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Rayleigh–Brillouin Light Scattering from Noble Gas Mixtures. 1. The Landau–Placzek Ratio

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We present the Rayleigh–Brillouin light scattering data for He + Xe mixtures of various compositions and pressures between 2 and 10 MPa. We compare our experimental data to calculations for a mixture that behaves according to the van der Waals equation of state. Our analysis shows that the contribution of concentration fluctuations to the Landau–Placzek ratio is very important. Furthermore, we demonstrate experimentally the relation between the Landau–Placzek ratio, the adiabatic velocity of sound, and the reduced second moment of the dynamic light scattering spectrum. We show that the van der Waals equation of state can be used to predict the Landau–Placzek ratio in these mixtures quantitatively for mixtures with compositions $x_{\text{Xe}} < 0.9$. For mixtures with higher xenon concentrations, experimental results agreed quantitatively up to 5 MPa with calculations.

I. Introduction

In recent years, the traditional method to measure the total light scattering intensity of a mixture to gain information on its thermodynamic properties has been supplemented with methods in which the scattering intensity is analyzed spectrally (or, equivalently, resolved in time). The analysis of light scattering spectra enables one to distinguish between different contributions to the spectra: the Brillouin lines, the Rayleigh line, or even the individual components that make up the Rayleigh line. Iwasaki et al.¹ studied the Rayleigh line intensity, and Dubois and Bergé² determined the relative contribution of entropy and concentration fluctuations to the Rayleigh line. In this pair of papers, our aim is to develop an additional method involving the Landau–Placzek ratio that lacks some of the disadvantages of the previous methods.

To attain this objective, we will proceed in two stages. We will check whether the thermodynamic description of the Landau–Placzek ratio can be made (semi)quantitative using a simple equation of state. This question will be covered in the first paper. In the second paper we will invert this analysis: how much information can be gained from the Landau–Placzek ratio concerning the thermodynamics of the scattering medium?

Besides the aforementioned goals of this study, we will achieve the first systematic study of the Landau–Placzek ratio over a wide range of thermodynamic circumstances in a binary gas mixture. Compared to earlier work on neat liquids by Cummins and Gammon³ and on binary liquid mixtures by Maguire, Michielsen, and Rakhorst,⁴ our study has the advantage that, due to the fact that we are considering noble gas mixtures, no corrections to the Landau–Placzek ratio need to be made to account for the internal degrees of freedom in the mixture.

This paper includes several introductory sections on dynamic light scattering (section II), on the experimental setup (section III), on our data analysis (section IV), and on the reduced second moment of a dynamic light scattering spectrum (section V). In section VI we will describe the van der Waals equation of state, and in section VII we will present some results for the Landau–Placzek ratio using this model. In section VIII we will present experimental results that can be compared to our calculations.

II. Dynamic Light Scattering

In a light scattering experiment an incoming light wave with $k_i = |\vec{k}_i| = 2\pi/\lambda_i$ is partially scattered by local fluctuations in the dielectric constant of the sample.⁵ Here, k_i is called the wave vector and λ_i is the wavelength of the incoming beam. Part of the scattered light, characterized by $\vec{k}_r$, is analyzed. The vectors

$\vec{k}_i$ and $\vec{k}_r$ determine the scattering angle θ and the scattering geometry. The wave vector $\vec{k} = \vec{k}_r - \vec{k}_i$ is associated with the fluctuations that cause scattering. As $|\vec{k}_i| \approx |\vec{k}_r|$, one can easily see from Figure 1 that

$$k = |\vec{k}| = (4\pi n/\lambda_i) \sin \theta/2 \quad (1)$$

where n is the refractive index of the scattering medium. In all our experiments we have chosen $\theta = 90^\circ$ and $\lambda_i = 514.5$ nm.

The frequency distribution of light is changed by the scattering process. In a typical dynamic light scattering experiment on a liquid or a dense gas, one observes the so-called Rayleigh–Brillouin triplet: a spectrum symmetrically around $\omega_i = 2\pi c/\lambda_i$, consisting of a central (Rayleigh) line and two shifted (Brillouin) lines. Here c is the speed of light. If the incoming beam is a delta function in frequency, the triplet is described in hydrodynamic fluctuation theory as a sum of Lorentzians—three for a pure fluid and four for a mixture—and a pair of associated asymmetric terms. In the small wave vector limit, the shift of the Brillouin lines is given by $c_s k$, where c_s is the adiabatic velocity of sound. If Rayleigh and Brillouin lines can be distinguished clearly, the asymmetric contribution will be small. In the limit $k \rightarrow 0$, the amplitudes of the various modes are determined by thermodynamic quantities. This is illustrated in Figure 2, where we have plotted two Rayleigh–Brillouin light scattering spectra under different thermodynamic circumstances. The quantity that describes the relative intensities of Rayleigh line and Brillouin lines, the Landau–Placzek ratio J , is a convenient measure to characterize these completely different appearances. For a binary mixture with no internal degrees of freedom the theoretical expression for J is given by^{6–8}

$$J = (\gamma - 1) + x_2 M c_s^2 \left(\frac{\partial x_1}{\partial \mu_1} \right)_{p,T} \left(\frac{1}{\rho} \left(\frac{\partial \rho}{\partial x_2} \right)_{p,T} + \mathcal{A} \right)^2 \quad (2)$$

where γ stands for the heat capacity ratio, x_i is the mole fraction of component i , M is the average molecular mass ($M = M_1 x_1 + M_2 x_2$), μ_i is the chemical potential of component i , ρ is the number density, and $\mathcal{A} = (\alpha_2 - \alpha_1)/(\alpha_1 x_1 + \alpha_2 x_2)$ where α_i is the molecular polarizability of component i . For a pure fluid, J is given by $\gamma - 1$ only. It is clear that J can become very large when either the isothermal or the osmotic compressibility diverges.

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Figure 1. Scattering geometry for a light scattering experiment. The dashed line indicates the incoming and outgoing beam. The scattering angle θ was chosen to be 90° in our experiments. The dotted line is the bisector of the angle $\angle(k_i, k_f)$ and is meant as a line to guide the eye.

Figure 2. Dynamic light scattering spectra of He + Xe mixtures at $T = 293$ K and $x_{Xe} = 0.99$: (a) $p = 0.83$ MPa; (b) $p = 6.63$ MPa.

III. Experiment

In our experiments we have used an argon ion laser operating single mode at a wavelength of 514.5 nm and at an output power of 200 mW. The main part of the beam was focused in the sample cell. A single-pass Fabry-Perot interferometer analyzes light scattered under an angle of 90° . The free spectral range of the interferometer was varied for different compositions. The finesse of the interferometer was typically 40. A Centronic Q4249B photomultiplier served as a detector, and the signal was fed into a Burleigh-DAS1 data acquisition and stabilization system. The analysis of the acquired data was performed on a personal computer. A smaller part of the beam was diverted to act as a signal to monitor the instrumental profile of the interferometer simultaneously. In Figure 3 we show the experimental setup. The sample cell was constructed from a block of stainless steel by drilling two perpendicular holes in it and fitting in four quartz windows. The incident light beam was passed through the cell along its long axis. Two small apertures (diameters 1 mm) were placed in the cell to reduce the amount of stray light coming from the entrance and exit windows. The volume of the cell was 15 cm³. Our gas samples were prepared from high-purity xenon obtained from Messer Griesheim and from helium that was evaporated from liquid helium. The mixtures were prepared by condensation of low-pressure gases in a small cold container. The composition was derived from the velocity of sound at 4.0 MPa for each series of density-dependent measurements. This was achieved by comparing the experimental values to calculations

Figure 3. Experimental setup: L, lens; M, mirror; BS, beam splitter; PH, pinhole; C, sample cell; CO, collimator; PM, photomultiplier; DISCR, amplifier and discriminator; P, pulse generator; AMP, amplifier; SW, optoacoustic switch.

using the van der Waals equation of state.

IV. Data Analysis

An experimentally obtained light scattering spectrum is a convolution of the instrumental profile of the experimental setup and an intrinsic line shape due to the processes that are probed

$$I_{\text{exp}}(k, \omega) = I_{\text{instr}}(\omega) * I(k, \omega) \quad (3)$$

where $*$ denotes the convolution and $I(k, \omega)$ represents the Fourier-Laplace transform of the dielectric autocorrelation function. For $I(k, \omega)$ we have used a sum of two unshifted Lorentzians and a pair of shifted Lorentzians with corresponding asymmetrical line shapes⁹

$$I(k, \omega) \sim A'_{D+} \frac{z'_{D+}}{z'^2_{D+} + \omega^2} + A'_{D-} \frac{z'_{D-}}{z'^2_{D-} + \omega^2} + \frac{(A'_s z'_s + A''_s(\omega + z''_s))}{z'^2_s + (\omega + z''_s)^2} + \frac{(A'_s z'_s - A''_s(\omega - z''_s))}{z'^2_s + (\omega - z''_s)^2} \quad (4)$$

where A_j and z_j refer to the amplitude and the eigenvalue of the j th eigenmode of the hydrodynamic matrix,⁹ respectively. The subscripts D+ and D- indicate diffusive modes, while s refers to the propagating sound mode. It is possible to reduce the number of parameters in the above equation by using the sum rule:¹⁰⁻¹²

$$z'_{D+} A'_{D+} + z'_{D-} A'_{D-} + 2z'_s A'_s - 2z''_s A''_s = 0 \quad (5)$$

Throughout the fitting procedure, we have assumed $A_{D-} = 0$. As Schaink discussed earlier,^{11,12} it always seems to be the case that either the amplitudes or one of both unshifted Lorentzians is small or their widths are comparable.

To compare our experimental results to the fitting function, we had to perform a background correction first. This was done by measuring the intensity of the spectrum halfway two adjacent orders of the interferogram. Although this correction was greater than expected if its value was determined by electronic noise alone, this additional contribution was negligible. Furthermore, some additional calculations showed that the wings of the instrumental profile were the main cause of this contribution. Suppression of the additional background should be possible either by increasing the finesse of the interferometer or by using a multipass interferometer, while varying the free spectral range would make no difference.¹³

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Having determined the background, we proceeded with fitting our data. Our aim was not only to fit the general shape of the spectrum but also to pay special attention to the shape of the wings of the spectrum. Although this difference in emphasis could have been attained by adjusting the weight function in the fit, we chose to multiply the spectrum by ω^2 , thus obtaining the longitudinal current autocorrelation function. This way, visual inspection of the fit was simplified. We fitted both $I(k, \omega)$ and $\omega^2 I(k, \omega)$ until both fits were satisfactory. Our automatic fitting procedure consisted of a simplex fitting routine. Having obtained a fit, the Landau-Placzek ratio J could be extracted from our data using

$$J = (A'_{D+} + A'_{D-})/2A'_s \quad (6)$$

V. The Reduced Second Moment

It can be shown that the second moment $\langle \omega^2 \rangle$ of the dynamic structure factor $S(k, \omega)$, which is essentially the integral over the current autocorrelation function¹⁴

$$\langle \omega^2 \rangle = \int \omega^2 S(k, \omega) d\omega \sim \int \omega^2 I(k, \omega) d\omega \quad (7)$$

is a constant for a mixture of fixed composition and temperature.

$$\langle \omega^2 \rangle = k^2 \frac{\alpha_1^2 x_1 k_B T / M_1 + \alpha_2^2 x_2 k_B T / M_2}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (8)$$

The quantity that can be extracted conveniently from a dynamic light scattering spectrum is the reduced second moment.

$$\langle \omega^2 \rangle / \langle \omega^0 \rangle = \int \omega^2 S(k, \omega) d\omega / \int S(k, \omega) d\omega \quad (9)$$

The reduced second moment is essentially the inverse scattering intensity because $\langle \omega^2 \rangle$ is a constant. In extracting the reduced second moment from a spectrum, there are a few things that have to be noted. Overlapping orders in the interferogram may seriously influence $\langle \omega^2 \rangle$, while there is hardly any influence on $\langle \omega^0 \rangle$. This is due to the fact that the main contributions to $\langle \omega^2 \rangle$ can be found at higher frequencies than the main contributions to $\langle \omega^0 \rangle$. When we extract this quantity, we should note that the value of $\langle \omega^2 \rangle / \langle \omega^0 \rangle$ is influenced by the shape of the instrumental profile (as is not the case with the Landau-Placzek ratio). To obtain the correct value for $\langle \omega^2 \rangle / \langle \omega^0 \rangle$, one should use the relation¹³

$$\left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{corrected}} = \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{exp}} - \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{instr}} \quad (10)$$

VI. The van der Waals Model

Anticipating the fact that we want to compare experiments and calculations, we will choose a system that does not have internal degrees of freedom and that can be described by a relatively simple (but not trivial) equation of state. The first requirement demands that we consider noble gas mixtures only. Systems like these can be represented by the van der Waals equation of state, which fulfills the second requirement. If we choose xenon for one of the components, we can observe the onset of critical phenomena under experimentally easily accessible circumstances.

The model for liquids and gases that was proposed by van der Waals in his famous thesis¹⁵ was extended later by him to binary mixtures.¹⁶ He retained the successful relation for pure fluids

$$p = \frac{\rho k_B T}{1 - \rho b} - a \rho^2 \quad (11)$$

and introduced the fact that this equation of state had to model a mixture only indirectly in the definition of the parameters a and b . (Note that throughout this paper we use ρ for number densities, and thus the dimensions of the van der Waals parameters a and

b are defined accordingly.) Nowadays we write¹⁷

$$\begin{aligned} a &= a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2 \\ b &= b_{11}x_1^2 + 2b_{12}x_1x_2 + b_{22}x_2^2 \end{aligned} \quad (12)$$

where the parameters with identical indexes are the pure fluid parameters and the others are interaction parameters. Often the latter are approximated by the pure fluid parameters, too.

$$a_{12} = (a_{11}a_{22})^{1/2} \quad b_{12} = \frac{1}{2}(b_{11}^{1/3} + b_{22}^{1/3})^3 \quad (13)$$

However, corrections to these interaction parameters can be substantial. For low-density He + Xe mixtures the correction to the related second virial cross-coefficient B_{12} is 40%.¹⁸ Fortunately, the effect on the resulting a 's and b 's is very small. Therefore, the details of the approximation for a_{12} and b_{12} do not influence the results of the thermodynamic calculations too much, as long as we do not perform calculations for mixtures that either consist mainly of He or are near critical.

Having established an equation of state, we are able to calculate the thermodynamic quantities that are of particular interest to us. For a few quantities we will elucidate the calculations.

The expression for the heat capacity at constant volume is given by¹⁹

$$c_{V,x} = c_{V,x}^{\text{ig}} + T \int_{-\infty}^V \left(\frac{\partial^2 p}{\partial T^2} \right)_{V,x} dV' \quad (14)$$

From the definition of the van der Waals equation, we can see that the second derivative of the pressure with respect to the temperature is zero. Thus, $c_{V,x}$ simplifies to the ideal gas result: $3/2 k_B$. From the standard thermodynamic relation

$$c_{p,x} = c_{V,x} + TV \frac{\alpha_{p,x}^2}{\chi_{T,x}} \quad (15)$$

where $\alpha_{p,x}$ is the isobaric expansion coefficient, we can calculate the heat capacity at constant pressure.

The chemical potential is also defined as the sum of an ideal term and an integral over deviations from ideality¹⁹

$$\begin{aligned} \mu_i(p, T) = & \mu_i(0, T) + k_B T \ln p x_i + \int_{-\infty}^V \left[\frac{1}{V'} \left(\frac{\partial p}{\partial \rho_i} \right)_{T, V, N_{j \neq i}} - \rho k_B T \right] dV' \end{aligned} \quad (16)$$

The integral term can be calculated analytically for a van der Waals mixture. The resulting expressions are, however, quite lengthy. If we define the fugacity f_i

$$f_i = \frac{1}{k_B T} [\mu_i(p, T) - \mu_i(0, T)] \quad (17)$$

we can write²⁰

$$f_i = \ln \left(x_i \frac{\rho k_B T}{1 - \rho b} \right) + \mathcal{B}_1 \frac{\rho}{1 - \rho b} - \mathcal{B}_2 \frac{\rho}{k_B T} \quad (18)$$

where

$$\begin{aligned} \mathcal{B}_1 &= b + \rho \left(\frac{\partial b}{\partial \rho_i} \right)_{T, V, N_{j \neq i}} = b_{ii} - x_j^2 (b_{ii} - 2b_{ij} + b_{jj}) \\ \mathcal{B}_2 &= 2a + \rho \left(\frac{\partial a}{\partial \rho_i} \right)_{T, V, N_{j \neq i}} = 2(a_{ii}x_i + a_{ij}x_j) \end{aligned} \quad (19)$$

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TABLE I: van der Waals Parameters a_{XeXe} , a_{HeHe} , b_{XeXe} , and b_{HeHe} , Molecular Masses, and Polarizabilities²¹ for He and Xe (N_A is Avogadro's Constant)

i	a_{ii}/N_A^2 , m ⁶ Pa	b_{ii}/N_A , m ³	M_i/N_A , kg	α_i , m ³
Xe	4.19×10^{-1}	5.15×10^{-5}	1.31×10^{-1}	4.170×10^{-30}
He	3.57×10^{-3}	2.40×10^{-5}	4.00×10^{-3}	0.207×10^{-30}

Figure 4. Landau-Placzek ratio for a He + Xe mixture in the ideal gas limit. The dashed line indicates the contribution to J due to $\gamma - 1$.

We will perform our calculations on mixtures of helium and xenon. For the numerical values used in our calculations we refer to Table I.

VII. Results of the Calculations

In the limit of an ideal binary gas mixture the expression for the Landau-Placzek ratio, eq 2, reduces to

$$J = \frac{2}{3} + \frac{5}{3} x_1 x_2 \left(\frac{\alpha_2 - \alpha_1}{\alpha_1 x_1 + \alpha_2 x_2} \right)^2 \quad (20)$$

which means that J is determined by the composition and the ratio of the polarizabilities of both components only. The maximum of this curve can be found at $x_1 = \alpha_2/(\alpha_1 + \alpha_2)$. Therefore, the curve is always asymmetrical with respect to x (or flat if $\alpha_1 = \alpha_2$). For He + Xe the curve is shown in Figure 4.

By increasing the pressure, we can observe the onset of nonideal behavior. In Figure 5a-d we show the pressure dependence on the Landau-Placzek ratio at various compositions. The pressure range is from 0 to 10 MPa. The dashed line indicates the contribution of $\gamma - 1$ to J . It is clear that J is strongly pressure dependent. In Figure 5a (the case for a pure fluid) $\gamma - 1$ grows in the neighborhood of the critical point as the entropy fluctuations increase. If we perform the calculations at higher He concentration, we observe the additional contribution due to concentration fluctuations. This contribution is small at small mole fractions of He. The calculations at a higher helium concentration show that the contribution to J due to concentration fluctuations increases while the contribution due to $\gamma - 1$ decreases. At $x_{\text{Xe}} = 0.75$, $\gamma - 1$ is a smooth function of pressure, while J is certainly not. If we increase the concentration of He still further, the pressure at which we encounter critical behavior shifts to still higher pressures. The width of the peak in J as a function of pressure increases with increasing mole fraction He.

A different way to look at the behavior of J is considering it as a function of composition at constant pressure (see Figure 6). At low pressures one finds essentially the ideal gas limit: a broad single hump at small molar fractions of xenon. If we increase the pressure, the shape of the curve of J changes mainly at the side of pure xenon. When we approach the critical pressure, the Landau-Placzek ratio increases sharply. If we increase the pressure still further, we find that the sharp increase develops into a second peak. The peak shifts to smaller mole fractions of xenon, broadening simultaneously, when the pressure increases.

VIII. Experimental Results and Discussion

In our experiments we measured Rayleigh-Brillouin light scattering spectra of He + Xe mixtures of various compositions and pressures up to 10 MPa. We will illustrate our results in some

Figure 5. Landau-Placzek ratio for a He + Xe mixture as a function of pressure at various compositions and $T = 293$ K, calculated according to the van der Waals equation of state: (a) $x_{\text{Xe}} = 1.00$; (b) $x_{\text{Xe}} = 0.90$; (c) $x_{\text{Xe}} = 0.75$; (d) $x_{\text{Xe}} = 0.25$. The dashed line indicates the contribution due to $\gamma - 1$.

detail with data obtained for one of these series. Our choice is a mixture with $x_{\text{Xe}} = 0.73 \pm 0.02$ at a temperature of 293 ± 0.5 K in the pressure range 2.0–10.0 MPa.

In Figure 7 we show the Landau-Placzek ratio J versus the pressure of the gas sample. This is a smoothly increasing function with increasing pressure. For low pressures one may calculate

Figure 6. Landau-Placzek ratio for a He + Xe mixture as a function of composition at various pressures and $T = 293$ K, calculated according to the van der Waals equation of state: (a) $p = 5.8$ MPa; (b) $p = 10.0$ MPa. The dashed line indicates the contribution due to $\gamma - 1$.

Figure 7. Landau-Placzek ratio J as a function of pressure for $x_{Xe} = 0.73$ and $T = 293$ K: ($\square$) experimental results; (—) J calculated according to the van der Waals equation of state; (---) $\gamma - 1$ calculated according to the van der Waals equation of state.

the ideal gas limit for J to be 1.2. As we estimate the absolute error in J to be 0.3, this means the extrapolation of J to the zero-pressure limit coincides within error with the calculated value. At higher pressures the data attain values that are over 5 times the ideal gas value. This is due to an increase in fluctuations in the mixture, both entropy fluctuations (that is, fluctuations in $\phi^{(2)}$) and concentration fluctuations. As there is no direct way to separate both contributions by Rayleigh-Brillouin light scattering, we will compare the experimental results to our calculations based on the van der Waals equation of state. The solid upper line in Figure 7 shows the Landau-Placzek ratio as is predicted by the van der Waals model, while the dashed lower line represents the contribution due to entropy fluctuations. Therefore, we may conclude that at this composition and temperature the pressure dependence of the Landau-Placzek ratio is determined more by the pressure dependence of the concentration fluctuations than by the pressure dependence of the entropy fluctuations.

The fact that the concentration fluctuations are much more sensitive to pressure than entropy fluctuations is reflected in the behavior of the velocity of sound in Figure 8. Usually, a large

Figure 8. Propagation frequency of the sound mode z''_s as a function of pressure for $x_{Xe} = 0.73$ and $T = 293$ K: ($\square$) experimental results; (—) $c_s k$ calculated according to the van der Waals equation of state.

Figure 9. Reduced second moment $\langle \omega^2 \rangle / \langle \omega^0 \rangle$ as a function of pressure for $x_{Xe} = 0.73$ and $T = 293$ K: ($\square$) experimental results; (—) $\langle \omega^2 \rangle / \langle \omega^0 \rangle$ calculated according to the van der Waals equation of state.

Figure 10. Experimental results for $(\langle \omega^2 \rangle / \langle \omega^0 \rangle)(J + 1)/(k^2 c_s^2)$ as a function of pressure for $x_{Xe} = 0.73$ and $T = 293$ K.

change in the heat capacity ratio γ is accompanied by a sudden decrease in the isothermal velocity of sound and a less pronounced, but nevertheless substantial, decrease in the adiabatic velocity of sound. However, from Figure 8 it follows that the adiabatic velocity of sound is virtually constant, variations being of the order of 5%. This rules out the possibility that variations in $\gamma - 1$ would be responsible for the increase in J in Figure 7. Thus, the data on the adiabatic velocity of sound support the same conclusion as the calculations do: Concentration fluctuations are more important than pressure fluctuations to explain the experimentally observed pressure dependence of the Landau-Placzek ratio at this composition.

In Figure 9 we display the results for $\langle \omega^2 \rangle / \langle \omega^0 \rangle$, which shows a smooth decreasing function with increasing pressure. This was to be expected as $\langle \omega^2 \rangle / \langle \omega^0 \rangle$ is proportional to the inverse normalized scattering intensity. Because $(J + 1)/c_s^2$ should be proportional to the scattering intensity,^{13,23} a test to find out whether this is indeed the case is to multiply $\langle \omega^2 \rangle / \langle \omega^0 \rangle$ by $(J + 1)/c_s^2$ and see whether the resulting function is a constant. In Figure 10 we plotted $(\langle \omega^2 \rangle / \langle \omega^0 \rangle)(J + 1)/(k^2 c_s^2)$. From ref 23, eq 14, we can calculate that the resulting constant should be 1.004, which is true within experimental error. Figure 10 demonstrates the accuracy and consistency of the data and data analysis. We will not use these reduced second moments any further but rather concentrate on the Landau-Placzek ratio and Brillouin shift to

(22) See refs 6 and 23 for the meaning of ϕ . It is not entirely correct to speak of entropy fluctuations if we mean fluctuations in ϕ , because fluctuations in ϕ can be written as a combination of entropy and concentration fluctuations. However, in analogy with pure systems we will use this nomenclature.

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Figure 11. Landau-Placzek ratio J as a function of pressure for various compositions and $T = 293$ K. From top to bottom: ($\diamond$) $x_{\text{He}} = 0.99$; ($\blacksquare$) $x_{\text{He}} = 0.97$; ($\star$) $x_{\text{He}} = 0.91$; (∇) $x_{\text{He}} = 0.83$; ($\triangle$) $x_{\text{He}} = 0.79$; ($\ast$) $x_{\text{He}} = 0.73$; ($\circ$) $x_{\text{He}} = 0.44$; ($\bullet$) $x_{\text{He}} = 0.39$; (—) S_{XeXe} calculated according to the van der Waals equation of state. Each subsequent graph has been shifted over a decade.

gain information on scattering intensities.

We have performed several series of experiments on mixtures of different compositions: $x_{\text{He}} = 0.99, 0.97, 0.91, 0.83, 0.79, 0.73$ (already discussed), 0.44, and 0.39 where the uncertainty in composition is 0.02. In Figure 11 we show our results for the Landau-Placzek ratio in these mixtures. The symbols indicate the data, and the solid lines indicate calculations according to the van der Waals equation of state. Note that in this logarithmic plot each subsequent curve has been shifted over a decade. From our data it is clear that for densities below the compressibility maximum the van der Waals model describes the data accurately. Since we do not attain this compressibility maximum in the lower five curves, the description is valid for these experiments over the full range of densities probed.

In the top three curves of Figure 11, deviations between calculations and experiment can be observed. For $x_{\text{He}} = 0.91$, the observed Landau-Placzek ratio is somewhat higher than the calculated one. For larger values of x_{He} , the deviations become more pronounced. The data seem to indicate that the model predicts a maximum in J at the wrong pressure. There are two possible reasons for the failure of the calculations. The first one is obvious and is related to the limitations of the van der Waals model. Near the critical region the results for the Landau-Placzek ratio become extremely sensitive to the shape of the isotherms predicted by the equation of state. Both the fact that the van der Waals equation itself is an approximation and the fact that we use mixing rule (13) will influence the reliability of the calcula-

Figure 12. Brillouin shift z''_s as a function of pressure for various compositions and $T = 293$ K: ($\diamond$) $x_{\text{He}} = 0.99$; ($\star$) $x_{\text{He}} = 0.91$; (∇) $x_{\text{He}} = 0.83$; ($\triangle$) $x_{\text{He}} = 0.79$; ($\ast$) $x_{\text{He}} = 0.73$; ($\circ$) $x_{\text{He}} = 0.44$; ($\bullet$) $x_{\text{He}} = 0.39$; (—) z''_s calculated according to the van der Waals equation of state.

tions. The second reason is experimental of origin and is related to the inaccuracy with which the composition of the mixtures is known. It can be seen from the top two figures, for which the uncertainty in composition of each mixture is the same as the difference in composition of both mixtures, that the difference between both calculations is of the same order of magnitude as the difference between calculation and experiment for a mixture. To be able to make more explicit assertions about the validity of the van der Waals model in this thermodynamic region, we should include results from other observables in the light scattering spectrum.

To this end we plotted the results for the Brillouin shifts and the corresponding calculations in Figure 12. In this graph results for $x_{\text{He}} = 0.97$ were omitted, because they nearly coincide with those for $x_{\text{He}} = 0.99$.

The graphs indicate that for higher He concentrations the data agree rather well with calculations. However, for smaller He concentrations clear deviations occur. In Figure 12, the data indicate that the $x_{\text{He}} = 0.99$ mixture at $p \approx 6$ MPa is nearer to the critical point than the van der Waals mixture. On the other hand, the comparison of the calculation and the experiments for the same circumstances in Figure 11 indicates the opposite. Therefore, the deviations between experiment and calculations cannot be due to an erroneous determination of composition but must be due to the difference between the van der Waals equation of state and experimental p, V, T data. In this region such a difference was to be expected.

The deviations for higher densities might have another origin. For pure xenon, one can see that the densities predicted by the van der Waals equation of state are smaller than the ones observed in experiment. Since we use density in the Clausius-Mossotti equation to calculate the refractive index for the mixture, the refractive index is underestimated in the model calculations. This

would lead to an underestimation of the wave vector k . Presumably, the same underestimation occurs for the mixture also (but to our knowledge no experimental data are available to check this), which would mean that our calculated curve is lower than it would have been if the correct value for the wave vector had been used. This question could be resolved if one would either measure the refractive index directly or use another design for the sample cell.²⁴

IX. Conclusions

In this paper we presented results from light scattering experiments on mixtures of helium and xenon. Our aim was to find out to what extent the van der Waals equation of state can be used to describe the thermodynamics of the mixture with respect to the quantities that are of importance in the description of a dynamic light scattering spectrum. We found that, over the range in which we performed our experiments, the van der Waals model always gives qualitative if not quantitative results.

To be more exact, for all our experiments with $x_{\text{Xe}} < 0.9$ results of experiments and calculations were (within error) identical up to the highest pressures probed. Thus, we can use the van der Waals model to predict the Landau–Placzek ratio and the Brillouin shifts in these cases. For compositions where $x_{\text{Xe}} > 0.9$, the correspondence between calculations and experiment is not always

quantitative. Up to 5.0 MPa agreement is found, but at higher pressures deviations occur. There are basically two possible causes for this. First, the van der Waals equation of state is incorrect near the critical point. However, deviations usually manifest themselves very near the critical point only. A second possibility is that the mixing rule (13) is inadequate, at least near the critical point. For higher pressures the underestimation of the density might introduce an error in the wave vector that is calculated, resulting in an incorrect prediction of the Brillouin shift.

The detailed analysis of J was necessary to check the theoretical framework upon which the description of the Landau–Placzek ratio is based. Having validated this description, we can proceed to inverse the scenario: can we use the Landau–Placzek ratio to extract thermodynamic data of a mixture? This is of course dependent on the number of independent parameters that can be retrieved from a dynamic light scattering spectrum and the number of other thermodynamic quantities that are known for the mixture. In the subsequent paper we will consider the “minimum” case: what information on the thermodynamics of a mixture can be gained from a single Rayleigh–Brillouin light scattering spectrum?

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Rayleigh–Brillouin Light Scattering from Noble Gas Mixtures. 2. Partial Structure Factors

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We derive a relation between the static structure factor for a mixture and experimental quantities that can be extracted from a Rayleigh–Brillouin light scattering experiment: the Landau–Placzek ratio and Brillouin shift. Partial structure factors are related to the thermodynamic quantities that characterize a mixture in a similar way as the Kirkwood–Buff integrals. In a He + Xe noble gas mixture, the spectrum is dominated by the contribution due to the Xe–Xe correlations in the mixture. We compare experimental results to calculations using the van der Waals equation of state. The other two partial structure factors can be obtained in an approximate way from a mixing rule for the partial static structure factors. Thus, it is possible to obtain approximate values for the isothermal compressibility, the osmotic compressibility, and the partial volume from a single experiment.

I. Introduction

Although thermodynamics constitutes a complete theory, there has always been an endeavor toward “understanding” the values of thermodynamic quantities in terms of molecular models. Fluctuation theory is among the most general of these models, and it can serve therefore as a first step to achieve such an understanding. It relates thermodynamic quantities to fluctuations in the number densities of particles present in a certain volume without specifying details of the interaction between those particles.

For a binary mixture the actual relations between compressibility, molar volume, osmotic compressibility, and fluctuations were given by Kirkwood and Buff.^{1,2} Only in the past decade have attempts been made to actually extract values for these so-called Kirkwood–Buff integrals from experimental data.^{3–20} A serious problem in extracting these integrals is that one needs several sets of thermodynamic data to obtain the integrals. One

would rather determine the Kirkwood–Buff integrals directly from an experiment.

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