Continuous demixing at liquid-vapor coexistence in a symmetrical binary fluid mixture

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We report a Monte Carlo finite-size scaling study of the demixing transition of a symmetrical Lennard-Jones binary fluid mixture. For equal concentration of species, and for a choice of the unlike-to-like interaction ratio $\delta = 0.7$, this transition is found to be continuous at liquid-vapor coexistence. The associated critical end point exhibits an Ising-like universality. These findings confirm those of earlier smaller scale simulation studies of the same model, but contradict the findings of recent integral equation and hierarchical reference theory investigations.

I. INTRODUCTION AND BACKGROUND

Symmetrical binary fluid mixtures are two-component fluid models in which the configurational energy is invariant with respect to the interchange of the particle species. One example is the symmetrical Lennard-Jones (LJ) mixture in which the interactions between particles of species 1 and 2 are controlled by an LJ potential with scale parameters $\sigma_{11} = \sigma_{22} = \sigma_{12} = \sigma$ and interaction strengths $\epsilon_{11} = \epsilon_{22} = \epsilon \neq \epsilon_{12}$. In common with all other symmetrical mixtures, the phase diagram of the LJ mixture is uniquely specified by the ratio of interaction strengths between the unlike and like species, $\delta \equiv \epsilon_{12}/\epsilon$.

Symmetrical mixtures have been the subject of considerable recent attention on account of their surprisingly rich phase behavior [1–5]. The phase diagram of the mixture is typically represented in terms of the temperature T, the overall number density $\rho = \rho_1 + \rho_2$, and the concentration $c = \rho_2/(\rho_1 + \rho_2)$. Most attention has been focused on the case of equal species concentration, $c = 0.5$. Within this particular symmetry plane of the full phase diagram, the ρ-T dependence of the phase behavior on the value of δ has been systematically studied using simulation and mean field theory for the case of a symmetrical square-well mixture [5]. The findings of that work are summarized in Fig. 1. of Ref. [5]. Three distinct classes of phase diagram were found depending on the choice of the parameter δ. Specifically, for large $\delta < 1$ [Fig. 1(a) of Ref. [5]] there occurs a "λ line" of critical demixing transitions, which intersects (and is truncated by) the liquid-vapor line at a critical end point (CEP). For small $\delta > 0$, on the other hand, the line of demixing transitions intersects the liquid-vapor line at the liquid-vapor critical point, forming a tricritical point [Fig. 1(c) of Ref. [5]]. Intermediate between these two regimes, one observes both the liquid-vapor critical point and (at higher densities) a tricritical point [Fig. 1(b) of Ref. [5]]. The tricritical point terminates a first-order line in which either of the demixed liquids coexists with a mixed liquid of lower density. This line intersects the liquid-gas line at a triple point in which the demixed liquid, the mixed liquid, and the gas all coexist. In the simulations the intermediate regime was observed to occur for $0.65 \lesssim \delta \lesssim 0.68$, while within the particular mean field theory employed it occurred for $0.605 \lesssim \delta \lesssim 0.708$.

It has been suggested [5] that the scenario of phase be-

havior outlined above for the square-well mixture might, in fact, be generic to all symmetrical fluids. On the theoretical side, support for this proposal has come from studies of a variety of model systems, including mean field studies of a lattice fluid model [6] and integral equation theories [7–10] of the hard core Yukawa fluid mixture (HCYFM). The same overall scenario was initially reported for the hard core plus Lennard-Jones mixture by Pini *et al.* [11] in a study employing the hierarchical reference theory (HRT)—a powerful fluctuation-inclusive approach based on renormalization group techniques [12]. In contrast, the available simulation data for models other than the square-well fluid is less comprehensive and has, in the main part, concentrated on the regime of large δ. Specifically, MC simulations of the symmetrical LJ fluid [4] found evidence for a CEP (and associated coexistence curve singularities) for the particular case $\delta = 0.7$. Similarly, a CEP has been reported in simulation studies of the HCYFM for $\delta = 0.9$ [10].

Very recently, however, the situation with specific regard to the CEP regime has become less clear following two theoretical studies that question its existence in the expected range of δ. In the first of these, Antonevych *et al.* [13] applied the modified hypernetted chain (MHNC) integral equation theory to the symmetrical LJ fluid, but found no evidence for a CEP at $c = 0.5$. Instead, they reported that the intermediate regime [Fig. 1(b) of Ref. [5]] persists right up to $\delta = 0.81$ (the limit of their study). This value of δ is considerably greater than that ($\delta = 0.7$) at which CEP behavior was originally found in the simulations of the same model. On this basis, Antonevych *et al.* suggested that the demixing transition could always be of first order at liquid-vapor coexistence, although they speculated that it might be only weakly so. Furthermore, they questioned the ability of simulation to distinguish this possibility from a true CEP.

In a separate study, Pini *et al.* [14] have applied the HRT approach to the HCYFM. They too observed no CEP, instead reporting (in accord with the finding of Antonevych *et al.* [13]) that the intermediate regime persists (albeit weakly) to $\delta = 0.8$, the limit of their study. Moreover, these authors report [15] that in their previous study of the LJ mixture [11], the apparent observation of a CEP was, in fact, an artifact stemming from the low resolution of the grid in the ρ-c plane on which the HRT equations were solved.

Clearly, therefore, the evidence emerging from the various

theoretical and simulation studies is contradictory with regard to the existence of a CEP and the range of values of δ for which it occurs. Most significant in our view is the failure of HRT to observe a CEP for $\delta < 0.8$. Given the fluctuation-inclusive nature of this approach (and its success in other contexts—see, e.g., Ref. [16]), one cannot simply ascribe discrepancies between the simulations and the MHNC study of the LJ fluid [13] to the neglect of critical fluctuations by the latter.

Questions have been raised, too, regarding the reliability of the simulation in distinguishing a CEP from a weak first-order transition [13]. While, in our opinion, the original work [4] *does* provide compelling evidence for CEP behavior, it is certainly the case that owing to the prevailing computational constraints, the range of system sizes studied was smaller than one might have wished. This in turn precluded an investigation of corrections to scaling and the approach to the limiting critical behavior.

In the light of the above considerations, it would seem worthwhile to revisit the original system in which a CEP was observed, with a view to performing a more comprehensive determination of the nature of the demixing transition along the liquid-vapor coexistence line. To this end, we have carried out a detailed MC finite-size scaling (FSS) simulation study of the symmetrical LJ fluid with $\delta = 0.7$, for which it was previously claimed that a CEP occurs [4]. The new study has been executed along similar lines to the original one, but employed a considerably larger range of systems sizes, thus permitting a more sophisticated finite-size scaling analysis. The results demonstrate (unambiguously, we believe) that the model does indeed exhibit a CEP of the expected Ising type.

II. METHOD AND RESULTS

The simulation methodology employed here is broadly similar to that described in Ref. [4], and we refer the reader to that paper for a detailed description. Briefly, we have performed a MC simulation study of the liquid-vapor coexistence line of the symmetrical LJ fluid mixture with $\delta = 0.7$ in the neighborhood of the demixing transition. The simulations were carried out within the grand canonical ensemble and the chemical potentials of the two species were constrained to be equal ($\mu_1 = \mu_2 = \mu$), implying on symmetry grounds that $\langle c \rangle = 0.5$. The system was confined to a cubic box of linear dimension L having periodic boundary conditions. In all, seven system sizes were studied having $L = 10\sigma$, 12.5σ, 15σ, 17.5σ, 20σ, 25σ, and 30σ. The largest of these systems contains some 1.6×10^4 particles in the liquid phase at the demixing point. The range of system sizes studied here is to be compared with that of the original study [4], for which the largest size attained was $L = 12.5\sigma$. The greater range of sizes studied here was partly facilitated by the use of high performance parallel computers.

The liquid-vapor coexistence curve $\mu_{cx}(T)$ was obtained using multicanonical extended sampling techniques [20]. These allow both the liquid and the vapor phases to be sampled (and thus connected) in a single simulation run. A suitable form for the requisite preweighting function was obtained using a variant of the recently proposed Wang-Landau
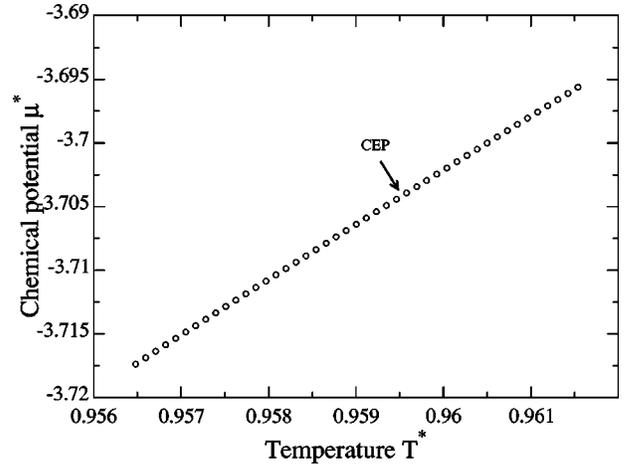
FIG. 1. The liquid-vapor coexistence curve in the neighborhood of the demixing transition, obtained for the $L = 25\sigma$ system. Statistical errors are considerably smaller than the symbol sizes. The location of the CEP, as determined in Sec. II, is also shown.

method [17]. To locate the coexistence line, the equal peak area criterion was applied to the measured form of the number density distribution function $p_L(\rho)$ [18,19]. Histogram reweighting techniques were employed to fine tune this procedure and to facilitate the mapping of a portion of the liquid-vapor coexistence curve in the neighborhood of the demixing transition.

Figure 1 shows the measured form of the liquid-vapor coexistence line $\mu_{cx}(T)$ [21]. To elucidate the nature of the demixing transition along the liquid branch of this tightly determined coexistence line, we have measured the probability distribution function $p_L(m)$ of the demixing order parameter m, where $m = (N_1 - N_2)/(N_1 + N_2)$, with N_1 and N_2 the instantaneous counts of the respective particle species. The form of $p_L(m)$, for the $L = 25\sigma$ system at temperatures spanning the demixing transition, is shown in Fig. 2. We find that $p_L(m)$ evolves smoothly between the strongly double peaked form (corresponding to a demixed liquid) at low temperature
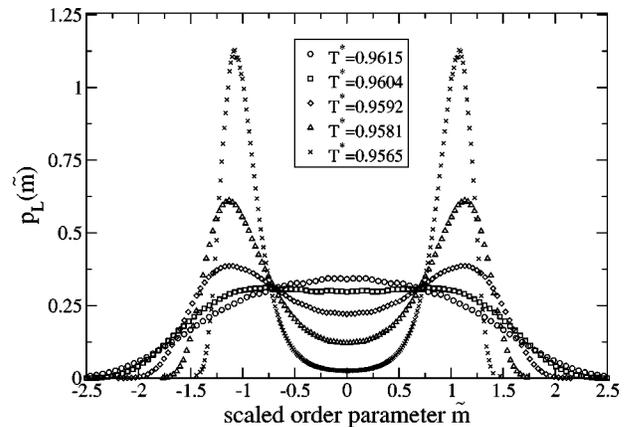
FIG. 2. The distribution of the order parameter obtained for the $L = 25\sigma$ system at a number of temperatures along the liquid branch of the coexistence curve. In each case, the order parameter has been scaled $m \rightarrow \tilde{m}$ to ensure that all distributions have a unit variance.
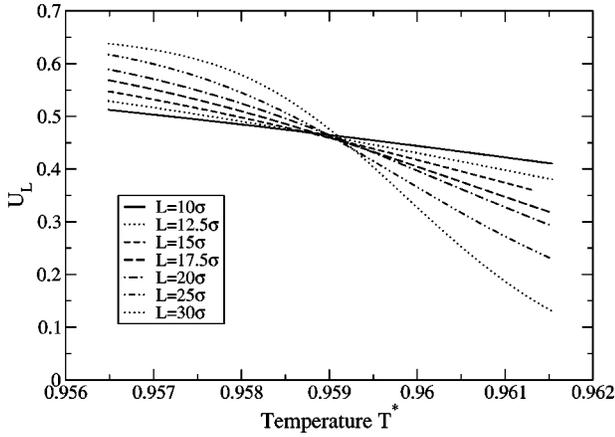
FIG. 3. The temperature dependence of the fourth-order cumulant ratio (see text) measured along the liquid branch of the coexistence curve.

and a singly peaked form (corresponding to a mixed liquid) at higher temperatures.

To quantify this evolution more precisely, we have measured the temperature dependence of the fourth-order cumulant ratio: $U_L = 1 - \langle m^4 \rangle / 3 \langle m^2 \rangle^2$, which provides a dimensionless measure of the shape of a distribution. The results (Fig. 3) demonstrate (for all system sizes) a smooth evolution of the concentration distribution from the ordered to the disordered phase. The rate of change increases with the system size, but there is no evidence of a jump discontinuity. More significantly, there is a fairly well-defined crossing point of the curves for $U_L \approx 0.46$ close to the reduced temperature $T^* \equiv 1/\epsilon = 0.959$. Such an intersection reflects a scale invariance in the concentration distribution and does not occur at a first-order phase transition. We note further that the magnitude of the cumulant ratio at the intersection point corresponds closely to the known Ising universal value, $U_L^{\text{Ising}} = 0.465$ [22].

Although the results of Fig. 3 constitute a strong evidence for a critical demixing transition, a close inspection reveals
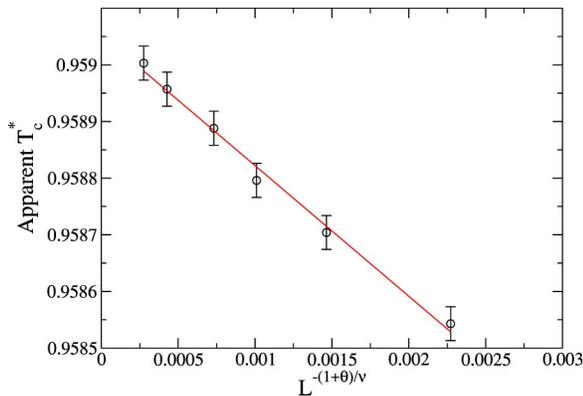
FIG. 4. The finite-size scaling behavior of the corrections to scaling obtained according to the method described in the text and Ref. [19]. The straight line is a linear fit to the data.
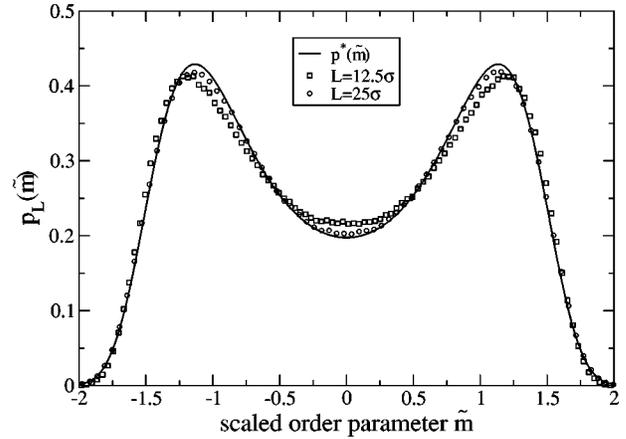
FIG. 5. Order parameter distribution for the $L = 12.5\sigma$ and $L = 25\sigma$ system sizes at the extrapolated parameters of the critical end point (cf. Fig. 4). Also shown (solid line) is the limiting universal fixed point form $p^*(\tilde{m})$ [22].

that the cumulant crossings do not occur precisely at a unique temperature for all system sizes. Such behavior mirrors those observed in other contexts (see, e.g., Refs. [19,16]), where it was found to be attributable to the corrections to finite-size scaling. Since these corrections have a known universal scaling form, one can attempt to fit them, thereby permitting an extrapolation to the thermodynamic limit. The procedure involves determining, for each system size, the coexistence state point for which the form of $p_L(m)$ on the liquid branch best matches the (independently known [22]) fixed point order parameter distribution function $p^*(m)$ appropriate to the Ising universality class. The matching temperature as a function of the system size is expected to scale like $T_c(L) \sim L^{-(1+\theta)/\nu}$ [19], where $\theta \approx 0.50(2)$ is the Ising correction-to-scaling exponent [23] and $\nu = 0.6294(4)$ is the correlation length exponent [24]. Figure 4 shows the data expressed in this form, which indeed exhibits the anticipated scaling behavior. Extrapolation of a linear fit to $L = \infty$ yields an estimate for the critical temperature T_{cep}
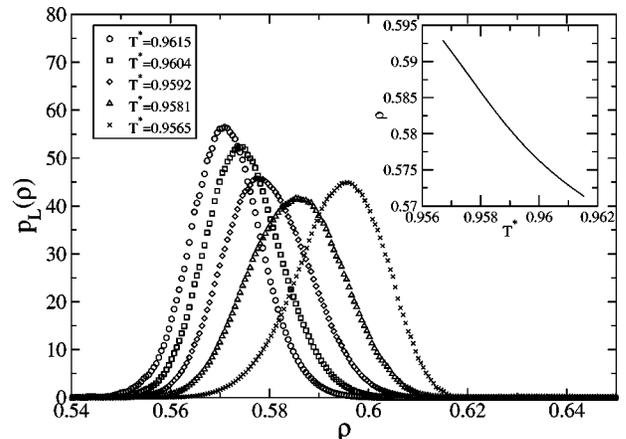
FIG. 6. The measured form of $p_L(\rho)$ on the liquid branch for the $L = 25\sigma$ system size for a number of temperatures spanning the demixing point. The inset shows the corresponding average number density as a function of temperature.

$=0.9595(3)$, which occurs for $\mu_{\mathrm{cep}}=-3.704(2)$. These coordinates are marked on the phase diagram of Fig. 1.

It is instructive to plot the finite-size forms of $p_L(m)$ at the estimated critical point in order to expose the scale and character of corrections to finite-size scaling. Figure 5 compares the distributions for the $L=12.5\sigma$ and $L=25\sigma$ system sizes with that of $p^*(m)$ [22]. One sees that the results for the larger system size closely match the limiting form.

Finally, we have considered the behavior of the number density along the liquid branch at coexistence. Were the demixing transition of first order along the coexistence line, one would expect that coupling between the concentration and the number density would engender a first-order phase transition in the liquid branch number density [cf. Fig. 1(b) of Ref. [5]]. This would be manifested as a discontinuity in the density of the coexisting liquid phase and by a splitting of the liquid-phase peak in the density distribution $p_L(\rho)$. Figure 6 shows the measured form of the liquid-phase peak for the $L=25\sigma$ system size for several coexistence state points spanning the demixing temperature. Also shown (inset) is the average liquid phase density. The distribution of the density in the liquid phase is singly peaked and we find no evidence of a discontinuity in the average density for any of the system sizes studied [25].

III. DISCUSSION AND CONCLUSIONS

In summary, we have performed a finite-size scaling analysis of the demixing transition of a symmetrical LJ fluid along the liquid branch of the liquid-vapor coexistence line. The results demonstrate that for the case $\delta=0.7$, this transition is continuous and of the expected Ising type [26]. Accordingly, we can conclude that this system does indeed exhibit a critical end point, as originally proposed in Ref. [4]. This clear finding should provide a benchmark for testing the reliability of theoretical approaches to the phase behavior of symmetrical mixtures.

With regard to the original motivation for this study, namely, the failure of both the MHNC integral equation study and the HRT to observe a CEP in the expected range of δ [13,14], it is difficult to comment definitively at this stage on the source of the discrepancies. We note, however, that problems with the accuracy of the MHNC approach for studying the liquid branch of the HCYFM have previously been reported [10]. With regard to the HRT, it would certainly be useful if this method could be applied to other symmetrical fluid models in order to determine whether there is any systematic model dependence on the qualitative features of the phase behavior.

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