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Collective Modes, Damping, and the Scattering Function in Classical Liquids

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An exact representation for the density–density response function is presented. This representation is a generalization of the result obtained in the mean field approximation and amounts to replacing the static, effective potential by one which is both wavenumber- and frequency-dependent. This potential possesses both a real and an imaginary part; the latter describes the collisional damping of collective modes. Analyticity and sum rule arguments are used to describe the basic properties of this complex potential. The formalism allows us to write an exact formula for the scattering function $S(k, \omega)$ in which the basic unknown is the collisional damping function. Using a small portion of the recent experimental data on coherent neutron scattering in liquid argon, we are able to calculate $S(k, \omega)$ and other quantities of interest and to make comparisons with the rest of the data.

KEY WORDS: Density–density response function; exact mean-field-type expression; van Hove scattering function; collisional damping function; Landau-type damping function.

1. INTRODUCTION

Some theoretical investigations of collective motions in simple liquids[1–4] in the region of high frequencies and short wavelengths have in part been based on approximate expressions for the complex density–density response function $\chi(k, z)$. Some of these approximations are in a sense mean field approximations (MFA) since they can be derived from a linearized kinetic equation for the single-particle distribution function. The mean-field-type

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approximation for $\chi(k, z)$, to be denoted by $\chi_{\mathrm{MF}}(k, z)$, is characterized by the expression

$$\chi_{\mathrm{MF}}(k, z) = \chi_0(k, z)/[1 + \psi(k)\chi_0(k, z)] \tag{1}$$

where $\chi_0(k, z)$ is the density–density response function for an ideal gas. Here $\chi(k, z)$ is defined in such a way that the limit $z \to \omega + i\epsilon$ (where ϵ is a positive infinitesimal) from above the real axis describes the linear response $\langle\rho(\mathbf{k}, \omega)\rangle$ of the density to an external potential $u(\mathbf{k}, \omega)$ according to

$$\langle\rho(\mathbf{k}, \omega)\rangle = -\chi(k, \omega + i\epsilon)u(\mathbf{k}, \omega) \tag{2}$$

The various approximations can be stated in terms of the expression used for the "effective" potential $\psi(k)$ [or the corresponding space-dependent form $\psi(r)$] as summarized in Table I. The MFA (1) is such that the first moment sum rule for the imaginary part of $\chi(k, \omega + i\epsilon)$ [to be denoted by $\chi''(k, \omega)$] is automatically satisfied. However, only the approximation in the second row of Table I is consistent with the elastic sum rule for all k [cf. Eq. (8)]. None of the expressions in Table I is consistent with the third or higher moment sum rules for $\chi''(k, \omega)$ (cf. Section 2).

In addition to discussions of collective motions, the MFA (1) has recently been used to investigate those density fluctuations which may be considered as precursors to freezing.[7]

As has been shown in Ref. 1 and is discussed further in Section 4.2 of this work, the scattering function $S_{\mathrm{MF}}(k, \omega)$ resulting from (1) shows well-defined side peaks for k values ranging from 0 to $\sim$1.6 Å^{-1} in liquid argon. However, recent experimental determinations of the scattering function $S(k, \omega)$ in liquid argon[8] by coherent neutron scattering in the region $1 \leqslant k \leqslant 4.4$ Å^{-1} and $0 \leqslant \omega \leqslant 16.1 \times 10^{12}\,\mathrm{sec}^{-1}$ do not reveal any side peaks. Comparison with the experimental results shows in fact the complete inadequacy of the MFA to describe even qualitatively the observed scattering intensity. The reason for this failure of the MFA lies in the fact that it only allows for Landau-type damping of the collective modes (see Section 4.2) and completely neglects the all-important collisional damping.

In this paper we use an exact representation for $\chi(k, z)$ which amounts to replacing the static, effective potential $\psi(k)$ in (1) by a wavenumber- and frequency-dependent effective potential $\phi(k, z)$. This potential possesses both a real and an imaginary part; the latter describes the collisional damping. Here we do not try to derive the form of $\phi(k, z)$ from a detailed microscopic equation of motion approach. Rather, we use analyticity and sum rule arguments to describe the basic properties of $\phi(k, z)$ and show that by making simple assumptions for its imaginary part, $\phi''(k, \omega)$, a correct quantitative description of the scattering function and other quantities of interest can be obtained.

At this point let us emphasize the basic difference between our approach and that of Pathak and Singwi.[9] These authors start from a formally exact expression of the form (1) in which $\chi_0(k, z)$ is replaced by a "screened" response function $\chi_{sc}(k, z)$. In their theory there are thus two unknown functions, $\chi_{sc}(k, z)$ and the effective potential $\psi(k)$, whereas in our theory there is only one unknown, the complex function $\phi(k, z)$. By using an appropriate ansatz for $\chi_{sc}(k, z)$ together with sum rule arguments, Pathak and Singwi[9] have obtained good argeement with molecular dynamics calculations and the experimental results of Sköld *et al.*[8] Their theory satisfies the zeroth, second, and fourth frequency moment sum rules for $S(k, \omega)$. In our approach these sum rules are built into the theory from the start. In principle our approach allows us also to be consistent with higher-order moment sum rules for $S(k, \omega)$. With a particularly simple ansatz for $\phi''(k, \omega)$ we can in fact satisfy all frequency moments up to the sixth. In practice, however, the lack of numerical data on the sixth and higher moments has led us to an "inversion" of the problem in the sense that we use a small portion of the experimental data in conjunction with the theory to extract some quantities of interest for which there exist thus far no reliable estimates (Section 6).

In Section 2 we review the basic relations, analytic properties, and sum rules connected with the response function $\chi(k, z)$. This section also defines some key quantities used throughout the analysis. In Section 3 we discuss the basic analytic properties of the complex effective interaction $\phi(k, z)$ and the sum rules satisfied by its imaginary part, $\phi''(k, \omega)$. Also given in Section 3 are some exact formulas relating the coherent scattering function $S(k, \omega)$ (or the closely related spectral function $\chi''(k, \omega)$) to the function $\phi''(k, \omega)$. Section 4.1 reviews the earliest speculations concerning collective modes and the shape of the scattering function in classical liquids, while Section 4.2 discusses in considerable detail the MFA description of collective modes and Landau damping.

In Section 5 we make contact with another exact representation for $\chi(k, z)$, that of Kadanoff and Martin,[10] in which the basic unknown is the complex damping or memory function $D(k, z)$. We show that the real part of this damping function, $D'(k, \omega)$, splits very naturally into a Landau-type part and a collisional part, involving $\phi''(k, \omega)$. We also give in Section 5 an exact formula for the longitudinal viscosity in terms of $\phi''(k, \omega)$.

In Section 6 we discuss two simple models for the collisional damping by introducing ansatz expressions for $\phi''(k, \omega)$ [or, equivalently, $\phi(k, z)$]. These ansatz expressions involve a quantity $\tau(k)$ which can be interpreted as a viscous relaxation time. Rather than using theoretical values for this quantity (which we deem unreliable) we have chosen to determine $\tau(k)$ from the experimental data for $S(k, \omega = 0)$. The $\tau(k)$ thus obtained shows considerable structure; in particular, there are pronounced minima near those values of k where $S(k)$ has maxima (cf. Fig. 5). Having thus obtained $\tau(k)$, we have computed $S(k, \omega)$ and $\omega^2 S(k, \omega)$ from the exact formulas given in Section 3 for the region of k and ω values investigated in the neutron scattering experiments of Sköld *et al.*[8] The results are shown in Figures 6–11.

In Section 6 we also try to answer quantitatively the question of whether the collective modes for $k \geqslant 1$ Å^{-1} can be considered to be propagating or not by calculating the real and imaginary parts of the corresponding frequency. This calculation makes use of the formalism of Kadanoff and Martin[10] and a semiphenomenological description of damping introduced originally by Maxwell and Drude. The results for the complex collective mode frequency are given in Table II and plotted in Fig. 2.

Section 7 contains a summary and discussion of the results obtained in this work and some ideas concerning the extension of the present method to other response functions of interest. Finally, in the Appendices A–C we discuss and amplify in detail some relevant points touched upon in the text.

2. ANALYTIC PROPERTIES AND SUM RULES

It is well known[10] that $\chi(k, z)$ is analytic in the upper half of the complex z plane and is given in terms of the spectral function $\chi''(k, \omega)$ by

$$\chi(k, z) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega - z} \tag{3}$$

In fact, the above integral also serves to define $\chi(k, z)$ in the lower plane so that $\chi(k, z)$ is an analytic function everywhere off the real axis. $\chi''(k, \omega)$ is related to van Hove's[12] coherent scattering function $S(k, \omega)$, defined here as the Fourier transform of the space- and time-dependent density–density correlation function,

$$S(k, \omega) = (1/\rho) \int d\mathbf{r} \int_{-\infty}^{\infty} dt \{\exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') + i\omega(t - t')]\} \times [\langle \rho(\mathbf{r}, t)\, \rho(\mathbf{r}', t') \rangle - \rho^2] \tag{4}$$

by the equation[10]

$$S(k, \omega) = 2\chi''(k, \omega)\hbar/\rho(1 - e^{-\beta\hbar\omega}) \tag{5}$$

which in the classical limit reads

$$S(k, \omega) = (2/\rho\beta\omega)\, \chi''(k, \omega) \tag{6}$$

($\beta = 1/k_B T$, where T is the temperature and k_B is Boltzmann's constant).

Because of the relation (3) and because $\chi''(k, \omega)$ has simpler properties, it is the more convenient function to deal with for our purposes. The function $\chi''(k, \omega)$ is a real, odd function of ω with the property[10] $\omega\chi''(k, \omega) \geqslant 0$. From (3) we see that the static, wavenumber-dependent susceptibility $\chi(k)$ is given by

$$\chi(k) \equiv \chi(k, 0) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega} \tag{7}$$

which may be regarded as a sum rule on $\chi''(k, \omega)$ (the so-called "elastic" sum rule). In the limit $k \to 0$, $\chi(k)$ is given by $\rho^2 K_T$, or, equivalently, ρ/mC_T^2, where K_T and C_T are the isothermal compressibility and sound velocity, respectively; the sum rule (7) is then referred to as the compressibility sum rule.

In the classical limit, to which we shall restrict ourselves hereafter, it follows from (6) and (7) that $\chi(k)$ is related to the static structure factor $S(k)$ by

$$\chi(k) = \beta\rho \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(k, \omega) = \beta\rho S(k) = \frac{\beta\rho}{1 - \rho C(k)} \tag{8}$$

where the last equality defines $C(k)$, the Fourier transform of the direct correlation function. If the approximate expression (1) is to be consistent with (8), the effective potential $\psi(k)$ must be taken as

$$\psi(k) = -k_B T C(k) = [1 - S(k)]/\beta\rho S(k) \equiv \phi_0(k) \tag{9}$$

the notation being chosen for convenience later. [We have used the fact that $\chi_0(k, 0) = \beta\rho$.] This is the expression for $\psi(k)$ used in Ref. 1 and indicated in Table I. The application of Eq. (9) thus requires knowledge of the structure factor $S(k)$. Alternatively, if by some means an expression for $\psi(k)$ as a functional of $S(k)$ [or of the radial distribution function $g(r)$] has been obtained,[6] then Eq. (9) allows a self-consistent theoretical determination of $S(k)$ [or $g(r)$], as stressed in Ref. 4.

Very useful, exact relations are provided by the moment sum rules for $\chi''(k, \omega)$ or $S(k, \omega)$. Let us define the moments

$$M_n(k) = \int_{-\infty}^{\infty} (d\omega/\pi)\, \omega^n \chi''(k, \omega) = \rho\beta \int_{-\infty}^{\infty} (d\omega/2\pi)\, \omega^{n+1} S(k, \omega) \tag{10}$$

The moment sum rules which have so far been calculated are the following.

1. Placzek[13]:

$$M_1(k) = \rho k^2/m \tag{11}$$

Table I. Expressions for Some Effective Mean Field Potentials $\psi(k)^a$:

Ref.	$\psi(r)$	$\psi(k)$
Vlasov[5]	$v(r)$	$v(k)$
Nelkin and Ranganathan[1]	$-k_B TC(r)$	$-k_B TC(k) = (1/\rho\beta)\{[1/S(k)] - 1\}$
Singwi, Tosi, *et al.*[6]	$\nabla\psi(r) = g(r)\,\nabla v(r)$	$-(4\pi/k^3)\int_0^\infty dr\, g(r)v'(r)\,[\sin kr - kr\cos kr]$
Singwi *et al.*[2]	$\nabla\psi(r) = \frac{1}{6}g(r)\,\nabla[3v(r) - rv'(r)]$	$-(4\pi/3k^3)\int_0^\infty dr\, g(r)[v'(r) - \frac{1}{2}rv''(r)]$ $\times\,[\sin kr - kr\cos kr]$
Schneider *et al.*[7]	$\nabla\psi(r) = [g(r) + \frac{1}{2}\rho\,\partial g(r)/\partial\rho]\,\nabla v(r)$	$-(4\pi/k^3)\int_0^\infty dr[g(r) + \frac{1}{2}\rho\,\partial g(r)/\partial\rho]\,v'(r)$ $\times\,[\sin kr - kr\cos kr]$

[a] The quantity $\psi(r)$ denotes the effective potential in real space and $\psi(k)$ its Fourier transform; $v(r)$ is the interparticle potential, $g(r)$ is the radial distribution function, $C(r)$ is the direct correlation function, and $S(k)$ is the static structure factor.

2. de Gennes[14]:

$$M_3(k) = (\rho k^2/m)[3k^2 v_T^2 + (\rho/m) \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k} \cdot \mathbf{r})(\hat{\mathbf{k}} \cdot \nabla)^2 v(r)]$$
$$= (\rho k^2/m)\langle \omega_l^2(k) \rangle \tag{12}$$

where $v_T = (k_B T/m)^{1/2}$ is the mean thermal velocity. For brevity we shall denote the quantity $\langle \omega_l^2(k) \rangle^{1/2}$ by $\omega_l(k)$.

3. Forster *et al.*[15]:

$$M_5(k) = (\rho k^2/m) \langle \omega_l^4(k) \rangle \tag{13a}$$

where

$$\langle \omega_l^4(k) \rangle = 15(kv_T)^4 + v_T^2(\rho/m) \int d\mathbf{r}\, g(r)\{15(\mathbf{k} \cdot \nabla)^2 v(r)$$
$$+ 6k(\sin \mathbf{k} \cdot \mathbf{r})(\hat{\mathbf{k}} \cdot \nabla)^3 v(r) + 2\beta(1 - \cos \mathbf{k} \cdot \mathbf{r})[\nabla(\hat{\mathbf{k}} \cdot \nabla v(r))]^2\}$$
$$+ (\rho^2/m^2) \int d\mathbf{r}_2 \int d\mathbf{r}_3\, g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)(1 + \cos \mathbf{k} \cdot \mathbf{r}_{23} - 2 \cos \mathbf{k} \cdot \mathbf{r}_{12})$$
$$\times [\nabla_1(\hat{\mathbf{k}} \cdot \nabla_1 v(r_{12}))] \cdot [\nabla_1(\hat{\mathbf{k}} \cdot \nabla_1 v(r_{13}))] \tag{13b}$$
$$\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 ; \qquad \mathbf{r}_{13} = \mathbf{r}_1 - \mathbf{r}_3$$

In Eqs. (12), (13a), and (13b) the subscript l stands for longitudinal and the notation has been chosen to be in accord with that of Forster *et al.*,[15] who defined the quantities $\langle \omega_l^{2n}(k) \rangle$ by the equation

$$M_{2n+1}(k) = M_1(k)\langle \omega_l^{2n}(k) \rangle \tag{14}$$

Sometimes the moment rules (10–14) are expressed in terms of the quantities $\overline{\omega^n(k)}$ defined by[14]

$$\overline{\omega^n(k)} = \int_{-\infty}^{\infty} (d\omega/2\pi)\, \omega^n S(k, \omega) \Big/ \int_{-\infty}^{\infty} (d\omega/2\pi)\, S(k, \omega) \tag{15}$$

and which are related to those defined in (14) by

$$\overline{\omega^{2n}(k)} = [k^2 v_T^2/S(k)]\langle \omega_l^{2n-2}(k) \rangle \tag{16}$$

It should be pointed out that none of the expressions for $\psi(k)$ given in Table I is consistent with the third moment sum rule (12) or any higher moment sum rule. In fact, with the approximate expression (1) for the response function it is impossible to satisfy the elastic sum rule (8) and third moment sum rule (12) simultaneously. One can either satisfy the elastic sum rule together with the f-sum rule (11) by making the choice (9), or one can satisfy the f-sum rule and the third moment sum rule by choosing the effective potential $\psi(k)$ of the form

$$\psi(k) = \phi_\infty(k) = (1/k^2) \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k} \cdot \mathbf{r})(\hat{\mathbf{k}} \cdot \nabla)^2 v(r)$$
$$= (4\pi/k^2) \int_0^\infty dr\, rg(r)(v'(r)\{1 - [(\sin kr)/kr]\}$$
$$- [v'(r) - rv''(r)] f(kr)) \tag{17}$$

where

$$f(kr) = \frac{1}{3} - \frac{\sin kr}{kr} + \frac{2(\sin kr - kr \cos kr)}{(kr)^3}$$

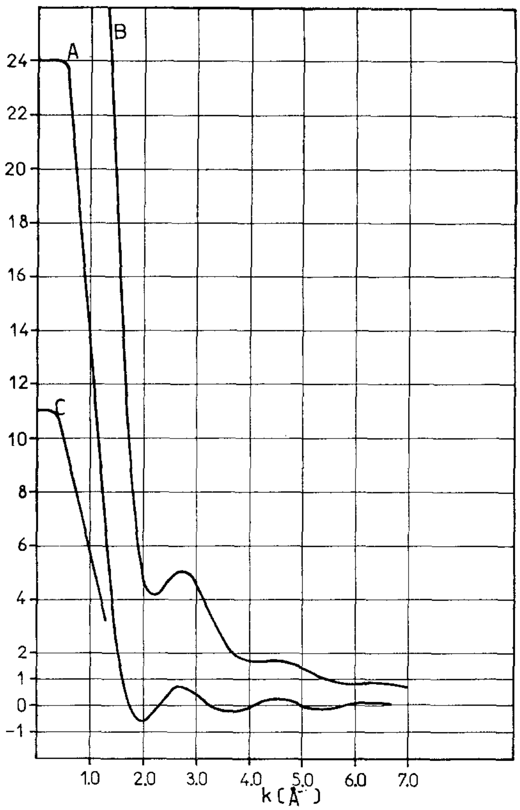

Fig. 1. Plot of the effective potentials $\rho\beta\phi_0(k)$ (curve A) and $\rho\beta\phi_\infty(k)$ (curve B). Curve C represents $\rho\beta\phi_\infty(k)$ divided by ten. The curves have been obtained from Rahman's[11] calculations for liquid argon.

and the notation $\phi_\infty(k)$ has been introduced for later purposes. If one tried to satisfy simultaneously (8) and (12) [in addition to (11)] by equating the expressions (9) and (17), the resulting integral equations for $g(r)$ would result in a value for $g(r)$ which is negative divergent at the origin. The fact that the potentials $\phi_0(k)$ and $\phi_\infty(k)$ differ greatly can be seen in Fig. 1, where we plot the effective potentials (9) and (17) for liquid argon ($T = 76°$K and mass density $\rho m = 1.407$ g/cm^3) as obtained from Rahman's molecular dynamics calculations.[11]

Plots for some of the other effective potentials given in Table I can be found in Ref. 2.

The statements leading to (17) can easily be verified by making use of the asymptotic expansions for $\chi(k, z)$ and $\chi^{-1}(k, z)$ for large z. From (3) and (10) one finds for large z

$$\chi(k, z) \sim -\frac{M_1}{z^2}\left(1 + \frac{M_3/M_1}{z^2} + \frac{M_5/M_1}{z^4} + \cdots\right) \tag{18}$$

$$\chi^{-1}(k, z) \sim -\frac{1}{M_1}\left[z^2 - \frac{M_3}{M_1} + \frac{(M_3/M_1)^2 - (M_5/M_1)}{z^2} + \cdots\right] \tag{19}$$

The large-z expansions of $\chi_0(k, z)$ and $\chi_0^{-1}(k, z)$ are obtained from (18) and (19) by replacing the moments $M_n(k)$ by the corresponding noninteracting values $M_n^{(0)}(k)$ [given by Eqs. (11)–(13) with $v(r) = 0$].

3. AN EXACT REPRESENTATION FOR $\chi(k, z)$ AND $\chi''(k, \omega)$

Instead of the approximate expression (1), we shall consider an exact representation for $\chi(k, z)$ of the form

$$\chi(k, z) = \chi_0(k, z)/[1 + \phi(k, z)\chi_0(k, z)] \tag{20}$$

or, equivalently,

$$\chi^{-1}(k, z) = \chi_0^{-1}(k, z) + \phi(k, z) \tag{21}$$

This equation has the form of the Dyson equation well known in the theory of Green's functions.[16,17] The function $\phi(k, z)$ may be considered an effective frequency- and wavenumber-dependent interaction, for the moment (21) may simply be regarded as the definition of $\phi(k, z)$. In Appendix A we discuss an equivalent space–time form for the representation (20) in terms of an exact ansatz for the equation of motion of the one-particle distribution function.

Basically, there exist three ways of determining $\phi(k, z)$: (a) the equation of motion method, (b) the method of diagrams, and (c) the use of sum rule arguments. The simplest example for (a) is the linearized kinetic equation[5] (or Vlasov equation) which leads to the frequency-independent form $\psi(k)$ (see the discussion in Appendix A). General methods of the types (a) and (b) have been explored and developed to a considerable extent recently by Forster and Martin[18] and Mazenko[19], using the quantum mechanical method of Green's functions. In this section we use the simpler and more pedestrian sum rule arguments to describe the basic properties which the effective interaction $\phi(k, z)$ must satisfy.

As will be shown explicitly below, the function $\phi(k, z)$ is linked to the scattering function $S(k, \omega)$ so that it may be possible to gain considerable information about the dynamic, frequency- and wavenumber-dependent interaction from light scattering and coherent neutron scattering experiments [cf. Eq. (40)]. Since (20) is an exact representation for the density response function, it follows that $\phi(k, z)$ must contain, in principle, all the information about hydrodynamic modes involving density fluctuations and associated transport coefficients. This is further discussed in Section 5. Another feature worth pointing out here is that the representation (20) ensures that the scattering function will have the correct free-particle behavior in the limit of large k, or when the interaction is switched off. This is not automatically the case with some other representations, as discussed in Sections 5 and 6.

From the fact that $\chi^{-1}(k, z)$ and $\chi_0^{-1}(k, z)$ are analytic functions of z off the real axis,[10] it follows that the same must be true of $\phi(k, z)$. From (19) and (21) it follows that for large z, $\phi(k, z)$ has the expansion

$$\phi(k, z) = \phi_\infty(k) - [\Phi_1(k)/z^2] + O(1/z^4) \tag{22}$$

where

$$\phi_\infty(k) \equiv \phi(k, \infty) = [1/M_1^2(k)][M_3(k) - M_3^{(0)}(k)] \tag{23}$$

is given explicitly by the expression (17), and

$$\begin{aligned}\Phi_1(k) &= \frac{1}{M_1(k)}\left\{\frac{M_3^2(k) - [M_3^{(0)}(k)]^2}{M_1^2(k)} - \frac{M_5(k) - M_5^{(0)}(k)}{M_1(k)}\right\} \\ &= -\frac{m}{\rho k^2}[\langle\omega_l^4(k)\rangle - \langle\omega_l^2(k)\rangle^2 - 6(kv_T)^4]\end{aligned} \tag{24}$$

On the other hand, for $z = 0$ we must have from (21) and (8)

$$\begin{aligned}\phi_0(k) \equiv \phi(k, 0) &= \chi^{-1}(k, 0) - \chi_0^{-1}(k, 0) \\ &= (1/\rho\beta)\{[1/S(k)] - 1\}\end{aligned} \tag{25}$$

which is the expression given by (9). The functions $\rho\beta\phi_0(k)$ and $\rho\beta\phi_\infty(k)$ have been plotted in Fig. 1.

Because $\phi(k, z) - \phi_\infty(k)$ is analytic off the real axis and vanishes for large z as $1/z^2$, we may write a spectral representation

$$\phi(k, z) - \phi_\infty(k) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\phi''(k, \omega)}{\omega - z} \tag{26}$$

where $\phi''(k, \omega)$ is a real, odd function of ω given by

$$\phi''(k, \omega) = (1/2i)[\phi(k, \omega + i\epsilon) - \phi(k, \omega - i\epsilon)] \tag{27}$$

From (26) follows immediately the sum rule

$$\phi_0(k) - \phi_\infty(k) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\phi''(k, \omega)}{\omega} \tag{28}$$

In Appendix B it is shown that for all values of k

$$\phi_0(k) - \phi_\infty(k) \leqslant 0 \tag{29}$$

By comparing (22) with the large-z expansion of (26) we obtain the first moment sum rule for $\phi''(k, \omega)$:

$$\Phi_1(k) = \int_{-\infty}^{\infty} (d\omega/\pi)\, \omega\phi''(k, \omega) \tag{30}$$

Higher-order moment sum rules for $\phi''(k, \omega)$ can, of course, be obtained in terms of the moments of $\chi''(k, \omega)$. The real part of the effective interaction, to be denoted by $\phi'(k, \omega)$, is related to the imaginary part, $\phi''(k, \omega)$, by a Kramers–Kronig relation:

$$\phi'(k, \omega) - \phi_\infty(k) = P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\phi''(k, \omega')}{\omega' - \omega} \tag{31}$$

where P denotes the principal value integral.

From (20) the spectral function $\chi''(k, \omega)$ is found to be given by

$$\chi''(k, \omega) = \frac{\chi_0'' - \phi''[(\chi_0')^2 + (\chi_0'')^2]}{[1 + \phi'\chi_0' - \phi''\chi_0'']^2 + [\phi''\chi_0' + \phi'\chi_0'']^2} \tag{32}$$

and the real part, $\chi'(k, \omega)$, of the complex response function $\chi(k, \omega + i\epsilon)$ is

$$\begin{aligned}\chi'(k, \omega) &= P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(k, \omega')}{\omega' - \omega} \\ &= \frac{\chi_0' + \phi'[(\chi_0')^2 + (\chi_0'')^2]}{[1 + \phi'\chi_0' - \phi''\chi_0'']^2 + [\phi''\chi_0' + \phi'\chi_0'']^2}\end{aligned} \tag{33}$$

In (32) and (33), all the arguments of the functions on the right are k, ω. The functions $\chi_0''(k, \omega)$ and $\chi_0'(k, \omega)$ are the corresponding free-particle functions given by

$$\begin{aligned} \chi_0''(k, \omega) &= \rho\beta(\pi/2)^{1/2}(\omega/kv_T)\exp(-\omega^2/2k^2v_T^2) \\ \chi_0'(k, \omega) &= \rho\beta[1 - 2xF(x)] \end{aligned} \tag{34}$$

$$x = \omega/\sqrt{2}kv_T = (\omega/k)(\tfrac{1}{2}m\beta)^{1/2}, \qquad F(x) = \exp(-x^2)\int_0^x dt \exp(t^2)$$

The function $F(x)$ is known as Dawson's integral and has been tabulated in the literature.[20] The free-particle density response function $\chi_0(k, z)$ in compact notation is given by

$$\chi_0(k, z) = \rho\beta[1 + \sqrt{\pi}(z/k)(\tfrac{1}{2}m\beta)^{1/2}\, W((z/k)(\tfrac{1}{2}m\beta)^{1/2})] \tag{35a}$$

where

$$W(z) = \int_{-\infty}^{\infty} \frac{dt}{\pi} \frac{\exp(-t^2)}{t - z} = \frac{z}{\pi}\int_{-\infty}^{\infty} dt \frac{\exp(-t^2)}{t^2 - z^2} \tag{35b}$$

is analytic in z off the real axis. A derivation of the above expressions for the free-particle response function can be found in Appendix A.

We will shortly make use of the asymptotic expansion for $\chi_0'(k, \omega)$ for large values of the ratio x. In this limit one has

$$\begin{aligned} \chi_0'(k, \omega) &\sim -\frac{\rho\beta}{2x^2}\left[1 + \frac{3}{2x^2} + \frac{15}{4x^4} + \cdots\right]; \qquad x \gg 1 \\ &= -\frac{\rho k^2}{m\omega^2}\left[1 + 3\frac{k^2v_T^2}{\omega^2} + 15\left(\frac{k^2v_T^2}{\omega^2}\right)^2 + \cdots\right]; \qquad \omega \gg kv_T \end{aligned} \tag{36}$$

Since $\phi'(k, \omega)$ is given in terms of $\phi''(k, \omega)$ by (31), the calculation of the spectral function $\chi''(k, \omega)$ is reduced to the problem of determining the wavenumber- and frequency-dependent function $\phi''(k, \omega)$. Being an exact representation for the spectral function, Eq. (32) must provide (at least in principle) the correct description of phenomena in the entire region of frequencies and wave numbers. In particular, for small values of its arguments k and ω, the function $\phi''(k, \omega)$ must contain a description of the hydrodynamic modes involving density oscillations.

The exact expression for the scattering function $S(k, \omega)$ is obtained from Eqs. (6) and (32). Because of what has been said above, the basic unknown function entering $S(k, \omega)$ is $\phi''(k, \omega)$ [assuming that $\phi_\infty(k)$ or $\phi_0(k)$ has been determined from a knowledge of $g(r)$ and $v(r)$]. In Section 6 we shall use these facts in a calculation of $S(k, \omega)$ using appropriate ansatz functions for $\phi''(k, \omega)$. Let us note here the exact expression for the function $S(k, \omega = 0)$, which is essentially the intensity of radiation scattered elastically by the system. From Eqs. (6), (32), and (25) one finds

$$S(k, \omega = 0) = S^2(k)\left[\frac{(2\pi)^{1/2}}{kv_T} - 2\rho\beta \lim_{\omega\to 0}\frac{\phi''(k, \omega)}{\omega}\right] \tag{37}$$

This equation will prove very useful in the discussion of Section 6. Various approximate expressions for $S(k, \omega = 0)$ are summarized in Ref. 9.

At this point let us discuss a possibly more direct method for the experimentalist to determine the dynamic interaction function $\phi''(k, \omega)$ from the measured $S(k, \omega)$. What this method amounts to is a prescription for separating out all the effects due to the interaction of the particles from those due to free-particle motion in the measured coherent neutron scattering or light scattering frequency spectrum.

From Eq. (21) we have

$$\phi(k, \omega + i\epsilon) = \chi^{-1}(k, \omega + i\epsilon) - \chi_0^{-1}(k, \omega + i\epsilon) \tag{38}$$

from which we obtain, by equating the imaginary parts of both sides,

$$\phi''(k, \omega) = -\chi''[(\chi')^2 + (\chi'')^2]^{-1} + \chi_0''[(\chi_0')^2 + (\chi_0'')^2]^{-1} \tag{39}$$

the arguments of all functions on the right being k, ω. The second term on the right, the free-particle term, can easily be calculated for all k, ω using (34). Since $\chi''(k, \omega) = \rho\beta\omega S(k, \omega)/2$ and since $\chi'(k, \omega)$ is given in terms of $\chi''(k, \omega)$ by (33), the function $\phi''(k, \omega)$ is in principle completely determined by the experimental $S(k, \omega)$. The only difficulty may lie in the evaluation of the principal value integral (33) since the latter requires knowledge of $S(k, \omega)$ over a large frequency range. Although we have not done so in this report, one could now attempt to calculate $\phi''(k, \omega)$ in the region $1 \leqslant k \leqslant 4.4$ Å^{-1} for liquid argon from the experimental values of $S(k, \omega)$ obtained by Sköld *et al.*[8] and compare this with the ansatz expressions for $\phi''(k, \omega)$ considered in Section 6.

In a sense, the discussion of the last two paragraphs amounts to a frequency dependent generalization of a procedure long used in the case of the static structure factor $S(k)$. Namely, experimental (or theoretical) knowledge of $S(k)$ allows one, via Eq. (9), to determine the direct correlation function $C(k)$; the latter is a measure of the correlation between two particles brought about by their mutual interaction as well as due to the interaction with other particles. Indeed, knowledge of $S(k)$ or $C(k)$ has been used to determine the interatomic potential $v(r)$.[21]

Equations (32) and (39) allow us to establish bounds on $\phi''(k, \omega)$.

Namely, the fact that $\omega\chi''(k, \omega) \geqslant 0$ and the above equations imply that for all k and ω

$$\frac{\omega\chi_0''}{(\chi_0')^2 + (\chi_0'')^2} \geqslant \omega\phi'' \geqslant -\frac{\omega}{\chi''} + \frac{\omega\chi_0''}{(\chi_0')^2 + (\chi_0'')^2} \tag{40}$$

4. COLLECTIVE MODES, NEGLECTING COLLISIONAL DAMPING

Even though we shall find that the effects of collisions as described by the function $\phi''(k, \omega)$ cannot be neglected in a classical liquid, it seems worthwhile to discuss and review some simple cases in which collisional effects are neglected. Comparison with experimental results will thus serve to emphasize the complete inadequacy of simple theories such as the mean field approximation (1) to account properly for observed density fluctuations in classical liquids.

4.1. Dispersion Relations, Neglecting All Damping

If one supposes the existence of collective modes for the density fluctuations in a simple liquid and neglects all damping, one can directly obtain estimates for the dispersion relations from the sum rules (8)–(12). Thus, the assumption that $\chi''(k, \omega)$ has sharp peaks located at $\pm\omega_0(k)$ and the requirement that the elastic sum rule (8) and first moment sum rule (11) be obeyed lead to

$$\chi''(k, \omega)/\omega = \tfrac{1}{2}\pi\rho\beta S(k)[\delta(\omega - \omega_0(k)) + \delta(\omega + \omega_0(k))] \tag{41}$$

where[14,22]

$$\omega_0^2(k) = k^2 k_B T/mS(k) = k^2 v_T^2/S(k) \tag{42}$$

The curve $\omega_0(k)$ versus k is shown in Fig. 2, as obtained from the values for $S(k)$ computed by Rahman.[11] The dispersion relation (42) can also be obtained starting from the equation of motion for the density fluctuation operator $\rho(\mathbf{k}, t) = \sum_i \exp[-i\mathbf{k} \cdot \mathbf{r}_i(t)]$ by applying a simple decoupling approximation.[23] In the limit $k \to 0$, Equation (42) predicts a linear relation between $\omega_0(k)$ and k characterized by the isothermal sound velocity C_T:

$$\lim_{k\to 0} \omega_0(k) = C_T k \tag{43}$$

Equations (41)–(43) are not in accord with experiment. In the region of k values ($k \geqslant 1.0$ Å^{-1}) covered by inelastic neutron scattering experiments it is uncertain if side peaks in $S(k, \omega)$ will be observed at all. In fact, the

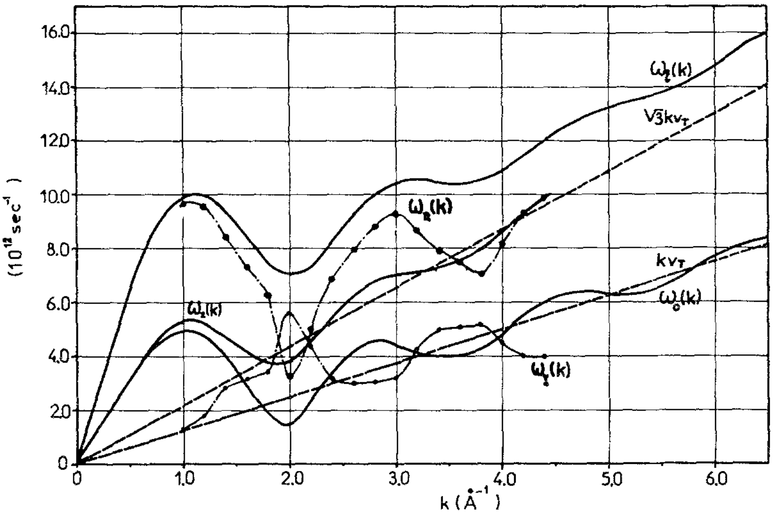

Fig. 2. Dispersion curves for density fluctuations in liquid argon. The curves $\omega_0(k)$, $\omega_2(k)$, and $\omega_l(k)$ (solid lines) are defined by Eqs. (42), (57), and (12), respectively. The curves $\omega_R(k)$ (heavy dots) and $\omega_I(k)$ (open circles) denote the real and imaginary parts of the complex collective mode frequency given in Table II.

recent experimental results of Sköld *et al.*[8] on liquid argon at 85.2°K in the range $1\ \text{Å}^{-1} \leqslant k \leqslant 4.4\ \text{Å}^{-1}$ do not reveal any structure in $S(k, \omega)$ in the wings. On the other hand, in the small k region ($k \to 0$) covered by optical (light scattering) experiments, the scattering function consists of three lines: one central line ($\omega = 0$) and two side lines at $\omega = \pm C_s k$ (the Brillouin doublet) characteristic of hydrodynamic sound modes propagating with the adiabatic sound velocity C_s (instead of C_T). Using these facts, de Gennes[14] has used the sum rules (8) and (11) to deduce the ratio I_1/I_0 of the itensities in the Brillouin doublet to the intensity in the central line, obtaining the well-known result of Landau and Placzek,

$$I_1/(I_0 + I_1) = C_T^2/C_s^2 = C_v/C_p \tag{44}$$

where C_v and C_p are the specific heats at constant volume and constant pressure, respectively.

Note that if instead of the elastic sum rule (8) one requires the third moment sum rule (12) to be satisfied along with (11), the assumption of sharp peaks leads to a spectral function given by

$$\chi''(k, \omega)/\omega = [\pi\rho k^2/2m\omega_l^2(k)][\delta(\omega - \omega_l(k)) + \delta(\omega + \omega_l(k))] \tag{45}$$

where $\omega_l(k)$ is defined by (12). The above form corresponds no better than

(41) to the observed scattering function. The dispersion relation $\omega_l(k)$ is originally due to Zwanzig,[24] whose derivation is based on an analogy with the phononlike excitations in solids and an approximate trial form for the eigenfunctions of the Liouville operator. The curve $\omega_l(k)$ has also been plotted in Fig. 2. In the limit $k \to 0$, $\omega_l(k)$ also leads to a linear dispersion,

$$\lim_{k \to 0} \omega_l(k) = C_l^{(\infty)} k \tag{46}$$

where

$$[C_l^{(\infty)}]^2 = 3v_T^2 + (2\pi\rho/5m) \int_0^\infty dr\, r^3 g(r)[rv''(r) + \tfrac{4}{3}v'(r)] \tag{47}$$

On the other hand, for large k, $\omega_l(k)$ is given by

$$\omega_l^2(k) = 3k^2 v_T^2 + \Omega_0^2 \tag{48}$$

where

$$\Omega_0^2 = (\rho/3m) \int d\mathbf{r}\, g(r)\, \nabla^2 v(r) \tag{49}$$

represents a sort of average square oscillation frequency for an atom oscillating in the field of all other atoms. In a harmonic solid this would correspond to the square of the Einstein frequency. Let us observe that both $\omega_0(k)$ and $\omega_l(k)$ show a strong dip at the value k_0 where $S(k)$ has it first maximum. The mode that corresponds to k_0 has recently been associated with those density fluctuations that may be considered as precursors to freezing.[7]

Next let us examine the predictions of the mean field approximation characterized by the expression (1).

4.2. Collective Modes in Mean Field Approximation; Landau Damping

First, let us compare the exact representation for $\chi''(k, \omega)$ given by (32) with the approximate expression resulting from the mean-field-type response function (1):

$$\chi''_{\mathrm{MF}}(k, \omega) = \chi_0''(k, \omega)/\{[1 + \psi(k)\, \chi_0'(k, \omega)]^2 + [\psi(k)\, \chi_0''(k, \omega)]^2\} \tag{50}$$

This expression is obtained from the exact expression (32) by putting $\phi''(k, \omega) = 0$ and taking for $\phi'(k, \omega)$ an effective potential $\psi(k)$, independent of ω. The scattering function $S(k, \omega)$ corresponding to (50) is given by

$$S_{\mathrm{MF}}(k, \omega) = \frac{(2\pi)^{1/2}}{kv_T} \frac{\exp(-x^2)}{\{1 + \rho\beta\psi(k)[1 - 2xF(x)]\}^2 + [\rho\beta\psi(k)\sqrt{\pi}x \exp(-x^2)]^2} \tag{51}$$

where x and $F(x)$ are defined in (34). With $\psi(k)$ given by (9) and with an

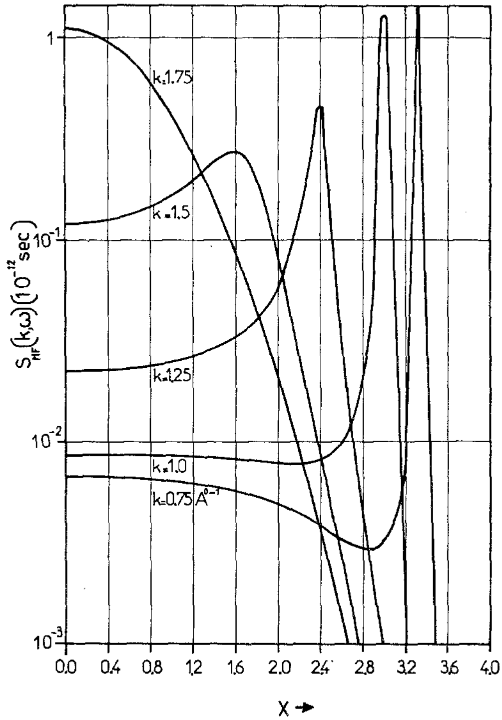

Fig. 3. Plot of the scattering function in mean field approximation as a function of the dimensionless variable $x = \omega/(\sqrt{2}kv_T)$ for various values of k, with the effective potential $\phi_0(k)$.

approximate analytic expression for $C(k)$, the expression (51) has been plotted in Ref. 1 both against wave number k (for various values of $\beta\hbar\omega$) and against frequency ω (for various values of k). In Fig. 3 we have plotted $S_{MF}(k, \omega)$ using the values for $S(k)$ obtained by Rahman.[11] For small k the characteristic feature is the existence of pronounced and very narrow side peaks and a broad, low-lying central plateau. The sharp peaks broaden with increasing k and disappear gradually. This behavior is characteristic of the mean field approximation and is in no way particular to the choice (9) for the effective potential $\psi(k)$. If one had chose the expression (17) for the effective potential in (51), the resulting plots would be similar to those in Fig. 3 except that for the same value of k the peaks in the latter case would be narrower and shifted more to the right with respect to those in Fig. 3. A comparison between the behavior of (51) resulting from the use of the effective potentials (9) and (17), respectively, for the same value of k is shown in Fig. 4.

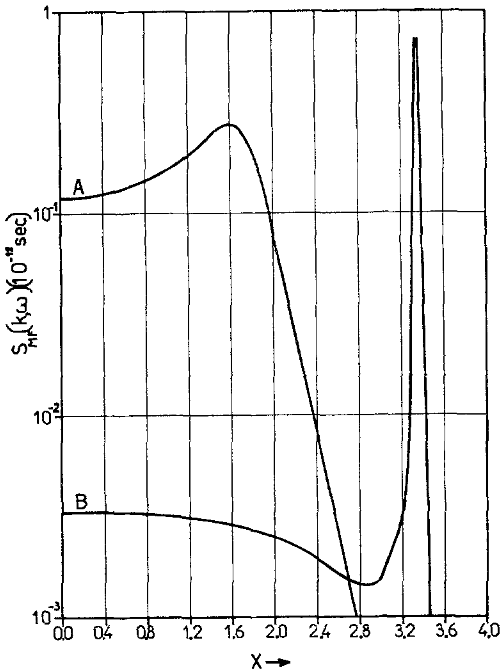

Fig. 4. Comparison of scattering functions in mean field approximation [Eq. (51)] for the potentials $\phi_0(k)$ (curve A) and $\phi_\infty(k)$ (curve B) for the same k value, 1.5 Å^{-1}.

It is of some interest to analyze the expression (50) in greater detail and to show how it predicts explicitly the dispersion relation and damping of collective modes in the mean field approximation. To see this, it is only necessary to substitute the asymptotic expansion (36) for the function $\chi_0'(k, \omega)$. For $\omega \gg kv_T$ one then has

$$\chi''_{\mathrm{MF}}(k, \omega) \simeq \frac{\omega^4\chi''_0(k, \omega)}{\{\omega^2 - (\rho k^2/m)\,\psi(k)[1 + (3k^2v_T{}^2/\omega^2)]\}^2 + [\psi(k)\,\omega^2\chi''_0(k, \omega)]^2} \tag{52}$$

From this expression we see that the spectral function may have peaks at the frequencies $\omega_R(k)$ given by the solutions of the equation

$$\omega^4 - \omega^2(\rho k^2/m)\psi(k) - 3(\rho k^4 v_T{}^2/m)\psi(k) = 0 \tag{53}$$

The physical solution gives

$$\begin{aligned}\omega_R{}^2(k) &= (\rho k^2/2m)\,\psi(k)\{1 + [1 + 12mk^2v_T{}^2/\rho k^2\psi(k)]^{1/2}\}\\ &\simeq (\rho k^2/m)\,\psi(k) + 3k^2v_T{}^2\end{aligned} \tag{54}$$

This solution will apply only for values such that $kv_T \ll \omega_R(k)$, i.e., for $k^2v_T^2 \ll \rho k^2\psi(k)/m$.

As an aside, let us note that in the special case of a plasma, where the interactions are Coulomb interactions described by the potential

$$\psi(k) = 4\pi e^2/k^2 \tag{55}$$

(e being the electronic charge), Eq. (54) predicts the well-known dispersion relation for plasma oscillations in the self-consistent field approximation[5]:

$$\omega_R^2(k) \simeq \omega_p^2 + 3k^2v_T^2 = \omega_p^2[1 + 3(k^2/k_D^2)] \tag{56}$$

where $\omega_p^2 = 4\pi\rho e^2/m$ is the square of the plasma frequency and k_D is the Debye screening wave number.[25]

In the case of classical liquids, however, Eq. (54) predicts a dispersion which varies linearly with k for small k. Depending on the form we choose for the effective potential $\psi(k)$ (cf. Table I), Eq. (54) will predict different values for $\omega_R(k)$. If we use the expression (9) (consistent with the elastic sum rule) in (54), we obtain

$$\omega_R^2(k) = [k^2v_T^2/S(k)] + 2k^2v_T^2 \equiv \omega_2^2(k) \tag{57}$$

Except for the small term $2k^2v_T^2$, this is the same dispersion relation as Eq. (42) obtained from the delta function ansatz. The dispersion curve predicted by (57) lies above the curve $\omega_0(k)$ and below the curve $\omega_l(k)$ as shown in Fig. 2 [this follows from the inequality (29) discussed in Appendix B]. Because of the restrictions imposed on the derivation of (54), the relation (57) will be valid only as long as $S(k) \ll 1$, which for liquid argon is the case only for values of $k < 1.5$ Å^{-1}, as confirmed in Fig. 3. In the limit $k \to 0$, Eq. (57) yields

$$\omega_R(k) = C_Tk[1 + (2v_T^2/C_T^2)]^{1/2} \tag{58}$$

Since the ratio v_T/C_T in liquids is in general much less than unity, Eq. (58) predicts the existence of collective modes propagating with a velocity which is only slightly larger than the isothermal sound velocity C_T. However, as already pointed out, in actual fact the long-wavelength modes are sound modes propagating with the adiabatic sound velocity C_s which is considerably larger than C_T. If we use for $\psi(k)$ the expression (17) [to be consistent with the third moment sum rule (12)], the dispersion relation (54) yields

$$\omega_R^2(k) = \omega_l^2(k) \tag{59}$$

which is the same expression as found by use of the delta function ansatz

(45). However, the present derivation restricts the validity of (59) to k values such that $kv_T \ll \omega_l(k)$.

The mean field approximation embodied by the expressions (50)–(54) also offers a simple description of the damping of the collective modes. For this purpose it is useful to rewrite (52) for ω near $\omega_R(k)$ in the form

$$\chi''_{\mathrm{MF}}(k, \omega) \simeq \frac{-\omega^2}{\psi(k)} \operatorname{Im}[\omega^2 - \omega_R{}^2(k) + i\psi(k)\,\omega^2\chi''_0(k, \omega)]^{-1}$$
$$= \frac{-\omega^2}{\psi(k)} \operatorname{Im}\left[\omega^2 - \omega_R{}^2(k) + i\psi(k)\left(\frac{\pi}{2}\right)^{1/2} \rho\beta\frac{\omega^3}{kv_T}\exp\left(-\frac{\omega^2}{2k^2v_T{}^2}\right)\right]^{-1} \tag{60}$$

In the neighborhood of the collective mode frequency $\omega_R(k)$, this may be further approximated by

$$\chi''_{\mathrm{MF}} \simeq -\frac{\rho k^2}{m}$$
$$\times \operatorname{Im}\left\{\omega^2 - \omega_R{}^2(k) + i\omega_R{}^2(k)\left(\frac{\pi}{2}\right)^{1/2}\left[\frac{\omega_R(k)}{kv_T}\right]^3 \exp\left[-\frac{\omega_R{}^2(k)}{2k^2v_T{}^2}\right]\right\}^{-1} \tag{61}$$

where we assumed $kv_T \ll \omega_R(k)$. To obtain more explicit expressions, one may substitute the various expressions for $\omega_R(k)$ corresponding to the different $\psi(k)$ discussed above. Since the exponential involved in the above expression is in general small, the mean field theory leads us to the existence of well-defined collective modes with small damping for which

$$\omega(k) \simeq \omega_R(k)\left\{1 - i\left(\frac{\pi}{8}\right)^{1/2}\left[\frac{\omega_R(k)}{kv_T}\right]^3 \exp\left[-\frac{\omega_R{}^2(k)}{2k^2v_T{}^2}\right]\right\} \tag{62}$$

The small damping of these collective modes is called Landau damping because it is analogous to the damping of plasma oscillations as described originally by Landau.[5] For this latter case one has [cf. Eq. (56)]

$$\omega(k) \simeq \omega_p\left[1 + \frac{3k^2}{k_{\mathrm{D}}{}^2} - i\left(\frac{\pi}{8}\right)^{1/2}\left(\frac{k_{\mathrm{D}}}{k}\right)^3 \exp\left(-\frac{k_{\mathrm{D}}{}^2}{2k^2}\right)\right] \tag{63}$$

Whereas the damping of the plamsa oscillations in mean field theory is exponentially small for $k \to 0$, that of the collective modes in classical liquids is proportional to k,[23] as is seen by using either Eq. (58) or Eq. (46) in the expression for the complex frequency (62). Thus, using (58) and neglecting terms of order $v_T{}^2/C_T{}^2$ compared to unity, we obtain

$$\omega(k) \simeq C_Tk\left[1 - i\left(\frac{\pi}{8}\right)^{1/2}\left(\frac{C_T}{v_T}\right)^3 \exp\left(-\frac{1}{2}\frac{C_T{}^2}{v_T{}^2}\right)\right] \tag{64}$$

Notice that the size of this damping depends crucially on the ratio C_T/v_T ; the larger this ratio, the smaller the damping. The reason for this result is as follows: As is well known, the Landau damping is due to a transfer of energy from the collective mode wave to those particles moving with the phase velocity of the wave, $\omega_R(k)/k \simeq C_T$. Because these particles are moving with the wave, they interact strongly with it and absorb energy from it. Now, the larger the ratio C_T/v_T, the less particles there will be in the tail of the Maxwellian velocity distribution with velocity C_T which can absorb energy from the wave, and therefore the smaller the damping of the wave.

The above description of collective modes in the mean field approximation is similar to the description of collisionless or zero sound modes in liquid ^{3}He, as described, for example, by the Landau theory of Fermi liquids.[26] A basic difference between the zero sound modes in liquid ^{3}He and collective motions in classical liquids is that while collisional damping can indeed be neglected in a Fermi liquid for $T \to 0$, this is by no means the case in classical liquids. As will be seen in Section 6, the sharp side peaks in $S_{\mathrm{MF}}(k, \omega)$ disappear as soon as one takes account of collisional damping through inclusion of a reasonable form for $\phi''(k, \omega)$ in the general formula (32).

In Appendix C we rederive some of the expressions for the Landau damped collective modes starting from another, very general formalism described in the next section.

5. ANOTHER EXACT REPRESENTATION FOR $\chi(k, z)$

We have already remarked that the function $\phi''(k, \omega)$ contains information about the dynamic effects of the particle interaction. In particular, as we shall see, $\phi''(k, \omega)$ describes the damping of collective modes brought about by collisions and, in the limit of small k and ω, must in principle provide us with information about the hydrodynamic behavior of the system. It is therefore useful to compare the representation (20) with another exact representation for $\chi(k, z)$ which has been of considerable use in analyzing the hydrodynamic expression for the spectral function[10] and in extending the latter [27] to larger values of k, ω. The representation of which we are speaking is

$$\chi(k, z) = \frac{-\rho k^2/m}{z^2 - [\rho k^2/m\chi(k)] + izk^2 D(k, z)} \tag{65}$$

or, equivalently,

$$\chi^{-1}(k, z) = \chi^{-1}(k) - (m/\rho k^2)[z^2 + izk^2 D(k, z)] \tag{66}$$

where $D(k, z)$, the complex longitudinal damping function, is analytic off the real axis and is given in terms of the real, wavenumber- and frequency-dependent damping function[2] $D'(k, \omega)$ (an even function of ω and positive for all k and ω) by

$$D(k, z) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi i} \frac{D'(k, \omega)}{\omega - z} \tag{67}$$

For the analysis presented in the next section it will be instructive to recast Eq. (65) in a general form for the equation of motion for the average density fluctuation $\langle \rho(\mathbf{k}, t) \rangle$ in the presence of an external potential $u(\mathbf{k}, t)$. From the definition of the linear response function we have [cf. Eq. (2)]

$$\langle \rho(\mathbf{k}, t) \rangle = - \int_{-\infty}^{\infty} dt' \, \tilde{\chi}(k, t - t') \, u(\mathbf{k}, t') \tag{68}$$

where

$$\begin{aligned} \tilde{\chi}(k, t - t') &= \int_{-\infty}^{\infty} (d\omega/2\pi) \, \chi(k, \omega + i\epsilon) \exp[-i\omega(t - t')] \\ &= \int_{-\infty}^{\infty} (d\omega/2\pi)[\chi'(k, \omega) + i\chi''(k, \omega)] \exp[-i\omega(t - t')] \end{aligned} \tag{69}$$

It is easily verified that (65) is equivalent to the following general equation of motion for $\langle \rho(\mathbf{k}, t) \rangle$:

$$\begin{aligned} &\langle \ddot{\rho}(\mathbf{k}, t) \rangle + \omega_0^2(k) \langle \rho(\mathbf{k}, t) \rangle + k^2 \int_{-\infty}^{\infty} dt' \, \tilde{D}(k, t - t') \langle \dot{\rho}(\mathbf{k}, t') \rangle \\ &\quad = -(\rho k^2/m) \, u(\mathbf{k}, t) \end{aligned} \tag{70}$$

where the dots denote time derivatives and $\omega_0^2(k) = \rho k^2 / m\chi(k) = k^2 v_T^2 / S(k)$. Equation (70) is the general equation of motion for an oscillator with "natural" frequency $\omega_0(k)$ subjected to a time- or, equivalently, frequency-dependent frictional force. The above equation is, in fact, equivalent to the generalized hydrodynamic equation for the longitudinal current fluctuation (when combined with the continuity equation for the conservation of particles derived recently from a heuristic physical argument by Ailawadi *et al.*[28] The time-dependent damping function is given by

$$\begin{aligned} \tilde{D}(k, t - t') &= \int_{-\infty}^{\infty} (d\omega/2\pi) \, D(k, \omega + i\epsilon) \exp[-i\omega(t - t')] \\ &= \int_{-\infty}^{\infty} (d\omega/2\pi)[D'(k, \omega) + iD''(k, \omega)] \exp[-i\omega(t - t')] \end{aligned} \tag{71}$$

and, since $D(k, \omega + i\epsilon)$ is analytic in the upper half ω plane, it follows that $\tilde{D}(k, t - t')$, just as $\tilde{\chi}(k, t - t')$, vanishes for $t < t'$.

[2] Reference 25, Chapters A–C.

We should emphasize that Eq. (70), being equivalent to (65), is an exact equation of motion for the average density fluctuation $\langle\rho(\mathbf{k}, t)\rangle$, requiring for its justification only the analyticity of $\chi(k, z)$ and $\chi^{-1}(k, z)$. The above equations were, of course, purposely designed[10] to provide a rigorous framework within which to examine some phenomenological descriptions such as that offered by hydrodynamics. However, the forms of Eqs. (65) and (70) make them suitable for describing density fluctuations, or collective motions even for values of k where hydrodynamics no longer applies.[27] In this connection it is appropriate to recall that the normal mode frequencies $\omega(k)$ (in general, complex) are obtained as the poles of the analytic continuation of $\chi(k, z)$ in the lower half of the complex z plane. Since we have defined $\chi(k, z)$ and $D(k, z)$ by Eqs. (3) and (67) to be analytic functions of z off the real axis, the above statement means, more precisely, that we must start with $\chi(k, z)$ and $D(k, z)$ defined for z in the upper half of the complex plane, analytically continue into the lower plane (to be denoted by the subscript a), and look for the solutions of the equation

$$z^2 - \omega_0^2(k) + izk^2D_a(k, z) = 0 \tag{72}$$

This equation is just a generalization of the simple, damped harmonic oscillator equation for the complex normal mode frequency [cf. Eq. (70)]. [In Appendix C we discuss a simplification of Eq. (72) for the case where the imaginary part of the frequency is very small.]

In the next section we shall apply the above discussion to the description of collective modes and their damping. First it is necessary to examine some properties of the real damping function $D'(k, \omega)$ and to show its relation to the function $\phi''(k, \omega)$.

By comparing the expansions for large z of both sides of Eq. (66) and making use of (19), one finds immediately the following sum rules for $D'(k, \omega)$[27]:

$$\int_{-\infty}^{\infty} (d\omega/\pi)\, D'(k, \omega) = (1/k^2)[\omega_l^2(k) - \omega_0^2(k)] \tag{73}$$

$$\int_{-\infty}^{\infty} (d\omega/\pi)\, \omega^2 D'(k, \omega) = (1/k^2)[\langle\omega_l^4(k)\rangle - \langle\omega_l^2(k)\rangle^2] \tag{74}$$

The exact expression for the spectral function $\chi''(k, \omega)$ which follows from (65) is

$$\chi''(k, \omega) = \frac{(\rho k^2/m)\, \omega k^2 D'(k, \omega)}{\{\omega^2 - [\rho k^2/m\chi(k)] - \omega k^2 D''(k, \omega)\}^2 + [\omega k^2 D'(k, \omega)]^2} \tag{75}$$

where

$$D''(k, \omega) = -P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{D'(k, \omega')}{\omega' - \omega} \tag{76}$$

Thus, the basic unknown function in this representation is $D'(k, \omega)$. The exact expression for the scattering function $S(k, \omega)$ in this representation is given by Eqs. (6) and (75). Let us note in particular the simple expression for $S(k, \omega = 0)$:

$$S(k, \omega = 0) = S^2(k)(2/v_T^2)[\lim_{\omega \to 0} D'(k, \omega)] \tag{77}$$

[compare Eq. (37)]. We shall make use of Eqs. (75) and (77) in Section 6. We obtain the relation between Martin's damping function $D'(k, \omega)$ and the collisional damping function $\phi''(k, \omega)$ by equating the right sides of (21) and (66) and taking the imaginary parts for $z \to \omega + i\epsilon$. This yields

$$D'(k, \omega) = D_0'(k, \omega) - (\rho/m\omega)\phi''(k, \omega) \tag{78}$$

where

$$D_0'(k, \omega) \equiv \frac{\rho}{m\omega} \frac{\chi_0''(k, \omega)}{[\chi_0'(k, \omega)]^2 + [\chi_0''(k, \omega)]^2} \tag{79}$$

These equations can be interpreted as follows: The total damping function $D'(k, \omega)$ consists of two parts, a part proportional to $\phi''(k, \omega)$ which represents the collisional damping arising entirely from the dynamic interaction between the particles, and a part $D_0'(k, \omega)$ which represents the Landau-type damping discussed previously; this latter type of damping is the only one which entered in the MFA. Using Eqs. (78), (79), and (34), it is easily verified that the expressions (77) and (37) are consistent with each other.

By comparing the sum rule expressions for $D'(k, \omega)$ with those for $\phi''(k, \omega)$ [Eqs. (28) and (30)], it is found that $D_0'(k, \omega)$ obeys the sum rules

$$\int_{-\infty}^{\infty} (d\omega/\pi)\, D_0'(k, \omega) = 2k_B T/m = 2v_T^2 \tag{80}$$

$$\int_{-\infty}^{\infty} (d\omega/\pi)\, \omega^2 D_0'(k, \omega) = 6k^2 v_T^4 \tag{81}$$

For the sake of completeness, we also state the relation obtained by equating the real parts of Eqs. (21) and (66) for $z = \omega + i\epsilon$:

$$\begin{aligned} \frac{m\omega}{\rho} D''(k, \omega) &= \phi'(k, \omega) - \chi^{-1}(k) + \frac{m\omega^2}{\rho k^2} + \frac{\chi_0'(k, \omega)}{[\chi_0'(k, \omega)]^2 + [\chi_0''(k, \omega)]^2} \\ &= \phi'(k, \omega) - \phi_0(k) + \frac{m\omega}{\rho} D_0''(k, \omega) \end{aligned} \tag{82}$$

These equations define the function $D_0''(k, \omega)$. It is easily verified that Eqs. (82) and (76) are indeed consistent with each other, as must be the case on account of the analyticity arguments employed. In Appendix C we show how the Landau-damped collective modes discussed in Section 4.2 are derived starting from (75) and the above expressions for $D_0'(k, \omega)$ and $D_0''(k, \omega)$.

It is interesting to compare the relative strength of collisional damping and Landau-type damping in the limits of small k and large k, respectively. Using (73) and the limiting values of $\omega_l^2(k)/k^2$ and $v_T^2S(k)^{-1}$ appropriate to liquid argon at $T = 76°$K and $\rho m = 1.407$g/cm^3 as calculated by Rahman,[11] one finds for the total weight of the damping function in the limit $k \to 0$

$$\begin{aligned}\lim_{k\to 0} \int_{-\infty}^{\infty} (d\omega/\pi)\, D'(k, \omega) &= \lim_{k\to 0} [\omega_l^2(k)/k^2] - C_T^2 \\ &= (180 - 39) \times 10^8 \quad \text{cm}^2/\text{sec}^2 = 141 \times 10^8 \quad \text{cm}^2/\text{sec}^2 \qquad (83)\end{aligned}$$

On the other hand, the weight of $D_0'(k, \omega)$ for argon at this temperature is

$$\int_{-\infty}^{\infty} (d\omega/\pi)\, D_0'(k, \omega) = 2v_T^2 = 3.2 \times 10^8 \quad \text{cm}^2/\text{sec}^2 \qquad (84)$$

independent of k. This shows the overwhelming dominance of the collisional damping in the limit of small k (hydrodynamic limit) as compared to Landau-type damping. On the other hand, in the opposite limit of large k, we find from (73) and (48)

$$\begin{aligned}\int_{-\infty}^{\infty} (d\omega/\pi)\, D'(k, \omega) &= (1/k^2)[3k^2v_T^2 + \Omega_0^2 - k^2v_T^2] \\ &= \int_{-\infty}^{\infty} (d\omega/\pi)\, D_0'(k, \omega) + (\Omega_0^2/k^2) \qquad (85)\end{aligned}$$

i.e., the damping for large values of k will be due almost entirely to Landau-type damping. The above analysis based on the sum rules (73) and (80) suggests therefore a quick and easy way for assessing the relative importance of collisional damping at any value of k.

The overwhelming dominance of the collisional type of damping in the small-k limit is even more apparent when we compare the second frequency moments of $D'(k, \omega)$ and $D_0'(k, \omega)$. Whereas the right side of (74) approaches a finite value in the limit $k \to 0$, that of (81) tends to zero.

To conclude this section, let us note how the longitudinal viscosity can be derived from a knowledge of the function $\phi''(k, \omega)$. As is well known, the longitudinal viscosity is given by the equivalent expressions (Ref. 25, Chapters A-C)

$$(1/\rho m)(\tfrac{4}{3}\eta + \zeta) = \lim_{\omega\to 0} [\lim_{k\to 0} (m\omega^3/\rho k^4)\, \chi''(k, \omega)]$$

$$= \lim_{\omega\to 0} [\lim_{k\to 0} D'(k, \omega)] \tag{86}$$

where ζ and η are bulk and shear viscosities, respectively. From Eqs. (78) and (34) we then find that

$$\tfrac{4}{3}\eta + \zeta = -\rho^2 \lim_{\omega\to 0} \{\lim_{k\to 0} [\phi''(k, \omega)/\omega]\} \tag{87}$$

Here we shall not pursue the calculation of these transport coefficients and associated hydrodynamic behavior any further. This will be considered in a subsequent paper.

6. COLLECTIVE MODES AND COLLISIONAL DAMPING

As we have already pointed out, all the dynamic effects of the particle interaction are contained in the function $\phi''(k, \omega)$, whose determination would be the task of detailed microscopic calculations. Much can be learned, however, by making assumptions about the behavior of $\phi''(k, \omega)$ and testing these assumptions by comparing the results obtained with experimental data. The simple models we shall discuss amount to considering only the viscous-type damping of collective modes, neglecting the damping due to thermal diffusion. It has been shown that for the region of k values investigated by neutron scattering experiments[8] ($k \geqslant 1$ Å^{-1}) the error due to omission of temperature fluctuations is small.[28] The latter fluctuations are important mainly in the hydrodynamic limit $k \to 0$.

The simple forms we consider are (*i*) a Lorentzian-type ansatz

$$\phi''(k, \omega) = [\phi_0(k) - \phi_\infty(k)]\omega\tau_1(k)/[1 + \omega^2\tau_1^2(k)] \tag{88}$$

for which

$$\phi(k, z) - \phi_\infty(k) = [\phi_0(k) - \phi_\infty(k)]/[1 \mp iz\tau_1(k)] \tag{89}$$

$$\phi'(k, \omega) - \phi_\infty(k) = [\phi_0(k) - \phi_\infty(k)]/[1 + \omega^2\tau_1^2(k)] \tag{90}$$

and (ii) a Gaussian-type ansatz

$$\phi''(k, \omega) = [\phi_0(k) - \phi_\infty(k)]\omega\tau_2(k) \exp[-\omega^2\tau_2^2(k)/\pi] \tag{91}$$

with corresponding

$$\phi(k, z) - \phi_\infty(k) = [\phi_0(k) - \phi_\infty(k)][1 + z\tau_2(k)W(z\tau_2(k)/\sqrt{\pi})] \quad (92)$$

$$\phi'(k, \omega) - \phi_\infty(k) = [\phi_0(k) - \phi_\infty(k)][1 - 2uF(u)] \quad (93)$$

where F and W are defined in Eqs. (34)–(35) and the variable $u = \omega\tau_2(k)/\sqrt{\pi}$.

Both the above forms (88) and (91) satisfy the basic sum rule (28). Note that because of the inequality $\phi_0 \leqslant \phi_\infty(k)$ proved in Appendix B, the right sides of (88), (90), and (91) are nonpositive quantities.

It should be pointed out that the form (88) does not have a finite first frequency moment as required by the sum rule (30). Moreover, the complex potential (89) [where the upper (lower) sign corresponds to z in the upper (lower) half complex plane, respectively] is not consistent with the form of the asymptotic expansion (22). Nevertheless, (88) and (90) lead to a very good description of the observed coherent scattering function $S(k, \omega)$.

The expression for $S(k, \omega)$ is obtained by substituting (88) and (90), or (91) and (93), into Eqs. (32) and (6). The resulting expressions satisfy the zeroth, second, and fourth frequency moment sum rules, regardless of how the relaxation times $\tau_1(k)$ or $\tau_2(k)$ are determined. Although there have been some theoretical attempts[29,30] at calculating the relaxation time for longitudinal density and current density fluctuations, we feel that none can be considered to be entirely satisfactory. In particular, in view of the results obtained below no simple interpolation expressions[27] for $\tau_1(k)$ or $\tau_2(k)$ will be adequate.

In the case of the Lorentzian form (88) we cannot employ any sum rule arguments to determine $\tau_1(k)$ in terms of microscopic quantities so that recourse will be made to experimental data (see below). On the other hand, for the Gaussian form (91) we can determine $\tau_2(k)$ by requiring that the first moment sum rule (30) for $\phi''(k, \omega)$ also be satisfied. When this is done we obtain $\tau_2(k)$ as

$$\tau_2^2(k) = \frac{\pi}{2}\frac{\phi_0(k) - \phi_\infty(k)}{\Phi_1(k)} = \frac{\frac{1}{2}\pi[\langle\omega_l^2(k)\rangle - \omega_2^2(k)]}{\langle\omega_l^4(k)\rangle - \langle\omega_l^2(k)\rangle^2 - 6(kv_T)^4} \quad (94)$$

With this choice for $\tau_2(k)$, the $S(k, \omega)$ determined by (91), (93), and (94) satisfies all moment sum rules up to and including the sixth.

Unfortunately, at present the calculation of $\tau_2(k)$ on the basis of (94) is very difficult on account of the unknown three-particle distribution function entering into $\langle\omega_l^4(k)\rangle$ [cf. Eq. (13b)]. Thus far only the limiting value for $k \to 0$ of $\langle\omega_l^4(k)\rangle/k^2$ has been obtained[15] using the superposition approximation for g_3. Knowledge of $\langle\omega_l^4(k)\rangle$ would be of general interest and provides for theoretical estimates of the longitudinal viscosity[31] [cf. Eqs. (86) and (87)].

In the absence of reliable theoretical values for $\tau_1(k)$, $\tau_2(k)$, or $\langle\omega_l^4(k)\rangle$ we have chosen to determine these quantities from experimental data. The most convenient and direct way for accomplishing this is to make use of the experimental results for the scattering function at zero energy transfer. The latter is given in general by the exact expression (37), which for the approximations (88) and (91) yields

$$S(k, \omega = 0) = S^2(k)\{[(2\pi)^{1/2}/kv_T] + 2\rho\beta[\phi_\infty(k) - \phi_0(k)]\tau(k)\} \tag{95}$$

where we have put $\tau_1(k) = \tau_2(k) = \tau(k)$. We have used the values for $S(k)$ and $\phi_\infty(k)$ obtained from Rahman's molecular dynamics calculations[11] on liquid argon at $T = 76°\text{K}$ and $\rho m = 1.407 \text{g/cm}^3$ (cf. Fig. 1) and the experimental values for $S(k, \omega = 0)$ for liquid argon 36 at $T = 85.2°\text{K}$ obtained by Sköld *et al.*[8] The resulting values for $\tau(k)$ are given in Table II and plotted in Fig. 5. Notice the structure in $\tau(k)$, in particular the strong dips for k values near those where the static structure factor $S(k)$ has maxima. At these k values the collisional damping is thus rather slowly varying over the frequency range of interest.

Table II. Values for $\tau(k)$, $\tau_D(k)$, and $\langle\omega_l^4(k)\rangle$ As Determined from Eqs. (95), (103), and (94), Respectively, Using the Experimental Values for $S(k, \omega = 0)$ Obtained by Sköld *et al.*[8] [a]

k, Å^{-1}	$\tau(k)$, 10^{-13} sec	$\tau_D(k)$, 10^{-13} sec	$\langle\omega_l^4(k)\rangle$, 10^{50} sec^{-4}	$\omega_R(k)$, 10^{12} sec^{-1}	$\omega_I(k)$, 10^{12} sec^{-1}
1.0	2.66	2.76	113	9.70	−1.33
1.2	1.96	2.09	129	9.58	−1.84
1.4	1.18	1.39	151	8.43	−2.87
1.6	1.05	1.32	127	7.29	−3.22
1.8	0.978	1.33	102	6.33	−3.47
2.0	0.243	0.839	962	3.33	−5.65
2.2	0.428	0.999	325	4.97	−4.38
2.4	0.842	1.24	136	6.88	−3.21
2.6	0.922	1.24	163	7.96	−3.06
2.8	0.970	1.23	198	8.82	−3.11
3.0	1.01	1.22	223	9.34	−3.25
3.2	0.633	0.953	380	8.74	−4.26
3.4	0.408	0.819	684	7.94	−5.00
3.6	0.302	0.783	1030	7.52	−5.14
3.8	0.166	0.730	2850	7.07	−5.22
4.0	0.296	0.803	971	8.20	−4.58
4.2	0.487	0.878	507	9.32	−4.04
4.4	0.480	0.850	582	9.90	−4.02

[a] $\omega_R(k)$ and $\omega_I(k)$ denote the real and imaginary parts of the complex normal mode frequency as determined from Eq. (104).

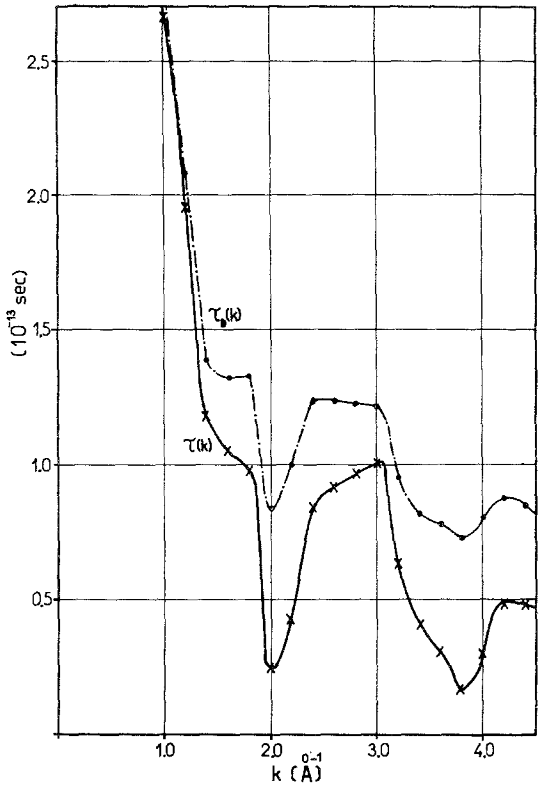

Fig. 5. Wavenumber dependence of the longitudinal, viscous relaxation times $\tau(k)$ and $\tau_D(k)$, as obtained from Eqs. (95) and (103). Smooth curves have been drawn through the discrete points (cf. Table II).

With the values $\tau_1(k) = \tau_2(k) = \tau(k)$ given in Table II one can now calculate the coherent scattering function $S(k, \omega)$ for all ω by substituting the Lorentzian forms (88) and (90) or the Gaussian forms (91) and (93) into the basic formulas (32) and (6). The results are shown by the solid lines (for the Lorentzian) and dashed lines (for the Gaussian) in Figs. 6–9 for various values for k. The experimental points of Sköld *et al.*[8] are also shown in these figures. Notice that for $k = 1.0$ and 1.2 Å^{-1} the calculated $S(k, \omega)$ shows remnants of a side peak, which we know must exist in the hydrodynamic limit. On the other hand, the experimental $S(k, \omega)$ for these k values does not give a clear indication for such remnants of a side peak although a trace of some structure seems to be borne out. In connection with Fig. 9 it should be noted that since this is a logarithmic plot, the discrepancy between experimental and calculated $S(k, \omega)$ for large ω (where the scattered intensity

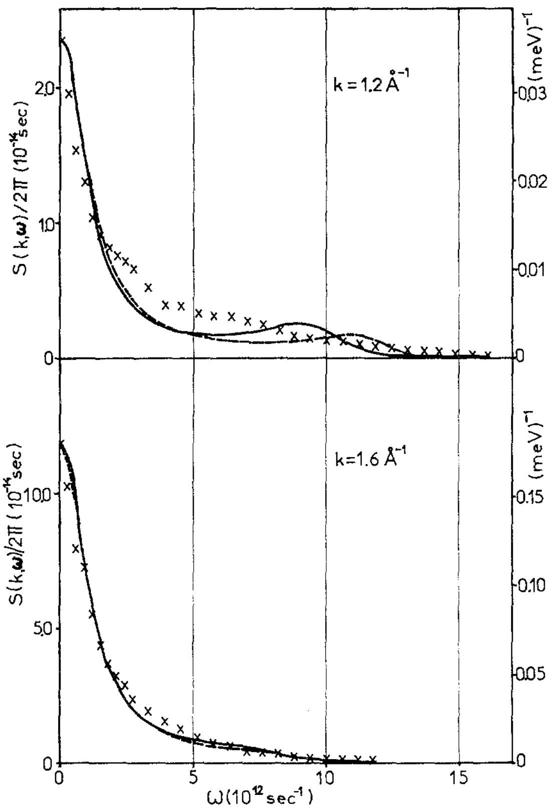

Fig. 6. Plot of the coherent scattering function $S(k, \omega)/2\pi$ as a function of ω for the k values indicated. The crosses denote the experimental results of Sköld *et al.*[8] for liquid argon 36 at $T = 85.2$ °K. The solid and dashed lines represent the results of the theory as described in Sections 3 and 6.

is small) is magnified. For the smallest wave numbers the Lorentzian-type ansatz gives somewhat better agreement with the experimental data then the Gaussian-type ansatz. However, for large ω the Gaussian would yield a better result for $S(k, \omega)$ since all frequency moments of the latter remain finite, in contrast to the $S(k, \omega)$ calculated with the Lorentzian form.

Having calculated $S(k, \omega)$, one can also obtain $\omega^2 S(k, \omega)$, which is proportional to the spectral function for the longitudinal current fluctuations. This function divided by $2k^2 v_T^2$ is plotted in Figs. 10 and 11, which also show the results based on the measured $S(k, \omega)$. The above function shows a maximum in its dependence on ω at a certain nonzero value of the frequency for all systems, including an ideal gas; for this last system the maximum of

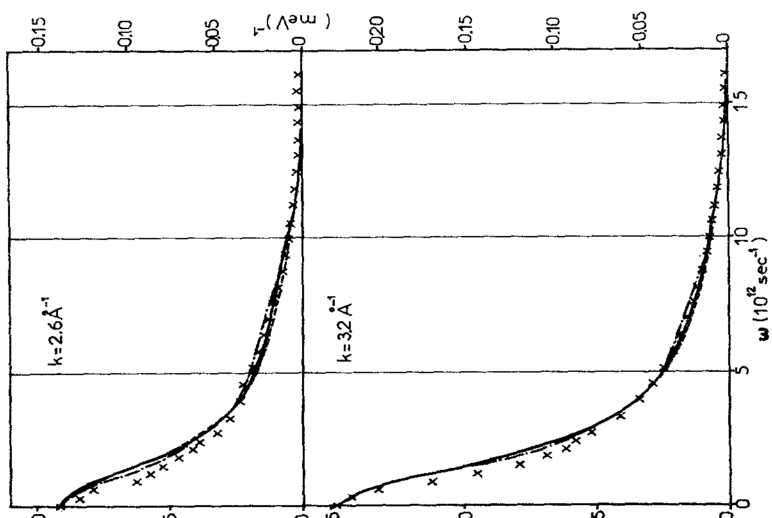

Fig. 7. See caption to Fig. 6. The dash-dotted lines represent the results of the theory described in Eqs. (98)–(103).

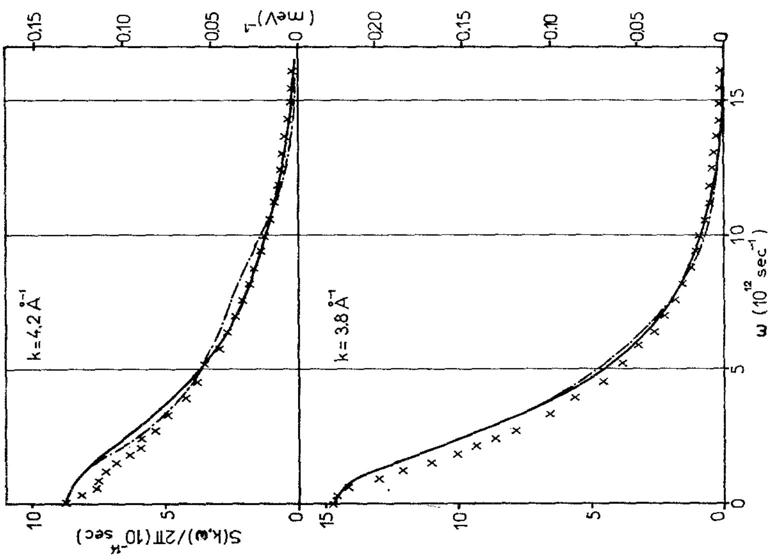

Fig. 8. See captions to Figs. 6 and 7.

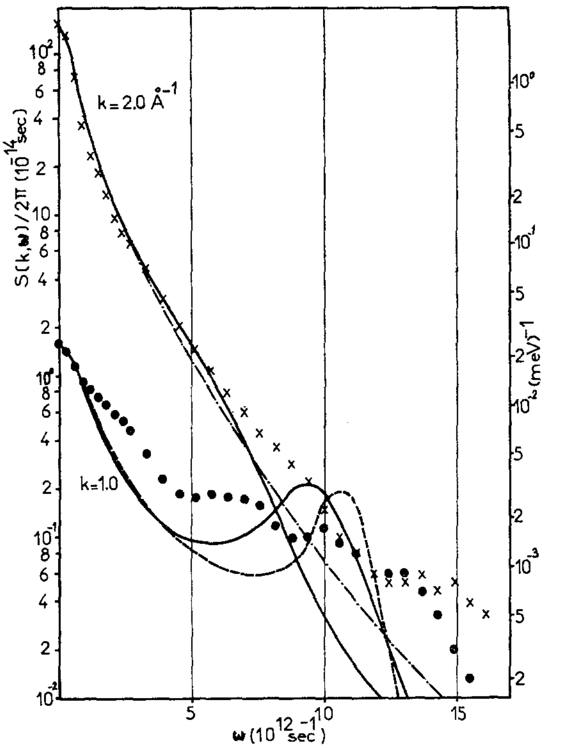

Fig. 9. Plot on a logarithmic scale of the coherent scattering function $S(k, \omega)/2\pi$ as a function of ω for $k = 1.0$ and 2.0 Å^{-1}. The solid circles and crosses denote the experimental results of Sköld *et al.*[8] The solid, dashed, and dash-dotted lines represent the results of the theory outlined in Section 6.

$\omega^2 S(k, \omega)$ occurs at $\sqrt{2} k v_T$. The values obtained from the above theory along with those obtained from the experimental $S(k, \omega)$ and by Rahman's[11] molecular dynamics calculations are shown in Fig. 12. We notice that for large ω the experimental values for $\omega^2 S(k, \omega)/(2k^2 v_T^2)$ lie consistently above the theoretical values in Figs. 10 and 11 and do not seem to approach zero rapidly enough, as required for consistency with the sum rules.

Using the values of $\tau_2(k) = \tau(k)$ obtained from (95), we have used Eq. (94) to calculate the quantity $\langle \omega_l^4(k) \rangle$. The results are given in Table II. Note that for $k = 1.0$ Å^{-1} we obtain from Table II

$$\langle \omega_l^4(k) \rangle / k^2 = 1.12 \times 10^{36} \quad \text{cm}^2/\text{sec}^4 \tag{96}$$

which is close to the value computed by Forster *et al.*[15] in the limit $k \to 0$

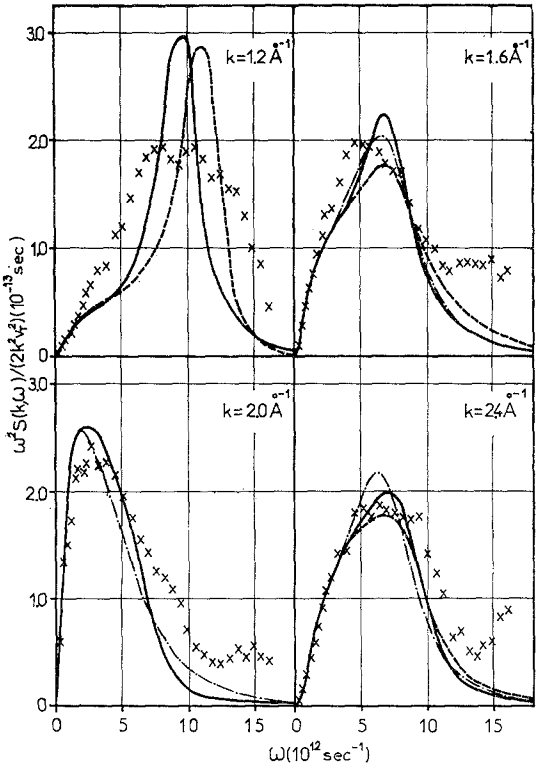

Fig. 10. Plot of the longitudinal current spectral function $\omega^2 S(k, \omega)/2k^2 v_T^2$ as a function of ω. The crosses denote the experimental results of Sköld *et al.*[8] The solid, dashed, and dash-dotted lines represent the results of the theory described in Section 6. The area under each curve is $\pi/2$.

using the superposition approximation for argon at $T = 79°\mathrm{K}$ and $\rho m = 1.415\ \mathrm{g/cm^3}$:

$$\lim_{k\to 0} [\langle \omega_l^4(k) \rangle / k^2] = 0.995 \times 10^{36} \quad \mathrm{cm^2/sec^4} \tag{97}$$

It is surprising to note that the function $\langle \omega_l^4(k) \rangle$ thus obtained has sharp maxima at or near those wave numbers where $S(k)$ has maxima, in contrast to $\omega_l^2(k)$, which has minima there.

To answer in a quantitative manner the question of whether the collective modes in liquid argon for $k \geqslant 1\ \text{Å}^{-1}$ are propagating or nonpropagating, it is more convenient to use the Kadanoff–Martin[10] representation discussed in Section 5. The basic equation we use is Eq. (72) for the complex normal

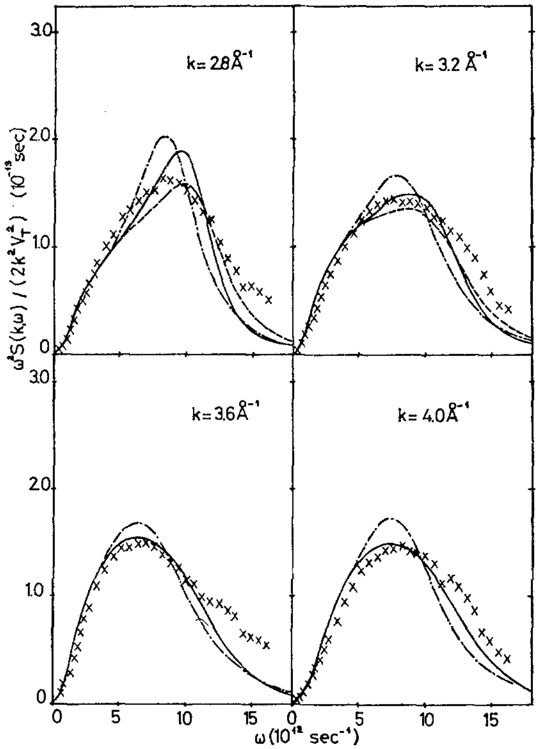

Fig. 11. See caption to Fig. 10.

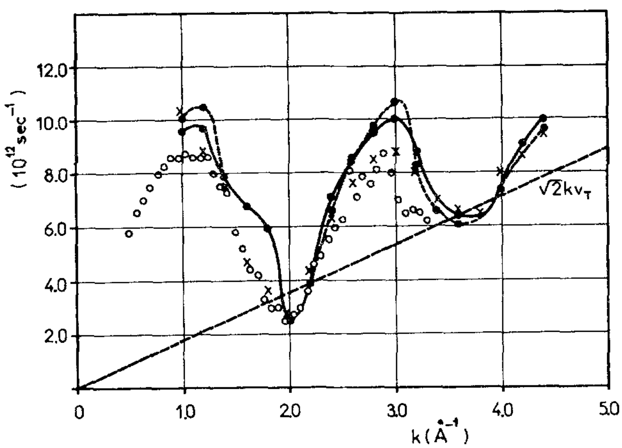

Fig. 12. Dispersion curves for longitudinal current fluctuations in liquid argon. The open circles denote the values obtained by Rahman.[11] The crosses denote the values obtained by Sköld *et al.*[8] The solid and dashed lines represent the results of the theory described in Section 6. The dashed straight line gives the result for an ideal gas at $T = 76\,^{\circ}\mathrm{K}$ and mass of argon 40.

mode frequency in the presence of a complex, frequency- and wavenumber-dependent damping function.

A particularly convenient phenomenological description of damping is that of Maxwell and Drude, where one assumes that[32]

$$D(k, z) = b(k)/[1 - iz\tau_D(k)], \qquad Im\, z > 0 \tag{98}$$

where $b(k)$ and $\tau_D(k)$ are functions to be determined. The above model for the viscous-type damping of collective modes has already been discussed by Chung and Yip,[27] though in a different manner from the discussion which follows.

From (98) we obtain for the real functions $D'(k, \omega)$ and $D''(k, \omega)$

$$D'(k, \omega) = b(k)/[1 + \omega^2\tau_D^2(k)] \tag{99}$$

$$D''(k, \omega) = b(k)\omega\tau_D(k)/[1 + \omega^2\tau_D^2(k)] \tag{100}$$

Notice that both the collisional and Landau-type damping effects [cf. Eqs. (78)–(82)] are here lumped together into the single expression (99). The latter will consequently not lead to the correct free-particle limit of the spectral function (75) for large values of k.

By requiring that the sum rule (73) be satisfied by the function (99), we obtain the relation

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} D'(k, \omega) = \frac{b(k)}{\tau_D(k)} = \frac{1}{k^2}[\omega_l^2(k) - \omega_0^2(k)] \tag{101}$$

which yields the function $b(k)$ in terms of ω_l^2, ω_0^2, and $\tau_D(k)$. For the last quantity Chung and Yip[27] have used a simple interpolation expression, which, however, turns out to be inadequate. We therefore proceed as in the above discussion for $\phi''(k, \omega)$ and determine $\tau_D(k)$ from the experimental values for $S(k, \omega = 0)$. We make use of the exact expression (77), which for the approximation (99) becomes

$$\begin{aligned} S(k, \omega = 0) &= S^2(k)[2\tau_D(k)/k^2v_T^2][\omega_l^2(k) - \omega_0^2(k)] \\ &= S^2(k)\, 2\tau_D(k)\{2 + \rho\beta[\phi_\infty(k) - \phi_0(k)]\} \end{aligned} \tag{102}$$

Comparing with the expression (95) which was used to determine $\tau(k)$, we find the following relation between $\tau_D(k)$ and $\tau(k)$:

$$\tau_D(k) = \frac{[(\frac{1}{2}\pi)^{1/2}/kv_T] + \rho\beta[\phi_\infty(k) - \phi_0(k)]\,\tau(k)}{2 + \rho\beta[\phi_\infty(k) - \phi_0(k)]} \tag{103}$$

The values for $\tau_D(k)$ thus obtained are also shown in Table II and plotted in Fig. 5.

With the functions $D'(k, \omega)$ and $D''(k, \omega)$ [Eqs. (99) and (100)] thus determined one can again calculate the scattering function $S(k, \omega)$ using the formulas (6) and (75). The resulting $S(k, \omega)$ satisfies the zeroth, second, and fourth frequency moment sum rules. The results are shown in Figs. 7–11 by the dash-dotted line. It turns out that for the smallest k values ($1 \leqslant k \leqslant 1.6$ Å^{-1}) the result for $S(k, \omega)$ is practically indistinguishable from the case considered at the beginning of this section [cf. Eqs. (88)–(90)) and indicated by the solid lines in Figs. 6–11. However, for the largest k values ($3.8 \leqslant k \leqslant 4.4$ Å^{-1}) the $S(k, \omega)$ resulting from (99) does not agree as well with the experimental data as does the approximation embodied by Eqs. (88)–(90). This, of course, is to be expected, since for large k the forms (99) and (100) cannot be correct.

Using the form for the complex damping function given by (98) and (101), the equation (72) for the complex collective mode frequencies becomes

$$z^2 - \omega_0^2(k) + iz\frac{[\omega_l^2(k) - \omega_0^2(k)]\,\tau_D(k)}{1 - iz\tau_D(k)} = 0 \tag{104}$$

This equation can be solved exactly. There are three roots, one of which turns out to be purely imaginary. Here we are only interested in the solution $\omega(k) = \pm\omega_R(k) + i\omega_I(k)$, possessing both a real and an imaginary part and characterizing a damped mode. The results for $\omega_R(k)$ and $\omega_I(k)$ are given in Table II and plotted in Fig. 2.

As a more precise criterion characterizing a propagating mode, we may take the following condition to be satisfied between the real and imaginary parts of the frequency:

$$\omega_R(k) > 2\pi\omega_I(k) \tag{105}$$

When this condition is satisfied the collective mode will propagate for at least several wavelengths before decaying away. From Table II we see that only the mode with the smallest k value, 1.0 Å^{-1}, starts to fulfill this condition. It is precisely for this k value that we find the remnant side peak in the calculated $S(k, \omega)$ as seen in Fig. 9. The "maximum" in the remnant side peak of the calculated $S(k, \omega)$ corresponding to the above k value occurs at $\omega \simeq 9.4 \times 10^{12}$ sec^{-1}, which is close to the corresponding value of $\omega_R(k)$ in Table II.

From Table II let us note in particular the large imaginary parts of the frequencies at or near the wave numbers where $S(k)$ has maxima. The corresponding modes resemble more a diffusion or relaxation-type process. It has been suggested[7] that these are the modes that lead to the dynamic instability connected with freezing and giving rise to critical fluctuations. Although the basic physical ideas expressed in Ref. 7 may be correct, the analysis presented there, however, is based on the mean field approximation (1), which we have shown to be inapplicable to the description of classical liquids.

7. DISCUSSION

In this paper we have presented a new approach to the calculation of the scattering function for classical liquids which is based on an exact representation for the density–density response function. The chief feature has been the introduction of an effective, frequency- and wavenumber-dependent interaction possessing both a real and an imaginary part. The latter has been associated with the collisional damping, which in classical liquids is quite large. With simple forms for the collisional damping function this theory permits one to satisfy all frequency moment sum rules for $S(k, \omega)$ up to and including the sixth. In principle, there is no difficulty in extending the present approach to yield an $S(k, \omega)$ satisfying still higher-order moment sum rules, although in practice the lack of knowledge concerning these moments seems to make this an unnecessary undertaking at the present time. Furthermore, the theory we have presented here allows one to extract useful information from the measured scattering function.

In particular, by fitting the theoretical expression for $S(k, \omega = 0)$ to the experimental data of Sköld *et al.*[8] we have obtained values for the viscous relaxation time and for the sixth frequency moment as functions of k. Using these values for $\tau(k)$, the calculated $S(k, \omega)$ is in very good agreement with the experimental one, except for the smallest k values, 1.0 and 1.2 Å^{-1}, where our calculated $S(k, \omega)$ shows remnants of a side peak for which there is no clear experimental evidence. The agreement between the calculated longitudinal current spectral function $\omega^2 S(k, \omega)$ and the experimental one can also be considered good, except for large ω, where the experimental values lie consistently above the calculated values. This lack of agreement may, however, be due to the uncertainty in the experimental data for large values of ω where the scattered intensity is low.

Since it is based on an exact representation, the theory presented in this paper is also applicable (at least in principle) to the hydrodynamic regime. If one took the existence of side peaks, corresponding to the Brillouin components, as marking the onset toward hydrodynamic behavior, we would conclude from the present calculations that the hydrodynamic regime extends for k values downward from 1 Å^{-1}. In this respect, our theory is in marked contrast to that of Pathak and Singwi,[9] who did not find any structure in $S(k, \omega)$ corresponding to Brillouin side peaks down to values for $k \leqslant 0.5$ Å^{-1}. Of course, to give a proper description of the hydrodynamic regime, in particular, for the limit $k \to 0$, it will be necessary to consider also the damping due to thermal diffusion[25,28] and this may present some difficulties in extending the present calculations to smaller k values. In this connection we should note that it may simply be the neglect of the latter type of damping which causes the appearance of a side peak at $k = 1.0$ Å^{-1} in our calculations.

The analysis of Ailawadi *et al.*,[28] however, suggests that for $k \geqslant 1.0$ Å^{-1} thermal diffusion should not lead to an important contribution to the damping. In any case, it would be very useful to have experimental data for $S(k, \omega)$ for argon, say, in the region $k < 1$ Å^{-1} since this would provide valuable information on the "transition" to the hydrodynamic regime.

In a subsequent paper we hope to apply the formalism presented in this paper to two other response functions of current interest, namely the self-motion response function $\chi_s(k, z)$ and the transverse momentum response function $\chi_t(k, z)$. Both of these response functions are in a sense much simpler than the density response function $\chi(k, z)$ discussed here. In particular both describe simple diffusion processes in the hydrodynamic limit.[25] The present approach allows one to obtain expressions for the corresponding transport coefficients, the self-diffusion constant D_s and shear viscosity η, which are similar to those obtained by Martin *et al.*[32,33]

Finally, let us note that the method presented in this paper could be applied to another exact representation for $\chi(k, z)$, namely one in terms of $\chi_s(k, z)$ with the form

$$\chi(k, z) = \chi_s(k, z)/[1 + \theta(k, z)\,\chi_s(k, z)] \tag{105}$$

[compare (20)]. This representation allows one to describe and separate off all the effects associated with the exact motion of a single particle from the total density response function. If the function $\theta(k, z)$ is assumed to be independent of z, one would obtain the approximations derived by Kerr[34] and Hubbard and Beeby[35] from a microscopic approach (see also Refs. 2 and 4). In fact the result of Kerr[34] corresponds to taking $\theta(k, z)$ as $\phi_0(k) = -k_B TC(k)$ [cf. Eq. (9)]. There is, of course, a difficulty associated with the representation (105) in that the exact $\chi_s(k, z)$ is not known, so that one has two unknown functions to deal with. However, since $\chi_s(k, z)$ is a simpler function and can more easily be approximated than $\chi(k, z)$, the representation (105) may well prove useful.

APPENDIX A

In this appendix we wish to recast the exact representation (20) in a space–time form involving the classical one-particle distribution function $f(\mathbf{p}, \mathbf{r}, t)$. This function is defined as the ensemble average of the one-particle phase space operator, i.e.,

$$f(\mathbf{p}, \mathbf{r}, t) = \sum_i \langle \delta(\mathbf{p} - \mathbf{p}_i(t))\, \delta(\mathbf{r} - \mathbf{r}_i(t)) \rangle \tag{A1}$$

where $\mathbf{p}_i(t)$ and $\mathbf{r}_i(t)$ denote the momentum and position of particle i at time

t and the summation extends over all particles in the system. At time $t_0 = -\infty$ we assume the system to have been in thermal equilibrium. We then apply an external time-dependent scalar potential giving rise to an extra term in the Hamiltonian of the form

$$H_{\mathrm{ex}}(t) = \sum_i u[\mathbf{r}_i(t), t] \tag{A2}$$

The angular brackets in (A1) then denote the expectation value of the operator with respect to a density matrix satisfying Liouville's equation in the presence of $H_{\mathrm{ex}}(t)$, with the initial condition stated above.

It is well known that $f(\mathbf{p}, \mathbf{r}, t)$ satisfies the exact equation of motion

$$\begin{aligned}[t][(\partial/\partial t) + (\mathbf{p}/m) \cdot \nabla_r - \nabla_r u(\mathbf{r}, t) \cdot \nabla_p] f(\mathbf{p}, \mathbf{r}, t)\\ = \int d\mathbf{r}' \, \nabla_r v(\mathbf{r} - \mathbf{r}') \cdot \int d\mathbf{p}' \, \nabla_p f_2(\mathbf{p}, \mathbf{r}, t; \mathbf{p}', \mathbf{r}', t)\end{aligned} \tag{A3}$$

where f_2 is the two-particle distribution function defined by

$$\begin{aligned}[t]&f_2(\mathbf{p}, \mathbf{r}, t; \mathbf{p}', \mathbf{r}', t)\\ &= \sum_{i \neq j} \langle \delta(\mathbf{p} - \mathbf{p}_i(t)) \, \delta(\mathbf{r} - \mathbf{r}_i(t)) \, \delta(\mathbf{p}' - \mathbf{p}_j(t)) \, \delta(\mathbf{r}' - \mathbf{r}_j(t)) \rangle\end{aligned} \tag{A4}$$

As an aside, let us note that in the derivation of the MFA given in Ref. 7, the function f_2 is approximated by

$$f_2(\mathbf{p}, \mathbf{r}, t; \mathbf{p}', \mathbf{r}', t) \simeq f(\mathbf{p}, \mathbf{r}, t) f(\mathbf{p}', \mathbf{r}', t)\{g(\mathbf{r} - \mathbf{r}') + [\rho \, \partial g(\mathbf{r} - \mathbf{r}')/2 \, \partial \rho]\} \tag{A5}$$

where $g(\mathbf{r} - \mathbf{r}')$ is the equilibrium radial distribution function. If the second term in the above curly bracket is replaced by zero, we obtain the approximation of Ref. 6 (cf. Table I). The original derivation of the MFA by Vlasov[5,36] corresponds to replacing $g(\mathbf{r} - \mathbf{r}')$ in (A5) by unity.

As the main point of this appendix, we claim that in the limit $u(\mathbf{r}, t) \to 0$, the representation (20) is equivalent to the following exact ansatz equation:

$$\begin{aligned}[t][(\partial/\partial t) + (\mathbf{p}/m) \cdot \nabla_r - \nabla_r u(\mathbf{r}, t) \cdot \nabla_p] f(\mathbf{p}, \mathbf{r}, t)\\ = \nabla_p f_0(p) \cdot \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, \nabla_r \Phi(\mathbf{r} - \mathbf{r}', t - t') \langle \rho(\mathbf{r}', t') \rangle\end{aligned} \tag{A6}$$

where $f_0(p)$ is the equilibrium one-particle distribution function given by

$$f_0(p) = \rho (2\pi m k_B T)^{-3/2} \exp(-\beta p^2/2m), \qquad \rho = \int d\mathbf{p} \, f_0(p) \tag{A7}$$

(ρ being the uniform equilibrium density) and

$$\langle\rho(\mathbf{r}, t)\rangle = \int d\mathbf{p}\, f(\mathbf{p}, \mathbf{r}, t) \tag{A8}$$

is the average density in the presence of the external field. The real space- and time-dependent effective potential (spherically symmetric in a spatially invariant system) $\Phi(r, t)$ is given by

$$\begin{aligned}\Phi(r, t) &= \int \frac{d\mathbf{k}}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \phi(k, \omega + i\epsilon) \exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t) \\ &= \int \frac{d\mathbf{k}}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, [\phi'(k, \omega) + i\phi''(k, \omega)] \exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t)\end{aligned} \tag{A9}$$

Note that because $\phi(k, \omega + i\epsilon)$ is analytic in the upper half of the complex ω plane (see Section 3), $\Phi(r, t)$ vanishes for $t < 0$. The time integral in (A6) can therefore be extended to $t = +\infty$. The meaning of the integral is that in establishing an effective field acting on a particle at $\mathbf{r}$, t, the system has a "memory" for the effect of the average density at a point $\mathbf{r}'$ at some prior time t'.

To show that (A6) is equivalent to (20), we write $f(\mathbf{p}, \mathbf{r}, t)$ as

$$f(\mathbf{p}, \mathbf{r}, t) = f_0(p) + f_1(\mathbf{p}, \mathbf{r}, t) \tag{A10}$$

where $f_1(\mathbf{p}, \mathbf{r}, t)$ represents the departure from the equilibrium distribution $f_0(p)$ caused by the infinitesimal external field $u(\mathbf{r}, t)$. According to linear response theory,[10] f_1 is itself linear in u and hence the product $f_1 u$ can be neglected. The rest the of the demonstration follows the well-known procedure[36] for the derivation of the mean field response function (1). First we rewrite (A6) in the form

$$\begin{aligned}&[(\partial/\partial t) + (\mathbf{p}/m)\cdot\nabla_r] f_1(\mathbf{p}, \mathbf{r}, t) - \nabla_r u(\mathbf{r}, t)\cdot\nabla_p f_0(p) \\ &\quad = \nabla_p f_0(p)\cdot \int d\mathbf{r}' \int_{-\infty}^{\infty} dt'\, \nabla_r \Phi(\mathbf{r} - \mathbf{r}', t - t')\langle\rho(\mathbf{r}', t')\rangle\end{aligned} \tag{A11}$$

or, in terms of the spatial Fourier components of f_1, u, and Φ,

$$\begin{aligned}&[(\partial/\partial t) + i\mathbf{k}\cdot\mathbf{p}/m] f_1(\mathbf{p}, \mathbf{k}, t) - i\mathbf{k}\cdot\nabla_p f_0(p)\, u(\mathbf{k}, t) \\ &\quad = i\mathbf{k}\cdot\nabla_p f_0(p) \int_{-\infty}^{\infty} dt'\, \Phi(k, t - t')\langle\rho(\mathbf{k}, t')\rangle\end{aligned} \tag{A12}$$

where the average density fluctuation $\langle\rho(\mathbf{k}, t)\rangle$ is related to $f_1(\mathbf{p}, \mathbf{k}, t)$ by the equation analogous to (A8). In terms of the Fourier frequency components, (A12) reads

$$[\omega + i\epsilon - (\mathbf{p}\cdot\mathbf{k})/m] f_1(\mathbf{p}, \mathbf{k}, \omega) + \mathbf{k}\cdot\nabla_p f_0(p)\, u(\mathbf{k}, \omega) \\ = -\mathbf{k}\cdot\nabla_p f_0(p)\, \phi(k, \omega + i\epsilon)\langle\rho(\mathbf{k}, \omega)\rangle \tag{A13}$$

where the positive infinitesimal ϵ has been added to ensure the causal response of the system to the external perturbation. Using the fact that the frequency components of the density fluctuation are given by

$$\langle\rho(\mathbf{k}, \omega)\rangle = \int d\mathbf{p}\, f_1(\mathbf{p}, \mathbf{k}, \omega) \tag{A14}$$

we finally obtain from (A13)

$$\langle\rho(\mathbf{k}, \omega)\rangle[1 + \phi(k, \omega + i\epsilon)\chi_0(k, \omega + i\epsilon)] = -u(\mathbf{k}, \omega)\chi_0(k, \omega + i\epsilon) \tag{A15}$$

where

$$\chi_0(k, \omega + i\epsilon) = \int d\mathbf{p}\, \mathbf{k}\cdot\nabla_p f_0(p)/[\omega - (\mathbf{p}\cdot\mathbf{k}/m) + i\epsilon] \tag{A16}$$

is the density response function for free particles. Recalling the definition (2) of the linear response function [cf. also Eq. (68)], we see the equivalence of Eq. (A15) [and hence (A6)] to the representation (20).

The fact that the definition (A16) of the free-particle response function is equivalent to the expressions (34)–(35) follows by considering the more general definition for complex z:

$$\chi_0(k, z) = \int d\mathbf{p}\, \frac{\mathbf{k}\cdot\nabla_p f_0(p)}{z - (\mathbf{p}\cdot\mathbf{k})/m} = \rho\beta - \beta z \int d\mathbf{p}\, \frac{f_0(p)}{z - (\mathbf{p}\cdot\mathbf{k})/m} \tag{A17}$$

where we have used (A7). After integration over angles and an integration by parts we obtain

$$\int d\mathbf{p}\, \frac{f_0(p)}{z - (\mathbf{p}\cdot\mathbf{k})/m} = \frac{\rho z}{(2\pi m k_B T)^{1/2}} \int_{-\infty}^{\infty} dp \exp\left(-\frac{\beta p^2}{2m}\right) \frac{1}{z^2 - (p^2k^2/m^2)} \tag{A18}$$

which is analytic off the real axis. Changing the variable of integration, the integral can be rewritten as

$$\int d\mathbf{p}\, \frac{f_0(p)}{z - (\mathbf{p}\cdot\mathbf{k})/m} = \frac{\rho}{\sqrt{\pi}} \frac{z}{\sqrt{2}kv_T} \int_{-\infty}^{\infty} d\omega\, \frac{\exp[-\omega^2/(2k^2v_T^2)]}{z^2 - \omega^2} \\ = -\frac{\rho\sqrt{\pi}}{\sqrt{2}kv_T} W\left(\frac{z}{\sqrt{2}kv_T}\right) \tag{A19}$$

where $W(z)$ is defined by (35b) and $v_T = (k_B T/m)^{1/2}$. Substituting the result (A19) into (A17), we recover the formula (35a). The expressions in (34) are easily obtained using the equivalent representations for $W(z)$[20]:

$$W(z) = \int_{-\infty}^{\infty} \frac{dt}{\pi} \frac{\exp(-t^2)}{t - z}$$
$$= -\frac{2\exp(-z^2)}{\sqrt{\pi}} \int_0^z dt \exp(t^2) \pm i \exp(-z^2) \tag{A20}$$

where the plus and minus signs correspond to z lying in the upper or lower half complex plane, respectively.

APPENDIX B

Here we wish to establish some inequalities related to the above work. First we note from the fact that $\omega\chi''(k, \omega) \geqslant 0$ that it follows that the damping function $D'(k, \omega) \geqslant 0$ [cf. Eq. (75)] and hence that all the even frequency moments of $D'(k, \omega)$ are nonnegative quantities. For the zeroth and second moments of $D'(k, \omega)$ this implies [cf. Eqs. (73) and (74)]

$$\langle \omega_l^2(k) \rangle \geqslant k^2 v_T^2 / S(k) \tag{B1}$$

$$\langle \omega_l^4(k) \rangle \geqslant \langle \omega_l^2(k) \rangle^2 \tag{B2}$$

the above quantities having been defined in Eqs. (12) and (13). Equation (B1) can be rewritten as

$$S(k) \geqslant \frac{k^2 v_T^2}{3k^2 v_T^2 + (\rho/m) \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k} \cdot \mathbf{r})(\hat{\mathbf{k}} \cdot \nabla)^2 v(r)} \tag{B3}$$

which can be recognized as a classical version of an inequality originally due to Bogoliubov[37] as applied to the density–density spectral function:

$$\rho\beta S(k) \geqslant \chi(k) \geqslant \frac{\int_{-\infty}^{\infty} (d\omega/\pi)\, \omega\chi''(k, \omega)}{\int_{-\infty}^{\infty} (d\omega/\pi)\, \omega^3\chi''(k, \omega)} \tag{B4}$$

Next we want to prove a stronger inequality than (B3), namely

$$S(k) \geqslant \frac{k^2 v_T^2}{k^2 v_T^2 + (\rho/m) \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k} \cdot \mathbf{r})(\hat{\mathbf{k}} \cdot \nabla)^2 v(r)} \geqslant 0 \tag{B5}$$

or, equivalently [cf. Eqs. (12) and (57)]

$$\omega_l^2(k) \geqslant \omega_2^2(k) \tag{B6}$$

Using the definitions (9) and (17), an equivalent statement of the inequality (B6) is

$$\phi_\infty(k) \geqslant \phi_0(k) \tag{B7}$$

To establish (B5), we shall use a slight modification of an inequality due to Mermin.[38] Starting with the Schwartz inequality

$$\langle | A |^2 \rangle \geqslant |\langle A^* \mathbf{B} \rangle|^2 / \langle | \mathbf{B} |^2 \rangle \tag{B8}$$

and taking the scalar function A and vector function $\mathbf{B}$ of the form

$$A = \sum_{i=1}^{N} \psi(\mathbf{r}_i) \tag{B9}$$

$$\mathbf{B} = -(e^{\beta V}/\beta) \sum_{i=1}^{N} \nabla_i [\phi(\mathbf{r}_i)\, e^{-\beta V}] \tag{B10}$$

Mermin[38] has derived the inequality (valid in classical statistics)

$$\left\langle \left| \sum_{i=1}^{N} \psi(\mathbf{r}_i) \right|^2 \right\rangle \geqslant \frac{| \sum_{i=1}^{N} \langle \phi(\mathbf{r}_i)\, \nabla_i \psi^*(\mathbf{r}_i) \rangle |^2}{\sum_{i=1}^{N} \langle | \nabla_i \phi(\mathbf{r}_i) |^2 \rangle + \beta \sum_{i,j=1}^{N} \langle \phi(\mathbf{r}_i)\, \phi^*(\mathbf{r}_j)\, \nabla_i \cdot \nabla_j V \rangle} \tag{B11}$$

V is the total potential energy. The function $\phi(\mathbf{r})$ is any twice differentiable function that either has the period of the cube of side L (assuming our system to be enclosed inside a cube) or vanishes on the surface of the cube, depending on whether one is using periodic or impenetrable wall boundary conditions. The function $\psi(\mathbf{r})$ is any differentiable function that has the period of the cube if one is using the periodic boundary conditions and is unrestricted if the impenetrable wall condition is used.

For simplicity we use periodic boundary conditions; however, since we are only interested in the thermodynamic limit, the results will be independent of our choice of boundary condition. The choice[38]

$$\phi(\mathbf{r}) = \psi(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}), \qquad \mathbf{k} = (2\pi/L)(n_1, n_2, n_3) \tag{B12}$$

with n_i an integer, is consistent with the periodicity requirements and reduces (B11) to

$$\left\langle \left| \sum_{i=1}^{N} \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right|^2 \right\rangle \geqslant \frac{N^2 k^2}{N k^2 + \beta \sum_{i,j=1}^{N} \langle \phi(\mathbf{r}_i)\, \phi^*(\mathbf{r}_j)\, \nabla_i \cdot \nabla_j V \rangle} \tag{B13}$$

In our case V is just a sum of pair potentials. Then, recalling the definition of $S(k)$, (B13) becomes[39]

$$S(k) \geqslant \frac{k^2 v_T^2}{k^2 v_T^2 + (\rho/m) \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k} \cdot \mathbf{r})\, \nabla^2 v(r)} \geqslant 0 \tag{B14}$$

[the last inequality resulting from the fact that both numerator and denominator in (B8), and hence (B11) and (B13), are positive quantities].

Inequality (B14) is not quite the same as the one we want, namely (B5). To prove the latter we choose instead of the vector function $\mathbf{B}$ given by (B10) a scalar function B given by

$$B = \hat{\mathbf{k}} \cdot \mathbf{B} = -(e^{\beta V}/\beta) \sum_{i=1}^{N} (\hat{\mathbf{k}} \cdot \nabla_i)[\phi(\mathbf{r}_i)\, e^{-\beta V}] \tag{B15}$$

Mermin's analysis[38] goes through as before, except that each gradient operator on the right side of (B11) is replaced by the scalar $\hat{\mathbf{k}} \cdot \nabla$. With the same choice for the functions $\phi(\mathbf{r}_i)$ and $\psi(\mathbf{r}_i)$ as in (B12), it is easily verified that we are led to (B5) and hence to (B6) and (B7), thus establishing the inequalities we set out to prove.

Finally, let us note that the inequalities (B5) and (B14) imply the following inequalities for the direct correlation function[39]:

$$\begin{aligned} 1 &\geqslant \rho C(k) \geqslant -\rho\beta\phi_\infty(k) = -\rho\beta k^{-2} \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k} \cdot \mathbf{r})(\hat{\mathbf{k}} \cdot \nabla)^2\, v(r) \\ 1 &\geqslant \rho C(k) \geqslant -k^{-2}\rho\beta \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k} \cdot \mathbf{r})\, \nabla^2 v(r) \end{aligned} \tag{B16}$$

APPENDIX C

Here we discuss the simplified form of the equation (72) for the complex normal mode frequency $\omega(k) = \omega_R(k) + i\omega_I(k)$ when the damping is very small and "rederive" the dispersion relations for the Landau-damped collective modes discussed in Section 4.2. When the damping is very small, i.e., $\omega_I \ll \omega_R$, we can write down explicitly the relations defining ω_R and ω_I from Eq. (72):

$$\omega_R^2 - \omega_0^2(k) - \omega_R k^2 D''(k, \omega_R) = 0 \tag{C1}$$

$$\omega_I = -\tfrac{1}{2} k^2 D'(k, \omega_R) \tag{C2}$$

In this case, as seen by comparing with the expression (15), the spectral function $\chi''(k, \omega)$, or scattering function $S(k, \omega)$, will have peaks at the frequencies $\omega = \pm\omega_R(k)$. If, however, the damping is such that ω_I and ω_R are of comparable size, we can no longer expect to find any peaks in $S(k, \omega)$ at $\pm\omega_R(k)$. Equations (C1) and (C2) apply in particular to the propagation and damping of the adiabatic sound modes in the limit $k \to 0$ [when one uses the phenomenological form of the damping function $D'(k, \omega)$ derived from hydrodynamics[25].

In terms of $\phi'(k, \omega)$ and $\phi''(k, \omega)$ the above equations read (making use of Eqs. (78) and (82)]

$$\omega_R^2 - k^2 v_T^2 - \omega_R k^2 D_0''(k, \omega_R) - (\rho k^2/m)\, \phi'(k, \omega_R) = 0 \tag{C3}$$

$$\omega_I = -\tfrac{1}{2}k^2[D_0'(k, \omega_R) - (\rho/m\omega_R)\, \phi''(k, \omega_R)] \tag{C4}$$

Using (34) and (36), it is easily verified that for values of the ratio $kv_T/\omega \ll 1$, $D_0'(k, \omega)$ is given by

$$D_0'(k, \omega) = (\tfrac{1}{2}\pi)^{1/2}[k_B T\omega^4/m(kv_T)^5] \exp(-\omega^2/2k^2 v_T^2) \tag{C5}$$

and the corresponding imaginary part $D_0''(k, \omega)$ by

$$\omega k^2 D_0''(k, \omega) = 2k^2 v_T^2 \tag{C6}$$

If we neglect the collisional damping term $\phi''(k, \omega)$, the imaginary part of the frequency for $kv_T \ll \omega_R$ is given by

$$\omega_I = -\tfrac{1}{2}k^2 D_0'(k, \omega_R) = -(\tfrac{1}{8}\pi)^{1/2}\, [\omega_R^4/(kv_T)^3] \exp(-\omega_R^2/2k^2 v_T^2) \tag{C7}$$

The expression we get for the real-part ω_R depends on how we use Eqs. (C1) and (C3). If in (C1) we replace $D''(k, \omega_R)$ by $D_0''(k, \omega_R)$, we obtain, using (C6),

$$\omega_R^2 = \omega_0^2(k) + 2k^2 v_T^2 \equiv \omega_2^2(k) \tag{C8}$$

$[kv_T \ll \omega_2(k)]$. This is the expression we obtained in (57) and which is consistent with the elastic sum rule (8). If, on the other hand, we use (C3), replacing $\phi'(k, \omega_R)$ by $\phi_\infty(k)$ [see (31)], we obtain

$$\omega_R^2 = 3k^2 v_T^2 + (\rho k^2/m)\, \phi_\infty(k) \equiv \omega_l^2(k) \tag{C9}$$

$[kv_T \ll \omega_l(k)]$, which is the relation we had found in (59), consistent with the third moment sum rule (12).

The spectral function $\chi''(k, \omega)$ corresponding to these approximations, for $kv_T \ll \omega$ and ω near $\omega_R(k)$, is given by [compare (75)]

$$\begin{aligned} \chi''(k, \omega) &\simeq \frac{(\rho k^2/m)\, \omega k^2 D_0'(k, \omega)}{[\omega^2 - \omega_R^2(k)]^2 + [\omega k^2 D_0'(k, \omega)]^2} \\ &\simeq -\frac{\rho k^2}{m} \operatorname{Im}[\omega^2 - \omega_R^2(k) + i\omega_R k^2 D_0'(k, \omega_R)]^{-1} \end{aligned} \tag{C10}$$

which is identical with the expression (61) obtained in the mean field approximation.

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NOTE ADDED IN PROOF

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