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Critical broadening of the vibrational linewidth by concentration fluctuations

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We report high pressure measurements of the half-width and shift of the vibrational Raman spectrum of nitrogen in the homogeneous helium-nitrogen fluid binary mixture. The measurements have been performed using a diamond anvil cell in a large range of pressure p, temperature T, and composition x including the critical region. In approaching the critical line a considerable broadening has been observed which is shown to be due to critical concentration fluctuations. This proves that the order parameter distribution can explicitly be determined by a general experimental method.

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When approaching a critical point, large fluctuations of the order parameter arise. Recently, interest has grown for determining the amplitude of these fluctuations [1], especially in terms of finite-size distribution functions [2–4]. From these one can calculate nonuniversal quantities such as the location of the critical point [2,3], aspects of the cross-over region [3], which are now currently of interest [5,6], or reaction dynamics [7], but also the universal critical exponents [3,4]. Many critical phenomena are in the same universality class as the Ising-spin system, e.g., [8] pure substances, mixtures, magnetism and [9] within a few K above T_c also polymers. A question of fundamental interest is then whether the distributions themselves possess a scaled universal form at criticality, while they fall off at some characteristic way to Gaussians far from criticality [3]. Recently, this was predicted for fluids and magnetic systems in two dimensions by means of Monte Carlo simulations [2].

Up to now, the only way to determine experimentally the amplitude of the critical fluctuations has been by means of Raman spectroscopy, which probes the local environment of the molecule. For pure substances an increase of the linewidth occurs [10–14], from which an order parameter (density) distribution can be extracted [11,12]. However, a similar experiment on the liquid mixture of 3-methylpentane and nitroethane (3MP-NE) [15], which is a model system for critical phenomena [16], showed no critical broadening at all. In their theoretical studies Hills and Madden [17,18] argued that the density fluctuations in a pure substance would give rise to a critical broadening, whereas for the critical concentration fluctuations in a mixture no effect was expected. Up to now this dissimilarity seemed to be in accordance with experiment.

In this paper we report measurements on the full width at half maximum (FWHM) and the shift of the vibrational Raman spectrum of nitrogen as a function of pressure, temperature, and composition in the homogeneous fluid phase of the helium-nitrogen mixture at very high density. In Fig. 1 the FWHM has been plotted as a function of the mole fraction of helium (x) at room temperature and three different pressures. The isobars exhibit a distinct maximum at about $x=0.8$, which corresponds to the critical composition. We will prove that this maximum is due to *critical* concentration fluctuations, taking into account the noncritical effects which influence the linewidth as discussed by, e.g., Oxtoby [19], Gallego *et al.* [20], and Knapp and Fischer [21]. We will estimate the amplitude of the concentration fluctuations with a method which is analogous to that of the pure substance [11,12] and which is applicable to any critical phenomenon in the Ising-spin universality class (three dimensional and two dimensional).

The critical composition of the fluid-fluid equilibrium of He-N_2 remains roughly constant ($x=0.8$) in the range from 2 to 10 GPa [22]. This makes it possible to follow well defined thermodynamic paths in (p,T,x) space with respect to the critical parameters. To measure the vibrational Raman peak of N_2 we used the same diamond anvil system as in previous investigations [23]. The absolute uncertainty in the ruby scale is 3%. The relative uncertainty in the pressure, which is of importance for this work, could be limited to 0.02 GPa, because we only used ruby chips, of which the ambient pressure values for the positions and half-widths of the spectrum at a well determined temperature were the same. The instrumental profile can be represented by a Gaussian with FWHM = 1.50 cm^{-1}. The spectra can also be represented with Gaussians rather than with Lorentzians, so the FWHM of the deconvoluted spectra was determined by subtracting the instrumental width quadratically from that

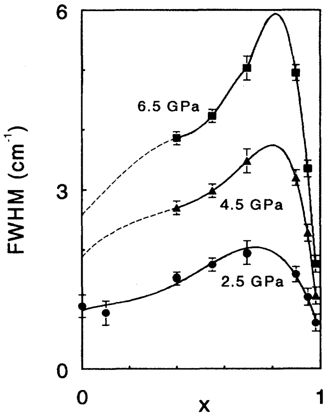

FIG. 1. The FWHM of the N_2 vibrational Raman line versus the mole fraction of helium (x) at $T=296$ K; error bar is σ of the corresponding fit.

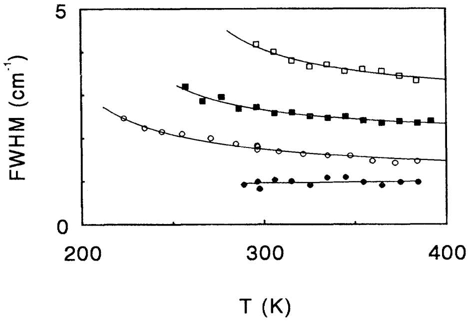

FIG. 2. The FWHM of N_2 versus T for pure N_2 at 2.25 GPa (full circles), $x=0.695$ at $p=2.3$ GPa (open circles), $x=0.400$ at $p=4.5$ GPa (full squares), and $x=0.695$ at $p=5.3$ GPa (open squares).

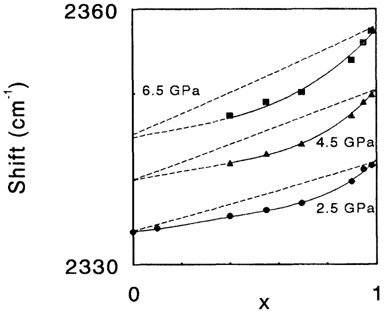

FIG. 3. The Raman shift of N_2 versus the mole fraction of helium (x) at $T=296$ K. The dashed lines are fits through the points if they are plotted versus the volume fraction.

of the Gaussians. For pure N_2 this method gave the same results as time-resolved techniques [24]. At the lower N_2 concentrations the time of recording was increased, such that the quality of the spectra remained about the same. Data have been collected at room temperature as a function of pressure and along six isobars as a function of temperature for eight different mole fractions. In total, 200 points have been obtained between 200 and 400 K and up to 10 GPa. During the measurements the mixture remained in the homogeneous phase, at least 5 K above the fluid-fluid surface.

Figure 1 has been obtained in the following way. The FWHM, which has been measured at room temperature for seven mixtures and pure nitrogen in a large pressure range, increases almost linearly with pressure. For all pressures the values for, e.g., $x=0.70$ appear to be much larger than those for $x=0.40$, while the ones for $x=0.98$ are smaller. A fit has been made of the FWHM as a function of pressure, for each composition separately. Since the data for the various compositions have not been obtained at exactly the same pressure, these fits [average standard deviation $(\sigma)=0.16$ cm^{-1}] were used to plot the FWHM versus x at a given pressure. For pure N_2 a proper fit can be made, which connects low pressure results [24], our data, and those at very high pressure and temperature [25,26]. The temperature dependence appears to be linear and very small $(+7\times10^{-4}\ \mathrm{cm}^{-1}/\mathrm{K})$.

Figure 1 shows some remarkable features. First, distinct maxima can be observed where the value of the FWHM is about three times that at $x=0.98$, the ratio being highest for the highest pressure. Second, the maximum occurs at the critical composition. Third, between $x=0.8$ and infinite dilution the FWHM decreases very fast.

In Fig. 2 the FWHM is plotted as a function of T for given pressure and composition. Pure nitrogen (lower curve) shows a small increase. In contrast, for $x=0.695$ and 0.400 the isobars show a decrease, which is most pronounced for $x=0.695$ and $p=5.3$ GPa and at the lowest temperatures. At higher T the FWHM tends to a constant value. The temperature behavior of the FWHM seems to imply that the broadening is due to critical fluctuations, because all theories predict an increase or at least a constant value of the FWHM as a function of T, except when a critical point is approached [12,14]. In that case the FWHM should increase when the critical point is approached, independent of the direction. Figure 1 proves this also to be the case for changes in pressure and composition. We note that the effects shown in Figs. 1 and 2 are much larger than the relative uncertainty (for Fig. 1 mainly given by the σ of the FWHM vs p fits; for Fig. 2 by the average scatter of 0.1 cm^{-1}).

The linewidth reflects fluctuations in the local field [12,14], so it is probable that the anomaly at criticality is due to critical concentration fluctuations; in order to be sure, other explanations have to be excluded. For that discussion the behavior of the Raman *shift* is important. At constant composition the Raman shift increases regularly with pressure and the data can be properly fitted ($\sigma=0.15$ cm^{-1}). Using these fits we can determine the composition dependence of the Raman shift at a given pressure. In Fig. 3 the results at room temperature have been plotted for $p=2.5$, 4.5, and 6.5 GPa. It is shown that there is an increase of the shift versus x which is more pronounced at higher compositions or higher pressures. Usually, in mixtures the volume fraction x_v is taken as the order parameter [27]. We use the definition as given in Ref. [27]. Employing the equations of state for N_2 [28] and He [29] x_v can be calculated. In Fig. 3 the dashed lines give the shift as a function of x_v instead of x; note that the dependence is almost linear. Along all isobars (and constant composition) the shift is constant as a function of temperature; only not too far from the critical line a very small increase has been measured.

The regular behavior vs x (Fig. 3) and vs T means that along the isobar the *average* interaction of a nitrogen molecule with its environment only gradually changes as a function of composition; it is constant as a function of T and so it does not show any anomaly in the critical region. Therefore there is no anomalous density effect [19]. Calculations of the density using perturbation theory show that it deviates slightly from linear behavior as a function of x [30].

It is expected that noncritical concentration fluctuations can cause a maximum in the FWHM as a function of x [20,21]. However, this maximum should occur at a mole fraction smaller than 0.5 [20] and the temperature dependence should be the same as that of pure N_2 [21,31]. According to Figs. 1 and 2 this is clearly not the case when we approach the critical line. We have performed measurements up to 400 K far from the critical line and indeed there the curve shows a shallow and broad maximum for values of x_v much lower than the critical one. The magnitude is 25% of the value near criticality. Therefore we finally conclude that the increase of the linewidth near the critical line is due to critical concentration fluctuations.

We now use the above results to make an estimate of the amplitude of the critical fluctuations as a function of p, T, and x. It is assumed that the decay time of the critical fluctuations is much larger than the relevant time scale given by the inverse linewidth, so this contribution has no significant motional narrowing [32]. This is a reasonable assumption, because the time scale given by our spectra is about 2 ps and that of the decay of the fluctuations in the mixture 3MP-NE is several orders of magnitude larger [16]. Moreover, the profiles of our spectra can be fitted better with Gaussians than with Lorentzians [32]. We now will use a finite-size method analogous to that of the pure substances [11,12]. We note that it is applicable to critical fluctuations in *any* system which is in the same universality class as the Ising-spin system (characterized by a short range interaction and a scalar order parameter). Then we can divide the sample space in small volumes with a length scale larger than the interaction range but much smaller than the wavelengths of the critical fluctuations. For a given *overall* value the *local* value of the order parameter then shows a certain distribution which (as we will show) is directly reflected in the spectral shape. We denote such a distribution by P [11,12].

One can expect that with x_v as order parameter $P(x_v)$ for mixtures will be almost symmetrical [27], so that a comparison can be made with the symmetrical $P(\rho)$ in pure substances [11,12]. Note that $P(0)$ and $P(1)$ need not be zero. Because of the linear behavior of the Raman shift (ω) as a function of the overall volume fraction x_{vo}, the relation between the local frequency $\omega(x_v)$ and the frequency corresponding to the overall concentration $\omega(x_{vo})$ in the sample is

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

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

$$I_{\text{cr}}(\omega)\sim[1-x_v(\omega)]P(x_v(\omega)), \tag{2}$$

where the factor $[1-x_v(\omega)]$ expresses the fact that the intensity of the signal is proportional to the number of nitrogen molecules in the part of the sample under consideration [11,12]. 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 $I_{\text{cr}}(\omega)$. We calculated this correction by modeling $P(x_v(\omega))$ with a Gaussian; it turns out that the resulting asymmetry is too small (<1.5%) to be detected, but the resulting negative shift of the peak position can be a few tenths of a cm^{-1}. We have probably observed this effect. The FWHM of $I_{\text{cr}}(\omega)$ was obtained by subtracting the noncritical contribution, as determined above, quadratically from the total width. The main source of uncertainty in the critical width originates from this procedure.

The results for the FWHM of $P(x_v)$ at room temperature have been plotted in Fig. 4 for three pressures (2.5, 4.5, and 6.5 GPa). If we define a reduced temperature ϵ by $\epsilon(T,p)=T/T_{\text{cr}}(p)-1$, where $T_{\text{cr}}(p)$ is the critical temperature at pressure p, the values of ϵ for these isobars are, respectively, 0.42, 0.17, and 0.026. Also, results for other temperatures and pressures have been determined. Figure 4 shows that within the accuracy the results seem similar for the same value of ϵ, nearly independent of p. Thus 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 a small change in critical composition.

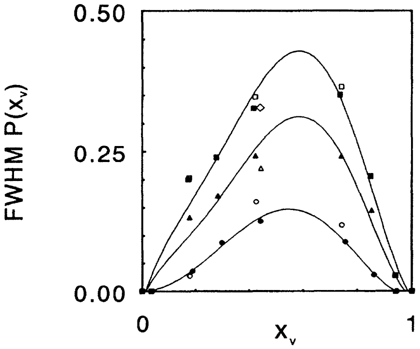

FIG. 4. The FWHM of the distribution function $P(x_v)$ versus x_v. Closed symbols are for $T=296$ K: circles, $p=2.5$ GPa; triangles, $p=4.5$ GPa; squares, $p=6.5$ GPa. Open symbols: circles, $p=4.5$ GPa and $T=360$ K ($\epsilon=0.42$); squares, $p=4.5$ GPa and $T=260$ K ($\epsilon=0.026$); triangle, $p=2.5$ GPa and $T=244$ ($\epsilon=0.17$); diamond, $p=2.5$ GPa and 213 K ($\epsilon=0.026$). The fits are through the room temperature results.

The isobar at 6.5 GPa comes close to the critical line. Here the FWHM of $P(x_v)$ is estimated to be 0.5, which is 0.9 times the critical value of x_v (0.57). The density (ρ) fluctuations in pure N_2 give a FWHM of $0.55\rho_{\text{cr}}$ [11]. Figure 4 also shows that at $1.4x_{v,\text{cr}}$ the effect is half of that at $x_{v,\text{cr}}$; the same ratio holds in pure N_2 [14]. Figure 2 ($x=0.695$ and $p=2.3$ GPa) suggests that the critical enhancement is still noticeable up to $\epsilon=0.8$; in pure N_2 this is $\epsilon=0.4$ [14]. In the mixture the effect seems to be larger than in the pure compound.

Hills and Madden [17] predicted for pure substances a critical broadening if the wavelength of the fluctuations is larger than the correlation length (ξ). But Hills [18] expected that for a mixture this was the case only rather far from the critical line, because in a mixture ξ is larger for a given value of ϵ than in a pure substance. However, for the system 3MP-NE close to the critical point the ξ value [16] appears to be only 1.5 times that for, e.g., carbon dioxide at the same ϵ.

From Eqs. (1) and (2) it appears that there will be no critical broadening if $(\partial\omega/\partial x_v)_{p,T}=0$. For the density fluctuations a similar correlation has been found between $\partial\omega/\partial\rho$ and the magnitude of the broadening effect [33]. If $(\partial\omega/\partial x_v)_{p,T}=0$ the critical fluctuations will not affect the local interactions, because these are then accidentally equivalent for both components. In the mixture 3MP-NE this is true for all the Raman lines [15] explaining the absence of the broadening effect. And so we have shown that the above scheme can be used for any critical phenomenon of the "Ising-spin universality class" under the important condition that the position of the spectrum changes as a function of the order parameter. This condition had already been found to hold for pure substances [33].

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