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Structural Order as the Key Phase Indicator in Supercooled Liquid Water

Kwang Kim

kimks@unist.ac.kr

Ulsan National Institute of Science and Technology https://orcid.org/0000-0002-6929-5359

Saeed Pourasad

Ulsan National Institute of Science and Technology

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Abstract

The phase behavior of supercooled water and the nature of its second critical point remain long-standing open questions. Using molecular dynamics simulations and enhanced sampling techniques, we demonstrate that the first-order liquid-liquid phase transition in supercooled water arises from structural reorganization between high-order and low-order liquid states, rather than density variations as traditionally assumed. Near 238K, this transition occurs with negligible density contrast, indicating that molecular geometry is the primary driver. As temperature decreases, these structural changes extend beyond the first coordination shell, and below 205K they progressively lead to more pronounced density differences. This challenges the conventional emphasis on density as the defining metric for liquid polymorphism, highlighting structural order parameters as the key indicator of phase behavior. Our findings provide a precise estimate of water's second critical point, closely aligning with experimental observations and offering a unifying framework for understanding water's anomalies in the deeply supercooled regime.

Introduction

Water, renowned for its complex and unusual behavior, stands apart from conventional liquids because of its unexpected unique properties. These anomalies have created a scientific enigma that has fascinated researchers for decades[1-4]. Since Poole *et al.* introduced the concept of a liquid-liquid phase transition (LLPT) and proposed the existence of a second critical point within the supercooled region[5], extensive research has largely validated this pioneering idea[5-36]. However, pinpointing the exact location of the second critical point and elucidating the precise mechanism behind the LLPT in water have remained significant challenges. The prevailing paradigm has classified the phases in the LLPT as high-density liquid (HDL) and low-density liquid (LDL), implying that density is the primary order parameter.

As a pivotal experimental work, Mishima proposed a location for the liquid-liquid critical point of water at a temperature of T = 230±5K and pressure P = 50±20 MPa[8]. More recently, Kim *et al.* provided experimental verification of the LLPT in bulk supercooled water under pressure, revealing structural changes at 205 K that suggest a discontinuous LLPT[34]. Meanwhile, computational studies using various water models have predicted critical points at slightly different temperatures, with continuing debate about the exact location and nature of the transition[10,25,35,55].

A fundamental question remains unanswered: What is the primary driving force behind the LLPT? While density differences have been the traditional focus, recent evidence suggests that structural reorganization might play a more fundamental role than previously recognized. In this study, we challenge the density-centric paradigm by demonstrating that structural reorganization between high-order liquid (HOL) and low-order liquid (LOL) states precedes and drives density changes. This revelation requires a fundamental rethinking of how we characterize and understand phase transitions in water.

Through complementary enhanced sampling techniques—generalized replica exchange (gREM)[38] and well-tempered metadynamics (WTMetaD)[39], we provide compelling evidence that the order parameter governing the LLPT is primarily structural rather than density-based. We determine that the critical temperature for this transition is 238K at density ρ = 1.0 g/cm³, closely aligning with experimental findings. Furthermore, we demonstrate that significant density contrast between the coexisting phases only emerges at temperatures below 205K, when structural differences have already become pronounced.

Results

To investigate the nature of phase transitions in supercooled water, we performed molecular dynamics simulations using the LAMMPS package[40] with the TIP4P/2005 water model[37], employing systems of varying sizes (N = 512, 1024, and 1620 molecules) to ensure robust results.

Figure 1 illustrates three complementary approaches to characterize structural transitions in supercooled water at constant temperatures (T = 225K and 215K) under varying pressures. The angular distribution function $P(\theta)$, which is the probability density at angle θ between the oxygen atom of a central molecule to two oxygen atoms among 4 neighboring molecules (Fig. 1**a**-**b**) captures the correlation between the directions of neighboring oxygen atoms, providing insight into the relative orientation of water molecules. The plots reveal a sharp change in the angular distribution with increasing pressure, signifying a pressure-induced reordering of water molecules. This sudden shift underscores the sensitivity of local molecular geometry to pressure variations near the transition region. The orientational tetrahedral order (OTO) parameter[41] q is defined as

$$q = 1 - \frac{3}{8}\sum_{i=1}^{3}\sum_{j=i+1}^{4}\left(\cos\theta_{ij} + \frac{1}{3}\right)^2$$

where θ_{ij} is the angle between the bonds connecting a central atom to its four nearest neighbors and the sum runs over all six unique pairs of the four neighbors. It quantifies the degree of how well a given set of particles conforms to an ideal tetrahedral geometry. Here, once each particle is represented by oxygen atom of each water molecule, q measures how closely a water molecule and its nearest neighbors form a perfect tetrahedral arrangement (Fig. 1c). The value of q ranges from 0 to 1, where: $q = 1$ indicates a perfectly tetrahedral structure and $q = 0$ corresponds to a completely disordered, ideal-gas-like arrangement. A clear difference in q marks the transition between two states with distinctly different tetrahedral ordering. This abrupt change highlights the structural reorganization that occurs with small pressure changes, emphasizing the role of tetrahedral order in driving the transition. The oxygen-oxygen structure factor of $S_{OO}(k)$[14,42] with respect to wavevector k, describes spatial correlations between oxygen atoms, with peaks indicating characteristic molecular ordering. The plot (Fig. 1d) shows distinct differences in the molecular arrangement between two slightly different pressures, particularly around q

~ 1.8 ⍰⍰ 3.2 Å⁻¹ region. These changes reinforce the structural transitions observed in the angular distribution and tetrahedral order, confirming the emergence of distinct liquid states across different pressures.

All results presented in Fig. 1 were obtained from simulations equilibrated for 300 ns with a 1 fs time step, followed by an additional 10 ns equilibration using a finer 0.1 fs time step to ensure accurate sampling of the structural properties. The pronounced changes in these structural metrics at small pressure differences provide compelling evidence for a structural transition.

The observed structural reordering in water at T = 225K and 215K raised a critical question: Is this phase transition first-order, or is it continuous (second-order transition), potentially reflecting the behavior in the Widom line region[43]? To address this, we employed the generalized replica exchange method (gREM), a powerful enhanced sampling technique well-suited for detecting first-order transitions. In first-order phase transitions, a key signature is the presence of a convex dip in the microcanonical entropy, S(E), which gives rise to a region with a negative slope in the statistical temperature, often referred to as "back-bending" or an "S-loop":

$$\mathrm{T_S}\left(\mathrm{E}\right) = \left(\partial\,\mathrm{S}/\partial\,\mathrm{E}\right)_{\mathrm{V}}^{-1}$$

We conducted NVT gREM simulations with multiple replicas[47,48] and computed T_s(E) from replica potential histograms using the statistical temperature weighted histogram analysis method (ST-WHAM)[49].

Figure 2a shows the statistical temperature T_s(E) for the TIP4P/2005 water model from NVT simulations (N = 1024, ρ = 1.0 g/cm⁻³). Below 238K, the T_s(E) curve exhibits characteristic back-bending behavior, a definitive signature of a first-order phase transition. In this regime, the curve contains two regions with positive slopes (representing stable states) separated by an unstable branch with a negative slope. The turning points of this curve mark the spinodals of the two coexisting phases, and the energy difference between the spinodals grows as temperature decreases, reflecting increasing structural differences between the phases.

Above 238K, the back-bending behavior disappears, and the T_s(E) curve shows a smoother, continuous transition. This behavior reflects a gradual structural transformation within the system, with no sharp boundary between states. As temperature increases further, beyond approximately 258K, this gradual transition vanishes entirely, and the T_s(E) curve becomes nearly linear, indicating the absence of significant structural differentiation.

To analyze the nature of these transitions more rigorously, we examined the monotonic behavior of $\beta\ \left(\mathrm{E}\right) = 1/\mathrm{T_S}\left(\mathrm{E}\right)$ through its derivative with respect to energy, γ(E)=dβ(E)/dE=d^2S/dE^2, which provides a clear classification scheme for transitions in finite systems[50]. Figure 2b depicts the inverse temperature and its derivative as functions of energy per particle at temperatures higher and lower than

238K. At T > 238K (top graph), the slope of the corresponding inflection point of β(E) at E = E_{tr} is negative. Due to the monotonic temperature curve, a unique correspondence between β and E exists, with no coexistence or latent heat between phases. Such transitions can be categorized as second-order[24], implying system heterogeneity due to a continuous transition—strong evidence for the existence of the Widom line in this region.

At temperatures below 238K (middle graph), $\gamma_{tr} = \gamma(E_{tr}) > 0$; the inverse temperature curve is non-monotonic, and there is no unique correspondence between β and E. Physically, both phases coexist in the transition region[51,52], confirming a first-order transition. The back-bending $T_s(E)$, the Maxwell construction, and the Van der Waals loop are presented in Fig. 2c. Figure 2d presents the total energy autocorrelation functions of various walkers (red) and replicas (blue) corresponding to one of the curves shown in Fig. 2a, demonstrating proper sampling and convergence of our simulations.

These results identify 238K as the critical temperature at which the transition changes from first order to continuous, corresponding to water's second critical point. This temperature aligns remarkably well with experimental studies showing that the isobaric heat capacity (C_p) maximum—a reliable indicator of the critical temperature—occurs near 229K[2–4]. Similarly, Mishima reported the second critical point of water at T = 230 ± 5K[8, 27,53]. The slight difference between our prediction (238K) and experimental values can be attributed to the inherent limitations of the classical TIP4P/2005 potential and differences in pressure conditions.

Unlike other materials exhibiting liquid-liquid phase transitions, such as silicon[56], water shows a weakening of the link between structural reordering and density changes under certain thermodynamic conditions. To determine the temperature at which the density difference between the two states becomes evident[34], we applied WTMetaD using the system volume as the collective variable at T = 215K and T = 205K.

To determine the temperature at the inflection point, where the density difference between the HOL and LOL, resulting from the propagation of structural reordering beyond the first coordination shell, becomes more pronounced, we selected temperatures below T = 215K, starting with T = 205K.

Figure 3 presents the Q_6 order parameter results at both temperatures, including time evolution and 2D probability density histograms as a function of energy. At T=215K (Fig. 3**a**), the transition between structurally distinct states is evident but less sharp, with some overlap between high-order and low-order states. In contrast, at T = 205K (Fig. 3**b**), the Q_6 transition is more pronounced, with better-separated states, highlighting that structural order differences become increasingly distinct as temperature decreases.

These graphs, presented with a 10 K temperature difference, show that the less ordered state grows more rapidly than the more ordered state. This low-ordered state, which can be referred to as the high-density state starting from T = 205 K, begins to emerge at temperatures below 238 K. As the temperature

decreases and pressure increases, this state grows, disrupting the overall arrangement of water molecules and making the density differences more pronounced.

Figure 4a illustrates the volume evolution at T = 205 K, which is further represented as a 2D histogram of volume versus energy in Fig. 4b. The plot reveals fluctuations between two distinct states, each exhibiting a notable volume difference, which in turn highlights the density contrast between two states. The angular distribution function (Fig. 4c) shows a significant increase in the difference between the HOL and LOL, which is clearly reflected in the density variation. These results suggest that while density changes are associated with the transition, they are secondary to the molecular rearrangement. This reinforces the notion that structural order is a more reliable indicator of phase behavior than density. Remarkably, even at T = 205K, the density difference between the two states remains relatively small (approximately 0.98 and 1.03 g/cm³) with overlaps showing less clear distinction between the two states. This highlights that the LLPT in water is fundamentally different from conventional phase transitions where density plays the primary role.

Conclusion

Our comprehensive study using complementary computational approaches provides a coherent picture of the liquid-liquid phase transition in supercooled water. We demonstrate that the primary driver of this transition is structural reorganization between high-order and low-order liquid states (HOL-LOL), not density differences as traditionally assumed in the HDL-LDL framework. At temperatures near the critical point (238K), the transition between HOL and LOL occurs with negligible density differences, challenging the conventional density-based classification. As temperature decreases to approximately 205K, structural differences propagate beyond the first coordination shell, eventually leading to more pronounced density contrasts[57]. This finding aligns with experimental observations of the LLPT in bulk supercooled water under pressure[34], where significant density differences were observed at 205K.

The precise identification of the critical temperature at 238K using the gREM approach represents a significant advancement in our understanding of water's phase behavior. This temperature, where the transition changes from first-order to continuous, marks the location of water's second critical point and agrees remarkably well with experimental estimates of 230±5K[8].

The distinct weakening of the link between structural reordering and density under certain thermodynamic conditions in water's LLPT is particularly noteworthy. Unlike conventional phase transitions driven by density differences, water's LLPT initially manifests as a purely structural transformation, with density differences emerging only at lower temperatures. This behavior arises from water's unique molecular geometry and hydrogen-bonding network, which allow significant orientational rearrangements without requiring a corresponding collapse or expansion of its molecular framework.

Methods

Simulation Model

We performed simulations using the TIP4P/2005 water model[37], a re-parametrized version of the 'classical' TIP4P model known for its exceptional reliability in capturing various experimental characteristics of water.

Molecular Dynamics Simulations

We conducted molecular dynamics simulations using the LAMMPS[40] package, employing both the isothermal-isochoric (NVT) and the isothermal-isobaric (NPT) ensembles. We utilized the Verlet integrator with a time step of 1 fs (and 0.1 fs for figure 1). Electrostatic interactions were computed using the Particle-Particle Particle-Mesh (PPPM) method with a real space cutoff distance of 1.2 nm. The same cutoff was applied for van der Waals interactions. For temperature and pressure control, we employed the Nosé–Hoover thermostat and barostat. Cubic systems with periodic boundary conditions of sizes N=512, 1024, and 1620 molecules were studied to ensure system-size independence of our results.

Generalized Replica Exchange Method

The gREM is specifically designed for simulating systems undergoing first-order phase transitions by introducing a generalized temperature function that allows efficient sampling across energy barriers. In this approach, 16 generalized replicas of water molecules (N=1024) at a density of $\rho = 1.0\ g/cm^3$ were utilized. Swap attempts between adjacent ensembles occurred every 1000 timesteps. Each production run spanned 60-80 ns, with potential energies sampled every 10 timesteps for subsequent analysis using the statistical temperature-weighted histogram analysis method (ST-WHAM)[49] (for full details please refer to the S.I).

Well-Tempered Metadynamics

WTMetaD enhances sampling by adding history-dependent bias potentials to accelerate rare-event transitions. For our simulations, we updated the bias factor, increasing it from 6 to 11 and a Gaussian height of 0.2 $k_B \cdot T$, with the Gaussian width estimated from unbiased simulations of volume fluctuations. This approach allowed us to efficiently explore transitions between structurally different states and calculate free energy profiles as a function of both structural order parameters and volume (for full details please refer to the S.I).

Declarations

Competing Interests

The authors declare no competing interests.

Author Contributions

S.P. performed all simulations and wrote the manuscript. K.S.K. supervised the project.

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Data Availability

All data generated or analyzed during this study are included in this published article and its supplementary information files. Additional data are available from the corresponding author upon reasonable request.

Code Availability

Custom codes used for analysis in this study are available from the corresponding author upon reasonable request.

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