International Journal of Thermophysics, Vol. 16, No. 3, 1995

Broadening of the Vibrational Linewidth in a Mixture Due to Critical Concentration Fluctuations[1]

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Vibrational Raman spectroscopy is a very usful technique for studying the dynamical behavior of a system, in particular in the critical region. In a mixture, composition fluctuations play an important role and on the basis of the results for pure substances one would expect an increase of the linewidth in approaching the critical point. However, in previous experiments such an effect was not detected. The reasons for this failure will be discussed. Recently, we have observed a considerable broadening of the linewidth in approaching the critical point in the system helium–nitrogen under high pressure. However, it is well-known that broadening may occur through various other mechanisms such as changes in density, composition fluctuations far from the critical point, aggregation, etc. On the basis of the helium–nitrogen data the pitfalls in the experimental determination of critical broadening are discussed. The data analysis takes into account the contribution of noncritical effects. Consequences are drawn for the interpretation of spectroscopic data in terms of concentration of species in supercritical solvents. Moreover, we discuss the possibility of a difference between the local composition and the bulk composition and demonstrate from our line shift data that this is not a critical effect.

KEY WORDS: concentration fluctuations; critical broadening; high pressure; line shape; line shift; local composition; mixtures; nitrogen–helium; Raman spectroscopy.

1. INTRODUCTION

The vibrational frequency of an isolated diatomic molecule is determined by the *intra*molecular forces. In a dense fluid the *inter*molecular forces can

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[1] Invited paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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cause a change not only in the molecular vibrational frequency [1], but also in the profile of the spectrum [2, 3]. The profile, characterized by, e.g., the linewidth, reflects the changes in the local environment of the molecule.

In a pure component the local environment varies due to fluctuations in the density. Well away from the critical point these fluctuations have a large wavevector and a high frequency, which result in motional narrowing of the spectral line. Near the critical point the amplitudes of the fluctuations with a small wavevector and low frequency increase, leading to broadening [4, 5]. The addition of a second component also changes the local environment. Since in the critical region of a mixture, concentration fluctuations play an important role one would expect a similar increase in linewidth in approaching the critical point of mixtures. However, in previous experiments on the system 3-methylpentane–nitroethane the linewidth turned out to be insensitive to critical concentration fluctuations [6], while in the case of argon–nitrogen a conclusion could not be drawn [7]. In a theoretical study it was concluded that line broadening due to critical concentration fluctuations did not exist [8].

Recently, we have performed experiments in a diamond-anvil cell on mixtures of helium and nitrogen in a large temperature, pressure, and composition range, including the critical region. The results are very interesting since a considerable broadening in the linewidth has been observed in approaching the gas–gas critical line. Moreover, the amplitude of the fluctuations can be estimated from the linewidth data.

To prove that the observed broadening is indeed due to critical fluctuations, and to show why other investigators did not find critical broadening in mixtures, other effects which influence the linewidth should also be considered. Therefore, a short discussion is presented of the linewidth, the line shift, and the choice of the system and the experimental conditions.

1.1. Linewidth

As pointed out by, e.g., Oxtoby [9], broadening may also occur through various other mechanisms such as changes in density, concentration fluctuations far from the critical point [10], resonance transfer [11], vibration–rotation coupling [12], aggregation [13] etc. In the past this has lead to an incomplete interpretation of the results [14]. Fortunately some of these contributions can be calculated; others are so small in the case of nitrogen that they can be neglected.

It has been shown experimentally that in pure nitrogen the contribution of resonance transfer to the linewidth is small [2]. In the mixture it is smaller and it is not to be expected that there is an anomalous behavior in this contribution in the critical region. The contribution of population (energy) relaxation can also be neglected [15]. At low densities the various rotational states manifest themselves as individual peaks in the spectrum. At higher densities these details will disappear due to motional narrowing. In this investigation the densities are such that motional narrowing has been completed.

More important is the maximum in concentration fluctuations which occurs even in a noncritical mixture. For instance, in a mixture of only 1% helium in nitrogen the chances are small that a nitrogen molecule has more than one helium molecule as its nearest neighbor, if there is no aggregation mechanism, and thus the fluctuation in concentration is small. On the other hand in a 50–50% mixture the local composition can easily be 30 or 70%. Callego et al. [16] have shown that for mixtures of hard spheres of equal size this maximum indeed occurs for $x = 0.5$. If the diameter ratio is increasing, the maximum shifts to lower concentrations of the smaller component. The calculation of these fluctuations, the possibility of aggregation and the effect of density are discussed later.

It should be noted that many investigators use the height of the peak of the sectrum as a measure of concentration. It must be clear from the above discussion that this is true only as long as the various contributions to the linewidth do not change since as soon as the line broadens the line height will decrease.

1.2. Line Shift

The line shift as a function of composition (at constant temperature and pressure) is closely related to the broadening of the linewidth due to concentration fluctuations. Since the local composition varies in space and time, the vibrational frequency of a diatomic molecule also varies. As a result one does not measure a single frequency (we discard for a moment the density fluctuations) but a whole spectrum. However, if there is no shift of the frequency as a function of composition, differences in local composition would not result in different frequencies. In that case there would be no effect of concentration fluctuations on the linewidth (see also Ref. 17). This explains the absence of a critical effect in 3-methylpentane–nitroethane. It is also clear that data on the concentration dependence of the line shift are needed to calculate the amplitude of the fluctuations from the linewidth.

The deviation of the local composition from the bulk composition is assumed to be the main reason for an enhanced reaction rate of chemical reactions in supercritical fluids [18]. Measurement of the Raman shift as a function of composition gives information about the local composition.

The density has also influence on the linewidth. Since the linewidth is measured as a function of composition at constant pressure (and temperature) and not at constant density, anomalous broadening might be due to anomalous density changes in the critical region, when the composition is changed. The behavior of the line shift as a function of composition (constant p and T) provides information about the change in density as explained later.

1.3. Choice of System

As mentioned before, line broadening may occur through various mechanisms. Thus it is important to follow an experimental path in p–T–x space which allows for a careful analysis of the data and to make a proper choice for the system to be investigated.

In a pure substance the distance to the critical point is expressed in terms of $T - T_c$ and $r - r_c$, where T_c and r_c are, respectively, the temperature and density at the critical point. In determining the critical line broadening, the critical point is approached at constant density r_c. This is a well-defined thermodynamic path along which only the temperature changes. In a mixture the distance to a point on the critical line should be expressed in terms of $T - T_c$, $x - x_c$, or $p - p_c$. The critical composition, x_c, generally changes considerably along the critical line. In practice, measurements can only be performed at constant composition (or along the coexistence surface). Then, in approaching the critical *point* corresponding to the (constant) experimental composition, the distance to the critical *line* can vary in a complicated way. In that case the interpretation of the data is very difficult.

In the system argon–nitrogen [7] the critical point of a mixture with arbitrary composition is always within 15 K of the critical point of one of the components. Thus not only critical concentration fluctuations but also critical density fluctuations play a role. Moreover, the critical composition changes from pure argon to pure nitrogen within 30 K. This explains why no conclusions could be drawn for this system [7].

In contrast, the system helium–nitrogen is appropriate for this study if the experiments are performed under high pressure. The system exhibits fluid–fluid equilibrium of the second type, with a temperature minimum in the critical line at about 120 K. It has the advantage that above 1 GPa the critical composition is nearly independent of pressure and temperature. In that pressure range the system is far from the critical point of both pure helium and pure nitrogen so that critical density fluctuations will not be of importance. The p–T–x diagram of the system in the relevant p–T range is given in Fig. 1 [19]. In this system the available pressure and temperature range for studying the behavior is very large, in contrast with systems

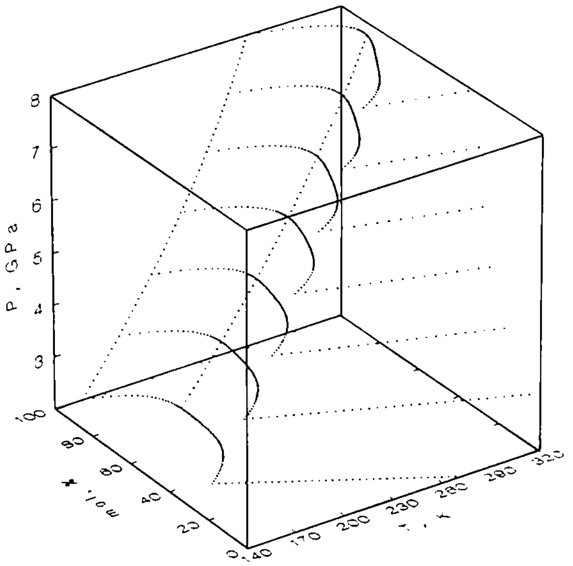

Fig. 1. The P–T–x diagram of the system helium–nitrogen. The composition is given as mole percentage helium. The strongly curved lines represent the fluid–fluid equilibrium. The curve in the p–T plane at 100 % is the melting line of helium. The dotted curve at about 80 mol % shows the critical line. The other (almost-straight) lines, which end at the melting line of nitrogen, represent the liquid branch of the solid–liquid equilibrium.

exhibiting liquid–liquid equilibrium which often disappears under the crystallization surface at relatively low pressures. This enables us to determine the extend of the crossover region (crossover from critical to noncritical behavior) and also to measure the noncritical contributions. Moreover, various values for the critical pressure or critical temperature can be selected.

The system consists of simple molecules which are amenable to theoretical treatment. The equation of state and the interaction potentials of the pure components are well-known and information on the unlike interactions is available so that computer simulations can be carried out and existing models for calculating the frequency shift can be applied. Moreover, a wealth of experimental data is available about the vibrational properties of pure nitrogen. As discussed before, the contribution to the linewidth of several mechanisms can be calculated or is so small that it can be neglected.

1.4. Amplitude of Fluctuations

Recently, Muller et al. [20] have shown that in mixtures far from the critical point the lifetime of the concentration fluctuations is about 5 ps. These are fluctuations with relatively small wavelength. The time scale of long-wavelength fluctuations is much longer and will increase in approaching the critical point [21]. Therefore, we may assume that the decay time of the critical concentration fluctuations is much larger than the relevant time scale given by the inverse linewidth, which is about 2 ps. Moreover, the profiles of our spectra can be fitted better with Gaussians than with Lorentzians. Thus we can conclude that the critical contribution to the linewidth has no significant motional narrowing [22]. In that case the shape of the vibrational spectrum represents the distribution of the local composition, where "local" means within an environment of a few atomic diameters.

2. RESULTS

We have determined [23] the full width at half-maximum (FWHM) and the shift of the vibrational polarized Raman spectrum of nitrogen as a function of pressure, temperature, and composition in the homogeneous fluid phase of the mixture helium–nitrogen at very high density. Data have been collected from 200 to 400 K and pressures up to 10 GPa for eight mixtures with compositions, in terms of the mole fraction of helium, of 0.0, 0.10, 0.40, 0.55, 0.70, 0.90, 0.95, and 0.98. Measurements have been performed as a function of temperature along six isobars and as a function of pressure at room temperature. The mixture was always in the homogeneous phase and at least 5 K above the fluid–fluid coexistence surface. The temperature stability, the temperature variation across the sample, and the uncertainty of the temperature are all about 0.1 K or less. The choice for the proper order parameter is often made by using the criterion of a symmetric coexistence curve [24]. In the case of helium–nitrogen our choice for the volume fraction instead of, for instance, the mole fraction does not only result in a more symmetric coexistence curve, but also in a nearly symmetric FWHM curve, while the frequency shift as a function of the volume fraction (at constant T and p) is then almost a straight line. At room temperature and 2.5 GPa the mole fractions mentioned above correspond to the following volume fractions: 0.00, 0.037, 0.188, 0.298, 0.442, 0.756, 0.861, and 0.945.

2.1. Linewidth

In Fig. 2 the FWHM has been plotted as a function of the volume fraction of helium (x_v) at room temperature and three pressures. The figure shows some remarkable features. The isobars have a pronounced maximum around the critical volume fraction, which is about 0.57. The value of the FWHM in the maximum is about twice that for pure nitrogen, the ratio being highest for the highest pressures. The FWHM decreases rapidly for the higher volume fractions and its value in dilute solutions is even smaller than in pure nitrogen. Finally, there is a small shoulder for volume fractions around 0.3.

In Fig. 3 the linewidth is shown as a function of pressure for two mixtures and for pure nitrogen at room temperature. The slope is always positive but for pure nitrogen it has the tendency to decrease, while for a curve with composition closer to the critical (90 mol%) the slope is clearly increasing in approaching the critical line. For all experimental pressures the FWHM is smaller for a dilute mixture with only 2% nitrogen than for pure nitrogen.

We have also determined the linewidth as a function of temperature (constant p) for nitrogen and a few mixtures. In nitrogen the linewidth shows a small increase at increasing T but in the mixtures there is a decrease, which is most pronounced for the near-critical composition. At high T the FWHM tends to a constant value in all cases.

2.2. Line Shift

The determination of the value of the Raman shift at constant pressure as a function of composition is necessary for a quantitative treatment of the concentration fluctuations. As discussed in the introduction, if there is no shift there is no critical broadening of the linewidth. These data are also needed in the discussion about a possible contribution to the linewidth of anomalous density changes as a function of composition in the critical region. The shift is presented as a function of volume fraction in Fig. 4 and as a function of T in Fig. 5. Figure 4 shows a regular increase in the shift versus x_v. Near the critical volume fraction (0.57) there is a small tendency for a negative deviation from the fitted curves. We will come back to this effect later. As a function of temperature the shift is essentially constant. A small increase has been measured at high pressure not too far from the corresponding critical composition.

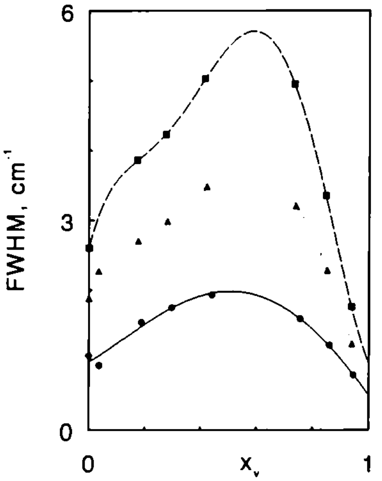

Fig. 2. The FHWM of the N_2 vibrational Raman line versus the volume fraction of helium at $T = 296$ K and $p = 2.5$ GPa (circles), $p = 4.5$ GPa (triangles), and $p = 6.5$ GPa (squares).

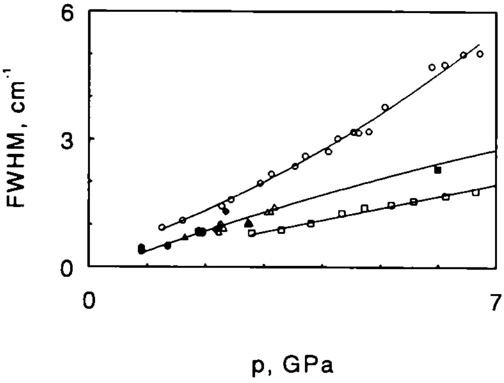

Fig. 3. The FWHM of N_2 versus p at 296 K. Open symbols: This work for $x = 0$ (triangles), $x = 0.695$ (circles), and $x = 0.980$ (squares). Filled symbols: Pure N_2 data obtained from the literature.

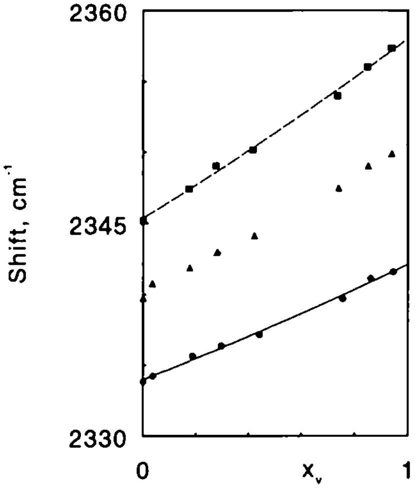

Fig. 4. The Raman shift of N_2 versus the volume fraction x_v of helium at $T = 296$ K and $p = 2.5$ GPa (circles), $p = 4.5$ GPa (triangles), and $p = 6.5$ GPa (squares). The lines are guides to the eye.

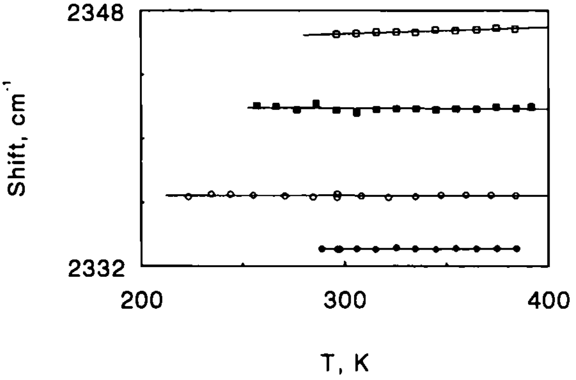

Fig. 5. The Raman shift on N_2 versus T. Pure N_2 at 2.25 GPa (filled circles), $x = 0.695$ at $p = 2.3$ GPa (open circles), $x = 0.400$ at $p = 4.5$ GPa (filled squares), and $x = 0.695$ at $p = 5.3$ GPa (open squares).

3. DISCUSSION

We proceed to prove that the maximum in the linewidth (Fig. 2) is due to *critical* concentration fluctuations. Both the behavior of the linewidth and the line shift are important in this respect.

3.1. Line Shift

It is mentioned in the introduction that concentration fluctuations have only influence on the linewidth if there is a shift of the vibrational frequency as a function of concentration [17]. Nitrogen in helium shows a considerable shift (Fig. 4). To explain the results of Petrula et al. in 3MP-NE [6] (*the absence of critical broadening*), *Hills* [8] *suggested that* the wavelength of the concentration fluctuations should be smaller than the correlation length (x) and that $kx > 1$ (k is wavenumber) to obtain critical broadening in mixtures. The measurements of Burstyn and Sengers [21] show that this is certainly not the case in the investigation of Petrula et al. For instance, for $k = 0.7 * 10^5$ cm^{-1} $kx < 1$ if $T - T_c > 0.01$ K. In fact, close to the critical point the x value of 3MP-NE is only 1.5 that of carbon dioxide [25] and thus in the mixture the relative temperature difference with the critical point needs to be only a factor of 2 larger to obtain the same qualitative behavior. The reason why no critical broadening was observed in this mixture is that there is no change in the frequency as a function of composition. This is the case for all the Raman lines of the components involved [6].

The curves of the linewidth in Fig. 2 are at constant pressure, and therefore the density will change as a function of composition. In particular, there might be anomalous changes in the bulk density as a function of composition in the critical region. Since the linewidth depends also on density, this will result in an anomalous linewidth which is not due to composition fluctuations. Such a density effect will as well have a direct influence on the vibrational frequency and thus on the line shift as a function of composition. From the regular behavior of the shift in Figs. 4 and 5 we can draw the conclusion that the *average* interaction of a particular nitrogen molecule with its environment does not show an anomaly in the critical region. A calculation, by means of a mean-field equation of state in which the unlike interaction is obtained from high-pressure sound velocity measurements in the mixture [26], also does not indicate any specific behavior of the density near the critical volume fraction. Therefore, the maximum in the FWHM is not due to anomalous density effects.

Another aspect is the behavior of the local composition near the critical point [18]. If, considering the bulk composition, there is an increase (decrease) in the local composition of helium around the nitrogen molecule in the critical region, the frequency will show an increase (decrease) in the same region. From the regular behavior of the shift and the symmetry of the spectrum, it follows that, although the local composition might be different from the bulk composition, there is no indication of an increased *average* local composition in the critical region as mentioned in Ref. 18.

The small negative deviation around the critical concentration (Fig. 4) can be explained as follows. The intensity of the Raman signal is proportional to the number of nitrogen molecules in the part of the sample under investigation. At higher helium concentrations this number decreases. Near the critical composition the concentration fluctuations are considerable and the intensity effect will result in a relative shift of the peak position towards lower values.

3.2. Linewidth

A necessary, but in general not sufficient, condition for the maximum in linewidth being due to critical concentration fluctuations is that the FWHM increases when the critical point is approached in any direction. We have shown in Section 2 that this condition is fulfilled along lines of constant pressure, temperature and composition (see also Figs. 2 and 3). In fact, since theories [2, 27] predict that the FWHM only increases at decreasing T, the experimentally observed decrease in the FWHM, if a critical point is approached from above, already implies that the broadening is due to critical fluctuations.

Essentially the only existing method to calculate the contribution of the noncritical concentration fluctuations to the linewidth for simple systems is provided by the Knapp–Fischer model [10]. In order to use this model the linewidth has been measured at higher temperatures (up to 450 K), where it is assumed that the FWHM is determined by non-critical effects. The experimental as well as the calculated results are presented in Fig. 6 for 4.5 GPa and 450 K. It must be noted that the model uses two experimental parameters: the linewidth of pure nitrogen and the linewidth of nitrogen in the infinitely dilute solution at the same p and T. Moreover, there is an adjustable parameter N, which takes into account the number of different (on a time scale large compared to that of the *density* fluctuations) environments of the molecule. Knapp and Fisher used $N = 3$–5 in their calculations. In a forthcoming article we will argue that in the case of mixtures of helium and nitrogen this number can be considerably higher. Here we use the model only as a correlation and Fig. 6 then shows that N could be adjusted such that the experimental results are well represented by

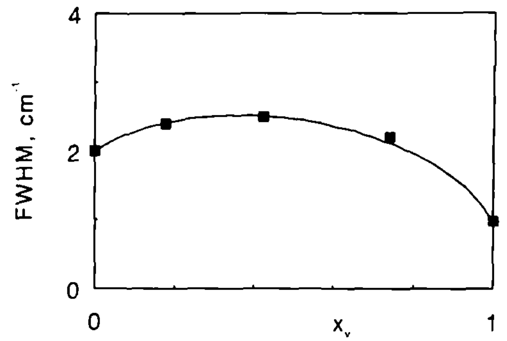

Fig. 6. Raman linewidth of N_2 at high T (450 K) and 4.5 GPa. Solid line calculated with the Knapp–Fischer model.

the fit. We now follow the model in assuming that the temperature behavior of this noncritical contribution to the linewidth is the same in the mixture as in pure nitrogen. The calculations show that under this assumption the noncritical contribution is only 25% of the experimental broadening. Our final conclusion is then that the broadening is mainly due to critical concentration fluctuations.

Figure 2 shows that in the dilute solution the linewidth is considerably smaller than in pure nitrogen and that the linewidth depends strongly on the composition. A narrow line gives a larger value for the height of the spectrum. This means that the height of the peak is not a good measure of the concentration. In fact the composition dependence increases for pressures close to the critical pressure. Therefore, one should be very careful in using the peak height as a measure of concentration.

3.3. Amplitude of Concentration Fluctuations

It is interesting to make an estimate of the amplitude of the critical concentration fluctuations. Because of the almost-linear behavior of the Raman shift (ω) as a function of the overall volume fraction x_{v0} (Fig. 4), the relation between the local frequency $\omega(x_v)$ and the frequency corresponding to the overall concentration $\omega(x_{v0})$ in the sample is

$$\omega(x_v) = \omega(x_{v0}) + (\partial\omega/\partial\omega_v)_{p,T}(x_v - x_{v0}) \tag{1}$$

This relation can be inverted to yield an expression for x_v as a function of the frequency. The critical contribution to the spectrum at a given p and T is then

$$I_{cr}(\omega) \sim (1 - x_v(\omega)) \cdot P(x_v(\omega)) \tag{2}$$

where $P(x_v(\omega))$ is the distribution of the local composition. The factor $(1-x_v(\omega))$ expresses the fact that intensity of the signal is proportional to the number of nitrogen molecules in the part of the sample under consideration. Because of this factor a small correction has to be made (1–5%) to obtain the width of $P(x_v(\omega))$ from that of $I_{cr}(\omega)$. We calculated this correction by modeling $P(x_v(\omega))$ with a Gaussian. The FWHM of $I_{cr}(\omega)$ was obtained by subtracting the noncritical contribution quadratically from the total width. The main source of uncertainty in the critical width originates from this procedure. It turns out that, as expected, the FWHM of $P(x_v)$ shows a maximum (almost 0.5) near the critical line. Moreover, the concentration fluctuations have been reduced by a factor 2 for $x_v = 1.4x_{v,cr}$. The behavior of the critical concentration fluctuations is analogous to the critical density fluctuations in a pure substance. The enhancement of the fluctuations in the mixture is still noticable up to a reduced temperature of 1.8, which seems to point to a larger crossover region than in a pure substance [27].

If the results for various temperatures and pressures are plotted in the same graph, within the accuracy the results seem similar for the same value of reduced temperature, nearly independent of pressure. Therefore, at a given composition one can approximately measure the distance to the critical line by regarding only the temperature. This is probably due to the steepness of the critical line and compensation by the small differences in critical composition.

It is assumed that the system is in the slow modulation regime with respect to the concentration fluctuations ($\Delta \cdot \tau_c \gg 1$; Δ is the amplitude and τ_c the correlation time of the concentration fluctuations). In that case the Raman linewidth directly reflects the magnitude Δ. If it was assumed that the system is in the fast modulation regime ($\Delta \cdot \tau_c \ll 1$), the line shape would be Lorentzian and Δ would be much larger than the Raman linewidth and thus much larger than calculated above. Of course, this is not possible.

4. SUMMARY

A consistent explanation of the experimentally observed broadening of the Raman linewidth in the critical region and the regular behavior of the shift can be given in terms of critical concentration fluctuations; there is no indication for a critically enhanced local composition, as suggested in Ref. 18; the peak height is often not a good measure of concentration.

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