

Unified Approximation for the Velocity Autocorrelation Function and the Structure Function of a Simple Liquid

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A theory of one-particle and two-particle motions in monatomic classical liquids, which employs the two-particle position-dependent Green's function in a fundamental way is developed. An equation of motion for the autocorrelation function is derived by assuming that a Brownian particle diffuses in a mean-time-dependent field. The motion of the atoms which generate the time-dependent field is described by the Green's function. In addition, the Green's function is directly related to the Van Hove scattering function in a simple way. The velocity autocorrelation function and neutron scattering cross sections are computed for liquid argon by assuming a relaxation approximation for the two-particle Green's function. Comparisons are made with recent experimental results.

I. INTRODUCTION

A description of the macroscopic consequences of the coupled motions of molecules in a simple liquid requires solution, either exact or approximate, of the N -body problem. Despite advances in our understanding of the N -body problem, it is not now possible to provide a completely satisfactory quantitative description of time dependent phenomena in simple liquids. The descriptions which exist are either exact and sterile, because evaluation in a form which may be compared with experiment is impossible, or approximate and therefore subject to controversy concerning the fundamental physical and mathematical assumptions made. In view of this situation, we believe it valuable to seek new representations from which may be derived qualitative constructs useful in the description of the properties of liquids. In this spirit, this paper is devoted to the presentation of a new approximation for the velocity autocorrelation function and the dynamic structure factor of a simple liquid. Our approximation is related to the concept of relaxation time in a fashion to be made precise later in this paper.

The formal theory of statistical mechanics¹ provides a relationship for the time and space evolution of the N -molecule distribution function, namely, the Liouville equation. We shall not be concerned with the exact solution of the Liouville equation, such as that presented by Prigogine and co-workers and others,² because the use of infinite-order perturbation theory does not lead to formulas useful for the description of liquids. Moreover, there is evidence that representation of the transport coefficients as a power series in the density is not fully satisfactory.³

Approximate solutions of the Liouville equation can, of course, be generated many different ways. First, the Liouville equation may be contracted to provide an evolution equation for the reduced distribution function for n molecules, $f^{(n)}$. One approach to the solution of the contracted hierarchy equation is to approximate $f^{(n+1)}$ in terms of $f^{(n)}$, thereby yielding an integral equation in $f^{(n)}$ which may be solved. For liquids in equilibrium, we thus derive the Yvon-Born-Green equation by employing the Kirkwood superposition approximation

in which the three-body distribution is approximated in terms of the several two-body distribution functions.⁴ The corresponding three-body integral equation, which represents the next higher approximation, cannot be solved using presently available computers.⁵ For liquids not in equilibrium, attempts to use approaches involving a time-dependent superposition approximation have not yet led to analytically tractable results.⁶

Alternatively, in 1946 Kirkwood demonstrated how the hierarchy equations can be simplified to yield a description of a particle undergoing Brownian motion.⁷ This work has been of considerable importance, and we shall find some of Kirkwood's ideas useful in our approximate theory.

Finally, relaxation methods have also been used to provide representations of particle motion.⁸⁻¹¹ In these analyses the detailed dynamical forces which act on a subsystem of particles are not specified. Instead it is assumed that the forces which are present tend to drive the system towards its equilibrium configuration, and the interaction term of the lowest hierarchy equation, or the flux equation arising from it, is replaced by a simpler form. The relaxation approximation we employ in this paper is quite similar to those recently proposed by Gray¹⁰ and by Singwi and Sjölander.¹¹ Here, however, by making a relaxation approximation for the two-particle Green's function, we are able to eliminate some of the conceptual and computational difficulties encountered by previous workers. The n -particle Green's function

$$K^{(n)}(\Gamma_n | \Gamma_n'; t)$$

gives the probability that a subsystem of n particles will undergo a transition from the state with phase Γ_n' to that with phase Γ_n in the time interval t .¹² Thus, we may find the n -particle distribution for any time if we know the distribution function at a previous time as well as the corresponding Green's function of the system. The function $P(\vec{R}', t | \vec{R}, t)$, which we introduce in Sec. II, is related to the Green's function $K^{(2)}$, being the integral of $K^{(2)}$ with respect to the momenta of both particles for both times and with respect to the position of one particle at the initial time.

Many studies of liquids have emphasized the cal-

culuation of the zero-frequency transport coefficients, which characterize the matter, momentum, and energy flows in liquids under gradients of density, flow velocity and temperature, respectively. The transport coefficients, however, do not contain a great deal of information concerning time-dependent processes in liquids. As a result, widely divergent approaches to the theory of liquids have led to comparably successful calculations of the transport coefficients.¹³ However, with the advent of high speed computers^{14,15} and the development of neutron scattering techniques,^{16,17} it has become possible to determine experimental distribution and correlation functions which contain a wealth of information concerning time-dependent processes in liquids. These new sources of information can be used to test the theoretical approaches in greater detail and to provide guidelines for the improvement of the conceptual structure of the theoretical analyses. In Sec. II of this paper, we introduce a formalism which we utilize to calculate the velocity autocorrelation function of a particle in a liquid (Sec. III) and the two-particle dynamic structure factor of a liquid (Sec. IV). The experimental and theoretical functions are then compared and the results discussed.

II. THE FORMALISM

We begin our analysis with the introduction of the function $P(\vec{R}', t | \vec{R}, t)$, which is defined to be the ensemble averaged conditional probability density that a particle is at the point \vec{R}' at time t , (\vec{R}, t) , given that a different particle which was at $(0, 0)$ has moved to (\vec{R}, t) .¹⁸ In order that $P(\vec{R}', t | \vec{R}, t)$ be properly normalized, we require that

$$\int d\vec{R}' P(\vec{R}', t | \vec{R}, t) = N - 1, \quad (1)$$

where N is the total number of particles in the system. In addition there is a boundary condition on P which defines the behavior as $t \rightarrow 0$. From the definition of $P(\vec{R}', t | \vec{R}, t)$, it is seen that

$$\lim_{t \rightarrow 0} P(\vec{R}', t | \vec{R}, t) = [\rho g(\vec{R}' - \vec{R})]_{t=0} = \rho g(\vec{R}') \quad (2)$$

where $\rho g(\vec{R}')$ is the ensemble-averaged probability density that a particle is at \vec{R}' if a different particle is simultaneously at the origin. The behavior of $P(\vec{R}', t | \vec{R}, t)$ as $t \rightarrow \infty$ is a bit more complicated. If we assert that we know nothing more about the motion of a particle than its positions at time zero and time t , then for very long times, when the particle has "forgotten" its position at time zero, it must be true that

$$\lim_{t \rightarrow \infty} P(\vec{R}', t | \vec{R}, t) = \rho g(\vec{R}' - \vec{R}). \quad (3)$$

In general, even for t large, $P(\vec{R}', t | \vec{R}, t)$ will be a complicated functional of the path of the particle in which the positions of the particle for t large will be more heavily weighted than the positions for t near $t = 0$.

In order to discuss the single particle motion, we introduce a mean force $\vec{F}(\vec{R}, t)$ which is defined to be the ensemble-averaged force acting on a particle which was $(0, 0)$ and has moved to (\vec{R}, t) .

If we assume that the interactions in a liquid are pairwise decomposable and that there are no external fields present, we find

$$\vec{F}(\vec{R}, t) = - \int d\vec{R}' \nabla V(\vec{R}' - \vec{R}) P(\vec{R}', t | \vec{R}, t), \quad (4)$$

where $V(\vec{R}' - \vec{R})$ is the two-body potential energy. In Sec. III, we shall assume that the average motion of a particle in a liquid may be found by solving the classical equation of motion for a particle experiencing the systematic force defined by (4), as well as a frictional force arising from random fluctuations in the force field of the diffusing particle.

The two-body correlations which arise from molecular interactions are most conveniently treated by introducing two additional functions, which were first used by Van Hove.¹⁹ Given that a particle is at $(0, 0)$ the ensemble-averaged probability density that the same particle may be found at (\vec{R}, t) is called $G_S(\vec{R}, t)$, and the ensemble-averaged probability density that a different particle may be found at (\vec{R}', t) is called $G_d(\vec{R}', t)$. From the definitions of these functions, we immediately obtain the relation

$$G_d(\vec{R}', t) = \int d\vec{R} G_S(\vec{R}, t) P(\vec{R}', t | \vec{R}, t). \quad (5)$$

In the work that follows, we generate approximate forms for $P(\vec{R}', t | \vec{R}, t)$ and use them to solve (4) and (5). To avoid the problems associated with direct solution of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy, we propose the following simple relaxation approximation for $P(\vec{R}', t | \vec{R}, t)$. If we know that there is a particle at the origin, the ensemble-averaged probability density of finding a particle at the same time at \vec{R}' is given by $\rho g(\vec{R}')$, provided there are no other constraints on the system. Let the particle at the origin diffuse to a point (\vec{R}, t) . If there is instantaneous relaxation in the liquid then the structure of the liquid about the diffusing particle will maintain its equilibrium configuration throughout the motion, and we find that (3) remains valid for all times. However, the forces in a liquid are not sufficiently strong to require instantaneous relaxation around the diffusing particle. The forces do, however, "drive" the liquid towards the equilibrium configuration. Therefore, without discussing the exact nature of the propagation and destruction of correlations in the liquid, it is suggestive to use the approximate representation

$$\frac{d}{dt} P(\vec{R}', t | \vec{R}, t) = \alpha [\rho g(\vec{R}' - \vec{R}) - P(\vec{R}', t | \vec{R}, t)] \quad (6)$$

which is the fundamental equation of this paper.

Equation (6) may be immediately integrated to yield²⁰

$$P(\vec{R}', t | \vec{R}, t) = \rho g(\vec{R}') e^{-\alpha t} + \alpha \int_0^t dt' e^{-\alpha(t-t')} \rho g[\vec{R}' - \vec{R}(t')], \quad (7)$$

where the integral is to be taken over all physical paths between times 0 and t . Equation (7) satisfies the normalization condition (1) and the boundary condition (2) as t approaches zero. For $t > 0$, $P(\vec{R}', t | \vec{R}, t)$ becomes a complicated functional of

the motion of the particle. In order to evaluate the integral in (7), we will find it necessary to find a representation of $g[\vec{R}(t) - \vec{R}(t')]$. Using a Taylor series expansion for $g[\vec{R}' - \vec{R}(t')]$ about $\vec{R}'(t)$, we find

$$g[\vec{R}'(t) - \vec{R}(t')] = g[\vec{R}'(t) - \vec{R}(t)] + [\vec{R}'(t) - \vec{R}(t')] \cdot \nabla_{\vec{R}' - \vec{R}(t)} g[\vec{R}'(t) - \vec{R}(t)] + \dots, \quad (8)$$

and substituting (8) in (7), it is found that

$$P(\vec{R}', t | \vec{R}, t) = \rho g(\vec{R}') e^{-\alpha t} + (1 - e^{-\alpha t}) \rho g[\vec{R}'(t) - \vec{R}(t)] + \alpha \int_0^t dt' e^{-\alpha(t-t')} \rho[\vec{R}'(t) - \vec{R}(t')] \cdot \nabla_{\vec{R}' - \vec{R}(t')} g[\vec{R}'(t) - \vec{R}(t')] + \dots \quad (9)$$

The reader should note the similarities between this approximation and the one recently proposed by Glass and Rice¹⁸

$$P(\vec{R}', t | \vec{R}, t) = f(t) \rho g(\vec{R}') + [1 - f(t)] \rho g(\vec{R}' - \vec{R}), \quad (10)$$

$$\lim_{t \rightarrow 0} f(t) = 1, \quad \lim_{t \rightarrow \infty} f(t) = 0,$$

where $f(t)$ is a function of time, one possible form of which is specified in Ref. 18. Equation (10) is useful in the description of the two-particle distribution function in liquids. We will defer justification for the implied truncation of the series in Eqs. (8) and (9) until a later section.

III. THE VELOCITY AUTOCORRELATION FUNCTION

A. The Modified Langevin Equation

In this section, we calculate the velocity autocorrelation function of a molecule in a simple liquid using the representation introduced in Sec. II. In order to carry out this calculation, it is necessary to specify the equation of motion of a particle. In the Kirkwood theory of transport in fluids, a friction coefficient is introduced to describe the influence of the fluctuating force field of $N-1$ molecules on the motion of some one selected molecule. Now the concept of a frictional force is introduced in the classical theory of Brownian motion,²¹ in which it is assumed that

$$\langle \vec{A}(0) \cdot \vec{A}(t) \rangle = 0, \quad (11a)$$

$$\langle \vec{v}(0) \cdot \vec{A}(t) \rangle = 0, \quad (11b)$$

where $\vec{A}(t)$ is a fluctuating force, and $\vec{v}(t)$ is the velocity of the Brownian particle under observation. The solution of the classical Langevin equation describing the motion of a massive Brownian particle with friction coefficient β ,

$$m d\vec{v}/dt = -m\beta\vec{v} + \vec{A}(t), \quad (12)$$

subject to (11a) and (11b), will be a good description for all times $t \gg \Delta t$, where Δt is the interval for which (11a) and (11b) are not satisfied.²¹ For a massive Brownian particle, $\Delta t \sim 10^{-21}$ sec is so

small relative to other characteristic times in the system ($\sim 10^{13} - 10^{-12}$ sec) that the use of (12) with (11a) and (11b) is accurate in the time domain of interest. On the other hand, when the Brownian particle is of the same mass as the surrounding particles no such clean-cut separation of time scales is possible within the dynamical framework defined by (12).

Attempts to modify (12) have proceeded in two separate directions. In one method, Mori²² and Kubo²³ postulate the existence of a force which satisfies (11b) but does not necessarily satisfy (11a). That is, the force acting on a particle is not correlated with the initial velocity of the particle, but the force is not necessarily rapidly fluctuating. When these assumptions are made, it is found that

$$\frac{d\vec{v}(t)}{dt} = -\int_0^t \Gamma(t-t') \vec{v}(t') + \frac{\vec{A}(t)}{m}, \quad (13)$$

$$\text{where } \Gamma(t) = (1/mk_B T) \langle \vec{A}(0) \cdot \vec{A}(t) \rangle. \quad (14)$$

Although (13) and (14) represent an elegant modification of (12), it should be noted that a large class of processes may be represented by (13), and that the force $\vec{A}(t)$ does not necessarily correspond to a simple physical process.²⁴

The other method of extending the Langevin equation separates the force field in which a particle in a liquid moves into two parts. One part is assumed to be rapidly fluctuating and satisfies the conditions of (11). The other part, however, does not fluctuate appreciably, and therefore need not fulfill the conditions cited in (11). It is simple to identify a force field in a liquid arising from the smoothed distribution determined by the local geometry, to which (11) does not apply. The existence of this systematic force has been implicit in many of the qualitative discussions of atomic motions in liquids. In particular, it is now generally accepted that, in the motion of an atom in a liquid, "backscattering" of the atom from the shell of nearest neighbors occurs, resulting in a negative region of the velocity autocorrelation function.^{15,25} The force responsible for the "backscattering" (in which large momentum transfers between atoms occur) is certainly correlated with the initial velocity of the particle, but in principle, it is also possible to define mathematically a random force which gives the same effect, as Mori and Kubo have done.²⁶

The preceding considerations lead us to consider describing the motion of a molecule in a liquid as if it were a Brownian particle in a nonrandom force field. Problems of this sort are not new; Ornstein and Uhlenbeck²⁷ considered the Brownian motion of a harmonically bound particle, and this simple model was recently used by Rahman, Singwi, and Sjölander to describe a liquid.²⁸ However, in the work of Rahman, Singwi, and Sjölander, care was not taken to make the velocity autocorrelation function obey the boundary conditions at zero time. Another closely related study is the computation, by Nossal, of the velocity autocorrelation function of a Brownian particle confined to a square well.²⁹ Finally, Sears and others have developed a model in which the "center of oscillation" of a particle in a liquid is assumed to undergo Brownian mo-

tion.^{30,31} We consider the concept that the particle is constantly bound to a center of oscillation to be somewhat artificial.

A model more closely related to that being proposed herein is present in the work of Rice, Allnatt, and coworkers.⁵ In the Rice-Allnatt model, two forces are identified: a rapidly fluctuating force arising from the motions of molecules moving only in the soft long-range part of the intermolecular potential, and the forces provided by the short-range strongly repulsive core collisions, which are responsible for the "backscattering" of the molecules. In the Rice-Allnatt theory the relaxation time due to the Brownian motion of the particles is considered to be sufficiently short (it is calculated to be $\sim 0.34 \times 10^{-13}$ sec in liquid Ar) that the successive strong repulsive collisions are dynamically uncorrelated with each other. This theory allows one to compute with good accuracy the zero-frequency transport coefficients of the liquid.

In this paper, we also assume that the fluctuations arising from motion of the molecules in the long-range soft part of the intermolecular field are sufficiently rapid to result in an irregular Brownian motion. However, we shall represent the effects of the strongly repulsive core collisions by a time-dependent average force field. The equation of motion thus obtained is identical to the one proposed by Chandrasekhar,²¹ and corresponds to the Langevin equation to which has been added a second systematic force term:

$$m d\vec{v}/dt = -m\beta\vec{v}(t) + \vec{F}(\vec{R}, t) + \vec{A}(t). \quad (15)$$

Eq. (15) is the equation of motion assumed to be valid for our model. We shall also assume that the systematic part of the intermolecular force is defined by the ensemble-averaged, two-particle, conditional distribution function $P(\vec{R}', t|\vec{R}, t)$, Eq. (4), and that the stochastic force results from rapid fluctuations in the soft part of the intermolecular potential field.

B. Calculation of the Velocity Autocorrelation Function

We now examine the calculation of the velocity autocorrelation function defined by

$$\psi(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle / \langle v^2 \rangle, \quad (16)$$

subject to the conditions³²⁻³⁴

$$\lim_{t \rightarrow 0} \psi(t) = 1, \quad (17a)$$

$$\lim_{t \rightarrow 0} \frac{d\psi}{dt} = 0, \quad (17b)$$

$$\lim_{t \rightarrow 0} \frac{d^2\psi}{dt^2} = -\frac{1}{3m} \langle \nabla^2 V \rangle \equiv -\omega_0^2, \quad (17c)$$

$$D = (k_B T / m) \int_0^\infty dt \psi(t). \quad (17d)$$

We obtain two differential equations for $\psi(t)$ by multiplying (13) and (15) by $\vec{v}(0)$, taking the ensemble average, and using (11) and (16). The two equations which result are

$$d\psi/dt = - \int_0^t dt' \Gamma(t-t') \psi(t') \quad (18)$$

and

$$d\psi/dt = -\beta\psi + \langle \vec{v}(0) \cdot \vec{F}(\vec{R}, t) \rangle / m \langle v^2 \rangle. \quad (19)$$

Although (18) can be shown to be isomorphous with an exact transcription of the classical equations of motion, and is therefore valid for all time if $\Gamma(t-t')$ is correctly interpreted, (19) is in principle not valid for all time. For the friction coefficient is only a meaningful concept for times which are long compared to the period of the rapidly fluctuating forces. Therefore, as $t \rightarrow 0$, (19) cannot be valid. If the failure of Eq. (19) is restricted to a small time interval near $t=0$, it is possible to use that equation over the larger time interval provided the correct values of $\psi(0)$ and $(d^2\psi/dt^2)_{t=0}$ are imposed. Despite the fact that (19) cannot be valid as $t \rightarrow 0$, we now assume that by differentiating (19) with respect to time we obtain a second-degree equation for $\psi(t)$ which is valid for all times. This procedure, in effect, allows us to introduce two constants of integration so that both of the boundary conditions displayed in (17a) and (17b) may be satisfied. We emphasize that in this way we can insure proper limiting values of the autocorrelation function for $t=0$ even though, formally, (19) is not valid for extremely short times. The justification for our procedure can only come, *a posteriori*, from a comparison between prediction and observation.

We may now substitute the approximation for $P(\vec{R}', t|\vec{R}, t)$, which was developed in Sec. II, into (4) in order to find the mean force under which the particle moves. Taking only the first three terms of (9) leads to

$$P(\vec{R}', t|\vec{R}, t) = e^{-\alpha t} \rho g(\vec{R}') + (1 - e^{-\alpha t}) \rho g(\vec{R}' - \vec{R}). \quad (20)$$

Substituting (20) into (4) and using the fact that the mean force acting on a particle in an equilibrium ensemble is zero, we immediately find that

$$\vec{F}(\vec{R}, t) = e^{-\alpha t} \int d\vec{R}' \rho g(\vec{R}') \nabla V[\vec{R}'(t) - \vec{R}(t)]. \quad (21)$$

Note that the strong short-ranged repulsive intermolecular forces are not hard-core forces, hence ∇V is well defined. Because the forces considered are of short range, ∇V is nonzero only when $\vec{R}'(t) - \vec{R}(t)$ is small. Moreover $\vec{R}(t)$ is itself small relative to an intermolecular spacing for times of the order of magnitude of the diffusion time. Then, consistent with the expansion displayed in Eq. (8), the expansion of (21) for $\vec{R}(t)$ small yields

$$\vec{F}(\vec{R}, t) = -\vec{R}(t) e^{-\alpha t} \rho \langle \nabla^2 V(R) \rangle + O(R^2). \quad (22)$$

Equation (22) describes a spherically symmetric harmonic-force field which decays exponentially as time increases. An examination of mean potentials found using the cell model shows that, for liquid argon at temperatures and densities near to the normal melting point, a harmonic potential should be a good approximation to the real potential.³⁵ However, at elevated temperatures (where the diffusion coefficient and hence $\vec{R}(t)$ is larger), the mean potential tends to flatten near the origin, and it may then be necessary to compute explicitly terms of order R^2 or higher in (22). Then, although it

would still be possible to adjust the well parameters to yield agreement with experiment, the simple equation which is solved below would no longer be valid, and the present computation would have to be extended. It will be instructive to compare the results obtained using the derived time dependent mean force in (22) with the results found for a Brownian particle diffusing in a static harmonic well. The latter results are reviewed in the Appendix.

Substituting (22) in (19), we find

$$\frac{d\psi}{dt} = -\beta\psi + \omega_0^2 e^{-\alpha t} \int_0^t dt' \psi(t'), \quad (23)$$

where ω_0^2 is defined in (17). However, neither (17) nor the theoretical relation between β and the autocorrelation functioning of the fluctuating force can currently be evaluated numerically with greater accuracy than about $\pm 10\%$, and the algebraic manipulations are greatly simplified if we regard ω_0^2 as a parameter. Dropping the subscript on ω_0 and differentiating (23) with respect to time, we find

$$\frac{d^2\psi}{dt^2} + (\alpha + \beta)\frac{d\psi}{dt} + (\omega_0^2 e^{-\alpha t} + \alpha\beta)\psi = 0. \quad (24)$$

To solve (24), subject to (17), we substitute³⁶

$$u = (2\omega/\alpha)e^{-\frac{1}{2}\alpha t} \quad (25)$$

to find

$$\psi(t) = e^{-\frac{1}{2}(\alpha + \beta)t} v(u), \quad (26)$$

where $v(u)$ is a solution of Bessel's equation

$$u^2 v'' + uv' + v[u^2 - (\alpha - \beta)^2/\alpha^2] = 0. \quad (27)$$

We have been describing a simple model of the atomic dynamics for which *a priori* calculation of α is not possible. We know that α is a molecular relaxation time, but we know little more. It is therefore convenient to now assume that the two relaxation times α and β are equal, since (27) then simplifies and may readily be solved analytically. From a physical point of view, this is a reasonable assumption. The decay of the mean force results from the loss of correlation of the surrounding first coordination shell and is due to the diffusion of the atoms of this shell. Since all atoms are equivalent, the relaxation time for the motion of these atoms should be about the same as the relaxation time for the motion of the initial particle. Therefore, assuming

$$\alpha = \beta, \quad (28)$$

we immediately find for the solution of (22)

$$\psi(t) = e^{-\beta t} [c_1 J_0(u) + c_2 Y_0(u)], \quad (29)$$

where J_0 and Y_0 are zero-order Bessel functions of the first and second kinds, respectively, c_1 and c_2 are constants of integration, and

$$u = 2\gamma e^{-\frac{1}{2}\beta t}, \quad \gamma = \omega/\beta. \quad (30)$$

In the following, we make use of the recursion relations for any zero-order Bessel function $Z_0(u)$ ³⁷:

$$\begin{aligned} Z_0'(u) &= -Z_1(u), \\ Z_0''(u) &= Z_1(u)/u - Z_0(u). \end{aligned} \quad (31)$$

Differentiating (30), applying the boundary conditions (17), and utilizing (31), we find

$$c_1 = \frac{Y_0(2\gamma) - \gamma Y_1(2\gamma)}{\gamma [J_0(2\gamma)Y_1(2\gamma) - J_1(2\gamma)Y_0(2\gamma)]}, \quad (32)$$

$$c_2 = \frac{J_0(2\gamma) - \gamma J_1(2\gamma)}{\gamma [J_0(2\gamma)Y_1(2\gamma) - J_1(2\gamma)Y_0(2\gamma)]}.$$

By taking the second derivative of (31) at $t=0$, and substituting the values of c_1 and c_2 found in (32), we now obtain

$$\omega^2(1 + 1/\gamma^2) = \langle \nabla^2 V \rangle / 3m. \quad (33)$$

In order to apply the condition displayed in (17) we note that³⁸

$$\begin{aligned} \int_0^1 dx x J_0(ax) &= J_1(a)/a, \\ \int_0^1 dx x Y_0(ax) &= Y_1(a)/a + 2/\pi a^2. \end{aligned} \quad (34)$$

The integrals found when (29) is substituted in (17) can readily be cast in this form. When the integration is performed, we find

$$(\beta/\omega^2)(1 + c_2/\pi) = mD/k_B T. \quad (35)$$

Substituting the definition for β_0 and ω_0 in (A6) and (A7), we find

$$\omega = \omega_0 \gamma (1 + \gamma^2)^{-1/2}, \quad (36)$$

$$\beta = \omega_0 (1 + \gamma^2)^{-1/2},$$

where γ is determined by solving the equation

$$1 + c_2/\pi = (\beta_0/\omega_0) \gamma^2 (1 + \gamma^2)^{-1/2}. \quad (37)$$

We noted earlier that the evaluation of the equation defining ω_0 is subject to errors of $\pm 10\%$. Instead of attempting an evaluation of ω_0 , we accept the re-

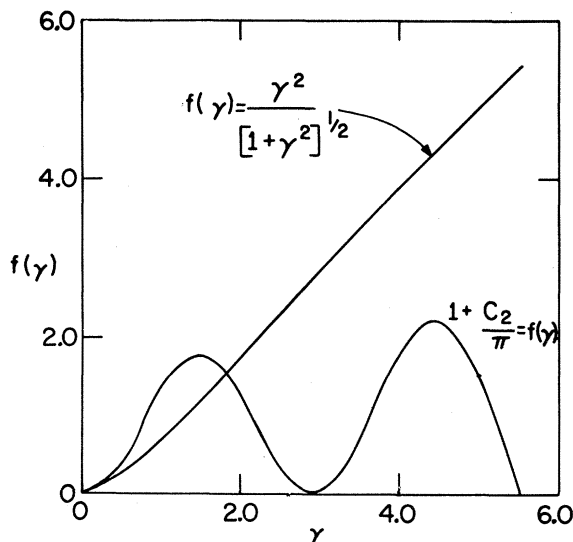


FIG. 1. Both sides of (43) are plotted as a function of γ for the case $\beta_0 = \omega_0$.

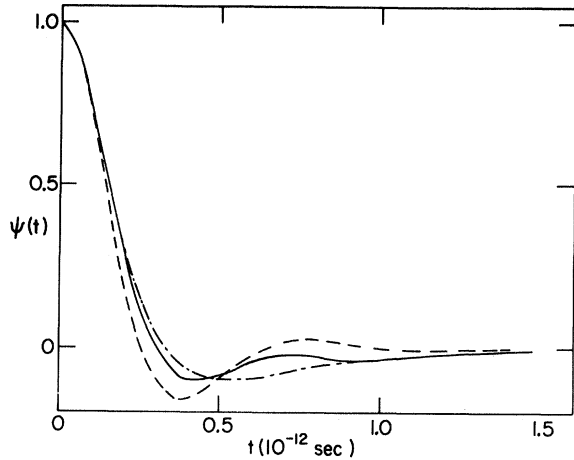


FIG. 2. The velocity autocorrelation function $\psi(t)$ as a function of time for argon at $T=85.5^\circ\text{K}$. The computer results, found by Nijboer and Rahman³³ (—) are compared with the results found using (A4) (-----) and the results found using (35) (- · - · -).

sult of the small-step diffusion approximation,^{39, 40} which seems to be reasonably accurate. Then, using

$$\beta_0 = \omega_0 = k_B T / mD, \quad (38)$$

we can solve (36) for γ . In Fig. 1 both sides of (37) are plotted as functions of γ . We note that there is one root, from which

$$\gamma = 1.795, \quad -c_1 = 1.864, \quad c_2 = 1.794. \quad (39)$$

We have now solved (24). The approximations displayed in (28) and (38) have eliminated two parameters so that the only remaining parameter is the diffusion coefficient, which is well known from experiment.

We may now compare the velocity autocorrelation function derived in this work with that derived from the simple harmonic model which is noted in the Appendix (A4). Displayed in Fig. 2 are the theoretical and experimental autocorrelation functions at $T=85^\circ\text{K}$, $D=1.88 \times 10^{-5} \text{ cm}^2/\text{sec}$ for liquid ar-

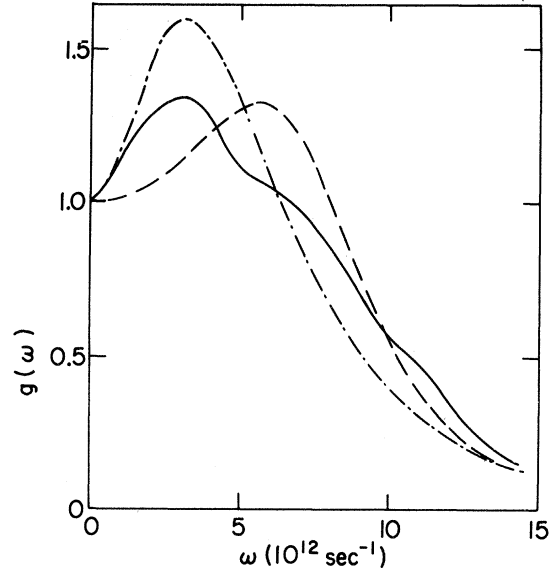


FIG. 3. The power spectrum $g(\omega)$ as a function of ω for argon at $T=94.4^\circ\text{K}$. The computer results, found by Rahman¹⁵ (—), are compared with the results found by substituting (A4) (-----), and (35) (- · - · -) in (46).

gon.³³ In Fig. 3, we plot the power spectrum defined by

$$g(\omega) = (k_B T / mD) \int_0^\infty dt \cos \omega t \psi(t) \quad (40)$$

for $T=94.4^\circ\text{K}$, $D=2.43 \times 10^{-5} \text{ cm}^2/\text{sec}$ for liquid argon.¹⁵ In the simple model of a Brownian particle in a static harmonic well, the oscillatory behavior of the autocorrelation function is over-emphasized, while, in the present formulation, using the approximations (28) and (38), the oscillatory motion seems to be somewhat underestimated. However, we consider the deviation from experimental results which we find to be small. By relaxing either (28) or (38), a better fit to the experimental data could have been achieved.

IV. THE DYNAMIC STRUCTURE FACTOR

In this section, we compute the dynamic structure factor for a simple liquid using the approximations described in Secs. II and III. Consider the scattering of neutrons by a simple liquid.¹⁶ Let $\hbar\kappa$ and $\hbar\omega$ be the momentum and energy loss of a scattered neutron and λ_i and λ the initial and final neutron wavelengths. Then

$$\omega = (2\pi^2 \hbar^2 / m_n) (1/\lambda_i^2 - 1/\lambda^2), \quad \kappa^2 = 4\pi^2 (\lambda_i^2 + \lambda^2 - 2\lambda_i \lambda \cos \theta) / \lambda_i^2 \lambda^2, \quad (41)$$

where m_n is the mass of the neutron and θ the angle between the directions of motion of the incoming and outgoing (scattered) neutron. Since we have used a classical representation of the liquid distribution function, it is necessary to correct the results for quantum effects in real systems. Several authors have discussed how this may be done.⁴¹⁻⁴³ For systems in which the first Born approximation is valid, the neutron scattering cross section is

$$\frac{d^2\sigma}{d\lambda d\Omega} = \frac{\pi \hbar \lambda_i}{m_n \lambda^4} \left[\exp\left(\frac{\hbar\omega}{2k_B T} - \frac{\hbar^2 \kappa^2}{8mk_B T}\right) \right] \left[\sigma^{\text{inc}} S^{\text{inc}}(\vec{\kappa}, \omega) + \sigma^{\text{coh}} S^{\text{coh}}(\vec{\kappa}, \omega) \right], \quad (42)$$

where σ^{inc} and σ^{coh} are the incoherent and coherent scattering cross sections, respectively, and the total scattering cross section is defined by

$$\sigma^{\text{tot}} = \sigma^{\text{inc}} + \sigma^{\text{coh}} \quad (43)$$

In (42) the dynamic structure functions $S^{\text{inc}}(\vec{k}, \omega)$ and $S^{\text{coh}}(\vec{k}, \omega)$ are related to the Van Hove distribution functions of (5) by

$$G(\vec{R}, t) = G_s(\vec{R}, t) + G_d(\vec{R}, t), \quad (44)$$

$$S^{\text{inc}}(\vec{k}, \omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \int d\vec{R} e^{-i\omega t} e^{i\vec{k} \cdot \vec{R}} G_s(\vec{R}, t), \quad (45)$$

$$S^{\text{coh}}(\vec{k}, \omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \int d\vec{R} e^{-i\omega t} e^{i\vec{k} \cdot \vec{R}} G_d(\vec{R}, t). \quad (46)$$

A. The Incoherent-Scattering Function

Before calculating the total neutron scattering cross section, we first must evaluate the cross section for incoherent scattering. For argon at 94.4°K, Rahman's computer experiment indicates that the non-Gaussian behavior of $G_s(\vec{R}, t)$ is rather small.¹⁵ Hence we assume that

$$G_s(\vec{R}, t) = [4\pi\rho(t)]^{-3/2} \exp[-R^2/4\rho(t)], \quad (47)$$

where $\rho(t)$ is, for classical liquids,

$$\rho(t) = \frac{3k_B T}{m} \int_0^t dt' (t-t') \psi(t'). \quad (48)$$

The velocity autocorrelation $\psi(t)$ has been discussed in Sec. III. It is important to note that the incoherent-scattering function is quite insensitive to the model which is used to calculate $\rho(t)$, because $\rho(t)$, defined in (48), reaches its asymptotic value after a rather short time ($\sim 10^{-13}$ sec). In Fig. 4 and 5 we compare, for two representative values of the momentum transfer, the computer simulated incoherent structure factor for argon at 85.5°K³³ with the theoretical incoherent-structure factor based on (29) and the simpler function (A4). Although the use of (29) does give a slightly better fit to the experimental data than does the use of (A4), the incoherent-scattering cross section is adequately represented by both approximations. In the following section, we use (A4) to calculate the coherent-scattering cross section.

B. The Coherent-Scattering Cross Section

It is instructive to consider some of the models which have been suggested for the computation of $G_d(\vec{R}', t)$. A more complete review may be found in Ref. 18 and a recent paper by Desai and Yip.⁴⁴ The earliest one of interest to us is the convolution approximation proposed by Vineyard in 1958.⁴⁵ Vineyard argued that the probability that a particle which was at a point $(\vec{R}, 0)$ would diffuse to (\vec{R}', t) is $G_s(\vec{R}' - \vec{R}, t)$. This leads to the approximation

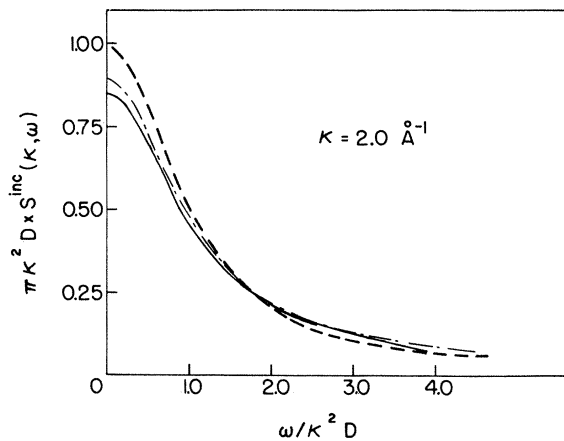


FIG. 4. $\pi\kappa^2 D S^{\text{inc}}(\kappa, \omega)$ as a function of $\omega/\kappa^2 D$ for $\kappa = 2.0 \text{ \AA}^{-1}$ computed for argon at $T = 85.5^\circ \text{K}$. The Gaussian results obtained by Nijboer and Rahman³³ are compared with the results found by substituting (A4) in (54) (-----) and the results found by substituting (35) in (54) (— · — · —).

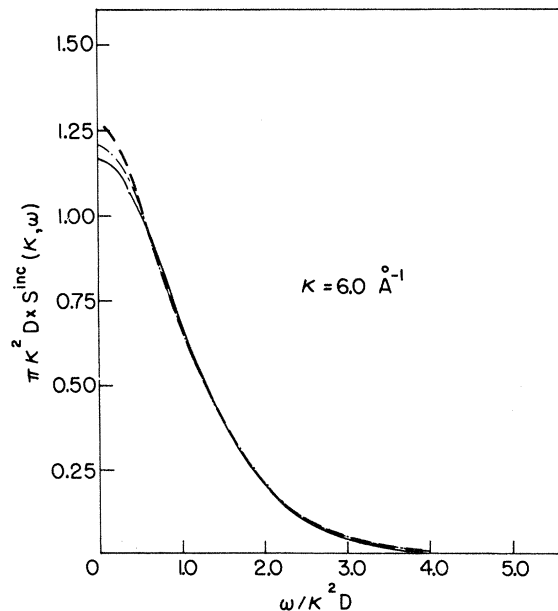


FIG. 5. Same as Fig. 4, for $\kappa = 6.0 \text{ \AA}^{-1}$.

$$G_d^c(\vec{R}', t) = \rho \int d\vec{R} G_s(\vec{R}' - \vec{R}, t) g(\vec{R}) = \rho \int d\vec{R} G_s(\vec{R}, t) g(\vec{R}' - \vec{R}). \quad (49)$$

$G_d^c(\vec{R}', t)$ is called the convolution approximation to $G_d(\vec{R}', t)$; the equivalence of both expressions on the right-hand side of (49) may be demonstrated by use of a change of variable. A comparison of (49) with (5) shows that the convolution approximation is equivalent to taking

$$P(\vec{R}', t | \vec{R}, t) = \rho g(\vec{R}' - \vec{R}) \quad (50)$$

for all times. In the discussion following (3) and preceding (6), we have noted that (50) can only be correct if we consider relaxation of the liquid about a moving molecule to be instantaneous. In fact, this is not the case. Therefore it is unrealistic to expect that the convolution approximation will give the correct sum rules, since the lower moments of $S(\vec{k}, \omega)$ are relevant to the behavior of the liquid only for short times.

In 1964, Rahman tested the convolution approximation using the results of computer simulated molecular dynamics experiments.¹⁵ He found that for liquid argon at 94.4°K the convolution approximation predicted a decay of $G_d(\vec{R}', t)$ which was too rapid. In order to correct this rapid decay, Rahman proposed that a delayed time be employed in place of the true time variable. In particular, he suggested that

$$G_d^R(\vec{R}', t) = G_d^c(\vec{R}', t_R), \quad (51)$$

$$\text{where } t_R = t - \tau [1 - e^{-t/\tau} - (t^2/\tau^2)e^{-t^2/\tau^2}]. \quad (52)$$

The particular form displayed in (52) was chosen to give the proper second-moment of $G_d(\vec{R}', t)$. By adjusting τ , Rahman found he could obtain good agreement with experiment for $\tau = 1.0 \times 10^{-12}$ sec.

More recently an alternative form has been suggested¹⁸ which successfully corrects the convolution approximation to give a less rapid temporal decay. The interpolation form displayed in (10) was deduced for $P(\vec{R}', t | \vec{R}, t)$ by requiring the correct limiting behavior for both long and short times. It is important to note that (10) is not strictly correct for long times although it does appear as the leading term of the expression in (9). Using (10), Glass and Rice find

$$G_d^{GR}(\vec{R}', t) = G_d^c(\vec{R}', t) + f(t)[g(\vec{R}') - G_d^c(\vec{R}', t)]. \quad (53)$$

Since $f(t)$ is a positive function for all times, (53) leads to an approximation for G_d which also decays less rapidly than does the convolution approximation. Glass and Rice attempted to use the sum rules to find $f(t)$. However, the present approximation is not valid for small \vec{k} (in the hydrodynamic range) and therefore fitting $f(t)$ by using the moment expansions valid for small \vec{k} may lead to spurious results.

It is clear that the dynamical model we have introduced is best suited for qualitative or semiquantitative descriptions of the behavior of a liquid. So as to emphasize the qualitative details rather than the numerical details, which are inevitably sensitive to parameter selection, in the present work we do not consider the power series expansion used in Sec. III, but rather evaluate approximately the integral in (7). If we define

$$\alpha \int_0^t dt' e^{-\alpha(t-t')} h(t') = (1 - e^{-\alpha t}) \langle h(t) \rangle, \quad (54)$$

Equation (7) immediately becomes

$$P(\vec{R}', t | \vec{R}, t) = e^{-\alpha t} \rho g(\vec{R}') + (1 - e^{-\alpha t}) \rho \langle g[\vec{R}'(t) - \vec{R}(t)] \rangle. \quad (55)$$

If we now approximate

$$\langle g[\vec{R}'(t) - \vec{R}(t)] \rangle = g[\vec{R}'(\bar{t}) - \vec{R}(\bar{t})], \quad (56)$$

$$\text{where } \bar{t} \equiv [t - (1/\alpha) + e^{-\alpha t}/\alpha](1 - e^{-\alpha t})^{-1}, \quad (57)$$

and substitute (55) in (5) we obtain

$$G_d(\vec{R}', t) = G_d^c(\vec{R}', \bar{t}) + e^{-\alpha t} [\rho g(\vec{R}') - G_d^c(\vec{R}', \bar{t})]. \quad (58)$$

It is important to note the similarities between this approximation and the two previously discussed approximations. The leading term here is analogous to the delayed time term in the Rahman approximation, and the second term is analogous to the second term in the results found by Glass and Rice. In addition, (58) contains only one parameter, which is the fundamental relaxation time introduced in (6).

In order to compute the cross sections using (42), we choose $\sigma^{\text{coh}}/\sigma^{\text{inc}} = 0.675$ found by Henshaw for argon at 84°K.⁴⁶ Then, once we have fixed a value for α , we can calculate the neutron scattering cross section. In the calculation reported in Sec. III, the value of α was found to be $4.61 \times 10^{12} \text{sec}^{-1}$ at $T = 85.5^\circ\text{K}$ and $3.93 \times 10^{12} \text{sec}^{-1}$ at $T = 94.4^\circ\text{K}$. As noted above, our intent is to understand the qualitative features of the scattering data. Because many approximations were made in Sec. III, no systematic effort was made to determine the best fit between theory and experiment. Therefore the values of α quoted should not be considered to be "best fits." An indication of the magnitude of α comes from Rahman's fit to the delayed time convolution approximation at 94.4°K.¹⁵ In order to make the function we use here give the same

asymptotic limit for long times, we would have to choose $\alpha = 1.0 \times 10^{12} \text{sec}^{-1}$. In Figure 6 we compare \bar{t} with t_{Ra} , (58) and (63), for $\alpha = 1.0 \times 10^{12} \text{sec}^{-1}$ and $\alpha = 3.93 \times 10^{12} \text{sec}^{-1}$. Since there are in our model two mechanisms which decrease the rate of decay of the two-body distribution function, we should expect that the data can be fit with our model using a smaller time delay than found by Rahman. We compare our theoretical cross sections with the neutron scattering results of Chen *et al.*⁴⁷ and the more recent results of Sköld and Larsson⁴⁸ in Figs. 7 and 8. The cross sections are plotted to give equal amplitude at $\lambda = 5.3 \text{\AA}$. There is rather good agreement with the latter set of results. Unfortunately, since these cross sections cover only a small region of space, a detailed analysis of the validity of the approximation we suggest herein is not now possible.

V. DISCUSSION

In this paper, we have presented a simple microscopic theory of molecular motion in classical monatomic liquids and shown how it may be used to compute correlation functions which are expected to be valid for the regions of (\vec{k}, ω) space which correspond roughly to those probed by neutron scattering experiments. In other theoretical descriptions of molecular motion in liquids, attempts have been made to introduce elementary "quasi-phonon" excitations in analogy with the behavior of solids.^{48, 49} However, it is not presently clear whether or not these formulations will prove to be adequate representations of the molecular motion in simple liquids. In this respect, it is important to note the following:

1. In his recent study of elementary excitations in a liquid, Zwanzig predicts lifetimes of "phonon-like" excitations in the limit $\kappa \rightarrow 0, \omega \rightarrow \infty$ of about 10^{-13}sec .

2. In Sec. III above, we show that the velocity autocorrelation function can be adequately calculated by assuming that the "period of oscillation" of a particle in the mean potential created by its neighbors is of the same order of magnitude as the lifetime against decay of the harmonic well.

The approach we use here does not in the present form provide an accurate description of the long-wavelength, low-frequency regions which are probed by light scattering experiments. These

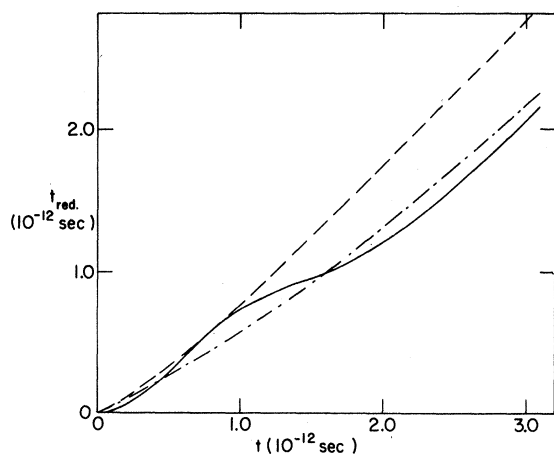


FIG. 6. A reduced time plotted as a function of time using various expressions in the text. We compare t_R , Eq. (52), (—) with t , Eq. (57), for $\alpha = 3.93 \times 10^{12} \text{sec}^{-1}$ (-----) and for $\alpha = 1.0 \times 10^{12} \text{sec}^{-1}$ (— · — · —).

regions of physical space can be accurately described by considering the fluid to be a continuum and by solving the linearized hydrodynamic equations.⁵⁰ However, it should be possible, and may not be difficult, to include the long-distance and long-time correlations corresponding to excitations with a (frequency-dependent) velocity of sound in the two-particle Green's function, $P(\vec{R}', t | \vec{R}, t)$. We have not yet accomplished this generalization. In addition to the hydrodynamic and neutron scattering limits, it should be remembered that there are large regions of physical space for which practically no theoretical or experimental results exist. In order to successfully treat the behavior of a liquid in these intermediate regions, it will be

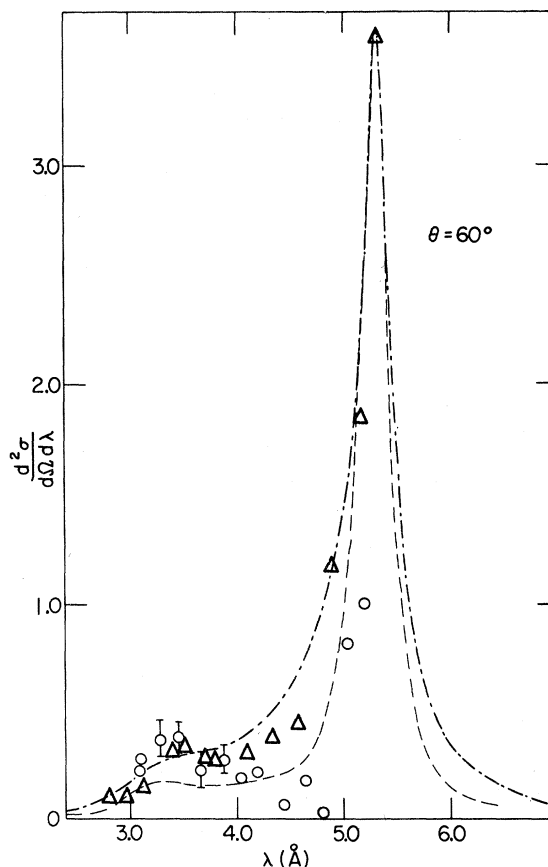


FIG. 7. Comparison of the neutron-scattering experimental results of Chen *et al.* (circles),⁴⁷ and Sköld and Larsson (triangles)⁴⁸ for $\theta = 60^\circ$, with the present approximation for $\alpha = 4.60 \times 10^{12} \text{sec}^{-1}$ (-----), and $\alpha = 1.0 \times 10^{12} \text{sec}^{-1}$ (— · — · —).

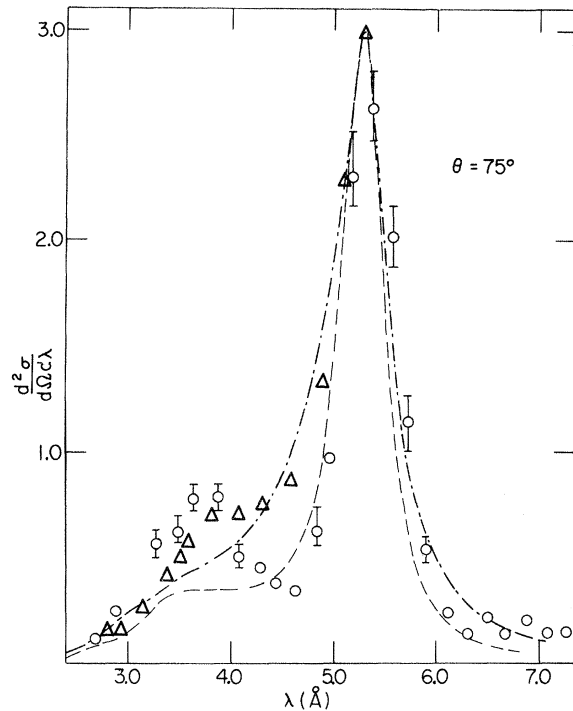


FIG. 8. Same as Fig. 7 for $\theta = 75^\circ$.

necessary to develop theoretical models of liquids which properly reproduce both the hydrodynamic and neutron scattering results.

Several additional extensions of this work seem feasible. From a formal point of view, it would be interesting to study the conditions which must be imposed to derive (15) from the BBGKY hierarchy. Equation (15) seems reasonable, but a formal derivation is lacking. It would also be interesting to investigate the ansatz proposed empirically, using computer simulation studies. By computing a mean force using the formulas in the text, it should be possible to see if the results could be fitted using a dynamical friction coefficient β . It is possible that the long-range, rapidly fluctuating, soft forces do not have a period of fluctuation sufficiently short so that they can be adequately described using a dynamical friction coefficient.

*USPHS Predoctoral Fellow, 1965–1967.

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⁴J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

⁵S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience Publishers, Inc., New York, 1965), Sec. 2.6.

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If this were the case one could introduce a retarded friction coefficient, in similar fashion to that proposed by Kubo, along with the mean force.

VI. ACKNOWLEDGMENTS

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APPENDIX

In analogy with the theory of solids, a simple model which may be considered for liquids is that of a Brownian particle diffusing in a harmonic well.^{27, 28} Substituting in (19) the representations

$$\vec{F}(\vec{R}, t) = -m\omega_0^2 \vec{R}(t), \quad (\text{A1})$$

$$\vec{R}(t) = \int_0^t dt' \vec{v}(t'), \quad (\text{A2})$$

where ω_0 is the characteristic frequency of the harmonic well, and differentiating, we obtain

$$\frac{d^2\psi}{dt^2} + \beta_0 \frac{d\psi}{dt} + \omega_0^2 \psi = 0. \quad (\text{A3})$$

Using the boundary conditions displayed in (17), this equation may be immediately solved to give

$$\psi(t) = e^{-\frac{1}{2}\beta_0 t} [\cos \xi t + (\beta_0/2\xi) \sin \xi t], \quad (\text{A4})$$

$$\text{where } \xi^2 = \omega_0^2 - \beta_0^2/4, \quad (\text{A5})$$

$$\omega_0^2 = \langle \nabla^2 V \rangle / 3m, \quad (\text{A6})$$

$$\text{and } \beta_0 = (mD/k_B T) \omega_0^2 \quad (\text{A7})$$

This result has also been obtained by assuming that the retarded friction coefficient in (18) is a simple exponential.^{34, 44} Substituting

$$\Gamma(t) = \omega_0^2 e^{-\beta_0 t} \quad (\text{A8})$$

in (22) and differentiating, we immediately obtain (A3).

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