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Two-state thermodynamics and the possibility of a liquid-liquid phase transition in supercooled TIP4P/2005 water

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Water shows intriguing thermodynamic and dynamic anomalies in the supercooled liquid state. One possible explanation of the origin of these anomalies lies in the existence of a metastable liquid-liquid phase transition (LLPT) between two (high and low density) forms of water. While the anomalies are observed in experiments on bulk and confined water and by computer simulation studies of different water-like models, the existence of a LLPT in water is still debated. Unambiguous experimental proof of the existence of a LLPT in bulk supercooled water is hampered by fast ice nucleation which is a precursor of the hypothesized LLPT. Moreover, the hypothesized LLPT, being metastable, in principle cannot exist in the thermodynamic limit (infinite size, infinite time). Therefore, computer simulations of water models are crucial for exploring the possibility of the metastable LLPT and the nature of the anomalies. In this work, we present new simulation results in the NVT ensemble for one of the most accurate classical molecular models of water, TIP4P/2005. To describe the computed properties and explore the possibility of a LLPT, we have applied two-structure thermodynamics, viewing water as a non-ideal mixture of two interconvertible local structures (“states”). The results suggest the presence of a liquid-liquid critical point and are consistent with the existence of a LLPT in this model for the simulated length and time scales. We have compared the behavior of TIP4P/2005 with other popular water-like models, namely, mW and ST2, and with real water, all of which are well described by two-state thermodynamics. In view of the current debate involving different studies of TIP4P/2005, we discuss consequences of metastability and finite size in observing the liquid-liquid separation. We also address the relationship between the phenomenological order parameter of two-structure thermodynamics and the microscopic nature of the low-density structure. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4944986>]

I. INTRODUCTION

The peculiar behavior of supercooled water is still a puzzle that continues to attract strong interest. In contrast to the behavior of ordinary substances, the thermodynamic response functions (namely, the isothermal compressibility, the isobaric heat capacity, and the magnitude of the thermal expansion coefficient) of liquid water show sharp increases on supercooling, suggesting their possible divergence just below the homogeneous ice nucleation temperature, T_H .^{1–12} Over the last few decades, several scenarios have been proposed to interpret this unusual thermodynamic behavior.^{12–20} One popular interpretation invokes a hypothetical first order liquid-liquid phase transition (LLPT) between two metastable liquid phases — high-density liquid (HDL) and low-density liquid (LDL) — a phenomenon known as “liquid water polyamorphism.”¹⁵ The proposed liquid-liquid transition line terminates at a critical point in the supercooled region. Thus, the anomalous behavior of thermodynamic response functions in supercooled water is attributed to the hypothetical liquid-liquid critical point (LLCP) at which the response functions should diverge. Direct experimental observation of the LLPT

and LLCP in bulk supercooled water is hampered by fast ice formation along T_H . Therefore, the hypothesized LLPT and LLCP are submerged in the “no-man’s land” (below T_H).¹²

The known existence of two distinct glass transitions of water at ambient pressure is consistent with the hypothesized existence of two different forms of liquid water.^{12,21–24} Experiments on confined water (confinement is known to prevent crystallization) also suggest the existence of a LLPT in bulk water.^{21,25} However, due to strong effects of interaction of water with the surface of confining walls, the predictions of such studies may not be directly relevant to bulk water. Recently, Sellberg *et al.*²⁶ used femtosecond X-ray laser pulses on micrometer-sized water droplets to probe the local structure of bulk supercooled water in “no man’s land” (water below T_H). Experiments on some supercooled aqueous solutions suggest the existence of a metastable liquid-liquid transition, presumably stemming from the original LLPT in pure supercooled water,^{27–31} though the interpretation of experiments on glycerol-water solutions remains controversial.^{30,32,33} In view of the enormous challenges that prevent direct access to the “no-man’s land,” computer simulations remain crucial for exploring the structure, dynamics, and phase behavior of supercooled water.

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Several computer simulation studies directly or indirectly suggest the existence of a metastable LLPT for some molecular models of water^{15,34–42} and for tetrahedral network-forming models.^{43–47} Recent state-of-the-art free-energy computations convincingly confirm the LLPT for the ST2 model^{38,41,48} and some coarse-grained water-like network-forming models.⁴⁶ Of special relevance is the work of Smallenburg and Sciortino:⁴⁸ these authors showed that the LLPT in the ST2 model persists upon making the crystal phase metastable with respect to the liquid by tuning the hydrogen bond angular flexibility. This disproves interpretations according to which the LLPT is generically a misinterpreted crystallization transition.^{49–52} On the other hand, metastable liquid-liquid separation is not observed in the coarse-grained mW model,^{49,53–55} a re-parametrized version of the Stillinger-Weber (SW) model.⁵⁶ Placing phenomenological (equation of state) calculations on firmer theoretical⁴² and computational ground,⁴¹ understanding the molecular basis underlying the existence⁴¹ or absence⁵⁴ of a LLPT in specific models, and elucidating the model-dependent time and length scales over which a metastable LLPT can be observed^{57–59} are current objects of activity and robust discussion.

The main focus of our work is the TIP4P/2005 water model.⁶⁰ This model reproduces satisfactorily the thermodynamics of liquid water and the complex, experimentally observed phase diagram of water in its numerous crystalline phases, and is considered to be one of the most accurate classical molecular models of liquid water. The existence of a LLPT in the TIP4P/2005 model is still a subject of debate. Abascal and Vega³⁶ reported the existence of a LLPT with critical parameters $T = 193$ K, $\rho = 1012$ kg/m³, and $P = 135$ MPa from molecular dynamics (MD) simulations in the NPT ensemble. The more recent study of Sumi and Sekino⁶¹ in the NPT ensemble also suggests a LLPT for the TIP4P/2005 model, but the critical parameters ($T \approx 182$ K, $\rho \approx 1020$ kg/m³, and $P = 158$ - 162 MPa) were found to be significantly different than those proposed by Abascal and Vega.³⁶ An equation of state based on the concept of the presence of two different local structures, proposed by Russo and Tanaka,⁶² also suggests the existence of a metastable LLPT for this model. Recently, Yagasaki *et al.*⁴⁰ have carried out MD simulations in the NVT ensemble and have observed a spontaneous low- and high-density liquid-liquid phase separation in three models: ST2, TIP5P, and TIP4P/2005. The critical temperature and density of TIP4P/2005 reported by Yagasaki *et al.*⁴⁰ are in agreement with the predictions of Sumi and Sekino.⁶¹ These authors also observed a clear separation of time scales between LLPT and crystallization. However, studies of Limmer and Chandler^{50,51} and Overduin and Patey^{58,59} found no evidence for two metastable liquid phases around the temperature-pressure range suggested by Abascal and Vega.³⁶ Overduin and Patey⁵⁸ also argued that the simulations of Abascal and Vega³⁶ are too short to obtain converged results. In recent studies, Limmer and Chandler⁵¹ and Overduin and Patey⁵⁹ have also challenged the results of Yagasaki *et al.*

Specifically, for TIP4P/2005⁶⁰ and TIP5P,⁶³ Overduin and Patey⁵⁹ show that the spontaneous liquid-liquid phase separation reported by Yagasaki *et al.*⁴⁰ exhibits a strong

system size dependence. For a system size of 4000 molecules, both studies, Refs. 40 and 59, observe regions of different densities separated by well-defined planar interfaces. However, Overduin and Patey⁵⁹ also observed that the density difference between these regions was sharply reduced with increasing system size and disappeared for a system size of 32 000 molecules. These authors further argue that, as the appearance of regions of low density is always accompanied by an excess of local ice-like molecules, the regions of different densities observed by Yagasaki *et al.*⁴⁰ are likely associated with appearance and coarsening of local ice-like structures, rather than with liquid-liquid phase separation. This argument supports the conclusion of Limmer and Chandler,⁵¹ who also argued that the density differences observed by Yagasaki *et al.*⁴⁰ are due to ice coarsening.

The fact that metastable phase behavior depends on the system size is not surprising. Obviously, a metastable phase separation cannot exist in the thermodynamic limit (infinite size and infinite time of equilibration). This is why the results and arguments of Overduin and Patey⁵⁹ require thorough analysis in light of the physics of metastability.

There is another aspect of the physics of supercooled water that is closely related to the discussion of the possibility of a metastable LLPT. This has to do with the physical nature of the thermodynamic anomalies, in particular, the trend toward diverging response functions. Currently, there is broad consensus based on the experimental^{64–69} and simulation^{62,70–73} studies that in supercooled water, two competing local structures indeed exist. Could this competition, which is assumed to be responsible for the thermodynamic anomalies, be sharp enough to trigger a metastable LLPT? This is the central question. Definitely, this possibility is strongly model-dependent and could also depend on specific experimental/simulation conditions.

Recently, two-structure thermodynamics has become increasingly popular for explaining the anomalous thermodynamic behavior of supercooled water.^{41,42,55,62,68,74–76} Liquid water is considered as a “mixture” of two types of local environments – LDL-like and HDL-like, with the fraction of each controlled by thermodynamic equilibrium. The competition between these two distinct configurations naturally explains the density anomaly along with other thermodynamic anomalies in the supercooled state. If the excess Gibbs energy of mixing of these two structures is positive, the non-ideality of mixing can overcome the ideal entropy of mixing, causing liquid-liquid phase separation. Recent studies show that the thermodynamic properties of metastable liquid water,⁷⁴ as well as of the ST2⁴² and mW⁵⁵ water models, can be well described by two-structure thermodynamics. It was shown that the liquid-liquid phase separation for the ST2 model is energy-driven; however, for the mW model, non-ideality of mixing is only entropy driven and is not strong enough to induce a LLPT. Bresme *et al.* used a two-structure equation of state with a LLPT and LLCPC to describe the TIP4P/2005 model in an investigation of the model’s thermal conductivity and found good agreement between the model and the simulation data.⁷⁷ So far, the best description of all currently available experimental data on thermodynamic properties of supercooled water is

achieved by an equation of state based on two-structure thermodynamics.^{74,78} A semi-empirical extension (up to 400 MPa) of this equation of state, reported in Ref. 78, has been adopted by the International Association for the Properties of Water and Steam (IAPWS) as an international guideline for scientific and industrial use. The recently observed bimodal distributions of molecular arrangements of inherent structures in the SPC/E⁷⁹ and TIP4P/2005⁷⁰ models strongly support the two-structure description of liquid water. The existence of a bimodal distribution of molecular configurations in water is also supported by X-ray absorption and emission spectroscopy^{66,68} and by an investigation of vibrational dynamics.⁶⁵ However, the mere existence and competition of the two local structures in water do not necessarily mean the existence of a metastable LLPT in “no-man’s land.”²⁰

In this work, we have carried out extensive computer simulations in order to explore the nature of the thermodynamic anomalies and, consequently, the possibility of a metastable LLPT in TIP4P/2005. To describe the computed properties, we have applied two-structure thermodynamics, viewing water as a non-ideal mixture of two interconvertible local structures. The thermodynamic behavior of the model in the one-phase region is fully consistent with the existence of an energy-driven LLPT in this model (at least for the simulated length and time scales). We have compared the behavior of TIP4P/2005⁶⁰ with the mW⁵³ and ST2⁸⁰ models, and with real water. We have also addressed the relation between the phenomenological order parameter of two-state thermodynamics and the microscopic nature of the low-density structure. In view of the current controversy between different studies of TIP4P/2005, the crucial role of metastability and finite size in observing liquid-liquid separation is emphasized.

II. COMPUTATIONAL MODEL AND SIMULATION DETAILS

We performed molecular dynamics (MD) simulations of 216 water molecules interacting via the TIP4P/2005 pair potential⁶⁰ in a cubic box at constant temperature and volume (*NVT* ensemble). We computed the properties of liquid water at approximately 200 state points at densities ranging from 1120–960 kg/m³ in steps of 20 kg/m³ and temperatures ranging from 300 K down to 185–180 K (depending on the density of the system) in steps of 5 K. This choice of ensemble was partly motivated by the possibility of observing van der Waals loops in the two-phase region (below LLC), in case they exist. It turned out that we were not able to relax the system in the region where one would expect to observe van der Waals loops. However, using many state points in the *NVT* ensemble enables us to follow different isochores throughout the one-phase region and to extrapolate them into the region where the slow relaxation of the system impedes reliable computation. We may thus distinguish between a system with a LLPT in which the isochores are projected to cross, and a system with competition between two structures but without a LLPT in which the isochores do not cross.

We have also performed MD simulations in the *NPT* ensemble with 512 water molecules at 0.1 MPa and temperatures ranging from 300 K to 200 K. All simulations were performed with use of GROMACS 4.6.5 molecular dynamics simulation package.⁸¹ In all cases, periodic boundary conditions were applied, and a time step of 2 fs was used. The short-range interactions were truncated at 8.5 Å for 216 water molecule system and 9.5 Å for 512 water molecule system. Long range electrostatic terms were computed by particle mesh Ewald with a grid spacing 1.2 Å. Long range corrections were applied to the short range Lennard-Jones interaction for both energy and pressure. Bond constraints were maintained using the LINCS (Linear Constraint Solver) algorithm.⁸² To maintain constant temperature, we used a Nose-Hoover thermostat^{83,84} with 0.2 ps relaxation time. Constant pressure was maintained by a Parrinello-Rahman barostat⁸⁵ with 2 ps relaxation time.

Molecular models of water are notorious for extremely slow structural relaxation in the supercooled state. This slow structural relaxation often leads to controversy over thermodynamic behavior of supercooled water observed in computer simulation studies.^{37,49,50,58} In this work, in order to ensure the relaxation of the system at each state point, we computed and carefully monitored the decay of the self-part of the intermediate scattering function ($F_s(k, t)$)⁸⁶ with time t (shown and discussed in the supplementary material⁸⁷). To ensure the relaxation of the system at each thermodynamic condition investigated in this work, MD trajectories are at least 400 times as long as the structural relaxation time (defined as the time at which $F_s(k^*, t) = 1/e$, k^* is the wavenumber corresponding to the first peak of structure factor). Depending on the thermodynamic condition, MD trajectory lengths vary between 20 ns and 15 μ s.

III. THERMODYNAMICS OF TWO STATES IN LIQUID WATER

The two-structure equation of state (TSEOS) treats liquid water as a “mixture” of two interconvertible structures (“states”), a high-density/high-entropy structure A and a low-density/low-entropy structure B . These two structures are interconvertible by a process that can be viewed as analogous to a “chemical reaction” $A \rightleftharpoons B$. This means that, unlike in binary mixtures, the fraction of each structure, $1 - x$ for A or x for B , is not an independent variable but rather is controlled by thermodynamic equilibrium. Our expression for the molar Gibbs energy of the system takes the form:^{42,55,74,78}

$$G = G^A + xG^{BA} + RT [x \ln x + (1 - x) \ln(1 - x) + \omega x(1 - x)], \quad (1)$$

where G^A represents the Gibbs energy of pure structure A and $G^{BA} = G^B - G^A$ represents the difference in Gibbs energy between structures B and A , respectively. The term G^A is treated empirically as a polynomial function of temperature and pressure. Since we are testing the possibility of the existence of a LLPT (terminating at a LLC) for the TIP4P/2005 model, the convenient variables are $\Delta\hat{T} = (T - T_c)/T_c$ and $\Delta\hat{P} = (P - P_c)/\rho_c RT_c$, where T is

the temperature, P is the pressure, T_c , P_c , and ρ_c are the critical temperature, pressure, and molar density, respectively. Therefore, G^A is represented as

$$G^A = \sum_{m,n} c_{mn} \Delta \hat{T}^m \Delta \hat{P}^n, \quad (2)$$

with $\{c_{mn}\}$ being adjustable coefficients. The difference G^{BA} determines the equilibrium constant K of the “chemical reaction” $A \rightleftharpoons B$ as $\ln(K(T, P)) = -G^{BA}/RT$. In the simplest non-linear approximation,

$$\frac{G^{BA}}{RT} = \lambda(\Delta \hat{T} + a\Delta \hat{P} + b\Delta \hat{T}\Delta \hat{P}), \quad (3)$$

where λ is associated with the difference in entropy between the two structures, a gives the slope $-(dT/dP)$ of the LLPT at the critical point and thus, asymptotically, the slope of the critical isochore, and b gives the curvature of the LLPT line and its analytic continuation, the “Widom line.”^{42,74} The condition $\ln K = 0$ describes the LLPT, LLC, and the Widom line.

The fraction x of molecules associated with structure B is controlled by the condition that the value of the Gibbs energy must be a minimum in thermodynamic equilibrium, so the equilibrium fraction x_e can be found from the equation

$$\left(\frac{\partial G(T, P; x)}{\partial x} \right)_{T, P} = 0. \quad (4)$$

In an ideal mixture, x_e will vary smoothly with T and P and there will be no phase transition.²⁰ If, however, the mixture is sufficiently non-ideal, the change in x_e may be discontinuous, signifying a first order phase transition between a high-density liquid (rich in structure A) and a low-density liquid (rich in structure B). In our case, the variation of the non-ideality yields a phase diagram with a curve of first-order LLPT terminating at a LLC. An extension of the LLPT curve into the one-phase region, where the non-ideality is not strong enough to induce phase separation, is commonly called the Widom line.¹⁸ Asymptotically close to the critical point, the Widom line coincides with the critical isochore, as well as with loci of maxima in the isobaric heat capacity C_P and isothermal compressibility κ_T .¹⁸

The term $RT[x \ln x + (1-x) \ln(1-x) + \omega x(1-x)]$ describes the Gibbs energy of mixing of structures A and B with $x \ln x + (1-x) \ln(1-x)$ being the ideal entropy of mixing.⁸⁸ The non-ideality is represented by a simple form, symmetric in x , with the parameter ω determining the nature and strength of the non-ideality. In this simple (symmetric) form of the TSEOS, the critical composition $x_c = 1/2$. If ω does not depend on temperature, then the non-ideality that leads to phase separation is entirely due to the non-ideal entropy of mixing (“athermal solution”). This form of the non-ideality has been used to describe both real water⁷⁴ and mW water.⁵⁵ If, on the other hand, $\omega \propto 1/T$, then the non-ideality arises due to non-ideal enthalpy of mixing (“regular solution”). Such a “regular solution” model has been used to describe two versions of the ST2 model of water, ST2(I) and ST2(II).⁴²

In principle, both non-ideal entropy and enthalpy of mixing could contribute. However, for TIP4P/2005, modification of the temperature dependence of ω , which is equivalent to the inclusion of non-ideal entropy of mixing,

introduced an additional adjustable parameter but did not yield an improvement in the description of the simulation data within their uncertainties. Therefore, for simplicity, we model the non-ideality as arising only from non-ideal enthalpy of mixing, as was done for ST2.⁴² In this model, phase separation occurs for $\omega > 2$, so we give ω the linear form

$$\omega = \frac{2 + \omega_0 \Delta \hat{P}}{\hat{T}}, \quad (5)$$

where $\hat{T} = T/T_c$, and ω_0 is the only adjustable parameter that controls the non-ideality of mixing.

Simple approximations, given by Eqs. (3) and (5), used for describing the TIP4P/2005 model, while enabling us to avoid a large number of adjustable parameters, obviously restrict the validity of the TSEOS within a reasonable vicinity of the LLC. In this work, we are deliberately using this restriction to describe the area of converging isochores and thus to emphasize the possibility of the existence of LLC in this model.

To obtain the values of thermodynamic properties from the TSEOS, we first solve Eq. (4) for x_e , and then use x_e to evaluate the desired derivative of the Gibbs energy. Because Eq. (4) is a transcendental equation with no closed-form solution, numerical methods must be used.

IV. DESCRIPTION OF THERMODYNAMIC PROPERTIES OF TIP4P/2005 WATER

In Fig. 1, we present the results of our NVT simulations (open circles) along with isochores predicted by the TSEOS (solid lines). The densities range from 960 to 1120 kg/m³ in steps of 20 kg/m³ and the temperatures range from 300 K down to 180–190 K (depending on the density) in steps of 5 K. The error bars of the simulation data points are approximately equal to the size of the circles. The shape of the isochores in the supercooled region strongly suggests the existence of a LLC for this model as predicted by the TSEOS. In Fig. 2, we have compared TSEOS predictions for the densities along isobars with the previously reported data by Sumi and Sekino⁶¹ as well as by Abascal and Vega³⁶ obtained by NPT simulations. We observe quantitatively good agreement between predictions of the TSEOS and simulation data for $T > 200$ K. However, for very low temperatures, the densities predicted by the TSEOS deviate significantly from previously reported data.⁶¹ This discrepancy most likely arises due to the approximations used in the current form of the TSEOS. In any case, both the new simulation data and the TSEOS strongly imply the existence of a liquid-liquid critical point near 182 K and 170 MPa, consistent with the recent simulation studies by Yagasaki *et al.*⁴⁰ and by Sumi and Sekino.⁶¹

In Figs. 1 and 2, we show the TSEOS prediction for the LLPT and LLC in the P - T and ρ - T planes, respectively. The TSEOS parameters are reported in Table I. The proposed phase diagram and its comparison with other studies for this model are discussed in more detail in Section VI.

In order to gain deeper insight into the thermodynamic behavior of the TIP4P/2005 model in the supercooled state, in Figs. 3(a) and 3(b), we demonstrate the behavior of

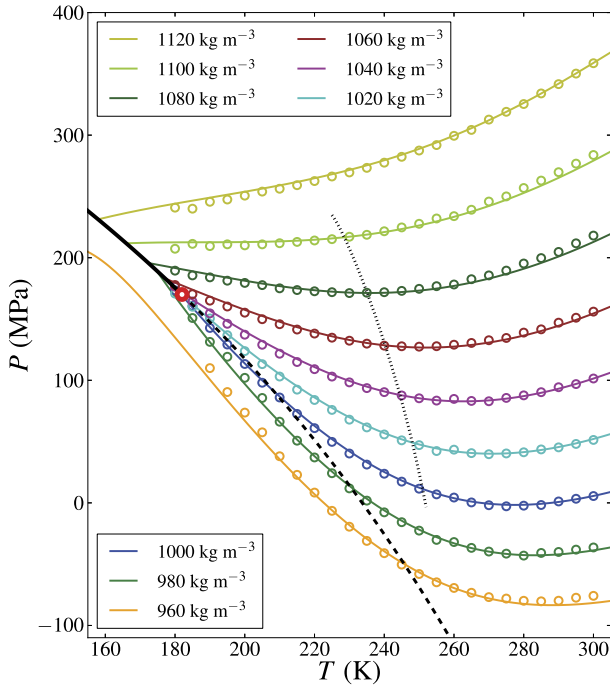


FIG. 1. Isochores in the P - T plane for TIP4P/2005 model. The open circles indicate simulation data, while the solid lines show the same isochores according to the TSEOS. The LLPT line, the LLCP, and the Widom line are shown as the solid black line, large red circle, and black dashed line, respectively. The thin dotted line is the melting line of TIP4P/2005 as reported in Ref. 36.

the isothermal compressibility (κ_T) and the corresponding predictions of the TSEOS. The isothermal compressibility, defined as $\kappa_T = -(1/V)(\partial V/\partial P)_T = \langle(\delta V)^2\rangle/k_B T V$ (k_B is Boltzmann's constant, V is the volume) is a measure of the mean-square volume fluctuations $\langle(\delta V)^2\rangle$ at constant temperature. The compressibility as a function of density along isotherms, shown in Fig. 3(a), is computed from the

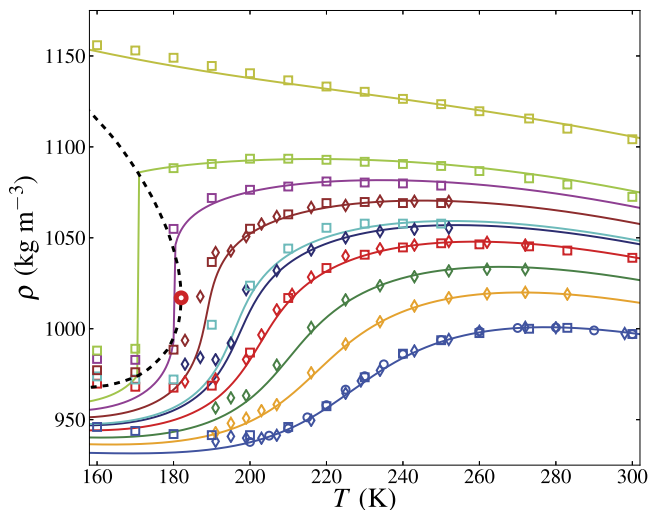


FIG. 2. Densities along isobars computed by Sumi and Sekino⁶¹ (open squares), Abascal and Vega³⁶ (open diamonds), in this work (open circles; 0.1 MPa), and fits by the TSEOS (solid lines). The black dashed line bounds the two phase region as predicted by the TSEOS, and the red circle shows the predicted location of the critical point. Isochores shown, from top to bottom, are 300, 200, 175, 150, 125, 120, 100, 70, 40, and 0.1 MPa.

TABLE I. Parameters for the two-structure equation of state.^a

Parameter	Value	Parameter	Value
T_c	182 K	\hat{c}_{20}	-5.348 1
P_c	170 MPa	\hat{c}_{12}	0.000 493
ρ_c	1017 kg/m ³	\hat{c}_{21}	0.109 4
λ	1.407	\hat{c}_{30}	1.329 3
a	0.171	\hat{c}_{22}	-0.021 29
b	-0.100	\hat{c}_{31}	-0.024 46
ω_0	0.071 7	\hat{c}_{40}	-0.131 73
\hat{c}_{01}	0.861 7	\hat{c}_{23}	0.003 687
\hat{c}_{02}	-0.003 412	\hat{c}_{32}	0.012 29
\hat{c}_{11}	0.013 51	\hat{c}_{33}	-0.003 513

^aThe adjustable coefficients of Eq. (2) are made dimensionless by the critical parameters.

simulation data. In Fig. 3(b), we show the compressibility data along the isobars reported by Abascal and Vega,³⁶ along with this work at 0.1 MPa, to compare with the predictions of the TSEOS. The results presented in these figures show that the two-structure thermodynamics successfully describes the observed anomalous behavior of thermodynamic response functions in the supercooled region.

In Fig. 4, we demonstrate the temperature dependence of the heat capacity at constant volume, C_V , along different isochores. The isochoric heat capacity C_V , defined as $(\partial E/\partial T)_V = \langle(\delta E)^2\rangle/k_B T^2$, is a measure of the total energy (E) fluctuations of the system. We observe excellent agreement between two-state thermodynamics and computer simulation predictions for higher densities (greater than 1040 kg/m³) and reasonably good agreement (considering the larger uncertainties involved in computing energy fluctuations) at lower densities and temperatures. From the figure, it is evident that unlike κ_T , C_V does not show any significant anomaly on supercooling down to 185 K. This is not surprising, as the anomaly of the isochoric heat capacity near the critical point is very weak. It originates solely from fluctuation effects associated with the divergence of the correlation length and does not exist in the mean-field approximation. According to scaling theory,⁸⁹ the weak divergence of C_V should only be noticeable in the close vicinity of the critical point (practically, within 1-2°, i.e., at $(T - T_c)/T_c < 10^{-2}$ ⁹⁰). Moreover, in a finite-size system, the correlation length cannot exceed the size of the box, and so the critical anomalies are rounded. Our system contains only 216 molecules, which is too small for weak (fluctuation-induced) anomalies to be observed. A crossover TSEOS that incorporates fluctuation effects upon approaching the critical point has recently been applied for the description of the ST2 model,⁴² and it was shown that within the accuracy of simulation data for that model, fluctuation effects are negligible.

V. LOW-DENSITY FRACTION AND THE NATURE OF THE ORDER PARAMETER

Two-structure thermodynamics makes use of the fraction x , an extent of reaction between two interconvertible structures, as a phenomenological order parameter. It does not, however, specify the microscopic nature of these two structures nor does it give a microscopic definition of the order

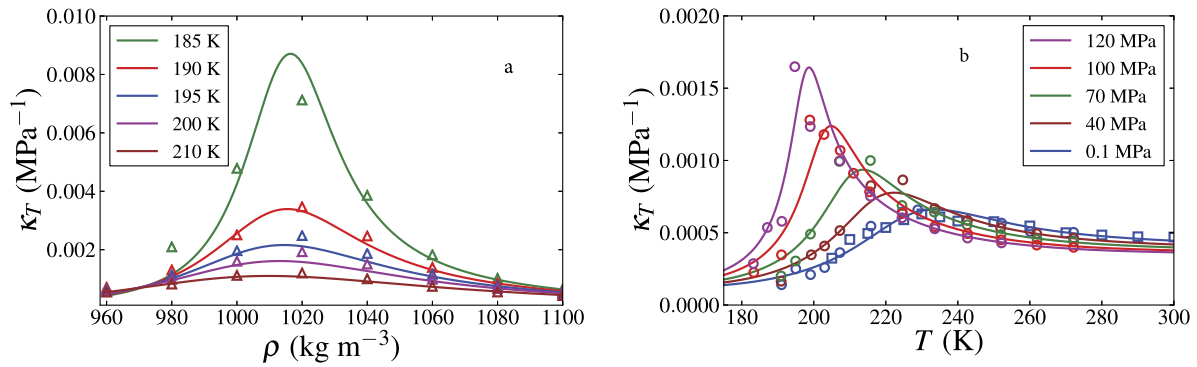


FIG. 3. (a) Isothermal compressibility along isotherms. Symbols are simulation data and the curves are predictions of the TSEOS (this work). (b) Isothermal compressibility along isobars. Symbols are simulation data by Abascal and Vega³⁶ (open circles) along with our work at 0.1 MPa (open squares). The curves are the predictions by the TSEOS.

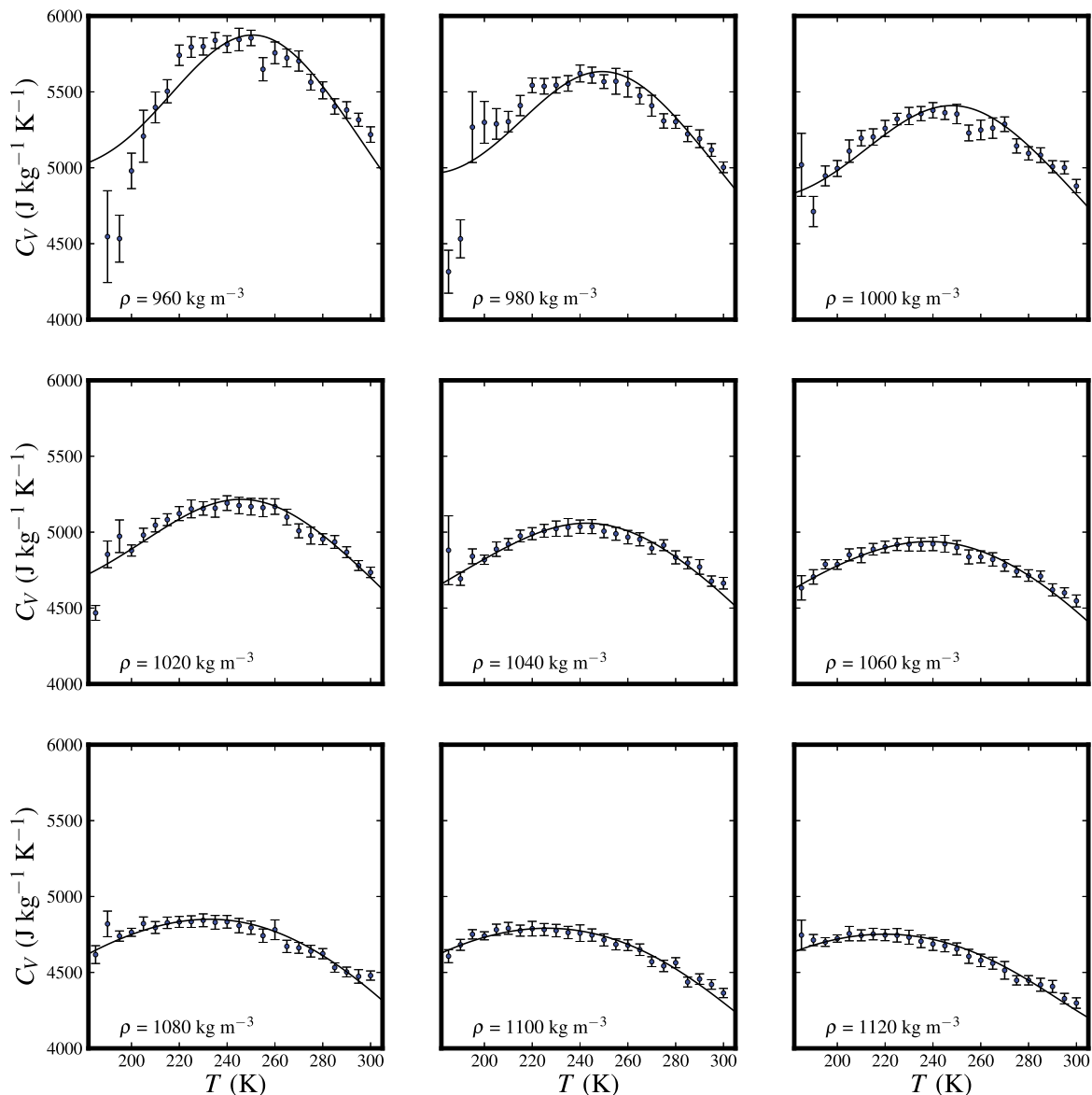


FIG. 4. Temperature dependence of the specific heat capacity at constant volume (C_V) along different isochores. Symbols are simulation data computed from total energy fluctuations and solid lines show the predictions of the TSEOS.

parameter. Different authors have suggested various ways to discriminate between the two arrangements of molecules in water.^{62,70,73,79,91}

In this work, we have computed the order parameter based on two different criteria: distance to the fifth nearest neighbor (d_5)⁷³ and local structure index (LSI, usually denoted by I).⁹²

The d_5 criterion assigns molecules to belong to “low density” when d_5 is greater than the cutoff distance, $r_0 = 3.5 \text{ \AA}$. This cutoff distance defines the first coordination shell and is estimated from the position of the minimum that separates the first and second coordination shells in the oxygen-oxygen radial distribution function. The parameter d_5 contains information about the local structure up to the first coordination shell (3.5 \AA) only.

In order to include structural information beyond the first shell, we have also computed the local structural index (LSI). The LSI of molecule i is obtained by ordering the oxygen-oxygen nearest neighbor distances between the central i th molecule and its j th nearest neighbor (denoted as r_j); $r_1 < r_2 < \dots < r_j < \dots < r_{n(i)} < 3.7 \text{ \AA} < r_{n(i)+1}$. The number $n(i)$ is chosen in such a way that $r_{n(i)} < 3.7 \text{ \AA} < r_{n(i)+1}$. Then, LSI is defined as⁹²

$$I(i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} [\Delta(j;i) - \bar{\Delta}(i)]^2, \quad (6)$$

where $\Delta(j;i) = r_{j+1} - r_j$ and $\bar{\Delta}$ is the average of $\Delta(j;i)$ over all the nearest neighbors j of molecule i . LSI is a measure of inhomogeneity between the first and second hydration shells of a tagged water molecule and thus probes the local structure

beyond the first shell. A large value of LSI implies that there is a structured first shell and that there is no inhomogeneity (that is, no trapped “interstitial” water molecules) between the first and second coordination shells. A small value of LSI implies either a disordered first coordination shell or a significant presence of inhomogeneities in between first and second coordination shells. We have used the same procedure followed by Wikfeldt *et al.*⁷⁰ for TIP4P/2005 and Appignanesi *et al.*⁷⁹ for SPC/E water to define LDL and HDL-like local environments in the system. However, unlike these studies, we have computed the LDL fraction in real dynamical trajectories, not in the inherent structures. The particles having LSI value less than 0.13 \AA^2 are assigned as HDL-like and particles having LSI values greater than 0.13 \AA^2 as LDL-like. The parameter d_5 requires merely that the low-density structures have a four-coordinated first shell, while the LSI criterion also requires local ordering beyond first coordination shell. Consequently, low-density fraction as computed by the LSI criterion will in general be lower than that computed according to the d_5 criterion.

In Fig. 5, we compare the low-density fractions computed using both the d_5 and LSI criteria along with the predictions of the TSEOS for the extent of reaction, x . The computed order parameters and the phenomenological low-density fraction show qualitatively similar pressure dependence along different isotherms. The computed low-density fraction based on the LSI criterion is significantly lower than that based on the d_5 criterion. LSI strongly underestimates the extent of reaction x , while d_5 slightly overestimates it. We also observe that the low-density fraction based on d_5 criteria is symmetric, showing

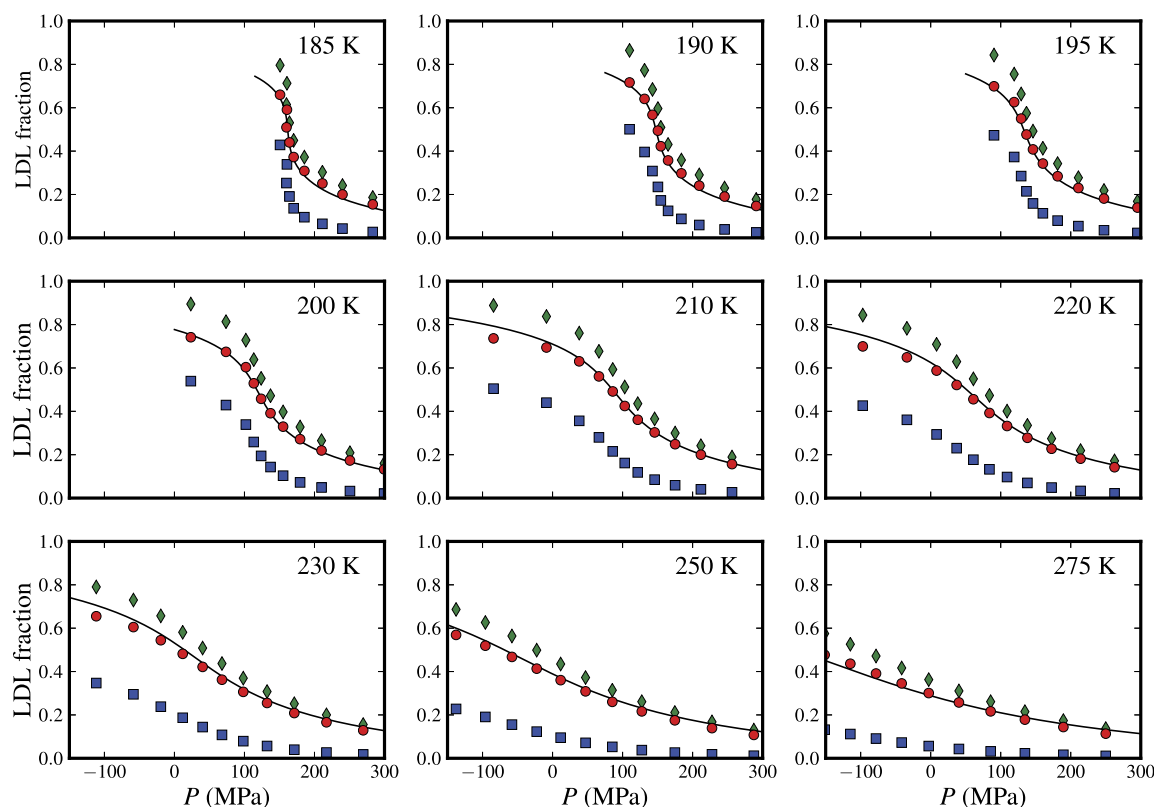


FIG. 5. Pressure dependence of low-density fraction computed using both d_5 (filled diamonds) and LSI (filled squares) criteria along different isotherms. Filled circles are d_5 multiplied by a factor of 0.82. Solid lines indicate predictions of TSEOS for the low-density fraction.

an inflection point at about $1/2$, which is in agreement with the TSEOS definition of the order parameter that is related to the low-density fraction as $x - x_c$ with the critical fraction $x_c = 1/2$. Low-density fractions computed for two versions of ST2⁴² were also based on d_5 and were in good agreement with the TSEOS. Similar behavior is demonstrated by the local density structural order parameter introduced by Russo and Tanaka⁶² which is also based on d_5 -like criteria.

Moreover, the low-density fraction, predicted by d_5 based criteria, multiplied by a factor ~ 0.82 is in remarkably good agreement with the phenomenologically defined order parameter. The discrepancy between the LDL fraction obtained by the d_5 criterion and $(x - x_c)$ may originate from both the approximations made in the TSEOS and the details of the microscopic definition of the order parameter. We also note that in the lowest approximation, the phenomenological order parameter $x - x_c$ is proportional to the change in molar volume (V) and entropy (S) as $x - x_c = a\lambda(V - V_c)/V_c$ and as $x - x_c = -\lambda(S - S_c)/R$.^{42,74}

VI. PHASE BEHAVIOR OF TIP4P/2005 WATER FROM TSEOS

In Fig. 6, we present the phase diagram summarizing the behavior of supercooled TIP4P/2005 in the P - T plane predicted by the TSEOS. In two-state thermodynamics, the locus of points with $\ln K = 0$ at $\omega > 2$ locates the LLPT line between HDL and LDL. The continuation of this line for $\omega < 2$ is the Widom line (see Section III). Using the language of the scaling theory of critical phenomena, $\ln K$ corresponds to the ordering field, while the conjugate variable $x - 1/2$ is the order parameter. The Widom line corresponds to zero field and zero order parameter and is the line of maximum fluctuations of the order parameter. Asymptotically, the Widom line coincides with the loci of the compressibility maxima and heat capacity maxima (see also Ref. 18). The estimated

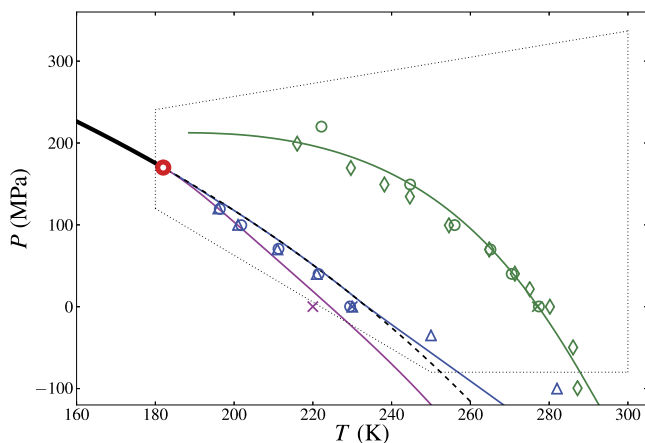


FIG. 6. Phase diagram for TIP4P/2005 water model predicted by TSEOS. The LLPT, critical point, and Widom line are shown by the thick black curve, the red circle, and the dashed black curve, respectively. The loci of maxima in ρ , κ_T , and C_P according to the TSEOS are shown by green, blue, and magenta curves, respectively. Corresponding data are shown as reported by Refs. 62 (open diamonds), 36 (open circles), 94 (open triangles), and as computed for this work (crosses). The dotted contour bounds the region of validity of the TSEOS.

critical temperature, pressure and density are $T_c = 182$ K, $P_c = 170$ MPa, and $\rho_c = 1017$ kg/m³, respectively. These critical parameters are in close agreement with the values reported by Sumi and Sekino⁶¹ and Yagasaki *et al.*⁴⁰ The temperature of maximum density (TMD) line predicted from two-structure thermodynamics also shows reasonable agreement with previously reported simulation data for this model.^{36,62} Our model predicts quite accurately (within ~ 5 K) the temperature of maximum of the isobaric heat capacity (≈ 220 K⁹³) and isothermal compressibility (≈ 230 K⁶⁸) at ambient pressure.

In Fig. 6, the dotted contour bounds the area of the validity of this form of the TSEOS. This restricted form becomes increasingly inaccurate for densities below 960 kg/m³ and at negative pressures. In the current work, we did not consider pressures below -80 MPa. Extending the validity of the TSEOS to lower densities and negative pressures will at least require the restrictions on the definitions of $\ln K$ and ω in Eqs. (3) and (5) to be relaxed. Such an extension could address the current discussions surrounding the behavior of water at extremely strong negative pressures.⁹⁴

VII. WATER-LIKE MODELS VERSUS REAL WATER

Our study, together with three previously published simulation results,^{36,40,61} shows that the TIP4P/2005 model in the range of pronounced thermodynamic anomalies behaves similarly to the ST2 model. This is clearly seen from the equally sharp behavior of isobars in the vicinity of the projected critical point as demonstrated in Figs. 7(a) and 2. Even without computational data obtained for the two-phase region, such van der Waals-like behavior of the isobars suggests the proximity of the critical point. Contrary to the ST2 and TIP4P/2005 models, in the mW model of water the isobars, shown in Fig. 7(b), only weakly change with changing pressure and never become steep enough to suggest criticality. Indeed, the presence of a LLPT is model-dependent. While in the mW model the non-ideality in mixing of the two structures never becomes strong enough to cause a metastable LLPT, the thermodynamics of the ST2 and TIP4P/2005 models strongly implies the existence of a metastable LLPT.

The thermodynamics of real supercooled water is more ambiguous. Properties of bulk supercooled water in the experimentally accessible region are well described by two-structure thermodynamics (for example, density data and theoretical predictions along isobars are presented in Fig. 8(a)). However, the projected phase separation is located so far below the homogeneous ice nucleation limit that the location of a LLPT and even its very existence become uncertain.⁷⁴ This problem with real water is clearly illustrated by comparison of Fig. 1, showing the convergence of isochores in TIP4P/2005 at a point that is interpreted as the LLCP, and Fig. 8(b) for real water in which such convergence is in principle allowed but far from certain. Obviously, the real-water dilemma cannot be resolved with the experimental data that are currently available. Future studies will need to either penetrate into “no-man’s land” or bring the critical point into experimentally accessible conditions by adding a solute.^{31,32,98}

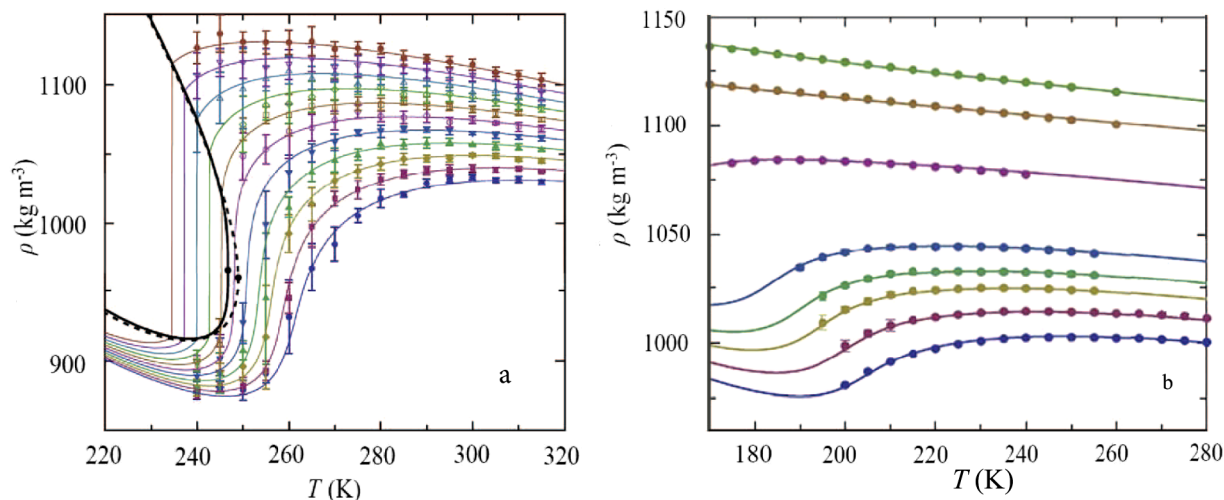


FIG. 7. Simulated data from the ST2 and mW model (symbols) are compared with the predictions (curves) of two-structure thermodynamics, as adapted for the respective models. (a) Temperature dependent density (ρ) along different isobars computed for the ST2(II) model. The thick black curve indicates two-phase coexistence (dashed: mean field equation, solid: crossover equation) and black dots represent the corresponding critical point. The isobar pressures vary from 100 MPa to 200 MPa in steps of 10 MPa. Adapted with permission from J. Chem. Phys. **140**, 104502 (2014). Copyright 2014 AIP Publishing LLC. (b) Temperature dependent density (ρ) along different isobars (from the top: 1013, 810, 507, 228, 159, 57, 0.1 MPa) computed for the mW model. Adapted with permission from J. Chem. Phys. **138**, 174501 (2013). Copyright 2013 AIP Publishing LLC.

VIII. DISCUSSION: DOES A METASTABLE LLPT EXIST IN TIP4P/2005?

We have investigated the thermodynamic behavior of the TIP4P/2005 water model in the supercooled region. The convergence of the isochores around a density of about 1020 kg/m³ and the steep van der Waals-like behavior of the order parameter (the low-density fraction) at about 180–185 K suggests the presence of a metastable LLPT in the TIP4P/2005 model.

Our results are supported by the data of Sumi and Sekino⁶¹ and consistent with the conclusions of Yagasaki *et al.*⁴⁰ The substantiation of this viewpoint will require free-energy calculations such as those that have yielded unambiguous evidence^{41,48} of a liquid-liquid transition in the ST2 model of water. Because the phenomenon under scrutiny is metastable,

the question of how sampling time and system size constrain the possibility of observing a liquid-liquid transition arises in addition to the question of its existence in a free-energy or equation-of-state calculation.

However, the most recent extensive study of the TIP4P/2005 and TIP5P models by Overduin and Patey,⁵⁹ which reported simulations in the projected two-phase region for systems ranging in size from 4000 to 32 000, found density differences between the regions of low and high densities to decrease with increasing system size. The difference finally disappeared for a system composed of 32 000 molecules. Overduin and Patey further argued that, as the appearance of regions of low density is always accompanied by small ice-like crystallites, the regions of different densities observed by Yagasaki *et al.*⁴⁰ might be associated with the appearance

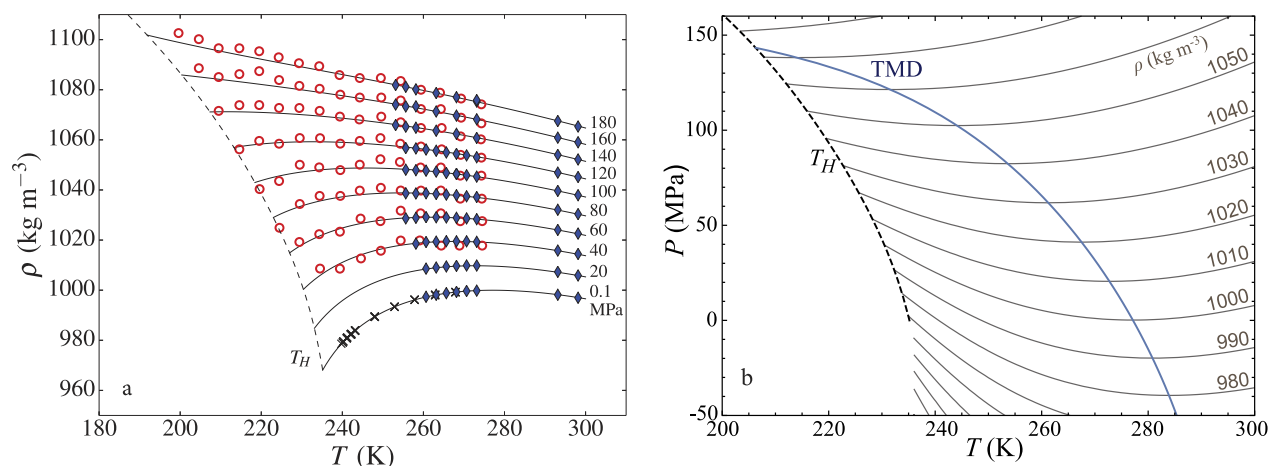


FIG. 8. (a) Density of cold and supercooled water as a function of temperature along different isobars (black lines are the predictions of an extended version of the TSEOS⁷⁸). Symbols are experimental data reported in Refs. **6** (crosses), **95** (open red circles), and **96** (filled blue diamonds). T_H indicates the homogeneous nucleation line. The data from Ref. **95** have been adjusted by at most 0.3% to correct for small systematic errors, as explained in Ref. **97**. (b) Isochores of cold and supercooled water computed with an extended version of the TSEOS.⁷⁸ The dashed curve is the homogeneous nucleation line and the blue curve is the TMD locus.

and coarsening of local ice-like structures, rather than with liquid-liquid phase separation. This argument is similar to that of Limmer and Chandler,⁵¹ who also argued that the density differences observed by Yagasaki *et al.*⁴⁰ are due to ice coarsening, rather than to spontaneous liquid-liquid phase separation.

This argument deserves serious consideration. However, we must note that separated liquid states observed in *NVT* simulations are always metastable with respect to ice formation. Consequently, as Overduin and Patey note,⁵⁹ the mere presence of ice-like crystallites (6-8% for TIP4P/2005 model at the lowest temperature studied by Overduin and Patey⁵⁹) having finite lifetime in the system does not provide unambiguous proof for the ice-coarsening hypothesis proposed by Limmer and Chandler.⁴⁹⁻⁵¹ Also, the computed fraction of ice-like particles or crystallites is very sensitive to the definition adopted for classifying a water molecule as ice-like. On the contrary, the observed excess local density of ice-like crystallites and strong correlations among them in low-density regions can also be understood without invoking the ice-coarsening hypothesis. Liquid-liquid phase separation leads to spatial heterogeneity in water, and it is to be expected that the ice-like fluctuations or crystallites will be more stable in the low-density regions due to a lower surface free-energy cost. In this context, the recent simulations of Smallenburg and Sciortino⁴⁸ have clearly demonstrated that the liquid-liquid transition in the ST2 model is not a misinterpreted crystallization transition, as had been claimed.^{49,50}

Moreover, the fact that phenomena observed in the metastable region depend on the system size and on the duration of observation time is not surprising. This is, in fact, an essential characteristic of metastability. A metastable phase separation cannot exist at all in the thermodynamic limit (infinite size and infinite time). If we denote by τ_{relax} the internal relaxation time in the metastable state, and τ_{out} the time it takes for the system to exit the metastable state and form the stable phase (i.e., a characteristic crystallization time in our case), then the metastable state is well defined if $\tau_{\text{relax}} \ll \tau_{\text{out}}$. When this condition is met, thermodynamics can be applied to a metastable state. As Overduin and Patey note, there are several reasons why the metastable LLPT might not be manifested in large enough systems.⁵⁹ In particular, as has been emphasized by Binder,⁹⁹ the divergence of the correlation length at the critical point causes the relaxation time to diverge, an effect known as critical slowing-down. Increasing the system size, on the other hand, decreases the lifetime of metastability, and thus at certain conditions prevents the manifestation of metastable phase separation. In addition, there is another characteristic time scale in this problem that could complicate observation of a liquid-liquid phase separation: the time of conversion between the two alternative liquid structures. At temperatures well below the liquid-liquid critical temperature, this time may become long enough that the formation of the low-density structure will not be completed during the time of observation.

The formation of two liquid phases can also be impeded by the unfavorable interfacial energy between them. Consequently, the extent of phase separation not only depends on the choice of initial density of the system but also on

the aspect ratio of the simulation box. Due to the large surface energy cost for the formation of well-defined stable interfaces, phase separation is not observed in cubic boxes, even in systems far below the LLC. In order to observe phase separation one always simulates rectangular boxes (1:1:4 in case of Yagasaki *et al.*⁴⁰ as well as Overduin and Patey⁵⁹ for 4000 molecules) to minimize interfacial free energy cost for formation of the LDL-HDL interface. It is thus very plausible that the observation of two different metastable liquid densities in water-like models, such as TIP4P/2005 and TIP5P, would involve length and time scale constraints that would also influence the pathway to homogeneous ice nucleation.

As explained above, attempts to directly observe metastable liquid-liquid separation in *NVT* simulations are subject to non-trivial limitations. We have used an alternative approach to evaluate the hypothesis of the metastable LLPT in supercooled water. We have studied a relatively small system of hundreds of molecules and performed a series of simulations (about 200) to obtain reliable information on the thermodynamic surface. Our study does not support one of the scenarios discussed by Overduin and Patey⁵⁹ in which “liquid-liquid coexistence is simply not a possibility” for the TIP4P/2005 water model. On the contrary, the clear convergence of the isochores around 1020 kg/m³ and the behavior of thermodynamic properties demonstrate the tendency to criticality. Furthermore, the equation of state that is built on the assumption of the existence of LLPT fits the simulation data very well. Moreover, the microscopic structural order parameters (d_5 and LSI) associated with the low-density fraction strongly support the two-structure nature of TIP4P/2005 and the approach to criticality around 180-182 K. This important simulation result is independent of any speculation regarding the shape of the thermodynamic surface.

An alternative hypothesis to the competition between two liquid structures would be to attribute supercooled water anomalies (the sharp increases of the response functions) to pre-crystallization effects.^{51,59} Indeed, the theory of so-called “weak crystallization,” which accounts for translational-order fluctuations, describes the properties of the supercooled mW model as well as two-structure thermodynamics does.⁵⁵ However, pre-crystallization effects cannot explain the convergence of isochores and the critical-like behavior of the low-density fraction that is clearly observed in the ST2 and TIP4P/2005 models.

There is another puzzling result of Overduin and Patey⁵⁹ that requires further studies. The correlation length characterizing fluctuations of density increases sharply upon supercooling in real water.^{100,101} In Ref. 59, Overduin and Patey examine this correlation length in both TIP5P and TIP4P/2005 and claim that it apparently diverges along the critical isochore in TIP5P, but does not exhibit such an anomaly in TIP4P/2005. We note that in our simulations, the isothermal compressibility increases by an order of magnitude along the critical isochore, which is a strong effect, especially in view of a relatively small size of the system (about 2 nm). The correlation length of density fluctuations is approximately proportional to the square root of the compressibility. Accordingly, the correlation length should increase by about three times, the effect indeed observed for TIP5P.⁵⁹

In conclusion, the results of our study strongly support the presence of a liquid-liquid critical point in the TIP4P/2005 model and are consistent with the possibility of a liquid-liquid phase transition for this model. Our study does not answer the questions regarding conditions under which the metastable LLPT can or cannot be observed in the region below the projected critical point. Systematic studies at various simulation conditions are required to further our understanding of this deep and important problem. As far as the one-phase metastable liquid region is concerned, investigation of finite-size effects on the shape of the thermodynamic anomalies would be highly desirable.

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- ¹C. A. Angell, J. Shuppert, and J. C. Tucker, *J. Phys. Chem.* **77**, 3092 (1973).
- ²R. J. Speedy and C. A. Angel, *J. Chem. Phys.* **65**, 851 (1976).
- ³H. Kanno and C. A. Angell, *J. Chem. Phys.* **70**, 4008 (1979).
- ⁴H. Kanno and C. A. Angell, *J. Chem. Phys.* **73**, 1940 (1980).
- ⁵C. A. Angell, W. J. Sichina, and M. Oguni, *J. Phys. Chem.* **86**, 998 (1982).
- ⁶D. E. Hare and C. M. Sorensen, *J. Chem. Phys.* **87**, 4840 (1987).
- ⁷C. A. Angell, *Science* **267**, 1924 (1995).
- ⁸P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, 1996).
- ⁹E. Tombari, C. Ferrari, and G. Salvetti, *Chem. Phys. Lett.* **300**, 749 (1999).
- ¹⁰F. Franks, *Water: A Matrix for Life* (Royal Society of Chemistry, Cambridge, 2000).
- ¹¹H. E. Stanley, S. V. Buldyrev, M. Canpolat, O. Mishima, M. R. Sadr-Lahijany, A. Scala, and F. W. Starr, *Phys. Chem. Chem. Phys.* **2**, 1551 (2000).
- ¹²P. G. Debenedetti, *J. Phys.: Condens. Matter* **15**, R1669 (2003).
- ¹³H. E. Stanley and J. Teixeira, *J. Chem. Phys.* **73**, 3404 (1980).
- ¹⁴R. J. Speedy and C. A. Angel, *J. Phys. Chem.* **86**, 982 (1982).
- ¹⁵P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, *Nature* **360**, 324 (1992).
- ¹⁶S. Sastry, P. G. Debenedetti, F. Sciortino, and H. E. Stanley, *Phys. Rev. E* **53**, 6144 (1996).
- ¹⁷L. P. N. Rebelo, P. G. Debenedetti, and S. Sastry, *J. Chem. Phys.* **109**, 626 (1998).
- ¹⁸L. Xu, P. Kumar, S. V. Buldyrev, S. Chen, P. H. Poole, F. Sciortino, and H. E. Stanley, *Proc. Nat. Acad. Sci. U. S. A.* **102**, 16558 (2005).
- ¹⁹B. Jana, R. S. Singh, and B. Bagchi, *Phys. Chem. Chem. Phys.* **13**, 16220 (2011).
- ²⁰H. Tanaka, *Faraday Discuss.* **167**, 9 (2013).
- ²¹O. Mishima and H. E. Stanley, *Nature* **396**, 329 (1998).
- ²²T. Loerting and N. Giovambattista, *J. Phys.: Condens. Matter* **18**, R919 (2006).
- ²³K. Amann-Winkel, C. Gainaru, P. H. Handle, M. Seidl, H. Nelson, R. Bhmer, and T. Loerting, *Proc. Nat. Acad. Sci. U. S. A.* **110**, 17720 (2013).
- ²⁴J. Wong, D. A. Jahn, and N. Giovambattista, *J. Chem. Phys.* **143**, 074501 (2015).
- ²⁵F. Mallamace, C. Branca, M. Broccio, C. Corsaro, J. Gonzalez-Segredo, N. Spooen, H. E. Stanley, and S. H. Chen, *Eur. Phys. J.: Spec. Top.* **161**, 19 (2008).
- ²⁶J. Sellberg, C. Huang, T. McQueen, N. Loh, H. Laksmono, D. Schlesinger, R. Sierra, D. Nordlund, C. Hampton, D. Starodub, D. DePonte, M. Beye, C. Chen, A. Martin, A. Barty, K. Wikfeldt, T. Weiss, C. Caronna, J. Feldkamp, L. Skinner, M. Seibert, M. Messerschmidt, G. Williams, S. Boutet, L. Pettersson, M. Bogan, and A. Nilsson, *Nature* **510**, 381 (2014).
- ²⁷J. R. Bruijn, T. H. van der Loop, and S. Woutersen, *J. Phys. Chem. Lett.* **7**, 795 (2016).
- ²⁸K. Murata and H. Tanaka, *Nat. Mater.* **11**, 436 (2012).
- ²⁹K. Murata and H. Tanaka, *Nat. Commun.* **4**, 2844 (2013).
- ³⁰Y. Suzuki and O. Mishima, *J. Chem. Phys.* **141**, 094505 (2014).
- ³¹Z. Zhao and A. Angell, *Angew. Chem.* **55**, 2474 (2016).
- ³²J. W. Biddle, V. Holten, and M. A. Anisimov, *J. Chem. Phys.* **141**, 074504 (2014).
- ³³L.-S. Zhao, Z.-X. Cao, and Q. Wang, *Sci. Rep.* **5**, 15714 (2015).
- ³⁴P. H. Poole, I. Saika-Voivod, and F. Sciortino, *J. Phys.: Condens. Matter* **17**, L431 (2005).
- ³⁵Y. Liu, A. Z. Panagiotopoulos, and P. G. Debenedetti, *J. Chem. Phys.* **131**, 104508 (2009).
- ³⁶J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **133**, 234502 (2010).
- ³⁷Y. Liu, J. C. Palmer, A. Z. Panagiotopoulos, and P. G. Debenedetti, *J. Chem. Phys.* **137**, 214505 (2012).
- ³⁸P. H. Poole, R. K. Bowles, I. Saika-Voivod, and F. Sciortino, *J. Chem. Phys.* **138**, 034505 (2013).
- ³⁹T. A. Kesselring, E. Lascaris, G. Franzese, S. V. Buldyrev, H. J. Herrmann, and H. E. Stanley, *J. Chem. Phys.* **138**, 244506 (2013).
- ⁴⁰T. Yagasaki, M. Matsumoto, and H. Tanaka, *Phys. Rev. E* **89**, 020301 (2014).
- ⁴¹J. C. Palmer, F. Martelli, Y. Liu, R. Car, A. Z. Panagiotopoulos, and P. G. Debenedetti, *Nature* **510**, 385 (2014).
- ⁴²V. Holten, J. C. Palmer, P. H. Poole, P. G. Debenedetti, and M. A. Anisimov, *J. Chem. Phys.* **140**, 104502 (2014).
- ⁴³S. Sastry and C. A. Angell, *Nat. Mater.* **2**, 739 (2003).
- ⁴⁴K. Stokely, M. G. Mazza, H. E. Stanley, and G. Franzese, *Proc. Nat. Acad. Sci. U. S. A.* **107**, 1301 (2010).
- ⁴⁵V. Vasisht, S. Saw, and S. Sastry, *Nat. Phys.* **7**, 549 (2011).
- ⁴⁶F. Smallenburg, L. Filion, and F. Sciortino, *Nat. Phys.* **10**, 653 (2014).
- ⁴⁷F. W. Starr and F. Sciortino, *Soft Matter* **10**, 9413 (2014).
- ⁴⁸F. Smallenburg and F. Sciortino, *Phys. Rev. Lett.* **115**, 015701 (2015).
- ⁴⁹D. Limmer and D. Chandler, *J. Chem. Phys.* **135**, 134503 (2011).
- ⁵⁰D. Limmer and D. Chandler, *J. Chem. Phys.* **138**, 214504 (2013).
- ⁵¹D. T. Limmer and D. Chandler, *Phys. Rev. E* **91**, 016301 (2015).
- ⁵²N. J. English, P. G. Kusalik, and J. S. Tse, *J. Chem. Phys.* **139**, 084508 (2013).
- ⁵³V. Molinero and E. B. Moore, *J. Phys. Chem. B* **113**, 4008 (2009).
- ⁵⁴E. B. Moore and V. Molinero, *Nature* **479**, 506 (2011).
- ⁵⁵V. Holten, D. T. Limmer, V. Molinero, and M. A. Anisimov, *J. Chem. Phys.* **138**, 174501 (2013).
- ⁵⁶F. H. Stillinger and T. A. Weber, *Phys. Rev. B* **31**, 5262 (1985).
- ⁵⁷S. D. Overduin and G. N. Patey, *J. Phys. Chem. B* **116**, 12014 (2012).
- ⁵⁸S. D. Overduin and G. N. Patey, *J. Chem. Phys.* **138**, 184502 (2013).
- ⁵⁹S. D. Overduin and G. N. Patey, *J. Chem. Phys.* **143**, 094504 (2015).
- ⁶⁰J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **123**, 234505 (2005).
- ⁶¹T. Sumi and H. Sekino, *RSC Adv.* **3**, 12743 (2013).
- ⁶²J. Russo and H. Tanaka, *Nat. Commun.* **5**, 3556 (2014).
- ⁶³M. W. Mahoney and W. L. Jorgensen, *J. Chem. Phys.* **112**, 8910 (2000).
- ⁶⁴A. K. Soper and M. A. Ricci, *Phys. Rev. Lett.* **84**, 2881 (2000).
- ⁶⁵A. Taschin, P. Bartolini, R. Eramo, R. Righini, and R. Torre, *Nat. Commun.* **4**, 2401 (2013).
- ⁶⁶T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L. G. M. Pettersson, A. Nilsson, and S. Shin, *Chem. Phys. Lett.* **460**, 387 (2008).
- ⁶⁷C. Huang, K. T. Wikfeldt, T. Tokushima, D. Nordlund, Y. Harada, U. Bergmann, M. Niebuhr, T. M. Weiss, Y. Horikawa, M. Leetmaa, M. P. Ljungberg, O. Takahashi, A. Lenz, L. Ojame, A. P. Lyubartsev, S. Shin, L. G. M. Pettersson, and A. Nilsson, *Proc. Nat. Acad. Sci. U. S. A.* **106**, 15214 (2009).
- ⁶⁸L. G. M. Pettersson and A. Nilsson, *J. Non-Cryst. Solids* **407**, 399 (2015).
- ⁶⁹A. Nilsson and L. G. M. Pettersson, *Nat. Commun.* **6**, 8998 (2015).
- ⁷⁰K. T. Wikfeldt, A. Nilsson, and L. G. M. Pettersson, *Phys. Chem. Chem. Phys.* **13**, 19918 (2011).
- ⁷¹A. Nilsson, C. Huang, and L. G. M. Pettersson, *J. Mol. Liq.* **176**, 2 (2012).
- ⁷²E. B. Moore and V. Molinero, *J. Chem. Phys.* **130**, 244505 (2009).
- ⁷³M. J. Cuthbertson and P. H. Poole, *Phys. Rev. Lett.* **106**, 115706 (2011).
- ⁷⁴V. Holten and M. A. Anisimov, *Sci. Rep.* **2**, 713 (2012).
- ⁷⁵C. E. Bertrand and M. A. Anisimov, *J. Phys. Chem. B* **115**, 14099 (2011).
- ⁷⁶H. Tanaka, *Europhys. Lett.* **50**, 340 (2000).
- ⁷⁷F. Bresme, J. W. Biddle, J. V. Sengers, and M. A. Anisimov, *J. Chem. Phys.* **140**, 161104 (2013).
- ⁷⁸V. Holten, J. V. Sengers, and M. A. Anisimov, *J. Phys. Chem. Ref. Data* **43**, 043101 (2014).
- ⁷⁹G. A. Appignanesi, J. Rodriguez Fris, and F. Sciortino, *Eur. Phys. J. E* **29**, 305 (2009).
- ⁸⁰F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60**, 1545 (1974).

- ⁸¹D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H. J. C. Berendsen, *J. Comput. Chem.* **26**, 1701 (2005).
- ⁸²B. Hess, H. Bekker, H. J. C. Berendsen, and J. G. E. M. Fraaije, *J. Comput. Chem.* **18**, 1463 (1997).
- ⁸³S. Nose, *Mol. Phys.* **52**, 255 (1984).
- ⁸⁴W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- ⁸⁵M. Parrinello and A. Rahman, *J. Appl. Phys.* **52**, 7182 (1981).
- ⁸⁶J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, 2006).
- ⁸⁷See supplementary material at <http://dx.doi.org/10.1063/1.4944986> for more detailed information on the relaxation of the systems, as evidenced by the decay in time of the self-intermediate scattering function.
- ⁸⁸J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures* (Butterworth Scientific, 1982).
- ⁸⁹M. E. Fisher, in *Critical Phenomena*, edited by F. J. W. Hahne, Lecture Notes in Physics (Springer, 1983), pp. 1–139.
- ⁹⁰M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach Science Publishers, 1991).
- ⁹¹J. R. Errington and P. G. Debenedetti, *Nature* **409**, 318 (2001).
- ⁹²E. Shiratani and M. Sasai, *J. Chem. Phys.* **108**, 3264 (1998).
- ⁹³S. Saito, I. Ohmine, and B. Bagchi, *J. Chem. Phys.* **138**, 094503 (2013).
- ⁹⁴G. Pallares, M. El Mekki Azouzi, M. A. Gonzalez, J. L. Aragones, J. L. F. Abascal, C. Valeriani, and F. Caupin, *Proc. Nat. Acad. Sci. U. S. A.* **111**, 7936 (2014).
- ⁹⁵O. Mishima, *J. Chem. Phys.* **133**, 144503 (2010).
- ⁹⁶T. Sotani, J. Arabas, H. Kubota, and M. Kijima, *High Temp. High Pressures* **332**, 433 (2000).
- ⁹⁷V. Holten, C. E. Bertrand, M. A. Anisimov, and J. V. Sengers, *J. Chem. Phys.* **136**, 094507 (2012).
- ⁹⁸D. Corradini, M. Rovere, and P. Gallo, *J. Chem. Phys.* **132**, 134508 (2010).
- ⁹⁹K. Binder, *Proc. Nat. Acad. Sci. U. S. A.* **111**, 9374 (2014).
- ¹⁰⁰C. Huang, T. M. Weiss, D. Nordlund, K. T. Wikfeldt, L. G. M. Pettersson, and A. Nilsson, *J. Chem. Phys.* **133**, 134504 (2010).
- ¹⁰¹K. T. Wikfeldt, C. Huang, A. Nilsson, and L. G. M. Pettersson, *J. Chem. Phys.* **134**, 214506 (2011).