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The Statistical Mechanical Theory of Transport Processes.

III. The Coefficients of Shear and Bulk Viscosity of Liquids*

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A molecular theory of the coefficients of shear and bulk viscosity of monatomic liquids is developed on the basis of the general theory of transport processes presented in the first article of this series. With the use of the Lennard-Jones potential and a reasonable analytic approximation to the experimental radial distribution function, calculations of the coefficients of shear and bulk viscosity of liquid argon at 89°K have been carried out. The theory leads explicitly to ratios of the coefficients to the friction constant of the theory of Brownian motion. With a preliminary estimate of the friction constant, a value of the shear viscosity of liquid argon in moderately good agreement with experiment is obtained.

I

THE general statistical mechanical theory of transport processes, developed in the first article (SMTI) of this series,¹ has as an objective the determination of the coefficients of viscosity, diffusion and heat conductivity of fluids in terms of molecular variables. It is the purpose of the present article to present a detailed theory of the coefficients of shear and bulk viscosity of liquids based upon the general theory. The starting point is provided by the differential equations of the Chandrasekhar² type for the probability distribution functions in the phase space of sets of one, two, and three molecules of the liquid, which were derived from the molecular standpoint in SMTI. An alternative approach is provided by the kinetic theory of liquids of Born and Green.³ While their theory parallels our own and duplicates many of its general results, it differs in the manner in which dissipative terms are introduced into the equations satisfied by the distribution functions. Although Born and Green have presented an interesting qualitative discussion of the coefficient of shear viscosity of liquids, they have not yet succeeded in constructing solutions of their equations for the distribution functions in sufficiently explicit form to yield concrete results.

The macroscopic hydrodynamics of viscous fluids is described by the equations of continuity and motion,

$$\begin{aligned}\nabla \cdot (\rho \mathbf{u}) + \partial \rho / \partial t &= 0, \\ \rho (d\mathbf{u}/dt) &= \mathbf{X} + \nabla \cdot \boldsymbol{\sigma},\end{aligned}$$

where ρ is the density, \mathbf{u} the particle velocity, \mathbf{X} the external body force, and $\boldsymbol{\sigma}$ the stress tensor, supplemented by the Newtonian expression for the stress tensor,

$$\boldsymbol{\sigma} = -\{p + [(2\eta/3)] - \phi\} \nabla \cdot \mathbf{u} \mathbf{I} + 2\eta \dot{\boldsymbol{\epsilon}},$$

where p is the equilibrium pressure of the fluid, $\dot{\boldsymbol{\epsilon}}$ the rate of strain, and η and ϕ are the coefficients of shear and bulk viscosity. The stress tensor is determined by molecular distribution functions and intermolecular forces in the manner described by Eq. (26) of SMTI. There are two types of terms, one arising from momentum transport and one from the direct transmission of intermolecular forces, which is determined by the average density of molecular pairs. In thermodynamic equilibrium the stress reduces to a uniform normal pressure, the first term of which is the ideal gas contribution. The second term arising from intermolecular forces has no shear components, since the pair density, proportional to the radial distribution function of the theory of liquids, possesses spherical symmetry. Departure from equilibrium resulting from hydrodynamic flow leads to perturbations in the molecular distribution functions proportional to the components of the rate of strain. In liquids the momentum transport contribution to these terms is very small relative to the contribution from intermolecular forces. The latter contribution arises from the perturbation in the pair density. This perturbation consists of two parts, one spherically symmetric, which determines the bulk viscosity ϕ , and one having the symmetry of a surface harmonic of order two, which determines the shear viscosity.

By means of the general equations of SMTI, the perturbations in the pertinent molecular distribution functions have been constructed and the ratios η/ζ and ϕ/ζ of the two coefficients of viscosity to the Brownian motion friction constant ζ have been expressed in terms of definite integrals involving the potential of intermolecular force and the equilibrium radial distribution function. Calculations have been carried out for liquid argon at 89°K with the use of the Lennard-Jones potential of intermolecular force and the Eisenstein-Gingrich radial distribution function. The result of the calculation is

$$\eta/\zeta = 2.63 \times 10^6 \text{ cm}^{-1}.$$

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¹ J. G. Kirkwood, *J. Chem. Phys.* **14**, 180 (1946).

² S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1945). (Chandrasekhar's equations are derived from the phenomenological theory of Brownian motion.)

³ M. Born and H. S. Green, *Proc. Roy. Soc. A* **188**, 10 (1946) and **190**, 455 (1947); H. S. Green, *Proc. Roy. Soc. A* **189**, 103 (1947).

Although the theory of the friction constant ζ was presented in SMTI, it has not yet been possible to calculate it accurately. Our preliminary estimate, $\zeta = 4.84 \times 10^{-10}$ g sec.⁻¹, leads to a shear viscosity η of 1.27×10^{-3} poise, in fair agreement with the experimental value, 2.39×10^{-3} poise. Calculations relating to the bulk viscosity are postponed for treatment in a subsequent article.

II

In SMTI, the macroscopic observables of a system of N molecules were put into correspondence with average values determined by probability densities $\tilde{f}^{(n)}(\mathbf{p}, \mathbf{q}; t)$ in the phase space (\mathbf{p}, \mathbf{q}) of subsets of n molecules

$$\begin{aligned} \tilde{f}^{(n)}(\mathbf{p}, \mathbf{q}; t) &= \int \int \tilde{f}^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t) d\mathbf{P} d\mathbf{Q}, \\ \tilde{f}^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t) &= \frac{1}{\tau} \int_0^\tau \tilde{f}^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t+s) ds, \end{aligned} \quad (1)$$

where (\mathbf{P}, \mathbf{Q}) is the phase space of the residual set of $N-n$ molecules and $\tilde{f}^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t)$ is the probability density in the complete phase space of an example of the appropriate statistical ensemble, from which a system is sampled in the process of preparation at time t with specified values of the molar variables determining its macroscopic state. The interval τ is determined by the time resolution of the instruments employed in the measurement of the macroscopic observables. If the shortest period macroscopically resolved is long relative to the Brownian motion correlation time, it was made plausible that in liquids, the macroscopic description would not sensibly depend upon the smoothing time τ , provided τ is long relative to the correlation time. For the representation of average values of functions of the configuration coordinates of small sets of n molecules, it is convenient to define number densities $\rho^{(n)}(\mathbf{q}; t)$ by the relation,

$$\rho^{(n)}(\mathbf{q}; t) = \frac{N!}{(N-n)!} \int \tilde{f}^{(n)}(\mathbf{p}, \mathbf{q}; t) d\mathbf{p}. \quad (2)$$

The mass density ρ of hydrodynamic theory at a point \mathbf{R} in a fluid and the particle velocity \mathbf{u} are then determined by the relation,

$$\begin{aligned} \rho(\mathbf{R}) &= m \rho^{(1)}(\mathbf{R}), \\ \rho \mathbf{u} &= N \int \mathbf{p} \tilde{f}^{(1)}(\mathbf{R}, \mathbf{p}) d\mathbf{p}, \end{aligned} \quad (3)$$

where m is the mass of a molecule. The distribution functions $\tilde{f}^{(n)}$ were shown to satisfy partial differential equations, SMTI, Eq. (60), of the type derived by Chandrasekhar² on the basis of the phenomenological theory of Brownian motion. The use of these equations to determine the molecular distribution functions of a fluid in a state of stationary viscous flow will be presented in Section III.

In a system of molecules for which the potential of intermolecular force V_N can be represented in the form,

$$V_N = \sum_{i < k=1}^N V(R_{ik}), \quad (4)$$

where $V(R_{ik})$ is a function, say of the Lennard-Jones type, of the distance R_{ik} between the pair of molecules (ik) , the stress tensor σ is given by SMTI, Eq. (26). In the notation of Eqs. (2) and (3), this equation becomes,

$$\begin{aligned} \sigma &= -\rho^{(1)} \left[\frac{\langle \mathbf{p}\mathbf{p} \rangle_{Av}}{m} - m\mathbf{u}\mathbf{u} \right] \\ &+ \frac{1}{2} \int \frac{\mathbf{R}_{12} \mathbf{R}_{12}}{R_{12}} \frac{dV}{dR_{12}} \rho^{(2)}(\mathbf{R}, \mathbf{R}_{12}) dv_{12}, \quad (5) \\ \rho^{(1)} \langle \mathbf{p}\mathbf{p} \rangle_{Av} &= N \int \mathbf{p} \tilde{f}^{(1)}(\mathbf{p}, \mathbf{R}) d\mathbf{p}, \end{aligned}$$

where $\rho^{(2)}(\mathbf{R}, \mathbf{R}_{12})$ is the number density of pairs, one member of which is situated at point \mathbf{R} and the other at point \mathbf{R}_{12} relative to the position of the first. The integration in the second term of Eq. (5), the contribution of intermolecular forces to the stress tensor, extends over the relative configuration space \mathbf{R}_{12} of the representative pair. The first term represents the momentum transfer contribution, important in gases, but almost negligible in liquids.

In a liquid in a state of stationary viscous flow, the distribution functions are perturbed in such a manner that the stress tensor takes on the extended Newtonian form. In Section III, it will be shown that with neglect of non-linear terms in the rate of strain, $\dot{\epsilon}$,

$$\begin{aligned} -\rho^{(1)} \left[\frac{\langle \mathbf{p}\mathbf{p} \rangle_{Av}}{m} - m\mathbf{u}\mathbf{u} \right] \rho^{(1)} &= -\rho^{(1)} kT \mathbf{I} + \rho \frac{kT}{\zeta} \dot{\epsilon}, \\ \zeta &= kT/D, \quad \dot{\epsilon} = \text{Sym} \nabla \mathbf{u}, \end{aligned} \quad (6)$$

where ζ is the Brownian motion friction constant and D is the coefficient of self-diffusion of the liquid. The pair density, $\rho^{(2)}$, determining the contribution of intermolecular forces to the stress tensor is conveniently written in the form,

$$\rho^{(2)}(\mathbf{R}, \mathbf{R}_{12}) = \rho^{(1)}(\mathbf{R}) \rho^{(1)}(\mathbf{R} + \mathbf{R}_{12}) g^{(2)}(\mathbf{R}, \mathbf{R}_{12}), \quad (7)$$

a relation defining the pair correlation function $g^{(2)}(\mathbf{R}, \mathbf{R}_{12})$. In Section III, it will be shown that $g^{(2)}$ can be expanded in the components of the rate of strain as,

$$\begin{aligned} g^{(2)} &= g_0^{(2)}(R_{12}) \left\{ 1 + \frac{\zeta}{2kT} \left[\frac{\mathbf{R}_{12} \cdot \dot{\epsilon} \cdot \mathbf{R}_{12}}{R_{12}^2} - \frac{1}{3} \nabla \cdot \mathbf{u} \right] \psi_2(R_{12}) \right. \\ &\quad \left. + \frac{\zeta}{6kT} (\nabla \cdot \mathbf{u}) \psi_0(R_{12}) \right\}, \quad (8) \end{aligned}$$

where $g_0^{(2)}(R_{12})$ is the radial distribution function of the fluid in thermodynamic equilibrium and $\psi_0(R_{12})$

and $\psi_2(R_{12})$ satisfy certain ordinary differential equations, presently to be derived from the general theory of the probability densities, $\bar{f}^{(n)}$.

Substitution of the momentum contribution of Eq. (6) and the perturbed pair density of Eqs. (7) and (8) into Eq. (5) yields the stress tensor,

$$\sigma = -[p + (2/3\eta - \phi)\nabla \cdot \mathbf{u}] + 2\eta\dot{\epsilon},$$

$$p = \frac{NkT}{V} - \frac{2\pi N^2}{3V^2} \int_0^\infty \frac{dV}{dR} R^3 g_0^{(2)}(R) dR, \quad (9)$$

where p is the equilibrium pressure of the liquid at the given temperature and uniform number density $\rho^{(1)}$, equal to the ratio of Avogadro's number N and the molal volume V . The coefficients of shear viscosity η and bulk viscosity ϕ are then given by the expressions

$$\eta = \rho \frac{kT}{2\zeta} + \frac{\pi\zeta}{15kT} \frac{N^2}{V^2} \int_0^\infty \frac{dV}{dR} R^3 \psi_2(R) g_0^{(2)}(R) dR,$$

$$\phi = \rho \frac{kT}{3\zeta} + \frac{\pi\zeta}{9kT} \frac{N^2}{V^2} \int_0^\infty \frac{dV}{dR} R^3 \psi_0(R) g_0^{(2)}(R) dR, \quad (10)$$

where, as subsequent calculations will show, the initial terms arising from momentum transport are of minor importance in liquids.

In order to evaluate the integrals of Eqs. (10), as well as to solve the differential equations determining the perturbation functions $\psi_0(R)$ and $\psi_2(R)$, it is necessary to know the equilibrium radial distribution function $g_0^{(2)}(R)$ and the potential of intermolecular force $V(R)$. The potential $V(R)$ is conveniently approximated by the Lennard-Jones expression,

$$V(R) = \epsilon \left(\frac{1}{x^n} - \frac{1}{x^6} \right), \quad (11)$$

$$x = R/a_0.$$

In applications of the theory presently to be made to liquid argon, we shall use parameters, n , ϵ , and a_0 , determined by Rushbrooke⁴ and Corner.⁵ The values are: $n=11.4$; $\epsilon=6.82 \times 10^{-14}$ erg; $a_0=3.43\text{\AA}$.

The radial distribution function $g_0^{(2)}(R)$ is of course determined by the potential of intermolecular force $V(R)$ and the thermodynamic variables.⁶ It is also accessible to experimental measurement, since it determines the intensity of x-rays scattered by a liquid as a function of scattering angle. In the applications to follow, we shall make use of the radial distribution function data for argon of Eisenstein and Gingrich.⁷ This function possesses a series of peaks with amplitude rapidly diminishing as R increases. Since it is found that

⁴ G. S. Rushbrooke, Proc. Roy. Soc. (Edin.) **60**, 182 (1940).

⁵ J. Corner, Trans. Faraday Soc. **35**, 711 (1939).

⁶ J. G. Kirkwood and E. M. Boggs, J. Chem. Phys. **10**, 394 (1942).

⁷ A. Eisenstein and N. S. Gingrich, Phys. Rev. **62**, 261 (1942).

the integrals of Eq. (10) are in the main determined by the first peak of the radial distribution function, the other factor being of very short range, we have constructed the following analytical approximation to $g_0^{(2)}(R)$,

$$g_0^{(2)}(R) = (a_1/R)^s \exp \left\{ \left(\frac{a_m}{a_1} \right)^t - \left(\frac{a_m}{R} \right)^t \right\};$$

$$= 1; \quad R < a_1, \quad 0 \leq R \leq a_1, \quad (12)$$

which represents quite well the first peaks of the Eisenstein-Gingrich curves. It has the important advantage of allowing the integration of the differential equations satisfied by the perturbation function ψ_0 and ψ_2 , in terms of confluent hypergeometric functions. Two of the parameters $a_1=4.5\text{\AA}$ and $t=14$ are determined from the Eisenstein-Gingrich data to be relatively insensitive to temperature. For liquid argon at 89°K and 1.2 atmos., the remaining parameters were determined with the use of the Lennard-Jones potential, Eq. (11), the theoretical equation of state, given by the second of Eq. (9), and the energy of vaporization,

$$E_v = -\frac{2\pi N^2}{V} \int_0^\infty R^2 V(R) g_0^{(2)}(R) dR. \quad (13)$$

They were found to have the values, $a_m=3.55\text{\AA}$ and $s=7.01$. This calibration was found to be necessary, since the Eisenstein-Gingrich functions fail to satisfy the equation of state, due to the extreme sensitivity of the cohesive pressure, arising from intermolecular forces, to the relative position of the first peak of $g_0^{(2)}(R)$ and the position of the minimum of the Lennard-Jones potential. With the adjusted parameters, the peak of the empirical function, Eq. (12), lies at 3.73\text{\AA} and corresponds to a coordination number of 8.1, both in good agreement with the experimental results of Eisenstein and Gingrich.

III

The determination of the perturbations from equilibrium of the distribution functions $\bar{f}^{(1)}(\mathbf{p}, \mathbf{R})$ and $\rho^{(2)}(\mathbf{R}, \mathbf{R}_{12})$ in a liquid in a state of stationary viscous flow is based upon the use of the Chandrasekhar equations, SMTI, Eq. (59) and Eq. (60), derived from the standpoint of molecular dynamics in the first paper of this series. In order to determine the momentum contribution to the stress tensor, we employ the equation [SMTI (59)]

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{R}} \bar{f}^{(1)} + \nabla_{\mathbf{p}} \cdot \mathbf{F}^{(1)} \bar{f}^{(1)}$$

$$= \left\{ \nabla_{\mathbf{p}} \cdot \left(\frac{\mathbf{p}}{m} - \mathbf{u} \right) \bar{f}^{(1)} + kT \nabla_{\mathbf{p}} \bar{f}^{(1)} \right\}, \quad (14)$$

$$\mathbf{F}^{(1)} = {}^{(1)}\langle \mathbf{F} \rangle_N + {}^{(1)}\mathbf{F}^+,$$

where ζ is the friction constant of the theory of Brownian motion, $\langle \mathbf{F} \rangle_{Av}^0$ is the average in the equilibrium ensemble of the total intermolecular force acting on a molecule situated at point \mathbf{R} , and $\langle \mathbf{F} \rangle^+$ is the perturbation arising from the departure of $\rho^{(2)}$ from equilibrium. Upon multiplication of both sides of Eq. (14) by $(\mathbf{p}/m - \mathbf{u})(\mathbf{p}/m - \mathbf{u})$ and integration over momentum space, we find with the use of Green's theorem that

$$\langle \Pi \Pi \rangle_{Av} - m k T I = - \frac{m}{2\zeta} \left\{ \langle \Pi \Pi \rangle_{Av} \cdot \nabla \mathbf{u} + \langle \Pi \cdot \nabla \Pi \rangle_{Av} + \mathbf{u} \cdot \nabla \langle \Pi \Pi \rangle_{Av} + \frac{\partial \langle \Pi \Pi \rangle_{Av}}{\partial t} \right\}, \quad (15)$$

$$\Pi = \mathbf{p} - m\mathbf{u},$$

with the neglect of non-linear terms in all perturbations from equilibrium. In the stationary case, Eq. (15) leads at once to Eq. (6), in the linear approximation, and the momentum transfer contribution to the stress tensor is evaluated.

In order to determine the pair density $\rho^{(2)}$, from which the intermolecular force contribution to the stress tensor is to be calculated, we employ Eq. (60) of SMTI in the form appropriate to $\tilde{f}^{(2)}(\mathbf{p}_1, \mathbf{R}_1, \mathbf{p}_2, \mathbf{R}_2; t)$ in the phase space of molecular pairs,

$$\begin{aligned} \frac{\partial \tilde{f}^{(2)}}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{p}_1} \tilde{f}^{(2)} + \frac{\mathbf{p}_2}{m} \cdot \nabla_{\mathbf{p}_2} \tilde{f}^{(2)} \\ + \nabla_{\mathbf{p}_1} \cdot \mathbf{F}_1^{(2)} \tilde{f}^{(2)} + \nabla_{\mathbf{p}_2} \cdot \mathbf{F}_2^{(2)} \tilde{f}^{(2)} \\ = \nabla_{\mathbf{p}_1} \cdot \boldsymbol{\zeta}_1^{(2)} \cdot \left\{ \left(\frac{\mathbf{p}_1}{m} - \mathbf{u}_1 \right) \tilde{f}^{(2)} + k T \nabla_{\mathbf{p}_1} \tilde{f}^{(2)} \right\} \\ + \nabla_{\mathbf{p}_2} \cdot \boldsymbol{\zeta}_2^{(2)} \cdot \left\{ \left(\frac{\mathbf{p}_2}{m} - \mathbf{u}_2 \right) \tilde{f}^{(2)} + k T \nabla_{\mathbf{p}_2} \tilde{f}^{(2)} \right\}; \end{aligned} \quad (16)$$

$$\mathbf{F}_1^{(2)} = {}^{(2)}\langle \mathbf{F}_1 \rangle_{Av}^0 + {}^{(2)}\mathbf{F}_1^+; \quad \mathbf{F}_2^{(2)} = {}^{(2)}\langle \mathbf{F}_2 \rangle_{Av}^0 + {}^{(2)}\mathbf{F}_2^+,$$

where ${}^{(2)}\langle \mathbf{F}_1 \rangle_{Av}^0$ is the mean force acting on the first molecule of the pair in the unperturbed equilibrium ensemble, subject to the condition that the configuration $(\mathbf{R}_1, \mathbf{R}_2)$ of the pair is fixed, and ${}^{(2)}\mathbf{F}_1^+$ is the perturbation arising from the departure of $\rho^{(3)}$, the density in triplet configuration space from equilibrium. The friction tensor $\boldsymbol{\zeta}^{(2)}$ is a second rank tensor in the six-dimensional configuration space of the pair, related to intermolecular forces in the manner prescribed in SMTI. The vectors \mathbf{u}_1 and \mathbf{u}_2 are the particle velocities of three-dimensional hydrodynamics, defined by Eq. (3), at the respective positions \mathbf{R}_1 and \mathbf{R}_2 of the pair. Integration of both sides of Eq. (16) over the momentum space of both molecules leads to the equation of continuity in pair configuration space,

$$\begin{aligned} \frac{\partial \rho^{(2)}}{\partial t} + \nabla_{\mathbf{R}_1} \cdot \mathbf{j}_1^{(2)} + \nabla_{\mathbf{R}_2} \cdot \mathbf{j}_2^{(2)} = 0, \\ \mathbf{j}_\alpha^{(2)} = \frac{N(N-1)}{m} \int \int \mathbf{p}_\alpha \tilde{f}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{R}_1, \mathbf{R}_2; t) d\mathbf{p}_1 d\mathbf{p}_2, \end{aligned} \quad (17)$$

with $\mathbf{j}_\alpha^{(2)}$ the number current density in pair space projected on the 3-space of molecule α . Multiplication of both sides of Eq. (16) by \mathbf{p}_1 and \mathbf{p}_2 respectively, followed by integration over momentum space yields the equations,

$$\begin{aligned} m \frac{\partial \mathbf{j}_1^{(2)}}{\partial t} &= -k T \nabla_{\mathbf{R}_1} \rho^{(2)} + \mathbf{F}_1^{(2)} \rho^{(2)} \\ &\quad - \boldsymbol{\zeta}_1^{(2)} \cdot [\mathbf{j}_1^{(2)} - \mathbf{u}_1 \rho^{(2)}], \\ m \frac{\partial \mathbf{j}_2^{(2)}}{\partial t} &= -k T \nabla_{\mathbf{R}_2} \rho^{(2)} + \mathbf{F}_2^{(2)} \rho^{(2)} \\ &\quad - \boldsymbol{\zeta}_2^{(2)} \cdot [\mathbf{j}_2^{(2)} - \mathbf{u}_2 \rho^{(2)}], \end{aligned} \quad (18)$$

with the neglect of non-linear terms in \mathbf{u}_1 and \mathbf{u}_2 and of terms of the order of $1/\zeta$ in the departure of the non-diagonal terms in $\langle \mathbf{p}_\alpha \mathbf{p}_\alpha \rangle_{Av}^{(2)}/m$ from their vanishing equilibrium values. Similar equations are obtained by the same procedure from Eq. (14),

$$\begin{aligned} m \frac{\partial \mathbf{j}_\alpha^{(1)}}{\partial t} &= -k T \nabla_{\mathbf{R}_\alpha} \rho^{(1)}(\mathbf{R}_\alpha) + \mathbf{F}_\alpha^{(1)} \rho^{(1)}(\mathbf{R}_\alpha), \\ \frac{\partial \rho^{(1)}(\mathbf{R}_\alpha)}{\partial t} + \nabla_{\mathbf{R}_\alpha} \cdot \mathbf{j}_\alpha^{(1)} &= 0, \quad \alpha = 1, 2, \\ \mathbf{j}_\alpha^{(1)} &= \rho^{(1)}(\mathbf{R}_\alpha) \mathbf{u}(\mathbf{R}_\alpha). \end{aligned} \quad (19)$$

We now introduce the simplifications,

$$\begin{aligned} \boldsymbol{\zeta}_1^{(2)} = \boldsymbol{\zeta}_2^{(2)} &= \zeta \mathbf{I}, \\ \mathbf{F}_\alpha^{(2)} - \mathbf{F}_\alpha^{(1)} &= k T \nabla_{\mathbf{R}_\alpha} \log g_0^{(2)}(\mathbf{R}_{12}); \quad \alpha = 1, 2, \end{aligned} \quad (20)$$

where ζ is the singlet friction constant of Eq. (14) and $g_0^{(2)}$ is the equilibrium radial distribution function. The first of Eqs. (20) implies the neglect of the dependence of the friction tensor $\boldsymbol{\zeta}^{(2)}$ on the relative configuration of the pair, and the second approximates the mean intermolecular force difference by its equilibrium value.⁸ Thus it is a well known result of equilibrium statistical mechanics that,

$$\begin{aligned} g_0^{(2)} &= \exp(-(W^{(2)} - W_1^{(1)} - W_2^{(1)})/kT), \\ {}^0\langle \mathbf{F}_\alpha \rangle_{Av} &= -\nabla_{\mathbf{R}_\alpha} W^{(2)}(\mathbf{R}_{12}), \quad \alpha = 1, 2, \\ {}^0\langle \mathbf{F}_\alpha \rangle_{Av}^{(1)} &= -\nabla_{\mathbf{R}_\alpha} W^{(1)}(\mathbf{R}_\alpha), \end{aligned} \quad (21)$$

where $W^{(1)}$ and $W^{(2)}$ are the potentials of mean force in singlet space and pair space, respectively.

Introduction of Eq. (7) into Eqs. (17) and (18) and elimination of $\rho^{(1)}(\mathbf{R}_1)$ and $\rho^{(2)}(\mathbf{R}_2)$ by means of Eqs. (19) leads, with neglect of the inertial terms, to the

⁸ See J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).

following equation for the correlation function,

$$\begin{aligned} \nabla \mathbf{R} \cdot \{ \nabla \mathbf{R} g^{(2)} - (\nabla \mathbf{R} \log g_0^{(2)}) g^{(2)} \} \\ - \frac{\zeta}{2kT} \frac{\partial g^{(2)}}{\partial t} = \frac{\zeta}{2kT} \mathbf{R} \cdot \dot{\mathbf{e}} \cdot \nabla \mathbf{R} g^{(2)}, \\ \mathbf{j}_{12}^{(2)} = - \frac{2kT}{\zeta} \{ \nabla \mathbf{R} g^{(2)} - (\nabla \mathbf{R} \log g_0^{(2)}) g^{(2)} \}, \end{aligned} \quad (22)$$

$$\begin{aligned} \rho^{(1)}(\mathbf{R}_1) \rho^{(1)}(\mathbf{R}_2) \mathbf{j}_{12}^{(2)} = [\mathbf{j}_2^{(2)} - \rho^{(2)} \mathbf{u}_2] \\ - [\mathbf{j}_1^{(2)} - \rho^{(2)} \mathbf{u}_1], \end{aligned}$$

$$g^{(2)}(\mathbf{R}_1, \mathbf{R}) = g^{(2)}(\mathbf{R}); \quad \mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1;$$

$$\mathbf{u}_2 - \mathbf{u}_1 = \mathbf{R} \cdot \nabla \mathbf{u},$$

where $\mathbf{j}_{12}^{(2)}$ is the excess probability current density in relative pair space, vanishing at $R \rightarrow \infty$ by definition and is conditioned by the absence of sources or sinks in the pair density distribution.

Introduction of Eq. (8) into Eq. (22) and linearization with respect to the components of the rate of strain $\dot{\mathbf{e}}$ leads, in the stationary case to the following ordinary differential equation for the functions $\psi_2(R)$ and $\psi_0(R)$,

$$\begin{aligned} \frac{d}{dR} \left(R^2 g_0^{(2)} \frac{d\psi_2}{dR} \right) - 6g_0^{(2)} \psi_2 = R^3 \frac{dg_0^{(2)}}{dR}, \\ \frac{d}{dR} \left(R^2 g_0^{(2)} \frac{d\psi_0}{dR} \right) = R^3 \frac{dg_0^{(2)}}{dR}. \end{aligned} \quad (23)$$

In coordinate representation $\psi_2(R)$ is the coefficient of surface harmonics of order two, arising from the shear component of the rate of strain, and $\psi_0(R)$ is the coefficient of the surface harmonic of order zero, arising from the dilatational component. The excess probability current density in the relative pair space is given by

$$\begin{aligned} \mathbf{j}_{12}^{(2)} = -g_0^{(2)} \left\{ \nabla \mathbf{R} \left[\frac{\mathbf{R} \cdot \dot{\mathbf{e}} \cdot \mathbf{R}}{R^2} - \frac{1}{3} \nabla \cdot \mathbf{u} \right] \psi_2(R) \right. \\ \left. + \frac{1}{3} (\nabla \cdot \mathbf{u}) \psi_0(R) \right\}. \end{aligned} \quad (24)$$

The requirement that $\mathbf{j}_{12}^{(2)}$ vanish at $R = \infty$ and that there be no sources or sinks in pair space leads to the

boundary conditions,

$$\lim_{R \rightarrow \infty} \psi_2(R) = 0, \quad (25a)$$

$$\lim_{R \rightarrow 0} R^2 g_0^{(2)} \frac{d\psi_2(R)}{dR} = 0, \quad (25b)$$

$$\lim_{R \rightarrow \infty} \frac{d\psi_0(R)}{dR} = 0, \quad (25c)$$

$$\lim_{R \rightarrow 0} R^2 g_0^{(2)} \frac{d\psi_0(R)}{dR} = 0, \quad (25d)$$

subject to which Eqs. (23) are to be solved. In addition, ψ_2 , $d\psi_2/dR$, and $d\psi_0/dR$ must be continuous for all $0 \leq R \leq \infty$, a condition which must be applied at the cut-off point, $R = a_1$, of the approximate radial distribution function, Eq. (12), in order to ensure continuity of the pair current at this point.

IV

The solution of the ψ_2 Eq. (23a) is based on use of the approximate representation of $g_0^{(2)}$ given in Eq. (12). Since $R^2/2$ is a particular solution, we only have to investigate the homogeneous equation

$$x^2 \frac{d^2 \psi_2}{dx^2} + \left\{ 2 + x \frac{d \log g_0^{(2)}}{dx} \right\} x \frac{d\psi_2}{dx} - 6\psi_2 = 0; \quad x = \frac{R}{a_0}. \quad (26)$$

For $x_1 < x$, Eq. (26) reduces to Euler's equation so that the solution satisfying the boundary condition at infinity, Eq. (25a), is given by

$$\psi_2 = K_2/x^3; \quad x_1 < x. \quad (27)$$

Substitution of the first peak approximation in Eq. (26) leads to the following differential equation for $0 \leq x \leq x_1$

$$\begin{aligned} z^2 \frac{d^2 \psi_2}{dz^2} + (2k - z) z \frac{d\psi_2}{dz} + (k + m - \frac{1}{2})(k - m - \frac{1}{2}) \psi_2 = 0, \\ k = \frac{1}{2} + \frac{s-1}{2t}; \quad m = \frac{1}{t} \left(\left(\frac{s-1}{2} \right)^2 + 6 \right)^{\frac{1}{2}}; \quad z = \left(\frac{x_m}{x} \right)^t. \end{aligned} \quad (28)$$

Two linearly independent solutions of this equation are found to be $e^{z/2} z^{-k} W_{k,m}(z)$ and $e^{z/2} z^{-k} W_{-k,m}(-z)$, where $W_{k,m}(z)$ is the Whittaker confluent hypergeometric function.⁹ We note that the generalized hypergeometric function is given by

$${}_p F_q(\alpha_1, \alpha_2, \dots, \alpha_p; \rho_1, \rho_2, \dots, \rho_q; z) = \sum_{n=0}^{\infty} \frac{\Gamma(\alpha_1+n) \Gamma(\alpha_2+n) \dots \Gamma(\alpha_p+n) \Gamma(\rho_1) \Gamma(\rho_2) \dots \Gamma(\rho_q) z^n}{\Gamma(\alpha_1) \Gamma(\alpha_2) \dots \Gamma(\alpha_p) \Gamma(\rho_1+n) \Gamma(\rho_2+n) \dots \Gamma(\rho_q+n) n!}. \quad (29)$$

⁹ For discussion of this function, see Whittaker and Watson, *Modern Analysis* (The Macmillan Company, New York, 1943).

In order to satisfy the boundary condition at the origin, Eq. (25b), it is seen from the asymptotic expansion of $W_{k,m}(z)$

$$W_{k,m}(z) \sim e^{-z/2} z^k {}_2F_0\left(\frac{1}{2}-m-k, \frac{1}{2}+m-k; -z^{-1}\right) \quad (30)$$

$|\arg z| < 3\pi/2$

that $e^{z/2} z^{-k} W_{-k,m}(-z)$ is not an admissible solution. Thus for $0 \leq x \leq x_1$, with

$$\begin{aligned} y_1(z) &= e^{z/2} z^{-k} W_{k,m}(z), \\ \psi_2 &= (a_0^2 x^2/2) + K_1 y_1(z). \end{aligned} \quad (31)$$

The derivative of $y_1(z)$ is readily obtained from the Mellin-Barnes type contour integral representation of $W_{k,m}(z)$

$$\begin{aligned} W_{k,m}(z) &= \frac{e^{-z/2} z^k}{2\pi i} \\ &\times \int_{-\infty-i}^{+\infty+i} \frac{\Gamma(v) \Gamma(-v-k+m+\frac{1}{2}) \Gamma(-v-k-m+\frac{1}{2}) z^v dv}{\Gamma(-k-m+\frac{1}{2}) \Gamma(-k+m+\frac{1}{2})}, \end{aligned} \quad (32)$$

with the result

$$\frac{dy_1(z)}{dx} = \frac{6}{tx} z^{-k} e^{z/2} W_{k-1,m}(z). \quad (33)$$

The constants K_1 and K_2 are determined by the requirement that ψ_2 and $d\psi_2/dx$ be continuous at x_1 . With use of Eq. (33) we find after some elementary calculations that

$$K_1 = -a_0^2 x_1^2 K_3 = -\frac{a_0^2 x_1^2 (5/2) z_1^k e^{-z_1}}{3W_{k,m}(z_1) + \frac{6}{t} W_{k-1,m}(z_1)},$$

$$K_2 = -a_0^2 x_1^5 K_4$$

(34)

$$\begin{aligned} & a_0^2 x_1^5 \left\{ W_{k,m}(z_1) - \frac{3}{t} W_{k-1,m}(z_1) \right\} \\ &= -\frac{6}{3W_{k,m}(z_1) + \frac{6}{t} W_{k-1,m}(z_1)}, \end{aligned}$$

$$z_1 = \left(\frac{x_m}{x_1} \right)^t.$$

Since in our numerical example $z_1 = 3.67 \times 10^{-2}$, $W_{k,m}(z_1)$ is easily computed by means of the relation

$$\begin{aligned} W_{k,m}(z) &= z^{(1/2)+m} e^{-z/2} \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} \\ &\times {}_1F_1\left(\frac{1}{2}+m-k; 1+2m; z\right) \\ &+ z^{(1/2)-m} e^{-z/2} \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} \\ &\times {}_1F_1\left(\frac{1}{2}-m-k; 1-2m; z\right), \end{aligned} \quad (35)$$

only a few terms in the power series being required.

Substitution of ψ_2 given by Eqs. (27) and (31) into Eq. (10) and use of the potential $V(x)$, Eq. (11), leads to the following result for the coefficient of shear viscosity,

$$\begin{aligned} \eta &= \frac{\zeta \pi N^2 a_0^5}{15 k T v^2} \left[\frac{1}{2} \int_0^{z_1} x^5 g_0^{(2)}(x) \frac{dV(x)}{dx} dx + K_4 x_1^5 V(x_1) \right. \\ &\quad \left. + K_3 \frac{\epsilon x_1^{2+s} e^{z_1}}{t x_m^{3+s}} \left\{ \frac{n I_{n-3}}{x_m^{n-6}} - 6 I_3 \right\} \right] + \frac{N m k T}{2 v \zeta}, \end{aligned} \quad (36)$$

$$I_\alpha = I_\alpha(\infty) - I(z_1),$$

$$I(z) = \int_0^z y_1(z) e^{-z_s(\alpha+s/t)-1} dz_s.$$

The value of $I_\alpha(\infty)$ is conveniently calculated with use of Eq. (32) and Barnes lemma (reference 9, p. 289).

$$\begin{aligned} I_\alpha(\infty) &= \frac{1}{2\pi i} \int_{-\infty-i}^{+\infty+i} \frac{\Gamma(v) \Gamma(-v-k-m+\frac{1}{2}) \Gamma(-v-k+m+\frac{1}{2}) \Gamma\left(v+\frac{\alpha+s}{t}\right) dv}{\Gamma(-k-m+\frac{1}{2}) \Gamma(-k+m+\frac{1}{2})} \\ &= \frac{\Gamma\left(\frac{\alpha+s}{t}-k-m+\frac{1}{2}\right) \Gamma\left(\frac{\alpha+s}{t}-k+m+\frac{1}{2}\right)}{\Gamma\left(\frac{\alpha+s}{t}+1-2k\right)}; \quad t > n-2. \end{aligned} \quad (37)$$

Use of Eq. (35) and Kummer's formula

$$\begin{aligned} e^{-z_1} {}_1F_1\left(\frac{1}{2}+m-k; 1+2m; z\right) \\ = {}_1F_1\left(\frac{1}{2}+m+k; 1+2m; -z\right), \end{aligned} \quad (38)$$

immediately leads to the result

$$I_\alpha(z_1) = I_\alpha^m(z_1) + I_\alpha^{-m}(z_1), \quad (39)$$

where

$$I_{\alpha^{\beta}}(z_1) = \frac{\Gamma(-2\beta)}{\Gamma(\frac{1}{2}-\beta-k)} \frac{z_1^{(\alpha+s/t)-k+1/2+\beta}}{\left(\frac{\alpha+s}{t}-k+\frac{1}{2}+\beta\right)} {}_2F_2\left(\frac{1}{2}+\beta+k, \frac{\alpha+s}{t}-k+\frac{1}{2}+\beta; 1+2\beta, \frac{\alpha+s}{t}-k+\frac{3}{2}+\beta; -z_1\right).$$

We have carried out the numerical calculation of η for liquid argon at 89°K

$$\eta = 2.63 \times 10^6 \zeta + \frac{8.53 \times 10^{-15}}{\zeta} \text{ poise}$$

the second term arising from momentum transport being negligible in comparison with the first. It is of interest to note that by defining an effective radius by the relationship $\zeta = 6\pi\eta R_{\text{eff}}$, $R_{\text{eff}} = 2.0\text{Å}$ at 89°K, while the actual radius, taken to be one half the distance between nearest neighbors is 1.9Å.

In order to check our theory with experiment it is necessary to calculate the friction constant. As a preliminary estimate we find that

$$\zeta^2 = \frac{4\pi a_0 \rho}{3} \int_0^\infty x^2 \left(\frac{d^2 V}{dx^2} + \frac{2}{x} \frac{dV}{dx} \right) g_0^{(2)} dx, \quad (40)$$

which for liquid argon at 89°K, using Eqs. (11) and (12) leads to $\zeta = 4.84 \times 10^{-10} \text{ g sec}^{-1}$. With this value of the friction constant, the calculated coefficient of shear viscosity for liquid argon at 89°K is $1.27 \times 10^{-3} \text{ poise}$ which is in moderately good agreement with the extrapolated experimental determination of $2.39 \times 10^{-3} \text{ poise}$.¹⁰

The solution of the ψ_0 Eq. (23b), subject to the boundary condition at the origin, Eq. (25d), is given by

$$\psi_0 = a_0^2 \int_\infty^x \frac{d\xi}{\xi^2 g_0^{(2)}} \int_0^\xi \frac{dg_0^{(2)}}{dw} w^2 dw + \psi_0(\infty), \quad (41)$$

$$\psi_0 \sim \frac{C}{x} + \psi_0(\infty) \quad \text{for } x \text{ large.}$$

¹⁰ N. S. Rudenko and L. W. Schubnikow, *Physik. Zeits. Sowjetunion* 6, 470 (1934).

In order to evaluate $\psi_0(\infty)$ we consider Eq. (22) for the case of a periodic dilation of frequency ω . For large x , we obtain

$$\frac{d}{dx} \left(x^2 \frac{d\psi_0}{dx} \right) - \frac{i\omega\zeta a_0^2}{2kT} x^2 \psi_0 = 0, \quad (42)$$

with the solution

$$\psi_0 \sim \frac{A(\omega)}{x} \exp \left(- \left[\frac{a_0}{2} \left(\frac{\omega\zeta}{kT} \right)^{\frac{1}{2}} x(1+i) \right] \right) - \frac{B(\omega)}{x} \exp \left(\left[\frac{a_0}{2} \left(\frac{\omega\zeta}{kT} \right)^{\frac{1}{2}} x(1+i) \right] \right). \quad (43)$$

The boundary condition at infinity Eq. (25c) requires that $B(\omega) = 0$. For the case of zero frequency of dilation

$$\psi_0 \sim \lim_{\omega \rightarrow 0} \frac{A(\omega)}{x} \exp \left\{ - \left[\frac{a_0}{2} \left(\frac{\omega\zeta}{kT} \right)^{\frac{1}{2}} x(1+i) \right] \right\} = \frac{C}{x}. \quad (44)$$

Comparison of (41) and (44) shows that ψ_0 vanishes at infinity. We thus obtain the following expression for the coefficient of bulk viscosity

$$\phi = \frac{Nm k T}{3v\zeta} + \frac{\zeta \pi a_0^5 N^2}{9kT} \int_0^\infty \frac{dV}{x^3} g_0^{(2)} dx \times \int_\infty^x \frac{d\xi}{\xi^2 g_0^{(2)}} \int_0^\xi \frac{dg_0^{(2)}}{dw} w^2 dw. \quad (45)$$

Numerical calculations of the coefficient of bulk viscosity are postponed for later treatment, since the result appears to be extraordinarily sensitive to the equilibrium radial distribution function and it is believed that a better approximation than that of Eq. (12) is required. For the same reason, our numerical estimate of the shear viscosity is to be considered preliminary and subject to revision. From recent ultrasonic absorption measurements of Galt,¹¹ an upper bound to the ratio ϕ/η is estimated to be $\frac{1}{3}$ for liquid argon at 85°K. However, in the absence of an experimental value of the heat conductivity, the calculation of the absolute value of ϕ is not possible.

¹¹ J. G. Galt, *J. Chem. Phys.* 16, 505 (1948).