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Collective Motions in Classical Liquids*

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A theory of collective motions in classical liquids, which is valid at short wavelengths and high frequencies, is presented. This theory is based on a self-consistent-field method, which can be viewed as a generalization of the random-phase approximation. The existence of collective effects is considered at the outset by introducing a self-consistent "polarization" potential that provides the restoring force and a "screened" response function. The density response function is expressed in terms of these two functions. The local field corrections enter the polarization potential via the static structure factor of the liquid. Various approximations for the polarization potential and the screened response function, and their relation to the first few moments of the spectral function of the density response, are examined. These approximations are tested by explicit numerical calculations of the spectral function of the longitudinal current correlations for liquid argon. It is found that an over-all good agreement with the data is obtained for the case in which the screened response function is equal to the response function for the self-motion of atoms and the polarization potential is determined through the zeroth-moment sum rule. There are no adjustable parameters in the theory.

I. INTRODUCTION

Recent inelastic neutron scattering experiments have furnished valuable information on the dynamic structure of liquids. There is a remarkable similarity[1] between the scattered-neutron spectrum of the liquid and that of the polycrystalline solid near the melting point. Since the spectrum in the solid can be understood in terms of its collective modes, i.e., the phonons, attempts have been made in the past to describe the spectrum in the liquid by means of solidlike phenomenological models.[2,3] Although these models have been reasonably successful in describing the observations,[4] the analogy between the solid and the liquid has, undoubtedly, been taken much too literally. Further evidence to the existence of collective effects in classical liquids in the region of high frequency and short wavelength has been provided by recent molecular-dynamics calculations[5] and neutron scattering data[6] in liquid argon. These have shown that the wave vector dependence of the peak in the spectrum of the longitudinal current correlations is correlated with the static structure factor, in a manner reminiscent of the ordinary dispersion curve for phonons in the solid. The purpose of this paper is to develop a theory for these collective aspects from basic considerations. While the theory attempts to explain the observations by postulating the existence of some collective motions, it does not interpret the observations in terms of "solidlike" phonons. In fact, an unambiguous interpretation of the observations[5] as a dispersion curve for collective modes would be possible only if the peaks in the spectrum were reasonably sharp.

The existence of collective motions in liquids in the domain of small frequency and long wavelength, i.e., in the hydrodynamic region, has been known for a long time and is well understood in terms of the Navier-Stokes equations. In the region of high frequencies and short wavelengths, the existence of a zero-sound mode was conjectured by Pines.[7] In this region, where hydrodynamics is inapplicable and where the microscopic structure of the liquid plays an important role, a self-consistent-field method, which can be viewed as a generalization of the random-phase approximation (RPA) for the electron liquid, has been used to describe the collective motions.[6] As in the RPA, one considers explicitly at the outset the existence of collective effects by introducing a self-consistent "polarization" potential that provides the restoring force for the collective mode and a "screened" response function which describes the response to the sum of the external potential and of the polarization potential. Of course, short-range correlation effects in the polarization potential, which are quite important in the electron liquid, are here essential because of the hard-core character of the interparticle potential.

The starting point of the theory is, in fact, formally equivalent to the formal generalization of hydrodynamics, valid for any frequency and wave vector, given by Kadanoff and Martin.[8] Since the polarization potential and the screened response function which occur in the theory are not known exactly, we shall in this paper examine the various approximations that we may consider for these two functions and their relation to the first few moments of the spectral function of the density response. These approximations are tested by explicit numerical calculations of the spectral function of the longitudinal current correlations for liquid argon. We find that an over-all good agreement with the data is obtained, except at very small wave vectors where in any case the theory is inapplicable, when one takes the screened response function equal to the response function for the self-motion of atoms[6] and one determines the polarization potential through the zeroth-moment sum rule.[8,9] We shall in Appendix A give a justification for the former choice using Kerr's approach[10] for the coherent motions in classical liquids. The conclusions arrived at in this paper are valid for frequencies greater than the inverse characteristic relaxation time for local thermal equilibrium and/or for wave vectors greater than the inverse mean free path, i.e., in the zero-sound region. In the former circumstance one is examining the behavior of the liquid over times shorter than the average time between collisions; in the latter, over distances shorter than the mean collision distance. No attempt has been made to join the theory to ordinary hydrodynamics.

II. THEORY

A. General Considerations

We shall consider the response of the system to a weak potential $V_{\text{ext}}(\vec{q}, \omega)$ which describes an external probe coupled to the density fluctuations in the system. In a translationally invariant system, the induced density change $\langle\rho(\vec{q}, \omega)\rangle$ is related to the external potential by

$$\langle\rho(\vec{q}, \omega)\rangle = \chi(\vec{q}, \omega)\, V_{\text{ext}}(\vec{q}, \omega) \quad , \tag{1}$$

where $\chi(\vec{q}, \omega)$ is the density response function. For the purpose of developing approximations to this function, it is useful to consider explicitly at the outset the collective aspects of the problem. This can be done by introducing the average self-consistent potential due to the polarization of the system in the form

$$V_{\text{pol}}(\vec{q}, \omega) = \Psi(\vec{q})\langle\rho(\vec{q}, \omega)\rangle \quad , \tag{2}$$

and by defining a new response function $\chi_{\text{sc}}(\vec{q}, \omega)$, which describes the response of the system to the sum of the external potential and of the polarization potential:

$$\langle\rho(\vec{q}, \omega)\rangle = \chi_{\text{sc}}(\vec{q}, \omega) \times [V_{\text{ext}}(\vec{q}, \omega) + V_{\text{pol}}(\vec{q}, \omega)] \,. \tag{3}$$

It then follows that the density response function is given by

$$\chi(\vec{q}, \omega) = \chi_{\text{sc}}(\vec{q}, \omega)/[1 - \Psi(\vec{q})\chi_{\text{sc}}(\vec{q}, \omega)] \,. \tag{4}$$

Of course, the functions $\Psi(\vec{q})$ and $\chi_{\text{sc}}(\vec{q}, \omega)$ are not known *a priori*. Expressions having the structure of Eq. (4) are very well known; for instance, in the case of the electron liquid, if one identifies $\Psi(\vec{q})$ with the bare Coulomb potential $4\pi e^2/q^2$, $\chi_{\text{sc}}(\vec{q}, \omega)$ in the language of the many-body perturbation theory is then given by the sum of the proper polarization diagrams. The simplest approximation for $\chi_{\text{sc}}(\vec{q}, \omega)$ consists in assuming that it is the density response function for a free-electron gas, which corresponds to the RPA of Bohm and Pines.[11] In this approximation, the interparticle interaction is accounted for only through the average Coulomb potential of polarization charges, exclusive of exchange and correlation effects. In a recent generalization[12] of the RPA, corrections in $\Psi(\vec{q})$ arising from short-range correlation effects were taken into account. As mentioned in the Introduction, these effects play an essential role when the interparticle potential has a hard-core component.

It is easy to show that Eq. (4) is equivalent to the expression of the density response function given by Kadanoff and Martin[8] by a generalization of hydrodynamics, provided that $\Psi(\vec{q})$ is chosen according to

$$\Psi(\vec{q}) = \chi_{\text{sc}}^{-1}(\vec{q}, 0) - \chi^{-1}(\vec{q}, 0) \,. \tag{5}$$

Indeed, Eq. (4) can then be written in the form

$$\chi^{-1}(\vec{q}, \omega) - \chi^{-1}(\vec{q}, 0) = \chi_{\text{sc}}^{-1}(\vec{q}, \omega) - \chi_{\text{sc}}^{-1}(\vec{q}, 0), \tag{6}$$

and the dispersion relation that Kadanoff and Martin have proved for $\chi^{-1}(\vec{q}, \omega) - \chi^{-1}(\vec{q}, 0)$ holds also for the screened response[13]:

$$\chi_{\text{sc}}^{-1}(\vec{q}, \omega) - \chi_{\text{sc}}^{-1}(\vec{q}, 0) = \frac{M\omega^2}{nq^2} + \frac{M}{n} i\omega\Gamma(\vec{q}, \omega) - \frac{M\omega}{n} P\int \frac{d\omega'}{\pi} \frac{\Gamma(\vec{q}, \omega')}{\omega - \omega'} \,. \tag{7}$$

Here, M is the particle mass, n is the number density, and $\Gamma(\vec{q}, \omega)$ is an unknown real function which in the hydrodynamic limit is related to the transport coefficients. Equations (4), (5), and (7) lead to

$$\operatorname{Im}\chi(\vec{q},\omega)=\frac{-(n/M)\,\omega q^4\Gamma(\vec{q},\omega)}{[\omega^2+nq^2/M\chi(\vec{q},0)-\omega q^2P\int(d\omega'/\pi)\;\Gamma(\vec{q},\omega')/\Gamma(\vec{q},\omega')/(\omega-\omega')(\omega-\omega')]^2+[\omega q^2\Gamma(\vec{q},\omega)]^2}\;. \tag{8}$$

This expression is the same as that given by Kadanoff and Martin. Equation (7) relates the function $\Gamma(\vec{q},\omega)$ to the screened response function. In the hydrodynamic regime where $\Gamma(\vec{q},\omega)$ has a direct physical meaning, it is preferable to use the formulation of Kadanoff and Martin.[14] On the other hand, in the zero-sound regime the screened response function has a more direct physical meaning and, as such, it is perhaps easier to envision physical approximations for this function.

B. Moments

According to the fluctuation-dissipation theorem, the dynamic structure factor $S(\vec{q},\omega)$ is related to the imaginary part of $\chi(\vec{q},\omega)$. In the classical limit this relation reads

$$S(\vec{q},\omega)=-(k_BT/\pi n\omega)\operatorname{Im}\chi(\vec{q},\omega), \tag{9}$$

where k_B is the Boltzmann constant and T is the temperature. Using the Kramers-Kronig relation,

$$\chi(\vec{q},\omega)=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega'\,\frac{\operatorname{Im}\chi(\vec{q},\omega')}{\omega'-\omega-i\eta}\;, \tag{10}$$

where η is a positive infinitesimal; one finds that the zeroth moment of $S(\vec{q},\omega)$, the static structure factor $S(\vec{q})$, is given by

$$S(q)=-(k_BT/n)\,\chi(q,0). \tag{11}$$

Using Eq. (4), this becomes

$$[S(q)]^{-1}=(n/k_BT)\{\Psi(q)-[\chi_{sc}(q,0)]^{-1}\}. \tag{12}$$

The above equation uniquely determines the polarization potential once one has made a choice for the screened response. The small-time behavior of the screened response is determined by the higher moments of $S(\vec{q},\omega)$.

From Eq. (9), the higher even moments of $S(\vec{q},\omega)$ are given by

$$\begin{aligned}\langle\omega^{2m}\rangle_{av}&\equiv\int_{-\infty}^{+\infty}\omega^{2m}S(\vec{q},\omega)\,d\omega\\&=-\frac{2k_BT}{n}\left(i\frac{\partial}{\partial t}\right)^{2m-1}\hat{\chi}_2(\vec{q},t)\Big|_{t=0},\end{aligned} \tag{13}$$

where $\hat{\chi}_2(\vec{q},t)$ is the Fourier transform of $\operatorname{Im}\chi(\vec{q},\omega)$. The odd moments, of course, vanish in the classical case. Using Eq. (10), it is straightforward to show that

$$\hat{\chi}(\vec{q},t)=2i\theta(t)\hat{\chi}_2(\vec{q},t), \tag{14}$$

where $\hat{\chi}(\vec{q},t)$ is the Fourier transform of $\chi(\vec{q},\omega)$, and $\theta(t)$ is the usual step function, $\theta(t)=1$ for $t>0$ and $\theta(t)=0$ for $t<0$. Therefore

$$\langle\omega^{2m}\rangle_{av}=(-1)^m\,\frac{k_BT}{n}\left(\frac{\partial}{\partial t}\right)^{2m-1}\hat{\chi}(q,t)\Big|_{t=0^+}. \tag{15}$$

From Eq. (4), it follows that

$$\begin{aligned}\hat{\chi}(\vec{q},t)&=\hat{\chi}_{sc}(\vec{q},t)+\Psi(\vec{q})\int_{-\infty}^{+\infty}dt'\\&\quad\times\hat{\chi}_{sc}(\vec{q},t-t')\,\hat{\chi}(\vec{q},t')\\&=\hat{\chi}_{sc}(\vec{q},t)+\Psi(\vec{q})\int_0^t dt'\\&\quad\times\hat{\chi}_{sc}(\vec{q},t-t')\,\hat{\chi}(\vec{q},t').\end{aligned} \tag{16}$$

The last step in the above equation follows by noting that both $\hat{\chi}_{sc}(\vec{q},t)$ and $\hat{\chi}(\vec{q},t)$ vanish for $t<0$. This equation can be solved by iteration. In practice, since only the first few moments of $S(\vec{q},\omega)$ are known, it is sufficient to consider the first few terms in the small-time expansion of $\hat{\chi}_{sc}(\vec{q},t)$. Writing

$$\hat{\chi}_{sc}(\vec{q},t)=-(nq^2/M)\,\theta(t)[t-\beta(\vec{q})t^3+\cdots], \tag{17}$$

where

$$\beta(\vec{q})=-\frac{M}{6\pi nq^2}\int_{-\infty}^{\infty}d\omega\,\omega^3\operatorname{Im}\chi_{sc}(\vec{q},\omega), \tag{18}$$

one finds that the second moment of $S(\vec{q},\omega)$ is already satisfied, and the fourth moment is given by

$$\langle\omega^4\rangle_{av}=q^2(k_BT/M)[6\beta(\vec{q})+(nq^2/M)\Psi(\vec{q})]. \tag{19}$$

The exact expression of the fourth moment is known.[15]

C. Approximations

We shall now consider various approximations for the screened response function. The simplest approximation is to take this function equal to the response function for a noninteracting gas:

$$\chi_{sc}(\vec{q},\omega)=\chi_g(\vec{q},\omega). \tag{20}$$

In this case, one has

$$\begin{aligned}\operatorname{Im}\chi_{sc}(\vec{q},\omega)&=-(\pi n\omega/k_BT)\,(M/2\pi k_BTq^2)^{1/2}\\&\quad\times\exp(-M\omega^2/2k_BTq^2),\end{aligned} \tag{21}$$

and, making use of the Kramers-Kronig relation, one obtains

$$\mathrm{Re}\chi_{\mathrm{sc}}(\vec{\mathrm{q}},\omega)=-\frac{n}{k_BT}\left\{1+i\left(\frac{\pi M\omega^2}{2k_BTq^2}\right)^{1/2}\right.$$
$$\left.\times\exp\left(\frac{-M\omega^2}{2k_BTq^2}\right)\mathrm{erf}\left[i\left(\frac{M\omega^2}{2k_BTq^2}\right)^{1/2}\right]\right\}. \qquad (22)$$

One also finds

$$\chi_{\mathrm{sc}}(\vec{\mathrm{q}},0)=-n/k_BT \qquad (23)$$

and $\beta(\vec{\mathrm{q}})=q^2(k_BT/2M)$. (24)

If one determines $\Psi(\vec{\mathrm{q}})$ from Eq. (12), one finds

$$\Psi(\vec{\mathrm{q}})=(k_BT/n)[1/S(\vec{\mathrm{q}})-1]\,. \qquad (25)$$

Thus, in this approximation, $\Psi(\vec{\mathrm{q}})$ is related to the direct correlation function.[9] Of course, with the above choice, the fourth-moment relation is not satisfied and one finds

$$\langle\omega^4\rangle_{\mathrm{av}}=(k_BT/M^2)q^4[3k_BT+n\Psi(\vec{\mathrm{q}})]\,. \qquad (26)$$

In Ref. 6 it was suggested that a more suitable approximation should be to relate $\chi_{\mathrm{sc}}(\vec{\mathrm{q}},\omega)$ to the self-motion of the atoms, i.e.,

$$\mathrm{Im}\chi_{\mathrm{sc}}(\vec{\mathrm{q}},\omega)=-(\pi n/k_BT)\,\omega S_s(\vec{\mathrm{q}},\omega), \qquad (27)$$

where $S_s(\vec{\mathrm{q}},\omega)$ is the Fourier transform of the self-correlation function. This suggestion was based on the physical idea that, having taken account explicitly of the collective aspects of the motion, one should also make some allowance for the fact that only in the large-wave-vector limit does the single-particle motion approach the free-particle behavior. At smaller wave vectors, this motion is rather complicated and has both diffusive and vibratory aspects. It will be shown in Appendix A that one indeed can obtain Eq. (4) with $\chi_{\mathrm{sc}}(\vec{\mathrm{q}},\omega)$ determined according to Eq. (27), and $\Psi(\vec{\mathrm{q}})$ determined according to Eq. (12) from the approach of Kerr.[10] From Eq. (27), one immediately finds that

$$\chi_{\mathrm{sc}}(\vec{\mathrm{q}},0)=\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{d\omega}{\omega}\,\mathrm{Im}\chi_{\mathrm{sc}}(\vec{\mathrm{q}},\omega)=-\frac{n}{k_BT}\,, \qquad (28)$$

and $\beta(\vec{\mathrm{q}})=(M/6k_BTq^2)\langle\omega_s{}^4\rangle_{\mathrm{av}}$, (29)

where $\langle\omega_s{}^4\rangle_{\mathrm{av}}$ is the fourth moment of $S_s(\vec{\mathrm{q}},\omega)$ and is given by[15]

$$\langle\omega_s{}^4\rangle_{\mathrm{av}}=\frac{k_BT}{M^2}q^4\left(3k_BT+\frac{n}{q^2}\int d\vec{\mathrm{r}}\;g(r)\frac{\partial^2\varphi(r)}{\partial x^2}\right)\,. \qquad (30)$$

Here, $g(r)$ is the pair correlation function, and $\varphi(r)$ is the interparticle potential. We see that in this approximation $\Psi(\vec{\mathrm{q}})$ is again given by Eq. (25). On the other hand, the fourth moment of $S(\vec{\mathrm{q}},\omega)$ is given by

$$\langle\omega^4\rangle_{\mathrm{av}}=\frac{k_BT}{M^2}\,q^4\left(3k_BT+\frac{n}{q^2}\int d\vec{\mathrm{r}}\right.$$
$$\left.\times g(r)\frac{\partial^2\varphi(r)}{\partial x^2}+n\Psi(\vec{\mathrm{q}})\right). \qquad (31)$$

The exact expression for the fourth moment is[15]

$$\langle\omega^4\rangle_{\mathrm{av}}=\frac{k_BT}{M^2}\,q^4\left(3k_BT+\frac{n}{q^2}\int d\vec{\mathrm{r}}\;g(r)\frac{\partial^2\varphi(r)}{\partial x^2}\right.$$
$$\left.-\frac{1}{q^2}\int d\vec{\mathrm{r}}\;g(r)\cos(qx)\frac{\partial^2\varphi(r)}{\partial x^2}\right). \qquad (32)$$

Clearly, in Eq. (31) one has approximated the "non-self" contribution to the fourth moment by $n\Psi(\vec{\mathrm{q}})$. Contrary to the results based on Eq. (20), this provides a rather good description of $\langle\omega^4\rangle_{\mathrm{av}}$ except at small wave vectors, as we shall see in Sec. III.

In the calculations presented in Ref. 6, the choice of $\Psi(\vec{\mathrm{q}})$ was based on an approximate analysis of the equation of motion[12] for the density fluctuations, rather than on the exact sum rule (12). The expression adopted for $\Psi(\vec{\mathrm{q}})$ in the large-wave-vector region was

$$\Psi(\vec{\mathrm{q}})=-\frac{4\pi}{q^3}\int_0^\infty[\sin(qr)-qr\cos(qr)]$$
$$\times g(r)\frac{d\varphi(r)}{dr}\,dr+\frac{0.6k_BT}{n}\,. \qquad (33)$$

The constant term in the above equation was added to fit the height of the first peak of the structure factor and was found to be of importance only in a narrow region of wave vectors around the position of this peak. On the other hand, in the small-wave-vector region, $\Psi(\vec{\mathrm{q}})$ was taken as

$$\Psi(q)=-\frac{4\pi}{3q^3}\int_0^\infty[\sin(qr)-(qr)\cos(qr)]g(r)$$
$$\times\left(\frac{d\varphi(r)}{dr}-\frac{1}{2}r\frac{d^2\varphi(r)}{dr^2}\right)dr\,. \qquad (34)$$

We shall show in Appendix B that this expression in the limit $q\to 0$ gives the correct potential contribution to the instantaneous compressibility.

Very recently, Hubbard and Beeby[16] have also used a zero-sound approach in developing a theory of collective motions in classical liquids. They calculate approximately the response function for a disordered static system and then extend the result to the nonstatic case. In their approximation, the screened response is related to the self-correlation function $G_s(\vec{q}, t)$ through

$$\hat{\chi}_{sc}(\vec{q}, t) = -(nq^2/M)\,\theta(t)\, t\, G_s(\vec{q}, t)\ . \tag{35}$$

This relation can also be expressed as

$$\mathrm{Im}\chi_{sc}(\vec{q}, \omega) = \pi \frac{nq^2}{M} \frac{\partial S_s(\vec{q}, \omega)}{\partial \omega}\ . \tag{36}$$

It then follows that

$$\chi_{sc}(\vec{q}, 0) = \frac{nq^2}{M} \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2}\, S_s(\vec{q}, \omega)\,, \tag{37}$$

while $\beta(\vec{q})$ is again given by Eq. (24). Therefore, in the approximation of Hubbard and Beeby, the fourth moment of $S(\vec{q}, \omega)$ is given by

$$\langle \omega^4 \rangle_{av} = (k_B T/M^2)\, q^4 \,[3k_B T + n\Psi(\vec{q})]\ . \tag{38}$$

In their approximate theory, $\Psi(\vec{q})$ is such that Eq. (38) gives the correct value of the fourth moment [Eq. (32)]. On the other hand, the determination of the zeroth moment from the sum rule (12) requires, in this approximation, an accurate knowledge of $S_S(\vec{q}, \omega)$ at small frequencies, as is apparent from Eq. (37). These authors disregard this sum rule on the ground that their theory is not applicable at small frequencies. We also note that in the limit of large q, where $S_S(\vec{q}, \omega)$ takes its free-gas value, Eqs. (36) and (27) are identical.

D. Computation

A knowledge of $\Psi(\vec{q})$ and $\chi_{sc}(\vec{q}, \omega)$ enables us to calculate the dynamic structure factor $S(\vec{q}, \omega)$. As we have seen in the preceding discussion, $\Psi(\vec{q})$ can be determined from the pair correlation function, which is known experimentally, and from the interparticle potential. On the other hand, a precise knowledge of the self-correlation function is not available. What is known with fair accuracy from molecular-dynamics calculations[17] is the velocity autocorrelation function in liquid argon. The Fourier transform of this function $f(\omega)$ gives $S_s(\vec{q}, \omega)$ in the limit of small wave vector and finite frequency, according to the relation[18]

$$S_s(\vec{q}, \omega) \cong (k_B T q^2/2M\omega^2) f(\omega) + O(q^4)\ . \tag{39}$$

In the other extreme of large wave vectors, $S_S(\vec{q}, \omega)$ is well represented by its free-gas value. In the following calculations, as was done in Ref. 6, we will use these two limiting behaviors and smoothly join their results in the intermediate region. One might take recourse to using a theoretical model for $S_S(\vec{q}, \omega)$, but because of lack of appropriate experimental data, one cannot reliably determine the parameters of the model. It would be highly desirable to have a complete knowledge of $S_S(\vec{q}, \omega)$, both from inelastic neutron scattering experiments and from molecular-dynamics calculations.

The calculations presented in Sec. III were carried out for liquid argon at 76 °K, for which temperature molecular-dynamics calculations of $g(r)$ and of the spectral function of the longitudinal current correlations $\omega^2 S(\vec{q}, \omega)$ are available.[5] We have adopted the 6-12 Lennard-Jones potential with the same values of the parameters as used by Rahman. We have used for $f(\omega)$ the values reported by Rahman[17] at 94.4 °K; the variation of this function with temperature does not seem to be such as to affect significantly our conclusions. These data can be represented analytically[19] by the formula

$$f(\omega) = \frac{2MD}{\pi k_B T}\left(e^{-\omega^2/\omega_0^2} + A'\omega^2 e^{-2|\omega|/\omega_m}\right), \tag{40}$$

where $\omega_0 = 0.25 k_B T/\hbar$, $\omega_m = 0.37 k_B T/\hbar$, $A' = 61.48\,(\hbar/k_B T)^2$, and D is the diffusion coefficient. Using Eqs. (39) and (40) in Eq. (27) and the Kramers-Kronig relation, one obtains

$$\mathrm{Re}\chi_{sc}(\vec{q}, \omega) = \frac{nDq^2}{\pi k_B T}\left[-\frac{i\pi}{\omega} e^{-\omega^2/\omega_0^2}\, \mathrm{erf}\left(\frac{i\omega}{\omega_0}\right) - A'\omega_m + 2A'\omega \int_0^\infty dy\, \sin\left(\frac{2\omega y}{\omega_m}\right)(1+y^2)^{-1}\right]. \tag{41}$$

This result holds only for finite frequencies because of the restrictions on the validity of Eq. (39). On the other hand, the calculation of $\chi_{sc}(\vec{q}, \omega)$ from Eqs. (36) and (39) is not possible because of the invalidity of the latter equation at small frequencies.

III. RESULTS

Figure 1 gives the values of $\Psi(\vec{q})$ as obtained from various approximations. These are, specifically, the results based on Eq. (25) (curve 1), Eq. (33) (curve 2), Eq. (34) (curve 3), and Eq. (38) (curve 4). Curve 1 could not be extended to small wave vectors because of large uncertainties in the experimental structure factor. It is apparent that the approximation (33) agrees quite well with the result based on the zeroth moment for $q \gtrsim 2$ Å^{-1}, as was anticipated. If the approximations (33) and (34) are smoothly joined, as was done in Ref. 6, the resulting curve provides a rather good representation of the zeroth-moment result, except at $q \lesssim 0.5$ Å^{-1}. This good agreement implies that the potential (33), together with the potential (34), gives a fairly good representation of the static structure factor $S(\vec{q})$, as was shown in Ref. 6 and is illustrated in Fig. 2. On the other hand, the potential obtained from the fourth moment [Eq. (38)] gives

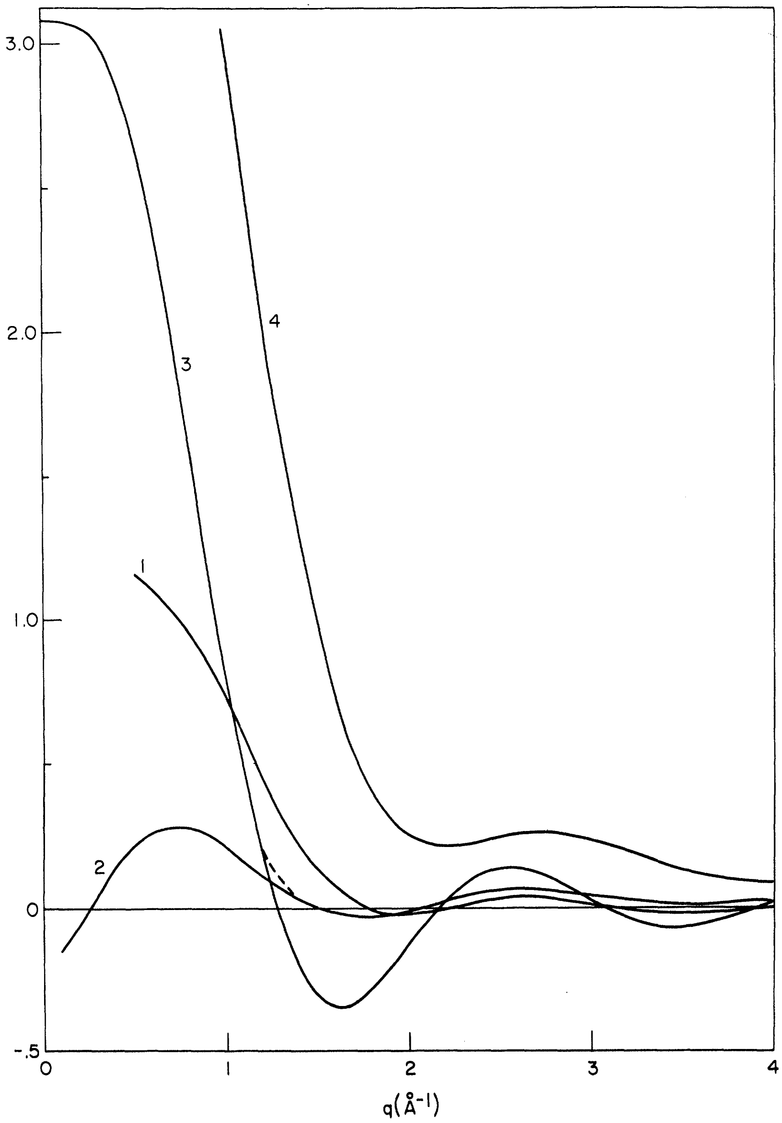

FIG. 1. Polarization potential $\psi(q)$ versus the wave vector q (curve 1), from Eq. (25); (curve 2), from Eq. (33); (curve 3), from Eq. (34); (curve 4), from Eq. (38). The broken curve shows the smooth joining of the potentials (33) and (34) discussed in the text.

a very poor $S(\vec{q})$. The latter result was obtained from Eq. (12) using the free-particle value for $\chi_{sc}(\vec{q}, 0)$.

Figure 3 compares the results for the fourth moment of $S(\vec{q}, \omega)$, obtained by various approximations, with those calculated from its exact expression [Eq. (32)]. Specifically, we give the results obtained from Eq. (31) with $\Psi(\vec{q})$ determined from Eq. (25) (curve 1), from Eq. (33) (curve 2), and from Eq. (34) (curve 3), as well as the results obtained from Eq. (26) with $\Psi(\vec{q})$ determined from Eq. (25) (curve 4). It should be stressed that curves 1, 2, and 3 do not involve any approximation on $\chi_{sc}(\vec{q}, \omega)$ except its representation in terms of $S_s(\vec{q}, \omega)$, given in Eq. (27). It is clear from the comparison of curves 1 and 4 that the difference between the two choices of $\chi_{sc}(\vec{q}, \omega)$ given in Eqs. (20) and (27) is far from trivial in the region of wave vectors of interest. Clearly, for all the potentials considered in Fig. 3, the expression (27) for $\chi_{sc}(\vec{q}, \omega)$ gives a good representation of the fourth moment, except for $q \lesssim 0.5\ \text{Å}^{-1}$. Since these different choices of $\Psi(\vec{q})$, which we have already seen give a reasonable or an exact account of the zeroth moment, do not affect significantly the fourth moment, one is led to conclude that the self-part of the fourth moment, accounted for by the approximation (27), gives the most relevant contribution in the region of wave vectors of interest.

Figure 4 presents the spectral function for the longitudinal current correlation $\omega^2 S(\vec{q}, \omega)$ as a function of frequency for selected values of the wave vector in various approximations. At large wave vectors, these are based on the approximation of Eq. (20) for $\chi_{sc}(\vec{q}, \omega)$ and on the values of

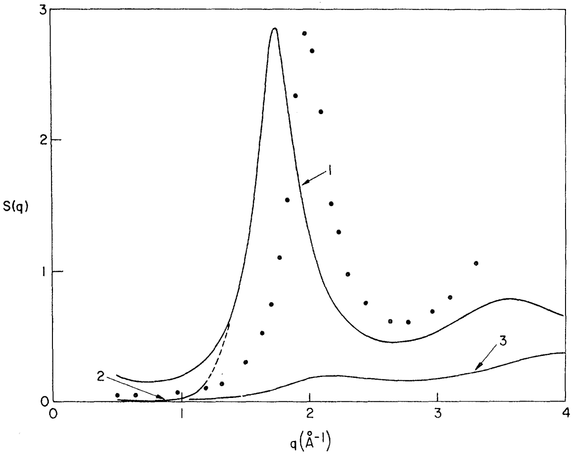

FIG. 2. Static structure factor $S(q)$ versus the wave vector q, as calculated from Eqs. (12) and (23) using $\psi(q)$ from Eq. (33) (curve 1), Eq. (34) (curve 2), and Eq. (38) (curve 3). The solid circles are the results of the machine computations of Rahman (Ref. 5).

$\Psi(\vec{q})$ given by Eq. (25) (curve 1), by Eq. (33) (curve 2), and by Eq. (38) (curve 3). At small wave vectors, we give, in addition, the results based on the approximation of Eq. (41) for $\chi_{SC}(\vec{q}, \omega)$ and on the values of $\Psi(\vec{q})$ given by Eq. (25) (curve 4) and by Eq. (34) (curve 5). The results of the machine computations of Rahman[5] are shown by solid circles. There are several points to note in this figure. First of all, the approximation of the screened response by the free-gas response gives a spectral function which is much too sharp for the whole range of wave vectors of interest. At large wave vectors, this merely implies that the high-frequency tail of the observed spectral function is missing from the calculated one, at least for those model potentials that account satisfactorily for the position of the peak. However, at small wave vectors, one would predict in the gas model the existence of very sharp collective modes, which is contrary to the observation. On the other hand, the description of the screened response through the self-motions [Eq. (27)] in the small-wave-vector approximation of Eq. (41) gives a fair account of the observed facts. It seems very likely that, if one had an expression for the true self-motion applicable at larger wave vectors, one would obtain a much better representation of the spectral function, including its high-frequency tail. This conjecture is based on the fact that the free-gas response, being a Gaussian function, falls off much too rapidly at high frequencies, whereas all the available evidence indicates that the spectral function for the self-motion falls off much more slowly.

The position of the peak of the spectral function of the longitudinal current correlations is plotted in Fig. 5 as a function of the wave vector. The various curves are labeled as in Fig. 4. In the same figure the crosses represent the experimental data[6] and the solid circles represent the results of the molecular-dynamics calculations of Rahman.[5] It may be noted that curves 4 and 5 tend to a finite frequency at small wave vectors as a consequence of the inapplicability of Eq. (41) at small frequencies. These curves would indeed pass through the origin if one were to use the proper choice of $S_S(\vec{q}, \omega)$. It is apparent that the choice of $\Psi(\vec{q})$ based on the zeroth moment gives an over-all fair description of these data, essentially independently of the choice made for $\chi_{SC}(\vec{q}, \omega)$. Of course, as we have seen in Fig. 4, the choice of $\chi_{SC}(\vec{q}, \omega)$ is essential in determining the shape of the spectral function. As was shown in Ref. 6, a smooth joining of the potentials of Eqs. (33) and (34) also provides a fair description of these data. On the other hand, the choice of $\Psi(\vec{q})$ based on Eq. (38) yields values of the peak position which are much too high at large wave vectors; this is, of course, a consequence of the fact that $\Psi(\vec{q})$ itself is rather large, as is evident from Fig. 1.

The position of the minimum in all these curves coincides with the position of the main peak of $S(q)$ given in Fig. 2.

IV. CONCLUDING REMARKS

We have seen that in the high-frequency and large-wave-vector region, where hydrodynamics is inap-

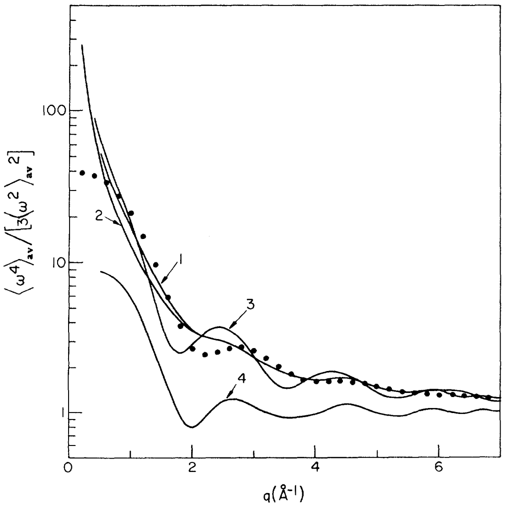

FIG. 3. Fourth moment of $S(q, \omega)$ versus the wave vector q, as calculated from Eq. (31) with $\psi(q)$ determined from Eq. (25) (curve 1), Eq. (33) (curve 2), and Eq. (34) (curve 3), and from Eq. (26) with $\psi(q)$ determined from Eq. (25) (curve 4). The solid circles are calculated from the exact expression of the fourth moment [Eq. (32)].

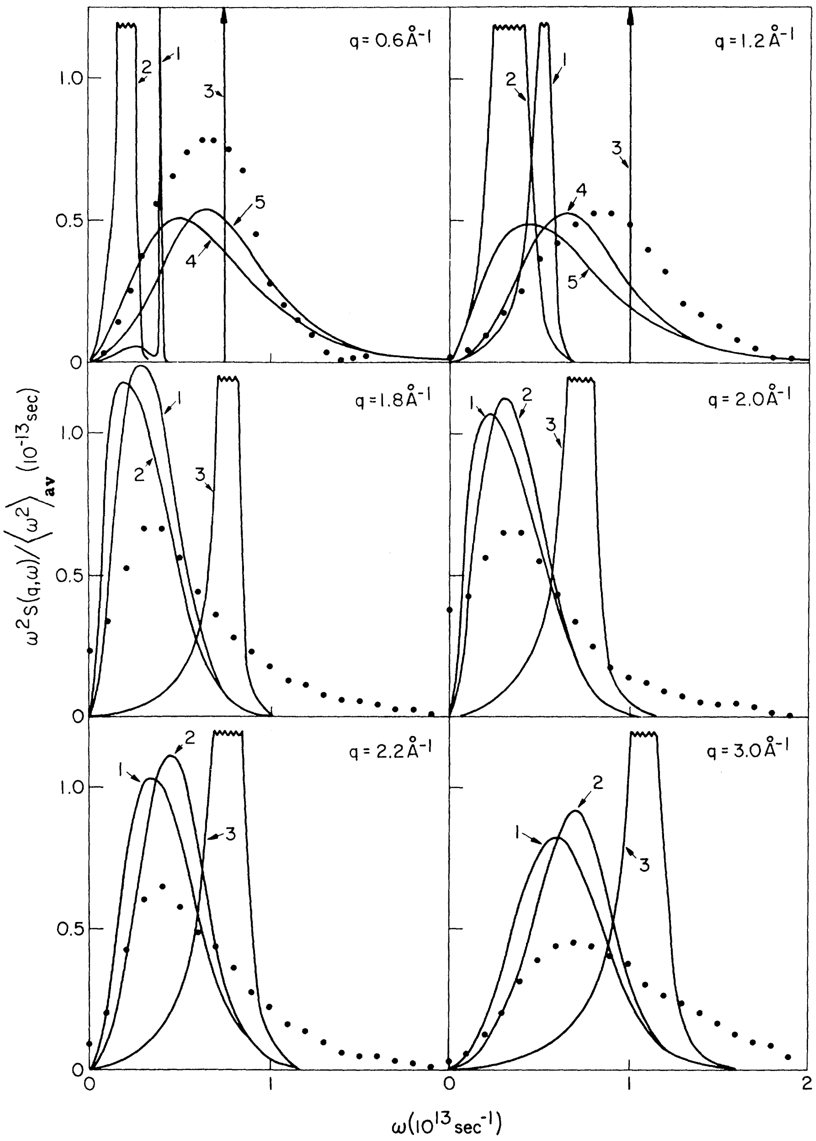

FIG. 4. Spectral function of the longitudinal current correlations $\omega^2 S(q, \omega)$ versus frequency for six values of the wave vector. The theoretical curves are calculated using Eq. (20) for $\chi_{sc}(q, \omega)$ and the values of $\psi(q)$ determined from Eq. (25) (curve 1), Eq. (33) (curve 2), and Eq. (38) (curve 3); and using Eq. (41) for $\chi_{sc}(q, \omega)$ and the values of $\psi(q)$ determined from Eq. (25) (curve 4) and Eq. (34) (curve 5). The solid circles give the results of the machine computations of Rahman (Ref. 5).

plicable, it is possible to account not only qualitatively but semiquantitatively for all the observed features of the dynamic structure factor on the basis of a zero-sound approach. In this approach, the self-consistent potential responsible for the collective motions is determined via the zeroth-moment sum rule, and the screened response is related to the single-particle motions. The damping of these collective modes is determined by the interplay of collective and single-particle motions. The agreement between theory and experiment in liquid argon is all the more gratifying if we consider the fact that the theory does not involve adjustable parameters. However, in some of the calculations, additional assumptions on $S_s(\vec{q}, \omega)$ had to be made, which could be avoided if one had a complete knowledge of this function. It would be interesting to test this theory on liquid metals, in which there are reasons to believe that the collective effects are more pronounced than in liquid argon. Unfortunately, there do not exist any reliable data on $S_s(\vec{q}, \omega)$ for liquid metals. It should be possible to extend the present theory to explain the recent observations of Woods and Cowley[20] on the inelastic scattering of neutrons in liquid He II in the region of large wave vectors where the departures from the free-gas behavior are small but interesting.

ACKNOWLEDGMENTS

Our thanks are due to Dr. A. Sjölander and Dr. W. C. Kerr for many interesting discussions.

APPENDIX A

In this Appendix, we shall show that our basic equation (4), with $\chi_{sc}(\vec{q}, \omega)$ related through Eq. (27)

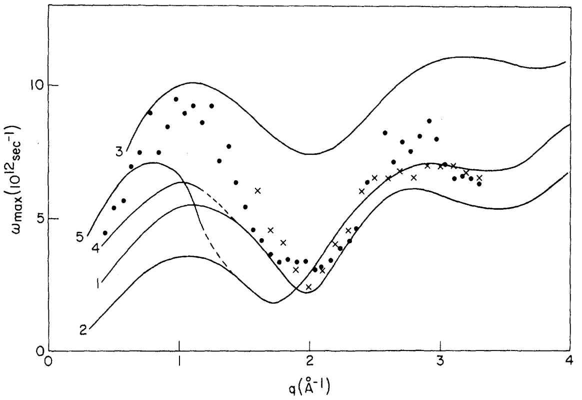

FIG. 5. Peak frequency in the spectral function of the longitudinal current correlations versus the wave vector. The theoretical curves are labeled as in Fig. 4. The solid circles give the results of the machine calculations of Rahman (Ref. 5), and the crosses give the experimental results of Sköld and Larsson (Ref. 4), as reported in Ref. 6.

(assumption made by Singwi *et al.*[6]) and $\Psi(\vec q)$ given by Eq. (25), is identical with Eq. (6.12) Kerr.[10] The latter equation was derived under certain simplifying assumptions discussed in detail by this author.

From Eqs. (9) and (14), it follows that

$$\chi(\vec q, t)=\frac{n}{k_B T}\,\theta(t)\,\frac{d}{dt}\int_{-\infty}^{+\infty} e^{-i\omega t}\, S(\vec q, \omega)\, d\omega\,. \qquad \text{(A1)}$$

Using the standard definition

$$S(\vec q, \omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\, F(\vec q, t)\, dt\,, \qquad \text{(A2)}$$

where $F(\vec q, t)$ is the intermediate scattering function, and (A1), it is easy to show that

$$\chi(\vec q, \omega)=(n/k_B T)\,[pF(\vec q, p)-S(q)]\,, \qquad \text{(A3)}$$

where $p=-i\omega$.

Similarly, we have for the self-part of the response function

$$\chi_s(\vec q, \omega)=(n/k_B T)\,[pF_s(\vec q, p)-1]\,. \qquad \text{(A4)}$$

Substituting (A3) and (A4) in Eq. (4) of the text and using Eq. (25) for $\Psi(\vec q)$ we have

$$F(\vec q, p)=\frac{S(q)F_s(\vec q, p)}{1+nC(q)\,[pF_s(\vec q, p)-1]}\,, \qquad \text{(A5)}$$

where $C(q)$ is the Ornstein-Zernike direct correlation function. Equation (A5) is identical with Eq. (6.12) of Kerr.[10] If, in the above equation, $F_S(\vec q, p)$ is replaced by its limit for free particles, we arrive at the result of Nelkin and Ranganathan,[9] who obtained it by solving the linearized Vlasov equation. It is important to realize, as has been shown in the text, that the latter approximation gives a poor quantitative agreement with experiment. The relation between our previous work[6] and that of Kerr[10] has also been pointed out independently by Nelkin.[21]

APPENDIX B

The classical equation of motion for the density fluctuations $\rho_{\vec q}$ is

$$\ddot\rho_{\vec q}+\sum_i (\vec q\cdot\vec v_i)^2\, e^{-i\vec q\cdot\vec r_i}+\sum_{\vec q\,'} \varphi(\vec q\,')(\vec q\cdot\vec q\,'/M)\,\rho_{\vec q-\vec q\,'}\rho_{\vec q\,'}=0\,, \qquad \text{(B1)}$$

where $\varphi(\vec q)$ is the Fourier transform of the interatomic potential. In the limit $q\to 0$, this equation should take the form of an undamped wave equation, i.e.,

$$\ddot\rho_{\vec q}=-\,\omega_{\vec q}^{\,2}\,\rho_{\vec q}\,, \qquad \text{(B2)}$$

with

$$\omega_{\vec q}^{\,2}=\frac{d}{dn}\left(\sum_i (\vec q\cdot\vec v_i)^2+\sum_{\vec q\,'} \varphi(\vec q\,')\frac{\vec q\cdot\vec q\,'}{M}\sum_{ij} e^{i\vec q\cdot\vec r_j}\, e^{i\vec q\,'\cdot(\vec r_i-\vec r_j)}\right). \qquad \text{(B3)}$$

The last term in the large parentheses can be written

$$\sum_{\vec q\,'} \varphi(\vec q\,')\frac{\vec q\cdot\vec q\,'}{M}\sum_{ij} \frac{i}{2}\,\vec q\cdot(\vec r_j-\vec r_i)\, e^{i\vec q\,'\cdot(\vec r_i-\vec r_j)}=\frac{i}{2}\sum_{\vec q\,'} \varphi(\vec q\,')\frac{\vec q\cdot\vec q\,'}{M}\int d\vec r\,\vec q\cdot\vec r\, e^{\,i\vec q\,'\cdot\vec r}{}_{i\neq j}$$

$$\times\sum_{i\neq j} \delta(\vec r+\vec r_i-\vec r_j)=-\frac{1}{2M}\int d\vec r\;\vec q\cdot\vec r\;\vec q\cdot\frac{\partial\varphi(r)}{\partial\vec r}\sum_{i\neq j} \delta(\vec r+\vec r_i-\vec r_j)$$

$$= -\frac{n^2}{2M}\int d\vec{r}\ \frac{(\vec{q}\cdot\vec{r})^2}{r}\ \frac{d\varphi(r)}{dr}g(r).$$

Equation (B3) becomes

$$\omega_{\vec{q}}^{\ 2} = \tfrac{1}{3}q^2\,\frac{d}{dn}\,\Big(\sum_i\ v_i^{\ 2}\Big) - \frac{4\pi n q^2}{3M}\int_0^\infty dr\ r^3 g(r)\,\frac{d\varphi(r)}{dr}$$

$$-\frac{2\pi n^2 q^2}{3M}\int_0^\infty dr\ r^3\,\frac{\partial g(r)}{\partial n}\ \frac{d\varphi(r)}{dr}\ , \tag{B4}$$

where the last term involves the implicit density dependence of the pair correlation function.

In the zero-sound regime, where we do not allow any relaxation to take place, we are interested in an "instantaneous" sound velocity[22] as opposed to the adiabatic sound velocity in the hydrodynamic regime. Mathematically, this implies that the density change occurs without any rearrangement of the particles, i.e.,

$$g(r,\ n+\delta n) = g(r - \frac{dr}{dn}\delta n, n). \tag{B5}$$

Substituting this result in Eq. (B4) and integrating by parts, we have

$$\omega_{\vec{q}}^{\ 2} = \frac{nq^2}{M}\left[\frac{M}{3n}\,\frac{d}{dn}\left(\ \sum_i\ v_i^{\ 2}\right) - \frac{4\pi}{9}\int_0^\infty dr\ r^3 g(r)\left(\frac{d\varphi(r)}{dr}\ - \frac{1}{2}\ \frac{d^2\varphi(r)}{dr^2}\right)\right]\ . \tag{B6}$$

The first term in Eq. (B6) is the kinetic contribution, which in our approach is accounted for in $\chi_{sc}(\vec{q}, \omega)$. The second term in the above equation is the potential contribution, which is the same as the expression of $\Psi(\vec{q})$ given in Eq. (34) in the limit $q \to 0$. Since we do not know how to join this value of $\Psi(\vec{q})$ at $q = 0$ with the expression given in Eq. (33), which we anticipate to be reasonably accurate at large wave vectors, in Eq. (34) we have assumed a tentative form. It may be noted that the second term in Eq. (B6) is identical with the potential contribution to the instantaneous compressibility expression given by Schofield.[22]

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