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# Water's two-critical-point scenario in the Ising paradigm

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# Water's two-critical-point scenario in the Ising paradigm

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**Note:** This paper is part of a JCP Special Topic on Chemical Physics of Supercooled Water.

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## ABSTRACT

We present a spin-1, three-state Ising model for the unusual thermodynamics of fluid water. Thus, besides vacant cells, we consider singly occupied cells with two accessible volumes in such a way that the local structures of low density, energy, and entropy associated with water's low-temperature "icelike" order are characterized. The model has *two* order parameters that drive *two* phase transitions akin to the standard gas-liquid transition and water's hypothesized liquid-liquid transition. Its mean-field equation of state enables a satisfactory description of results from experiments and simulations for the ST2 and TIP4P/2005 force fields, from the phase diagram, the density maximum, or the deeply "stretched" states to the behavior of thermodynamic response functions at low temperatures at which water exists as a supercooled liquid. It is concluded that the model may be regarded as a most basic prototype of the so-called "two-critical-point scenario."

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## I. INTRODUCTION

Water exhibits an unusual pattern of thermodynamic behavior both at ambient conditions and in the low-temperature region where it exists as a supercooled liquid.<sup>1</sup> Underlying this phenomenology are the specific features of hydrogen bonding, which are known to lead to transient "icelike" molecular arrangements in the liquid state.<sup>2,3</sup> Such icelike structural order propagates to longer distances as temperature is lowered. In fact, recent experimental work on deeply supercooled water reports<sup>4</sup> a growing correlation length consistent with the sharp increase in thermodynamic response functions observed long ago at  $\sim 240$  K.<sup>5–7</sup>

It has been conjectured<sup>8</sup> that this behavior reflects that supercooled water *should* undergo a liquid-liquid phase transition terminating at a critical point at which, as usual, the correlation length and the response functions diverge. This physical picture, often referred to as "two-critical-point scenario," has gained significant support over the last years from experimental, computational, and theoretical studies (see for review Refs. 9–12). A strong implication is that

a (one-component) substance can exist as a liquid in two distinct forms. This has been proved by careful computational analyses<sup>13–15</sup> of the ST2 force field of water<sup>16</sup> as well as for tetrahedral patchy colloids<sup>17</sup> and model fluids of particles interacting via a variety of core-softened pair potentials.<sup>18</sup>

Incorporating water's unusual thermodynamics into a tractable equation of state is a challenging task. Early approaches to this problem successfully reproduced the two-critical-point scenario from a model free energy composed of a van der Waals part and an additional contribution accounting for the effect of hydrogen bonding in water.<sup>19,20</sup> On the other hand, regarding liquid water, a regular mixture of two species of distinct local structure yields an expression for the Gibbs free energy that describes satisfactorily experimental data as well as results from simulations of water models.<sup>21,22</sup>

All this theoretical work exploits the fact that water's icelike order is characterized by local structures of low energy, entropy, and density. Using the concept of "fluctuating cell volumes in lattice models" introduced by Fisher and co-workers,<sup>23,24</sup> such features have been implemented in a spin- $\frac{1}{2}$  Ising-like model in which,

instead of employing occupied and vacant cells for describing the dense states of liquid water, singly occupied cells with two accessible volumes and an appropriate energy-entropy-volume coupling are used.<sup>25</sup> It was concluded that such a *compressible cell* model may serve as an Ising prototype of the hypothesized liquid-liquid phase transition, while its mean-field solutions were shown to provide hints on the analytical form of the equation of state of water.

Here, we further elaborate upon this by analyzing a spin-1 (or three-state) Ising-like model in which, in addition to occupied cells with two distinct volumes, vacant cells are considered. Its mean-field solutions lead to an equation of state which reproduces the two-critical-point scenario, ranging from the unusual thermodynamics at supercooling and ambient conditions to standard-fluid behavior at high enough temperatures. Results are found to be consistent with evidence available from experiments and simulations for the ST2 and TIP4P/2005<sup>26</sup> water force fields. Furthermore, to deepen on the comparison with TIP4P/2005 water, we augment the database of this model by performing simulations for the thermodynamic response functions at low temperatures.

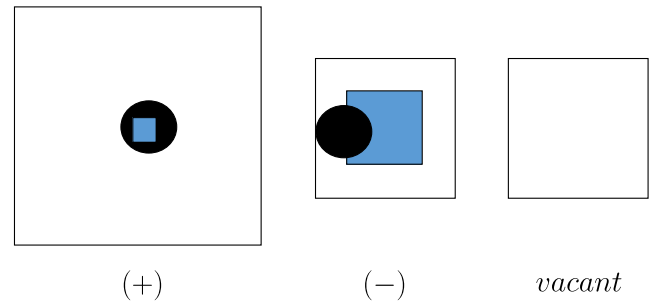
Spin-1 Ising models have been used to study a great variety of problems, from magnetic phase transitions<sup>27</sup> to the interplay between superfluid ordering and phase separation in <sup>3</sup>He-<sup>4</sup>He mixtures<sup>28</sup> or the phase behavior and criticality in three-component solutions.<sup>29,30</sup> The idea of employing a variant of the class for describing water's unusual thermodynamics goes back to the work by Ciach *et al.*<sup>31</sup> which, indeed, inspired our present approach.

The manuscript is organized as follows. The model is described in Sec. II. Its performance is analyzed in Sec. III: this includes comparison with available information on the phase behavior and the thermodynamic response functions as well as a theoretical analysis of certain model's specific features. Section IV contains some concluding remarks. Technical details and results of simulations are placed as the [supplementary material](#).

## II. MODEL

Let us consider a three-dimensional regular lattice of coordination number  $c$ . At each of its  $\mathcal{N}$  sites, there is a cell that can be empty or accommodate one classical particle of fixed size and shape. But, occupied cells are labeled as (+) or (-) as done in Ref. 25. Thus, we set  $v_+ = v_0 + \delta v$  and  $v_- = v_0$ , with  $\delta v > 0$ , the volume of a vacant cell being  $v_0$  (see Fig. 1). As a next step, we interpret our three-state scheme as a *continuum model*.<sup>23-25</sup> Thus, a particle in a (-) cell is allowed to move freely throughout the entire cell volume so that it explores a free volume  $\dot{v}_- \leq v_0$ , with the equality holding for the marginal case of point particles. On the other hand, we consider that the motion of a particle in a (+) cell is restricted to a narrow volume centered at the cell site so as to have the constraint  $\dot{v}_+ < \dot{v}_-$ . Finally, particles only interact when they are in nearest-neighbor cells, with interaction energies being  $\varepsilon_{--} = \varepsilon_{+-} = -\varepsilon_0$  and  $\varepsilon_{++} = -\varepsilon_0 - \delta\varepsilon$  ( $\varepsilon_0, \delta\varepsilon > 0$ ).

Note that a particle in a (+) cell has a surrounding volume devoid of other particles while, at the same time, its reduced free volume introduces a geometrical selectivity. Thus, (++) configurations have lower energy, entropy, and density than (+-) or (-) ones. As a result, assemblies of adjacent (+) cells mimic the local icelike structures characteristic of liquid water at low temperatures.



**FIG. 1.** Single-cell (+), (-), and “vacant” states of our waterlike spin-1 Ising model (see text). Pictures are two-dimensional for the sake of simplicity. The shaded (blue) areas are the free volumes a particle can explore in its cell.

The state of each cell is specified by a spin-1 Ising variable  $s_i = -1, 0, 1$ , with  $s_i = 1$  for the (+) state,  $s_i = -1$  for the (-) state, and  $s_i = 0$  for a vacant cell. Then, the number of (+) and (-) cells,  $N_+$  and  $N_-$ , the number of particles  $N$ , the volume  $V$ , and the configurational energy  $U_{\text{conf}}$  fulfill

$$N_+ = \sum_{i=1}^{\mathcal{N}} \frac{1}{2}(1 + s_i)s_i, \quad N_- = \sum_{i=1}^{\mathcal{N}} \frac{1}{2}(s_i - 1)s_i, \quad (1)$$

$$N = N_+ + N_- = \sum_{i=1}^{\mathcal{N}} s_i^2, \quad (2)$$

$$V = \mathcal{N}v_0 + N_+\delta v = \mathcal{N}v_0 + \delta v \sum_{i=1}^{\mathcal{N}} \frac{1}{2}(1 + s_i)s_i, \quad (3)$$

$$U_{\text{conf}} = - \sum_{\langle ij \rangle} [\varepsilon_0 s_i^2 s_j^2 + \frac{1}{4} \delta\varepsilon (1 + s_i)(1 + s_j)s_i s_j]. \quad (4)$$

An exact statistical mechanical treatment entails summing  $e^{-(U+pV-\mu N)/k_B T}$  factors, with  $p$  the pressure,  $T$  the temperature,  $\mu$  the chemical potential, and  $k_B$  the Boltzmann constant. But, we will confine ourselves to the solutions in the Bragg-Williams, mean-field approximation.

Thus, we start from

$$\mu = u - Ts + pv, \quad (5)$$

where  $u \equiv U/N$ ,  $s \equiv S/N$ , and  $v \equiv V/N$  denote the energy, the entropy, and the volume *per particle*,<sup>32</sup> and define the averages

$$n \equiv \left\langle \frac{N}{\mathcal{N}} \right\rangle \quad \text{and} \quad n_+ \equiv \left\langle \frac{N_+}{\mathcal{N}} \right\rangle. \quad (6)$$

The energy per particle splits into kinetic and configurational contributions,

$$u = u_{\text{kin}} + u_{\text{conf}}. \quad (7)$$

For classical particles without internal structure,

$$u_{\text{kin}} = \frac{3}{2}k_B T, \quad (8)$$

while according to standard mean-field arguments,

$$u_{\text{conf}} = -\frac{\varepsilon}{2}(\varepsilon_0 n + \delta\varepsilon n_+^2 n^{-1}). \quad (9)$$

Now, the entropy has a configurational term accounting for the distinct ways in which objects (or cells) of three distinct types can be randomly placed at the lattice. There is also a “free volume” contribution arising from integrations over momenta and over the volumes accessible to the center of each particle in its cell. Hence,

$$s = s_{\text{conf}} + s_{\text{fv}}, \quad (10)$$

$$\frac{s_{\text{conf}}}{k_B} = -n^{-1} [n_+ \ln n_+ + (n - n_+) \ln(n - n_+) + (1 - n) \ln(1 - n)], \quad (11)$$

$$\frac{s_{\text{fv}}}{k_B} = \frac{1}{2} [\ln(\dot{v}_+ \dot{v}_- \Lambda_T^{-6}) + n^{-1} (2n_+ - n) \ln \lambda], \quad (12)$$

where  $\lambda = \dot{v}_+/\dot{v}_- < 1$  and  $\Lambda_T = h/\sqrt{2\pi mk_B T}$ , with  $h$  the Planck constant and  $m$  the mass of a particle. Finally, from (2), (3), and (6), one finds

$$v = n^{-1} v_0 + n_+ n^{-1} \delta v, \quad (13)$$

its inverse yielding the number density  $\rho$ .

The parameters  $n$  and  $n_+$  attain the values that minimize  $\mu$  for given  $T$  and  $p$ . Necessary conditions are

$$\left( \frac{\partial \mu}{\partial n} \right)_{T,p,n_+} = 0 \quad \text{and} \quad \left( \frac{\partial \mu}{\partial n_+} \right)_{T,p,n} = 0, \quad (14)$$

which lead to the following two expressions relating  $p$ ,  $T$ ,  $n$ , and  $n_+$ :

$$p(v_0 + \delta v n_+) = k_B T \{ n_+ \ln[\lambda(n - n_+)n_+^{-1}] - \ln(1 - n) \} - \frac{\varepsilon}{2} \varepsilon_0 n^2 + \frac{\varepsilon}{2} \delta \varepsilon n_+^2, \quad (15)$$

$$p \delta v = k_B T \ln[\lambda(n - n_+)n_+^{-1}] + c \delta \varepsilon n_+. \quad (16)$$

These two equations can be rearranged to get

$$p v_0 = -k_B T \ln(1 - n) - \frac{\varepsilon}{2} \varepsilon_0 n^2 - \frac{\varepsilon}{2} \delta \varepsilon n_+^2, \quad (17)$$

$$k_B T = \frac{\varepsilon}{2} \delta v [v_0 \ln \phi]^{-1} [\varepsilon_0 n^2 + \delta \varepsilon n_+ (n_+ + 2v_0 \delta v^{-1})], \quad (18)$$

$$\phi = n_+ [\lambda(n - n_+) (1 - n) \frac{\delta v}{v_0}]^{-1}, \quad (19)$$

which together with (13) yield the model's  $p v T$  relation.

### III. RESULTS AND DISCUSSION

#### A. Phase behavior

To get explicit results, we adopted a single set of values of the model parameters, which is shown in Table I. There is more to be said about this choice but, for now, we note that the physical picture it leads to remains for varied sets of parameter values.

Given  $T$  and  $v$  (or, equivalently,  $\rho$ ), (13), (17), and (18) were solved numerically for  $p$ ,  $n$ , and  $n_+$ . This way, isotherms in the  $p$ - $v$  plane are generated. Figure 2 shows a variety of such isotherms. Starting at very low densities (not shown) at which ideal-gas behavior holds, the pressure increases monotonically as  $v$  is decreased. For the isotherm corresponding to the highest temperature, this behavior remains throughout the whole  $v$  range. At lower temperatures, a “van der Waals loop” is found, with Maxwell equal-area

TABLE I. Model parameters.<sup>a</sup>

$c$	$\varepsilon_0$	$\delta \varepsilon$	$v_0$	$\delta v$	$\lambda$
6	3400	900	$1.68 \times 10^{-5}$	$0.632 \times 10^{-5}$	0.3

<sup>a</sup>Energies in J mol<sup>-1</sup> and volumes in m<sup>3</sup> mol<sup>-1</sup>. For calculation of the entropy,  $\dot{v}_- = 5.983 \cdot 10^{-9}$  m<sup>3</sup> mol<sup>-1</sup> was used.

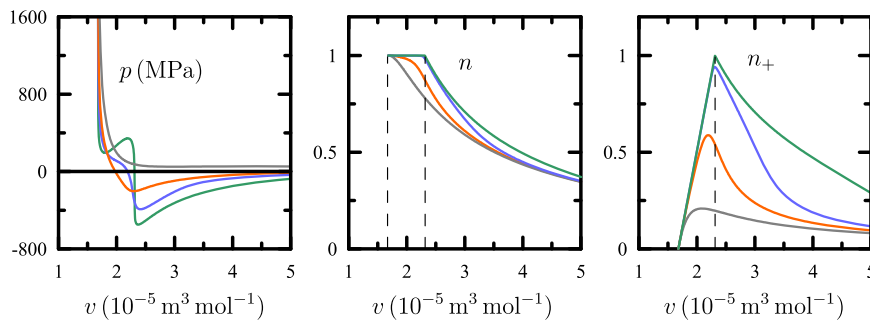
construction yielding  $v$  values for the coexisting phases that are typical of gas and liquid. In addition, a second loop with  $v$  values for the coexisting phases characteristic of liquid appears at sufficiently low temperatures. It transpires that the model exhibits two first-order phase transitions, each of which associated with the coexistence of two phases of distinct density and terminating at an upper critical point. They can be reasonably identified as the standard gas-liquid transition and water's hypothesized liquid-liquid transition. Using standard terminology in water thermodynamics, we will henceforth refer to the coexisting liquid phases as the high-density liquid (HDL) and the low-density liquid (LDL).

The corresponding phase diagram in the  $p$ - $T$  and  $T$ - $\rho$  planes is shown in Fig. 3. The densities along the binodal,  $\rho'$  and  $\rho''$ , and the pressure and chemical potential at coexistence were obtained at each prescribed  $T$  by imposing  $\mu' = \mu''$  and  $p' = p''$ , with algebraic expressions for  $\mu$ ,  $p$ , and  $T$  given by (5), (17), and (18). (This entails calculating  $n'$ ,  $n''$ ,  $n'_+$ , and  $n''_+$ .) The spinodal curves were computed by locating the points at which isotherms in the  $p$ - $v$  plane display extrema (see Fig. 2).

Numerical results may be summarized as follows. The gas-liquid critical temperature and pressure are  $T_c^{GL} \approx 624$  K and  $p_c^{GL} \approx 60$  MPa, respectively, their liquid-liquid counterparts being  $T_c^{LL} \approx 162$  K and  $p_c^{LL} \approx 170$  MPa. We have observed that the coordinates of the gas-liquid critical point do not deviate substantially from the ones obtained from a standard lattice gas with the same values of  $\varepsilon_0$  and  $v_0$ . On the other hand, it comes out from Fig. 2 that  $n \approx 1$  (i.e., almost no vacant cells) along liquid-liquid coexistence, implying that the model reduces to the spin- $\frac{1}{2}$  compressible cell model presented in Ref. 25, with  $\delta \varepsilon$ ,  $\delta v$ , and  $\lambda$  as parameters. Since in the standard lattice gas  $T_c^{GL} \propto \varepsilon_0$  (see, e.g., Ref. 24) and in the compressible cell model  $T_c^{LL} \propto \delta \varepsilon$ ,<sup>25</sup> we chose the  $\varepsilon_0$  and  $\delta \varepsilon$  values in Table I so as to get a  $T_c^{GL}$  value around the experimental one and a  $T_c^{LL}$  value around 200 K. On the other hand,  $v_0$ ,  $\delta v$ , and  $\lambda$  were fixed so as to get a reasonable description of the temperature dependence of the density and the  $p_c^{LL} \approx 170$  MPa value reported by Biddle *et al.*<sup>22</sup> in their analysis of simulation data of TIP4P/2005 water.

As Fig. 3 shows, the gas-liquid binodal in the  $p$ - $T$  plane has a positive slope which, according to the Clapeyron equation, indicates that the denser phase (that is, liquid) is the one with lower entropy. Following the same reasoning, the negative slope of the liquid-liquid binodal indicates that the LDL has lower entropy. Remarkably, the region of the phase diagram in the  $p$ - $T$  plane associated with the liquid-liquid transition agrees qualitatively with that for ST2 water (cf. Fig. 2 of Ref. 11).

It also comes out from Fig. 3 that the liquid branches of the gas-liquid binodal and spinodal in the  $T$ - $\rho$  plane exhibit a temperature of maximum density (TMD). The existence of a TMD in water's liquid binodal was experimentally observed long ago.<sup>36</sup> Its spinodal counterpart has been shown to be consistent with the low-temperature



**FIG. 2.** Isotherms in the pressure-volume  $p$ - $v$  plane for  $T = 100$  K (green),  $T = 200$  K (blue),  $T = 300$  K (orange), and  $T = 600$  K (gray). Also shown are the model's order parameters  $n$  and  $n_+$  as a function of  $v$  along each isotherm. The thin dashed lines correspond to  $v = v_- = v_0$  and  $v = v_+ = v_0 + \delta v$ .

behavior of thermodynamic response functions along isochores in TIP4P/2005 water.<sup>37</sup> Both maxima were already found in early theoretical work<sup>19,20</sup> and obviously associated with them is the TMD of liquid water along isobars, which is central in water's unusual thermodynamics and defines a TMD line in the  $p$ - $T$  plane that is plotted in Fig. 3. [Such a TMD line has been calculated from (13) upon fixing  $T$  and  $p$  and solving (17) and (18) for  $n$  and  $n_+$ .]

The absence of a TMD in the gas branches of the binodal and spinodal embodies an evident gas-liquid asymmetry far from criticality. Such an asymmetry is known to be also reflected near the gas-liquid critical point by the temperature dependence of the binodal diameter.<sup>23,24,38-40</sup> Despite an exact analysis of this issue being prevented by the mean-field nature of our approach, it is important to mention that our spin-1 model contemplates the local free volume fluctuations that were shown in Refs. 23 and 24 to underlie the singular behavior of the binodal diameter and the related Yang-Yang asymmetries in gas-liquid criticality.

## B. Order parameters and low- $T$ behavior

Theoretical work and simulations evidence that two order parameters are relevant for understanding water's unusual thermodynamics.<sup>21,41-43</sup> In this connection, one remarkable feature of spin-1 Ising models is that they are characterized by two order parameters.<sup>28</sup> In our present approach, they are  $n$  and  $n_+$ , which, as found, lead to two phase transitions, each of which terminating at a

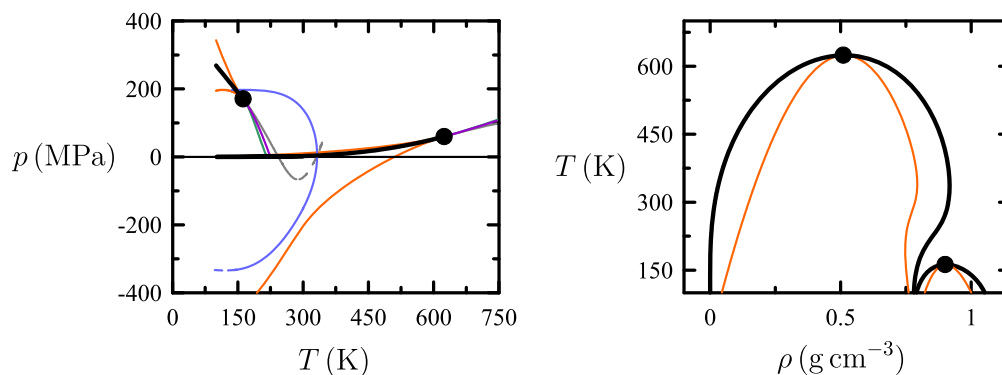
critical point. This is how the two-critical-point scenario appears in the Ising paradigm.<sup>44,45</sup>

As noted in Sec. II,  $n$  quantifies lattice cell occupancy, while  $n_+$  is a measure of icelike structural order. It is important to recall from Fig. 2 that  $n \approx 1$  along liquid-liquid coexistence. Hence,  $n$  is only relevant to the gas-liquid transition, while the liquid-liquid transition is solely driven by  $n_+$ . Implications of this result regarding the nature of the liquid-liquid phase transition are described as follows. First, the LDL and HDL coexisting phases are fully characterized by  $n_+$ , with the LDL being the one with greater  $n_+$  (cf. Fig. 1). Second, one readily finds from (13) that along liquid-liquid coexistence,  $n_+$  is directly related to the volume per particle via  $n_+ \approx (v - v_0)\delta v^{-1}$ , implying that the model's  $p$  $v$  $T$  relation reduces to

$$p\delta v = k_B T \ln \left( \lambda \frac{v_0 + \delta v - v}{v - v_0} \right) + c\delta\varepsilon \frac{v - v_0}{\delta v}, \quad (20)$$

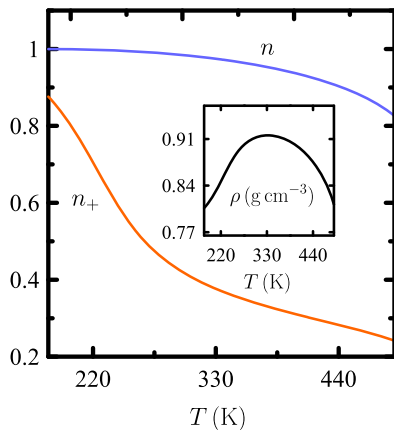
where we have used Eq. (16). Third, the cell volumes  $v_+ = v_0 + \delta v$  and  $v_- = v_0$  set upper and lower bounds for the  $v$  of the coexisting phases (cf. Fig. 2). Certainly, they define the *two length scales* that have been shown to be relevant to one-component liquid-liquid transitions.<sup>2,18</sup>

Figure 4 shows  $\rho(T)$ ,  $n(T)$ , and  $n_+(T)$  at  $p = 0.1$  MPa. As can be seen, both  $n$  and  $n_+$  increase as  $T$  is decreased, but in the low-temperature region,  $n_+$  does it at a significantly faster rate than  $n$ . Then, Eq. (13) straightforwardly allows us to understand how  $n(T)$



**FIG. 3.** Binodal (bold solid, black) and spinodal (solid, orange) curves in the pressure-temperature  $p$ - $T$  and temperature-density  $T$ - $\rho$  planes. Also shown are the line of temperature of maximum densities (TMDs) along isobars (solid, blue), the lines of isobaric extrema of  $C_p$  (solid, green),  $\alpha_p$  (solid, violet), and  $\kappa_T$  (solid, gray) emanating from each critical point, and the lines of isobaric minima of the density (dashed, blue) and  $\kappa_T$  (dashed, gray). Some loci have been deliberately cut off for the sake of clarity, while both the high-pressure termination of the TMD line and the intersection between the line of isobaric  $\kappa_T$  minima and the TMD line satisfy thermodynamic constraints.<sup>33-35</sup>





**FIG. 4.** Model's order parameters  $n$  and  $n_+$  at  $p = 0.1$  MPa as a function of temperature  $T$ . The inset shows the resulting temperature dependence of the density  $\rho$  according to Eq. (13). Note that a 30% fraction of icelike cells at a temperature as high as 400 K seems unreasonably large (see comments in Sec. IV).

and  $n_+(T)$  combine to produce the  $\rho(T)$  maximum. Thus, at high temperatures, the temperature dependence of  $\rho$  is mainly governed by  $n(T)$ , whereas at low temperatures, it is  $n_+(T)$  which dominates. Indeed, both icelike order and lattice vacancies make the density to decrease, with the former effect dominating at low temperatures and the latter at high temperatures so that, inevitably, a  $\rho(T)$  maximum occurs. The  $\rho(T)$  maxima of the liquid branches of the binodal and spinodal are rationalized exactly in the same way.

Back to Fig. 2, we note that low-temperature isotherms display a quasivertical portion in between the two van der Waals loops at  $v \approx v_+$ . Thus, around  $v_+$ , the compressibility is so small that a wide pressure range is spanned. More specifically, negative pressures that are large in magnitude can be attained for  $v$  close to (but lower than)  $v_+$ , while for  $v$  close to (but higher than)  $v_+$ , the pressure can be large and positive until liquid-liquid coexistence is reached. Since at low temperatures  $v \approx v_+$  corresponds to  $n_+ \approx 1$ ,  $\rho_{\text{opt}} = v_+^{-1}$  may be regarded an “optimal density for full icelike order.”<sup>46</sup> Certainly, icelike order and its concomitant large cohesive energy allow the liquid to be able to sustain large tensions, but it also demands large pressures for the LDL to be converted into the HDL. Accordingly, the fact that water can bear unusually large tensions (see, e.g., Ref. 37) is consistent with the two-critical-point scenario. Indeed, the connection between the “stretched water” and the liquid-liquid transition has stimulated recent experimental work.<sup>47</sup>

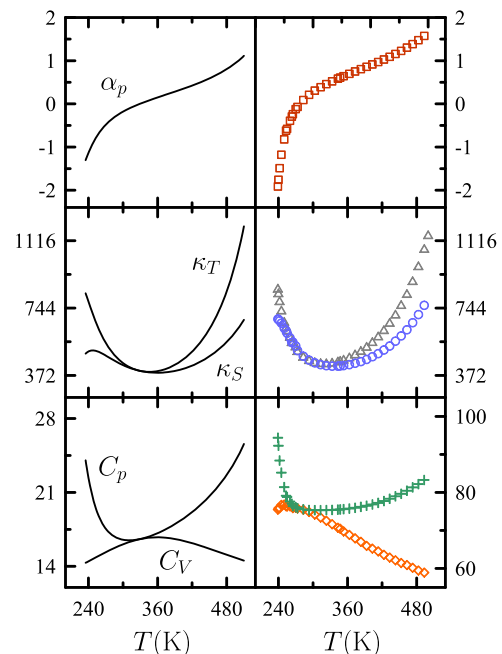
### C. Response functions

The temperature dependence of thermodynamic response functions for the (one-phase) liquid along isobars has been extensively studied in connection with water's unusual thermodynamics.<sup>4-7,48,49</sup> To make progress, we shall examine what the model predicts about it. Specifically, our attention will be focused on the isothermal and isentropic compressibilities,  $\kappa_T \equiv -v^{-1}(\partial v/\partial p)_T$  and  $\kappa_S \equiv -v^{-1}(\partial v/\partial p)_S$ , the isobaric thermal expansivity,  $\alpha_p \equiv v^{-1}(\partial v/\partial T)_p$ , and the isobaric and isochoric heat capacities,  $C_p \equiv T(\partial s/\partial T)_p$  and  $C_V \equiv T(\partial s/\partial T)_V$ . To calculate them, given  $T$  and  $p$ , (17) and (18) were solved for  $n$  and  $n_+$  so that  $v$  and  $s$

were obtained from (10) to (13). Then, via numerical differentiation,  $\kappa_T$ ,  $\alpha_p$ , and  $C_p$  were determined. These led to  $\kappa_S$  and  $C_V$  with the aid of the exact thermodynamic relations  $\kappa_S = \kappa_T - Tv\alpha_p^2 C_p^{-1}$  and  $C_V = C_p - Tv\alpha_p^2 \kappa_T^{-1}$ .

Figure 5 shows the results over a wide temperature range at  $p = 50$  MPa, that is, at a pressure which is lower than both  $p_c^{GL} \approx 60$  MPa and  $p_c^{LL} \approx 170$  MPa. The condition  $p < p_c^{GL}$  implies that the liquid branch of the gas-liquid spinodal is approached as  $T$  is increased. On the other hand,  $p < p_c^{LL}$  implies that the Widom line associated with the liquid-liquid critical point<sup>52-54</sup> is approached as  $T$  is lowered. This latter statement may be understood as follows. As Fig. 3 shows, the negatively sloped liquid-liquid coexistence line in the  $p$ - $T$  plane implies that starting at criticality, lines of isobaric extrema of each response function (as a function of temperature) develop toward temperatures higher than  $T_c^{LL}$  and pressures lower than  $p_c^{LL}$ . Asymptotically close to criticality, all such lines converge into a single line, the so-called Widom line, which serves to measure the proximity to the critical region for  $p < p_c^{LL}$ . (Also shown in Fig. 3 is the gas-liquid Widom line, useful to quantify the proximity to the gas-liquid critical region for  $p > p_c^{GL}$ .)

Accordingly, the high-temperature increases in  $C_p$ ,  $\alpha_p$ , and  $\kappa_T$  in Fig. 5 merely reflect the diverging behavior of these properties over the spinodal limit.<sup>55</sup> Since at a one-component liquid-liquid critical point with a negatively sloped  $p$ - $T$  binodal line  $C_p, \kappa_T \rightarrow +\infty$  and  $\alpha_p \rightarrow -\infty$  (see, e.g., Ref. 25), at intermediate temperatures,  $C_p(T)$

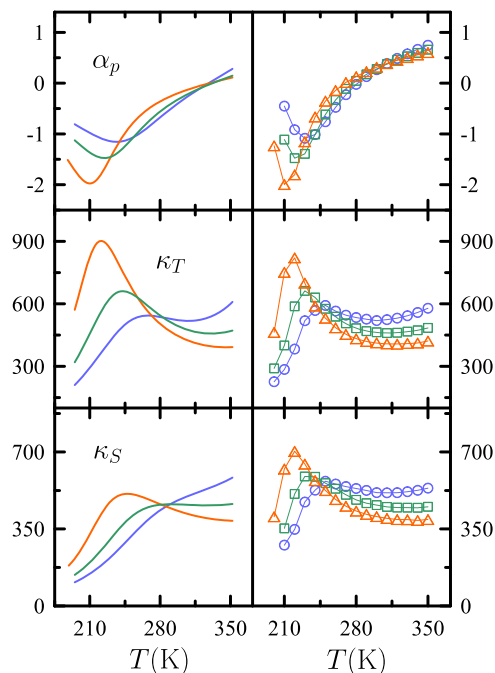


**FIG. 5.** Isobaric thermal expansivity  $\alpha_p$  (in  $10^{-3} \text{ K}^{-1}$ ), isothermal compressibility  $\kappa_T$  (in  $10^{-12} \text{ Pa}^{-1}$ ), isentropic compressibility  $\kappa_S$  (in  $10^{-12} \text{ Pa}^{-1}$ ), isobaric heat capacity  $C_p$  (in  $\text{J mol}^{-1} \text{ K}^{-1}$ ), and isochoric heat capacity  $C_V$  (in  $\text{J mol}^{-1} \text{ K}^{-1}$ ) as a function of temperature  $T$ . Left: spin-1 Ising model values at  $p = 50$  MPa obtained using the parameters shown in Table I; right: literature experimental data at atmospheric pressure.<sup>5-7,50,51</sup>

and  $\kappa_T(T)$  must inevitably exhibit a minimum and  $\alpha_p(T)$  an inflection point. On the other hand,  $C_V$  and  $\kappa_S$  remain finite at the liquid spinodal<sup>55</sup> but also, in mean-field approximation, at liquid-liquid criticality. However, in contrast to  $C_V$ ,  $\kappa_S$  noticeably increases at both extremes of the temperature range, implying that  $\kappa_S(T)$  also exhibits a minimum at intermediate temperatures.

Figure 5 also illustrates that the model's behavior is in accord with experimental data. However, using the values for the model parameters of Table I, such a consistency has been achieved by shifting the pressure up 50 MPa. While this situation could be improved by changing the parameter setting, we have concluded that an accurate approach to water's experimental data demands a careful analysis that is beyond the scope of the present work.

Certainly, assuming that one-component liquid-liquid criticality belongs to the Ising universality class,<sup>56</sup> it must be recognized that our approach suffers from the limitations inherent to the mean-field approximation. One such limitation was mentioned above and has to do with the so-called weakly diverging properties such as  $\kappa_S$  and  $C_V$ ,<sup>57</sup> which are otherwise nondiverging in mean-field theory. Accordingly, it is to be expected that the low-temperature increase in these properties is underestimated by the model, as it can be inferred from Fig. 5 for  $\kappa_S$ . On the other hand, the model does not consider either vibrational and rotational degrees of freedom or nuclear quantum effects,<sup>58</sup> while it also lacks from any detailed account of the contribution of dispersion forces to the heat capacities.<sup>59</sup>



**FIG. 6.** Isobaric thermal expansivity  $\alpha_p$  (in  $10^{-3} \text{ K}^{-1}$ ), isothermal compressibility  $\kappa_T$  (in  $10^{-12} \text{ Pa}^{-1}$ ), and isentropic compressibility  $\kappa_S$  (in  $10^{-12} \text{ Pa}^{-1}$ ) as a function of temperature  $T$ . Left: spin-1 Ising model values at  $p = -50$  MPa (blue lines),  $p = 0.1$  MPa (green lines), and  $p = 50$  MPa (orange lines) obtained using the parameters shown in Table I; right: TIP4P/2005 water at  $p = -50$  MPa (circles),  $p = 0.1$  MPa (squares), and  $p = 50$  MPa (triangles). The lines joining points in TIP4P/2005 plots are only intended to guide the eye.

To further test the model's capabilities, we focus on the behavior at lower temperatures than those experimentally accessible. This naturally entails comparison with results from water force fields, which has led us to perform simulations of TIP4P/2005 water for temperatures ranging from 200 to 350 K at  $p = -50, 0.1,$  and 50 MPa isobars. The results are shown in Fig. 6 together with model values within the same temperature and pressure ranges. Because of the just-mentioned model's limitations for a quantitative description of  $C_p$  and  $C_V$ , we have restricted ourselves to  $\alpha_p$ ,  $\kappa_T$ , and  $\kappa_S$ . For these, the consistency between our model and TIP4P/2005 water is remarkably good. It has been achieved with the only expediency of choosing the spin-1 Ising model parameters so as to get values of  $T_c^{LL}$  and  $p_c^{LL}$  similar to those reported by Biddle *et al.*<sup>22</sup> in their mean-field "two-structure thermodynamics" analysis of simulation data of TIP4P/2005.

#### IV. CONCLUSIONS

It was already realized at early stages<sup>60–62</sup> that in its distinct versions, the Ising model contemplates the essential microscopic features underlying quite diverse phenomena such as ferromagnetism, antiferromagnetism, gas condensation, or demixing in binary solutions or alloys. But the status of the "Ising paradigm" goes even beyond this. Indeed, the confidence levels it has gained over the years are so great that sometimes newly revealed phase behaviors (by experiment, etc.) encourage looking for Ising models describing them, whereas the mere existence of Ising prototypes displaying uncovered physical phenomena constitutes a strong suggestion that such phenomena may be observed in nature. It is on this footing that consistently placing water's two-critical-point scenario in the Ising framework—as we have done in the present work—proves certainly meaningful.

Our approach consists of a spin-1 Ising variant—mathematically equivalent to the Blume-Capel,<sup>27</sup> Blume-Emery-Griffiths,<sup>28</sup> and "three-component"<sup>29,30</sup> models—in which we have taken advantage of the concept of fluctuating cell volumes introduced recently<sup>23,24</sup> to characterize the energetic, entropic, and volumetric effects of water's icelike order. As such, it stresses the value of rather "crude" models and, in particular, of the relations among different models in the theory of condensed matter.<sup>63</sup>

A natural extension should be a comparative study between our spin-1 model and the spin- $\frac{1}{2}$  variant by Sastry *et al.*<sup>35</sup> accounting for the so-called "singularity-free scenario"—in which water's unusual thermodynamics are *not* associated with a liquid-liquid critical point. Unambiguously elucidating which of these two Ising approaches describing mutually exclusive scenarios proves better is of obvious relevance. On the other hand, preliminary calculations have shown that upon lowering the  $\lambda$  value, the model is able to reproduce the "critical-point-free scenario."<sup>10</sup> But, whatever the situation regarding these competing physical pictures may be, we stress that our present approach relies on the explicit distinction between icelike and disordered local arrangements in water, which, as long recognized, is essential for describing its unusual thermodynamics.

Before a detailed analysis along those lines can be undertaken, refining our model with a view to attain a more accurate description of experimental data than the one actually provided by Fig. 5 is in order. For that purpose, recent work<sup>64</sup> suggests that a spin- $\frac{3}{2}$ ,



four-state model should be promising. Such a variant would eventually correct the unreasonably large fraction of water molecules in the icelike configuration indicated in Fig. 4.

Future work should also address one-component liquid-liquid criticality as well as water's analytical tractability. The former problem may be readily attacked by simply recalling that at low temperatures, our spin-1 model reduces to the spin- $\frac{1}{2}$  compressible cell model presented in Ref. 25, for which one can straightforwardly explore its "exact" solutions. As for the latter subject, the simplicity of the mean-field equation of state given by Eqs. (13), (17), and (18) suggests that studying water's unusual thermodynamics within the theory of liquids may not be regarded a hopeless task. Concrete progress on all these topics pertaining to the advancing field of water physics is highly desirable.

## SUPPLEMENTARY MATERIAL

See [supplementary material](#) for technical details of simulations and numerical results in tabulated form.

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- <sup>45</sup>Note also that spin-1 Ising models can lead to very complex phase diagrams, as it is the case of three-component systems.<sup>29,30</sup> But recall that we are dealing with a one-component fluid.
- <sup>46</sup>The existence of such an optimal density was first postulated by Poole *et al.*<sup>19</sup>
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