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Metastable liquid-liquid coexistence and density anomalies in a core-softened fluid

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Linearly sloped or "ramp" potentials belong to a class of core-softened models which possess a liquid-liquid critical point (LLCP) in addition to the usual liquid-gas critical point. Furthermore, they exhibit thermodynamic anomalies in their density and compressibility, the nature of which may be akin to those occurring in water. Previous simulation studies of ramp potentials have focused on just one functional form, for which the LLCP is thermodynamically stable. In this work we construct a series of ramp potentials, which interpolate between this previously studied form and a ramp-based approximation to the Lennard-Jones (LJ) potential. By means of Monte Carlo simulation, we locate the LLCP, the first order high density liquid (HDL)–low density liquid (LDL) coexistence line, and the line of density maxima for a selection of potentials in the series. We observe that as the LJ limit is approached, the LLCP becomes metastable with respect to freezing into a hexagonal close packed crystalline solid. The qualitative nature of the phase behavior in this regime shows a remarkable resemblance to that seen in simulation studies of accurate water models. Specifically, the density of the liquid phase exceeds that of the solid; the gradient of the metastable LDL-HDL line is negative in the pressure (p)-temperature (T) plane; while the line of density maxima in the p-T plane has a shape similar to that seen in water and extends into the *stable* liquid region of the phase diagram. As such, our results lend weight to the "second critical point" hypothesis as an explanation for the anomalous behavior of water.

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I. INTRODUCTION

Multiple liquid phases are a common feature of the phase diagrams of multicomponent mixtures [1]. However, there is a growing body of experimental and computational evidence to indicate that they can also occur in *single component* systems. In elemental systems, a liquid-liquid (LL) transition has been reported in phosphorus [2–4], while for carbon a maximum occurs in the p-T melting curve [5] which has been linked to a probable LL transition [6]. Indirect evidence for LL transitions (mainly through electrical conductivity data, but also via anomalies in the melting curves) has been obtained for sulphur [7–9] and selenium [10]. Additionally, tentative evidence has recently emerged for LL transitions in molecular liquids such as n-butanol and triphenyl phosphite [11].

Arguably, however, the most intriguing example of a molecular system exhibiting signs of a liquid-liquid (LL) transition is water. Here the "second critical point" hypothesis [12] proposes that the LL transition is wholly metastable with respect to freezing and that the associated liquid-liquid critical point (LLCP) is responsible for the celebrated thermodynamic anomalies in its density and compressibility in the stable and metastable liquid region near the freezing boundary. Support for this proposal comes from molecular dynamics simulations of the (generally successful) TIP5P interaction potential [13]. These find a metastable LL transition and associated critical point, with a line of density maxima which seems to emanate from near the LLCP. Moreover, it has been suggested that at very low temperatures the LL boundary evolves into a transition between low density and high density glassy phases. While transitions between amorphous phases of different densities have been observed experimentally, their relationship to the liquid phases is still a matter of some debate (see, e.g., Refs. [14,15]). To date, however, the LL transition has not been observed in real water, possibly because the metastable lifetime of these phases is too small to be resolvable experimentally.

Notwithstanding the progress in identifying and characterizing LL phase transitions and thermodynamic anomalies across a variety of disparate systems, it remains unclear as to whether these phenomena are pluralistic in physical origin, or can instead be traced to a single common underlying mechanism. Furthermore, the connection between LL transitions and thermodynamic anomalies seems at present rather tenuous: in some systems density maxima have been reported without (as yet) clear evidence of an LL transition, as is the case in SiO_2 [16]; while in other (indeed in *most*) systems for which LL transitions have been reported, they appear unaccompanied by anomalies (see, e.g., Refs. [7,17] for reviews). Only in water do the two phenomena seem fairly firmly linked. It is therefore of interest to enquire as to whether there exist simple model potentials that capture the general qualitative behavior of an LL transition and thermodynamic anomalies, and to elucidate their properties in detail.

Work in this direction has concentrated on the so-called core-softened potentials, originally introduced by Hemmer and Stell [18]. The functional form of these potentials is engineered to favor two distinct interparticle separations—thereby providing impetus for a transition between two liquids of differing densities. Core-softened potentials can usefully be subdivided into two classes: "shoulder" potentials in which the hard core exhibits a region of negative curvature (or a step), and "ramp" potentials in which the hard core is softened via a linear slope. To date, the majority of work on core-softened potentials has concentrated on the shoulder form. Simulation and theory [19–23] show that (given favorable choices of potential parameters) these do indeed possess a metastable LLCP. However, to date, no firm evidence of thermodynamic anomalies in shoulder potentials has been reported [24]. Initial indications of anomalies in two-dimensional (2D) shoulder models [25] were subsequently shown [26] to be an artifact of the quasicontinuous nature of the 2D freezing transition in the case when the solid has a lower density than the liquid.

In contrast to their shouldered counterparts, ramp potentials are known to exhibit both an LLCP and thermodynamic anomalies. They therefore appear a potentially more fruitful route to determining whether the qualitative features of the LL transition in systems such as water can be described by a very simple model, as well as for investigating the more general aspects of the relationship between the LL phase behavior and thermodynamic anomalies. As we shall show in the present paper, a ramp model can indeed capture (to a remarkable degree) the qualitative features of the metastable LL transition and density maxima seen in simulations of accurate water models.

II. RAMP POTENTIALS

The phase behavior of particles interacting via an isotropic pair potential, in which the steep repulsive core is softened by a linear ramp, was first considered 35 years ago by Hemmer and Stell [18]. Their calculations for a one-dimensional system revealed a range of parameters for which two phase transitions occurred, and they speculated that the same might be true in high dimensions. More recently, interest in such potentials has been rekindled following computer simulation and mean field studies of ramp potentials in two and three dimension by Jagla [27]. These revealed evidence of HDL and LDL phases in addition to the expected liquid and gas phases, and the presence of density and compressibility anomalies. A subsequent detailed Monte Carlo (MC) simulation study of the same system by one of us [26], accurately mapped a portion of the HDL-LDL phase boundary, the liquid-gas boundary, and the locus of the lines of density and compressibility maxima. A more recent study of the same potential has used molecular dynamics simulations to investigate the relationship between the line of specific heat maxima emanating from the LLCP and a region of dynamic crossover [28]. The case of a purely repulsive ramp potential has also been studied [29,30]; this system exhibits thermodynamic anomalies but no direct evidence of an LL transition was found.

The form of ramp potential we consider in the present work is given by

$$\tilde{U}(r)=\infty; \quad r<r_0,$$

$$\tilde{U}(r)=\frac{(r_0-r)(D+0.69)}{(r_1-r_0)}+0.69; \quad r_0\leq r<r_1,$$

$$\tilde{U}(r)=D(r_2-r)/(r_1-r_2); \quad r_1\leq r<r_2,$$

$$\tilde{U}(r)=0; \quad r\geq r_2, \tag{1}$$

where $\tilde{U}(r)=U(r)/\epsilon$ is a dimensionless potential (measured in units of some parameter ϵ which serves to set the energy scale, and which we set equal to unity in what follows). Given a constant hard-core radius r_0 and contact value $\tilde{U}(r\rightarrow r_0^+)$, the form of the potential is determined by the position of the minimum r_1, the maximum range of the potential r_2, and the magnitude of the well depth $D=-\tilde{U}(r_1)$. In the original work of Refs. [26,27], this potential was studied for the parameters values $r_1=1.72r_0$, $r_2=3.0r_0$, $D=0.1984$. In the present work we study the properties of a *family* of such potentials, the members of which are chosen such as to interpolate between the original form and a ramp potential approximation to the LJ potential. The interpolation simultaneously reduces the radius of the potential minimum and the maximum range, while increasing the potential depth. This is done in such a way as to maintain approximate constancy of the second virial coefficient, thereby ensuring that the potentials are comparable in a corresponding states sense [31,32].

TABLE I. Forms of the ramp potentials studied in this work (cf. Fig. 1). The well depth is given by $D(r_1)=-\tilde{U}(r_1)=1.1578-0.5578r_1$, while the maximum range r_2 is tuned such as to maintain the second virial coefficient at the value $B_2\approx 1.52$.

r_1	$D(r_1)$	r_2
1.72	0.1984	3.0
1.7	0.209556	2.92483
1.68	0.220711	2.8549
1.66	0.231867	2.78963
1.65	0.237444	2.75859
1.64	0.243022	2.72853
1.63	0.2486	2.69941
1.62	0.254178	2.67118
1.61	0.259756	2.6438
1.60	0.265333	2.61721
1.59	0.270911	2.5914
1.58	0.276489	2.56631
1.5	0.321111	2.38847
1.4	0.376889	2.21068
1.3	0.432667	2.06848

We define our family of ramp potentials as follows. The limiting value of the potential at the hard core contact is held constant at $\tilde{U}(r\rightarrow r_0^+)=0.69$. Choosing to label each member of the family of potentials by the radius of the minimum r_1, the associated well depth $D(r_1)$ is given by $D(r_1)=1.1578-0.5578r_1$, while the value of r_2 is tuned such as to maintain the second virial coefficient at the value $B_2=1.52$. The resulting values of $D(r_1)$ and r_2 are listed in Table I, and a selection of potentials is shown in Fig. 1.

III. COMPUTATIONAL METHODS

Monte Carlo simulation studies of the phase behavior of a selection of potentials in the family have been performed within the constant-NpT ensemble. In the results reported below, we quote a reduced temperature k_BT/ϵ, and reduced pressure pr_0^3/ϵ. The particle number density (ρ) is expressed

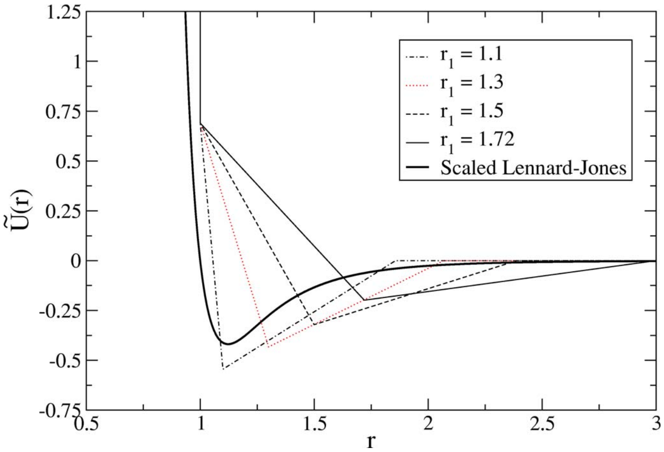

FIG. 1. (Color online) A selection from the family of ramp potentials studied in this work and listed in Table I. Also shown for comparison is the Lennard-Jones (LJ) potential whose well depth has been scaled such that the second virial coefficient takes the value $B_2 = 1.52$.

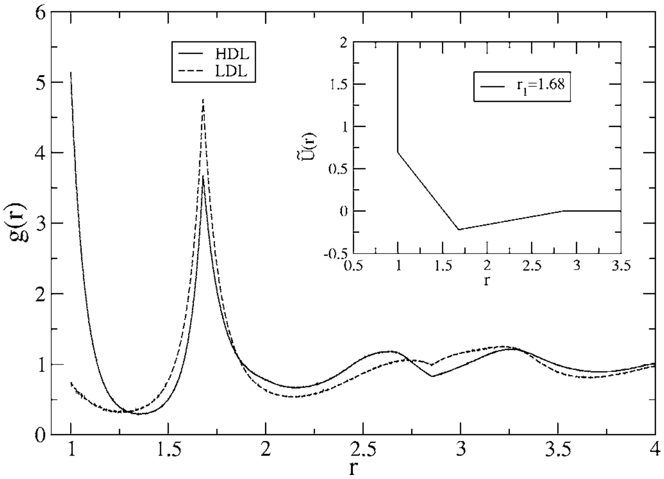

FIG. 2. Comparison of the forms of $g(r)$ for coexisting points on the LL phase boundary. Parameters are $r_1 = 1.68$, $T = 0.0644 = 0.944T_c$, $p = 0.05021$. The density of the HDL phase is $\rho = 0.484(1)$, while that of the LDL phase is $\rho = 0.313(1)$. The inset shows the corresponding form of the interaction potential.

in units of r_0^{-3}. All simulations were performed for systems of $N = 300$ particles.

The principal aim was to locate the liquid-liquid coexistence line and critical point for each potential and to map the line of density maxima. The coexistence boundaries were obtained from the fluctuation spectra of the number density using multicanonical Monte Carlo techniques and histogram extrapolation in the well established manner [33–36]. To estimate critical parameters, we have employed a crude version of the finite-size scaling (FSS) analysis described in Ref. [37]. The analysis involves scanning a range of pressure p and temperature T until the observed probability distribution of the fluctuating instantaneous particle density matches the independently known universal fixed point form appropriate to the Ising universality class in the FSS limit. Owing to the relatively low temperature at which the liquid-liquid critical point generally occurs, the acceptance rate for volume updates in the constant-*NpT* ensemble are very low, resulting in extended correlation time for the density fluctuations. Consequently we were able neither to study a wide range of system sizes nor obtain data of sufficient statistical quality to permit a more sophisticated FSS analysis. Nevertheless, it transpires that our estimated uncertainties for the critical point parameters are sufficient to resolve clearly the trends that occur as the form of the potential is altered.

Lines of density maxima were mapped by measuring the density as a function of temperature along isobars. The task of tracking the line of maxima was again aided by histogram extrapolation techniques.

IV. RESULTS

A. LDL-HDL transition and the density anomaly

It is natural to enquire, first of all, as to the structural differences between the LDL and HDL phases. In Fig. 2 we show the form of the radial distribution function $g(r)$ at an LL coexistence point for the $r_1 = 1.68$ potential. The temperature is some 5% below that of the LLCP. From Fig. 2 it is evident that, in the LDL phase, the majority of first neighbors are located at the potential minimum, whereas, in the HDL phase, there is a much greater number of neighbors at the hard core diameter and fewer at the potential minimum.

In Refs. [26,27] it was shown that for the ramp potential a density maximum occurs as the temperature is lowered isobarically though the LDL phase. An example is shown in Fig. 3(a) for the case $r_1 = 1.72$ at $p = 0.0247$. For these parameters the density maximum occurs at $T_{\mathrm{MD}} = 0.095(5)$. Also included in this figure is the form of the radial distribution function $g(r)$ for three temperatures on this isobar: one below, one above, and one at T_{MD}. At the hard core contact value, one sees that $g(r_0)$ is greatest for $T = T_{\mathrm{MD}}$. Thus the anomalous density increase with increasing T is apparently due, in part at least, to an increase in the number of particles choosing the shorter of the two separation distances and settling at the hard core, despite the higher energy cost.

We have traced the locus of the density maxima in the p-T plane for three of the potentials studied. These are discussed in connection with the phase diagram in the following subsection.

B. Phase behavior

Figure 4 shows the location of the LLCP for a selection of values of r_1, together with (in some instances) a portion of the associated LL coexistence line. One sees that as r_1 is decreased, the LLCP shifts to lower temperatures and higher pressures. On tracking the LL boundary down in temperature from the critical point, we observed spontaneous freezing to a hexagonal close packed (hcp) structure. This solid has a density lower than that of either liquid phase [38].

The freezing point on the LL boundary shifts to higher temperatures as r_1 is decreased. This, coupled with the concomitant decrease in the critical temperature, rapidly narrows the temperature range over which the LL transition is stable

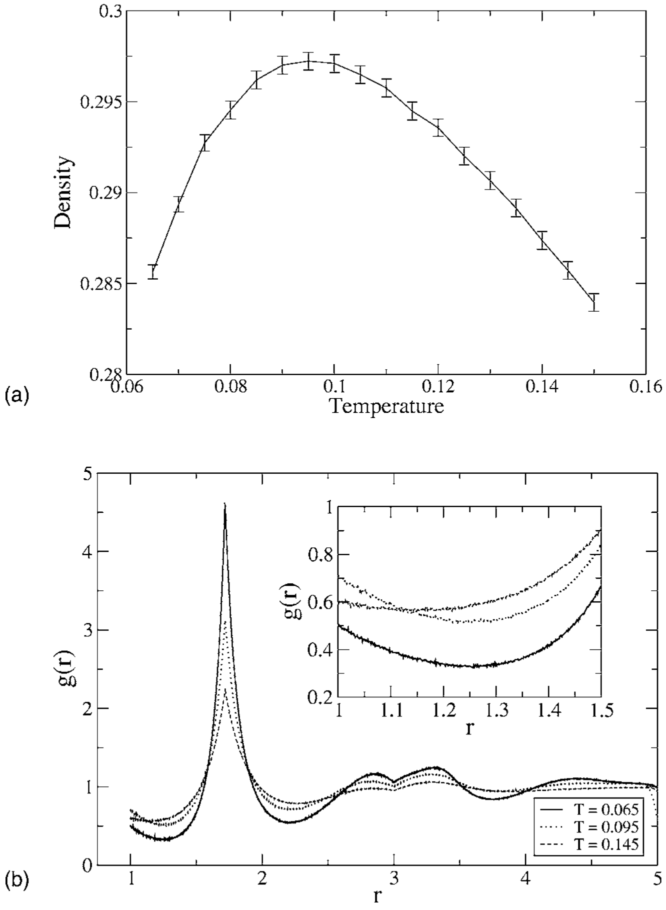

FIG. 3. (a) The measured number density as a function of temperature for $p=0.0247$, for the potential having $r_1=1.72$. (b) The measured form of the radial distribution function $g(r)$ for the same potential at three temperatures on the $p=0.0247$ isobar spanning $T_{MD}=0.095(5)$.

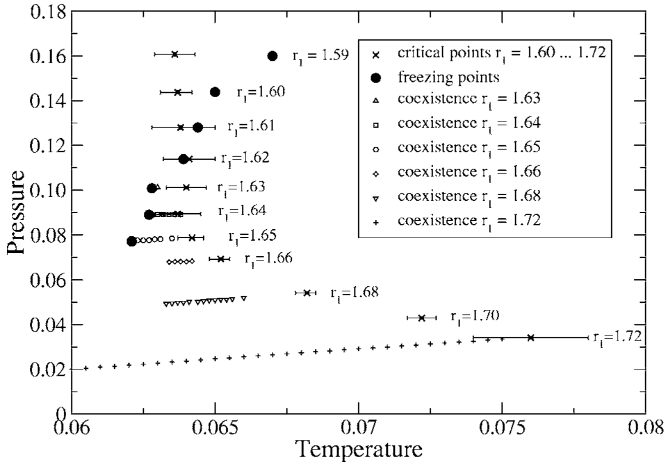

FIG. 4. The near-critical region of the phase diagram for each of the ramp potentials studied. Shown in each instance is the estimated location of the LLCP. For certain larger values of r_1 in the range studied, a segment of the LDL-HDL phase boundary has also been estimated. The point of intersection of the LL phase boundary with the freezing line is shown for potentials in which the LLCP is either metastable or only moderately stable with respect to freezing. Error bars represent the uncertainties in the critical temperature. Uncertainties in the critical pressure, as well as in the location of the LL line and the freezing points, are comparable with the symbol sizes.

as r_1 is reduced. For $r_1 \lesssim 1.62$, the critical point became metastable with respect to the stable hcp solid phase. For $r_1=1.61$ and $r_1=1.60$, simulations initiated in the liquid phase were able to sample the near critical point fluctuations for a limited period, before eventually spontaneous crystallization occurred. Freezing occurred very rapidly in the critical region for $r_1 \leqslant 1.59$, preventing accurate estimates of critical point parameters or indeed the value of r_1 at which the critical point becomes completely unstable rather than simply metastable.

In order to obtain a flavor for the types of freezing behavior which may occur in our model potentials, we have estimated the locus of the liquid-solid coexistence boundary in the p-T plane for the case $r_1=1.61$ (for which the LLCP is barely metastable). The results presented in Fig. 5(a) show that in addition to the freezing to an hcp structure already identified, a face centred cubic (fcc) can form at low pressure. Figure 5(b) shows for both a high and low pressure, the time evolution of the simulation density starting from an initial liquidlike configuration for two temperatures either side of the freezing point. In the case of the higher pressure ($p=0.1$), the system freezes to an hcp solid of lower density, while for lower pressure ($p=0.001$), the solid is fcc, having a density greater than that of the liquid. One thus expects that the gradient of the freezing boundary in the p-T plane is negative at high pressure and positive at low pressure. This is indeed confirmed by Fig. 5(a): within the rather limited accuracy of our measurements, the gradient of the freezing boundary appears to change sign at $p \simeq 0.02$, suggesting that this marks a triple point between hcp, fcc, and liquid phases. We have not attempted to map the hcp-fcc coexistence line within the solid region.

It is interesting to note that as r_1 is decreased, the initially positive gradient of the LDL-HDL line in the p-T plane reduces in magnitude and changes sign for $r_1 \approx 1.60$, which is about the point at which the LDL-HDL critical point itself becomes metastable. This trend is quantified in Fig. 6. Thus the gradient of the *metastable* LDL-HDL line is negative, as has also been reported to be the case for water [39]. We find that the change in the sign of the gradient occurs because the enthalpy difference between the two phases changes sign, rather than the density difference.

Figure 7 superimposes the lines of density maxima on the phase diagrams (cf. Fig. 4) of several of the ramp potentials studied. At high pressures, the lines of anomalies for the various potentials become rather flat and appear to approach the respective LLCP. As the line is followed to lower pressures, it passes through a temperature maximum before bending back on itself, and reaching a pressure minimum below which no density anomaly occurs [40]. The maximum temperature attained by the line of maxima increase strongly with decreasing r_1. It is noteworthy that the shape of the line of density maxima in each case is similar to that found in MD simulations of TIP5P water [13]. Furthermore, for the case $r_1=1.60$, for which the LDL-HDL critical point is significantly buried within the stable solid region, the density

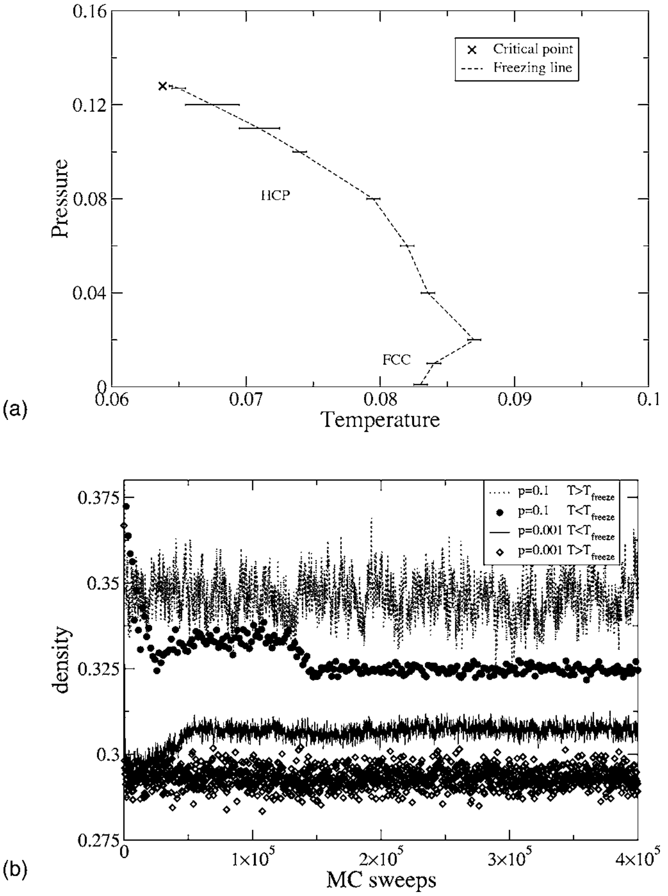

FIG. 5. (a) The liquid-solid coexistence boundary and location of the LLCP for $r_1=1.61$. (b) The time evolution of the system density close to the freezing transition, as described in the text. The figure shows the freezing to a solid of higher (lower) density for low (high) pressures, respectively. Time is measured in units of Monte Carlo sweeps.

anomaly is nevertheless observable over a wide range of the stable liquid phase.

The point of minimum pressure separates the line of density maxima from a line of density *minima*, the latter being the locus of points in the *p*-*T* plane at which the behavior returns to "normal," i.e., increasing density with decreasing *T*. Figure 8(a) illustrates this feature for the $r_1=1.72$ potential via isobaric measurements of ρ against *T*, which exhibits both a density maximum and a minimum. The associated lines of density extrema are plotted on the *p*-*T* phase diagram in Fig. 8(b). Following the line of density minima for $r_1=1.72$ past the point of minimum pressure, the system freezes to an hcp solid structure. We find that the extent to which the line of density minima occupies the stable fluid region depends strongly on the value of r_1: for $r_1=1.72$ it is observable over a significant range of fluid densities, while for $r_1=1.63$ and $r_1=1.61$ freezing occurs (this time to an fcc solid) close to the location of the point of minimum pressure. We note that observations of lines of density maxima transforming into lines of density minima have also recently been reported in simulations of the ST2 model of water [41].

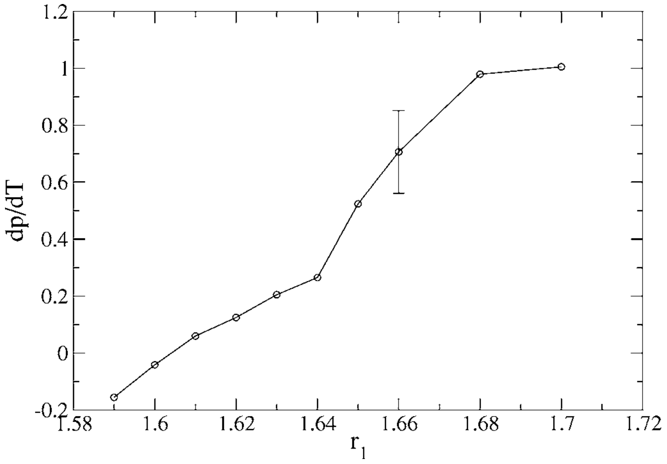

FIG. 6. Estimates of the near-critical gradient of the LDL-HDL coexistence boundary in the *p*-*T* plane, for the family of potentials shown in Fig. 1. A representative error bar is shown.

Whilst the LDL-HDL transition becomes wholly metastable for $r_1\lesssim1.62$, the line of density anomalies is nevertheless observable in the stable liquid region for this value of r_1 and indeed for a considerable range of smaller ones. However, since no density anomaly occurs for the Lennard-Jones potential, it is pertinent to ask how the anomaly disappears as we approach this limit. To answer this question we have studied the potentials having r_1 in the range $r_1=1.5-1.3$ (cf. Fig. 1), which are much closer to the LJ limit than the potentials discussed so far. Here we find that freezing occurs at much higher temperatures than found for our studies of the range $r_1=1.72-1.60$. For $r_1=1.4$, the maximum temperature attained by the line of density maxima is very close to the freezing line, while for $r_1=1.3$, no anomalies are seen. Furthermore, there is no indication of a metastable liquid-liquid transition for potentials in the range $r_1=1.5-1.3$. It thus appears that a rapid increase in the freezing temperature occurs with decreasing r_1 (as already hinted at in Fig. 4). As a result the stable solid region engulfs the temperature range in which the anomalies would otherwise be found. This occurs despite the fact that the maximum temperature attained by

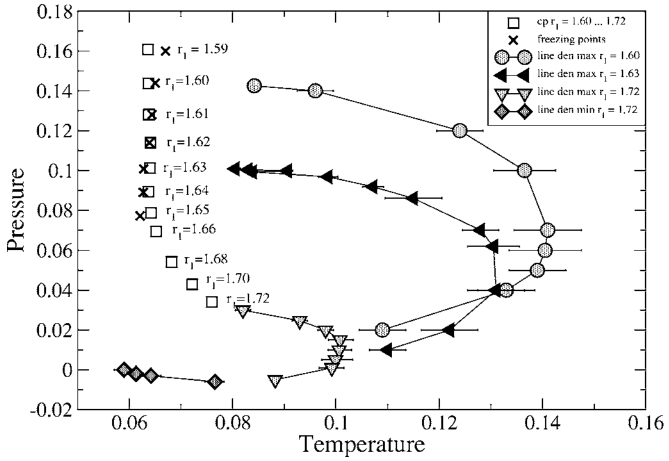

FIG. 7. Lines of density maxima for a selection of the potentials studied, superimposed upon the phase diagrams of Fig. 4. Also shown for the case $r_1=1.72$ is the line of density minima (cf. Fig. 8).

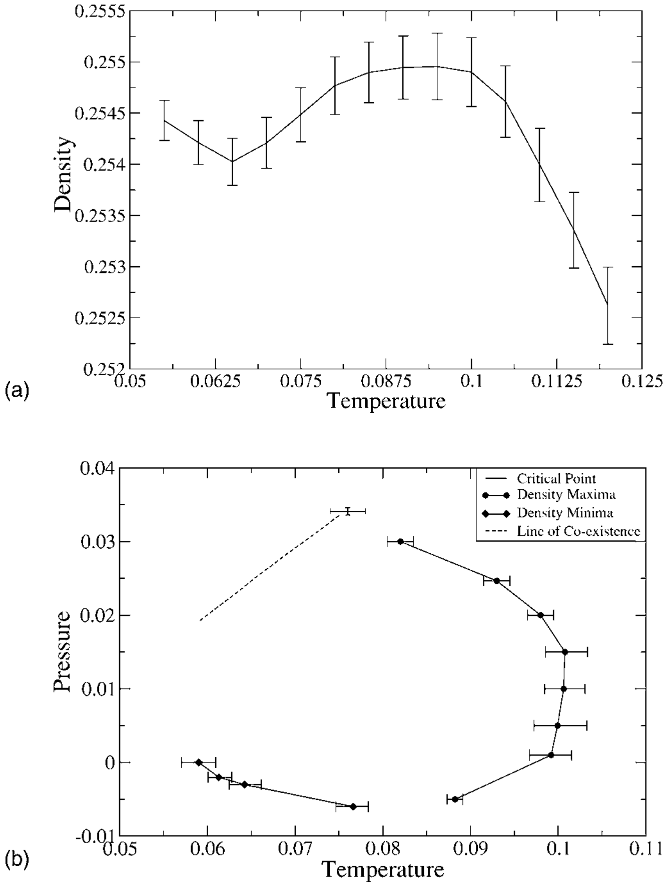

FIG. 8. (a) The measured number density as a function of temperature at $p=-0.003$, for the potential having $r_1=1.72$. Two extrema are found, a maximum and a minimum. The system freezes to an hcp solid at $T=0.055(1)$. (b) The lines of density maxima and density minima for the case $r_1=1.72$. Also shown is the location of the LLCP and HDL-LDL coexistence line.

the line of anomalies also appears (initially at least) to increase strongly as r_1 decreases (cf. Fig. 7).

V. DISCUSSION AND CONCLUSIONS

To summarize: previous simulation work on LL transitions for ramp potentials [26,27] has been confined to the situation in which the LLCP occupies the stable fluid region. Here the LL phase boundary has a positive gradient in the pressure-temperature plane of the phase diagram. We have shown that by judicious choice of ramp parameters, one can render the LLCP metastable with respect to freezing to a crystalline solid of density lower than that of the liquid. A line of density maxima emanates from near the metastable LLCP and extends well into the *stable* fluid region, before bending back in the p-T plane as the pressure is reduced. In contrast to its stable counterpart, the gradient of the metastable LL phase boundary is *negative*. All these features are in qualitative agreement with the results of simulations of water, and as such, our results lend substantial weight to the "second critical point" hypothesis for water.

It is probably fair to say that there is currently no clear picture regarding the factors controlling (i) the existence or otherwise of density anomalies in terms of the form of the interparticle potential; and (ii) the detailed relationship between any such line of anomalies and the LL phase boundary. In situations where a line of density maxima exists, this is thought to be a sufficient, but not a necessary condition for an LLCP to occur, at least for supercooled states [45]. However, it remains unclear why shoulder potentials exhibit an LL transition, but no density anomaly, while ramp potentials exhibit both. As regards the locus of the line of density maxima, thermodynamic considerations limit the number of ways in which it can terminate [42,43]; specifically it must either intersect a phase boundary or transform smoothly into a line of density minima. For the family of ramp potentials studied in the present work, the line of density anomalies was always found to approach the LLCP at its high pressure end. Indeed the same appears to be true for a number of other distinct models exhibiting LL transitions [44], although there are yet other models where the intersection appears to occur at a point further down the LL boundary [45,46]. We have recently obtained preliminary results for a series of ramp potentials which may shed some light on this matter. Specifically we find that if the interaction range is increased to values greater than those studied here, the line of density anomalies detaches from the LLCP; its intersection with the LL boundary then occurs at subcritical temperatures and in a region of negative pressure. We hope to report on this finding in greater detail in a future publication.

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