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# Generalized Hydrodynamics and Analysis of Current Correlation Functions[*,†]

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A generalization of the Navier-Stokes equation, valid for wavelengths and times of a molecular order of magnitude, is discussed on the basis of viscoelastic behavior of simple classical liquids. In this theory, transport coefficients are replaced by appropriate viscoelastic memory functions. The theory is verified by analyzing the data on current-correlation functions obtained from computer experiments. Three different models for the time dependence of the viscoelastic memory are investigated, namely, a single-exponential decay, a modified-exponential decay, and a Gaussian decay. It is observed that the memory functions are approximately Gaussian, at least for times of the order of one or two relaxation times. This is in agreement with a conjecture of Forster, Martin, and Yip. The wave-number dependence of the half-width of the Gaussian decay, and of the longitudinal- and shear-viscosity coefficients, are found from computer experiments. The extrapolated values of these transport coefficients, in the limit $k \rightarrow 0$, are in good agreement with experiments on liquid argon.

## I. INTRODUCTION

In recent years, the dynamics of density fluctuations in simple classical liquids has been a subject of considerable interest. In particular, several theoretical attempts[1-4] have been made to reproduce the data obtained from computer experiments on fluctuations of the current density in liquid argon.[5,6] Our reasons for presenting still another article on the same topic are twofold: (i) We provide a simple heuristic argument leading to the generalized hydrodynamic equations that have been derived previously by more elaborate statistical-mechanical methods; and (ii) we present a more detailed and complete analysis of the data provided by computer experiments.

As is well known, the familiar Navier-Stokes equation gives a good description of transport phenomena in liquids for long wavelengths and low frequencies. This description may be expected to fail at wavelengths of a few angstroms and frequencies of the order of $10^{12}$ Hz. The original motivation for the present work was to find the appropriate generalization of the Navier-Stokes equation so as to include short-wavelength and high-frequency phenomena satisfactorily.[7] Since the inception of this investigation, a number of authors have in fact found the desired generalization.[1-4] The essential point is to include nonlocal behavior in space and time. In particular, viscoelastic behavior must be taken into account. This has been done by various forms of linear response theory, for example, by Mori's theory of generalized Brownian motion[4,8] and by methods of Kadanoff and Martin.[1,9]

The generalized hydrodynamic equations that have been derived and discussed in this article are

$$\frac{d}{dt} J_{\parallel}(\vec{k}, t) = \frac{k_B T}{mS(k)} ik\rho(\vec{k}, t) - \int_0^t ds\, k^2 \phi_{\parallel}(k, t-s) J_{\parallel}(\vec{k}, s), \qquad (1.1a)$$

$$\frac{d}{dt} \vec{J}_{\perp}(\vec{k}, t) = -\int_0^t ds\, k^2 \phi_{\perp}(k, t-s) \vec{J}_{\perp}(\vec{k}, s)\ , \qquad (1.1b)$$

where $J_{\parallel}(\vec{k}, t)$ and $\vec{J}_{\perp}(\vec{k}, t)$ are, respectively, the $k$th Fourier components of the longitudinal and transverse current density; $\rho(\vec{k}, t)$ is the $k$th Fourier component of particle density. $\phi(k, t)$ is a memory function representing the retarded response of the current to a change in the stress tensor. [If the memory function is independent of $k$ and is a $\delta$ function in time and the value of $S(k)$, the structure factor, is taken in the limit $k \to 0$, Eqs. (1.1) reduce to the longitudinal and transverse components of the ordinary linearized Navier-Stokes equation.] Fluctuations in the current density are described by a correlation function $\overleftrightarrow{C}(k, t)$,

$$\overleftrightarrow{C}(k, t) = \langle \vec{J}^*(\vec{k}, 0)\vec{J}(\vec{k}, t)\rangle\ , \qquad (1.2)$$

where $\langle\cdots\rangle$ denotes average over an equilibrium ensemble. The longitudinal current-correlation function obeys the equation

$$\frac{d}{dt} C_{\parallel}(k, t) = -\int_0^t ds \left( \frac{k_B T}{mS(k)} k^2 + k^2 \phi_{\parallel}(k, t-s) \right) \times C_{\parallel}(k, s) \qquad (1.3)$$

and the transverse current-correlation function satisfies the equation

$$\frac{d}{dt} C_{\perp}(k, t) = -\int_0^t ds\, k^2 \phi_{\perp}(k, t-s) C_{\perp}(k, s)\ , \qquad (1.4)$$

which is exactly the equation obeyed by transverse current density itself.

We find that the memory function $\phi(k, t)$ has the following properties. First, the initial value for the memory function in the longitudinal case is $[\omega_l^2(k) - \omega_0^2(k)]/k^2$ and for the transverse case is $\omega_t^2(k)/k^2$. The quantities $\omega_l^2(k)$, $\omega_t^2(k)$, and $\omega_0^2(k) = k^2[k_B T/mS(k)]$ can be found from an equilibrium calculation involving the radial distribution function and the intermolecular potential; alternatively, the quantities $\omega_l^2(k)$ and $\omega_t^2(k)$ can be calculated from the initial second derivative of the correlation function $C(k, t)$. Second, the time dependence of the memory function can be approximated reasonably well by a Gaussian (in agreement with a conjecture of Forster, Martin, and Yip[10]); the half-width can be found either from an equilibrium calculation or, alternatively, from the initial fourth derivative of $C(k, t)$.

## II. COMPUTER EXPERIMENTS

Before proceeding to the details of the analysis, we present some background information on the computer experiments[11] which investigate the dynamics of a classical system of interacting particles.

The data presented in this paper pertain to a calculation on a system of 500 particles in a box with periodic boundary conditions. The total intermolecular potential is taken to be a sum of (6-12) Lennard-Jones pair potentials,

$$4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]\ , \qquad (2.1)$$

with $\epsilon/k_B = 120\ ^\circ\mathrm{K}$ and $\sigma = 3.4$ Å. The mass of a single particle is the atomic mass of argon. The density is 1.407 $g/\mathrm{cm}^3$. Because of the corresponding states relationship arising out of Eq. (2.1), the results should be applicable to a variety of liquified noble gases at appropriate temperatures and densities.

Trajectories of this system of particles were obtained by numerical integration of the coupled differential equations of motion. The time step for integration was $2\times 10^{-14}$ sec. The system was in thermal equilibrium at a temperature of 76 °K (and therefore simulates liquid argon in a slightly supercooled state). Having determined the trajectories of the 500 particles as functions of time, one can then compute the time dependence of various dynamical variables, in particular, the current density

$$\vec{J}(\vec{k}, t) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \dot{\vec{R}}_j(t) e^{i\vec{k}\cdot\vec{R}_j(t)}\ . \qquad (2.2)$$

Here $N = 500$, and $\vec{R}_j(t)$ and $\dot{\vec{R}}_j(t)$ are the position and velocity of the $j$th particle at time $t$ in an $N$-

particle system. $J_{\parallel}(\vec{k}, t)$ is then the component of $\vec{J}(\vec{k}, t)$ in the direction of $\vec{k}$ and $\vec{J}_{\perp}(\vec{k}, t)$ in a direction normal to $\vec{k}$.

From the time dependence of $J(\vec{k}, t)$ [here $J(\vec{k}, t)$ stands for either longitudinal or transverse current density], we compute a moving time average

$$C(k, t) = (1/T) \int_0^T ds\, J^*(\vec{k}, s) J(\vec{k}, s+t) \qquad (2.3)$$

for the longitudinal as well as transverse current-correlation functions. Here $T$ is of the order of $2\times 10^{-12}$ sec. Figures 1(a) and 1(b) show the shapes of these correlation functions for several values of $k$ in reciprocal angstroms.[6] For convenience these curves have all been normalized to unity $t=0$. Shortly after the first minimum, the curves appear to be dominated by statistical noise. The data presented in Figs. 1 are the raw material for our analysis. The statistical problems arising in the calculation of these correlation functions have been investigated elsewhere.[12]

## III. THEORY

In this section, we present a theory in support of Eqs. (1). We use a heuristic argument, based on physical intuition.

The dynamical variables with which we shall be concerned in this analysis are the particle and current densities. Fourier components of the particle density $\rho$ and current density $\vec{J}$ are defined to be

$$\rho(\vec{k}, t) = N^{-1/2} \sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{R}_j(t)} \qquad (3.1)$$

and

$$\vec{J}(\vec{k}, t) = N^{-1/2} \sum_{j=1}^{N} \dot{\vec{R}}_j(t) e^{i\vec{k}\cdot\vec{R}_j(t)} . \qquad (3.2)$$

As stated earlier, the longitudinal and transverse components of the current density $\vec{J}(\vec{k}, t)$ are defined with respect to the direction of the wave vector $\vec{k}$. The current-correlation function $\overleftrightarrow{C}(k, t)$ defined in Eq. (1.2) can be decomposed into longitudinal and transverse components $C_{\parallel}$ and $C_{\perp}$. Because of isotropy in a liquid, both these correlation functions depend only on the magnitude of $\vec{k}$ and not its direction. We now study the longitudinal and transverse current-correlation functions separately.

### A. Longitudinal Current-Current Correlation

In ordinary hydrodynamics, the time dependence of the longitudinal current density $J_{\parallel}(\vec{R}, t)$ at the position $\vec{R}$ and time $t$ is determined by the longitudinal component of the linearized Navier-Stokes equation[13]

$$\frac{d}{dt} J_{\parallel}(\vec{R}, t) = -\frac{1}{m} \vec{\nabla} P(\vec{R}, t) + \nu_l \nabla^2 J_{\parallel}(\vec{R}, t) , \qquad (3.3)$$

where $\nu_l$ is the kinematic longitudinal viscosity, related to the shear viscosity $\eta$ and volume viscosity $\eta_v$ by

$$\nu_l = (\tfrac{4}{3}\eta + \eta_v)/m\rho , \qquad (3.4)$$

$m\rho$ being the mass density. (Transverse and longitudinal fields are not coupled in linear response theory.)

Also, conservation of particles leads to the continuity equation for $\rho(\vec{R}, t)$,

$$\frac{\partial}{\partial t} \rho(\vec{R}, t) + \vec{\nabla}\cdot\vec{J}(\vec{R}, t) = 0 , \qquad (3.5)$$

or its $k$th Fourier component

$$\frac{\partial}{\partial t} \rho(\vec{k}, t) = ikJ_{\parallel}(\vec{k}, t) . \qquad (3.6)$$

We do not consider the effects of temperature fluctuations. We show in the Appendix that for the region of interest to us in this analysis ($k \sim 10^8\,\mathrm{cm}^{-1}$), the error due to omission of temperature fluctuations is small and falls within the reliability of our results.

We assume that the pressure variations are entirely due to density fluctuations; the pressure gradient then is

$$\vec{\nabla} P(\vec{R}, t) = (\partial P/\partial\rho) \vec{\nabla}\rho(\vec{R}, t) . \qquad (3.7)$$

A generalization of the ordinary hydrodynamics is suggested along the following lines.

(i) A change in pressure at position $\vec{R}$ should not be determined completely by density variations at the same position $\vec{R}$ but also by density variations in neighboring positions. In other words, the pressure gradient due to a density gradient is nonlocal and should really be a functional derivative

$$\vec{\nabla} P(\vec{R}) = \vec{\nabla}_{\vec{R}} \int d\vec{R}' \frac{\delta P(\vec{R})}{\delta\rho(\vec{R}')} \delta\rho(\vec{R}') . \qquad (3.8)$$

Because of the translational invariance in liquids, the functional derivative depends on the relative separation only. On taking a Fourier transform in space, this becomes

$$(\vec{\nabla} P)_k = ik\rho(k)(\delta P/\delta\rho)_k . \qquad (3.9)$$

This functional derivative is related to the direct correlation function of the liquid or its equilibrium structure factor $S(k)$ by

$$(\delta P/\delta\rho)_k = k_B T/S(k) . \qquad (3.10)$$

In effect, $S(k)$ determines a $k$-dependent compressibility.

(ii) Another generalization is suggested by the observation that liquids have viscoelastic behavior; the viscosity coefficients are really complex functions of frequency,[14,15]

$$\nu_l(\omega) = \int_0^\infty dt\, e^{-i\omega t} \phi_{\parallel}(t) , \qquad (3.11)$$

where $\phi_{\parallel}(t)$ is an after effect or memory function describing the delayed response of the longitudinal

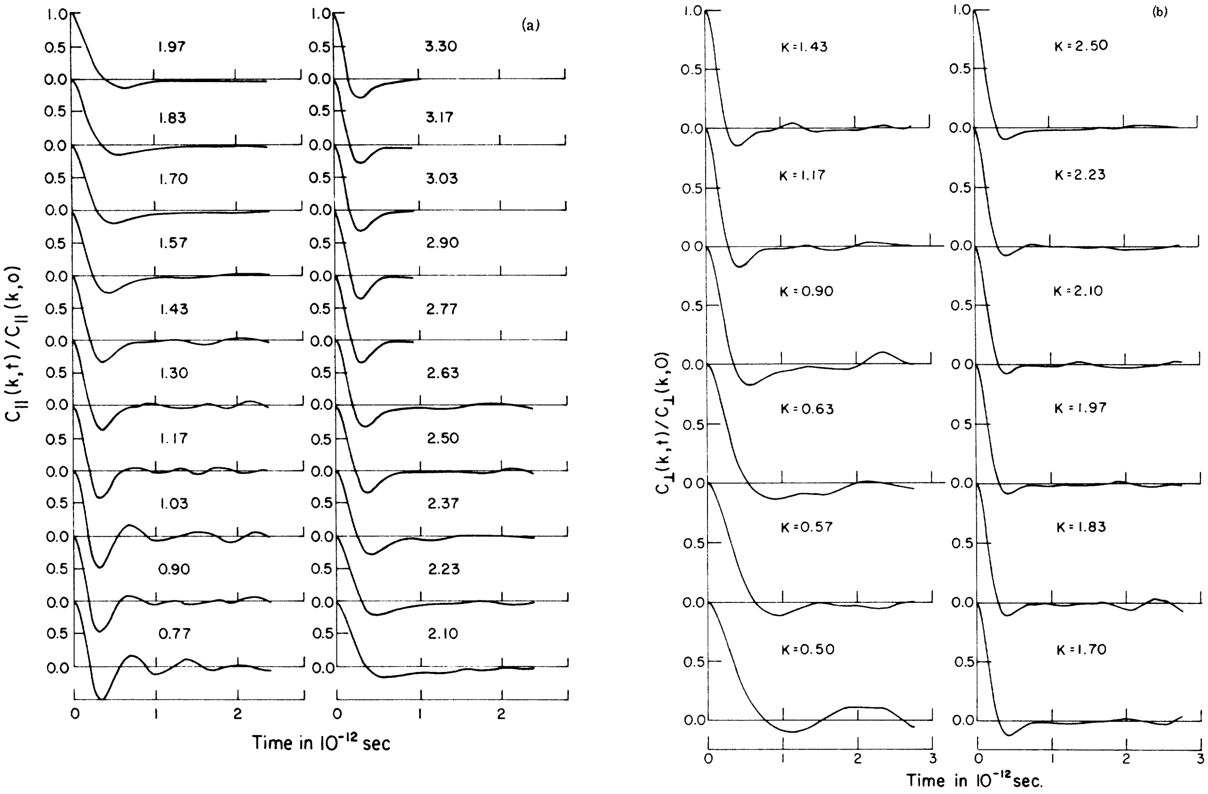

FIG. 1. (a) Time dependence of the data $C_{\parallel}(k, t)/C_{\parallel}(k, 0)$ for several values of $k$. (b) Time dependence of the data $C_{\perp}(k, t)/C_{\perp}(k, 0)$ for different values of $k$.

part of the stress tensor to a change in the rate of shear. We may therefore replace the constant longitudinal viscosity $\nu_l$ in Eq. (3.3) by a memory function in the form of a convolution in time. At the same time, the memory function $\phi_{\parallel}$ can be made a function of $k$ to allow for nonlocal effects in space.

Allowing for these generalizations, the longitudinal component of the linearized Navier-Stokes equation (3.3) becomes

$$\frac{d}{dt}J_{\parallel}(\vec{k}, t) = ik\frac{k_BT}{mS(k)}\rho(\vec{k}, t) - k^2\int_0^t dt'\phi_{\parallel}(k, t-t') \times J_{\parallel}(\vec{k}, t') \,, \tag{3.12}$$

which is just Eq. (1.1a). A closed equation for the current density can be obtained by making use of the continuity Eq. (3.6). In order to get the longitudinal current-correlation function, we multiply this equation by the initial value $J_{\parallel}^*(\vec{k}, 0)$ and average over an equilibrium distribution.

The contribution from the initial value of the particle density $\rho(\vec{k}, 0)$ vanishes by symmetry

$$\langle J_{\parallel}^*(\vec{k}, 0)\rho(\vec{k}, 0)\rangle = 0 \,. \tag{3.13}$$

The longitudinal current-correlation function thus obeys the equation

$$\frac{d}{dt}C_{\parallel}(k, t) = -\int_0^t dt' K_l(k, t-t')C_{\parallel}(k, t') \,, \tag{3.14}$$

with the memory kernel

$$K_l(k, t) = k^2[k_BT/mS(k) + \phi_{\parallel}(k, t)] \,. \tag{3.15}$$

This may be written as

$$K_l(k, t) = \omega_0^2(k) + [\omega_l^2(k) - \omega_0^2(k)]\Psi_{\parallel}(k, t) \,, \tag{3.16}$$

where $\omega_0^2(k) = k^2[k_BT/mS(k)]$ is the "isothermal" dispersion curve, and the time dependence of the memory function $\Psi_{\parallel}(k, t)$ is normalized to unity at its initial value. The frequency $\omega_l(k)$ is defined by the initial value $K_l(k, 0)$ of the memory kernel and is given by the initial second derivative of $C_{\parallel}(k, t)$,

$$\omega_l^2(k) = -\ddot{C}_{\parallel}(k, 0)/C_{\parallel}(k, 0) \,, \tag{3.17a}$$

or, equivalently,

$$\omega_l^2(k) = \langle|\dot{J}_{\parallel}(\vec{k}, 0)|^2\rangle/\langle|J_{\parallel}(\vec{k}, 0)|^2\rangle \,. \tag{3.17b}$$

### B. Transverse Current-Current Correlation

The derivation of Eqs. (1.1b) and (1.4) follows along the same lines as that of the longitudinal current density. In ordinary hydrodynamics, the transverse part of the linearized Navier-Stokes equation[13] gives the time dependence of the transverse current density $\vec{J}_\perp(\vec{R}, t)$ at a position $\vec{R}$ and time $t$

$$\frac{d}{dt}\vec{J}_\perp(\vec{R}, t) = \nu\nabla^2\vec{J}_\perp(\vec{R}, t) , \tag{3.18}$$

where $\nu$ is the kinematic shear viscosity $\nu = \eta/m\rho$. The Fourier transform in space of this equation is

$$\frac{d}{dt}\vec{J}_\perp(\vec{k}, t) = -\nu k^2\vec{J}_\perp(\vec{k}, t) . \tag{3.19}$$

Note that Eq. (3.19) leads to an exponential decay of the transverse current-correlation function $C_\perp(k, t)$; this is far from correct as can be seen from the inspection of Fig. 1(b). We must therefore modify the transverse part of the Navier-Stokes equation (3.19). This is generalized so as to include the viscoelastic behavior of liquids. Following the arguments used to get Eqs. (3.11) and (3.12), we replace the constant viscosity $\nu$ in Eq. (3.19) by a memory function, in the form of a convolution in time and a function of $k$ (to allow for nonlocal effects in space)

$$\frac{d}{dt}\vec{J}_\perp(\vec{k}, t) = -k^2\int_0^t ds\, \phi_\perp(k, t-s)\,\vec{J}_\perp(\vec{k}, s) . \tag{3.20}$$

The corresponding equation for the transverse current-correlation function is

$$\frac{d}{dt}C_\perp(k, t) = -k^2\int_0^t ds\, \phi_\perp(k, t-s)C_\perp(k, s) . \tag{3.21}$$

We define, as before, a frequency $\omega_t(k)$ as

$$\omega_t^2(k) \equiv k^2\phi_\perp(k, 0) , \tag{3.22}$$

so that

$$k^2\phi_\perp(k, t) = \omega_t^2(k)\Psi_\perp(k, t) , \tag{3.23}$$

where $\Psi_\perp(k, t)$ is the time dependence of the memory function and has been normalized to unity at its initial value. This frequency $\omega_t(k)$ can be found either from initial second derivative of the correlation function $C_\perp(k, t)$ or, alternatively, from an equilibrium calculation:

$$\begin{aligned}\omega_t^2(k) &= -\ddot{C}_\perp(k, 0)/C_\perp(k, 0)\\ &= \langle|\vec{J}_\perp(\vec{k}, 0)|^2\rangle/\langle|\vec{J}_\perp(\vec{k}, 0)|^2\rangle .\end{aligned} \tag{3.24}$$

Equations (3.14) and (3.21) are the equations we investigate by means of computer experiments.

## IV. CALCULATION AND ANALYSIS

An *a priori* calculation of the memory function $\Psi(k, t)$ is difficult and little progress has been made. For this reason, we take an experimentalist's point of view. Information obtained from computer experiments tells us something about the structure of the current-correlation function. On using Eqs. (3.14) and (3.21), the structure of the memory functions can be deduced. The simplest procedure, and the one we use here, is to assume a mathematical form for $\Psi(k, t)$ containing an undetermined parameter, and then to test the validity of the assumed form by curve fitting.

We use three different models for the time dependence of the memory function $\Psi(k, t)$ in Eqs. (3.14) and (3.21): (i) a simple exponential function

$$e^{-t/\tau_E(k)} , \tag{4.1a}$$

(ii) a modified exponential function

$$[1 + 2t/\tau_{\mathrm{ME}}(k)]e^{-2t/\tau_{\mathrm{ME}}(k)} , \tag{4.1b}$$

and (iii) a Gaussian,

$$\exp[-\pi t^2/4\tau_G^2(k)] . \tag{4.1c}$$

### A. Analysis in Terms of Power Spectrum

The power spectrum of the current-correlation function is defined as

$$C(k, \omega) = \int_0^\infty dt\, \cos\omega t\, C(k, t) \tag{4.2}$$

and can be related to the corresponding memory functions by Eqs. (3.14) and (3.21). The frequencies $\omega_l(k)$, $\omega_0(k)$, and $\omega_t(k)$ are obtained by an equilibrium calculation and are considered as input data. The relaxation times $\tau_E(k)$, $\tau_{\mathrm{ME}}(k)$, and $\tau_G(k)$ appearing in the three models are considered as parameters, and are determined by the method of least-squares fitting to the molecular dynamics data on power spectrum $C(k, \omega)$. This is repeated for several values of $k$. The theoretical curves for the power spectrum $C(k, \omega)$ are then obtained by substituting these computed values of the parameters $\tau(k)$. A comparison of the theoretical power spectrum with the molecular dynamics data on $C(k, \omega)$ indicates that the Gaussian model for the time dependence of the memory function gives the best fit at least for large $\omega$ (or short times). In Figs. 2 and 3 we show the theoretical power spectrum for the longitudinal as well as transverse current-correlation function computed by assuming a Gaussian model for the time dependence of the memory function; this is compared with the "experimental" data.

### B. Analysis in Terms of Initial Time-Dependence of Correlation Function

In this part of the analysis, the parameter $\tau(k)$ is computed directly from the data on the time dependence of $C(k, t)/C(k, 0)$(and not from its power spectrum). We use the Gaussian model for the time dependence of the memory function and compare the results with those obtained from the analysis of the power spectrum. A least-squares method is used to obtain a polynomial fit to the data $C(k, t)/C(k, 0)$. The coefficients of $t^2$ and $t^4$ give the second and the fourth moments of the correlation functions. From Eqs. (3.17a) and

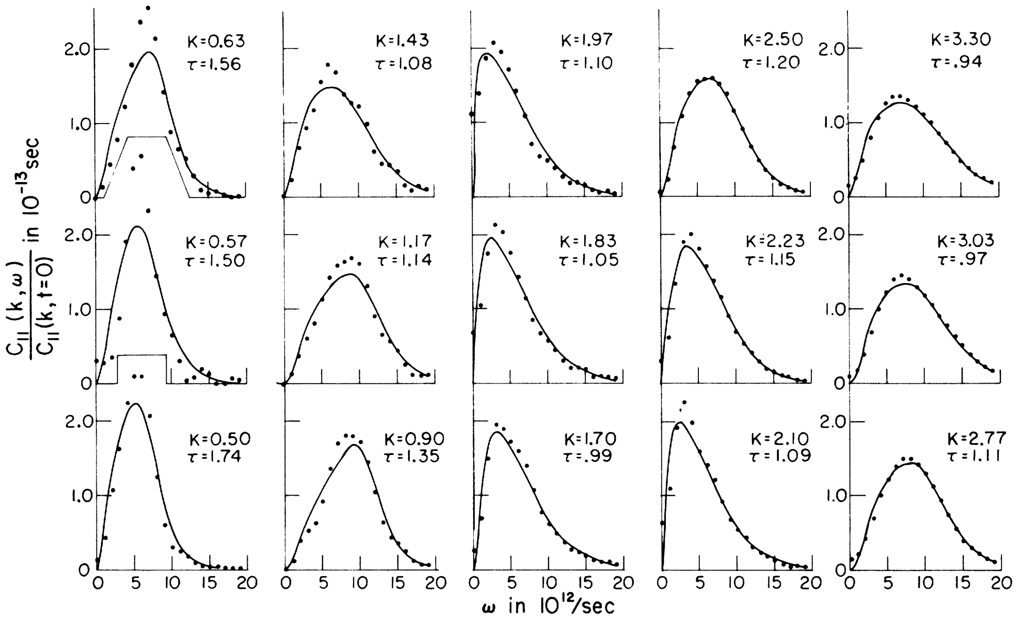

FIG. 2. Power spectrum of the longitudinal current-correlation function $C_{\parallel}(k,\omega)/C_{\parallel}(k,0)$ for several $k$ values; for each $k$, the frequencies $\omega_0(k)$, $\omega_l(k)$, and the parameter $\tau^{\text{long}}(k)$ are determined from an equilibrium calculation. The time dependence of the memory function is assumed to be Gaussian. The solid lines are the computed power spectrum, and dots are data [Fourier transform of functions shown in Fig. 1(a)].

(3.24), we can therefore compute the frequencies $\omega_l^2(k)$ and $\omega_t^2(k)$. The fourth initial derivatives are (Gaussian model)

$$\frac{[(d^4/dt^4)C_{\parallel}(k,t)]_{t=0}}{C_{\parallel}(k,t=0)}$$

$$= \omega_l^4(k) + \tfrac{1}{2}\pi[\omega_l^2(k) - \omega_0^2(k)][1/\tau_G^{\text{long}}(k)]^2 \qquad (4.3)$$

and

$$\frac{[(d^4/dt^4)C_{\perp}(k,t)]_{t=0}}{C_{\perp}(k,t=0)}$$

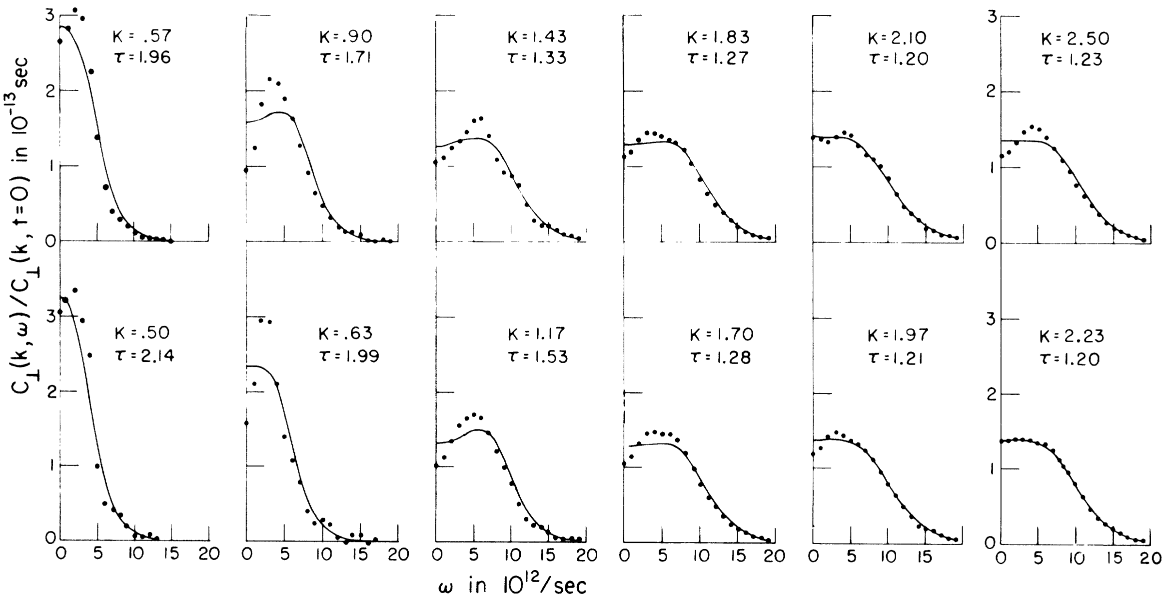

FIG. 3. Power spectrum of the transverse current-correlation function $C_{\perp}(k,\omega)/C_{\perp}(k,0)$ for several $k$ values; for each $k$, the frequency $\omega_t(k)$ and the parameter $\tau^{\text{tran}}(k)$ are determined by an equilibrium calculation. A Gaussian model is assumed for the time dependence of the memory function. The solid lines are the computed power spectrum, and dots are data [Fourier transform of functions shown in Fig. 1(b)].

$$= \omega_t^4(k) + \tfrac{1}{2}\pi\omega_t^2(k)[1/\tau_G^{\,\mathrm{tran}}(k)]^2 \qquad (4.4)$$

for the longitudinal and transverse current-correlation functions, respectively. Thus, a knowledge of the initial fourth derivative (fourth moment) of the current-correlation function gives an opportunity to compute $\tau_G^{\mathrm{long}}(k)$ and $\tau_G^{\mathrm{tran}}(k)$. [Note that a previous knowledge of $\omega_0^2(k)$ is essential for the longitudinal case.] In Tables I and II, we compare the values of the parameters $\tau_G^{\mathrm{long}}(k)$ and $\tau_G^{\mathrm{tran}}(k)$ as computed from the best fit to the power spectrum with those from the best polynomial fit to the time dependence of the current-correlation function. The agreement seems to be quite good.

From the foregoing analysis, we find that the time dependence of the memory function $\Psi(k, t)$ can be approximated reasonably well by a Gaussian; this is particularly true for short times of the order of one or two relaxation times.

## V. RESULTS

We find from this analysis that a one parameter description of the time dependence of the memory function is reasonable. We find also that Eqs. (3.12) and (3.20) are valid generalizations of the Navier-Stokes equations for the longitudinal as well as transverse current density, and give a good description of the dynamic behavior of simple classical liquids for small wavelengths and short times.

We find that the time dependence of the memory function is reasonably well approximated by a Gaussian, at least for times of the order of one or two relaxation times. The half-width $\tau(k)$ can be found from a calculation using the entire power spectrum of the current-correlation function; alternatively, we can use the initial fourth derivative of the time dependence of the current-correlation function $C(k, t)$.

TABLE I. Comparison of $\tau^{\mathrm{long}}(k)$ and $\eta_l(k, 0)$ using Gaussian memory.

| $k$ (Å$^{-1}$) | $\tau^{\mathrm{long}}(k)$ best fit to power spectrum ($10^{-13}$ sec) | $\tau^{\mathrm{long}}(k)$ from initial derivatives ($10^{-13}$ sec) | $\eta_l(k, 0)$ best fit to power spectrum ($10^{-3}$ P) | $\eta_l(k, 0)$ from initial derivatives ($10^{-3}$ P) |
|---|---|---|---|---|
| 0.23 | 3.02 | 0.96 | 5.54 | 4.12 |
| 0.50 | 1.74 | 1.52 | 3.19 | 2.63 |
| 0.57 | 1.50 | 1.53 | 2.52 | 2.31 |
| 0.63 | 1.56 | 1.54 | 2.52 | 2.52 |
| 0.90 | 1.36 | 1.38 | 1.60 | 1.66 |
| 1.17 | 1.14 | 1.28 | 0.91 | 0.96 |
| 1.43 | 1.09 | 1.20 | 0.52 | 0.55 |
| 1.70 | 0.99 | 1.10 | 0.27 | 0.28 |
| 1.83 | 1.05 | 1.03 | 0.22 | 0.21 |
| 1.97 | 1.10 | 1.11 | 0.20 | 0.18 |
| 2.10 | 1.09 | 1.07 | 0.17 | 0.15 |
| 2.23 | 1.15 | 1.20 | 0.17 | 0.17 |
| 2.50 | 1.20 | 1.26 | 0.17 | 0.17 |
| 2.77 | 1.11 | 1.21 | 0.15 | 0.15 |
| 3.03 | 0.97 | 1.15 | 0.13 | 0.15 |
| 3.30 | 0.94 | 1.10 | 0.11 | 0.13 |

TABLE II. Comparison of $\tau^{\mathrm{tran}}(k)$ and $\eta(k, 0)$ using Gaussian memory.

| $k$ (Å$^{-1}$) | $\tau^{\mathrm{tran}}(k)$ best fit to power spectrum ($10^{-13}$ sec) | $\tau^{\mathrm{tran}}(k)$ from initial derivatives ($10^{-13}$ sec) | $\eta(k, 0)$ best fit to power spectrum ($10^{-3}$ P) | $\eta(k, 0)$ from initial derivatives ($10^{-3}$ P) |
|---|---|---|---|---|
| 0.23 | 3.02 | 1.27 | 2.63 | 1.21 |
| 0.50 | 2.14 | 1.90 | 1.72 | 1.45 |
| 0.57 | 1.96 | 1.92 | 1.53 | 1.27 |
| 0.63 | 1.99 | 1.70 | 1.50 | 1.31 |
| 0.90 | 1.71 | 1.42 | 1.09 | 0.91 |
| 1.17 | 1.53 | 1.42 | 0.79 | 0.72 |
| 1.43 | 1.36 | 1.32 | 0.53 | 0.52 |
| 1.70 | 1.28 | 1.29 | 0.38 | 0.37 |
| 1.83 | 1.27 | 1.29 | 0.32 | 0.32 |
| 1.97 | 1.21 | 1.24 | 0.27 | 0.27 |
| 2.10 | 1.20 | 1.23 | 0.22 | 0.24 |
| 2.23 | 1.20 | 1.22 | 0.20 | 0.21 |
| 2.50 | 1.23 | 1.22 | 0.17 | 0.17 |

We therefore discuss all our results assuming a Gaussian model:

$$\Psi(k, t) = \exp[-\pi t^2/4\tau_G^2(k)] .$$

We use this analysis to obtain the zero-frequency $k$-dependent longitudinal and shear viscosities

$$\eta_l(k, 0) = m\rho[\omega_l^2(k) - \omega_0^2(k)]\tau^{\mathrm{long}}(k)/k^2 , \qquad (5.1)$$

$$\eta(k, 0) = m\rho\omega_t^2(k)\tau^{\mathrm{tran}}(k)/k^2 . \qquad (5.2)$$

In Fig. 4, we show as a function of $k$ the quantities $\omega_0(k)$, $\omega_l(k)$, $\tau^{\mathrm{long}}(k)$, and $\eta_l(k, 0)$. Figure 5 shows the quantities $\omega_t(k)$, $\tau^{\mathrm{tran}}(k)$, and $\eta(k, 0)$ each as a function of $k$. Note that all the quantities except $\omega_0(k)$ can be calculated either from the power spectrum (Sec. IV A) or from initial derivatives (Sec. IV B). The agreement between the two procedures is quite good. The extrapolated values of the shear viscosity $\eta$ and the longitudinal viscosity $\eta_l = (\frac{4}{3}\eta + \eta_v)$ in the limit $k \to 0$ are

$$\eta = \lim_{k \to 0} \eta(k, 0) = 3.0 \times 10^{-3} \text{ P}$$

and

$$\eta_l = \lim_{k \to 0} \eta_l(k, 0) = 5.6 \times 10^{-3} \text{ P} .$$

They compare favorably with the experimental values obtained by Naugle *et al.*[16]: $\eta = 2.80 \times 10^{-3}$ P and $\eta_l = (\frac{4}{3}\eta + \eta_v) = 6.03 \times 10^{-3}$ P at density 1.408 g/cm$^3$ and temperature 85.0 °K. Forster, Martin, and Yip[10] get a theoretical value of $1.63 \times 10^{-3}$ P at density 1.37 g/cm$^3$ and temperature 98.5 °K for the shear viscosity of liquid argon.

Our scheme does not work as well for the smaller values of $k$, particularly, $k = 0.23$ Å$^{-1}$, as it does for larger values of $k$, for example, $k = 1.83$ Å$^{-1}$. This seems to indicate, as might be anticipated, that our generalization of the Navier-Stokes equation so as to include nonlocal effects in space and time is valid for short times and short wavelengths only. For smaller wave numbers, temperature fluctuations may be important and should be considered. (However, it should be remembered that the computer experiments are not reliable for such small values of $k$.)

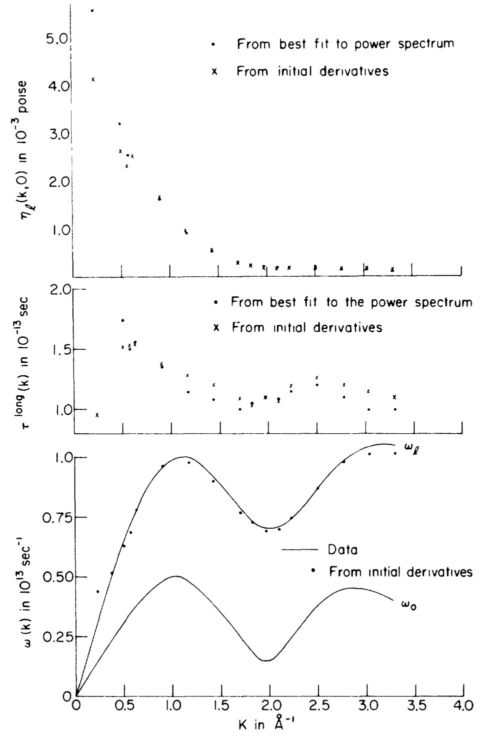

FIG. 4. (a) Dispersion curves $\omega_0(k)$ and $\omega_l(k)$ for the longitudinal current-correlation function. (b) Half-width $\tau^{\rm long}(k)$ of the Gaussian (for the time dependence of the memory function) versus $k$. (c) Zero-frequency wavelength-dependent longitudinal viscosity $\eta_l(k, 0)$ as a function $k$.

## VI. DISCUSSION

From the foregoing analysis, we conclude that one can use a scheme based on hydrodynamics to describe short-wavelength and high-frequency cooperative motions in simple classical liquids, provided that one generalizes the Navier-Stokes equation so as to include nonlocal behavior in space and time. In other words, viscoelastic properties of a liquid play an important role in its dynamic behavior in the region where distances and times are of a molecular order of magnitude.

We have also seen an indication that temperature fluctuations may be important at long wavelengths. In the region of interest to us, these fluctuations are unimportant.

Our analysis is similar to those of Chung and Yip[1] and Akcasu and Daniels.[4] However, these workers were concerned with only a simple exponential model of the memory function; they used different prescriptions to estimate $\tau(k)$. Our analysis is more detailed in that we investigate three different models for the memory function and use the method of least squares to estimate $\tau(k)$.

Singwi, Sköld, and Tosi[2] used a theory based on self-consistent-field method which may be viewed as a generalization of the random-phase approximation. Such an approach was used earlier by Hubbard and Beeby[17] in developing a theory of collective motions in classical liquids. Duderstadt and Akcasu[3] apply a kinetic approach for the analysis. Both these latter approaches give a relatively poorer agreement with the molecular dynamics data, essentially because it is much more difficult to model either the screened response function[2] or the damping operator[3] than to model a function of $k$ as in the hydrodynamic description. A more recent improved model for the screened response function[2] used by Pathak and Singwi[18] fits the molecular dynamics data to a much greater degree. No attempt, however, is made to connect these theories with ordinary hydrodynamics.

Using computer molecular dynamics experiments, one can obtain information about the transverse current-correlation function; neutron-scattering experiments are inherently incapable of giving such information. However, molecular dynamics data is currently available only up to about $10^{-12}$ sec. It is therefore desirable to obtain molecular dynamics data for a longer time interval.

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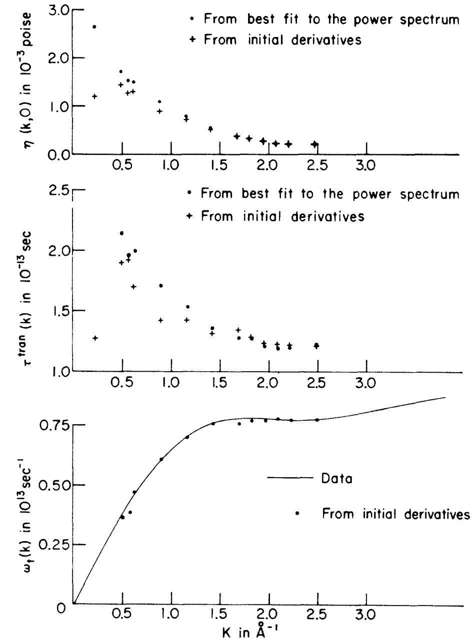

FIG. 5. (a) Dispersion curve $\omega_t(k)$ for the transverse current-correlation function. (b) Half-width $\tau^{\rm tran}(k)$ of the Gaussian as a function of $k$. (c) Zero-frequency wavelength-dependent shear viscosity $\eta(k, 0)$ as a function of $k$.

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## APPENDIX: EFFECT OF TEMPERATURE FLUCTUATIONS

In this appendix, we consider the effect of temperature fluctuations on the longitudinal current-correlation function. We first consider the long-wavelength long-time behavior of the correlation function. For this purpose, we start with the linearized hydrodynamic equations

$$\frac{d}{dt}\rho(\vec{k},\, t)=ikJ_{\parallel}(\vec{k},\, t)\ , \tag{A1}$$

$$\frac{\partial}{\partial t}J_{\parallel}(\vec{k},\, t)=\frac{ik}{\gamma}C_0^2\rho(\vec{k},\, t)+\frac{C_0^2\beta\rho_0}{\gamma}ikT(\vec{k},\, t) - \frac{k^2(\frac{4}{3}\eta+\eta_v)}{m\rho_0}J_{\parallel}(\vec{k},\, t)\ , \tag{A2}$$

$$\rho_0 c_v\frac{\partial}{\partial t}T(\vec{k},\, t)=\frac{C_v(\gamma-1)}{\beta}\frac{\partial}{\partial t}\rho(\vec{k},\, t)-\frac{k^2}{m}\lambda T(\vec{k},\, t)\ , \tag{A3}$$

where $\beta$ is the coefficient of thermal expansion, $C_0$ is the ordinary adiabatic sound velocity, and $\gamma = c_p/c_v$; $\rho_0$ is the equilibrium value of the particle number density. The quantities $\rho(\vec{k},\, t)$, $T(\vec{k},\, t)$, and $J_{\parallel}(\vec{k},\, t)$ are the $k$th Fourier components of fluctuations in particle number density, temperature, and the longitudinal current density.

We solve the set of equations (A1)–(A3) by Laplace transforms

$$\hat{A}(s)=\int_0^{\infty}dt\, e^{-st}A(t)\ . \tag{A4}$$

The Laplace transform of the longitudinal current-correlation function is easy to obtain:

$$\frac{C_{\parallel}(k,s)}{C_{\parallel}(k,\, t=0)} = \left(s+\frac{C_0^2k^2}{\gamma}\frac{1}{s}+bk^2+\frac{C_0^2k^2}{\gamma}(\gamma-1)\frac{1}{s+ak^2}\right)^{-1}, \tag{A5}$$

where

$$a=\lambda/m\rho_0 c_v\, ,\quad b=(\tfrac{4}{3}\eta+\eta_v)/m\rho_0\ . \tag{A6}$$

Since the long-wavelength limit of $\omega_0(k)$ is determined by

$$\omega_0^2(k)=k^2[k_BT/mS(k)]\xrightarrow{k\to 0}C_T^2k^2 \tag{A7}$$

($C_T$ being the isothermal sound velocity), in the long-wavelength limit

$$\gamma\omega_0^2(k)=C_0^2k^2\ . \tag{A8}$$

In Eq. (A5), we can now replace $C_0^2k^2$ by $\gamma\omega_0^2(k)$, i.e.,

$$\frac{\hat{C}_{\parallel}(k,\, s)}{C_{\parallel}(k,\, t=0)} = \left(s+\frac{\omega_0^2(k)}{s}+bk^2+(\gamma-1)\omega_0^2(k)\frac{1}{s+ak^2}\right)^{-1}\ . \tag{A9}$$

If Eq. (A7) were to be written in the form of the memory function equation (3.14) the memory function $K_l(k,t)$ would be given by

$$K_l(k,\, t)=\omega_0^2(k)+bk^2\delta(t)+(\gamma-1)\omega_0^2(k)e^{-ak^2t}\ . \tag{A10}$$

This is the long-wavelength long-time limit of the memory function for the longitudinal current-correlation function. Notice that the memory function due to viscosity is a $\delta$ function in time and does not persist beyond $t=0$, whereas the memory function due to temperature fluctuations (thermal conduction) persists for rather long times.

If we replace the $\delta$ function in the viscous memory function by a finite function with a range of not more than $10^{-13}$–$10^{-12}$ sec, the long-time long-wavelength hydrodynamic behavior of the longitudinal current-correlation function should not be affected. For this purpose, we can replace the $\delta$ function by a Gaussian,

$$\delta(t)\to(1/\sqrt{\pi})\mathcal{E}e^{-\mathcal{E}^2t^2}\, , \tag{A11}$$

where $\mathcal{E}$ may be of the order of $10^{13}$ sec$^{-1}$. Equation (A10) can now be written as

$$K_l(k,\, t)=\omega_0^2(k)+(bk^2/\sqrt{\pi})\mathcal{E}e^{-\mathcal{E}^2t^2} + (\gamma-1)\omega_0^2(k)e^{-ak^2t}\ . \tag{A12}$$

The quantity $\mathcal{E}$ can be evaluated from the initial value of the memory function $K_l(k,\, t)$; from (3.16) and (A12), it is easy to see that

$$\mathcal{E}=\sqrt{\pi}\,[\omega_l^2(k)-\gamma\omega_0^2(k)]/bk^2\ . \tag{A13}$$

In the limit of long wavelengths, $\omega_l^2(k)$ is given by[19]

$$\omega_l^2(k)=C_3^2k^2,\quad C_3^2=(\tfrac{4}{3}G_\infty+K_\infty)/m\rho_0\ , \tag{A14}$$

where $G_\infty$ and $K_\infty$ are the long-wavelength limits of the high-frequency shear modulus and bulk modulus, respectively. From Eqs. (A7) and (A14), it follows that in the limit $k\to 0$, Eq. (A13) reduces to

$$\mathcal{E}=\sqrt{\pi}\,(C_3^2-C_0^2)/b\ . \tag{A15}$$

For liquid argon, $b\sim 10^{-3}$ cm$^2$sec$^{-1}$, $C_3^2/b\sim 10^{13}$ sec$^{-1}$, and $C_0^2/b\sim 10^{12}$ sec$^{-1}$. Thus, we see that $\mathcal{E}\sim 10^{13}$ sec$^{-1}$ in the limit $k\to 0$. Hydrodynamic behavior of the longitudinal current-correlation function is, therefore, not affected by using Eq. (A12) instead of Eq. (A10) for the memory function. Equation (A12) for the memory function $K_l(k,\, t)$ is now

$$K_l(k,\, t)=\omega_0^2(k)+[\omega_l^2(k)-\gamma\omega_0^2(k)]$$

$$\times \exp\left( - \frac{\pi[\omega_l^2(k) - \gamma\omega_0^2(k)]^2}{b^2k^4} t^2 \right)$$

$$+ (\gamma - 1)\omega_0^2(k)e^{-ak^2t} \text{ .} \qquad \text{(A16)}$$

This memory function in the limit $k \rightarrow 0$ yields correct hydrodynamics. The second term in Eq. (A.16) is large initially, and decays very fast ($\sim 10^{-13}$ sec); the third term, on the other hand, is small initially and decays very slowly. All three parts of the memory function $K_l(k, t)$ are essential to obtain the long-wavelength behavior of the dynamic structure factor $S(k, \omega)$. For example, in the region of $\omega$ away from the origin, the slowly decaying component $K_3(k, t) = (\gamma - 1)\omega_0^2(k)e^{-ak^2t}$ appears almost like a constant, $(\gamma - 1)\omega_0^2(k)$; this, when added to the constant term $\omega_0^2(k)$, yields $\gamma\omega_0^2(k)$. Therefore in the long-wavelength limit, the Brillouin peak occurs at $C_0k$.

The situation is markedly different for large $k$. At about $k = 1$ Å$^{-1}$, since $a \approx 10^{-3}$ cm$^2$ sec$^{-1}$, $ak^2 \approx 10^{13}$ sec$^{-1}$; also

$$[\omega_l^2(k) - \gamma\omega_0^2(k)] \approx 10^{13} \text{ sec}^{-1} \text{ .}$$

Beyond $k = 1$ Å$^{-1}$, $ak^2$ continues to increase whereas

$$[\omega_l^2(k) - \gamma\omega_0^2(k)]/bk^2$$

tends to stay stable around $10^{13}$ sec$^{-1}$. Thus the roles "fast" and "slow" are interchanged between the second and the third terms in Eq. (A16). We therefore expect that a memory function of the form

$$K_l(k, t) = \omega_0^2(k) + [\omega_l^2(k) - \omega_0^2(k)]e^{-\alpha(k)t^2} \qquad \text{(A17)}$$

is sufficient for our purpose.

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