Confinement effects on the liquid-liquid phase transition and anomalous properties of a monatomic water-like liquid

Gang Sun, Nicolas Giovambattista, and Limei Xu

Citation: The Journal of Chemical Physics 143, 244503 (2015); doi: 10.1063/1.4937486
View online: http://dx.doi.org/10.1063/1.4937486
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/143/24?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Effects of confinement on anomalies and phase transitions of core-softened fluids

The putative liquid-liquid transition is a liquid-solid transition in atomistic models of water

Core-softened fluids, water-like anomalies, and the liquid-liquid critical points

Theoretical evidence for a first-order liquid-liquid phase transition in gallium

Effect of confinement on the liquid-liquid phase transition of supercooled water
Confinement effects on the liquid-liquid phase transition and anomalous properties of a monatomic water-like liquid

Gang Sun, Nicolas Giovambattista and Limei Xu
International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, China
Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210, USA
Ph.D. Programs in Chemistry and Physics, The Graduate Center of the City University of New York, New York, New York 10016, USA
Collaborative Innovation Center of Quantum Matter, Beijing, China

(Received 29 September 2015; accepted 27 November 2015; published online 24 December 2015)

We use molecular dynamics simulations to study the effects of confinement on the phase behavior of a water-like monatomic liquid that exhibits a liquid-liquid phase transition (LLPT) and a liquid-liquid critical point (LLCP). The liquid is confined between parallel walls and we focus on the effects of wall separation and surface chemistry (solvophobicity/solvophilicity) on the location of the LLCP, temperature of maximum density (TMD) line, and loci of compressibility maxima (CM). It is found that, independently of the surface solvophobicity/solvophilicity, the LLCP, TMD, and CM lines shift rapidly towards higher pressures and lower temperatures as the wall separation is reduced. It follows that the effects of confinement on the TMD and CM lines are indicative of the confinement effects on the LLPT. Confinement effects are observable already when the liquid particles form ≈15 layers between the walls. For the case of water, this corresponds to a separation of ≈4–5 nm between the surfaces, larger than the confining dimension of the nanopores commonly used to study the hypothesized LLPT in confined water. Hence, our results suggest that such experiments should not be interpreted in terms of the phase diagrams proposed for bulk water.

© 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4937486]

I. INTRODUCTION

Water is a polyamorphic substance with at least two glass or amorphous solid states.1–5 Experiments indicate that these amorphous solids, if heated at appropriate pressure and heating rate, can transform into two different liquids, low-density liquid (LDL) and high-density liquid (HDL).6–12 A scenario that explains the liquid and glass polymorphisms in water as well as many of water anomalous properties is the liquid-liquid phase transition (LLPT) hypothesis,13,14 where LDL and HDL are considered to be two different liquid phases separated by a first-order phase transition line. In this view, the LLPT line ends at a liquid-liquid critical point (LLCP), which is regarded as the source of many of water anomalous properties.13 The LLPT scenario for water has been extended to explain the (anomalous) behavior of other substances, such as phosphorous and metallic glasses.15–17 Alternative scenarios to explain water’s complex behavior, which do not assume the presence of a LLPT, are also available (see, e.g., Refs. 18 and 19).

Scientists have been searching for the LLCP in supercooled water for more than 20 yr. Yet, the experimental confirmation of such a LLCP in real water has been elusive due to unavoidable crystallization.20 This led experimentalists to explore alternative approaches which could suppress water crystallization while preserving the phase behavior of water in the liquid state. Among these methodologies are the study of emulsified water in the supercooled liquid and amorphous ice21 and the study of nanoconfined water (see, e.g., Refs. 22–25). In the first case, water is confined in droplets of ≈1–10 μm in size.21,26 Remarkably, the phase diagram of water in the supercooled liquid and glassy state remains practically unaltered by the addition of the emulsifier,26 while the crystallization temperature is shifted to lower temperatures. In the case of nanoconfined systems, water is usually confined in cylindrical pores of ≈1.5–2 nm in diameter.22,24,27–30 In these severely confined systems, it is unclear whether water retains the properties of bulk water (see, e.g., Refs. 31–33).

One would expect that surface chemistry and confinement geometry may affect, to some degree, the behavior of water under nanoscale confinement.31 Nonetheless, it is not evident to what extent surface chemistry and confinement geometry may affect the phase behavior of liquid water and particularly, how confinement may alter the location in the P-T plane of the hypothesized LLPT line and LLCP (see, e.g., Refs. 32 and 33). Experiments in triphenyl phosphate indicate that LLPTs can indeed be altered by confinement.34 Computational studies of water confined in nanoscale hydrophobic slits with separation of 1.1 nm indicate that confinement suppresses the LLCP and LLPT.35,36 Similar results have been obtained in other hydrophobic environments.37 Computational studies of water confined in hydrophilic pores show diverse results. For example, mW water shows no LLCP,38 while the simulations of Ref. 39 using the ST2 water model suggest that the LLCP temperature and pressure shift to higher values upon hydrophilic confinement.

Most computational studies are limited to a few confining dimensions and one type of confining surface (solvophobic...
or solvophilic). Moreover, in many of such studies, the water model employed does not exhibit an accessible LLCP in the bulk. All these limitations make it difficult to determine how the hypothesized LLCP (and LLPT) of water, if it can be accessed experimentally, should be affected by confinement. As far as we know, a LLCP in computer simulations of confined water has not been observed and its existence has only been inferred, e.g., by detecting a LLPT at fixed pressure or by extrapolations of isochores in the P-T plane to low temperatures. In some cases, confinement effects on the LLPT/LLCP have been inferred based on the effects of confinement on the liquid anomalous properties, such as the temperature of maximum density (TMD) line.36,38

In this work, we perform molecular dynamics (MD) simulations of a monatomic liquid with isotropic pair interactions confined between two parallel surfaces. The liquid exhibits a LLCP in bulk conditions, allowing us to track its location in the P-T plane as function of the confining dimension and surface chemistry (solvophobic/solvophilicity). In addition, we are able to identify the critical confining dimension below which the LLPT phenomenology is affected and the effects of confinement on the liquid anomalous properties, such as the TMD line.

II. SIMULATION DETAILS

Our system consists of $N$ particles confined between two amorphous confining surfaces. The same model system was used in Ref. 40 to study the effects of confinement on crystallization and computer simulation details can be found in that work. Briefly, particles in the liquid interact with the Fermi-Jagla (FJ) potential,41 a smooth version of the extensively studied Jagla pair potential that was originally proposed to model the properties of water and silica.42–48 The Fermi-Jagla potential is defined by

$$U(r) = \epsilon_0 \left[ \frac{1}{r^n} + \frac{A_0}{1 + \exp\left(\frac{A_2}{A_0}(r/a - A_2)\right)} - \frac{B_0}{1 + \exp\left(B_1/B_0(r/a - B_2)\right)} \right],$$

where $A_i$ and $B_i$ ($i = 0, 1, 2$) are parameters provided in Table I. As shown in Fig. 1(a), the FJ potential is a spherically symmetric pair potential that exhibits both a repulsive and an attractive hard-core with radius $a$ of the FJ particles, and a core-softened part that extends approximately over distances $a < r < b \approx 2a$. Relevant to this work is the fact that the FJ liquid exhibits accessible LLPT and LLCP41 as well as two glass states.49,50 In particular, the phase behavior of this model system in the glass and liquid states is remarkably similar to the phase behavior of ST2 water13,51,52 and hence, its behavior is in agreement with the LLPT hypothesis proposed for the case of water.13,14

As explained in Ref. 40, the surfaces are composed of immobile particles and the interactions between surface and liquid particles are represented by a Lennard-Jones pair potential with energy parameter $\epsilon$ and distance parameter $\sigma$.

While $\sigma = 1$ for all surfaces considered (i.e., equal to the hard-core radius $a$ of the FJ particles), the parameter $\epsilon$ is tuned in order to model surfaces with different chemistries, from solvophobic to solvophilic. The degree of solvophobicity of these surfaces is quantified by the contact angle of the FJ liquid, $\theta(\epsilon)$. Surfaces are solvophobic for $\theta(\epsilon) > 90^\circ$ and solvophilic for $\theta(\epsilon) < 90^\circ$. Fig. 1(b) indicates that for $\epsilon = 0.1$, the surface is solvophobic ($\theta \approx 150^\circ$), while for $\epsilon = 0.8$, the surface is solvophilic ($\theta \approx 0^\circ$). For $\epsilon = 0.2$, $\theta \approx 90^\circ$, hence, this surface has neutral solvophobicity/solvophilicity. Most of the results in this work are obtained for the cases $\epsilon = 0.1$ (solvophobic), 0.2 (neutral), and 0.8 (solvophilic).

The confining surfaces expand across the system and are oriented perpendicularly to the x-axis. Periodic boundary conditions are applied along the $y$ and $z$ directions. Simulations are performed at different surface separations $d_0 (= 8a, 10a, 15a, 20a)$, where $a$ is the hard core radius of the particles with mass $m$.41 The surfaces have an area $A = L_y \times L_z$, where $L_y = L_z = 20a$. For given $d_0$ and

<table>
<thead>
<tr>
<th>$n$</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$B_0$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.56</td>
<td>0.72</td>
<td>1.36</td>
<td>1.00</td>
<td>0.28</td>
<td>2.36</td>
</tr>
</tbody>
</table>

TABLE I. Parameters for the Fermi-Jagla pair interaction potential defined in Eq. (1).

FIG. 1. (a) Fermi-Jagla pair potential interaction.41 This potential is characterized by a hard-core with radius $r = a$, a core-softened part at approximately $a < r < b \approx 2a$, and a weak attractive part of depth $\epsilon_0$. (b) Contact angle of the FJ liquid, $\theta(\epsilon)$, for amorphous surfaces of interaction strength $\epsilon$. Surfaces are solvophobic (i.e., $\theta(\epsilon) > 90^\circ$) for approximately $\epsilon \leq 0.2$. Snapshots from simulations are included for specific values of $\epsilon$. 

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to  IP: 162.105.145.47 On: Fri, 25 Dec 2015 00:46:25
surface chemistry $\epsilon$, we perform MD simulations at different temperatures and for different number of particles in the range $N = 800–3500$, allowing us to construct complete phase diagrams for different surface separations and surface chemistry. Each simulation lasts for at least $1.0 \times 10^7$ time steps, starting from an equilibrated high-temperature liquid configuration. The mean-square displacement obtained at a given temperature $T$ indicates that particles diffuse for at least 2–3 particle diameters, suggesting that simulations are sufficiently long to reach equilibrium. The simulation time step is $dt = 0.001$ and a cutoff distance $r_c = 4.0$ is used in the calculation of the pair interactions. Units of energies and temperatures are $e_0$ and $e_0/k_B$, respectively, where $k_B$ is the Boltzmann constant. Time is given in unit of $a(m/e_0)^{1/2}$ and density unit is $m/a^3$. The temperature is controlled by rescaling the velocities of liquid particles, as explained in Ref. 40. The pressure parallel to the surfaces is calculated using the Virial expression applied to the $y$- and $z$-axes. The pressure perpendicular to the surfaces is obtained by calculating the net force along the $x$-axis (per unit area) acting on the walls. For liquids confined in slab geometry, it can be shown that it is the pressure parallel to the surfaces and not the pressure perpendicular to the surfaces, which plays the role of the isotropic pressure in bulk liquids. Thus, in this work, $P$ refers to the pressure parallel to the surfaces.

### III. RESULTS

The main effects of surface solvophobicity/solvophilicity and confinement on the LLCP and compressibility maximum (CM) lines are summarized in Fig. 2. Figs. 2(a)–2(c) show the location of the LLCP and CM lines in the P-T plane for liquid-wall interaction strengths $\epsilon = 0.1$ (solvophobic), $\epsilon = 0.2$ (neutral), and $0.8$ (solvophilic), and for different surface separations. The main point of Fig. 2 is that independently of the surface solvophobicity/solvophilicity, confinement shifts the LLCP and CM lines to higher pressures and lower temperatures as the separation between two surfaces decreases, consistent with previous reports (see, e.g., Refs. 54, 56, and 57). In particular, the LLCP pressure and temperature are very sensitive to the confining dimension, $d_0$. We note that only separations in the range $d_0 = 10–20$ are included in Fig. 2 since, for $d_0 < 10$, the LLCP becomes inaccessible due to rapid crystallization and, for $d_0 > 20$, the LLCP coordinates are very close to the critical pressure and temperature reported previously for the bulk FJ liquid, $T_c \approx 0.18$ and $P_c \approx 0.35$ [see, e.g., Fig. 2(b)]. Thus, for roughly $d_0 > 20$, confinement effects on the LLCP and CM lines become less obvious. The effects of surface chemistry on the location of the LLCP are shown in Fig. 3. Interestingly, it is found that for fixed surface separations, both $T_c$ and $P_c$ decrease as the surface becomes more solvophobic ($\epsilon$ decreases).

The LLCPs shown in Figs. 2(a)–2(c) are obtained from the $P - V$ isotherms. Accordingly, the condition of stability for the confined liquid is $(\partial P(V)/\partial V)_{A,d_0,T} < 0$. It follows that the LLCP coordinates, for a fixed separation $d_0$, are defined by the $(T, P, V)$ values at which $P(V)$ exhibits an inflection point. As an example of the behavior of $P(V)$ with $T$ and $d_0$, we show the $P - V$ isotherms for $\epsilon = 0.2$ in Fig. 4. There is no inflection point in $P(V)$ for the case $d_0 = 8$ [Fig. 4(a)], and such an inflection point (and hence, a LLCP) can only be identified for $d_0 > 8$ [Figs. 4(b)–4(d)]. Along isothermal lines below the LLCP, one can see that there is a range of volumes for which $(\partial P(V)/\partial V)_{A,d_0,T} > 0$ [Figs. 4(b)–4(d)], i.e., the liquid is unstable and the system phase separates into two liquids.

Also included in Figs. 2(a)–2(c) is the CM line. This line indicates the pressure at which the isothermal compressibility,
Isothermal compressibility

Isotherms in the P-V plane for the FJ liquid confined between neutral and convergent surfaces converge to the LLCP temperature and pressure of the bulk FJ liquid, \( P_{\text{C}}(b) \). Pressure is approached and diverge at the LLCP. The isothermal compressibility should increase as the LLCP temperature (see Fig. 5). If the liquid indeed exhibits a LLCP, the liquid-surface interaction strength \( \epsilon \) at different temperatures and pressures define the compressibility maxima shown in Fig. 2(b).

\[
\kappa_T(P) = -V^{-1}(\partial V/\partial P)_{\epsilon, d_0, T},
\]

reaches a maximum at a given temperature (see Fig. 5). If the liquid indeed exhibits a LLCP, the isothermal compressibility should increase as the LLCP is approached and diverge at the LLCP.\(^{44}\) Figs. 5(a)-5(d) show that this is indeed the case for the surfaces characterized by \( \epsilon = 0.2 \) (similar results hold for other values of \( \epsilon \)). That is, for all separations, the peak in \( \kappa_T(P) \) becomes sharper as the temperature decreases and the LLCP is approached. Thermodynamics requires that the CM line ends at the LLCP and this is fully consistent with Figs. 2(a)-2(c). In particular, the CM line moves to lower temperatures and higher pressures as \( d_0 \) decreases, independently of the surface solvophobicity/solvophilicity, as is the case of the LLCP location. We also include \( \kappa_T(P) \) for \( d_0 = 8 \) in Fig. 5(a). Interestingly, even when the LLCP is inaccessible at this wall separation, one can still observe that the peak in \( \kappa_T(P) \) increases upon cooling, indicating that the location of the LLCP in the \( P - T \) plane has moved below the crystallization temperature.

It has been shown that the TMD line of water confined by either hydrophobic or hydrophilic surfaces shifts to lower temperatures compared to bulk water.\(^{36,56,58-62}\) This observation, together with the absence of the LLCP, has been used to support the view that hydrophobic and hydrophilic confinements shift the LLCP to low temperatures.\(^{54,56,59,63}\) In agreement with these works, our simulations show that for severe confinement, i.e., \( d_0 = 8a \), the TMD line shifts to lower temperatures [Figs. 6(a)-6(c)]. For such severe confinements, the changes in the TMD line are indeed indicative of the effect that confinement and surface chemistry have on the LLCP and LLPT. However, the TMD line shifts monotonically to lower temperatures, as \( d_0 \) decreases, only for solvophobic [\( \epsilon = 0.1 \); Fig. 6(a)] and neutral [\( \epsilon = 0.2 \); Fig. 6(b)] surfaces. In the case of solvophilic surfaces [\( \epsilon = 0.8 \); Fig. 6(c)], as \( d_0 \) decreases, the TMD line is first (\( d_0 > 10 \)) shifted toward higher temperatures and then (\( d_0 < 10 \)) to lower temperatures. Thus, in the case of the FJ liquids, we find that, for all surface chemistry considered, reducing \( d_0 \) shifts the TMD line monotonically to higher pressures compared to those of bulk liquids. We also point out that, for a fixed surface separation \( d_0 \), as the surface becomes more solvophilic (e.g., \( \epsilon \) varies from 0.1 to 0.8), the TMD line shifts monotonically to higher temperatures, with only a weak shift in pressure; see Fig. 7.
FIG. 6. Effects of confinement and surface chemistry on the TMD line for the case of FJ liquids confined between (a) solvophobic ($\epsilon = 0.1$), (b) neutral ($\epsilon = 0.2$), and (c) solvophilic surfaces ($\epsilon = 0.8$). In all cases, the TMD line shifts to higher pressures and lower temperatures as $d_0 \to 8$ (i.e., severe confinement).

For hydrophobic confinement, the TMD lines shift to lower temperature compared to that of bulk liquids, consistent with that reported in Ref. 56. We find that in the case of the FJ liquid, independently of the surface solvophobicity/solvophilicity, the TMD lines move to lower temperatures and higher pressures as the surfaces separation decreases, which is consistent with the experiments (see, e.g., Refs. 59 and 60). Instead, we note that for the hydrophilic particle-surface interaction potentials in the work of Krott et al., the TMD lines are shifted to higher temperatures, compared with the bulk values.

IV. SUMMARY AND DISCUSSION

In this work, we studied the LLPT of the FJ liquid confined between two parallel amorphous surfaces with surface chemistry ranging from solvophobic to solvophilic. We found that independently of the surface chemistry, decreasing the surfaces separation shifts the LLCP/LLPT, CM, and TMD lines to lower temperatures and higher pressures, relative to the case of bulk water. Surprisingly, confinement effects become relevant already at $d_0 \approx 15-20a$ ($d_0 \sim 20a$ corresponds to 15 layers of liquid particles between the surfaces) and the LLCP disappears for surface separations $d_0 \leq 8a$ (corresponding to 5 layers of liquid particles between the surfaces). To get an estimation of what these surface separations ($d_0 = 8a$ and $20a$) correspond to the case of water, we follow Ref. 64 and identify the radius of the FJ particle, $a$, with the typical oxygen-oxygen distance of nearest-neighbor water molecules, $\approx 0.27$ nm. This implies that for water, confinement effects should become relevant for confining dimensions smaller than $\approx 5.4$ nm; the LLCP should disappear for confining dimensions below $\approx 2.2$ nm. We note that 5.4 nm is larger than the confining dimensions of the nanopores commonly used experimentally to study nanoconfined water (the pore diameters are typically in the range 1.4–2 nm). Although such experiments employed cylindrical pores, while we consider a slab geometry, the present results suggest that the phase behavior of nanoconfined water cannot be directly mapped to that of bulk water. Our results suggest that the phase diagram of confined water may correspond to the phase behavior of bulk water shifted to higher pressures and lower temperatures.

Our results also indicate that confinement effects on the location of the CM and TMD lines of a polymorphic liquid mimic the confinement effects on the location of the LLPT/LLCP. In other words, independently of the surface chemistry, decreasing the surfaces separation shifts the LLCP/LLPT, CM, and TMD lines to lower temperatures and higher pressures, relative to the case of bulk water. Therefore, one can estimate how severe confinement shifts the location of the LLCP by studying how confinement shifts the CM and TMD lines, which may be more accessible experimentally. We note that confinement is not the only way to shift the LLCP and TMD lines. The LLCP and TMD lines in aqueous solution have been found to move to higher temperatures...
and lower pressures (see Refs. 65 and 66), opposite to that of confinement. Thus, the aqueous solutions also provide the possibility to detect the hypothesized LLCP of water in experiments.

Finally, we point out that our work considers only amorphous surfaces. As shown in Ref. 40, employing structureless confining surfaces favors the crystallization of the confined liquid. Indeed, we performed similar MD simulations to those reported in this work using the structureless surfaces employed in Ref. 40 (in this case, the surface interacts with the liquid particles via a 9-3 Lennard-Jones potential). We found that the LLCP/LLPT in these systems becomes inaccessible due to crystallization, which is different from that reported in Ref. 56. It was previously stated that the attractive surfaces induce crystallization more easily than the repulsive surfaces. The interaction between particles and surfaces is attractive in our case, while it is repulsive in Ref. 56. Thus, we believe such difference is mainly due to the different interactions between liquid particles and surfaces.

Acknowledgments

We thank the National Science Foundation of China (Grant Nos. 11174006, 11290162, and 11525520) and MOST (Grant Nos. 2012CB921404 and 2015CB856801) for financial supports. The work was supported by the National Supercomputer Center in Tianjin, China.