Supercooled fluid-fluid phase transition in three dimensions from a soft-core potential

G. Franzese\textsuperscript{1}, G. Malescio\textsuperscript{2}, A. Skibinsky\textsuperscript{1}, S. V. Buldyrev\textsuperscript{1}, and H. E. Stanley\textsuperscript{1}

\textsuperscript{1}Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215, USA

\textsuperscript{2}Dipartimento di Fisica, Università di Messina and Istituto Nazionale Fisica della Materia, 98166 Messina, Italy

(November 21, 2018)

Abstract

To study the possibility of a fluid-fluid phase transition, we analyze a three-dimensional soft-core isotropic potential for a one-component system. We utilize two independent numerical approaches, (i) integral equation in the hypernetted-chain approximation and (ii) molecular dynamics simulations, and find for both approaches a fluid-fluid phase transition as well as the conventional gas-liquid critical point. We also study the possible existence of a triple point in the supercooled fluid phase at which three phases—gas, high-density fluid, and low-density fluid—coexist.

PACS numbers: 61.20.Gy, 61.25.Em, 65.70.+y, 64.70.Ja
Recent experiments on phosphorus [1] show that a fluid-fluid phase transition is present at a temperature above the gas-liquid critical temperature. The transition is between two stable fluids at different densities. This sort of transition between low-density (LD) and high-density (HD) fluids has been proposed for many different materials, including supercooled H$_2$O, Al$_2$O$_3$-Y$_2$O$_3$, SiO$_2$, GeO$_2$, C, S, Ga, Se, Te, I$_2$, Cs, Bi and Si [2]. Experimental and theoretical studies support this hypothesis, and some suggest (e.g. for H$_2$O and C) the presence of a fluid-fluid critical point (CP) [1,3–7].

Theoretical and numerical studies take into account, as accurately as possible, the anisotropies of the molecular interactions, depending on the relative molecular orientations [2]. An alternative approach to the problem consists of investigating simple isotropic potentials which might be able to give rise to the LD-HD fluid transition. This makes it possible to find out which are the ingredients of the inter-particle interaction related to LD-HD fluid transition.

Here we study an isotropic potential in three dimensions (3D) using two methods: (i) integral equations in the hypernetted-chain (HNC) approximation and (ii) molecular dynamics (MD) simulations. These approaches agree qualitatively, showing a phase diagram with a gas-liquid CP and a LD-HD fluid transition with a second CP. The results suggest the presence of a gas-LD-HD triple point. The MD simulations reveal that both transitions are in the supercooled fluid phase, i.e. where the fluid phase is metastable with respect to the solid.

Stell and Hemmer [8] proposed the possibility that an isotropic potential with a region of negative curvature in the repulsive core (“core-softened potential”) might have two transitions. Recently it was shown, using analytic solutions in 1D and MD in 2D, that a Stell-Hemmer type of interaction gives rise to water-like fluid anomalies that can be related to the existence of two different local structures in the fluid phase [9]. Furthermore, the behavior of spherical particles, interacting in 3D through an isotropic potential with a hard-core and a linear repulsive shoulder, has been investigated through Monte Carlo. [10]. It was also shown that the addition of an infinite range van der Waals type attractive term
may give rise to a second CP. The attraction, however, was not explicitly included in the simulation and was taken into account in a mean field type scheme [10].

One feature of LD-HD transition is that there is a competition between an expanded structure and a compact structure. In water, for example, the former is due to hydrogen-bond formation and is preferred at low pressures and low temperatures, while the latter is favored at high pressures and high temperatures. This suggests a potential with two characteristic radii [3]. Here we consider a 3D potential (Fig. 1, inset) with a hard-core radius $a$ and a soft-core radius $b$. Depending on the value of pressure and temperature, the effective hard-core will be $a$ or $b$. The soft-core is given by a repulsive square shoulder with height $\lambda \epsilon$. The attractive part of the potential is given by a square well, with depth $\epsilon$ and an interaction cut-off at distance $c$. Choosing $a$ as length unit and $\epsilon$ as energy unit, the potential has three free parameters: $\lambda$ (we set $\epsilon = 1$) and ratios $b/a$, $c/a$. Their possible combinations are too many to be investigated directly by means of MD. Therefore, it is advisable to use a faster, way of estimating the phase diagram. In this way it is possible to have a first indication of the phase diagram dependence on the potential's parameters. This allows one to perform MD simulation in an systematic fashion.

Integral equations [11] for the radial distribution function may provide a convenient tool for estimating the phase stability of the fluid. In particular, the HNC equation [11] has often been used for relating phase diagrams and potentials [12]. For this theory there exists a region in the density-temperature ($\rho$-$T$) plane in which no solution can be found. When this region is approached from high temperatures, there is a strong increase of the isothermal compressibility $K_T$. Since there is no genuine divergence in $K_T$, this region cannot be identified in a rigorous way with the spinodal decomposition region of the fluid. However, for a large variety of potentials, its shape resembles qualitatively the fluid spinodal [12]. This allows us to have a first hint of the topology of the fluid instability region.

The instability line, below which no solution of the HNC can be found, is shown in Figs. 1, 2. For $b/a = 1.4$, $c/a = 1.7$ and $\lambda = -0.5$, the potential considered in Ref. [9], the shape of the instability line is similar to that of a standard gas-liquid spinodals and does not change
significantly by varying the value of $\lambda$. However, for other combinations of the parameters, the shape can change dramatically (Fig. 2). For example, for $b/a = 2$ and $c/a = 2.2$, we have a bifurcated instability line at intermediate values of $\lambda$. The HNC instability line is not a true spinodal, but its bifurcation, with two distinct maxima, supports the existence of two CPs \[13\]. Note that the bifurcation in the instability line disappears by increasing $\lambda$ (as shown in Fig. 2.A) or by changing only one of the other parameters. Therefore, the phase diagram depends drastically on the delicate interplay between the parameters.

Based on the HNC results, we performed extensive MD simulations for a system of particles interacting through the potential with $b/a = 2.0$, $c/a = 2.2$ and $\lambda = 0.5$ \[13\]. At high density the stable phase is solid, but the MD allows us to study the supercooled fluid phase before the crystallization occurs. The life-time of this metastable phase depends on $(\rho-T)$. To be sure that our estimates are done in the fluid phase, we study the structure factor $S(\vec{Q}, t) \equiv [\rho_{\vec{Q}}^*(t)\rho_{\vec{Q}}(t)]/N$ where $\rho_{\vec{Q}} \equiv \sum_j \exp(i\vec{Q} \cdot \vec{r}_j(t))$, $N$ is the number of particles, $\vec{Q}$ is the wave vector \[18\] and $\vec{r}_j(t)$ is the position of particle $j$ at time $t$. The growth of $S(\vec{Q}, t)$ for wave vectors with $Q \rightarrow 0$ indicates a phase separation. Furthermore, for finite $Q$, it marks the onset of the crystal phase. Our simulations show the occurrence of a phase separation without a crystal formation (time interval labeled with B in Fig. 3), followed by the onset of crystal phase (C in Fig. 3) marked by a dramatic increase of $S(\vec{Q}, t)$ for $Q \simeq 6$ and 12 (in $a^{-1}$ units) \[19\]. Our calculations are done in the (metastable) fluid phase before the crystallization.

The study of the static structure factor $S(Q) \equiv \langle S(Q, t) \rangle$, where $\langle \cdot \rangle$ is the average over $\vec{Q}$ vectors, and $[\cdot]$ is the average over a time interval, done on different time intervals (A, B and C in Fig. 3), confirms the previous analysis. To emphasize the phase separation occurring in the fluid phase, we show in Fig. 3 the snapshot corresponding to the larger peak in time-interval B in Fig. 3.a. The histograms of the number of particles in the system for the three planar projections of the snapshot show a clear separation in density. Therefore, the phase separation marked by the increasing of $S(Q)$ at low values of $Q$ is associated with the coexistence of LD and HD fluids.
The MD phase diagram is shown in Fig. 5. At low densities and high temperature, the system is in the gas phase. Increasing the density or decreasing the temperature, the system undergoes a first order gas-solid transition. In the supercooled fluid phase, we observe two regions with negatively-sloped isotherms. The first region is for temperatures $k_B T/\epsilon < 0.61$ in the low density regime. The second region is for temperatures $k_B T/\epsilon < 0.645$ in the high density regime. These regions correspond to thermodynamically unstable states and their borders are the spinodal lines. In the region of low density the coexisting fluids are the gas and the liquid. In the region of high density the analysis presented above allows one to conclude that the coexisting phases are a LD and a HD fluid. The points at highest pressure on the spinodal lines correspond to the CPs. In both HNC and MD approaches the merging of instability regions below the critical temperatures suggests the merging of coexisting lines, i.e. the existence of a gas-liquid-liquid triple point.

Within our precision we find that the gas-liquid critical point is at $k_B T_{c1}/\epsilon = 0.605 \pm 0.005$, $a^3 P_{c1}/\epsilon = 0.018 \pm 0.002$ and $a^3 \rho_{c1}/m = 0.115 \pm 0.015$ corresponding to a packing fraction $\eta_{c1} = 0.06 \pm 0.01$ ($\eta = \pi a^3 \rho / 6$). Note that $T_{c1}$ and $\rho_{c1}$ are in good agreement with the HNC results. The second instability region occurs at packing fraction $\eta > 0.08$, deep in the solid phase, where the metastable fluids phases have short lifetimes. Within our precision the critical temperature is $k_B T_{c2}/\epsilon = 0.650 \pm 0.005$, the critical pressure is $a^3 P_{c2}/\epsilon = 0.08 \pm 0.01$ and the critical packing fraction is $\eta_{c2} = 0.16 \pm 0.01$. Note that $T_{c2}$ is consistent with the HNC result, while $\rho_{c2}$ is smaller.

Since the MD calculations show that $T_{c2} > T_{c1}$, the above set of parameters is not able to reproduce a fluid-fluid critical point. Nevertheless the HNC analysis suggests that other sets of parameters can lead to $T_{c2} < T_{c1}$ as shown in Fig. 2.b. Preliminary calculation on a second set of parameters with $b/a = 2.2$, $c/a = 2.4$ and $\lambda = 0.5$ show that both CPs are lowered in temperature and pressure.

In conclusion, we studied an isotropic soft-core potential with a repulsive shoulder and an attractive well by means of integral equations in the hypernetted-chain approximation (HNC) and molecular dynamics (MD) simulations. Both approaches show, in the super-
cooled fluid phase, a gas-liquid critical point (at low density, low pressure, low temperature) and a transition (at high density, high pressure, high temperature) between a low-density (LD) and a high-density (HD) fluid with a second critical point. This second transition resembles the fluid-fluid transition discovered recently in experiments with phosphorus [1]. However, in phosphorus the fluid-fluid transition occurs between stable phases, while in our case it is in the supercooled phase as in H$_2$O. Furthermore, both numerical approaches used here suggest the existence of a gas-liquid-liquid triple point. Therefore, the potential proposed here, despite its simplicity, is able to reproduce many intriguing features of materials with a second fluid-fluid transition, leading to a new way to explore the existence of a second critical point.

We wish to thank P.V. Giaquinta, G. Pellicane, A. Scala, F. Sciortino, F. W. Starr, for helpful suggestions and for interesting and stimulating discussions. We thank NSF for support and CNR grant N.203.15.8/204.4607 (Italy) for partial support.
REFERENCES

[1] Y. Katayama et al., Nature 403, 170 (2000).

[2] P.G. Debenedetti, *Metastable Liquids: Concepts and Principles*, Princeton University Press, Princeton (1998).

[3] O. Mishima and H.E. Stanley, Nature 396, 329 (1998); *ibid.* 392, 164 (1998).

[4] M.-C. Bellissent-Funel, Europhys. Lett. 42, 161 (1998); S. Aasland and P.F. McMillan, Nature 369, 633 (1994).

[5] M. Togaya, Phys. Rev. Lett. 79, 2474 (1997).

[6] P.H. Poole et al. Nature 360, 324 (1992); Phys. Rev. Lett. 73, 1632 (1994); Science 275, 322 (1997); S. Harrington et al. Phys. Rev. Lett. 78, 2409 (1997).

[7] J.N. Ghosli and F.H. Ree, Phys. Rev. Lett. 82, 4659 (1999).

[8] P.C. Hemmer and G. Stell, Phys. Rev. Lett. 24, 1284 (1970); G. Stell and P.C. Hemmer, J. Chem. Phys. 56, 4274 (1972).

[9] M.R. Sadr-Lahijany et al. Phys. Rev. Lett. 81, 4895 (1998).

[10] E.A. Jagla, J. Chem. Phys. 111, 8980 (1999).

[11] J.P. Hansen and I.R. McDonald *Theory of simple liquids*, Academic Press London (1976).

[12] See C. Caccamo, Phys. Rep. 274, 1 (1996) and references therein.

[13] We observe that the overall shape of the bifurcated instability line is consistent with the phase diagram derived by Tejero and Baus [[14] within a van der Waals approach for an effective density-dependent potential.

[14] C.F. Tejero and M. Baus, Phys. Rev. E 57, 4821 (1998).

[15] The MD simulations are performed fixing the number of particles $N = 490$, the volume
\( V \) and the average temperature \( k_B T/\epsilon \) (\( k_B \) is the Boltzmann constant). We use a standard collision event list algorithm \([16]\) to evolve the system and a modified Berendsen method to achieve the desired temperature \([17]\). To study the equilibrium phase diagram for each \( V \) we equilibrate the system at low enough temperature (e.g. \( k_B T/\epsilon = 5 \) for \( a^3 \rho/m = 0.04 \) with \( m \) unitary mass) to form a crystal seed in the liquid phase. Starting from this configuration, we perform simulations at different \( T \) to see which phase prevails and to find the phase separation line. To study the (metastable) fluid phase at each \( V \) we quench the system starting from a high \( T \) configuration. We observe that, in the (\( \rho-T \)) region considered here, \( \Delta t = 2 \times 10^3 \) updating per particle (UPP) are enough on average to equilibrate the system toward a stable (metastable) state in the (supercooled) fluid phase. Therefore we discarded the first \( \Delta t \) UPP of any simulation and averaged each data point over at least \( 10^5 - 10^6 \) UPP.

[16] D.C. Rapaport, *The Art of Molecular Dynamics Simulation*, (Cambridge University Press, Cambridge, 1995).

[17] H.J.C. Berendsen et al., J. Chem. Phys. 81, 3684 (1984).

[18] We consider up to \( 9 \times 10^4 \) wave vectors \( \vec{Q} \) with \( |\vec{Q}| \leq 100 \ a^{-1} \).

[19] We tested that corresponding to the large increase in \( S(\vec{Q}, t) \), there is also a dramatic step-like decrease (increase) of energy (pressure).
FIGURES

FIG. 1. Instability line in ($\rho$-$T$) plane of the HNC equation for $b/a = 1.4$, $c/a = 1.7$ $\epsilon = 1$ and $\lambda$ given by the label of the curves. Inset: general form of the soft-core potential.

FIG. 2. As in Fig.1 with (A) $b/a = 2.0$, $c/a = 2.2$ and (B) $b/a = 2.5$, $c/a = 3.0$ and $\lambda$ given by the label of the curves.

FIG. 3. Structure factor versus time for (a) wave vectors with $Q \simeq 1$ and (b) $Q \simeq 12$ (in $a^{-1}$ units) at density $a^3\rho/m = 0.27$ and $k_BT/\epsilon = 0.62$ up to $3 \times 10^4$ UPP; (c) The static structure factor $S(Q)$ averaged over different time intervals: labels (A,B,C) stands for the time intervals shown in panels (a,b). For A (B) we averaged over a low (high) density fluctuation time interval; for C over an interval after the crystal seed formation. The curves for $S(Q)$ are shifted for the sake of comparison.

FIG. 4. Histograms of number of particles as function of one coordinate for the snapshot corresponding to the large value of $S(Q = 1, t)$ in time interval B of previous figure. The corresponding projections of the snapshot are also shown. Histogram and snapshots are shifted for the sake of clarity. The horizontal line shows the average density.

FIG. 5. Pressure-density isotherms from the MD simulation for the potential with $b/a = 2.0$, $c/a = 2.2$ and $\lambda = 0.5$. Full points represent stable fluid. Open points represent supercooled fluid. The inset emphasizes the instability region with negatively-sloped isotherms (and a van der Waals loops at $k_B T/\epsilon = 0.6$) associated with the gas-liquid CP. It is possible to see a high density region with the van der Waals loops associated with the second CP. The lines connecting the points are just guides for the eyes. Temperature is measured in $\epsilon/k_B$. 
