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A theory for discriminating the mechanism responsible for the water density anomaly

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Abstract

We propose a model elucidating the mechanisms at the origin of the density anomaly of water. We start from a model of Sastry et al., with no correlation between the hydrogen bonds (HBs), that rationalizes the experiments with an anomalous behavior of the line of temperatures of maximum density (TMD), i.e., with a singularity-free scenario. We introduce the correlation of HBs and solve the model within a mean-field approach. The resulting phase diagram shows the same anomalous behavior of the TMD line but also the occurrence of a phase transition between a high- and a low-density liquids ending in a critical point. Therefore, the introduction of the HBs correlation is enough to pass from the singularity-free scenario to the second critical point scenario. Since experiments on water show the presence of HBs correlation, this result suggests that the relevant mechanism for the density anomaly is the liquid–liquid phase transition.

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1. Introduction

Liquid water expands under isobaric cooling, showing a line of temperatures of maximum density (TMD line) [1]. This anomaly has been extensively investigated with experiments, theories and numerical simulations [2]. However, the mechanism responsible for the anomaly is not fully understood [2].

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Two interpretations, among the others, have been considered as alternative theories. One, the *singularity-free scenario* [3], rationalizes the anomalous behavior of water with a TMD line that retraces in the pressure–temperature P – T plane, i.e., that has a negative derivative at high P (in the stable liquid phase) and positive derivative at lower P (in the superheated liquid phase). A number of theoretical approaches [3–7] have predicted this scenario in specific ranges of model parameters. In particular, in the Sastry et al. model [5] the proposed mechanism is based on a local expansion of the system as consequence of the formation of a hydrogen bond (HB).

Another interpretation, the *two critical points hypothesis* [8], relates the anomaly to the presence of a first-order phase-transition line between a low-density liquid (LDL) and a high-density liquid (HDL), with a possible critical point, in the supercooled liquid region. This scenario has been inspired by numerical simulations for realistic model of water [8] and has been rationalized by theoretical models [4,9,10] receiving some partial experimental confirmations [11]. Recently, clear experimental evidences of a liquid–liquid phase transition for phosphorus have been presented [12] and confirmed by specific numerical simulations [13]. Other numerical results on carbon and silica suggest a liquid–liquid critical point [14].

It has been shown that both scenarios can be derived within the same theoretical framework [4,9,7] and that they arise from the same microscopic description [4,7]. However, it is still an open problem which of the two is the correct interpretation for water. Our goal is to show that a way to discriminate between them is to consider the effect of the HBs correlation. By introducing this effect, the second critical point is recovered, supporting this interpretation as the one describing the water case.

2. The model

A network-forming liquid with correlated bonds depending on the orientation, such as water, can be described by the Hamiltonian

$$H = -\varepsilon \sum_{\langle i,j \rangle} n_i n_j - \mu \sum_i n_i - J \sum_{\langle i,j \rangle} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}} - J_\sigma \sum_i n_i \sum_{(k,l)_i} \delta_{\sigma_{ik}, \sigma_{il}}, \quad (1)$$

where the system is partitioned in N cells of equal size on a regular lattice, each with a variable n_i , $i = 1, \dots, N$, with $n_i = 1$ if the cell is occupied by a molecule, $n_i = 0$ otherwise. The first term describes the van der Waals attractive interaction between the molecules, with energy $\varepsilon > 0$, and the sum is extended to nearest-neighbors (nn) cells $\langle i, j \rangle$. The second term determines the average density in the system via the chemical potential μ .

The third term, introduced by Sastry et al. [5], describes the HB formation, occurring only if the molecules are correctly oriented [2]. We associate to each molecule four arms, one per HB in the ground state, and consider a lattice with coordination number 4. The orientation of the arm of the molecule in the cell i and facing the molecule in the cell j is represented by a Potts variable $\sigma_{ij} = 1, \dots, q$, with q orientational states, interacting only with the facing arm σ_{ji} . A HB is formed, and the energy decreases

($-J < 0$), when the facing arms have the appropriate orientation (i.e., $\delta_{\sigma_{ij}, \sigma_{ji}} = 1$, with $\delta_{a,b} = 1$ if $a = b$, otherwise $\delta_{a,b} = 0$).

The fourth term, new with respect to the Sastry et al. [5] model, is introduced because the experiments show a narrow distribution in the H–O–H angle at low T [2], suggesting that the relative orientations of the HBs on the same molecules are strongly correlated. We, therefore, propose this *intra-molecular* term that gives a negative contribution ($-J_\sigma < 0$) to the energy when two arms on the same molecule are in the appropriate orientational state ($\delta_{\sigma_{ik}, \sigma_{il}} = 1$ assuming, for simplicity, that they have to be in the same state). This 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 .

To take into account the experimentally motivated local increase of volume associated to the HB, following Sastry et al. [5], we express the (liquid) volume as $V = V_0 + v_{HB} \sum_{\langle i,j \rangle} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}}$, where V_0 is the volume of the liquid with no HBs, v_{HB} is the specific volume per HB and the sum is the total number of HBs in the system. Since the formation of HBs decreases the number of possible Potts configurations for the system, the entropy S decreases for increasing V .

If $J_\sigma = 0$, we recover the Sastry et al. model, where each HB, once formed, is independent on the other HBs. Therefore, the model in this case takes into account the inter-molecular orientational correlation, the expansion and the anticorrelation between V and S , upon HB formation, but the Potts variables have no long-range correlation and the only relevant order parameter is the liquid molar density $\rho = nN/V$, where $n = \sum_i n_i/N$ is the number density. As a consequence, for $J < \varepsilon$, at high T , V is almost constant, while n increases by decreasing T . Hence, ρ increases and has a discontinuity in correspondence of the gas–liquid first-order transition, if P is below the critical pressure. At low T , also V increases, as a consequence of the formation of HBs, and ρ is no longer monotonic, showing a maximum at a T that depends on P and retraces in the P – T phase diagram. Therefore, the Sastry et al. model predicts the singularity-free scenario with retracing TMD line [5]. However, this prediction is valid in the approximation of non-correlated HBs.

3. The mean-field results with the intra-molecular term

For $J_\sigma > 0$, there are two relevant order parameters. One, $m \in [-1, 1]$, describes the ordering of the variables n_i and is proportional to the number density n . The other, $m_\sigma \in [0, 1]$, describes the orientational order of the variables σ_{ij} and is proportional to the number density n_σ of Potts variables in the appropriate state for HB. In mean field (MF) they can be expressed as $n = (1 + m)/2$ and $n_\sigma = [1 + (q - 1)m_\sigma]/q$.

To calculate the phase diagram of the system we minimize, with respect to the order parameters m and m_σ , the molar Gibbs free energy for the liquid $g = u - Ts + Pv \equiv \mu$, where $-s/k_B = \ln n + [(1 - n)/n] \ln(1 - n) + 4\{n_\sigma \ln n_\sigma + (q - 1)(1 - n_\sigma) \ln[(1 - n_\sigma)/(q - 1)]\}$ is the molar entropy $s \equiv S/(nN)$ of N variables n_i and $4nN$ variables σ_{ij} , $u = -2[\varepsilon n + (Jn + 3J_\sigma)p_\sigma]$ is the molar energy, $v \equiv 1/\rho \equiv V/nN = (2V_0/N + 4v_{HB}n^2 p_\sigma)/(1 + m)$, is the molar volume, n^2 is the probability of having two nn molecules and

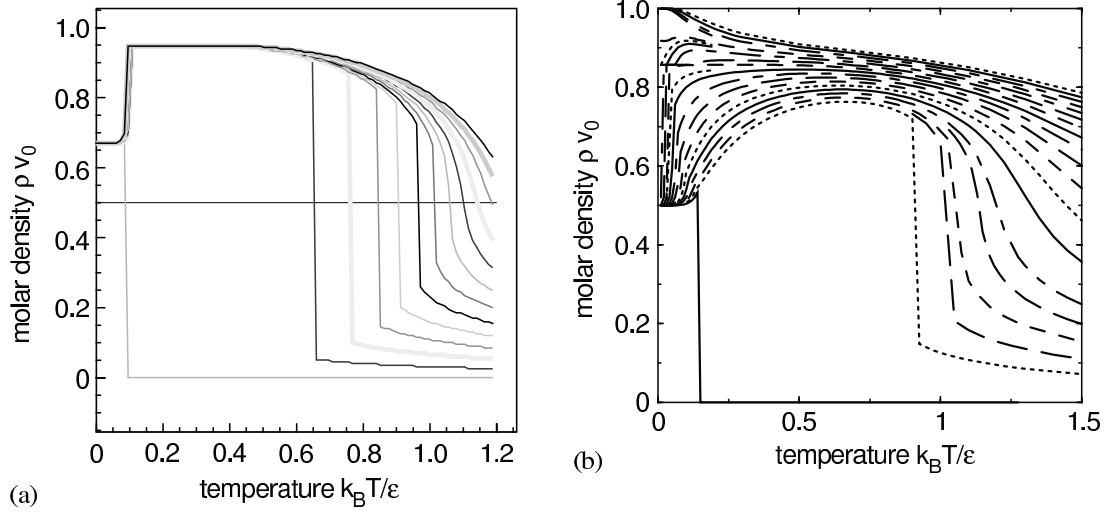


Fig. 1. The molar density ρ as function of the temperature T along isobars, calculated in the mean field approximation at different orders. (a) The zeroth-order approximation for pressures (top to bottom) $Pv_0/\epsilon = 0.36, 0.33, 0.30, 0.27, 0.24, 0.21, 0.18, 0.15, 0.12, 0.09, 0.06, 0.03, -0.007$, for the model with $J/\epsilon = 0.5$, $J_\sigma/\epsilon = 0.01$, $v_{HB}/v_0 = 0.25$ and $q = 10$. The low- T discontinuity in ρ marks the LDL–HDL first-order phase transition, occurring at a T that decreases linearly for increasing P . (b) The first-order approximation for pressures (top to bottom) $Pv_0/\epsilon = 1.6, 1.5, 1.4, 1.35, 1.3, 1.275, 1.25, 1.2, 1.1, 1.0, 0.95, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.1, 0$, for the model with $J/\epsilon = 0.5$, $J_\sigma/\epsilon = 0.05$, $v_{HB}/v_0 = 0.5$ and $q = 6$. At low T and low P , there is a continuous decrease of ρ . Above a critical P , a discontinuity appears as in panel (a).

$p_\sigma \equiv n_\sigma^2 + (q-1)(1-n_\sigma)^2/(q-1)^2 \equiv [1 + (q-1)m_\sigma^2]/q$ is the probability of having the facing arms of the two molecules in the same Potts state.

The minimization of g , as defined above and as a function of T and P , gives values of $m^{(0)}(T, P)$ and $m_\sigma^{(0)}(T, P)$ that allow us to calculate $\rho^{(0)}(T, P)$ (Fig. 1a) [15]. The result is that a HDL–LDL phase transition appears in the liquid region below a maximum P . However, this transition instead of ending in critical point, ends in a liquid–liquid–gas triple point. This result, different from the Sastry et al. prediction, is a consequence of our MF approximation, where p_σ has no explicit dependence on P .

To find an explicit dependence of p_σ on P and T , we note that p_σ increases for decreasing T , going from $1/q$ for $T \rightarrow \infty$ to 1 for $T \rightarrow 0$, as a consequence of the interactions between Potts variables. To include the cooperativity effect, we consider that each Potts variable interacts with a mean field h 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 h proportional to the density of particles in the preferred state n_σ , with a proportionality factor given by the Potts interaction strength and the number of nn variables. The solution in Fig. 1a, that is for $h=0$, therefore can be considered as the zeroth-order approximation. We can consider explicitly the field generated by the first shell of variables around a center 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. By iterating the process we can calculate higher orders of the approximation.

To the first order, the field generated by three of the Potts variables in a molecule acting on the fourth Potts variable is $h = 3J_\sigma n_\sigma$. Writing the partition function for two facing arms under the action of h , we find [15]

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

with $k_B T \ln w_P = (J - Pv_{HB})$ and $qk_B T \ln w_T = 3J_\sigma[1 + m_\sigma(q - 1)]$, that, from the general relation between p_σ and n_σ , allows us to find the first order solution for $m^{(1)}(T, P)$, $m_\sigma^{(1)}(T, P)$ and $\rho^{(1)}(T, P)$ (Fig. 1b) [15].

In Fig. 1b the low- T discontinuity in ρ , marking the HDL–LDL phase transition, disappears at low P in a critical point, without changing the high- T and high- P parts of the phase diagram. Therefore, the model presented here shows the singularity-free scenario if the intra-molecular interaction is $J_\sigma = 0$, while predicts the liquid–liquid phase transition for $J_\sigma > 0$. Within the first-order approximation, we predict the second critical point. This result shows that the two interpretations differ only in the assumption about the importance of the intra-molecular interaction. Since the experiments on water suggest a finite J_σ , this theory supports the liquid–liquid phase transition scenario.

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