Abstract

We have developed a scaled parametric equation of state to describe and predict thermodynamic properties of supercooled water. The equation of state, built on the growing evidence that the critical point of supercooled liquid-liquid water separation exists, is universal in terms of theoretical scaling fields and is shown to belong to the Ising-model class of universality. The theoretical scaling fields are postulated to be analytical combinations of the physical fields, pressure and temperature. The equation of state enables us to accurately locate the “Widom line” (the locus of stability minima) and determine that the critical pressure is considerably lower than predicted by computer simulations.

Upon supercooling, water exhibits anomalous behavior with sharply increasing heat capacity, isothermal compressibility, and the magnitude of negative thermal expansivity [1]. A thermodynamically consistent view on the global phase behavior of supercooled water was formulated by Poole et al. [2]. According to this view, the observed anomalies are associated with density and entropy fluctuations diverging at a critical point of liquid-liquid coexistence that terminates the line of first-order transitions between two liquid aqueous phases: low-density liquid and high-density liquid. This ”second-critical-point” scenario is supported by
extensive Monte Carlo and molecular dynamic simulations [3], by a modified van der Waals model that includes hydrogen-bond contributions [4], and by the limited but impressive experimental evidence [5,6]. An alternative interpretation of the phase behavior of water, the "singularity-free" scenario, attributes the increase in response functions upon supercooling, through a thermodynamic consistency argument, to the existence of a negatively-sloped locus of density maxima in the P-T plane [7]. However, the second-critical-point scenario seems more plausible in view of the experimental evidence of a first-order phase transition between two amorphous-water glasses [1,5,6]. The global phase diagram of water is shown in Fig. 1. Two remarkable features make the second critical point in water phenomenologically different from the well-known gas-liquid critical point. The negative slope of the liquid-liquid phase transition line in the P-T plane means that the higher density liquid water is the phase with larger entropy. A very large value of the slope at the critical point (about 30 times larger than for the vapor-liquid transition at the critical point) indicates the significance of the entropy change with respect to the density change, and correspondingly, the importance of the entropy fluctuations. However, the location of the liquid-liquid critical point, especially the value of the critical pressure is uncertain. The simulation data yields a variety of the critical-pressure values, from negative pressures to 3.4 kbar [1,8].

In this Letter, we present a scaled parametric equation of state to describe and predict thermodynamic properties of supercooled water. The equation of state is universal and belongs to the Ising-model class of universality. The equation of state enables us to accurately locate the critical point and the “Widom line” [9] (the locus of stability minima and order-parameter fluctuation maxima). In particular, we conclude that the critical pressure is considerably lower than obtained by computer simulations and we predict thermodynamic properties in the regions inaccessible to experiments.

It is commonly accepted that the critical behavior of all fluids, simple and complex, belong to the universality class of the three-dimensional Ising model [10]. Water is not an exception [11]. Near the critical point the critical (fluctuation-induced) part, Ψ_{cr}, of an appropriate field-dependent thermodynamic potential Ψ is a universal function of two
scaling fields, “ordering”, $h_1$, and “thermal”, $h_2$ [10]:

$$\Psi_{cr} \simeq h_2^{2-\alpha} f \left( \frac{h_1}{h_2^{\beta+\gamma}} \right),$$

where $\alpha = 0.109$, $\beta = 0.326$, $\gamma = 1.239$, are universal exponents (interrelated as $\alpha + 2\beta + \gamma = 2$) in the scaling power laws (as a function of $h_2$ at $h_1 = 0$) for the “weak” susceptibility, the order parameter and the “strong” susceptibility, respectively. The first derivatives of the thermodynamic potential with respect to the scaling fields define two scaling densities, the “order parameter” $\phi_1 = -\partial \Psi_{cr}/\partial h_1$ and the “thermal density” $\phi_2 = -\partial \Psi_{cr}/\partial h_2$. Respectively, the second derivatives define three susceptibilities, “strong” $\chi_1 = (\partial \phi_1/\partial h_1)_{h_2}$, “weak” $\chi_2 = (\partial \phi_2/\partial h_2)_{h_1}$, and “cross” $\chi_{12} = (\partial \phi_1/\partial h_1)_{h_2} = (\partial \phi_2/\partial h_1)_{h_2}$.

The universal scaling function $f$ contains two system-dependent amplitudes that originate from the initial Hamiltonian. In the mean-field approximation ($\alpha = 0$, $\beta = 1/2$, $\gamma = 1$), the critical part of the thermodynamic potential is represented by a Landau expansion,

$$\Psi_{cr} = \frac{1}{2}a_0 h_2 \phi_1^2 + \frac{1}{4}u_0 \phi_1^4 - h_1 \phi_1,$$

where the constants $a_0$ and $u_0$ (the same coefficients as in the initial Hamiltonian) play the role of the mean-field system-dependent amplitudes.

To apply the universal expression (1) for describing the liquid-liquid critical point in supercooled water, we assume the scaling fields are analytical combinations of physical fields, the pressure $P$ and the temperature $T$:

$$h_1 = a_1 \Delta \hat{P} + a_2 \Delta \hat{T} + a_3 \Delta \hat{P}^2$$

$$h_2 = b_1 \Delta \hat{T} + b_2 \Delta \hat{P}$$

with $\Delta \hat{P} = (P - P_c) / (\rho_c RT_c)$ and $\Delta \hat{T} = (T - T_c) / T_c$ (where the subscript “c” here and below indicates the critical parameters) and $a_i$ and $b_i$ are system-dependent coefficients.

Representation of scaling fields through linear mixing of physical fields is commonly used to incorporate asymmetric fluid criticality into the symmetric Ising model [?,13]. To account for the strong curvature of the liquid-liquid transition line, defined as $h_1 = 0$, we added a non-linear pressure term, $a_3 \Delta \hat{P}^2$, in $h_1$. 

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Such a representation of the scaling fields corresponds to the practically convenient choice of the molar Gibbs energy (chemical potential) as the field-dependent potential so that $\Psi = \Psi(P, T)$ and $\Psi_{cr} = \Psi_{cr}(h_1, h_2)$. In this formulation we neglect the difference between $-\Delta \hat{V} \equiv -(V - V_c)/V_c = (\rho - \rho_c)/\rho$ and $(\rho - \rho_c)/\rho_c$, a reasonable approximation for weakly compressible liquids. Any two coefficients in the scaling fields may be absorbed in two system-dependent amplitudes of the scaling function $f$, so that we adopt $a_2 = 1$ and $b_2 = -1$. The negative sign of $b_2$ indicates that the liquid-liquid phase separation in supercooled water occurs with increase of pressure (Fig. 1), in contrast to the vapor-liquid phase separation. The value of $a_1$, $a_3$, and $b_1$ can be determined from the shape of the liquid-liquid first-order transition curve. The “Widom line” in the one-phase region, $h_1 = 0$, is an analytical continuation of the liquid-liquid transition curve from $C^*$ to lower pressures and higher temperatures.

The mixing of physical fields into the scaling fields, defined by Eqs. (2) and (3), means that the order parameter is a combination of molar entropy and molar volume. In the linear approximation

$$
\phi_1 = \frac{b_1 \Delta \hat{V} + b_2 \Delta \hat{S}}{a_2 b_2 + (a_1)_{eff} b_1}, \quad \phi_2 = \frac{a_2 \Delta \hat{V} + b_2 \Delta \hat{S}}{a_2 b_2 - (a_1)_{eff} b_1},
$$

where $\Delta \hat{S} \equiv (S - S_c)/R$, with $R$ being the gas constant, and $(a_1)_{eff} = \left(\partial h_1/\partial \hat{P}\right)_T = a_1 + 2a_3 \Delta \hat{P}$.

As far as the physical fields are mixed into the scaling fields, the physical properties, such as the isobaric heat capacity $C_P$, the isothermal compressibility $\kappa_T$, and the thermal expansivity $\alpha_P$, will not exhibit universal power laws when measured along isotherms or isobars; instead, their apparent behavior will be determined by a thermodynamic path and by the values of the mixing coefficients in Eqs. (2) and (3). As follows from Eqs. (2) and (3), the critical (fluctuation induced) parts of the dimensionless isobaric heat capacity, isothermal compressibility, and thermal expansivity are expressed through the scaling susceptibilities:
\begin{align*}
(\hat{C}_P)_{cr} &= \hat{T} \left( \frac{\partial \hat{S}}{\partial \hat{T}} \right)_{\hat{P}} - (\hat{C}_P)_b \\
&= -\hat{T} \left( a_2^2 \chi_1 + 2a_2 b_1 \chi_{12} + b_1^2 \chi_2 \right), \\
(\hat{\kappa}_T)_{cr} &= -\frac{1}{V} \left( \frac{\partial \hat{V}}{\partial \hat{P}} \right)_{\hat{T}} - (\hat{\kappa}_T)_b \\
&= \frac{1}{V} \left( (a_1)^2_{\text{eff}} \chi_1 + 2 (a_1)_{\text{eff}} b_2 \chi_{12} + b_2^2 \chi_2 \right), \\
(\hat{\alpha}_P)_{cr} &= \frac{1}{V} \left( \frac{\partial \hat{V}}{\partial \hat{T}} \right)_{\hat{P}} - (\hat{\alpha}_P)_b \\
&= -\frac{1}{V} \left( (a_1)_{\text{eff}} a_2 \chi_1 + ((a_1)_{\text{eff}} b_1 + a_2 b_2) \chi_{12} + b_1 b_2 \chi_2 \right).
\end{align*}

where \( \hat{T} = T/T_c, \hat{P} = P/\rho_c RT_c, \) and the subscript "b" indicates the property backgrounds.

We use the simplest form of a scaled parametric equation of state, the so-called “linear model”, which represents the scaling fields and scaling susceptibilities as functions of the “polar” variables \( r \) and \( \theta \) [13,14]:

\begin{align*}
h_1 &= ar^{\beta+\gamma} \left( 1 - \theta^2 \right), \quad h_2 = r \left( 1 - b^2 \theta^2 \right), \\
\chi_1 &= k r^{-\gamma} c_1(\theta), \quad \chi_{12} = kr^{-\beta} c_{12}(\theta), \quad \chi_2 = akr^{-\alpha} c_2(\theta) - B_{cr}
\end{align*}

where the coefficient \( b^2 = (\gamma - 2\beta)/\gamma (1 - \beta) \simeq 1.36 \) is a universal constant, while \( a \) and \( k \) are system-dependent amplitudes, and \( B_{cr} \) is the so-called “critical background” of order \( ak \) [13]. The analytical functions \( c_1(\theta), \) \( c_2(\theta), \) and \( c_{12}(\theta) \) are calculated in ref. [13]. A remarkable feature of the “linear model” is that the singularities in the thermodynamic functions are only related to the variable \( r \), while the properties are analytical with respect to \( \theta \).

This model offers a consistent scaling description of the available experimental data in supercooled water. Using high-resolution experimental heat-capacity data [15] shown in Fig. 2, we optimized the location of the critical point and the system dependent amplitudes. Based on the most recent estimate of the liquid-liquid phase transition curve given by Mishima [6], we have obtained the coefficients \( a_1 = b_1 = 0.0078 \) and \( a_3 = 0.062 \). These particular numbers correspond to \( P_c = 27 \) MPa, the value optimized by our equation of state.
We assume that the “Widom line” is described by the same coefficients. Furthermore, to reduce the number of adjustable parameters, we assume that the ratio \( k/a = 1 \), as obtained for the three dimensional Ising model with short range interactions [16]. Hence, only two adjustable parameters, namely, \( P_c \) and \( a = k \), have been used to describe the anomalous parts of the thermodynamic properties. The non-critical background of the heat capacity was approximated as a linear function of temperature. We obtained \( a = k = 0.47 \) and \( P_c = 27 \) MPa with the critical temperature corresponding to this pressure \( T_c = 232 \) K. The critical point, obtained from our equation of state, is located at a much lower pressure than previously predicted from computer simulations (see Fig. 1a).

With the given amplitudes and location of the critical point, we predict the behavior of the compressibility and expansivity, shown in Figs. 3 and 4, by adjusting only their non-critical backgrounds. The molar volume as a function of temperature was taken from ref. [17]. The predictions appear to have excellent agreement with the experimental data [18,19]. While it is difficult to establish the error bars for the obtained \( P_c \) value, the parametric equation of state certainly excludes the critical pressure above 50 MPa or below 10 MPa. We also conclude that the mean-field scenario is unlikely. The mean-field scenario cannot predict the anomalous behavior of isothermal compressibility within our model. While the major contribution in the heat-capacity anomaly is strong susceptibility, \( \chi_1 \), \((b_1 \text{ is small})\) diverging both in mean-field and in scaling theory, the major contribution in the isothermal compressibility anomaly is the weak susceptibility \( \chi_2 \), \((a_1 \text{ is small})\) which shows no anomaly in mean-field approximation. The major contribution in the critical part of the expansivity comes from the cross susceptibility \( \chi_{12} \) as both \( a_1 \) and \( b_1 \) are small. These features make the second critical point in water essentially different from the liquid-vapor critical point where \( C_P, \kappa_T, \) and \( \alpha_P \) all diverge strongly, as \( \chi_1 \), and from the liquid-liquid critical points in binary fluids where \( C_P, \kappa_T, \) and \( \alpha_P \) all diverge weakly, as \( \chi_2 \).

There are obvious limitations of our equation of state. First, the model used in this work is accurate only asymptotically close to the critical point \( r << 1 \) while all measurements in supercooled water have been taken far beyond the asymptotic region. The
experimental range of \( r \), the parametric distance to the critical point, may be as large as 0.5. However, this is the first estimate of the critical parameters for the second critical point in water based on experimental data, and not on computer simulations of “water like” models. Including non-asymptotic corrections to the parametric equation of state would change the adjustable backgrounds while not significantly affecting the critical parameters. To more accurately describe and predict the properties in a broader range of pressures and densities in supercooled water, a “global” crossover equation of state [14], based on a reliable mean-field equation of state, such as a modified van der Waals model [4], is required. Moreover, we did not address an intriguing possibility of the existence of multiple critical points in supercooled water, as predicted by some simulated water models [20].

In this work, the order parameter is phenomenologically expressed through molar volume and entropy, with entropy being the major contribution. A clarification of the relation between this phenomenology and the microscopic nature of the order parameter [21] would help in better understanding the physics of phase transitions in supercooled water.

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Captions of figures

Figure 1. (a) Phase diagram for water with vapor-liquid and liquid-liquid critical points. Solid curves are vapor-liquid, liquid-liquid, and liquid-solid phase transitions; dashed is the Widom line; dotted is the compressibility maxima; crosses are literature estimates for the liquid-liquid critical point. C is the vapor-liquid critical point; C’ is the liquid-liquid critical point predicted by our equation of state. (b) The vicinity of the liquid-liquid critical point.

Figure 2. Heat capacity measurements (stars) [15] compared to the heat capacity predicted by our scaling parametric equation of state (solid curve) for a critical point of $P_c = 27$ MPa, $T_c = 232$ K. Non-critical background plotted as a thin solid curve.

Figure 3. Isothermal compressibility experimental data [18] at 10 MPa (○), 50 MPa (∆), 100 MPa (◇), 150 MPa (★), and 190 MPa (□), compared with our prediction at the same pressures (solid curves).

Figure 4. Thermal expansivity experimental data [19] (▲), at ambient pressure, compared with our prediction (solid curve). Non-critical background plotted as a thin solid curve.
$P=1\text{ atm}$
$P=1\text{ atm}$

Temperature (K)

$\alpha_p \times 10^3 (K^{-1})$