

Evidence for a liquid-solid critical point in a simple monatomic system

Måns Elenius^{1,a)} and Mikhail Dzugutov²

¹*Department of Numerical Analysis, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

²*Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

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It is commonly believed that the transition line separating a liquid and a solid cannot be interrupted by a critical point. This opinion is based on the traditional symmetry argument that an isotropic liquid cannot be continuously transformed into a crystal with a discrete rotational and translational symmetry. We present here a molecular-dynamics simulation of a simple monatomic system suggesting the existence of a liquid-solid spinodal terminating at a critical point. We show that, in the critical region, the isotropic liquid continuously transforms into a phase with a mesoscopic order similar to that of the smectic liquid crystals. We argue that the existence of both the spinodal and the critical point can be explained by the close structural proximity between the mesophase and the crystal. This indicates a possibility of finding a similar thermodynamic behavior in gelating colloids, liquid crystals, and polymers. © 2009 American Institute of Physics. [doi:10.1063/1.3213616]

I. INTRODUCTION

In many systems, a domain of spinodal instability can be observed where a liquid phase coexists in equilibrium with a gas phase. The spinodal terminates at a critical point (CP),¹ which manifests a possibility of a continuous transformation between the two phases. Whether a single-component system can exhibit a spinodal where a liquid and a crystalline solid phase coexist in equilibrium, and a respective CP, still remains an unanswered question of a significant conceptual interest. A liquid-solid CP has never been observed hitherto, and its existence is commonly regarded impossible based on the argument that a continuous transformation from an isotropic liquid to a crystal with a discrete symmetry is inconceivable.¹

The results of a molecular dynamics simulation of a simple monatomic system that we report here indicate the existence of a spinodal domain separating a stable liquid and the crystalline solid phase. Moreover, evidence is presented suggesting the existence of a low-density CP terminating the first-order transition between the two phases. We also demonstrate that, upon constant-density cooling toward the vicinity of the CP, the isotropic liquid continuously transforms into a low-density phase with a mesoscopic order similar to that of smectic liquid crystals.² Furthermore, we observed a close structural proximity between the mesophase and the crystal, which extends much beyond the local order of nearest neighbors. We argue that this structural peculiarity of the mesophase can account for the existence of both the spinodal and the CP. It also makes it possible to conjecture that a liquid-solid CP like the one we observe here might exist in liquid crystals, polymers, and in gelating colloidal systems.

The following crystallization scenario suggested by the classical nucleation theory is commonly accepted. In a metastable supercooled liquid, nuclei of the lower free energy

crystalline phase are being spontaneously created by virtue of thermal fluctuations. Because the two phases are symmetry-unrelated, appearance of a nucleus involves creation of an interface. The free-energy cost of the interface blocks the growth of the nucleus unless the latter exceeds a critical size. In this scenario, the entire volume of a metastable supercooled liquid rapidly crystallizes as soon as a critical nucleus has been created. The existence of a spinodal instability domain where no single phase can be in a stable or metastable equilibrium implies that the interfacial free-energy barrier vanishes.

In general, there are two independent order parameters involved in a first-order phase transition: density and the local structural symmetry. The former controls fluid-fluid phase transitions where a spinodal instability domain is commonly observed, whereas the latter plays the key role in crystallization of dense liquids. However, it was pointed out that density fluctuations seen in the vicinity of a metastable liquid-liquid spinodal with a CP may cause a dramatic increase in the nucleation rate, indicating a reduction of the interfacial barrier for crystallization.^{3–5} The possibility of a liquid-solid spinodal was also inferred from the crystallization anomalies in simple liquids under deep supercooling^{6–8} and phase transformations in atomic clusters.^{9–12} It was also predicted, based on analytic arguments, that a fluid-solid spinodal region may appear in the system of hard spheres in higher dimensions.¹³

A possible microscopic mechanism for the density-driven spinodal domain in the liquid-solid transition of a simple single-component system was conjectured by Debenedetti *et al.*¹⁴ based on a lattice model. A pair potential, attractive at the nearest-neighbor distance and repulsive at the second-nearest neighbor distance, was shown to induce low-density open structures, associated with the liquid phase, which collapse into a dense solid phase under pressure. Due to a significant difference in density, the two phases can coexist within a spinodal domain of infinite compressibility.

^{a)}Electronic mail: elenius@csc.kth.se.

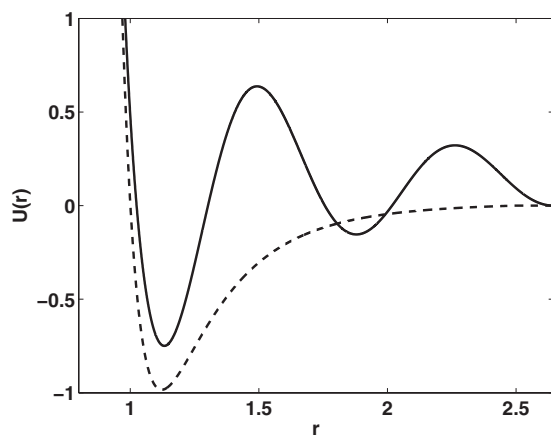


FIG. 1. The Z2 potential (Ref. 15) used in this study (solid line) compared to the Lennard-Jones potential (dashed line).

II. SIMULATION DETAILS

In the present study, we performed a molecular dynamics simulation of a single-component system exploring a pair potential of the type suggested in the above conjecture. The pair potential¹⁵ (denoted as Z2 in that reference) is presented in Fig. 1. It has been found to induce a pronounced icosahedral local ordering of the nearest neighbors due to the design of its short-range attraction, while the repulsion incorporated in its longer-range part inhibits bulk packing of icosahedra.

In this simulation, we used a system of 3456 identical particles in the constant number of atoms, volume, and temperature (NVT) ensemble. All results here are presented in reduced simulation units following from the definition of the pair potential.¹⁵

III. RESULTS

The phase behavior of the simulated system was explored within a wide range of densities by cooling it at constant density ρ from the high-temperature isotropic liquid state. The cooling was performed stepwise, with comprehensive equilibration at each temperature point. The isochoric variation of enthalpy H as a function of temperature T is shown in Fig. 2(a). For each isochore where $\rho > 0.32$ we observe a discontinuity in $H(T)$ indicating a first-order freezing transition into a low-temperature state. The first-order character of this transition is confirmed by distinct hysteresis loops in the $H(T)$ isochores that are observed when the system is heated from the low-temperature state toward the high-temperature liquid.

Both the freezing and melting temperatures derived from the isochoric enthalpy variations are shown in the ρ - T phase diagram, Fig. 2(b). A distinctive anomaly of the observed phase transition is that the melting line and the freezing line confining the metastability domain converge at $\rho = 0.33$ and $T = 0.31$. The first-order phase transition apparently disap-

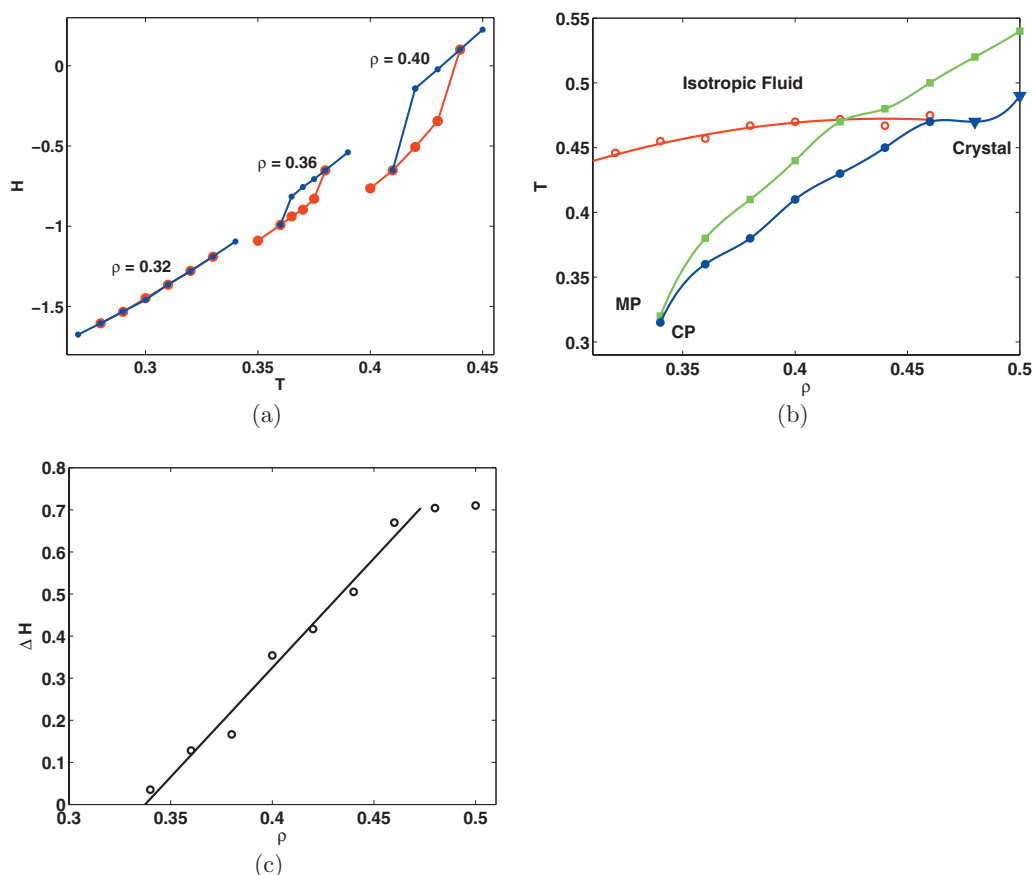


FIG. 2. Liquid-solid phase transformation. (a) Isochoric temperature variations of the enthalpy H at indicated densities. Small blue dots and line: cooling; large red dots and line: heating. (b) Density-temperature phase diagram of the simulated system. Blue symbols and line: the freezing transition; triangles: crystallization; and circles: spinodal. Green symbols and line: melting transition. Red line and symbols denote maximum of C_V in the liquid phase. MP and CP, respectively, abbreviate mesophase and CP. (c) Density dependence of the latent heat ΔH for the freezing transition.

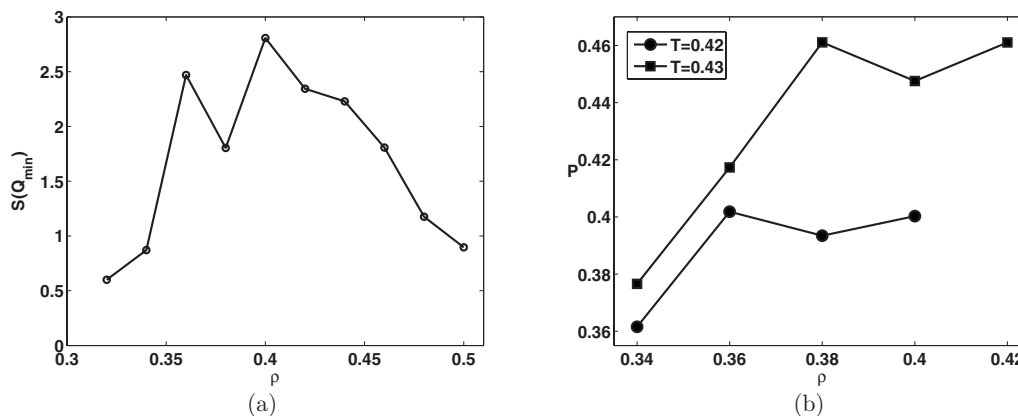


FIG. 3. (a) Density dependence of the estimated small- Q limit of the structure factor $S(Q)$ along the freezing line. (b) Two isotherms suggesting the spinodal decomposition discussed in the text.

appears at densities below $\rho=0.33$. This is confirmed in Fig. 2(c) that shows the density dependence of the latent heat ΔH of this transition. That quantity reduces in an apparently linear manner with the reduction of density, eventually vanishing at the indicated density point. Indeed, no trace of discontinuity or hysteresis can be discerned in the isochoric variation of enthalpy within the relevant temperature interval at $\rho=0.32$ presented in Fig. 2(a). These observations can be interpreted as evidence that at $\rho=0.33$ and $T=0.31$ the first-order transition line is terminated by a CP.

Another interesting anomaly we observe is that the described phase transition results in divergence of the isothermal compressibility χ_T . In a macroscopic system, χ_T is related to the low- Q limit of the structure factor $S(Q)$ by the compressibility equation:

$$\chi_T = \rho TS(0), \quad (1)$$

where $S(Q) = \langle \rho(Q)\rho(-Q) \rangle$ and $\rho(Q)$ is the Fourier transform of the system's density:

$$\rho(Q) = \frac{1}{N} \sum_{k=1}^N \exp(-iQr_k), \quad (2)$$

N being the number of particles and r_k the position of particle k . The compressibility equation thus links divergence of χ_T with the presence of density fluctuations of macroscopic spatial scale giving rise to the divergence of $S(0)$. We note that in a system with a fixed number of particles, the system size L determines the long-wavelength limit of the density fluctuations, and, respectively, the minimum value of Q for which $S(Q)$ is defined as $Q_{\min}=2\pi/L$. In such a system, when χ_T diverges, $S(Q_{\min})$ increases to a finite value dependent on the system size. Figure 3(a) shows an anomalous increase in $S(Q_{\min})$ in the low-temperature state along the freezing line, within the density interval above the estimated critical density, indicating the system's large-scale decomposition into domains of different density characteristics of spinodal instability. This conclusion is supported by the divergence of the χ_T by zero slope of the P - ρ isotherm shown in Fig. 3(b). We stress that this result was obtained after a thorough equilibration of the low-temperature state and, therefore, cannot be regarded as a transient effect of the phase transition.

In order to gain an insight into the microscopic mechanism of these thermodynamic anomalies, we now analyze the structural aspects of the observed phase transformation by directly inspecting the atomic configurations of the low-temperature state. We note that, to get rid of the thermal noise, all the configurations investigated here were subjected to steepest-descent minimization of potential energy.

Figure 4 depicts a set of configurations representing the system's states equilibrated at T immediately below the freezing transition, at different densities. At $\rho=0.5$, the tran-

sition evidently produces a structure characterized by a well-defined global periodic order. This is a low-density crystalline phase with a local order apparently dominated by tetrahedral close packing. The central element of its unit cell is a cubically symmetric configuration composed of eight icosahedra, which are kept apart by low-dimensional arrangements of tetrahedra. In a similar manner, low-dimensional tetrahedral bridges link the described cubes into a periodic structure. To the best of our knowledge, this crystalline structure has not been reported so far. A detailed crystallographic description of this phase will be reported elsewhere.

Other atomic configurations shown in Figs. 4(b)–4(d) represent the density domain of diverging isothermal compressibility that we identified as spinodal. Within each of these configurations, we are able to discern a distinct compact domain of the same crystalline structure as the one observed at $\rho=0.5$. These crystalline domains are marked by

red in the plots. The rest of the volume of the molecular dynamics simulation cell outside the crystalline domains is occupied by an apparently different structure that is visibly less dense and does not exhibit any immediately detectable global order. Its local order, however, appears to be quite similar to that of the crystalline structure, being dominated by the same kind of tetrahedral close packing with a high number of icosahedra linked in a low-dimensional manner. The plots in Fig. 4 also demonstrate that the relative volume occupied by the crystalline phase shrinks approximately linearly with reduction of density, eventually vanishing at the CP. This observation is evidently consistent with the respec-

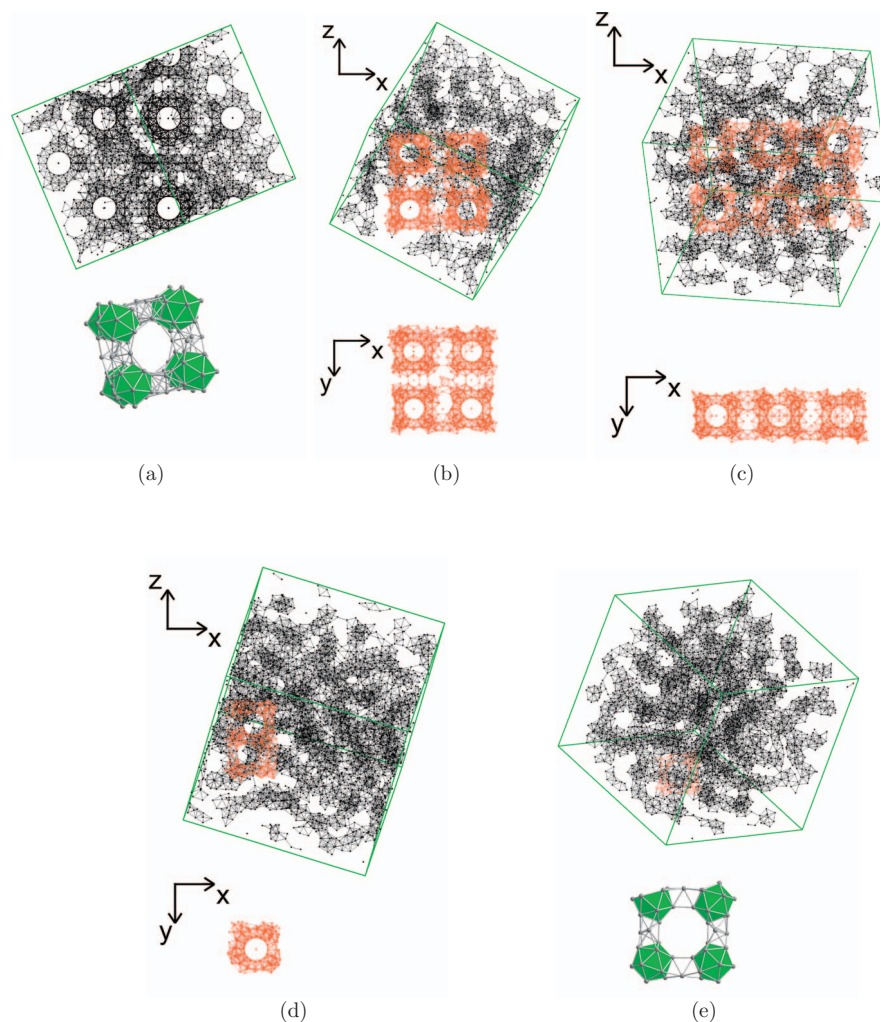


FIG. 4. Instantaneous configurations of the low temperature state. (a) $\rho=0.5$, $T=0.48$. (b) $\rho=0.4$, $T=0.41$. (c) $\rho=0.36$, $T=0.36$. (d) $\rho=0.34$, $T=0.3125$. (e) $\rho=0.32$, $T=0.28$. The cubic arrangement of eight icosahedra shown separately in (a) represents the central element of the crystalline phase. In (b)–(d), red color marks crystalline domains coexisting with the liquid phase. Separate plots present the same domains in a different projection. In e, the configuration domain marked by red, also shown in a separate plot, is an arrangement of four icosahedra, with some defects, representing a rudiment of the crystalline structure.

tive variation of the latent heat shown in Fig. 2(c). It suggests that the liquid phase can be continuously transformed into a crystal via the CP.

We now analyze the transformation of the liquid phase under cooling. First, we consider the isochore $\rho=0.32$, i.e., below the critical density. Temperature variations of the specific heat C_V at that density, shown in Fig. 5(a), display a pronounced maximum at $T_m=0.45$. The density dependence of T_m is shown in the phase diagram, Fig. 2(b). The line of C_V maximum extends to higher densities until it eventually encounters the freezing transition line. The appearance of excess specific heat under cooling is an indicator of the development of bonded structures, and a common precursor of percolation.^{16,17} Indeed, a steep increase in the number of icosahedra can be observed below T_m , Fig. 5(b). This leads to the development of extended clusters and a rapid growth of the correlation length, as it is demonstrated by the temperature-dependence of the maximum cluster size, Fig. 5(b). These clusters are extended low-dimensional structures composed of interconnected icosahedra and face sharing tetrahedra, like the one exemplified in Fig. 5(c). Upon further

cooling, the maximum cluster size diverges, and at $T=0.28$, a continuous tetrahedrally packed network is formed that includes approximately 90% of all the atoms. An example of that network is shown in Fig. 4(e). Another interesting structural feature developed in this liquid state under cooling is a low- Q prepeak of $S(Q)$, Fig. 5(d). This anomaly, as well as the maximum of C_V , is commonly observed in the context of gelation in colloidal systems.¹⁸

Figure 5(e) presents the ratio of the number of icosahedra in the high temperature state to the respective number in the low temperature state within the metastability domain, as a function of density. It indicates that, as the density is reduced, the difference in the local order between the two states shrinks, vanishing at the CP. A considerable degree of local structural similarity between the liquid in the critical-point region and the crystal is exemplified by the ringlike arrangement of icosahedra depicted in Fig. 4(e). A trend for the formation of similar structural arrangement, although in a more defective rudimentary form, can be detected in the higher-temperature cluster, Fig. 5(c). Moreover, the liquid exhibits an instantaneous mesoscopic-scale periodicity con-

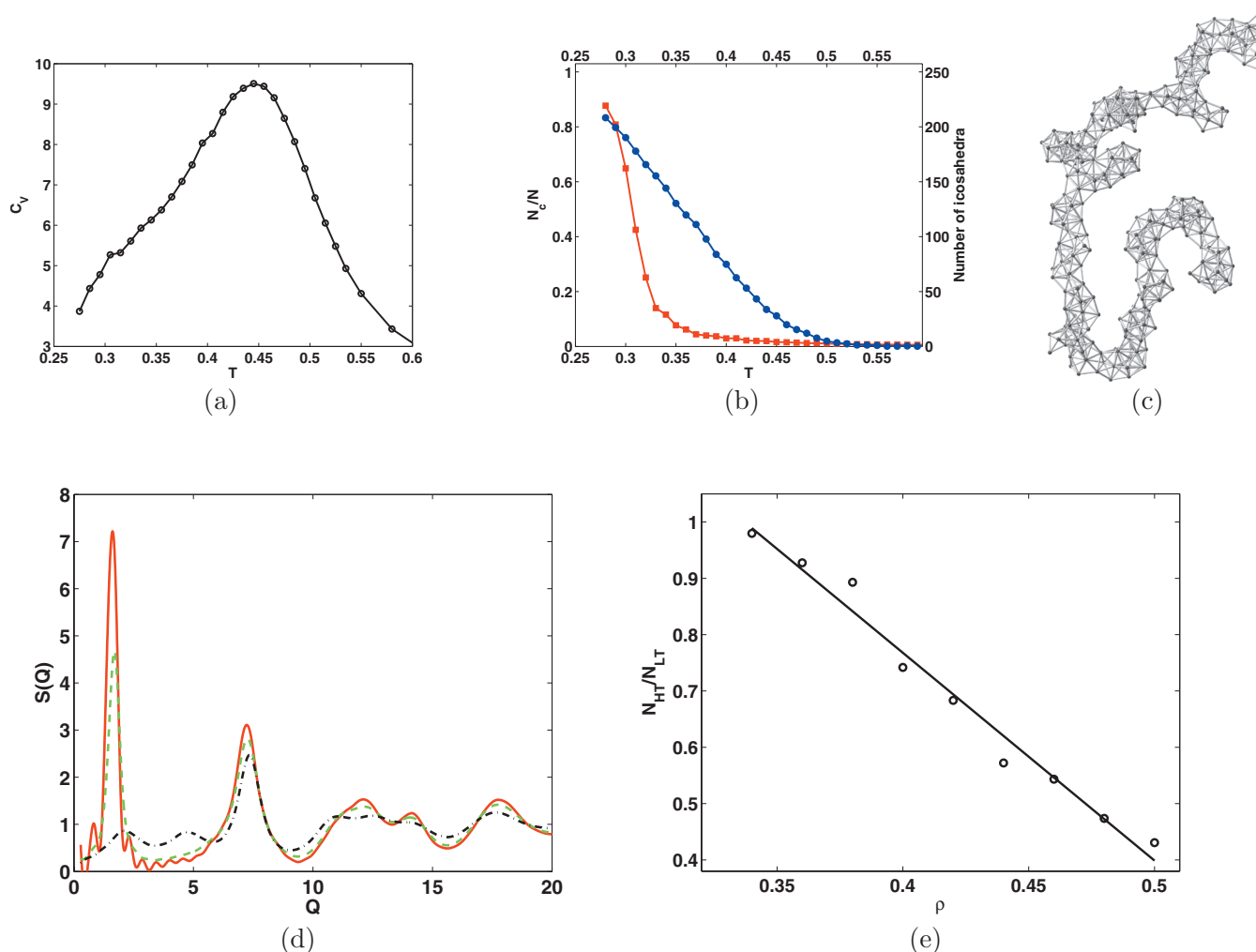


FIG. 5. Evolution of the liquid phase under cooling. (a) Temperature variation of the liquid specific heat C_V along the isochore $\rho=0.32$. (b) Temperature variation, along the isochore $\rho=0.32$, of the number of icosahedra (blue circles) and the number of atoms N_c in the maximum-size cluster composed of face sharing tetrahedra, scaled by the total number of atoms in the system N (red squares). (c) A maximum-size tetrahedral cluster observed at $\rho=0.32$, $T=0.34$. (d) Temperature variation of the structure factor $S(Q)$. Black dash-dotted line, $T=1.10$; green dashed line, $T=0.40$; red solid line, $T=0.28$. (e) The ratio of the number of icosahedra in the high temperature state, N_{HT} , to the respective number in the low temperature state, N_{LT} , within the metastability domain, as a function of density.

sistent with that of the crystal. Figure 6(a) shows the intensity pattern of the liquid's $S(Q)$ on a sphere in the Q -space, with a radius equal to Q_{pp} , the position of the low- Q prepeak of $S(Q)$; Fig. 6(b) shows the respective pattern exhibited by the crystal on the Q -sphere of the same radius. The liquid diffraction pattern shows a sizable degree of periodicity along two perpendicular axes, consistent with the respective periodicity pattern in the crystal. The observed periodic order in the liquid is however limited in both time and space. Its dissipation in time is demonstrated in Fig. 6(c) where we present the decay of the respective component of the density-density correlator $F(Q_{pp}, t) = \langle \rho(Q_{pp}, 0) \rho(-Q_{pp}, t) \rangle$, for a set of temperatures. The density-correlation pattern manifested by the prepeak of $S(Q)$ evidently dissipates. The relaxation time exhibits a strong temperature-dependence, and exceeds the timescales accessible in our simulation for temperatures below $T=0.28$.

IV. DISCUSSION

The liquid phase formed by cooling from the high-temperature liquid at $\rho=0.32$ can be classified as a

mesophase similar to the smectic phases² observed in polymeric liquids. We note that the large-scale equilibrium fluctuations of periodic order, consistent with the periodicity of the crystalline phase, that were demonstrated in Fig. 6 can be compared with the critical fluctuations of structure observed at the tricritical point terminating the line of first-order nematic-smectic transition in liquid crystals.² In those systems, the critical fluctuations of the structural order give rise to a singularity in the specific heat. In the present system, the existence of a similar singularity can be inferred from the evolution of the enthalpy step in Fig. 2(a). We also mention that a liquid-crystal smectic phase interposed between the isotropic liquid and the crystalline solid was discussed¹⁹ as a possible scenario for the bond ordering in the supercooled liquid state. Both melting of such a phase and its transformation to a crystal were conjectured to be continuous. The present result supports that conjecture. Another possible candidate for the observation of a liquid-solid CP may be polymers where a liquid-solid spinodal was recently observed.²⁰

Based on the observations we presented here, we can

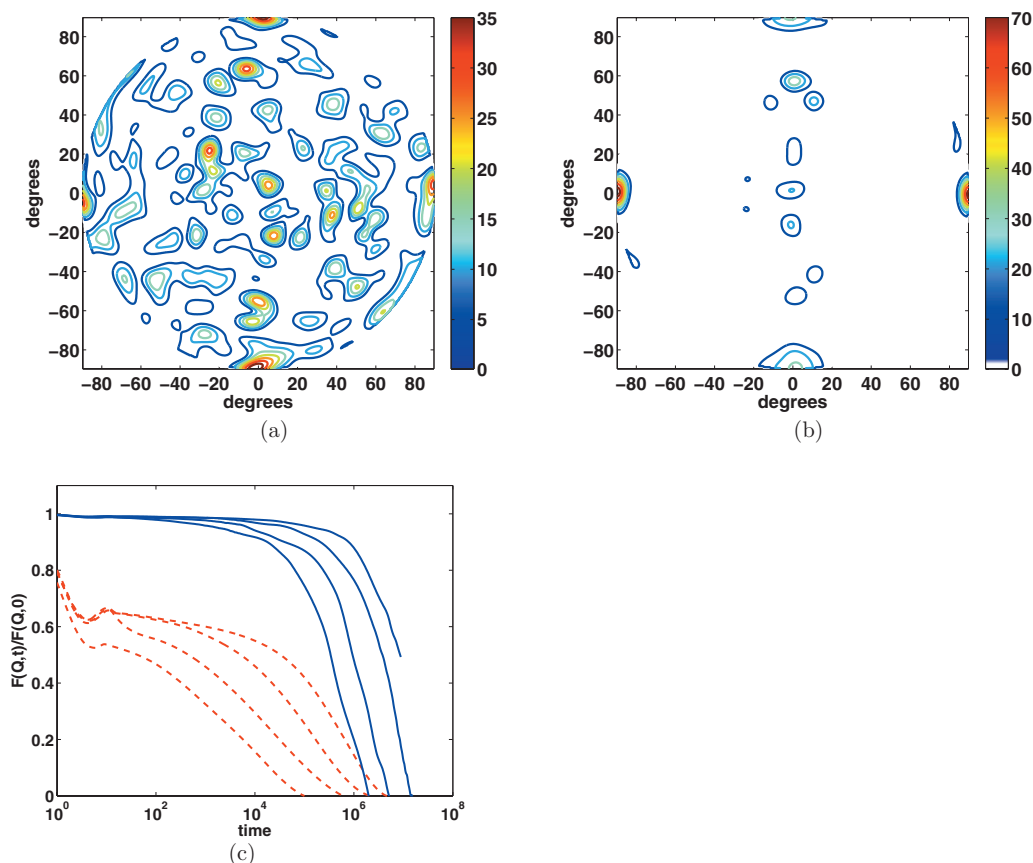


FIG. 6. Mesoscopic-scale anisotropy in the low-temperature liquid phase. (a) Intensity of the structure factor $S(Q)$ on a Q -space sphere of the radius Q_{pp} , the position of the low- Q prepeak of $S(Q)$ for a liquid configuration at $\rho=0.32$, $T=0.28$. (b) The same plot as Fig. 4(a) but for the crystalline phase at $\rho=0.5$, $T=0.48$. (c) The decay of the density-density correlator $F(Q,t)$ at $\rho=0.32$. Red dashed lines: Q corresponding to the position of the main peak of $S(Q)$. Blue solid lines: $Q=Q_{pp}$. From left to right, $T=0.30, 0.29, 0.28, 0.27$.

understand the existence of a spinodal domain where the mesophase coexists with the crystal, and the corresponding CP considering two factors. First, there is a significant difference in density between the two coexisting phases. The characteristic low-density open structure of the mesophase is induced by the pair potential, which enforces a strong tendency for icosahedral ordering of the nearest neighbors while keeping the icosahedra apart due to the repulsion incorporated in its long-range part. Second, the structural proximity between the mesophase and the crystal that extends well beyond the nearest-neighbors' configurations can be expected to greatly reduce the free-energy cost for the interface separating the two structural domains. These two factors render the system unstable with respect to density fluctuations of a large spatial scale, making possible both an equilibrium coexistence of the two phases within the spinodal domain and the existence of the CP at its low-density limit. In this way, the present observation can be compared with the coexistence of structurally similar liquid phases discriminated by density, and a respective CP observed in a simulation of a one-component system using a pair potential with a long-range repulsion.²¹

The structural similarity between the mesoscopic liquid state formed by the present system under cooling at subcritical density and gel-forming colloidal systems that we have already mentioned deserves an additional comment. It was found²² that the appearance of spanning clusters involved in

gelation in low-density systems of colloidal particles with short-range interaction can be interpreted in terms of density fluctuations caused by the existence of a liquid-gas spinodal instability. A possible relation between that instability and the higher-density liquid-solid CP we report here looks quite intriguing and deserves to be investigated in future studies. In particular, a question of significant interest is whether the tetrahedrally packed colloidal clusters demonstrating gelation at low densities^{17,18} would at higher densities display coexistence between a disordered phase and a crystal, and a respective liquid-solid CP like the one we report here.

V. CONCLUSIONS

In summary, the molecular dynamics simulation presented here provides evidence for a novel kind of phase behavior in a simple one-component system. The results suggest that the phase diagram includes a spinodal domain separating a stable liquid phase and a crystalline solid phase. Moreover, evidence is presented suggesting that the spinodal terminates at a CP. The existence of a liquid-solid CP implies that an isotropic liquid can be transformed into a crystal without crossing the line of first-order phase transition. We argue that the existence of both the spinodal and the CP that we conclude based on the presented evidence can be explained by the structural transformation of the liquid phase.

Upon cooling toward the CP, the liquid is found to develop a mesoscopic order, reminiscent of that in smectic liquid crystals, which demonstrates a strong structural similarity with the crystalline phase. We conjecture that the observed phase behavior can be expected in other systems possessing a similar kind of mesoscopic order, including liquid crystals, polymers, and gelating colloidal systems.

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