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Single-Particle Motion in Simple Classical Liquids*

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We use the memory-function formalism to investigate $\tilde{G}_s(\vec{k}, \vec{p}, \vec{p}', t)$, the time autocorrelation function for the single-particle density in phase space and $S_s(\vec{k}, w)$, the incoherent scattering function of Van Hove. Following a recent treatment for coherent neutron scattering by Akcasu and Duderstadt, we derive a formally exact equation for $\tilde{G}_s$. If we assume that the relevant memory function is separable and given by $\tilde{\varphi}_s(\vec{k}, \vec{p}, \vec{p}', t) = \tilde{\varphi}_s(\vec{p}, \vec{p}', o)\, \tilde{\Phi}(\vec{k}, t)$, then the equation for $\tilde{G}_s$ reduces to a generalized Fokker-Planck equation which can be exactly solved. We use two simple forms for $\tilde{\Phi}(\vec{k}, t)$, a Gaussian and an exponential, to study the analytical solution both numerically and in various limits. We also compare these results with those obtained in the molecular dynamics computations by Nijboer and Rahman and discuss the extent of validity of the separability assumption for the memory function.

I. INTRODUCTION

Slow-neutron-scattering experiments[1] and more recently the molecular dynamics experiments[2] have renewed the interest in understanding the basic nature of the dynamical correlations in liquids. The Van Hove theory[3] for slow neutron scattering expresses observed cross sections in terms of the dynamical structure factor $S(\vec{k}, w)$ and the single-particle (incoherent) scattering function $S_s(\vec{k}, w)$. The early phenomenological approach using the convolution approximation,[4] as well as more recent mean-field theories and related approaches[5] for calculating $S(\vec{k}, w)$, require the knowledge of $S_s(\vec{k}, w)$.

$S_s(\vec{k}, w)$ as well as $\Psi(t)$ the normalized velocity autocorrelation function describe the single-particle correlations which are of central interest in the present work. Both $S_s(\vec{k}, w)$ and $\Psi(t)$ can be deduced from slow-neutron-scattering experiments on purely incoherent scatterers and also, after some analysis, from similar experiments on substances like argon[6] and sodium which are mixed coherent and incoherent scatterers. However, a cleaner and more direct "measurement" of these functions has been obtained by their computation in the molecular-dynamics studies[2,7] where the conditions for the state of the system, as well as the basic interaction, are under direct control.

Most calculations of $S_s(\vec{k}, w)$ use some physical model which prescribes $\Psi(t)$, and hence the mean-square displacement $\langle r^2(t)\rangle$ for the particle; from $\langle r^2(t)\rangle$, $S_s(\vec{k}, w)$ is deduced by using the phenomenological Gaussian approximation.[4] Such a procedure is accurate about 10–15%. The molecular-dynamics experiments of Rahman[2] have given some guidance about the corrections to the Gaussian approximation for liquid argon. Moreover, in a dilute gas, where one has a kinetic equation (Boltzmann equation) available, calculations have been performed[8–10] to evaluate these corrections. When such a gas model is extended to liquid densities, the non-Gaussian corrections look quantitatively similar[10] to those obtained by Rahman.[2] It is thus possible to do a calculation[11] of $S_s(\vec{k}, w)$ with some confidence for a liquid. However a better microscopic understanding of the Gaussian approximation, of the non-Gaussian corrections, and of the detailed behavior of single-particle correlations in the transition region between the ideal gas and hydrodynamic limits is desirable and is still lacking for a liquid.

In the last few years, a number of studies[11–18] have been made which attempt to calculate the velocity-autocorrelation function from first principles. Some of these studies have used the memory function approach of Zwanzig[19] and Mori.[20]

In this paper, we use the memory-function approach to study $S_s(\vec{k}, w)$ and compare the results with those obtained in the molecular-dynamics experiment of Nijboer and Rahman.[7] Akcasu and Duderstadt[21,22] have used this approach to calculate $S(\vec{k}, w)$ and longitudinal as well as transverse current correlation functions, and have compared their results with the molecular-dynamics results of Rahman[23] for liquid argon. Their procedure[21] can be trivially extended to derive a formally exact equation for the evolution of the (Fourier component of) single-particle density in phase space denoted here by $\delta g_k(\vec{p}, t)$. In Sec. II we write this equation and discuss its consequences. We then consider an approximate equation obtained by making a separability assumption [Eq. (7)] for the memory function. The approximate equation which is analogous to the usual Fokker-Planck equation, is solved in Sec. III to give analytical result for $S_s(\vec{k}, w)$.

The resulting expression for $S_s(\vec{k}, w)$ offers a clean way of assessing the extent of validity of the separability assumption for the memory function. In Sec. IV, we use two simple forms for the memory function which are generalizations of the forms used by Berne, Boon, and Rice[12] and by Singwi and

Tosi[13] for evaluating the velocity autocorrelation function. We then show the numerical results obtained by using these functions and compare them with those obtained by Nijboer and Rahman.[7]

The modeled kinetic equation [Eq. (8)] which results from the separability assumption is very similar to the kinetic equation obtained by Lebowitz, Percus, and Sykes[24] (LPS), who use a different approach starting from Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy equations. The approximation made in their Eq. (8.1) is analogous to the separability assumption and their resulting Eq. (8.6) is analogous to our Eq. (8); the crucial difference is that the friction coefficient $\omega_0^2\,\Phi(\vec{k},\epsilon)$ in Eq. (8) depends not only on frequency but also on wave vector. From the numerical results presented in Sec. IV, we find that the wave-vector dependence in the friction coefficient is essential in obtaining the liquidlike behavior for $S_s(\vec{k},w)$; if in the modeled kinetic equation one uses a friction coefficient which is only frequency dependent, a gaslike behavior results.

LPS have also solved their modeled kinetic equation using Fourier transforms in momentum and have expressed the solution in a closed form [see their Eq. (8.16)]. The first form of their solution can be shown, by expanding e^{-x}, to be identical to the infinite-series form of our solution [Eq. (37)]. For the discussion given in Sec. III, the infinite-series form is more convenient; moreover, the series is rapidly convergent for most (k,w) values of interest and is thus not inconvenient in the numerical study given in Sec. IV.

After this work was submitted for publication, we received a preprint by Akcasu, Corngold, and Duderstadt[25] in which their earlier work[21,22,26] is extended to the calculation of $S_s(\vec{k},w)$ via generalized hydrodynamic[26] and kinetic[21,22] approaches. They find (see Ref. 25, Figs. 3 and 4) that among the two approaches, the kinetic approach (used also in this work) gives better agreement with the molecular-dynamics results. The work presented here partially overlaps with their results from the kinetic approach; they have used an exponential form for the memory function, whereas we investigate both the exponential and Gaussian forms and also present an analysis for the frequency moments of $S_s(\vec{k},w)$.

II. EVOLUTION OF SINGLE-PARTICLE DENSITY IN PHASE SPACE

In this section we study the evolution of the single-particle phase-space density $\delta g_k(\vec{p},t)$ via the generalized Langevin equation[20] (GLE). Akcasu and Duderstadt[21,22] (AD) have recently applied the GLE to the evolution of the total phase-space density and have evaluated the corresponding time-correlation functions appropriate for describing the collective behavior of the fluid as measured, for example, in the coherent slow-neutron-scattering experiments and simulated in the molecular-dynamics experiments. The analysis of AD can be trivially extended to derive the formally exact GLE for our case. The continuous set of dynamical variables considered here is $\delta g_k(\vec{p},t)$ defined[27] as

$$\delta g_k(\vec{p},t)=e^{i\vec{k}\cdot\vec{r}_1(t)}\,\delta(\vec{p}-\vec{p}_1(t))\,, \tag{1}$$

where $\vec{r}_1(t)$, $\vec{p}_1(t)$ are the position and momentum (at time t) of the test particle whose evolution we wish to follow. It is easy to show, following an analysis similar to that of AD, that $\delta g_k(\vec{p},t)$ satisfies the GLE

$$\left(\frac{\partial}{\partial t}-\frac{i\vec{k}\cdot\vec{p}}{m}\right)\delta g_k(\vec{p},t)+\int_0^t d\tau\int d\vec{p}\,'\;\tilde{\varphi}\,(\vec{k},\vec{p},\vec{p}\,',\tau)\times\;\delta g_k(\vec{p}\,',t-\tau)=f_k(\vec{p},t), \tag{2}$$

where the random force $f_k(\vec{p},t)$ propagates in time via the thermal propagator[20] and is explicitly given by

$$f_k(\vec{p},t)=e^{it(1-P)L}\left(e^{i\vec{k}\cdot\vec{r}_1}\,\vec{F}_1\cdot\frac{\partial}{\partial\vec{p}_1}\;\delta(\vec{p}-\vec{p}_1)\right)\,, \tag{3}$$

and the memory function $\tilde{\varphi}\,(\vec{k},\vec{p},\vec{p}\,',\tau)$ is given by

$$\tilde{\varphi}\,(\vec{k},\vec{p},\vec{p}\,',\tau)=\langle f_k^*(\vec{p}\,',0)\,f_k(\vec{p},\tau)\rangle/M(p'). \tag{4}$$

In Eqs. (3) and (4), L is the Liouville operator for the one-component system of N identical particles for mass m enclosed in volume V and interacting classically via pairwise interaction $u(r)$; P is the projection operator explicitly defined by AD; $\vec{F}_1$ is the total force on the test particle; $\langle\cdots\rangle$ is the canonical ensemble average, and $M(p')$ the equilibrium Maxwellian distribution normalized to unity. It is interesting to note that initially the memory function is independent of $\vec{k}$ and is given by

$$\tilde{\varphi}\,(\vec{k},\vec{p},\vec{p}\,',0)\equiv\tilde{\varphi}\,(\vec{p},\vec{p}\,',0)=\omega_0^2\,M(p)\times\left(\vec{p}\cdot\frac{\partial}{\partial\vec{p}}-\frac{m}{\beta}\,\frac{\partial}{\partial\vec{p}}\cdot\frac{\partial}{\partial\vec{p}}\right)\frac{\delta(\vec{p}\,'-\vec{p})}{M(p')}\;, \tag{5}$$

where $\beta=1/k_B T$ is the inverse temperature in energy units and ω_0^2 is related to the mean-square force on the test particle as $\omega_0^2=(N-1)\langle\nabla^2 u\rangle/(3m)$.

The time correlation function appropriate for studying the various properties related to the single-particle motion in liquids is

$$\tilde{G}_s(\vec{k},\vec{p},\vec{p}\,'',t)=\langle\delta g_k(\vec{p},t)\;\delta g_k^*(\vec{p}\,'',0)\rangle.$$

Its inverse Fourier transform $\overline{G}_s(\vec{r},\vec{p},\vec{p}\,'',t)$ is the conditional probability that at time t the test particle will be at the phase point $(\vec{r},\vec{p})$, given that initially it was at $(0,\vec{p}\,'')$. $\overline{G}_s(\vec{r},\vec{p},\vec{p}\,'',t)$, when integrated over $\vec{p},\vec{p}\,''$, becomes identical to the Van Hove correlation function,[3] $G_s(\vec{r}, t)$. Now since the random force $f_k(\vec{p}, t)$ is orthogonal to $\delta g_k(\vec{p}'', 0)$ at all times, and since initially $\tilde{G}_s(\vec{k}, \vec{p}, \vec{p}'', t)$ has the value. $M(p)\,\delta(\vec{p}-\vec{p}'')$, the Laplace transformed function

$$G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon) \equiv \int_0^\infty dt\, e^{-\epsilon t}\, \tilde{G}_s(\vec{k}, \vec{p}, \vec{p}'', t)$$

satisfies the equation

$$\left(\epsilon - \frac{i\vec{k}\cdot\vec{p}}{m}\right) G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon) = M(p)\,\delta(\vec{p}-\vec{p}'') - \int d\vec{p}'\, \varphi(\vec{k}, \vec{p}, \vec{p}', \epsilon)\, G_s(\vec{k}, \vec{p}', \vec{p}'', \epsilon). \tag{6}$$

While applying the memory-function formalism to the collective motion in liquids, Rahman and co-workers[28] as well as Akcasu and co-workers[22,26] found it convenient to use a model description for the appropriate memory functions. We shall follow here a similar procedure and make the assumption of separability that

$$\tilde{\varphi}(\vec{k}, \vec{p}, \vec{p}', \tau) = \tilde{\varphi}(\vec{p}, \vec{p}', 0)\, \tilde{\Phi}(\vec{k}, \tau). \tag{7}$$

This approximation implies that the random force correlation in Eq. (4) decays at the same rate regardless of the initial and final momenta of the test particle. We expect that such an approximation would be reasonably good if we are interested in the low-order momentum moments of the correlation function $G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon)$, but it will not be particularly appropriate if we are interested in the detailed behavior of $G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon)$ in the momentum space. Using Eq. (5), the approximation in Eq. (7) reduces Eq. (6) to

$$\{\epsilon - [i\vec{k}\cdot\vec{p}/m + m\omega_0^2\, \Phi(\vec{k}, \epsilon)\, \Omega(\vec{p})]\}\, G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon) = M(p)\,\delta(\vec{p}-\vec{p}''), \tag{8}$$

where

$$\Omega(\vec{p}) = \frac{\partial}{\partial\vec{p}}\cdot\left(\frac{1}{\beta}\frac{\partial}{\partial\vec{p}} + \frac{1}{m}\vec{p}\right), \tag{9}$$

is the well-known Fokker-Planck operator. Thus Eq. (8) is similar to the Fourier-Laplace transform of the usual Fokker-Planck equation[29] with the difference that the friction coefficient $m\omega_0^2\Phi(\vec{k}, \epsilon)$ in Eq. (8) depends on both $\vec{k}$ and ϵ.

Two limiting situations clearly emerge from Eq. (8). In the absence of any interactions, $\Phi(\vec{k}, \epsilon)$ is zero and Eq. (8) reduces to the correct ideal-gas description. For a dilute and weakly interacting gas, the memory function $\tilde{\Phi}(\vec{k}, \tau)$ can be approximated by a δ function in time so that $\Phi(\vec{k}, \epsilon)$ is exactly 1. In this limit, Eq. (8) reduces to the usual Fokker-Planck equation. This result is consistent with the fact that in the limit of weak interactions, the dilute-gas Boltzmann equation reduces to the ordinary Fokker-Planck equation. This description is also equivalent to the model in which $\langle r^2(t)\rangle$ is obtained from the ordinary Langevin equation and the Gaussian approximation of Vineyard[4] used to obtain $S_s(\vec{k}, w)$. Such a model was used by Singwi and Sjolander[30] and our solution for $G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon)$ in this limit is consistent with their result. It is interesting to note that for a dilute gas the weak-interaction limit implies the neglect of the non-Gaussian corrections in calculating $S_s(\vec{k}, w)$.

In Sec. III, we discuss the analytical solution of Eq. (8). The solution enables us to study the extent of validity of the separability assumption in Eq. (7) in a rather clean way by comparing the results of the molecular-dynamics experiments[7] for liquid argon with the results derived from Eq. (8).

III. GENERALIZED FOKKER-PLACK EQUATION AND $S_s(\vec{k}, \omega)$

$S_s(\vec{k}, w)$, the double Fourier transform of Van Hove's $G_s(\vec{r}, t)$, is related to $G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon)$ as

$$S_s(\vec{k}, w) = (1/\pi) \lim_{\eta\to 0^+} \mathrm{Re}\, S_s\ (\vec{k}, \epsilon = iw + \eta), \tag{10}$$

where

$$S_s(\vec{k}, \epsilon) = \int d\vec{p}'' \int d\vec{p}\, G_s(\vec{k}, \vec{p}, \vec{p}'', \epsilon), \tag{11}$$

$$S_s(\vec{k}, \epsilon) \equiv \int_{-\infty}^{\infty} dp_z\, Y_s(k, p_z, \epsilon), \tag{12}$$

and Z axis is chosen to be in the direction of $\vec{k}$. Because of their connection with the velocity autocorrelation function $\Psi(t) \equiv \langle\vec{p}_1(0)\cdot\vec{p}_1(t)\rangle/\langle p_1^2\rangle$, longitudinal and transverse single-particle current-correlation functions are also of some interest. These are, respectively, defined as

$$\tilde{J}_{s\parallel}(k, t) = \frac{\beta}{m}\langle p_{1z}(0)\, e^{-i\vec{k}\cdot\vec{r}_1(0)}\, p_{1z}(t)\, e^{i\vec{k}\cdot\vec{r}_1(t)}\rangle, \tag{13}$$

$$J_{s\parallel}(k, t) = \frac{\beta}{m}\int d\vec{p}'' \int d\vec{p}\, p_z''\, p_z\, \tilde{G}_s(\vec{k}, \vec{p}, \vec{p}'', t), \tag{14}$$

$$J_{s\parallel}(k, t) \equiv \frac{\beta}{m}\int_{-\infty}^{\infty} dp_z\, p_z\, \tilde{V}_s(k, p_z, t) \tag{15}$$

and

$$\tilde{J}_{s\perp}(k, t) = \beta/m\,\langle p_{1x}(0)\, e^{-i\vec{k}\cdot\vec{r}_1(0)}\, p_{1x}(t)\, e^{i\vec{k}\cdot\vec{r}_1(t)}\rangle, \tag{16}$$

$$\tilde{J}_{s\perp}(k, t) = \frac{\beta}{m}\int d\vec{p}'' \int d\vec{p}\, p_x''\, p_x\, \tilde{G}_s(\vec{k}, \vec{p}, \vec{p}'', t), \tag{17}$$

$$\tilde{J}_{s\perp}(k, t) \equiv \int_{-\infty}^{\infty} dp_z\, \tilde{X}_s(k, p_z, t). \tag{18}$$

In the limit $k \to 0$, both $\tilde{J}_{s\parallel}$ and $\tilde{J}_{s\perp}$ reduce to $\Psi(t)$. However, for nonzero k they satisfy different equations and are, in general, different. It can be shown that the longitudinal current correlation function is related to $S_s(\vec{k}, w)$ as

$$J_{s\parallel}(k, w) = \pi m\beta w^2 S_s(k, w)/k^2, \tag{19}$$

where

$$J_{s\parallel}(k,w)=\lim_{\eta\to0^+}\operatorname{Re}J_{s\parallel}\;(k,\epsilon=iw+\eta). \tag{20}$$

Starting from Eq. (8) and using the definitions in Eqs. (12), (15), and (18), it is seen that Y_s, V_s, and X_s satisfy the following equations:

$$[\epsilon-ikp_z/m-m\omega_0^2\,\Phi(k,\epsilon)\,\Omega\;(p_z)]$$

$$\times\;Y_s(k,p_z,\epsilon)=M(p_z), \tag{21}$$

$$[\epsilon-ikp_z/m-m\omega_0^2\,\Phi(k,\epsilon)\,\Omega\;(p_z)]$$

$$\times\;V_s(k,p_z,\epsilon)=p_zM(p_z), \tag{22}$$

and

$$[\epsilon-ikp_z/m-m\omega_0^2\,\Phi(k,\epsilon)\,\Omega_1(p_z)]$$

$$\times\;X_s(k,p_z,\epsilon)=M(p_z), \tag{23}$$

where $\Omega(p_z)$ is the one-dimensional analog of the three-dimensional Fokker-Planck operator defined in Eq. (9) and

$$\Omega_1(p_z)=\left(\frac{1}{\beta}\frac{\partial^2}{\partial p_z^2}+\frac{1}{m}p_z\,\frac{\partial}{\partial p_z}\right). \tag{24}$$

In the $k\to0$ limit, starting from either Eq. (22) or Eq. (23), we can show after integration with respect to p_z that $\Psi(\epsilon)$ is given by

$$\Psi(\epsilon)=[\epsilon+\omega_0^2\,\Phi\;(k=0,\epsilon)]^{-1}, \tag{25}$$

which is identical to the exact form derived by Berne, Boon, and Rice.[12] Thus, $\omega_0^2\Phi(0,\epsilon)$ is the memory function for which various simple forms[12,13] have been tried and which is also numerically available from the molecular-dynamics experiments.[17,31] Moreover, it has recently been a subject of some first principles studies.[14–18] We note that Eq. (25) has also been obtained by Lebowitz *et al.* [see Ref. 24, Eq. (8.13)].

In what follows we restrict ourselves to $Y_s(k,p_z,\epsilon)$ and $V_s(k,p_z,\epsilon)$ although Eqs. (8) and (21)–(23) can be solved along similar lines. The solutions of Eqs. (21) and (22) are found by constructing the eigenvalues and eigenfunctions of the non-Hermitian operator

$$\mathcal{O}(p_z)\equiv[ikp_z/m+m\omega_0^2\,\Phi\;(k,\epsilon)\;\Omega\;(p_z)]\;. \tag{26}$$

Treating k, ϵ as parameters, the solution can be found by following a procedure identical to that used by Resibois[32] with the result

$$\mathcal{O}(p_z)\;\Psi_n(k,\epsilon,p_z)=\Lambda_n(k,\epsilon)\;\Psi_n(k,\epsilon,p_z), \tag{27}$$

where

$$\Lambda_n(k\epsilon)=-(n+X)/D_{k\epsilon}\,,\quad n=0,1,2,\ldots, \tag{28}$$

$$\Psi_n(k,\epsilon,p_z)=H_n(u-i\,(2X)^{1/2})\;e^{-[u-i\;(X/2)^{1/2}]^2}, \tag{29}$$

with

$$X=(k\,D_{k\epsilon})^2/(\beta m), \tag{30}$$

$$U=(\beta/2m)^{1/2}\,p_z\,, \tag{31}$$

$$D_{k\epsilon}=[\omega_0^2\,\Phi\;(k,\epsilon)]^{-1}, \tag{32}$$

and where $H_n(Z)$ are the Hermite polynomials. Using these results, it is easy to show that the solution to Eq. (21) is given by

$$Y_s(k,p_z,\epsilon)=\sum_{n=0}^{\infty}\;Y_n(k,\epsilon)\;\Psi_n(k,\epsilon,p_z), \tag{33}$$

where

$$Y_n(k,\epsilon)=C_n(k,\epsilon)/[\epsilon-\Lambda_n(k,\epsilon)], \tag{34}$$

and

$$C_n(k,\epsilon)=\frac{\beta}{2\pi m}\,\frac{1}{2^n n!}\;e^X\int_{-\infty}^{\infty}d\,p_z\;\Psi_n(k,\epsilon,p_z), \tag{35}$$

$$C_n(k,\epsilon)\equiv\left(\frac{\beta}{2\pi m}\right)^{1/2}\frac{(-i)^n}{2^n n!}\;e^X\,(2X)^{n/2}. \tag{36}$$

The above solution for $Y_s(k,p_z,\epsilon)$, taking Eq. (12) into account, implies that

$$S_s(k,\epsilon)=e^X\sum_{n=0}^{\infty}\frac{(-X)^n}{n!}\;\frac{1}{\epsilon-\Lambda_n(k,\epsilon)}\;. \tag{37}$$

Similar analysis for Eq. (22) leads to the result that

$$J_{s\parallel}(k,\epsilon)=\epsilon\,D_{k\epsilon}\;e^X\sum_{n=0}^{\infty}\frac{(-X)^n}{n!}\;\frac{(1+n/X)}{\epsilon-\Lambda_n(k,\epsilon)}\;, \tag{38}$$

which is consistent with the expected relation

$$J_{s\parallel}(k,\epsilon)=\beta m\epsilon\,[1-S_s(k,\epsilon)]/k^2. \tag{39}$$

Solutions for $S_s(\vec{k},\epsilon)$, $J_{s\parallel}(\vec{k},\epsilon)$, and $J_{s\perp}(\vec{k},\epsilon)$ have also been obtained by Lebowitz, Percus, and Sykes in Sec. VIII of their paper.[24]

When $\Phi(k,\epsilon)$ and $D_{k\epsilon}$ are replaced by constant values, the exact result in Eq. (37) reduces to the previously known[8,30] Langevin equation result for $S_s(k,w)$. Also, if in Eq. (37) one replaces all the eigenvalues by the smallest magnitude eigenvalue $\Lambda_0(k,\epsilon)$, then one gets the simple result

$$S_s(k,\epsilon)=(\epsilon+k^2\,D_{k\epsilon}/\beta m)^{-1}\;, \tag{40}$$

which gives

$$S_s(k,w)=\frac{1}{\pi}\;\frac{[D'(k,w)\,k^2]}{[D'(k,w)\,k^2]^2+[w+D''(k,w)\,k^2]^2}\;, \tag{41}$$

where we have defined the real functions D' and D'' as

$$D_{k\epsilon}\xrightarrow[\epsilon\to iw+0^+]{}\beta m\;[D'(k,w)+i\,D''(k,w)]\;. \tag{42}$$

In the hydrodynamic limit, one expects Λ_0 to be the dominant eigenvalue; also $D'(k,w)$ would approach the self-diffusion coefficient D_0, and $D''(k,w)$ would go to zero, giving the well-known[4] hydrodynamic form for $S_s(k,w)$.

Recently, Chung and Yip[33] have used the generalized hydrodynamic approach on the basis of Martin's formalism[34] to write down various correlation functions. Their form of $S_s(k,w)$ is the same as that in Eq. (40). Thus, within the present framework of the memory-function formalism with the approximation in Eq. (7), the Chung-Yip study ignores the distribution of eigenvalues $\Lambda_n(k,\epsilon)$. For the range of k,w encountered in the incoherent-neutron-scattering experiments and used in the molecular-dynamics studies, the absolute magnitude of X is of the order of 10^{-2}– 10^{-1}. Thus, we can see from Eqs. (28) and (37) that the relative importance of $\Lambda_n(k,\epsilon)$, $n\neq 0$, may not be great.

It is also of interest to note that Eq. (38) reduces to Eq. (25) in the limit $k=0$; only the $n=1$ term in Eq. (38) survives in this limit.

To conclude this section, we consider the frequency moments of $S_s(k,w)$. [For the remaining part of this section, $\langle\cdots\rangle$ denotes an average over $S_s(k,w)$.] These moments have been calculated exactly by many authors.[7] For a classical fluid, all odd-order frequency moments vanish and the first few even moments are given as

$$\langle w^0\rangle = 1, \tag{42a}$$

$$\langle w^2\rangle = (kv_0)^2\ , \tag{42b}$$

$$\langle w^4\rangle = 3(kv_0)^4 + \omega_0^2(kv_0)^2\ , \tag{42c}$$

$$\langle w^6\rangle = 15\,(kv_0)^4\,[(kv_0)^2+\omega_0^2] + B\,(kv_0)^2\ , \tag{42d}$$

where $v_0^2=(\beta m)^{-1}$, ω_0^2 is defined previously, and B is $\langle \dddot{X}_1(0)^2\rangle/\langle \dot{X}_1(0)^2\rangle$ as given by Nijboer and Rahman.[35] For liquid argon at 85.5 °K, they estimate that ω_0^2 is about 45×10^{24} sec^{-2} and B is about $[4!\times277\times10^{48}]$ sec^{-4}. For the description given by Eq. (8) or equivalently by Eq. (21) or Eq. (37), we have evaluated the first six frequency moments. For an arbitrary $\tilde{\Phi}(k,\tau)$, the description gives $\langle w^n\rangle$ correctly for $n\leqslant 4$, provided $\tilde{\Phi}(k,0)=1$. If we define $\Phi^{(n)}(k)$ by the small time expansion

$$\tilde{\Phi}(k,\tau) = 1 + \sum_{n=1}^{\infty}\Phi^{(n)}(k)\frac{\tau^n}{n!}\ , \tag{43}$$

then

$$\langle w^5(k)\rangle = -i\,(kv_0)^2\,\omega_0^2\,\Phi^{(1)}(k), \tag{44}$$

and

$$\langle w^6(k)\rangle = 15\,(kv_0)^6 + 10\,(kv_0)^4\,\omega_0^2 + (kv_0)^2\,\omega_0^2\,[\omega_0^2 - \Phi^{(2)}(k)]\ . \tag{45}$$

Thus one way of satisfying the first six moments of $S_s(k,w)$ is to choose such a function $\tilde{\Phi}(k,\tau)$ in Eq. (7) that

$$\Phi^{(1)}(k) = 0, \tag{46a}$$

and

$$\Phi^{(2)}(k) = [5\,(kv_0)^2 + B/\omega_0^2 - \omega_0^2]\ . \tag{46b}$$

In the Sec. IV, we show the results of the numerical study for $S_s(k,w)$ from Eq. (37) and compare them with the molecular dynamics results of Nijboer and Rahman.[7]

IV. RESULTS AND DISCUSSION OF THE NUMERICAL STUDY FOR $S_s(\vec{k},\omega)$

The molecular-dynamics experiment with which we compare our results is the one reported by Nijboer and Rahman[7] (NR). It simulates liquid argon at 85.5 °K with a density of 1.407 g cm^{-3} with exp(−6) potential. Thus in all our calculations we use a value of 0.188×10^{-4} cm^2/sec for D_0 (the self-diffusion coefficient) and a value of 45×10^{24} sec^{-2} for ω_0^2 (the frequency related to the mean-square force).

Using Eqs. (10), (37), (42), (28), and (30) we have

$$S_s(\vec{\mathrm{k}},w) = (\pi v_0^2)^{-1}\exp\left[\left(\frac{k}{v_0}\right)^2(D'^2 - D''^2)\right] \times\sum_{n=0}^{\infty}\frac{(-1)^n S_n(k,w)}{n!}\ , \tag{47a}$$

where

$$S_n(k,w) = (k/v_0)^{2n}\,(D'^2+D''^2)^{n+1/2} \times\cos\,[\theta-\xi_n+(2n+1)\,\gamma]/(A_n^2+B^2)^{1/2} \tag{47b}$$

with

$$\gamma = \arctan\,[D''(k,w)/D'(k,w)]\ , \tag{48a}$$

$$\theta = 2\,(k/v_0)^2\,D'(k,w)\,D''(k,w), \tag{48b}$$

$$\xi_n = \arctan\,(B/A_n)\ , \tag{48c}$$

$$A_n = n - w\,D''/v_0^2 + (k/v_0)^2\,(D'^2 - D''^2)\ , \tag{48d}$$

and

$$B = D'\,\frac{[w+2(k/v_0)^2D'']}{v_0^2}\ . \tag{48e}$$

We have used this analytical form to calculate $S_s(k,w)$, $S_s(k,0)$, and $w_{1/2}(k)$, the half-width of $S_s(k,w)$, under various conditions. In all the cases $S_s(k,w)$ is a monotonically decreasing function of w as expected. Thus most of the information is revealed by examining the two dimensionless functions $[w_{1/2}(k)/D_0k^2]$ and $[\pi D_0k^2S_s(k,0)]$. For the case of a diffusing atom both these functions (labeled SD in all the figures) are unity for all values of k; whereas for an ideal gas, the former decreases as $1/k$ and the latter increases linearly as k.

NR have computed the half-width $w_{1/2}(k)$ of $S_s(k,w)$ and also the half-width of $S_s^G(k,w)$, which is $S_s(k,w)$, under the Gaussian approximation. We reproduce

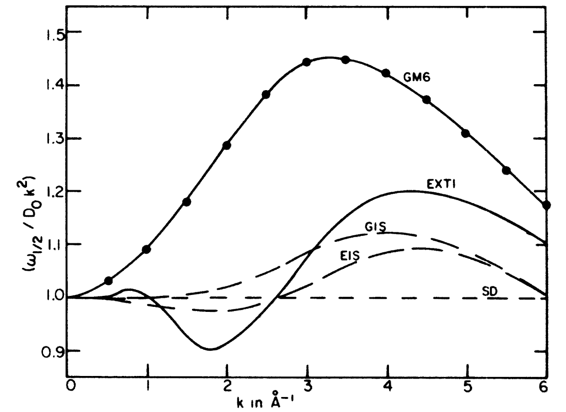

FIG. 1. The half-width function $w_{1/2}/D_0k^2$ versus k for the full non-Gaussian $S_s(k, w)$. EXT 1 – molecular-dynamics results of NR; GM6 – Φ_{Gauss} with $\tau_1(k)$ determined from the exact sixth frequency moment of $S_s(k, w)$; G1S – Φ_{Gauss} with $\tau_1(k)$ determined from $S_s(k, 0)$ of NR; E1S – Φ_{exp} with $\tau_2(k)$ determined from $S_s(k, 0)$ of NR; SD – simple diffusion.

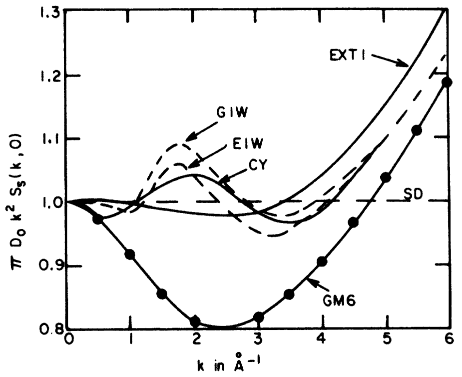

FIG. 3. The zero-frequency function $\pi D_0k^2S_s(k, 0)$ versus k for the full non-Gaussian calculation. EXT 1, GM6, and SD same as in Fig. 1; G1W – Φ_{Gauss} with $\tau_1(k)$ determined from $w_{1/2}(k)$ of EXT 1 in Fig. 1; E1W – Φ_{exp} with $\tau_2(k)$ determined from $w_{1/2}(k)$ of EXT 1 in Fig. 1; CY – using Eqs. (4.6) and (4.16) and $\tau(k)$ in curve C of Fig. (4.2) in the work of Chung and Yip (Ref. 33).

the former half-width in Fig. 1 (labeled EXT 1) and the latter one in Fig. 2 (labeled EXT 2). The characteristic features of the half-width are the minimum around $k = 1.8$ Å^{-1} in the EXT 1 curve and the maxima around $k = 4$ Å^{-1} in both EXT 1 and EXT 2 curves. Since $S_s(k, 0)$ values have not been given by NR, we have computed them numerically from the relation[7]

$$S_s(k,w) = \frac{1}{\pi}\int_0^\infty dt\cos(wt)\, F_s(k,t), \tag{49a}$$

where

$$F_s(k,t) = \exp(-y)\{1 + \alpha_2(t)(y^2/2!) - [\alpha_3(t) - 3\alpha_2(t)](y^3/3!) + [\alpha_4(t) - 4\alpha_3(t) + 6\alpha_2(t)](y^4/4!) - \cdots\}\ , \tag{49b}$$

with

$$y = \tfrac{1}{6}k^2\langle r^2(t)\rangle\ , \tag{49c}$$

$$\alpha_n(t) = \langle r^{2n}(t)\rangle / C_n\langle r^2(t)\rangle^n - 1\ , \tag{49d}$$

$$C_n = 1\times 3\times 5\times\cdots(2n+1)/3^n\ . \tag{49e}$$

In Eq. (49), $\langle\cdots\rangle$ implies an average over the correlation function $G_s(\vec{r}, t)$. The result in the Gaussian approximation, $S_s^G(k, w)$, is obtained by setting $\alpha_n(t) = 0$. The numerical procedure is described elsewhere.[11] $\langle r^2(t)\rangle$ is taken from NR; the non-Gaussian corrections $\alpha_n(t)$, $n = 2$, 3, 4 are taken from an earlier calculation by Rahman[2] for liquid argon under slightly different conditions. Since these corrections are found to be quantitatively similar in gases and liquids,[10] the slight difference in the two[2,7] molecular-dynamics calculations is not expected to change $\alpha_n(t)$ significantly. The results for $[\pi D_0k^2S_s(k, 0)]$ and $[\pi D_0k^2S_s^G(k, 0)]$ are shown in Figs. 3 and 4 and are denoted by EXT 1 and EXT 2, respectively. Both are qualitatively similar with a minimum around $k = 2.5$ Å^{-1}, the minimum being much deeper in the function with a Gaussian approximation.

In studying the solution given in Eqs. (47) and (48), we have used two simple forms for the memory function $\Phi(k, t)$ which is defined in Eq. (7) and which is related to $D'(k, w)$ and $D''(k, w)$. These

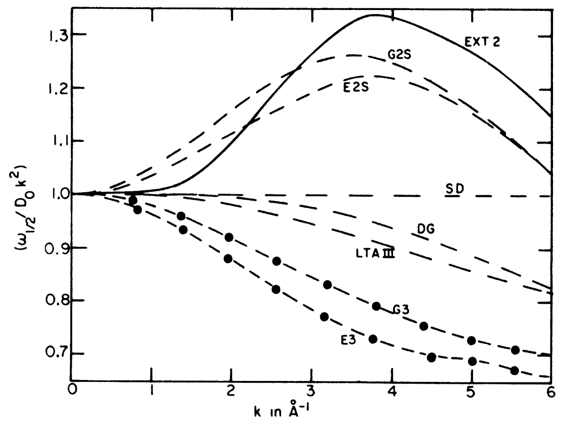

FIG. 2. The half-width function $w_{1/2}/D_0k^2$ versus k for the Gaussian approximation $S_s^G(k, w)$. EXT 2 – molecular-dynamics results of NR; G2S – Φ_{Gauss} with $\tau_1(k)$ determined from $S_s^G(k, 0)$ of NR; E2S – Φ_{exp} with $\tau_2(k)$ determined from $S_s^G(k, 0)$ of NR; DG – dilute-gas model; LTA III – long time approximation of Sears (Ref. 37); G3 – Φ_{Gauss} with $\tau_1(k) = \tau_1(0) = 0.235\times10^{-12}$ sec; E3 – Φ_{exp} with $\tau_2(k) = \tau_2(0) = 0.208\times10^{-12}$ sec; SD – simple diffusion.

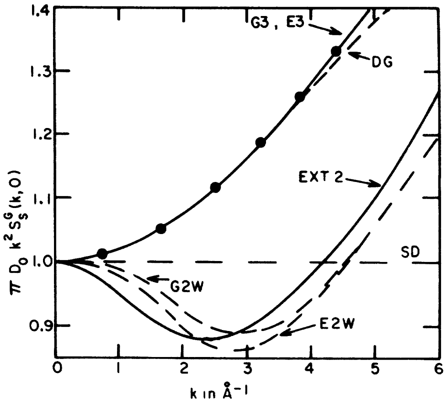

FIG. 4. The zero-frequency function $\pi D_0 k^2 S_s^G(k, 0)$ versus k for the calculation with Gaussian approximation (Ref. 4). EXT 2, G3, E3, SD same as in Fig. 2. G2W – Φ_{Gauss} with $\tau_1(k)$ determined from $w_{1/2}(k)$ of EXT 2 in Fig. 2; E2W – Φ_{exp} with $\tau_2(k)$ determined from $w_{1/2}(k)$ of EXT 2 in Fig. 2.

forms are the generalizations of the earlier models[12,13] for the memory function $\tilde{\Phi}(k=0,t)$ used in evaluating the velocity autocorrelation function $\Psi(t)$. These two forms are

$$\tilde{\Phi}_{\text{Gauss}}(k,t) = \exp\{-[t/\tau_1(k)]^2\} \tag{50}$$

and

$$\tilde{\Phi}_{\text{exp}}(k,t) = \exp[-t/\tau_2(k)] \;. \tag{51}$$

It is easy to show using Eqs. (32), (42), and (50) that

$$D'_{\text{Gauss}}(k,w) = \frac{\sqrt{\pi}\, v_0^2}{2\omega_0^2 \tau_1(k)} \, \frac{\exp(-x^2)}{\frac{1}{4}\pi \exp(-2x^2) + [F(x)]^2} \;, \tag{52a}$$

$$D''_{\text{Gauss}}(k,w) = \frac{v_0^2}{\omega_0^2 \tau_1(k)} \, \frac{F(x)}{\frac{1}{4}\pi \exp(-2x^2) + [F(x)]^2} \;, \tag{52b}$$

where

$$x(k,w) = \tfrac{1}{2} w\, \tau_1(k) \tag{52c}$$

and

$$F(x) \equiv e^{-x^2} \int_0^x dt\, e^{t^2} \;, \tag{52d}$$

is the Dawson's integral.[36] Similarly, for the exponential form we find

$$D'_{\text{exp}}(k,w) = v_0^2 / \omega_0^2 \tau_2(k) \tag{53a}$$

and

$$D''_{\text{exp}}(k,w) = v_0^2 w / \omega_0^2 \;. \tag{53b}$$

Both the Gaussian and the exponential forms in Eqs. (50) and (51) satisfy the requirement that $\tilde{\Phi}(k,0)=1$ and thus satisfy the first four frequency moments of $S_s(k,w)$ automatically. $\tilde{\Phi}_{\text{exp}}$ violates the fifth frequency sum rule and if this violation is ignored, then a purely imaginary value of $\tau_2(k)$ is required in order to satisfy the sixth frequency sum rule. Thus in determining $\tau_2(k)$, these sum rules have to be ignored. On the other hand, $\tilde{\Phi}_{\text{Gauss}}$ gives the fifth frequency moment correctly, and the exact value of the sixth frequency moment can be used as one of the ways to determine $\tau_1(k)$. Using Eq. (46b), such a determination gives

$$\tau_1(k) = [\tfrac{5}{2} v_0^2 k^2 + \tfrac{1}{2}(B/\omega_0^2 - \omega_0^2)]^{-1/2} \;, \tag{54a}$$

$$= \{\tfrac{5}{2} v_0^2 k^2 + [\tau_2(0)]^{-2}\}^{-1/2} \;. \tag{54b}$$

For given values of D_0 and ω_0^2, the values of $\tau_1(0)$ and $\tau_2(0)$ are fixed from Eqs. (52) and (53), since $D'(0,0)=D_0$. For our case, $\tau_1(0) = 0.235\times 10^{-12}$ sec and $\tau_2(0) = 0.208\times 10^{-12}$ sec. These values are used in our calculations. Thus from Eq. (54) we would estimate the value of the constant B to be about 3660×10^{48} sec^{-4} which compares favorably with the value 6650×10^{48} sec^{-4} quoted by NR. $\tau_1(k)$ as determined by Eq. (54b) is shown in Fig. 5 (labeled GM6).

Once the form of $\tilde{\Phi}(k,t)$ is determined, calculation of $S_s(k,w)$ is self-contained in Eqs. (47) and (48); the desired functions $[w_{1/2}/D_0 k^2]$ and $[\pi D_0 k^2 S_s(k,0)]$ can be determined from $S_s(k,w)$. These functions are shown in Figs. 1 and 3 (both denoted by GM6), respectively, for $\tilde{\Phi}_{\text{Gauss}}$ [with $\tau_1(k)$ obtained from the sixth frequency moment]. When compared with the exact NR result (EXT 1), $w_{1/2}(k)$ is overestimated while the zero-frequency value of $S_s(k,w)$ is underestimated for all values of k in this calculation. Because of the non-Gaussian effects, the characteristic minimum in the half-width is not reproduced. This is not entirely unexpected, since the leading non-Gaussian correction $\alpha_2(t)$ behaves as t^8 for small t. Thus in order to reproduce the minimum quantitatively one would need a description which gives the correct eighth frequency moment, in addition to the features of the present solution. Apart from the lack of this minimum, the GM6 results do bear a qualitative resemblance to the EXT 1 results.

Another way of determining both $\tau_1(k)$ and $\tau_2(k)$ is to require that the NR results for $S_s(k,0)$ [EXT 1 curve in Fig. 3] are reproduced exactly for all k values. We find numerically that such a determination of $\tau(k)$ is unique [i.e., $S_s(k,0)$ is a single-valued functional of $\tau(k)$]. $\tau_1(k)$ so found is shown in Fig. 5 (labeled G1S) and $\tau_2(k)$ so found is shown in Fig. 6 (labeled E1S). The half-widths of $S_s(k,w)$ as determined by using $\tau_1(k)$ and $\tau_2(k)$ and the appropriate forms of $\tilde{\Phi}(k,t)$ are shown in Fig. 1, denoted, respectively, as G1S and E1S. The exponential form of $\tilde{\Phi}(k,t)$ gives the half-width (E1S) which qualitatively resembles the exact results of

NR (EXT 1) with the positions of the minimum and the maximum remarkably close; actual magnitudes of $[w_{1/2}/D_0k^2]$ however disagree by about 10%. The Gaussian form of $\tilde{\Phi}(k,t)$ does not reproduce the minimum and underestimates the position of the maximum slightly; the difference in the actual magnitude of $[w_{1/2}/D_0k^2]$ is again about 10%.

An identical calculation is also made using the Gaussian-approximation molecular-dynamics results $S_s^G(k,0)$, which were obtained using $\langle r^2(t)\rangle$ of NR (EXT 2 curve in Fig. 4). The determined $\tau_1(k)$ and $\tau_2(k)$ are shown in Fig. 5 (labeled G2S) and in Fig. 6 (labeled E2S). Corresponding half-widths are shown in Fig. 2 under the labels G2S for $\tilde{\Phi}_{\text{Gauss}}(k,t)$ and E2S for $\tilde{\Phi}_{\text{exp}}(k,t)$. Again the results are qualitatively similar to that of NR, the quantitative difference being about 10% or less; the position of the maximum is reproduced slightly better by the exponential form.

Curves labeled G3 and E3 in Figs. 2 and 4 show the results of the two calculations, where $\tau_1(k)$ and $\tau_2(k)$ were assumed to be k independent with their values fixed at $\tau_1(0)$ and $\tau_2(0)$, respectively. These results do not show the characteristic behavior of NR results (EXT 2), thereby indicating that in the present formalism [with the approximation in Eq. (7)] the k dependence in the memory function $\tilde{\Phi}(k,t)$ is essential for reproducing the results obtained with the phenomenological Gaussian approximation for $G_s(r,t)$. It is also interesting to compare these results (E3, G3) with those obtained from a dilute-gas model (labeled DG in Figs. 2 and 4), as discussed in Sec. II, in which we assume $\tilde{\Phi}(k,t)$ to be a δ function in time. This calculation [which is equivalent to Langevin equation coupled with the Gaussian approximation] gives rise to $[\pi D_0k^2S_s(k,0)]$ which is almost identical to that given by G3, E3. The difference in the time dependence of the memory function has some consequence only in the half-width (Fig. 2). Also shown in Fig. 2 are the results of Sears[37] (curve labeled LTA III) who has applied Mori's continued fraction representation in order to calculate, among other quantities, the half-width of $S_s(k,w)$. In Sear's notation, the DG model is identical to the LTA II representation and the SD model to LTA I.

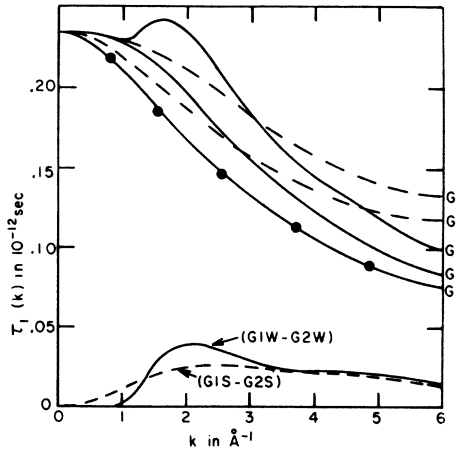

FIG. 5. $\tau_1(k)$, the relaxation time of $\tilde{\Phi}_{\text{Gauss}}(k,t)$ versus k. G1S, GM6 as in Fig. 1, G2S as in Fig. 2, G1W as in Fig. 3, G2W as in Fig. 4. (G1W-G2W) – difference of G1W and G2W; (G1S-G2S) – difference of G1S and G2S.

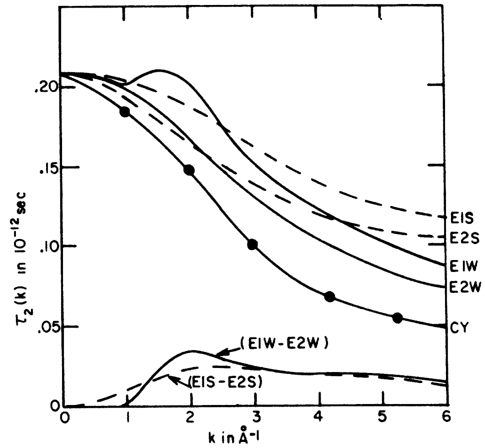

FIG. 6. $\tau_2(k)$, the relaxation time of $\tilde{\Phi}_{\text{exp}}(k,t)$ versus k. E1S as in Fig. 1, E2S as in Fig. 2, E1W and CY as in Fig. 3, E2W as in Fig. 4. (E1W-E2W) – difference of E1W and E2W; (E1S-E2S) – difference of E1S and E2S.

We have also performed another set of calculations via a procedure which is the same as that followed by Chung and Yip.[33] In this procedure, by repeating the trials for each value of k, we find the value of $\tau(k)$ that precisely gives the value of the half-width obtained in molecular-dynamics calculations of NR. The results are shown in Figs. 3–6 under the labels of G1W, G2W, E1W, and E2W. Results with G in the label use $\tilde{\Phi}_{\text{Gauss}}$ and the results with E in the label use $\tilde{\Phi}_{\text{exp}}$; results with 1 reproduce the non-Gaussian half-width EXT 1 of Fig. 1 and those with 2 reproduce the Gaussian approximation half-width EXT 2 of Fig. 2. Chung and Yip[33] have used the formalism by Martin; curves labeled CY in Figs. 3 and 6 are obtained by using (i) *their* Eqs. (4.6) and (4.16) and (ii) the curve labeled C in *their* Fig. 4.2. The conditions under which the CY calculations were done correspond quite closely to those for the E1W calculation. Again the CY values of $\tau_2(k)$ in Fig. 6 are chosen to reproduce the non-Gaussian half-widths of NR (EXT 1 in Fig. 1) exactly. The qualitative similarity of $[\pi D_0k^2S_s(k,0)]$ in Fig. 3 for the three curves G1W, E1W, and CY is striking. All the three show an extra maximum and an extra minimum as compared to the molecular-dynamics result EXT 1. The difference arising due to the two different forms of $\tilde{\Phi}(k,t)$ used is of the same order as the difference arising from the approximation, $[\Lambda_n(k,\epsilon)=\Lambda_0(k,\epsilon)$ for all $n]$ which is needed to reduce our results to those of Chung and Yip,[33] as discussed in Sec. III.

Comparing the various results for the relaxation times $\tau_1(k)$ and $\tau_2(k)$ [Figs. 5 and 6], we see that they are all qualitatively similar. The effect of the non-Gaussian corrections is to make $\tau(k)$ larger, implying a longer memory time during which the initial phase information is retained by the test particle. In Figs. 5 and 6 we also show the quantities $(\tau_{G1W}-\tau_{G2W})$, $(\tau_{G1S}-\tau_{G2S})$, $(\tau_{E1W}-\tau_{E2W})$, and $(\tau_{E1S}-\tau_{E2S})$, all of which arise because of the non-Gaussian effects. Although these effects arise mainly because of the dynamical correlations, the striking peaks around $k=2$ Å^{-1} in $(\tau_{G1W}-\tau_{G2W})$ and $(\tau_{E1W}-\tau_{E2W})$ tend to make us speculate that this behavior is the manifestation of the local structure of the bath particles around the test particle. Around $k=2$ Å^{-1}, when the surrounding local structure is favorable, the test particle tends to retain the initial phase memory longer.

In conclusion we can make a general remark about the simple approximation in Eq. (7) for the memory function. By using the simple forms for $\tilde{\Phi}(k,t)$, one is capable of reproducing most of the qualitative features of the molecular-dynamics results; quantitative agreements are within about 10%. All the details regarding the connection with the basic interaction are however hidden in the average relaxation time $\tau(k)$. Thus, we can speculate that for better basic and quantitative understanding of $S_s(k,w)$ and its half-width, one requires an ansatz for $\phi(\vec{k},\vec{p},\vec{p}',t)$ that uses Eqs. (3) and (4) explicitly and which describes the behavior of the test particle in momentum space more accurately than Eq. (7), rather than more involved forms for $\tilde{\Phi}(k,t)$ within the framework of the approximation in Eq. (7). The calculations presented here can also be extended to study the correlations in the rotational single-particle motion. Work is in progress in both these directions.

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