Collective Modes in Simple Liquids: A Semiempirical Model

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A semiempirical model for the dynamical structure factor, $S(Q,\omega)$, in a simple liquid is presented. This is a modification of the Lorentzian form predicted by linear hydrodynamics that enables it to be extended into the viscoelastic region while still retaining finite moments. The model leads directly to a criterion for the existence of a sound mode which includes the possibility of soft modes and dispersion gaps. By a suitable choice of parameters the experimental results for liquid Ar and molten Rb may be explained.

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The dynamical structure factor $S(Q,\omega)$ (wave vector Q, frequency ω) of a fluid contains information about the positions and motions of the particles in that fluid. The motions involved may include all possible types from single-particle diffusion at one extreme to collective vibrational modes at the other. In the hydrodynamic region ($Q<0.1$ Å^{-1}) $S(Q,\omega)$ for a simple monatomic fluid consists of a central (Rayleigh) peak broadened by thermal diffusivity and two noncentral (Brillouin) lines broadened by viscosity. The frequency of the noncentral lines is determined by the sound velocity. In the region accessible to inelastic-neutron-scattering experiments ($Q>0.4$ Å^{-1}) side peaks may be observed in $S(Q,\omega)$ for some liquids such as He[1] and Rb,[2] but not for others such as Ar.[3] In Rb these side peaks broaden and disappear at $Q\cong 1.0$ Å^{-1} while in He they extend up to $Q\cong 4.0$ Å^{-1}.

The question of whether sound modes exist in a liquid at Q values where they are not directly observable as side peaks in $S(Q,\omega)$ is a subject of some controversy. Accurate neutron-scattering data have been obtained for Ar by van Well *et al.*[3] de Schepper *et al.*[4] argue, on the basis of the generalized Enskog theory developed by de Schepper and Cohen[5] and from fits to the experimental data, that $S(Q,\omega)$ may be described by a sum of three Lorentzians (one extended heat and two extended sound modes), as in the true hydrodynamic region, up to at least $Q=4.0$ Å^{-1}. The parameters derived from the fit predict that sound modes are present in liquid Ar in this region even though no side peaks are observed in $S(Q,\omega)$. The frequency of these modes softens rapidly at $Q\cong 1.6$ Å^{-1} and there is a dispersion gap where they have zero frequency up to $Q\cong 2.3$ Å^{-1}.

Lovesey[6] argues that these predictions may be an artifact of the form of the function fitted and suggests that linear hydrodynamics, and hence the description of $S(Q,\omega)$ by a sum of three Lorentzians, should only be valid below $Q\cong 0.3$ Å^{-1} and that the line shapes will differ in the viscoelastic region at higher Q. de Schepper *et al.*[7] have shown that the experimental data for Ar are described better by three Lorentzians satisfying the first three moments, hence with three independent parameters, than satisfying five moments with one independent relaxation time as in viscoelastic theory. They point out that the higher moments are strongly dependent on data outside of the experimental range. van Well and de Graaf[8] stress that higher moments should be satisfied by the inclusion of additional Lorentzians, though this is not found to be necessary within the experimental region. The direct measurement of mode softening in molten $MgCl_2$ by McGreevy and Mitchell[9] suggests that the results of de Schepper *et al.*[4] are not simply artifacts of the theory. However, there are still a number of problems. In particular, for the sum of three Lorentzians to have the required finite moments there are relations between the parameters that lead to negative amplitudes for the extended sound modes at $Q\cong 1.0$ Å^{-1}. This could not be the case in liquid Rb where the sound modes are observed to have positive amplitudes.[2] Lovesey[10] has shown that including up to the fourth moment reduces the form of $S(Q,\omega)$ to that predicted by simple viscoelastic theory but that this form is no longer valid in the hydrodynamic region.

In this paper we discuss an empirical modification of the Lorentzian form of $S(Q,\omega)$ predicted by linear hydrodynamics that enables it to be extended to higher Q and ω while still retaining finite moments. This modification, based on a function originally proposed by Egelstaff and Schofield[11] to describe single-particle motion in fluids, has been used by Bunten *et al.*[12] to fit the light-scattering spectra of a number of molten salts. While we accept the empirical nature of the model we show that it can account for the observed differences between Ar and Rb and for the existence of soft modes. We suggest, therefore, that it may have a wide applicability.

From linear hydrodynamics the (symmetrized) intermediate scattering function $S(Q,t)=\int S(Q,\omega)\times e^{i\omega t}d\omega$ has the form

$$S(Q\to 0,t)=S(Q\to 0)[ae^{-t/\tau_a}+(1-a)e^{-t/\tau_b}\cos(\omega_0 t)], \quad (1)$$

where $S(Q)=\int S(Q,\omega)\,d\omega$ is the static structure factor and

$$S(Q\to 0)=\rho k_B T K_T,\quad a=(\gamma-1)/\gamma,\quad \tau_a=1/D_T Q^2,\quad \tau_b=1/\Gamma Q^2,\quad \omega_0=CQ, \tag{2}$$

with ρ the number density, k_B Boltzmann's constant, T the temperature, and K_T the isothermal compressibility. $\gamma=C_p/C_v$ is the ratio of specific heats, D_T the thermal diffusivity, Γ the sound-wave damping constant, and C the sound velocity. This gives the Landau-Plazcek form for the dynamical structure factor

$$S(Q\to 0,\omega)=\frac{\rho k_B T K_T}{\pi}\left[\frac{\gamma-1}{\gamma}\,\frac{D_T Q^2}{\omega^2+(D_T Q^2)^2}+\frac{1}{2\gamma}\left[\frac{\Gamma Q^2}{(\omega-CQ)^2+(\Gamma Q^2)^2}+\frac{\Gamma Q^2}{(\omega+CQ)^2+(\Gamma Q^2)^2}\right]\right]. \tag{3}$$

Equation (1) is strictly valid only for small Q and large t. We propose a modification such that

$$S(Q,t)=S(Q)\left[a\exp\{-[(t^2+\tau_1^2)^{1/2}-\tau_1]/\tau_2\}+(1-a)\exp\{-[(t^2+\tau_3^2)^{1/2}-\tau_3]/\tau_4\}\cos(\omega_0 t)\right], \tag{4}$$

which has the Gaussian behavior expected for a free particle in the limit $t\to 0$ but reduces to (1), with $\tau_a\equiv\tau_2$ and $\tau_b\equiv\tau_4$, for $t\gg\tau_1,\tau_3$. (All parameters a, τ, and ω_0 are in general functions of Q.) The dynamical structure factor is then

$$S(Q,\omega)=\frac{S(Q)}{\pi}\left[ae^{\tau_1/\tau_2}\frac{\tau_1^2}{\tau_2}\,\frac{K_1(x)}{x}+\frac{(1-a)}{2}e^{\tau_3/\tau_4}\frac{\tau_3^2}{\tau_4}\left[\frac{K_1(y)}{y}+\frac{K_1(z)}{z}\right]\right], \tag{5}$$

where $x=\tau_1(\omega^2+1/\tau_2^2)^{1/2}$ and $y,z=\tau_3[(\omega\mp\omega_0)^2+1/\tau_4^2]^{1/2}$. K_1 is a modified Bessel function of the second kind.

The parameters in the model are not all independent but are related by the moments of $S(Q,\omega)$:

$$\langle\omega^n S\rangle=\int\omega^n S(Q,\omega)\,d\omega=(i)^n\frac{d^n S(Q,t)}{dt^n}\bigg|_{t=0}. \tag{6}$$

The odd moments are all zero as $S(Q,t)$ is even in t. The first three even moments are

$$\langle\omega^0 S\rangle=S(Q), \tag{7a}$$

$$\langle\omega^2 S\rangle=S(Q)\left[\frac{a}{\tau_1\tau_2}+\frac{(1-a)}{\tau_3\tau_4}+(1-a)\omega_0^2\right], \tag{7b}$$

$$\langle\omega^4 S\rangle=S(Q)\left[3\left[\frac{a}{\tau_1^3\tau_2}+\frac{(1-a)}{\tau_3^3\tau_4}\right]+3\left[\frac{a}{\tau_1^2\tau_2^2}+\frac{(1-a)}{\tau_3^2\tau_4^2}\right]+(1-a)\omega_0^2\left[\frac{6}{\tau_3\tau_4}+\omega_0^2\right]\right], \tag{7c}$$

which are finite as long as all time constants τ are nonzero. The classical value of the second moment (ignoring recoil effects) is

$$\langle\omega^2 S\rangle=Q^2 k_B T/M, \tag{8}$$

where M is the atomic mass. Combining this with (7b) gives the sound mode frequency

$$\omega_0^2=\frac{1}{(1-a)}\left[\frac{Q^2 k_B T}{MS(Q)}-\frac{a}{\tau_1\tau_2}-\frac{(1-a)}{\tau_3\tau_4}\right]. \tag{9}$$

In the limit $Q\to\infty$ [$S(Q)\to 1$] we expect that $S(Q,\omega)$ is a single Gaussian with $a=1$, $\omega_0=0$, and $\tau_1\tau_2=M/Q^2 k_B T$. For intermediate Q we may choose (as an example) $\tau_1\tau_2=\tau_3\tau_4=M/\alpha Q^2 k_B T$. We then have

$$\omega_0^2=\frac{1}{(1-a)}\,\frac{Q^2 k_B T}{M}\left[\frac{1}{S(Q)}-\alpha\right], \tag{10}$$

which predicts a dispersion gap ($\omega_0^2<0$) for $1/S(Q)>\alpha$. If $\alpha=1$ the mode softens when $S(Q)=1$, approximately the position observed by de Schepper *et al.*[2] and McGreevy and Mitchell.[5] In order to recover the correct sound velocity we require that $\alpha\to 0$ as $Q\to 0$ but also that $\tau_2^2\gg\tau_1\tau_2$ and $\tau_4^2\gg\tau_3\tau_4$ to retain the Lorentzian form of hydrodynamics. Since, from (2), $\tau_2\to\tau_a=1/D_T Q^2$ and $\tau_4\to\tau_b=1/\Gamma Q^2$ at low Q then a choice of $\alpha\propto Q$ will satisfy both requirements. The model can therefore be extended directly from the hydrodynamic to the viscoelastic region while retaining the required moments. The condition for the existence of a sound mode is $\omega_0^2>0$. Side peaks in $S(Q,\omega)$ disappear when the mode becomes overdamped (which we define as when the half width at half height of the peak is greater than ω_0).

We have compared the model with experimental data for liquid Ar[3] and Rb.[2] For Ar a direct fit to the experimental $S(Q,\omega)$ has been carried out and the deviation found is within experimental error, provided that a collective-mode term is included. The data for Rb are not sufficiently accurate for a direct fit to

$S(Q,\omega)$ and so to determine the parameters we have used $S(Q)$, the width at half height of $S(Q,\omega)$, and ω_c, the frequency of the peak in $C^L(Q,\omega)=\omega^2 \times S(Q,\omega)$, or ω_s, the frequency of the side peak in $S(Q,\omega)$ when it is directly observable. (This is the case in Rb for $Q \lesssim 1.0$ Å^{-1}.) For Rb we have also assumed $\tau_1\tau_2=\tau_3\tau_4$. For both liquids the fit is required to satisfy the second moment via Eq. (9); we have not used $\langle\omega^4 S\rangle$ because the calculation would require a knowledge of the interatomic potential. If we use the indirect procedure, i.e., as used for Rb, for Ar we obtain a reasonable fit to $S(Q,\omega)$ with parameters similar to the direct fit.

The Q dependence of the parameters determined is shown in Fig. 1 for both liquids. At low Q the parameters tend to the limiting forms discussed above [Eq. (2)]. Although in the experimental Q range there is no side peak in $S(Q,\omega)$ for Ar the parameters indicate that a side peak should occur for $Q \lesssim 0.25$ Å^{-1}. In the case of Rb a side peak is observed for $Q < 1.0$ Å^{-1} with $\omega_0 \cong \omega_s$. At low Q we have $\omega_0 = CQ$; as Q increases ω_0 has a maximum at $Q \cong Q_P/2$, where Q_P is the Q value of the first peak in $S(Q)$. The mode softens for $Q > Q_P/2$ and $\omega_0 \to 0$ for $S(Q) \cong 1$. ω_c is always slightly greater than ω_0 and remains finite with a minimum when $\omega_0 = 0$, the height of the minimum being determined by the width of the central line in $S(Q,\omega)$.

As noted above the Ar data cannot generally be fitted within experimental error without including a

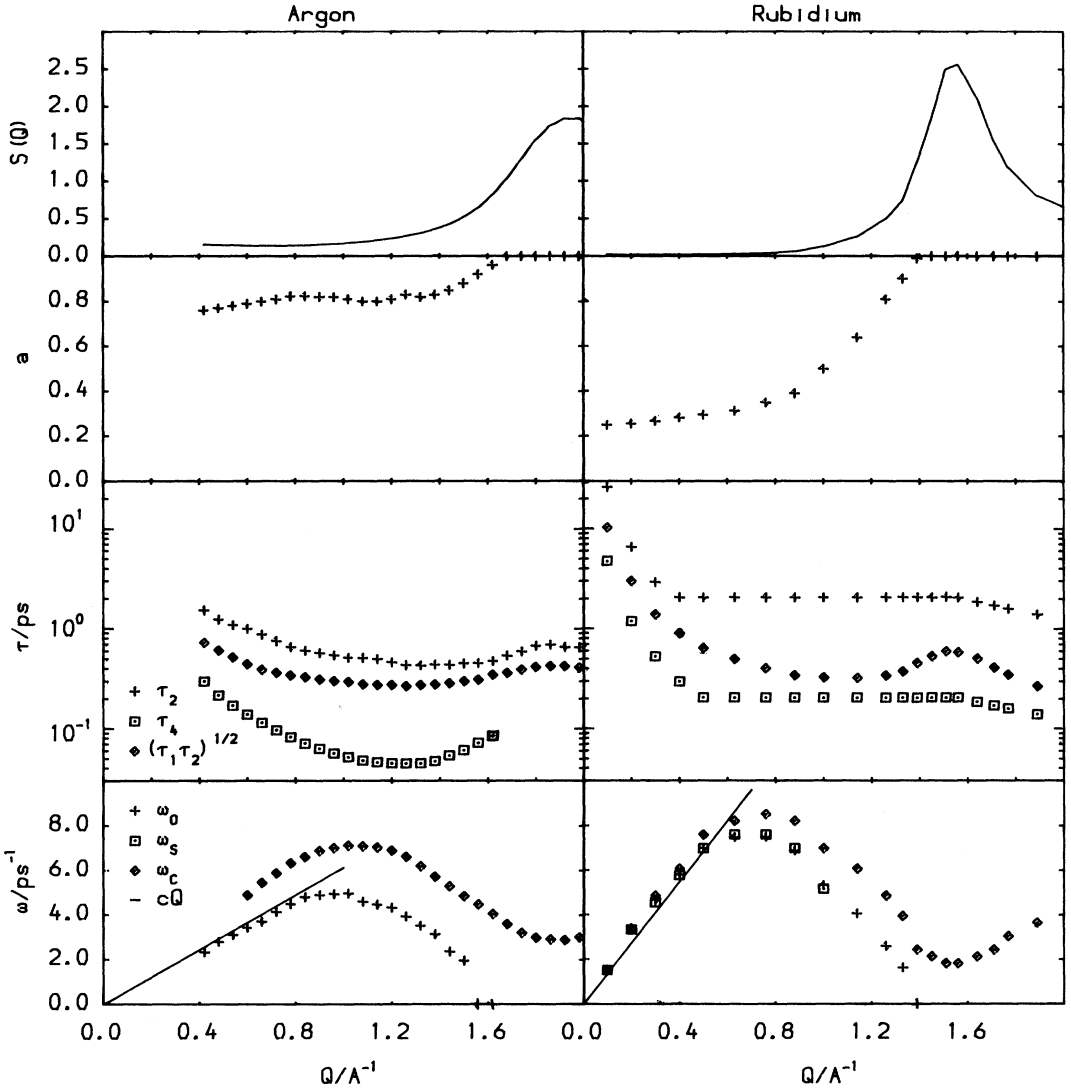

FIG. 1. Representative parameters used in the model and as defined in the text. ω_0 is calculated from the second moment [Eq. (9)]. ω_s and ω_c are then determined by the resulting $S(Q,\omega)$.

collective-mode term, although the amplitude of the mode tends to zero in the region where $\omega_0 \rightarrow 0$. The mode is overdamped so that a side peak is not directly observable in $S(Q,\omega)$. Because the mode amplitude becomes zero $(1-a \rightarrow 0)$ in the mode-softening region $(\omega_0 \rightarrow 0)$ it is not possible to determine unambiguously whether ω_0 reaches zero or exhibits a deep minimum. Although there appears to be a tendency for the mode to have a negative amplitude $(1-a<0)$ for $Q > 1.7$ Å^{-1} there is also a tendency towards $\omega_0^2 < 0$ in the same region, in which case $S(Q,\omega)$ does not have an analytic form. However a negative amplitude for the mode is *not* required to fit the data at any Q value.

In the low-Q limit the constants τ_2 and τ_4 are given by hydrodynamics as the relaxation times associated respectively with thermal diffusion and sound waves. At higher Q the various τ are generally in the range 0.1–1.0 ps; these are reasonable magnitudes although it is not clear what physical processes they refer to. For Ar as Q approaches Q_P, $\tau_2 \cong S(Q)/DQ^2$, where D is the diffusion constant $(0.68\times10^{-8}\ \mathrm{m^2\,s^{-1}}$ at the experimental temperature and pressure), indicating a "structurally inhibited" diffusion mechanism. In the same region $\tau_4 \cong S(Q)\rho M/\eta Q^2$, where η is a generalized viscosity ($\cong 2.5\times10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}$, about $\frac{1}{4}$ of the shear viscosity). In the case of Rb the limitations of the fitting procedure mean that individual time constants should only be taken as representative; even so they are of plausible magnitudes. We have not extended the model to high Q because the values of the parameters determined for Ar for $Q > 2.3$ Å^{-1} indicate that here the model is unrealistic. It is possible that higher-order terms ("multiphonon effects") may have to be introduced in this region, as is the case in liquid ^{4}He(II) [1] and in high-temperature solids.

Our major conclusion is that, by a simple modification of terms involving relaxation times, the results of linear hydrodynamics may be extended into the viscoelastic region while retaining finite moments for $S(Q,\omega)$ and positive amplitudes for sound modes. The model agrees well with experimental data for liquid Ar and Rb. Furthermore, from the second moment the model leads directly to a criterion for the existence of sound modes which includes the possibility of dispersion gaps.

The possible existence of such gaps in classical fluids is of considerable interest. The quantum fluid ^{4}He(II) is observed[1] to have a *minimum* (not a gap) in the dispersion for $Q \cong Q_P$, as has also been observed in some disordered solids such as metallic glasses.[13] In the case of classical fluids the diffusive broadening of the central line in $S(Q,\omega)$ means that a collective-mode side peak cannot generally be resolved when ω_0 is less than the central line width. The determination of whether a collective mode exists, and if so whether is has a dispersion gap or a minimum, depends, therefore, on the fitting of theoretical models. We suggest that in these respects the form proposed here has certain advantages, as described, over the purely hydrodynamic form.

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