A STATISTICAL MECHANICAL THEORY OF THE COEFFICIENTS OF SHEAR AND BULK VISCOSITY OF MONATOMIC LIQUIDS

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1949

ACKNOWLEDGMENT

It is a great pleasure to acknowledge my profound indebtedness to Professor John G. Kirkwood, not only for suggesting this problem, but also for the constant friendly advice and constructive criticism which made this work possible. My conferences with Professor Kirkwood and Professor Don M. Yost always provided new concepts and I consider it a rare privilege to have been in contact with these inspiring teachers.

ABSTRACT

A detailed 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 proposed by Kirkwood. The coefficients are expressed explicitly in terms of the potential of intermolecular force and the perturbations in the pair number density produced by viscous fluid flow. These perturbations are obtained from the steady state solutions of an equation of forced diffusion, derived from the generalized Chandrasekhar equations determining the distribution functions of sets of one and two molecules. This procedure leads to a set of ordinary differential equations, which are solved in terms of the Whittaker confluent hypergeometric function by means of a reasonable analytic approximation to the experimental radial distribution function.

With the use of the Lennard-Jones potential and the approximate radial distribution function, calculations of the coefficients of shear and bulk viscosity of liquid argon at $89^{\circ}K$ and 1.2 atm. have been carried out. The theory leads explicitly to ratios of the coefficients to the friction constant of the theory of Brownian motion. With an estimate of the friction constant, a value of the shear viscosity of liquid argon in moderately good agreement with experiment is obtained.

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I.

INTRODUCTION

The macroscopic behavior of a system of molecules may be described in two ways. The first is the phenomenological description, and the other is the more fundamental approach in terms of the molecular structure of the system. A small number of molar variables, such as the temperature, composition and parameters of external force specify the macroscopic state.

It is to be noted that a complete phenomenological description, without reference to the molecular structure, is possible. When the system is in equilibrium, its behavior is described by thermodynamics. Furthermore, when the state of the system is inconsistent with the conditions of thermodynamic equilibrium, transport processes occur, such as fluid flow, diffusion and heat transfer. These transport processes may then be described in terms of the macroscopic equations of hydrodynamics, which are supplemented by empirical relations connecting the stress tensor and heat and mass currents with functions of the local macroscopic state of the system. The parameters entering into these supplementary expressions are the various transport coefficients. The solutions of the transport equations, subject to specified initial and boundary conditions, then determine the macroscopic state of the system as a function of position and time. On the other hand, if a description in molecular terms is desired, the macroscopic behavior of the system requires interpretation from the standpoint of statistical mechanics since its dynamical state is incompletely defined by the molar variables. The main objectives of this approach are the derivation of the equations of hydrodynamics from molecular dynamics, the investigation of the validity of the supplementary empirical relations, the determination of the transport coefficients in terms of the forces acting between the molecules of which the system is composed, and the molecular interpretation of the relaxation time spectrum produced by time dependent external forces.

In the following treatment a detailed molecular theory of viscous fluid flow will be presented. At the outset we will limit our discussion to monatomic liquids which may be adequately treated by means of classical statistical mechanics. It is hoped that our theory will help in the elucidation of the properties of fluids such as liquid helium, even though a quantum mechanical approach is necessary in these problems.

The natural development of the theory came from the investigations of the viscosity coefficients in dilute monatomic gases. In 1867, Maxwell(1) published the first accurate theoretical discussion of the coefficient of shear viscosity and his prediction, since experimentally verified, that the coefficient is independent of pressure at a given temperature was one of the early triumphs of the kinetic theory of gases. The problem received its rigorous formulation in 1872, when Boltzmann(2) first derived the integro-differential equation appropriate when the behavior of the molecules is amenable to binary collision analysis. Due to the mathematical difficulties involved in solving this equation, it was not until 1911-1916 that D. Enskog(3) and S. Chapman(4) independently succeeded in obtaining general solutions valid for any type of spherically symmetric molecule possessing only translational degrees of freedom. Both men were guided by the investigations of D. Hilbert(5), who first called this equation, the Maxwell-Boltzmann integro-differential equation.

These, as well as later treatments, calculated the coefficient of viscosity by considering the momentum transmitted across an arbitrary surface in the fluid. However, as early as 1885, Graetz(6) suggested that in the case of liquids the mechanism of viscous flow also involves the resistance against deformation due to the intermolecular forces. In order to substantiate his argument, he cited the decrease of viscosity due to an increase of temperature, a relation which was later found to follow an exponential law.

An important extension of the general theory was made by Enskog(7) in 1922, who indicated a development valid for dense gases. Despite the partial success of this work, it could not be readily applied to liquids. In view of these complexities, various models were postulated to account for the experimental results. With use of the Graetz mechanism, J. Frenkel(8) developed a model theory which qualitatively led to the exponential temperature dependence. This approach was later formulated more elaborately by Andrade, Furth and Eyring(9). In particular, Eyring and his coworkers discovered some useful semi-empirical relationships by applying the transition state method to the free volume theory of liquids. These expressions have recently been critically reexamined by Brunner(10).

In 1946, Kirkwood(11) and Born and Green(12) formulated alternative approaches to molecular theories of transport processes. While the two theories duplicate many of the general results, they differ in the manner in which dissipative terms are introduced into the equations satisfied by the distribution functions. Although Born and Green have presented interesting qualitative discussions, they have not yet succeeded in constructing solutions of their equations for the distribution functions in sufficiently explicit form to yield concrete results.

The detailed molecular theory of viscous flow to be presented is based on Kirkwood's theory of irreversible processes, which combines many features of the kinetic theory of gases and the theory of Brownian motion. A starting point is provided by the differential equations of the Chandrasekhar type for the probability distribution functions in the phase space of sets of one, two and three molecules, which were derived by him from the molecular standpoint.

The coefficients of viscosity are defined by the empirical Newtonian law relating the stress tensor entering into the hydrodynamical equation of motion to the rate of strain. On the other hand, the stress tensor is determined by molecular distribution functions and intermolecular forces in the manner to be described in Part III. There are two types of terms, one arising from momentum transport and one from the direct transmission of intermolecular forces, the latter being determined by the average density of molecular pairs for the monatomic liquids to be treated. 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 consists of two parts, one spherically symmetric, which determines the bulk viscosity,and one having the symmetry of a surface harmonic of order two which determines the shear viscosity.

By means of the Chandrasekhar type of equations the perturbations in the pertinent molecular distribution functions have been constructed and the ratios of the two coefficients of viscosity to the Brownian motion friction constant 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 use of the Lennard-Jones potential and a reasonable analytic approximation to the radial distribution function. It has not yet been possible to calculate the friction constant accurately, but a preliminary estimate leads to a shear viscosity of 1.27×10^{-3} poise, in moderately good agreement with the experimental value, 2.39×10^{-3} poise. The results of these calculations are summarized in Table III.

II.

DEFINITION OF MOLECULAR DISTRIBUTION FUNCTIONS

In the field of classical statistical mechanics the dynamical states of a system of N molecules constitute a phase space and the ensemble representing a distribution in initial conditions is characterized by a probability density $f^{(N)}(\vec{P}, \vec{Q}; t)$ in phase space. For molecules possessing only translational degrees of freedom, the momentum vector $\vec{P}$ is then defined in 3N- dimensional momentum space and is composed of N vectors $\vec{p}_1 \ldots \vec{p}_N$, its projections on the 3- momentum spaces of the individual molecules. Similarly, the configuration vector $\vec{Q}$ is a vector in the 3N- dimensional configuration space with components $\vec{q}_1 \ldots \vec{q}_N$ specifying the positions of the centers of gravity in the 3- configuration spaces of the several molecules.

From operational considerations Kirkwood concludes that the appropriate distribution function involved in the non-equilibrium statistical expectation value of a macroscopic observable is to be smoothed over a microscopically short time interval of sufficient duration to average out certain fluctuations. Thus the macroscopic observables of a system of N molecules are put into correspondence with average values determined by the probability density

$$\bar{f}^{(N)}(\vec{P}, \vec{Q}; t) = \frac{1}{\tau} \int_0^{\tau} f^{(N)}(\vec{P}, \vec{Q}; t+s)\, ds \qquad (1)$$

where $\bar{f}^{(N)}(\vec{P}, \vec{Q}; t)$ is the probability density in the 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 is reasonable that in liquids, the macroscopic description will not sensibly depend upon the smoothing time τ, provided τ is long relative to the correlation time.

For the process of obtaining average values of a property $\varphi(\vec{p}_n, \vec{q}_n)$, depending not on all coordinates in phase space, but only on those of a subset of n molecules, we may employ a distribution function of lower order. Denoting the coordinates of the subset by $\vec{p}_n$ and $\vec{q}_n$ and letting $\vec{p}_{N-n}$ and $\vec{q}_{N-n}$ denote those of the set of N-n molecules comprising the remainder of the system, the distribution function of order n is defined by

$$\bar{f}^{(n)}(\vec{p}_n, \vec{q}_n; t) = \iint \bar{f}^{(N)}(\vec{p}_n, \vec{q}_n, \vec{p}_{N-n}, \vec{q}_{N-n}; t)\, d\vec{p}_{N-n}\, d\vec{q}_{N-n} \quad (2)$$

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

$\rho^{(n)}(\vec{q}_n;t)$ by the relation

$$\rho^{(n)}(\vec{q}_n;t) = \frac{N!}{(N-n)!}\int f^{(n)}(\vec{p}_n,\vec{q}_n;t)\,d\vec{p}_n \qquad (3)$$

The probability density in the configuration space of the subset is related to the number density by the expression

$$\varphi^{(n)}(\vec{q}_n;t) = \frac{(N-n)!}{N!}\,\rho^{(n)}(\vec{q}_n;t) \qquad (4)$$

We will denote by $\vec{X}_i$ the external force acting on a molecule i of the system, dependent only on the coordinates of that molecule. The intermolecular force exerted on a specified molecule i by the other molecules of the system will be denoted by $\vec{F}_i$. We will assume that for the type of systems to be treated, the force $\vec{F}_i$ may be derived from a potential of intermolecular force $V^{(N)}$ of the form

$$V^{(N)} = \sum_{\substack{i<l\\=1}}^{N} V_{il}(R_{il}) \qquad (5)$$

where $V_{il}(R_{il})$ is a function, say of the Lennard-Jones type, of the distance R_{il} between the pair of molecules (il) . For this potential, $\vec{F}_i$ is given explicitly by

$$\vec{F}_i = -\sum_{\substack{l=1\\ \neq i}}^{N} \nabla_{\vec{R}_i} V_{il} = \sum_{\substack{l=1\\ \neq i}}^{N} \frac{\vec{R}_{il}}{R_{il}}\,\frac{dV_{il}}{dR_{il}} \qquad (6)$$

$$\vec{R}_{il} = \vec{R}_l - \vec{R}_i$$

The potential (5) suggests the definition of a pair correlation function $g^{(2)}(\vec{R}_1, R_{12}; t)$ by the relation

$$\rho^{(2)}(\vec{R}_1, \vec{R}_2; t) = \rho^{(1)}(\vec{R}_1; t)\, \rho^{(1)}(\vec{R}_2; t)\, g^{(2)}(\vec{R}_1, \vec{R}_{12}; t) \qquad (7)$$

In the course of our treatment we will frequently deal with distributions representing statistical equilibrium to be represented by the Gibbs canonical ensemble. For a one component system the equilibrium probability density in the phase space of the ensemble is given by

$$f_0^{(N)}(\vec{P}, \vec{Q}) = e^{-\beta H^{(N)}} \Big/ \iint e^{-\beta H^{(N)}} d\vec{P}\, d\vec{Q} \qquad (8)$$

where $\beta = \frac{1}{kT}$ and $H^{(N)}$ is the Hamiltonian of the system. For a potential of intermolecular force $V^{(N)}$ of the form (5), the probability density in the configuration space of a subset of n molecules reduces to

$$\varphi_0^{(n)}(\vec{q}_n) = \frac{\int e^{-\beta V^{(N)}} d\vec{q}_{N-n}}{\int e^{-\beta V^{(N)}} d\vec{Q}} \qquad (9)$$

The expression $e^{-\beta w^{(n)}(\vec{q}_n)}$ is defined by

$$e^{-\beta w^{(n)}(\vec{q}_n)} = v^n \varphi_0^{(n)}(\vec{q}_n) \qquad (10)$$

where v is the volume of the system. $W^{(n)}(\vec{q}_n)$ is the potential of the equilibrium average force acting on the molecules of the set n, for the force, ${}^{(n)}\langle \vec{F}_i \rangle^{\circ}$ acting on a specified molecule i of the set n, keeping the members of the set fixed, is

$$ {}^{(n)}\langle \vec{F}_i \rangle^{\circ} = - \nabla_{\vec{R}_i} W^{(n)} = - \frac{\int \nabla_{R_i} V^{(N)} e^{-\beta V^{(N)}} d\vec{q}_{N-n}}{\int e^{-\beta V^{(N)}} d\vec{Q}} \qquad (11) $$

For a liquid in the absence of external forces, the equilibrium pair correlation function, $g_0^{(2)}(\vec{R}_1, \vec{R}_{12})$ is identical with the radial distribution function $g_0^{(2)}(R_{12})$

$$ g_0^{(2)}(\vec{R}_1, \vec{R}_{12}) = g_0^{(2)}(R_{12}) = e^{-\beta W^{(2)}(R_{12})} \qquad (12) $$

It is also accessible to experimental measurement, since it determines the intensity of X-rays scattered by a liquid as a function of the scattering angle.

III.

GENERAL THEORY

After this necessary preliminary discussion, we may proceed with the formulation of our investigation. The macroscopic hydrodynamics of viscous fluids is described by the equations of continuity and motion, supplemented by the Newtonian expression. The hydrodynamical equation of continuity embodies the conservation of mass,

$$\frac{\partial}{\partial t}\rho + \nabla\cdot\rho\vec{u} = 0 \tag{13}$$

where ρ is the mass density of the fluid and $\vec{u}(\vec{R})$ is the fluid velocity at the point $\vec{R}$. Furthermore the hydrodynamical equation of motion is obtained by equating the volume and surface forces acting on a fixed but arbitrary volume to the sum of the rate of change of momentum inside the volume and the rate of transfer of momentum out through the surface,

$$\frac{\partial}{\partial t}\rho\vec{u} + \nabla\cdot\rho\vec{u}\vec{u} = \vec{X} + \nabla\cdot\underset{\sim}{\sigma} \tag{14}$$

where $\vec{X}$ is the external force per unit volume and $\underset{\sim}{\sigma}$ is the stress tensor. For example, σ_{xy} is the x component of the force transmitted per unit area across a surface whose normal is in the y direction. An empirical expression of rather general applicability for the stress of a homogeneous isotropic fluid is the Newtonian law,

$$\underset{\sim}{\sigma} = -\left(p + \frac{2}{3}\eta\,\nabla\cdot\vec{u} - \phi\,\nabla\cdot\vec{u}\right)\underset{\sim}{1} + 2\eta\,\underset{\sim}{\epsilon} \tag{15}$$

where p is the equilibrium pressure of the fluid, η and ϕ are the coefficients of shear and bulk viscosity, $\underset{\sim}{1}$ is the unit tensor and $\underset{\sim}{\dot{\varepsilon}}$ is the rate of strain tensor, whose nine components are symmetrical,

$$\underset{\sim}{\dot{\varepsilon}} = \mathrm{Sym}\,\nabla\vec{u} \qquad (16)$$

$$\dot{\varepsilon}_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)$$

Substitution of (15) into (14) leads to the Navier-Stokes equation of motion,

$$\frac{\partial}{\partial t}\rho\vec{u} + \nabla\cdot\rho\vec{u}\vec{u} = -\nabla p + \left(\frac{\eta}{3} + \phi\right)\nabla(\nabla\cdot\vec{u}) - \nabla^2\vec{u} + \vec{X} \qquad (17)$$

It might be noted that the coefficient of bulk viscosity, related to the non-steady state behavior of the fluid, is ordinarily omitted, since Stokes in his early writings in hydrodynamics omitted this term, although later in his life he admitted its existence. Recently Tisza(13) has reemphasized the importance of a phenomenological bulk viscosity. The sign of this coefficient is determined by the requirement that the dissipation function φ be positive. Since $\varphi = \underset{\sim}{\mathcal{T}} : \nabla\vec{u} + p\,\nabla\cdot\vec{u}$, the bulk viscosity contribution is $\phi\left(\nabla\cdot\vec{u}\right)^2$ when the Newtonian law is in the form (15).

The derivation of the hydrodynamical equation of continuity and motion from statistical mechanics will now be briefly outlined, since this procedure will enable us to express the stress tensor in terms of molecular variables, a necessary step for a molecular theory of viscous flow. In the spirit of Kirkwood's operational considerations, the mass density ρ at a point $\vec{R}$ in the fluid and the particle velocity $\vec{u}$ are then determined by the relations

$$\begin{aligned} \rho(\vec{R}; t) &= m\,\rho^{(1)}(\vec{R}; t) \\ \rho\,\vec{u} &= N \int \vec{p}\, \bar{f}^{(1)}(\vec{p}, \vec{R}; t)\, d\vec{p} = \rho^{(1)} \langle \vec{p} \rangle \end{aligned} \qquad (18)$$

where m is the mass of a molecule.

By Liouville's theorem, embodying the equation of continuity in phase space and the laws of mechanics, the probability distribution function $f^{(N)}(\vec{P}, \vec{Q}; t)$ satisfies the partial differential equation

$$\sum_{i=1}^{N} \left\{ \frac{p_i}{m} \cdot \nabla_{\vec{R}_i} f^{(N)} + \left(\vec{X}_i + \vec{F}_i\right) \cdot \nabla_{\vec{p}_i} f^{(N)} \right\} + \frac{\partial f^{(N)}}{\partial t} = 0 \qquad (19)$$

Since $\vec{P}$ and $\vec{Q}$ are fixed during the time averaging process, the equation for $\bar{f}^{(N)}(\vec{P}, \vec{Q}; t)$ is identical with (19). By means of the Dirac delta function, the number of particles at the point $\vec{R}$ in the fluid may be expressed by $\sum_{k=1}^{N} \delta(\vec{R}_k - \vec{R})$. Upon multiplication of Liouville's equation by this expression, followed by integration over the complete phase space and restricting our analysis to distributions $\bar{f}^{(N)}$ for which the surface integrals vanish on the boundary of the phase space accessible to the system, we obtain with use of Green's theorem

$$\frac{\partial}{\partial t}\sum_{i=1}^{N}\int \bar{f}^{(1)}(\vec{p}_i,\vec{R}_i;t)\,\delta(\vec{R}_i-\vec{R})\,d\vec{p}_i\,d\vec{R}_i$$

$$+\nabla\cdot\sum_{i=1}^{N}\int\frac{\vec{p}_i}{m}\,\bar{f}^{(1)}(\vec{p}_i,\vec{R}_i;t)\,\delta(\vec{R}_i-\vec{R})\,d\vec{p}_i\,d\vec{R}_i=0 \qquad (20)$$

i.e.

$$\frac{\partial}{\partial t}\rho^{(1)}(\vec{R};t)+\nabla\cdot\rho^{(1)}(\vec{R};t)\,\vec{u}=0$$

After multiplication of the last equation by the mass of a molecule, m, we recover the hydrodynamical equation of continuity (13).

Similarly, the momentum of the system at the point $\vec{R}$ is given by $\sum_{k=1}^{N}\delta(\vec{R}_k-\vec{R})\,\vec{p}_k$. In the following analysis we restrict ourselves to central forces of the type (6) and we note that by Green's theorem

$$\iint\sum_{k=1}^{N}\delta(\vec{R}_k-\vec{R})\,\vec{p}_k\,(\vec{F}_i+\vec{X}_i)\cdot\nabla_{\vec{p}_i}\,\bar{f}^{(N)}\,d\vec{P}\,d\vec{Q}= \qquad (21)$$

$$-\int(\vec{F}_i+\vec{X}_i)\,\delta(\vec{R}_i-\vec{R})\,\varphi^{(N)}(\vec{Q};t)\,d\vec{Q}$$

Thus, after multiplication of equation (20) by the momentum and integration over phase space, we find, using relation (21) and noting that the external force $\vec{X}_i$ depends only on the coordinates of molecule i, that

$$\frac{\partial}{\partial t}\rho\vec{u}+\nabla_{\vec{R}}\cdot\frac{\rho^{(1)}}{m}\langle\vec{P}\vec{P}\rangle=\vec{X}+\sum_{i=1}^{N}\int\vec{F}_i\,\delta(\vec{R}_i-\vec{R})\,\varphi^{(N)}\,d\vec{Q}$$

$$\rho^{(1)}\langle\vec{P}\vec{P}\rangle=N\int\vec{P}\vec{P}\,\bar{f}^{(1)}(\vec{P},\vec{R};t)\,d\vec{P} \qquad (22)$$

The last sum may be appreciably simplified,

$$\sum_{i=1}^{N} \int \vec{F}_i \, \delta(\vec{R}_i - \vec{R}) \, \varphi^{(N)} \, d\vec{Q} = \tag{23}$$

$$\sum_{i=1}^{N} \sum_{\substack{\ell=1 \\ \neq i}}^{N} \iint \frac{\vec{R}_{i\ell}}{R_{i\ell}} \frac{dV_{i\ell}}{dR_{i\ell}} \, \delta(\vec{R}_i - \vec{R}) \, \varphi^{(2)}(\vec{R}_i, \vec{R}_\ell; t) \, d\vec{R}_i \, d\vec{R}_\ell =$$

$$= \frac{1}{2} \iint \rho^{(2)}(\vec{R}_1, \vec{R}_2; t) \frac{\vec{R}_{12}}{R_{12}} \frac{dV_{12}}{dR_{12}} \left\{ \delta(\vec{R}_1 - \vec{R}) - \delta(\vec{R}_2 - \vec{R}) \right\} d\vec{R}_1 \, d\vec{R}_2$$

Upon changing the variable of integration $\vec{R}_1$ to $\vec{R}_{12}$, with transformation Jacobian unity, this expression reduces to

$$\frac{1}{2} \int \frac{\vec{R}_{12}}{R_{12}} \frac{dV_{12}}{dR_{12}} \left\{ \rho^{(2)}(R, R_{12}; t) - \rho^{(2)}(\vec{R} - \vec{R}_{12}, \vec{R}_{12}; t) \right\} d\vec{R}_{12} \tag{23}$$

In view of the short range of intermolecular forces, by means of a Taylor expansion about $\vec{R}$, we finally obtain

$$\sum_{i=1}^{N} \int \vec{F}_i \, \delta(\vec{R}_i - \vec{R}) \, \varphi^{(N)} \, d\vec{Q} = \nabla_{\vec{R}} \cdot \frac{1}{2} \int \rho^{(2)}(\vec{R}, \vec{R}_{12}; t) \frac{\vec{R}_{12} \vec{R}_{12}}{R_{12}} \frac{dV(R_{12})}{dR_{12}} \, d\vec{R}_{12} \tag{24}$$

Substitution of equation (24) into equation (22), addition of the term $\nabla_{\hat{R}} \cdot \rho \vec{u} \vec{u} = \nabla_{\vec{R}} \cdot \frac{\rho^{(1)}}{m} \langle \vec{P} \rangle \langle \vec{P} \rangle$ to both sides of equation (22) and comparison with the hydrodynamical equation of motion, (14), leads to the following relations(11),(12) for the stress tensor in terms of molecular variables,

$$\underset{\sim}{\sigma} = -\frac{\rho^{(1)}}{m} \langle \vec{\pi} \vec{\pi} \rangle + \frac{1}{2} \int \frac{\vec{R}_{12} \vec{R}_{12}}{R_{12}} \frac{dV(R_{12})}{dR_{12}} \, \rho^{(2)}(\vec{R}, \vec{R}_{12}; t) \, d\vec{R}_{12} \tag{25}$$

$$\vec{\Pi} = \vec{p} - \langle \vec{p} \rangle \qquad (25)$$

where $\rho^{(2)}(\vec{R}, \vec{R}_{12}; t)$ is the number density of pairs, one member of which is situated at point $\vec{R}$ and the other at the point $\vec{R}_{12}$ relative to the position of the first. The integration in the second term of equation (25), the contribution of intermolecular forces to the stress tensor, extends over the relative configuration space $\vec{R}_{12}$ of the representative pair. The first term represents the momentum transfer contribution, important in gases, but almost negligible in liquids. The vector $\vec{\Pi}$ is the familiar peculiar momentum of the kinetic theory of gases.

It is seen from equation (25) that the development of a molecular theory of viscous flow requires the determination of the perturbation from equilibrium resulting from hydrodynamic flow of the number density of pairs and the singlet distribution function. The detailed calculation of these perturbations will be based on the pertinent solutions of the general Chandrasekhar type equations determining the molecular distribution functions of small sets of molecules, first derived by Kirkwood$^{(11)}$ from the molecular standpoint. At this point it is desirable to briefly review these equations and to consider the fundamental assumptions necessary for their derivation.

Following Kirkwood we will find it convenient to use the concepts of the theory of Brownian motion to describe the dissipative mechanisms in liquids. This theory, which describes transport processes in dilute solutions, is based upon the Langevin equation describing the motion of a Brownian particle in an environment in statistical equilibrium. The Langevin equation has the form

$$\frac{d\vec{p}_i}{dt} + \frac{\zeta_i^\circ}{m}\vec{p}_i = \vec{X}_i + \vec{G}_i \qquad (26)$$

where $\vec{p}_i$ is the momentum of a specified molecule i, m its mass, $\vec{X}_i$ the external force acting on it and $\vec{G}_i$ is a fluctuating intermolecular force, the time average of which vanishes over a macroscopically short interval τ, and which is uncorrelated in successive intervals of magnitude τ. The friction constant ζ_i° appearing in the dissipative term $\zeta_i^\circ \frac{\vec{p}_i}{m}$ is a phenomenological constant, determined by intermolecular forces, which has heretofore been estimated only for macromolecules dispersed in solvents of low molecular weight, where macroscopic hydrodynamics may reasonably be expected to apply. Thus for a spherical molecule of radius a, in a solvent of viscosity coefficient η, Stokes law yields the estimate $6\pi\eta a$ for the friction constant ζ_i°.

Kirkwood succeeded in deriving the Langevin equation from statistical mechanics by the assumptions, also implicit in the phenomenological theory, that the environment of molecule i is in equilibrium and that the momentum change of the specified molecule is very small during the smoothing time τ_i, $\tau_i << T$. By this analysis he was able to explicitly express the Brownian motion friction constant ζ_i° in terms of the intermolecular forces characteristic of the system of molecules under consideration,

$$\zeta_i^{\circ} = \zeta_i - 2mkT \frac{d\zeta_i}{dp_i^2}$$

$$\zeta_i = \frac{1}{3kT} \int_0^{\tau_i} {}^{i}\langle \vec{F}_i(t) \cdot \vec{F}_i(t+s) \rangle^{\circ} ds = \zeta^{(1)} \qquad (27)$$

$${}^{i}\langle \vec{F}_i(t) \cdot \vec{F}_i(t+s) \rangle^{\circ} = \frac{\iint \vec{F}_i(t) \cdot \vec{F}_i(t+s)\, f_0^{(N)}(\vec{P}, \vec{Q})\, d\vec{p}_{N-i}\, d\vec{q}_{N-i}}{f_0^{(1)}(\vec{p}_i, \vec{R}_i)}$$

For the determination of the sequence of distribution functions $\bar{f}^{(n)}$, from which the average values characterizing macroscopic transport processes in liquids are to be evaluated, methods closely related to those of the theory of Brownian motion are utilized. The starting point of the analysis is provided by the integration of the Liouville equation (19) over the partial phase space $(\vec{p}_{N-n}, \vec{q}_{N-n})$ of the remainder of the molecules not belonging to set n, followed by a time smoothing of the distribution functions. For central forces of the form (6), the resulting sequence of integro-differential equations, independently derived by Kirkwood and Born and Green, is given by

$$\frac{\partial \bar{f}^{(n)}}{\partial t} + \frac{\vec{p}}{m} \cdot \nabla_{\vec{q}} \bar{f}^{(n)} + \vec{X} \cdot \nabla_{\vec{p}} \bar{f}^{(n)} = \nabla_{\vec{p}} \cdot \vec{\Omega}^{(n)} \qquad (28)$$

$$\vec{\Omega}^{(n)} = -\sum_{\substack{i,k=1 \\ i \neq k}}^{n} \vec{F}_{ki} \bar{f}^{(n)} - \sum_{i=1}^{n} \sum_{\ell=n+1}^{N} \iint \vec{F}_{\ell i}(\vec{R}_{\ell i}) \bar{f}^{(n+1)}(\vec{p}_n, \vec{q}_n, \vec{p}_\ell, \vec{R}_{\ell}, t) \, d\vec{p}_\ell \, d\vec{R}_\ell$$

where $\vec{X}$ denotes the total external force regarded as vectors in the n-configuration space of set n, $\frac{\vec{p}}{m}$ represents a vector in the n- momentum space with projections $\frac{\vec{p}_1}{m} \ldots \frac{\vec{p}_n}{m}$ on the 3- spaces of the several molecules of the set and the vectors $\vec{F}_{\ell i}$ are to be treated as vectors in the 3- configuration space of molecule i of the set n. The dissipative mechanism affecting the behavior of the distribution functions $\bar{f}^{(n)}$ is concealed in the time averaged function of highest order, $\bar{f}^{(N)}$. In order to obtain useful results, the terms in $\vec{\Omega}^{(n)}$ have to be transformed with the aid of solutions of the Liouville equation for $\bar{f}^{(N)}$. Kirkwood performed this transformation by means of the plausible hypothesis of local equilibrium, i.e., the assumption that the environment of the set of n molecules is in statistical equilibrium, and the additional assumption that the change of momentum of the individual molecules of the set is small during the Brownian motion correlation time τ. The latter hypothesis appears reasonable in view of the quasi-localized nature of the molecules in a liquid.

As a result of these Brownian motion approximations, the dissipative terms concealed in the mean currents due to intermolecular forces, $\vec{\Omega}^{(n)}$, appear as integrals related to the friction constant previously obtained in the derivation of the Langevin equation. It is of particular importance to note that this procedure closes the sequence of integro-differential equations and leads to partial differential equations in $\bar{f}^{(n)}$ alone. These equations in the phase space of a subset of n molecules are generalizations of a singlet distribution function equation first derived by Chandrasekhar$^{(14)}$ from the standpoint of the phenomenological theory of Brownian motion, and will be called the generalized Chandrasekhar equations.

For the development of our theory of viscosity we will require the singlet and pair equations. In order to evaluate the momentum contribution to the stress tensor we employ

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{\vec{p}_1}{m}\cdot\nabla_{\vec{R}_1}\bar{f}^{(1)} + \nabla_{\vec{p}_1}\cdot\vec{F}_1^{(1)*} = \nabla_{\vec{p}_1}\cdot\zeta^{(1)}\left\{\frac{\vec{\Pi}_1}{m}\bar{f}^{(1)} + kT\nabla_{\vec{p}_1}\bar{f}^{(1)}\right\} \tag{29}$$

$$\vec{\Pi}_1 = \vec{p}_1 - \langle\vec{p}_1\rangle\,; \quad \vec{F}_1^{(1)*} = -\nabla_{\vec{R}_1}W^{(1)} + \vec{X}_1 + \vec{F}_1^{(1)+}$$

where $\vec{X}_1$ is the external force acting on molecule 1, $\vec{F}_1^{(1)+}$ is the average force due to the departure from equilibrium of the environment of the set of 1 molecule, and $-\nabla_{\vec{R}_1} W^{(1)}$ is the average in the equilibrium ensemble of the total intermolecular force acting on a molecule situated at point $\vec{R}_1$, varying only over distances of macroscopic magnitude. The singlet friction constant $\zeta^{(1)}$ is determined from intermolecular forces by equation (27) of the theory of the Langevin equation. For the determination of the pair density $\rho^{(2)}$, from which the intermolecular force contribution to the stress tensor is to be calculated, we employ the equation appropriate to $\bar{f}^{(2)}(\vec{P}_1, \vec{R}_1, \vec{p}_2, \vec{R}_2; t)$ in the phase space of molecular pairs,

$$\frac{\partial \bar{f}^{(2)}}{\partial t} + \frac{\vec{p}}{m} \cdot \nabla_{\vec{q}} \bar{f}^{(2)} + \nabla_{\vec{p}} \cdot \vec{F}^{(2)*} \bar{f}^{(2)} = \nabla_{\vec{p}} \cdot \underset{\sim}{\zeta}^{(2)} \cdot \left\{ \left(\frac{\vec{p}}{m} - \vec{u}^{(1)} \right) \bar{f}^{(2)} + kT \nabla_{\vec{p}} \bar{f}^{(2)} \right\}$$

$$\vec{F}^{(2)*} = \vec{X} + \vec{F}^{(2)+} - \nabla_{\vec{q}} W^{(2)}$$

$$\underset{\sim}{\zeta}^{(2)} = \frac{1}{kT} \sum_{\alpha=1}^{2} \int_0^{\tau_{12}} {}^{12}\left\langle \vec{F}_\alpha'(t)\, \vec{F}_\alpha'(t+s) \right\rangle^{\circ} ds \qquad (30)$$

$$\vec{F}_\alpha' = \sum_{l=3}^{N} \vec{F}_{l\alpha}$$

$${}^{12}\left\langle \vec{F}_\alpha'(t) \vec{F}_\alpha'(t+s) \right\rangle^{\circ} = \frac{\iint \vec{F}_\alpha'(t)\, \vec{F}_\alpha'(t+s)\, f_0^{(N)}(\vec{P}, \vec{Q})\, d\vec{p}_{N-2}\, d\vec{q}_{N-2}}{f_0^{(2)}(\vec{P}_1, \vec{R}_1, \vec{P}_2, \vec{R}_2)}$$

where, for example, $\vec{p}$ represents a vector in the 2-momentum space with projections $\vec{p}_1$ and $\vec{p}_2$ on the 3-spaces of the molecules of the pair, $-\nabla_{\vec{R}_\alpha} W^{(2)}$ is the mean force acting on molecule α of the pair in the unperturbed equilibrium ensemble, subject to the condition that the configuration $(\vec{R}_1, \vec{R}_2)$ of the pair is fixed, and $\vec{F}^{(2)+}$ is the perturbation arising from the departure of $\rho^{(3)}$, the density in triplet configuration space, from equilibrium. The friction tensor $\underset{\sim}{\zeta}^{(2)}$ is a second rank tensor in the six dimensional configuration space of the pair and the vectors $\vec{u}_1$ and $\vec{u}_2$, the projections of $\vec{u}^{(1)}$, are the particle velocities of three dimensional hydrodynamics, defined by equation (18) at the respective positions $\vec{R}_1$ and $\vec{R}_2$ of the pair.

At this point we may anticipate certain results to be obtained subsequently. In a liquid in a state of stationary viscous flow, the distribution functions are disturbed in such a manner that the stress tensor takes on the extended Newtonian form. It will be shown that the momentum contribution may be directly evaluated from equation (29). With neglect of nonlinear terms in the rate of strain, $\dot{\underset{\sim}{\varepsilon}}$,

$$-\rho^{(1)}\frac{\langle\vec{\pi}\vec{\pi}\rangle}{m} = -\rho^{(1)}kT\underset{\sim}{1} + \frac{\rho^{(1)}mkT}{\zeta}\dot{\underset{\sim}{\varepsilon}} \qquad (31)$$

The pair density $\rho^{(2)}$ is obtained from an equation of forced diffusion resulting from the six dimensional hydrodynamics of the pair. We will find that the pair correlation function $g^{(2)}(\vec{R}, \vec{R}_{12})$, defined by equation (7), can be expanded in the components of the rate of strain as,

$$g^{(2)} = g_0^{(2)}(R_{12})\left\{1 + \frac{\zeta}{2kT}\left[\frac{\vec{R}_{12}\cdot\dot{\underset{\sim}{\varepsilon}}\cdot\vec{R}_{12}}{R_{12}^2} - \frac{1}{3}\nabla\cdot\vec{u}\right]\psi_2(R_{12}) + \frac{\zeta}{6kT}(\nabla\cdot\vec{u})\,\psi_0(R_{12})\right\} \tag{32}$$

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.

Substitution of the momentum contribution of equation (31) and the perturbed pair density of equations (7) and (32) into equation (25) yields the stress tensor

$$\underset{\sim}{\sigma} = -\left[p + \left(\frac{2}{3}\eta - \phi\right)\nabla\cdot\vec{u}\right]\underset{\sim}{1} + 2\eta\,\dot{\underset{\sim}{\varepsilon}} \tag{33}$$

$$p = \frac{NkT}{v} - \frac{2\pi N^2}{3v^2}\int_0^\infty R^3\frac{dV}{dR}\,g_0^{(2)}(R)\,dR \tag{34}$$

where p is the equilibrium pressure of the liquid at the given temperature and uniform number density $\rho_0^{(1)}$, 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,

$$\eta = \frac{\rho k T}{2\zeta} + \frac{\pi \zeta N^2}{15 k T v^2} \int_0^\infty R^3 \frac{dV}{dR} \psi_2(R)\, g_0^{(2)}(R)\, dR \qquad (35)$$

$$\phi = \frac{\rho k T}{3\zeta} + \frac{\pi \zeta N^2}{9 k T v^2} \int_0^\infty R^3 \frac{dV}{dR} \psi_0(R)\, g_0^{(2)}(R)\, dR \qquad (36)$$

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

IV.

MOMENTUM CONTRIBUTION TO STRESS TENSOR

For the evaluation of the momentum contribution to the stress tensor by means of the singlet Chandrasekhar equation (29), the assumption is made that the friction constant γ is momentum independent. This approximation is analogous to the one common to the Langevin equation of Brownian motion. The procedure of multiplying equation (29) by the respective tensors 1, $\vec{\pi}$, $\vec{\pi}\vec{\pi}$ and $\vec{\pi}\vec{\pi}\vec{\pi}$, integration over the momentum space and summation over all the molecules permits the direct calculation of $-\frac{\rho^{(1)}}{m}\langle\vec{\pi}\vec{\pi}\rangle$. Denoting by the operator "Sym" the symmetrization of the tensor following it, we find at the point $\vec{R}$, at time t, with use of Green's theorem,

$$\frac{\partial}{\partial t}\rho^{(1)} + \nabla\cdot\rho^{(1)}\frac{\langle\vec{p}\rangle}{m} = 0 \tag{37}$$

$$\rho^{(1)}\left\{\frac{\partial}{\partial t}\langle\vec{p}\rangle + \frac{\langle\vec{p}\rangle}{m}\cdot\nabla\langle\vec{p}\rangle\right\} + \nabla\cdot\frac{\rho^{(1)}}{m}\langle\vec{\pi}\vec{\pi}\rangle = \vec{F}^{(1)*}\rho^{(1)} \tag{38}$$

$$\frac{\partial}{\partial t}\rho^{(1)}\langle\vec{\pi}\vec{\pi}\rangle + \nabla\cdot\frac{\rho^{(1)}}{m}\langle\vec{\pi}\vec{\pi}\vec{\pi}\rangle + \nabla\cdot\frac{\rho^{(1)}}{m}\langle\vec{p}\rangle\langle\vec{\pi}\vec{\pi}\rangle + 2\frac{\rho^{(1)}}{m}\,\mathrm{Sym}\left\langle\left(\vec{\pi}\cdot\nabla\langle\vec{p}\rangle\right)\vec{\pi}\right\rangle = -\frac{2\gamma}{m}\rho^{(1)}\left\{\langle\vec{\pi}\vec{\pi}\rangle - mkT\underset{\sim}{1}\right\} \tag{39}$$

$$\frac{\partial}{\partial t}\rho^{(1)}\langle\vec{\pi}\vec{\pi}\vec{\pi}\rangle + 3\frac{\rho^{(1)}}{m}\,\mathrm{Sym}\left\langle\vec{\pi}\vec{\pi}\left(\vec{\pi}\cdot\nabla\langle\vec{p}\rangle\right)\right\rangle + \nabla\cdot\frac{\rho^{(1)}}{m}\langle\vec{p}\rangle\langle\vec{\pi}\vec{\pi}\vec{\pi}\rangle + $$

$$+ 3\frac{\rho^{(1)}}{m}\,\mathrm{Sym}\left\langle\vec{\pi}\vec{\pi}\left(\langle\vec{p}\rangle\cdot\nabla\langle\vec{p}\rangle\right)\right\rangle + \tag{40}$$

$$+\nabla\cdot\frac{\rho^{(1)}}{m}\langle\vec{\pi}\vec{\pi}\vec{\pi}\vec{\pi}\rangle = 3\rho^{(1)}\,\mathrm{Sym}\langle\vec{F}^{(1)*}\vec{\pi}\vec{\pi}\rangle - 3\frac{\rho^{(1)}}{m}\zeta\langle\vec{\pi}\vec{\pi}\vec{\pi}\rangle \qquad (40)$$

It will be noted that equation (37) is the equation of continuity, equation (38) is the equivalent of the hydrodynamic equation of motion, and equation (39) is independent of $\vec{F}^{(1)*}$. Substitution of (38) into (40) shows that $\nabla\cdot\frac{\rho^{(1)}}{m}\langle\vec{\pi}\vec{\pi}\vec{\pi}\rangle$ will not contribute to a linear theory of viscosity so that with use of the equation of continuity (37), with neglect of nonlinear terms in all perturbations from equilibrium, equation (39) simplifies to

$$\langle\vec{\pi}\vec{\pi}\rangle - mkT\underset{\sim}{1} = -\frac{m}{2\zeta}\Big\{\langle\vec{\pi}\vec{\pi}\rangle\cdot\nabla\vec{u} + \langle\vec{\pi}\cdot\nabla\vec{u}\,\vec{\pi}\rangle + \vec{u}\cdot\nabla\langle\vec{\pi}\vec{\pi}\rangle + \frac{\partial}{\partial t}\langle\vec{\pi}\vec{\pi}\rangle\Big\} \qquad (41)$$

$$\vec{\pi} = \vec{p} - m\vec{u}$$

For the stationary case, the solution of this equation is obtained by substituting the first approximation $\langle\vec{\pi}\vec{\pi}\rangle = mkT\underset{\sim}{1}$ into the terms on the right-hand side,

$$-\frac{\rho^{(1)}}{m}\langle\vec{\pi}\vec{\pi}\rangle = -\rho^{(1)}kT\underset{\sim}{1} + \frac{\rho^{(1)}mkT}{\zeta}\dot{\underset{\sim}{\varepsilon}}$$

$$\dot{\underset{\sim}{\varepsilon}} = \mathrm{Sym}\,\nabla\vec{u}$$

This result reduces to $-\rho^{(1)}kT\underset{\sim}{1}$ in the absence of fluid flow. In terms of the coefficient of self diffusion $D = \frac{kT}{\zeta}$

and the mass density ρ, the momentum contribution to the stress tensor becomes,

$$\underset{\sim}{\sigma}_p = -\rho \frac{kT}{m} \underset{\sim}{1} + \rho D \dot{\underset{\sim}{\varepsilon}} \tag{43}$$

The analogous expression for rigid spheres derived in the kinetic theory of gases(15) is given by

$$\underset{\sim}{\sigma}_p = -\rho \frac{kT}{m} \underset{\sim}{1} + \frac{5}{3} \rho D \left(\dot{\underset{\sim}{\varepsilon}} - \frac{1}{3} \nabla \cdot \vec{u} \, \underset{\sim}{1} \right) \tag{44}$$

Despite the different approach employed in our theory, it is surprising that similar results are obtained. The main difference is that the Brownian motion approximation does not lead to a divergenceless viscous flow contribution and thus gives rise to a bulk viscosity.

V.

INTERMOLECULAR FORCE CONTRIBUTION TO STRESS TENSOR

The calculation of the pair number density $\rho^{(2)}$, required for the intermolecular force contribution, will be undertaken with the simplifications that the pair friction tensor $\underset{\sim}{\zeta}^{(2)}$ is momentum independent, independent of the relative configuration of the pair, and is furthermore assumed to be numerically equal to the singlet friction constant ζ,

$$\underset{\sim}{\zeta}_1^{(2)} = \underset{\sim}{\zeta}_2^{(2)} = \zeta \underset{\sim}{\underline{1}} \tag{45}$$

With this approximation the pair Chandrasekhar equation (30) reduces to

$$\frac{\partial \bar{f}^{(2)}}{\partial t} + \frac{\vec{p}}{m} \cdot \nabla_{\vec{q}} \bar{f}^{(2)} + \nabla_{\vec{p}} \cdot \vec{F}^{(2)*} \bar{f}^{(2)} = \nabla_{\vec{p}} \cdot \zeta \left\{ \left(\frac{\vec{p}}{m} - \vec{u}^{(2)} \right) \bar{f}^{(2)} + kT \nabla_{\vec{p}} \bar{f}^{(2)} \right\} \tag{46}$$

For the purpose of evaluating the pair correlation function $g^{(2)}(\vec{R}_1, \vec{R}_{12}; t)$ from this equation it is convenient to utilize the previously defined notation for the six dimensional hydrodynamics of the pair and to introduce the number current density of the pair, $\vec{j}^{(2)}$,

$$\vec{j}^{(2)} = \frac{N(N-1)}{m} \iint \vec{p}\, \bar{f}^{(2)}(\vec{p}_1, \vec{p}_2, \vec{R}_1, \vec{R}_2; t)\, d\vec{p}_1\, d\vec{p}_2 \tag{47}$$

Upon multiplication of equation (46) by 1, $\vec{p}$ and $\vec{p}\vec{p}$, followed by integration over the momentum space of both molecules and summation over the particles, the following set of equations is obtained,

$$\frac{\partial \rho^{(2)}}{\partial t} + \nabla_{\vec{q}} \cdot \vec{j}^{(2)} = 0 \qquad (48)$$

$$m \frac{\partial \vec{j}^{(2)}}{\partial t} + \nabla_{\vec{q}} \cdot \frac{\rho^{(2)}}{m} \langle \vec{p}\vec{p} \rangle^{(2)} = \rho^{(2)} \vec{F}^{(2)*} - \zeta \left(\vec{j}^{(2)} - \rho^{(2)} \vec{u}^{(1)} \right) \qquad (49)$$

$$\frac{\partial}{\partial t} \rho^{(2)} \langle \vec{p}\vec{p} \rangle^{(2)} + \nabla_{\vec{q}} \cdot \frac{\rho^{(2)}}{m} \langle \vec{p}\vec{p}\vec{p} \rangle^{(2)} = 2 \,\mathrm{Sym}\, m \vec{j}^{(2)} \vec{F}^{(2)*} -$$

$$- \frac{2\zeta}{m} \rho^{(2)} \langle \vec{p}\vec{p} \rangle^{(2)} + 2 m \zeta \,\mathrm{Sym}\, \vec{j}^{(2)} \vec{u}^{(1)} + 2 \zeta k T \rho^{(2)} \underset{\sim}{1}^{(2)} \qquad (50)$$

$$\rho^{(2)} \langle \vec{p}\vec{p} \rangle^{(2)} = N(N-1) \iint \vec{p}\vec{p} f^{(2)} d\vec{p}_1 d\vec{p}_2$$

It follows from equation (50) that the neglect of non-linear terms in $\vec{u}^{(1)}$ and of terms of the order of $1/\zeta$ in the departure of the non-diagonal terms in $\frac{\langle \vec{p}\vec{p} \rangle^{(2)}}{m}$ from their vanishing equilibrium values leads to $\frac{\rho^{(2)}}{m} \langle \vec{p}\vec{p} \rangle^{(2)} = kT\rho^{(2)} \underset{\sim}{1}^{(2)}$ Substitution of this estimate into equation (49) leads to

$$m \frac{\partial \vec{j}^{(2)}}{\partial t} = -kT \nabla_{\vec{q}} \rho^{(2)} + \vec{F}^{(2)*} \rho^{(2)} - \zeta \Delta \vec{j}^{(2)}$$

$$\Delta \vec{j}^{(2)} = \vec{j}^{(2)} - \rho^{(2)} \vec{u}^{(1)} \qquad (51)$$

Similar equations are obtained by the same procedure from equation (29),

$$\frac{\partial}{\partial t} \rho^{(1)}(\vec{R}_\alpha) + \nabla_{R_\alpha} \cdot \rho^{(1)}(\vec{R}_\alpha) \vec{u}(\vec{R}_\alpha) = 0 \quad ; \qquad \alpha = 1,2 \qquad (52)$$

$$m\frac{\partial}{\partial t}\rho^{(1)}(\vec{R}_\alpha)\vec{u}(\vec{R}_\alpha) = -kT\nabla_{\vec{R}_\alpha}\rho^{(1)}(\vec{R}_\alpha) + \vec{F}_\alpha^{(1)*}\rho^{(1)}(\vec{R}_\alpha) \qquad (52)$$

Apart from nonlinear terms and with introduction of the pair correlation function $g^{(2)}(\vec{R}_1, \vec{R}_{12}; t)$, equation (52) may be written in the form

$$m\frac{\partial}{\partial t}\rho^{(2)}\vec{u}^{(1)} = \rho^{(2)}\vec{F}^{(1)*} - g^{(2)}kT\nabla_{\vec{q}}\,\rho^{(1)}(\vec{R}_1)\rho^{(1)}(\vec{R}_2) \qquad (53)$$

Combination of equations (51) and (53) and use of the definitions of $\vec{F}^{(2)*}$ and $\vec{F}^{(1)*}$ yields

$$\Delta\vec{j}^{(2)} + \frac{m}{\zeta}\frac{\partial}{\partial t}\Delta\vec{j}^{(2)} = \rho^{(1)}(\vec{R}_1)\rho^{(1)}(\vec{R}_2)\Big\{-\frac{kT}{\zeta}\nabla_{\vec{q}}\,g^{(2)} + \frac{g^{(2)}}{\zeta}\left(\vec{F}^{(2)+} - \vec{F}^{(1)+}\right) - \frac{g^{(2)}}{\zeta}\nabla_{\vec{q}}\left(W^{(2)} - W_1^{(1)} - W_2^{(1)}\right)\Big\} \qquad (54)$$

an expression independent of the external force $\vec{X}$. The term $\frac{\partial}{\partial t}\Delta\vec{j}^{(2)}$ will be neglected since its coefficient, $\frac{m}{\zeta}$, is of the order of magnitude of the Brownian motion correlation time. The equilibrium radial distribution function $g_0^{(2)}$ is related to the potentials of mean force $W^{(2)}$ and $W^{(1)}$ by equations (2) and (10),

$$g_0^{(2)}(R_{12}) = e^{-(W^{(2)} - W_1^{(1)} - W_2^{(1)})/kT} \qquad (55)$$

so that

$$-\nabla_{\vec{q}}\left(W^{(2)}-W_1^{(1)}-W_2^{(1)}\right) = kT\nabla_{\vec{q}}\log g_0^{(2)}(R_{12}) \qquad (56)$$

With use of equation (56) and introduction of the perturbation in the correlation function produced by viscous flow, $g_1^{(2)}$, defined by the relation

$$g^{(2)} = g_0^{(2)}\left(1+g_1^{(2)}\right) \qquad (57)$$

equation (54) simplifies to

$$\Delta j^{(2)} = \rho^{(1)}(\vec{R}_1)\,\rho^{(1)}(\vec{R}_2)\left\{-\frac{kT}{\zeta}\,g_0^{(2)}\nabla_{\vec{q}}\,g_1^{(2)} + \frac{g^{(2)}}{\zeta}\left(\vec{F}^{(2)+}-\vec{F}^{(1)+}\right)\right. \qquad (58)$$

For the evaluation of $g_1^{(2)}$ we note that by the equations of continuity (37) and (48),

$$\nabla_{\vec{q}}\cdot\Delta\vec{j}^{(2)} = -\rho^{(1)}(\vec{R}_1)\,\rho^{(1)}(\vec{R}_2)\left\{g_0^{(2)}\frac{\partial g_1^{(2)}}{\partial t} + \vec{u}^{(1)}\cdot\nabla_{\vec{q}}\,g^{(2)}\right\} \qquad (59)$$

Thus by taking the divergence of equation (58), the equation determining $g_1^{(2)}$ becomes for a linear theory,

$$\nabla_{\vec{q}}^2\,g_1^{(2)} + \nabla_{\vec{q}}\,g_1^{(2)}\cdot\nabla_{\vec{q}}\log g_0^{(2)} = \frac{\zeta}{kT}\,\vec{u}^{(1)}\cdot\nabla_{\vec{q}}\log g_0^{(2)} + \frac{\zeta}{kT}\frac{\partial g_1^{(2)}}{\partial t}$$

$$+\frac{1}{kT g_0^{(2)}}\,\nabla_{\vec{q}}\cdot\left[\left(\vec{F}^{(2)+}-\vec{F}^{(1)+}\right)g^{(2)}\right] \qquad (60)$$

Furthermore, for a linear theory $g^{(2)}$ depends only on the relative coordinates $\vec{R}=\vec{R}_2-\vec{R}_1$, so that $\nabla_{\vec{R}_2}=-\nabla_{\vec{R}_1}=\nabla_{\vec{R}}$ when operating on the correlation function. In view of the short range of intermolecular forces, it is adequate to retain the first term in the Taylor expansion of the velocity of molecule 2, $\vec{u}(\vec{R}_2)$, about $\vec{R}_1$,

$$\vec{u}^{(1)} \cdot \nabla_{\vec{q}} g_0^{(2)} = \left\{ \vec{u}(\vec{R}_2) - \vec{u}(\vec{R}_1) \right\} \cdot \nabla_{\vec{R}} g_0^{(2)} = \frac{\vec{R} \cdot \dot{\underset{\sim}{\varepsilon}} \cdot \vec{R}}{R} \frac{d g_0^{(2)}}{dR} \qquad (61)$$

The treatment to follow will be based upon the neglect of $\vec{F}^{(2)+} - \vec{F}^{(1)+}$, i.e., the average force arising from the departure from equilibrium of the environment of sets of three molecules. With these approximations we finally obtain the equation of forced diffusion determining the perturbation $g_1^{(2)}$,

$$\nabla^2 g_1^{(2)} + \frac{d g_1^{(2)}}{dR} \frac{d \log g_0^{(2)}}{dR} = \frac{\zeta}{2kT} \frac{\vec{R} \cdot \dot{\underset{\sim}{\varepsilon}} \cdot \vec{R}}{R^2} R \frac{d}{dR} \log g_0^{(2)} + \frac{\zeta}{2kT} \frac{\partial g_1^{(2)}}{\partial t} \qquad (62)$$

The complete solution of this equation leads to the molecular interpretation of the relaxation time spectrum due to viscous fluid flow. For the determination of the coefficients of viscosity it suffices to consider the steady state solutions. For this purpose we note that the term $\frac{\vec{R} \cdot \dot{\underset{\sim}{\varepsilon}} \cdot \vec{R}}{R^2}$ may be expressed in terms of surface harmonics of order two and zero,

$$\begin{aligned} \frac{\vec{R} \cdot \dot{\underset{\sim}{\varepsilon}} \cdot \vec{R}}{R^2} &= \tfrac{1}{3} \dot{\varepsilon}_{xy} P_2^2(\cos\theta) \sin 2\varphi + \tfrac{2}{3} \dot{\varepsilon}_{xz} P_2^1(\cos\theta) \cos\varphi + \\ &\quad + \tfrac{2}{3} \dot{\varepsilon}_{yz} P_2^1(\cos\theta) \sin\varphi + \left(\dot{\varepsilon}_{zz} - \tfrac{1}{3} \nabla \cdot \vec{u} \right) P_2^0(\cos\theta) \qquad (63) \\ &\quad + \tfrac{1}{6} \left(\dot{\varepsilon}_{xx} - \dot{\varepsilon}_{yy} \right) P_2^2(\cos\theta) \cos 2\varphi + \tfrac{1}{3} \nabla \cdot \vec{u}\, P_0^0(\cos\theta) \end{aligned}$$

In view of this relationship, the perturbation $g_1^{(2)}$ is given by

$$g_1^{(2)} = \frac{J}{2kT}\left\{\left(\frac{\vec{R}\cdot\dot{\underset{\sim}{\varepsilon}}\cdot\vec{R}}{R^2} - \frac{1}{3}\nabla\cdot\vec{u}\right)\psi_2(R) + \frac{1}{3}\nabla\cdot\vec{u}\,\psi_0(R)\right\} \qquad (64)$$

In coordinate representation $\psi_2(R)$ is the coefficient of surface harmonics of order two, arising from the shear components of the rate of strain, and $\psi_0(R)$ is the coefficient of the surface harmonic of order zero, arising from the dilatational component. Introduction of equation (64) into equation (62) and linearization with respect to the components of the rate of strain, $\dot{\underset{\sim}{\varepsilon}}$, leads, in the stationary case, to the following ordinary differential equations for the functions $\psi_2(R)$ and $\psi_0(R)$,

$$\frac{d}{dR}\left(R^2 g_0^{(2)} \frac{d\psi_2}{dR}\right) - 6 g_0^{(2)}\psi_2 = R^3 \frac{dg_0^{(2)}}{dR} \qquad (65)$$

$$\frac{d}{dR}\left(R^2 g_0^{(2)} \frac{d\psi_0}{dR}\right) = R^3 \frac{dg_0^{(2)}}{dR} \qquad (66)$$

The boundary conditions subject to which these equations are to be solved are derived from the conditions imposed on the excess probability current density in relative pair space, $\vec{j}_{12}^{(2)}$. This vector is the difference of the projection of $\Delta\vec{j}^{(2)}$ on the configuration spaces of molecules 2 and 1, respectively,

$$\rho^{(1)}(\vec{R}_1)\,\rho^{(1)}(\vec{R}_2)\,\vec{j}_{12}^{(2)} = \left[\vec{j}_2^{(2)} - \rho^{(2)}\vec{u}_2\right] - \left[\vec{j}_1^{(2)} - \rho^{(2)}\vec{u}_1\right] \qquad (67)$$

By means of equations (58) and (64) the excess probability density in the relative pair space may be expressed in terms of $\psi_2(R)$ and $\psi_0(R)$,

$$\dot{\vec{j}}_{12}^{(2)} = -g_0^{(2)} \nabla_{\vec{R}} \left\{ \left[\frac{\vec{R}\cdot\dot{\underline{\epsilon}}\cdot\vec{R}}{R^2} - \frac{1}{3}\nabla\cdot\vec{u} \right] \psi_2(R) + \frac{1}{3}\nabla\cdot\vec{u}\, \psi_0(R) \right\} \tag{68}$$

The relative current $\dot{\vec{j}}_{12}^{(2)}$ vanishes at $R \to \infty$ by definition and is conditioned by the absence of partial sources or sinks in pair space. These requirements lead to the boundary conditions,

$$\lim_{R\to\infty} \psi_2(R) = 0 \tag{69}$$

$$\lim_{R\to 0} R^2 g_0^{(2)} \frac{d\psi_2}{dR} = 0 \tag{70}$$

$$\lim_{R\to\infty} \frac{d\psi_0}{dR} = 0 \tag{71}$$

$$\lim_{R\to 0} R^2 g_0^{(2)} \frac{d\psi_0}{dR} = 0 \tag{72}$$

In addition, in order to ensure continuity of the pair current at any point q_1, $0 < q_1 \leq \infty$,

$$\begin{aligned} \lim_{\epsilon\to 0} g_0^{(2)}(q_1-\epsilon)\, \psi_2(q_1-\epsilon) &= \lim_{\epsilon\to 0} g_0^{(2)}(q_1+\epsilon)\, \psi_2(q_1+\epsilon) \\ \lim_{\epsilon\to 0} g_0^{(2)}(q_1-\epsilon)\, \frac{d\psi_2}{dR}(q_1-\epsilon) &= \lim_{\epsilon\to 0} g_0^{(2)}(q_1+\epsilon)\, \frac{d\psi_2}{dR}(q_1+\epsilon) \end{aligned} \tag{73}$$

The stress tensor is derived by substitution of equations (64) and (57) into the expression for the intermolecular force contribution, equation (25), and the result, equation (42),

$$\underset{\sim}{\sigma} = -\underset{\sim}{1}\left(\rho^{(1)}kT - \frac{2\pi}{3}\rho^{(1)2}\int_0^\infty R^3\frac{dV}{dR}\,g_0^{(2)}\,dR\right) \tag{74}$$

$$+2\left(\underset{\sim}{\dot{\varepsilon}} - \frac{1}{3}\nabla\cdot\vec{u}\,\underset{\sim}{1}\right)\left(\frac{\rho^{(1)}mkT}{2\zeta} + \frac{\zeta\pi}{15kT}\rho^{(1)2}\int_0^\infty R^3\frac{dV}{dR}\,g_0^{(2)}\psi_2\,dR\right)$$

$$+\underset{\sim}{1}\,\nabla\cdot\vec{u}\left(\frac{\rho^{(1)}mkT}{3\zeta} + \frac{\zeta\pi}{9kT}\rho^{(1)2}\int_0^\infty R^3\frac{dV}{dR}\,g_0^{(2)}\psi_0\,dR\right)$$

Equations (34), (35) and (36), giving the equation of state and the coefficients of viscosity, follow directly by comparison of the stress tensor (74) with the empirical Newtonian law and use of the equilibrium value for the singlet number density $\rho_0^{(1)} = \frac{N}{v}$. Since the tensor $\vec{R}\vec{R}$ may be expanded in terms of surface harmonics of order two and zero in the same manner as $\frac{\vec{R}\cdot\underset{\sim}{\varepsilon}\cdot\vec{R}}{R^2}$, the numerical coefficients resulting from the angular integration follow from the orthogonality of surface harmonics and the relation

$$\int_0^\pi\int_0^{2\pi}\left[P_n^m(\cos\theta)\right]^2 \begin{matrix}\cos^2 m\varphi\\ \sin^2 m\varphi\end{matrix}\, d\varphi\,\sin\theta\, d\theta = \frac{2\pi}{2n+1}\frac{(n+m)!}{(n-m)!} \tag{75}$$

VI.

EQUILIBRIUM RADIAL DISTRIBUTION FUNCTION

In order to evaluate the integrals (35) and (36), as well as to solve the differential equations determining the perturbation functions $\psi_2(R)$ and $\psi_0(R)$, 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,

$$V(R) = \varepsilon\left(\frac{1}{X^n} - \frac{1}{X^6}\right) \qquad (76)$$

$$X = \frac{R}{a_0}$$

The theory to be presented has been applied numerically to liquid argon. This fluid satisfies the requirements that the individual molecules have spherically symmetric fields of force, and furthermore its properties may be calculated by means of classical statistical mechanics. In applications of the theory to be made to liquid argon, we will use parameters ε, n and a_0, determined by Rushbrooke(16) and Corner(17). The values are:

$n = 11.4;\ \varepsilon = 6.82 \times 10^{-14}\ \text{ergs};\ a_0 = 3.43\ \text{Å}.$

It is to be emphasized that the Lennard-Jones expression is not a true representation of the potential, but is commonly used because of its analytical properties.

The radial distribution function $g_0^{(2)}(R)$ is determined by the potential of intermolecular force V(R) and the thermodynamic variables. In Part II it was shown that for a liquid in the absence of external forces,

$$\rho_0^{(2)} = \frac{N^2}{V^2} g_0^{(2)}(R_{12}) = N(N-1) \frac{\int e^{-\beta V^{(N)}} d\vec{q}_{N-2}}{\int e^{-\beta V^{(N)}} d\vec{Q}} \qquad (77)$$

$$\beta = \frac{1}{kT}$$

For a potential of intermolecular force of the form (5), the dependence of $g_0^{(2)}$ on the thermodynamic variables may be easily determined by taking the gradient of both sides of equation (77) with respect to molecule 2 of the pair,

$$\nabla_{\vec{R}_2} \rho_0^{(2)}(R_{12}) = -\rho_0^{(2)} \beta \nabla_{\vec{R}_2} V(R_{12}) - \beta N(N-1) \int \sum_{i=3}^{N} \nabla_{\vec{R}_2} V(R_{2i}) \varphi_0^{(N)} d\vec{q}_{N-2}$$

$$= -\beta \rho_0^{(2)} \nabla_{\vec{R}_2} V(R_{12}) - \beta \int \nabla_{\vec{R}_2} V(R_{23}) \rho_0^{(3)} d\vec{R}_3 \qquad (78)$$

By defining a correlation function for a set of three molecules by the relation $\rho_0^{(3)} = \frac{N^3}{V^3} g_0^{(3)}(\vec{R}_{12}, \vec{R}_{13}, \vec{R}_{23})$, and using the potential $V(R) = \varepsilon\left(\frac{1}{x^n} - \frac{1}{x^6}\right) = \varepsilon f(x)$, the equation for $g_0^{(2)}$ becomes

$$\nabla_{\vec{R}_2} \log g_0^{(2)}(R_{12}) = -\beta \nabla_{\vec{R}_2} V(R_{12}) - \frac{\beta N}{V} \int \nabla_{\vec{R}_2} V(R_{23}) \frac{g_0^{(3)}(R_{12}, R_{13}, R_{23})}{g_0^{(2)}(R_{12})} d\vec{R}_3$$

$$(79)$$

$$\nabla_{\vec{x}_2} \log g_0^{(2)} = -\frac{\varepsilon}{kT} \nabla_{\vec{x}_2} f(x_{12}) - \frac{\varepsilon}{kT} \frac{N a_0^3}{V} \int \nabla_{\vec{x}_2} f(x_{23}) \frac{g_0^{(3)}(x_{12}, x_{13}, x_{23})}{g_0^{(2)}(x_{12})} d\vec{x}_3$$

It is thus seen that $g_0^{(2)}$ depends on the combinations $\alpha_1 = \frac{\varepsilon}{kT}$ and $\alpha_2 = \frac{N a_0^3}{V}$. The normalization condition imposed on $g_0^{(2)}$ (appendix) has the same dependence on the thermodynamic variables.

All theoretical investigations of $g_0^{(2)}$ carried out thus far have been based on the "Kirkwood(18) superposition approximation", which terminates the integro-differential equation (79) by the approximation

$$g_0^{(3)}(R_{12}, R_{13}, R_{23}) = g_0^{(2)}(R_{12})\, g_0^{(2)}(R_{13})\, g_0^{(2)}(R_{23}).$$

In view of the mathematical difficulties involved in solving this nonlinear integral equation, solutions have only been obtained for the hard sphere(19) case up until now. Thus, at the present time, accurate theoretical distribution functions are not available.

However, $g_0^{(2)}$ 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 applications to follow, we will make use of the radial distribution function data for liquid argon of Eisenstein and Gingrich(20). This function approaches zero at an effective collision diameter and possesses a series of peaks with amplitude rapidly diminishing as R increases. For large R, the value of the function approaches unity.

The experimental results of Eisenstein and Gingrich were checked by substituting their values into the equation of state (34). It was found that with use of their curves, the integral determining the cohesive pressure yields a negative value at a condition requiring a positive result. This clearly demonstrates a difficulty encountered in problems of this type. The representative integrals are very sensitive to the relative variation of the first peak of the radial distribution function to the position and value of the minimum of the potential of intermolecular force, the latter being always somewhat arbitrarily chosen. One could partly circumvent this difficulty by adjusting the experimental $g_0^{(2)}$ so as to give correct results for the integrals determining the equation of state and the energy of vaporization, likewise determined by $g_0^{(2)}$.

The solution of equations (65) and (66) could be based on this improved $g_0^{(2)}$, but this procedure would entail a very extensive numerical program. We have selected a different line of attack on this problem. The analytical approximation to $g_0^{(2)}(R)$,

$$\begin{aligned} g_0^{(2)}(R) &= \left(\frac{a_1}{R}\right)^s e^{\left\{\left(\frac{a_m}{a_1}\right)^t - \left(\frac{a_m}{R}\right)^t\right\}} ; \quad 0 \leq R \leq a_1 \\ &= 1 ; \quad a_1 < R \end{aligned} \tag{80}$$

represents the first peaks of the Eisenstein-Gingrich curves quite well, and has the important advantage of allowing integration of the differential equations satisfied by the perturbations ψ_2 and ψ_0 in terms of confluent hypergeometric functions. Due to the short range of intermolecular forces, the subsidiary maxima and minima in $g_0^{(2)}$ will not contribute appreciably to the desired results.

The two parameters a_1 and t were determined from the Eisenstein-Gingrich data to be relatively insensitive to temperature. On the basis of their curves, the values $a_1=4.5A^{\circ}$ and $t=14$ were selected. For liquid argon at 89°K and 1.2 atm., the remaining parameters were determined with use of the Lennard-Jones potential, equation (76), the theoretical equation of state, equation (34), and the energy of vaporization of the liquid into a perfect gas,

$$-\Delta E_v = E_\ell - \frac{3}{2}RT = 2\pi\frac{N^2}{V}\int_0^\infty R^2 g_0^{(2)}(R)\, V(R)\, dR \tag{81}$$

Equation (81) may be easily derived from the result that the kinetic energy of a classical monatomic fluid is $\frac{3}{2}RT$ and from the statistical average of the potential energy. Thus the energy, E_l, of the liquid is given by

$$\begin{aligned} E_\ell &= \frac{3}{2}RT + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\int V_{ij}(R_{ij})\,\varphi_0^{(N)}\,d\vec{Q} \\ &= \frac{3}{2}RT + \frac{1}{2}\int V(R_{12})\,\rho^{(2)}\,d\vec{R}_{12}\,d\vec{R}_1 \qquad (82) \\ &= \frac{3}{2}RT + 2\pi\frac{N^2}{V}\int_0^\infty R^2\, V(R)\, g_0^{(2)}(R)\, dR \end{aligned}$$

Table I summarizes the best available data for liquid argon in equilibrium with the vapor needed for the subsequent calculations of the thermodynamic variables.

TABLE I

T	P (atm)	$\rho_{liq}\left(\frac{gm}{cm^3}\right)$	E_{vap} (cal/mol)
84.0	.6793	1.409	1,425
86.0	.8520	1.397	1,411
88.0	1.1099	1.385	1,396
90.0	1.329	1.374	1,382
95.0	2.120	1.343	1,347
100.0	3.210	1.309	1,311
110.0	6.566	1.239	1,236

The pressure was calculated from the equation given by F. Born(21) (84° - 86°K), and from the equation in the International Critical Tables(22) (88° - 110°K). Densities of the liquid were taken from the compilations of Mathias, Kamerlingh Onnes and Crommelin(23). The energies of vaporization were calculated from the heat of vaporization at 87.29°K determined by Frank and Clusius(24), and the heat capacities of the liquid given by Clusius(25) (86.0°-88.0°K) and Eucken and Hauck(26) (90°- 110°K). Gas corrections were made from the second virial coefficient obtained by Cath and Kamerlingh Onnes(27).

For the determination of the parameters a_m and s of equation (80), it is convenient to transform the theoretical expressions for the equation of state and energy of vaporization. Quite generally with use of the Lennard-Jones potential (76),

$$L_E = \frac{\frac{3}{2}RT - E_\ell}{2\pi a_0^3 \frac{N}{V}^2 \varepsilon} = -\int_0^\infty x^2\left(\frac{1}{x^n} - \frac{1}{x^6}\right) g_0^{(2)}\, dx \qquad (83)$$

$$L_p = \frac{RT - pv}{\frac{2\pi}{3} a_0^3 \frac{N}{V}^2 \varepsilon} = -\int_0^\infty x^2\left(\frac{n}{x^n} - \frac{6}{x^6}\right) g_0^{(2)}\, dx \qquad (84)$$

By means of some elementary algebraic operations we find that

$$L_n = \frac{6L_E - L_p}{n-6} = \int_0^\infty \frac{g_0^{(2)}}{x^{n-2}}\, dx \qquad (85)$$

$$L_6 = \frac{nL_E - L_p}{n-6} = \int_0^\infty \frac{g_0^{(2)}}{x^4}\, dx \qquad (86)$$

Substitution of the analytical approximation to $g_0^{(2)}$, equation (80), into equations (85) and (86), leads to the following transcendental equations:

$$L_n - \frac{1}{n-3}\frac{1}{x_1^{n-3}} = x_m^{3-n} z_1^{-\frac{s}{t}} e^{z_1} \Gamma\left(\frac{s+n-3}{t} ; z_1\right) \qquad (87)$$

$$L_6 - \frac{1}{3x_1^3} = x_m^{-3} z_1^{-\frac{s}{t}} e^{z_1} \Gamma\left(\frac{s+3}{t} ; z_1\right) \qquad (88)$$

$$x_1 = \frac{a_1}{a_0} \; ; \; x_m = \frac{a_m}{a_0} \; ; \; z_1 = \left(\frac{a_m}{a_1}\right)^t ;$$

$$\Gamma(\alpha, z_1) = \int_{z_1}^{\infty} e^{-z} z^{\alpha-1} dz$$

$$= \Gamma(\alpha) - \gamma(\alpha, z_1)$$

The functional relation between a_m and s was derived by solving the equation obtained from the division of equation (87) by equation (88). Resubstitution of this relation into equation (87) led to the values of the parameters. Table II summarizes the results of these calculations for liquid argon at 89°K and 1.2 atm.

TABLE II

a_1	a_m	t	s
4.5 A°	3.554 A°	14	7.007

With these parameters the maximum of the first peak occurs at 3.73 A° and the coordination number corresponding to nearest neighbors is 8.1, both in good agreement with the Eisenstein-Gingrich experiments. It should be noted that the procedure adopted, partly compensates for the arbitrariness of the constants in the potential V(R).

VII.

SOLUTION OF SHEAR VISCOSITY EQUATION

In this section we will derive the solution of the ψ_2 equation (65) based on use of the approximate representation of $g_0^{(2)}$ given in equation (80). Since $\frac{R^2}{2}$ is a particular solution, we only have to investigate the homogeneous equation,

$$x^2 \frac{d^2\psi_2}{dx^2} + \left\{ 2 + x \frac{d}{dx} \log g_0^{(2)} \right\} x \frac{d\psi_2}{dx} - 6\psi_2 = 0 \qquad (89)$$

$$x = \frac{R}{a_0}$$

For $x_1 < x$, equation (89) reduces to Euler's equation,

$$x^2 \frac{d^2\psi_2}{dx^2} + 2x \frac{d\psi_2}{dx} - 6\psi_2 = 0 \qquad (90)$$

so that the solution satisfying the boundary condition at infinity, equation (69), is given by

$$\psi_2 = \frac{K_2}{x^3} \quad ; \quad x_1 < x \qquad (91)$$

Substitution of the first peak approximation into equation (89) leads to the following differential equation for $0 \leq x \leq x_1$,

$$z^2 \frac{d^2\psi_2}{dz^2} + (2k - z) z \frac{d\psi_2}{dz} + \left(k + m - \tfrac{1}{2}\right)\left(k - m - \tfrac{1}{2}\right)\psi_2 = 0$$

$$k = \frac{1}{2} + \frac{s-1}{2t} \; ; \quad m = \frac{1}{t}\sqrt{\left(\frac{s-1}{2}\right)^2 + 6} \; ; \quad z = \left(\frac{x_m}{x_1}\right)^t \qquad (92)$$

The two linearly independent solutions of this equation are found to be $e^{\frac{z}{2}} z^{-k} W_{k,m}(z)$ and $e^{\frac{z}{2}} z^{-k} W_{-k,m}(-z)$ where $W_{k,m}(z)$ is the Whittaker$^{(28)}$ confluent hypergeometric function. Thus,

$$\psi_2 = \frac{q_0^2 x^2}{2} + K_1 y_1(z) + K_5 y_2(z) \qquad (93)$$

$$y_1(z) = e^{\frac{z}{2}} z^{-k} W_{k,m}(z)$$

$$y_2(z) = e^{\frac{z}{2}} z^{-k} W_{-k,m}(-z)$$

We note that the generalized hypergeometric function is given by

$${}_pF_q(\alpha_1, \alpha_2, \ldots, \alpha_p; \rho_1, \rho_2, \ldots, \rho_q; z) = \qquad (94)$$

$$\sum_{n=0}^{\infty} \frac{\Gamma(\alpha_1+n)\,\Gamma(\alpha_2+n)\cdots\Gamma(\alpha_p+n)\;\Gamma(\rho_1)\,\Gamma(\rho_2)\cdots\Gamma(\rho_q)\, z^n}{\Gamma(\alpha_1)\;\Gamma(\alpha_2)\cdots\Gamma(\alpha_p)\;\Gamma(\rho_1+n)\,\Gamma(\rho_2+n)\cdots\Gamma(\rho_q+n)\, n!}$$

By means of this abbreviated notation we can easily summarize the more important properties of the Whittaker function.

1) The asymptotic expansion of $W_{k,m}(z)$ is

$$W_{k,m}(z) \sim e^{-\frac{z}{2}} z^{k}\, {}_2F_0\left(\tfrac{1}{2}-m-k, \tfrac{1}{2}+m-k; -z^{-1}\right) \qquad (95)$$

for large value of $|z|$ when $|\arg z| < \frac{3\pi}{2}$

2) When $|\arg z| < \frac{3\pi}{2}$ and 2m is not an integer

$$W_{k,m}(z) = \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} M_{k,m}(z) + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} M_{k,-m}(z) \qquad (96)$$

$$M_{k,\pm m}(z) = z^{\frac{1}{2}\pm m} e^{-\frac{z}{2}} {}_1F_1\left(\tfrac{1}{2} \pm m - k ; 1 \pm 2m ; z\right)$$

3) When $|\arg z| < \frac{3\pi}{2}$ and neither of the numbers $k \pm m + \frac{1}{2}$ is a positive integer or zero, $W_{k,m}(z)$ may be represented by a contour integral of the Mellin-Barnes type,

$$W_{k,m}(z) = \qquad (97)$$

$$\frac{e^{-\frac{z}{2}} z^{k}}{2\pi i} \int_{-\infty i}^{+\infty i} \frac{\Gamma(v)\,\Gamma(-v-k+m+\frac{1}{2})\,\Gamma(-v-k-m+\frac{1}{2})\, z^{v}\, dv}{\Gamma(-k+m+\frac{1}{2})\,\Gamma(-k-m+\frac{1}{2})}$$

4) Kummer's formula states that when 2m is not a negative integer

$$e^{-z} {}_1F_1\left(\tfrac{1}{2}+m-k ; 1+2m ; z\right) = {}_1F_1\left(\tfrac{1}{2}+m+k ; 1+2m ; -z\right) \qquad (98)$$

It follows readily from the asymptotic expansion (95) that

$$\lim_{x\to 0} x^{2} g_0^{(2)} \frac{dy_1}{dx} = 0$$

$$(99)$$

$$\lim_{x\to 0} x^{2} g_0^{(2)} \frac{dy_2}{dx} = \text{constant}$$

so that in view of the boundary condition at the origin (70), y_2 is not an admissible solution. The constants K_1 and K_2 are determined by the requirement (73) that ψ_2 and

$\frac{d\psi_2}{dx}$ be continuous at x_1. The derivative of $y_1(z)$ may be most conveniently calculated by means of relation (97),

$$\frac{dy_1(x)}{dx} = -\frac{t}{x} z \frac{dy_1(z)}{dz}$$

$$\frac{dy_1(z)}{dz} = \frac{1}{2\pi i}\int_{-\infty i}^{+\infty i} \frac{v\,\Gamma(v)\,\Gamma(-v-k-m+\frac{1}{2})\,\Gamma(-v-k+m+\frac{1}{2})\,z^{v-1}}{\Gamma(-k-m+\frac{1}{2})\,\Gamma(-k+m+\frac{1}{2})}\,dv \tag{100}$$

$$= \frac{1}{z^2\,2\pi i}\int_{-\infty i}^{\infty i} \frac{\Gamma(v)\,\Gamma(-v-k+1-m+\frac{1}{2})\,\Gamma(-v-k+1+m+\frac{1}{2})\,z^{v}}{\Gamma(-k-m+\frac{1}{2})\,\Gamma(-k+m+\frac{1}{2})}\,dv$$

$$= \left\{ \left(k-\tfrac{1}{2}\right)^2 - m^2 \right\} e^{\frac{z}{2}} z^{-k-1}\, W_{k-1,m}(z)$$

Since $\left(k-\frac{1}{2}\right)^2 - m^2 = -\frac{6}{t^2}$, we finally obtain the result

$$\frac{dy_1(x)}{dx} = \frac{6}{tx} W_{k-1,m}(z)\, e^{+\frac{z}{2}} z^{-k} \tag{101}$$

With use of the preceding expression, the constants K_1 and K_2 are found to be

$$K_1 = -a_0^2 x_1^2 K_3 = -\frac{a_0^2 x_1^2 \frac{5}{2} z_1^{k} e^{-z_1}}{3\,W_{k,m}(z_1) + \frac{6}{t} W_{k-1,m}(z_1)} \tag{102}$$

$$K_2 = -a_0^2 x_1^5 K_4 = -a_0^2 x_1^5 \frac{\left\{ W_{k,m}(z_1) - \frac{3}{t} W_{k-1,m}(z_1) \right\}}{3\,W_{k,m}(z_1) + \frac{6}{t} W_{k-1,m}(z_1)} \tag{103}$$

Since in our numerical example $z_1 = 3.67 \times 10^{-2}$, $W_{k,m}(z_1)$ is easily computed by means of relation (96), only a few terms in the power series being required.

Substitution of ψ_2 given by equations (91) and (93) into equation (35) and use of the potential V(x), equation (76), leads to the following result for the coefficient of shear viscosity,

$$\eta = \frac{\zeta \pi N^2 a_0^5}{15 k T v^2} \Bigg[\frac{1}{2} \int_0^{x_1} x^5 g_0^{(2)}(x) \frac{d\,V(x)}{d\,x}\, dx + K_4 x_1^5 V(x_1) + \frac{K_3 \varepsilon x_1^{2+s} e^{z_1}}{t\, x_m^{3+s}} \left\{ \frac{n I_{n-3}}{x_m^{n-6}} - 6 I_3 \right\} \Bigg] + \frac{NmkT}{2v\zeta} ; \tag{104}$$

$$\int_0^{x_1} x^5 g_0^{(2)}(x) \frac{dV(x)}{dx}\, dx = - \frac{\varepsilon x_1^s e^{z_1}}{t\, x_m^{s+1}} \left[\frac{n \Gamma\left(\frac{s+n-5}{t}, z_1\right)}{x_m^{n-6}} - 6 \Gamma\left(\frac{s+1}{t}, z_1\right) \right]$$

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

$$I_\alpha(z) = \int_0^z y_1(z)\, e^{-z} z^{\frac{\alpha+s}{t} - 1}\, dz$$

The value of $I_\alpha(\infty)$ may be calculated with use of equation (97),

$$I_\alpha(\infty) = \int_0^\infty e^{\frac{z}{2}} z^{-k} W_{k,m}(z)\, e^{-z} z^{\frac{\alpha+s}{t}-1}\, dz$$

$$= \frac{1}{2\pi i} \int_{-\infty i}^{+\infty i} \frac{\Gamma(v)\,\Gamma(-v-k-m+\tfrac{1}{2})\,\Gamma(-v-k+m+\tfrac{1}{2})\,\Gamma(v+\tfrac{\alpha+s}{t})\, dv}{\Gamma(-k-m+\tfrac{1}{2})\,\Gamma(-k+m+\tfrac{1}{2})}$$

$$= \frac{\Gamma(\tfrac{\alpha+s}{t}-k-m+\tfrac{1}{2})\,\Gamma(\tfrac{\alpha+s}{t}-k+m+\tfrac{1}{2})}{\Gamma(\tfrac{\alpha+s}{t}+1-2k)} \qquad (105)$$

$t > n-2$

The last step follows from Barnes' Lemma (ref. 28, p. 289), which states that

$$\int_{-\infty i}^{+\infty i} \Gamma(\beta_1+v)\,\Gamma(\beta_2+v)\,\Gamma(\beta_3-v)\,\Gamma(\beta_4-v)\, dv = \qquad (106)$$

$$\frac{\Gamma(\beta_1+\beta_3)\,\Gamma(\beta_1+\beta_4)\,\Gamma(\beta_2+\beta_3)\,\Gamma(\beta_2+\beta_4)}{\Gamma(\beta_1+\beta_2+\beta_3+\beta_4)}$$

when the poles of $\Gamma(\beta_1+v)\,\Gamma(\beta_2+v)$ do not coincide with the poles of $\Gamma(\beta_3-v)\,\Gamma(\beta_4-v)$.

The correction term $I_\alpha(z_1)$ is readily evaluated from equation (96) and Kummer's formula, equation (98),

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

where

$$I_\alpha^{\beta}(z_1) = \frac{\Gamma(-2\beta)}{\Gamma(\frac{1}{2} - \beta - k)} \frac{z_1^{\frac{\alpha+s}{t} - k + \frac{1}{2} + \beta}}{\left(\frac{\alpha+s}{t} - k + \frac{1}{2} + \beta\right.} \times \tag{107}$$

$$\times {}_2F_2\left(\frac{1}{2} + \beta + k, \frac{\alpha+s}{t} - k + \frac{1}{2} + \beta; 1 + 2\beta, \frac{\alpha+s}{t} - k + \frac{3}{2} + \beta; -z_1\right)$$

only a few terms in the power series being required for the numerical computation.

VIII.

SOLUTION OF BULK VISCOSITY EQUATION

The differential equation (66) for the bulk viscosity perturbation $\psi_0(R)$ may be integrated directly. The solution satisfying the boundary condition at the origin, equation (72), is given by

$$\psi_0 = a_0^2 \int_{\infty}^{x} \frac{d\xi}{\xi^2 g_0^{(2)}} \int_0^{\xi} \frac{dg_0^{(2)}}{dv} v^3 dv + \psi_0(\infty) \qquad (108)$$

$$\psi_0 \sim \frac{c}{x} + \psi_0(\infty) \qquad \text{for x large}$$

In order to evaluate $\psi_0(\infty)$ we must utilize the fact that the coefficient of bulk viscosity only enters into non-steady state fluid flow. For the case of a periodic dilation of frequency ω, the equation of forced diffusion (62) reduces to the following differential equation for $\psi_0(R)$ when x is large and thus $g_0^{(2)} = 1$,

$$\frac{d}{dx}\left(x^2 \frac{d\psi_0}{dx}\right) - \kappa^2 x^2 \psi_0 = 0$$

$$\kappa^2 = \frac{i\omega \zeta a_0^2}{2kT} \qquad (109)$$

The substitution $\psi_0 = \dfrac{\chi}{x}$ reduces this equation to the form

$$\chi'' - \kappa^2 \chi = 0$$

Hence the asymptotic solution of ψ_0 is readily seen to be

$$\psi_0 \sim \frac{A(\omega)}{x} e^{-\left[\frac{a_0}{2}\sqrt{\frac{\omega\zeta}{kT}}\, x(1+i)\right]} + \frac{B(\omega)}{x} e^{+\left[\frac{a_0}{2}\sqrt{\frac{\omega\zeta}{kT}}\, x(1+i)\right]} \tag{110}$$

The boundary condition at infinity, equation (71), requires that $B(\omega) = 0$ and in the limiting case of zero frequency of dilation

$$\psi_0 \sim \lim_{\omega \to 0} \frac{A(\omega)}{x} e^{-\left\{\frac{a_0}{2}\sqrt{\frac{\omega\zeta}{kT}}\, x\,(1+i)\right\}} = \frac{c}{x} \tag{111}$$

By comparison of (111) and (108), ψ_0 vanishes at infinity so that the coefficient of bulk viscosity is given by

$$\phi = \frac{NmkT}{3v\zeta} + \\ + \frac{\pi\zeta a_0^5 N^2}{9kTv^2}\int_0^\infty x^3 \frac{dV}{dx}\, g_0^{(2)}\, dx \int_\infty^x \frac{d\xi}{\xi^2 g_0^{(2)}} \int_0^\xi V^3 \frac{dg_0^{(2)}}{dV}\, dV \tag{112}$$

While we have succeeded in deriving this expression without recourse to our analytical approximation to $g_0^{(2)}$, for the purpose of evaluating (112) numerically it is convenient to introduce this simplication. Upon partial integration of (108) with $\psi_0(\infty) = 0$,

$$\psi_0 = a_0^2 \int_\infty^x \left[\xi\, d\xi - \frac{3\, d\xi}{\xi^2 g_0^{(2)}(\xi)} \int_0^\xi x^2 g_0^{(2)}\, dx \right] \tag{113}$$

In the region where $g_0^{(2)} = 1$,

$$\psi_0(x) = \frac{3a_0^2}{x}\int_0^{x_1} x^2\left(g_0^{(2)}-1\right)dx \qquad x_1 < x \qquad (114)$$

Similarly for $x < x_1$,

$$\psi_0(x) = \psi_0(x_1) + \frac{a_0^2}{2}\left(x^2 - x_1^2\right) + 3a_0^2\int_x^{x_1}\frac{d\xi}{\xi^2 g_0^{(2)}(\xi)}\int_0^{\xi} x^2 g_0^{(2)}\,dx \qquad (115)$$

The last term, which gives rise to the principal computational difficulties, simplifies by means of the first peak approximation, equation (80),

$$H(x) = 3\int_x^{x_1}\frac{d\xi}{\xi^2 g_0^{(2)}}\int_0^{\xi} x^2 g_0^{(2)}\,dx = \frac{3x_m^2}{t^2}\int_{z_1}^{z} e^{\xi}\,\xi^{\frac{1-s}{t}-1}\,d\xi\int_{\xi}^{\infty} e^{-x}\,x^{\frac{s-3}{t}-1}\,dx \qquad (116)$$

With use of the relation$^{(28)}$

$$\Gamma(n,\xi) = \Gamma(n) - \frac{\xi^n e^{-\xi}}{n}\,{}_1F_1(1;n+1;\xi) \qquad (117)$$

we find that

$$H(x) = k(z) - k(z_1) \qquad (118)$$

$$k(z) = 3x_m^2\left[\frac{\Gamma\left(\frac{s-3}{t}\right)}{(1-s)\,t}\, z^{\frac{1-s}{t}}\,{}_1F_1\left(\frac{1-s}{t}; 1+\frac{1-s}{t}; z\right) + \right.$$

$$\left. + \frac{z^{-\frac{2}{t}}}{2(s-3)}\,{}_2F_2\left(1, -\frac{2}{t}; 1-\frac{2}{t}, 1+\frac{s-3}{t}; z\right)\right.$$

Substitution of (114), (115) and (118) into the general relation (112) for the coefficient of bulk viscosity results in the approximation,

$$\phi = \frac{NmkT}{3v\zeta} + \frac{\zeta\pi N^2 a_2^5}{9kTv}\Big\{3\Big[\int_0^{x_1} x^2\big(g_0^{(2)}-1\big)dx\Big]\Big[\int_{x_1}^{\infty} x^2\frac{dV}{dx}dx\Big] +$$

$$+\Big[\frac{3}{x_1}\int_0^{x_1} x^2\big(g_0^{(2)}-1\big)dx - \frac{x_1^2}{2} - K(z_1)\Big]\Big[\int_0^{x_1} x^3\frac{dv}{dx}g_0^{(2)}dx\Big] + \qquad (119)$$

$$+\frac{1}{2}\int_0^{x_1} x^5\frac{dV}{dx}g_0^{(2)}dx - \frac{3e^{z_1}z_1^{-\frac{s}{t}}}{t x_m}\Big[\frac{nJ_n}{x_m^{n-6}} - 6J_6\Big]\Big\}$$

where(29)

$$J_\alpha = \int_{z_1}^{\infty} e^{-z} z^{\frac{\alpha+s-3}{t}-1}\frac{K(z)}{3x_m^2}dz = J_\alpha(\infty) - J_\alpha(z_1)$$

$$J_\alpha(z_1) = \frac{\Gamma\left(\frac{s-3}{t}\right)}{t^2}\sum_{j=0}^{\infty}\frac{\gamma\left(\frac{\alpha-2}{t}+j;z_1\right)}{\left(j+\frac{1-s}{t}\right)j!} - \sum_{j=0}^{\infty}\frac{\gamma\left(\frac{s-5+\alpha}{t}+j;z_1\right)\Gamma\left(\frac{s-3}{t}\right)}{t^2\Gamma\left(j+1+\frac{s-3}{t}\right)\left(j-\frac{2}{t}\right)} \qquad (120)$$

$$J_\alpha(\infty) = \frac{\Gamma\left(\frac{s-3}{t}\right)}{t(1-s)}\,{}_2F_1\left(\frac{\alpha-2}{t},\frac{1-s}{t};1+\frac{1-s}{t};1\right) +$$

$$+\frac{\Gamma\left(\frac{s-5+\alpha}{t}\right)}{2(s-3)}\,{}_3F_2\left(\frac{s-5+\alpha}{t},-\frac{2}{t},1;1-\frac{2}{t},1+\frac{s-3}{t};1\right)$$

In the foregoing expressions, $K(z_1)$ and $J_\alpha(z_1)$ are evaluated by means of a few terms in the power series. The first term of $J_\alpha(\infty)$ is greatly simplified with use of the Gauss summation formula(28) for the ${}_2F_1$ function of argument unity and the relation $\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin \pi z}$, i.e.

$$ {}_2F_1(a, b; c; 1) = \frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)} \qquad (121)$$

$$c > a+b$$

with the result

$$\frac{\Gamma\left(\frac{s-3}{t}\right)\Gamma\left(\frac{\alpha-2}{t}\right)}{t(1-s)}\, {}_2F_1\left(\frac{\alpha-2}{t}, \frac{1-s}{t}; 1+\frac{1-s}{t}; 1\right) = \frac{\Gamma\left(\frac{s-3}{t}\right)\Gamma\left(\frac{1-s}{t}\right)\pi}{t^2\,\Gamma\left(1+\frac{3-\alpha-s}{t}\right)\sin\pi\left(\frac{\alpha-2}{t}\right)} \qquad (122)$$

Since the ${}_3F_2$ function of argument unity cannot be summed in an analogous manner, the direct summation procedure must be carried out.

IX.

FRICTION CONSTANT AND SUMMARY OF RESULTS

By means of our molecular theory of viscous flow, we have verified the extended Newtonian law and we have succeeded in expressing the coefficients of viscosity in terms of the potential of intermolecular force, V(R), the equilibrium radial distribution function, $g_0^{(2)}$, and the friction constant, ζ. The friction constant appears as a factor in the formulas for the coefficients of viscosity and it remains to express this function in a form readily amenable to calculation in terms of molecular variables. With the assumption that ζ is momentum independent, the diffusion friction constant was derived by Kirkwood, equation (27),

$$\zeta = \langle \zeta_i \rangle = \frac{\beta}{3} \int_0^{\tau_i} \langle \vec{F}_i(t) \cdot \vec{F}_i(t+s) \rangle^0 \, ds \tag{123}$$

$$\langle \vec{F}_i(t) \cdot \vec{F}_i(t+s) \rangle^0 = \iint \vec{F}_i(t) \cdot \vec{F}_i(t+s) \, f_0^{(N)} \, d\vec{P} \, d\vec{Q}$$

In view of the extreme generality of this formula for the dissipation, it has not yet been possible to evaluate ζ rigorously. We are thus forced to turn to a plausible approximation which is expected to yield results of the correct order of magnitude. If the structure of the dynamical system is such that ζ exists, then we may define a correlation time θ such that

$$\langle \zeta_i \rangle = \frac{\theta}{3kT} \langle F_i^2(t) \rangle^\circ \qquad (124)$$

For a potential of total intermolecular force, $V^{(N)}$, of the form (5),

$$\langle F_i^2(t) \rangle^\circ = \frac{\int \nabla_i V^{(N)} \cdot \nabla_i V^{(N)} e^{-\beta V^{(N)}} d\vec{Q}}{\int e^{-\beta V^{(N)}} d\vec{Q}}$$

$$= -\frac{1}{\beta} \frac{\int \nabla_i V^{(N)} \cdot \nabla_i e^{-\beta V^{(N)}} d\vec{Q}}{\int e^{-\beta V^{(N)}} d\vec{Q}} \qquad (125)$$

$$= \frac{1}{\beta} \int \nabla_i^2 V^{(N)} \varphi_0^{(N)} d\vec{Q}$$

where we have applied Green's theorem in the third step. Upon performing the indicated integration,

$$\langle F_i^2(t) \rangle^\circ = \frac{4\pi \rho_0^{(1)}}{\beta} \int_0^\infty R^2 \nabla^2 V(R)\, g_0^{(2)}(R)\, dR \qquad (126)$$

The estimate that the correlation time θ is equal to the relaxation time $\frac{m}{\zeta}$ enables one to express the friction constant by the simple formula,

$$\zeta^2 = \frac{4\pi\rho}{3} \int_0^\infty R^2 \left(\frac{d^2V}{dR^2} + \frac{2}{R}\frac{dV}{dR} \right) g_0^{(2)}(R)\, dR \qquad (127)$$

where ρ is the mass density. This result is to be considered a preliminary estimate.

It will be convenient at this point to summarize the results of our theory as applied to liquid argon at 89°K and 1.2 atm. With use of parameters ε, n and a_0, given by Rushbrooke, and parameters a_1, a_m, t and s, given in Table II, we obtain for the coefficient of shear viscosity, η, and the coefficient of bulk viscosity, ϕ,

$$\eta = 2.63 \times 10^{6} \zeta + \frac{8.53 \times 10^{-15}}{\zeta} \text{ poise} \tag{128}$$

$$\phi = 1.95 \times 10^{7} \zeta + \frac{4.68 \times 10^{-15}}{\zeta} \text{ poise} \tag{129}$$

The preliminary estimate for the friction constant ζ leads to the value,

$$\zeta = 4.84 \times 10^{-10} \text{ gm. sec.}^{-1} \tag{130}$$

Reference to these results shows that the momentum contribution to the coefficients of viscosity is negligible in comparison with the contribution arising from intermolecular forces.

By defining an effective radius by the relationship $\zeta = 6\pi\eta R_{eff}$, suggested by the Stokes estimate for the friction constant, the evaluation of R_{eff} may be carried out by equation (128). The result, $R_{eff} = 2.0\text{Å}$ at 89°K, is strikingly similar to the actual radius, 1.9 A°, taken to be one-half the distance between nearest neighbors.

A final test of our theory of shear viscosity is available with the estimate for γ, equation (130). The theoretical value for liquid argon at 89°K, $\eta = 1.27\times10^{-3}$ poise, is in moderately good agreement with the extrapolated experimental determination(30), 2.39×10^{-3} poise.

The coefficient of bulk viscosity calculated similarly leads to the value $\phi = 9.37\times10^{-3}$ poise. By dividing equation (129) by equation (128), the friction constant cancels and we find for the ratio $\phi/\eta = 7.4$. From recent ultrasonic absorption measurements of Galt(31), an upper bound to the ratio ϕ/η is estimated to be 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. Results of these calculations are summarized in Table III.

TABLE III

Viscosity Coefficients of Liquid Argon at 89°K and 1.2 atm.

	$\frac{\phi}{\gamma}$ cm.$^{-1}$	$\frac{\eta}{\gamma}$ cm.$^{-1}$	$\frac{\phi}{\eta}$	ϕ poise	η poise
Calc.	1.95×10^{7}	2.63×10^{6}	7.4	9.38×10^{-3}	1.27×10^{-3}
Exp.			$<\frac{1}{3}$		2.39×10^{-3}

In view of the approximate nature of our $g_0^{(2)}$ and Υ, these values are to be considered as preliminary estimates. At such a later time when a more satisfactory $g_0^{(2)}$ will be available, it is expected that better agreement will be obtained by deriving the first peak parameters from the theoretical $g_0^{(2)}$ curves. The coefficient of bulk viscosity is particularly sensitive to the choice of $g_0^{(2)}$ so that the ratio ϕ/η may be smaller. This is apparent by reference to equation (114), which indicates that the coefficient of bulk viscosity is strongly affected by the fluctuation integral (see appendix)

$$4\pi \rho_0^{(1)} \int_0^\infty R^2 (g_0^{(2)}-1)\, dR = -1 + kT\kappa \rho_0^{(1)} \qquad (131)$$

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

The parameters selected by the procedure given in Part VI do not satisfy this additional restriction and thus the unsatisfactory value for the coefficient of bulk viscosity is not unexpected. However, the fluctuation integral does not enter into the theory of the coefficient of shear viscosity.

A qualitative investigation of the effect of the fluctuation integral on the results of the theory has been carried out. A starting point was provided by transforming the differential equation for the perturbation ψ_2, subject to the appropriate boundary conditions, into a Fredholm integral equation of the second kind. It was possible to solve this integral equation by representing $g_0^{(2)}$ by the three parameter approximation

$$g_0^{(2)} = \begin{cases} 0 ; & 0 \le R < b_0 \\ h ; & b_0 \le R \le b_1 \qquad\qquad h > 1 \\ 1 ; & b_1 < R \end{cases} \tag{132}$$

The details of this calculation will not be presented, since it was demonstrated that the constants b_0, b_1 and h could not be determined numerically from equations (85), (86) and (131). Physically this means that the step approximation to $g_0^{(2)}$, equation (132), is inconsistent with a potential of intermolecular force of the Lennard-Jones type.

We thus conclude that better numerical agreement will only be possible on the basis of a reliable radial distribution function. However, the results already obtained indicate the success of the molecular theory of viscous flow formulated in the preceding sections.

APPENDIX

We will conclude this presentation by investigating the important normalization condition imposed on the non-equilibrium pair distribution function. The approach which has been adopted is the generalization of a method due to Yvon(32) and is based on fluctuation theory.

Consider a fluid composed of N identical molecules contained in a volume v. The configuration probability distribution function of the ensemble at time t will again be denoted by $\varphi^{(N)}(\vec{Q};t)$. We note that by definition $\int^{v} \varphi^{(N)}(\vec{Q};t)\,d\vec{Q} = 1$. Next we focus our attention on an arbitrary volume ν, wholly contained within v, and we define the quantity P_j by the relation

$$\begin{aligned} P_j &= 1 \qquad \text{if molecule } j \text{ is in the volume } \nu \\ P_j &= 0 \qquad \text{if molecule } j \text{ is not in the volume } \nu \end{aligned} \tag{133}$$

Thus the number of molecules contained within ν at time t, $N(\nu;t)$ may be expressed in the form,

$$N(\nu;t) = \sum_{j=1}^{N} P_j \tag{134}$$

The average number of molecules within ν, $\overset{\nu}{\langle} N(\nu;t)\rangle$, is calculated from the statistical average of equation (134). In view of the identical nature of the molecules,

$$\begin{aligned} {}^{\nu}\langle N(\nu;t)\rangle &= \int^{V}\!\!\cdots\int^{V} N(\nu;t)\,\varphi^{(N)}(\vec{Q};t)\,d\vec{Q} \\ &= \int^{\nu} d\vec{R}_1\; N \int^{V}\!\!\cdots\int^{V} \varphi^{(N)}(\vec{Q};t)\,d\vec{q}_{N-1} \\ &= \int^{\nu} d\vec{R}_1\,\rho^{(1)}(\vec{R}_1;t) \end{aligned} \qquad (135)$$

The deviation from the mean ΔN, of molecules contained in the volume ν at time t is defined by

$$\Delta N = N(\nu;t) - {}^{\nu}\langle N(\nu;t)\rangle \qquad (136)$$

Since ${}^{\nu}\langle \Delta N\rangle \equiv 0$, we consider the mean square deviation, ${}^{\nu}\langle (\Delta N)^2\rangle$,

$${}^{\nu}\langle (\Delta N)^2\rangle = {}^{\nu}\langle N^2(\nu;t)\rangle - \left[{}^{\nu}\langle N(\nu;t)\rangle\right]^2 \qquad (137)$$

The first term of equation (137) is readily evaluated,

$$\begin{aligned} {}^{\nu}\langle N^2(\nu;t)\rangle &= \int^{V} \sum_{i,j=1}^{N} P_i P_j\, \varphi^{(N)}(\vec{Q};t)\,d\vec{Q} \\ &= \int^{V} \sum_{j=1}^{N} P_j^2\, \varphi^{(N)}(\vec{Q};t)\,dQ \; + \\ &\quad + \int^{V} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} P_i P_j\, \varphi^{(N)}(\vec{Q};t)\,d\vec{Q} \\ &= {}^{\nu}\langle N(\nu;t)\rangle + \int^{\nu}\!\!\int^{\nu} \rho^{(2)}(\vec{R}_1,\vec{R}_2;t)\,d\vec{R}_1\,d\vec{R}_2 \end{aligned} \qquad (138)$$

Substitution of equation (138) into equation (137) leads to the final result of our analysis,

$$\begin{aligned} {}^{\nu}\langle(\Delta N)^2\rangle &= {}^{\nu}\langle N\rangle + \int^{\nu}\!\!\int^{\nu}\left\{\rho^{(2)}(\vec{R}_1,\vec{R}_2;t) - \rho^{(1)}(\vec{R}_1;t)\,\rho^{(1)}(\vec{R}_2;t)\right\} d\vec{R}_1\,d\vec{R}_2 \\ &\doteq {}^{\nu}\langle N\rangle + \int^{\nu_1}\!\!\int^{\nu_{12}} \rho^{(1)}(\vec{R}_1;t)\,\rho^{(1)}(\vec{R}_1+\vec{R}_{12};t)\left\{g^{(2)}(\vec{R}_1,\vec{R}_{12};t)-1\right\} d\vec{R}_1\,d\vec{R}_{12} \end{aligned} \tag{139}$$

An important expression is derived when the system is in thermodynamic equilibrium in the absence of external forces. When $\nu << V$, the Einstein-Smoluchowski theory of density fluctuations, based on the Gibbs canonical ensemble, leads to the result

$${}^{\nu}\langle(\Delta N)^2\rangle = \frac{kT\kappa}{\nu}\,{}^{\nu}\langle N\rangle^2 \tag{140}$$

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

where κ is the compressibility.

The limiting process $\nu \to \infty$, keeping the ratio of ν to v constant, and use of equation (140), permits the calculation of the normalization integral

$$4\pi\rho_0^{(1)}\int_0^{\infty} R^2\left(g_0^{(2)}(R)-1\right) dR = kT\kappa\rho_0^{(1)} - 1 \tag{141}$$

Our analysis thus provides us with a restriction to be imposed on $g_0^{(2)}$, and furthermore yields an expression for the fluctuations in the non-equilibrium case. For viscous fluid flow it has been previously shown that for a linear theory,

$$g^{(2)} = g_0^{(2)}\left[1 + \left\{ \frac{\vec{R}_{12}\cdot\underline{\dot{\varepsilon}}(\vec{R}_1)\cdot\vec{R}_{12}}{R_{12}^2} - \frac{1}{3}\nabla\cdot\vec{u}(\vec{R}_1)\right\} f_\eta(R_{12}) + \nabla\cdot\vec{u}(\vec{R}_1) f_\phi(R_{12})\right]$$

Since the shear viscosity perturbation involves surface harmonics of order two and the bulk viscosity perturbation involves surface harmonics of order zero, our general equation (139) leads to the interesting conclusion that the fluctuation is only affected by dilational viscous flow. This result is intimately related to the previous observation that the value of the coefficient of bulk viscosity is affected by the value of the normalization integral of the equilibrium radial distribution function.

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Propositions submitted by Frank P. Buff

Ph. D. Oral Examination, May 5, 1949, 1:30 P.M., Crellin Conference Room

Committee: Professors Kirkwood (Chairman), Epstein, Lucas,
Pauling, Yost

* * * * * *

1) The thermodynamics of multi-component azeotropes, pseudo-azeotropes, etc. may be formulated rigorously by Gibbsian methods. Among several interesting results it is found that for binary azeotropes the composition-pressure diagram shows a maximum when $\Delta\bar{H}_2 \Delta\bar{v}_1 = \Delta\bar{H}_1 \Delta\bar{v}_2$, where $\Delta\bar{H}$ is the change in partial molal enthalpy and $\Delta\bar{v}$ is the change in partial molal volume.

2) The statistical mechanical theory of surface tension of Kirkwood and Buff may be used to calculate the surface tension of binary solutions. With the usual assumptions for "regular" solutions $\sqrt{\gamma} = \varphi_1\sqrt{\gamma_1} + \varphi_2\sqrt{\gamma_2}$ where γ is the surface tension of the mixture, γ_1 and γ_2 are the surface tensions of the pure components and φ_1 and φ_2 are the volume fractions.

J. G. Kirkwood and F. P. Buff, J. Chem. Phys., 17, 338 (1949)

3) a) Mott's theory relating the change of resistance of a metal upon melting to the entropy of fusion cannot be directly extended to allotropic transitions. It is suggested that this is partly due to the resultant change in the number of "free"conduction electrons and hence the electron ratio may be calculated from experimental data.

b) A survey of the physical properties of the liquid alkali metals suggests that they may not be unambiguously classified as monatomic fluids.

N.F. Mott, Proc. Roy. Soc., A, 146, 465 (1934)

4) The temperature derivative of the equilibrium radial distribution function is of interest in investigations of the liquid state. This derivative may be calculated by statistical mechanics, and for monatomic liquids is determined by the potential of intermolecular force and number densities of sets of 2, 3 and 4 molecules.

5) a) It is suggested that a new titration curve with possibly sharper inflection points is obtained by subtracting corresponding pH readings of two titration curves obtained at different ionic strengths.

5) b) The instability of some solutions containing cerium reagents should be investigated.

6) A statistical mechanical theory of solutions may be based on:

a) The Kirkwood expression for the chemical potential and his integro-differential equation for number densities, both being in terms of a coupling parameter.

b) A direct transformation of the Gibbs phase integral.

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

7) a) By means of a Tolman-Stewart type arrangement with simultaneous cooling it should be possible to induce currents in a superconductor.

b) The method devised by Yost and Johnston for the study of rapid gas phase reactions may be used to follow clock reactions.

H. S. Johnston and D. M. Yost, J. Chem. Phys., 17, 386 (1949)

8) a) The approximate treatment of shear viscosity given by Born and Green has attracted considerable attention. The starting point of their unjustified peak integration may be actually shown equivalent to $\eta \propto \frac{\gamma}{\sqrt{T}}$, where η is the viscosity coefficient and γ is the surface tension. However, the modified expression, $\frac{\eta T}{\gamma}$ = constant, appears to reproduce experimental data satisfactorily.

b) Kirkwood's new theory of the friction constant leads to a certain ordinary differential equation. Approximate solutions of this equation in terms of confluent hypergeometric functions may be obtained with use of the first peak approximation (this thesis) to the radial distribution function.

M. Born and H. S. Green, Proc. Roy. Soc., A, 190, 455 (1947)

9) It is suggested that a table of potential functions permitting solution of the Schroedinger equation in terms of known functions may facilitate some quantum mechanical problems. By means of this method, a smooth symmetrical potential well problem may be treated with some success.

10) I propose that the final oral examination be restricted to the defense of the thesis and a small number of propositions.