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Observation of Fast Sound in Disparate-Mass Gas Mixtures by Light Scattering

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We performed light-scattering experiments on a mixture of hydrogen and argon. By varying the density of the sample, we can probe the range of reduced wave vectors in which Campa and Cohen [Phys. Rev. A **39**, 4909 (1989)] predicted, in dilute disparate-mass gas mixtures, the onset of a mode supported by the light particles: the fast sound mode. The presence of the additional sound mode can be established most conveniently by analyzing $\omega^2 I(k,\omega)$ rather than $I(k,\omega)$. Our results for the shift of fast and slow sound match the theoretical predictions very well.

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Recent investigations have revealed a sound mode which, at sufficiently large wave vectors, is carried by the lightest particles only. This mode is often referred to as "fast sound." Bosse *et al.*[1] were the first who identified this phenomenon. In their molecular-dynamics study of $Li_{0.8}Pb_{0.2}$, they have shown that the partial dynamic structure factor of the lithium particles exhibits a distinct peak at a frequency which is much higher than that of the ordinary sound mode. The other partial dynamic structure factors are featureless at the fast sound frequency, indicating that the effect is due to dynamical processes in lithium only. More recent work concerning the fast sound mode include kinetic calculations,[2,3] new molecular-dynamics simulations,[4] and the first experimental observation of fast sound by neutron scattering.[5] Most of this work is restricted to mixtures at liquid densities. However, Campa and Cohen have pointed out that a fast sound mode is also to be expected in dilute gas mixtures, and that it can be measured by light-scattering spectroscopy.[6] In this Letter we will present the first experimental results concerning fast sound in dilute gas mixtures.

The relation between a light-scattering spectrum and the partial dynamic structure factors $S_{ij}(k,\omega)$ is given by

$$\begin{aligned} I(k,\omega) \sim{} & \alpha_1^2 x_1 S_{11}(k,\omega) \\ & + 2\alpha_1\alpha_2 (x_1 x_2)^{1/2} S_{12}(k,\omega) \\ & + \alpha_2^2 x_2 S_{22}(k,\omega) . \end{aligned} \qquad (1)$$

Here x_i represents the mole fraction of component i. From Eq. (1) it is evident that the spectral line shape $I(k,\omega)$ is affected by the partial dynamic structure factor of the light component only when the polarizability $\alpha_{\rm light}$ is not too small. Therefore our experiments are performed on a gas mixture with a small polarizability ratio: $H_2 + Ar$ $(\alpha_{Ar}/\alpha_{H_2} \approx 2)$.[6]

In our experiments we use an argon-ion laser operating single mode at a wavelength of 514.5 nm and at an output power of 200 mW. A Fabry-Perot interferometer analyzes light scattered under an angle of 90°. The free spectral range of the interferometer is 1.00×10^{11} rad/s and its finesse is 40. Details of the setup can be found elsewhere.[7,8] The experiments are performed at room temperature $(T = 292$ K).

We have studied light-scattering spectra of a $H_2 + Ar$ mixture with $x_{Ar} = 0.23 \pm 0.02$ in the pressure range 0.1 MPa $< p <$ 4.78 MPa. In earlier studies[7-10] we have shown that the eigenvalues of the hydrodynamic matrix, which determine the shape of $I(k,\omega)$ for small wave vectors, are a function of the product of wave vector k and mean free path l. We will use the mean free path of a hydrogen molecule:

$$l_{H_2} = [\pi n \{ x_{Ar} \sigma^2_{ArH_2} (m_{H_2}/m_{\rm red})^{1/2} + \sqrt{2} x_{H_2} \sigma^2_{H_2} \}]^{-1} , \qquad (2)$$

with $\sigma_{Ar} = 0.3659$ nm, $\sigma_{H_2} = 0.2760$ nm,[6] $\sigma_{ArH_2} = (\sigma_{Ar} + \sigma_{H_2})/2$, and $m_{\rm red}$ represents the reduced mass $m_{\rm red} = m_{Ar} m_{H_2}/(m_{Ar} + m_{H_2})$. It should be noted that the mean free path is inversely proportional to the number

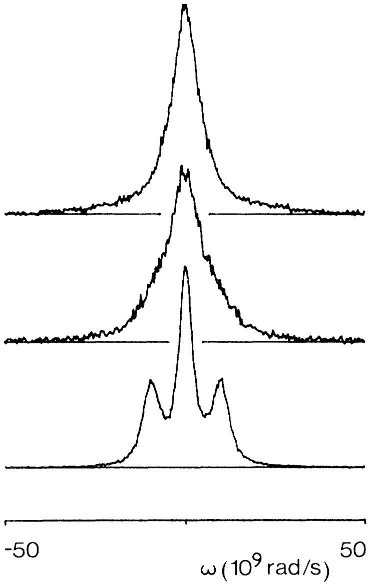

FIG. 1. $I(k,\omega)$ at fixed k at various thermodynamic circumstances. From bottom to top: $kl_{H_2}=0.04$ ($p=4.78$ MPa), $kl_{H_2}=0.21$ ($p=0.88$ MPa), and $kl_{H_2}=1.87$ ($p=0.10$ MPa).

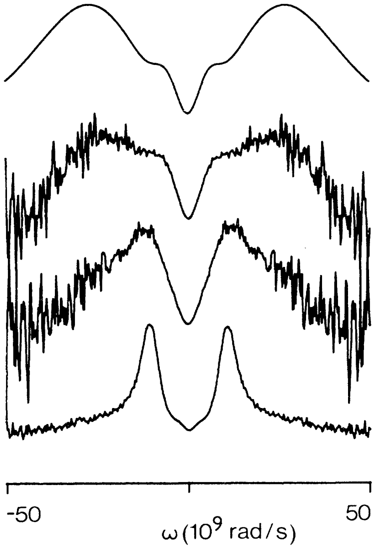

FIG. 2. $\omega^2 I(k,\omega)$ at fixed k at various thermodynamic circumstances. From bottom to top: $kl_{H_2}=0.04$, $kl_{H_2}=0.21$, $kl_{H_2}=1.87$, and the limit $kl_{H_2}\rightarrow\infty$.

density n. Then, using this scaling property it is possible to obtain "dispersion relations" over a larger range of kl_{H_2} values than is possible by varying the wave vector through the scattering angle only. In particular, we are interested in the way in which quantities that can be extracted from $I(k,\omega)$ will deviate from their $k\rightarrow 0$ values as the reduced wave vector kl_{H_2} increases.

In Fig. 1 we show light-scattering spectra of H_2+Ar mixtures at various densities. It is clear that spectra taken at low pressures appear rather featureless due to excessive broadening. The broad wings serve as a qualitative indication of the occurrence of fast sound. The exact shape of the wings can be studied in more detail when spectral line shape is multiplied by ω^2. The function $\omega^2 I(k,\omega)$ is closely related to the longitudinal current-current autocorrelation function.[11] This function has well-defined peaks for all wave vectors, even when the Brillouin lines are no longer discernible. In our study of He+Xe mixtures we have shown that in the hydrodynamic region the peak position in $\omega^2 I(k,\omega)$ follows closely the wave-vector dependence of the propagation frequency of the sound mode.[7,8] In the limit of very large wave vectors the spectral line shape $I(k,\omega)$ can be represented by a sum of two Gaussians due to the velocity distributions of the two species of particles.[11] As a result $\omega^2 I(k,\omega)$ can become a doubly peaked function with maxima near $\pm v_{H_2}k\sqrt{2}$ and $\pm v_{Ar}k\sqrt{2}$, where v_i represents the thermal velocity of component i: $v_i=(k_B T/m_i)^{1/2}$. It depends on the composition of the mixture and the polarizabilities of the components whether or not both maxima can be detected simultaneously in a light-scattering experiment.

In Fig. 2 some examples of the function $\omega^2 I(k,\omega)$ are shown typical for the various kl_{H_2} regions. At high densities (i.e., small kl_{H_2}) a peak of $\omega^2 I(k,\omega)$ is located at a frequency that is slightly higher than the shift of the Brillouin lines. We will refer to the absolute maximum of $\omega^2 I(k,\omega)$ as $\omega_{m,1}(k)$. From Fig. 2 it is evident that as the density decreases high-frequency contributions to $\omega^2 I(k,\omega)$ become more pronounced. For the region $kl_{H_2}>0.35$ the function $\omega^2 I(k,\omega)$ consists of two unresolved contributions. We will refer to the peak position of the low-frequency contribution as $\omega_{m,2}(k)$. At the largest reduced wave vector probed, the high-frequency contribution at $\omega_{m,1}(k)$ is centered near $\pm v_{H_2}k\sqrt{2}$, while the low-frequency contribution at $\omega_{m,2}(k)$ is centered around the frequency which corresponds to the thermal velocity of pure argon. For comparison we also show the calculated shape of $\omega^2 I(k,\omega)$ in the limit of very large wave vectors. It can be seen that the experimental line shape of $\omega^2 I(k,\omega)$ converges to the line shape which corresponds to the large wave-vector limit of $I(k,\omega)$, although it never reaches it in the density regime we have studied.

In Fig. 3 we have plotted the behavior of $\omega_{m,1}^*(k)$ and $\omega_{m,2}^*(k)$ as a function of the reduced wave vector. Throughout this Letter quantities that are labeled with a superscript * are reduced with respect to $c_s k$, where $c_s=579$ m/s is the experimentally determined value of the adiabatic sound velocity of the mixture in the limit $kl_{H_2}\rightarrow 0$. We can extract $\omega_{m,1}^*(k)$ throughout the full kl_{H_2} range and we observe that its value increases with increasing reduced wave vector. On the other hand, $\omega_{m,2}^*(k)$ can be extracted for $kl_{H_2}>0.35$ only, and in

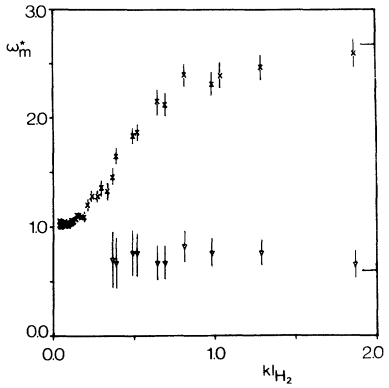

FIG. 3. The reduced peak positions of $\omega^2 I(k,\omega)$ as a function of the reduced wave vector. The horizontal bars indicate frequencies that correspond to the thermal velocities of hydrogen and argon. ×, $\omega^*_{m,1}(k)=\omega_{m,1}(k)/c_s k$; ∇, $\omega^*_{m,2}(k)=\omega_{m,2}(k)/c_s k$.

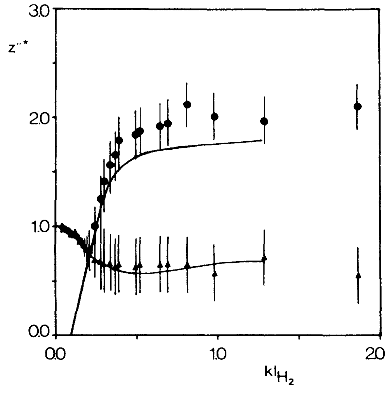

FIG. 4. The reduced propagation frequencies $z_s''^*(k)$ and $z_f''^*(k)$ as a function of the reduced wave vector. The drawn lines are extracted from Fig. 1 of Ref. 6. △, $z_s''^*(k)=z_s''(k)/c_s k$; ●, $z_f''^*(k)=z_f''(k)/c_s k$.

that range it does not show much dispersion. Such behavior is not found for He+Xe mixtures.[7,8] For these mixtures (polarizability ratio $\alpha_{\mathrm{Xe}}/\alpha_{\mathrm{He}} \approx 20$) the light-scattering spectrum is dominated by the contributions from the fluctuations in the xenon density. As a result only one contribution can be observed in the shape of $\omega^2 I(k,\omega)$. In He+Xe mixtures we have found that the position of the peak in $\omega^2 I(k,\omega)$ shifts to lower frequencies as the reduced wave vector increases.[7,8] The qualitatively different behavior of the peak positions of $\omega^2 I(k,\omega)$ in H_2+Ar indicates that a fast sound mode is indeed observed in this mixture.

Having thus established the existence of two contributions for large kl_{H_2}, we proceed to a detailed analysis of the spectrum itself. We are now looking for the frequencies of the propagating modes which can be compared with the calculations of Campa and Cohen.[6] To this end, we fitted our light-scattering spectra by a convolute of the experimentally determined instrumental profile and a sum of Lorentzians:

$$I(k,\omega)=I_{\mathrm{instr}}(\omega)*\mathrm{Re}\left[\sum_j A_j/(i\omega-z_j)\right], \qquad (3)$$

where $j=D,s\pm,f\pm$ and A_j represents the wave-vector-dependent amplitude of the jth eigenmode and z_j the wave-vector-dependent jth eigenfrequency. The eigenfrequencies $z_{s\pm},z_{f\pm}$ of the sound mode and the fast sound mode and the corresponding amplitudes are complex: $z_{i\pm}=z_i'\pm iz_i''$ and $A_{i\pm}=A_i'\pm iA_i''$. The imaginary part of the complex frequency z_i is the propagation frequency of eigenmode i. It can be seen that Eq. (3) reduces to the well-known expression for the Rayleigh-Brillouin triplet[11] when the amplitudes of the fast sound mode $A_{f\pm}=0$. In our fitting procedure we have used the sum rule $\sum_i A_i z_i=0$,[7,8,12] and we have taken into account the shape of $I(k,\omega)$ as well as the shape of $\omega^2 I(k,\omega)$. For small reduced wave vectors we have found that $I(k,\omega)$ and $\omega^2 I(k,\omega)$ can be fitted well with the expression of the Rayleigh-Brillouin triplet (i.e., $A_{f\pm}=0$). However, for large reduced wave vectors it is necessary to use a second propagating mode in order to analyze $\omega^2 I(k,\omega)$.

In Fig. 4 we have plotted in the reduced wave-vector dependence of the reduced propagation frequencies $z_s''^*(k)$ and $z_f''^*(k)$, which we have extracted from our experiments. For $kl_{H_2}<0.25$ only one propagating mode can be distinguished, while at high kl_{H_2} there are obviously two propagating modes. In the limit of small reduced wave vectors, the eigenfrequency of the propagating mode equals the produce of the wave vector and the adiabatic sound velocity of the mixture. It can be seen that this eigenfrequency becomes smaller as the reduced wave vector increases. Around $kl_{H_2}=0.3$ a second propagating mode emerges. However, it is not possible to determine unambiguously the kl_{H_2} value at which this happens since the error bars in the frequencies and amplitudes are rather large in this kl_{H_2} region. For $kl_{H_2}>0.35$, the two eigenfrequencies are well separated. For $kl_{H_2}=1.87$ we find that $z_{f\pm}''/k=1214$ m/s and $z_{s\pm}''/k=317$ m/s. These values of $z_{f\pm}''/k$ and $z_{s\pm}''/k$ are close to the adiabatic sound velocities calculated for pure hydrogen ($c_x=1306$ m/s) and pure argon ($c_x=318$ m/s),[13] respectively. Therefore, we conclude that the fast sound mode propagates mainly through the hydrogen, while the slow sound mode propagates through the argon. Our experiments show that the slow sound mode is a continuation of the hydrodynamic sound mode. This behavior of the sound mode is similar to that of the only sound mode that can be detected in He+Xe mixtures. For the H_2+Ar mixture we find, in addition to this slow sound mode, a fast sound mode emerging in the wave-vector region in which Navier-Stokes hydrodynamics[7,10,14] ceases to be valid.

In Fig. 4 we compare our experimental results with the calculations of Campa and Cohen.[6] We find a good correspondence to their sound mode (in Ref. 6 labeled with s) and their kinetic mode (in Ref. 6 labeled with k_1). The small quantitative differences might be explained by two effects. First, the composition of the mixture in our experiments was slightly different from that in the calculations of Campa and Cohen. Second, the neglect of internal degrees of freedom in hydrogen might cause subtle deviations in propagation frequencies and amplitudes of the sound modes.[15,16]

We conclude that our experiments give evidence for the existence of a fast sound mode in dilute disparate-mass gas mixtures. Our results concerning $\omega^2 I(k,\omega)$ show clearly that the manifestation of a fast sound mode is related to a decoupling of the eigenmodes which occurs as the limit is approached in which $I(k,\omega)$ reflects the dynamics of individual particles. Such a decoupling might be expected in any mixture with components which differ in mass. However, a fast sound mode can be detected more clearly when the difference in mass becomes larger, though for observation by light scattering it is essential that the difference in the polarizability of the components is not too large. Therefore, a less favorable polarizability ratio must be compensated by the mass ratio. As an example, we have performed light-scattering experiments on a mixture of H_2+Xe ($x_{\mathrm{Xe}}=0.17\pm0.02$, $\alpha_{\mathrm{Xe}}/\alpha_{\mathrm{H}_2}=5$, $m_{\mathrm{Xe}}/m_{\mathrm{H}_2}=65$). These experiments have revealed for large reduced wave vectors a shape of $\omega^2 I(k,\omega)$ in which the contributions of hydrogen and xenon are well resolved. We will present a further analysis of this system in the future.

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[1] J. Bosse, G. Jacucci, M. Ronchetti, and W. Schirmacher, Phys. Rev. Lett. **57**, 3277 (1986).

[2] A. Campa and E. G. D. Cohen, Phys. Rev. Lett. **61**, 853 (1988).

[3] P. B. Lerner and I. M. Sokolov, Physica (Amsterdam) **150C**, 465 (1988).

[4] W. Montfrooij, P. Westerhuijs, and I. M. de Schepper, Phys. Rev. Lett. **61**, 2155 (1988).

[5] W. Montfrooij, P. Westerhuijs, V. O. de Haan, and I. M. de Schepper, Phys. Rev. Lett. **63**, 544 (1989).

[6] A. Campa and E. G. D. Cohen, Phys. Rev. A **39**, 4909 (1989).

[7] H. M. Schaink, thesis, University of Amsterdam, 1989 (unpublished).

[8] G. H. Wegdam and H. M. Schaink, Phys. Rev. A (to be published).

[9] H. M. Schaink and G. H. Wegdam, Physica (Amsterdam) **141A**, 211 (1987); **160A**, 117 (1989).

[10] G. H. Wegdam and H. M. Schaink, Mol. Phys. **65**, 531 (1988).

[11] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

[12] I. M. de Schepper, P. Verkerk, A. A. van Well, and L. A. de Graaf, Phys. Rev. Lett. **50**, 974 (1983).

[13] These values for the adiabatic sound velocity are calculated using the equation of state for ideal gases which is valid within 2% in this density range. For hydrogen we have included the contributions of the internal degrees of freedom using a phenomenological equation given by W. J. Moore, *Physical Chemistry* (Longman, London, 1972), p. 68.

[14] C. Cohen, J. W. H. Sutherland, and J. M. Deutch, Phys. Chem. Liq. **2**, 213 (1971).

[15] M. Hubert and A. D. May, Can. J. Phys. **55**, 23 (1977).

[16] J. van der Elsken and A. Bot, J. Appl. Phys. **66**, 2118 (1989).