Observable Fast Kinetic Eigenmode in Binary Noble-Gas Mixtures?

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It is suggested that a fast kinetic mode should be observable in a whole class of disparate-mass fluid mixtures, such as gaseous He-Xe, by neutron scattering experiments, at not too high densities and Xe concentrations.

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Many years ago Grad[1] pointed out that in dilute disparate-mass mixtures, i.e., binary mixtures of dilute gases, where the two components have very different masses, the slow exchange of kinetic energy between the two components should lead to two temperatures: one associated with the light component and one associated with the heavy component. This idea was further developed by others, especially, by Johnson and coworkers[2] and Kamgar-Parsi and Cohen,[3] who studied the behavior of forced sound modes as a function of the frequency ω of an external disturbance in dilute binary mixtures of He and Xe. For He concentrations $x_1 > 0.45$ and frequencies $\omega > 10^8$ Hz, a sharp increase in the sound velocity was found.

Recently Bosse *et al.*[4] have found a very fast propagating soundlike mode—which they called fast sound—at a wave number higher than a critical wave number $k_c \approx 2\ \mathrm{nm}^{-1}$, in a computer simulation of a model of a liquid $\mathrm{Li_{0.8}Pb_{0.2}}$ alloy. This eigenmode was deduced from the presence of a pronounced Brillouin-type peak in the partial dynamic structure factor $S_{11}(k,\omega)$, associated with the light (Li) component, at a position that corresponded to a velocity 3 times that of the velocity of sound. No such peak was found in $S_{22}(k,\omega)$, associated with the heavy component (Pb). To what extent this fast-sound peak would be present in the total $S(k,\omega)$ of actual Li-Pb alloys was left open.

In this Letter, we want to point out that a fast propagating kinetic mode should be observable in the neutron spectrum of a whole class of fluid disparate-mass mixtures. We take He-Xe mixtures at sufficiently high He concentrations (around $x_1 = 0.75$) and not too high densities (reduced densities below 0.5) as a typical example. The predictions are based on a hard-sphere fluid model of the He-Xe mixtures, which has been used before for the neutron scattering of simple noble-gas fluids.[5] An advantage of our using a hard-sphere model is that a kinetic theory is available for all densities, so that a more detailed discussion of the dynamical processes in the fluid can be made. The work on forced modes in disparate-mass mixtures indicates that the occurrence of a fast kinetic mode need not be restricted to such large mass ratios as in He-Xe mixtures.[3]

The quantities of interest are the partial dynamic structure factors, the Fourier transforms of the density-density correlation functions:

$$S_{ij}(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \delta n_i^*(\mathbf{k},0)\, \delta n_j(\mathbf{k},t)\rangle .$$

Here $i,j = 1,2$ and $\delta n_i(\mathbf{k},t)$ is the fluctuation of the number density of the ith component, which is, for $k \neq 0$ ($k = |\mathbf{k}|$), given by

$$\delta n_i(\mathbf{k},t) = \frac{1}{\sqrt{N_i}} \sum_{p=1}^{N_i} e^{-i\mathbf{k}\cdot\mathbf{r}_p(t)},$$

where $\mathbf{r}_p(t)$ is the position of particle p of species i at time t and N_i is the number of particles of species i. For classical fluids, all S_{ij} are real and $S_{12} = S_{21}$.

The dynamics of a hard-sphere fluid is governed by a pseudo Liouville operator,[6] which in kinetic theory is approximated by a single-particle operator $L_E(\mathbf{k})$ that permits us to write the $S_{ij}(k,\omega)$ in the form[5,7-9]

$$S_{ij}(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle\langle \boldsymbol{\psi}_i(\mathbf{v}_1,\mathbf{v}_2;k)\, e^{tL_E(\mathbf{k})}\, \boldsymbol{\psi}_j(\mathbf{v}_1,\mathbf{v}_2;k)\rangle_1\rangle_2;$$

each one of the two functions $\boldsymbol{\psi}_i(\mathbf{v}_1,\mathbf{v}_2;k)$ (for $i = 1,2$) is a two-component function depending parametrically on k. A general two-component function $\boldsymbol{\phi}(\mathbf{v}_1,\mathbf{v}_2)$ is defined as follows:

$$\boldsymbol{\phi}(\mathbf{v}_1,\mathbf{v}_2) = \begin{pmatrix} \phi_1(\mathbf{v}_1) \\ \phi_2(\mathbf{v}_2) \end{pmatrix},$$

where $\phi_1(\mathbf{v}_1)$ and $\phi_2(\mathbf{v}_2)$ are its components. The scalar product $\langle\langle \cdots \rangle_1\rangle_2$ between two functions $\boldsymbol{\phi}(\mathbf{v}_1,\mathbf{v}_2)$ and $\boldsymbol{\phi}'(\mathbf{v}_1,\mathbf{v}_2)$ is defined by

$$\langle\langle \boldsymbol{\phi}(\mathbf{v}_1,\mathbf{v}_2), \boldsymbol{\phi}'(\mathbf{v}_1,\mathbf{v}_2)\rangle_1\rangle_2 = \int d^3v_1\, \phi_0(\mathbf{v}_1) \int d^3v_2\, \phi_0(\mathbf{v}_2) [\phi_1(\mathbf{v}_1)\phi_1'(\mathbf{v}_1) + \phi_2(\mathbf{v}_2)\phi_2'(\mathbf{v}_2)],$$

where $\phi_0(v_i)$ is the Maxwell velocity distribution for component i. We should note that actually the two particular functions $\psi_i(\mathbf{v}_1,\mathbf{v}_2;k)$ in $S_{ij}(k,\omega)$ are independent of $\mathbf{v}_1$ and $\mathbf{v}_2$, but for the sake of mathematical generality, we maintain the notation $\psi(\mathbf{v}_1,\mathbf{v}_2;k)$; their components are such that

$$\langle\langle \psi_i(\mathbf{v}_1,\mathbf{v}_2;k),\psi_j(\mathbf{v}_1,\mathbf{v}_2;k)\rangle\rangle_1\rangle_2 = S_{ij}(k),$$

where $S_{ij}(k)$ are the partial static structure factors. For details we refer to a later publication. The differential cross section for neutron scattering is proportional to a weighted average of the $S_{ij}(k,\omega)$:

$$d^2\sigma/d\omega\, d\Omega \sim x_1 b_1^2 S_{11}(k,\omega) + x_2 b_2^2 S_{22}(k,\omega) + 2(x_1x_2)^{1/2} b_1 b_2 S_{12}(k,\omega), \tag{1}$$

where b_i is the effective scattering length of a nucleus of the ith component.

The computation of the $S_{ij}(k,\omega)$ for the k values of interest here is performed by matrix inversion[9] or by a spectral decomposition of the time-evolution operator $L_E(\mathbf{k})$ in terms of discrete eigenmodes. The latter leads to an expression for $S_{ij}(k,\omega)$ as a sum of Lorentzians[5,9]:

$$S_{ij}(k,\omega) = \frac{1}{\pi}\,\mathrm{Re}\sum_n \frac{M_{ij}^{(n)}(k)}{i\omega - z_n(k)}, \tag{2}$$

where the sum runs over the eigenvalues $z_n(k)$ and the amplitudes $M_{ij}^{(n)}(k)$ can be expressed in terms of the eigenfunctions of $L_E(\mathbf{k})$. In our calculations we determined eight eigenmodes of the mixture on the basis of the Bernstein-Greene-Kruskal method.[5,9] The details will be given elsewhere.

The reduced eigenvalues, corresponding to the first two propagating eigenmodes—the ordinary sound mode and its extension, and a kinetic mode—are given in Fig. 1. These modes are plotted as functions of a reduced wave number for a He concentration $x_1 = 0.8$ and a reduced density $n^* = n_1\sigma_1^3 + n_2\sigma_2^3 = 0.4$, where the equivalent hard-sphere diameter of the He and Xe are taken to be $\sigma_1 = 2.163$ Å and $\sigma_2 = 4.801$ Å, respectively. To each propagating mode in Fig. 1 correspond two eigenvalues, which have the same negative real part, that ensures the damping out of the corresponding fluctuations, and imaginary parts with opposite signs, that represent propagation in opposite directions. In the following, the imaginary part of a mode is understood to be the absolute value of the imaginary part of its eigenvalues. For k sufficiently close to zero, there is only one propagating mode, corresponding to ordinary sound. However, for $k\sigma_{12} > k_c\sigma_{12} \approx 0.01$ $[\sigma_{12} = (\sigma_1+\sigma_2)/2]$, a second propagating mode appears, the imaginary part of which has a sudden steep increase in slope at $k\sigma_{12} \approx 0.6$, where a third propagating mode (not shown in Fig. 1) appears. For $k\sigma_{12} > 0.6$ the propagation velocity [ω/k or $d\omega(k)/dk$, where $\omega = \mathrm{Im}z$] of the second propagating mode is about 3 times that of the velocity of the extension of the sound mode in this k regime. This new propagating mode is a kinetic mode, because the real part of its eigenvalue does not vanish for $k \to 0$, contrary to the eigenvalues of the sound modes. From the corresponding coefficients $M_{ij}^{(n)}(k)$ one can deduce that the fast mode only occurs in component 1.

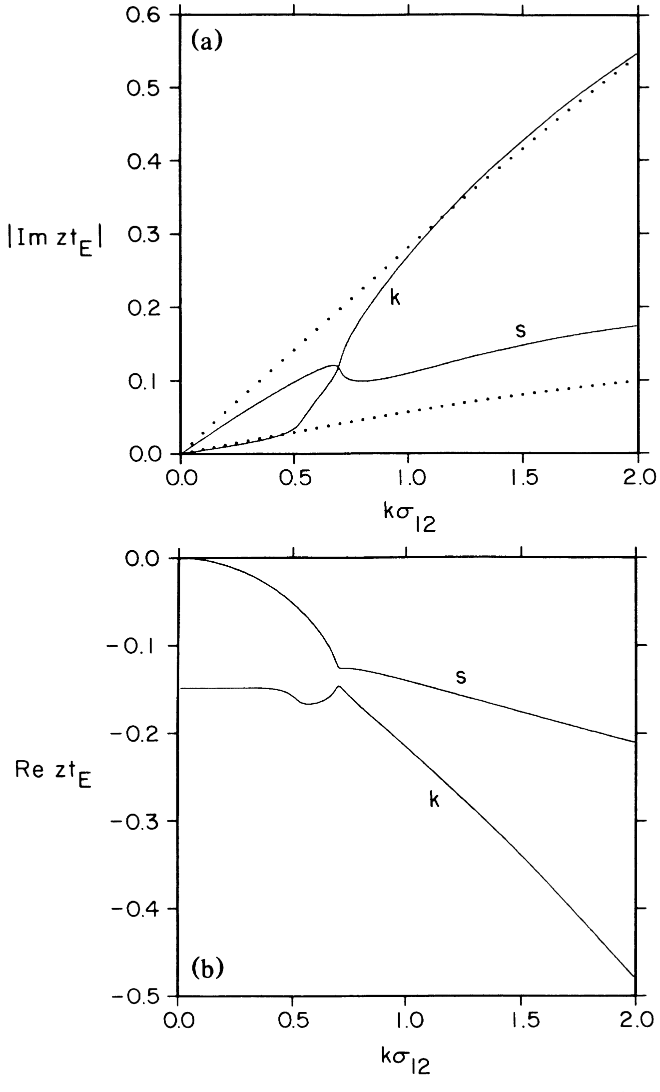

FIG. 1. Reduced eigenvalues of the first two propagating modes: (a) absolute value of imaginary part; (b) real part. t_E (Ref. 5) is the Enskog mean free time; $\sigma_{12} = (\sigma_1+\sigma_2)/2$; s, sound mode; k, kinetic mode. The dotted lines in (a) are the modes obtained by a 4×4 moment method (see text).

The propagating modes, in particular the fast propagating mode, manifest themselves directly in the correlation functions $S_{ij}(k,\omega)$. In Fig. 2, the partial correlation functions $S_{11}(k,\omega)$ and $S_{22}(k,\omega)$ are given in different approximations for a typical value $k\sigma_{12}=1.5$. Eight Lorentzians, i.e., eight eigenmodes or $n=8$ in Eq. (2), give a result identical to that obtained by matrix inversion. Approximation with six Lorentzians, leaving out the fast kinetic mode, clearly shows that the fast mode contributes only to S_{11}. The right-hand side of Eq. (1) is plotted in Fig. 3, where the large contribution of the fast kinetic mode to $S(k,\omega)$ is clearly visible.

We note that (at temperature $T=293$ K) the group velocity of the fast propagating mode is about 1.20×10^5 cm/s, very close to the sound velocity of 1.261×10^5 cm/s in a single-component fluid (at the same temperature) obtained by removal of all the Xe atoms from the mixture (ratio 0.95), but quite different from all the sound velocity of 0.77×10^5 cm/s in the mixture (ratio 0.61).

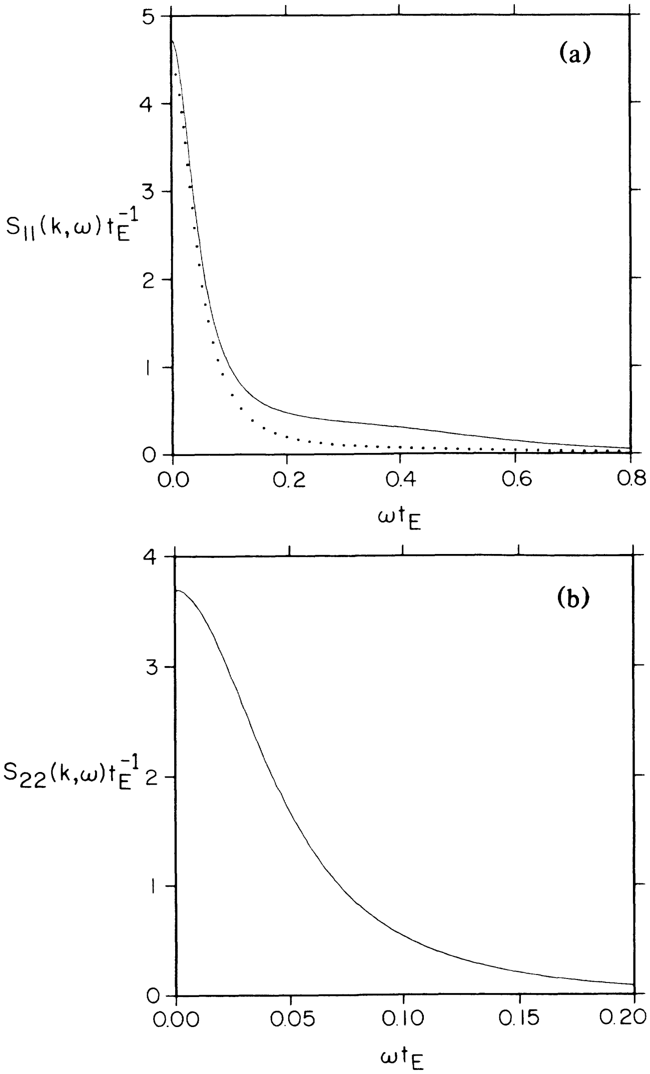

FIG. 2. Reduced partial dynamic structure factors as functions of the reduced frequency. (a) He (S_{11}): solid line, matrix inversion; dotted line, six Lorentzians without fast kinetic mode. (b) Xe (S_{22}): matrix inversion and six Lorentzians give the same curve.

Concluding, we make the following remarks:

(1) The partial dynamic structure factors $S_{ij}(k,\omega)$ can be determined experimentally by variation of the isotopic composition of the mixture. The detection of a shoulder in $S_{11}(k,\omega)$ and $S(k,\omega)$ but not in $S_{22}(k,\omega)$ at a frequency much higher than ck (c is the velocity of sound) would be an indication for a fast propagating mode.

(2) The above analysis for a hard-sphere model of the disparate-mass mixture shows that a kinetic fast mode is present over a wide range of densities ($0.1<n^*<0.5$) and concentrations ($0.6\leq x_1\leq 0.85$). One would expect these results also to obtain for actual He-Xe as well as for other disparate-mass mixtures (H_2-Xe, He-Ar) under comparable conditions, since a comparison of (pure) liquid argon with a corresponding hard-sphere fluid indicates that propagation is much more pronounced in liquid Ar than in the corresponding hard-sphere fluid, while damping is similar for the two fluids.[9-11]

(3) The fast-sound mode discussed here differs from the fast-sound mode discussed by Johnson and coworkers[2] in two respects: Here it concerns an eigenmode rather than a forced mode, and the k,ω regimes differ by 4 orders of magnitude.

(4) The connection with the model alloy $Li_{0.8}Pb_{0.2}$ discussed by Bosse *et al.* is that in that case the damping of the relevant eigenmodes appears to be much less than in our fluid mixtures. Consequently, the side peak in $S_{11}(k,\omega)$ is much more pronounced for the model alloy and an analysis considering only the propagating parts of the eigenmodes, or equivalently the $S_{ij}(k)$, is possible.[4] In fact, it can easily be shown that their calculation is equivalent to our using the moment method[12] in the Enskog kinetic theory, and one approximates the operator L_E by a 4×4 matrix that describes only the coupled fluc-

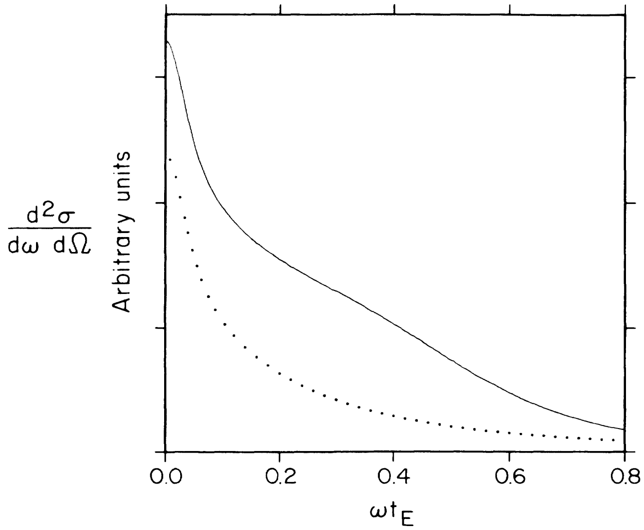

FIG. 3. Differential scattering cross section as a function of reduced frequency. Symbols as in Fig. 2(a).

tuations of the density and the longitudinal (component parallel to **k**) velocity of each component, but neglects the damping given by the collision terms in L_E.

The modes obtained this way are given in Fig. 1(a), where one sees that the fastest of the two modes is very close to our fast kinetic mode for $k\sigma_{12} > 1$. That one can obtain to a good approximation the propagating part of the fast mode, in the relevant k regime, in spite of the neglect of the collision term in the kinetic operator suggests again that a fast propagating mode could well be present in a large class of disparate-mass fluid mixtures.

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