Relationship between the liquid–liquid phase transition and dynamic behaviour in the Jagla model

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Abstract

Using molecular dynamics simulations, we study a spherically symmetric 'two-scale' Jagla potential with both repulsive and attractive ramps. This potential displays a liquid–liquid phase transition with a positively sloped coexistence line ending at a critical point well above the equilibrium melting line. We study the dynamic behaviour in the vicinity of this liquid–liquid critical point. Below the critical point, we find that the dynamics in the more ordered high density liquid (HDL) are much slower then the dynamics in the less ordered low density liquid (LDL). Moreover, the behaviour of the diffusion constant and relaxation time in the HDL phase follows approximately an Arrhenius law, while in the LDL phase the slope of the Arrhenius fit increases upon cooling. Above the critical pressure, as we cool the system at constant pressure, the behaviour of the dynamics smoothly changes with temperature. It resembles the behaviour of the LDL at high temperatures and resembles the behaviour of the HDL at low temperatures. This dynamic crossover happens in the vicinity of the Widom line (the extension of the coexistence line into the one-phase region) which also has a positive slope. Our work suggests a possible general relation between a liquid–liquid phase transition and the change in dynamics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Water is the most important solvent for biological functions [1, 2], yet it possesses many properties that are not well understood. An open question of general interest concerning liquid water is the relation between a liquid–liquid (LL) phase transition [3, 4] and dynamic properties [5–10]. Based on analogies with other network-forming liquids and with the thermodynamic properties of the amorphous forms of water, it has been suggested that, at ambient pressure, liquid water should show a crossover between fragile behaviour at high T to
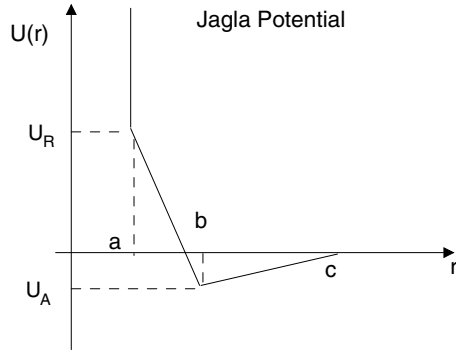
Figure 1. The 'two-scale' Jagla ramp potential with attractive and repulsive ramps. Here $U_R = 3.5U_0$, $U_A = -U_0$, a is the hard core diameter, $b = 1.72a$ is the soft core diameter, and $c = 3a$ is the long distance cutoff. In the simulation, we use a as the unit of length, and U_0 as the unit of energy.

strong behaviour at low T [5, 6, 8, 11–13] in the deep supercooled region of the phase diagram below the homogeneous nucleation line. This region, called the 'no-man's land', may contain an LL critical point [3], the terminal point of a line of first-order LL phase transitions. One current hypothesis concerns the possibility that water's anomalies are related to the existence of this LL critical point and its associated LL phase transition line [3, 7, 14, 15]. Thus far there has been no direct experimental proof of this hypothesis, but recent experiments in nanoscale hydrophilic pores [6] showing a line of sharp crossover in water diffusivity were interpreted in terms of the effects of the LL critical point. A dynamic crossover has also been associated with the LL phase transition in silicon and silica [16, 17]. The relation between the LL phase transition and dynamics properties may not be limited to tetrahedral liquids, but may be a general feature of all liquids near the LL critical point. Here we review the results of [7] on the Jagla model of a liquid which models intermolecular interactions using a spherically symmetric soft-core potential. We also study phase segregation and dynamics below the LL critical point.

2. Two-scale spherically symmetric Jagla ramp potential

A spherically symmetric potential with two different length scales has been studied recently [7, 18–27]. Here, we study the linear ramp potential with both attractive and repulsive parts [20]. The potential is defined as

$$U(r) = \begin{cases} \infty & r < a \\ U_A + (U_A - U_R)(r - b)/(b - a) & a < r < b, \\ U_A(c - r)/(c - b) & b < r < c, \\ 0 & r > c \end{cases} \quad (1)$$

where $U_R = 3.5U_0$ is the repulsive energy, $U_A = -U_0$ is the attractive part, a is the hard core diameter, $b = 1.72a$ is the well minimum, and $c = 3a$ is the cutoff at large distance (figure 1).

We approximate the potential of equation (1) by a step function with small steps $\Delta U = U_0/8$ and implement the standard discrete molecular dynamics algorithm for particles interacting with step potentials [22, 28, 29]. We use a as the unit of length, particle mass m as the unit of mass and U_0 as the unit of energy. The simulation time is therefore measured in units of $a\sqrt{m/U_0}$, temperature in units of U_0/k_B, pressure in units of U_0/a^3 and density ρ in units of Na^3/L^3, where L is the size of the system and $N = 1728$ is the number of particles.
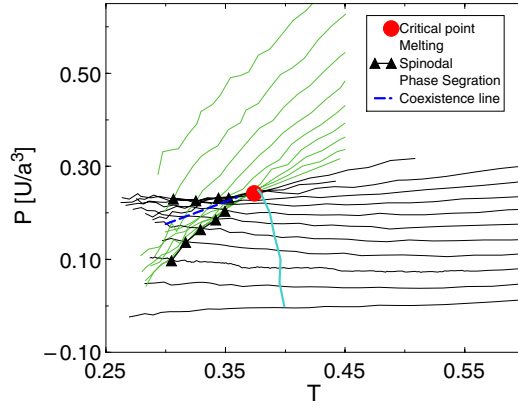
Figure 2. The equation of state $P(T, \rho)$ for the ramp potential in the vicinity of the LL phase transition. Lines indicate 21 different $P(T)$ isochores with densities $\rho = Na^3/L^3$, where $L = 15.0a, 15.2a, 15.4a, \ldots, 19.0a$ from top to bottom, with the number of particles $N = 1728$. The LL critical point (closed circle) is located at $P = 0.243$, and $T = 0.375$, corresponding to the point at the highest temperature isochore crossing.
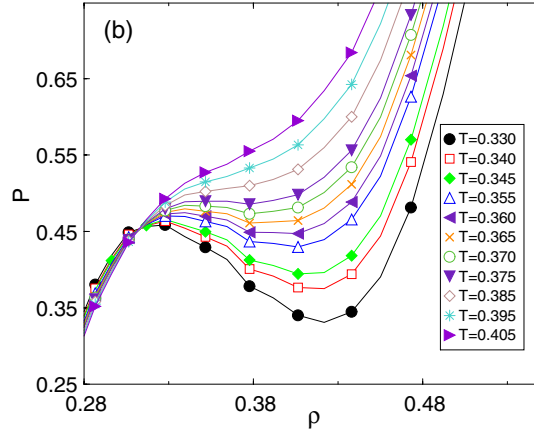
Figure 3. The van der Waals equation of state of the Jagla potential. The positively sloped LL coexistence line is obtained by the Maxwell rule construction of the van der Waals equation of state.

We use the Berendsen thermostat and barostat for constant temperature and constant pressure simulations [30].

3. Results

The equation of state of the Jagla model (figure 2) is obtained by using constant volume and constant temperature simulations (NVT-ensemble). The model displays a LL critical point located at $P_c = 0.243 \pm 0.003$, $T_c = 0.375 \pm 0.002$, and $\rho_c = 0.37 \pm 0.01$. We determine the LL coexistence line by Maxwell construction on the isotherms (figure 3). The coexistence line has a positive slope of $0.96 \pm 0.02 \, k_B a^{-3}$. According to the Clapeyron equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}, \tag{2}$$

hence the entropy in the HDL phase is lower than the entropy in the LDL phase. Thus the
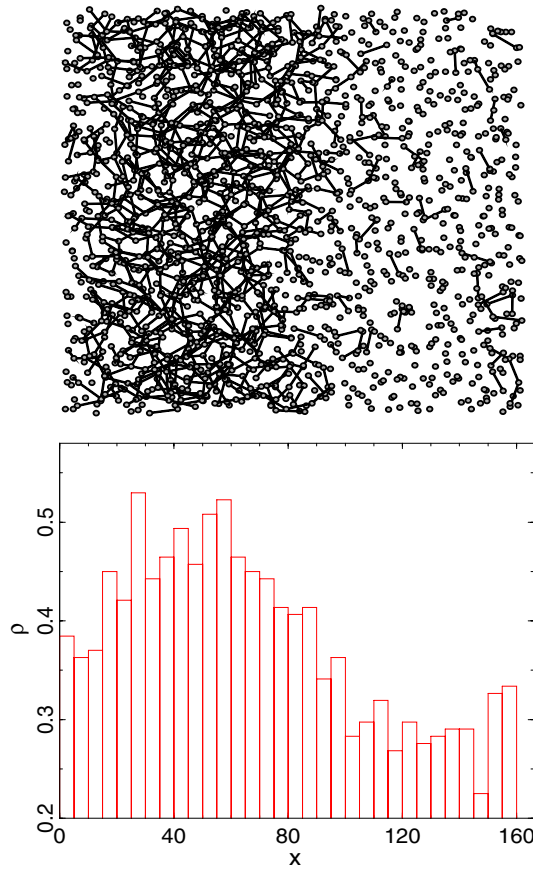
Figure 4. Phase segregation for a system with $L = 16.6$ at $T = 0.285$. In the top panel, we present bonds between particles within a distance $d < 1.2$, indicating that the left side is the HDL phase and the right side corresponds to the LDL phase. The bottom panel is the histogram of densities along the horizontal direction, with a high density on the left and lower density on the right.

HDL phase is more ordered than the LDL phase, which is opposite to the LL transition found in simulations for water [4] and silicon [16]. The position of the melting line is estimated as the temperature at which the solid–liquid first-order phase transition occurs upon gradually heating a system initially consisting of a crystal configuration obtained by spontaneous crystallization at low temperature. The equilibrium melting line is about 15% below the upper limit melting temperatures [31, 32]. Very recently, it has been suggested that by shrinking the attractive and repulsive ramp parameters of the Jagla model it is possible to change the sign of the slope of the LL coexistence line as well as to move the position of the critical point into the supercooled region as in water [25]. The stability limits are defined by the HDL and low LDL spinodal lines at which

$$(\partial P / \partial \rho)_T = 0. \tag{3}$$

We examine the LL phase segregation along each isochore as we cool the system down in the two-phase region. We did not observe any signs of the phase segregation at temperatures higher than the spinodal temperature for a given density. In figure 2, the isochores terminate at points where the phase segregation is clearly visible (figure 4). We show the structure of the
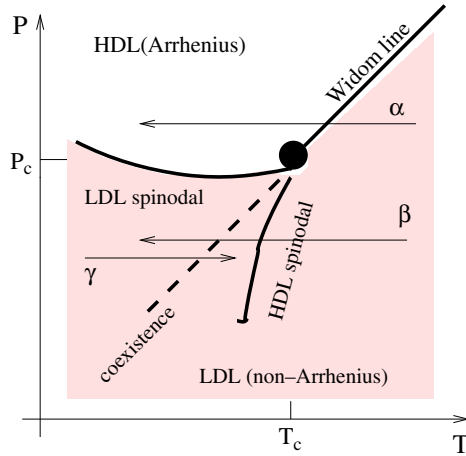
Figure 5. A sketch of the P–T phase diagram for the two-scale Jagla model. Upon cooling along path β, the liquid can remain in the LDL phase (non-Arrhenius) before crossing the LDL stability limit (LDL spinodal line). Upon heating along path γ, the liquid may remain in the HDL phase up to the HDL spinodal line. Thus one does not expect any dramatic change in the dynamic behaviour along the path β and γ in this case. Upon cooling at constant pressure above the critical point (path α), a dynamic crossover occurs from LDL-like behaviour at the high-temperature side to HDL-like behaviour at the low-temperature side upon crossing the Widom line [7].

$N = 1728$ system upon phase segregation, for $L = 16.6a$ at $T = 0.285$. The liquid separates into two types of liquids—HDL and LDL—with a clear phase boundary. The density of each phase is consistent with the density at the coexistent line. We present a clear visualization of the phase boundary by displaying the bonds between particles within the range $d < 1.2a$. In the LDL phase, there are practically no such particles, while in the HDL phase any particle has at least one neighbour within this range. This can be reflected in the high peak in the radial distribution function of the HDL phase.

We also study the diffusivity D:

$$D \equiv \lim_{t \to \infty} \frac{\langle [\mathbf{r}(t' + t) - \mathbf{r}(t')]^2 \rangle_{t'}}{6t}, \tag{4}$$

where $\langle \cdots \rangle_{t'}$ denotes an average over all particles and over all t' along constant pressure paths in three different regions: (i) $P = 0.250$ path α above the critical point in the one-phase region (figure 5), (ii) $P = 0.225$ path β (figure 5), below the critical point in the LDL phase, and (iii) $P = 0.225$ path γ, in the HDL phase (figure 5).

Below the LL critical point along path γ, the diffusivity D exhibits a temperature behaviour different from the behaviour in the LDL phase along path β. The behaviour of the diffusion constant and relaxation time in the HDL phase follows an approximately Arrhenius law, while in the LDL phase the slope of the Arrhenius fit increases upon cooling. As we cool along path β, we can achieve very low temperatures without phase segregation so that we can measure the dynamic properties of the LDL in a metastable region below the coexistence line (figure 6(a)).

On the other hand, by heating the HDL phase along path γ, we can reach the stability limit of the HDL denoted by the HDL spinodal line. As we cross the HDL spinodal at constant pressure, the density abruptly increases and the diffusivity of the system becomes equal to that of the LDL (figure 6(a)). In contrast, along path α in the one-phase region above the LL critical point, D exhibits a dynamic crossover from LDL-like behaviour on the high-temperature side of
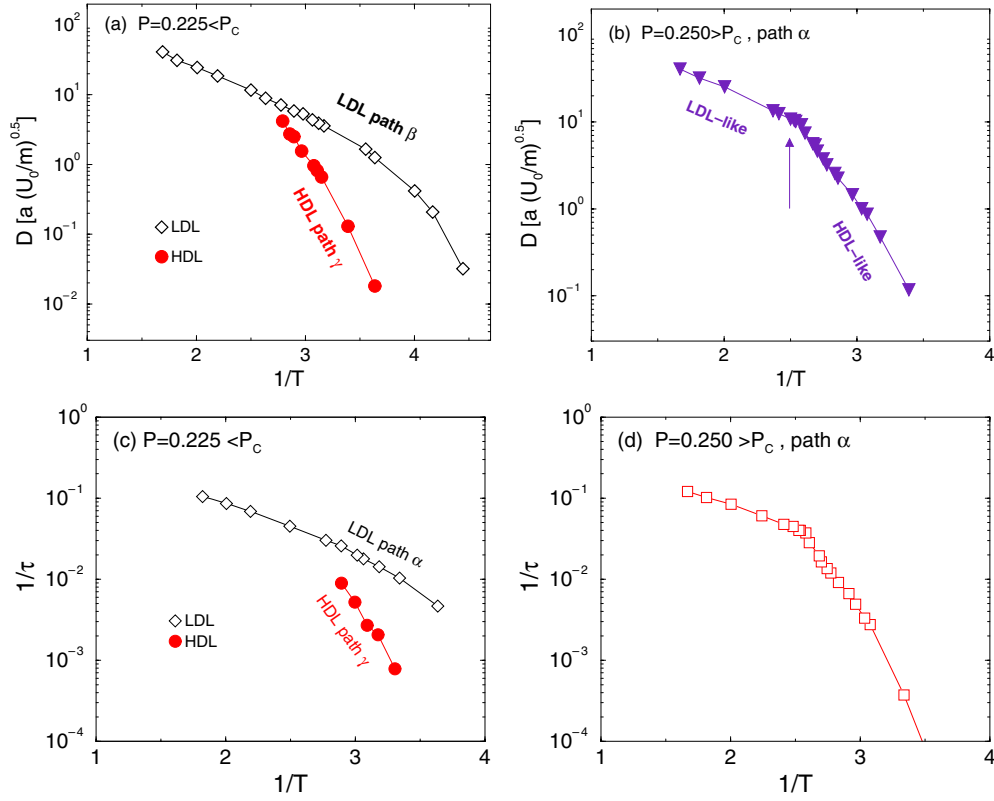
Figure 6. Dynamic behaviour for Jagla potential. The T-dependence of diffusivity along constant pressure paths. (a) Path β with $P = 0.225 < P_c$ (open diamonds), and path γ with $P = 0.225 < P_c$ (closed circles). D in the HDL phase differs from its behaviour in the LDL phase. (b) Path α with $0.250 > P_c$. A dynamic crossover occurs when the Widom line is crossed upon cooling [7]. (c) Relaxation time τ as a function of $1/T$ for $P = 0.225$. Similar to D, the relaxation time τ in the HDL (path γ) differs from τ in the LDL (path β). (d) Relaxation time τ along path α with $P = 0.250$. A dynamic crossover, as found in D, occurs as the system changes from 'LDL-like' behaviour to 'HDL-like' behaviour.

the Widom line to HDL-like behaviour on the low-temperature side (figure 6(b)). This dynamic crossover is an indication of crossing the Widom line above the LL critical point [7].

We also present results for the relaxation time τ along different paths, where τ is defined as the time when the intermediate scattering function decays by a factor of e for a certain q (the first peak of the static structure factor) [33]. Along path γ with $P = 0.225$ (figure 6(c)), τ differs from its behaviour in the LDL phase along path β. Above the LL critical point, along path α with $P = 0.250$, we find that τ displays a crossover from LDL-like behaviour on the high-temperature side to HDL-like behaviour on the low-temperature side (figure 6(d)), which is similar to the crossover found in D (figure 6(b)).

4. Summary

In summary, we study a simple spherically symmetric two-scale Jagla potential with both repulsive and attractive parts. The system displays an LL phase transition well above the equilibrium melting line. The phase segregation shows direct evidence of the coexistence of

two metastable states—HDL phase and LDL phase. The dynamic behaviours in the LDL and HDL phases are different from each other below the critical pressure, and change from LDL-like behaviour to HDL-like behaviour upon cooling above the critical pressure, suggesting the association of the changes in dynamic behaviour with the LL critical point similar to the changes observed in water in nanopores [6].

Acknowledgments

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