Fast Sound in Two-Component Liquids

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A new high-frequency and short-wavelength collective mode specific to binary liquid mixtures with large mass difference is observed in a computer simulation of $Li_{0.8}Pb_{0.2}$ and discussed within the framework of the Mori-Zwanzig formalism. The mode shows linear dispersion in a wave-number regime $0.1\ \text{Å}^{-1} \leq q \leq 0.6\ \text{Å}^{-1}$, but its propagation velocity is higher than the ordinary sound velocity by more than a factor of 3. Its attenuation is only weakly q dependent in contrast to the damping of ordinary sound. In $Li_{0.8}Pb_{0.2}$ "fast sound" entails motion of the lighter atoms only.

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We report the existence of an additional propagating collective mode in binary liquid mixtures, confined to high frequencies and large wave numbers well beyond the hydrodynamic regime. It can be observed in inelastic neutron-scattering experiments or in computer simulation studies of two-component systems with large atomic-mass difference. Some of these systems may respond to a high-frequency short-wavelength perturbation with a density wave, which is supported by the light particles alone, essentially, without the heavy particles participating in the collective motion. Since the dispersion law of this excitation mode is much steeper in the linear region than that of the Brillouin peak of ordinary sound, we call the new mode "fast sound." We have observed fast sound in a computer simulation study[1] of a liquid alloy system of 250 particles in a periodic cell modeling $Li_{0.8}Pb_{0.2}$[2] at temperature $T=1085$ K and total number density $n=0.04558\ \text{Å}^{-3}$.

Results for the partial dynamic structure factors

$$S_{ss'}(q;\omega) = \frac{1}{2\pi(N_s N_{s'})^{1/2}} \int_{-\infty}^{+\infty} dt\, e^{it\omega} \langle \delta N_s^*(\mathbf{q};t)\, \delta N_{s'}(\mathbf{q}) \rangle$$

are plotted in Figs. 1–3. N_s is the particle number of species s (Li or Pb) and $\delta N_s(\mathbf{q};t)$ is a density fluctuation of wave vector $\mathbf{q}$.

We observe a well-defined propagating high-frequency excitation in the lithium density-fluctuation spectrum which is absent in the lead spectrum. The latter consists of a central peak with a pronounced shoulder, the dispersion of which roughly corresponds to the measured ordi-

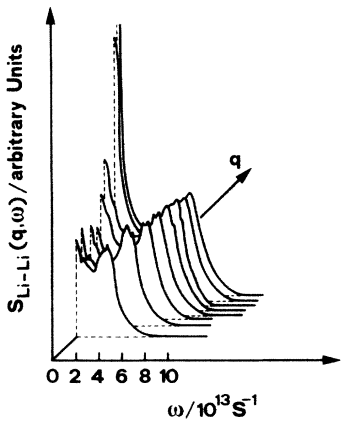

FIG. 1. Representative dynamical-structure factors $S_{LiLi}(q;\omega)$ for q values ranging between 0.2 and 1.0 Å^{-1}.

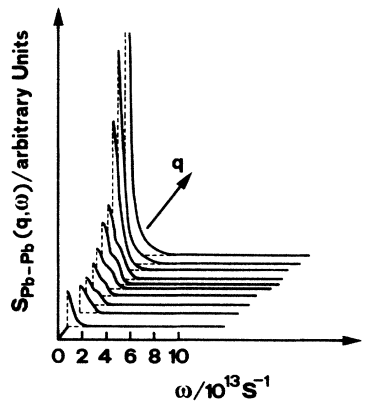

FIG. 2. As in Fig. 1 for $S_{PbPb}(q;\omega)$.

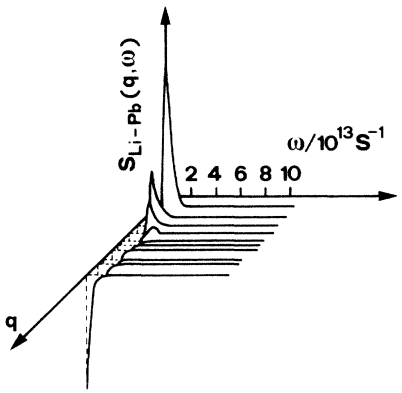

FIG. 3. As in Fig. 1 for $S_{LiPb}(q;\omega)$.

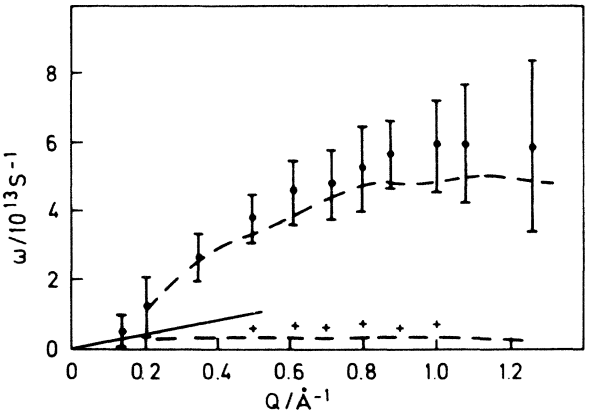

FIG. 4. Positions of high-frequency peak in $S_{LiLi}(q;\omega)$ are denoted by dots; vertical bars indicate half-widths. Positions of shoulders in $S_{PbPb}(q;\omega)$ are marked by crosses. Dashed lines: frequencies $\omega_1(q)$ and $\omega_2(q)$ determined from the larger and smaller eigenvalues of $\Omega^2(q)$, respectively. The slope of the full straight line corresponds to the sound velocity as estimated from Ref. 3.

nary sound velocity.[3] The positions of this shoulder and the fast-sound dispersion are depicted in Fig. 4. The linear region of the fast-sound dispersion extends up to 0.6 $Å^{-1}$, and its slope corresponds to a value for the velocity of propagation more than three times higher than that of ordinary sound.

In the following we explain the origin and dispersion properties of the new high-frequency mode. This is done in terms of the Mori-Zwanzig formalism.[4,5] The dynamical partial structure factors of Figs. 1–3 are expressed in terms of three correlation functions which constitute the three independent matrix elements of the (2×2) correlation matrix Φ:

$$S_{ss'}(q;\omega)=\frac{k_BT}{\pi(N_sN_{s'})^{1/2}}\mathrm{Im}[\Phi(q;z=\omega+i0)]_{ss'}, \quad (1)$$

where

$$[\Phi(q;z)]_{ss'}=i\int_0^\infty dt\, e^{izt}\langle\sigma N_s^*(\mathbf{q};t)\sigma N_{s'}(\mathbf{q})\rangle$$

for $\mathrm{Im}z>0$. Φ is now rewritten[4] in terms of a restoring-force matrix $\Omega^2(q)$ and a generalized friction matrix $\Gamma(q;z)$ (matrix of memory kernels)

$$\Phi(q;z)=\frac{-1}{z+\{-1/[z+\Gamma(q;z)]\}\Omega^2(q)}X(q). \quad (2)$$

The susceptibility matrix $X(q)$ is determined by the static partial structure factors, $X(q)_{ss'}=(N_sN_{s'})^{1/2}S_{ss'}(q)/k_BT$, and the restoring-force matrix elements are given by

$$\Omega^2(q)_{ss'}=q^2N_s/m_s[X(q)^{-1}]_{ss'}, \quad (3)$$

where m_s is the mass of the s particles.

In a one-component system $\Gamma(q;z)$ reduces to a single friction function $\Gamma(q;z)$ which vanishes as q^2 in the hydrodynamic limit, as a consequence of momentum conservation leading to the ordinary hydrodynamic sound mode at $\Omega(q)\simeq c_0q$. [The correct adiabatic sound velocity $c=c_0(c_p/c_v)^{1/2}$ would result if coupling to energy density fluctuations were properly taken into account.]

In a two-component system, momentum can be exchanged between the two species; only the total momentum is conserved. This fact complicates evaluation of Eq. (2) for liquid mixtures in the hydrodynamic limit, since $z\Gamma(q;z)$ is no longer negligible compared to $\Omega^2(q)$ for small q. Besides the ordinary sound mode at frequency c_0q (again neglecting coupling to energy-density fluctuations for simplicity) one finds a second mode of zero frequency corresponding to the interdiffusion of particles of the two species.

The situation may, however, simplify as the wave number q is increased beyond the hydrodynamic regime. If one of the eigenvalues of the matrix $\Omega^2(q)$, say $\omega_1^2(q)$, becomes large compared to the damping [as characterized by the norm of $z\Gamma(q;z)$ taken at $z=\omega_1(q)$] for a certain q range, there will appear a nonoverdamped high-frequency collective mode. We argue that this is exactly what happens in the case of $Li_{0.8}Pb_{0.2}$. In Fig. 4 we have plotted the maxima of $S_{LiLi}(q;\omega)$ against q together with the characteristic frequencies $\omega_{1,2}(q)$ resulting from the eigenvalues of $\Omega^2(q)$ given by

$$\omega_{1,2}^2(q)=[\Omega^2(q)_{11}+\Omega^2(q)_{22}]/2\pm\{[\Omega^2(q)_{11}-\Omega^2(q)_{22}]^2+4\Omega^2(q)_{12}\Omega^2(q)_{21}\}^{1/2}/2, \quad (4)$$

with $\omega_1^2(q)\geq\omega_2^2(q)\geq 0$.

The $\Omega^2(q)_{ss'}$ were evaluated according to Eq. (3) by use of static structure factors supplied by the simulation.[6] It is remarkable that the dispersion of fast sound follows closely that of the larger eigenvalue. The strong difference be-

tween ω_1 and ω_2 obviously is due to a Born-Oppenheimer-type separation of time scales which results from the large mass difference. This pushes the Li dispersion way out of the region of damping leading to the appearance of fast sound. As opposed to the well-known optic modes common to ionic systems, let us note that fast sound is a *propagating* high-frequency mode with nearly constant propagation velocity. In accordance with Eq. (2) the dynamical variable

$$A(\mathbf{q}) = N_1(\mathbf{q}) + \alpha(q) N_2(\mathbf{q}) \tag{5a}$$

associated with the high-frequency mode is determined by the left eigenvector belonging to the eigenvalue $\omega_f^2(q)$. One finds

$$\alpha(q) = \Omega^2(q)_{12} / [\omega_f^2(q) - \Omega^2(q)_{22}], \tag{5b}$$

which is very small in the relevant q regime ($\alpha = -0.035$ for $q = 0.52$ Å^{-1}). So the new mode in $Li_{0.8}Pb_{0.2}$ must be interpreted as a propagating lithium density fluctuation in a background of heavy lead ions, which do not participate to an essential extent in the high-frequency motion.

Regarding the situation at small q in Fig. 4, as discussed above, one expects a central peak (interdiffusion plus heat conduction) in addition to the ordinary sound peak in the limit $q \to 0$. On the other hand, the frequencies $\omega_{1,2}(q)$ vanish linearly with q. So there will be a transition from fast sound ($q \gtrsim 0.2$ Å^{-1}) to hydrodynamic ($q \lesssim 0.05$ Å^{-1}) behavior. Theoretical prediction of the spectra in this transition regime would require detailed knowledge of the kernel matrix $\Gamma(q,z)$ which is not available yet. It is not clear *a priori* whether the fast-sound mode will disappear as the wave number decreases while the ordinary sound peak appears at still smaller wave numbers, or alternatively, whether the fast-sound mode will change its slope continuously in the transition regime to merge into the ordinary Brillouin peak without ever disappearing. This latter possibility would be consistent with our data at the smallest wave number $q = 0.12$ Å^{-1} attainable in the simulation because of system-size restrictions.[1]

An application of this treatment to the liquid alloy $Na_{0.5}K_{0.5}$ shows that fast sound should be absent there as in fact shown in a computer simulation.[7] In $Li_{0.8}Pb_{0.2}$ the fast-sound mode was not open to experimental observation in a recent neutron-scattering experiment[8] because it would show up at much higher frequencies than the ones monitored. (The energy transfer was less than 5 meV in the relevant q regime corresponding to frequencies $\omega < 0.76 \times 10^{13}$ s^{-1}.)

Finally, we wish to recall that in a previous occasion indications were found in a computer simulation study of the existence of a higher-frequency sound in a system characterized by two species having a large mass difference: water.[9] This feature never has properly been explained and it has not received further confirmation. However, we think that, if real, it may be closely connected to fast sound in binary mixtures. In spite of the fact that the considered model of water consists of rigid molecules, a density wave within the light hydrogen atoms alone could be achieved by an appropriate rotation of the molecules about the heavy-oxygen centers.

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