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Kinetic-sound propagation in dilute gas mixtures

A. Campa and E. G. D. Cohen
The Rockefeller University, New York, New York 10021
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Kinetic sound is predicted in dilute disparate-mass binary gas mixtures, propagating exclusively in the light compound and much faster than ordinary sound. It should be detectable by light-scattering experiments, as an extended shoulder in the scattering cross section for large frequencies. As an example, H_2-Ar mixtures are discussed.

In a recent Letter[1] we reported the possibility of observing a fast kinetic eigenmode in disparate-mass binary fluid mixtures at moderately high densities through neutron-scattering experiments. The aim of this Rapid Communication is to point out that this phenomenon can be more easily observed performing light-scattering experiments on dilute binary gas mixtures in equilibrium. A previous suggestion of this was published in Ref. 2. The interest in this new phenomenon lies in that this appears to be the first time that a nonhydrodynamic eigenmode associated with a nonconserved quantity can be observed in a fluid. In addition, this eigenmode is not a collective mode in the sense of an ordinary sound mode, in that it propagates only in the light component, not involving the heavy component at all. Furthermore, this eigenmode is heavily damped, because it is associated with a nonconserved quantity, yet it propagates twice as fast as ordinary sound.

Our predictions are based on a hard-sphere model of the mixtures. This model has the advantage that a kinetic treatment is available and that for the densities considered here, corresponding to pressures p of $0<p<10$ bars, this model is expected to be a good model for the mixture.

Light-scattering experiments probe dynamical processes in the fluid; in fact, the differential cross section for light scattering is directly related to the correlations in space and time of the density fluctuations in the fluid. The quantities of interest here are the partial dynamic structure factors, the Fourier transforms of the density-density correlation functions, given by

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

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

$$\delta n_i(\mathbf{k},t)=\frac{1}{(N_i)^{1/2}}\sum_{p=1}^{N_i} e^{-i\mathbf{k}\cdot\mathbf{r}_p(t)} ,$$

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 and the angular brackets indicate an equilibrium average. 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,[3] which is approximated, in kinetic theory, by a single-particle operator $L_E(\mathbf{k})$.[4]

The differential cross section for light scattering is proportional to a weighted average of the $S_{ij}(k,\omega)$:

$$\frac{d^2\sigma}{d\omega\, d\Omega}\sim x_1a_1^2S_{11}(k,\omega)+x_2a_2^2S_{22}(k,\omega)+2\sqrt{x_1x_2}a_1a_2S_{12}(k,\omega) , \qquad (1)$$

where a_i and x_i are, respectively, the polarizability and the relative concentration of atoms (or molecules) of the ith component.

The computation of the $S_{ij}(k,\omega)$ is performed by matrix inversion or by a spectral decomposition of the time-evolution operator $L_E(\mathbf{k})$ in terms of discrete eigenmodes.[5,6] The latter leads to an expression for $S_{ij}(k,\omega)$ as a sum of Lorentzians:

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

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 $L_E(\mathbf{k})$.

The eigenvalues $z_n(k)$ are real for purely damped modes and complex for propagating modes. To each propagating mode correspond two eigenvalues with the same real part but with imaginary parts of opposite signs, representing propagation in opposite directions. In the following, the imaginary part of the eigenvalue of a propagating mode is understood to be the absolute value of the imaginary parts of its two eigenvalues. The modes can further be classified into hydrodynamic or kinetic modes, depending on whether their eigenvalues go to zero for $k\rightarrow 0$ or not, respectively.[1,5]

For a fast propagating kinetic mode to be present, in addition to the always present sound mode, it is necessary that the mass ratio of the heavy to the light component is significantly larger than 1 (disparate mass mixtures). However, in order to observe this mode, which propagates exclusively in the light component, it is also necessary that the polarizabilities of the heavy and the light components are comparable. In disparate-mass noble-gas mixtures, such as He-Xe and He-Kr, only $S_{22}(k,\omega)$ is practically observable in light-scattering experiments because of the large polarizability ratio ($a_{\mathrm{Xe}}/a_{\mathrm{He}}\approx 20$ and $a_{\mathrm{Kr}}/a_{\mathrm{He}}\approx 12$). A much more suitable mixture is therefore H_2-Ar, in which the mass ratio is very similar to He-Kr, but the polarizability ratio $a_{\mathrm{Ar}}/a_{\mathrm{H_2}}\approx 2$, i.e., such that the contribution to the differential cross section of $S_{11}(k,\omega)$ is of

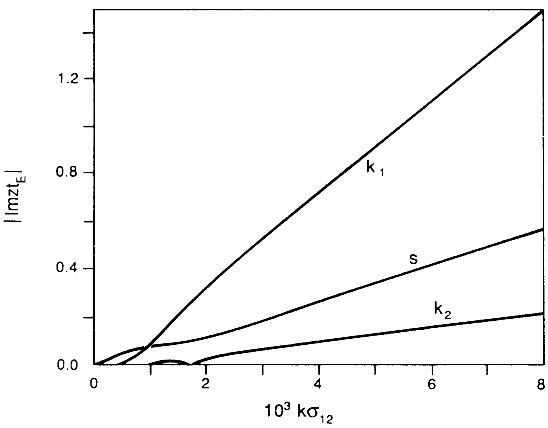

FIG. 1. Imaginary parts of the first few propagating eigenmodes: the sound mode (s) and two kinetic modes (k_1 and k_2); k_2 exhibits a propagation gap around $k\sigma_{12}=0.00175$. t_E is the Enskog mean-free time and $\sigma_{12}=(\sigma_1+\sigma_2)/2$.

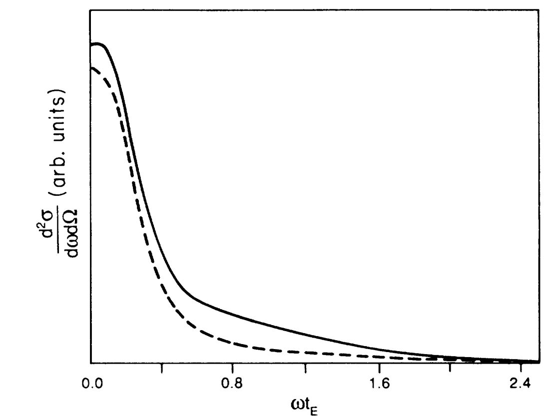

FIG. 3. Differential scattering cross section $d^2\sigma/d\omega d\Omega$ as a function of the reduced frequency: matrix inversion or eight Lorentzians (——); with six Lorentzians (---).

the same order as that of $S_{22}(k,\omega)$.

In Fig. 1 we plot the imaginary parts of the eigenvalues z_n of the first few propagating eigenmodes. The propagation velocities are $|\mathrm{Im} z_n|/k$. The modes are plotted as a function of a reduced wave number $k\sigma_{12}$ for a H_2 concentration $x_1=0.8$ and a typical reduced density $n^*=n_1\sigma_1^3+n_2\sigma_2^3=0.001$, corresponding to a pressure of about 1.5 atmospheres, where the equivalent hard-sphere diameters of H_2 and Ar are taken to be $\sigma_1=2.760$ Å and $\sigma_2=3.659$ Å, respectively, with $\sigma_{12}=(\sigma_1+\sigma_2)/2$. The results do not change appreciably when the density is varied, as long as one remains in the dilute gas regime. We see from Fig. 1 that one of the kinetic modes has, beyond a certain k value, a velocity of propagation much larger (by a factor 2) than that of the sound mode. From the corresponding coefficients $M_{ij}^{(n)}(k)$ one can deduce that this fast mode ($n=k_1$) only occurs in the light component.

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 $k\sigma_{12}=0.006$. Eight Lorentzians, i.e., eight eigenmodes [or $n=8$ in Eq. (2)], give a result indistinguishable from that obtained by matrix inversion. Approximating S_{11} by only six Lorentzians, leaving out the fast kinetic mode, clearly shows the important contribution of the fast mode to S_{11}, as opposed to S_{22}. The right-hand side of Eq. (1) is plotted in Fig. 3, where the large contribution of the fast kinetic mode to the scattering cross section is again clearly visible.

We note two important characteristics of Fig. 2, which could allow one to disentangle, at least approximately, the contribution of $S_{11}(k,\omega)$ to the differential cross section, in spite of the fact that the $S_{ij}(k,\omega)$ cannot be measured individually. First, the contribution of $S_{11}(k,\omega)$ to $d^2\sigma/d\omega d\Omega$ appears as a pronounced shoulder for the frequency range, in which the fast mode occurs. Second, computing $S_{\mathrm{Ar}}(k,\omega)$ for pure argon gas, at the same k value but at a density corresponding to $n_2\sigma_2^3$ (which would

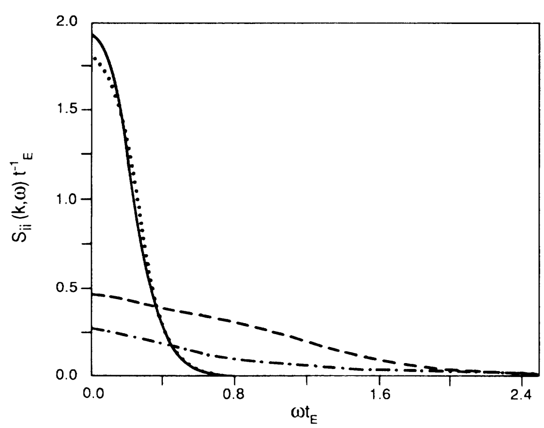

FIG. 2. Reduced partial-dynamic-structure factors as functions of the reduced density: S_{11} by matrix inversion or eight Lorentzians (---); S_{11} by six Lorentzians without fast kinetic mode (-·-·); S_{22} by matrix inversion or eight Lorentzians (——), which is identical to S_{22} using only six Lorentzians; $S_{\mathrm{Ar}}(k,\omega)$ in a pure argon fluid (····) (see text).

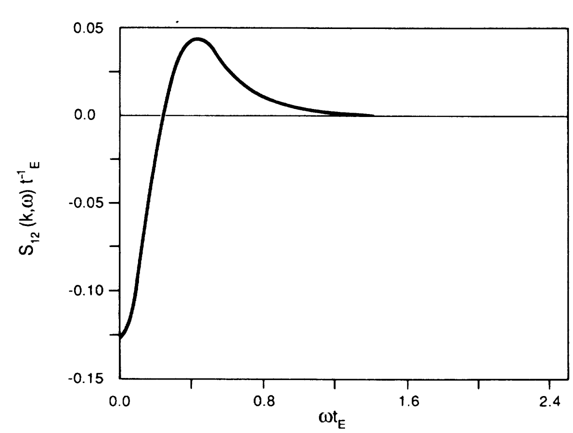

FIG. 4. Reduced cross partial dynamic structure factor as a function of the reduced frequency.

correspond to removing the H_2 molecules from the mixture), we found that $S_{Ar}(k,\omega)$ for pure argon as well as $S_{22}(k,\omega)$ in the mixture, are both different from zero in about the same ω range $0 \leq \omega t_E < 0.8$, that does *not* include the ω values relevant for the fast mode, $0.8 < \omega t_E < 2.4$. This is clearly another indication that, at least in this range of k and ω values and in this range of relative concentrations, where the fast propagating mode is present, the dynamics of the two components are partly decoupled. Thus, the heavy component is unable to follow the rapid oscillations of the light molecules due to the fast mode, and the presence of the light component does not influence the dynamical behavior of the heavy component. Moreover, at these densities, $S_{12}(k,\omega)$ is usually smaller in absolute value than $S_{11}(k,\omega)$ and $S_{22}(k,\omega)$ (see Fig. 4). This is to be expected, since the integral of $S_{12}(k,\omega)$ over the frequency gives $S_{12}(k)$, the static cross structure factor, which is a small quantity at low densities, since then $S_{12} \propto n^*$. Therefore, in a light-scattering experiment one could deduce the presence of a fast propagating mode from a side peak or a shoulder in the scattering cross section, and by estimating the contribution of $S_{22}(k,\omega)$ in the manner outlined above, it would be possible to assign this mode uniquely to the light component.

Our conclusions are the following.

(1) We predict that fast sound will be present in dilute binary (disparate-mass) gas mixtures, at high concentrations of the light component.

(2) It is, in principle, possible by light-scattering experiments to detect the fast mode and to see that it contributes to the dynamical processes of the light component only. In order to attain this, it is necessary to perform experiments with mixtures, where the polarizability of the heavy component is not much larger than that of the light component.

(3) Since a similar fast sound mode has been predicted for disparate-mass liquid mixtures,[1] one could wonder whether such a mode would not also exist in disparate mass solid mixtures. One would then have fast phonons propagating exclusively in the light component with a velocity greater than the sound velocity of the mixture.

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