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

H.M. Gibson and N.B. Wilding

Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom

I. INTRODUCTION

Multiple liquid phases are a common feature of the phase diagrams of multi-component mixtures [1]. However, there is a growing body of experimental and computational evidence to indicate that they can also occur in single component systems. Examples of such have, to date, been found in a number of elemental systems including (inter alia) Sulphur [2, 3, 4], Phosphorous [5, 6, 7], Hydrogen [8, 9, 10] and Selenium [11]. Additionally, tentative evidence has recently emerged for the existence of liquid-liquid transitions in molecular liquids such as n-butanol and triphenyl phosphate [12].

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 [13] 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 the 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 [14]. 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 temperature the LL boundary evolves into a transition between low density and high density glassy phases. Whilst 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 eg. [12, 16]). 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) evidence of a LL transition, as is the case in SiO$_2$ [17]; while in other (indeed in most) systems for which LL transitions have been reported, they appear unaccompanied by anomalies (see eg. [2, 18] 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 captures the general qualitative behaviour of a 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 [19]. 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, and "ramp" potentials in which the hard core is softened via a linear slope. To date, the majority of work on core softened potential has concentrated on the shoulder form. Simulation and theory [20, 21, 22, 23, 24] show that these do indeed (given a favorable choices of potential parameters) possess a metastable LLCP. However, to date, no firm evidence of thermodynamic anomalies has been reported.
In the original work of refs. [26, 27], this potential was shown to be an artifact of the quasi-continuous nature of the 2d freezing transition in the case when the solid has a density less than the liquid.

In contrast to their shouldered counterparts, ramp potentials are known to exhibit both a 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 behaviour 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 behaviour of particles interacting via an isotropic pair potentials in which the steep repulsive core is softened by a linear ramp, was first considered 35 years ago by Hemmer and Stell [19]. 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 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.

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

\[ U(r) = \begin{cases} \infty & r < r_0 \\ \frac{(r_0 - r)(D + 0.69)}{(r_1 - r_0)} + 0.69 & r_0 \leq r < r_1 \\ D(r_2 - r)/(r_1 - r_2) & r_1 \leq r < r_2 \\ 0 & r > r_2 \end{cases} \]

where \( U(r) \) is measured in units of \( k_BT \). Given a constant hard-core radius \( r_0 \) and contact value \( U(r \to r_0) \), 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 \( D = -U(r_1) \). In the original work of refs. [26, 27], this potential was studied for the parameters values \( r_1 = 1.72 \, r_0 \), \( r_2 = 3.0 \, r_0 \), \( D = 0.1984 \). In the present work we study the properties of a family of such potentials, the members of which are chosen such as 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, whilst 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 [28, 29].

We define our family of ramp potentials as follows. The limiting value of the potential at the hard core contact is held constant at \( U(r \to r_0) = 0.69 \). 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 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 tab. II and a selection of potentials is shown in fig. II.

![Graph showing ramp potentials](image)

FIG. 1: A selection from the family of ramp potentials studied in this work and listed in tab. II. Also shown for comparison is the LJ potential whose well depth has been scaled such that the second virial coefficient takes the value \( B_2 = 1.52 \).

III. COMPUTATIONAL METHODS

Monte Carlo simulation studies of the phase behaviour of a selection of potentials in the family have been performed within the constant-\( NpT \) ensemble. In the results reported below, temperature (\( T \)) is measured in units of the well depth, particle number density (\( \rho \)) is measured in units of \( r_0^3 \) and the pressure (\( p \)) in units of \( k_BT/r_0^3 \). All simulations were performed for systems of \( N = 300 \) particles.

The principal aim was to locate the liquid-liquid (LL) coexistence line and critical point for each potential and to map the line of density maxima. The coexistence boundaries were obtained using multicanonical Monte Carlo techniques and histogram extrapolation in the well established manner [30, 31, 32, 33]. To estimate cri-
The temperature is some 5% below that of the LLCP.

1. Maintain the second virial coefficient at the value $B$

We show the form of the radial distribution function $g(r)$ at a LL coexistence point for the $r_1 = 1.68$ potential. The temperature is some 5% below that of the LLCP.

| $r_1$ | $D(r_1)$ | $r_2$ |
|-------|----------|-------|
| 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|
| 1.58  | 0.276489 | 2.56631|
| 1.5   | 0.321111 | 2.38847|
| 1.4   | 0.376889 | 2.21068|
| 1.3   | 0.432667 | 2.06848|

TABLE I: Forms of the ramp potentials studied in this work (cf. fig. 1). The well depth is given by $D(r_1) = -U(r_1) = 1.11578 - 0.568$, while the maximum range $r_2$ is tuned such to maintain the second virial coefficient at the value $B_2 \approx 1.52$.

...cal parameters, we have employed a crude version of the finite-size scaling (FSS) analysis described in ref. \[34\]. The analysis involves scanning the range of pressure $p$ and temperature $T$ until the observed probability distribution of the fluctuating instantaneous particles density matches the independently known universal fixed point form appropriate to the Ising universality class in the FSS limit. Owing to the relatively small 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 of the phase diagram. The task of tracking the line of maxima was again aided by histogram extrapolation techniques.

IV. RESULTS

A. The 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 a LL coexistence point for the $r_1 = 1.68$ potential. The temperature is some 5% below that of the LLCP.

From the figure, 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 larger number of neighbors at the hard core diameter and fewer at the potential minimum.

In refs. \[26, 27\] it was shown that the ramp potential exhibits a maximum in the density as the temperature is lowered isobarically though the LDL phase. An example is shown in fig. 4(a) for the case $r_1 = 1.72$ at $p = 0.0247$. For these parameters the density maximum occurs at $T_{MD} = 0.095(5)$. 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 $T = T_{MD}$. 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 several of the potentials studied. These are discussed in connection with the phase diagram in the following subsection.

B. Phase behaviour

Fig. 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 \[35\].

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 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 was able to sample the near critical point fluctuations for a limited time, before eventually spontaneous crystallization occurred. Freezing occurred very rapidly in the critical region for \( r_1 < 1.60 \), 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.

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 close to the point at which the LDL-HDL critical point becomes metastable. This trend is quantified in fig. 5. Thus the gradient of the metastable LDL-HDL line is negative, as has also been reported to be the case for water \[36\]. 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.

![Diagram](https://example.com/diagram1.png)

**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 \( T_{MD} = 0.095 \).

![Diagram](https://example.com/diagram2.png)

**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.

![Diagram](https://example.com/diagram3.png)

**FIG. 5:** Estimates of the near-critical gradient of the LDL-HDL coexistence boundary in the \( p-T \) plane, for the family of potentials shown in 4. A representative error bar is shown.

![Diagram](https://example.com/diagram4.png)

**FIG. 6:** Superimposes the lines of density maxima on the phase diagrams of several of the ramp potentials studied. The gradient of these lines changes from negative to positive values in the \( p-T \) plane as pressure is reduced. We observe a strong increase in the temperature of the turning point as \( r_1 \) decreases. It is noteworthy that the shape of the line of density maxima is similar to that found in MD simulations of TIP5P water \[14\]. 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 anomaly is nevertheless observable over a wide range of the stable liquid phase.

We have estimated the locus of the liquid-solid coexistence boundary in the \( p-T \) plane for the potential having \( r_1 = 1.61 \), for which the LLCP is metastable; the results are presented in fig. 8(a). Fig. 8(b) shows for both a high and low pressure, the time evolution of the simulation density starting from an initial liquid-like configuration for two temperatures either side of the freezing point. In the case of the higher pressure (\( p = 0.1 \)), the system freezes to a hcp solid of lower density, while for lower pressure (\( p = 0.001 \)), the solid is fcc in structure 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. 8(a): within the rather limited accuracy of our measurements, the gradient of the freezing boundary appears to change sign at \( p \approx 0.02 \), 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, although on cooling the fcc structure, we find it transforms to hcp suggesting the gradient of the boundary is positive in the \( p-T \) plane.

At high pressure, the lines of anomalies for the various potentials becomes rather flat and appear to approach the respective LLCP. At low pressure we find that the line is truncated by freezing to a face centered cubic (fcc) solid structure at slightly negative pressures. For most of the potentials studied, the anomalous decrease in density continues right up to the stable solid region as \( T \) is lowered isobarically; there is no subsequent density minimum, i.e. a return to “normal” behaviour, as has been recently reported in simulations of the ST2 model of water \[37\]. An exception is the case of \( r_1 = 1.72 \) at small negative pressure. Here the density maximum flattens and a small minimum appears, followed by a clear increase in the density as freezing is approached, as is shown in fig. 8.

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**FIG. 6:** Lines of density maxima for a selection of the potentials studied, superimposed upon the phase diagrams of fig. 4.

**FIG. 7:** The measured number density as a function of temperature at \( p = -0.005 \), for the potential having \( r_1 = 1.72 \). The system freezes as \( T = 0.055 \).

**FIG. 8:** (a) The liquid-solid coexistence boundary and line of anomalies in the \( p-T \) plane 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.
Whilst the LDL-HDL transition becomes wholly metastable for $r_1 \lesssim 1.62$, the lines of density anomalies is nevertheless observable in the stable liquid region for this value of $r_1$ and indeed 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 case $r_1 = 1.3$ (cf. fig. 1), which is 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 $r_1 = 1.72 - 1.62$, no anomalies are seen and there is no indication of a metastable liquid-liquid transition. It thus appears that a rapid increase in the freezing temperature occurs with decreasing $r_1$ (as already hinted at in fig. 1). As a result the stable solid region engulfs the temperature range in which the freezing temperature occurs with decreasing $r_1$ and indeed a considerable range of smaller $r_1$. We estimate that the anomalies are lost for $r_1 \lesssim 1.4$.

V. DISCUSSION AND CONCLUSIONS

To summarize, previous simulation work on ramp potentials 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. The line of density maxima bends back in the $p-T$ plane as pressure is reduced. Furthermore (and 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 a LLCP to occur, at least for supercooled states. However, it remains unclear why shoulder potentials exhibit a LL transition, but no density anomaly, while ramp potentials exhibit both. As regards the locus of the line, thermodynamic considerations limit the number of ways in which it can terminate specifically it must either intersect a spinodal 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 their high pressure end. Indeed the same appears to be true for a number of other distinct models exhibiting LL transitions, although there are yet other models where the intersection appears to occur at a point further down the LL boundary. We have recently obtained preliminary results for the ramp potential which may potentially 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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