Thermodynamic Anomalies in Stretched Water

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ABSTRACT: Via molecular dynamics simulations of the TIP4P/2005 water model, we study liquid water’s anomalous behavior at large negative pressure produced through isochoric cooling. We find that isochores without a pressure minimum can display "reentrant" behavior whereby a system that cavitates upon cooling can then rehomogenize upon further cooling. This behavior is a consequence of the underlying density maximum along the spinodal, but its actual manifestation in simulations is strongly influenced by finite size effects. These observations suggest that water under strong hydrophilic confinement may display richer phase behavior than hitherto assumed. This also suggests that propensity toward cavitation does not always correlate with greater tension, contrary to the prevailing assumption for interpreting water stretching experiments. We also show that a maximum spinodal density in water results in a locus of maximum compressibility and a minimum speed of sound that are independent from any in pressure.

I. INTRODUCTION

Liquid water is often described as anomalous because its behavior frequently departs from that of conventional “simple” liquids. Examples of water anomalies include a temperature of maximum density (TMD) and increases in thermodynamic response functions (e.g., isothermal compressibility $\kappa_T$ and isobaric heat capacity $C_V$) upon isobaric cooling. While departures from simple liquid behavior are certainly not unique to water, the plethora of such deviations makes this substance an extraordinary simple liquid behavior are certainly not unique to water, the abundance of work on water at positive pressure, this region is rather vast, as the strong degree of cohesion a liquid spinodal at its pressure minimum. While thermodynamic arguments make a retracing spinodal at positive pressures problematic, there is still much interest in characterizing whether the TMD increases with decreasing pressure or eventually retraces to lower temperatures. Note that a retracing spinodal is possible for single component substances that contain a second, low-temperature liquid/gas critical point and a negatively sloped liquid/gas coexistence locus at low temperature, which exist in some computational models of patchy colloids.

The two most frequently invoked interpretations of water anomalies in the supercooled region are the second critical point hypothesis and the singularity-free scenario. The former posits the existence of a liquid–liquid phase transition (LLPT) between high- and low-density liquids (HDL, LDL) that terminates at a liquid–liquid critical point (LLCP) deep in the supercooled region. Water’s anomalies are then consequences of being supercritical with respect to this second critical point. The singularity-free scenario shows that an increase of thermodynamic response functions upon cooling is a thermodynamic necessity for a liquid with a negatively sloped TMD in the pressure–temperature ($P-T$) plane. Note that this scenario is also equivalent to the existence of an LLCP at zero absolute temperature.

Both scenarios predict a locus of extrema in thermodynamic response functions with respect to temperature along isobars,
which in the case of the second critical point hypothesis are often called Widom lines. The loci of response function extrema become arbitrarily close to each other upon approaching the critical point,12,22 and hence, a common term is often used to refer to all such lines. Recent proposals12,22 suggest that defining the Widom line as the locus along which there is a 1:1 ratio of HDL:LDL-like water molecules provides less ambiguity. We adopt this usage here (see section VI) and clarify when discussing studies where the authors refer to the locus of extrema of a thermodynamic response function as the Widom line. Computational studies routinely observe such extrema in molecular models of water.12,21 However, only an increase upon isobaric cooling, without extrema, is observed experimentally.1,2 This may be because at ambient and elevated pressures such extrema are below the temperature limit determined by homogeneous ice nucleation in a region often referred to as “no man’s land.” A recent study has suggested that the line of maximum compressibility emerges from no man’s land at negative pressure, suggesting that the doubly metastable regime (i.e., metastable to cavitation and to crystallization) may provide fresh insights into the anomalous behavior of liquid water.8 In addition, experiments on supercooled water confined in silica nanopores, which suppresses crystal nucleation, may require reinterpretation if the recent suggestion that such water is in fact under considerable tension proves to be correct.23

Here, we employ molecular dynamics to study the thermodynamic behavior of water under strongly stretched conditions, produced through isochoric cooling. In section II, we revisit water’s phase diagram in the temperature—density ($T$–$ho$) plane and highlight the fact that the shape of the liquid binodal and spinodal allow for isochores to exhibit “reentrant” phase behavior, whereby a system that cavitates upon isochoric cooling can then rehomogenize upon further cooling. In addition, isochores have a temperature of maximum propensity toward cavitation in the metastable region. Section III briefly describes the computational methods employed in this study. In section IV, we demonstrate that, in the TIP4P/2005 water model, isochores without a TMD can exhibit reentrant phase behavior, suggesting that greater tension along an isochore does not necessarily imply a greater propensity toward cavitation, as has been assumed in the interpretation of water stretching experiments.7,11 Such behavior displays appreciable finite size effects and suggests that water may display richer phase behavior under hydrophilic confinement than previously assumed. We then show in section V that a maximum propensity toward cavitation can result in extrema in the compressibility and the speed of sound that are independent of any signatures of an LLCP emanating from elevated pressure. Finally in section VI, we show that structural signatures of an LLCP do extend to deeply negative pressure, however they are only observed upon sampling water’s potential energy landscape. Section VII contains concluding remarks as well as suggestions for further study.

II. WATER’S $T$–$ho$ PHASE DIAGRAM

Figure 1 contains a schematic of water’s liquid/vapor phase boundaries in the temperature-density ($T$–$ho$) plane, including its metastable low-temperature extension. The feature in this plot that serves as the focal point for much of the following discussion is that the liquid binodal exhibits a maximum density $\rho_{\text{binodal}}^\text{max} \sim 4$ °C in real water). A $\rho_{\text{binodal}}^\text{max}$ in water has been known for a long time26 and is reproduced in both theoretical descriptions27,28 and simulations of molecular models of water.23,25 In addition, the supercooled metastable branch of the liquid binodal and cavitation lines (the kinetic spinodal) have also recently been reported.11

Water with $\rho > \rho_{\text{max}}$ is never thermodynamically favored to cavitate. Below $\rho_{\text{max}}$, the equilibrium liquid can be subdivided into two portions: a high-$T$ and a low-$T$ region (see Figure 1). In the former, the liquid becomes metastable with respect to the vapor upon isochoric cooling; in the latter, it does so by isochoric heating. A range of isochores below $\rho_{\text{max}}$ can exhibit “reentrant” behavior whereby upon cooling the system would phase separate and then rehomogenize upon further cooling (assuming crystallization is avoided). In fact, homogenization upon cooling as well as cavitation upon heating have been directly observed in synthetic quartz inclusions.11 The density range over which separate stable liquid branches exist in water is rather narrow and has been exaggerated in the figure for clarity. We stress that the low-$T$ region, while stable with respect to cavitation, is largely metastable with respect to crystallization.

A consequence of $\rho_{\text{max}}$ is a maximum spinodal density $\rho_{\text{spinodal}}^\text{max}$ and liquid water above $\rho_{\text{spinodal}}^\text{max}$ is never thermodynamically unstable (as opposed to metastable) with respect to the vapor. We are not aware of any model with a $\rho_{\text{spinodal}}^\text{max}$ in the absence of a $\rho_{\text{spinodal}}^\text{max}$ and numerous studies suggest that both exist for liquid water.1,23,27,28 A $\rho_{\text{spinodal}}^\text{max}$ means that isochores above this density contain a point which is “closest” to the spinodal, resulting in a temperature of maximum propensity toward cavitation.

The method that has been shown to produce the highest tensions in liquid water is isochoric cooling. In order to develop tension this way, the liquid must have a positive coefficient of thermal expansion, which in the case of water, requires that temperatures not be too low. Using a microscopic Berthelot tube,23 water trapped in tiny mineral inclusions develops tension as it is cooled isochorically, with tensions up to $-140°C$.
MPa reported. The exact pressures achieved remain uncertain because their determination often requires extrapolation of a given equation of state (e.g., IAPWS-95). A more accurate method employs thermodynamic integration using the speed of sound.

The pioneering work of Angell and co-workers on water at negative pressure in quartz inclusions noted that a particular isochore would "nucleate randomly in the range 40–47 °C and occasionally not at all." In subsequent work, Caupin and co-workers studied a single isochore that exhibited a temperature with a minimum free energy barrier to cavitation $T_{\text{min}}$. Both cases were interpreted as the consequence of a TMD, as isochores will exhibit a minimum in pressure (i.e., largest tension) at such a point. The assumption in this case is that along an isochore, a more stretched liquid is more prone to cavitate. While $T_{\text{min}}$ does not exactly coincide with the TMD, due to the temperature variation of surface tension, the existence of $T_{\text{min}}$ is described as being the result of a pressure minimum along an isochore. In section IV, we present the results of molecular dynamics simulations of TIP4P/2005 water, (generally considered the most accurate classical model of water) that suggest that a larger tension in liquid water does not necessarily imply it is more prone to cavitate.

III. METHODS

Molecular dynamics simulations were performed using the GROMACS 4.6.5 simulation package. For the equation of state computation (Figure 2), we simulated 4000 water molecules interacting via TIP4P/2005 potential in the NVT ensemble. SETTLE was used to constrain the covalent bonds in water molecules. Depending on the temperature, the simulation times varied from 10 ns to 2 μs. To compute thermodynamic response functions (Figure 3), we simulated 500 water molecules in both the NVT and NPT ensembles, and the simulation times varied between 20 ns to 4 μs.

Throughout the study, we employed a 2 fs time step. Temperature was maintained using a Nose–Hoover thermostat with a 0.2 ps time constant, and pressure was controlled using Parrinello–Rahman barostat with a 2 ps time constant. Periodic boundary conditions were applied in all three dimensions in a cubic simulation cell. The short-range interactions were truncated at 0.95 nm, and long-range dispersion corrections were applied for both pressure and energy. Long range electrostatic terms were computed by using particle mesh Ewald with a grid spacing of 0.12 nm.

IV. ISOCHORES OF TIP4P/2005 WATER

Figure 2 shows the pressure–temperature equation of state for isochores ranging from 0.840 to 0.920 g/cm$^3$. Isochores with $\rho \geq 0.890$ g/cm$^3$ exhibit no phase transitions. In addition, a pressure minimum (i.e., a TMD), observed at $\rho = 0.900$ and 0.920 g/cm$^3$, disappears at lower densities. In fact, $\rho = 0.900$ g/cm$^3$ exhibits a maximum in pressure around 230 K, indicating a temperature of minimum density, a feature seen in several molecular models of water but has not been observed experimentally in bulk water. For $\rho \leq 0.885$ g/cm$^3$, cavitation occurs as the liquid cools, resulting in a phase-separated system. For $\rho = 0.885$ and 0.880 g/cm$^3$, lowering the temperature of the two-phase system results in spontaneous homogenization to a single liquid phase, consistent with the reentrant coexistence line and spinodal shown in Figure 1. Note that these isochores do not contain a TMD, meaning that reentrant behavior is not simply the consequence of a minimum pressure. For isochores below 0.880 g/cm$^3$, we no longer observe spontaneous homogenization upon cooling on the simulation time scales employed here. However, homogeneous systems launched at low temperature are kinetically stable and only spontaneously cavitate upon heating.

Isochores that homogenize upon cooling exhibit hysteresis upon heating, a feature indicative of a first-order phase transition. Upon further heating of the two-phase system, we observe homogenization without any hysteresis, which is likely a result of our coarse temperature resolution and long equilibration times. However, this still suggests that the temperature range that separates the high temperature homogeneous and cavitated states (e.g., between 320 and 330 K for $\rho = 0.885$ g/cm$^3$) contains a temperature where a first-order phase transition occurs.

A key observation is that isochores that rehomogenize produce a low-T liquid that is more stretched than the corresponding high-T liquid. The difference between the most stretched liquid on the high-T branch and the least stretched liquid of the low-T branch is significant: 58 MPa for $\rho = 0.885$ g/cm$^3$ and 103 MPa for $\rho = 0.880$ g/cm$^3$. The highest liquid tension, achieved by preparing a low-temperature homogeneous sample at $\rho = 0.860$ g/cm$^3$ and $T = 210$ K, is ~340 MPa (see Figure 2), a value more than double the limiting tensions that have been reported in the literature and in theoretical predictions. The difference between this extreme value and the tension at which this isochore initially cavitated upon cooling from much higher temperature (see Figure 2) is roughly 200 MPa.

An outstanding issue to reconcile at this point is that a bulk liquid under tension is never stable with respect to a vapor. However, we have shown that a range of low-density isochores contain two temperatures corresponding to a first order phase transition, both occurring at negative pressure. Thus, both the high and low temperature phase transitions observed along isochores (Figure 2), although originating in the reentrant behavior permitted for a range of isochores due to a TMD, cannot be strictly interpreted solely in terms of water’s phase diagram (Figure 1). Evidently, the finite system size constrained to fixed volumes allows for such behavior. Since both of these...
temperatures correspond to states of tension (see Figure 2), neither can correspond to equal chemical potential between liquid and vapor. Rather, they mark a point of equal Helmholtz free energy between two systems under different tensions: a homogeneous liquid and a system that contains a bubble for a collection of 4000 water molecules at the same temperature and overall density.

A likely explanation for the existence of such transitions under tension is a marked influence of interfacial effects. The thermodynamic contributions of interfaces are known to shift phase boundaries or promote new phases for small and confined systems.41–47 The relative thermodynamic cost of forming a new interface (especially for water) is formidable for small systems. Thus, the finite system must develop significant tension before cavitation becomes thermodynamically favorable. As the thermodynamic penalty of breaking hydrogen bonds becomes more costly as water is cooled, water’s interfacial tension then increases upon further cooling. Eventually, the increasing cost of maintaining an interface promotes dissolution of the bubble.

From the simulation results of TIP4P/2005 water presented above, it appears that larger tension along a given isochore does not imply a greater propensity to cavitate, which has been the common assumption in interpreting the results in water stretching experiments.6–8,13 However, it is clear that the finite system size allows for something akin to a liquid/vapor phase transition at negative pressure that by definition do not exist in a bulk sample, since a vapor cannot exist under tension. While mineral inclusion water is typically viewed as bulk, it has been found that the homogenization temperature can depend on the size of the inclusion,48 with smaller inclusions at the same density having lower homogenization temperatures. This observation has been rationalized through thermodynamic analyses that suggests that the size of the critical nucleus can approach that of the inclusion.48–50 Such analyses also suggest that the influence of surface tension can result in cavitation followed by homogenization upon cooling small systems along isochores with a pressure minimum.49 Here, we have shown that such behavior is possible for isochores without a pressure minimum, and the tension upon homogenization continues to increase upon further cooling. Therefore, it may be possible to observe greater tensions than previously assumed in sufficiently small, low-density isochores. More broadly, this work suggests that water’s phase behavior under strong hydrophilic confinement may be richer than previously assumed. Specifically, it demonstrates the possibility of first-order transitions between a homogeneous liquid and liquid/bubble system at negative pressure.

V. CONSEQUENCES OF $\rho_{\text{spinodal}}^{\max}$ FOR THERMODYNAMIC RESPONSE FUNCTIONS

Next, we consider the influence of a $\rho_{\text{spinodal}}^{\max}$ on the behavior of thermodynamic response functions. A single component fluid’s $\kappa_T$ and $C_p$ diverge at a limit of thermodynamic stability, which include spinodal curves and critical points.31 Accordingly, isochores in the vicinity of $\rho_{\text{spinodal}}^{\max}$ may exhibit maxima in thermodynamic response functions due to a minimum in proximity to a limit of stability (see example of such an isochore, labeled $T_A, T_B$ in Figure 1). Such a locus of the extrema in thermodynamic functions would be in direct analogy to the lines of $C_p^{\max}$ and $\kappa_T^{\max}$ (often generically called Widom lines) that emanate from a critical point and extend into the supercritical region.

In Figure 3 we present plots of the speed of sound $c$, isothermal compressibility $\kappa_T$, and $C_p$ sampled along a selection of isochores that remain homogeneous (i.e., $\rho \geq 0.890 \text{ g/cm}^3$). $c$ is calculated through $c = \sqrt{\frac{C_p}{\rho \kappa_T}}$. 

Figure 3. Isocohoric temperature dependence of the speed of sound $c$, isothermal compressibility $\kappa_T$, and isobaric heat capacity $C_p$ generated using 300 water molecules. $c$ displays a minimum that weakens upon compression. For $\rho \leq 0.9332 \text{ g/cm}^3$, this minimum is due to a maximum in $\kappa_T$, which itself is a result of a maximum spinodal density. Signatures of a locus of maximum $\kappa_T$ emanating from higher pressure are observed at lower temperatures than spinodal-induced maxima, and $\rho = 0.9525$ and 0.960 g/cm3 display two maxima (see inset) corresponding to these separate contributions. Such contributions are not well-separated in $C_p$, resulting in a nonmonotonicity in the height of the maximum upon compression. All lines are empirical guides to the eye.
where \( C_V \) is the isochoric heat capacity, \( C_P \), \( C_V \), and \( \kappa_T \) are calculated through their respective fluctuation relations

\[
\begin{align*}
C_V &= \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}, \quad C_P &= \frac{\langle H^2 \rangle - \langle H \rangle^2}{k_B T^2}, \\
\kappa_T &= \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle k_B T}
\end{align*}
\]

(1)

where \( E \) is the total energy, \( H \) is the enthalpy, \( V \) is volume, and \( k_B \) is Boltzmann’s constant. \( C_V \) is calculated using the total energy under NVT conditions. Then to calculate \( C_P \) and \( \kappa_T \), NPT simulations are performed using the average pressure obtained from the corresponding NVT simulation. We note here that results for two of the isochores, 0.9332 and 0.9525 g/cm\(^3\), have been previously reported.\(^7\)

The lowest density isochore \((\rho = 0.890 \text{ g/cm}^3)\) exhibits a strong maximum in \( \kappa_T \) at roughly 340 K. As density increases, the maximum steadily weakens and disappears at \( \rho = 0.975 \text{ g/cm}^3 \). We attribute \( \rho_{\text{spinodal}}^{\text{max}} \) as the source of the maxima in \( \kappa_T \) upon cooling along isochores, as these maxima weaken upon compression. While not shown, we have also observed a spinodal-induced maximum in \( \kappa_T \) for the mW model.\(^52\)

Of particular interest are the \( \rho = 0.9525 \) and 0.960 g/cm\(^3\) isochores, which exhibit two maxima in \( \kappa_T \) (see inset in Figure 3). The higher temperature maximum at roughly 320 K is clearly a point on the \( \kappa_T^{\text{max}} \) line emanating from the liquid spinodal. However, the lower temperature maxima around 220 K (0.960 g/cm\(^3\)) are points on the \( \kappa_T^{\text{max}} \) line that emanate from higher pressure.\(^2,22\)

While we do not observe separate peaks in \( C_P \), the strength of the maximum weakens and then increases with increasing density, suggesting that while there is no clean separation between a spinodal-induced and an LLCP-induced \( C_P^{\text{max}} \), there is clear evidence of the effect of the spinodal. This strongly suggests that spinodal induced fluctuations affect \( C_P \) in this regime. We must note that lines of \( C_P^{\text{max}} \) and \( \kappa_T^{\text{max}} \) are not necessarily indicative of criticality, however, in this water model there is reasonable evidence to suggest the existence of a second critical point.\(^2,22\) In addition, secondary maxima in heat capacity have been observed in a coarse-grained lattice model of water subject to extreme confinement.\(^13\)

Between \( \rho = 0.890 \) and 0.960 g/cm\(^3\), isochores display a minimum in the speed of sound, a result of either a maximum in \( \kappa_T \) or minimum in \( C_P/C_V \). \( C_P/C_V \) exhibits a roughly density-independent minimum at 280 K. The minima in \( c \) for \( \rho = 0.890, 0.910, \) and 0.9332 g/cm\(^3\) coincide with the corresponding \( \rho_{\text{spinodal}}^{\text{max}} \) along these isochores and are thus a consequence of \( \rho_{\text{spinodal}}^{\text{max}} \). However, the 0.9525 and 0.960 g/cm\(^3\) isochores display minima near the temperature of minimum \( C_P/C_V \), where the influence of the liquid spinodal and a possible LLCP are interwoven.

Recent experiments of isochorically stretched water found a minimum speed of sound in the 0.9332 g/cm\(^3\) isochore.\(^7\) The authors then performed simulations with TIP4P/2005 along this isochore and found a minimum speed of sound that is due to a compressibility maximum, a result we have reproduced in this study. The authors suggested that this point was the negative pressure extension of the \( \kappa_T^{\text{max}} \) locus that had previously been computed for TIP4P/2005 water.\(^22\) They then proposed that the experiments had observed a point on the \( \kappa_T^{\text{max}} \) locus, which had previously eluded observation on account of rapid crystallization, and which “emerges from the no man’s land at negative pressure”.\(^7\) Our extensive computational investigation suggests that, depending on the particular isochore under investigation, this high temperature minimum in the speed of sound can originate either from a \( \rho_{\text{spinodal}}^{\text{max}} \) or a minimum in \( C_P/C_V \). However, \( \kappa_T^{\text{max}} \) is not the negative pressure extension of a line emanating from higher pressure. Instead, it is due to the peculiar behavior of water’s spinodal in its \( T−p \) phase diagram and originates at negative pressure. We stress that this assessment is limited to the behavior of TIP4P/2005 water and that the origin of the minimum in \( c \) in the experiments remains to be clarified. If one were to observe that the minimum speed of sound intensifies upon decompression from 0.9332 g/cm\(^3\) and disappears upon compression, similar to the behavior seen in Figure 3 (top), it is then likely that such minima in \( c \) are spinodal-induced.

Thus, one can include an additional line of \( \kappa_T^{\text{max}} \) to TIP4P/2005’s phase diagram of anomalies in the \( P−T \) plane (Figure 4).

![Figure 4](image)

Figure 4. Phase diagram of anomalies in TIP4P/2005 water. A maximum spinodional density results in a locus of compressibility maxima that is well-separated from the \( \kappa_T^{\text{max}} \) originating at high pressure. However, the spinodal-induced \( \kappa_T^{\text{max}} \) is only observed through isochorich sampling, which is the typical pathway for experiments of stretched water. The locus of equal proportions of HDL and LDL water molecules in water’s potential energy landscape follows the Widom line well into the negative pressure regime and suggests that a crossover from HDL to LDL dominance in the structure of water could be observed at higher temperatures than the \( C_P^{\text{max}} \) in highly stretched water. All curves aside from the spinodal-induced \( \kappa_T^{\text{max}} \) and 1:1 HDL:LDL in the potential energy landscape are two-structure equation of state fits originally published in ref 12.

However, this additional \( \kappa_T^{\text{max}} \) line is limited to isochorich paths, the relevant pathway for experiments achieving such high tensions. This line is well separated from the previously calculated \( \kappa_T^{\text{max}} \) that is suspected to emanate from an LLCP\(^2,23\) (shown in Figure 4). While an LLCP-induced \( \kappa_T^{\text{max}} \) does not extend below ~100 MPa, we have found that signatures of an LLCP, observed by sampling water’s potential energy landscape, extend much deeper into water’s stretched regime as well as higher temperatures.

VI. STRUCTURAL SIGNATURES OF A WIDOM LINE IN THE POTENTIAL ENERGY LANDSCAPE

We now present a structural analysis that demonstrates how signatures of the Widom line, which can be interpreted as the analytical extension of the liquid–liquid coexistence line,\(^22\) extend to extreme negative pressures. Specifically, we consider
the structure of water’s potential energy landscape. Sampling a system’s potential energy landscape by producing a representative ensemble of potential energy minima (i.e., inherent structures) can clarify structural features that are otherwise obscured by thermal fluctuations.\textsuperscript{54,55} A liquid’s inherent structures correspond physically to the “glass” produced through an infinitely rapid isochoric quench to $T = 0 \text{ K}$. Recent studies have shown that water’s inherent structures display a bimodal distribution of local structure index (LSI), a local structural order parameter that quantifies the degree of separation between the first and second hydration shells, in both SPC/E\textsuperscript{56,57} and TIP4P/2005.\textsuperscript{58} LSI for a given water molecule $i$ is defined by

\[
\text{LSI}(i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} [\Delta(j; i) - \bar{\Delta}(i)]^2
\]

where $\Delta(j;i) = r_{j+1} - r_j$ [i.e., the oxygen–oxygen distance of the $j$th nearest neighbor subtracted from the $(j+1)$th] and $\bar{\Delta}(i)$ is the average over the $n(i)$ nearest neighbors defined to be within a cutoff of 3.7 Å.\textsuperscript{59} Weak bimodality in the equilibrated liquid is observed only at extreme supercooling. A smaller LSI value implies a more disordered, HDL-like environment, and a larger LSI value corresponds to a more ordered, LDL-like environment. Thus, generating inherent structures appears to clarify the underlying structural features corresponding to these two distinct local environments.

It was shown that, in TIP4P/2005 water, the Widom line, defined in this case as the $\kappa_T^\text{max}$ line generated along isobars, closely corresponds to a 1:1 distribution of HDL:LDL in the inherent structures for pressures from 1 to 1500 bar.\textsuperscript{58} Note that in this pressure range, the lines of $c_p^\text{max}$, $\kappa_T^\text{max}$, and the Widom line differ by at most 10 K, so they are often collectively called the Widom line. As pressure decreases, these lines grow further apart, and only the Widom line is expected to intersect the spinodal in the deeply stretched region (see Figure 4).

Through steepest descent potential energy minimization, we have generated the inherent structures along isochores that avoid cavitation (i.e., $\rho > 0.885$ g/cm$^3$) and calculated their LSI. In agreement with previous observations,\textsuperscript{60,61} we observe a bimodal LSI distribution with a minimum around 0.13, a value that is independent of the thermodynamic conditions. In Figure S, we have provided an example of the LSI distributions sampled along the 0.890 g/cm$^3$ isochore. Using 0.13 as the cutoff to distinguish a water molecule as either HDL or LDL-like, we estimate the temperature of 1:1 HDL:LDL ratio along an isochore by mapping the equilibrated liquid onto the underlying potential energy landscape and performing the LSI calculation on the resulting inherent structures. We then find the corresponding pressure of the equilibrated liquid from its equation of state. Here, we have extended the line of 1:1 HDL:LDL in the $P$–$T$ plane from elevated pressure well into the negative pressure regime (Figure 4).

In agreement with earlier work,\textsuperscript{58} we observe that the 1:1 HDL:LDL line follows the line of $\kappa_T^\text{max}$ at positive pressure. At negative pressure, this trend breaks down, as the locus of 1:1 HDL:LDL in inherent structures appears to roughly follow the Widom line predicted by two-structure equation of state fitting.\textsuperscript{12} If this were to be the case for real water, this would suggest that signatures of an LLCP would be accessible in the deeply stretched region at higher temperature than $c_p^\text{max}$. Molecular simulations have found that the HDL:LDL ratio estimated from the inherent structures is in the neighborhood of estimates from X-ray adsorption\textsuperscript{60} and emission\textsuperscript{61} of liquid water at ambient conditions.\textsuperscript{58} While HDL is the predominant local structure at elevated temperatures, the LDL fraction grows upon cooling. The present work suggests that a crossover from HDL to LDL dominance may be observed in liquid water at extreme negative pressures.

\section{VII. Conclusions}

One way in which water deviates from conventional liquids is in the fact that the liquid binodal has a maximum density, allowing in principle for isochors to exhibit homogenization upon cooling. In finite isochoric systems, an analogous transition occurs in the absence of a TMD. However, since such transitions occur at negative pressure, they are more faithfully interpreted as a homogeneous to cavitated transition rather than a liquid to vapor transition. It is expected that such transitions can be realized in sufficiently small mineral inclusions.\textsuperscript{49,50} In addition, this work suggests that much smaller inclusions may be a route to producing liquid water under much greater tension than theory\textsuperscript{40} and experiment.\textsuperscript{5,13} have so far suggested to be possible. Whether small enough isochoric systems are experimentally feasible remains to be clarified.

A maximum spinodal density gives rise to a line of $\kappa_T^\text{max}$ that is independent of any Widom line emanating from higher pressure, with the latter associated with an LLCP. While signatures of a possible LLCP-induced $\kappa_T^\text{max}$ line have been observed in the TIP4P/2005 model,\textsuperscript{12,22–24} they exist at significantly lower temperature and extend to $-100$ MPa. However, we have shown that structural signatures of a Widom line extending to much larger negative pressures lie hidden in water’s energy landscape. If the Widom line in real water crosses the homogeneous nucleation line at negative pressure, it is unlikely to emerge as a locus of extrema in thermodynamic response functions. Rather one would seek to observe a locus of 1:1 HDL:LDL-like water molecules, which may be possible with existing experimental techniques.\textsuperscript{50,61}
Much of what we have discussed here, specifically reentrant behavior and spinodal-induced extrema in thermodynamic response functions, is relevant to any liquid that contains a \( \rho_{\text{binodal}}^{\text{max}} \) which should exist in liquids with density anomalies. This includes other tetrahedrally coordinated liquids (e.g., silicon and germanium) as well as the numerous patchy colloidal models. Some patchy colloids have also been shown to have a minimum “vapor” binodal density \( \rho_{\text{vapor}} \) which should also result in lines of extrema of thermodynamic response functions.

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### Notes

The authors declare no competing financial interest.

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