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Fast and slow sound in binary fluid mixtures

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Abstract. We present new data on H_2 + Xe mixtures that support the existence of a fast sound mode in binary gas mixtures. In addition we show that using an approriate scaling, the behaviour of the slow sound mode in systems with different mass ratios, i.e. H_2 + Xe, H_2 + Ar and He + Xe, is identical.

In their theoretical work on binary disparate mass fluid mixtures Campa and Cohen [1–3] predicted the existence of a fast sound mode in liquids as well as in gases. Their paper triggered a considerable amount of experimental work which confirmed their results: both in liquid noble gas mixtures (He + Ne [4]) and gaseous mixtures (H_2 + Ar [5–7]) fast sound modes were observed. In addition, slow sound modes were identified in binary gas mixtures (He + Xe [8–10] and H_2 + SF_6 [6]).

Since the fast sound mode contributes only to the partial structure factor of the light species, Campa and Cohen [2] concluded that the wave is carried by the light particles. The partial structure factor of the heavy species is characterized by a slow propagating mode [10]. These two propagating modes can exist from a minimum value of the wave vector up to higher values. This minimum value is given roughly by the condition $kl \approx 1$, where l is a suitable chosen mean free path for the mixture and k is the wave vector of the density fluctuations probed. The picture that emerges is a decoupling of the dynamics of both components at high wave vectors. It seems as if the system consists of two subsystems—the heavy and light particles respectively—each carrying their own sound mode. The two modes have propagation velocities that tend towards values approximately equal to the sound velocities of the pure components. At high reduced wave vectors the propagation velocities are roughly independent of kl. The presence of the other component is visible only through an enhanced attenuation of the sound modes with respect to the attenuation in the pure system. This causes a considerable broadening of the spectral features.

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

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

where x_i is the mole fraction and α_i is the polarizability of component i. By a careful

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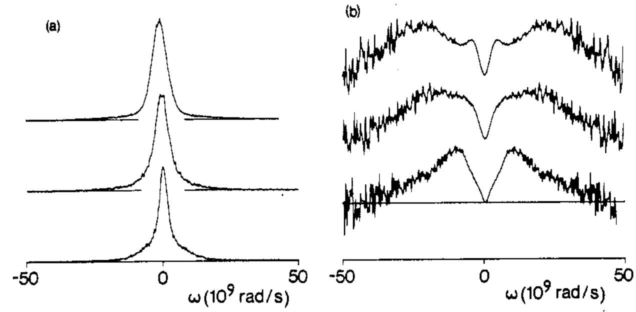


Figure 1. (*a*) Three Rayleigh–Brillouin spectra of H_2 + Xe, $x_{Xe} = 0.17$. Thermodynamic circumstances from bottom to top: $P = 2.65$ MPa, $p = 1.17$ MPa and $p = 0.05$ MPa ($T = 294$ K). (*b*) The longitudinal current autocorrelation function ($= \omega^2 I(k, \omega)$) of the H_2 + Xe spectra. Thermodynamic circumstances as in figure 1(*a*).

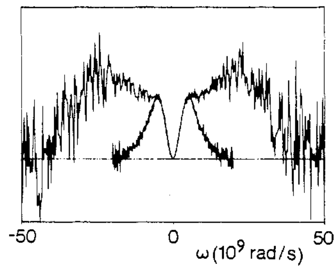
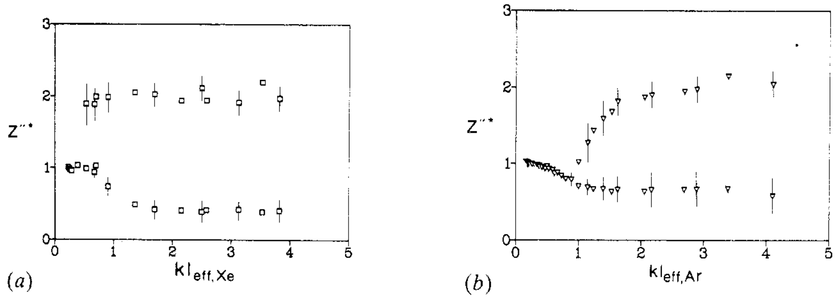


Figure 2. Current autocorrelation functions of H_2 + Xe, $x_{Xe} = 0.17$ (outer spectrum) and He + Xe, $x_{Xe} = 0.22$ (inner spectrum). The spectra were recorded at the same temperature, $T = 294$ K, and the same partial xenon pressure, $p_{Xe} = 0.17$ MPa.

choice of masses, polarizabilities and mole fractions of the constituents it is possible to observe a slow and a fast sound mode. We have performed light scattering experiments on He + Xe, H_2 + Ar and H_2 + Xe. In this paper we will focus mainly on the results of the H_2 + Xe system. Results of the other two systems as well as details of the experimental set-up can be found in [5] and [9].

In our experiments the scattering angle is kept constant (90°) and the pressure, i.e. the mean free path, is varied. The spectra and the quantities derived from them are represented as a function of the reduced wave vector $kl_{\mathrm{eff},i}$, where i refers to the heavy component. The effective mean free path we use is the ordinary mean free path of the heavy particles between collisions, corrected for the persistence of velocity. Details on scaling behaviour can be found elsewhere [11].

In figure 1(*a*) we show some typical light scattering spectra of a H_2 + Xe mixture. The existence of two propagating modes is not directly evident. The exact shape of the wings can be studied in more detail when the spectral line shape has been multiplied by ω^2, as is shown in figure 1(*b*). By performing this multiplication a Lorentzian located at $\omega = 0$ cannot lead to a maximum in $\omega^2 I(k, \omega)$ for finite ω. Therefore, any maxima in the current autocorrelation function $\omega^2 I(k, \omega)$ must be associated with a shifted Lorentzian. At low densities, that is at high reduced wave vectors, a second local maximum occurs in the current autocorrelation function. This can be considered an even more convincing proof of the occurrence of two sound modes at high wave vectors than in the case of H_2 + Ar [5]. The fact that the high frequency part is due to the hydrogen contribution to the spectrum is illustrated in figure 2, where $\omega^2 I(k, \omega)$ for a H_2 + Xe mixture and for a He + Xe ($\alpha_{He}/\alpha_{Xe} \approx 0.05$, whereas $\alpha_{H_2}/\alpha_{Xe} \approx 0.2$), only the contribution of Xe to the current autocorrelation function can be observed for He + Xe mixtures.



(*a*) (*b*)

Figure 3. (*a*) Reduced eigenvalues, $z''^* = z''_j/c_s k$, of the fast and slow modes of H_2 + Xe, $x_{Xe} = 0.17$, $c_s k = 7.65 \times 10^9$ rad s^{-1}. (*b*) As (*a*) but for H_2 + Ar, $x_{Ar} = 0.23$, $c_s k = 1.00 \times 10^{10}$ rad s^{-1}.

The propagation frequencies of the spectrum were extracted from our data by fitting our light scattering by a convolution of the experimentally determined instrumental profile and a sum of Lorentzians [9]:

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

where A_j and z_j are the amplitude and the eigenvalue of the jth mode. The subscript j stands for D, s±, f±; the diffusive, the slow and the fast propagating modes, respectively. The imaginary part of z_s and z_f are the propagation frequencies of the slow and the fast sound mode. The spectrum as well as the current autocorrelation function are used in our fitting procedure. We did not take into account any contribution from the internal degrees of freedom, such as a Mountain line [12]. The results of the fits are shown in figure 3. We have plotted

$$z''^*_j = z''_j/(c_s k)$$

where j = s, f and $c_s k$ is the $k \to 0$ limit of z''_s. For high values of the reduced wave vector two propagating sound modes exist. Like in the He + Xe experiments it seems that the slow sound mode is a continuation of the ordinary hydrodynamic sound mode [9, 10]. The fast sound mode appears at roughly $kl_{\text{eff},i} = 0.8$, which coincides with the value at which hydrodynamic theory ceases to be valid [7, 11]. The propagation velocity of the fast mode tends towards a value somewhat lower than the adiabatic sound velocity of pure hydrogen. The propagation frequency of the slow sound mode equals $c_{\text{s,heavy}}k$ for large reduced wave vectors, where $c_{\text{s,heavy}}$ is the adiabatic velocity of sound for the neat heavy component. The results on H_2 + Ar and H_2 + Xe showed similar behaviour. In order to compare the slow sound modes of these systems, with different mass ratios and concentrations, we have plotted in figure 4 the propagation frequency reduced according to

$$\tilde{z}''_s = (z''_s/k - c_{\text{s,heavy}})/(c_s - c_{\text{s,heavy}})$$

where c_s is the experimental adiabatic sound velocity of the mixture. The propagation frequencies for the three systems collected in this graph coalesce onto a single curve. We omitted the error bars for clarity, but the deviations of the H_2 + Ar data are within experimental uncertainty.

We have examined the scaling behaviour of the fast sound mode as well. The results were not as convincing as for the slow mode, but here a note of caution should be made: (i) we used only hydrogen as a light component, so no comparison (like with the slow

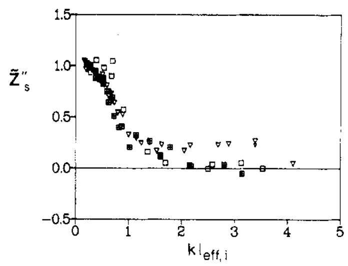


Figure 4. Reduced eigenvalues of the slow modes of three systems: (⊞) He + Xe, $x_{Xe} = 0.45$, (□) H_2 + Xe, $x_{Xe} = 0.17$ and (▽) H_2 + Ar, $x_{Ar} = 0.23$.

mode scaling) can be made, (ii) the internal degrees of freedom of H_2 were not taken into account, (iii) although the fitting procedure renders accurate results in the high and low kl regions, the number of parameters involved affects the reliability of the fitting results around $kl_{\mathrm{eff},i} = 0.8$.

The analysis of the slow sound mode in this system showed that its behaviour is similar to the behaviour of the slow sound mode in He + Xe and H_2 + Ar. Striking is the fact that, using an appropriate scaling procedure, the results for the slow sound mode of He + Xe, H_2 + Ar and H_2 + Xe can be reduced to a single curve. Our results confirm the theoretical predictions [5] and the physical picture outlined by Campa and Cohen [2].

Acknowledgments

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