# Rayleigh-Brillouin light-scattering study of both fast and slow sound in binary gas mixtures

R. P. C. Schram and G. H. Wegdam<sup>\*</sup>

Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, NL-1018 WS Amsterdam, The Netherlands

Arjen Bot

# FOM-Institute for Atomic and Molecular Physics, P.O. Box 41883, NL-1009 DB Amsterdam, The Netherlands (Received 8 July 1991)

We present Rayleigh-Brillouin scattering results of  $H_2+Ar$ ,  $H_2+Xe$ , and He+Xe mixtures that support the existence of fast and slow sound in binary gas mixtures. An experimental dispersion relation of both the fast and slow sound modes is given. The approach to the Gaussian limit is also investigated. An alternative characteristic length scale is used as the scaling parameter of the sound modes. This length scale proved to be a proper choice as a scaling parameter of the dispersion relation of different gas mixtures.

PACS number(s): 05.20. - y, 33.20.Fb, 51.70. + f, 78.35. + c

# I. INTRODUCTION

When Brillouin derived the formula that predicted a shift in frequency of scattered light with respect to the incoming light [1], his results were received with skepticism [2]. It took more than 15 years before his predictions were verified experimentally by Gross [3]. Gross was not only the first to observe the so-called Brillouin lines, he was also the first who claimed to have observed multiple sound modes. With respect to that last point his experiments turned out to be incorrect [4], and it would take almost 60 years before new claims would be made about the observation of more than a single bulk sound mode in a Rayleigh-Brillouin light-scattering spectrum of a fluid [5]. This time, however, there was a sound physical basis for such an assertion. Recent developments in the fields of computer simulations, kinetic theory, neutron scattering, and light scattering contributed to this basis.

First of all, Bosse *et al.* [6] performed simulations on a liquid Li+Pb alloy, and found, unexpectedly, indications for the existence of a fast-propagating collective mode of the Li particles. The propagation velocity of this mode was more than three times larger than the ordinary sound velocity of the mixture. The subsequent theoretical work by Campa and Cohen was the important breakthrough. They showed that calculations based on revised Enskog theory predicted a fast sound mode in dense He+Xe mixtures [7,8]. Later they were able to show that fast sound should also occur in low-density gas mixtures [8,9]. These results suggested that the existence of fast sound is a general property of both high- and low-density binary fluid mixtures [8].

The calculations triggered a considerable amount of additional work. Montfrooij, Westerhuijs, and de Schepper performed a molecular-dynamics simulation on a dense He+Ne mixture [10] and observed fast sound. Later they were the first to present experimental evidence of fast sound from neutron-scattering experiments on a dense He+Ne mixture [11]. In their experimental paper, they suggested that the negative dispersion observed in He+Xe gas mixtures by Schaink and Wegdam [12,13] could be the onset of slow sound: a sound mode to which only the heavy particles contribute. The existence of both sound modes was demonstrated for a H<sub>2</sub>+Ar gas mixture by our group [5]. We observed a fast sound mode and also a heavily damped slow sound mode for large reduced wave vectors. Independently, Clouter *et al.* [14] showed the existence of fast sound in H<sub>2</sub>+Ar and of slow sound in H<sub>2</sub>+SF<sub>6</sub>. More recently, we added preliminary results on H<sub>2</sub>+Xe mixtures [15].

We investigated binary mixtures of  $H_2+Ar$  and  $H_2+Xe$  at different compositions and established the dispersion relations of the propagating modes. In this paper we present these results and our attempts to find the scaling parameters—for frequency and wave vector—to scale the dispersion relations onto a single curve independent of kind and composition of the mixture. A proper length scale, the so-called effective mean free path, was found by us and suggested in an earlier publication [16].

The relatively simple picture that emerges from these experiments confirms the suggestion of Campa and Cohen [9]. At small wave vectors the system behaves as a homogeneous mixture with just one propagating sound mode. From certain wave vectors on, the system decouples dynamically and two propagating modes are observed: a slow sound mode supported by the heavy particles and a fast mode carried mainly by the light particles. Kinetic calculations on binary fluid mixtures point out that this behavior appears to be quite general and should appear in any disparate-mass mixture provided the mass difference is large enough [8].

The outline of this paper is as follows. In Sec. II we will discuss in what way the polarizability influences the observability of the fast and slow sound modes. In Sec. III we discuss the  $kl \rightarrow 0$  and  $kl \rightarrow \infty$  limit of the light-scattering spectrum and which mean free path is the appropriate scaling length for the sound dispersion relations. In Sec. IV we present some experimental details.

44

TABLE I. Parameters used in the calculations of Eqs. (7) and (11). The hard-sphere diameters  $\sigma$  are obtained from Campa [38]. The polarizability volumes are taken from Burns, Graham, and Weller [39], except for hydrogen [40].

Component	$\sigma$ (nm)	<i>m</i> (g/mol)	$\alpha (10^{-30} \text{ m}^3)$
He	0.2163	4.003	0.2069
$H_2$	0.2760	2.016	0.8051
Ār	0.3659	39.95	1.674
Xe	0.4801	131.30	4.170

Section V is dedicated to data analysis and our experimental results. Discussion and conclusions can be found in Secs. VI and VII.

## **II. OBSERVABILITY OF THE SOUND MODES**

The scattering intensity  $I(k,\omega)$  for a binary mixture is given by

$$I(k,\omega) \propto xa^{2}S_{11}(k,\omega) + 2x^{1/2}aS_{12}(k,\omega) + S_{22}(k,\omega) , \quad (1)$$

where  $x = x_1/x_2$  is the composition ratio,  $a = \alpha_1/\alpha_2$  the polarizability ratio, and  $S_{ii}(k,\omega)$  are the partial dynamic structure factors. In this paper, the subscripts 1 and 2 will refer to the light and heavy particles, respectively. Since the polarizability increases roughly linearly with increasing mass for noble gases, the polarizability ratio a is a small number for disparate-mass noble-gas mixtures. For example, a = 0.05 for He+Xe (see Table I). Thus it will be very hard to observe  $S_{11}(k,\omega)$ , the structure factor of the light particles, by light scattering. On the other hand, the structure factor of the heavy particles  $S_{22}(k,\omega)$ can be studied with ease in this system. Results for this system at various compositions were published previously [17,18]. For  $H_2$ +Ar and  $H_2$ +Xe systems, however, the polarizability ratio a equals 0.5 and 0.2, respectively, so the behavior of  $S_{11}(k,\omega)$  can be studied in more detail.

The fast sound mode is associated with the fluctuations in the density of the light particles and is observed only in  $S_{11}(k,\omega)$ , so that the observability of the fast mode then depends on the composition and polarizability ratios xand a. With a proper choice of x and a, two propagating modes can indeed be observed, though unambiguously only in a limited number of systems. This will be illustrated in Sec. V for two different compositions of the  $H_2+Xe$  system.

#### **III. THEORY**

In a light-scattering experiment of a gas mixture two important length scales are present that determine the features of the dynamic behavior that can be observed experimentally. We can distinguish a "molecular" length scale, a mean free path l, and a "collective" length scale given by the inverse of the wave vector  $k^{-1}$ , the wavelength of the propagating density fluctuations. The ratio of these two quantities, expressed as the reduced wave vector kl, is the key parameter in light-scattering experiments.

In two cases the expressions for the light-scattering spectrum are known exactly: in the limit for small kl and the limit for kl to infinity. We will treat both cases in this section. In addition we will dwell upon the most convenient definition of the mean free path that can be used to describe our experiments in Sec. III D.

# A. Hydrodynamic limit: $kl \rightarrow 0$

The scattered light intensity  $I(k,\omega)$  can in general be represented by a sum of Lorentzians [19]

$$I(k,\omega) \propto S(k,\omega) = \frac{1}{\pi} \operatorname{Re} \sum_{j} \frac{A_{j}}{i\omega + z_{j}} , \qquad (2)$$

where  $A_j = A'_j + iA''_j$  and  $z_j = z'_j + iz''_j$  represent the amplitude and eigenvalue of the *j*th mode. Note that  $A_j$  is the contribution of the *j*th mode to the total area of  $S(k,\omega)$ . In the hydrodynamic limit,  $I(k,\omega)$  for a binary gas mixture can be represented by four Lorentzians [20]. Two central Lorentzians represent the heat and concentration mode, two shifted Lorentzians represent the Brillouin lines. A few of the quantities that can be obtained directly from the hydrodynamic spectrum are the Brillouin shift, the Landau-Placzek ratio, and the second moment of the spectrum. The thermodynamic relation between these three experimental parameters can serve as a consistency check for fitting procedures and was found to work quite well for He+Xe mixtures [21].

#### B. Intermediate regime: $kl \approx 1$

In this intermediate regime  $(kl \approx 1)$  a second sound mode appears [5,14,15]. Since propagating sound modes always appear as conjugate pairs, we have to add one pair of Lorentzians to account for the second sound mode. Then the formal expression for the scattering intensity consists in the intermediate regime of six Lorentzian contributions with associated asymmetric terms,

$$I(k,\omega) \propto A'_{D} + \frac{z'_{D+}}{(z'_{D+})^2 + \omega^2} + A'_{D} - \frac{z'_{D-}}{(z'_{D-})^2 + \omega^2} + [A'_s z'_s \pm A''_s (\omega \pm z''_s)] \frac{1}{(z'_s)^2 + (\omega \pm z''_s)^2} + [A'_f z'_f \pm A''_f (\omega \pm z''_f)] \frac{1}{(z'_f)^2 + (\omega \pm z''_f)^2} .$$
(3)

Here the subscripts D + and D - and s and f refer to the diffusive and the propagating modes and the slow and fast sound modes. For example,  $z'_f$  and  $z''_f$  represent the damping and the propagation frequency of the fast sound mode.

The corresponding spectrum of  $\omega^2 I(k,\omega)$  can also be expressed as a sum of Lorentzians

8064

$$\omega^{2}I(k,\omega) \propto -A'_{D+}(z'_{D+})^{2} \frac{z'_{D+}}{(z'_{D+})^{2} + \omega^{2}} - A'_{D-}(z'_{D-})^{2} \frac{z'_{D-}}{(z'_{D-})^{2} + \omega^{2}} - [B'_{s}z'_{s} \pm B''_{s}(\omega \pm z''_{s})] \frac{1}{(z'_{s})^{2} + (\omega \pm z''_{s})^{2}} - [B'_{f}z'_{f} \pm B''_{f}(\omega \pm z''_{f})] \frac{1}{(z'_{f})^{2} + (\omega \pm z''_{f})^{2}},$$
(4)

with

$$B'_{j} = A'_{j}[(z'_{j})^{2} - (z''_{j})^{2}] - 2A''_{j}z'_{j}z''_{j},$$
  
$$B''_{j} = A''_{j}[(z'_{j})^{2} - (z''_{j})^{2}] + 2A'_{j}z'_{j}z''_{j},$$

where j refers to the fast (f) or the slow (s) sound mode. In the small wave-vector limit the maxima in  $\omega^2 I(k,\omega)$  are located at the eigenvalue of the hydrodynamic sound mode:  $\omega_m(k \rightarrow 0) = z''_s = c_s k$ . In the intermediate regime,  $kl \approx 1$ , the maxima in  $\omega^2 I(k,\omega)$  are related to the eigenvalues of the sound modes in a very complicated manner. In the Gaussian limit, however, the positions of these maxima are known, which will be discussed in Sec. III C.

#### C. Gaussian limit: $kl \rightarrow \infty$

As kl increases an increasing number of Lorentzians are needed to describe  $I(k,\omega)$  properly [19]. It can be shown that in the limit of free-particle flow  $I(k,\omega)$  for an *N*-component gas mixture can then be represented by *N* Gaussians [22]

$$I(k,\omega) \propto \sum_{i=1}^{N} \frac{x_i (\partial \epsilon / \partial n_i)_{n_j \neq i}, T}{\sqrt{2\pi} k v_i} \exp\left[-\frac{1}{2} (\omega / k v_i)^2\right], \qquad (5)$$

where *i* refers to component *i*, and  $n_i$  and  $v_i$  represent the number density of species *i* and the thermal velocity of particle *i*, respectively. The thermal velocity  $v_i = \sqrt{RT/m_i}$ , where *R*, *T*, and  $m_i$  are the gas constant, the absolute temperature, and the molar mass of species *i*, respectively. We use the well-known Clausius-Mossotti equation for the calculation of the dielectric constant  $\epsilon$ . Furthermore, we ignore the temperature fluctuations because the temperature derivative of the dielectric constant is very small compared to the density derivative. Then Eq. (5) can be rewritten for a binary mixture

$$I(k,\omega) \propto xa^{2}m^{1/2} \exp[-\frac{1}{2}(\omega/kv_{1})^{2}] + \exp[-\frac{1}{2}(\omega/kv_{2})^{2}],$$
(6)

where m is the mass ratio  $m_1/m_2$ . The widths and the ratio of the intensities in the Gaussian limit are

$$\frac{I_2}{I_1} = (xa^2)^{-1}, \quad \Gamma_i = kv_i \quad (i = 1, 2) \;. \tag{7}$$

The intensity  $I_i$  is defined as the contribution of component *i* to  $I(k,\omega)$  in Eq. (5). Note that the full width at half maximum (FWHM) is  $2\sqrt{2 \ln 2}$  times the width used in Eq. (7). One can calculate the intensity ratio from the parameters in Table I and find that for the He+Xe system  $I(k,\omega)$  can be represented properly by a single Gaussian throughout almost the whole composition range. For H<sub>2</sub>+Ar and H<sub>2</sub>+Xe, however, two Gaussians must be used over practically the whole composition range. If the contribution to  $I(k,\omega)$  of both components is substantial, this will result in a longitudinal current autocorrelation function, which is related to  $\omega^2 I(k,\omega)$ , that is doubly peaked. The peak positions are located at  $\omega_{m,i}(k) \approx \sqrt{2}kv_i$ .

## D. A characteristic length scale: the effective mean free path

Earlier studies of He+Xe gas mixtures have shown already that kl is a proper scaling parameter of the dispersion relation [17,23]. However, there is some freedom in the exact definition of the mean free path that is used. In this paper we will use the effective mean free path  $l_{eff}$  of the fluctuations of the heavy-particle density, in which the persistence of velocity is taken into account [24]. For He+Xe mixtures this length scale has the property that the reduced wave vector  $kl_{eff}$  at which the hydrodynamic description ceases to be valid is virtually independent of the composition of the mixture [16].

In disparate-mass gas mixtures there is a very inefficient exchange of kinetic energy between unlike particles. If one considers a collision between a light and a heavy particle, the heavy particle will be hardly disturbed by the collision. On the other hand, the collision has a dramatic effect on the change in the velocity of the light particle. This feature of disparate-mass gas mixtures can be quantitatively described by the persistence of velocity. The mean persistence ratio  $\Omega_{ij}$ , defined as the mean of the ratio of the component of velocity along the incident direction of velocity to the velocity before the collision, is given by [25]

$$\Omega_{ij} = \frac{1}{2} \{ M_i + M_i^2 M_j^{-1/2} \ln[(M_j^{-1/2} + 1) M_i^{1/2}] \} , \quad (8)$$

where  $M_i = m_i / (m_i + m_j)$ . The definition of  $\Omega_{ij}$  allows us to calculate the average number of collisions after which a particle no longer has a velocity component in the incident direction. We define  $\tau_{ij}$ , the mean free time of a collision between the tagged particle *i* and one of the particles of type *j*, as

$$\tau_{ij} = 1/(n_j \pi \sigma_{ij}^2 \langle v \rangle), \quad \langle v \rangle^2 = 8RT/(\pi m_{\rm red}) , \qquad (9)$$

where the average hard-sphere diameter  $\sigma_{ij}$  equals  $\frac{1}{2}(\sigma_i + \sigma_j)$  and  $m_{red}$  is the reduced molar mass. The average number of collisions needed for the "randomization" of the incident velocity vector  $\overline{p}_{ij}$  can be calculated using a Poisson distribution [26]

$$\overline{p}_{ij} = \frac{\sum_{p=1}^{\infty} (\Omega_{ij})^p p}{\sum_{p=1}^{\infty} (\Omega_{ij})^p} = \frac{1}{1 - \Omega_{ij}} .$$

$$(10)$$

We can now calculate an effective mean free path which



FIG. 1. Composition-dependence of the mean free paths for  $H_2+Xe$  (assuming ideal-gas behavior): ----,  $l_{light}$ ; ...,  $l_{heavy}$ ; ---,  $l_{eff,light}$ ; ----,  $l_{eff,heavy}$ . Thermodynamic circumstances: p = 0.10 MPa; T = 294 K.

takes collisions between both like and unlike particles into account

$$l_{\mathrm{eff},i} = \overline{p}_i l_i \quad , \tag{11}$$

where  $l_i (=\tau_i v_i)$  represents the mean free path of particle *i*, and  $\overline{p}_i$  is the average persistence of velocity of particle *i*, weighted by mean free times

$$\bar{p}_{i} = \frac{\bar{p}_{ii}/\tau_{ii} + \bar{p}_{ij}/\tau_{ij}}{1/\tau_{ii} + 1/\tau_{ij}} .$$
(12)

This definition of  $l_{eff,i}$  is a generalization of an expression given by Sharma *et al.* [26]. Details on this effective mean free path can be found in Ref. [16]. The different length scales are calculated with the parameters in Table I and are shown for the H<sub>2</sub>+Xe system in Fig. 1. All length scales in this paper are calculated assuming idealgas behavior. The length scale  $l_{eff,heavy}$  is almost independent of the composition for  $x_{heavy} < 0.6$ . This statement holds for the H<sub>2</sub>+Ar system as well.

One of the aims of this paper is to test whether an effective mean free path is only useful in the comparison of data from a single mixture for different compositions [16], or that it can be used to compare data of different mixtures also. If the latter would be the case the effective mean free path would be an extremely useful concept in the study of the dynamics of binary mixtures.

### **IV. EXPERIMENT**

The light-scattering spectra are measured in a 90° scattering geometry. An argon-ion laser operating single mode at 514.5 nm and with an output power of 200 mW is used as a light source and the scattered light is analyzed with a single-pass Fabry-Perot interferometer equipped with flat plates. The value of the wave vector can be calculated by  $k = (4\pi n / \lambda_i) \sin(\theta / 2)$ , where  $n, \lambda_i$ , and  $\theta$  are the refractive index, the wavelength of the incoming light, and the scattering angle. The wave vector equals  $1.73 \times 10^7 m^{-1}$  for all experiments on H<sub>2</sub>+Ar and  $H_2 + Xe$  reported in this paper. The plate separation was 0.94 cm, resulting in a free spectral range of  $1.00 \times 10^{11}$ rad/s. The finesse of the interferometer was 40. The experiments are carried out at room temperature (294 K). The recorded interferograms contain the instrumental profile and two orders of the scattering spectrum. Details of the experimental circumstances of the He+Xe results can be found elsewhere [17].

We used high-grade gases in our experiments, obtained from Messer Griesheim. The mixtures are made as follows: the sample cells are filled with hydrogen up to  $p_{\rm H_2}$ , then the heavy component (Ar or Xe) is added up to a pressure  $p_{\rm tot}$ . The mole fractions are calculated assuming ideal-gas behavior. Another method of calculating mole fractions is using the experimental adiabatic sound velocity of the mixture as a reference [27,28]. The latter method cannot be applied for H<sub>2</sub>+Xe mixtures since the Brillouin lines did not appear as distinct peaks which hampers an accurate determination of the adiabatic sound velocity. The samples are allowed to equilibriate at least 24 h before the first measurements start. The spectra are recorded at different pressures in the pressure ranges given in Table II.

#### V. DATA ANALYSIS AND RESULTS

In Figs. 2 and 3 we show several light-scattering spectra for  $H_2+Xe$  and  $H_2+Ar$ . From these spectra it is evident that by lowering the pressure the spectra become more and more featureless. This is due to the heavy damping of the sound modes. For the  $H_2+Xe$  mixture no distinct Brillouin peaks are visible, not even at the highest density. This will be discussed in Sec. VI.

In order to study the spectral features of the wings in more detail, we multiply the spectrum by  $\omega^2$ . The obtained spectrum  $\omega^2 I_{expt}(k,\omega)$  is related to the spectrum of the longitudinal current autocorrelation spectrum [22] and is shown in Figs. 4 and 5. In the hydrodynamic re-

TABLE II. A summary of the mixtures we studied. Only the pressure was varied. The last column is the conversion factor in  $kl_{\text{eff, heavy}} = p^*/p$  which is calculated using Eq. (11) assuming ideal-gas behavior. p is the pressure, the temperature is 294 K.

System	Xheavy	p (MPa)	No. of spectra	<i>p</i> * (MPa)
$H_2 + Ar$	0.23±0.02	0.1-4.78	36	0.799
$\mathbf{H}_{2}^{2} + \mathbf{X}\mathbf{e}$	$0.17{\pm}0.02$	0.1-2.70	16	1.050
$\tilde{\mathbf{H}_{2} + \mathbf{X} \mathbf{e}}$	$0.18{\pm}0.02$	0.1-4.54	19	1.054
$H_2 + Xe$	$0.33 {\pm} 0.02$	0.1-4.10	22	1.126



FIG. 2. Three Rayleigh-Brillouin spectra of  $H_2+X_e$ ,  $x_{Xe}=0.17$ . Thermodynamic circumstances from bottom to top: p=2.65 MPa, p=1.17 MPa, and p=0.10 MPa (T=294 K).

gime, the position of the maximum in  $\omega^2 I_{\text{expt}}(k,\omega)$  resembles the Brillouin shift very closely [17]. Although no distinct Brillouin peaks are visible for the  $H_2$ +Xe mixtures, a good estimate for the Brillouin shift can still be obtained from the spectrum of  $\omega^2 I_{expt}(k,\omega)$ . A doubly peaked structure appears when the pressure is decreased, that is, when the reduced wave vector kl increases. This is a qualitative proof of the existence of a fast sound mode. The fact that the high-frequency contribution must be attributed to hydrogen is illustrated by comparing  $\omega^2 I_{expt}(k,\omega)$  of He+Xe and H<sub>2</sub>+Xe mixtures with the same partial Xe pressure (Fig. 6). As was pointed out before, the scattering function  $I_{\text{expt}}(k,\omega)$  of He+Xe essentially represents  $S_{22}(k,\omega)$ . The difference between the two spectra in Fig. 5 must therefore be attributed to hydrogen.

An experimentally obtained light-scattering spectrum is a convolution of the instrumental profile of the experimental setup and a line shape due to the processes which are probed,

$$I_{\text{expt}}(k,\omega) = I_{\text{instr}}(\omega) \otimes I(k,\omega) .$$
(13)

To extract the values for  $z_j$  and  $A_j$  from our experiments we used a fitting procedure. The scattering intensity was approximated by the form given in Eq. (3). This fitting



FIG. 3. Three Rayleigh-Brillouin spectra of  $H_2+Ar$ ,  $x_{Ar}=0.23$ . Thermodynamic circumstances from bottom to top: p=4.78 MPa, p=0.88 MPa, and p=0.10 MPa (T=294 K).



FIG. 4. The longitudinal current autocorrelation function  $[=\omega^2 I_{expt}(k,\omega)]$  of the H<sub>2</sub>+Xe spectra. Thermodynamic circumstances as in Fig. 2.

function for  $I(k,\omega)$  was convoluted with the instrumental profile and fitted to the experimental scattering intensity using a simplex fitting routine. The  $\chi^2$  merit function was minimized by fitting both  $I_{\text{expt}}(k,\omega)$  and  $\omega^2 I_{\text{expt}}(k,\omega)$ .

Throughout all fitting procedures we have assumed only one central component in the spectrum, so  $A_{D-}=0$ . Hydrodynamic calculations on the He+Xe system showed that the Rayleigh line is always dominated by one of the possible diffusive modes [23]. This prediction holds for H<sub>2</sub>+Ar and H<sub>2</sub>+Xe as well. Furthermore, we assume that the amplitude of the asymmetric term of the fast sound mode  $A''_{f}$  can be neglected. The amplitude of the asymmetric term of the slow sound mode  $A''_{s}$  is calculated using the n = 1 sum rule [29]

$$2A_{s}''z_{s}'' = A_{D+}'z_{D+}' + 2A_{s}'z_{s}' + 2A_{f}'z_{f}' . \qquad (14)$$

For small reduced wave vectors, the scattering spectrum can be described by the well-known Rayleigh-Brillouin triplet. Equation (3) reduces to the Rayleigh-Brillouin triplet when  $A_f$  equals zero. At higher reduced wave vectors we allow  $A'_f$  to have a nonzero value in our fitting routine in order to account for the contribution of the fast sound mode.

It is known from hydrodynamics that the propagation frequency of the sound mode in the small wave-vector



FIG. 5. The longitudinal current autocorrelation function of the  $H_2$ +Ar spectra. Thermodynamic circumstances as in Fig. 3.



FIG. 6. 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.

limit is given by

$$\lim_{k \to 0} z_s^{\prime\prime} = c_{s,\min} k \quad , \tag{15}$$

where  $c_{s,\text{mix}}$  is the adiabatic sound velocity of the mixture. In Figs. 7 and 8 we have plotted the sound propagation frequency vs  $kl_{\text{eff},i}$  (*i*=Ar,Xe) for various mixtures and compositions. From the propagation frequency in the limit of small  $kl_{\text{eff},\text{heavy}}$ , that is at the highest densities, one can obtain the adiabatic sound velocity of the mixture (Table III). A remarkable result, that was already noted for He+Xe system [13], is that the value for  $z_s''$ tends towards the adiabatic sound velocity of the heavy component times k,

$$z_{s}^{\prime\prime} \rightarrow c_{s,\text{heavy}} k$$
 , (16)

for large values of  $kl_{\text{eff, heavy}}$ . The propagation frequencies of the fast sound modes (Fig. 9), however, do not reach  $c_{s,H_2}k$  for the largest values of  $kl_{\text{eff, heavy}}$  (see discussion). In order to make a comparison between the slow sound modes for the different systems, we make use of the behavior in both kl limits. We therefore used the following scaling formula for the propagation frequency:

$$\tilde{z}_{s}^{\prime\prime} = \frac{z_{s}^{\prime\prime}/k - c_{s,\text{heavy}}}{c_{s,\text{mix}} - c_{s,\text{heavy}}} , \qquad (17)$$

where  $c_{s,\text{mix}}$  is the experimental adiabatic sound velocity of the mixture and  $c_{s,\text{heavy}}$  is the calculated adiabatic sound velocity of the heavy component assuming idealgas behavior. The results for the  $\tilde{z}''_s$  scaling of the y axis and  $kl_{\text{eff},i}$  scaling of the x axis are shown in Figs. 10 and



FIG. 7. The propagation frequency of the slow sound modes for  $H_2+Xe$ ; ( $\Box$ )  $x_{Xe}=0.18$ ; ( $\blacksquare$ )  $x_{Xe}=0.33$ . Horizontal line denotes  $c_{s,Xe}$ , assuming ideal-gas behavior.

11. We can see the sound-mode behavior of the different mixtures and compositions coalesce onto a single curve.

Clouter et al. [14] have shown unambiguously the existence of both fast and slow sound in the spectrum of  $I_{expt}(k,\omega)$ . Their results for the slow mode in the  $H_2+SF_6$  mixture obey the same scaling behavior as the mixtures we studied. The experimental data points obtained from Fig. 3 of Ref. 14 coalesce with our results when scaled according to Eq. (11) and Eq. (17), like in Figs. 10 and 11.

In Figs. 12 and 13 we show the results for both the fast and slow sound mode. The fast sound mode appears at  $kl_{eff,Xe} \approx 0.5$  for the H<sub>2</sub>+Xe mixture and at  $kl_{eff,Ar} \approx 1$ for the H<sub>2</sub>+Ar mixture. Due to the larger mass ratio *m* of H<sub>2</sub>+Xe the peaks in  $\omega^2 I_{expt}(k,\omega)$  are better separated than in the case of H<sub>2</sub>+Ar. This makes the observation of the fast sound contribution in H<sub>2</sub>+Xe easier. The fast sound mode appears roughly at  $kl_{eff,heavy} \approx 0.8$ , the value where the hydrodynamic description breaks down [16]. The fast sound mode appears around this kl value whereas the slow sound mode seems to be the continuation of the ordinary hydrodynamic sound mode in the low-density gas mixtures we studied [15].

The advantage of analyzing  $\omega^2 I_{\text{expt}}(k,\omega)$  rather than the light-scattering spectrum itself is that the two sound modes can still be distinguished at low pressures. This can be done even when the sound modes are overdamped. At the lowest pressures, at large  $kl_{\text{eff,heavy}}$  values, the spectrum of  $\omega^2 I_{\text{expt}}(k,\omega)$  is very similar to the longitudinal-current autocorrelation function in the Gaussian limit. The question that arises is: "At which kl

TABLE III. Results for the adiabatic sound velocities at the highest pressure of each series (see Table II) and at T = 294 K. For the calculation of the adiabatic sound velocities, see text.

System		Adiabatic sound velocity in m/s			
	$x_{\rm heavy}$	C <sub>s, expt</sub>	$c_{s,\mathrm{calc}}^{\mathrm{0}}$	$c_{s, calc}^{\infty}$	
$H_2 + Ar$	$0.23 {\pm} 0.02$	579	572	614	
$H_2 + Xe$	$0.17{\pm}0.02$	460	381	417	
$H_2 + Xe$	$0.18{\pm}0.02$	440	371	422	
$H_2 + Xe$	$0.33 {\pm} 0.02$	320	282	305	



FIG. 8. The propagation frequency of the slow sound modes for  $H_2$ +Ar; ( $\bigtriangledown$ )  $x_{Ar}$ =0.23. Horizontal line denotes  $c_{s,Ar}$ , assuming ideal-gas behavior.



FIG. 9. The propagation frequency of the fast sound modes: ( $\blacksquare$ ) H<sub>2</sub>+Xe,  $x_{Xe}$ =0.17; ( $\checkmark$ ) H<sub>2</sub>+Ar;  $x_{Ar}$ =0.23. Horizontal line denotes  $c_{s,H_2}$ , assuming ideal-gas behavior.



FIG. 10. Reduced eigenvalues  $\overline{z}_{s}^{''}$  [see Eq. (17)] vs  $kl_{\text{eff},i}$  (*i* is the heavy component) of the slow modes of three systems: ( $\boxplus$ ) He+Xe,  $x_{Xe}$ =0.45, ( $\square$ ) H<sub>2</sub>+Xe,  $x_{Xe}$ =0.17, and ( $\bigtriangledown$ ) H<sub>2</sub>+Ar,  $x_{Ar}$ =0.23.



FIG. 11. Reduced eigenvalues  $\tilde{z}_{s}^{\prime\prime}$  [see Eq. (17)] of the slow modes of He+Xe for three compositions: ( $\Box$ )  $x_{Xe} = 0.22$ ; ( $\nabla$ )  $x_{Xe} = 0.45$ , and ( $\Diamond$ )  $x_{Xe} = 0.61$ .

values does the Gaussian-like behavior start?"

In order to check if the  $kl \rightarrow \infty$  limit was already reached at the lowest pressures, we fitted a sum of two Gaussians to our data. We convoluted this function with the instrumental profile and followed the fitting procedure mentioned above. The relevant experimental parameters are the intensity ratios and the widths as given by Eq. (7). The fitting results for  $H_2 + Ar$  are given in Figs. 14 and 15. Similar results were found for the  $H_2$ +Xe mixtures. Although  $\Gamma_{2'}$ , the width of the heavycomponent velocity distribution, resembles the Gaussian width quite well,  $\Gamma_1$  does not reach its Gaussian value  $(=kv_1)$  at the highest  $kl_{\text{eff, heavy}}$  values. The intensity ratio is close to the Gaussian value. This is not surprising since, at these densities, only  $S_{11}(k)$  and  $S_{22}(k)$  contribute to the integrated intensity [see Eq. (1)]. The ratio of these contributions has the same value. The suggestion is that at the largest  $kl_{\rm eff,heavy}$  values (lowest densities), the Gaussian limit is gradually approached. However, for  $kl_{\rm eff, heavy}$  < 3, we can safely state that the Gaussian limit is not applicable. This proves that we have examined an intermediate regime in between hydrodynamic and the free flight limit. Kinetic calculations on dilute pure gases show that Gaussian behavior is reached for kl > 4 [19] (for pure gases  $l_{\rm eff}/l = 1.6$ ). In hard-sphere fluids, Gaussian behavior is found for kl > 3 [30]. We find that the mixtures we studied approach gradually the Gaussian re-



FIG. 12. Reduced eigenvalues,  $(z'')^* = z_j''/c_s k$ , of the fast and slow modes (j = s, f) of H<sub>2</sub>+Xe,  $x_{Xe} = 0.17$ , and  $x_{Xe} = 0.18$ ,  $c_s k = 7.65 \times 10^9$  rad/s.

8069



FIG. 13. As in Fig. 12 for  $H_2 + Ar$ ,  $x_{Ar} = 0.23$ ,  $c_s k = 1.00 \times 10^{10} \text{ rad/s.}$ 



FIG. 14. Widths  $\Gamma_i$  (i=1,2) of the Gaussians vs  $kl_{eff,Ar}$  for  $H_2$ +Ar;  $x_{Ar}$ =0.23. Horizontal bar denotes the Gaussian limit [Eq. (7)].



FIG. 15. Intensity ratio  $I_2/I_1$  of the Gaussians vs  $kl_{eff,Ar}$  for  $H_2 + Ar$ ;  $x_{Ar} = 0.23$ . Horizontal bar denotes the Gaussian limit [Eq. (7)].

gime at  $kl_{\text{eff, heavy}} \approx 5$ . For one H<sub>2</sub>+Xe mixture,  $x_{\text{Xe}} = 0.33$ , we did not observe a fast sound mode. The high-frequency contribution in the longitudinal-current autocorrelation function did not appear, not even at the lowest pressures. Although the fast mode may be present, the observation will be hampered by the low hydrogen mole fraction. This can be illustrated by Eq. (1), where one can see that the observability of  $S_{11}(k,\omega)$  does not only depend on the polarizability ratio a, explaining the absence of an observable fast sound mode in He+Xe, but also on the composition ratio x.

### VI. DISCUSSION

In Figs. 10 and 11 one can see that the scaling with  $\tilde{z}_{s}^{\prime\prime}$ using the experimental value for  $c_{s,mix'}$  works quite well. We have used the experimental value for  $c_{s,mix}$  instead of the calculated one because of a relatively large difference between the calculated and experimental adiabatic sound velocity for  $H_2$ +Xe (see Table III). None of the spectra of the H<sub>2</sub>+Xe series shows distinct Brillouin peaks, contrary to the spectra of  $H_2$  + Ar (Figs. 2 and 3). There are several plausible explanations of experimental origin for this problem. The combination of a low adiabatic sound velocity of this mixture and a relatively large free spectral range causes overlap of the Rayleigh and Brillouin lines, which may result in the disappearance of the Brillouin peaks. During these experiments the free spectral range had to be large in order to observe the fast sound mode. In addition, the instrumental function was slightly broader during the measurements of the  $H_2 + Xe$  series.

In Table III the experimental as well as calculated adiabatic sound velocities are given. Since H<sub>2</sub> has internal degrees of freedom, the adiabatic sound velocity is frequency dependent. The low-frequency adiabatic sound velocity  $c_{s,calc}^{0}$  was calculated using the van der Waals equation of state. The high-frequency adiabatic sound velocity  $c_{s,calc}^{\infty}$  was calculated from the ideal-gas isothermal sound velocity and the specific-heat ratio  $\gamma^{\infty}$ . The specific-heat ratio  $\gamma^{\infty}$  was calculated from numberaveraged values for  $C_p$  and  $C_{p'}$  where we took experimental specific-heat values for hydrogen [31] and ideal-gas specific-heat values for the noble-gas component. The experimental adiabatic sound velocity for H<sub>2</sub>+Ar coincides with the calculated zero-frequency result for  $c_s$ . For all  $H_2 + Xe$  series we found that the experimental adiabatic sound velocities are higher than the calculated  $c_{s, calc}^{\infty}$ values. If these differences would be ascribed to uncertainties in the composition, than these uncertainties should be of the order of 20-30 %, which is very unlikely. Neither can it be ascribed to an error in the experimentally determined Brillouin shift since the error in this shift in the limit for small wave vectors is typically of the order of 2-3 %.

In general the fitting results can be influenced by the presence of a central component such as a Mountain line [32]. Since we use only one central Lorentzian in our fitting procedure to account for all possible nonpropagating modes, an offset in the fitted position of the Brillouin lines may be suspected. This may also explain the discrepancies between the experimental and calculated adiabatic sound velocities. A precise prediction for the contribution of the different nonpropagating modes can probably be given by hydrodynamics for mixtures with internal relaxation [33]. Although this may introduce systematic errors in the absolute values of the experimentally determined sound velocities, use of the experimental sound velocity does not affect the scaling behavior. The same holds for the scaling behavior of the fast sound mode.

We have examined the scaling behavior of the fast sound mode as well. For both mixtures the propagation frequency of the fast mode tends towards roughly two times the propagation frequency of the mixture for large kl values. The fast mode is not analogous to the slow mode in the sense that the propagation frequency of the fast mode does not reach  $c_{s,H_2}k$  at large  $kl_{eff,heavy}$  values. In our fitting procedures we have neglected the asymmetric contribution of the fast sound mode  $A''_f$ . The asymmetric term shifts the top of the fast sound mode contribution to a value that is somewhat smaller than  $z''_{f}$ . Neglect of the asymmetric term thus suppresses the experimental value of  $z''_f$ . Around  $kl_{\text{eff,heavy}} \approx 1$ , the fast modes of the two mixtures exhibit qualitative different behavior. Although the fitting procedure renders accurate results in the high and low kl regimes, it is less accurate around  $kl_{\rm eff, heavy} \approx 1$ . In this regime the fast sound mode appears but its contribution to the spectrum is still small. As a consequence we could not distinguish the contributions of the fast and slow sound mode very clearly in the  $\omega^2 I_{\text{expt}}(k,\omega)$  spectrum, which affects the reliability of the fitting results.

At this stage we wish to refer to kinetic calculations of Campa and Cohen on the dilute  $H_2$ +Ar mixture. They point out that above a certain concentration of the light component, the fast sound mode no longer exists [8]. As the hydrogen concentration increases, the difference between the sound velocity of the mixture and that of pure hydrogen becomes small. They state that the extended hydrodynamic sound mode becomes fast propagating for compositions with  $x_{\rm H_2} > 0.9$ . We have performed calculations based on a simple four-moment model proposed by Bowler and Johnson [34] and found the same qualitative behavior. The extended sound mode is a fast propagating mode for  $x_{\rm H_2} > 0.84$  and 0.92 for  $\rm H_2 + Ar$  and  $H_2 + Xe$ , respectively. Maybe the qualitative different behavior of the experimentally determined fast sound mode of the  $H_2$ +Ar and  $H_2$ +Xe mixture is associated with the above described phenomena. The composition of the  $H_2 + Xe$  mixtures ( $x_{H_2} = 0.82$  and 0.83) might be too close to a critical composition  $x_{H_2,crit}$ . Below this critical composition the hydrodynamic sound mode goes over into slow sound, above this composition it goes over into a fast propagating mode.

Johnson and co-workers [35,36] have found anomalous dispersion in dilute He + Xe mixtures by ultrasonic experiments. They found two different forced sound modes that can be predicted fairly well by two-temperature hy-

drodynamics. The anomalous dispersion arises from a competition between a diffusive mode and a sound mode and seems to be a typical feature of disparate-mass gas mixtures. It would be interesting to carry out a normal-mode analysis of two-temperature hydrodynamics and compare the eigenvalues with our results. Good agreement was already found for light scattering results of He+Xe gas mixtures [37].

Earlier results of the He+Xe system proved that hydrodynamics is applicable for  $0 \le k l_{\text{eff, heavy}} \le 0.8$  [16]. The present results indicate that Gaussian behavior starts at  $k l_{\text{eff, heavy}} \approx 5$ . In the intermediate regime, demarked by  $1 \le k l_{\text{eff, heavy}} \le 5$ , we have found both qualitative and quantitative evidence of a fast and slow sound mode. The physical interpretation of fast and slow sound, however, is still not entirely clear.

Campa and Cohen proposed an interpretation of fast and slow sound in terms of decoupled sound waves [9]. The light particles are moving in a background of heavy particles. Due to the fact that the heavy particles are unable to follow the rapid oscillations of the light particles, there is a decoupling of the dynamics of the light and heavy subsystem allowing two separate sound modes to propagate through the gas mixture.

### **VII. CONCLUSIONS**

We have found qualitative evidence for the existence of both fast and slow sound modes in gaseous  $H_2$ +Ar and  $H_2$ +Xe systems. For one of the examined  $H_2$ +Xe mixtures,  $x_{Xe}$ =0.33, we have not observed a fast sound mode. This is due to an unfavorable combination of the polarizability ratio and the composition of the mixture. The slow sound mode seems to be the continuation of the hydrodynamic sound mode in the examined gas mixtures. The fast and slow sound mode were observed in an intermediate regime in between the hydrodynamic and the Gaussian regime.

Using a newly developed length scale that includes the effects of the persistence of velocity in disparate-mass gas mixtures, we found that the behavior of the slow sound mode of  $H_2$ +Ar and  $H_2$ +Xe is very similar to the slow sound mode in He+Xe, which was intensively studied earlier [17]. This led us to believe that we have separated the "universal" mixture behavior from trivial mass effects. The scaling behavior of the fast sound mode is still not clear but may be elucidated by further experiments.

Until now we may conclude that revised Enskog theory gives, at least qualitatively, an accurate description of the light-scattering spectra in the intermediate regime between hydrodynamics and free flight. In the case for which calculations were published, correspondence between theory and experiment was even quantitative [5]. Fortunately, experimental and theoretical results not only allow us to compare experiment with a highly complicated formal framework, but also allow us to develop an appealing physical picture of the dynamics of a gas mixture at high reduced wave vectors.

#### ACKNOWLEDGMENTS

The authors wish to thank Dr. H. M. Schaink for critically reading the manuscript. Experiments were performed at the Laboratory for Physical Chemistry at the University of Amsterdam. This work is part of the scientific program of the Foundation for Fundamental Research of Matter (FOM) and the Netherlands Foundation for Chemical Research (SON) with financial support from the Netherlands Organization for Research (NWO).

\*Author to whom correspondence should be addressed.

- [1] L. Brillouin, C. R. Acad. Sci. 158, 1331 (1914).
- [2] L. Brillouin, in Light Scattering Spectra of Solids, edited by G. B. Wright (Springer, Heidelberg, 1969), p. xvii.
- [3] E. Gross, Nature 126, 201 (1930); *ibid.* 126, 400 (1930); *ibid.* 126, 603 (1930).
- [4] E. Gross, Phys. Rev. 42, 579 (1932).
- [5] G. H. Wegdam, A. Bot, R. P. C. Schram, and H. M. Schaink, Phys. Rev. Lett. 63, 2697 (1989).
- [6] J. Bosse, G. Jacucci, M. Ronchetti, and W. Schirmacher, Phys. Rev. Lett. 57, 3277 (1986).
- [7] A. Campa and E. G. D. Cohen, Phys. Rev. Lett. 61, 853 (1988).
- [8] A. Campa and E. G. D. Cohen, Phys. Rev. A 41, 5451 (1990).
- [9] A. Campa and E. G. D. Cohen, Phys. Rev. A 39, 4909 (1989).
- [10] W. Montfrooij, P. Westerhuijs, and I. M. de Schepper, Phys. Rev. Lett. 61, 2155 (1988).
- [11] W. Montfrooij, P. Westerhuijs, V. O. de Haan, and I. M. de Schepper, Phys. Rev. Lett. 63, 544 (1989).
- [12] H. M. Schaink and G. H. Wegdam, Physica A 141, 211 (1987).
- [13] G. H. Wegdam and H. M. Schaink, Phys. Rev. A 41, 3419 (1990).
- [14] M. J. Clouter, H. Luo, H. Kiefte, and J. A. Zollweg, Phys. Rev. A 41, 2239 (1990).
- [15] R. P. C. Schram, A. Bot, H. M. Schaink, and G. H. Wegdam, J. Phys.: Condens. Matter 2, SA157 (1990).
- [16] G. H. Wegdam and H. M. Schaink, Physica A 169, 353 (1990).
- [17] G. H. Wegdam and H. M. Schaink, Phys. Rev. A 40, 7301 (1989).
- [18] A. Bot, Ph.D. thesis, University of Amsterdam, 1990.
- [19] B. Kamgar-Parsi and E. G. D. Cohen, Physica A 138, 249 (1986).
- [20] C. Cohen, J. W. H. Sutherland, and J. M. Deutch, Phys. Chem. Liq. 2, 213 (1971).
- [21] A. Bot and G. H. Wegdam, J. Phys. Chem. 95, 4679

(1991).

- [22] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
- [23] G. H. Wegdam and H. M. Schaink, Mol. Phys. 65, 531 (1988).
- [24] H. M. Schaink, Ph.D. thesis, University of Amsterdam, 1990.
- [25] S. Chapman and T. G. Cowling, *The Mathematical Theory* of Non-Uniform Gases (Cambridge University Press, Cambridge, 1970).
- [26] K. C. Sharma, S. Ranganathan, P. A. Egelstaff, and A. K. Soper, Phys. Rev. A 36, 809 (1987).
- [27] H. M. Schaink and G. H. Wegdam, Physica A 160, 117 (1989).
- [28] A. Bot, H. M. Schaink, R. P. C. Schram, and G. H. Wegdam, J. Phys. Chem. 95, 4673 (1991).
- [29] I. M. de Schepper, P. Verkerk, A. A. van Well, and L. A. de Graaf, Phys. Rev. Lett. 50, 974 (1983).
- [30] B. Kamgar-Parsi, E. G. D. Cohen, and I. M. de Schepper, Phys. Rev. A 35, 4781 (1987).
- [31] A. Michels, W. de Graaf, and G. J. Wolkers, Physica 25, 1097 (1959).
- [32] R. D. Mountain, J. Res. Natl. Bur. Stand. Sect. A 70, 207 (1966).
- [33] (a) J. W. H. Sutherland and J. M. Deutch, Chem. Phys. 1, 447 (1973); (b) R. Kapral and R. C. Desai, Chem. Phys. 3, 141 (1974).
- [34] J. R. Bowler and E. A. Johnson, Proc. R. Soc. London Ser. A 408, 79 (1986).
- [35] J. R. Bowler and E. A. Johnson, Phys. Rev. Lett. 54, 329 (1985).
- [36] E. A. Johnson, J. Stat. Phys. 57, 647 (1989).
- [37] E. A. Johnson, Phys. Rev. A 27, 1146 (1983).
- [38] A. Campa, Ph.D. thesis, The Rockefeller University, 1989.
- [39] R. C. Burns, C. Graham, and A. R. M. Weller, Mol. Phys. 59, 41 (1986).
- [40] R. H. Orcutt and R. H. Cole, J. Chem. Phys. 46, 697 (1967).