Dynamical Correlations in Simple Liquids and Cold-Neutron Scattering by Argon*

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Recent inelastic neutron-scattering measurements on liquid argon at 94.4°K are quantitatively analyzed in terms of velocity autocorrelation functions obtained from computer molecular-dynamics experiments and from a simple model which has no adjustable parameters. The model is derived using dispersion-relation and sum-rule arguments, and a single, operationally well-defined approximation. Physically it corresponds to treating the motions as if the atoms were moving in a relaxing cage. The model description is tested against computer results, and both are employed in the cross-section calculation, in which two recent convolution-type approximations are considered. Over-all agreement between present analysis and experiments is quite satisfactory. Moreover, detailed comparisons show that the results are not very sensitive to the differences in the model and computer velocity correlation functions, and that the observed discrepancies arise mainly from the existing methods of relating coherent and incoherent scattering functions.

I. INTRODUCTION

INELASTIC neutron-scattering measurements and computer molecular-dynamics experiments are the most direct methods with which atomic motions in liquids can be studied in detail. These investigations are closely related in that they both provide information about the density correlation functions $G(r,t)$ and $G_s(r,t)$.[1] In computer calculations[2] one constructs the density correlation functions as well as the velocity autocorrelation function $\psi(t)$ and the mean-square displacement $\langle r^2(t)\rangle$ from a knowledge of the particle positions and velocities at various time intervals. In neutron experiments[3,4] one measures the space-time Fourier transform of G and G_s, although usually not separately. From the neutron data it is possible to infer $\langle r^2(t)\rangle$ [5–7] or the frequency spectrum of $\psi(t)$,[8] but this is a difficult problem and the results obtained thus far can not be considered very precise.

It is physically meaningful and mathematically convenient to discuss molecular dynamics in liquids in terms of $\psi(t)$ and $\langle r^2(t)\rangle$. Any vibratory component present in the motions would appear in $\psi(t)$ as a negative region, or in its frequency spectrum $f(\omega)$ as a peak away from the origin. The diffusive component, always present in a liquid, would give rise to a linear growth of $\langle r^2(t)\rangle$ with time. These characteristics clearly manifest themselves in the computer results, and to a lesser degree they also have been observed in the neutron data.

Since neutron scattering is capable of furnishing microscopic details about atomic motions, it can be expected that interpretation of the data will not be simple. Conventionally one first attempts to compute the incoherent scattering cross section by means of a model for $G_s(r,t)$. The result would be sufficient for the analysis of experiments on liquids containing hydrogen, an element with a large scattering cross section that is almost entirely incoherent. For liquids which also scatter coherently, a knowledge of $G(r,t)$ is needed. This is a more complex problem in that phenomenological descriptions are difficult to formulate. Fortunately, in both cases one now has the aid of computer results to motivate and test approximate calculations.

The computation of $G_s(r,t)$ can be reduced to the problem of determining $\psi(t)$ or $\langle r^2(t)\rangle$ through the assumption that G_s is a spatially Gaussian distribution. This is a useful procedure which can be made quite accurate because reliable methods for estimating the non-Gaussian corrections have been developed. In the Gaussian approximation, model calculations therefore begin at the level of $\psi(t)$ or $\langle r^2(t)\rangle$. Initial attempts to describe both solidlike oscillations and diffusive motions in this way were made by Rahman, Singwi, and Sjolander[9] using stochastic arguments. Later models which involve more formal and elaborate procedures have been proposed by Ardente, Nardelli, and Reatto,[10]

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and by Sears.[11] All these calculations have the common feature that two distinct types of motions were introduced into the description *ab initio*. We observe, on the other hand, that if the atom vibrating initially is to be the same particle diffusing at later times, then oscillations and diffusion should result from a single unified treatment. Moreover, there should be an intimate connection between the two processes.

Although a good deal is known about the properties of $G(r,t)$, its computation generally involves an indirect approach. The most common procedure is to express $G(r,t)$ in terms of $G_s(r,t)$ and the equilibrium pair distribution function $g(r)$, the first approximation of this kind being the convolution approximation suggested by Vineyard.[12] Modifications of this approximation have been made notably by Singwi[13] and by Rahman.[2] Rahman suggested a delayed convolution approximation (DCA) which was primarily motivated by his computer results. More recently, another approximate relation between G and G_s has appeared in the literature.[14,15] This procedure, which we shall call the effective-mass approximation (EMA), has the attractive feature of introducing no additional parameter or function relative to the original convolution approximation. Both DCA and EMA have not been used in any extensive calculation, but initial results[14–16] obtained with these phenomenological prescriptions have been encouraging.

The purpose of this paper is to consider a model that is mathematically simple and also qualitatively correct, to test the model against computer experiments, and to apply both model and computer results in a quantitative analysis of neutron-scattering measurements. Our specific discussions will be concerned with liquid argon since this is the only system for which computer and neutron-scattering data are presently available. In the next section we begin with the correlation function formalism of Martin.[17] The model is derived using dispersion-relation and sum-rule arguments, and the assumption of a single relaxation process. It is an interpolation description which has the correct asymptotic behavior at short and long times. This description is not entirely new in that similar results for $\psi(t)$ and $f(\omega)$ have already been obtained elsewhere[18]; however, the present formulation enables us to give a simple interpretation of the model and to emphasize the fact that it has no adjustable parameters. The comparison of model and computer results for $\psi(t)$, $f(\omega)$, and $\langle r^0(t)\rangle$ is discussed in Sec. III. We also present results for the incoherent-scattering function computed in the Gaussian approximation. The actual calculation of the double differential neutron-scattering cross section using DCA and EMA is described in Sec. IV. The computed spectra are compared with neutron data in several ways in Sec. V. It is found that the most serious approximation in the calculational procedure is the treatment of coherent effects. We then conclude the paper with a number of remarks in Sec. VI.

II. INTERPOLATION MODEL

To develop our model description it is necessary to first introduce a number of basic definitions and relations.[17] We consider the liquid as a spherically symmetric classical system. The Fourier transforms of the displacement response and correlation functions are defined by

$$\chi''(\omega)=\int_{-\infty}^{\infty} dt\, e^{i\omega t}\tfrac{1}{2}i\langle[x(t),x(0)]_{\mathrm{PB}}\rangle, \tag{2.1}$$

$$\Phi(\omega)=\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle x(t)x(0)\rangle, \tag{2.2}$$

where $[\ ]_{\mathrm{PB}}$ denotes the Poisson bracket and $\langle\ \rangle$ an equilibrium ensemble average. These two quantities are not independent but are related through the fluctuation-dissipation theorem[19]

$$\chi''(\omega)=\tfrac{1}{2}\beta\omega\Phi(\omega), \tag{2.3}$$

where β is the inverse temperature in energy units. We next define the complex susceptibility function

$$\chi(z)=\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{\chi''(\omega')}{\omega'-z}, \tag{2.4}$$

with $z=w+i\epsilon$, a complex variable in the upper half-plane. In terms of real and imaginary parts one has, on taking limit $\epsilon\to 0^+$,

$$\chi(\omega)=\chi'(\omega)+i\chi''(\omega), \tag{2.5}$$

with

$$\chi'(\omega)=P\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{\chi''(\omega')}{\omega'-\omega}, \tag{2.6}$$

where P denotes the principal value. It can be shown that $\chi''(\omega)$ is real and odd in ω, hence $\chi'(\omega)$ and $\Phi(\omega)$ are both real and even.

An essential part of Martin's formalism is the dispersion relation. This equation is motivated by considering certain analytic properties of $\chi(z)$. In our

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case we write

$$Mz^2\chi(z)=-[1+\lambda(z)/z]^{-1}, \tag{2.7}$$

where M is the particle mass and

$$\lambda(z)=\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{\lambda''(\omega')}{\omega'-z}. \tag{2.8}$$

Formally, (2.7) merely defines a new complex function $\lambda(z)$. However, it is possible to give an interpretation to this relation, and we will discuss this point later in the context of a model. Note that the imaginary part of $\lambda(\omega)$ is $\lambda''(\omega)$, which will be taken to be even. As a result, the real part

$$\mathrm{Re}[\lambda(\omega)]\equiv\lambda'(\omega)=\omega P\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{\lambda''(\omega)}{\omega'^2-\omega^2} \tag{2.9}$$

is obviously an odd function.

As an immediate consequence of Eq. (2.7) one can derive a number of moment relations involving χ'' and λ''. The first three relations obtained from a high z expansion are

$$\frac{M}{\pi}\int_{-\infty}^{\infty}d\omega\,\omega\chi''(\omega)=1, \tag{2.10}$$

$$\frac{M}{\pi}\int_{-\infty}^{\infty}d\omega\,\omega^3\chi''(\omega)=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\lambda''(\omega), \tag{2.11}$$

$$\frac{M}{\pi}\int_{-\infty}^{\infty}d\omega\,\omega^5\chi''(\omega)=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^2\lambda''(\omega)+\left[\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\lambda''(\omega)\right]^2. \tag{2.12}$$

Another quantity of basic interest in the discussion of liquid dynamics is the velocity autocorrelation function $\langle v(t)v(0)\rangle$. Its spectral representation is simply related to the displacement functions,

$$\begin{aligned}f(\omega)&=\frac{2}{\pi}\int_0^{\infty}dt\,\cos\omega t\frac{\langle v(t)v(0)\rangle}{\langle v^2\rangle}\\&=(\beta M/\pi)\omega^2\Phi(\omega)\\&=(2/\pi)M\omega\chi''(\omega).\end{aligned} \tag{2.13}$$

Therefore, the dispersion relation (2.7) implies the expression

$$f(\omega)=\frac{2}{\pi}\frac{\lambda''(\omega)}{[\omega+\lambda'(\omega)]^2+[\lambda''(\omega)]^2}. \tag{2.14}$$

From Eq. (2.10) one sees that $f(\omega)$ over all positive frequencies has unit normalization. The connection between $\lambda''(\omega)$ and the mean-square force is given by (2.11),

$$\begin{aligned}\omega_0^2&=\int_0^{\infty}d\omega\,\omega^2 f(\omega)\\&=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\lambda''(\omega)\\&=(1/3M)\langle\nabla^2U\rangle,\end{aligned} \tag{2.15}$$

where U is the interaction potential. Finally a relation exists between λ'' and the self-diffusion coefficient D,

$$\begin{aligned}D&=\int_0^{\infty}dt\,\langle v(t)v(0)\rangle\\&=\tfrac{1}{2}\pi\langle v^2\rangle f(0)\\&=\langle v^2\rangle/\lambda''(0).\end{aligned} \tag{2.16}$$

The foregoing results are all exact and completely general for a classical liquid. We now show how they can be applied to formulate model calculations. Since the various functions are interrelated, a model description can be introduced by simply assuming a particular functional form for $\lambda''(\omega)$. Suppose we take for $\lambda''(\omega)$ a Lorentzian

$$\lambda''(\omega)=\alpha\tau_0/[1+(\omega\tau_0)^2]. \tag{2.17}$$

Because of Eqs. (2.11) and (2.16) the constants α and τ_0 are not free parameters; instead one finds

$$\alpha=\omega_0^2, \tag{2.18}$$

$$\tau_0=\langle v^2\rangle(\omega_0^2D)^{-1}. \tag{2.19}$$

The dispersion function $\lambda(\omega)$ is obtained from Eq. (2.8),

$$\lambda(\omega)=i\omega_0^2\tau_0/(1-i\omega\tau_0), \tag{2.20}$$

or, equivalently,

$$\lambda'(\omega)=-\omega\omega_0^2\tau_0^2/[1+(\omega\tau_0)^2]. \tag{2.21}$$

The spectral function $f(\omega)$ then becomes, for the model,

$$f(\omega)=\frac{2}{\pi}\frac{\omega_0^2/\tau_0}{(\omega^2-\omega_0^2)^2+(\omega/\tau_0)^2}, \tag{2.22}$$

from which we can immediately evaluate the normalized velocity correlation function,

$$\begin{aligned}\psi(t)&\equiv\langle v(t)v(0)\rangle/\langle v^2\rangle\\&=\int_0^{\infty}d\omega\,\cos\omega t f(\omega)\\&=e^{-t/2\tau_0}[\cos\Omega t+(1/2\tau_0\Omega)\sin\Omega t],\end{aligned} \tag{2.23}$$

with $\Omega^2=\omega_0^2-1/4\tau_0^2$. The displacement correlation $\langle x(t)x(0)\rangle$ is of no direct interest; however, the mean-

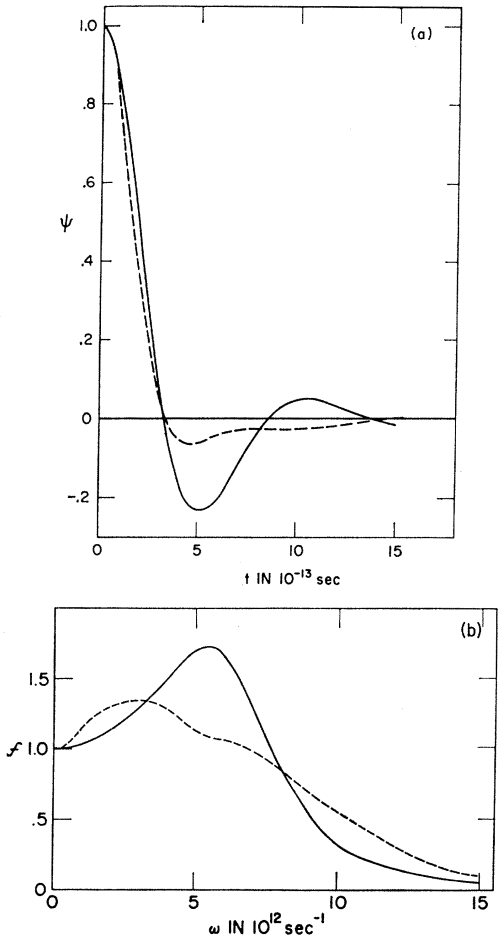

FIG. 1. (a) Comparison of normalized velocity autocorrelation function $\psi(t)$ between the model (solid line) and the computer experiment (dashed line) at 94.4°K. (b) Same as (a) for the frequency spectrum of $\psi(t)$.

square displacement, which can be expressed as

$$\tfrac{1}{3}\langle r^2(t)\rangle \equiv \langle [x(t)-x(0)]^2\rangle = 2\int_0^t dt'(t-t')\langle v(t')v(0)\rangle \quad (2.24)$$

for a stationary system, is essential to the calculation of $S(\kappa,\omega)$ discussed in later sections. One has in this case

$$\tfrac{1}{6}\frac{\langle r^2(t)\rangle}{\langle v^2\rangle} = \frac{\omega_0^2-1/\tau_0^2}{\omega_0^4} + \frac{1}{\omega_0^2\tau_0}t + \omega_0^{-4}e^{-t/2\tau_0} \times\left[\left(\frac{1}{8\tau_0^3\Omega}-\frac{3\Omega}{2\tau_0}\right)\sin\Omega t - \left(\omega_0^2-\frac{1}{\tau_0^2}\right)\cos\Omega t\right]. \quad (2.25)$$

The model description based on Eq. (2.17) will be used throughout the present work. The simplicity of $\lambda''(\omega)$ has made it possible to obtain analytic expressions for all the relevant quantities. As mentioned in the Introduction, Berne, Boon, and Rice[18] have arrived at basically the same model using a memory-function formalism. These authors have compared the model results for $f(\omega)$ and $\psi(t)$ with those obtained by computer molecular-dynamics calculations. We will consider a similar comparison for $\langle r^2(t)\rangle$, and also discuss certain physical interpretation of the description.

The physical content of the model is most simply discussed in terms of the dispersion relation of Eq. (2.7). Rewriting it as

$$z^2\chi(z)+z\lambda(z)\chi(z) = -M^{-1}, \quad (2.26)$$

we observe that $z\lambda(z)$ in this case is expressible as

$$z\lambda(z) = \omega_0^2[1/(1-iz\tau_0)-1]. \quad (2.27)$$

Thus Eqs. (2.26) and (2.27) lead to

$$\frac{d^2\chi(t)}{dt^2} - \frac{\omega_0^2}{\tau_0}\int_0^t dt'\,\chi(t')e^{-(t-t')/\tau_0} + \omega_0^2\chi(t) = \frac{1}{M}\delta(t) \quad (2.28)$$

as the equation describing the displacement response to a unit impulsive external force at $t=0$. Equation (2.28) is similar to the generalized Langevin equation discussed by Kubo.[19] It is useful to regard Eq. (2.28) as an equation of motion corresponding to the generalized force

$$F(t) = -\omega_0^2\left[\chi(t) - \frac{1}{\tau_0}\int_0^t dt'\,\chi(t')e^{-(t-t')/\tau_0}\right]. \quad (2.29)$$

For $t\ll\tau_0$, $F(t)\sim\omega_0^2\chi(t)$, whereas for $t\gg\tau_0$ one can show that $F(t)\sim\omega_0^2\tau_0\dot{\chi}(t)$. Therefore, it is clear that the model describes the behavior of $\chi(t)$ as an oscillator

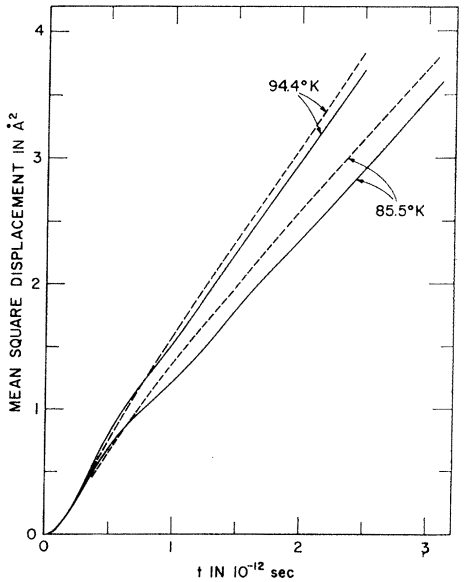

FIG. 2. Comparison of mean-square displacement $\langle r^2(t)\rangle$ as a function of time between the model (solid line) and the computer experiment (dashed line).

with characteristic frequency ω_0 during short times, and as a diffusing particle with friction coefficient $\omega_0^2\tau_0$ at long times. The time constant τ_0 which determines the two types of asymptotic behavior appears in the role of a relaxation time. If we associate the behavior of $\chi(t)$ with the motion of an atom in the liquid, then the present description corresponds to putting the atom in an external parabolic potential which relaxes in time so that eventually the atom experiences only a frictional force.

III. COMPARISON OF MODEL WITH COMPUTER EXPERIMENTS

To determine the utility of the interpolation model and to illustrate the interpretive remarks of Sec. II, we consider a comparison with computer experiments on liquid argon. Machine solutions of Newton's equations of motion for 864 argon atoms have been obtained by Rahman[2,20] and the results used to determine the velocity autocorrelation function $\psi(t)$, its frequency spectrum $f(\omega)$, and the mean-square displacement $\langle r^2(t)\rangle$. Using the $f(\omega)$ given by Rahman at 94.4°K we have obtained the constants ω_0 and τ_0 from Eqs. (2.15), (2.16), and (2.19). Numerical integration gives $\omega_0^2=45\times10^{24}$ sec^{-2}, and combining this with $D=2.43\times10^{-5}$ cm^2/sec we find τ_0 to be 1.78×10^{-13} sec. The comparison of model and computer results for $\psi(t)$ and $f(\omega)$ is shown in Fig. 1. We see that the velocity autocorrelation functions are in good agreement at short times, but the oscillatory behavior in the model $\psi(t)$ is not as heavily damped. The fact that the interpolation description also allows for diffusive motions is more apparent in $f(\omega)$, which has an appreciable value at $\omega=0$. Since we are using the computer value of D, the two frequency spectra are constrained to coincide at the origin. In Fig. 2 we compare the displacement functions at 94.4 and 85.5°K. For the lower temperature the constants are $\omega_0^2=45\times10^{24}$, $D=1.88\times10^{-5}$, and $\tau_0=2.05\times10^{-13}$. The more pronounced discrepancy at 85.5°K suggests that our simple model becomes less valid as the triple point (83.8°K) is approached.

In the analysis of inelastic neutron-scattering experiments one needs to know the scattering function $S_s(\kappa,\omega)$, the space-time Fourier transform of the van Hove self-correlation function $G_s(r,t)$. If one assumes that G_s is a Gaussian distribution in r, then S_s is completely determined in terms of $\psi(t)$ or $\langle r^2(t)\rangle$. Nijboer and Rahman[20] have evaluated S_s for liquid argon at 85.5°K in this approximation using computer results for for $\langle r^2(t)\rangle$. A comparison with model calculations at $\kappa=2$ Å^{-1} is shown in Fig. 3(a). Since the shape of S_s is not a sensitive criterion, we have also examined the variation of the width at half-maximum, $\omega_{1/2}$, as a function of κ. The model and computer results are given in Fig. 3(b). It can be observed that maximum error in the width occurs in the region $\kappa\sim3$ Å^{-1}, where the model gives an underestimate of about 15%. It is somewhat surprising that in this region the model result is actually in better agreement with the width of S_s when non-Gaussian corrections have also been included. To our knowledge this behavior is fortuitous.

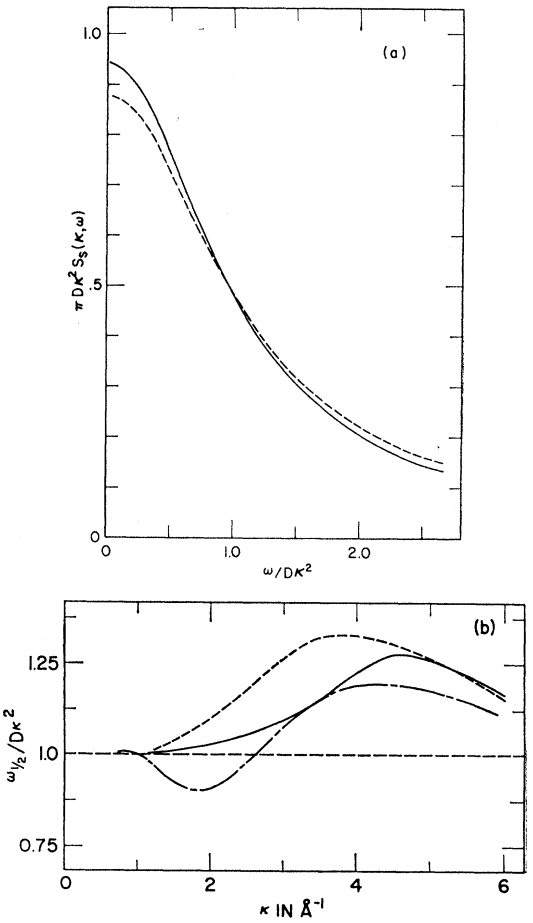

FIG. 3. (a) $\pi D\kappa^2 S_s(\kappa,\omega)$ as a function of $\omega/D\kappa^2$ under Gaussian approximation (GA): model (solid line), computer experiment (dashed line). (b) $(\omega_{1/2}/D\kappa^2)$ as a function of κ: model+GA (solid line), computer experiment+GA (dashed line), computer experiment—non-Gaussian (broken line).

On the basis of the above considerations we may conclude that the simple interpolation model is consistent with general requirements at short and long time, and that the essential features of computer experiments can be reasonably well reproduced. We consider next the application of the model to an analysis of neutron-scattering experiments. In the following two sections we describe the calculation of scattering cross sections and a detailed comparison with recent measurements on liquid argon.

IV. CALCULATION OF NEUTRON-SCATTERING CROSS SECTION

In an inelastic neutron-scattering experiment the quantity directly measured is the double differential

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

cross section

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{k_f}{k_i}e^{-\beta\hbar\omega/2}e^{-\beta\hbar^2\kappa^2/8M}\times[\langle a\rangle^2 S(\kappa,\omega)+(\langle a^2\rangle-\langle a\rangle^2)S_s(\kappa,\omega)], \quad (4.1)$$

where k_i and k_f are initial and final neutron wave numbers, $\hbar\mathbf{k}=\hbar(\mathbf{k}_f-\mathbf{k}_i)$ and $\hbar\omega=\hbar(\omega_f-\omega_i)$ are neutron momentum and energy gains, and M is the mass of the scattering atom. The scattering lengths $\langle a\rangle^2$ and $\langle a^2\rangle$ are averaged quantities whenever there is a distribution of isotopes present. Since the coherent- and incoherent-scattering functions, $S(\kappa,\omega)$ and $S_s(\kappa,\omega)$, will be computed classically, one needs to include the two exponential factors in Eq. (4.1) to take into account recoil effects and to preserve the property of detailed balance.[21] For calculational purposes it is more convenient to consider the intermediate scattering functions, $F(\kappa,t)$ and $F_s(\kappa,t)$, defined by

$$S_s(\kappa,\omega)=\frac{1}{\pi}\int_0^\infty dt\,\cos\omega t F_s(\kappa,t), \quad (4.2)$$

$$S(\kappa,\omega)=\frac{1}{\pi}\int_0^\infty dt\,\cos\omega t F(\kappa,t). \quad (4.3)$$

These functions are in fact the transform of the van Hove density-correlation functions $G(r,t)$ and $G_s(r,t)$.

A practical representation of $F_s(\kappa,t)$ is [20]

$$F_s(\kappa,t)=e^{-\kappa^2\gamma_1(t)}\{1+\alpha_2(t)[\kappa^2\gamma_1(t)]^2/2!-[\alpha_3(t)-3\alpha_2(t)][\kappa^2\gamma_1(t)]^3/3!+[\alpha_4(t)-4\alpha_3(t)+6\alpha_2(t)]\times[\kappa^2\gamma_1(t)]^4/4!-\cdots\}, \quad (4.4a)$$

where

$$\gamma_1(t)=\tfrac{1}{6}\langle r^2(t)\rangle, \quad (4.4b)$$

$$\alpha_n(t)=\langle r^{2n}(t)\rangle/c_n\langle r^2(t)\rangle^n-1, \quad (4.4c)$$

$$c_n=1\times3\times5\times\cdots\times(2n+1)/3^n, \quad (4.4d)$$

$$\langle r^{2n}(t)\rangle=\int_0^\infty r^{2n}G_s(r,t)4\pi r^2dr. \quad (4.4e)$$

The first term in Eq. (4.4a) corresponds to the Gaussian approximation originally proposed by Vineyard. Our result for S_s shown in Fig. 3(a) was obtained in this way. The non-Gaussian corrections, characterized by the $\alpha_n(t)$, have been studied by Rahman for liquid argon.[2] They have also been computed for dilute gases.[22] When the $\alpha_n(t)$ are expressed in terms of a reduced time scale which partly takes into account the density dependence, the dilute-gas results are quantitatively similar to those found for liquid argon. Moreover, it was found that the leading correction, $\frac{1}{2}\alpha_2(t)[\kappa^2\gamma_1(t)]^2$, gives almost all the non-Gaussian effects in S_s. Accordingly, we have devised a procedure for evaluating the time transform in Eqs. (4.2) and (4.3), and this method is described in the Appendix.

It should be noted that our method of computing $S_s(\kappa,\omega)$ preserves the frequency-moment sum rules

$$\bar{\omega}_s{}^n\equiv\int d\omega\,\omega^n S_s(\kappa,\omega) \quad (4.5)$$

for $n\leqslant4$. This is because the non-Gaussian corrections to frequency moments first appear[23] at $n=8$ and because our model $\langle r^2(t)\rangle$ is correct to t^4 at short times.

The calculation of the coherent-scattering function $S(\kappa,\omega)$ for liquids is a difficult and still not satisfactorily resolved problem. A number of phenomenological approaches have been suggested whereby $F(\kappa,t)$ is expressed in terms of $F_s(\kappa,t)$ and the equilibrium pair distribution function $g(r)$. Suppose one writes

$$F(\kappa,t)=F_s(\kappa,t)+\Gamma(\kappa)F_s(\kappa,t'(t)), \quad (4.6)$$

where $\Gamma(\kappa)$ is the Fourier transform of $n[g(r)-1]$, n being the number density. The convolution approximation corresponds to setting $t'(t)=t$.[12] For the DCA, Rahman[2] has suggested the empirical relation

$$t'=t-\tau[1-\exp(-t/\tau)-(t/\tau)^2\exp(-t^2/\tau^2)], \quad (4.7)$$

with $\tau=10^{-12}$ sec for liquid argon at 94.4°K. If one uses instead the expression

$$F(\kappa,t)=[1+\Gamma(\kappa)]\exp\{-\kappa^2\gamma_1(t)/[1+\Gamma(\kappa)]\}, \quad (4.8)$$

one obtains the EMA.[14,15]

The contents of these various prescriptions can be at least partly discussed in terms of frequency-moment sum rules.[24] It is well known that the convolution approximation fails to satisfy the second moment, and therefore does not predict the deGennes narrowing effect.[25] Since the sum rules are essentially the coefficients of time expansion of $F(\kappa,t)$, the requirement that $\bar{\omega}^2$ be preserved is equivalent to the statement that $F_d=F-F_s$ should not contain a term proportional to t^2 in the expansion. This condition is satisfied by EMA without introducing any additional quantity besides $\Gamma(\kappa)$ and $\langle r^2(t)\rangle$. Another interpretation of this condition is that the initial damping of F_d should be slower than that of F_s; consequently, in DCA a delay is introduced through Eq. (4.7), where τ is the delay time. With either EMA or DCA, $\bar{\omega}^4$ is not given correctly,[24] but in the latter approximation τ may be

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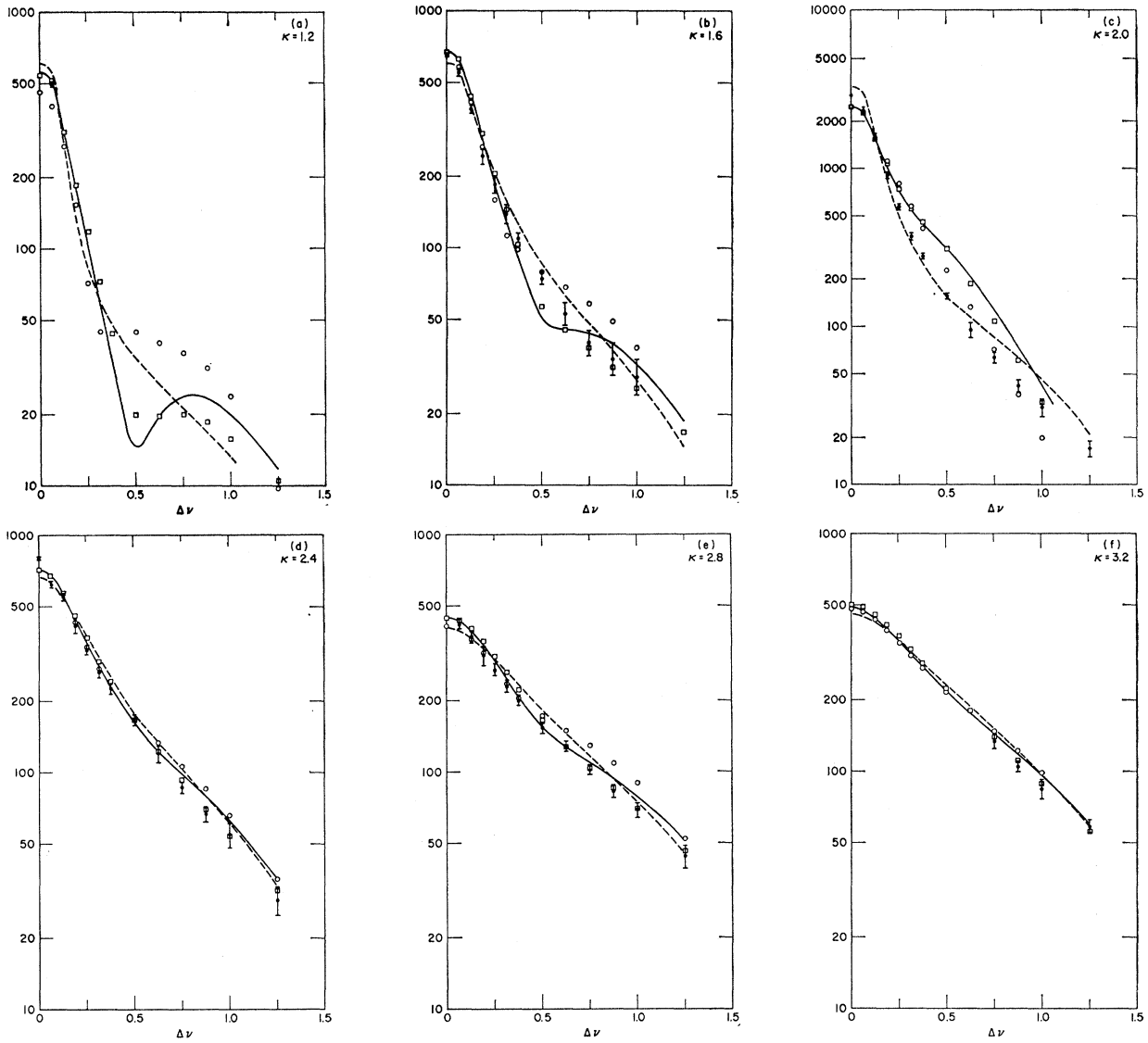

FIG. 4. Neutron-scattering cross section, $J(\kappa,\omega_f)$ in units of 2.2×10^{-40} cm^2/(sr sec^{-1} atom) as a function of $\Delta\nu=(\omega_f-\bar{\omega}_i)/2\pi$, in units of 10^{12} sec^{-1}, for liquid argon at 94.4°K: bar-circle, experiment; solid line, model +DCA($\tau=10^{-12}$ sec); dashed line, model+EMA; ○, Model +DCA($\tau=2\times10^{-12}$ sec); □, computer experiment +DCA($\tau=10^{-12}$ sec). (a) $\kappa=1.2$ Å^{-1}, (b) $\kappa=1.6$ Å^{-1}, (c) $\kappa=2.0$ Å^{-1}, (d) $\kappa=2.4$ Å^{-1}, (e) $\kappa=2.8$ Å^{-1}, (f) $\kappa=3.2$ Å^{-1}. Effects of non-Gaussian corrections and incident spectrum have been included in all the theoretical cross sections.

appropriately chosen to give a reasonable fit to the exact result. This procedure leads to a value of τ twice as large as that suggested by Rahman. Moreover, if τ is allowed to vary with κ, then one can even satisfy $\bar{\omega}^4$ exactly.

The spectra of inelastically scattered neutrons from liquid argon at 94.5°K have been extensively measured by Skold and Larsson.[26] In comparing theoretical results with experiment we first compute $F(\kappa,t)$ from $F_s(\kappa,t)$ using DCA or EMA. Then following the method described in the Appendix we evaluate $S_s(\kappa,\omega)$ and $S(\kappa,\omega)$, and these are inserted into Eq. (4.1) to give the double differential cross section. For scattering lengths we use $\langle a^2\rangle=5.57\times10^{-26}$ cm^2 and $\langle a\rangle^2/\langle a^2\rangle=0.675$, and we take measured[27] values of $\Gamma(\kappa)$ for liquid argon at 84°K ignoring a slight temperature correction. The cross section is then averaged over the experimental incident spectrum (taken from Skold)[14,26] which has its mean at $\bar{\omega}_i=7.38\times10^{12}$ sec^{-1}. The cross sections thus computed are denoted as $J(\kappa,\omega_f)$ and these are the quantities which are compared with measurements in Sec. V. It should be emphasized that the present procedure gives absolute cross sections and requires no normalization of any kind.

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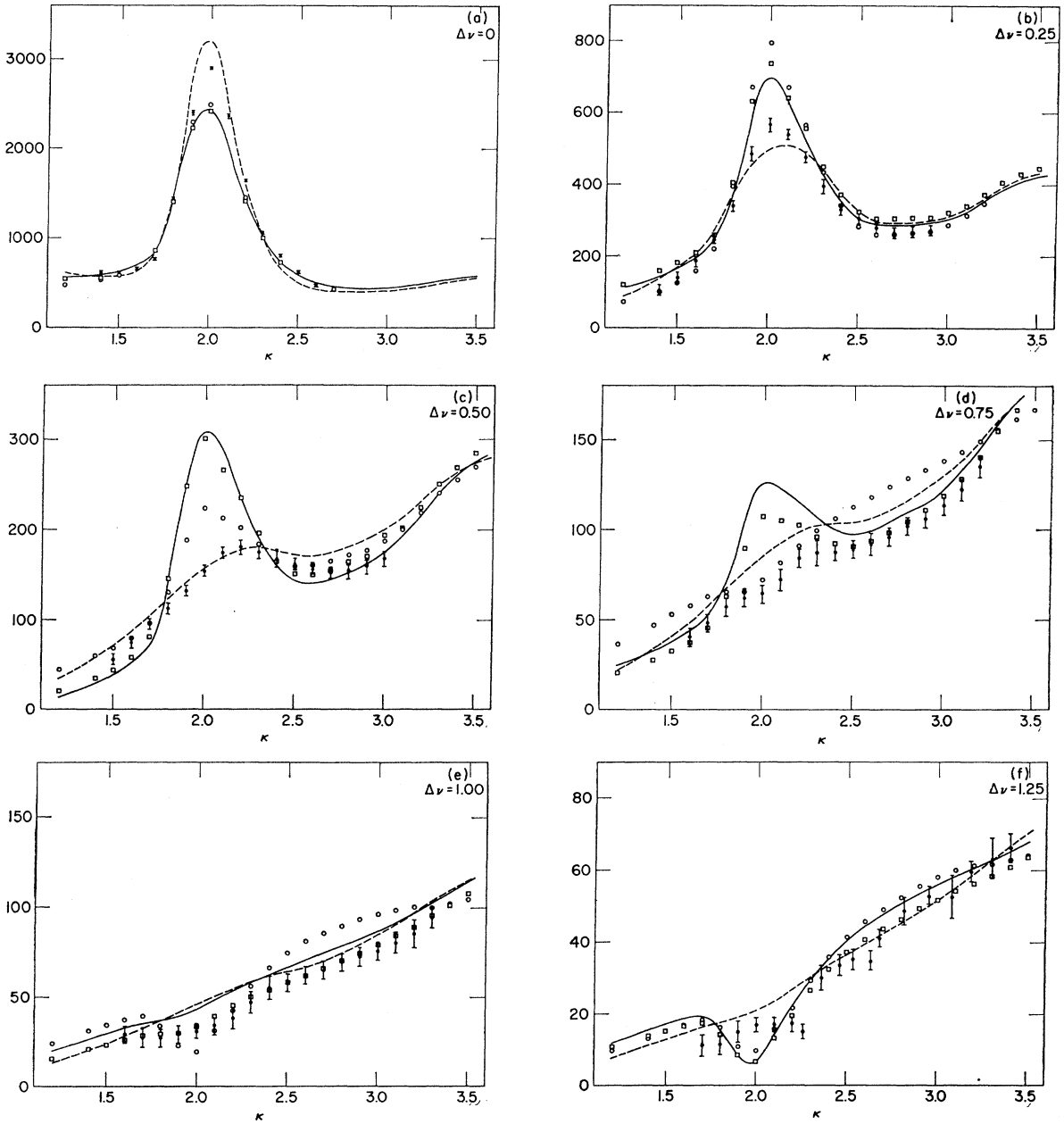

FIG. 5. $J(\kappa,\omega_f)$ as a function of κ. All symbols and units are the same as in Fig. 4. (a) $\Delta\nu=0$, (b) $\Delta\nu=0.25$, (c) $\Delta\nu=0.50$, (d) $\Delta\nu=0.75$, (e) $\Delta\nu=1.00$, (f) $\Delta\nu=1.25$.

V. COMPARISON WITH NEUTRON-SCATTERING EXPERIMENT

The neutron-scattering cross sections of liquid argon measured by Skold and Larsson extend over a considerable range of momentum and energy transfers. To fully analyze these data we consider the variations of the cross section with both κ and ω. In Figs. 4 and 5 the measured and computed spectra are compared. We have used the displacement function $\langle r^2(t)\rangle$ obtained from computer calculations as well as that derived from the interpolation model. The computed cross sections include results based on these $\langle r^2(t)\rangle$ in conjunction with DCA ($\tau=10^{-12}$). In addition, we also show the effects of EMA and DCA ($\tau=2\times10^{-12}$) using the model $\langle r^2(t)\rangle$. In all the calculations displayed in Figs. 4 and 5, non-Gaussian corrections have been taken into account. The variation of the width of $J(\kappa,\omega_f)$ at half-maximum is of interest because of the narrowing behavior first predicted by deGennes. The theoretical and experimental widths are shown in Fig. 6.

On an over-all basis the calculated cross sections using either computer or model $\langle r^2(t)\rangle$ are in reasonable agreement with experiment. In some instances [see Fig. 5(e)] the agreement between measurement and results obtained with computer $\langle r^2(t)\rangle$ and DCA is remarkable. At small and intermediate values of energy transfer and in the region of the first diffraction maximum ($\kappa\sim 2$ Å^{-1}), EMA results are in better agreement than DCA with either τ. Beyond $\kappa\sim 2.3$ Å^{-1}, DCA ($\tau=10^{-12}$) appears to give better results. It is known[16] that DCA ($\tau=10^{-12}$) reproduces the inelastic structure found by Chen *et al.*[28] quite well, whereas EMA seems to give a less pronounced structure. As seen from Fig. 4(a), this structure is also very sensitive to the value of τ in DCA. It is interesting to note that the computed spectra in Fig. 5 always intersect at $\kappa\simeq 1.8$ Å^{-1} and $\kappa\simeq 2.3$ Å^{-1}; these are also the values where the fourth frequency moments, $\bar{\omega}^4$, intersect.[24] In fact, the superiority of EMA over DCA ($\tau=10^{-12}$) in the region $1.8\leqslant\kappa\leqslant 2.3$ is consistent with the fourth-moment behavior; however, the striking improvement in $\bar{\omega}^4$ when $\tau=2\times10^{-12}$ is not evident in the cross sections. The most serious disagreement between DCA calculations and experiment occurs around $\kappa\sim 2$ Å^{-1}. Here and at $\kappa\sim 1.2$ Å^{-1} the results are sensitive to a variation in τ; otherwise the cross sections as well as the half-width shown in Fig. 6 apparently do not change significantly with τ.

We have not explicitly indicated the magnitude of the non-Gaussian corrections. Generally speaking, these are appreciable only in the quasi-elastic region, and even here the qualitative behavior of the cross section is not affected. The contribution of the non-Gaussian terms at $\kappa=2$ Å^{-1} was 10% at $\omega=0$ and 1% at $\omega=3.1\times10^{12}$ sec^{-1}. At larger ω the contribution was noticeable only at large κ, which are beyond the experimental range.

VI. DISCUSSION

In this paper we have presented a detailed analysis of inelastic neutron-scattering measurements on liquid argon. The calculations, which include incoherent and coherent contributions, divide naturally into two distinct parts. The main problem in incoherent scattering is the determination of the velocity autocorrelation function $\psi(t)$ of an atom in the liquid. For this purpose we have proposed a simple interpolation model which is consistent with general requirements and has no free parameters. In the case of liquid argon at 85.5 and 94.5°K the model has been subjected to a thorough test by comparison with computer molecular-dynamics calculations.

The interpolation model is derived from a rigorous correlation-function formalism and follows directly from a single approximation. The assumption of a single relaxation process is hardly new; in different context it was probably first discussed by Maxwell and Drude.[29] More recently, Berne, Boon, and Rice have investigated a memory-function approach to correlation functions. They obtained essentially the same results as our $\psi(t)$ and $f(\omega)$ by assuming an exponentially decaying (in time) memory function. Similar calculations also have been reported by Singwi and Tosi[30] using a Gaussian memory. When the parameters are determined in the same way as in Sec. III, the Gaussian assumption gives qualitatively the same type of results as shown in Fig. 1. However, it has the advantage that it gives finite sum rules whereas with the exponential memory one knows that Eq. (2.12) and all high-order frequency moments diverge. It is of interest to point out that if an exponential or Gaussian form for $\lambda''(\omega)$ is assumed, Eqs. (2.11) and (2.12) can be used to determine the two parameters and one then obtains a "calculation" of D. of course, one may employ a three-parameter description to accomodate the two sum rules and preserve the correct value of D.

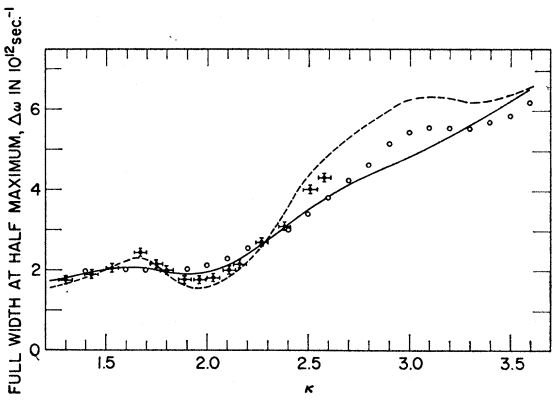

FIG. 6. Full width at half-maximum $\Delta\omega$ of $J(\kappa,\omega_f)$ as a function of κ. All symbols and units are the same as in Fig. 4.

The advantage of the simple interpolation model is that it leads to analytical expressions for $\psi(t)$, $f(\omega)$, and $\langle r^2(t)\rangle$. While these functions have the same basic behavior as the computer results, the extent to which the model is useful depends largely on the intended application. For the purpose of analyzing neutron-scattering spectra, our results indicate that close agreement in $\psi(t)$ or even $\langle r^2(t)\rangle$ between model and computer results may be too stringent a requirement since they are not directly observable. Fig. 3(b) shows that the width at half-maximum of S_s calculated from the model has a maximum error of about 15%. This deviation will be further reduced in an actual experiment when broadening due to incident-spectrum and instrument-resolution effects is considered. Calculations are pres-

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ently underway to apply the model to neutron spectra[31] of liquid argon containing hydrogen as an impurity. In this case, the scattering is dominated by the hydrogen and is therefore mainly incoherent.

The present computation of the coherent-scattering function, $S(\kappa,\omega)$, is based on two empirical prescriptions, DCA and EMA. Both approximations may be viewed as modifications of the convolution approximation, but numerically they could give quite different results. As can be observed from the detailed comparisons shown in Figs. 4 and 5, EMA is clearly superior around $\kappa\sim 2$ Å^{-1}, whereas DCA ($\tau=10^{-12}$) gives slightly better results at larger κ. Deviations between experiment and $J(\kappa,\omega_f)$ obtained with computer $\langle r^2(t)\rangle$ and DCA are most pronounced around $\kappa\sim 2$. These are almost certainly due to the use of DCA, and one should expect improved agreement had EMA been used. In fact, the failure of DCA around the diffraction maximum raises serious questions regarding its value as a general calculational procedure. On the other hand, the simplicity of EMA and the fact that it gives reasonable results over practically the entire range of (κ,ω) considered appear to make this a more attractive procedure for future calculations.

As a final remark we note that a direct study of $G(r,t)$ is needed for a more fundamental understanding of coherent neutron scattering or detailed explanation of computer results on correlation functions. The formalism discussed in Sec. II, which provided a convenient basis for formulating an interpolation description of single-particle motions, should be equally well suited for this problem. Other approaches to compute $G(r,t)$ have been used,[32] but no conclusive results have been obtained.

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APPENDIX

In this Appendix we summarize the procedure which is followed in performing the cosine transforms of Eqs. (4.2) and (4.3). Let us denote, for brevity, the series in Eq. (4.4) by

$$F_s(\kappa,t)=e^{-\kappa^2\gamma_1(t)}(1+A_2-A_3+A_4-\cdots). \quad \text{(A1)}$$

First we approximate

$$F_s(\kappa,t)\approx e^{-\kappa^2\gamma_1(t)}(1+A_2-A_3+\tfrac{1}{2}A_4), \quad \text{(A2)}$$

since $\alpha_n(t)$ are known only for $n=2$, 3, and 4. Next we formally rewrite Eq. (4.2) as

$$\pi S_s(\kappa,\omega)=\sum_{l=1}^{N} I_l(\kappa,\omega)+\int_{NH}^{\infty} dt\,\cos\omega t F_s(\kappa,t), \quad \text{(A3)}$$

where

$$I_l(\kappa,\omega)=\int_{(l-1)H}^{lH} dt\,\cos\omega t F_s(\kappa,t). \quad \text{(A4)}$$

The numerical procedure consists in fitting $F_s(\kappa,t)$ to a function $\{\exp[-(a_l+b_lt)]\}(A_l+B_lt)$ in each interval $(l-1)H\leqslant t\leqslant lH$ and it is assumed that a_l, b_l, A_l, and B_l are constants within the interval. Then

$$I_l(\kappa,\omega)=\left\{\frac{F_s(\kappa,t)(\omega\sin\omega t-b_l\cos\omega t)}{\omega^2+b_l^2}+B_le^{-(a_l+b_lt)}\frac{[(\omega^2-b_l^2)\cos\omega t+2\omega b_l\sin\omega t]}{(\omega^2+b_l^2)^2}\right\}_{t=(l-1)H}^{t=lH}. \quad \text{(A5)}$$

Note that

$$(a_l+b_lt)=\kappa^2\gamma_1(t), \quad \text{(A6)}$$

$$b_l=\kappa^2[\gamma_1(lH)-\gamma_1(H(l-1))]/H, \quad \text{(A7)}$$

and

$$B_l=H^{-1}\{[1+A_2(lH)-A_3(lH)+\tfrac{1}{2}A_4(lH)]-[1+A_2((l-1)H)-A_3((l-1)H)+\tfrac{1}{2}A_4((l-1)H)]\}. \quad \text{(A8)}$$

In order to elucidate the chosen form of integrand in each subinterval $(l-1)H\leqslant t\leqslant lH$, and to evaluate the infinity correction given by the integral from NH to ∞ in Eq. (4.6) we note that for large t, (i) $\gamma_1(t)$ increases linearly with t, and (ii) the terms A_2 and A_3 of Eq. (4.5) are linear functions of time for dilute gases.[33] If we assume that for $NH\leqslant t\leqslant\infty$, a_l, b_l, A_l, and B_l are constants and are same as those found in the interval $(N-1)H\leqslant t\leqslant NH$, we get the value of infinity correction as just the negative of the bracketed expression in Eq. (4.7) evaluated at $t=NH$. In all the numerical work, t was measured in units of 10^{-12} sec, ω in units of 10^{-2} sec^{-1}, κ in units of Å^{-1}, and γ in units of Å^2; N was taken to be 400 and H was chosen to be 0.05. The above procedure was checked for the single relaxation model of Nelkin and Ghatak.[34] For this model, $S_s(\kappa,\omega)$ is analytically known. Agreement between the numerical and analytical answers was found to be very satisfactory.

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