

PRESENT STATE OF THE THEORY OF LIQUIDS

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1. INTRODUCTION

THE present stage in the development of the theory of the liquid state originated for the most part in the numerous researches of Jacob Il'ich Frenkel, which he summarized in his classical book "Kinetic Theory of Liquids."^[1] He was one of the first to point out that the approximately equal particle density in solid and fused crystals, and the consequent approximate equality of their intermolecular interaction intensity, is bound to make the structure and the character of thermal motion of the atoms and molecules nearly the same in both phases. This gives rise to the known parallelism between the physical properties of solids and liquids, and creates a real basis for the theory of the processes that relate both phases. The views developed by Frenkel proved equally fruitful for both the theory of crystals and the theory of liquids. These views presupposed the increasing disorder in real crystals with rising temperature, and the presence of elements of order in liquids. The notion of defects (in the broad sense) in crystals and of their role in thermodynamic, electric, kinetic, and optical properties of real solids was a most important step in the development of solid-state theory. On the other hand, the ideas of short-range order and strong interaction between the particles of a liquid, and their specific influence on its physical properties, has given rise to a new branch of physics, the statistical theory of liquids.

We shall attempt to review briefly the present status of statistical theory of simple liquids, confining ourselves to non-quantum theory. Except for liquid helium and to some extent liquid neon, all monatomic liquids can be satisfactorily described by classical methods.

The lack of a simple and readily visualized model for liquids, one capable of serving as the "zereth approximation" in the building of a theory of liquids (in contrast with the perfect-gas and ideal-crystal models in the theory of gases and solids) makes the development of the theory extremely difficult. The mathematical difficulties encountered on the path towards the development of the theory of the liquid state of matter are so great, that only a statistical theory of simple monatomic liquids is feasible at present. Liquefied inert gases and fused metals are real examples of simple liquids. We can also include, with some degree of approximation, certain monatomic liquids with molecules and force fields that have some measure of specific symmetry.

Many problems in the statistical theory of liquids have been recently discussed in detail in reviews and books.^[2-6] We have therefore attempted to pay more attention here to questions that are relatively new or insufficiently explained in the review literature. Many problems in the theory of liquids were not touched upon at all.

2. EQUILIBRIUM CORRELATIVE FUNCTIONS

1. Definition of correlative functions. The mathematical tool of modern theory of liquids and dense gases is that of molecular distribution functions or correlative functions,^[2,3,7] the main properties of which will be listed briefly. For an equilibrium system of N particles contained in a volume V and having a temperature T , the coordinate part of the Gibbs distribution function is equal to

$$D_N(\mathbf{q}_1, \dots, \mathbf{q}_N) = Q_N^{-1} \exp \left\{ -\frac{U_N(\mathbf{q}_1, \dots, \mathbf{q}_N)}{kT} \right\}, \quad (2.1)$$

where Q_N — configuration integral that normalizes D_N to unity and U_N — total interaction energy of the system particles. As already mentioned, we assume that the position of each particle is completely characterized by the coordinates of its center of mass. The correlative functions $F_s(\mathbf{q}_1, \dots, \mathbf{q}_s)$ can be defined as

$$F_s(\mathbf{q}_1, \dots, \mathbf{q}_s) = V^s \int_V \dots \int_V D_N(\mathbf{q}_1, \dots, \mathbf{q}_N) d\mathbf{q}_{s+1} \dots d\mathbf{q}_N, \quad (2.2)$$

so that the expressions

$$dW(\mathbf{q}_1, \dots, \mathbf{q}_s) = F_s(\mathbf{q}_1, \dots, \mathbf{q}_s) \frac{d\mathbf{q}_1 \dots d\mathbf{q}_s}{V^s}, \quad (2.3)$$

$$s = 1, 2, \dots, N,$$

define the probabilities of definite configurations of groups comprising s particles, regardless of the positions of the remaining $N-s$ particles of the system. This leads to the normalization conditions

$$\frac{1}{V} \int_V F_1(\mathbf{q}) d\mathbf{q} = 1, \quad (2.4)$$

$$\frac{1}{V} \int_V F_{s+1}(\mathbf{q}_1, \dots, \mathbf{q}_{s+1}) d\mathbf{q}_{s+1} = F_s(\mathbf{q}_1, \dots, \mathbf{q}_s). \quad (2.5)$$

In addition, the functions F_s are, by definition, symmetrical with respect to permutation of the coordinate triplets of the different particles, and should satisfy the conditions of weakening correlation

$$F_s(\mathbf{q}_1, \dots, \mathbf{q}_s) \rightarrow F_1(\mathbf{q}_1) \dots F_s(\mathbf{q}_s) \quad (2.6)$$

as the distance between particles increases.^[7]

From (2.1) and (2.2) we can obtain an integro-differential equation connecting various functions F_s with different indices. If we assume that the total interaction energy U_N is the sum of paired interactions

$$U_N = \sum_{1 \leq i < j \leq N} \Phi_{ij} = \sum_{1 \leq i < j \leq N} \Phi(|\mathbf{q}_i - \mathbf{q}_j|), \quad (2.7)$$

then we obtain as equations for F_s [7]

$$kT \frac{\partial F_s}{\partial \mathbf{q}_i} + F_s \frac{\partial U_s}{\partial \mathbf{q}_i} + \frac{1}{v} \int \frac{\partial \Phi_{1,s+1}}{\partial \mathbf{q}_i} F_{s+1} d\mathbf{q}_{s+1} = 0, \quad (2.8)$$

where $v = V/N$, the limit being taken as N and V become infinite. U_s denotes the interaction energy of the chosen group of s particles

$$U_s = \sum_{1 \leq i < j \leq s} \Phi_{ij}. \quad (2.9)$$

In the homogeneous case, far from the walls bounding the system, all positions of a single particle are equally likely. For a pair of particles, likewise, only the relative distance is significant, and not the general position or orientation. In this case, thus,

$$F_1(\mathbf{q}) = 1, \quad (2.10)$$

$$F_2(\mathbf{q}, \mathbf{q}') = g(|\mathbf{q} - \mathbf{q}'|). \quad (2.11)$$

Similar simplifications hold also for F_s with $s > 2$ (but $s \ll N$). We can also introduce the conditional correlative functions $F_s(\mathbf{q}_1, \dots, \mathbf{q}_s | \mathbf{q}_{s+1}, \dots, \mathbf{q}_{s+p})$, which would define the conditional probabilities of the positions of a group of s particles for fixed positions of a different group of p particles, independently of the positions of the remaining $N - s - p$ particles of the system. The rule for the product of probabilities then yields

$$F_s(\mathbf{q}_1, \dots, \mathbf{q}_s | \mathbf{q}_{s+1}, \dots, \mathbf{q}_{s+p}) = \frac{F_{s+p}(\mathbf{q}_1, \dots, \mathbf{q}_s, \mathbf{q}_{s+1}, \dots, \mathbf{q}_{s+p})}{F_p(\mathbf{q}_{s+1}, \dots, \mathbf{q}_{s+p})}. \quad (2.12)$$

For example, in the homogeneous case with $s = p = 1$ we obtain therefore

$$F_1(\mathbf{q} | \mathbf{q}') = F_2(\mathbf{q}, \mathbf{q}') = g(|\mathbf{q} - \mathbf{q}'|), \quad (2.13)$$

so that the function $g(r)$ of (2.11) is simultaneously also the conditional simple (unitary) correlative function and is therefore called the radial distribution function of the system particles. The probability that the relative distance between an arbitrary pair of particles will increase from r to $r + dr$ is

$$d\omega(r) = g(r) \frac{4\pi r^2 dr}{V}. \quad (2.14)$$

The deviation of the function $g(r)$ from unity is the simplest and most important characteristic of the order existing in a liquid.

2. Mean values. Knowledge of the functions F_s enables us to determine mean values M_s of the type

$$M_s = \sum_{1 \leq i_1 < i_2 < \dots < i_s \leq N} f(\mathbf{q}_{i_1}, \dots, \mathbf{q}_{i_s}). \quad (2.15)$$

By simple calculation we obtain from (2.1) and (2.2) [7]

$$\bar{M}_s = \frac{N(N-1)\dots(N-s+1)}{V^s s!} \int_V \dots \int_V f(\mathbf{q}_1, \dots, \mathbf{q}_s) \times F_s(\mathbf{q}_1, \dots, \mathbf{q}_s) d\mathbf{q}_1 \dots d\mathbf{q}_s. \quad (2.16)$$

We are interested principally in quantities of the additive type, M_1 , and of the binary type, M_2 , with $f(\mathbf{q}, \mathbf{q}') = f(|\mathbf{q} - \mathbf{q}'|)$ in the homogeneous case. We then obtain from (2.10), (2.11), and (2.16)

$$M_1 = \frac{1}{v} \int f(\mathbf{q}) d\mathbf{q}, \quad (2.17)$$

$$\bar{M}_2 = \frac{2\pi N}{V} \int_0^\infty f(r) g(r) r^2 dr, \quad (2.18)$$

where it is assumed that N and V are very large.

The simplest example of a quantity of type M_2 is the interaction energy U_N of the system particles as given by (2.7). Along with the kinetic contribution we obtain from (2.18) for the total energy of the system

$$E = N \left\{ \frac{3}{2} kT + \frac{2\pi}{v} \int_0^\infty \Phi(r) g(r) r^2 dr \right\}. \quad (2.19)$$

In similar fashion, but with a somewhat more complicated proof, we obtain also an equation for the pressure in the system [7]

$$p = \frac{kT}{v} - \frac{2\pi}{3v^2} \int_0^\infty \Phi'(r) g(r) r^3 dr, \quad (2.20)$$

where the prime denotes differentiation. The last equation is a particular case of a more complicated expression for the elastic tensions in the liquid in terms of the function F_2 . [3,4] A simple expression can be obtained in terms of $g(r)$ for the quadratic fluctuations of the number of particles in a certain volume G inside the system

$$\overline{(\Delta N_G)^2} = \bar{N}_G \left\{ 1 + \frac{4\pi}{v} \int_0^\infty (g(r) - 1) r^2 dr \right\}. \quad (2.21)$$

In view of the known relation between the density fluctuations and the compressibility, we obtain furthermore

$$\frac{kT}{v^2} \left(- \frac{\partial v}{\partial p} \right)_T = 1 + \frac{4\pi}{v} \int_0^\infty (g(r) - 1) r^2 dr. \quad (2.22)$$

Many other thermodynamic and mechanical characteristics of a liquid or a dense gas can be expressed in terms of the functions F_1 and F_2 . Thus, for most liquids of interest in our theory, it is sufficient to know only the two lowest-order correlative functions F_1 and F_2 .

3. Scattering of light and x rays by liquids. The correlations existing between the particle positions in a liquid determine the character of the scattering of electromagnetic waves by an entire aggregate of particles, and this can also be translated into the language of the radial distribution function. Familiar calculations [1,3,4] yield for the intensity of the scattered waves:

$$I(s) = I_0 \left\{ 1 + \frac{4\pi}{v} \int_0^{\infty} (g(r) - 1) \frac{\sin(sr)}{sr} r^2 dr \right\}, \quad (2.23)$$

where

$$s = \frac{4\pi}{\lambda} \sin \frac{\phi}{2}, \quad (2.24)$$

and I_0 is the intensity of scattering by a system of independent particles. In (2.24), λ is the wavelength and ϕ the scattering angle.

For waves in the optical region, the length $1/s$ (except for very small angles ϕ) is much larger than the "correlation radius," at which $g(r)$ differs from unity. Consequently the function $[\sin(sr)]/sr$ can be replaced by its value for $r = 0$ (i.e., by unity), and we obtain

$$I(s) = I_0 \left\{ 1 + \frac{4\pi}{v} \int_0^{\infty} (g(r) - 1) r^2 dr \right\}. \quad (2.25)$$

This expression is independent of the scattering angle and we obtain, in connection with (2.21) and (2.22), the same result as in the usual thermodynamic theory of scattering of light by density fluctuations.

The situation is different in the case of x rays, where the length $1/s$ is commensurate with the interatomic distances in the liquid, so that further simplification of (2.23) is impossible. If we introduce the relative scattering intensity $i(s) = I(s)/I_0$, we can write

$$(i(s) - 1) s = \frac{4\pi}{v} \int_0^{\infty} (g(r) - 1) r \sin(sr) dr. \quad (2.26)$$

Here the right half can be regarded as a sine-transformation of the Fourier function $[(4\pi/v)(g(r) - 1)]r$. The inverse transformation yields

$$(g(r) - 1) r = \frac{v}{2\pi^2} \int_0^{\infty} (i(s) - 1) s \sin(rs) ds. \quad (2.27)$$

Consequently, if we determine the function $i(s)$ experimentally for some liquid, we can calculate $g(r)$ for this liquid.

3. STRUCTURE OF SIMPLE LIQUIDS

For many monatomic liquids, x-ray diffraction data indeed yielded the radial distribution functions $g(r)$, and in some cases the temperature dependence of $g(r)$ can be established over a wide range of temperatures (see the reviews [8,9]). A typical $g(r)$ curve is shown schematically in the figure. It follows from these data that a short-range density (radial) order exists in simple liquids within a distance of several atomic dimensions, with preferred stratified distribution of the neighbors of each particle. The impossibility of resolving the peaks of the function $g(r)$ is directly connected with the displacements of the particles from certain layers in the closest vicinity of a certain particle to other layers. At distances exceeding several atomic dimensions, $g(r) = 1$, and the relative distribution of the particles is completely disordered. With

increasing temperature or with decreasing density of the liquid, the picture shown in the figure becomes more diffuse, the peaks become less pronounced, and this corresponds to a decrease in the degree of short-range order. However, traces of order of the same type remain also in the gaseous state of matter (except for the case of infinite dilution).

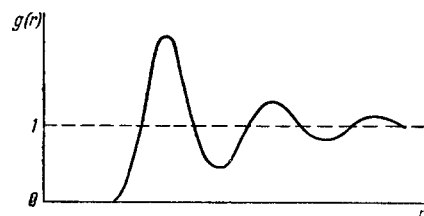
It was found that near the melting temperature the distances to the first peak of $g(r)$, and sometimes also to the second peak, very nearly correspond in many cases to the distances between the nearest sites (or correspondingly to the next-nearest sites) in crystal lattices of the same substances before the melting. We can further introduce the quantities

$$z_1 = \frac{4\pi}{v} \int_0^{r_1 \min} g(r) r^2 dr, \quad (3.1)$$

where $r_1 \min$ —abscissa of the first minimum on the $g(r)$ curve, equal to the average number of nearest neighbors of a certain particle in the corresponding liquid ("first coordination number" of the liquid). We can analogously define some of the next higher coordination numbers z_2, z_3, \dots . The numbers z_1 , and sometimes also z_2 , or z_2 and z_3 , were also found in many cases to be close to (but somewhat smaller than) the coordination numbers in the corresponding crystals.^[8-10]

These properties are manifestations of the "quasi-crystalline" short-range order in simple liquids. Of course, these properties still do not indicate in any way the presence, even in small volumes, of an approximate crystalline order in the sense of structural-anisotropy effects or translational periodicity. The absence of such quasi-crystallinity, at least in simple liquids with non-directional and non-saturating interparticle forces, actually follows from estimates of the rms fluctuations of the coordination numbers z_k .^[3,11] The coordination numbers in a liquid, unlike in a crystal, are not constants characterizing the type of crystal lattice, but merely mean values of the number of nearest neighbors, and should be subject to thermal fluctuations. If H is a certain region that is immovably connected with some particle at the point q_0 , then the quadratic fluctuation of the number of particles in this region is

$$\begin{aligned} \overline{(\Delta N_H)^2} &= \bar{N}_H + \frac{1}{v^2} \int_H \int_H \{ F_2(q, q' | q_0) \\ &\quad - F_1(q | q_0) F_1(q' | q_0) \} dq dq'. \end{aligned} \quad (3.2)$$



With proper choice of the region H , we can obtain from this estimates of the fluctuations of the coordination number z_1, z_2, \dots . In this case the function $F_1(\mathbf{q} | \mathbf{q}_0) = g(|\mathbf{q} - \mathbf{q}_0|)$ can be taken directly from x-ray diffraction data, and the function $F_2(\mathbf{q}, \mathbf{q}' | \mathbf{q}_0) = F_3(\mathbf{q}, \mathbf{q}', \mathbf{q}_0)$ can be approximately expressed in terms of combinations of $g(r)$ with the aid of the "superposition approximation" (see below); it can further be shown that this leads only to a reduction in the estimate for $(\overline{\Delta N_H})^2$. Such calculations were carried out for a large number of monatomic liquids and it turned out that in almost all cases z_1 fluctuates by about 20% and more, while z_2 fluctuates by 35–40% and more.^[11] So high a level of coordination-number fluctuation is utterly incompatible with the notion of approximate crystalline order of liquid particles in a small volume, and the short-range order in simple liquids must be understood only in the density sense.

4. SUPERPOSITION APPROXIMATION

1. Integral equation for the radial distribution function. The fundamental equations (2.8) interrelate the infinite totality of correlative functions F_s , $s = 1, 2, \dots$, which cannot be solved in the case of a liquid. But we have seen that it would be sufficient to know only the functions F_1 and F_2 for most problems, and only the function $g(r)$ in the homogeneous case. It would therefore be of importance to the theory of liquids to obtain a closed equation for $g(r)$. The simplest approximate method of obtaining such an equation involves terminating the chain of equations (2.8) at the equation with $s = 2$ by introducing Kirkwood's "superposition approximation"

$$F_3(\mathbf{q}, \mathbf{q}', \mathbf{q}'') = g(|\mathbf{q} - \mathbf{q}'|) g(|\mathbf{q} - \mathbf{q}''|) g(|\mathbf{q}' - \mathbf{q}''|) \quad (4.1)$$

(it is assumed that $F_1 = 1$). With the aid of the conditional correlative functions this can also be written in the form

$$F_1(\mathbf{q} | \mathbf{q}', \mathbf{q}'') = F_1(\mathbf{q} | \mathbf{q}') F_1(\mathbf{q} | \mathbf{q}''), \quad (4.2)$$

from which it is clear that the approximation (4.1) does not take into account the correlation in the influences that the particles at the points \mathbf{q}' and \mathbf{q}'' have on the probability of the position of the third particle at the point \mathbf{q} . Therefore the superposition approximation can reflect only very crudely the actual correlations between the particles in the liquid. Nonetheless, the construction of a theory of liquids in such an approximation is of certain interest, and this problem has been the subject of many investigations. We note that the approximation (4.1) turns out to be sufficiently accurate in the case of a gas that is not too dense, and also in a dense gas or liquid with large distances between particles, as is clear from the remark made in connection with (4.2).

The substitution of (4.1) in (2.8) with $s = 2$ leads after some transformations to a closed nonlinear integral equation for the function $g(r)$, namely^[7]

$$kT \ln g(r) + \Phi(r) + \frac{2\pi}{rv} \int_0^\infty \left\{ \int_{|r-q|}^{r+q} \mathcal{E}(t) t dt \right\} (g(q) - 1) q dq = 0, \quad (4.3)$$

where

$$\mathcal{E}(t) = \int_{-\infty}^t \Phi'(t) g(t) dt. \quad (4.4)$$

Thus, the kernel of the integral equation is itself dependent on the unknown function. Equation (4.3), with specified thermodynamic parameters v and T , determines the radial distribution function $g(r; v, T)$ from the specified intermolecular potential $\Phi(r)$, and thereby solves in principle (in the approximation considered) the basic problem in the theory of simple liquids. Equation (4.3) with different notation was derived also in^[12].

The actual solution of (4.3) for a specified function $\Phi(r)$ can be obtained only by numerical means. Detailed solutions were obtained by Kirkwood and his co-workers for the case of a model of solid noninteracting spheres^[13] and for a model of solid spheres with Lennard-Jones interaction.^[14]

$$\left. \begin{aligned} \Phi(r) &= +\infty && \text{for } r < a, \\ \Phi(r) &= 4\epsilon \left\{ \left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^6 \right\} && \text{for } r > a. \end{aligned} \right\} \quad (4.5)$$

In this case the parameters a and ϵ were chosen to make the potential $\Phi(r)$ correspond most closely to the properties of the actual potential in gaseous argon (this can be done by comparing the calculated and experimental values of the Joule-Thomson coefficient and other properties).

The results of calculations for a "realistic" potential (4.5) and their discussions can be found in^[14] and other papers,^[2,3,6,15] and will not be discussed in detail here. We note merely that the function $g(r, v, T)$, obtained for large intervals of v and T , together with the thermodynamic properties of the studied model calculated from this function, agrees qualitatively with the known properties of real simple liquids, including such complicated phenomena as the liquid-gas phase transition and the critical phenomena. The quantitative results, however, are not quite so satisfactory; for example, the calculated pressure and entropy in the liquid state were found to be noticeably lower than their actual values in liquid argon.

2. Behavior of $g(r)$ at large distances and stability limit of the homogeneous phase. At large values of r , the function $g(r)$ deviates little from unity, and if in addition the potential $\Phi(r)$ vanishes with sufficient speed, then (4.3) can be linearized and investigated in general.^[3,16] Analysis shows that the asymptotic form of $g(r)$ for large r is

$$g(r) = 1 + \frac{1}{r} \sum_{(n)} A_n e^{-\alpha_n r} \cos(\beta_n r + \delta_n), \quad (4.6)$$

where α_n and β_n are determined by the properties of $\Phi(r)$ and $g(r)$ for small r , while A_n and δ_n remain indeterminate in the linear approximation. It is obvious that, in accordance with (4.6), the general character of $g(r)$ represents correctly the experimentally known properties of $g(r)$. It is possible to show further that the solutions of (4.3) retain the physical meaning of a binary distribution function of a certain stable system only if all $|\alpha_n| \neq 0$. In the opposite case, if at least one α_n vanishes, the functions $g(r)$ described by (4.3) correspond to absolutely unstable, i.e., nonexistent, states.^[16]

The foregoing property can be used to define the stability limits of a homogeneous phase (gas or liquid) as the lines on the v - T plane, where the smallest of the α_n vanishes. This leads to the following analytical conditions for the limit of absolute stability of a homogeneous phase^[3]

$$-\frac{4\pi}{v k T} \int_0^{\infty} \frac{\sin \beta r}{\beta r} \left\{ \int_0^r \Phi'(t) g(t) dt \right\} r^2 dr = 1, \quad (4.7)$$

$$\int_0^{\infty} \frac{\sin \beta r - \beta r \cos \beta r}{\beta r} \left\{ \int_0^r \Phi'(t) g(t) dt \right\} r^2 dr = 0. \quad (4.8)$$

These equations in parametric form (in terms of the parameter β) determine the line $v = v(T)$ of the stability limit of the system. With the aid of (2.20) we can then obtain an analogous line on the p - T plane. Equation (4.7) was first derived in^[17].

The foregoing method can be used, in particular, to determine the melting-crystallization line of a simple substance. If the repulsion forces between molecules are approximated by a power law, this leads to the following approximate expression for the melting curve^[18]

$$p_m = -A + BT^m, \quad (4.9)$$

where A , B , and m can be expressed in terms of the parameters of intermolecular interaction. The law (4.9) agrees well with the experimental data for simple substances.^[19]

5. MORE ACCURATE APPROXIMATIONS IN THE THEORY OF LIQUIDS

1. Review of different theories. Many attempts were made recently to obtain for the lower-order correlative functions closed equations which are more accurate than the superposition approximation. Some of these could apparently serve in fact as a basis for the construction of a more exact theory of simple liquids, but as far as we know, there is still no published paper, with detailed calculations and with discussions, employing this theory. We list some of the new theories.

A general method of constructing approximations to the exact equations in (2.8) was investigated in^[20]. These approximations, which are appreciably better

than the superposition approximation, led to exceedingly complicated and cumbersome equations, which were not investigated further. A new formalism using special correlative functions relating only the particles that interact directly with a chosen particle, was introduced in^[21]. For strictly short-range forces this leads to a system of twelve equations with twelve unknown functions (in accord with the largest number of geometrically possible nearest neighbors).

Since the superposition approximation is exact when the particle density in the system is low, it is natural to attempt to make this approximation more suitable for larger densities by introducing into the right half of (4.1) a correction factor

$$F_3(\mathbf{q}, \mathbf{q}', \mathbf{q}'') = g(|\mathbf{q} - \mathbf{q}'|) g(|\mathbf{q} - \mathbf{q}''|) g(|\mathbf{q}' - \mathbf{q}''|) \varphi(\mathbf{q}, \mathbf{q}', \mathbf{q}''). \quad (5.1)$$

A function φ in the form of a certain infinite series in powers of the density, constructed with the aid of the group integrals of the theory of real gases, was formally obtained in^[22]. This series can be used in practice only for a gas.

In^[23] there was introduced a "hypersuperposition" approximation

$$F_4(\mathbf{q}, \mathbf{q}', \mathbf{q}'', \mathbf{q}''') = \frac{F_3(\mathbf{q}, \mathbf{q}', \mathbf{q}'') F_3(\mathbf{q}, \mathbf{q}', \mathbf{q}''') F_3(\mathbf{q}, \mathbf{q}'', \mathbf{q}''') F_3(\mathbf{q}', \mathbf{q}'', \mathbf{q}''')}{F_2(\mathbf{q}, \mathbf{q}') F_2(\mathbf{q}, \mathbf{q}'') F_2(\mathbf{q}, \mathbf{q}''') F_2(\mathbf{q}', \mathbf{q}'') F_2(\mathbf{q}', \mathbf{q}''') F_2(\mathbf{q}'', \mathbf{q}''')}, \quad (5.2)$$

by which the infinite chain (2.8) is terminated one link farther than in (4.1). In conjunction with (5.1), this leads to a system of two equations for φ and $g(r)$. It is shown that in the case of a gas these equations yield correct values for the first virial coefficients. The first terms of the expansion of φ in powers of the density are

$$\varphi(\mathbf{q}, \mathbf{q}', \mathbf{q}'') = 1 + \frac{1}{v} \int f(|\mathbf{q} - \mathbf{q}''|) f(|\mathbf{q}' - \mathbf{q}''|) f(|\mathbf{q}'' - \mathbf{q}''|) d\mathbf{q}'' + \dots, \quad (5.3)$$

$$\text{where } f(|\mathbf{q}|) = e^{-\frac{\Phi(|\mathbf{q}|)}{kT}} - 1, \quad (5.4)$$

which corresponds to a similar approximation given in^[22].

Approximate expressions for $g(r)$, which are more accurate for a gas than (4.3), can be obtained by a partial summation of the diagrams of the theory of real gases.^[24-26] For example, the equation derived in^[26] can be written in the form

$$kT \ln g(r) + \Phi(r) + \frac{2\pi}{rv} \int_0^{\infty} \left\{ \int_{|r-Q|}^{r+Q} [\Phi(t) + kT(1-g(t)) + \ln g(t)] t dt \right\} (g(Q) - 1) Q dQ = 0 \quad (5.5)$$

and takes account of more simple diagrams than in the case of (4.3). Equations similar in form are given in^[24,25]. Although in principle all these equations are exact only for a gas that is not too dense, one can hope that in the case of a liquid they lead to better approximate results than in the superposition approximation.

2. Variational theories. The free energy of a large but finite system of particles can be expressed in terms of the highest order correlative function F_N in the form

$$A_N = A_N^0 + \frac{1}{V^N} \int_V \dots \int_V \{U_N + kT \ln F_N\} F_N d\mathbf{q}_1 \dots d\mathbf{q}_N, \quad (5.6)$$

where A_N^0 —free energy of a perfect gas. Regarding A_N as a functional of F_N , requiring that A_N be minimal with respect to variations of F_N , and imposing the normalization condition on F_N we can readily obtain a solution for F_N in the form of a Gibbs distribution (2.1), namely $F_N = V_N D_N$.

A variational theory for the determination of correlative functions, which reduces to an approximate representation of F_N in terms of a product of a certain number of auxiliary functions of simpler structure and subsequent determination of the "best" such functions by solving the corresponding variational problem, was proposed in [27]. Depending on the number and character of the factors in which F_N is expanded, approximations of different degrees of accuracy can be obtained. Actually, only a few very rough approximations were calculated in that paper. An analogous theory, based on a grand canonical distribution and using the thermodynamic potential Ω_N in place of the free energy A_N , was developed in [28].

It is pointed out even in [27] that a difficulty arises in variational theory on going over to a system that expands without limit (at constant density), in view of the appearance of improper integrals in the free energy, with values that depend on the method used to go to the limit as $V, N \rightarrow \infty$. A more rigorous analysis shows [29,30] that the initial versions of the variational theory are incorrect in many other respects; for example, a very complicated problem (and one incorrectly solved in [27,28]) is that of accounting in the variation of the free energy for the relations between the auxiliary functions employed, relations needed to satisfy the normalization conditions for (2.5) or for their limiting expressions as $V \rightarrow \infty$.

A correct variational theory leading to integral equations for the correlation functions was developed in [29,30]. For a large but finite system of particles, the author introduces a system of "correlation" functions $\varphi_3, \varphi_4, \dots$ and a system of "pseudocorrelation" functions ψ_2, ψ_3, \dots defined by the relations

$$F_s = \prod_{(1 \leq i < j \leq s)} F_2(\mathbf{q}_i, \mathbf{q}_j) \prod_{(1 \leq i < j < k \leq s)} \varphi_3(\mathbf{q}_i, \mathbf{q}_j, \mathbf{q}_k) \dots \varphi_s(\mathbf{q}_1, \dots, \mathbf{q}_s), \quad (s > 2), \quad (5.7)$$

$$F_N = \prod_{(1 \leq i < j < N)} \psi_2(\mathbf{q}_i, \mathbf{q}_j) \prod_{(1 \leq i < j < k < N)} \psi_3(\mathbf{q}_i, \mathbf{q}_j, \mathbf{q}_k) \dots \psi_N(\mathbf{q}_1, \dots, \mathbf{q}_N). \quad (5.8)$$

Because of the connections existing between the F_s and between F_s and F_N , the functions ψ_s and F_2 or φ_s can in principle be expressed in terms of each

other, and it is assumed that this can actually be done. To obtain real approximate results it is necessary to impose some limitations on the functions φ_s and ψ_s in the course of minimizing the free energy. The following approximations are considered in [29,30]:

1) $\varphi_{n+1} = 1$ for all $n \geq \alpha$, and 2) $\psi_m = 1$ for all $m \geq \beta$, where α and β are certain integers. For example, the approximation $\{\alpha = 3, \beta + 4\}$ reduces to the approximate relations

$$F_N = \prod_{1 \leq i < j \leq N} \psi_2(\mathbf{q}_i, \mathbf{q}_j) \prod_{(1 \leq i < j < k \leq N)} \psi_3(\mathbf{q}_i, \mathbf{q}_j, \mathbf{q}_k), \quad (5.9)$$

$$F_2 = \frac{1}{V^{N-2}} \int_V \dots \int_V F_N d\mathbf{q}_3 \dots d\mathbf{q}_N, \quad (5.10)$$

$$F_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = F_2(\mathbf{q}_1, \mathbf{q}_2) F_2(\mathbf{q}_1, \mathbf{q}_3) F_2(\mathbf{q}_2, \mathbf{q}_3) \varphi_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3), \quad (5.11)$$

and the value of (5.9) should be substituted in the right half of (5.10). By going over to continuously increasing values of α and β , we can obtain a sequence of more and more accurate approximations. The question of the limiting transition $N, V \rightarrow \infty$ and the functional relationships between the φ_s or between the ψ_s remains vital in this theory, too. Its author was able, however, to develop a rigorous theory of "renormalization" of the free energy, which eliminates these difficulties and yields reliably correct results.

6. NONEQUILIBRIUM CORRELATIVE FUNCTIONS

1. Correlative functions in phase space. We proceed now to review the status of the theory of kinetic properties of simple liquids. The theory can be expressed in the language of correlative functions of particle groups. These functions should now be defined in the phase space of the group, and can depend explicitly on the time. If $\mathbf{q}_i, \mathbf{p}_i$ is the assembly of coordinates and momenta of the i -th particle and $d\tau_i = d\mathbf{q}_i d\mathbf{p}_i$, then the correlative function $F_s = F_s(\mathbf{q}_1, \dots, \mathbf{q}_s; \mathbf{p}_1, \dots, \mathbf{p}_s; t)$ is defined by the relation

$$dW(\mathbf{q}_1, \dots, \mathbf{q}_s; \mathbf{p}_1, \dots, \mathbf{p}_s; t) = F_s \frac{d\tau_1 \dots d\tau_s}{V^s}, \quad s = 1, 2, \dots, N, \quad (6.1)$$

where $dW(\mathbf{q}_1, \dots, \mathbf{q}_s; \mathbf{p}_1, \dots, \mathbf{p}_s; t)$ is the probability of observing simultaneously the coordinates and the momenta of the selected s particles at the instant t near the specified values, independently of the positions and momenta of the remaining $N-s$ particles. As in the equilibrium case, the functions F_s should be symmetrical and should satisfy normalization conditions such as (2.4) and (2.5), except that integration in coordinate space is replaced by integration in the total phase space of the corresponding particles. In the special case of statistical equilibrium, the distributions of the coordinates and of the momenta are independent, and for a Maxwellian momentum distribution we obtain

$$F_s = F_s^0(\mathbf{q}, \dots, \mathbf{q}_s) (2\pi mkT)^{-\frac{3}{2}s} \prod_{(1 \leq i \leq s)} \exp\left(-\frac{\mathbf{p}_i^2}{2mkT}\right), \quad (6.2)$$

where F_S^0 —ordinary equilibrium correlation functions in the space of the particle coordinates.

Conditional correlative functions of various types can also be introduced in the absence of equilibrium. Some of these will be encountered below.

In analogy with the equilibrium case, the function pairs F_S and S_{S+1} must satisfy a certain integro-differential relationship between them. If we assume the system as a whole to be closed, we have on the basis of the Liouville theorem

$$\frac{dF_N}{dt} = \frac{\partial F_N}{\partial t} + \sum_{(1 \leq i \leq N)} \frac{\partial F_N}{\partial q_i} \frac{p_i}{m} + \sum_{(1 \leq i \leq N)} \frac{\partial F_N}{\partial p_i} \mathbf{K}_i = 0, \quad (6.3)$$

where \mathbf{K}_i —force acting on the i -th particle. Multiplying this by $V^{-(N-s)} d\tau_{S+1} \dots d\tau_N$ and integrating over all the phase space of the $(s+1)$ -st, \dots N -th particles, we obtain after simple transformations in the limit as $N, V \rightarrow \infty$ the following equations:^[7,31]

$$\begin{aligned} \frac{\partial F_s}{\partial t} + \sum_{(1 \leq i \leq s)} \left\{ \frac{\partial F_s}{\partial q_i} \frac{p_i}{m} + \frac{\partial F_s}{\partial p_i} \left(X_i - \frac{\partial U_s}{\partial q_i} \right) \right\} \\ = \frac{1}{v} \sum_{(1 \leq i \leq s)} \int \frac{\partial \Phi_{i, s+1}}{\partial q_i} \frac{\partial F_{s+1}}{\partial p_i} d\tau_{s+1} \quad (s = 1, 2, \dots). \end{aligned} \quad (6.4)$$

Here U_s is defined in (2.9), and \mathbf{X}_i denotes the external force acting upon the i -th particle. It is easy to check that when $\mathbf{X}_i = 0$ the equilibrium functions (6.2) satisfy the equations in (6.4).

As in the equilibrium case, only the two functions F_1 and F_2 are of primary interest. We note that the kinetic theory of gases is based exclusively on knowledge of the function F_1 , because in a rarefied gas the transport of mass, momentum, and energy is effected almost completely by the motion of the particles themselves. In a liquid, to the contrary, the greater part of the momentum and energy flow is connected with the interaction between particles, and knowledge of the function F_2 is essential for most problems.

2. Initial conditions. Reversibility and irreversibility. Except for stationary nonequilibrium states and a few other special problems, it is necessary to solve (6.4) subject to definite initial conditions. A typical case is when the distribution of the particle groups is specified at some initial instant of time $t = t_0$: $F_S(\mathbf{q}_1, \dots, \mathbf{q}_S; \mathbf{p}_1, \dots, \mathbf{p}_S; t_0) = f_S(\mathbf{q}_1, \dots, \mathbf{q}_S; \mathbf{p}_1, \dots, \mathbf{p}_S)$. We single out here a case when the initial state of a group of particles is specified precisely, for example, for $s = 1$

$$F_1(\mathbf{q}, \mathbf{p}; t_0) = V \delta(\mathbf{q} - \mathbf{q}_0) \delta(\mathbf{p} - \mathbf{p}_0), \quad (6.5)$$

where \mathbf{q}_0 and \mathbf{p}_0 are two constant vectors. In this case the solution should have the form $F_1(\mathbf{q}, \mathbf{p}, t | \mathbf{q}_0, \mathbf{p}_0, t_0)$ and has the meaning of a conditional probability of observing a particle near the phase point \mathbf{q}, \mathbf{p} at the instant t , if we know that the particle was at the point $\mathbf{q}_0, \mathbf{p}_0$ at the instant t_0 . An analogous problem can also be formulated for $s > 1$.

If the initial distribution f_S was not an equilibrium one, as for example in (6.5), then in accordance with

the proposed ergodic properties of the investigated system, we expect that in the absence of external forces the system will arrive after a corresponding relaxation time at an equilibrium state with a probability distribution (6.2). However, the equations (6.4) present certain difficulties in the investigation of such relaxation processes, and also stationary irreversible processes such as viscosity, heat conduction, etc, since these equations are reversible in time and remain invariant under the simultaneous substitutions $t \rightarrow -t$ and $\mathbf{p}_i \rightarrow -\mathbf{p}_i$. Essentially, like the initial Liouville equation (6.3), these are still dynamic and not statistical equations. The situation remains the same, of course, even if the infinite chain of equations (6.4) is terminated, for example, with the aid of the superposition approximation, as was done in^[32] in the hope of obtaining irreversible kinetic equations for F_1 and F_2 in liquids.

In order to obtain solutions that describe irreversible processes it is necessary either to solve (6.4) under initial or other supplementary conditions for F_S which are asymmetrical with respect to the past and to the future, or else change over to new distribution functions \bar{F}_S or to equations that are explicitly irreversible with respect to time for these functions. The latter can be attained by using functions \bar{F}_S obtained by averaging or spreading the exact functions F_S and their equations of motion over suitably chosen microscopically-small time intervals. The irreversible equations obtained in this manner for \bar{F}_S are called kinetic.

A typical and well known example where the relaxation problem is solved with the aid of reversible equations, but the supplementary conditions have a preferred direction in time, is Landau's calculation of the damping of plasma oscillations.^[33] Green has similarly demonstrated that irreversible phenomena in simple liquids can be studied in principle by starting from the reversible equations (6.4).^[5] A more general method is that of the kinetic equations. A highly perfected theory of kinetic equations was developed by Bogolyubov,^[7] but is effective only for gas systems. Kirkwood proposed for the functions \bar{F}_S in a liquid kinetic equations modeled after the equations of the theory of Brownian motion. In spite of the approximate character of this theory, it is at present the best developed. A brief description of this method will be given in the following sections.

3. Scattering of slow neutrons in a liquid. It is interesting in many problems to know, along with the functions F_S defined above, the nonequilibrium distribution functions only in configuration or only in momentum space, for example

$$\begin{aligned} F_s(\mathbf{q}_1, \dots, \mathbf{q}_s; t) \\ = \int \dots \int F_s(\mathbf{q}_1, \dots, \mathbf{q}_s; \mathbf{p}_1, \dots, \mathbf{p}_s; t) d\mathbf{p}_1 \dots d\mathbf{p}_s, \end{aligned} \quad (6.6)$$

and analogously for $F_S(\mathbf{p}_1, \dots, \mathbf{p}_S; t)$, and also to know

different conditional distribution functions in each of these spaces.

Of particular interest are the two functions $F_1(\mathbf{q}, t | \mathbf{q}^0, t_0)$ and $F_1(\mathbf{q}, t | \mathbf{q}'^0, t_0)$, where \mathbf{q}^0 corresponds to the initial position of the same particle as in the main argument F_1 , and \mathbf{q}'^0 corresponds to the initial position of some other particle. In a homogeneous system which is in equilibrium on the whole, these functions can depend only on the distances between the points \mathbf{q} and \mathbf{q}^0 or \mathbf{q}'^0 and on the time interval $t - t_0$:

$$F_1(\mathbf{q}, t | \mathbf{q}^0, t_0) = V \varrho(|\mathbf{q} - \mathbf{q}^0|, t - t_0), \quad (6.7)$$

$$F_1(\mathbf{q}, t | \mathbf{q}'^0, t_0) = g(|\mathbf{q} - \mathbf{q}'^0|, t - t_0). \quad (6.8)$$

The functions $\rho(\mathbf{r}, t)$ and $g(\mathbf{r}, t)$ are natural kinetic generalizations of the number density (per particle) and the radial distribution function $g_0(\mathbf{r})$ of the static theory, into which they go over when t vanishes

$$\left. \begin{array}{l} \varrho(\mathbf{r}, t) \rightarrow \delta(\mathbf{r}) \\ g(\mathbf{r}, t) \rightarrow g_0(\mathbf{r}) \end{array} \right\} \text{ as } t \rightarrow 0. \quad (6.9)$$

The sum

$$G(\mathbf{r}, t) = \varrho(\mathbf{r}, t) + g(\mathbf{r}, t) \quad (6.10)$$

corresponds to the average density of all the particles at the instant t , at a distance r from the point where a certain chosen particle was situated at $t = 0$. As $t \rightarrow \infty$ or $r \rightarrow \infty$ we have $\rho(\mathbf{r}, t) \rightarrow 0$ and $g(\mathbf{r}, t) \rightarrow 1$, respectively.

Just as the function $g_0(\mathbf{r})$ for a real liquid can be reconstituted from the results of x-ray scattering, the functions $\rho(\mathbf{r}, t)$ and $g(\mathbf{r}, t)$ can be reconstituted from the results of slow-neutron scattering.^[34] If we denote by $d^2\sigma/d\Omega d\epsilon$ the effective cross section (per particle) for elastic scattering in a unit solid angle and a unit energy interval, we obtain for the coherent and incoherent scattering, respectively,

$$\frac{d^2\sigma'}{d\Omega d\epsilon} = \frac{\langle a \rangle^2 k}{2\pi\hbar k_0} \int \int \exp[i(\boldsymbol{\kappa}\mathbf{r} - \omega t)] G(|\mathbf{r}|, t) d\mathbf{r} dt, \quad (6.11)$$

$$\frac{d^2\sigma''}{d\Omega d\epsilon} = \frac{[\langle a^2 \rangle - \langle a \rangle^2] k}{2\pi\hbar k_0} \int \int \exp[i(\boldsymbol{\kappa}\mathbf{r} - \omega t)] \varrho(|\mathbf{r}|, t) d\mathbf{r} dt. \quad (6.12)$$

Here \mathbf{k}_0 and \mathbf{k} are the wave numbers of the incoming and scattered neutrons, $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}_0$, $\omega = \epsilon/\hbar$, a — length for the scattering of a neutron by nuclei of a given kind, and the brackets $\langle \dots \rangle$ denote averaging over the spin and isotopic states of the nuclei. The inverse Fourier transformation with respect to $\boldsymbol{\kappa}$ and ω yields $G(\mathbf{r}, t)$ and $\rho(\mathbf{r}, t)$, and consequently also $g(\mathbf{r}, t)$.

Thus, a detailed investigation of the scattering of slow neutrons can yield in principle more complete information on the structure and thermal motion in a liquid than x-ray methods. The reason lies in the simple fact that the time necessary for the slow neutron to traverse the average interatomic distance in the liquid is comparable with the characteristic times of thermal motion of the atoms, whereas the x-ray quantum covers this distance too rapidly and its scattering is determined by the instantaneous distribution

of the particles. Unfortunately, a reliable experimental determination of the energy spectrum of neutrons scattered at different angles is a very complicated problem, as yet unsolved. One can hope, however, for success in this direction in the nearest future.

7. LANGEVIN EQUATION FOR THE MOTION OF A LIQUID MOLECULE

1. Derivation of the Langevin equation. Kirkwood has proposed a theory for the kinetic processes in simple liquids, constructed in close analogy with the well known theory of Brownian motion. In this section we consider the equation of motion of an individual liquid particle, following^[35]. This makes graphically clear how the time averaging procedure as applied to reversible laws of dynamics leads to irreversible dissipative effects.

We isolate a certain particle in the liquid, say the first, and write its law of motion

$$\frac{d\mathbf{p}_1}{dt} = \mathbf{K}_1, \quad (7.1)$$

where \mathbf{K}_1 is the total force exerted on the isolated particle by all the remaining particles. For simplicity we assume that there are no external forces and that the liquid itself is in equilibrium. We represent the force \mathbf{K}_1 as the sum of its mean value and a fluctuating part

$$\mathbf{K}_1 = {}^1\langle \mathbf{K}_1 \rangle_\tau + G_1(t), \quad (7.2)$$

where $(\dots)_\tau$ denotes time averaging over an interval of length τ , and ${}^1\langle \dots \rangle$ denotes statistical averaging over the states of all the remaining particles with the phase position of the first particle fixed:

$$\begin{aligned} {}^1\langle \mathbf{K}_1 \rangle_\tau &= \frac{1}{V^{N-1}} \int \dots \int \left\{ \frac{1}{\tau} \int_0^\tau \mathbf{K}_1(t+s) ds \right\} \\ &\times F_{N-1}^{(0)}(\mathbf{Q}^0, \mathbf{P}^0 | \mathbf{q}_1^0, \mathbf{p}_1^0) d\mathbf{Q}^0 d\mathbf{P}^0. \end{aligned} \quad (7.3)$$

For the sake of brevity, \mathbf{Q} and \mathbf{P} denote the totality of coordinates and momenta of all $N-1$ particles, except the first, and the zero superscript denotes that a variable belongs to the initial instant of time t , for which the equation of motion (7.1) has been written out. The zero superscript of $F_{N-1}^{(0)}$ indicates equilibrium distribution. The duration τ is assumed very small on a microscopic time scale, but covering a large number of changes in the values of the instantaneous force \mathbf{K}_1 .

We interchange the sequence of integration with respect to the time and with respect to the initial states in (7.3), and go over to integration in the total phase space of the system, introducing the corresponding δ -functions

$$\begin{aligned} {}^1\langle \mathbf{K}_1 \rangle_\tau &= \frac{1}{V^{N-1}} \int_0^\tau ds \int \dots \int \mathbf{K}_1(t+s) F_{N-1}^{(0)}(\mathbf{Q}^0, \mathbf{P}^0 | \mathbf{q}_1^0, \mathbf{p}_1^0) \\ &\times \delta(\mathbf{q}_1^0 - \mathbf{q}_1^0) \delta(\mathbf{p}_1^0 - \mathbf{p}_1^0) d\mathbf{Q}^0 d\mathbf{P}^0 d\mathbf{q}_1^0 d\mathbf{p}_1^0. \end{aligned} \quad (7.4)$$

We then change over from the phase variables at the

initial instant of time to the phase variables at the instant $t+s$. The Jacobian of such a transformation is equal to unity, and from the Liouville theorem and from the rule for the product of probabilities we have furthermore

$$F_{N-1}^{(0)}(\mathbf{Q}^0, \mathbf{P}^0 | \mathbf{q}_1^0, \mathbf{p}_1^0) F_N^{(0)}(\mathbf{q}_1^0, \mathbf{p}_1^0) = F_N^{(0)}(\mathbf{q}_1^0, \mathbf{p}_1^0, \mathbf{Q}^0, \mathbf{P}^0) \\ = F_{N-1}^{(0)}(\mathbf{Q}, \mathbf{P} | \mathbf{q}_1', \mathbf{p}_1') F_1^{(0)}(\mathbf{q}_1', \mathbf{p}_1'). \quad (7.5)$$

We can therefore write

$${}^1\langle (\mathbf{K}_1)_\tau \rangle = \frac{1}{\tau^{N-1}} \int_0^\tau ds \int \dots \int \mathbf{K}_1(t+s) F_{N-1}^0(\mathbf{Q}, \mathbf{P} | \mathbf{q}_1', \mathbf{p}_1') \\ \times \frac{F_1^0(\mathbf{q}_1', \mathbf{p}_1')}{F_1^0(\mathbf{q}_1^0, \mathbf{p}_1^0)} \delta(\mathbf{q}_1' - \mathbf{q}_1^0) \delta(\mathbf{p}_1' - \mathbf{p}_1^0) d\mathbf{Q} d\mathbf{P} d\mathbf{q}_1' d\mathbf{p}_1'. \quad (7.6)$$

But the equilibrium function F_1^0 is merely the Maxwellian momentum distribution function, so that

$$\frac{F_1^0(\mathbf{q}_1', \mathbf{p}_1')}{F_1^0(\mathbf{q}_1^0, \mathbf{p}_1^0)} = \exp\left(-\frac{\mathbf{p}_1'^2 - \mathbf{p}_1^{02}}{2mkT}\right) = 1 - \frac{\mathbf{p}_1^0}{mkT} \int_0^s \mathbf{K}_1(t+s') ds' \\ + O[(\Delta \mathbf{p}_1')^2], \quad (7.7)$$

where

$$\Delta \mathbf{p}_1' = \mathbf{p}_1' - \mathbf{p}_1^0 = \int_0^s \mathbf{K}_1(t+s') ds'. \quad (7.8)$$

An analogous expansion for the δ -functions yields

$$\delta(\mathbf{p}_1^0 - \mathbf{p}_1') = \delta(\mathbf{p}_1' - \mathbf{p}_1^0 - \Delta \mathbf{p}_1') = \delta(\mathbf{p}_1' - \mathbf{p}_1^0) - \Delta \mathbf{p}_1' \frac{\partial}{\partial \mathbf{p}_1^0} \delta(\mathbf{p}_1' - \mathbf{p}_1^0) \\ + O[(\Delta \mathbf{p}_1')^2], \\ \delta(\mathbf{q}_1^0 - \mathbf{q}_1') = \delta(\mathbf{q}_1' - \mathbf{q}_1^0 - \Delta \mathbf{q}_1') = \delta(\mathbf{q}_1' - \mathbf{q}_1^0) + O(\Delta \mathbf{q}_1'). \quad (7.9)$$

Substituting all this into (7.6) and recognizing that in the case of equilibrium the mean value of the force \mathbf{K}_1 is equal to zero, we obtain after some calculations

$${}^1\langle (\mathbf{K}_1)_\tau \rangle = - \left(\frac{\mathbf{p}_1^0}{mkT} - \frac{\partial}{\partial \mathbf{p}_1^0} \right) \frac{1}{V^{N-1}} \\ \times \int \dots \int \left\{ \frac{1}{\tau} \int_0^\tau ds \int_0^s \mathbf{K}_1(t+s) \mathbf{K}_1(t+s') ds' \right\} \\ \times F_{N-1}^{(0)}(\mathbf{Q}, \mathbf{P} | \mathbf{q}_1^0, \mathbf{p}_1^0) d\mathbf{Q} d\mathbf{P}. \quad (7.10)$$

We have left out small terms that vanish as $\tau \rightarrow 0$. The integrand contains a tensor-dyad. For a homogeneous liquid this tensor is proportional to the unit tensor, and it is natural to introduce a scalar quantity β equal to

$$\beta = \frac{1}{3kT} \frac{1}{\tau} \int_0^\tau ds \int_0^s {}^1\langle \mathbf{K}_1(t+s) \mathbf{K}_1(t+s') \rangle ds', \quad (7.11)$$

where the integrand contains the usual scalar products, and where a simple change in the variable of integration was made relative to (7.10). The substitution of (7.10) and (7.11) into (7.1) and (7.2) leads to an equation of motion for a single particle in the form

$$\frac{d\mathbf{p}_1}{dt} = -\frac{\beta}{m} \mathbf{p}_1 + kT \frac{\partial \beta}{\partial \mathbf{p}_1} + \mathbf{G}_1(t), \quad (7.12)$$

which is accurate to terms that vanish as $\tau \rightarrow 0$, and in which the zero superscript of \mathbf{p}_1 was omitted.

If there exists a small time interval τ^* such that the forces $\mathbf{K}_1(t)$ and $\mathbf{K}_1(t+s')$ are not correlated over a time $s' > \tau^*$, then the quantity

$$\int_{-s}^0 {}^1\langle \mathbf{K}_1(t+s) \mathbf{K}_1(t+s+s') \rangle ds' = \int_0^s {}^1\langle \mathbf{K}_1(t+s) \mathbf{K}_1(t+s+s') \rangle ds' \quad (7.13)$$

does not depend on s when $s > \tau^*$ (and by virtue of the homogeneity, it is also independent of t) so that

the operation $\frac{1}{\tau} \int_0^\tau (\dots) ds$ in (7.11) is superfluous,

and we have

$$\beta = \frac{1}{3kT} \int_0^\infty {}^1\langle \mathbf{K}_1(0) \mathbf{K}_1(s) \rangle ds. \quad (7.14)$$

For the same reason, in accord with (7.2), the random force $\mathbf{G}_1(t)$ is uncorrelated at the instants $t=0$ and $t=s > \tau^*$, and since in accord with (7.2) we also have ${}^1\langle (\mathbf{G}_1)_\tau \rangle = 0$, Eq. (7.12) is the ordinary Langevin equation, known from the theory of Brownian motion,^[36] and the two coincide when $\beta = \text{const}$. The stochastic equation (7.12) contains the dissipative effects explicitly, owing to the first two terms in the right half.

2. **Friction coefficient.** The quantity β , defined by (7.14) as an integral of the autocorrelation function of the force \mathbf{K}_1 , depends generally speaking on the momentum of the first particle, owing to the method used for averaging (fixed values of \mathbf{q}_1 and \mathbf{p}_1). From (6.4) we readily see that β can depend only on \mathbf{p}_1^2 . If we therefore introduce the quantity

$$\beta^* = \beta - \frac{2kT}{m} \frac{\partial \beta}{\partial \mathbf{p}_1^2}, \quad (7.15)$$

then (7.12) turns into the ordinary Langevin equation

$$\frac{d\mathbf{p}_1}{dt} = -\frac{\beta^*}{m} \mathbf{p}_1 + \mathbf{G}_1(t), \quad (7.16)$$

but with a velocity-dependent friction coefficient β^* . The question of the difference between β^* and β is discussed in^[35], where it is shown that for condensed systems the dependence of the friction coefficient on the velocity is not very important.

More interesting is the question of the magnitude and temperature dependence of β . Direct calculation by means of (7.14) is impossible at present, since we do not know the exact solutions of (6.4) under the initial conditions of interest to us. An estimate of β in terms of the molecular potential $\Phi(r)$ and the equilibrium radial distribution function $g_0(r)$ is given in^[35] in the form

$$\beta = \left[\frac{4\pi m}{3v} \int_0^\infty \Delta \Phi(r) \cdot g_0(r) r^2 dr \right]^{1/2}, \quad (7.17)$$

where Δ is the Laplace operator. Thus, the temperature dependence of β is determined completely by the temperature dependence of $g_0(r)$. Analogous estimates were obtained also in^[37,38].

In view of Einstein's relation, we have $D = kT/\beta$, where D is the self-diffusion coefficient. If D is known for a certain liquid, the theoretical result (7.17) can be directly verified. Thus, for argon near the triple point we have $D_{\text{exp}} = 2.06 \times 10^{-5}$ cm²/sec,

whereas the value calculated from (7.17) is $D_{\text{theor}} = 2.60 \times 10^{-5} \text{ cm}^2/\text{sec}$,^[5] which is quite satisfactory. An experimentally obtained function $g_0(r)$ and the Lennard-Jones potential for argon were used in the calculations. Analogous calculations were carried out in^[38] for neopentane, which also led to results having the same order of magnitude, but with a greater difference between D_{theor} and D_{exp} than in the case of argon.

In connection with the estimates of the reliability of the theory made in the references just mentioned, the following remark is in order. The use of Einstein's relations is valid only for an ideal gas or for truly Brownian particles. In the general case it should be replaced by the relation^[39]

$$D = v^2 \left(-\frac{\partial p}{\partial v} \right)_T \frac{1}{\beta}, \quad (7.18)$$

which depends essentially on the isothermal compressibility of the medium. Therefore the results mentioned above for D_{theor} should be recalculated, and this may influence appreciably the comparison with D_{exp} .

8. KIRKWOOD'S THEORY OF TRANSPORT PROCESSES IN SIMPLE LIQUIDS

1. Equations for the averaged correlative functions.

From the theory of Brownian motion it is known that in principle any problem in this theory can be solved with the aid of the stochastic equation (7.16), provided the distribution law is known for the random force $\mathbf{G}_1(t)$. A simpler method of solving problems in the theory of Brownian motion, however, is to study the partial differential equations for the partition functions of the Brownian particle.^[36] It is desirable to obtain a similar method for the theory of liquids. This was done in^[35], where the generalized Fokker-Planck equations were used as the kinetic equations for the liquid particles.

In accordance with the physical ideas developed in the preceding section, the irreversible motion of liquid particles should be described in terms of correlative functions in phase space, averaged over microscopically small time intervals:

$$\begin{aligned} \bar{F}_s(\mathbf{q}_1, \dots, \mathbf{q}_s; \mathbf{p}_1, \dots, \mathbf{p}_s; t) \\ = \frac{1}{\tau} \int_0^\tau F_s(\mathbf{q}_1, \dots, \mathbf{q}_s; \mathbf{p}_1, \dots, \mathbf{p}_s; t+t') dt'. \end{aligned} \quad (8.1)$$

Applying such an averaging operation to any of the equations in (6.4) we obtain, after certain transformations similar to those of the preceding section, a system of kinetic equations for the functions \bar{F}_s . A completely rigorous but very cumbersome derivation of these equations is given in^[35], while a simplified derivation is given in^[40]. The equations obtained are generalized Fokker-Planck equations. Thus, for \bar{F}_1 we have

$$\frac{\partial \bar{F}_1}{\partial t} + \frac{\partial \bar{F}_1}{\partial \mathbf{q}} \frac{\mathbf{p}}{m} + \frac{\partial \bar{F}_1}{\partial \mathbf{p}} \mathbf{X}^* = \frac{\partial}{\partial \mathbf{p}} \left\{ \beta \left[\frac{\mathbf{p}}{m} \bar{F}_1 + kT \frac{\partial \bar{F}_1}{\partial \mathbf{p}} \right] \right\}, \quad (8.2)$$

where \mathbf{X}^* is the sum of the external force and of the additional force of statistical origin connected with the non-equilibrium nature of the system. For simplicity it was assumed in (8.2) that the mean velocity of liquid flow \mathbf{u} is equal to zero at the given place. Otherwise \mathbf{p}/m in the right half of (8.2) must be replaced by $(\mathbf{p}/m) - \mathbf{u}$. The friction coefficient β in (8.2) is defined by (7.14); the terms that vanish as $\tau \rightarrow 0$ are again neglected.

Analogously, we obtain for \bar{F}_2

$$\begin{aligned} \frac{\partial \bar{F}_2}{\partial t} + \sum_{(1 \leq i \leq 2)} \left\{ \frac{\partial \bar{F}_2}{\partial \mathbf{q}_i} \frac{\mathbf{p}_i}{m} + \frac{\partial \bar{F}_2}{\partial \mathbf{p}_i} \left(\mathbf{X}_i^* - \frac{\partial \Phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_i} \right) \right\} \\ = \sum_{i \leq j \leq 2} \frac{\partial}{\partial \mathbf{p}_i} \left\{ \beta \left[\frac{\mathbf{p}_i}{m} \bar{F}_2 + kT \frac{\partial \bar{F}_2}{\partial \mathbf{p}_i} \right] \right\}, \end{aligned} \quad (8.3)$$

and similar equations can be obtained for \bar{F}_s with $s > 2$. The remarks made above concerning Eq. (8.2) are valid for these equations, too. In addition, in accordance with^[35], it is assumed that in the six-dimensional configuration space of the particle pair the friction-coefficient tensor breaks up into two diagonal (and isotropic) three-dimensional tensors, so that the scalar quantity β is the same in (8.3) as in (8.2). The validity of such an assumption is not obvious, and this question is discussed in^[41].

An interesting feature of Eqs. (8.2) and (8.3) is that, in contrast to the initial equations (6.4), they are no longer coupled, and each equation contains only one function \bar{F}_s . The different functions \bar{F}_s are connected with each other only implicitly, through the friction coefficient (more accurately, friction tensors).

2. Viscosity and heat conduction of simple liquids.

The question of determining the coefficients of viscosity and heat conduction from the kinetic equations (8.2) and (8.3) was considered in^[42,43], and a simplified variant of the theory was developed in^[44]. Certain preliminary general results concerning the viscosity and heat conduction in liquids were obtained in^[4] (see also^[5]). To simplify the problem, which is complicated enough without this, it is assumed in all these papers that $\beta = \text{const}$ and the effective external force connected with the non-equilibrium nature of the system and contained in \mathbf{X}_i^* is neglected.

The momentum or energy transfer consists of two parts—"kinetic," connected with the motion of the particles, as in a rarefied gas, and "potential," connected with the interaction between particles and of principal interest in the case of a liquid. The most important part of the problem is to find the nonequilibrium binary distribution function \bar{F}_2 . Assuming the causes tending to disturb the system equilibrium to be small, we can put

$$\bar{F}_2 = g_0(r) \{1 + \chi\} \quad (8.4)$$

and use the smallness of the nonequilibrium correction χ . For example, in discussing the viscosity of a liquid this leads to the following structure of the function χ ^[43]

$$\chi = \frac{\beta}{2kT} \left[\frac{1}{r^2} \left(\mathbf{r} \frac{\partial \mathbf{u}}{\partial \mathbf{q}} \mathbf{r} \right) - \frac{1}{3} \operatorname{div}_{\mathbf{q}} \mathbf{u} \right] \psi_2(r) + \frac{\beta}{6kT} \operatorname{div}_{\mathbf{q}} \mathbf{u} \cdot \psi_0(r), \quad (8.5)$$

where $r = |\mathbf{r}|$, \mathbf{r} —vector distance between the particle pair, \mathbf{q} —vector of the center of mass of the particle pair, $\mathbf{u} = \mathbf{u}(\mathbf{q})$ —mean velocity at the point \mathbf{q} , and $\psi_0(r)$ and $\psi_2(r)$ —two auxiliary functions, which must be determined from equations obtained by substituting (8.5) in (8.3). These functions were actually determined and tabulated in [43] for liquid argon, by numerical solution of the derived equations. Calculation of the viscous-stress tensor with the aid of (8.4) and (8.5) leads then to the following expressions for the shear and bulk viscosity coefficients (the "kinetic" contributions are also taken into account)

$$\eta = \frac{mkT}{2v\beta} + \frac{\pi\beta}{15v^2kT} \int_0^\infty \Phi'(r) g_0(r) \psi_2(r) r^5 dr, \quad (8.6)$$

$$\xi = \frac{mkT}{3v\beta} + \frac{\pi\beta}{9v^2kT} \int_0^\infty \Phi'(r) g_0(r) \psi_0(r) r^5 dr, \quad (8.7)$$

where $\Phi'(r)$ is the intermolecular potential.

Numerical calculation of the coefficient of shear viscosity for liquid argon using Eq. (8.6) yielded a result highly dependent on the friction coefficient β . [42] Two different estimates for β gave for η calculated values 1.27×10^{-3} poise and 0.73×10^{-3} poise, respectively, whereas the experimental value of η for argon is 2.39×10^{-3} poise. No calculations were made for the coefficient of bulk viscosity. The temperature dependence of η and ξ is essentially contained in $g_0(r)$, and consequently the second term in (8.6) and (8.7) has principally an exponential temperature dependence, in agreement with the experimental data.

It should be noted that the question of the boundary conditions at $r = 0$ for the auxiliary functions ψ_0 and ψ_2 is not fully clear. The papers cited require that these functions be finite when $r = 0$. This question was discussed in [41, 45, 46], and the possibility of other boundary conditions was demonstrated.

The coefficient of heat conduction in a simple liquid was calculated in [43]. A very cumbersome computation has yielded

$$\kappa = \frac{k^2T}{2v\beta} + \frac{k^2T^2}{6\beta v^2} \left(\frac{\partial v}{\partial T} \right)_p + \frac{\pi kT}{3v^2\beta} \int_0^\infty \left(\frac{\Phi(r)}{r} \right)' g_0(r) \left(r \frac{\partial}{\partial r} - 1 \right) \frac{\partial \ln g_0(r)}{\partial T} r^4 dr. \quad (8.8)$$

Numerical calculation for liquid argon gives $\kappa = 4.1 \times 10^{-4}$ cal/g-sec-deg, which is in satisfactory agreement with the experimental value 2.9×10^{-4} cal/g-sec-deg.

3. General remarks on Kirkwood's theory. Kirkwood's theory is at present the only one that permits the kinetic coefficients for a liquid to be expressed in terms of intermolecular forces and the partition function of the liquid particles. In addition to the problems mentioned above, this theory was also used to calcu-

late the optical anisotropy occurring in a flowing liquid, [46] and the results were again in satisfactory agreement with experiment. Much work was done on a generalization of Kirkwood's theory to include multi-component systems and on applications of this theory to irreversible processes in these systems.

Nevertheless, Kirkwood's theory remains only approximate because of the very method it employs, since the model of Brownian motion it uses cannot be fully representative of the motion of a molecule in a liquid. This is particularly manifest in the fact that Eq. (8.2) does not yield the correct expression (7.18), but of necessity leads to Einstein's relation in the form $D = kT/\beta$. [36] One might therefore expect the theory developed to be more correct for a rarefied gas, but this is not the case. In the limit of vanishing interaction, the equations for the viscosity and heat conduction coefficients do not coincide with the known expressions from kinetic theory of gases. [5] Further development of the theory of kinetic processes in liquids still remains a very important problem.

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