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Transport Coefficients from Dissipation in a Canonical Ensemble

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Expressions for the transport coefficients are obtained by studying the average changes with time which occur in members of a canonical ensemble when the initial state of one particle is partially specified. One calculates, both hydrodynamically and statistical mechanically, an appropriately weighted average of the spread of the initial knowledge. In this way expressions analogous to the Einstein equation for the self-diffusion of a Brownian particle are obtained; viz., the viscosity is proportional to a mean-square center of momentum displacement and the thermal conductivity is related to a mean-square center of energy displacement. These expressions may be converted into the integral of autocorrelation function formulas derived previously by others.

1. INTRODUCTION

THE path to construction of nonequilibrium distribution functions, the goal of the Kirkwood transport theory,[1] appears to be strewn with difficulties. The question thus arises as to whether irreversible phenomena can be described with equilibrium ensembles, the distributions of which are well known. Efforts in this direction have met with considerable success in recent years. Generally speaking, the result is the following. The transport coefficients may be expressed as equilibrium ensemble averages of dynamical variables whose explicit specification requires a solution of the N-body equation of motion. Equations (2.14) and (2.20) are illustrations. The field is thus open to various approximate solutions, or evaluations in the limit, of the mechanical equations, such as Mori's[2] binary encounter calculation or Montroll and Ward's[3] cluster development. This paper, however, will not be concerned with that problem. What will be discussed is a derivation of the transport coefficient expressions based on what we feel is a more pictorial argument than has previously been presented. It is hoped that greater physical insight into not only the final results but also the approximations may be gleaned. Let us begin by briefly reviewing the previous work.

The problems encountered may be classified into two types. Properties such as conductivity and magnetic susceptibility are related to the admittance of the system to an external conservative force. (Such admittances have been shown by Callen and Welton,[4] Kubo,[5] and others, to be related through the so-called fluctuation-dissipation theorem to time correlation functions.) Concisely put, the derivation is based on a solution of the Liouville equation (or its quantum analog, the equation of motion of the density matrix) for the linear deviations from equilibrium induced by the switching on of the external force. The possibility for such a solution arises from the fact that the external forces are derivable from a potential which may be made an additive part of the Hamiltonian. Possessing the distribution function, one may use standard methods of statistical mechanics to calculate the response to the force, then identify the admittance as the constant of proportionality.

The other type of problem deals with properties such as viscosity and thermal conductivity which are not strictly admittances. McLennan[6] has extended the above technique by assuming that nonequilibrium states are maintained by reservoirs which may be considered, on the average, as acting through external forces, albeit nonconservative ones. While it is not possible to detail

[1] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. 22, 817 (1950).

[2] H. Mori, Phys. Rev. 111, 694 (1958).

[3] E. W. Montroll and J. C. Ward, Physica 25, 268 (1959).

[4] H. B. Callen and T. A. Welton, Phys. Rev. 83, 34 (1951).

[5] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957); M. Lax, Phys. Rev. 109, 1921 (1958).

[6] J. A. McLennan, Phys. Rev. 115, 1405 (1959).

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completely the nature of these forces, fortunately one can obtain just the information about them which is necessary for the solution of Liouville's equation. Using the distribution function arrived at in this manner the fluxes may be evaluated to terms linear in the forces; the constants of proportionality are identified as the transport coefficients.

Mori[7] had developed a different technique for determining the distribution function. He hypothesizes that an ensemble artificially constructed at a given time with a local equilibrium canonical distribution will relax to the nonequilibrium ensemble appropriate to the given temperature, chemical potential, and velocity distribution in a time short on the scale of macroscopic variations. This provides an initial condition for the solution of Liouville's equation (or the quantum analog). The time derivatives of the local energy, density, and velocity which arise are replaced by divergences of flows according to the macroscopic equations of motion (conservation equations).

Two approaches to this problem have appeared in which calculation of the distribution function is not required. The work of Kubo, Yokota, and Nakajima[8] is based on the Onsager assumption that the average regression of fluctuations follows the macroscopic linear laws. One may then invert the linear laws wherein the time derivative is written as a finite difference quotient. One studies the entropy production in order to identify the variables. Equivalence between the behavior of macroscopic thermodynamic fluctuations and their corresponding microscopic mechanical variables is implicitly assumed.

Green[9] begins by deriving a Fokker-Planck type equation to describe the time evolution of a Markoffian set of variables ("complete set of gross variables" in his terminology). If the long wavelength components of the microscopic particle, momentum, and energy density are considered to be such a set, then the dissipation coefficients of these Fokker-Planck equations, which are expressible as time integrals of correlation functions, may be related to the transport coefficients.

While all the above work has appeared rather recently, description of a transport process by means of an equilibrium ensemble actually dates back to Einstein's study of diffusion of a Brownian particle.[10] This work was based on a physical picture which it is our purpose to extend to the description of phenomena such as viscosity and thermal conductivity in a classical system. The result will be expressions for the transport coefficients which emphasize their nature as measures of dissipation. The new equations can be shown to be

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[7] H. Mori, Phys. Rev. **112**, 1829 (1958).

[8] R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. Japan **12**, 1203 (1957).

[9] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954).

[10] A. Einstein, Ann. Physik **17**, 549 (1905). R. Furth, in his notes to A. Einstein, *Theory of the Brownian Movement* (E. P. Dutton and Company, New York, 1926), p. 99, presents a clear description of the model upon which the Einstein calculation was based.

equivalent to the previous ones when an assumption about fluctuations of the wall forces is made.

2. SELF-DIFFUSION

To arrive at an expression for the self-diffusion coefficient we will attempt to describe the average spread with time in our knowledge about the location of a particle. Comparison between a phenomenological and a statistical mechanical approach to this problem will yield the desired formula.

Consider an ensemble of systems canonically distributed. At time $t=0$ in each of the systems measure the x position of the particle which has been designated as the ith. The ensemble may be divided into subensembles such that at $t=0$ the ith particle of every member of a subensemble has the same x position. (Physically we have in mind allowing a range about this x position and having the range approach zero.) Characterize the subensembles by this position, for example x_{i0}'. Now allow the systems to evolve for a time t, after which the x position of the ith particle is again measured. The number of systems in a subensemble which have i between x and $x+dx$ at time t, divided by the total number of systems in that subensemble is

$$c_i(x,t\,|\,x_{i0}')A_x dx,$$

where A_x is the cross-sectional area perpendicular to the x direction. The notation has been chosen to indicate that c_i is the concentration of i at any point on the plane x after a time t in the subensemble characterized by x_{i0}'.

Being a concentration, c_i satisfies the equation of continuity

$$\partial c_i/\partial t = -\nabla\cdot\mathbf{j}_i, \tag{2.1}$$

where $\mathbf{j}_i$ is the particle diffusion current. As will become evident, except at zero time, gradients of c_i are small, so if we assume that the average behavior of i follows the macroscopic laws, then

$$\mathbf{j}_i = -D\nabla c_i, \tag{2.2}$$

D being the self-diffusion constant. Combining Eqs. (2.2) and (2.3) yields the usual diffusion equation, which, after a consideration of the symmetry of the problem, is

$$\partial c_i/\partial t = D\partial^2 c_i/\partial x^2. \tag{2.3}$$

One boundary condition is that at $t=0$, i is definitely at x_{i0}', or

$$c_i(x,0\,|\,x_{i0}') = \delta(x-x_{i0}')/A_x. \tag{2.4}$$

Let us consider throughout a system which is infinite in extent in such a way that l_x, l_y, l_z, and $N \rightarrow \infty$ while $N/V = c$, where the volume V is the product of the lengths l_x, l_y, l_z, and $A_x = l_y l_z$, etc. In this case the second and third boundary conditions arise from the fact that the particle i cannot arrive at infinity in finite time, so that

$$c_i(\pm\infty, t\,|\,x_{i0}') = 0. \tag{2.5}$$

The solution to this problem is well known to be

$$c_i = \frac{1}{2A_x(\pi Dt)^{\frac{1}{2}}} \exp\left[-\frac{(x-x_{i0}')^2}{4Dt}\right]. \quad (2.6)$$

This distribution is a Gaussian, representing a broadening of the original delta function, which may be regarded as the limit of a Gaussian.

The product of D and t characterizes the spread of the concentration or its second moment which, by (2.6), is

$$M_2{}^{(D)} = \int_{-\infty}^{\infty} (x-x_{i0}')^2 c_i(x,t\,|\,x_{i0}')dx = 2Dt/A_x. \quad (2.7)$$

In order to set the pattern for succeeding work, although it adds nothing in this case, let us reassemble the ensemble by multiplying this second moment by the probability density of each subensemble, integrate over all initial positions of i, and sum over i. The required probability density is

$$f^{(1,0)}(x_{i0}') = 1/l_x. \quad (2.8)$$

We find

$$I^{(D)} = \sum_{i=1}^{N} \int_0^{l_x} M_2{}^{(D)} f^{(1,0)}(x_{i0}')dx_{i0}',$$

$$= 2NDt/A_x. \quad (2.9)$$

A statistical mechanical analysis of the same phenomenon may also be performed. The concentration, c_i, is the average over the appropriate subensemble distribution function of the dynamical variable $\delta(x_i-x)/A_x$. If the subensemble distribution function at time t is $f^{(N)}(\mathbf{R}^N,\mathbf{P}^N,t\,|\,x_{i0}')$ then c_i is given by

$$c_i(x,t\,|\,x_{i0}') = \int\int [\delta(x_i-x)/A_x]$$
$$\times f^{(N)}(\mathbf{R}^N,\mathbf{P}^N,t\,|\,x_{i0}')d\mathbf{R}^N d\mathbf{P}^N. \quad (2.10)$$

For a canonical transformation of the variables of integration to zero time variables, Liouville's theorem tells us that $d\mathbf{R}^N d\mathbf{P}^N = d\mathbf{R}_0{}^N d\mathbf{P}_0{}^N$ and $f^{(N)}(\mathbf{R}^N,\mathbf{P}^N,t\,|\,x_{i0}') = f^{(N)}(\mathbf{R}_0{}^N,\mathbf{P}_0{}^N,0\,|\,x_{i0}')$, where we consider the phase point $\mathbf{R}^N\mathbf{P}^N$ as a function of $\mathbf{R}_0{}^N\mathbf{P}_0{}^N$ and t. By the method of construction the exact zero time distribution function is known to be

$$f^{(N)}(\mathbf{R}_0{}^N, \mathbf{P}_0{}^N, t=0\,|\,x_{i0}')$$
$$= \delta(x_{i0}-x_{i0}')f^{(N,0)}(\mathbf{R}_0{}^N,\mathbf{P}_0{}^N)/f^{(1,0)}(x_{i0}), \quad (2.11)$$

the zero superscripted distribution functions being those appropriate to an equilibrium canonical ensemble. This relation expresses the fact that at zero time particle i was definitely at x_{i0}', instead of being distributed with probability $f^{(1,0)}(x_{i0})$. The concentration is given by

$$c_i(x,t\,|\,x_{i0}') = \int\int (l_x/A_x)\delta(x_{it}-x)\delta(x_{i0}-x_{i0}')$$
$$\times f^{(N,0)}(\mathbf{R}_0{}^N,\mathbf{P}_0{}^N)d\mathbf{R}_0{}^N d\mathbf{P}_0{}^N. \quad (2.12)$$

The second moment $M_2{}^{(D)}$ and the integral $I^{(D)}$ may be written in terms of (2.12). After performing the integrations over the δ functions and equating the statistical result to the quasi-phenomenological expression of Eq. (2.9) one finds that

$$D = (1/2t)\int\int (x_{it}-x_{i0})^2$$
$$\times f^{(N,0)}(\mathbf{R}_0{}^N,\mathbf{P}_0{}^N)d\mathbf{R}_0{}^N d\mathbf{P}_0{}^N, \quad (2.13)$$

where $x_{it} = x_{it}(\mathbf{R}_0{}^N,\mathbf{P}_0{}^N,t)$ is a solution of the mechanical equations of motion. Introducing a more succinct notation in which $\Delta x_i = x_{it}-x_{i0}$, and $\langle\ \rangle$ denotes equilibrium ensemble averaging over zero time variables, we have

$$D = (1/2t)\langle(\Delta x_i)^2\rangle. \quad (2.14)$$

A few words should be said about the duration t. It must be of sufficient length to allow the hydrodynamical processes employed in the initial part of the derivation to become predominant. Thus t must at least be long compared with a mean collision time. A more quantitative estimate, following from the work of Uhlenbeck and Ornstein[11] with the Langevin equation, is $t \gg mD/kT$. This estimate also suffices for the considerations of the next paragraph. Difficulties of an upper limit are avoided in the infinite system since Poincaré recurrence times probably go at least exponentially with size.

Expressions such as Eq. (2.14) for D may be converted to a form involving an integration over time of an autocorrelation function. We carry out the derivation with a general dynamical variable, $G(R^N,P^N)$, for future use. Write

$$\Delta G = \int_0^t J_\tau d\tau, \quad (2.15)$$

where

$$J_\tau = dG(\mathbf{R}_\tau{}^N,\mathbf{P}_\tau{}^N)/d\tau,$$

and examine

$$\langle(\Delta G)^2\rangle = \int_0^t\int_0^t \langle J_\tau J_{\tau'}\rangle d\tau d\tau'. \quad (2.16)$$

Due to the stationarity of the equilibrium ensemble and the time symmetry of the equations of mechanical motion we have

$$\langle J_\tau J_{\tau'}\rangle = \langle J_{\tau-\tau'}J_0\rangle = \langle J_{\tau'-\tau}J_0\rangle. \quad (2.17)$$

After a change of variables to $\sigma = \tau'-\tau$, a change of order of integration, and the performance of one integration, Eq. (2.16) becomes

$$\langle(\Delta G)^2\rangle = 2t\int_0^t \left(1-\frac{\sigma}{t}\right)\langle J_0 J_\sigma\rangle d\sigma. \quad (2.18)$$

If the autocorrelation function $\langle J_0 J_t\rangle$ vanishes in sufficiently strong a manner for infinite time then the t

[11] G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930).

may be chosen large enough for the upper limit of integration to be extended to ∞, and Eq. (2.18), becomes asymptotically

$$\langle (\Delta G)^2 \rangle = 2t \int_0^\infty \langle J_0 J_\sigma \rangle d\sigma. \tag{2.19}$$

Specifically applying this result to Eq. (2.14) for D, one has

$$D = (1/m^2) \int_0^\infty \langle p_{ix0} p_{ixt} \rangle dt, \tag{2.20}$$

where p_{ix} is the x component of momentum.

Equations (2.14) and (2.20) are well-known results. They have been developed here for the sake of illustrating the technique which will now be applied to a study of the shear viscosity.

3. SHEAR VISCOSITY

At time $t=0$ in each system of a canonical ensemble, observe the x position and simultaneously the y momentum of the ith particle, and make subensemble divisions based on the results of this measurement; for example, group those with x_{i0}', p_{iy0}'. At a time t later measure the y velocity of the fluid at each plane x in the systems. [The precise meaning of this measurement is clarified in the statistical mechanical section by Eq. (3.10).] Form a subensemble average to determine the mean y velocity, $u_y(x,t\,|\,x_{i0}',p_{iy0}')$. After sufficient time this velocity satisfies the equation of motion

$$\partial \rho \mathbf{u}/\partial t = \nabla \cdot (\boldsymbol{\sigma} - \rho \mathbf{u}\mathbf{u}) + c\mathbf{K}, \tag{3.1}$$

where $\mathbf{K}$ is the external force per particle and $\rho = mc$ is the mass density. For the stress tensor $\boldsymbol{\sigma}$ we will assume the Newtonian form

$$\boldsymbol{\sigma} = -P\mathbf{1} + \varphi(\nabla \cdot \mathbf{u})\mathbf{1} + 2\eta \boldsymbol{\varepsilon}, \tag{3.2}$$

where P is the pressure, $\boldsymbol{\varepsilon} = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^\dagger) - \frac{1}{3}(\nabla \cdot \mathbf{u})\mathbf{1}$ is the divergenceless symmetric part of $\nabla \mathbf{u}$ (known as the rate of shear tensor), and η and φ are, respectively, the shear and bulk viscosities.

By the symmetry of the problem all variables are functions of x and t only. The walls are at infinity, in the previously defined limit, so that the external force term may be neglected. Employing these facts in Eqs. (3.1) and (3.2), and linearizing in $\mathbf{u}$, one obtains as the y component of (3.1)

$$\frac{\partial u_y}{\partial t} = \frac{\eta}{\rho} \frac{\partial^2 u_y}{\partial x^2}. \tag{3.3}$$

The boundary conditions are

$$u_y(x,0\,|\,x_{i0}',p_{iy0}') = p_{iy0}' \delta(x - x_{i0}')/\rho A_x, \tag{3.4}$$

and

$$u_y(\pm \infty, t\,|\,x_{i0}', p_{iy0}') = 0. \tag{3.5}$$

The equation and boundary conditions are identical with those encountered in Sec. 2, so that the solution is

$$u_y = \frac{p_{iy0}'}{2A_x(\pi \eta \rho t)^{\frac{1}{2}}} \exp\left[-\frac{\rho(x - x_{i0}')^2}{4\eta t} \right]. \tag{3.6}$$

The spread of this Gaussian is proportional to ηt and may be characterized by the second moment

$$M_2{}^{(\eta)} = \int_{-\infty}^\infty (x - x_{i0}')^2 u_y(x,t\,|\,x_{i0}',p_{iy0}')dx$$

$$= 2p_{iy0}' \eta t/\rho^2 A_x. \tag{3.7}$$

Note that when we consider $A_x \to \infty$, then $u_y \to 0$ and the use of linearized equations is justified. What this amounts to physically is that while, in general, individual member of the ensemble do not have transition probabilities given by solution of a linearized hydrodynamic equation (or for that matter a nonlinearized hydrodynamic equation), the average behavior is described by such an equation.

The ensemble is now reassembled in the following manner. Multiply the second moment by p_{iy0}' and average over the probability density

$$f^{(1,0)}(x_{i0}',p_{iy0}')$$
$$= l_x{}^{-1}(2\pi m k T)^{-\frac{1}{2}} \exp[(p_{iy0}')^2/2mkT]. \tag{3.8}$$

To symmetrize in particle name, sum over i. The result is

$$I^{(\eta)} = \sum_{i=1}^N \int\int p_{iy0}' M_2{}^{(\eta)} f^{(1,0)}(x_{i0}',p_{iy0}')dx_{i0}'dp_{iy0}',$$

$$= 2kTl_x \eta t/\rho. \tag{3.9}$$

Note that failure to multiply the second moment by p_{iy0}' leads to a zero.

Next, consider the statistical mechanical description of the same procedure. The mean velocity, u_y, is expressible as a subensemble average of the dynamical variable $(1/N)\sum_j (p_j/m)l_x \delta(x_j - x)$; viz.,

$$u_y(x,t\,|\,x_{i0}',p_{iy0}')$$

$$= \frac{1}{N}\sum_{i=1}^N \int\int \frac{p_{jy}}{m} l_x \delta(x_j - x)$$

$$\times f^{(N)}(\mathbf{R}^N,\mathbf{P}^N,t\,|\,x_{i0}',p_{iy0}')d\mathbf{R}^N d\mathbf{P}^N. \tag{3.10}$$

A canonical transformation may be made to zero time variables. The subensemble distribution function at $t=0$ is, by construction,

$$f^{(N)}(\mathbf{R}_0{}^N,\mathbf{P}_0{}^N,0\,|\,x_{i0}',p_{iy0}')$$
$$= \delta(x - x_{i0}')\delta(p_{iy0} - p_{iy0}')$$
$$\times f^{(N,0)}(\mathbf{R}_0{}^N,\mathbf{P}_0{}^N)/f^{(1,0)}(x_{i0}',p_{iy0}'). \tag{3.11}$$

Therefore, we may write

$$u_y = \frac{1}{N}\sum_{j=1}^{N}\int\int\left[\frac{p_{jyt}}{m}l_x\delta(x_{jt}-x)\delta(x_{i0}-x_{i0}')\right.$$

$$\times\delta(p_{iy0}-p_{iy0}')$$

$$\left.\times f^{(N,0)}(\mathbf{R}_0^N,\mathbf{P}_0^N)/f^{(1,0)}(x_{i0}',p_{iy0}')\right]d\mathbf{R}_0^N d\mathbf{P}_0^N. \quad (3.12)$$

The second moment $M_2^{(\eta)}$ and the integral $I^{(\eta)}$ are easily calculated due to the presence of the δ functions. Equating the result so obtained to the phenomenological Eq. (3.9) we find for large t

$$\eta = [1/(2VkTt)]\langle\sum_{i,j=1}^{N}(x_{jt}-x_{i0})^2 p_{jyt}p_{iy0}\rangle. \quad (3.13)$$

Let us review the origin of the factors: $(x_{jt}-x_{i0})^2$ arises in taking the second moment; p_{jyt} is from the dynamical variable which defines u_y in Eq. (3.10); p_{iy0} originates from the weighting employed in the definition of $I^{(\eta)}$. Using conservation of momentum it is possible to transform the shear viscosity to

$$\eta = [1/(2VkTt)]\langle[\sum_{i=1}^{N}(x_{it}p_{iyt}-x_{i0}p_{iy0})]^2\rangle, \quad (3.14)$$

by the procedure outlined in Appendix I. The shear viscosity is found to be proportional to the mean-square x displacement of the center of y momentum.

Equation (2.19) may be applied to this last result with

$$G^{(\eta)} = \sum_{i=1}^{N}x_i p_{iy}, \quad (3.15)$$

$$J^{(\eta)} = \sum_{i=1}^{N}[(p_{ix}p_{iy}/m)+x_iF_{iy}+x_iK_{iy}], \quad (3.16)$$

so that in autocorrelation function form

$$\eta = (1/VkT)\int_0^\infty\langle J_0^{(\eta)}J_t^{(\eta)}\rangle dt. \quad (3.17)$$

In definition (3.16) the force on i has been divided into an intermolecular part, $\mathbf{F}_i$, and an external part, $\mathbf{K}_i$.

To obtain correspondence between this autocorrelation function equation and previous results[7] it is necessary to assume that the fluctuations of $\sum_i x_iK_{iy}$ from the average value have short relaxation time or are small compared with fluctuations of $\sum_i[(p_{ix}p_{iy}/m)+x_iF_{iy}]$, and that these two quantities are uncorrelated. Then $\sum_i x_iK_{iy}$ may be replaced by its average value, zero.

The necessity of including external forces in the mechanical equation of motion, whereas they were neg-

lected in the hydrodynamical equation, (3.3), is evident from the case of bulk viscosity discussed below.

4. BULK VISCOSITY

The calculation of the bulk viscosity proceeds along lines similar to the previous two derivations, although some additional complications enter. At time zero the x position and x momentum of the ith particle of each system of a canonical ensemble is measured, and subensembles constructed on the basis of this result. After a time t the velocity in the x direction at every point in the fluid is determined and subensemble averaged to yield a quantity $u_x(x,t\,|\,x_{i0}',p_{ix0}')$ satisfying the equation of motion (3.1). Considering the symmetry of the problem and employing the Newtonian stress tensor, (3.2) we arrive at the linearized equation

$$\frac{\partial u_x}{\partial t} = \frac{\psi}{\rho}\frac{\partial^2 u_x}{\partial x^2} - \frac{1}{\rho}\frac{\partial P}{\partial x}, \quad (4.1)$$

where $\psi = \varphi + \frac{4}{3}\eta$. We shall drop the term $\rho^{-1}\partial P/\partial x$. The reason for the neglect of this term will be examined in detail later.

The calculation goes through in complete analogy to Sec. 3 with p_x replacing p_y. For ψ we find

$$\psi = [1/(2VkTt)]\langle\sum_{i,j=1}^{N}(x_{jt}-x_{i0})^2 p_{jyt}p_{iy0}\rangle, \quad (4.2)$$

or, following the argument of Appendix I,

$$\psi = [1/(2VkTt)]\langle[\sum_{i=1}^{N}(x_{it}p_{ixt}-x_{i0}p_{ix0})]^2\rangle. \quad (4.3)$$

This, in turn, may be converted to the autocorrelation function form

$$\psi = (1/VkT)\int_0^\infty\langle J_0^{(\psi)}J_t^{(\psi)}\rangle dt, \quad (4.4)$$

where

$$J^{(\psi)} = \sum_{i=1}^{N}[(p_{ix}p_{ix}/m)+x_iF_{ix}+x_iK_{ix}]. \quad (4.5)$$

Note that $J^{(\psi)}$ and $J^{(\eta)}$ are, respectively, the xx and xy terms of a dyadic which we might label $\mathbf{J}^{(\mathrm{visc})}$.

Again, this is the result of previous authors[7] when $\sum_i x_iK_{ix}$ is replaced by its average value, $-PV$.

In order to understand the reason for neglecting the term $-\rho^{-1}\partial P/\partial x$ in Eq. (4.1) let us examine the effect of its inclusion. The assumption will tentatively be made that the average behavior of u_x is governed by the hydrodynamic equations of change under isothermal conditions, in keeping with the employment of a canonical ensemble. We shall assume, for argument's sake, that the pressure is in instantaneous equilibrium with the density (later we shall point the finger of accusation at this assumption for yielding the erroneous results). Under these terms the equation of continuity,

(2.1), may be written as

$$\frac{\partial P}{\partial t} = -\rho \left(\frac{\partial P}{\partial \rho}\right)_T \frac{\partial u_x}{\partial x}. \qquad (4.6)$$

Details of the simultaneous solution of this equation with Eq. (4.1) are discussed in Appendix II. One finds that the second moment of the velocity distribution is

$$M_2^{(\psi)} = \int_{-\infty}^{\infty} (x - x_{i0}')^2 u_x dx$$
$$= (2p_{ix0}'/\rho A_x)[(\psi/\rho)t + \tfrac{1}{2}c_s^2 t^2], \quad (4.7)$$

where c_s is the isothermal sound velocity, $c_s^2 = (\partial P/\partial \rho)_T$. Physically this result is easily understood. The solution for u_x can be approximately decomposed into a propagation in the positive and negative directions, with velocity c_s, of the disturbance originated at x_{i0}', and Gaussian spreading about these centers, $x_{i0}' \pm c_s t$. There are further terms which represent a crossing of the two effects but these do not contribute to the second moment. The term proportional to ψt in Eq. (4.7) arises from the dissipative spreading, while the term containing the factor $c_s^2 t^2$ is due to the nondissipative propagation.

If Eq. (4.7) for the second moment replaced the analog of Eq. (3.7) in the phenomenological part of the ψ calculation then we would have obtained instead of the final result (4.4) the equation

$$\psi + \tfrac{1}{2}\rho c_s^2 t = \frac{1}{VkT}\int_0^t \left(1 - \frac{\sigma}{t}\right)\langle J_0^{(\psi)} J_\sigma^{(\psi)}\rangle d\sigma, \quad (4.8)$$

where the σ/t of Eq. (2.18) has been retained. From the equilibrium statistical mechanics of the pressure, based on the virial theorem,[12] we see that trace $\mathbf{J}^{(\mathrm{visc})}$ has the character of a pressure fluctuation. If we wish to be consistent in employing Eq. (4.1) to describe the time evolution of average mechanical properties, then we would predict that as σ becomes large the autocorrelation function $\langle J_0^{(\psi)} J_\sigma^{(\psi)}\rangle$ does not approach zero but rather has the coherent part $\langle (V\Delta P)^2\rangle$. The fact that pressure fluctuations are conserved by the equations of motion (4.1) and (4.6) is demonstrated in Appendix III. The short time part of the autocorrelation function may be considered as giving rise to the viscosity coefficient ψ by the method employed in the initial paragraphs of this section, so that the remainder of Eq. (4.8) which must be examined is

$$\tfrac{1}{2}\rho c_s^2 t = \frac{1}{VkT}\langle (V\Delta P)^2\rangle \int_0^t \left(1 - \frac{\sigma}{t}\right) d\sigma. \quad (4.9)$$

Regarding P and T as the independent variables we find,

by the method outlined in Landau and Lifshitz,[13] that the isothermal mean square fluctuation $\langle (\Delta P)\rangle^2$ are $-kT(\partial P/\partial t)_T$ or $kT\rho c_s^2/V$. The validity of Eq. (4.9) is thus confirmed.

The above argument is, of course, not physically meaningful, but the mathematical manipulations do give us an insight into its faults and the reason for not retaining the $\partial P/\partial x$ part of the hydrodynamic equations of motion. While these equations of motion do appear to be useful in describing the average spread of a microscopic mechanical fluctuation, in some cases they also erroneously predict a conservation of the magnitude of the fluctuation. The difficulty is that the microscopic variables do not behave like thermodynamic variables in that they do not tend to drive the pressure to new local thermodynamic values. Thus the pressure should not be regarded as in equilibrium with the density, as implied by the equation of continuity, (4.6), but rather as remaining uniform as implied by the neglect of $\partial P/\partial x$ in Eq. (4.1).

5. THERMAL CONDUCTIVITY

The now familiar pattern of dividing a canonical ensemble into subensembles according to the results of a measurement is repeated. In this case at zero time the x position and total energy of a single particle is to be measured. Typical results of this determination might be x_{i0}' and $\tilde{E}_{i0}'$, where the tilde denotes excess above the average particle energy; i.e.,

$$\tilde{E}_{i0}' = E_{i0}' - \langle E_i\rangle,$$
$$E_i = (p_i^2/2m) + \tfrac{1}{2}\sum_{j\neq i} V_{ij}. \qquad (5.1)$$

At a time t later measure the excess energy density at each point in the fluid and take subensemble averages to determine a quantity $\tilde{E}(x,t\,|\,x_{i0}',\tilde{E}_{i0}')$.

This average energy satisfies the conservation equation

$$c(\partial \tilde{E}/\partial T) + c\mathbf{u}\cdot\nabla\tilde{E} = \boldsymbol{\sigma}:\nabla\mathbf{u} - \nabla\cdot\mathbf{j}_E, \qquad (5.2)$$

where c is the concentration in particles per unit volume The energy flow, $\mathbf{j}_E$, we will assume to be given by the linear law

$$\mathbf{j}_E = -(\kappa/c_v)\nabla\tilde{E}, \qquad (5.3)$$

where c_v is the heat capacity $(\partial E/\partial T)_v$, and κ is the coefficient of thermal conductivity. Combining Eqs. (5.2) and (5.3), linearizing in deviations from equilibrium, simplifying the vectors by means of the system's symmetry, and neglecting the nondissipative ideal fluid term, $-p\partial u_x/\partial x$, yields the diffusion type equation

$$\partial \tilde{E}/\partial t = (\kappa/cc_v)(\partial^2 \tilde{E}/\partial x^2). \qquad (5.4)$$

[12] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, New York, 1954), p. 134.

[13] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, 1958), Sec. 111. Here, too, the assumption of thermodynamic equilibrium among the fluctuations is made. This may account for the lack of the nonthermodynamic term for this external reaction fluctuation [R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, Cambridge, 1955), p. 755].

The boundary conditions are

$$\bar{E}(x,0\,|\,x_{i0}',\bar{E}_{i0}') = (\bar{E}_{i0}'/cA_x)\delta(x-x_{i0}'), \quad (5.5)$$

$$\bar{E}(\pm\infty,t\,|\,x_{i0}',\bar{E}_{i0}') = 0. \quad (5.6)$$

Actually, the first condition involves neglect of the correlation of the energy and position of the other particles with that of i. This will be discussed more fully below.

In analogy to previous sections one finds the second moment of $\bar{E}$ to be

$$M_2^{(\kappa)} = \int_{-\infty}^{\infty} (x-x_{i0}')^2 \bar{E}\,dx$$

$$= 2\bar{E}_{i0}'\kappa t/c^2 c_v A_x. \quad (5.7)$$

In reassembling the ensemble we weight each subensemble with a factor $\bar{E}_{i0}'$ and its probability of occurrence, $f^{(1,0)}(x_{i0}')f(\bar{E}_{i0}')$, integrate over x_{i0}', $\bar{E}_{i0}'$, and sum over i, to obtain

$$I^{(\kappa)} = \sum_{i=1}^{N} \int_{-\infty}^{\infty} \bar{E}_{i0}' M_2^{(\kappa)} (1/l_x) f(\bar{E}_{i0}') dx_{i0}' d\bar{E}_{i0}'$$

$$= \frac{2\kappa t}{c^2 c_v A_x} \sum_{i=1}^{N} \int_{-\infty}^{\infty} (\bar{E}_{i0}')^2 f(\bar{E}_{i0}') d\bar{E}_{i0}'. \quad (5.8)$$

The integral shall be evaluated in an approximation equivalent to the previous one, namely, independence of particle energy.

Consider the fluctuations in energy in a canonical ensemble of systems:

$$\langle (E-\langle E\rangle)^2\rangle$$

$$= kT^2 N c_v$$

$$= \sum_i \int\int \bar{E}_i^2 f^{(N,0)} d\mathbf{R}^N d\mathbf{P}^N$$

$$+ \sum_i \sum_{j\neq i} \int\int \bar{E}_i \bar{E}_j f^{(N,0)} d\mathbf{R}^N d\mathbf{P}^N. \quad (5.9)$$

If the particle energies are independent, the second term on the right-hand side may be neglected so that

$$NkT^2 = \frac{1}{c_v} \sum_{i=1}^{N} \int_{-\infty}^{\infty} (\bar{E}_{i0}')^2 f(\bar{E}_{i0}') d\bar{E}_{i0}', \quad (5.10)$$

and

$$I^{(\kappa)} = 2NkT^2\kappa t/c^2 A_x. \quad (5.11)$$

Previous authors have seemingly circumvented the explicit neglect of particle energy correlations by a coarse graining in space.[14] That argument as applied to the present method would introduce a modification of technique as follows. Instead of locating one particle at

[14] For the most complete discussion see Sec. A and the appendix to reference 9.

x_{i0}' and measuring its energy we would measure the energy in a macroscopically narrow but microscopically wide region about x_{i0}'. We could then argue that the energy correlations decrease in importance inversely with the width of the region. If we did this, however, difficulties of particle energy correlation would enter in the statistical calculation which follows, so it is not clear that the approximation can be avoided here.

Paralleling the technique of previous sections we may derive a statistical mechanical expression for the integral $I^{(\kappa)}$ or, equivalently, κ. No assumption about independence of particle energy is necessary. We find

$$\kappa = [1/(2VkT^2 t)]\langle \sum_{i,j} (x_{jt}-x_{i0})^2 \bar{E}_{jt}\bar{E}_{i0}\rangle. \quad (5.12)$$

The origins of the terms are again easily perceived [see the discussion following Eq. (3.13)].

With the principle of conservation of momentum replaced by conservation of energy the method of Appendix I may be employed to convert κ to

$$\kappa = [1/(2VkT^2 t)]\langle [\sum_{i=1}^{N} (x_{it}\bar{E}_{it} - x_{i0}\bar{E}_{i0})]^2\rangle, \quad (5.13)$$

a form analogous to Eqs. (4.3), (3.14) and the Einstein relation (2.14). The thermal conductivity is proportional to the mean square x displacement of the center of energy.

Another transformation may be made by Eq. (2.19) to yield the autocorrelation expression

$$\kappa = (1/VkT^2)\int_{0}^{\infty} \langle J_{x0}^{(\kappa)} J_{xt}^{(\kappa)}\rangle dt, \quad (5.14)$$

where the flow $\mathbf{J}^{(\kappa)}$ is given by

$$\mathbf{J}^{(\kappa)} = \frac{d}{dt}\sum_i \mathbf{r}_i \bar{E}_i$$

$$= \sum_{i=1}^{N} \left(\frac{p_i^2}{2m}\mathbf{1} + \tfrac{1}{2}\sum_{j\neq 1} [V(r_{ij})\mathbf{1} + \mathbf{r}_{ij}\mathbf{F}_{ij}]\right.$$

$$\left. - \langle E_i\rangle\mathbf{1} + \mathbf{r}_i\mathbf{K}_i\right)\frac{\mathbf{p}_i}{m}. \quad (5.15)$$

The force, $\mathbf{F}_i$, has been resolved into pair components

$$\mathbf{F}_i = \sum_{j\neq 1} \mathbf{F}_{ji},$$

and use has been made of the Newton law

$$\mathbf{F}_{ji} = -\nabla_{\mathbf{r}_i} V(r_{ij}) = \nabla_{\mathbf{r}_j} V(r_{ij}) = -\mathbf{F}_{ij}.$$

The vector separation is defined as $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. To achieve identity between Eqs. (5.14–15) and the results of previous workers[7] $\sum_i \mathbf{r}_i \mathbf{K}_i \cdot \mathbf{p}_i$ must be identified with its spatially averaged value, $-(1/N)\sum_i (PV)\mathbf{p}_i$.

6. CONCLUSION

The purpose of this work has been to present a simple, somewhat more pictorial basis for recent theories of irreversible processes. The transport coefficients have been shown to be measures of the average spread with time of knowledge after the microscopic state of a single particle has been specified. In the cases studied the average transition probabilities followed a Gaussian law. Attention was fixed on the second moment which turned out to be proportional to the transport coefficient and the time. The equivalence of these second moment expressions to the usual forms involving autocorrelation functions was demonstrated.

The question arises as to whether the second moment expressions have greater validity than the Gaussian curves upon which they are based.[15] Consider the simplest case, which is self-diffusion. If the Gaussian distribution for c_i, Eq. (2.6), was rigorously valid then one should be free to characterize it, for example, by the fourth moment instead of the second. If this had been done we would have found the expression

$$D^2 = (1/12t^2)\langle(\Delta x_i)^4\rangle, \qquad (6.1)$$

which for equivalence with Eq. (2.4) requires that

$$\langle(\Delta x_i)^4\rangle = 3[\langle(\Delta x_i)^2\rangle]^2. \qquad (6.2)$$

Uhlenbeck and Ornstein[11] have shown that the Langevin equation implies this result as well as the entire Gaussian distribution for c_i for times $t\gg 1/\beta$ and distances $(x-x_{i0}')\gg u_x^*/\beta$ where $m\beta$ is the friction constant equal to kT/D, and u_x^* is the x component of some characteristic molecular velocity; i.e., $u_x^* \approx (kT/m)^{\frac{1}{2}}$.

There appears to be a further degree of arbitrariness in our work, the significance of which is not fully understood. In "reassembling the ensemble" for the shear viscosity calculation we found that by weighting each subensemble with p_{iy0}' we avoided an odd integrand which would have yielded zero. At the time there appeared to be nothing unique about this manner of weighting, and yet later we found that this particular procedure was essential in deriving the mean square displacement expression, (3.14), and the autocorrelation equation, (3.17). A similar situation arises in bulk viscosity, thermal conductivity, and even self-diffusion (where the weight unity is employed). This does not imply that there is anything wrong with the final results but rather that other expressions of the same type may be valid.

APPENDIX I

This Appendix is devoted to outlining the procedure which transforms Eq. (3.13) into Eq. (3.14). We begin with

$$A = \langle \sum_{i,j=1}^{N} (x_{jt}^2 - 2x_{i0}x_{jt} + x_{i0}^2)p_{jyt}p_{iy0}\rangle, \qquad (A1.1)$$

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[15] A similar question has been raised by M. Lax, Revs. Modern Phys. **32**, 25 (1960).

from Eq. (3.13). The equalities

$$\langle \sum_j x_{jt}^2 p_{jyt} \sum_i p_{iy0}\rangle = \langle \sum_{i,j} x_{jt}^2 p_{jyt}p_{iyt}\rangle, \qquad (A1.2)$$

$$= \langle \sum_{i,j} x_{j0}^2 p_{jy0}p_{iy0}\rangle, \qquad (A1.3)$$

$$= \langle \sum_i x_{i0}^2 p_{iy0}^2\rangle, \qquad (A1.4)$$

follow, respectively, from conservation of momentum, a canonical transformation, and the evenness of the distribution function in momentum. Similarly we find

$$\langle \sum_{i,j} x_{i0}^2 p_{jyt}p_{iy0}\rangle = \langle \sum_i x_{i0}^2 p_{iy0}^2\rangle. \qquad (A1.5)$$

In Eq. (3.14) there appears the factor

$$B = \langle \sum_{i,j=1}^{N} (x_{jt}x_{it}p_{jyt}p_{iyt} - 2x_{jt}x_{i0}p_{jyt}p_{iy0}$$
$$+ x_{j0}x_{i0}p_{jy0}p_{iy0})\rangle. \qquad (A1.6)$$

The equalities

$$\langle \sum_{i,j} x_{jt}x_{it}p_{jyt}p_{iyt}\rangle = \langle \sum_{i,j} x_{j0}x_{i0}p_{jy0}p_{iy0}\rangle, \qquad (A1.7)$$

$$= \langle \sum_i x_{i0}^2 p_{iy0}^2\rangle, \qquad (A1.8)$$

follow by a canonical transformation and the evenness of the distribution function in momentum. Putting pieces together it is seen that $A = B$.

Since total momentum is not strictly conserved due to wall interactions we have assumed above that the correlation of the deviations with the other factors are either small or short lived.

APPENDIX II

We wish to find a simultaneous solution of Eqs. (4.1) and (4.6). The zero of pressure in these equations may be regarded as the constant value at infinite distance since only derivatives of P appear. The Fourier transform with respect to x of these two equations may be written as the one matrix equation

$$\partial\mathfrak{Z}/\partial t = \mathbf{M}\mathfrak{Z}, \qquad (A2.1)$$

where

$$\mathfrak{Z} = \begin{pmatrix} \mathfrak{u}_x(k,t) \\ \mathfrak{P}(k,t) \end{pmatrix}, \qquad (A2.2)$$

$$\mathbf{M} = \begin{pmatrix} -k^2\psi/\rho & ik/\rho \\ i\rho c_s^2 k & 0 \end{pmatrix}, \qquad (A2.3)$$

k is the transform variable and the German type denotes transform. The initial condition is

$$\mathfrak{Z}_0 = \begin{pmatrix} \mathfrak{u}_x(k,0) \\ \mathfrak{P}(k,0) \end{pmatrix}. \qquad (A2.4)$$

The boundary condition analogous to Eq. (3.4) would be

$$u_x(x,0) = p_{ix0}'\delta(x-x_{i0}')/\rho A_x, \qquad (A2.5)$$

so that

$$\mathfrak{u}_x(k,0)=p_{ix0}'e^{ik x_{i0}'}/\rho A_x. \qquad (A2.6)$$

The initial pressure condition turns out to be immaterial for the final result and a reasonable choice is

$$\mathfrak{P}(k,0)=0, \qquad (A2.7)$$

corresponding to uniform pressure initially. The solution of Eq. (A2.1) is

$$\mathfrak{Z}=\exp(\mathbf{M}t)\mathfrak{Z}_0. \qquad (A2.8)$$

It is easily shown that the second moment is related to the Fourier transform by

$$M^{(\psi)}=\int_{-\infty}^{\infty}(x-x_{i0})^2\mathfrak{u}_x(x,t)dx$$

$$=-\frac{\partial^2}{\partial k^2}[\mathfrak{u}_x(k,t)e^{-ik x_{i0}'}]_{k=0}. \qquad (A2.9)$$

One finds that

$$\int_{-\infty}^{\infty}(x-x_{i0}')^2 Z(x,t)dx$$

$$=-\frac{\partial^2}{\partial k^2}[\mathfrak{Z}(k,t)e^{-ik x_{i0}'}]_{k=0}, \qquad (A2.10)$$

$$=-\left[t\frac{\partial^2\mathbf{M}}{\partial^2 k}+t^2\left(\frac{\partial\mathbf{M}}{\partial k}\right)^2\right]_{k=0}(\mathfrak{Z}_0 e^{-ik x_{i0}'}), \qquad (A2.11)$$

$$=\left[t\begin{pmatrix}2\psi/\rho & 0\\ 0 & 0\end{pmatrix}+t^2\begin{pmatrix}c_s^2 & 0\\ 0 & c_s^2\end{pmatrix}\right]\begin{pmatrix}p_{ix0}'/\rho A_x\\ 0\end{pmatrix}, \qquad (A2.12)$$

from which Eq. (4.7) follows.

APPENDIX III

By conservation of a pressure fluctuation we mean that the integral of the instantaneous pressure over all space is independent of time. To show that Eqs. (4.1) and (4.6) imply this result we must examine

$$\int_{-\infty}^{\infty}P(x,t)dx=\mathfrak{P}(0,t). \qquad (A3.1)$$

The matrix $\mathbf{M}$ is zero for $k=0$ so that Eq. (A2.8) expresses the conservation condition in the form $\mathfrak{P}(0,t)=\mathfrak{P}(0,0)$. (We are no longer assuming that at zero time there are no pressure fluctuations.)

Effect of the λ Transition on the Atomic Distribution in Liquid Helium by Neutron Diffraction

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Neutron diffraction patterns for samples of liquid helium at 1.06°K, 2.29°K, and 2.46°K have been measured over the angular range 4° to 64° using 1.06₄ A neutrons. The liquid structure factor $i(s)+1$ was deduced for each curve and these show a change which is associated with the λ transition which indicates that the spatial order in the liquid is smaller below the λ point than above. The measurements were transformed to give the radial distribution function $4\pi r^2[\rho(r)-\rho_0]$ from which was deduced the number of neighbors under the first shell of atoms and the nearest distance of approach of two atoms in the liquid. These lie between 8.₅ atoms and 9.₃ atoms and 2.35 A and 2.40 A, respectively.

1. INTRODUCTION

A KNOWLEDGE of the atomic distributions, atomic motions and effective potentials in liquids is important in the theory of condensed systems. Information about the atomic distribution in liquids can be obtained from either neutron or x-ray diffraction patterns while information about the atomic motions can be obtained from determinations of the change in energy of inelastically scattered neutrons. Such informations are of particular importance in the case of liquid helium because the details of the λ transition have not been explained and because liquid helium at low temperatures is essentially in its ground state and therefore

the liquid most amenable to theoretical investigations. Both neutrons[1] and x-rays[2-5] have been used to investigate the atomic distribution in liquid helium while the excitation curve has been obtained through measurements of the change in wavelength of neutrons inelasti-

[1] D. G. Hurst and D. G. Henshaw, Phys. Rev. **100**, 994 (1955).
[2] W. H. Keesom and K. W. Taconis, Physica **5**, 270 (1938).
[3] J. Reekie, Proc. Cambridge Phil. Soc. **36**, 236 (1940).
[4] J. Reekie and T. S. Hutchinson, Phys. Rev. **92**, 827 (1953); T. S. Hutchison, C. F. A. Beaumont, and J. Reekie, Proc. Phys. Soc. (London) A**66**, 409 (1953); C. F. A. Beaumont and J. Reekie, Proc. Roy. Soc. (London) A**228**, 363 (1955).
[5] W. L. Gordon, C. H. Shaw, and J. G. Daunt, J. Phys. Chem. Solids **5**, 117 (1958).