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Collective Motions in Classical Liquids. II*†

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An improved version of the theory of Singwi *et al.* for the collective motions in classical liquids is described. The theory is based on a generalized mean-field approximation involving the polarization potential and the screened response function. The latter, instead of having a free-particle form or that corresponding to the true self-motion of the particle in a liquid, is assumed to be a sum of Gaussian functions weighted by the momentum distribution of the particles. The zero and fourth moments of the scattering law determine the polarization potential and the width of the Gaussians. Numerical calculations have been made for the spectral function of the longitudinal current correlations, quasielastic scattering, and absolute intensities for liquid argon in the range of momentum transfer 0.5–6.3 $\mathrm{\AA}^{-1}$. The results are in excellent agreement with the molecular-dynamics calculations and recent experiments on a purely coherent sample of liquid argon.

I. INTRODUCTION

In an earlier paper,[1] hereafter referred to as I, a simple theory for the dynamic-structure factor $S(q, \omega)$ for classical liquids which is valid in the region of high frequencies and short wavelengths was described. This theory is based on a generalized mean-field approximation involving the polarization potential and the screened response function. The imaginary part of the latter is assumed to describe the true self-motion of particles in the liquid, i.e., $S_s(q, \omega)$. The theory satisfies the zero and second moments of $S(q, \omega)$ exactly, whereas the fourth moment is only approximately satisfied. Although an over-all good agreement with the data for the longitudinal current correlations for liquid argon is obtained, the theory is lacking in a quantitative description.

In the present paper we propose a refinement of our earlier theory.[1] The refinement consists in choosing for the imaginary part of the screened response function a sum of Gaussian functions weighted by the momentum distribution of the particles. The zero and fourth moments of the scattering law determine the polarization potential and the width of the Gaussians. The low-order sum rules are *exactly* satisfied by the theory – a requirement which is minimal for any satisfactory theory. Numerical calculations have been made for the dynamical structure factor for momentum transfers greater than 0.2 $\mathrm{\AA}^{-1}$, and a remarkable improvement over the earlier theory of I has been achieved. The agreement with data can now be considered as at least a semiquantitative one. The predictions of the present theory in the range of momentum transfer 3.5–4.6 $\mathrm{\AA}^{-1}$, for which no data were available until very recently, have now been verified in an experiment by Rowe *et al.*[2] on a completely coherent argon sample.

Section II contains the formal discussion of the scattering law, sum rules, and the details of our model. In Sec. III, $S(q, \omega = 0)$ of the present theory is compared with that of the other theories of collective motions in classical liquids. Numerical results are presented in Sec. IV, and Sec. V contains the critique.

II. FORMULATION

A. General Considerations

Since the principles underlying the mean-field approach have been discussed previously in I, the description here is very brief. The density response function $\chi(q, \omega)$ may be written as[3]

$$\chi(q, \omega) = \chi_{sc}(q, \omega)/[1 - \Psi(q)\, \chi_{sc}(q, \omega)] , \qquad (1)$$

where $\chi_{sc}(q, \omega)$ is defined to give the response of the density to the sum of the external potential and the polarization potential. The latter is defined through the equation

$$\langle V_{\mathrm{Pol}}(q, \omega) \rangle = \Psi(q)\, \langle \rho(q, \omega) \rangle. \qquad (2)$$

The functions $\Psi(q)$ and $X_{sc}(q, \omega)$ are not known *a priori*. In the usual random phase approximation (RPA), $\chi_{sc}(q, \omega)$ is taken as the response function of a noninteracting system and $\Psi(q)$ is the Fourier transform of the bare interparticle potential.

From the analytic properties of the response function it follows that

$$\chi(q, \omega) = \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \, \frac{\chi''(q, \omega')}{\omega' - \omega - i\eta} , \qquad (3)$$

where $\eta = 0^+$. The imaginary part of the density response function $\chi''(q, \omega)$ is related to its real part $\chi'(q, \omega)$ through the Kramers-Kronig dispersion relation. The fluctuation-dissipation theorem provides the relation between the dynamical-structure factor $S(q, \omega)$ and $\chi''(q, \omega)$, which in the classical limit ($\hbar\omega \ll k_BT$) simplifies to

$$S(q,\omega) = -(k_BT/n\pi)/[\chi''(q,\omega)/\omega], \tag{4}$$

where n is the number density and T the absolute temperature.

B. Model Form for $\chi(q,\omega)$

In the present approach the mean field, arising as a result of mutual interaction between the particles of the condensed system, should tend to organize their motion in a coherent fashion and should thus lead to some sort of collective oscillations. This collective behavior is described by the denominator of Eq. (1), which vanishes for well-defined collective modes. In a classical liquid in the region of large wave vectors ($q > 0.5$ Å^{-1}), although we do not find good collective modes, the denominator of Eq. (1), as we shall see, has a marked influence.

The precise form of the screened response function $\chi_{sc}(q,\omega)$ is not known to us. We have only intuitive physical arguments and approximate theoretical considerations to guide us. The simplest approximation[1,4] in the standard RPA theory is to take for this function the response function for a noninteracting gas. A somewhat better approximation[1,5] is to relate the imaginary part of $\chi_{sc}(q,\omega)$ with the actual self-motion of particles, i.e., with $S_s(q,\omega)$. A theoretical justification[1,6] for this approximation can be given from a general and more formal approach due to Kerr.[7] Then there is a related approximation due to Hubbard and Beeby.[8] All these approximations have been considered in detail and their consequences have been examined in I. Here we present another approximation for $\chi_{sc}(q,\omega)$ which at present has only *a posteriori* justification. The approximation seems physically reasonable and has the merit that the scattering law satisfies *exactly* the low-order sum rules and gives a semiquantitative fit to all the experimental data available so far for liquid argon.

The imaginary part of the free-particle response function is given by

$$\chi''_{\text{Free}}(q,\omega) = -\frac{\pi}{\hbar}\sum_{\vec{p}} n_p\,[\delta(\omega-\omega_{\vec{p}+\vec{q}}+\omega_{\vec{p}}) - \delta(\omega+\omega_{\vec{p}+\vec{q}}-\omega_{\vec{p}})], \tag{5}$$

where the symbols have their usual meaning. In the classical case with n_p given by Maxwell-Boltzmann distribution function and neglecting recoil, Eq. (5) reduces to the standard formula. Having taken into account explicitly the collective aspects of the motion as expressed mathematically by the denominator of Eq. (1), there will still be left some residual interactions between the particles. These residual interactions will have the physical effect of modifying the free-particle behavior. Mathematically, this is expressed here by broadening the δ functions in Eq. (5) by Gaussian functions. We therefore assume the following form for $\chi''_{sc}(q,\omega)$:

$$\chi''_{sc}(q,\omega) = -\frac{\pi}{\hbar}\sum_{\vec{p}} n_p\,[\pi\Gamma(q)]^{-1/2} \times \{\exp[-(\omega-\omega_{\vec{p}+\vec{q}}+\omega_{\vec{p}})^2/\Gamma(q)] - \exp[-(\omega+\omega_{\vec{p}+\vec{q}}-\omega_{\vec{p}})^2/\Gamma(q)]\}, \tag{6}$$

where $\Gamma(q)$ is the width of the Gaussian. We have particularly chosen Gaussians rather than Lorentzians because we want to make use of the frequency moments, which do not exist for a Lorentzian. In the limit $\Gamma(q)\to 0$, Eq. (6) goes over to Eq. (5). In general, $\Gamma(q)$ will also depend on frequency, and therefore our assumption implies some kind of average over the frequency. We are forced to make this assumption in order to make the calculation tractable. Renormalization of the energy of the particles has also been neglected. It appears that the main effect of the residual interactions is to produce damping of the free-particle motion.

For the classical case under consideration, performing the integration and neglecting recoil, Eq. (6) becomes

$$\chi''_{sc}(q,\omega) = -\frac{2n\omega q^2}{2q^2k_BT+m\Gamma(q)}\left(\frac{\pi m}{2q^2k_BT+m\Gamma(q)}\right)^{1/2} \times \exp\left(\frac{-m\omega^2}{2q^2k_BT+m\Gamma(q)}\right). \tag{7}$$

For $\Gamma(q)=0$, the above expression reduces to that of a free gas. Making use of the Kramers-Kronig dispersion relation, the real part $\chi'_{sc}(q,\omega)$ of $\chi_{sc}(q,\omega)$ is given by

$$\chi'_{sc}(q,\omega) = -\frac{2nq^2}{2q^2k_BT+m\Gamma(q)}\left\{1+i\left(\frac{\pi m\omega^2}{2q^2k_BT+m\Gamma(q)}\right)^{1/2} \times \exp\left(\frac{-m\omega^2}{2q^2k_BT+m\Gamma(q)}\right) \times \operatorname{erf}\left[i\left(\frac{m\omega^2}{2q^2k_BT+m\Gamma(q)}\right)^{1/2}\right]\right\}. \tag{8}$$

Here the result has been expressed in terms of the error function of purely imaginary argument for convenience of our numerical calculations. It is also expressible in terms of Dawson's integral which is tabulated in the literature.

From Eq. (8), it follows that

$$\chi_{sc}(q,0) = \chi'_{sc}(q,0) = -\frac{2nq^2}{2q^2k_BT+m\Gamma(q)}. \tag{9}$$

C. Sum Rules

From Eqs. (1), (3), and (4) we have

$$\Psi(q)=k_BT/n\,S(q)+1/\chi_{sc}(q,0), \tag{10}$$

which is the zero-moment sum rule. On using Eq. (9), Eq. (10) becomes

$$n\Psi(q)=k_BT\,[1/S(q)-1]-m\,\Gamma(q)/2q^2. \tag{11}$$

In the classical limit the odd moments of $S(q,\omega)$ vanish and the even moments are defined as

$$\begin{aligned}\langle\omega^{2l}\rangle &\equiv\int_{-\infty}^{+\infty}\omega^{21}S(q,\omega)d\omega\\ &=-(k_BT/n)\int_{-\infty}^{+\infty}(d\omega/\pi)\,\omega^{2l-1}\,\chi''(q,\omega),\end{aligned} \tag{12}$$

which follows from Eq. (4). Large-ω expansion of $\chi(q,\omega)$ can be obtained from Eq. (3), and using Eq. (12) it can be written as

$$\chi(q\,\omega)=\frac{n}{k_BT}\sum_{l=1}^{\infty}\frac{\langle\omega^{2l}\rangle}{\omega^{2l}}\quad. \tag{13}$$

Similarly, for the screened response function we have

$$\chi_{sc}(q,\omega)=\sum_{l=1}^{\infty}\langle\omega_{sc}^{2l-1}\rangle/\omega^{2l}, \tag{14}$$

where we have defined $\langle\omega_{sc}^{2l-1}\rangle$ as

$$\langle\omega_{sc}^{2l-1}\rangle=-\int_{-\infty}^{+\infty}(d\omega/\pi)\,\omega^{2l-1}\,\chi_{sc}''(q,\omega). \tag{15}$$

The even moments of $\chi_{sc}''(q,\omega)$ obviously vanish. Large-ω expansion of Eq. (1) can be written as

$$\chi(q,\omega)=\frac{\langle\omega_{sc}\rangle}{\omega^2}+\frac{1}{\omega^4}\,[\langle\omega_{sc}^3\rangle+\Psi(q)\,\langle\omega_{sc}\rangle^2]+0\,\frac{1}{\omega^6}\,. \tag{16}$$

Comparing Eqs. (13) and (16), we have

$$\langle\omega_{sc}\rangle=(n/k_BT)\,\langle\omega^2\rangle, \tag{17}$$

$$\langle\omega_{sc}^3\rangle+\Psi(q)\,\langle\omega_{sc}\rangle^2=(n/k_BT)\,\langle\omega^4\rangle. \tag{18}$$

Similar relations may be obtained for higher moments. It may be noted that the above relations are independent of any specific form for the screened response function. This suggests that all the moments of $\chi_{sc}''(q,\omega)$ must exist, and hence our choice for the Gaussian form. The fact that the right-hand sides of Eqs. (17) and (18) are exactly known is of great help.

Using Eq. (7) in Eq. (15) one immediately finds that

$$\langle\omega_{sc}\rangle=nq^2/m, \tag{19}$$

$$\langle\omega_{sc}^3\rangle=(3nq^2/2m^2)\,[2q^2k_BT+m\,\Gamma(q)]. \tag{20}$$

We note from Eqs. (17) and (19) that the second moment of $S(q,\omega)$ is automatically satisfied. We also note from Eqs. (18) and (20) that the fourth moment of $S(q,\omega)$ will be exactly satisfied if

$$3\,q^2k_BT+\tfrac{3}{2}m\,\Gamma(q)+nq^2\,\Psi(q)=(m^2/q^2k_BT)\,\langle\omega^4\rangle. \tag{21}$$

Substituting the exact expression[9] of the fourth moment in the above equation, we have

$$3m\Gamma(q)/2q^2+n\Psi(q)=n\,P_4(q), \tag{22}$$

where the potential part $P_4(q)$ of the fourth moment is given by

$$P_4(q)=\int d\vec{r}\,g(r)[(1-\cos\vec{q}\cdot\vec{r})/q^2]\,(\hat{q}\cdot\nabla)^2\,\phi(r). \tag{23}$$

Here $g(r)$ is the pair correlation function and $\phi(r)$ is the interparticle potential. Solving the simultaneous equations (11) and (22) for $\Psi(q)$ and $\Gamma(q)$, we get

$$\Psi(q)=\frac{3k_BT}{2n}\left(\frac{1}{S(q)}-1\right)-\frac{P_4(q)}{2}, \tag{24}$$

$$\Gamma(q)=\frac{q^2}{m}\left[nP_4(q)-k_BT\left(\frac{1}{S(q)}-1\right)\right]. \tag{25}$$

With the above choice of $\Psi(q)$ and $\Gamma(q)$ our theory satisfies exactly the low-order moments up to the fourth.

III. COMPARISON OF $S(q,\omega=0)$ IN VARIOUS THEORIES

From Eqs. (1) and (4), it follows that

$$S(q,\omega)=-\frac{k_BT}{\pi n\omega}\times\frac{\chi_{sc}''(q,\omega)}{[1-\Psi(q)\,\chi_{sc}'(q,\omega)]^2+[\Psi(q)\chi_{sc}''(q,\omega)]^2}\,. \tag{26}$$

The expression for $S(q,\omega)$ in the present theory as well as in other theories is far too complicated to allow any instructive comparison to be made. Nevertheless, the expression for $S(q,\omega=0)$ is simple and transparent enough to allow such a comparison. We shall do so in the following.

From Eqs. (7), (8), and (26) and using Eqs. (11) and (22) it is straightforward to show that

$$S(q,\omega=0)=S^2(q)\left(\frac{m}{4\pi k_BTq^2}\right)^{1/2}\left(3-\frac{1}{S(q)}+\frac{nP_4(q)}{k_BT}\right)^{1/2}. \tag{27}$$

This expression has an interesting structure.

In Nelkin's model[1,4] where $\chi_{sc}(q,\omega)$ is taken to be the response of a free gas, one finds

$$S(q,\omega=0)=S^2(q)\,(m/2\pi k_BTq^2)^{1/2}\,. \tag{28}$$

In the limit of q large, Eq. (27) indeed goes over to Eq. (28) as it should. In the earlier theory of Singwi *et al.*,[1,5] it is easy to show that

$$S(q,\omega=0)=S^2(q)\,S_s(q,\omega=0), \tag{29}$$

where $S_s(q,\omega)$ is the Van Hove self-correlation function. In the convolution approximation of Vineyard[10] we have

$$S(q,\omega=0)=S(q)\,S_s(q,\omega=0), \tag{30}$$

which is very different from the corresponding expression based on other theories.

Sometime ago Sköld,[11] in attempt to explain his quasielastic scattering data in liquid argon, proposed a recipe for $S(q, \omega)$. His expression is

$$S(q, \omega=0)=S(q)\; S_s\{q/[S(q)]^{1/2}, \omega=0\}\;. \tag{31}$$

It is interesting to note that for a simple diffusive model for $S_s(q, \omega)$, Eqs. (29) and (31) are identical. However, for a finite ω, this is not the case.

Recently, Ortoleva and Nelkin[12] and Kurkijarvi[13] have derived, based on the memory-function approach, an expression for $S(q, \omega)$. Their theory also satisfies the low-order moments. Their result is

$$S(q, \omega=0)=S^2(q)\; S_s(q, \omega=0)\left(3-\frac{1}{S(q)}+\frac{nP_4(q)}{k_BT}\right)\times\left(2+\frac{n}{q^2k_BT}\langle\nabla^2\phi(r)\rangle\right)^{-1}, \tag{32}$$

where

$$\langle\nabla^2\phi(r)\rangle=\int d\vec{r}\, g(r)\,\nabla^2\phi(r).$$

Ailawadi *et al.*[14] and Chung and Yip[15] have used a generalized hydrodynamic approach to derive an expression for $S(q, \omega)$. The approach of the latter authors is based on the formalism of Kandanoff and Martin,[16] which has the merit that it approaches rigorously to the hydrodynamic limit as both q and ω tend to 0. In the theory of Ailawadi *et al.*[14] we have

$$S(q, \omega=0)=S^2(q)\left(3-\frac{1}{S(q)}+\frac{nP_4(q)}{k_BT}\right)\frac{\tau(q)}{\pi}, \tag{33}$$

where $\tau(q)$ is the "generalized" relaxation time and is a parameter of the theory. In the limit of large q, $\tau(q)$ must be of the form

$$\tau(q)=\left(\frac{m\pi}{8k_BTq^2}\right)^{1/2}.$$

On the other hand, the corresponding expression in the theory of Chung and Yip[15] is

$$S(q, \omega=0)=S^2(q)\,\frac{1}{\pi}\left[\left(3+\frac{nP_4(q)}{k_BT}-\frac{\gamma}{S(q)}\right)\tau(q)+\frac{\gamma-1}{S(q)}\,\tau'(q)\right], \tag{34}$$

where γ is the ratio of the specific heats and τ's are the "generalized" relaxation times. For $\tau(q)=\tau'(q)$, Eq. (34) reduces to Eq. (33) as expected, since in the approach of Ailawadi *et al.*[14] thermal diffusion is neglected.

IV. CALCULATIONS AND RESULTS

A. Longitudinal Current Correlations

The calculations presented in this section have been done for liquid argon at 76 °K and for a density of 1.407 g/cm^3. For this temperature and density, molecular-dynamics computations of Rahman[17] for $S(q)$, $P_4(q)$ and for the spectral function of the longitudinal current correlations, $\omega^2S(q, \omega)$, are available. Using the values of $S(q)$ and $P_4(q)$ provided by Rahman,[17] we have calculated $\Gamma(q)$ and $\Psi(q)$ from Eqs. (24) and (25) for various values of the wave vector q. These are plotted in Figs. 1 and 2. Note that $\Psi(q)$ is negative and has minor oscillations in it. For a good collective mode $\Psi(q)$ is positive. $\Gamma(q)$ has very pronounced oscillations in it which arise from oscillations in $P_4(q)$ and $S(q)$ as is evident from Eq. (25). It may be mentioned that there are some uncertainties in the values of the structure factor $S(q)$ for very small values of the wave vector. We have taken $S(q)=0.04$ for values of q ranging from 0 to 0.63 Å^{-1}.

Having determined the functions $\Psi(q)$ and $\Gamma(q)$, we have calculated, using Eqs. (8), (9), and (26), the spectral function $\omega^2S(q, \omega)$ as a function of frequency for various values of q, ranging from 0.23 to 6.57 Å^{-1}. In Figs. 3(a) and 3(b) are plotted the values of $\omega^2S(q, \omega)/\langle\omega^2\rangle$ versus ω for arbitrarily selected values of q. For the sake of comparison we have also shown by a dashed curve the corresponding results of I. The solid circles represent the results of the molecular-dynamics "experiments" of Rahman,[17] whose data extend only up to $q=3.3$ Å^{-1}. Rahman's data are avilable for five different time cutoffs of the Fourier transform of the longitudinal current correlation function for the values of q between 0.23 and 2.63 Å^{-1}. For q's between 2.7 and 3.3 Å^{-1}, data are available for only one value of the time cutoff. Ailawadi[18] has made a detailed statistical analysis of Rahman's data and has concluded that for the time cutoff corresponding to 1.6×10^{-12} sec, the spectral functions of the longitudinal and transverse current correlations are smooth functions of the frequency for all values of the wave vec-

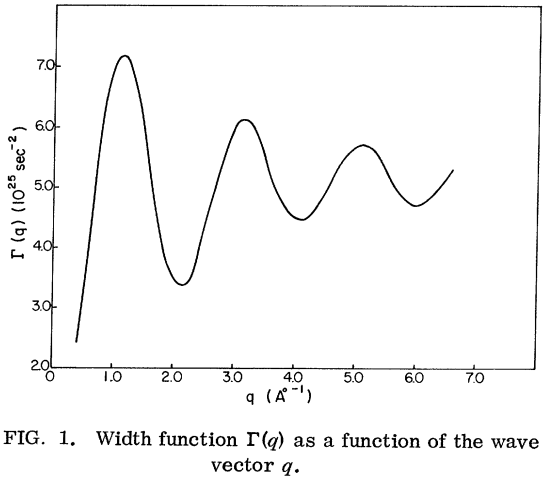

FIG. 1. Width function $\Gamma(q)$ as a function of the wave vector q.

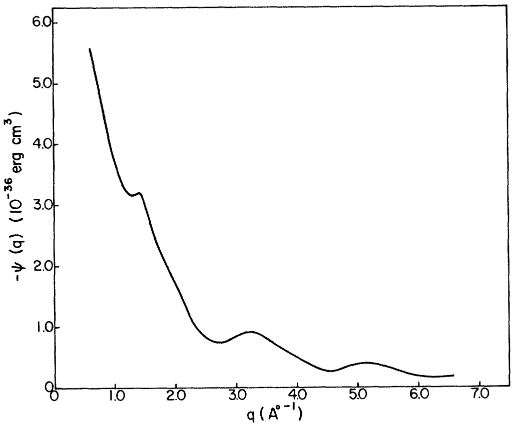

FIG. 2. Effective potential $\Psi(q)$ versus the wave vector q.

tors. The solid circles in Fig. 3(a) and (b) correspond to this time cutoff.

From an inspection of Fig. 3, it is clear that the present results show a remarkable improvement over the earlier results of Singwi *et al.*[1] The agreement with the results of molecular-dynamics calculation can now be considered more than semiquantitative. For the largest value of q shown in Fig. 3, the results of the present theory have not yet approached their free-gas value.

In Fig. 4 the position of the peak in the spectral function of the longitudinal current correlation is plotted as a function of the wave vector. The straight line gives the corresponding free-gas behavior. The solid circles represent the average of the molecular-dynamics data by using five different time cutoffs. The vertical bars indicate the spread of the molecular-dynamics data as a result of using different time cutoffs. The crosses in Fig. 4 are the experimental results of Sköld and Larson.[19] The agreement between theory and experiment is very good and again shows a remarkable improvement over the results of Singwi *et al.*[1] A very interesting result of the present theory is that there exist further maxima and minima in the $\omega_{\max}(q)$ versus q curve beyond $q = 3\,\text{Å}^{-1}$, which should be observable. If the curve of Fig. 4 is extrapolated for values of $q < 0.23\,\text{Å}^{-1}$, it passes through the origin. This has been indicated by a dashed line. The slope of this line is 9×10^4 cm sec^{-1} – a result which is in agreement with the extrapolated value of the molecular-dynamics data.[17]

In Fig. 5 is plotted the maximum height of the spectral function of the longitudinal current correlations as a function of the wave vector. The corresponding curve for the case of a free gas is also shown. The solid circles represent the computer data of Rahman.[17] The agreement between the two results is again quite good. The height is a rough

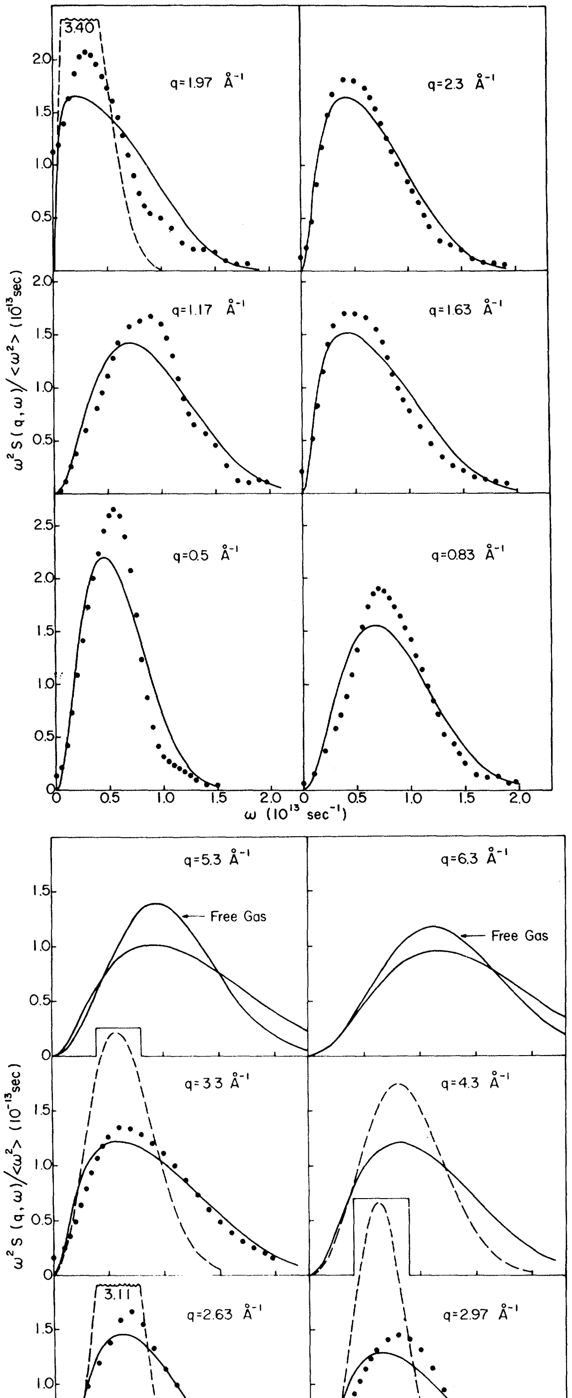

FIG. 3. Spectral function of the longitudinal current correlations $\omega^2 S(q,\omega)/\langle\omega^2\rangle$ plotted as a function of the frequency for some arbitrarily selected values of the wave vector. Area under each curve is normalized to $\frac{1}{2}\pi$. The dashed curves are the results of Singwi *et al.* (Ref. 1). The solid circles denote the results of the molecular-dynamics calculation of Rahman.

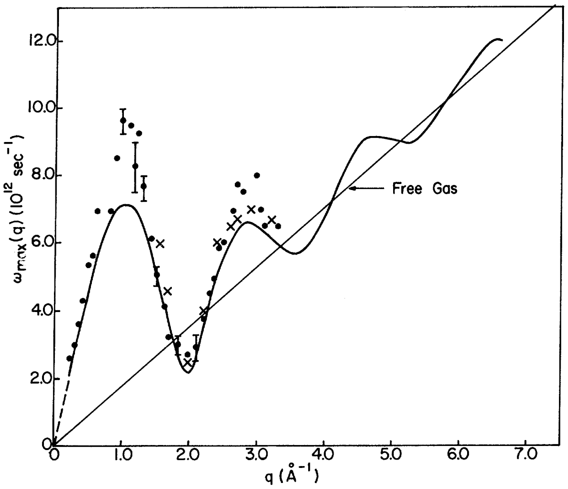

FIG. 4. Dispersion curve $\omega_{\rm max}(q)$ versus q for the longitudinal current fluctuations. The solid circles denote the results of the molecular-dynamics calculation of Rahman, and crosses are the experimental results of Sköld and Larsson (Ref. 19).

measure of the lifetime of the longitudinal current fluctuations.

B. Quasielastic Scattering

In Fig. 6 we have plotted the full width at half-maximum of $S(q,\omega)$ as a function of the wave vector q. The straight line represents the corresponding value for the case of a free gas. A very important feature of this width function is the presence of maxima and minima for certain characteristic values of q. The pronounced minimum at $q = 2\ \text{Å}^{-1}$ corresponds to the maximum in the structure factor $S(q)$. The existence of such a minimum was predicted many years ago by de Gennes[9] and was first experimentally observed by Brockhouse *et al.*[20] And since then many attempts[11,21] have been made to explain the characteristic features of the width function on the basis of phenomenological models. It is worth noting that even for a value of q as large as $7\ \text{Å}^{-1}$ the departure of the calculated width function from its free-gas value is appreciable.

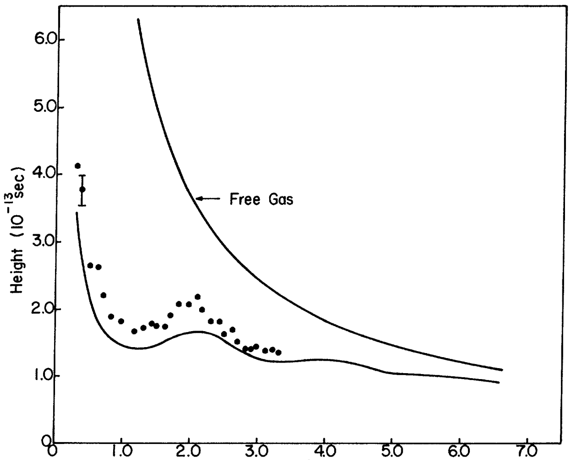

FIG. 5. Height of the peak position of the spectral function of the longitudianl current correlations as a function of the wave vector q. The solid circles denote the results of the molecular-dynamics calculation of Rahman.

After the present calculations were finished, we were fortunately furnished by Rowe and his collaborators[2] their recent neutron inelastic scattering experimental results of $S(q,\omega)$ on a purely coherent sample of liquid argon (atomic mass 35.97). As far as we know this is the first time such an experiment has been done. This makes it possible for us to compare our results directly with their experimental data without worrying about the incoherent part of the scattering which is always present in an ordinary sample of liquid argon. Their results are shown by crosses in Fig. 6. The data have been taken at 85.2 °K whereas our calculations have been made for 76 °K. We have been informed by Rowe that these are raw data in the sense that they have not yet been corrected for energy resolution and multiple scattering. The latter correction, we are told, is not going to alter the values of the width

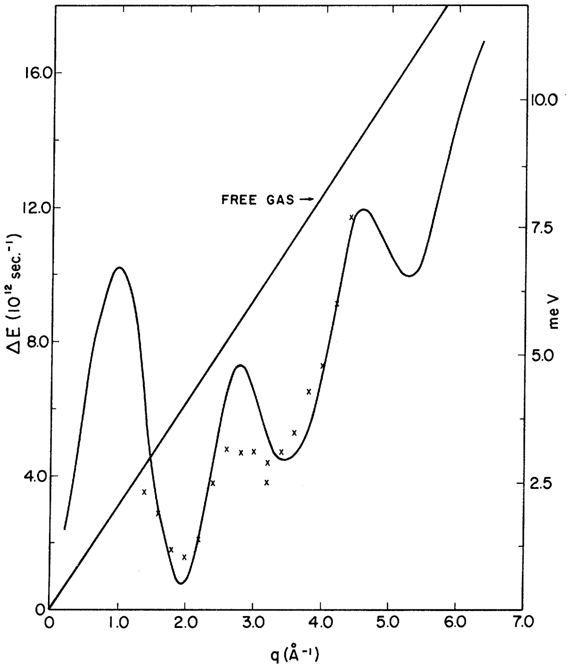

FIG. 6. Full width ΔE at half-maximum of $S(q,\omega)$ versus wave vector q for a coherent sample of liquid argon (atomic mass 35.97) at 76 °K and density of 1.407 g/cm^3. The experimental points of Rowe (Ref. 2) denoted by crosses are for $T = 85.2$ °K.

function, but the energy resolution correction will reduce somewhat the values in the neighborhood of $q=2\,\text{Å}^{-1}$ where the width is smallest. It is very gratifying to note that the predictions of the theory have been confirmed by this experiment. We shall reserve further judgment until the time the data of Rowe and collaborators have been fully analyzed and until more data are available in the region of both small ($q<1.5\,\text{Å}^{-1}$) and large ($q>4.5\,\text{Å}^{-1}$) wave vectors. In Fig. 7 the absolute value of the intensity for $\omega=0$, i.e., $S(q, \omega=0)$ is plotted as a function of q. The crosses are the data of Rowe and collaborators.[2] Again, the agreement between theory and experiment is fairly good. The experimental value at $q=2\,\text{Å}^{-1}$ falls much below the theoretical value, but the former is expected to go up after it is corrected for energy resolution.

V. CRITIQUE

In this paper we have presented an improved version of the theory of Singwi *et al.*[1] for the collective motions in classical liquids. The basic assumption of the model theory is the use of the Gaussian forms for the imaginary part of the screened response function whose width depends on wave number only. The assumption relies more on intuitive and physical considerations and as yet lacks a first-principle derivation. A detailed comparison of the theoretical results with all the available experimental data for liquid argon that we have presented here gives *a posteriori* justification to our basic assumption. The merit of the present theory lies in its great simplicity and in requiring minimal outside information. The latter consists in knowing the static structure factor $S(q)$ of the liquid and the interatomic potential. Moreover, the theory satisfies *exactly* the low-order sum rules and is free from any adjustable parameters. A quantum-mechanical version of the present theory has also recently been applied[22] with reasonable success to explain the experiments of Woods and Cowley[23] on neutron scattering from liquid He II at large momentum transfers. There is sufficient reason to believe that the theory when applied to liquid metals should also yield good results.

The weakness of the present theory is that it is not applicable in the hydrodynamic regime. We have calculated $S(q, \omega)$ in the region of momentum transfers less than $0.5\,\text{Å}^{-1}$ and did not find any structure in it corresponding to the two Brillouin components. Of course, it is not yet known where the hydrodynamic regime ends and the zero-sound

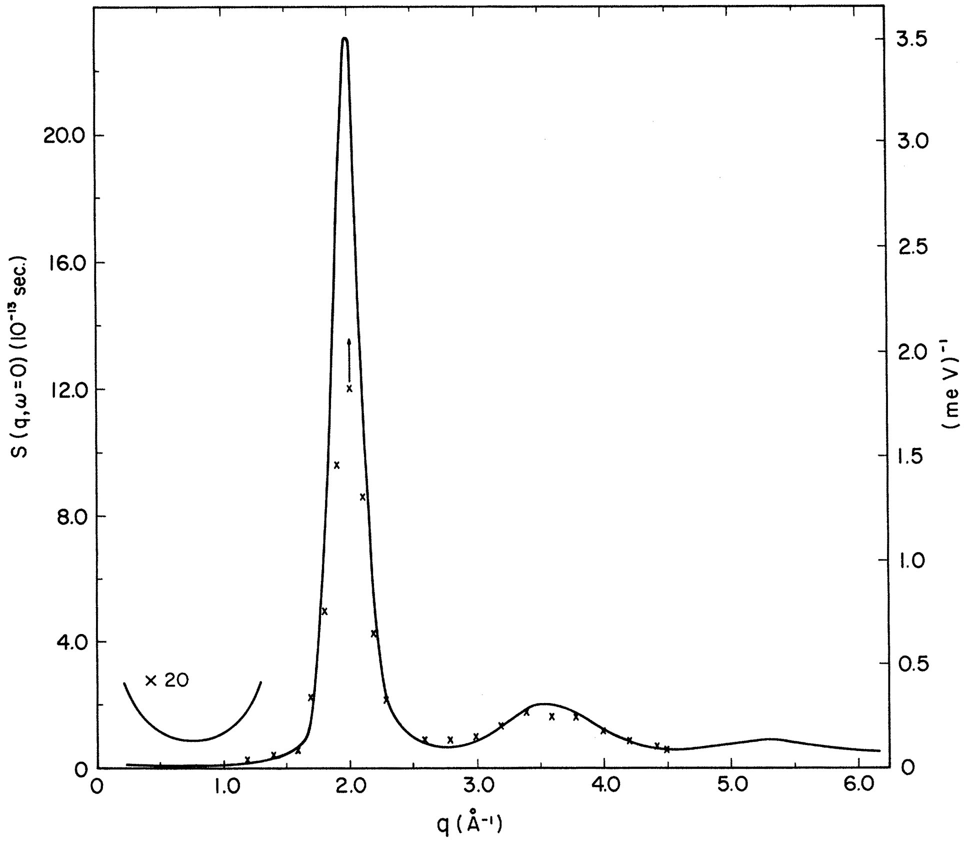

FIG. 7. Absolute intensity $S(q, \omega=0)$ versus wave vector. Experimental points of Rowe (Ref. 2) are denoted by crosses.

regime begins.

Recently, Chung and Yip[15] have successfully analyzed the molecular dynamics and neutron scattering data for liquid argon using the formalism of Kadanoff and Martin,[16] which has the merit of giving the correct hydrodynamic limit. In their attempt to use the generalized hydrodynamic expressions, Chung and Yip[15] introduce concepts such as the wave number and frequency-dependent relaxation times, whose physical meaning in the high-frequency and large wave number region is not very clear. The work of Ailawadi *et al.*[14] is also based on a generalized hydrodynamic approach. The ideas of these authors are of interest in the domain not too far from the hydrodynamic region.

In the region of large wave vectors where the microscopic structure of the liquid plays an important role, and where very probably $\omega\tau \sim 1$, it is our belief that the mean-field approach of the present theory and that of Hubbard and Beeby[8] is the more appropriate one. The concepts in this approach are well understood from our experience in other fields. However, the physical meaning of the oscillatory behavior of our $\Gamma(q)$ is not clear. Mathematically, it arises due to the structure in $S(q)$ and $P_4(q)$ [see Eq. (25)]. It could also be due to our basic simplifying assumptions regarding $\Gamma(q)$.

Although we have not attempted, it should be possible to establish a connection between our theory and the memory-function approach of Ortoleva and Nelkin[12] and Kurkijarvi.[13]

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