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Self-Diffusion Model for Memory Functions in Classical Fluids[*]

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The Mori memory-function formalism is used to derive systematically a hierarchy of approximations relating the dynamic structure factor $S(k, \omega)$ of a dense classical fluid to its self-part $S_s(k, \omega)$. The formalism is applied to a column vector of dynamical variables whose components include the self and distinct parts, ρ_s and ρ_d, of the fluctuating density plus N time derivatives of these variables. Increasing N is analogous to a continued-fraction expansion of the memory functions, and builds in more short-time information about the correlation functions. In this manner approximations generated earlier by Vineyard, by Kerr, and by Ortoleva and Nelkin are concisely stated, and a new approximation which gives the first six frequency moments of $S(k, \omega)$ correctly is obtained. Since the sixth frequency moment of $S(k, \omega)$ is not known from molecular-dynamics calculations, it is used as a parameter to fit these calculations. Agreement for $S(k, \omega)$ to within a few percent is obtained for several k values and two thermodynamic states. The deduced value of the sixth frequency moment has a reasonable dependence on k, and may give useful information about the three-particle static correlation function.

I. INTRODUCTION

The dynamical structure factor $S(k, \omega)$ for a simple classical liquid is a convenient focal point for the study of collective motion in a strongly interacting disordered system. Its self-motion counterpart $S_s(k, \omega)$ gives similarly detailed information on the single-particle motion. The qualitative behavior of these functions is well understood, but there is considerable interest in a quantitatively accurate description of their behavior. For values of k greater than about 10^7 cm^{-1}, experimental information is available from neutron inelastic scattering, and accurate theoretical information comes from molecular-dynamics calculations of the classical motion of several hundred atoms interacting through a Lennard-Jones potential.[1-3] In particular the self-function $S_s(k, \omega)$ has been very accurately calculated for several thermodynamic states,[2] and this information has been analyzed in terms of a memory function with only a few parameters. A quantitative description of this function is thus now generally available, greatly facilitating further attempts at its theoretical understanding.

There have been several recent theoretical descriptions of collective motion in liquids. Nossal and Zwanzig[4] constructed approximate collective modes as variational eigenfunctions of the Liouville operator. The frequencies of these modes are closely related to the wave-number–dependent elastic moduli for the fluid introduced by Schofield.[5] The introduction of approximate collective modes allows the possibility of a microscopic theoretical analog to the viscoelastic models which so often give a useful phenomenological description. One such approach was carried out by Ortoleva and Nelkin.[6] They considered approximate equations of motion for the single-particle distribution function $f(\vec{k}, \vec{p}, \vec{p}', t)$. The interaction term was expanded, keeping only terms linear in the Nossal-Zwanzig collective coordinates. The result is a simple analytic expression for $S(k, \omega)$ which expresses the damping of these collective modes due to free-particle motion. The first four frequency moments of $S(k, \omega)$ are given correctly since the approximate collective modes chosen allow an accurate short-time description.

The Ortoleva-Nelkin result corresponds to a solid-like description of the collective motion combined with a gas-like description of the single particle motion. In a solid the short-time behavior of a dynamical variable determines its subsequent harmonic motion. The use of the short-time behavior in a liquid to define the collective mode frequencies led to the picturesque title of liquid phonon model.[6] The principal defect of the model is not in its choice of collective modes, but in the fact that the only damping considered is due to free-particle motion.

Another pattern for approximate theories has been to relate the collective motion as given by $S(k, \omega)$ to the single-particle motion as given by $S_s(k, \omega)$. The first result of this kind was Vineyard's convolution approximation.[7] This was extended using explicit consideration of test particle motion by Kerr,[8] and using an effective field argument by Singwi, Sköld, and Tosi.[9] (The physical arguments of these last two papers are very different, but the result is the same.) We will present the Vineyard and Kerr results in yet another way in the following as the lowest order in a hierarchy of memory-function approximations.

The memory-function formalism[10,11] has long been recognized as a convenient tool for the analysis of time-correlation functions. It was noticed[12] that this formalism gives a particularly concise statement of the approximate theoretical results mentioned above. This readily allowed the extension of these results to generate more accurate approximations, though no new microscopic physical insight is thus obtained. For example, the above-mentioned approximation by Ortoleva and Nelkin[6] corresponds to choosing the memory function for the current autocorrelation function to have its correct value at $t=0$, but to evolve in time as it would for a perfect gas. The correct value at $t=0$ gives the correct fourth frequency moment of $S(k, \omega)$. It is natural to extend this approximation so that the memory function evolves in time as does the memory function for the actual self-motion in the liquid. This "extended liquid phonon" (ELP) model leads to an expression relating $S(k, \omega)$ and $S_s(k, \omega)$ only slightly more complicated than that given by Kerr. Since the principal collective effects are now included through the zero time value of the memory function, and the damping is more realistically described in terms of the actual single-particle motion, the description should be more accurate than for the other models described above. This is in fact true, as shown by Kurkijärvi,[3] who compared the ELP model predictions with his molecular-dynamics results.

By working with model memory functions, a natural synthesis of the earlier collective variable and self-motion theories is achieved. The result is a rather accurate description of $S(k, \omega)$ with a considerable degree of intuitive plausibility. There are, however, several disadvantages. The microscopic theoretical basis for the approximations given is far from clear. A great deal of information about the system is used as input: The structure factor $S(k)$, the fourth frequency moment of $S(k, \omega)$, and the detailed self-function $S_s(k, \omega)$ are all taken as known from molecular-dynamics calculations. Finally, the modeling of memory functions as carried out in Refs. 6 and 12 is not sufficiently systematic. Thus the structure of the approximations made needs further clarification, and a systematic procedure for extending to more accurate calculations of the same kind is needed.

Only the last of these difficulties is surmounted in the present paper. We examine certain structural aspects of self-motion approximations within the Mori[11] formalism. A hierarchy of approximations is generated proceeding from Vineyard to Kerr to the ELP model to a new and more accurate approximation. Numerical comparisons are then given.

In Sec. II we briefly review the Mori formalism. We then consider various choices for the column vector of dynamical variables and the associated matrix of memory functions. In Sec. III we take a one-component description with ρ_s, the self-part of the density, as the dynamical variable. In this description there is only one memory function. It is possible to generate equations of motion for correlation functions other than $S_s(k, \omega)$ from the generalized Langevin equation for ρ_s. The extra degree of freedom is in the random force term in the generalized Langevin equation. Neglecting this random force term in a particular case gives the Vineyard approximation. Including it allows for a new set of approximations which has not yet been explored in detail.

A more natural use of the Mori formalism is to choose a column vector of dynamical variables such that matrix elements among them give all the correlation functions of interest. The matrix of equations for the correlation functions then contains no contribution from the random force terms in the generalized Langevin equation. For our purpose this requires a two-component description with

$$\rho_s = e^{i\,\vec{k}\cdot\vec{r}_1}\ ,\quad \rho_d = \sum_{j=2}^{N} e^{i\vec{k}\cdot\vec{r}_j}$$

as the two components. This is studied in Sec. IV. With this choice of components there are only two independent correlation functions and thus only two independent memory functions. If the memory functions for the self and coherent motion are set equal, the Vineyard approximation results. If they are normalized to their correct values at $t=0$ and then set equal, the Kerr approximation results.

We want to include more information about the short-time behavior of the correlation functions. This can be done by making a continued fraction expansion of the memory functions.[13] We follow an equivalent procedure of expanding the number of components in the column vector of dynamical variables to include time derivatives of ρ_s and ρ_d. If the first time derivatives are included, the four-component description of Sec. V results. Equating memory functions now gives the Kerr approximation. Normalizing at $t=0$ and then equating gives the ELP result. If first and second time derivatives of ρ_s and ρ_d are included we get the six-component description of Sec. VI. Still there are only two independent correlation functions and two independent memory functions. Equating memory functions (for the self-part and coherent part of the autocorrelation function of the longitudinal stress tensor) now gives the ELP approximation. Normalizing at $t=0$ and then equating gives a new approximation [Eq. (6.17)] which is still algebraically quite simple. This expression contains an additional parameter ξ defined by Eq. (6.14) which depends on the sixth frequency moment of $S(k,\omega)$. This in turn depends on the three-particle static correlation function, which has not yet been explicitly determined from molecular-dynamics calculations.

In Sec. VII we present numerical calculations of $S(k,\omega)$ using the approximation developed in Sec. VI. The parameter ξ is fitted to $S(k,\omega=0)$ taken from molecular-dynamics calculations. The resulting agreement with the full $S(k,\omega)$ curve is within a few percent in all cases. The resulting $\xi(k)$ can be considered as a prediction of the sixth frequency moment of $S(k,\omega)$ to be checked by more precise molecular-dynamics calculations in the short-time regime. The predictions given here of $\xi(k)$ may give useful information about three-particle static correlations in the liquid.

II. MEMORY-FUNCTION FORMALISM

In order to allow a more concise presentation of our results, we begin with a brief review of the memory-function formalism.[10,11]

Consider a function space whose elements are column vectors, each component describing a fluctuating classical dynamical variable (i.e., a function of the coordinates and momenta of the N particles in the system). The scalar product is defined for any two components $A_i(t)$ and $B_j(t)$ by

$$\langle A_i(t)\,|\,B_j(t)\rangle = (A_i(t)B_j^*(t))\ , \tag{2.1}$$

where $(\cdots)$ on the right-hand side denotes an average over a classical canonical ensemble. All elements are taken to have D components, and the $D\times D$ matrix of scalar products defined by Eq. (2.1) is abbreviated by $\langle\vec{A}(t)\,|\,\vec{B}(t)\rangle$. The projection operator P_0 which projects out the part of any element $\vec{G}(t)$ along $\vec{A}$ is defined by

$$P_0\vec{G}(t) = \langle\vec{G}(t)\,|\,\vec{A}\rangle\langle\vec{A}\,|\,\vec{A}\rangle^{-1}\vec{A}\ . \tag{2.2}$$

In Eq. (2.2), $\vec{A}$ denotes $\vec{A}(t=0)$, and the second factor on the right-hand side is the inverse of the matrix whose elements are $\langle A_i\,|\,A_j\rangle$. The Liouville equation for $\vec{A}(t)$ is then recast in a form more convenient for approximate solution. The resulting exact equation of motion for $\vec{A}(t)$ may be regarded as a generalization of the Langevin equation familiar from the stochastic theory of Brownian motion. This equation is

$$\frac{d}{dt}\vec{A}(t) - i\hat{\Omega}\cdot\vec{A}(t) + \int_0^t d\tau\,\hat{M}(t-\tau)\cdot\vec{A}(\tau) = \vec{f}(t)\ , \tag{2.3}$$

where the frequency matrix $i\hat{\Omega}$, the memory matrix $\hat{M}(t)$, and the random force $\vec{f}(t)$ are defined by

$$i\hat{\Omega} = \langle iL\vec{A}\,|\,\vec{A}\rangle\langle\vec{A}\,|\,\vec{A}\rangle^{-1}\ , \tag{2.4}$$

$$\hat{M}(t) = \langle\vec{f}(t)\,|\,\vec{f}\rangle\langle\vec{A}\,|\,\vec{A}\rangle^{-1}\ , \tag{2.5}$$

$$\vec{f}(t) = \exp[t(1-P_0)iL](1-P_0)iL\vec{A}\ , \tag{2.6}$$

and L is the usual Liouville operator given by

$$iL = \sum_{j=1}^{N}\left(\frac{\partial H}{\partial\vec{p}_j}\cdot\frac{\partial}{\partial\vec{r}_j} - \frac{\partial H}{\partial\vec{r}_j}\cdot\frac{\partial}{\partial\vec{p}_j}\right)\ , \tag{2.7}$$

where H is the Hamiltonian for the system.

When postmultiplied by $\vec{A}^*$, and averaged over a canonical ensemble, the generalized Langevin equation, Eq. (2.3), becomes an equation of motion for the correlation matrix

$$\hat{\Xi}(t) = \langle\vec{A}(t)\,|\,\vec{A}\rangle\ . \tag{2.8}$$

The random force $\vec{f}(t)$ has been explicitly constructed so that

$$\langle \vec{f}(t) | \vec{A} \rangle = 0 \ . \tag{2.9}$$

The equation of motion for $\hat{\Xi}(t)$ thus simplifies to

$$\frac{d}{dt}\hat{\Xi}(t) - i\hat{\Omega}\cdot\hat{\Xi}(t) + \int_0^t d\tau\, \hat{M}(t-\tau)\cdot\hat{\Xi}(\tau) = 0 \ . \tag{2.10}$$

We usually find it more convenient to work with the Laplace transform

$$\hat{\Xi}(z) = \int_0^\infty dt\, e^{-zt}\hat{\Xi}(t) \ ,$$

which is given by

$$z\hat{\Xi}(z) - \hat{\Xi}(t=0) - i\hat{\Omega}\cdot\hat{\Xi}(z) + \hat{M}(z)\cdot\hat{\Xi}(z) = 0 \ . \tag{2.11}$$

In order for this formally exact result to be useful, it is necessary that relatively simple approximate results for the memory matrix $\hat{M}(z)$ be combined with exact results for the frequency matrix $i\hat{\Omega}$ to give reasonably accurate approximate results for the correlation matrix $\hat{\Xi}(z)$. There is accumulating evidence that this is a fruitful procedure in classical liquids. In the following we analyze further the structure of some existing memory-function approximations, and propose a new one.

III. ONE-COMPONENT DESCRIPTION

We consider first a single-component column vector. The single component is taken as the self-part ρ_s of the density fluctuation

$$\rho_s = e^{i\vec{k}\cdot\vec{r}_1} \ , \tag{3.1}$$

where we specify particle number one as a test particle. The projection operator P_0 in this case has the property

$$P_0 G(t) = \langle G(t) | \rho_s \rangle \cdot \rho_s \tag{3.2}$$

for an arbitrary dynamical variable $G(t)$. The generalized Langevin equation for $\rho_s(k,t)$ is

$$\frac{d}{dt}\rho_s(k,t) + \int_0^t d\tau\, m_s(k,t-\tau)\rho_s(k,\tau) = f_s(k,t) \ . \tag{3.3}$$

(In a single-component description, when the single component is either odd or even in momentum, the frequency matrix $i\Omega$ vanishes.) When postmultiplied by $\rho_s^*(k,0)$ and averaged (all averages are with respect to the equilibrium classical canonical ensemble), Eq. (3.3) gives an equation of motion for $G_s(k,t)$,

$$\frac{d}{dt}G_s(k,t) + \int_0^t d\tau\, m_s(k,t-\tau)G_s(k,\tau) = 0 \ , \tag{3.4}$$

where the self-correlation function $G_s(k,t)$, the random force $f_s(k,t)$, and the memory function $m_s(k,t)$ are defined by

$$G_s(k,t) = \langle \rho_s(k,t) | \rho_s(k) \rangle \ , \tag{3.5}$$

$$f_s(k,t) = e^{t(1-P_0)iL}(1-P_0)iL\rho_s(k) \ , \tag{3.6}$$

$$m_s(k,t) = \langle f_s(k,t) | f_s(k) \rangle \ . \tag{3.7}$$

Equation (3.3) can also be used to generate an exact equation of motion for the time-dependent pair-correlation function $G_d(k,t)$. We introduce the distinct part $\rho_d(k,t)$ of the density fluctuation defined through

$$\rho(k,t) = \rho_s(k,t) + \rho_d(k,t) = \sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{r}_j(t)} \ . \tag{3.8}$$

The functions $G_s(k,t)$, $G_d(k,t)$, and the density-density correlation function $G(k,t)$ are defined by Eq. (3.5) and

$$G_d(k,t) = \langle \rho_s(k,t) | \rho_d(k) \rangle \ , \tag{3.9}$$

where

$$G(k,t) = N^{-1}\langle \rho(k,t) | \rho(k) \rangle = G_s(k,t) + G_d(k,t) \ . \tag{3.10}$$

At zero time these correlation functions become

$$G_s(k,0) = 1 \ , \quad G_d(k,0) = S(k) - 1 \ , \tag{3.11}$$

where $S(k)$ is the static structure factor of the fluid.

If postmultiplied by $\rho_d^*(k)$ and averaged, Eq. (3.3) gives an exact equation of motion for $G_d(k,t)$

$$\frac{d}{dt}G_d(k,t) + \int_0^t d\tau\, m_s(k,t-\tau)G_d(k,\tau) = \langle f_s(k,t) | \rho_d(k) \rangle \ . \tag{3.12}$$

In Eq. (3.12) the memory function is the same as for the self-motion, but the right-hand side does not vanish since the random force acting on the self-motion is not orthogonal to the correlated motion of pairs of particles.

When Laplace transformed with respect to time, Eqs. (3.4) and (3.12) become

$$zG_s(k,z) - 1 + m_s(k,z)G_s(k,z) = 0 \ , \tag{3.13}$$

$$zG_d(k,z) - [S(k) - 1] + m_s(k,z)G_d(k,z) = \langle f_s(k,z) | \rho_d(k) \rangle \ . \tag{3.14}$$

Within our one-component description, it is natural to relate the collective motion to the single-particle motion by approximating the right-hand side of Eq. (3.14). To lowest order we neglect entirely the overlap term $\langle f_s(k,z) | \rho_d(k) \rangle$. Eliminating the memory function $m_s(k,z)$ in favor of $G_s(k,z)$ through Eq. (3.13), this approximate form of Eq. (3.14) becomes

$$G_d(k,z) = [S(k) - 1]\,G_s(k,z) \quad \text{or} \quad G(k,z) = S(k)G_s(k,z) \ , \tag{3.15}$$

which can be recognized as the Vineyard convolution approximation.[7] This approximation has many well-known deficiencies, the most striking being that it does not correctly give the second frequency moment of $S(k,\omega)$. This can be remedied by correctly including particle conservation. In the present context, this corresponds to correctly including the leading term (of order z^{-2}) in a large z expansion of the right-hand side of Eq. (3.14). This expansion is considered in Appendix A, and could be used to generate improved approximations. We turn instead to a multicomponent description where we build particle conservation into approximate relations between memory functions. It is interesting to note, however, that a description with a single memory function, where the approximations are made on the random force term, is also possible. The physical meaning and quantitative accuracy of such a description are deserving of further study.

IV. TWO-COMPONENT DESCRIPTION

A more natural choice of column vector for relating $G_d(k, t)$ to $G_s(k, t)$ has $\rho_s(k, t)$ and $\rho_d(k, t)$ as its two components

$$\vec{A} = \mathrm{col}[\rho_s, \rho_d] \ . \tag{4.1}$$

Noting that

$$i\hat{\Omega} = 0 \tag{4.2}$$

for this choice of $\vec{A}$, and that

$$\begin{aligned}\langle \rho_s(k, t) | \rho_d(k) \rangle &= \langle \rho_d(k, t) | \rho_s(k) \rangle \\ &= N^{-1} \sum_{l \neq j}^{N} \langle e^{iLt} e^{i\vec{k}\cdot\vec{r}_l} | e^{i\vec{k}\cdot\vec{r}_j} \rangle = G_d(k, t) \ ,\end{aligned} \tag{4.3}$$

$$\begin{aligned}\langle \rho_d(k, t) | \rho_d(k) \rangle &= NG(k, t) - 2G_d(k, t) - G_s(k, t) \\ &= [N + O(1)] G(k, t) \ ,\end{aligned} \tag{4.4}$$

we obtain

$$\begin{bmatrix} zG_s - 1 & zG_d - (S(k) - 1) \\ zG_d - (S(k) - 1) & N(zG - S(k)) \end{bmatrix} + \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} G_s & G_d \\ G_d & NG \end{bmatrix} = 0 \tag{4.5}$$

as the Laplace transformed equation of motion for the correlation matrix. All components depend on k and z, but this is not explicitly written.

The essential particular feature of this choice of column vector is that the correlation matrix contains only two independent correlation functions. Thus Eq. (4.5) can represent only two independent equations of motion, and the memory matrix also contains only two independent components. This is most conveniently expressed by relating the off-diagonal components of the memory matrix to its diagonal components

$$M_{12} = N^{-1}(M_{22} - M_{11}) \ , \tag{4.6}$$

$$M_{21} = M_{22} - M_{11} \ . \tag{4.7}$$

The two independent equations of motion are most conveniently written as

$$zG_s - 1 + M_{11} G_s = 0 \ , \tag{4.8}$$

$$zG - S + M_{22} G = 0 \ . \tag{4.9}$$

In both Eq. (4.8) and Eq. (4.9) we have neglected a term containing $N^{-1}(M_{22} - M_{11})G_d$ since this term is of order N^{-1} compared to the terms retained.

We thus have two uncoupled equations of motion for $G_s(k, z)$ and $G(k, z)$. The equation for $G_s(k, z)$ is the same as Eq. (3.13) so that $M_{11}(k, z)$ as introduced here is the same as $m_s(k, z)$ introduced in Sec. III. The two-component description introduced here thus contains the same information as two separate one-component descriptions with $\rho_s(k, t)$ and $\rho(k, t)$ as the two single-component vectors. It is natural in this description to consider simple approximate relations between $M_{11}(k, z)$ and $M_{22}(k, z)$. This has been done in an earlier paper,[6] but we repeat the results briefly here to show the structural pattern.

To lowest order we set the memory function M_{22} for the density autocorrelation equal to its counterpart M_{11} for the single-particle motion. With this approximation, we can eliminate the memory functions from Eqs. (4.8) and (4.9) and relate $G(k, z)$ to $G_s(k, z)$. The result is the Vineyard convolution approximation Eq. (3.15).

The principal defect of this approximation is easily remedied by examining the short-time (large-z) behavior of the relevant functions:

$$G_s(k, z) = z^{-1} - k^2 v_T^2 z^{-3} + \cdots \ ,$$

$$G(k, z) = S(k) z^{-1} - k^2 v_T^2 z^{-3} + \cdots \ ,$$

$$M_{11}(k, z) = k^2 v_T^2 z^{-1} + \cdots \ ,$$

$$M_{22}(k, z) = k^2 v_T^2 S^{-1}(k) z^{-1} + \cdots \ ,$$

where the thermal speed v_T is defined by

$$v_T^2 = k_B T/m \ . \tag{4.10}$$

The natural approximation to next order is

$$M_{11}(k, z) = S(k) M_{22}(k, z) \ . \tag{4.11}$$

Combining Eqs. (4.8), (4.9), and (4.11) gives

$$G(k, z) = \frac{S(k) G_s(k, z)}{1 + c(k)[zG_s(k, z) - 1]} \ . \tag{4.12}$$

The approximate result Eq. (4.12) was previously obtained by Kerr[8] by a method whose physical relationship to the present derivation is not at all clear. The Kerr approximation gives the correct second frequency moment of $S(k, \omega)$, and thus properly includes particle conservation. We consider its quantitative predictions in Sec. VII.

V. FOUR-COMPONENT DESCRIPTION

To build particle conservation automatically into the formalism we take a four-component column vector

$$\vec{\mathrm{A}} = \mathrm{col}[\rho_s, \rho_d, iL\rho_s, iL\rho_d] = \mathrm{col}[\rho_s, \rho_d, ikj_s, ikj_d]\ , \tag{5.1}$$

where the self-part j_s and distinct part j_d of the longitudinal current density j are defined by

$$j_s = (\vec{\mathrm{k}} \cdot \vec{\mathrm{p}}_1/km)e^{i\vec{\mathrm{k}} \cdot \vec{\mathrm{r}}_1}\ , \tag{5.2}$$

$$j_d = \sum_{j=2}^{N} \frac{\vec{\mathrm{k}} \cdot \vec{\mathrm{p}}_j}{km} e^{i\vec{\mathrm{k}} \cdot \vec{\mathrm{r}}_j}\ . \tag{5.3}$$

The introduction of two new components which are time derivatives of the two already considered does not introduce any new memory functions. Thus we still have only two independent memory functions, and can get the same results by considering the algebraically simpler formulation in terms of two separate two-component column vectors given by

$$\vec{\mathrm{A}}_s = \mathrm{col}[\rho_s, ikj_s]\ , \tag{5.4}$$

$$\vec{\mathrm{A}}_c = \mathrm{col}[\rho, ikj]\ . \tag{5.5}$$

The Laplace transformed equation of motion for $\hat{\Xi}_c(z)$, defined by Eqs. (5.5) and (2.10), is

$$z\hat{\Xi}_c(z) - \hat{\Xi}_c(t=0) - i\hat{\Omega}_c \cdot \hat{\Xi}_c(z) + \hat{M}_c(z) \cdot \hat{\Xi}_c(z) = 0\ , \tag{5.6}$$

where the correlation matrix $\hat{\Xi}_c(z)$, its zero time value $\hat{\Xi}_c(t=0)$, the frequency matrix $i\hat{\Omega}_c$, and the memory matrix $\hat{M}_c(z)$ are given by

$$\hat{\Xi}_c(z) = N \begin{bmatrix} G & k^2 v_T^2 z^{-1} J \\ zG - S(k) & k^2 v_T^2 J \end{bmatrix}, \tag{5.7}$$

$$\hat{\Xi}_c(t=0) = N \begin{bmatrix} S(k) & 0 \\ 0 & k^2 v_T^2 \end{bmatrix}\ , \tag{5.8}$$

$$i\hat{\Omega}_c = \begin{bmatrix} 0 & 1 \\ -k^2 c_I^2 & 0 \end{bmatrix}\ , \tag{5.9}$$

$$\hat{M}_c(z) = \begin{bmatrix} 0 & 0 \\ 0 & M_c \end{bmatrix}\ . \tag{5.10}$$

The thermal speed v_T, the isothermal sound speed c_I, and the longitudinal current-current correlation function $J(k, t)$ are defined by Eq. (4.10) and

$$c_I^2(k) = v_T^2/S(k)\ , \tag{5.11}$$

$$J(k, t) = \langle j(k, t) | j(k) \rangle \langle j(k) | j(k) \rangle^{-1}\ . \tag{5.12}$$

In writing Eq. (5.7) we have used

$$G(k, z) = S(k)z^{-1} - k^2 v_T^2 z^{-2} J(k, z) \tag{5.13}$$

which is a direct consequence of the particle conservation law

$$iL\rho = ikj\ .$$

Making full use of Eq. (5.13), the 2×2 matrix equation Eq. (5.6) contains only one independent equation of motion. This is most conveniently expressed in terms of $J(k, z)$, and is

$$zJ - 1 + k^2 c_I^2 z^{-1} J + M_c J = 0\ . \tag{5.14}$$

In an entirely similar way we define the self-part of the longitudinal current-current correlation function by

$$J_s(k, t) = \langle j_s(k, t) | j_s(k) \rangle \langle j_s(k) | j_s(k) \rangle^{-1}, \tag{5.15}$$

and make use of particle conservation expressed through

$$G_s(k, z) = z^{-1} - k^2 v_T^2 z^{-2} J_s(k, z) \tag{5.16}$$

to get a single equation of motion for $J_s(k, z)$ which is equivalent to the 2×2 matrix equation for $\hat{\Xi}_s(z)$.[14] This equation is

$$zJ_s - 1 + k^2 v_T^2 z^{-1} J_s + M_s J_s = 0\ . \tag{5.17}$$

As the lowest-order approximation we equate M_c in Eq. (5.14) with M_s in Eq. (5.17). The resulting expression for $J(k, z)$ in terms of $J_s(k, z)$ can be rewritten to give $G(k, z)$ in terms of $G_s(k, z)$ using Eqs. (5.13) and (5.16). The result is just the Kerr approximation of Eq. (4.12). As the next-order approximation we let

$$M_c(k, t) = \gamma M_s(k, t)\ , \tag{5.18}$$

where the constant γ is chosen so that Eq. (5.18) is satisfied exactly at $t = 0$. The appropriate value of γ is

$$\gamma = ({\omega_l}^2 - k^2 c_I^2)/({\omega_s}^2 - k^2 v_T^2)\ , \tag{5.19}$$

where the frequencies ω_l and ω_s are defined by

$${\omega_l}^2 = \langle iLj | iLj \rangle \langle j | j \rangle^{-1}\ , \tag{5.20}$$

$${\omega_s}^2 = \langle iLj_s | iLj_s \rangle \langle j_s | j_s \rangle^{-1} \tag{5.21}$$

and are studied in greater detail in Appendix B.

With γ given by Eq. (5.19), longitudinal momentum conservation is properly included, and the fourth frequency moment of $S(k, \omega)$ is correctly given. Combining Eqs. (5.18), (5.19), (5.14), and (5.17) we obtain the next-order approximation relating $J(k, z)$ to $J_s(k, z)$;

$$J(k, z) = \frac{({\omega_s}^2 - k^2 v_T^2) J_s(k, z)}{[({\omega_s}^2 - k^2 v_T^2 - {\omega_l}^2 + k^2 c_I^2)z + ({\omega_s}^2 k^2 c_I^2 - {\omega_l}^2 k^2 v_T^2)z^{-1}]\, J_s(k, z) + ({\omega_l}^2 - k^2 c_I^2)}\ . \tag{5.22}$$

Equation (5.22) was previously derived by Ortoleva and Nelkin,[6] in essentially the same way. Because of the way it extended an approximation derived from a set of phononlike collective coordinates, they called it the ELP model. Kurkijärvi[3] has compared the predictions of the ELP and Kerr models with molecular-dynamics calculations of $S(k, \omega)$ for liquid and dense gaseous argon. In Sec. VI we present an improvement on the ELP model, and in Sec. VII we extend Kurkijärvi's comparison to this improved model.

VI. SIX-COMPONENT DESCRIPTION

To build longitudinal momentum conservation automatically into the formalism we take a six-component column vector, namely,

$$\vec{A} = \mathrm{col}[\rho_s, \rho_d, iL\rho_s, iL\rho_d, (iL)^2\rho_s, (iL)^2\rho_d]$$
$$= \mathrm{col}[\rho_s, \rho_d, ikj_s, ikj_d, -(k^2/m)\sigma_{33,s}, -(k^2/m)\sigma_{33,d}] \tag{6.1}$$

where the microscopic stress tensor density σ_{33} is defined by

$$\frac{ik}{m}\sigma_{\alpha 3} = iLj_\alpha = \frac{1}{m}\sum_{l=1}^{N}\left(-\frac{\partial U}{\partial r_{l,\alpha}} + ik\frac{p_{l,\alpha}p_{l,3}}{m}\right)e^{i\vec{k}\cdot\vec{r}_l}, \tag{6.2}$$

j_α being the α component of $\vec{j}$ and U the total potential energy of interaction. (In the following we will consider only the components j_3 and σ_{33}, and will drop the subscripts to simplify notation.) We note that the six-component column vector of Eq. (6.1) has been obtained simply by adding two more time derivatives to the four-component column vector of Eq. (5.1), and thus no new memory functions are introduced. We can thus get the same results by considering two three-component column vectors $\vec{A}_s$ and $\vec{A}_c$ defined by

$$\vec{A}_s = \mathrm{col}[\rho_s, iL\rho_s, (iL)^2\rho_s], \tag{6.3}$$

$$\vec{A}_c = \mathrm{col}[\rho, iL\rho, (iL)^2\rho]. \tag{6.4}$$

We introduce the longitudinal stress tensor correlation function $\Sigma(k, z)$ and its self-part $\Sigma_s(k, z)$ defined by

$$\Sigma(k, t) = \omega_l^2 \langle \sigma(k, t) | \sigma(k) \rangle \langle \sigma(k) | \sigma(k) \rangle^{-1}, \tag{6.5}$$

$$\Sigma_s(k, t) = \omega_s^2 \langle \sigma_s(k, t) | \sigma_s(k) \rangle \langle \sigma_s(k) | \sigma_s(k) \rangle^{-1}. \tag{6.6}$$

Longitudinal momentum conservation implies that

$$J_s(k, z) = z^{-1} - z^{-2}\Sigma_s(k, z), \tag{6.7}$$

$$J(k, z) = z^{-1} - z^{-2}\Sigma(k, z). \tag{6.8}$$

Making full use of particle and momentum conservation, the 3×3 matrix of memory functions appropriate to the column vectors of Eqs. (6.3) and (6.4) take the form

$$\hat{M}_s(z) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ k^2 v_T^2 \mathfrak{M}_s & 0 & \mathfrak{M}_s \end{bmatrix}, \tag{6.9}$$

$$\hat{M}_c(z) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ k^2 c_I^2 \mathfrak{M}_c & 0 & \mathfrak{M}_c \end{bmatrix}. \tag{6.10}$$

After some straightforward algebra[14] which is entirely parallel to Secs. III–V, the two 3×3 matrix equations of motion corresponding to Eq. (2.11) reduce to two independent equations which are most conveniently expressed in terms of $J(k, z)$ and $J_s(k, z)$:

$$z(zJ_s - 1) + \omega_s^2 J_s + \mathfrak{M}_s[(z + k^2 v_T^2 z^{-1})J_s - 1] = 0, \tag{6.11}$$

$$z(zJ - 1) + \omega_l^2 J + \mathfrak{M}_c[(z + k^2 c_I^2 z^{-1})J - 1] = 0. \tag{6.12}$$

As the lowest-order approximation we equate $\mathfrak{M}_c$ in Eq. (6.12) to $\mathfrak{M}_s$ in Eq. (6.11). The resulting expression for $J(k, z)$ in terms of $J_s(k, z)$ is just Eq. (5.22), the ELP approximation of Ortoleva and Nelkin. As the next order approximation we let

$$\mathfrak{M}_c(k, t) = \xi \mathfrak{M}_s(k, t) \tag{6.13}$$

and choose ξ so that Eq. (6.13) is exactly satisfied at $t = 0$. This guarantees that the sixth moment of $S(k, \omega)$ is given correctly. After some algebra the value of ξ is found to be

$$\xi = \frac{\omega_s^2 - k^2 v_T^2}{\omega_l^2 - k^2 c_I^2}\,\frac{\langle \omega_l^4 \rangle - \omega_l^4}{\langle \omega_s^4 \rangle - \omega_s^4}, \tag{6.14}$$

where $\langle \omega_l^4 \rangle$ and $\langle \omega_s^4 \rangle$ are defined by

$$\langle \omega_l^4 \rangle = \langle (iL)^2 j | (iL)^2 j \rangle \langle j | j \rangle^{-1}, \tag{6.15}$$

$$\langle \omega_s^4 \rangle = \langle (iL)^2 j_s | (iL)^2 j_s \rangle \langle j_s | j_s \rangle^{-1} \tag{6.16}$$

and are studied in greater detail in Appendix B.

With ξ given by Eq. (6.14) the expression relating $J(k, z)$ to $J_s(k, z)$ becomes

$$J(k, z) = \frac{[(\xi - 1)z^2 + \xi\omega_s^2 - k^2 v_T^2]J_s(k, z) - (\xi - 1)z}{[(\xi - 1)z^3 + Az + Bz^{-1}]J_s(k, z) - (\xi - 1)z^2 + C}, \tag{6.17}$$

where

$$A = \xi(\omega_s^2 + k^2 c_I^2) - (\omega_l^2 + k^2 v_T^2),$$
$$B = \xi\omega_s^2 k^2 c_I^2 - \omega_l^2 k^2 v_T^2, \tag{6.18}$$
$$C = \omega_l^2 - \xi k^2 c_I^2.$$

As can be easily checked the new approximation Eq. (6.17) reduces to the ELP approximation Eq. (5.22) when $\xi = 1$.

VII. NUMERICAL RESULTS

We turn now to the numerical predictions of the

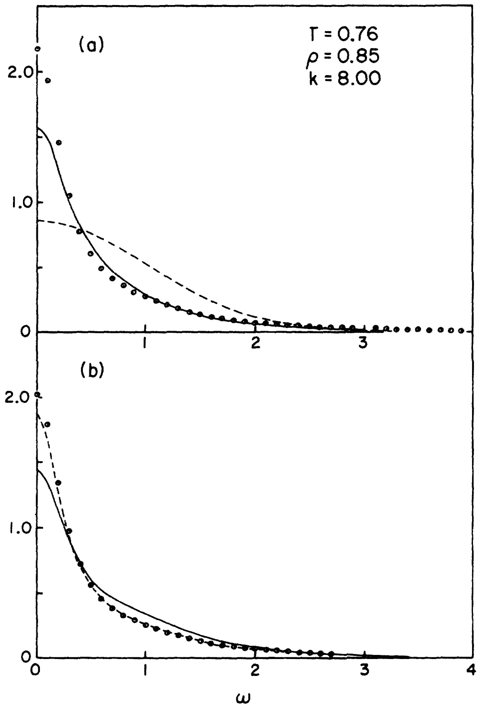

FIG. 1. The dynamic structure factor $S(k, \omega)$ [scaled by $2/S(k)$] as a function of frequency ω at the wave vector $k = 8.00$ for the liquid ($\rho = 0.85$, $T = 0.76$): (a) the molecular-dynamics result of the Orsay group (Refs. 2, 3) (solid line), the self-part $S_s(k, \omega)$ (dashed line), the perfect gas result (circles); (b) the ELP (solid line), Kerr (dashed line), and Vineyard (circles) approximations.

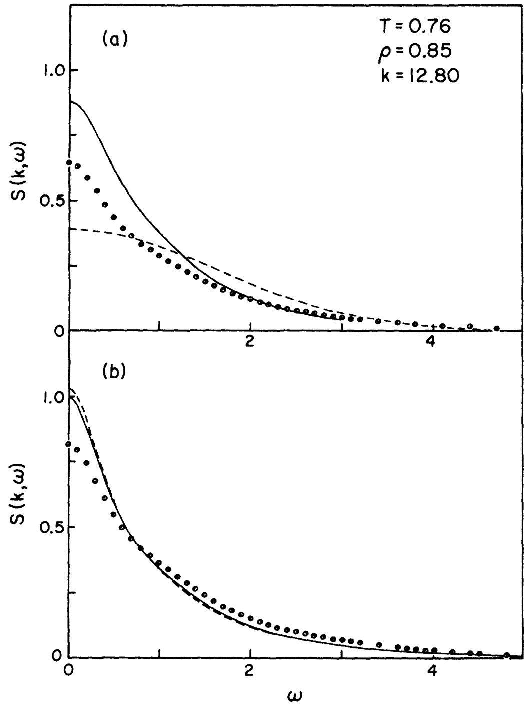

FIG. 2. The same as Fig. 1 except that $k = 12.80$.

various approximate theories discussed in Secs. III–VI. We consider a Lennard-Jones fluid with interaction potential

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \ . \tag{7.1}$$

For argon appropriate values of ϵ and σ are

$$\epsilon/k_B = 119.8\ ^\circ\mathrm{K}\ , \quad \sigma = 3.405\ \text{Å}\ .$$

Following the Orsay group,[2,3] we use reduced units with densities in units of σ^{-3}, wave numbers in units of σ^{-1}, temperatures in units of ϵ/k_B, and frequencies in units of t_0^{-1} where

$$t_0 = (m\sigma^2/48\epsilon)^{1/2} = 3.112\times 10^{-13}\ \text{sec}\ .$$

We consider two thermodynamic states, ($\rho = 0.85$, $T = 0.76$) corresponding to a liquid near the triple point, and ($\rho = 0.65$, $T = 1.827$) corresponding to a dense gas at temperature above the critical temperature. Molecular-dynamics studies of both the self-motion and $S(k, \omega)$ have been carried out for these two states. (For the first state a slight interpolation of the self-motion results was used.) For actual calculation from Eqs. (5.22) and (6.17) we use the parameterization of $J_s(k, z)$ given by Levesque and Verlet,[2] namely,

$$J_s(k, z) = [z + k^2 v_T^2 z^{-1} + N_s(k, z)]^{-1}\ , \tag{7.2}$$

$$N_s(k, t) = (2k^2 v_T^2 + \Omega_0^2)\, e^{-Bt^2/2}[1 - k^4 v_T^4 \varphi(k v_T t)] + At^4 e^{-\alpha t}\ , \tag{7.3}$$

where

$$\Omega_0^2 = \omega_s^2 - 3k^2 v_T^2 = (\rho/3m)\int d^3r\, g(r) \nabla^2 u(r)\ ,$$

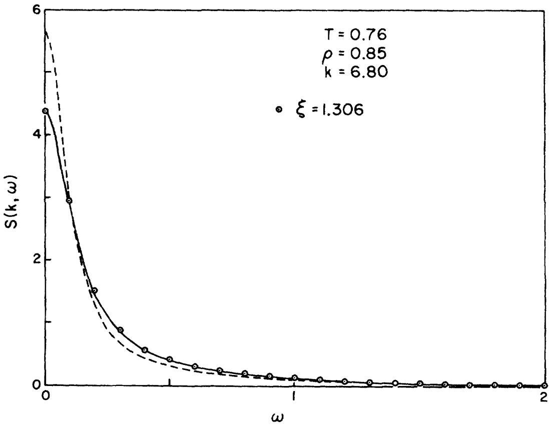

FIG. 3. The dynamic structure factor $S(k, \omega)$ (scaled) as a function of ω for the liquid ($\rho = 0.85$, $T = 0.76$) at $k = 6.80$: the molecular-dynamics result (solid lines); the best fit (circles); the ELP approximation (dashed lines).

$$B=\frac{1.65+10.43T+3k^2v_T^2(3+2k^2v_T^2/\Omega_0{}^2)}{1+2k^2v_T^2/\Omega_0{}^2} ,$$

$$\varphi(s)=0.7258-0.1876\,s^2 .$$

$$A=A_0\exp[-(k\lambda_c/2\pi)^2],$$

where $A_0=0.88$ and $\lambda_c\simeq 0.46$ for the state ($\rho=0.85$, $T=0.76$) [since $S(k,\omega)$ was found to be rather insensitive to λ_c, the value of λ_c for the state ($\rho=0.8442$, $T=0.722$) was used for the state ($\rho=0.85$, $T=0.76$)] and $A_0=-0.67$ and $\lambda_c=2.0$ for the state ($\rho=0.65$, $T=1.827$),

$$\alpha=4.12-2.61\rho .$$

The dynamic structure factor $S(k,\omega)$ is then given in terms of $J_s(k,z)$ through Eqs. (5.22) and (6.17), and

$$\pi S(k,\omega)=k^2v_T^2\omega^{-2}\,\mathrm{Re}J(k,z=-i\omega) . \qquad (7.4)$$

Before showing the results of our more refined models it is useful to indicate some typical simple theoretical results, and some typical "experimental" curves from molecular dynamics. We do this for the liquid at two different k values in Figs. 1 and 2. Figure 1(a) shows the molecular-dynamics results for $S(k,\omega)$ and for the self-part $S_s(k,\omega)$ taken from Refs. 3 and 2, respectively. The perfect gas result is plotted for comparison. Figure 1(b) compares the Vineyard, Kerr, and ELP approximations for the same k value and thermodynamic state as Fig. 1(a). The Vineyard result is of course the same as $S_s(k,\omega)$, but is normalized to give the correct $S(k)$. The progression from Vineyard to Kerr to ELP improves the agreement with the molecular dynamics $S(k,\omega)$. The residual disagreement of the ELP model with the exact results is displayed in detail in later figures. Figure 2 repeats the results of Fig. 1 for a larger k value. This is already twice the k value corresponding to the main peak in $S(k)$, but significant dynamic effects characteristic of the liquid are still present.

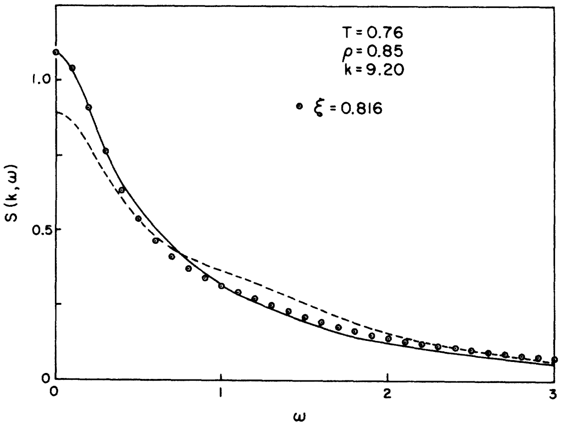

FIG. 4. The same as Fig. 3 except that $k=9.20$.

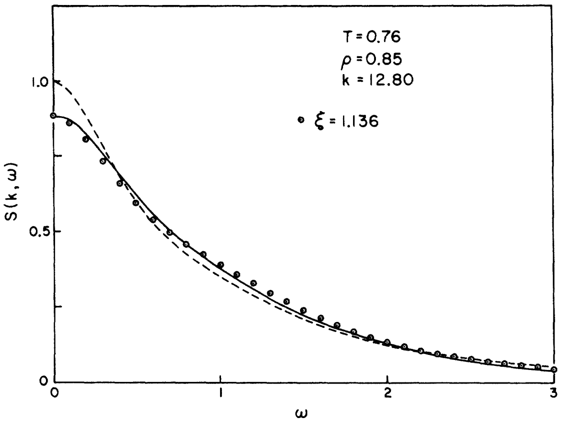

FIG. 5. The same as Fig. 3 except that $k=12.80$.

To calculate with our new approximation, Eq. (6.17), we need a value for the parameter ξ. This depends on the sixth frequency moment of $S(k,\omega)$, which in turn depends on the three-particle correlation function. Molecular-dynamics calculations to date have not been analyzed for this parameter, and are probably not sufficiently accurate to justify such an analysis. We thus treat ξ as a parameter to be fitted to $S(k,\omega)$. This fit must be carried out separately for each k value. No elaborate best fit criterion seems justified for this process, so we carry out the fit at $\omega=0$, where we have

$$S(k,\omega=0)=\xi^{-1}\frac{\omega_l{}^2-k^2c_l^2}{\omega_s{}^2-k^2v_T^2}\,S^2(k)S_s(k,\omega=0) . \qquad (7.5)$$

Equation (7.5) is a direct consequence of Eqs.

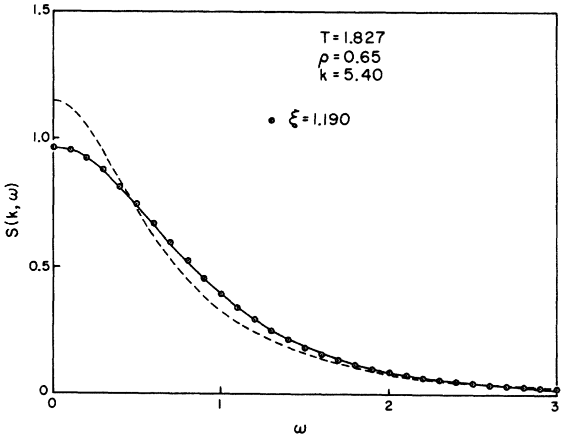

FIG. 6. The dynamic structure factor $S(k,\omega)$ (scaled) as a function of ω at $k=5.40$ for the dense gas ($\rho=0.65$, $T=1.827$): the molecular-dynamics result (solid line); the best fit (circles); the ELP approximation (dashed line).

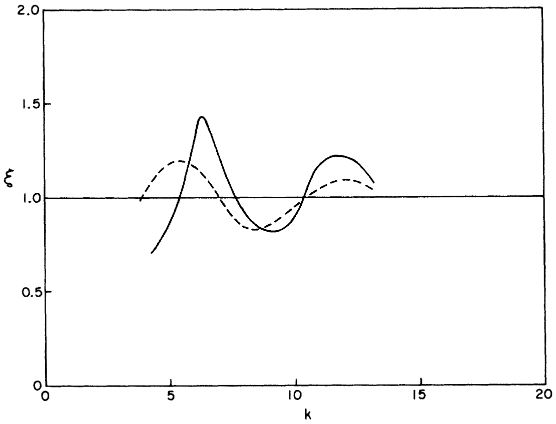

FIG. 7. The fitted value of ξ as a function of k. The solid line represents the ξ values for the liquid ($\rho = 0.85$, $T = 0.76$), while the dashed line, those for the dense gas ($\rho = 0.65$, $T = 1.827$).

(6.17) and (7.4).

In Figs. 3–6 we illustrate the fit to $S(k, \omega)$ obtained in this way. Figures 3, 4, and 5 are for the liquid, and Fig. 6 is for the dense gas. In all cases we plot the molecular-dynamics result, the ELP result of Eq. (5.22) and our new result from Eq. (6.17) with the value of ξ determined by Eq. (7.5). Recall that the ELP result corresponds to our new approximation with $\xi = 1.0$. The characteristic disagreement between the model calculations and the exact molecular dynamics is reduced from about 15% for $\xi = 1$ to a few percent for the best fit value of ξ. This latter agreement is within the precision of the molecular-dynamics results.

In Fig. 7 we plot the fitted value of ξ as a function of k. It has the oscillations characteristic of frequency moments of $S(k, \omega)$, but there is no information available to tell us if it is quantitatively correct. A clear test of the model given here would require a very accurate calculation of $J(k, t)$ at short times from which the parameter ξ could be directly evaluated through Eq. (6.14). If the model introduced here is applicable, this directly calculated value of ξ would agree with the value fitted to $S(k, \omega)$.

We have given a rather elaborate phenomenological analysis leading to Eq. (6.17). The only step which is not exact is the approximate scaling of memory functions in Eq. (6.13). This step has been taken with no theoretical justification. It was based on the observation that the equivalent step at a cruder level of approximation[6,12] [expressed by Eq. (5.18)] gave good numerical results. Even at the phenomenological level it is not clear how sensitive our fit to $S(k, \omega)$ is to the time dependence of the memory function given by Eq. (6.13). This point is now under investigation. For the present we have a procedure for fitting the dynamic structure factor $S(k, \omega)$ which works very well numerically, and which strongly indicates certain properties of the three-particle correlation function. We plan to compare our numerical results with those of other recent phenomenological theories.[15,16] This comparison should aid in pointing out the essential features of a more microscopic theory, and in defining more clearly the ranges of k and ω and the needed accuracy for future molecular-dynamics calculations and for neutron inelastic scattering experiments.

ACKNOWLEDGMENTS

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APPENDIX A: COUPLING BETWEEN RANDOM FORCE AND DENSITY FLUCTUATION

We make here a short-time expansion of the coupling term $\langle f_s(k, t) | \rho(k) \rangle$ between the random force for the single-particle motion at time t and the density fluctuation at $t = 0$ [note that $\langle f_s(k, t) | \rho_d(k) \rangle = \langle f_s(k, t) | \rho(k) \rangle$] which was entirely neglected in Sec. III to obtain the Vineyard convolution approximation Eq. (3.15). From its definition

$$f_s(k, t) = \exp[t(1 - P_0)iL](1 - P_0)iL\rho_s \,, \tag{A1}$$

with the projection operator P_0 defined for any $G(t)$ by

$$P_0 G(t) = \langle G(t) | \rho_s \rangle \rho_s \,. \tag{A2}$$

On a short-time scale we therefore have

$$\begin{aligned}\langle f_s(k, t) | \rho(k) \rangle &= \langle \{1 + t[1 - P_0]iL + (t^2/2!)[(1 - P_0)iL]^2 \\ &\quad + (t^3/3!)[(1 - P_0)iL]^3 + \cdots\}(1 - P_0)iL\rho_s(k) | \rho(k) \rangle \\ &= k^2 v_T^2 [S(k) - 1]t + k^2 v_T^2 \{\omega_l{}^2 - S(k)\omega_s{}^2 \\ &\quad + [S(k) - 1]k^2 v_T^2\} t^3/6 + \cdots \,. \end{aligned} \tag{A3}$$

Or equally well, a large-z expansion of $\langle f_s(k, z) | \rho(k) \rangle$ is

$$\begin{aligned}\langle f_s(k, z) | \rho(k) \rangle &= k^2 v_T^2 (S(k) - 1) z^{-2} \\ &\quad + k^2 v_T^2 [\omega_l{}^2 - S(k)\omega_s{}^2 + (S(k) - 1)k^2 v_T^2] z^{-4} + \cdots \,. \end{aligned}$$

APPENDIX B: FREQUENCY PARAMETERS

The longitudinal frequency parameters $\omega_l{}^2$, $\omega_s{}^2$, $\langle \omega_l{}^4 \rangle$, and $\langle \omega_s{}^4 \rangle$, or, more generally, $\omega_\alpha{}^2$, $\omega_{\alpha s}{}^2$, $\langle \omega_{\alpha\beta}{}^4 \rangle$, and $\langle \omega_{\alpha\beta, s}{}^4 \rangle$ with α and β being the directions either parallel or perpendicular to $\vec{k}$, may be expressed in terms of the static correlation functions and the pair potential $u(r)$. (The total interaction potential is taken as a sum of pairwise potentials.) From its definition

$$\omega_\alpha{}^2 = \langle iLj_\alpha | iLj_\alpha \rangle \langle j_\alpha | j_\alpha \rangle^{-1}$$

$$= (1+2\delta_{\alpha 3})k^2 v_T^2 + \frac{n_0}{m}\int d^3r\, g(r)(1-\cos\vec{k}\cdot\vec{r})\frac{\partial^2 u(r)}{\partial r_\alpha^2}, \tag{B1}$$

where n_0 is the mean density N/V and $g(r)$ is the static pair-correlation function.

Similarly for the self-part $\omega_{\alpha s}{}^2$ we have

$$\omega_{\alpha s}{}^2 = \langle iLj_{\alpha s} | iLj_{\alpha s} \rangle \langle j_{\alpha s} | j_{\alpha s} \rangle^{-1}$$

$$= (1+2\delta_{\alpha 3})k^2 v_T^2 + \frac{n_0}{m}\int d^3r\, g(r)\frac{\partial^2 u(r)}{\partial r_\alpha^2}\ . \tag{B2}$$

The frequency parameter $\langle \omega_{\alpha\beta}{}^4 \rangle$ by its definition

$$\langle \omega_{\alpha\beta}{}^4 \rangle = \langle (iL)^2 j_\alpha | (iL)^2 j_\beta \rangle \langle j_\beta | j_\beta \rangle^{-1}$$

$$= \delta_{\alpha\beta}(3+12\delta_{\alpha 3})k^4 v_T^4$$

$$+ \delta_{\alpha\beta} v_T^2 \frac{n_0}{m}\int d^3r\, g(r)\left[(6+8\delta_{\alpha 3})k^2 \frac{\partial^2 u(r)}{\partial r_\alpha^2} + k^2 \frac{\partial^2 u(r)}{\partial r_3^2} + 6k \sin\vec{k}\cdot\vec{r}\,\frac{\partial^3 u(r)}{\partial r_\alpha^2 \partial r_3} + 2\beta(1-\cos\vec{k}\cdot\vec{r})\sum_{\mu=1}^{3}\left(\frac{\partial^2 u(r)}{\partial r_\mu \partial r_\alpha}\right)^2\right]$$

$$+ \delta_{\alpha\beta}\left(\frac{n_0}{m}\right)^2 \iint d^3r\, d^3r'\, g(\vec{r},\vec{r}\,')[1+\cos\vec{k}\cdot(\vec{r}-\vec{r}\,') - \cos\vec{k}\cdot\vec{r} - \cos\vec{k}\cdot\vec{r}\,']\sum_{\mu=1}^{3}\frac{\partial^2 u(r)}{\partial r_\mu \partial r_\alpha}\,\frac{\partial^2 u(r')}{\partial r'_\mu \partial r'_\beta}\ , \tag{B3}$$

where $g(\vec{r},\vec{r}\,')$ is the static three-body correlation function.

The self-part $\langle \omega_{\alpha\beta,s}{}^4 \rangle$ is similarly given by

$$\langle \omega_{\alpha\beta,s}{}^4 \rangle = \langle (iL)^2 j_{\alpha s} | (iL)^2 j_{\beta s} \rangle \langle j_{\beta s} | j_{\beta s} \rangle^{-1}$$

$$= \delta_{\alpha\beta}(3+12\delta_{\alpha 3})k^4 v_T^4 + \delta_{\alpha\beta} v_T^2 \frac{n_0}{m}\int d^3r\, g(r)\left[(6+8\delta_{\alpha 3})k^2 \frac{\partial^2 u(r)}{\partial r_\alpha^2} + k^2 \frac{\partial^2 u(r)}{\partial r_3^2} + 2\beta\sum_{\mu=1}^{3}\left(\frac{\partial^2 u(r)}{\partial r_\mu \partial r_\alpha}\right)^2\right]$$

$$+ \delta_{\alpha\beta}\left(\frac{n_0}{m}\right)^2 \iint d^3r\, d^3r'\, g(\vec{r},\vec{r}\,')\sum_{\mu=1}^{3}\frac{\partial^2 u(r)}{\partial r_\mu \partial r_\alpha}\,\frac{\partial^2 u(r')}{\partial r'_\mu \partial r'_\beta}\ . \tag{B4}$$

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