Ising Universality Class for the Liquid-Liquid Critical Point of a One Component Fluid: A Finite-Size Scaling Test

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We present a finite-size scaling study of the liquid-liquid critical point in the Jagla model, a prototype model for liquids that present the same thermodynamic anomalies which characterize liquid water. Performing successive umbrella sampling grand canonical Monte Carlo simulations, we evaluate an accurate density of states for different system sizes and determine the size-dependent critical parameters. Extrapolation to infinite size provides estimates of the bulk critical values for this model. The finite-size study allows us to establish that critical fluctuations are consistent with the Ising universality class and to provide definitive evidence for the existence of a liquid-liquid critical point in the Jagla potential. This finding supports the possibility of the existence of a genuine liquid-liquid critical point in anomalous one-component liquids like water.

The question of whether supercooled water would undergo a liquid-liquid (LL) first order transition terminating in a second order LL critical point (LLCP) if crystallization could be prevented is still highly debated [1–5]. The LLCP hypothesis, formulated back in 1992, was put forward to interpret molecular dynamics simulations of the classical ST2 model [6] for water which showed evidence of a van der Waals loop observed in low temperature T supercooled isotherms [7]. Such unconventional behavior has since then been confirmed in more detailed studies of the same model [3,4,8] as well as in studies of different water models [9–11]. The idea of a LLCP and the associated elegant explanation of water anomalies (including the density maximum and the compressibility minimum) and of the amorphous forms of water has been supported, with no definitive proof, by experiments [12–16] and theoretical studies [2]. It has also been suggested that the LLCP can be a feature of several network forming liquids, including silica [17], silicon [18–21], and tetrahedral DNA constructs [22]. A second critical point (besides the ordinary gas-liquid one) has also been discussed as a feature of models in which a competition between two local structures of distinct density, differing in local order (entropy) and energy, exists. Spherical models with competing length scales [23–26] and in particular ramp potentials [27] have indeed been proposed as candidates for investigating the physics of LL transitions.

Recently, Limmer and Chandler [1] questioned the idea of a LLCP in the ST2 model, calling attention on the absence of any finite-size scaling study of the critical fluctuations close to the LLCP. Indeed, interference from both the close-by glass transition, which makes equilibration of the low density phase difficult, as well as the spontaneous nucleation of ice, the rate of which is proportional to the system size, makes finite-size scaling studies very difficult

for classical water models, even if electrostatic forces are treated with the computationally less expensive reaction field method. The criticisms posed by Limmer and Chandler can be applied to all models, including the spherical ones, challenging the accumulated evidence in favor of LL transitions. In light of such criticisms, it is thus particularly important to establish whether the existence of a LLCP can be unambiguously proved with a proper finite-size scaling investigation. In this Letter, we report a detailed numerical study of the critical fluctuations for the Jagla potential [28–30], a model which shows both water anomalies and polyamorphism in the glass phase [31]. Evidence of a LLCP, located in the stability field of the fluid has been reported in previous studies [32–34]. By investigating systems of different sizes (from 100 to 1600 particles), we are able to prove that such a LLCP does exist and that the behavior of the fluctuations close to the critical point is consistent with the Ising universality class. Extrapolating the size-dependent critical parameters we evaluate the location of the bulk critical point. We thus provide an unmistakable evidence of a LLCP in a one component system.

The pair-wise Jagla ramp interaction potential [28–30] is shown in Fig. 1. It has two characteristic lengths, the hard-core distance $r = a$ and the soft-core distance $r = b$. The minimum of the energy U_0 corresponds to the soft-core distance. An attractive tail extends up to $r = c$. In the present Letter, the parameters of the ramp potential have been set to $b/a = 1.72$ and $c/a = 3$. $U_R = 3.56U_0$ is defined as the value of the potential energy at $r = a$ [33]. Quantities in the following are expressed in reduced units. Distances are in units of a, energies in units of U_0. The density, defined as $\rho \equiv N/L^3$, where N is the number of particles and L is the edge of the cubic simulation box, is measured in units of a^{-3}, the pressure in units of U_0/a^3, and the temperature in units of U_0/k_B, where k_B is the
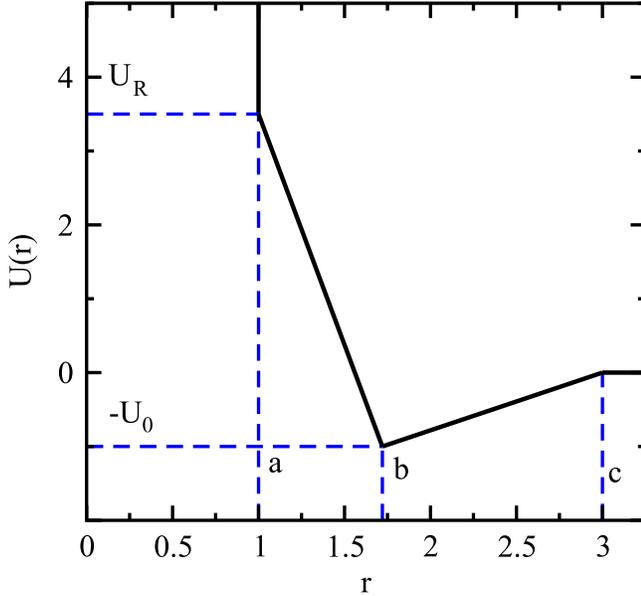
FIG. 1 (color online).   Representation of the radial dependence of the Jagla ramp potential for the parameters chosen in the present study.

Boltzmann constant. Molecular dynamics simulations suggest that with this choice of the parameters, a LLCP occurs at $T_C = 0.375$, $\rho_C = 0.37$, and $P_C = 0.243$ [32], in a region where the liquid is stable (as opposed to metastable) with respect to crystal ordering [32,33]. For a different choice of parameters, isothermal-isobaric constant-NPT Monte Carlo simulations also suggest the existence of a LLCP in the stable liquid phase at $T_C = 0.076$, $\rho_C = 0.378$, and $P_C = 0.0341$ [34].

To evaluate the distribution of density and energy fluctuations close to the critical point we perform grand canonical Monte Carlo (GCMC) simulations in a cubic box of side L at fixed T and chemical potential μ. Translation, insertion, and deletion moves are attempted with ratios 200:1:1. The translation move consists of randomly displacing a particle up to $0.1a$ in each direction. To effectively harvest the computational abilities offered by computer clusters and to sample all possible states with similar statistics, we implement the successive umbrella sampling (SUS) technique [35]. In the SUS technique the range of number of particles investigated is divided into many small overlapping windows $(N, N + \Delta N)$. For each window, a separate GCMC simulation monitors how often a state of N particles is visited. Deletions or insertions that would cause N to vary outside the range assigned to that window are rejected. Since the windows are independent, simulations can be run in parallel, with a gain in throughput that scales linearly with the number of processors employed. In our case, approximately 30 years on a single CPU are required to obtain the data presented here. By imposing the equality of the probability at the overlapping boundaries, the energy and particle histograms for each

TABLE I.   SUS GCMC simulations performed close to the size-dependent LLCP. We report the box size, the interval in the number of particles ($N_{\mathrm{Min}} - N_{\mathrm{Max}}$) studied, the temperature T and the fugacity z selected in the simulations.

Box Size	N_{Min}	N_{Max}	T	z
8	100	291	0.363	6.30×10^{-6}
10	250	537	0.368	7.98×10^{-6}
12	466	808	0.370	8.50×10^{-6}
15	1000	1600	0.370	8.61×10^{-6}

window $P(\rho, E)$ can be combined to obtain the full $P(\rho, E)$ histogram. Such a coupled density-energy histogram allows us to estimate $P(\rho)$ at different T and μ using temperature reweighting techniques [36], changing the fugacity $z = e^{\beta\mu}$ as well as T. We have selected $\Delta N = 1$ for $L = 8$, 10, and 12 and $\Delta N = 2$ for the $L = 15$ system. Table I reports the range of number of particles spanned during our SUS GCMC simulations for each box, and the values of T and z at which the systems were simulated.

Figure 2 shows $P(\rho)$ calculated starting from the raw SUS GCMC data for the $L = 8$ system at $T = 0.363$ and $z = 6.30 \times 10^{-6}$ (see Table I). It also shows different curves calculated at the low-density liquid high-density liquid coexistence via data reweighting, imposing equal area under the two peaks, up to the size-dependent LLCP.

The location of the critical point for each size is estimated through best-fit comparison of the probability distribution of the ordering operator M at the critical point
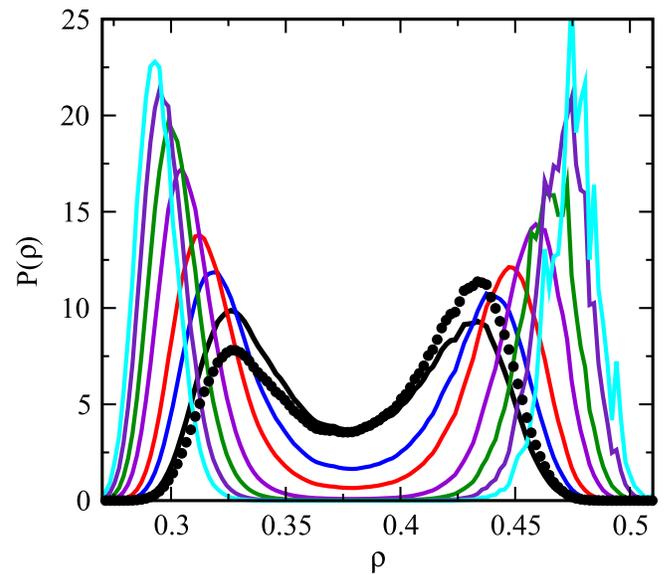

FIG. 2 (color online).   Density distribution functions $P(\rho)$ for $L = 8$. The filled symbols show the raw $P(\rho)$ resulting from the GCMC simulation at $T = 0.363$ and $z = 6.30 \times 10^{-6}$. The lines show $P(\rho)$ along the LL coexistence, obtained via T and z reweighting of the filled symbols. The lowest curve is the critical density distribution.
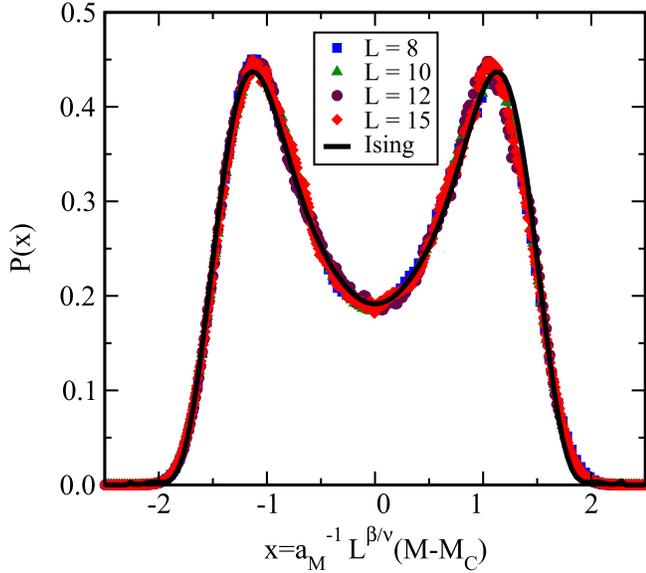
FIG. 3 (color online).   Matching to the Ising distribution (continuous line) of all the density distribution function at the critical point (symbols) for all the box sizes ($L = 8, 10, 12,$ and 15). The factor $a_M^{-1} = 0.34$ has been chosen to scale $P(x)$ to unit variance. The theoretical curve is from Ref. [38].
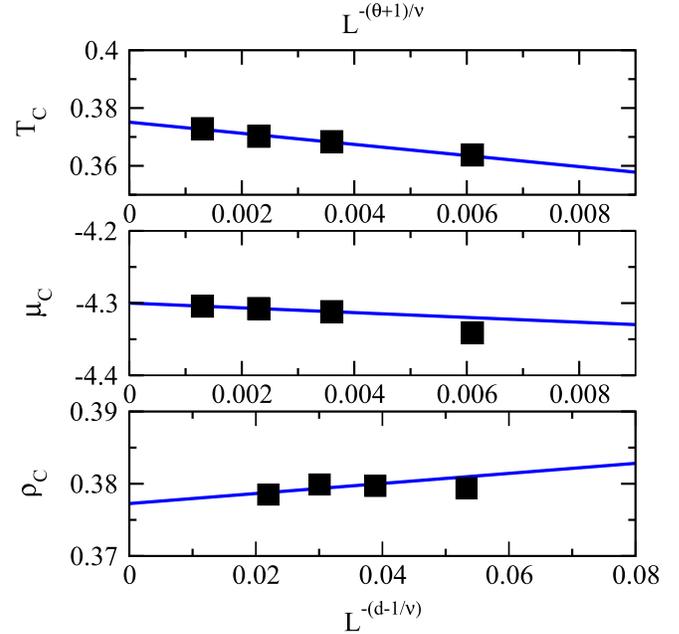

FIG. 4 (color online).   Size dependence of the apparent critical temperature, chemical potential, and density (symbols) for the four sizes, 8, 10, 12, and 15, investigated. The lines are best fit to straight lines and are performed considering only the three largest sizes, $L = 10, 12,$ and 15.

with the universal distribution characterizing the Ising universality class [37]. The ordering operator M of the LL transition is considered to be, analogously to the gas-liquid transition, a linear combination $M \sim \rho - su$, where u is the energy density of the system and s is the field-mixing parameter. Exactly at the critical point, fluctuations of M follow a known universal distribution, the same that characterizes the fluctuations of the magnetization in the Ising model. The result of the fitting procedure provides values for T_C, z_C, s and implicitly also for ρ_C. In all cases, the size-independent parameter s has been found to assume values close to zero, so that for the present model $M \sim \rho$ to a good approximation.

Figure 3 shows the distribution of density fluctuations at the (size-dependent) critical point for all investigated system sizes. All the distributions are shown as a function of the rescaled variable $x = a_M^{-1} L^{\beta/\nu}(M - M_C)$. Here ν is the critical exponent of the correlation length and β the critical exponent of the order parameter. For the three dimensional Ising universality class $\nu = 0.629$ and $\beta = 0.326$ [38]. All curves follow the Ising universal distribution very precisely.

Finite-size scaling predicts $T_C \sim L^{-(\theta+1)/\nu}$ and $\mu_C \sim L^{-(\theta+1)/\nu}$, where $\theta = 0.54$ is the universal correction to the scaling exponent [37]. Finite-size scaling also predicts $\rho_C \sim L^{-(d-1/\nu)}$. The size dependence of (T_C, μ_C, ρ_C) is shown in Fig. 4. As we can see the size dependence of the critical parameters is consistent with the Ising 3D universality class. By extrapolating the behavior of the critical parameters to $L \to \infty$, we find $T_C^{\text{bulk}} = 0.3751(3)$,

$\mu_C^{\text{bulk}} = -4.2999(1)$, and $\rho_C^{\text{bulk}} = 0.377(5)$, in very good agreement with the corresponding values estimated from molecular dynamics simulations for the same model [32]. We have used for the extrapolation only the three largest
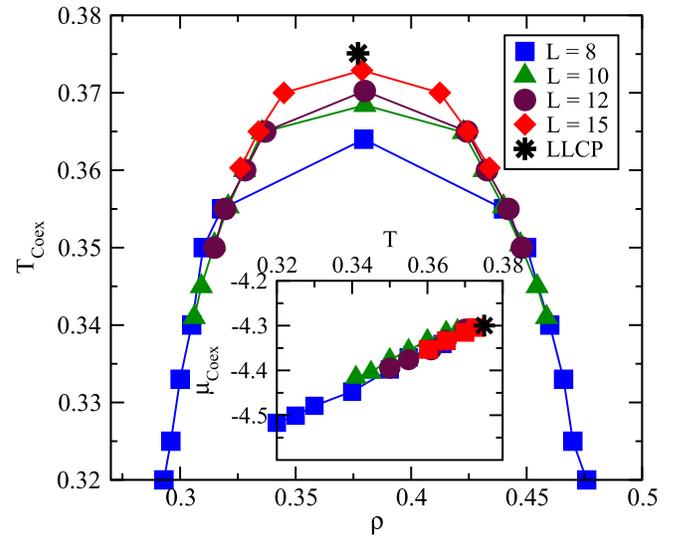

FIG. 5 (color online).   Liquid-liquid coexistence as calculated from histogram reweighting for all box sizes and LLCP as calculated from finite-size scaling. In the inset, the values of the chemical potential at coexistence and at the LLCP are also reported as a function of temperature.

systems to be sure to be within the range of L for which the scaling is valid.

Further implementing histogram reweighting techniques, it is possible to calculate the LL coexistence for all the investigated sizes, by estimating for each T the value of z at which the area under the peaks of the two phases are identical (see Fig. 2). Fig. 5 shows the LL coexistence curve in (T, ρ) as well as the values of the chemical potential along the coexistence curve. The coexistence lines of all sizes superpose far from the critical point, confirming that finite-size effects are progressively more and more negligible.

The data reported in this Letter rigorously prove via finite-size scaling that a second order LLCP, consistent with the three-dimensional Ising universality class—i.e., the same universality class of the gas-liquid transition— does exist in the one-component Jagla model. The present findings also prove that stable (or metastable) LLCPs can indeed exist in models with competing structures. By analogy our Letter supports the interpretation of the observed shape of the critical fluctuations recently reported for the case of long-range water models [3,5,8] in terms of a genuine LLCP.

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