Revisiting waterlike network-forming lattice models

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I. INTRODUCTION

Water is extremely abundant in nature, and it is of enormous importance from a biological, technological as well as environmental point of view, because of its various anomalous properties [1]. For instance, it is well known that liquid water exhibits unusually large heat capacity and dielectric constant. Furthermore, at ordinary pressures, the solid phase (ice) is less dense than the corresponding liquid phase, while the latter displays a temperature of maximum density, slightly above the freezing transition. In spite of great research efforts on water [2, 3, 4], a fully consistent theory of such (and many other) anomalies from first principles is not yet available. Nonetheless, it is well established that most anomalies are related to the ability of water molecules to form a network of hydrogen bonds.

Following this view, so-called network-forming fluids have been the subject of several theoretical investigations. Among different possible approaches, a number of studies have been developed in the framework of simplified lattice models [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. Various types of model molecules with orientation-dependent interactions have been used, in either two [5, 6, 7, 8, 9, 10] or three [11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31] dimensions. A natural choice for water is a 3-dimensional model molecule with four bonding arms arranged in a tetrahedral symmetry [11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27]. Two arms represent the hydrogen (H) atoms, which are positively charged and act as donors for the H bond, whereas the other two represent the negatively charged regions of the H$_2$O molecule (“lone pairs”), acting as H-bond acceptors. As far as the lattice is concerned, the body-centered cubic (bcc) lattice is suitable for the tetrahedral molecule, as the latter can point its arms toward four out of eight nearest neighbors of each given site. The above features are common to several models, which differ in the form of interactions and in the set of allowed configurations.

In the early model proposed by Bell [11, 12, 13, 14], molecules can point their arms only toward nearest neighbor sites. An attractive energy is assigned to every pair of occupied nearest neighbors, with an extra contribution if a H bond is formed, i.e., if a donor arm points toward an acceptor arm. Moreover, a repulsive energy is assigned to certain triplets of occupied sites, in order to account for the difficulty of forming H bonds by closely-packed water molecules. Minor variations of this model have also been investigated: Bell and Salt [14], and subsequently Meijer and coworkers [15, 16], have replaced the three-body interaction with a simple next-nearest-neighbor repulsion, whereas Lavis and Southern [17] have defined a simplified model with no distinction between donors and acceptors. All these studies predict a liquid-vapor coexistence and two different low-temperature phases, characterized by orientational order and different densities. At zero temperature, the low-density phase is an ideal diamond network made up of H-bonded water molecules, with half the lattice sites left empty, resembling the structure of ice Ic (cubic ice). Conversely, the high-density phase is made up of two interpenetrating diamond structures, with all the sites occupied, resembling the structure of ice VII (a high pressure form of ice). If the models retain bond asymmetry, i.e., donors and acceptors are distinguished, then both zero-temperature phases possess a residual entropy.

Debenedetti and coworkers have studied a similar model [20, 21, 22], in which water molecules have an extra number of nonbonding configurations and the close-packing energy penalty occurs only when two molecules
in a triplet form a H bond. At zero temperature, this model still predicts the two ordered H-bond networks of the Bell model. At finite temperature, these (ice-like) phases have not been investigated, as the cited works were mainly focused on metastable liquid water. Indeed, the model seems to support the popular “second critical point” conjecture [32, 33], originally proposed by Stanley and coworkers [34]. Two authors of the present paper have also studied a simplified version of this model, without the donor-acceptor asymmetry [23, 24].

A variation of the Bell model has been considered by Besseling and Lyklema [18, 19], who have taken into account only nearest-neighbor interactions, namely, an attractive term for H-bonded molecules and a repulsive term for nonbonded molecules. Even in this case, the two different ordered phases described above are stable at zero temperature, but they have not been investigated at finite temperature. The cited studies were indeed devoted to liquid-vapor interface properties [18] and to hydrophobic hydration thermodynamics [19], for which the authors found good agreement with experiments. These results were obtained in the so-called quasi-chemical or Bethe approximation, i.e., a first-order approximation which takes into account correlations over clusters made up of two nearest-neighbor sites.

Girardi and coworkers [25] have recently performed extensive Monte Carlo simulations for the above model, in the simplified version with symmetric bonds. This work claims the onset of two liquid phases of different densities, which can coexist in equilibrium, in agreement with Stanley’s conjecture [34]. The coexistence line seems to terminate in a critical point, while the lower-density phase exhibits a temperature of maximum density, depending on pressure.

In our previous paper [27] we analyzed the latter model by a generalized first-order approximation, based on a four-site tetrahedral cluster. Such semi-analytical calculation turns out to reproduce, with remarkable accuracy, most physical properties obtained by simulations. Nevertheless, the resulting phase diagram is quite different from the one proposed in the original paper [25]. The two different condensed phases exhibit orientational order, which suggests to identify them as a temperature evolution of the two zero-temperature network structures introduced above. Furthermore, the two claimed critical points turn out to be in fact tricritical, and two critical lines appear, related to two different kinds of symmetry breaking. In conclusion, the phase diagram is more complex and richer than expected, but unfortunately quite far from the real water phase diagram.

In the current paper, we exploit the effectiveness of our approximation scheme, with a twofold purpose. On the one hand, we reconsider more complex models with asymmetric bonds, such as the Besseling-Lyklema (BL) model and the original Bell model.

Several investigations devoted to this kind of models have hypothesized a fully homogeneous (i.e., site-independent) probability distribution of molecular configurations, thus excluding the possibility of orientational ordering of the type observed in the GBHB model [27]. Conversely, we find out that analogous ordered phases occur even in the BL and Bell models. The liquid phase reported by previous papers [11, 18] (displaying water-like density anomalies) turns out to be an artifact of the aforementioned homogeneity assumption. Furthermore, density anomalies appear in the lower-density ordered phase, which makes it questionable to regard this phase as a representation of some real ice form. Let us note that density anomalies in an icleike phase have been previously noticed by Meijer and coworkers [16], investigating the Bell-Salt model [14]. We discuss the reasons underlying these difficulties, which we argue to be common to a wide class of network-forming lattice models for water, and finally suggest a possible way to circumvent the problem.

The paper is organized as follows. In Section II we introduce a generic model Hamiltonian incorporating the three models under investigation. In Section III we describe in more detail the ground states of the models. In Section IV we explain the cluster-variation technique employed for the calculation. Section V reports the results, and a comparison to previous semi-analytical [18] and numerical [13] investigations. Section VI contains the conclusions.

II. THE MODEL HAMILTONIAN

As mentioned in the Introduction, we study three different models of increasing complexity (GBHB, BL, and Bell), defined on a bcc lattice (Fig. 1). It is possible to write a single Hamiltonian incorporating the three models. For all the models, a lattice site can be empty or occupied by a molecule having a tetrahedral structure (4 bonding arms, which can point toward 4 out of 8 nearest neighbors of each given site).

In the simplest case (GBHB model), a hydrogen bond is formed, yielding an attractive energy $-\eta < 0$, whenever two nearest-neighbor molecules point an arm toward each other, with no distinction between donor and acceptor. Each molecule can thus have only two different configurations, which we simply denote as 1 and 2 (see Fig. 2). Moreover, a repulsive energy $-\epsilon > 0$ is assigned to every pair of nearest-neighbor sites occupied by water molecules. This term is meant to penalize neighbor molecules not forming H bonds. Finally, a chemical potential contribution $-\mu$ is taken into account for every occupied site (in this paper we always consider a grandcanonical description).

In the BL model [18], the above picture is a little more
FIG. 1: Two conventional (cubic) cells of the body centered cubic (bcc) lattice. A, B, C, D denote four interpenetrating face-centered cubic (fcc) sublattices.

FIG. 2: Two model molecules in a bonding configuration. The arm configuration is \( i = 1 \) for the lower molecule and \( i = 2 \) for the upper one (see the text).

complex. The bonding arms of each molecule are “decorated” by a sign (two “+” and two “−”), respectively denoting donors and acceptors. A H bond is formed only if the two bonding arms, pointing toward each other, carry one “+” sign and one “−” sign, or vice versa. As a consequence, a water molecule can assume 6 distinguishable “sign configurations” for each of the 2 “arm configurations” described above, adding up to 12 different configurations.

The Bell model [11] is equivalent to the BL model in the bonding mechanism, but incorporates different orientation-independent interactions. The two-molecule interaction is attractive \((-\epsilon < 0\)) whereas a repulsive energy \(-\gamma > 0\) is assigned to any (fully occupied) 3-site cluster, made up of two second neighbors plus one of their common first neighbors.

We can write the general model hamiltonian as

\[
H = -\epsilon \sum_{(r,s)} n_{i_r}n_{i_s} - \mu \sum_r n_{i_r} \\
-\eta \sum_{(r,s)} h_{i_r,i_s} - \gamma \sum_{(r,s,t)} n_{i_r}n_{i_s}n_{i_t},
\]

where \( r, s, t \) denote lattice sites, \( i_r, i_s, i_t \) denote their respective configurations, \( n_i \) is an “occupation function”, defined as \( n_i = 0 \) if \( i = 0 \) (empty site), \( n_i = 1 \) otherwise (occupied site), and \( h_{ij} \) is a “bond function”, defined as \( h_{ij} = 1 \) if the pair configuration \((i, j)\) represents a H bond, and \( h_{ij} = 0 \) otherwise. The summations denoted by \( r \), \((r, s)\), and \((r, s, t)\) respectively run over sites, nearest neighbor pairs, and the 3-site clusters defined above. Let us note that the first line of Eq. (1) is formally equivalent to a lattice-gas hamiltonian, although the GBHB and the BL models are characterized by a repulsive interaction energy \((-\epsilon < 0\)). The first term of the second line represents the H-bond energy, which is always attractive \((\eta > 0)\), whereas the last term takes into account the 3-body repulsive interaction \((-\gamma < 0\)). As mentioned above, the latter occurs only in the Bell model, whereas the GBHB and BL models are characterized by \( \gamma = 0\). Concerning configuration indices, we can always denote a vacancy (empty site) by \( i = 0 \), but molecular configurations need to be defined in different ways, depending on whether the model assumes asymmetric bonds (donor-acceptor distinction) or symmetric bonds (no distinction). In the latter case (GBHB model), the two possible arm configurations, which we respectively denote by \( i = 1, 2 \) (see Fig. 2), provide a full description of the molecule configurations. In the other case we have to understand that \( i \) is in fact a multi-index \((i, i')\), where \( i' \) denotes the sign configuration. As a consequence, in general the precise definition of the bond function \( h_{ij} \) turns out to depend on the spatial orientation of the lattice bond considered. It can be made unambiguous in the symmetric bond case, by defining a special order for the sites in each nearest neighbor pair. Such order may be for instance the one indicated by the arms of a molecule in the \( i = 1 \) configuration, in which case we obtain the following simple definition: \( h_{ij} = 1 \) if \( i = 1 \) and \( j = 2 \), and \( h_{ij} = 0 \) otherwise.

III. GROUND STATES

The models under investigation can exhibit two different ground states with different densities, in which the bonding arms of the molecules form ordered network structures, as described in the Introduction. Such
ordered structures naturally split the bcc lattice into four (mutually exclusive) interpenetrating fcc sublattices, which we denote by $A, B, C, D$ (see Fig. 1). Assuming here that $i, j, k, l$ denote the arm configurations of all sites placed on the $A, B, C, D$ sublattices, respectively, one can see that the low density structure (single diamond network) is fourfold degenerate and can be represented by the four alternative sublattice configurations $(i, j, k, l) = (1, 2, 0, 0), (0, 1, 2, 0), (0, 0, 1, 2), (2, 0, 0, 1)$ (which can be obtained from one another by a circular permutation). In each structure, two sublattices (respectively, $AB, BC, CD, DA$) are occupied, while the other two sublattices are empty. Conversely, the high-density structure (two intertwined diamond networks) turns out to be twofold degenerate and can be represented by the two alternative sublattice configurations $(i, j, k, l) = (1, 2, 0, 0), (2, 1, 2, 1)$. Both these configurations have all lattice sites occupied, but they differ in the pairs of bonded sublattices, which is, $AB$ and $CD$, in the former case, or alternatively $BC$ and $DA$ in the latter.

In this paper, we do not investigate in detail the ground state phase diagrams, which depend on the interaction parameters of each different model. Let us only remark an important difference between the simpler GBHB model, with symmetric bonds, and the other two models with asymmetric bonds. In the former case, molecule configurations are fully defined by their arm configurations, so that the formation of a diamond network immediately implies that all molecules are maximally bonded (each molecule can participate in four bonds at most). Conversely, in the latter case, molecules still have the freedom of arranging their ring configurations in order to respect the ice rule (i.e., to realize the correct donor-acceptor pairings), giving rise to an exponential number of global configurations with equal energy, and therefore to a residual ground-state entropy. An approximate calculation of this entropy was first performed in 1935 by Pauling, who obtained a value of $\ln(3/2)$ per molecule [33]. This value turns out to be in extremely good agreement with both experimental measurements and simulations (see Ref. [32] and references therein).

IV. CLUSTER-VARIATION APPROXIMATION

The ground state structures described above suggest to write the average (grand-canonical) energy per site in the following form

$$w = \sum_{i,j,k,l} p_{ijkl} H_{ijkl},$$

where $p_{ijkl}$ denotes the joint probability distribution for the configurations of a tetrahedral cluster like the one depicted in Fig. 3, whose sites are placed respectively on the four different $A, B, C, D$ sublattices, and $H_{ijkl}$ is a suitable function, which we denote as tetrahedron hamiltonian. The sum is understood to run over all possible configurations of the four sites. By grand-canonical energy, we mean $w = u - \mu \rho$, where $u$ is the internal energy per site and $\rho$ is the density, i.e., the average occupation probability

$$\rho = \sum_{i,j,k,l} p_{ijkl} \frac{n_i + n_j + n_k + n_l}{4}.$$  (3)

At first, let us consider the model with symmetric bonds (GBHB model), so that the configuration indices denote only arm configurations. It is easy to verify that the tetrahedron hamiltonian can be written as follows,

$$H_{ijkl} = H_{ij} + H_{jk} + H_{kl} + H_{ij},$$  (4)

where

$$H_{ijk} = -\epsilon n_i n_j - \mu n_i/4 - \eta h_{ij} - 3\gamma n_i n_j n_k.$$  (5)

Eq. (4) shows that the tetrahedron hamiltonian turns out to be invariant under circular permutation of the configuration indices $i, j, k, l$. As far as Eq. (5) is concerned, numerical coefficients are meant to adjust counting of the different terms. The one-site (chemical potential) term is divided by 4, which is, the number of sites in the tetrahedron. The two-site terms have a unit coefficient, because there are exactly 4 nearest-neighbor pairs in the tetrahedron and 4 nearest-neighbor pairs per site in the lattice. Finally, the three-site term is multiplied by 3, because there are 4 triangle clusters in the tetrahedron, but 12 triangle clusters per site in the lattice.

Let us note that the meaning of Eq. (2), and of the related definition of the tetrahedron hamiltonian, is that every elementary tetrahedron is assumed to give on average the same contribution to the energy of the system. In other words, we assume that possible breaking of translational invariance in the thermodynamic state of the system can only occur at the level of the four sublattices identified by the ground states, whereas the thermodynamic state of each individual sublattice is assumed to remain translationally invariant. This assumption is supported by Monte Carlo simulations, performed for the GBHB model [27].

As far as entropy is concerned, we make use of the very same approximation employed for the GBHB

![Diagram](https://via.placeholder.com/500)

**FIG. 3:** Tetrahedral cluster, made up of four sites placed on the four different $A, B, C, D$ sublattices. $AB, BC, CD,$ and $DA$ are nearest-neighbor pairs; $AC$ and $BD$ are next-nearest-neighbor pairs.
model \cite{27}. In the cited paper, we deduced the approximation as an instance of Kikuchi’s cluster-variation method \cite{37,38,39}. The latter is a generalized mean-field theory, which describes correlations up to the size of certain maximal clusters. In general, one obtains a free-energy functional in the cluster probability distributions, to be minimized, according to the variational principle of statistical mechanics. Here, we derive the variational free energy, according to a heuristic argument analogous to the one originally suggested by Guggenheim \cite{40}. One assumes that the entropy per site can be evaluated as a difference of two terms. The former is the information entropy associated with the 4-site probability distribution $p_{ijkl}$, which takes into account correlations among 4 configuration variables on a tetrahedral cluster (i.e., on the 4 different sublattices). The latter can be viewed as a correction term, which ensures that, if the tetrahedron distribution factorizes into a product of single-site probabilities, the mean-field (Bragg-Williams) entropy approximation is recovered.

The variational grand-canonical free energy per site
\[
\omega = \sum_{i,j,k,l} p_{ijkl} \left[ \mathcal{H}_{ijkl} / T + \ln p_{ijkl} - \frac{3}{4} \ln \left( \frac{p_i^A p_j^B p_k^C p_l^D}{p_{ijkl}} \right) \right],
\]
where $p_i^X$ is the probability of the $i$ configuration for a site on the $X$ sublattice ($X = A, B, C, D$). These probabilities are of course defined as marginals of the tetrahedron distribution as
\[
\begin{align*}
 p_i^A &= \sum_{j,k,l} p_{ijkl}, & p_i^B &= \sum_{k,l,i} p_{ijkl}, \\
 p_i^C &= \sum_{l,i,j} p_{ijkl}, & p_i^D &= \sum_{i,j,k} p_{ijkl}.
\end{align*}
\]  

The variational free energy in Eq. (6) is thus a function of the only tetrahedron distribution $p_{ijkl}$. Let us note that such a free energy is also sometimes referred to as (generalized) first-order approximation (on the tetrahedron cluster), and turns out to be exact for a suitable Husimi lattice \cite{41,42}, with the (tetrahedral) building blocks arranged as in Fig. 4.

The free energy minimization, taking into account the normalization constraint
\[
\sum_{i,j,k,l} p_{ijkl} = 1,
\]
can be performed by the Lagrange multiplier method, yielding
\[
p_{ijkl} = \zeta e^{-\mathcal{H}_{ijkl} / T} \left( \frac{p_i^A p_j^B p_k^C p_l^D}{p_{ijkl}} \right)^{3/4},
\]
where $\zeta$ is related to the Lagrange multiplier, and can be determined by imposing the constraint Eq. (8).

By finding (numerically) a change of sign in some eigenvalue of the Hessian matrix of the variational free energy. The elements of the latter can be written as
\[
\frac{1}{T} \frac{\partial^2 \omega}{\partial p_{ijkl} \partial p_{i'j'k'l'}} = \delta_{i,i'} \delta_{j,j'} \delta_{k,k'} \delta_{l,l'} \frac{\delta_{ii'}}{p_i^A} + \frac{\delta_{jj'}}{p_j^B} + \frac{\delta_{kk'}}{p_k^C} + \frac{\delta_{ll'}}{p_l^D},
\]
where $\delta$ denotes Kronecker delta.

As mentioned above, these calculations are valid in the case of symmetric bonds (GBHB model), but they have
to be generalized, in order to deal with the asymmetric-bond models (BL and Bell models). In the latter cases one has to take into account both arm and sign configurations. We make the simplifying assumption that all sign configurations are equally probable, for a molecule in a given arm configuration. Such assumption is reasonable, since it turns out to lead to a very good approximation for the zero-point entropy of perfect ice (where correlations among sign configurations are expected to be maximal). Indeed, in Ref. [18] Besseling and Lyklema showed that Pauling’s calculation is exactly equivalent to the quasi-chemical (Bethe) approximation, with the extra assumption of equally probable sign configurations. A simple, though quite tedious, calculation proves that the same result is recovered by our cluster approximation. In a few words, this is related to the fact that each tetrahedral (4-site) cluster contains only 2 molecules in the same diamond network. Therefore, for perfect ice (i.e., fixed arm configuration), the tetrahedral cluster approximation describes sign-configuration statistics in the very same way as the Bethe (2-site) approximation does.

According to these arguments, we restrict the minimization procedure to a subspace of the probability distribution space, characterized by equally probable sign configurations. It is possible to show that such a calculation leads to a set of equations for the probability distribution of arm configurations, that are formally equivalent to Eqs. (9) and (10). In these equations, the tetrahedron hamiltonian $H_{ijkl}$ can still be evaluated by Eqs. (4) and (5), but the H bond energy $\eta$ is replaced by the effective temperature-dependent parameter

$$\tilde{\eta}(T) = T \ln \frac{1 + e^{\eta/T}}{2},$$

while the chemical potential $\mu$ is replaced by

$$\tilde{\mu}(T) = \mu + T \ln 6,$$

(recall that we have 6 sign configurations for each arm configuration). These parameters contain entropic contributions, which take into account the extra degrees of freedom related to the sign configurations. Such contributions must not be taken into account in the evaluation of the (grand-canonical) average energy. It turns out that the latter can still be computed by Eqs. (2), (4), and (5), with $\eta$ replaced by

$$\tilde{\eta}(T) = \eta \frac{e^{\eta/T}}{1 + e^{-T}}.$$  

The latter parameter represents the H-bond energy, averaged over the sign configurations.

Let us finally recall that we are also interested in studying the effect of a homogeneity constraint, i.e., of forcing site probability distributions $p^X_i$ to be independent of the sublattice $X$. It is easy to see that, if the latter condition is verified in the right-hand side of Eq. (9) the resulting tetrahedron distribution (left-hand side) turns out to be invariant under circular permutation of the indices, due to the same invariance property of the tetrahedron hamiltonian $H_{ijkl}$. As a consequence, the marginals computed by Eqs. (7) will verify the homogeneity condition as well. This observation clearly shows that the cluster-variational free energy actually admits “homogeneous” stationary points. In order to determine such points, preventing numerical instabilities which might drive the iterative procedure toward more stable symmetry-broken solutions, it is sufficient to compute marginals according to the following prescription

$$p_i^A = p_i^B = p_i^C = p_i^D = \frac{\sum_j p_{ijkl} + p_{ijlk} + p_{klij} + p_{ljki}}{4},$$

rather than Eqs. (7).

V. RESULTS

A. Phases

Let us consider the probability distributions $p^X_i$ of the arm configuration $i$ on the $X$ sublattice, as defined in Eqs. (7). Due to normalization, each distribution can be represented by two parameters, which can be conveniently defined as

$$\rho^X = p^X_1 + p^X_2,$$

$$\xi^X = p^X_1 - p^X_2.$$

The former is an occupation probability, restricted to the $X$ sublattice, so that we may call it sublattice density. The latter characterizes preference for the water arm configuration 1 rather than 2 on the $X$ sublattice. For the benefit of readers that are familiar with spin models, let us note that the arm configuration variables of the current models admit a “natural” mapping onto spin-1 variables, namely, $S = \pm 1$ spin values representing the two water configurations, and $S = 0$ representing empty sites. In this view, the above parameters turn out to be the usual order parameters of spin-1 models, i.e., the quadrupolar order parameter $(S^2)$ and the magnetization $(S)$, respectively. It is possible to characterize the different phases of our models by the set of sublattice order parameters $\rho^X, \xi^X$, for $X = A, B, C, D$. Let us stress the fact that the same characterization is valid for all the models under investigation, both with symmetric and asymmetric bonds.

At high temperature and low pressure, we always observe a fully homogeneous (gaslike or liquidlike) phase, which we simply denote as fluid (F), where the order parameters $\rho^X, \xi^X$ are independent of the sublattice. The $\xi^X$ parameters vanish, revealing that there is no preference between the two alternative arm configurations of a water molecule. In summary, we can write

$$\begin{bmatrix} p^A & p^B & p^C & p^D \\ \xi^A & \xi^B & \xi^C & \xi^D \end{bmatrix} = \begin{bmatrix} \rho_F & \rho_F & \rho_F & \rho_F \\ 0 & 0 & 0 & 0 \end{bmatrix},$$

(18)
where the matrix notation has been chosen for reasons of clarity. In the low-temperature region, we observe two different phases, which we denote as high density (HD) and low-density (LD) phases. These phases can be regarded as a temperature evolution of the two (HD and LD) ground-state ordered network structures, respectively.

As far as the HD phase is concerned, we have

\[
\begin{bmatrix}
\rho^A & \rho^B & \rho^C & \rho^D \\
\xi^A & \xi^B & \xi^C & \xi^D
\end{bmatrix} = \begin{bmatrix}
\rho_{HD} & \rho_{HD} & \rho_{HD} & \rho_{HD} \\
\xi_{HD} & -\xi_{HD} & \xi_{HD} & -\xi_{HD}
\end{bmatrix},
\]

with \(\rho_{HD} = \xi_{HD} = 1\) at zero temperature. The density is still homogeneous, whereas the preference parameters reveal that H bonds are more likely formed within the sublattice pairs \(AB\) and \(CD\), respectively. In other words, this phase can be viewed as an ideal HD structure (two interpenetrating diamond networks), in which defects are progressively introduced by thermal fluctuations.

In the ground state, this phase turns out to be twofold degenerate. The degenerate solution, having defects in the diamond H bond network on the \(AB\) sublattices, and begin to populate the \(CD\) sublattices, which are rigorously empty at zero temperature. This phase is fourfold degenerate, and the alternative solutions can be obtained from Eq. (19) by performing all possible circular permutations.

The LD phase is characterized by

\[
\begin{bmatrix}
\rho^A & \rho^B & \rho^C & \rho^D \\
\xi^A & \xi^B & \xi^C & \xi^D
\end{bmatrix} = \begin{bmatrix}
\rho'_{LD} & \rho'_{LD} & \rho''_{LD} & \rho''_{LD} \\
\xi'_{LD} & -\xi'_{LD} & \xi''_{LD} & -\xi''_{LD}
\end{bmatrix}.
\]

Assuming for instance \(\rho'_{LD} > \rho''_{LD}\), the sublattice pair \(AB\) turns out to be more populated than \(CD\), whereas the preference parameters reveal the formation of preferential bonding within the same sublattice pairs. This phase can be viewed as a temperature evolution of the zero temperature LD structure, characterized by \(\rho'_{LD} = \xi'_{LD} = 1\) and \(\rho''_{LD} = \xi''_{LD} = 0\). Thermal fluctuations introduce defects in the diamond H bond network on the \(AB\) sublattices, and begin to populate the \(CD\) sublattices, which are rigorously empty at zero temperature. This phase is fourfold degenerate, and the alternative solutions can be obtained from Eq. (20) by performing all possible circular permutations.

In certain conditions, we also observe a peculiar phase, which we denote as "modulated" fluid (MF) phase, characterized by the following parameters

\[
\begin{bmatrix}
\rho^A & \rho^B & \rho^C & \rho^D \\
\xi^A & \xi^B & \xi^C & \xi^D
\end{bmatrix} = \begin{bmatrix}
\rho_{MF} & \rho_{MF} & \rho_{MF} & \rho_{MF} \\
0 & 0 & 0 & 0
\end{bmatrix}.
\]

Assuming \(\rho_{MF} > \rho_{MF}\), the two sublattices \(A\) and \(C\) are more populated than \(B\) and \(D\) (whence the term "modulated"), while there is no preference between the two arm configurations (whence the term "fluid"). This phase can be viewed as a temperature evolution of a zero temperature state with \(\rho_{MF} = 1\) (two fully populated sublattices) and \(\rho_{MF} = 0\) (two empty sublattices), or vice versa. Note that the two populated sublattices are next nearest neighbors, so that there is no interaction energy in these states. One can verify that these can actually be ground states of the GBHB and BL models, only if the two-body repulsive interaction is larger than the H bond energy, i.e., \(\epsilon/\eta < -1\).

Let us finally remark that, except the fully homogeneous F phase, all the phases described above (HD, LD, and MF) are symmetry-broken phases, which do not possess the full translational symmetry of the bcc lattice.

### B. GBHB model

In Fig. 5 we report the phase diagram of the GBHB model, for \(\epsilon/\eta = -0.5\). This ratio corresponds to the parameters chosen by Girardi and coworkers in the original paper [25]. In the \(T-P\) diagram (Fig. 5a), we observe three different first-order transition lines. The first one separates the F and LD phases, whereas the other two occur between the LD and HD phases. All these lines are mapped onto coexistence regions in the \(T-\rho\) diagram (Fig. 5b). Both the LD-HD first-order transition lines terminate in tricritical points, which are connected by a second-order line (i.e., a line of critical points) enclosing the LD phase. Another critical line separates the F phase from the HD phase, and terminates in a critical end-point. The LD phase exhibits a density anomaly, namely, a temperature of maximum (or minimum) den-
sity (TMD), at constant pressure. In the $T$-$P$ diagram, the TMD locus is bounded between a minimum and a maximum pressure. The portion of the TMD line joining these two points corresponds to density maxima, whereas the remaining two branches of the line to density minima.

Fig. 5 also reports some data points obtained by the Monte Carlo study of Ref. [25]. We find a remarkably good agreement both for first-order transitions (transition lines and coexistence regions in the $T$-$P$ and $T$-$\rho$ diagrams, respectively), and for the TMD locus. Such an agreement suggests that the tetrahedral cluster approximation is able to take into account the most relevant correlations present in the system. Let us recall that in Ref. 25 the authors could not detect second-order transitions, and interpreted the tricritical points as critical points terminating first-order transitions between homogeneous fluid phases of different densities. The misinterpretation was probably due to the fact that no order parameter was investigated. Indeed, in Ref. 27 we collected several evidences supporting the existence of the ordered phases predicted by the cluster approximation, and the validity of the corresponding phase diagram.

The previous results show that unfortunately the phase diagram of the GBHB model is quite far from that of real water. The main difficulty is that the density anomaly appears in a region where the system still exhibits orientational order (i.e., the icelike LD phase). Furthermore, the LD phase is never less dense than the corresponding fluid phase, as shown by the slope of the F-LD transition line in the $T$-$P$ diagram, and no liquid-vapor coexistence is observed. We have explored the possibility of removing at least the first difficulty, by reducing the relative importance of the attractive H-bond interaction (which is, the one responsible for orientational order), with respect to the repulsive close-packing interaction.

In Fig. 6 we report the phase diagram for $\epsilon/\eta = -0.8$. It turns out that the stability of the LD phase with respect to temperature is actually reduced, but our difficulty is not solved, since the TMD locus is displaced toward lower temperatures, remaining inside the LD phase region. Furthermore, a modulated fluid (MF) phase becomes stable at finite temperature, which makes the phase diagram even more complex. The MF phase is separated from the ordinary fluid (F) phase by a second-order transition and from the LD and HD phases by two different first-order transitions. The physical mechanism underlying the onset of the MF phase can be qualitatively understood by energetic arguments. On the one hand, the increased importance of nearest-neighbor repulsion favors configurations in which occupied sites have empty neighbors (by the way, this also enhances stability of the LD phase with respect to pressure). On the other hand, the reduced importance of H bonding favors thermodynamic states with no preference for particular molecule orientations.

We have also investigated the opposite regime, in which the H-bond interaction dominates with respect to the close-packing interaction (i.e., $\eta \gg |\epsilon|$). We have observed that the pressure and density ranges on which the LD phase is stable become smaller and smaller, but the phase diagram does not exhibit significant changes with respect to the case $\epsilon/\eta = -0.5$.

### C. BL model

As mentioned in the Introduction, the BL model can be viewed as a version of the GBHB model, with asymmetric bonds. The interaction parameters chosen by BL in the original paper [18], based on a fit to real thermodynamic properties, correspond to $\epsilon/\eta = -0.08$, which is, to a regime of dominating H-bond interaction. The phase diagram we have obtained for this case is reported in Fig. 7. This phase diagram is, both qualitatively and quantitatively, very similar to the one of the GBHB model for the same $\epsilon/\eta$ value. We just observe a sort of “rescaling” of the whole phase diagram toward lower temperatures. This effect is of entropic nature, and is related to the presence of the sign configurations.

Apart from these changes, the most remarkable fact in the above phase diagram is that we find no trace of the vapor-liquid coexistence, claimed by BL [18]. We have already mentioned that the reason of such a discrepancy is a homogeneity hypothesis, on which the cal-
Calculations of the cited paper are based. As shown in the previous Section, our approach allows one to impose an analogous homogeneity constraint in a straightforward way. We have repeated the phase diagram calculation, taking into account this constraint, and the results are reported in Fig. 8. Of course, we no longer observe the ordered phases, but only homogeneous (fluid) phases. At low temperature, there appear two first-order transition lines (and related coexistence regions), allowing us to distinguish three phases with different densities. In particular, the transition between the lowest density phase and the intermediate density one might be identified with the vapor-liquid transition. The other transition, between the intermediate and the highest density phases, reminds us of the conjecture about the liquid-liquid transition in metastable water, put forward by Stanley and coworkers [34]. Unfortunately, a more detailed analysis shows that this “homogeneous” phase diagram carries several inconsistencies. First of all, one can observe that the entropy is negative below a certain temperature, which depends on pressure. The TMD locus and most part of the supposed liquid-liquid coexistence region (including the critical point), lie below the zero-entropy line. Moreover, making use of Eq. (11), it is possible to compute the continuation of the F-HD critical line in the stability region of the LD phase. This line marks a boundary, beyond which the free-energy minimum associated to the homogeneous solution becomes a saddle point, i.e., the homogeneous phase becomes thermodynamically unstable. As shown in Fig. 8, such a condition comes true in a very large portion of the phase diagram. By the way, let us also remark that, although for brevity we do not report the results, totally analogous phase diagrams have been obtained for the “homogeneous” GBHB model.

We have also reproduced BL’s original calculation [18], in order to compare the results with those obtained by our approach, in the homogeneity assumption. Fig. 9 reports the vapor-liquid binodals and some coexistence lines in the density-temperature and density-entropy planes. It turns out that, for not too high densities, the two methods yield very similar results. Conversely, a relevant discrepancy appears in the high density regime, which is, the phase diagram computed by BL [18] does not exhibit the “liquid-liquid” transition at all. Such a discrepancy is ultimately due to the different cluster considered for the approximation, namely, a nearest-neighbor pair in BL’s calculation and the tetrahedral cluster in the current one. The (pseudo) liquid-liquid transition is indeed a reminiscence of the distinction between the LD and HD structures, which the tetrahedron approximation is able to account for (although, in the homogeneous assumption, only at the level of local correlations), at odd with the pair approximation.

Let us finally remark that, according to Fig. 9, even BL’s solution turns out to suffer from the negative-entropy problem. More generally, one can see that all the aforementioned inconsistencies do not depend on the type of approximation (except the fact that the pair ap-
proximation does not reveal the liquid-liquid transition but rather on the artificial homogeneity constraint.

D. Bell model

The Bell model is quite different from the GBHB and BL models, as the nearest-neighbor interaction is attractive, while the close-packing repulsion effect is modeled by a three-body interaction (see Section II). For the parameter set of the original paper [11], we have obtained the phase diagram reported in Fig. 10. We can indeed observe several differences, with respect to the phase diagrams presented above. First of all, there appears a coexistence region between two homogeneous (fluid) phases at different densities, which we can identify with a vapor and a liquid phase, respectively. This new feature is likely to be related to the quite strong orientation-independent attractive interaction ($\epsilon > 0$), which is absent in the other models. The ordered LD and HD phases are still present, but with clearly different phase transitions. The F phase turns out to be more stable with respect to pressure, so that a direct F-LD transition takes place, at odd with the GBHB and BL models. Such a transition is partially first-order (at lower pressure) and partially second-order (at higher pressure). As a consequence, a multicritical point appears, at which three critical lines (F-LD, LD-HD, and F-HD) merge. Density anomalies can still be observed in the LD phase. The TMD locus is made up of two different branches: a lower pressure one, corresponding to density maxima, and a higher pressure one, corresponding to density minima. The F phase does not display any density anomaly.

Let us now consider the phase diagram obtained imposing the homogeneity constraint (Fig. 11). Of course, no ordered phase is present, whereas the vapor-liquid coexistence region continues down to zero temperature. Let us note that Bell’s original calculation [11] is equivalent to the tetrahedral cluster approximation for homogeneous phases, so that the vapor-liquid binodals, obtained by the former, turn out to be exactly superimposed to those reported in Fig. 11. In the very low temperature region, we also observe a “liquid-liquid” coexistence, like in the BL and GBHB models. The latter feature was not pointed out by Bell [11], most likely because at that time the exploration of supercooled water physics was at the very beginning [44], and the “second critical point” conjecture had not been proposed yet [34]. Anyway, the
entropy computed by the cluster approximation turns out to be negative in this region. Conversely, the TMD locus lies mostly in the positive entropy region, and exhibits the correct experimental slope. The latter was indeed one of the most striking results of the Bell model. Unfortunately, the stability limit, which in this case is made up of both the F-HD and F-LD second-order transition lines (and a metastable continuation of the latter), suggests that, even for the Bell model, all the interesting anomalies take place in a region where the homogeneous F phase is thermodynamically unstable.

We have compared our results for the Bell model with some Monte Carlo data obtained by Whitehouse and coworkers [13]. In Fig. 12 we report the density as a function of the chemical potential at fixed temperature \( T/\eta = 0.5 \). At a first glance, it turns out that the tetrahedral cluster approximation does not fit the Monte Carlo results so closely as for the GBHB model. This fact is probably to be ascribed to stronger correlations, present in the Bell model, arising from the three-site interaction. We expect that the observed discrepancy is not so relevant to affect the qualitative structure of the phase diagram. Anyway, it is evident that the symmetry-broken solution (solid line) is much closer to the Monte Carlo results than the homogeneous one (dashed line). In particular, the LD-HD symmetry change (see Subsection A) provides an explanation for the transition observed at higher chemical potential. Therefore, we argue that the simulations of Whitehouse and coworkers [13] actually describe ordered phases of the same type predicted by our approximation. This fact was not recognized in the cited paper, most likely because the authors did not investigate any kind of order parameter.

VI. CONCLUSIONS

The basic ideas of the present paper originated in a previous one [27], in which we showed that a generalized first-order approximation on a tetrahedral cluster was able to reproduce several Monte Carlo results for a waterlike network-forming lattice model (GBHB model) [25]. The approximate theory also predicted that the two denser phases, identified as liquid in Ref. 25, were in fact characterized by two different ordered H-bond-network structures. In the current work, we have exploited the same cluster approximation, to extend the analysis of the GBHB model to different parameter values and to revisit other models with similar features (tetrahedral molecules, bcc lattice), already known in the literature (BL and Bell models).

We find that analogous ordered phases are present in all the models investigated. As mentioned in the text, several previous investigations did not point out these phases. In particular, while Girardi and coworkers did not recognize order-disorder transitions in their simulations [25], as they did not compute order parameters, other studies ignored the ordered phases by imposing homogeneity in an analytical way [11, 18, 19]. Our results show that the onset of orientational order produces substantial changes in the phase diagrams, which turn out to be very complex and rich, but quite far from real water.

Let us recall that, in principle, the ordered phases are an interesting feature of the current models, since they might be regarded as a description of two different ice forms. Unfortunately, such an interpretation gives rise
to some difficulties. The most relevant one is that the icelike LD phase exhibits a temperature of maximum density, which would be indeed expected in the liquidlike F phase. Conversely, the F phase turns out to be rather trivial, as it does not exhibit any density anomaly, and, in the GBHB and BL models, not even a vapor-liquid transition. These difficulties seem to be somewhere related to the fact that, in these models, orientational order is exceedingly stable with respect to thermal fluctuations.

We have explored the possibility that a suitable choice of the parameter set could yield a more realistic phase diagram, in the framework of the same models. Several failed attempts have led us to believe that this is likely not to be the case. Indeed, the physical mechanism underlying density anomalies (which is, correlation between low energy and high specific-volume configurations) is also responsible for enhancing thermodynamic stability of the ordered LD phase. Accordingly, a parameter change oriented, for instance, to lowering the LD-F transition temperature, usually turns out to lower the temperature of maximum density as well. In Section VIA we have reported an example of such an effect for the GBHB model.

Let us remark that analogous arguments might probably hold for other similar models, not studied in this paper. For instance, Bell and Salt (14) have shown that their model predicts open- and close-packed ice-like phases, which are respectively equivalent to the LD and HD phases of the current models. More recently, it was noticed (21) that the liquidlike phase of the Roberts-Debenedetti model is metastable at “ordinary” temperatures. Indeed, the authors of Ref. 21 devise particular techniques to prevent the Monte Carlo dynamics from “falling” into ordered states. Two authors of the present paper have verified the onset of analogous ordered states in a simplified (symmetric bonds) version of the Roberts-Debenedetti model, although this result has not been published yet. All these facts suggest that a quite large class of waterlike lattice models should be critically reconsidered.

Concerning the stability of the H-bond network structures, let us note that, in the models under investigation, this is necessarily overemphasized by the regular bcc lattice, which imposes a strong directional correlation on the bonds. Such a correlation is not present in the real (off-lattice) system. In particular, it is known from experiments that directional correlation in real water is almost completely lost after the second consecutive bond (see Ref. 1 and references therein). Therefore, a more realistic model might be provided by a suitable random lattice, preserving the local geometric structure of the H-bond network (up to the second consecutive bond). We expect that such a lattice might hinder the onset of orientational order, though retaining the essential physical properties of the liquidlike phase. Of course, even in a random-lattice description involves a simplification, because, in principle, directional disorder should not be an a-priori assumption, but rather a prediction of the theory.

In any case, a very simple realization of the random lattice, satisfying the requirement on the local tetrahedral geometry, is the Husimi lattice made up of tetrahedral blocks, which we have mentioned in Section IV (Fig. 1). As noted there, the tetrahedral cluster approximation happens to be exact for this particular lattice. Furthermore, it is known that, in general, Husimi and Bethe lattices are characterized by a random graph structure, which is locally treelike, but contains closed loops of different (even and odd) lengths. The latter fact can produce frustration, which is expected to forbid periodically ordered states (14) like those appearing on a regular lattice. As a consequence, it turns out that the different models treated in this paper, properly redefined on the Husimi lattice, cannot exhibit ordered phases at all. The exact thermodynamic equilibrium states for these models are given by the “homogeneous” stationary points of the corresponding Husimi lattice models.

At first sight, the above idea might look a bit tricky, but in fact a random lattice is not much more arbitrary than any regular lattice, for modeling a fluid. Both types of lattice should be regarded as simplifying assumptions, which affect the model predictions in opposite ways. In the regular lattice case, the stability of the ordered phases is underestimated, whereas, in a generic random lattice, it is underestimated. In the simplest case of a Husimi lattice, whose exact solution is almost analytically available, periodically ordered states turn out to be rigorously forbidden. In other words, the price paid for simplicity is that the model is no longer able to describe ice-like phases. Let us also remind that a Husimi lattice is an infinite-dimensional system, so that all its properties have necessarily a mean-field nature. As a consequence, the model cannot yield realistic estimates of critical exponents, which turn out to belong to the mean-field universality class.

Let us also stress the fact that the tetrahedral cluster is not the only possible choice for the building block of the Husimi lattice. This choice turns out to be quite effective for the current models, as it is able to distinguish two different (low- and high-density) local molecular packings. As mentioned in Section VIA these two packings are not only the elementary structures of the ideal LD and HD networks (which are not relevant on the random lattice), but they are also expected to play a role in the possible onset of a liquid-liquid phase transition.

Let us finally note that, in the light of the new interpretation, the negative-entropy phenomenon suggests that the waterlike Husimi lattice models might predict a replica symmetry breaking, in analogy with the models studied by Mézard and coworkers (43, 44). This possibility might even be relevant for describing the glassy
states of water (amorphous ices), which have been studied intensively in the last years by both experiments and simulations [47]. We are going to investigate this issue in a future work.

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