Crossover behavior in ^{3}He and Xe near their liquid-vapor critical point

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(Received 25 January 2000)

We present a detailed discussion of the crossover from mean-field to Ising critical behavior upon approach of the critical point, both for ^{3}He and Xe. By combining different sets of experimental data, we are able to cover an unusually large temperature range on either side of the critical temperature T_c. Below T_c, we thus can make an accurate comparison with a recent calculation for the crossover of the coexistence curve. For the regime above T_c, an analysis of the compressibility demonstrates that the crossover regime in ^{3}He is unexpectedly widened by a subtle interplay between quantum and critical fluctuations.

PACS number(s): 64.60.Fr, 05.70.Jk, 67.55.Cx

Recently, there has been a renewed interest in the nature of the crossover from mean-field-like (''classical'') to Ising-like critical behavior that occurs upon approach of the critical point. Although this phenomenon can be observed in a wide variety of experimental systems, including simple fluids, micellar solutions, and polymer mixtures, much of the recent attention has been focused on its theoretical description. An important reason for this lack of experimental data is the width of the crossover region, which extends over several decades in the reduced temperature $t \equiv (T-T_c)/T_c$, where T_c is the critical temperature. The crossover depends on the ratio between t and the (system-dependent) Ginzburg number G: Ising critical behavior occurs for $t \ll G$ and mean-field critical behavior is expected for $t \gg G$. Throughout the crossover region, however, one has to stay within the critical regime, i.e., $t \lesssim 0.1$. Hence, the full crossover can be observed only if G is sufficiently small. On the other hand, if G is *extremely* small, as for conventional superconductors which have $G \approx 10^{-16}$, the nonclassical region is so narrow that it becomes impossible to observe. Ideally, thus, one would need a system with a tunable Ginzburg number, as can actually be realized in polymer mixtures, where the Ginzburg number is inversely proportional to the molecular weight. Measurements of the crossover have indeed been reported for such systems [1,2], essentially confirming the existence of a crossover between the two universality classes. However, few studies have actually addressed the *shape* of the crossover curves. In Ref. [2] the concentration susceptibility χ as a function of t/G was shown to be well described by a phenomenological crossover function obtained by Belyakov and Kiselev (BK) [3], but it must be pointed out that χ increases by more than 5 orders of magnitude in the crossover region, making it difficult to judge even the qualitative agreement from a logarithmic plot. The *effective* susceptibility exponent, which is defined as the logarithmic derivative of χ, $\gamma_{\rm eff} \equiv -d \ln \chi / d \ln |t|$ [4], is clearly a much more sensitive quantity. However, very few papers [5,6] have endeavored to discuss the shape of the crossover in experimental systems in terms of this parameter.

It is the objective of this work to present an alternative description of experimental data exhibiting (part of) the crossover between mean-field-like and Ising-like (asymptotic) critical behavior. Our description differs from previous ones in several aspects. First, those of Refs. [3,6] possess essentially phenomenological features and rely on extensions of low-order renormalization-group (RG) results [3] or on the so-called RG matching procedure [6]. Note that for simple liquids (as studied in this work) the crossover function used in Ref. [6] closely resembles the equation obtained by BK (cf. Ref. [7]). In addition, both the field-theoretic results obtained in Ref. [8] and the description by BK are only valid in the limit where t/G is varied but where both $t \to 0$ and $G \to 0$, a restriction that is certainly not fulfilled by liquids and liquid mixtures, for which G is a finite, fixed quantity. In contrast, we use here theoretical crossover curves that have been obtained from numerical calculations for model systems in which G was a tunable parameter [9]. A second aspect concerns our choice of experimental systems, *viz.* ^{3}He and Xe. Whereas the latter system was already considered for $t>0$ in Refs. [5,6], it is the former that exhibits two features that make it stand apart from other fluids: (i) its coexistence curve is almost symmetrical with respect to ρ_c in the ρ-$|t|$ plane, thereby eliminating important corrections to scaling; (ii) the magnitude of its bare correlation length suggests a relatively small Ginzburg number. In addition, there is a great abundance of available data close to the liquid-vapor critical point for these two systems, extending over a larger range in $t \gtrless 0$ than for most other fluids. They can be thought of as representing extremes in both mass density and molar mass for simple fluids near the critical point, ^{3}He having the largest de Boer parameter Λ^* of any fluid [10], implying a ''near-quantum'' behavior, and Xe a very small one, leading one to expect ''classical'' (in the sense of non-quantum) behavior. Both, however, show the predicted critical exponents and amplitude ratios in the asymptotic critical regime. Our comparison now allows exploration of the influence of quantum effects on the nature of the crossover. A final noteworthy aspect is the fact that we consider the two-phase region $T<T_c$ as well. To our knowledge, this is one of

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the first comparisons between a theoretical description of the crossover of the coexistence curve and experimental results presented together with the crossover above T_c. An important feature of the low-temperature region is that one can clearly identify the end of the critical regime. By contrast, for $T>T_c$, the region where the compressibility exhibits mean-field-like *critical* behavior, i.e., $\gamma_{\rm eff}=1$, cannot be distinguished from the regular high-temperature behavior $\chi\sim 1/T$. Thus, a system that actually has left the critical region can incorrectly be interpreted as having completed the full crossover. An important point in this context is the expected degree of universality of crossover scaling functions, which may be legitimately doubted because of the decrease of the correlation length in the crossover regime. See Ref. [11] for a detailed analysis of the nature of nonuniversal corrections. Here we just note that recent numerical work [12] has provided evidence that the actual crossover scaling functions may be remarkably insensitive to the detailed nature of the interactions.

For the study of crossover phenomena in ^{3}He and Xe, we consider two properties, namely the isothermal compressibility $\kappa_T=\rho^{-1}(\partial\rho/\partial P)_T$ along the critical isochore above T_c and the coexistence curve below T_c. Here ρ is the mass density and P the pressure. The data are presented in the form of the dimensionless ''reduced'' compressibility $\chi_T^*=P_c\kappa_T$ and (for Xe) the density difference $\Delta\rho^*=(\rho_{\rm liq}-\rho_{\rm vap})/2\rho_c$ as a function of $|t|$. The densities are those of the coexisting liquid and vapor phases. This representation eliminates the effect of the slope of the rectilinear diameter. For ^{3}He, where this slope is much smaller than in Xe (cf. Fig. 7 of Ref. [13]), we use the individual liquid and vapor data in the form $\Delta\rho_+^*=(\rho_{\rm liq}-\rho_c)/\rho_c$ and $\Delta\rho_-^*=(\rho_c-\rho_{\rm vap})/\rho_c$. Inevitably, some accuracy is lost if one extracts effective exponents by means of numerical differentiation of the actual data, and hence we have divided out the leading singularity instead, which yields an equally sensitive comparison with the theoretical models. Thus, the quantities are plotted as $\chi_T^*/t^{-\gamma}$ and $\Delta\rho^*/(-t)^\beta$ with $\gamma=1.240$ and $\beta=0.327$, the asymptotic singular exponents predicted for the three-dimensional Ising model [14]. In a fully logarithmic plot versus $|t|$, the local slopes are then, respectively, $(\gamma-\gamma_{\rm eff})$ and $(\beta_{\rm eff}-\beta)$. The influence of the uncertainties in the exponents β and γ and in the respective critical temperatures of the examined fluids turns out to be small.

For Xe, the critical parameters are $P_c=58.40$ bar, $\rho_c=1.110$ g/cm^3, and $T_c=289.73$ K. Excellent compressibility data along the critical isochore have been obtained from light scattering experiments by Güttinger and Cannell [15] for $10^{-4}<t<10^{-1}$. The range of these data overlaps that covered by density measurements versus pressure along several isotherms between 25 and 150 °C by Michels *et al.* [16]. From the tabulated data, χ_T^* was obtained by numerical differentiation. A small (systematic) adjustment of 4.5% was required to bring the results in line with those of Ref. [15]. The combined range for Xe extends over $3\frac{1}{2}$ decades in t and exhibits a clear crossover in $\gamma_{\rm eff}$ as we shall see. For $\Delta\rho^*(-t)$, we used the data of Ref. [17], where the densities of both the coexisting phases were obtained simultaneously with a visual method. These data cover the range $3.0\times10^{-3}<-t<2.9\times10^{-1}$. Closer to the critical point, we used the most recent data [18], obtained by an optical interferometric technique. In addition to a high precision, these data exhibit a good agreement with those of Hocken and Moldover [19] in the asymptotic regime ($|t|<5\times10^{-5}$) and are consistent with those from nuclear magnetic resonance experiments by Hayes and Carr [20].

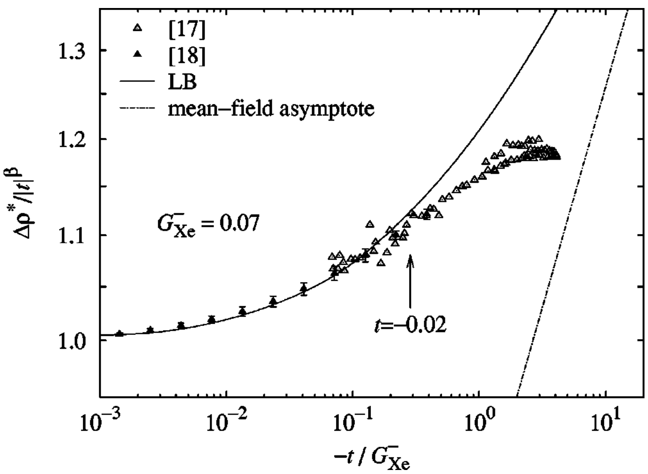

FIG. 1. Comparison between experimental data for the coexistence curve of Xe and the predicted universal crossover function calculated by Luijten and Binder (LB). The vertical arrow calibrates the scale of t. The data were normalized by dividing out the critical amplitude $B_{\rm Xe}=1.475$.

For ^{3}He ($P_c=1.168$ bar, $\rho_c=0.0414$ g/cm^3, $T_c=3.317$ K on the T_{90} scale), compressibility data above T_c were obtained from density measurements along isotherms over the range $0.05<t\lesssim 2$ [21] and from measurements of the vertical density gradient in the gravitational field [13]. For the latter experiments, the determination of χ_T is limited to the temperature range where the density gradient over the distance h is constant within the experimental error. As the stratification diminishes with increasing T, the scatter increases and the useful data were confined to $4\times10^{-4}<t<3\times10^{-2}$. The data are consistent with earlier ones [22,23]. In both experiments, the dielectric-constant method was used. Also for the coexistence curve $\Delta\rho^*(-t)$ the results of Ref. [13] were used, where the density of both phases could be measured simultaneously. The range of the data was $3\times10^{-5}<-t\lesssim 0.1$ and could be extended by measurements of $\rho_{\rm liq}$ at saturated vapor below 3.2 K ($0.05<-t<1.0$) [24], and of the vapor density $\rho_{\rm vap}$ in equilibrium with the liquid above 1.4 K [25]. These measurements used a volumetric method and join on smoothly to those of Ref. [13]. Below 1.4 K, $\rho_{\rm vap}$ was obtained by using the ideal gas law as a reasonable approximation.

We now proceed with a comparison of these experimental data to theoretical predictions, starting with the coexistence curves. Figure 1 displays $\Delta\rho^*/|t|^\beta$ for Xe. The solid curve indicates the crossover function as predicted from numerical data for the Ising-like systems studied in Ref. [9]. The closed symbols, which were recreated from the fit expression of Ref. [18] with parameters that were taken as the average for the two samples, follow the predicted curve very closely. These data are joined smoothly by those of Ref. [17], making the data span a total range of approximately 80 K. For

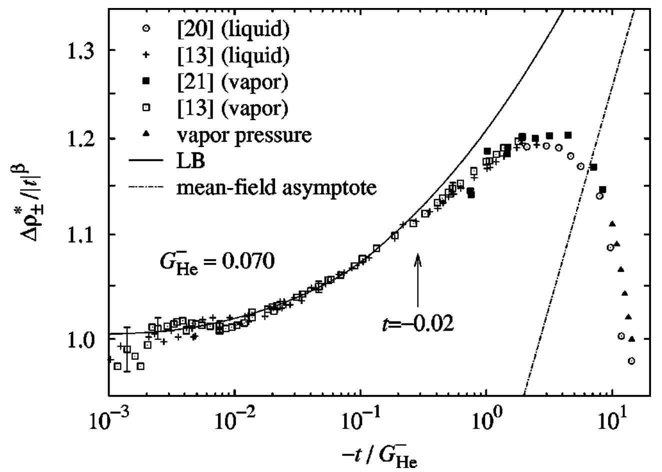

FIG. 2. Crossover of the coexistence curve for ^{3}He. We adopted the critical amplitude $B_{\rm He}=1\,000$ and hence no further normalization of the data was required.

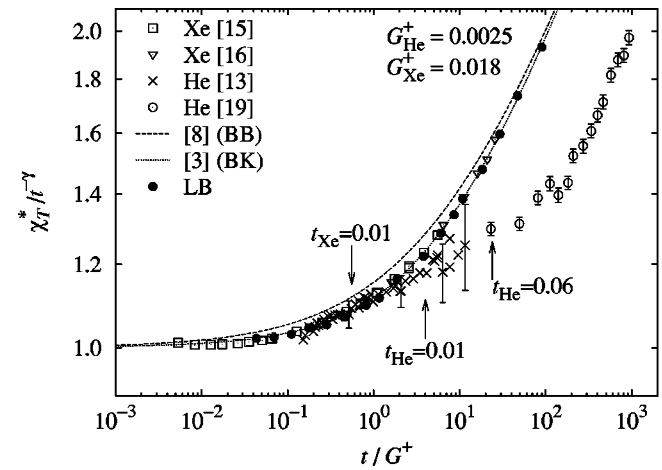

FIG. 3. Crossover of the compressibility of Xe and ^{3}He for $T>T_c$. For Xe, the error bars do not exceed the symbol size. The data were normalized by dividing out the respective critical amplitudes $\Gamma^+_{\rm Xe}=0.0594$ and $\Gamma^+_{\rm He}=0.139$.

$|t|\lesssim 0.02$ there is good agreement with the theoretical curve; for $|t|>0.02$ the latter continues its trend toward the mean-field asymptote, whereas the experimental data already start to leave the critical region, presumably because of the finite width of the low-temperature regime. Indeed, the distance between the onset of the deviation and absolute zero is less than 2 decades on this logarithmic scale. Note that there is only one adjustable parameter in the form of the Ginzburg parameter $G^-_{\rm Xe}$, estimated as 0.07 ± 0.02.

The data for ^{3}He, shown in Fig. 2, exhibit a close similarity to those for Xe. For $10^{-4}<|t|<0.02$ the agreement with the prediction is comparable with that for Xe and for larger $|t|$ a similar changeover to regular low-temperature behavior is observed. The downward trend upon approach of absolute zero simply results from the saturation of the order parameter. The Ginzburg parameter turns out to be the same as that for Xe within the fitting uncertainty, with $G^-_{\rm He}=0.070\pm0.008$. The close agreement of the experimental data for both Xe and ^{3}He with the theoretical curve confirms the expectation that, due to the predominance of the critical fluctuations, the initial crossover behavior is essentially unaffected by quantum statistics. Unfortunately, the very small width of the critical regime makes it impossible to identify the influence of quantum effects on the crossover behavior at somewhat larger distances from the critical point.

Next, we turn our attention to the high-temperature regime, where the crossover of the compressibility upon approach of T_c is considered. We compare the experimental data to three theoretical descriptions, namely the field-theoretical approach of Bagnuls and Bervillier (BB) [8], the phenomenological extension of low-order RG calculations of Ref. [3], and the numerical calculation of Luijten and Binder (LB) [9]. The latter calculation has been improved compared to Ref. [9] by leaving out the results for systems with very short interaction ranges, which cannot exhibit the crossover to mean-field-like behavior due to their location with respect to the Wilson–Fisher RG fixed point. The improved calculation exhibits a very close agreement with the BK curve. In view of the phenomenological nature of the latter, this must be coincidental to some extent. The normalization of the Ginzburg number in the theoretical expressions has been chosen such that the curves coincide in the asymptotic (Ising) regime. The main remaining difference then essentially lies in the width of the crossover regime, where the asymptotic crossover described by the field-theoretic curve pertains to the strict limit $G\to0$. Systems with a finite Ginzburg number will appear to exhibit a *faster* crossover, due to the fact that one leaves the critical region before completing the full crossover and hence enters the noncritical high-temperature regime, as has, e.g., been illustrated in Fig. 4 of Ref. [26]. Additional deviations, however, may result from neglected irrelevant couplings and analytic corrections to scaling [27] and it remains to be seen which theoretical expression actually provides the best description of experimental measurements. The admirable accuracy of the Xe data from Refs. [15] and [16], and the large temperature range that is spanned by the total data set, enable an accurate matching with the theoretical expressions. As can be seen from Fig. 3, the LB and BK calculations turn out to yield a strikingly good description of the data over the full temperature range. The BB expression exhibits a slower crossover toward the classical critical regime, as was already found in Ref. [5]. We note here that the agreement is very sensitive to the choice of the critical amplitude; the value $\Gamma^+=0.0577\pm0.0001$ [15] for $\gamma=1.241$ appears very low. Upon omission of the data points for $t>0.02$, which are presumably not described by the first few Wegner corrections, a fit yields $\Gamma^+=0.0587\pm0.0002$; for $\gamma=1.240$ this even increases to $\Gamma^+=0.0594\pm0.0002$. A smaller value improves the agreement with the BB curve for intermediate temperatures, but leads to poor agreement for very small t. It should be stressed that the horizontal offset between the curves and the experimental data should *not* be regarded as a failure by itself, since the matching involves adjustment of the Ginzburg parameter G, here estimated as $G^+_{\rm Xe}=0.018\pm0.002$. The essential point is that there exists no value of G for which the experimental data coincide with the BB curve over the full temperature range. Note that even the data point at the highest temperature is located at $t<0.5$, and thus lies definitely not far outside the critical regime.

The data for ^{3}He (also shown in Fig. 3) exhibit a completely different behavior. Whereas the initial increase of the data is again well described by the BK and LB calculations, with $G^{+}_{\mathrm{He}}=0.0025\pm0.0010$, a systematic deviation sets in around $t=0.005$, which is not captured by any of the theoretical expressions. The experimental data continue their upward trend, but at a markedly slower rate. Unlike for $t<0$, there is no reason to expect a deviation at such a small t. In the rightmost part of the graph the data run roughly parallel to the predicted curves, but shifted by an order of magnitude in t. At this point, the system has obviously left the critical region and one is observing the changeover to regular high-temperature behavior. This effect by itself, however, would rather *hasten* the (apparent) crossover and can certainly not explain the slowing down in the crossover behavior; the Xe results (with a seven times higher G!) only reinforce this conclusion.

We suggest that one is actually observing the interplay between the critical and the quantum fluctuations. While the former are dominating close to T_c (and thus lead to Ising-like critical behavior), the contribution of the latter cannot be neglected in this temperature range and leads to a considerable enhancement of the compressibility, as follows from the critical amplitude $\Gamma^{+}=0.139\pm0.003$, which is more than twice as large as for Xe. Indeed, the thermal de Broglie wavelength λ_{dB} is, at T_c, 4.5 times larger than the van der Waals radius, compared to a corresponding ratio of only 0.062 for Xe at criticality. However, the absolute temperature changes appreciably within the crossover region and so does the quantum-natured contribution to the compressibility. Since the data in Fig. 3 are normalized by the critical amplitude, this then obviously leads to an apparent *depression* of the compressibility at higher t and to a corresponding ''widening'' of the crossover regime. Although a proper description of crossover behavior is clearly beyond the scope of the van der Waals equation, it is still instructive to consider the quantum corrections to the second virial coefficient [10]. In first approximation, these corrections are indeed found to be proportional to $\lambda^2_{\mathrm{dB}}\propto T^{-1}$. Exchange effects, which will tend to *decrease* the compressibility for ^{3}He, are proportional to λ^3_{dB} but expected to become important only below 1 K. The compressibility of ^{4}He [28] lends strong support to this scenario, as it shows essentially the same behavior as ^{3}He, except that the high-temperature data lie somewhat higher, i.e., closer to the theoretical curve. This is consistent with the reduced importance of quantum effects in ^{4}He due to its higher mass. A quantitative description of this phenomenon will require a more fundamental understanding of the contribution of quantum-mechanical fluctuations to the critical divergence of the compressibility, which is essentially driven by *thermal* fluctuations! Of particular interest will be a study of the compressibility in the two-phase region, where the above-mentioned mechanism should rather have an opposite effect.

For completeness we remark that a rather different fit of the ^{3}He data to the Monte Carlo results might be attempted, in which a considerably higher critical amplitude $\Gamma^{+}\approx0.15$ is used. This leads to a larger Ginzburg number and diminishes the deviations at higher t, but entails two undesirable consequences: Γ^{+} lies certainly 3 standard deviations above the value quoted in Ref. [13] and a considerable part of the data at very small t has to be omitted from the analysis, even though there is no reason to expect stratification effects at these temperatures. With regard to the Ginzburg numbers found in our analysis, we note that the $G^{+}_{\mathrm{Xe}}/G^{+}_{\mathrm{He}}>1$, whereas $G^{-}_{\mathrm{Xe}}/G^{-}_{\mathrm{He}}$ (as obtained from the coexistence curve) lies much closer to unity; this is consistent with the corresponding first Wegner corrections, to which the Ginzburg parameter can be related, but seems to contradict the expected universality in the ratio of Ginzburg numbers above and below T_c [29].

We wish to thank H. Carr and M. Durieux for supplying us with data tabulations for Xe and ^{4}He, A. Kogan for help with scaled plots, and K. Binder, M. Anisimov, and M. E. Fisher for stimulating comments and helpful discussions. The provision of computing resources by the NIC and support by NASA Grant No. NAG3-1838 are gratefully acknowledged.

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