Liquid–liquid phase transition in deeply supercooled Stillinger–Weber silicon

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Abstract

The existence of a phase transition between two distinct liquid phases in single-component network-forming liquids (e.g., water, silica, silicon) has elicited considerable scientific interest. The phase transition, both for experiments and simulations, is that the liquid–liquid phase transition (LLPT) occurs under deeply supercooled conditions, where crystallization occurs very rapidly. Thus, early evidence from numerical equation of state studies was challenged with the argument that slow spontaneous crystallization had been misinterpreted as evidence of a second liquid state. Rigorous free-energy calculations have subsequently confirmed the existence of a LLPT in some models of water, and exciting new experimental evidence has since supported these computational results. Similar results have so far not been found for silicon. Here, we present results from free-energy calculations performed for silicon modeled with the classical, empirical Stillinger-Weber potential. Through a careful study employing state-of-the-art constrained simulation protocols and numerous checks for thermodynamic consistency, we find that there are two distinct metastable liquid states and a phase transition. Our results resolve a long-standing debate concerning the existence of a liquid–liquid transition in supercooled liquid silicon and address key questions regarding the nature of the phase transition and the associated critical point.

Keywords: liquid–liquid phase transition, supercooled liquids, Stillinger–Weber silicon, network-forming liquids, free-energy

Significance Statement:

The debate around the existence of a phase transition between distinct liquid phases in single-component liquids has elicited considerable scientific interest in recent years. The most recent evidence from investigations of water, both computational and experimental, strongly suggests the existence of a liquid–liquid phase transition (LLPT). However, similar results have not been available for silicon, which has been argued to be an extreme case in the family of network-forming liquids that may exhibit a liquid–liquid transition. The phase transition is expected to occur at very deeply supercooled conditions, presenting methodological challenges which we address. Our demonstration of the LLPT in model liquid silicon represents a definitive step in establishing the generality of liquid–liquid transitions in network forming liquids.

Introduction

The possibility of a phase transition between distinct liquid states in a single-component liquid has been the subject of intense scientific investigation and debate (1). Liquid silicon, which we study here, is one such case where a number of experimental and computational studies have addressed the existence of such a liquid–liquid phase transition (LLPT) (2–6). The most prominent example of a liquid undergoing a LLPT is water. The possibility of a liquid–liquid transition in water was first discussed while attempting to understand the apparent divergence of isothermal compressibility and other quantities in the supercooled state (7, 8). Based on molecular dynamics simulations for the ST2 model of water, Poole et al. (9) proposed the existence of a liquid–liquid critical point under metastable conditions. Other scenarios have also been proposed, including those not invoking any singular behavior (10). The possibility of a liquid–liquid transition has since been explored in a large variety of substances, and efforts made to understand its origins (11,11). Verifying the existence of a LLPT experimentally has proved to be immensely challenging both for water (12–14) and for silicon (5, 15). A number of numerical studies have reported the existence of a LLPT in silicon, both using first-principles or ab initio methods (6) and using molecular dynamics with a classical empirical potential (3,4). However, the body of numerical evidence pointing to a LLPT was brought into question by the work of Limmer and Chandler (16, 17), who argued that the appearance of a second liquid phase was due to the misinterpretation of slow and spontaneous crystallization. Their study included results on models of water, including the ST2 model, as well as silicon modeled by the classical, empirical Stillinger–Weber (SW) potential (18). The debate around water has since been resolved and the existence of the LLPT confirmed in a comprehensive study of the free-energy surface for the ST2 potential by Palmer et al. (19).
and for other realistic potentials \( (20) \). Equally compelling results have also been reported for models of silica \( (21, 22) \). For SW silicon, the question has remained open, with recent investigations with free-energy calculations similar to those performed by Limmer and Chandler and Palmer et al. showing only one liquid state before the free-energy barrier with respect to crystallization vanishes at conditions where the phase transition is expected \( (23) \). This scenario of spontaneous, barrier-less, crystallization in silicon has since been ruled out in the work of Goswami et al. \( (24) \).

In that work, the choice of a global order parameter \( Q_6 \)—typically used in such contexts—to constrain the system to reversibly sample states with different degrees of crystallinity was demonstrated to give misleading results and we believe, as supported by free-energy calculations in ref. \( (25) \), that similar considerations would also apply to the mW model, another system for which spontaneous crystallisation has been argued to rule out the liquid–liquid transition \( (26) \). However, the question of whether there are in fact two metastable liquid states remains an open and challenging one. Starr and Sciortino \( (27) \) set out to understand the relative propensity of different model network forming liquids to display either a stable or metastable LLPT based on the angular rigidity of the tetrahedral bonds. This analysis led to the successful design of a patchy colloidal model that exhibits a LLPT without the intervention of crystallization \( (28) \). The analysis in ref. \( (27) \) revealed that the angular rigidity for SW silicon was the highest among the models considered. Thus, any phase transition between two metastable liquids would be expected in the deeply metastable regime, possibly prevented by the onset of spontaneous crystallisation. Silicon thus assumes special significance among the class of network-forming liquids that have been investigated.

Here, we present results from numerical free-energy calculations for SW silicon at conditions where the possibility of a LLPT is discussed. We use a combination of a constrained sampling protocol and an appropriate order parameter, which has been demonstrated to accurately determine the free-energy barriers to crystallization at deep supercooling \( (24, 29) \). We develop an extension to that methodology to effectively sample both the liquid state(s) and the transition state with respect to crystallization. Our results show clear evidence of the coexistence between two metastable liquid states, with the characteristic double-well feature in the free-energy surface of the liquid state at the relevant conditions. Through rigorous checks for thermodynamic consistency, including simulations at larger system sizes, we are able to demonstrate that the free-energy reconstructions are robust and consistent with expectations concerning a LLPT \( (19) \). We further investigate the behavior of the relevant order parameter \( (30) \) and characterize the associated critical fluctuations \( (20) \), which behave in accordance with the 3D Ising universality class.

We perform umbrella sampling Monte Carlo \( (31) \) (USMC) simulations of silicon modeled using the 3-body SW potential \( (18) \) in the constant pressure, temperature, and particle number (NPT) ensemble. The density and the size of the largest crystalline cluster \( n_{\text{max}} \) are constrained within overlapping hardwall constraints \( [n^c, n^h] \), while the density is constrained with harmonic bias potentials. Parallel tempering swaps are performed between adjacent windows in \( n_{\text{max}} \), density, and temperature. Total simulation run lengths are in excess of \( 10^8 \) MC steps for each case (at all system sizes) and are compared to the autocorrelation time, number of swaps performed along each axis, and the mean duration required for parallel tempering swaps to "return" to the initial window (see Supplementary Material Figures S3 and S4).

In Figure 1(A), we show the free-energy barrier to crystallization [obtained from the full cluster size distribution, \( P(n) \)] with a finite free-energy cost to the formation of the critical nucleus at each of the temperatures considered.

The choice of temperatures is based on estimates of the LLPT line reported in \( (4) \), where the estimated transition temperature for \( P = 0.75 \) GPa is \( T \approx 990 \) to 995 K. We then construct the density distribution subject to the constraint \( n_{\text{max}} \leq 4 \), integrating over the multivariate distribution to get

\[
P(n_{\text{max}}) = \sum_{\rho} F(n_{\text{max}}, \rho).
\]

(1)

The corresponding free energies obtained from \( \beta \Delta G(n) = -\ln(P(n)) \) are shown in Figure 1(B), displaying a jump in the most probable density of the liquid across \( T = 992 \) K, and a double-well form at \( T = 992 \) K, indicative of coexistence between two liquids. In Figures 1(C and D), we present two order parameter free-energy reconstructions as a function of the size of crystalline clusters along \( x \) and the density along \( y \). The liquid state(s) can be observed by considering the small \( n \) region, while the transition state [critical cluster for which \( \beta \Delta G(n) \) is maximum] and the beginnings of the globally stable crystalline basin are observed by scanning along the \( x \) axis. In these reconstructions, we compute the free-energy from the relative probability of observing a cluster of size \( n \) in the liquid at density \( \rho \) (see the "Materials and methods" section and Supplementary Material for more details). Figure 1(C) shows the free-energy at the lowest temperature considered, \( T = 965 \) K, where the metastable liquid is purely in the LDL, with a barrier with respect to the growth of crystalline order centered at \( n = 8 \). In Figure 1(D), for \( T = 992 \) K, two basins are visible at HDL and LDL densities, respectively, in the low \( n \) region. Integrating over \( n \) (or \( n_{\text{max}} \)) will yield the contracted surface, i.e. the projection of the global \( Q_6 \) \( (32) \). Further, visit and excursion statistics from the parallel tempering swaps are also monitored to determine the efficacy of sampling. Free-energy estimates from the different bias windows and simulation conditions are reweighted using an in-house implementation of the weighted histogram analysis method \( (20, 36) \) to both obtain unbiased free-energy estimates and reweight across temperature and pressure. Errors are obtained by estimating the number of decorrelated samples based on the integrated autocorrelation time for the slowly relaxing variables, density, and \( Q_6 \) \( (19, 36, 37) \). Finally, this reweighting procedure is used to compare directly obtained free-energy profiles with those obtained by reweighting from other conditions, giving identical results (see Supplementary Material). This is a strong indication of converged, equilibrium sampling.

**Free-energy reconstruction from constrained sampling**

Free-energies are reconstructed, in the first instance, for systems of \( N = 512 \) atoms along the \( P = 0.75 \) GPa isobar. The size of the largest crystalline cluster, \( n_{\text{max}} \), is constrained within overlapping hardwall constraints \( [n^c, n^h] \), while the density is constrained with harmonic bias potentials. Parallel tempering swaps are performed between adjacent windows in \( n_{\text{max}} \), density, and temperature. Total simulation run lengths are in excess of \( 10^8 \) MC steps for each case (at all system sizes) and are compared to the autocorrelation time, number of swaps performed along each axis, and the mean duration required for parallel tempering swaps to "return" to the initial window (see Supplementary Material Figures S3 and S4).

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two-order parameter free-energy along the $\rho$ axis shown in Figure 1(B).

**Free-energy reconstructions at larger system sizes**

In Figure 2, we show the free-energy profile as a function of density along the $P = 0.75$ GPa isobar at different system sizes ranging from $N = 512$ to $N = 2000$. Convergence is monitored as discussed in the “Materials and methods” section (see Supplementary Material) by using S17, S18, and S19. Free-energy estimates at exact coexistence conditions are obtained by reweighting from the available data directly simulated at $P = 0.75$ GPa (see Supplementary Material). We note a slight shift (of $<3$ K) to higher temperatures for the coexistence conditions at larger system sizes, as also noted in (30). The coexistence temperature mentioned in Figure 2 is for $N = 512$.

The formation of a stable interface between two liquid phases will result in a scaling of the barrier height with $N$ as $N^{2/3}$ (19, 38). Results shown in the bottom inset in Figure 2 are consistent with this scaling with system size. Additionally, for the low-density phase to be a disordered phase, the degree of global orientational ordering should scale as $N^{-1/2}$ (17, 19). We find this to be the case from inspection of the top inset of Figure 2 where the error bars are obtained from the SD of $Q_6$ measured under the conditions and constraints specified (see also Supplementary Material Figure S20).

**Trends across other state points—absence of bi-modality beyond the critical point**

We perform USMC simulations constraining only the largest cluster size with a hardwall bias at conditions far from coexistence, where a single liquid phase exists. A set of overlapping bias windows is used to constrain $n_{\text{max}}$ and the density distribution is measured subject to a constraint on $n_{\text{max}} \leq 4$. Parallel tempering swaps across temperatures enhance the sampling of different values of density and convergence is monitored (see Supplementary Material, Figures S8, S9, S10, and S11). Away from coexistence this procedure gives quantitatively similar estimates of $\beta \Delta G(\rho)$ as the procedure where both $n_{\text{max}}$ and $\rho$ are constrained (see Supplementary Material Figure S12 and Supplementary Material text for details). We perform similar USMC computations (both variants) along the $P = 0$ GPa and $P = 1.5$ GPa isobars for a range of temperatures straddling the LLPT (see Supplementary Material Figures S13, S14, S15, and S16) as well as at a negative pressure of $P = -1.88$ GPa, which is in the supercritical region of the phase diagram reported in ref. (4). In this region, the extension of the LLPT line corresponds to a locus of maximum compressibility, also known as the Widom line (4, 39). No phase separation is expected to occur, though weak bi-modality in the density distribution may be observed at small system sizes when measured in close proximity to the critical point. One finds no indication of a double-well feature in the free-energy reconstructions along the $P = -1.88$ GPa isobar shown in Figure 3A suggesting a fully continuous change in the character of the liquid across the Widom line. From the equilibrium sampling distribution of the fraction of 4-coordinated (LDL-like) atoms, $\phi_4$ (see Supplementary Material), we extract the mean and standard deviation and plot $(\phi_4)$ as a function of temperature along isobars, as shown in Figure 3B. At coexistence conditions, the liquid is composed of equal fractions of LDL-like and HDL-like atoms, enabling an estimate of the LLPT temperature across which the fraction of 4-coordinated atoms changes

![Fig. 1. Panel (A) shows the free-energy barrier to crystal nucleation from NPT USMC simulations of $N = 512$ atoms at $P = 0.75$ GPa at the temperatures shown. The free-energy is obtained from the full cluster size distribution using $\Delta G(n) = -kT \ln(p(n))$ with the condition $\beta \Delta G(0) = 0$ fixing the value of the constant. The free-energy barrier is finite at all temperatures, with the height at the lowest temperature being 6 to 7 kBT. Panel (B) shows the free-energy as a function of density, obtained from the negative log of the contracted distribution defined in Eq. (1), from the same simulations. Errors are obtained from estimates of the number of decorrelated samples in each constrained simulation. The double well feature at $T = 992$ K is indicative of coexistence of the LDL (low-density state) and the HDL (high-density state). Panel (C) shows the free-energy from the joint distribution of density and cluster size at $T = 965$ K, $P = 0.75$ GPa. The liquid has a low density of 2.37 g cc$^{-1}$ even when the degree of crystallinity is zero. Contour lines are placed at the values mentioned in the legend. Panel (D) shows a two order parameter free-energy reconstruction zoomed into the low $n$ region, showing a bi-modal feature along density.

![Fig. 2. $\beta \Delta G(\rho)$ from USMC simulations at $T = 992$ K at $N = 512$, 800, 1000, and 2000 atoms. Density is sampled subject to the constraint on $n_{\text{max}}$. Error bars are a measure of the number of uncorrelated samples obtained for the free-energy calculation (see Supplementary Material). The bottom inset shows the height of the barrier as a function of system size. The barrier height scales as $N^{2/3}$, as expected when a stable interface can form between two phases. Error bars indicate the uncertainty arising from measurements at the bottom of the well and the top of the barrier and the variation in depth of the LDL basin and HDL basin. The top inset shows the scaling of average $Q_6$ with system size when measured in the low-density basin. The value of $Q_6$ decreases with $N$ as $N^{-1/2}$, demonstrating that the low-density phase is disordered. The error bars are the standard deviation obtained from the same samples.](image-url)
The LLPT line obtained by estimating the point of crossing \( s \) = 0.5 for each isobar, shown with symbols of the corresponding color. The LLPT line obtained from \( \sigma_A G(\rho) \) along each of the 3 isobars, \( P = 0 \) GPa, 0.75, and 1.5 GPa (see Supplementary Material for data at \( P = 0 \) and 1.5 GPa), is shown with violet diamonds. Estimates are found to be consistent with each other and with the equation of state data reported in (4).

**Comparison with analyses for other models**

Free-energy investigations of the LLPT for similar tetrahedrally ordered liquids have shown typical barriers of \( \sim 1 \) to \( 4 \) k\(_B\)T. While the barrier height increases with system size, performing constrained simulations at arbitrarily large system sizes is prohibitively expensive. For ST2 water, Palmer et al. (19) report a barrier height of \( \sim 4 \) k\(_B\)T with \( N = 192 \) molecules at conditions of coexistence far from the critical point. Poole et al. (44) have reported similar barrier heights earlier with \( N = 216 \) molecules. Simulations of silica by Chen et al. (21) have identified a barrier of less than \( 4 \) k\(_B\)T away from the critical point, but for a system size of \( N = 1500 \) atoms. Recent work with two variants of the TIP4P model (which also report analysis of critical fluctuations as belonging to the Ising universality class) has reported density histograms corresponding to a barrier height of less than \( 2 \) k\(_B\)T for \( N = 300 \) (20). The barrier heights we obtain of 0.8 k\(_B\)T for \( N = 512 \) and 1.9 k\(_B\)T for \( N = 2000 \) are thus comparable to these earlier reported values.

**Discussion**

In summary, we find through rigorous free-energy calculations and extensive analysis of the consistency of our results, that two well-defined metastable liquid states, with corresponding free-energy minima, exist in supercooled SW silicon. Coexistence conditions are identified in the subcritical part of the phase diagram that are in agreement with estimates reported previously from equation of state studies. At each of the state points considered, a clear and significant free-energy barrier to crystal nucleation is observed, ruling out the possibility that the low-density liquid is a transient artifact resulting from slow, spontaneous crystallization. At several state points [in particular \( T = 965 \) K, \( P = 0.75 \) GPa shown in Figure 1(C)] we observe a free-energy minimum corresponding to the low-density liquid phase, with a large fraction of tetrahedrally coordinated atoms and zero crystallinity, decisively
Fig. 4. Negative log of the distribution of density and potential energy per atom obtained subject to the constraint of $n_{\text{max}} \leq 4$ along the $P = 0.75$ GPa isobar at five temperatures, $T = 965$ K (A), $T = 975$ K (B), $T = 985$ K (C), $T = 992$ K (D), and $T = 1005$ K (E). Data are obtained from NPT USMC simulations of $N = 512$ atoms. The two liquid phases differ both energetically and in density. Panel (F) shows a comparison of the distribution of the field-mixing order parameter with the reference Ising 3D distribution at the critical point. The critical point and the field mixing coefficient, $s$, are estimated by iteratively reweighting free-energy estimates, obtained directly from umbrella sampling simulations at $P = 0$ GPa, to different $T, P$, and minimising the difference between $P(M)$ and $P_{\text{ising}}(M)$ (see Supplementary Material), where $M = \rho + sE$ is rescaled to have unit variance. The estimate of the critical point obtained from this procedure is $T_c = 1085.5$ K, $P_c = 0.5$ GPa, ruling out the slow crystallization scenario. The free-energy barrier between the two liquids is found to scale with the size of the simulated system—an important test of the presence of a first-order transition. Reweighting of free-energy profiles across conditions results in identical results, providing a strong test of converged equilibrium sampling. We also find that the same analysis finds no evidence of phase separation when performed along an isobar in the super-critical region of the phase diagram, also consistent with the two-critical point scenario (4, 9). We note that the density difference between the two liquids is small and remains small as distance from the critical point increases, in contrast to the case of other similar network-forming liquids such as ST2 water (19, 44) and WAC silica (21, 22). Given the low barriers to crystallization for silicon under these conditions and the small difference in the densities of the two liquid phases, the barrier separating the two phases is expected to be small. However, the scaling of barrier height with system size shown here confirms the existence of two well-defined metastable liquid phases. The barrier heights are of comparable order to these and to other cases such as ST2 water (19, 44), TIP4P water (20), and silica (21). The two liquid states do not differ in density alone, as shown by a free-energy reconstruction along two order parameters, density and potential energy per atom, subject to the constraint of low $n_{\text{max}}$. These point to the interplay of energy and entropy in driving the transition, as discussed in the context of other liquids showing a LLPT. Our work thus provides a comprehensive analysis that resolves the long-standing debate concerning the existence of a liquid–liquid transition in supercooled SW silicon. Taken together with the simulation investigations in the case of water and silica, and experimental results concerning water and silicon, there is now a preponderance of evidence in support of LLPTs in pure substances.

Materials and methods

Interaction potential and simulation protocol

We use the classical three-body SW potential to model silicon (18). Parametrization is shown in Supplementary Material Table S1. Monte Carlo simulations are performed in the NPT ensemble. Enhanced reversible sampling is achieved by using the umbrella sampling scheme (31). An in-house code with an efficient double-sum implementation (45) of the three-body SW potential was used for the USMC simulations. The bias variables are the size of the largest crystalline cluster, $n_{\text{max}}$, and the density $\rho$. A hard wall bias (which is zero within prescribed limits and infinite outside) is used to constrain the $n_{\text{max}}$ values as used in refs. (24, 29) and a harmonic bias constrains the density. Parallel tempering swaps are performed across temperature, $n_{\text{max}}$ bias, and density bias windows. In simulations where only $n_{\text{max}}$ is constrained, far from coexistence conditions, parallel tempering swaps are only performed across temperature and $n_{\text{max}}$ bias windows. Swaps are performed between adjacent windows in $n_{\text{max}}$, density and adjacent temperatures every $2 \times 10^5$ MC steps, $10^5$ MC steps, and $2 \times 10^3$ MC steps, respectively. Convergence is determined by monitoring the decay of the time-autocorrelation functions of the density and of the global bond orientational order parameter, $Q_6$ (32). These are found to decay in less than $\tau \sim 10^5$ to $10^6$ MC sweeps at all conditions and system sizes considered. Simulations lengths...
exceed $10^8$ MC steps at all the conditions studied, with histograms sampled over $\sim 100$ to $200r$ for each window. Statistics of traversal due to parallel tempering swaps are also used to determine adequate sampling. More than $10^4$ parallel tempering swaps are performed in each direction, with observed mean return times being $\sim 10^4$ to $10^6$ MC steps for simulations in each window. The return time is the number of MC steps before a simulation returns to its initial temperature or bias potential after being swapped out as a result of the replica exchanges. Further details on the umbrella sampling and parallel tempering scheme are provided in the Supplementary Material.

**Defining atom types**

Bulk crystalline atoms are identified as those with high degree of local tetrahedral ordering and also surrounded by similarly tetrahedrally ordered atoms. We use the cut-offs described in the Supplementary Material and also in (24, 35, 46) (see Supplementary Material Figure S1). The local order is identified by using the local bond orientational order for each atom, $q_3(i)$. Neighbouring atoms with correlated neighbourhoods are said to be “bonded”, with the correlation function used being $q_3(i)q_3(j)$. Atoms bonded to three or more neighbors are defined as bulk crystalline atoms. A 4-coordinated or “LDL” atom is identified as one with high local $q_3$ but bonded to fewer than three of its neighbors. The fraction of such 4-coordinated liquid-like atoms, $\phi_4$, is also used to estimate coexistence conditions. At coexistence, the fraction of such 4-coordinated atoms in LDL-like local structures is expected to be $\sim 0.5$ (40, 42). The details of the cut-offs used and the relevant distributions are shown in the Supplementary Material.

**Free-energy as a function of cluster size and density**

We measure the unbiased probability of observing a cluster of size $n$ in the liquid at density $\rho$ and take the negative log to obtain a free-energy as shown below:

$$\Delta G(n, \rho) = -k_B T \ln(P(n, \rho)). \quad (2)$$

To obtain this, one is required to obtain the following equilibrium probability distribution:

$$P(n, \rho) = \frac{1}{\tau_T} \sum_{t=0}^{\infty} N(n, t) \rho(t) \rho(\rho(t) - \rho) \quad if \quad n_{\max}^l \leq n \leq n_{\max}. \quad (3)$$

Sampling is performed in the biased ensemble and we use the iterative scheme of the weighted histogram analysis method (36, 37) (described in the following section) to obtain the unweighted, normalised distribution, $P(n, \rho)$ from which we obtain the free-energy surfaces shown in Figures 1(C) and (D). Note that the contracted free-energy surface in Figures 1(B) and 4(A to E) are obtained by first constructing the unbiased estimate for $P(n_{\max}, \rho)$ from free-energy reweighting. Then the contracted free-energy, $\beta \Delta G(\rho)$, is obtained by summing $P(n_{\max}, \rho)$ up to the chosen largest value of $n_{\max}$ and taking the negative logarithm (see Eq. 1).

**Reweighting and stitching free-energy surfaces**

For umbrella sampling runs with two order parameters, we employ an in-house code that implements the self-consistent iterative scheme of the WHAM equations (36, 37) (see Supplementary Material Figure S2 and Supplementary Material text for details). Errors are estimated from the number of decorrelated samples and the integrated autocorrelation times. Tests for thermodynamic consistency are performed by comparing reweighted estimates of the free-energy to directly measured estimates at different conditions (see Supplementary Material Figure S5, S6, and S7). For single order parameter umbrella sampling simulations only the largest cluster size is constrained with parallel tempering across temperatures enhancing sampling of density (see Supplementary Material). The two methods agree quantitatively for conditions far from coexistence, whereas only the full two-order parameter US simulations give reliable results at or near coexistence conditions (see Supplementary Material for details).

**Critical fluctuations of the order parameter**

We investigate whether the liquid–liquid critical point belongs to the 3D-Ising universality class by comparing the probability distribution of the relevant order parameter with the reference distribution for the 3D-Ising model. In the case of the Ising model, the magnetisation, $M$, undergoes critical fluctuations in the vicinity of the critical point. In the case of the LLPT, the relevant order parameter is a linear combination of density and the potential energy ($\rho + sE$) (30). The following general expression is found to be a good approximation to the distribution of $M$ (43)

$$P_{\text{sing}}(M) \propto \exp\left\{-\left(\frac{M^2}{M_0^2} - 1\right)^2 \left(\frac{\rho}{\rho_0} + c\right)^2\right\}. \quad (4)$$

The appropriate choice of constants yields a distribution of unit variance (see Supplementary Material for details). The distribution of the order parameter, $M = \rho + sE$, is expected to match the reference distribution at the critical point. The critical point is identified by finding the optimal set of $T_c$, $\rho_c$, $s$ that minimizes the root-mean-squared error of $P(M)$ with respect to $P_{\text{sing}}(M)$ (see Supplementary Material for details). This procedure gives both an estimate of the critical point as well as the field-mixing parameter, $s$.

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**Supplementary Material**

Supplementary material is available at PNAS Nexus online.

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Authors’ Contributions
Y.G. and S.S. designed the research; Y.G. performed the research; Y.G. and S.S. analyzed the data; and Y.G. and S.S. wrote the paper.

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Data Availability
All data are included in the manuscript and/or supplementary Material.

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