

# Liquid–liquid critical point in a Hamiltonian model for water: analytic solution

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## Abstract

Water is characterized by a density anomaly whose origin is a matter of debate. Theoretical works have shown that two of the proposed explanations, the *second-critical-point hypothesis* and the *singularity-free scenario*, have the same microscopic origin, but arise from different choices of parameters, such as the hydrogen bond strength or geometry. We consider a Hamiltonian model proposed by Sastry *et al* that supports the singularity-free scenario and was solved in an approximation where the intra-molecular interactions are neglected. We show that, by including these interactions, the second critical point is recovered, elucidating the differences in the mechanisms at the origin of the two interpretations.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Water shows an anomalous behavior at low temperatures [1–3], that has led to an extensive experimental [1–16], theoretical [1, 2, 17–32] and numerical [1–3, 33–42] study. The main anomalies are a rapid increase of the absolute magnitude of isothermal compressibility [5], isobaric heat capacity [7] and thermal expansion coefficient [8] in the supercooled (metastable) liquid water below the melting line, and a density maximum that is observable even at ambient pressure and 4 °C, and that occurs along a line of temperatures of maximum density (TMD line) [6, 9].

Three major theories have been proposed to explain this phenomenon, but none of them has been definitively confirmed or refuted, as a consequence of the difficulty of probing metastable water without encountering inevitable crystallization [12]. These three theories are known as

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the stability-limit conjecture [20], the second-critical-point hypothesis [33] and the singularity-free scenario [18, 29].

The *stability-limit conjecture* [20–22] assumes that the limits of stability (spinodal lines) of the superheated, supercooled and stretched liquid water form a single spinodal line, with negative derivative in the  $P$ – $T$  phase diagram at low  $T$  and positive derivative at high  $T$  (retracing spinodal). This conjecture predicts a divergence for the response functions in correspondence to the supercooled liquid-to-liquid spinodal. This prediction is consistent with experimental data, but the experiments cannot discriminate between a genuine divergence and a fast increase with a maximum. No experimental or numerical evidence of a retracing spinodal is available for realistic models of water [42], but the mean field solutions of lattice models [23, 24, 28] and a modified van der Waals equation for weak-hydrogen-bonding liquids [25] show a liquid spinodal that retraces where it meets the TMD line, as predicted by the stability-limit conjecture.

The *two-critical-point hypothesis* [33–35] interprets the increasing in the response functions as a divergence associated with a critical point in the supercooled liquid region. This critical point, at temperature lower than the gas–liquid critical point, is predicted at the end of a first-order phase-transition line that separates two liquid phases, a low-density liquid (LDL) and a high-density liquid (HDL), considered as metastable counterparts of a low-density amorphous and a high-density amorphous, whose first-order transition line has been studied experimentally [14]. The second critical point has been inspired by numerical simulations for realistic model of water [33–35] and has been rationalized by theoretical models [25, 26, 28, 31, 32] receiving some partial experimental confirmation [15, 16]. Recently clear experimental evidence of a liquid–liquid phase transition for phosphorus has been presented [43, 44] and then confirmed by specific numerical simulations [45]. Other numerical results on carbon [46] and silica [47] suggest a liquid–liquid critical point.

In the *singularity-free scenario* [17, 18] the response functions are not considered to diverge, but merely to have maxima. This behaviour can be associated with a TMD line that retraces in the  $P$ – $T$  plane, with negative derivative at high  $P$  (in the stable liquid phase) and positive derivative at lower  $P$  (in the super-heated liquid phase). A number of theoretical approaches [17, 18, 28, 29, 31, 36, 37] have predicted this scenario in specific ranges of model parameters. It is consistent with the lack of experimental evidence for an increasing correlation length [10], but there is no direct experimental confirmation of the existence of a part of the TMD line with negative slope. Even an experimental observation of a retracing TMD line will not give a definitive answer, since the TMD line is retracing also in the two-critical-point hypothesis.

From the theoretical point of view, it is possible to see that these different scenarios can be reconciled without inconsistencies [25, 28, 31, 37]; however, increasing evidence [1, 42] shows that the stability-limit conjecture is not a probable interpretation of the experimental data, and many models [28, 31, 37] suggest that the singularity-free and the second-critical-point scenarios arise from the same microscopic description, with different choices of the hydrogen bond strength or geometry. Nevertheless it is still an open problem which of the two is the correct description for water.

Here we consider a model for water introduced by Sastry *et al* [29], and supporting, in an approximated solution, the singularity-free scenario. We show that by including an interaction, neglected for sake of simplicity in the original model but motivated by experimental results, the two-critical-point scenario is predicted, suggesting that this interpretation is the one describing the water case.

## 2. The model

A fluid can be represented by partitioning the system into  $N$  cells of equal size. With each cell  $i = 1, \dots, N$  a variable  $n_i$  is associated, with  $n_i = 1$  if the average density of the cell is above a threshold,  $n_i = 0$  otherwise. The threshold is by definition such as to discriminate between liquid and gas densities. The van der Waals attractive interaction between the molecules is given by the lattice-gas Hamiltonian

$$\mathcal{H}_{\text{LG}} = -\epsilon \sum_{\langle i, j \rangle} n_i n_j - \mu \sum_i n_i \quad (1)$$

where  $\epsilon > 0$  is the characteristic energy, the first sum is extended to nearest-neighbour (nn) cells  $\langle i, j \rangle$ , the second term determines the average density in the system through the chemical potential  $\mu$  (greater  $\mu$  favours the liquid state) and the cells are represented by sites on a regular lattice.

The Hamiltonian  $\mathcal{H}_{\text{LG}}$  describes a simple fluid with the gas–liquid critical point. Defining the liquid (number) density as  $\rho_l = \sum_i n_i / N$  and the gas (number) density as  $\rho_g = 1 - \rho_l$ , the relevant order parameter of the transition is  $m = \rho_l - \rho_g = 2\rho_l - 1$ , that is 1 for a uniform liquid system, and  $-1$  for a uniform gas system. Above the critical temperature  $T_c$  the discontinuity disappears and is<sup>2</sup>  $m = 0$ .

Liquid water forms a dynamic network of hydrogen bonds (HBs), with each molecule bonded to four other molecules [1]. Even though it is known that a molecule in excited states can have more than four HBs, as a first approximation Sastry *et al* [29] associate with each molecule four arms, one per HB in the ground state, and consider cells with the size of a water molecule and with coordination number  $z = 4$ .

Since two molecules can form an HB only if they are correctly oriented [1], Sastry *et al* describe this *inter-molecular* interaction by introducing an orientational variable per each arm. The orientation of the arm of the molecule on the site  $i$  that faces the site  $j$  is represented by a (discrete) Potts variable  $\sigma_{ij} = 1, \dots, q$ , with a finite number  $q$  of possible orientational states, as suggested by other theoretical works [19]. The Potts variable  $\sigma_{ij}$  interacts only with the variable  $\sigma_{ji}$  of the arm of the molecule (if any) on the site  $j$  facing the site  $i$  [29].

Therefore, in addition to equation (1), the attractive term in the Hamiltonian

$$\mathcal{H}_{\text{HB}} = -J \sum_{\langle i, j \rangle} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}} \quad (2)$$

accounts for the energy decrease  $-J < 0$  due to the HB formed when two nearest-neighbour cells are occupied by a molecule ( $n_i n_j = 1$ ) and the two arms  $\sigma_{ij}$  and  $\sigma_{ji}$  have the appropriate orientation (i.e.  $\delta_{\sigma_{ij}, \sigma_{ji}} = 1$ , with  $\delta_{a,b} = 1$  if  $a = b$ , otherwise  $\delta_{a,b} = 0$ ). For the sake of simplicity, Sastry *et al* [29]<sup>3</sup> assume that to form an HB the arms must be in the same state.

The experimental oxygen–oxygen correlation function shows that an HB is formed if the inter-molecular distance is within a characteristic range, and that it is not formed below this range [3]. Since, to minimize the energy, the HBs are preferred at low  $T$ , this observation is crucial to understand the density anomaly (expansion upon isobaric cooling)  $(\partial V / \partial T)_P < 0$ , because the formation of an HB leads to a local expansion. This is consistent with the fact that the solid, and fully hydrogen-bonded, phase (ice) has a specific volume larger than the liquid phase. To take into account the increase of volume associated with the HB, Sastry *et al* proposed to express the (liquid) volume as

$$V = V_0 + N_{\text{HB}} v_{\text{HB}} \quad (3)$$

<sup>2</sup> The solid phase has no representation in the LG model and, for  $T$  going to zero,  $m$  goes to 1, i.e. the model is in a uniform liquid phase at zero temperature.

<sup>3</sup> By considering that other specific patterns of orientations minimize the energy, one changes only the multiplicity (entropy) of the ground state by a factor.

where  $V_0$  is the volume of the liquid with no HBs,

$$N_{\text{HB}} = \sum_{(i,j)} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}} \quad (4)$$

denotes the total number of HBs in the system and  $v_{\text{HB}}$  is the specific volume per HB. Since the formation of HBs decreases the number of possible Potts configurations for the system, the entropy decreases for increasing  $N_{\text{HB}}$ . Therefore the Sastry *et al* model,  $\mathcal{H}_{\text{LG}} + \mathcal{H}_{\text{HB}}$  with the equation (3), takes into account the inter-molecular orientational correlation (equation (2)), the expansion and the anticorrelation between  $V$  and  $S$ , upon HB formation (equations (3), (4)). The model predicts the singularity-free scenario, in the approximation with the arms of the same molecule completely independent.

However, experiments [3] show that the relative orientations of the arms of the same molecules are strongly correlated at low  $T$ . Hence the interaction between the arms of each single molecule must be taken into account.

To this goal, we add to  $\mathcal{H}_{\text{LG}} + \mathcal{H}_{\text{HB}}$  an *intra-molecular* term that, for each occupied cell ( $n_i = 1$ ), gives a negative contribution ( $-J_\sigma < 0$ ) to the energy when two of its arms are in the appropriate orientational state ( $\delta_{\sigma_{ik}, \sigma_{il}} = 1$  assuming, for simplicity, that they have to be in the same state):

$$\mathcal{H}_I = -J_\sigma \sum_i n_i \sum_{(k,l)_i} \delta_{\sigma_{ik}, \sigma_{il}} \quad (5)$$

where the term is summed over all the cells and over all the six different pairs  $(k, l)_i$  of the four arms belonging to the same molecule  $i$ . Therefore the model considered here is defined by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{LG}} + \mathcal{H}_{\text{HB}} + \mathcal{H}_I \quad (6)$$

given by equations (1), (2), (5) and by the volume definition equation (3).

Since the number of liquid cells  $\mathcal{N} = \sum_i n_i$ , the volume  $V$ , the entropy  $S$  and the total energy  $U = \mathcal{H} + \mu\mathcal{N}$  are not constant, the equation of state is implicitly given by

$$U - TS + PV - \mu\mathcal{N} = 0 \quad (7)$$

where the left-hand side is the relevant thermodynamic potential for the system. By using the equations (1)–(6), we obtain

$$TS - PV_0 = - \sum_{(i,j)} \epsilon'_{ij}(P, \sigma) n_i n_j - \sum_i \mu'_i(\sigma) n_i \quad (8)$$

with the effective attraction energy, depending on  $P$  and the local Potts configuration,

$$\epsilon'_{ij}(P, \sigma) = \epsilon + J'(P) \delta_{\sigma_{ij}, \sigma_{ji}} \quad (9)$$

where

$$J'(P) = J - P v_{\text{HB}} \quad (10)$$

can be seen as the effective HB interaction energy due to the HB volume increase, and

$$\mu'_i(\sigma) = \mu + J_\sigma \sum_{(k,l)_i} \delta_{\sigma_{ki}, \sigma_{li}} \quad (11)$$

is the effective chemical potential depending on the (local) configuration of Potts variables on the molecule  $i$ .

For  $q > 1$  and  $J_\sigma = 0$  the model recovers the Sastry *et al* case, in which each Potts variable on a molecule arm interacts *only* with the facing Potts variable on the nn molecule (if any) and does not interact with the other arms of the same molecule. Therefore the Potts variables are on a *disconnected* lattice and there is no Potts transition. Nevertheless at low  $T$ ,

to minimize the free energy, the Potts variables match in pairs and  $N_{\text{HB}}$  (and the volume) increases giving the density anomaly reported in [29]. The characteristic temperature of this ordering process is given by  $k_{\text{B}}T \sim O(J')$  (where  $k_{\text{B}}$  is the Boltzmann constant), suggesting that this characteristic temperature decreases for increasing  $P$  (equation (10)), as seen in the experiments, and that for  $P \simeq P_0$ , with

$$P_0 = \frac{J}{v_{\text{HB}}} \quad (12)$$

such that  $J'(P_0) = 0$ , there are no HBs.

### 3. Analytic approach, results and conclusions

For the general case with  $q > 1$  and finite  $J_{\sigma}$  we consider the model described in equations (3), (6), and associate an order parameter  $m \in [-1, 1]$  with the LG variables  $n_i$ , and an order parameter  $m_{\sigma} \in [0, 1]$  with the orientational Potts variables  $\sigma_{ij}$ . The order parameter  $m$  is proportional to the (liquid) number density  $n = \sum_i n_i/N$ , while  $m_{\sigma}$  is proportional to the number density  $n_{\sigma}$  of Potts variables in the appropriate state for HB. A mean field approximation consists in assuming that the relations between  $n$  and  $m$  and between  $n_{\sigma}$  and  $m_{\sigma}$  are linear, i.e.

$$n = (1 + m)/2 \quad \text{and} \quad n_{\sigma} = [1 + (q - 1)m_{\sigma}]/q. \quad (13)$$

In this approximation, the (liquid) molar density  $\rho = nN/V$  is

$$\rho = \frac{1 + m}{2v_0 + v_{\text{HB}} p_{\text{HB}} \gamma} \quad (14)$$

where  $v_0 = V_0/N$ ,  $\gamma = 4$  is the number of arms of the molecules and  $p_{\text{HB}}$  is the probability of forming an HB between two nn molecules. Since by definition all the nn molecules are at a distance within the HB interaction range it is,  $p_{\text{HB}} = n^2 p_{\sigma}$  where  $n^2$  is the probability of having two nn molecules, and  $p_{\sigma}$  is the probability of having the facing arms of the two molecules in the same Potts state.

To find the expression for  $p_{\sigma}$  we note that at low enough  $T$  the Potts variables order in the same state, as a consequence of the interactions between them, and  $m_{\sigma}$  goes to 1. Therefore  $p_{\sigma}$  increases for decreasing  $T$  as an effect of the cooperativity between the Potts variables, going to 1 for  $T \rightarrow 0$  and going to  $1/q$  for  $T \rightarrow \infty$ .

To include the cooperativity effect, we consider that each Potts variable interacts with a mean field generated by all the surrounding Potts variables. Since the system breaks the symmetry, ordering in the preferred state for the HB, a choice is to consider the field proportional to the density of particles in the preferred state  $n_{\sigma}$  with a proportionality factor given by the Potts interaction strength and the number of nn variables<sup>4</sup>.

In the first-order approximation the field generated by three of the Potts variables in a molecule and acting on the fourth Potts variable is<sup>5</sup>

$$h = 3J_{\sigma} n_{\sigma}. \quad (15)$$

<sup>4</sup> In principle we can consider explicitly the field generated by the first shell of variables around a centre one, and include the effect of all the others in a field acting on the variables in the first shell in an approximation *a la* Bethe-Peierls [48]. The latter can be separated as the field of the second shell and the field of the outer shells, and so on in a shell expansion, getting higher orders of the approximation. We shall report on the higher-order approximations elsewhere. Note that we considered the zeroth-order approximation (i.e. no effect of surrounding field) in [49], finding a line of first-order phase transitions to a low-density state inside the liquid region with negative slope in the  $P$ - $T$  plane and at  $T$  below the liquid-gas critical temperature.

<sup>5</sup> In this approximation  $h$  does not depend on  $T$  explicitly, but the dependence is implicit via  $n_{\sigma}$  that turns out to be a function of  $T$ .

Writing the partition function  $Z_h$  for the fourth Potts variable (e.g.  $\sigma_{ij}$ ) interacting with the facing Potts variable ( $\sigma_{ji}$ ) on the  $nn$  molecule, with both variables in the field  $h$ , the probability  $p_\sigma$  in this case can be expressed as

$$Z_h p_\sigma = \sum_{\sigma_{ij}, \sigma_{ji}} \delta_{\sigma_{ij}, \sigma_{ji}} \exp\{[(J - P v_{\text{HB}})\delta_{\sigma_{ij}, \sigma_{ji}} + h(\delta_{\sigma_{ij}, 1} + \delta_{\sigma_{ji}, 1})]/(k_B T)\} \quad (16)$$

where

$$Z_h = \sum_{\sigma_{ij}, \sigma_{ji}} \exp\{[(J - P v_{\text{HB}})\delta_{\sigma_{ij}, \sigma_{ji}} + h(\delta_{\sigma_{ij}, 1} + \delta_{\sigma_{ji}, 1})]/(k_B T)\} \quad (17)$$

and where the symbol  $\sum_{\sigma_{ij}, \sigma_{ji}}$  denotes the sum over all the possible states of the two Potts variables.

The resulting expression for  $p_\sigma(T, P)$  is

$$p_\sigma(T, P) = \left[ 1 + (q - 1) \frac{2w_T + q - 2}{w_{P,T}[w_T^2 + q - 1]} \right]^{-1} \quad (18)$$

where

$$\begin{aligned} w_{P,T} &= \exp[(J - P v_{\text{HB}})/(k_B T)] & \text{and} \\ w_T &= \exp[3J_\sigma(1 + m_\sigma)/(q k_B T)] \end{aligned} \quad (19)$$

with  $p_\sigma \rightarrow 1/q$  for  $T \rightarrow \infty$  and  $p_\sigma = 1$  for  $T = 0$ , as expected. We assume that the equation (18) is an approximation for  $p_\sigma$  in the general case in which each cell is interacting with the surrounding cells and without the field  $h$ , i.e.  $(n_\sigma^2 + (q - 1)(1 - n_\sigma)^2)/(q - 1)^2$ . Therefore the solution of the equation

$$p_\sigma(T, P) = n_\sigma^2 + (q - 1) \left( \frac{1 - n_\sigma}{1 - q} \right)^2 \equiv \frac{1 + (q - 1)m_\sigma^2}{q} \quad (20)$$

gives a new expression for  $m_\sigma(T, P)$  and  $n_\sigma(T, P)$ . The equation (20) has no solution at high enough  $P$ , i.e. above a limiting value  $P_{\text{max}}(T)$  there is no Potts transition and with  $m_\sigma = 0$  and  $n_\sigma = 1/q$ . It turns out that at  $T = 0$ ,  $P_{\text{max}}(0) \gtrsim P_0$  (equation (12)) and that  $P_{\text{max}}(T)$  decreases with  $T$  approximately as a linear function of  $m_\sigma$ .

To calculate the phase diagram of the system we minimize, with respect to the order parameters  $m$  and  $m_\sigma$ , the molar Gibbs free energy for the liquid<sup>6</sup>  $g = u - Ts + Pv \equiv \mu$ , where  $u$  is the molar energy,  $s$  is the molar entropy and  $v = 1/\rho$  is the molar volume. The molar energy  $u$ , the total energy divided by  $nN$ , has contributions from the LG term equation (1), the inter-molecular term equation (2) and the intra-molecular term equation (5):

$$u = -\frac{\gamma}{2} \{ \epsilon n + [Jn + (\gamma - 1)J_\sigma] p_\sigma \}. \quad (21)$$

The molar entropy  $s = S/(nN)$  has a contribution from the  $(N)$  LG variables, that in the mean field approximation is

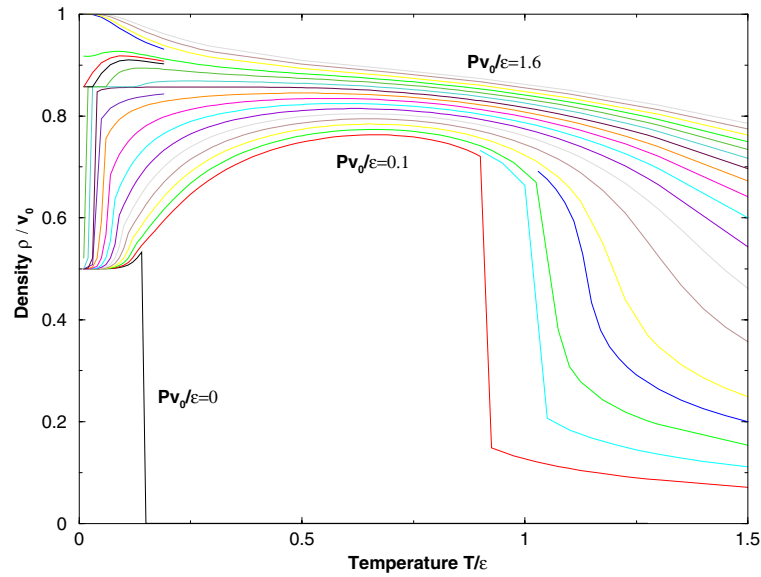
$$-\frac{S_{\text{LG}}}{k_B N} = n \ln n + (1 - n) \ln(1 - n) \quad (22)$$

and a contribution from the  $\gamma nN$  Potts variables

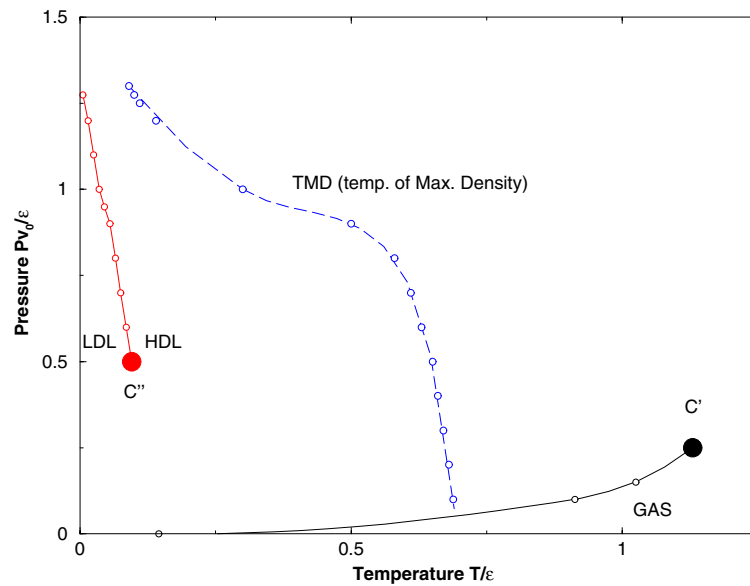
$$-\frac{S_\sigma}{k_B \gamma n N} = n_\sigma \ln n_\sigma + (q - 1)(1 - n_\sigma) \ln \frac{1 - n_\sigma}{q - 1} \quad (23)$$

where  $n_\sigma = n_\sigma(T, P)$  is given by the solution of equation (20) for  $P \leq P_{\text{max}}(T)$  and by  $1/q$  elsewhere. The resulting total molar entropy, to the leading order in  $\mathcal{N}$ , is  $s \equiv (S_{\text{LG}} + S_\sigma)/(nN)$ .

<sup>6</sup> The liquid is described by the canonical ensemble where  $P$ ,  $T$  and the number of particles is fixed. Nevertheless the number  $\mathcal{N}$  of liquid cells is changing since the volume is changing.



**Figure 1.** The density  $\rho$  as a function of the temperature  $T$  for pressures (top to bottom)  $Pv_0/\epsilon = 1.6, 1.5, 1.4, 1.35, 1.3, 1.275, 1.25, 1.2, 1.1, 1.0, 0.95, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.1, 0$ , from the analytic solution of the model with parameters  $q = 6$ ,  $J/\epsilon = 0.5$ ,  $J_\sigma/\epsilon = 0.05$ ,  $\gamma = 4$  and  $v_{HB}/v_0 = 0.5$ .



**Figure 2.** The  $P$ - $T$  phase diagram for the model with the parameters in figure 1. The HDL-LDL phase transition line is approximately linear, with negative slope, ending in the critical point  $C''$ . The liquid-gas critical point is  $C'$  at the end of the liquid-gas phase transition line. Circles along the two transition lines are estimated from the discontinuities in figure 1. The TMD (dashed) curve shows the  $P(T)$  of the maxima in  $\rho$  in figure 1. Note that  $P_0 = 1\epsilon/v_0$  is only a rough estimate of  $P_{\max}$ , the maximum pressure at which the TMD occurs. Circles are estimated from the maxima in figure 1. The curves are only guides for the eyes.

From the minimization of  $g(T, P)$  we find the equilibrium  $m(T, P)$ ,  $m_\sigma(T, P)$  and  $\mu(T, P)$ . Then, by using equation (14) for the equilibrium values of  $m$  and  $m_\sigma$ , we calculate the equilibrium value of  $\rho(T, P)$  (figure 1). At high  $P$  the density  $\rho$  is monotonically decreasing with  $T$ . At lower  $P$ ,  $\rho$  has a maximum. Decreasing  $P$ , the maximum shifts to higher  $T$ , and at lower  $T$  a discontinuity in  $\rho$  appears. The discontinuity at low  $T$  disappears for lower  $P$ , and at high  $T$  another discontinuity in  $\rho$  occurs. The latter discontinuity (at high  $T$ ) shows the liquid–gas first-order phase transition, disappearing in the liquid–gas critical point  $C'$  (figure 2). The maximum in  $\rho$  is the TMD line, shifting at higher  $T$  for decreasing  $P$ , as seen in the range of the experimental measurements [6, 9]. The low- $T$  discontinuity in  $\rho$  shows the HDL–LDL first-order phase transition, disappearing in the HDL–LDL critical point  $C''$ . The slope of the line of HDL–LDL phase transitions is negative (figure 2) as predicted by the two-critical-point hypothesis.

In conclusion, the Hamiltonian model for water proposed by Sastry *et al* [29] and analysed with the approximation that the HBs on a molecule can form any angle, independently of the temperature, supports the free-singularity scenario. However the experiments suggest that the HB angles are strongly correlated at low  $T$ . We therefore introduce a new Hamiltonian term to take into account this correlation. We have presented here the analytic solution of this new model in a first-order approximation, in which the cooperativity effect is included by a mean field for the four Potts variables describing the orientations of the four hydrogen-bonding arms of a molecule. The resulting phase diagram shows the occurrence of an HDL–LDL phase transition ending in a critical point. Therefore the correlation in the HBs leads to a model supporting the second-critical-point hypothesis as the most reasonable explanation for the anomalies of water instead of the singularity-free scenario, elucidating the difference between these two possible scenarios.

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