around the respective rectangles for each of the two integrands will vanish so that (C2) may be written as

$$\chi(\omega)=-2C\sinh\tfrac{1}{2}\beta\hbar\omega\int_0^{\infty+i0}d\tau$$
$$\times e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}+C\bigg\{e^{-\beta\hbar\omega/2}\int_{0+i\beta\hbar/2}^{0}d\tau$$
$$\times e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}-e^{\beta\hbar\omega/2}\int_{0-i\beta\hbar/2}^{0}d\tau$$
$$\times e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}\bigg\}.\quad\text{(C3)}$$

The above terms can now be combined into the form which is Eq. (42),

$$\chi(\omega)=-2C\sinh\tfrac{1}{2}\beta\hbar\omega\int_0^{\infty}dt$$
$$\times e^{-i\omega t}\left[\frac{\beta u}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+t^2\right]^{-5/2}$$
$$-2C\int_0^{\beta\hbar/2}dy\,\cosh\omega(y-\tfrac{1}{2}\beta\hbar)$$
$$\times\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2-y^2\right]^{-5/2}.\quad\text{(C4)}$$

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New Approximation for the Calculation of Neutron Scattering from a Simple Liquid

LEON GLASS* AND STUART A. RICE
Department of Chemistry and James Franck Institute, University of Chicago, Chicago, Illinois

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A conceptually simple and easily applied approximation is made for the Van Hove distribution function $G(\mathbf{R},t)$ of a classical liquid. This approximation gives a less rapid temporal decay of $G(\mathbf{R},t)$ than is found in the Vineyard convolution approximation. In addition, by requiring that the sum rules be satisfied, we find that for t smaller than about 0.5×10^{-13} sec the "correlations" in a liquid may be said to be increasing. Comparisons are made with recent neutron scattering experiments. There is fair agreement between the theoretical and experimental results.

I. INTRODUCTION

IN 1954, in a study of neutron-diffraction phenomena, Van Hove introduced the time-dependent generalization of the equilibrium radial distribution function.[1] This function, denoted $G(\mathbf{R},t)$, represents the ensemble averaged time evolution of the spatial distribution of pairs of molecules in a liquid. $G(\mathbf{R},t)$, and its space and time transform $S(\boldsymbol{\kappa},\omega)$, contain a wealth of information concerning the properties of a liquid. For example, by use of the first Born approximation $S(\boldsymbol{\kappa},\omega)$ may be shown to be proportional to the probability of creating an excitation of momentum $\hbar\boldsymbol{\kappa}$ and energy $\hbar\omega$ in a scattering experiment.[1,2] As expected, then, $S(\boldsymbol{\kappa},\omega)$ appears in the theoretical expressions for the scattering of light[3,4] and neutrons[1,5] by a liquid.

There have been two approaches to the computation of $S(\boldsymbol{\kappa},\omega)$. In one, the hydrodynamic equations have been solved to find the time-dependent distribution functions. As might be expected, such analyses lead to quite good agreement between theory and observation in the hydrodynamic regime,[6] and even to agreement in the case of the long-time behavior probed by neutron-scattering experiments.[7,8] However, since a hydrodynamic theory avoids study of the microscopic dynamics of the liquid and uses only the coarse-grained hydrodynamic equations of motion, such an analysis is not capable of predicting the behavior of the liquid for short times.

In the other approach, attempts have been made to determine $G(\mathbf{R},t)$ by examining the microscopic behavior of the system.[9–15] Because of the complicated

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[*] U. S. Public Health Service Predoctoral Fellow.

[1] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[2] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), Chap. 19.

[3] L. I. Komarov and I. Z. Fisher, Zh. Eskperim i Teor. Fiz. **43**, 1927 (1962) [English transl.: Soviet Phys.—JETP **16**, 1358 (1963)].

[4] R. Pecora, J. Chem. Phys. **40**, 1604 (1964).

[5] A. Sjölander, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., London, 1965). This article is an excellent theoretical review of neutron scattering by liquids.

[6] R. D. Mountain, Rev. Mod. Phys. **38**, 205 (1966).

[7] R. K. Osborn and A. Z. Akcasu (unpublished).

[8] J. H. Ferziger and D. L. Feinstein, Phys. Rev. **158**, 97 (1967).

[9] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

[10] P. A. Egelstaff, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 25.

[11] P. A. Egelstaff, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 65.

[12] A. Rahman, Phys. Rev. **136**, 405 (1964).

[13] K. S. Singwi, Phys. Rev. **136**, 969 (1964); Physica **31**, 1257 (1965).

[14] R. J. Nossal, Phys. Rev. **143**, 74 (1966).

[15] R. C. Desai and M. Nelkin, Phys. Rev. Letters **16**, 839 (1966).

coupling that exists between the motions of particles in the liquid, it is difficult to carry through this analysis despite the simple physical meaning attached to the function $G(\mathbf{R},t)$. Shortly after the appearance of Van Hove's pioneering paper, Vineyard[9] proposed an approximation designed to factor the many-body problem and to give $G(\mathbf{R},t)$ as a function of a single-particle time-dependent distribution function and the equilibrium radial distribution function. As we will show, the Vineyard convolution approximation is only accurate for long times. Indeed, this approximation fails to satisfy the sum rules for the lower moments of $S(\boldsymbol{\kappa},\omega)$, which depend only on the limiting behavior of $S(\boldsymbol{\kappa},\omega)$ as $t\rightarrow 0$.[5] In addition, because the convolution approximation is a poor representation of the behavior of $S(\boldsymbol{\kappa},\omega)$ for short times, propagation of coherent excitations is impossible. Thus, the convolution approximation fails to predict the Brillouin-Mandelstam components of the light scattered from density fluctuations in a liquid,[16,17] or the coherent peaks observed in neutron scattering from simple liquids.[18]

Recent attempts to improve the convolution approximation have met with some success. Egelstaff has proposed an expression designed to satisfy the sum rules.[10,11] Rahman, observing that the convolution approximation leads to a decay of initial correlations which is too rapid, has proposed a time-delayed form of the convolution approximation which is in better agreement with the results of his computer experiments.[12] Desai and Nelkin have used this latter approximation to study neutron scattering from argon.[15] Singwi and Nossal have attempted to include the many-body dynamics by adding terms neglected in the convolution approximation.[13,14] Singwi finds good agreement with experiment.

In this paper we adopt a different approach to the computation of $S(\boldsymbol{\kappa},\omega)$. In Sec. II we present elementary considerations which show that the Vineyard convolution approximation fails to accurately represent the behavior of the liquid for short times. We propose an interpolation formula which represents the motion of a particle properly for both long and short times. The sum rules for $S(\boldsymbol{\kappa},\omega)$ are presented in Sec. III. These are then used in Sec. IV to establish an approximate form for the interpolation function. In Sec. V we compute the incoherent scattering function by employing a velocity autocorrelation function recently introduced by Berne, Boon, and Rice.[19] We use these results to compute in Sec. VI the neutron-scattering cross sections for argon at 85°K, and compare our results to recent experimental work.[18,20] We find the predicted scattering cross sections to be in reasonable (but by no means exact) agreement with experimental data.

II. A NEW APPROXIMATION

Given that there is a particle at the origin of the coordinate system at time zero, the probability density for finding the same particle at the point $\mathbf{R}$ at time t, $(\mathbf{R},t)$, is $G_s(\mathbf{R},t)$. The probability density that a different particle is at $(\mathbf{R}',t)$ given the same initial conditions is $G_d(\mathbf{R}',t)$. Finally, the conditional probability that a different particle is at $(\mathbf{R}',t)$ if the first, which had been at $\mathbf{R}=\mathbf{0}$ at $t=0$, is at $(\mathbf{R},t)$ is $P(\mathbf{R}',t|\mathbf{R},t)$. In order that $P(\mathbf{R}',t|\mathbf{R},t)$ be properly normalized we must have

$$\int d^3R'\, P(\mathbf{R}',t|\mathbf{R},t)=N-1. \tag{1}$$

It is also necessary that the boundary conditions

$$\lim_{t\to 0} P(\mathbf{R}',t|\mathbf{R},t)=g(\mathbf{R}'), \tag{2a}$$

$$\lim_{t\to \infty} P(\mathbf{R}',t|\mathbf{R},t)=g(\mathbf{R}'-\mathbf{R}) \tag{2b}$$

[where $g(\mathbf{R})$ is the equilibrium pair correlation function] be satisfied. The connection between $P(\mathbf{R}',t|\mathbf{R},t)$ and the functions $G_s(\mathbf{R}',t)$ and $G_d(\mathbf{R},t)$ is established by the definition

$$\int d^3R\, P(\mathbf{R}',t|\mathbf{R},t)G_s(\mathbf{R},t)=G_d(\mathbf{R}',t). \tag{3}$$

$P(\mathbf{R}',t|\mathbf{R},t)$ is not known for a fluid. We may, however, approximate it in terms of known functions making sure that Eqs. (1) and (2) are satisfied. It is then possible to use Eq. (3) to generate an approximate $G_d(\mathbf{R}',t)$. The Vineyard convolution approximation[9] is equivalent to setting

$$P(\mathbf{R}',t|\mathbf{R},t)=g(\mathbf{R}'-\mathbf{R}). \tag{4}$$

This yields the equations

$$\int d^3R\, g(\mathbf{R}'-\mathbf{R})G_s(\mathbf{R},t)=\int d^3R\, g(\mathbf{R})G_s(\mathbf{R}'-\mathbf{R},\, t) =G_d{}^C(\mathbf{R}',t), \tag{5}$$

where $G_d{}^C(\mathbf{R}',t)$ is the convolution approximation to $G_d(\mathbf{R}',t)$, and the equivalence of both expressions on the left-hand side of (5) may be demonstrated by use of a change of variable. Vineyard presented the second expression and pointed out that the behavior of the system for short times is not properly represented.

If we examine the behavior of $P(\mathbf{R}',t|\mathbf{R},t)$ as a function of time, we can clearly see where the problem lies. In the short-time limit the dominant term of $P(\mathbf{R}',t|\mathbf{R},t)$ should be simply $g(\mathbf{R}')$, not $g(\mathbf{R}'-\mathbf{R})$ as in the convolution approximation. In the long-time limit, the convolution approximation is valid. Clearly, we should

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[16] P. G. DeGennes, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p.239.

[17] K. S. Singwi and A. Sjölander, Phys. Letters **9**, 120 (1964).

[18] S. H. Chen, O. J. Elder, P. A. Egelstaff, B. C. G. Haywood, and F. J. Webb, Phys. Letters **19**, 269 (1965).

[19] B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. **45**, 1086 (1966).

[20] B. A. Dasannacharya and K. R. Rao, Phys. Rev. **137**, A417 (1965).

choose a form for $P(\mathbf{R}',t|\mathbf{R},t)$ which has the proper behavior for both long and short times. Here we choose

$$P(\mathbf{R}',t|\mathbf{R},t)=f(t)g(\mathbf{R}')+[1-f(t)]g(\mathbf{R}'-\mathbf{R}), \quad (6)$$

where $f(t)$ is a function of time. This form for $P(\mathbf{R}',t|\mathbf{R},t)$ guarantees that the normalization condition of Eq. (1) will be satisfied. If in addition we require that

$$\lim_{t\to 0} f(t)=1,$$

$$\lim_{t\to\infty} f(t)=0, \quad (7)$$

we ensure that the boundary conditions of Eq. (2) are obeyed.

Equation (6) represents the new approximation introduced in this paper. In Sec. IV we will discuss $f(t)$ in some detail. It is pertinent, however, to comment briefly on the structure of $P(\mathbf{R}',t|\mathbf{R},t)$ as represented by Eq. (6). First, we must realize that Eq. (6) is an interpolation formula. The behavior for intermediate times is not explicitly defined by Eqs. (6) and (7), and we must hope that a judicious choice of $f(t)$ will approximate the true function for this time regime. In addition, for a hard-sphere fluid, $P(\mathbf{R}',t|\mathbf{R},t)$ should be zero whenever $|\mathbf{R}'-\mathbf{R}|$ is smaller than the hard-core diameter σ. Of course, in the long-time limit and in the short-time limit the volume exclusion which requires that $P(\mathbf{R}',t|\mathbf{R},t)=0$ for $|\mathbf{R}'-\mathbf{R}|<\sigma$ is entirely contained in $g(\mathbf{R}'-\mathbf{R})$ and $g(\mathbf{R}')$, respectively. It is only in the intermediate time domain, when the particle originally at the origin has moved some distance, but not enough to make (2b) valid, that Eq. (6) is in error. A fully valid form of Eq. (6) is obtained if the right-hand side is multiplied by the Heaviside function $\Theta(|\mathbf{R}'-\mathbf{R}|-\sigma)$. Use of this form introduces complications in the analysis, so we shall not in fact multiply (6) by Θ. A dimensional analysis of the integrals involved suggests that the error we make is tolerably small because the calculation of $G_d(\mathbf{R}',t)$ involves an integration of $P(\mathbf{R}',t|\mathbf{R},t)$ over all $\mathbf{R}$. In this integration the volume for which $|\mathbf{R}'-\mathbf{R}|$ is greater than the hard-core diameter is most important, and hence discrepancies which exist in the intermediate time domain when $|\mathbf{R}'-\mathbf{R}|$ is smaller than the hard-core diameter will introduce only minor error.

By substituting Eq. (6) in Eq. (3), we obtain

$$G_d(\mathbf{R}',t)=f(t)g(\mathbf{R}')+[1-f(t)] \times\int_0^\infty d^3R\, g(\mathbf{R}'-\mathbf{R})G_s(\mathbf{R},t). \quad (8a)$$

This may be rewritten, using Eq. (5), in the form

$$G_d(\mathbf{R}',t)=f(t)g(\mathbf{R}')+[1-f(t)]G_d{}^c(\mathbf{R}',t). \quad (8b)$$

We will return to this equation after we have established the sum rules which are to be used in determining $f(t)$.

III. SUM RULES

There are a number of conditions which it is necessary that the function $G_d(\mathbf{R},t)$ satisfy in order that it be considered physically correct. Perhaps the most useful of these conditions gives the theoretical values of the moments of the space-time transformed distribution function. Let

$$G(\mathbf{R},t)=G_s(\mathbf{R},t)+G_d(\mathbf{R},t), \quad (9)$$

and define the space transforms, called the intermediate scattering functions, of $G_s(\mathbf{R},t)$ and $G(\mathbf{R},t)$ by

$$F_s(\boldsymbol{\kappa},t)=\int d^3R\, e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}G_s(\mathbf{R},t), \quad (10)$$

$$F(\boldsymbol{\kappa},t)=\int d^3R\, e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}G(\mathbf{R},t), \quad (11)$$

and the space and time transforms of $G_s(\mathbf{R},t)$ and $G(\mathbf{R},t)$ by

$$S^{\text{inc}}(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}F_s(\boldsymbol{\kappa},t), \quad (12)$$

$$S^{\text{coh}}(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}F(\boldsymbol{\kappa},t). \quad (13)$$

By inverting Eqs. (12) and (13) and differentiating with respect to time, we may derive the well-known relationships

$$\langle\omega^n\rangle_{\text{inc}}=\int_{-\infty}^{\infty} d\omega\, \omega^n S^{\text{inc}}(\boldsymbol{\kappa},\omega) =\lim_{t\to 0}\,(-i\partial/\partial t)^n F_s(\boldsymbol{\kappa},t), \quad (14)$$

$$\langle\omega^n\rangle_{\text{coh}}=\int_{-\infty}^{\infty} d\omega\, \omega^n S^{\text{coh}}(\boldsymbol{\kappa},\omega) =\lim_{t\to 0}\,(-i\partial/\partial t)^n F(\boldsymbol{\kappa},t). \quad (15)$$

The values of the lowest moments of ω are well-known functions in both classical mechanics and quantum mechanics.[21–23] In fact, since the detailed balancing condition requires that[24]

$$S(\boldsymbol{\kappa},-\omega)=e^{-\beta\hbar\omega}S(\boldsymbol{\kappa},\omega) \quad (16)$$

[where $\beta\equiv(k_BT)^{-1}$], it is possible, using the techniques introduced by Egelstaff,[5,10] to derive the nth quantum mechanical moment to order $\hbar^n$ if we know the lowest $2n$ classical mechanical moments. In this paper, we can consider either the quantum mechanical or classical mechanical moments without changing any of the conclusions reached in Sec. IV. However, since the expres-

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[21] P. G. DeGennes, Physica **25**, 825 (1959).

[22] G. Placzek, Phys. Rev. **86**, 377 (1952).

[23] A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962).

[24] P. Schofield, Phys. Rev. Letters **4**, 239 (1960).

sions we obtain are somewhat simpler in form for the classical case, and the physical interpretation is more transparent, we will couch our argument in classical terms. First, we note that all moments of odd order vanish.[21] Then, defining

$$\gamma(\boldsymbol{\kappa})=\int d^3R\, e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}g(\mathbf{R})\,, \tag{17}$$

we find[21]

$$\langle 1\rangle_{\text{inc}}=1\,, \tag{18}$$

$$\langle 1\rangle_{\text{coh}}=1+\gamma(\boldsymbol{\kappa})\,, \tag{19}$$

$$\langle \omega^2\rangle_{\text{inc}}=\kappa^2/\beta m\,, \tag{20}$$

$$\langle \omega^2\rangle_{\text{coh}}=\kappa^2/\beta m\,, \tag{21}$$

$$\langle \omega^4\rangle_{\text{inc}}=\frac{\kappa^4}{\beta m^2}\left[\frac{3}{\beta}+\frac{4\pi}{3\kappa^2}\int_0^\infty dR\, R^2 g(R)\left(\frac{\partial^2V}{\partial R^2}+\frac{2}{R}\frac{\partial V}{\partial R}\right)\right], \tag{22}$$

$$\langle \omega^4\rangle_{\text{coh}}=\frac{\kappa^4}{\beta m^2}\left[\frac{3}{\beta}+\frac{2\pi}{15}\int_0^\infty dR\, g(R)\left(3\frac{\partial^2V}{\partial R^2}+\frac{2}{R}\frac{\partial V}{\partial R}\right)\right]+O(\kappa^6)\,. \tag{23}$$

In Eqs. (20), and those following, m is the mass of the particle and V is the intermolecular potential. Equations (22) and (23) may be rewritten in various ways. Using the small step diffusion approximation introduced by Rice and Kirkwood,[25,26] we find that the diffusion coefficient D is given by

$$D=\frac{1}{\beta}\left[\frac{4\pi m}{3}\int_0^\infty dR\, R^2 g(R)\left(\frac{\partial^2V}{\partial R^2}+\frac{2}{R}\frac{\partial V}{\partial R}\right)\right]^{-\frac{1}{2}}. \tag{24}$$

Substituting Eq. (24) in Eq. (22), we find

$$\langle \omega^4\rangle_{\text{inc}}=\frac{\kappa^4}{\beta m^2}\left(\frac{3}{\beta}+\frac{1}{m\beta^2D^2\kappa^2}\right). \tag{25}$$

Equation (23), which has been expanded for small κ, may be simply written in terms of the shear and bulk moduli of the system for infinite frequency, K_∞ and G_∞, respectively. Using the expressions presented by Zwanzig and Mountain,[27] and Schofield,[28] we find

$$\langle \omega^4\rangle_{\text{coh}}=\frac{\kappa^4}{\beta m^2\rho}(K_\infty+\tfrac{4}{3}G_\infty)+O(\kappa^6)\,, \tag{26}$$

where ρ is the number density. Still another rewriting of Eq. (22) is possible. Although we do not use this last form herein, we mention it briefly in the Appendix.

IV. THE INTERPOLATION FUNCTION

We shall now return to the problem of determining $f(t)$. First, since all the odd moments of the scattering cross section vanish, $f(t)$ must be an even function of the time. A simple even function which satisfies the boundary conditions displayed in Eq. (7) is the Gaussian function

$$f(t)=e^{-\alpha^2t^2}. \tag{27}$$

Although this choice leads to a form of $S(\boldsymbol{\kappa},\omega)$ which does not obey the fourth sum rule (see below), it is a very good approximation to the proper function for intermediate times. It is instructive to substitute Eq. (27) in Eq. (8b). We obtain

$$G_d(\mathbf{R}',t)=G_d{}^C(\mathbf{R}',t)+e^{-\alpha^2t^2}[g(\mathbf{R}')-G_d{}^C(\mathbf{R}',t)]\,. \tag{28}$$

In his computer experiments Rahman found that a major defect of the convolution approximation is that it leads to a decay of $g(\mathbf{R})$ which is too rapid.[12] From Eq. (28) we see that the effect of our simple substitution is to decrease the rate of decay of the convolution approximation. It is, therefore, qualitatively correct. In fact, by substituting the values found by Rahman for $G_d{}^C(\mathbf{R},t)$ and $g(\mathbf{R})$ for argon at 94.4°K at the first maximum of the distribution function ($t=1.0\times10^{-12}$ sec), we find $\alpha\approx1.5\times10^{12}$ sec^{-1}.

In order to apply the sum rules, we shall work with the intermediate scattering function. Taking the space transform of Eq. (8) we find

$$F_d(\boldsymbol{\kappa},t)=\gamma(\boldsymbol{\kappa})\{1-[F_s(\boldsymbol{\kappa},t)-1][f(t)-1]\}\,, \tag{29}$$

where $F_d(\boldsymbol{\kappa},t)$ is the space transform of $G_d(\mathbf{R},t)$. We write Eq. (29) in this way for two reasons. First, in this form we see the similarities that exist between our approximation and those proposed by Egelstaff[10,11] and Singwi.[13] Secondly, the sum rules for coherent scattering can be verified easily. Since we know that both $F_s(\boldsymbol{\kappa},t)$ and $f(t)$ have power series expansions in time that start as $1+O(t^2)$, we immediately verify the two lowest sum rules embodied in Eqs. (19) and (21). Equation (21), which is not satisfied by the convolution approximation, is satisfied here solely by properly representing the boundary condition on $f(t)$ for short times without making further assumptions about its structure.

Now we must determine the second-order term in the expansion of $f(t)$ in powers of t. Let

$$f(t)=1+a^2t^2+O(t^4)\,. \tag{30}$$

Substitution of (30) and the exact expansion of $F_s(\boldsymbol{\kappa},t)$ in powers of t in Eq. (29) leads to

$$F_d(\boldsymbol{\kappa},t)=\gamma(\boldsymbol{\kappa})[1+(a^2\kappa^2t^4/2\beta m)+O(t^6)]\,. \tag{31}$$

We require that our approximate form of $S(\boldsymbol{\kappa},\omega)$ have the correct fourth moment. Therefore, we use the

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[25] S. A. Rice and J. G. Kirkwood, J. Chem. Phys. **31**, 901 (1959).

[26] S. A. Rice, J. Chem. Phys. **33**, 1376 (1960).

[27] R. Zwanzig and R. D. Mountain, J. Chem. Phys. **43**, 4464 (1965).

[28] P. Schofield, Proc. Phys. Soc. (London) **88**, 149 (1966).

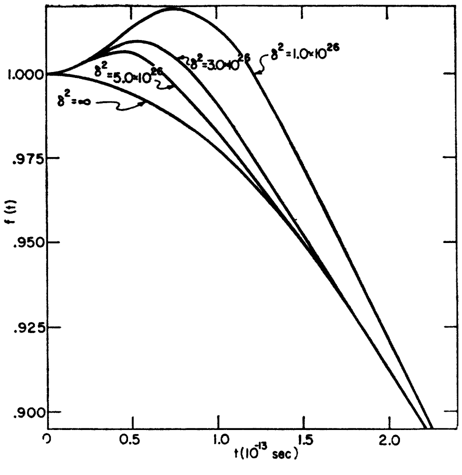

FIG. 1. $f(t)$ as a function of time for short times using Eq. (34). The values of c and α are as cited in the text.

appropriate sum rule to replace the left-hand side of Eq. (31) and solve for a^2. However, since we do not know the left-hand side of Eq. (31) to all orders in κ, it is also necessary to expand both sides in a power series in κ. From the theory of thermodynamic fluctuations we know that

$$\gamma(\kappa)=(\rho/m\beta K_T)-1+\rho(2\pi)^3\lim_{\kappa\to0}\delta(\kappa)+O(\kappa^2), \quad (32)$$

where K_T is the isothermal bulk modulus. For our purposes we can neglect the delta function, since we are examining the expressions only for κ different from zero. Using (14), (15), (25), and (26) and taking the fourth time derivative of (31), we have, letting $t\to0$, equating powers of κ^2, and solving for a^2,

$$a^2=\{[1-(\rho/\beta mK_T)]12\beta^2m^2D^2\}^{-1}. \quad (33)$$

Since $1>\rho/m\beta K_T>0$ for a liquid, we find that a^2 must be positive, and therefore that $f(t)$ must increase when t is very small. This is contrary to the naive expectation that $f(t)$ is a monotonically decreasing function of time, and that the correlations in the liquid decay monotonically. On the contrary, for small t and small κ (large R), we see from Eq. (31) that the correlations in the fluid increase.

[*Note added in proof.* Professor Egelstaff has suggested to us that the argument defining the sign of a^2 may be invalid because the form of $f(t)$ chosen may not be adequate in the limit $\kappa\to0$. See Sec. VII.]

This result is sufficiently unexpected that a few words of explanation are necessary. We start by noting that a formal analysis of memory effects in liquids by Boon and Rice[29] leads to the same conclusion. These investigators use the theory of irreversible processes, as developed by Prigogine and co-workers,[30,31] to derive the transport equation describing the time evolution of the autocorrelation function of a phase function. It is then shown that the memory function which enters the master equation derived by Nakajima[32] and Zwanzig[33] can be formally expressed in terms of the collision operator and the destruction operator which appear in the master equation of Prigogine and Resibois. Calculations based on a simple model show that the time dependence of the destruction fragment is such that the initial correlations propagate for a short time before they are destroyed by molecular collisions. It may be said, then, that in the short period of time for which the particle motion is essentially free, correlations increase. Only when molecular interactions come into play do the correlations decrease as in the naive picture. It is important to note that the time scale on which the correlations grow and then decrease is a fraction of the average time between collisions. Although Boon and Rice deduce these consequences from a simple model, they believe the results to be more general than the analysis. Application of their model analysis to liquid Ar leads to both an autocorrelation function of momentum and a power spectrum in reasonable agreement with Rahman's computer experiment.[12]

In accord with the Boon-Rice analysis and Eq. (33) we now introduce a form for $f(t)$ which has two time scales. The first time scale corresponds to the buildup of correlations, and the second to the decay of the correlations. In pictorial terms, we note that at extremely short times few of the atoms have undergone any collisions. In this domain of free particle motion, the initial correlations propagate and tend to make the fluid appear as if it were more ordered. As t increases, collisions occur and act to destroy the order in the fluid.

An interpolation function which is consistent with these considerations is

$$f(t)=(1+c^2t^2e^{-\delta^2t^2})e^{-\alpha^2t^2}, \quad (34)$$

where $\delta^2\gg\alpha^2$. Equation (34) is adopted for $f(t)$ in the remainder of this paper. For t small we immediately obtain from Eq. (33)

$$c^2-\alpha^2=\left[\left(1-\frac{\rho}{\beta mK_T}\right)12\beta^2m^2D^2\right]^{-1}. \quad (35)$$

For intermediate time the second term in the brackets in Eq. (34) approaches zero. In this regime we may compare the t^2 term with that obtained in Rahman's delayed time convolution approximation,[12] and thereby obtain a value for α. We find

$$\alpha=3/2\tau. \quad (36)$$

For argon at 94.4°K, Rahman found that $\tau=1.0\times10^{-12}$ sec. Although α is expected to be temperature-depen-

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[29] J. P. Boon and S. A. Rice, J. Chem. Phys. **47**, 2480 (1967).

[30] I. Prigogine and P. Resibois, Physica **27**, 629 (1961).

[31] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962).

[32] S. Nakajima, Progr. Theoret. Phys. (Kyoto) **20**, 948 (1958).

[33] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); in *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1961).

dent, we have not found a better way of computing it than by comparison with the computer experiment, and hence we will use $\alpha=1.5\times10^{12}$ sec^{-1} in Sec. VI. From Eq. (35) and the values quoted in Cook[34] we now find that $c=3.16\times10^{12}$ sec^{-1} for a temperature of 85°K. We could find δ by appealing to the higher-order sum rules. Unfortunately, the higher-order sum rules rapidly become quite complicated in form. In the absence of simple physical approximations to the functions involved we choose to avoid this method of evaluating δ. Furthermore, the time scale on which the second term in the brackets in Eq. (33) contributes is so short that inclusion of the second term has practically no effect on the neutron-scattering cross section and merely serves to satisfy the sum rules. In Fig. 1 we display $f(t)$ for short times and several values of δ^2. It should be noticed that for $t=2\times10^{-13}$ sec. Equation (34) reduces to Eq. (27) for the values we have used for the parameters. To carry out the computations in Sec. VI, we choose $\delta^2=3\times10^{26}$ sec^{-2}. In Fig. 2 we plot $f(t)$ for this value of δ^2.

V. INCOHERENT SCATTERING CROSS SECTION

Before considering the total neutron scattering cross section we first must establish the cross section for incoherent scattering. Although this constitutes a formidable problem in itself, we will bypass many of the deeper difficulties involved by adopting an approximate form. For argon at 94.4°K Rahman's computer experiment indicates that the non-Gaussian behavior of $G_s(\mathbf{R},t)$ is rather small.[12] Hence, we assume that

$$G_s(\mathbf{R},t)=\frac{1}{[4\pi\rho(t)]^{3/2}}e^{-R^2/4\rho(t)}, \tag{37}$$

where $\rho(t)$ is to be determined, should be a good approximation. By taking the space transform of (37) we find that

$$F_s(\boldsymbol{\kappa},t)=e^{-\kappa^2\rho(t)}. \tag{38}$$

Comparing (38) with the frequently used expansion expressing $F_s(\boldsymbol{\kappa},t)$ in terms of the autocorrelation function we find, for the classical case,[21,23]

$$\rho(t)=\frac{1}{\beta m}\int_0^t dt'(t-t')\psi(t'), \tag{39}$$

where the velocity autocorrelation function $\psi(t)$ is defined by

$$\psi(t)=\frac{\langle \mathrm{v}(0)\cdot\mathrm{v}(t)\rangle}{\langle v^2\rangle}. \tag{40}$$

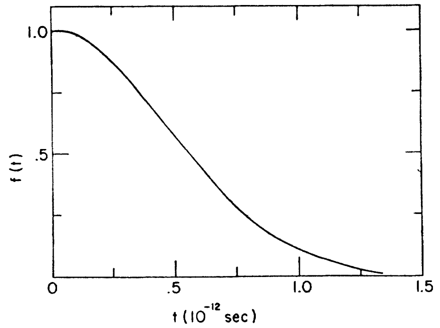

FIG. 2. $f(t)$ as a function of time using Eq. (34). The values of c and α are as cited in the text and $\delta^2=3.0\times10^{26}$/sec^2.

By judiciously choosing the autocorrelation function, we should be able to generate an accurate incoherent scattering cross section. DeGennes[21] has considered the possibility of using a Gaussian autocorrelation function. He showed that with the introduction of one parameter both the asymptotic and short time behaviors of the scattering function can be accurately reproduced. However, the Gaussian autocorrelation function does not properly represent the behavior of the dense fluid. As recent computer studies and theoretical analyses both show, one of the major characteristics of the velocity autocorrelation function of a liquid is the negative region corresponding to backscattering from the first coordination shell.[12,35] In a recent paper, Berne, Boon, and Rice have computed an autocorrelation function which has a negative region and is supposed to include the "memory" effects inherent in the molecular dynamics in the liquid.[19] Their correlation function has two parameters. However, if we make the approximations represented by Eq. (24) and define

$$\xi=1/2D\beta m, \tag{41}$$

we find

$$\psi(t)=e^{-\xi|t|}(\cos\sqrt{3}\xi|t|+(1/\sqrt{3})\sin\sqrt{3}\xi|t|). \tag{42}$$

In the Berne, Boon, and Rice analysis, the approximation represented by Eq. (24) is applicable to liquid Ar at 94°K, and the two-parameter form which they derive reduces to the one-parameter form of Eq. (42). Substituting Eq. (42) in Eq. (39) and integrating, we find

$$\rho(t)=\frac{1}{\beta m}\left[\frac{|t|}{2\xi}-\frac{e^{-\xi|t|}\sin\sqrt{3}\xi|t|}{2\xi^2\sqrt{3}}\right]. \tag{43}$$

As a final test of internal consistency, we substitute Eq. (43) in Eq. (38) and examine both the asymptotic and short time behavior of the intermediate scattering function. We find that for large t this form for the intermediate scattering function is valid only if Eq. (41) is correct. Further, by expanding the intermediate scattering function for t small we find that the sum rules presented in Eqs. (18) and (20) are satisfied. Further, the fourth sum rule, Eq. (22), is satisfied only if Eq. (24) is correct. Hence, we have an internally

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[34] *Argon, Helium and the Rare Gases* edited by G. A. Cook (Interscience Publishers, Inc., New York, 1961).

[35] J. H. Dymond and B. J. Alder, J. Chem. Phys. 45, 2061 (1966).

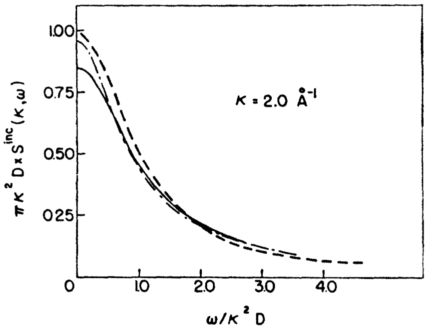

FIG. 3. $\pi\kappa^2 DS^{\mathrm{inc}}(\kappa,\omega)$ as a function of $\omega/\kappa^2 D$ for $\kappa=2.0$ Å^{-1}. Computed for argon at $T=85.5$°K using $D=1.88\times10^{-5}$ cm^2/sec. The Gaussian results obtained by Nijboer and Rahman, Ref. 36 (———) are compared with the results obtained as described in the text (- - - -), and the exact results (— · —) from Ref. 36.

consistent one-parameter approximation which represents "memory" effects as well as the short and long time behavior of the liquid. Substituting for the value of D at 85.5°K, $D=1.88\times10^{-5}$ cm^2/sec, we may now compute the incoherent scattering cross section. In Figs. 3–6 we compare our calculations and the results obtained by Nijboer and Rahman in their computer experiment for liquid argon at $T=85.5$°K.[36] The solid line represents the results found by Nijboer and Rahman when they made the Gaussian approximation for $F_s(\kappa,t)$, [Eq. (38)] and found $\rho(t)$ using the root-mean-square displacements derived from the computer data. The dashed line is what we obtain by substituting Eq. (43) in Eq. (38) and taking the transform. The agreement is very good over a wide range of values of κ and ω. Only for small ω does there seem to be a significant difference between the two sets of results. This is to be expected for Nijboer and Rahman find the asymptotic form $\rho(t)=D|t|+C$ where C is a constant, and here we have $\rho(t)=D|t|$. However, it should be noted that for $\kappa=2.0$ Å^{-1} for which there is an exact computation of $S^{\mathrm{inc}}(\kappa,\omega)$ (dash-dot line in Fig. 3), our results are in better agreement with the exact form than with the form derived from the Gaussian approximation.

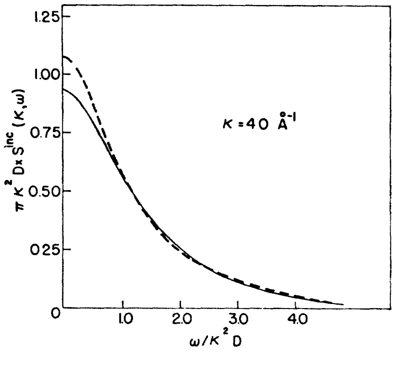

FIG. 4. $\pi\kappa^2 DS^{\mathrm{inc}}(\kappa,\omega)$ as a function of $\omega/\kappa^2 D$ for $\kappa=4.0$ Å^{-1} computed for argon at $T=85.5$°K using $D=1.88\times10^{-5}$ cm^2/sec. The Gaussian results obtained by Nijboer and Rahman, Ref. 36 (———) are compared with the results obtained as described in the text (- - - -).

VI. NEUTRON SCATTERING CROSS SECTION

We can now proceed to compute the theoretical neutron scattering cross sections, and compare our results with recent experimental work. Defining $\hbar\kappa$ and $\hbar\omega$ as the momentum and energy loss of the neutron, respectively, and λ_i and λ as the initial and final neutron wavelengths, respectively, we may easily derive the formulas[18,20]

$$\omega=\frac{2\pi^2\hbar}{m_n}\left(\frac{1}{\lambda_i^2}-\frac{1}{\lambda^2}\right), \tag{44}$$

$$\kappa^2=4\pi^2\left(\frac{\lambda_i^2+\lambda^2-2\lambda_i\lambda\cos\theta}{\lambda_i^2\lambda^2}\right), \tag{45}$$

where m_n is the neutron mass, and θ is the angle between the incoming and scattered neutron. Since we are calculating the distribution function using classical mechanics it is necessary to correct the results for quantum effects in real systems. Several authors have discussed how this may be done.[24,37,38] It may be shown that

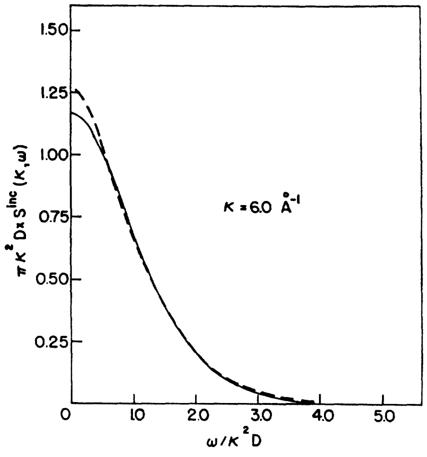

FIG. 5. Same as Fig. 4 for $\kappa=6.0$ Å^{-1}.

$$\frac{d^2\sigma}{d\lambda d\Omega}=\frac{\pi\hbar\lambda_i}{m_n\lambda^4}\left[e^{(\beta\hbar\omega/2)-(\beta\hbar^2\kappa^2/8m)}\right]\times\left[\sigma^{\mathrm{inc}}S^{\mathrm{inc}}(\kappa,\omega)+\sigma^{\mathrm{coh}}S^{\mathrm{coh}}(\kappa,\omega)\right], \tag{46}$$

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

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[36] B. R. A. Nijboer and A. Rahman, Physica **32**, 415 (1966).

[37] K. S. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).

[38] R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, Phys. Rev. **126**, 1165 (1962).

scattering cross section is defined by

$$\sigma^{\text{inc}}+\sigma^{\text{coh}}=\sigma^{\text{tot}}. \qquad (47)$$

Examination of Eqs. (46) and (47) shows that by specifying the ratio between any two of the quantities in Eq. (47), we may calculate the neutron scattering to within a multiplicative constant. Here, we choose $\sigma^{\text{coh}}/\sigma^{\text{tot}}=0.675$ ($\sigma^{\text{coh}}/\sigma^{\text{tot}}=0.66$ in Ref. 20) found by Henshaw for argon at 84°K.[39] In addition, to compute the absolute magnitude of the neutron-scattering cross section we choose $\sigma^{\text{inc}}=0.210$ b, $\sigma^{\text{coh}}=0.436$ b, corresponding to a scattering cross section of 73 b for Ar^{40} and of 0.40 b for Ar^{36}.

In Figs. 7 and 8 we plot $d^2\sigma/d\Omega d\lambda$ using our approximation and compare it with the results found using the convolution approximation, delayed-time convolution approximation, and the experimental data reported by Chen *et al.* for Ar at $T=85°\text{K}$. Several points should noted. First, contrary to commonly held opinion, the convolution approximation does predict the existence of a subsidiary peak for this particular experiment. In Chen's experiment $\boldsymbol{\kappa}$ is not held constant and as one scans through the energy $\boldsymbol{\kappa}$ also varies. Thus, at the mean peak in $S(\boldsymbol{\kappa})$, i.e., for $\kappa=2.0$ Å^{-1}, the form of the convolution approximation leads to the prediction of a maximum in $d^2\sigma/d\Omega d\lambda$. The predictions of the delayed-time convolution approximation and our results are seen to be very similar. The delayed-time approximation does give a differential cross section in slightly better agreement with the observed position of the peak arising from coherent scattering. However, the location of this peak is sensitive to the value of the parameter α, and by varying α we could achieve better agreement with experiment. There is, unfortunately, a considerable difference between the experimental and theoretical intensities of the peaks. We cannot at present explain this discrepancy. In Fig. 9 we plot the full half-width of the theoretical scattering function $d^2\sigma/d\Omega d\omega$ and compare it with the experimental results of Dasannacharya and Rao,[20] and also with the full-half-width computed using the convolution approximation and assuming simple diffusion to be a valid description at all times. Although we find a slight flattening in our results for $\kappa=2.0$ Å^{-1}, we do not reproduce the extreme variation in half-widths found by Dasannacharya and Rao.

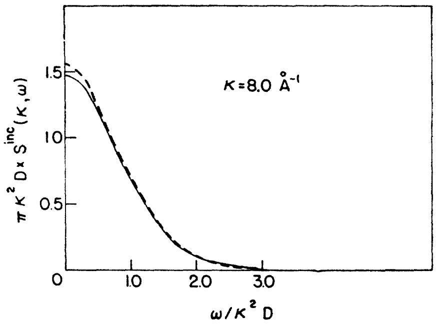

FIG. 6. Same as Fig. 4 for $\kappa=8.0$ Å^{-1}.

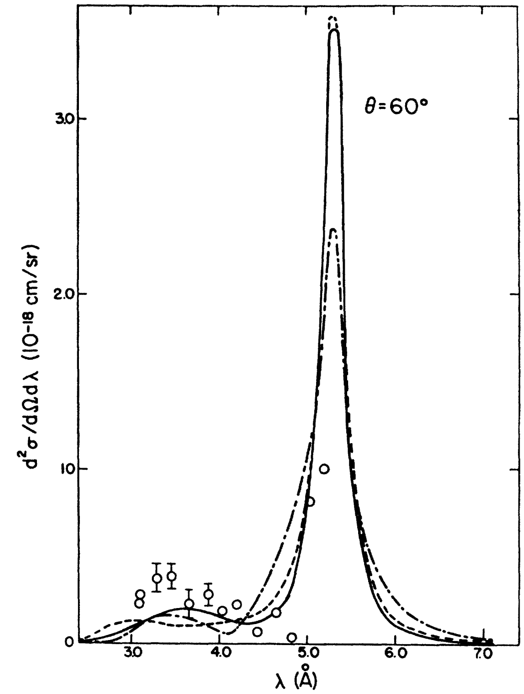

FIG. 7. Comparison of the neutron scattering results experimental of Chen *et al.*, Ref. 18 (points) for a scattering angle $\theta=60°$, with the present approximation (————), the Vineyard convolution approximation (- - - -), and the delayed time convolution approximation (— · —). The vertical scale of this experimental curve is arbitrary.

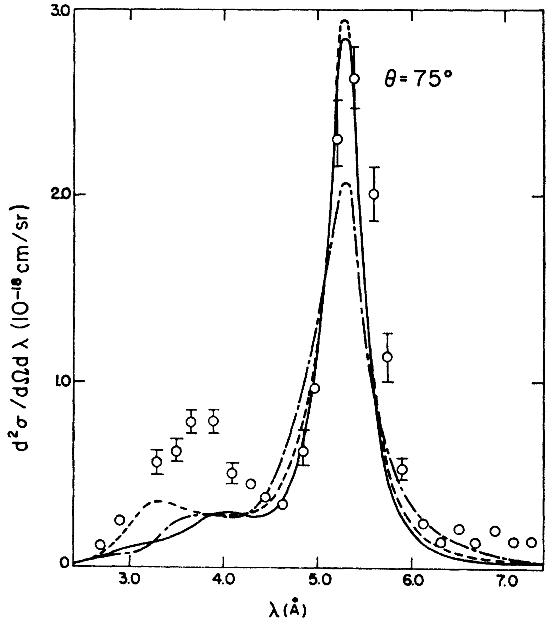

FIG. 8. Same as Fig. 7 for $\theta=75°$.

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[39] D. G. Henshaw, Phys. Rev. **105**, 976 (1957).

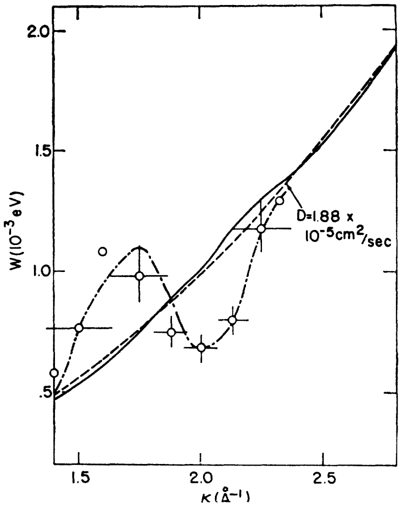

FIG. 9. Comparison of the full width at half-maximum in the neutron scattering experiment of Dasannacharya and Rao, Ref. 20 (— · —), with those found in the text (———) and those expected for simple diffusion for $D=1.88\times10^{-5}$ cm²/sec (- - - -).

VII. CONCLUSIONS

Our purpose in this paper has been to present a conceptually simple and easily applied modification of the Vineyard convolution approximation and to show how it may be used to compute the neutron scattering from a simple liquid. We believe that the application of these results to other systems may prove to be fruitful. Some modifications may, however, be necessary. The hard-sphere volume exclusion factor which was briefly discussed in Sec. II could easily be included at the expense of simplicity of the analytic expressions. The extension of this work to the hydrodynamic regime might be more difficult. Recent work based on solution of the hydrodynamic equations of motion is of considerable use here.[7,8] In order to obtain the correct hydrodynamic behavior we must include terms in Eq. (6) such that if the velocity of the particle at the origin at time zero were specified a positive correlation would exist with the velocity of a particle 100 Å away 10^{-11} sec later. Such a correlation corresponds to the propagation of an excitation with the speed of sound. Our approximation does not include this correlation, and therefore will not account for the Brillouin-Mandelstam components observed in light scattering experiments.

As a result of examining a formalism which should be accurate for short times, we have found that for t smaller than about 0.5×10^{-13} sec the "correlations" may be said to be increasing. We consider this to be an important result, the verification of which should prove a challenge to experimentalists in view of the small magnitudes involved.

ACKNOWLEDGMENTS

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APPENDIX

Another relationship has often been employed in the study of the function $S(\kappa,\omega)$ for liquids. The relationship between the mean square velocity of an atom in the classical and quantal representations is

$$\langle v^2\rangle_{\text{Q.}}=\langle v^2\rangle_{\text{Cl.}}+\frac{\pi\beta\hbar^2}{3m^2}\int_0^\infty dR\,R^2g(R)\left(\frac{\partial^2V}{\partial R^2}+\frac{2}{R}\frac{\partial V}{\partial R}\right),\qquad\text{(A1)}$$

where

$$\langle v^2\rangle_{\text{Cl.}}=3/\beta m.\qquad\text{(A2)}$$

Substituting Eq. (A1) in Eq. (24) we find

$$D=\frac{\hbar}{2m}\left(\frac{1}{\beta m}\right)^{1/2}(\langle v^2\rangle_{\text{Q.}}-\langle v^2\rangle_{\text{Cl.}})^{-1/2}.\qquad\text{(A3)}$$

It is often assumed that, for certain purposes, a liquid may be approximately represented as a solid with a Debye temperature Θ_D.[5,11,23] The formula[22]

$$\langle v^2\rangle_{\text{Q.}}-\langle v^2\rangle_{\text{Cl.}}=\frac{3}{20\beta m}\left(\frac{\Theta_D}{T}\right)^2,\qquad\text{(A4)}$$

which is valid in a solid where $T\gg\Theta_D$, is then introduced. However, substituting (A4) in (A3), we find that

$$D=\frac{\hbar}{m}\left(\frac{5}{3}\right)^{1/2}\frac{T}{\Theta_D}.\qquad\text{(A5)}$$

Using the value of D at 85.5°K for liquid argon, $D=1.88\times10^{-5}$ cm²/sec, we find $\Theta_D=93.4$°K. For this value of Θ_D, Eq. (A4) is invalid. Finally, we note that substitution of Eq. (A1) in Eq. (22) leads to

$$\langle\omega^4\rangle_{\text{inc}}=\frac{\kappa^4}{\beta m^2}\left[\frac{3}{\beta}+\frac{4m^2}{\beta\hbar^2\kappa^2}(\langle v^2\rangle_{\text{Q.}}-\langle v^2\rangle_{\text{Cl.}})\right].\qquad\text{(A6)}$$