A system with multiple liquid–liquid critical points

Sergey V. Buldyrev*, H. Eugene Stanley

Department of Physics, Center for Polymer Studies, Boston University, Boston, MA 02215, USA

Abstract

We study a three-dimensional system of particles interacting via spherically symmetric pair potentials consisting of several discontinuous steps. We show that at certain values of the parameters describing the potential, the system has three first-order phase transitions between fluids of different densities ending in three critical points.
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Much attention has been focused on the topic of liquid–liquid phase transitions [1]. Recently, a liquid–liquid phase transition was found experimentally in phosphorus [2]. Liquid–liquid phase transitions also can exist in other materials with tetrahedral symmetry such as carbon [3,4], silica, [5] and silicon [6,7].

The possibility of a sharp amorphous–amorphous transition between low-density amorphous ice (LDA) and high-density amorphous ice (HDA) has been known for a long time [8]. Computer simulations of the ST2 water model [9] suggest that the transition line between LDA and HDA can be extended to higher temperatures above the glass transition, where it would become a first-order liquid–liquid phase transition line ending at a critical point at about 200 K [10]. However, in this temperature range, water immediately crystallizes and this phase transition cannot be observed in direct experiments. More recently, a distinct amorphous phase of water, called *very high-density amorphous ice*, has been observed experimentally [11–13]. New simulations of the ST2 model [14] in the restricted NPT ensemble suggest that instead of one

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* Corresponding author. Tel.: +1-617-353-4518; fax: +1-617-353-9393.
E-mail address: buldyrev@bu.edu (S.V. Buldyrev).

previously observed liquid–liquid phase transition, there might be three liquid–liquid phase transition lines between four liquids with different densities roughly correspond-ing to the densities of the three known amorphous ices. It has been suggested [15] that systems with rich polymorphic solid phase diagrams may have several liquid phases with local particle arrangements corresponding to various crystalline structures.

We propose here a simple model with at least two liquid–liquid phase transitions in addition to the known liquid–gas phase transition. This model is based on the double step soft-core potential model previously used to study systems with two fluid–fluid critical points [16–19]. Two fluid–fluid critical points were also observed by Monte Carlo simulations of a similar model with a continuous soft-core potential [20].

We perform constant volume V collision-driven molecular dynamic simulations [17,18,21] on a system of $N = 1728$ spherically symmetric particles interacting via the discontinuous pair potential

$$
U(r) = \begin{cases}
\infty & \text{for } r < a \,, \\
U_1 & \text{for } a \leqslant r < b_1 \,, \\
U_2 & \text{for } b_1 \leqslant r < b_2 \,, \\
-U_A & \text{for } b_2 \leqslant r < c \,, \\
0 & \text{for } c \leqslant r \,,
\end{cases} \tag{1}
$$

where $U(r)$ is a potential energy of a pair of particles at distance r, $U_A > 0$ is the energy of attraction, $U_1 = 3U_A$, $U_2 = U_A$, $b_1 = 1.4a$, $b_2 = 2.1a$, and $c = 2.8a$. (see Fig. 1, inset). We keep temperature T constant using a modified Berendsen
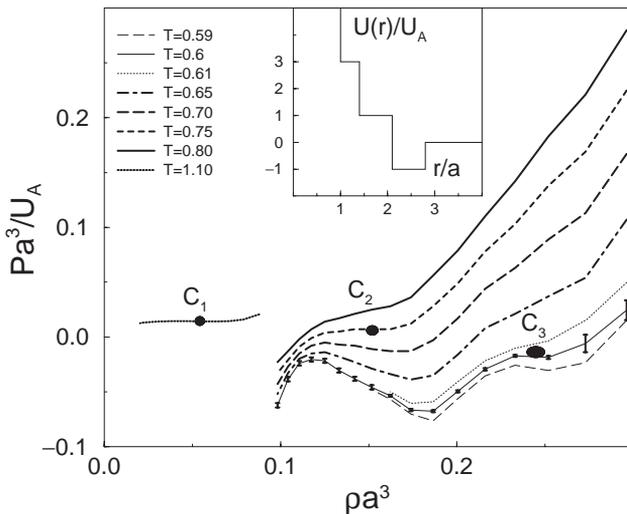

Fig. 1. Isotherms and critical points for the system of spherically symmetric particles interacting via the potential shown as an inset.

method [22] periodically (after each N collisions) rescaling the velocities of all the particles so that the average kinetic energy approaches the desired value. To speed up the simulation, we achieve this effect by rescaling the unit of time and parameter U_A, so that the numerical values of the velocities remain unchanged and the collision table is preserved. We compute pressure P the same way as in Refs. [16,17], averaging it over $2 \times 10^4 (ma^2/U_A)^{1/2}$ time units, where m is particle mass. Throughout this paper, we measure density, pressure, and temperature in units of a^{-3}, $U_A a^{-3}$, and U_A/k_B, respectively, where k_B is the Boltzmann constant. We investigate several state points for systems with different densities $\rho \equiv N/V$ along several isotherms (see Fig. 1) and find three distinct sets of van Der Waals loops, each ending in a specific critical point characterized by an isotherm with an inflection point. Note that the negatively sloped regime of the isotherms is an artifact of the constant volume simulations with periodic boundary conditions. It is caused by the surface tension of the fluctuating phase boundary. For large enough system, it splits into several regimes corresponding to different surface topology: planar, cylindrical, and spherical causing apparent jumps on the isotherms which can be mistakenly identified as separate phase transitions. We observe these regimes below the gas–liquid critical point C_1. We check that the system remains homogeneous in the vicinity of the critical points C_2 and C_3.

Note that the isotherm for $T = 0.60$ almost entirely corresponds to a stretched metastable liquid with $P < 0$. In addition, at this temperature, the system spontaneously crystallizes for $\rho > 0.23$. Nevertheless, we are able to find equilibrium liquid pressures by averaging pressure before the crystallization onset, using the same technique as in Ref. [17]. We quench five independent configurations equilibrated at $T = 0.9$ to $T = 0.6$, skip initial 800 time units (the correlation time at this temperature), and average the pressure until the onset of crystallization, indicated by the sharp decrease of potential energy. The average existence time $\langle t \rangle$ of the metastable liquid is $\langle t \rangle = 1.5 \times 10^4$ time units at $\rho = 0.23$, $\langle t \rangle = 4.5 \times 10^3$ at $\rho = 0.25$, $\langle t \rangle = 1.5 \times 10^3$ at $\rho = 0.27$, and $\langle t \rangle = 10^3$ at $\rho = 0.30$. The error bars of the pressure are assumed to be equal to the standard deviation of the pressure measurements for five independent runs.

Accordingly, we find a liquid–gas critical point C_1 at $T_1 = 1.10$, $P_1 = 0.014$, $\rho_1 = 0.054$, a stable high-density critical point C_2 at $T_2 = 0.75$, $P_2 = 0.0056$, $\rho_2 = 0.152$, and a third very high-density critical point C_3 at $T_3 = 0.60$, $P_3 = -0.014$, $\rho_3 = 0.245$. The third critical point is metastable with respect to gas–crystal coexistence, but by varying the parameters of the potential [19], it may be possible to shift the position of the third critical point to a stable region of the phase diagram.

Fig. 2 shows radial distribution functions for the three liquids at temperature $T = 0.59$, corresponding to the low-density liquid (LDL) with density $0.098a^{-3}$, high-density liquid (HDL) with density $0.186a^{-3}$, very high-density liquid (VHDL) with density $0.272a^{-3}$ and a crystal with density $0.296a^{-3}$. One can see a dramatic difference between the structures of LDL and HDL.

Integrating radial distribution function for LDL, we find that 11 neighbors stay in the attractive well, almost not penetrating into soft cores.

In contrast, in HDL, particles penetrate into a larger soft core. The average number of neighbors in the smaller soft core is 0.6. The average number of neighbors in the larger soft core is 2.7. The number of particles in the attractive well also increases to 17.
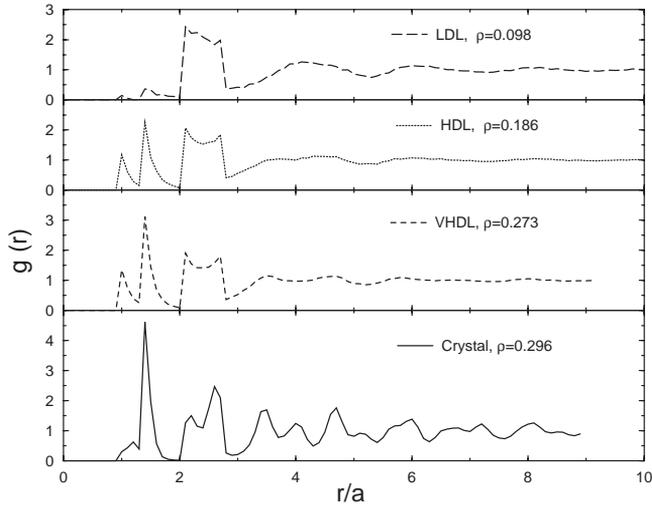
Fig. 2. Radial distribution functions for a system shown in Fig. 1 at temperature $T = 0.59$ at four different densities, corresponding to three different liquids and a crystal.

The difference between the structures of HDL and VHDL is less pronounced. Nevertheless, one can see the development of an extra peak for VHDL at a distance $3.5a$. In addition, the number of particles in the smaller and larger soft cores increases to 1 and 5, respectively, and the number of particles in the attractive well increases to 23.

The choice of parameters is motivated by our preliminary studies of simpler systems with $U_1 = \infty$, which have a gas–liquid critical point $\tilde{C}_1$ ($T = 1.06$, $P = 0.013$, $\rho = 0.052$) and a stable liquid–liquid critical point $\tilde{C}_2$ ($T = 0.67$, $P = 0.059$, $\rho = 0.144$) (see Fig. 3). The potential of this system is the soft-core potential [16], with b_1 playing the role of the hard core and b_2 playing the role of the soft core. Note that the positions of these critical points are very similar to those of C_1 and C_2 in the three-step potential. Thus, adding a second soft core $a < b_1 < b_2$ to the potential, creates a third critical point at higher densities without a significant change in the position of the two original critical points.

One can speculate that adding more steps to a potential can create more critical points at different densities corresponding to the interparticle distances of these steps if the parameters of these steps are carefully selected. However, if the steps become much smaller than $k_B T$, their individual effects become negligible and the phase diagram of such a system converges to the phase diagram of a system with a continuous potential which these discontinuous potentials approximate. We test our collision-driven molecular dynamic algorithm approximating the continuous Gaussian repulsive rump [23] and the linear repulsive rump [20] by the step-functions of $n \leqslant 256$ steps and observe an excellent quantitative agreement, including density anomalies associated with these potentials. We find that the pressure $P_n(V, T)$ for a potential with n steps converges to the corresponding pressure for a continuous potential $P_\infty(V, T)$ as $1/n^2$, while the diffusion coefficient converges as $1/n$.
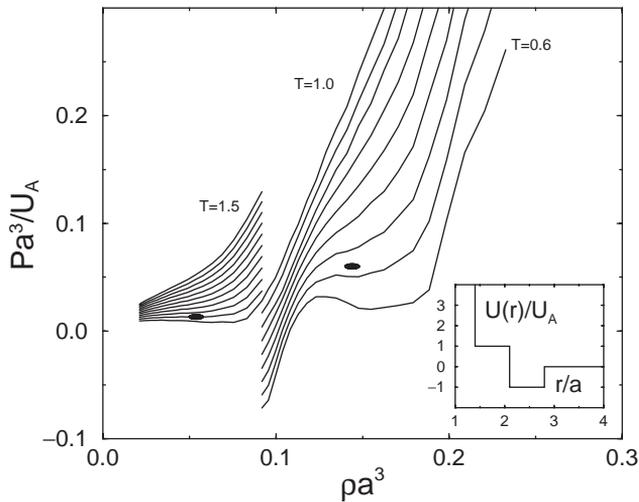
Fig. 3. Isotherms and critical points for temperatures $T = 1.5, 1.45, 1.4, 1.35, 1.30, 1.25, 1.20, 1.15, 1.10,$ $1.05, 1.00, 0.95, 0.90, 0.85, 0.80, 0.75, 0.70, 0.65, 0.60$ for a simplified potential shown in the inset with one soft core b_2 and a hard core $b_1 = 1.4a$. Isotherms for $T > 1.00$ are computed only for small densities, while isotherms for $T < 1.00$ are computed only for large densities. The isotherm corresponding to $T = 1.00$ is computed for the entire range of densities. The systems for $\rho > 0.23$ spontaneously crystallize at $T < 0.75$ into crystalline structures similar to the crystalline structure of the system with two soft cores shown in Fig. 2.

In summary, we show that systems interacting via spherically symmetric potentials with three characteristic repulsive distances playing the role of soft cores may have three liquid phases of three increasing densities characterized by the penetration of particles into a soft core of smaller diameter.

References

[1] V. Brazhkin, S.V. Buldyrev, V. Ryzhov, H.E. Stanley (Eds.), New kinds of phase transitions: transformations in disordered substances; Proceedings of the NATO Advanced Research Workshop, Volga River, Kluwer, Dordrecht, 2002.

[2] Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata, K. Funakoshi, Nature 403 (2000) 170.

[3] M. Togaya, in: V. Brazhkin, S.V. Buldyrev, V. Ryzhov, H.E. Stanley (Eds.), New kinds of phase transitions: transformations in disordered substances; Proceedings of the NATO Advanced Research Workshop, Volga River, Kluwer, Dordrecht, 2002, p. 255.

[4] J.N. Glossili, F.H. Ree, Phys. Rev. Lett. 82 (1999) 4659.

[5] I. Saika-Voivod, F. Sciortino, P.H. Poole, Phys. Rev. E 63 (2001) 011 202.

[6] S.S. Borick, P.G. Debenedetti, S. Sastry, J. Phys. Chem. 99 (1995) 3781.

[7] C.A. Angell, S. Borick, M. Grabow, J. Non-Cryst. Solids 207 (1996) 463.

 [8] O. Mishima, L.D. Calvert, E. Whalley, Nature 314 (1985) 76;
     O. Mishima, J. Chem. Phys. 100 (1994) 5910–5912.
 [9] P.H. Poole, F. Sciortino, U. Essmann, H.E. Stanley, Nature 360 (1992) 324.
[10] O. Mishima, H.E. Stanley, Nature 396 (1998) 329.
[11] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker, Phys. Chem. Chem. Phys. 3 (2002) 5355.
[12] J.L. Finney, D.T. Bowron, A.K. Soper, T. Loerting, E. Mayer, A. Hallbrucker, Phys. Rev. Lett. 89 (2002) 205 503.
[13] D.D. Klug, Nature 420 (2002) 749.
[14] I. Brovchenko, A. Geiger, A. Oleinikova, J. Chem. Phys. 118 (2003) 9473.
[15] V.V. Brazhkin, R.N. Voloshin, S.V. Popova, A.G. Lyapin, in: V. Brazhkin, S.V. Buldyrev, V. Ryzhov, H.E. Stanley (Eds.), New kinds of phase transitions: transformations in disordered substances; Proceedings of the NATO Advanced Research Workshop, Volga River, Kluwer, Dordrecht, 2002, p. 239.
[16] G. Franzese, G. Malescio, A. Skibinsky, S.V. Buldyrev, H.E. Stanley, Nature 409 (2001) 692.
[17] G. Franzese, G. Malescio, A. Skibinsky, S.V. Buldyrev, H.E. Stanley, Phys. Rev. E 66 (2002) 051 206.
[18] S.V. Buldyrev, G. Franzese, N. Giovambattista, G. Malescio, M.R. Sadr-Lahijany, A. Scala, A. Skibinsky, H.E. Stanley, Physica A 304 (2002) 23.
[19] A. Skibinsky, G. Franzese, G. Malescio, S.V. Buldyrev, H.E. Stanley, cond-mat/0309632 (2003).
[20] E.A. Jagla, Phys. Rev. E 63 (2001) 061 501.
[21] D.C. Rapaport, The Art of Molecular Dynamics Simulation, Cambridge University Press, Cambridge, 1995.
[22] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. Di Nola, J.R. Haak, J. Chem. Phys. 81 (1984) 3684.
[23] F.H. Stillinger, D.K. Stillinger, Physica A 244 (1997) 358.