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

Nigel B. Wilding
Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom

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 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.

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I. INTRODUCTION AND BACKGROUND

Symmetrical binary fluid mixtures are two-component fluid models in which the configurational energy is invariant with respect to interchange of the two 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 a LJ potential with scale parameters \( \sigma_{11} = \sigma_{22} = \sigma, \epsilon_{11} = \epsilon_{22} = \epsilon \neq \epsilon_{12} \). The phase diagram of the 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 behaviour \([1, 2, 3, 4, 5]\). 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 focused on the case of equal species concentration, \( c = 0.5 \). Within this particular symmetry plane of the full phase diagram, the \( \rho-T \) dependence of the phase behaviour on the value of \( \delta \) has been systematically studied using simulation and mean field theory for the case of a symmetrical square-well mixture \([6]\). The findings of that work are summarized in fig. 1. of ref. \([6]\). Three distinct classes of phase diagram were found depending on the choice of the parameter \( \delta \). Specifically, for large \( \delta < 1 \) (fig. 1(a) of ref. \([6]\)) there occurs a “\( \lambda \)-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 critical point, forming a tricritical point (fig. 1(c) of ref. \([6]\)). Intermediate between these two regimes, one observes both a liquid-vapor critical point and a tricritical point at higher densities (fig. 1(b) of ref. \([6]\)). In the simulations this latter 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 \([6]\) that the scenario of phase behaviour 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 variety of model systems, including mean field studies of a lattice fluid model \([6]\) and integral equation theories \([6, 7, 8, 9, 10, 11]\) of the hard core Yukawa fluid mixture (HCYFM). The same overall scenario was initially reported for the hard core + 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 \([12]\). By 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 \( \delta \). Specifically, MC simulations of the symmetrical LJ fluid \([6]\) 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 which question its existence in the expected range of \( \delta \). 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. \([6]\)) persists right up to \( \delta = 0.81 \), (the limit of their study). This value of \( \delta \) is considerably greater than that (\( \delta = 0.7 \)) at which CEP behaviour was originally found in the simulations of the same model. On this basis, Antonevych et al. suggested that the demixing transition could always be 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 \([14]\) that in their previous study of the LJ mixture \([11]\), the apparent observation of a CEP was an artifact stemming from the low resolution of the grid in the \( \rho-c \) plane on which the HRT equations were solved.

\[ \sigma_{11} = \sigma_{22} = \sigma, \epsilon_{11} = \epsilon_{22} = \epsilon \neq \epsilon_{12} \]
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 $\delta$ 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. [13]), 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 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 behaviour, 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 behaviour.

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 at liquid-vapor coexistence. To this end we have carried out a detailed Monte Carlo (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 system 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 $L = 10\sigma, 12.5\sigma, 15\sigma, 17.5\sigma, 20\sigma, 25\sigma$ and $30\sigma$. The largest of these systems contains some $1.6 \times 10^4$ 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 $\mu_{\text{cs}}(T)$ was obtained using multicanonical extended sampling techniques [20]. These allow both the liquid and 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 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.

Fig. 1 shows the measured form of the liquid-vapor coexistence line $\mu_{\text{cs}}(T)$ [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 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 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 strong evidence for a critical demixing transition, a close inspection reveals that the cumulant crossings do not occur precisely at a unique temperature for all system sizes. Such behaviour mirrors that observed in other contexts (see eg. [16, 19]) where it was found to be attributable to 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 system size is expected to scale like $T_c(L) \sim L^{-(1+\theta)/\nu}$, where $\theta \approx 0.50(2)$ is the Ising correction-to-scaling exponent 22, and $\nu = 0.6294(4)$ is the correlation length exponent 22. Fig. 4 shows the data expressed in this form, which indeed exhibits the anticipated scaling behaviour. Extrapolation of a linear fit to $L = \infty$ yields an estimate for the critical temperature $T_{cep} = 0.9595(3)$, which occurs for $\mu_{cep} = -3.704(2)$.

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 behaviour of the number density along the liquid branch at coexistence. Were the demixing transition 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 manifest as a discontinuity in the density of the coexisting liquid phase and by a splitting of the liquid-phase peak in the density distribution $p_L(\rho)$. Fig. 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 22.

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 20. 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 behaviour of symmetrical mixtures.

With regard to the original motivation for this study, namely the failure of both the MHNC integral equation study and HRT to observe a CEP in the expected range of $\delta$ 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 14. 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 behaviour.

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Singularity are expected to occur in certain derivatives of the phase boundary locus at a critical end point [4].
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.

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 unit variance.
FIG. 3: The temperature dependence of the fourth order cumulant ratio (see text) measured along the liquid branch of the coexistence curve.

FIG. 4: The finite-size scaling behaviour 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 $p^*(\tilde{m})$.  

FIG. 6: The measured form of $p_L(\rho)$ on the liquid branch for the $L = 25\sigma$ system size for a number of temperature spanning the demixing point. The inset shows the corresponding average number density as a function of temperature.