(0) \rangle_{ds}$$

where c is a constant and the average is over an equilibrium ensemble.

This expression is compatible with the linear regression law

$$a_i = \sum_j L_{ij} x_j$$

which is related to the Onsager expressions for irreversible thermodynamics.

4.4.3. Evolution of Local Thermodynamic Equilibrium.

Conditions about each point can be expressed in terms of thermodynamic functions according to the concept of local equilibrium.

The time evolution of the phase distribution, which determines the local conditions, is specified by the Liouville equation. The fluxes follow from the ensemble average (1) once the Liouville equation has been solved and expressions for the transport coefficients are derived in this way. If T_{ij} is the i -th component of the momentum flux in the j -th direction and Q is the energy flux the following expressions result

$$\begin{aligned}\eta &= (1/vk_B T) \int \langle T_{ij}(t) T_{ij}(0) \rangle dt \\ \zeta - (2/3)\eta &= (1/vk_B T) \int \langle T_{jj}(t) T_{jj}(0) \rangle dt \\ \lambda &= - (1/vk_B T) \int \langle Q(t) \cdot Q(0) \rangle dt.\end{aligned}$$

The essential ingredient is the solution of the Liouville equation.

4.5. Stochastic Theories: The Brownian Motion

The importance of the autocorrelation function in the description of liquid structure suggests the use of specific stochastic theories in the elucidation of liquid properties. The classical model is the semi-macroscopic theory of the Brownian motion.

4.5.1. The Langevin Equation.

Consider a semi-macroscopic colloidal particle suspended in a liquid. The particle shows random movement as the result of bombardment by the (smaller) molecules of the suspending liquid. The suspended particle suffers acceleration due to molecular collisions but simultaneously retardation due to the viscous effect of the suspending fluid. These two effects, both molecular in their origins, are nevertheless accounted for in different ways.

The fluctuating stochastic acceleration of the particle is represented by the vector $\underline{A}(t)$ referring to the time t , and is assumed independent of the location. The deceleration results from a macroscopic friction proportional to the instantaneous velocity of the

particle; explicitly the retardation is written $-\underline{u}(t)$ where $\underline{u}(t)$ is the velocity of the particle at the time t . Here ζ is a dynamical constant of macroscopic friction. The resultant acceleration $\underline{a}(t)$ of the particle at the time instant t was expressed by Langevin in the form

$$\underline{a}(t) = -\zeta \underline{u}(t) + \underline{A}(t) + \underline{K}(\underline{r}, t)$$

where $\underline{K}(t)$ is the acceleration due to external forces (which may depend on the location), such as gravity. Random energy from the molecules of the suspending liquid is transferred to the Brownian particle by collisions and the resulting kinetic energy of the Brownian particle is passed back to the molecules of the liquid again by viscous friction. There is a reversibility as far as the mechanics is concerned but the macroscopic process of the Brownian motion is strictly irreversible.

It follows from the Langevin equation by making an average over a time interval t (so we in a sense "course-grain" the equations of motion of the particle) that the mean and mean square displacements of the colloidal particle during the time interval t are given by

$$\langle \underline{\Delta r} \rangle = - \left(\zeta \underline{u} - \underline{K} \right)$$

$$\langle \underline{\Delta r} \cdot \underline{\Delta r} \rangle = [6k_B T / m \zeta] \left(t - \frac{1}{\zeta} [1 - \exp(-\zeta t)] \right).$$

The momenta are supposed to have reached an average value within a time period for which the mean square displacement does not change very much; during this time interval the fluctuating force can also be supposed constant. There are, then, three distinct time scales involved in the theory: one is the short time over which the velocity and fluctuating force reach their time average values; a second is the time over which the mean square displacement is calculated; and the third is the time of observation of the system. It is seen that $\underline{\Delta r} \propto$

t for all times. For small times $\langle \Delta \underline{r}, \Delta \underline{r} \rangle$ is proportional to t^2 , but for large values of t it follows that

$$\langle \Delta \underline{r}, \Delta \underline{r} \rangle = (6k_B T / m \beta) [1 - 1/\beta] t$$

If $\beta \gg 1$ this reduces further to

$$\langle \Delta \underline{r}, \Delta \underline{r} \rangle = (6k_B T / m \beta) t$$

a result well confirmed by experiment. The proportionality to t is a characteristic feature of the Brownian motion and is also characteristic of an irreversible process. Interpreting the macroscopic motion of the particle as an example of random flights we can associate the formulae with the diffusion of many particles. The diffusion coefficient D is then found to be

$$D = k_B T / m \beta,$$

and the mobility coefficient is $m \beta$.

The same arguments are applied to the autocorrelation of the velocity, on the assumption that the velocity and fluctuating force are uncorrelated, to give

$$\langle \underline{v}(t) \cdot \underline{v}(0) \rangle = [k_B T \beta / m] \exp(-\beta t)$$

and

$$\beta = mk_B T / 6 \int_0^\infty \langle \underline{A}(t) \cdot \underline{A}(0) \rangle dt.$$

These results are characteristic of random motions of the Brownian type and will be referred to later.

4.5.2. Transition Probabilities.

The stochastic motion of a Brownian particle can be described by generalising the Liouville equation to include the stochastic motion. This introduces the notion of the probability W that the particle will suffer a change of phase $\Delta \underline{p}$ about the phase point \underline{p} during the time interval s. Let $f(\underline{p}, \underline{r}, t) d\underline{p} d\underline{r}$ be the probability of finding the particle with momentum \underline{p} at the position \underline{r} at the time t within the

elementary phase range $d\underline{p} d\underline{r}$. After the time interval s the transition to the later phase is given by

$$f(\underline{p} + \Delta \underline{p}, \underline{r} + \Delta \underline{r}, t+s) = \int f(\underline{p}, \underline{r}, t) W(\Delta \underline{p}, \Delta \underline{r}) d(\Delta \underline{p}) d(\Delta \underline{r}).$$

If the increments $\Delta \underline{p}$ and $\Delta \underline{r}$ are sufficiently small the function f and W can be expanded in a Taylor series to yield the integral equation

$$\frac{\partial f}{\partial t} + \underline{p} \cdot \frac{\partial f}{\partial \underline{r}} = - \frac{\partial}{\partial \underline{p}} \cdot \left[\frac{\langle \Delta \underline{p} \rangle}{\tau} f + \frac{1}{2} \frac{\partial}{\partial \underline{p}} \cdot \frac{\langle \Delta \underline{p} \cdot \Delta \underline{p} \rangle}{\tau} f \right] - K \cdot \frac{\partial f}{\partial \underline{p}}$$

where

$$\langle \Delta \underline{p} \rangle = \int \Delta \underline{p} W(\Delta \underline{p}) d(\Delta \underline{p})$$

$$\langle \Delta \underline{p} \cdot \Delta \underline{p} \rangle = \int (\Delta \underline{p} \cdot \Delta \underline{p}) W(\Delta \underline{p}) d(\Delta \underline{p}).$$

This equation was first explored by Fokker and Planck, and later by Kramers and Chandrasekhar - it is often known as the Fokker-Planck equation. It is applied to the Brownian motion by making particular assignments of the mean and mean square momentum increments.

4.5.3. The Smoluchowski Equation.

Integrating the phase function f over the momentum gives the configuration distribution $n(\underline{r}, t)$ according to

$$n(\underline{r}, t) = \int f(\underline{p}, \underline{r}, t) d\underline{p}.$$

Again introducing the appropriate transition probability $w(\Delta \underline{r})$ we have the expression of continuity

$$n(\underline{r} + \Delta \underline{r}, t+s) = \int n(\underline{r}, t) w(\Delta \underline{r}) d(\Delta \underline{r}).$$

Performing the Taylor expansion as before we find the equation

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial \underline{r}} \cdot \left[\frac{\langle \Delta \underline{r} \cdot \Delta \underline{r} \rangle}{\tau} \frac{\partial n}{\partial \underline{r}} - \frac{\langle \Delta \underline{r} \rangle}{\tau} n \right]$$

named after von Smoluchowski. Application to the Brownian motion is made by making the appropriate assignments for the mean and mean square displacements during the time interval s .

If β is large enough the momenta reach an equilibrium distribution before the configuration has reached one and the configuration equation is the one that is to be solved for the description of the motion. The Langevin equation can be integrated and arranged into a form relating explicitly to the correlations of particle velocity and fluctuating force. Then, as seen above in connection with the Brownian motion, the expressions for the diffusion coefficient and the Stokes friction constant follow in the form

$$D = 1/3 \int \langle \underline{u}(t+s) \cdot \underline{u}(t) \rangle ds$$

$$\beta = m/6k_B T \int \langle \underline{A}(t+s) \cdot \underline{A}(t) \rangle ds$$

both for large time intervals.

The representation of diffusion as a random motion of many particles has allowed such processes to be investigated by computer experiments of various kinds. The studies are able to explore the range of time intervals that are not necessarily very large.

4.6. Stochastic Motion in Liquids

The theory of the Brownian movement is important for two reasons. First, it gives a detailed insight into the workings of one theory of irreversible processes. Second, it includes a stochastic element that can be expected broadly to be relevant for the treatment of the motion of molecules in a liquid. The interaction between the many molecules in a liquid can be expected to lead to motion of the general Brownian type but with the difference that the "particle" (being a representative molecule like the others) will not be more massive than the molecules which give it apparent "life": all

molecules will be assumed to have the same mass m . In particular, the representative molecule will have less inertia than the surroundings, being a group of n molecules in continual interaction. This approach was pioneered particularly by Kirkwood.

4.6.1. The Phase Equation.

Viscous friction is introduced through a friction constant $\beta^{(n)}$ which refers to the force correlation on a molecule which is a member of a group of n ($< N$) molecules according to

$$\beta^{(n)} = 1/3mk_B T \int \langle \underline{F}(t) \cdot \underline{F}(t+s) \rangle_{N-n} ds.$$

Provided the force correlation vanishes after some time t_c which is macroscopically small the integral will achieve a constant value for $t > t_c$ which is interpreted as a friction constant of the Stokes type. Kirkwood showed how this hypothesis allows the Liouville equation for the group of N molecules contained in a volume V to be reduced to the form of a Fokker-Planck or Smoluchowski equation for a single molecule or a pair of molecules.

The appropriate distribution function is the time-averaged form and the corresponding Liouville equation is integrated over the phase of $N-1$ "unwanted" molecules to form the singlet equation, or over the phase of $N-2$ unwanted molecules to form the pair equation. The distribution of two molecules in phase can be expressed as the relative distribution for one molecule relative to the other taken as the origin so the construction of an equation for the singlet distribution has particular interest. This equation has the form

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{\underline{p}}{m} \cdot \frac{\partial \bar{f}^{(1)}}{\partial \underline{r}} = \frac{\Delta \bar{f}^{(1)}}{\tau}$$

where $\Delta \bar{f}^{(1)}$ contains the contributions due to interactions between

the molecules. The form of this term is determined by the nature of the interactions. If the molecular movement in a liquid during the small time interval t is supposed to be associated with only a small increment of momentum then $\Delta \vec{f}^{(1)}$ takes the form

$$\frac{\Delta \vec{f}^{(1)}}{t} = \zeta^{(1)} \frac{\partial}{\partial \vec{p}} \cdot \left[\left(\frac{\vec{p}}{m} - \underline{u} \right) \vec{f}^{(1)} + k_B T \frac{\partial \vec{f}^{(1)}}{\partial \vec{p}} \right]$$

$\zeta^{(1)}$ is the appropriate friction constant as is found by tracing back to the appropriate Langevin equation for the system.

4.6.3. Expression for the Friction Constant.

Various attempts have been made in evaluating the friction constant and the last word has yet to be said.

Originally Kirkwood suggested writing

$$\langle \underline{F}(t) \cdot \underline{F}(t+s) \rangle = \langle \underline{F}(t) \cdot \underline{F}(t) \rangle \phi(s)$$

assuming $\phi(s)$ will decay in the same way as the average momentum so that $\phi(s) = m / (1)$. Accepting that the environment is in local thermodynamic equilibrium the mean square force is expressed in terms of the static radial distribution function

$$\langle F^2 \rangle / k_B T = 4\pi n \int_0^\infty g^{(2)}(\nabla^2 \psi) r^2 dr.$$

Then

$$(\zeta^{(1)})^2 = 4\pi m / 3 \int_0^\infty g^{(2)}(\nabla^2 \psi) r^2 dr,$$

which is an expression first proposed by Rice and Kirkwood. Alternative expressions have also been obtained but the numerical magnitudes of them all are general similar, falling in the range 10^{-10} to $10^{-11} s^{-1}$.

4.6.4. Configuration Equation.

The Smoluchowski equation has the form of the balance equation

$$\partial n^{(1)} / \partial t = -\partial j / \partial r$$

where the mass current j is, retaining only terms of order $(1/\beta)$

$$j = \partial / \partial r [k_B T n^{(1)} / m] - \langle F \rangle n^{(1)} / \beta m + O(1/\beta^2)$$

and $\langle F \rangle$ is the mean force on the molecule. If this is written in terms of the potential of the mean force $\bar{\Phi}$

$$\langle F \rangle = -\partial \bar{\Phi} / \partial r = \partial / \partial r [k_B T \log g^{(2)}]$$

the result is a configuration equation for $n^{(1)}$. The form of the boundary conditions to be applied depend on the particular non-uniformities being studied.

Terms of higher power in $(1/\beta)$ can be included and the result is a differential equation of higher order; they have all proved too complicated to solve in practice but have had importance in connection with the boundary conditions to be applied.

4.6.5. Equations for the Pair Distribution.

Suppose the deviation from equilibrium is not too great. If $\bar{g}^{(2)}$ is the relative non-equilibrium pair distribution then this is related to the corresponding equilibrium function $g^{(2)}$ according to

$$\bar{g}^{(2)}(r) = g^{(2)}(r) [1 + w(r)].$$

For laminar viscous flow over a flat surface we suppose with time rate of shear $\dot{\epsilon}$ we can write

$$w(\underline{r}) = \frac{\beta}{k_B T} \left[\frac{r_i \dot{\epsilon}_{ij} r_j}{r^2} - \frac{1}{3} \frac{\partial u_i}{\partial r_i} \delta_{ij} \right] w_2(r) P_2(\cos \theta) + \frac{\beta}{6 k_B T} \frac{\partial u_i}{\partial r_i} w_0(r)$$

where w_2 and w_0 are two unknown functions referring respectively to pure shear and pure dilatation. Inserting this expression into the Smoluchowski equation gives the two equations associated with the two angular functions

$$\begin{aligned} \frac{d^2 w_2}{dr^2} + \left(\frac{2}{r} - \frac{1}{k_B T} \frac{d\psi}{dr} \right) \frac{dw_2}{dr} - \frac{6w_2}{r} &= -\frac{r}{k_B T} \frac{d\psi}{dr} \\ \frac{d^2 w_0}{dr^2} + \left(\frac{2}{r} - \frac{1}{k_B T} \frac{d\psi}{dr} \right) \frac{dw_0}{dr} &= -\frac{r}{k_B T} \frac{d\psi}{dr} \end{aligned}$$

These are to be solved subject to the boundary conditions

$$\begin{aligned} r^2 g^{(2)}(r) \frac{dw_0}{dr} &= 0 \quad (r \rightarrow \infty) & w_0(r) &= 0 \quad (r \rightarrow 0) \\ r^3 w_2(r) &= 0 \quad (r \rightarrow \infty) & \frac{dw_2(r)}{dr} &= 0 \quad (r \rightarrow 0) \end{aligned}$$

For a linear temperature gradient $T = T_0(1 + \underline{a} \cdot \underline{r})$ the form of the Smoluchowski equation is

$$\frac{d^2 w_1}{dr^2} + \left(\frac{2}{r} - \frac{1}{k_B T} \frac{d\psi}{dr} \right) \frac{dw_1}{dr} - \frac{2w_1}{r} = \frac{a}{(k_B T)^2} \frac{d\psi}{dr}$$

with the boundary conditions

$$\frac{w_1}{r} = \frac{dw_1}{dr} = -|a| \quad (r \rightarrow \infty)$$

4.6.6. Expressions for the Transport Coefficients.

Insert the expression for the non-equilibrium pair distribution into the expressions for the fluxes: the result is the expressions for the coefficients of viscosity and for thermal conduction λ_T

$$\eta = \frac{n m k_B T}{2\beta} + \frac{\pi\beta}{15 k_B T} n^2 \int_0^\infty \frac{d\psi(r)}{dr} w_2(r) g^{(2)}(r) r^3 dr$$

$$\zeta = \frac{\pi\beta}{k_B T} n^2 \int_0^\infty \frac{d\psi(r)}{dr} w_0(r) g^{(2)}(r) r^3 dr$$

$$\lambda_T = \frac{n^2 m k_B T}{\beta} \left[\frac{1}{3} \int_0^\infty r \frac{\partial \psi(r)}{\partial r} - \psi(r) g^{(2)}(r) \frac{\partial w_1}{\partial r} r^3 dr + \int_0^\infty \left(\psi(r) - \frac{r}{3} \frac{\partial \psi}{\partial r} \right) w_1 r^2 dr \right]$$

These formulae are applicable to monatomic insulating liquids and require for their evaluation a knowledge of the corresponding equilibrium pair distribution and the interparticle pair potential of the force. The evaluation of the formulae in non-equilibrium statistical mechanics depend on a knowledge of the corresponding equilibrium data.

4.7. Using the Liouville Equation

The formulae could be evaluated if the full solution of the Liouville equation were known. We consider briefly now some attempts that have been made to achieve this. We consider the operator form of the equation.

4.7.1. The Bromwich Integral Approach.

The Liouville operator is defined by the expansion

$$\exp\{-i\tilde{L}t\} = 1 + \sum_j (-1)^j (i\tilde{L}t)^j (j!)^{-1}$$

which is often called the time propagator operator. If $L^{(N)}$ is the Laplace transform of the distribution function $f^{(N)}$ then

$$\hat{f}^{(N)}(k) = \int f^{(N)}(t) \exp(-kt) dt$$

and the Laplace transform is

$$ik \hat{f}^{(N)} - \tilde{L} \hat{f}^{(N)}(0) = \tilde{L} \hat{f}^{(N)}(k)$$

remembering \tilde{L} is independent of the time. Rearrangement of this last expression gives

$$\hat{f}^{(N)}(k) = -i(\tilde{L} - ik)^{-1} \hat{f}^{(N)}(0)$$

which is the Laplace transform of the propagator equation. The operator $(\tilde{L} - ik)^{-1}$ is the inverse of the operator $(\tilde{L} - ik)$. The integral inverse of $\hat{f}^{(N)}(k)$ is the expression for $f^{(N)}$ itself

$$f^{(N)}(t) = -\frac{i}{2\pi i} \int_{-\infty + i\epsilon}^{\infty - i\epsilon} (\tilde{L} - z)^{-1} \exp(-zt) \hat{f}^{(N)}(0) dz$$

where $z = ik$ is the complex variable. This is an example of the Bromwich integral well known in the theory of the complex variable.

This is the formal solution of the Liouville equation referred to before but is mathematically too difficult to solve in the case (which interests us now) of many particles in continuous interaction. If such an evaluation were, in fact, possible this would solve the problem.

4.6.2. Perturbation Expansion.

We have already seen that the Liouville equation has many mathematical similarities with the Schrödinger equation of quantum theory and the associated mathematical techniques developed for that equation can be exploited here.

A much used approach is to divide the Liouville operator into a purely kinetic and purely (potential) interactive term. If λ is a parameter which measures the magnitude of the interaction forces we write

$$L = L_0 + \lambda \delta L.$$

We write the identity

$$(L - z)^{-1} - (L_0 - z)^{-1} = (L - z)^{-1}[(L_0 - z) - (L - z)](L - z)^{-1}.$$

This means

$$(L - z)^{-1} = (L_0 - z)^{-1} + (L - z)^{-1}(\lambda \delta L)(L - z)^{-1}.$$

The rearrangement of this expression to give $(L - z)^{-1}$ in terms of L_0 requires some approximation.

The approximation for non-interacting particles is $\lambda = 0$ so that

$$(L - z)^{-1} = (L_0 - z)^{-1}.$$

The next approximation arises by inserting this into the right hand side of () and the iteration process continued. This gives

$$(L - z)^{-1} = (-\lambda)^n (L_0 - z)^{-1} [\delta L (L_0 - z)^{-1}]^n$$

where

$$\delta L = i\lambda \sum_j \sum_k \left[\nabla_{\mathbf{r}_k} \psi(j, \mathbf{r}_k) \cdot (\mathbf{v}_{\mathbf{r}_j} - \mathbf{v}_{\mathbf{r}_k}) \right].$$

The interaction terms can now be included piecemeal in a systematic

way and the single integration necessary for the solution of the original Liouville equation is introduced as a large number of integrations over restricted particle interactions. Each complete interaction is accounted for by evaluating all the components of the series separately, and in practice this has presented the most severe difficulties. The analysis outlined above has been given a graphical representation in terms of the so-called Feynmann diagrams.

The complete interaction is specified in terms of the three parameters: (i) the coupling parameter λ ; (ii) the particle number density $n = N/V$; and (iii) the time t . The following conclusions have been found:

- (a) The Boltzmann equation for a dilute gas is obtained when the repulsive contribution to the interparticle force dominates the others;
- (b) If a weak repulsion is included in the interparticle force, the Fokker-Planck equation follows if terms of order $(\lambda n t)^s$, with $s > 0$ are accounted for in the limit of long times compared with the time for a single interaction between a pair of particles;
- (c) For short times, including all terms of order $(\lambda n)^s$ the theory provides the Vlasov equation which forms the basis for the theory of the gaseous plasma.

The total interaction potential can be treated through its effects on the other particle of an interaction. If, relative to the first, the second particle suffers a small change of momentum such that the succession becomes important after many interactions the result is the Fokker-Planck equation. If, on the other hand, the second particle suffers a large momentum change during one collision the theory provides the Boltzmann equation. The intermediate cases,

of particular interest in the extended and continuous interactions of liquid structure, have not really been treated and remain largely unexplored.

4.7. Other approaches.

A variety of approximate theories have been developed by including the diagrams that can be summed. The equations, of uncertain physical association, which result from this approach are called master equations. The earliest can be obtained by including terms of order $(\lambda^2 t)^n$ to all orders of the density and refers to the momentum evolution in a weak coupling approximation. Although we have used classical theory so far the most general arguments are based on quantum mechanics.

Another approach involves the projection operators where unwanted information is disregarded by moving from many to fewer dimensions. Generalisations of the Langevin equation can also be included within the scheme.

There are many developments of the theory but all, in the end, amount to the evaluation of specific contributions of the total interaction and the neglect of the remainder.

A heuristic theory is the cell model. Here emphasis is placed on the confinement of each molecule into a small volume (called a cell) by the neighbours. The potential energy field in the cell is determined by the neighbours and the entrapped molecule moves in this force field. By accounting for a mean field due to neighbours (assumed located in their mean positions) together with a superposed fluctuating field to account for thermal movements, the movement of a representative molecule within its cell can be calculated. The approach provides a quantitative understanding of the behaviour

of molecules and of the energy from which various properties can be calculated using the formulae already set out. The results are in fair agreement with experiment near the melting point.

