Hydration of an apolar solute in a two-dimensional waterlike lattice fluid

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In a previous work, we investigated a two-dimensional lattice-fluid model, displaying some waterlike thermodynamic anomalies. The model, defined on a triangular lattice, is now extended to aqueous solutions with apolar species. Water molecules are of the “Mercedes Benz” type, i.e., they possess a $D_3$ (equilateral triangle) symmetry, with three equivalent bonding arms. Bond formation depends both on orientation and local density. The insertion of inert molecules displays typical signatures of hydrophobic hydration: large positive transfer free energy, large negative transfer entropy (at low temperature), strong temperature dependence of the transfer enthalpy and entropy, i.e., large (positive) transfer heat capacity. Model properties are derived by a generalized first order approximation on a triangle cluster.

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I. INTRODUCTION

The term hydrophobicity [1] refers to peculiar thermodynamic properties of the transfer process of an apolar solute into water. In such a process, one generally observes large positive transfer free energy, large negative transfer entropy (at room temperature), and strong temperature dependence of the transfer enthalpy and entropy, i.e., large (positive) transfer heat capacity. Such anomalous behavior seems to play a central role for relevant phenomena taking place in aqueous solutions, such as folding of macromolecules and proteins, and formation of micelles and membranes [2]. For example, biopolymers such as proteins contain a significant fraction of apolar chemical groups, and it is well established that the effective attraction between apolar groups, due to hydrophobicity, gives an important contribution both to the folding process and to stabilization of the folded protein.

Despite several decades of research, the theory of the hydrophobic effect is still incomplete. Different theoretical models have been proposed to explain the anomalous behavior of water itself and hydrophobic interactions, which have been recognized to be closely related. A straightforward approach relies on the application of molecular dynamics or Monte Carlo simulation methods to models with more or less realistic three-dimensional water geometry [3, 4, 5, 6, 7]. This approach is powerful, but has some limitations. First of all, large computational effort is needed, and properties involving multiple derivatives of the free energy (such as transfer heat capacity, whose behavior is a fingerprint of hydrophobicity) cannot be determined easily. Moreover, the amount of different interactions and geometric parameters included in the model makes it difficult to find out relevant physical mechanisms which determine observable properties.

A complementary approach involves investigation of simplified models [8, 9, 10], with fewer parameters, geometric details, and degrees of freedom. Such models should better allow to trace connections between microscopic structure and observed properties, while the latter can be usually analyzed in full detail, and in a large range of thermodynamic conditions, with relatively small computational effort. One of these attempts is based on the application of scaled-particle theory [11] to hydrophobic hydration [12, 13]. These studies suggest that the hydrophobic effect results mostly from the small size of water molecules, and not from water structuring by the solute. A recent and interesting descendant of scaled-particle theory is the information theory approach by Pratt and coworkers [14, 15], based on previous knowledge of water properties, such as the pair correlation function, obtainable either by experiments or by simulations. The latter approach suggests that water structuring induced by the solute, though existing, may be scarcely relevant for a description of the hydrophobic effect. The simplified molecular thermodynamic theory of Ref. [6] is essentially in agreement with this conclusion. On the contrary, different theories stress that the large positive heat capacity variation, observed upon insertion of apolar solutes into water, can only arise from a cooperative phenomenon, that is from induced ordering of water molecules, so that a theory of the hydrophobic effect should be based on a description of this phenomenon. It can be observed that, at room temperature, hydration of apolar solutes is energetically favorable but sufficiently unfavorable entropically, with a resulting increased free energy. A simplified way to reproduce this effect is for instance the one-dimensional lattice model by Kolomeisky and Widom [16], extended also to two and three dimensions [17]. In that case, entropy penalty is achieved by lowering the large number of possible orientations of a water molecule, if it has to accommodate a neighboring hydrophobic solute. Another possibility is to give water molecules a geometric structure, as in the two-dimensional Mercedes Benz (MB) model, first introduced by Ben-Naim in 1971 [18]. In the latter model, water molecules possess three equivalent bonding arms arranged as in the Mercedes logo, and a geometric constraint (arm alignment) is required for bond formation. An MB model has been investigated
The paper is organized as follows. In Sec. II we define the model and recall the first-order approximation. In Sec III we introduce the thermodynamic quantities used to characterize the solvation process, and compute them in the framework of the model. In particular, we analyze transfer quantities for an inert molecule, comparing them to the case in which hydrogen bonding interaction is “turned off”. Model predictions about solvation of water in its own pure liquid are also reported. In Sec. IV we investigate hydrogen bond coordination, drawing a comparison with the results of the off-lattice MB model. Sec. V contains some concluding remarks.

II. THE MODEL AND THE FIRST ORDER APPROXIMATION

The model is defined on a two dimensional triangular lattice. A lattice site can be empty or occupied by molecules of two different chemical species, water (\( w \)) or solute (\( s \)). A water molecule has three equivalent bonding arms, separated by \( 2\pi/3 \) angles, whereas a solute molecule is assumed to have no internal structure. Two nearest-neighbor (NN) molecules of species \( x, y \) (with \( x, y = w, s \)) interact with an attractive energy \( -\epsilon_{xy} < 0 \), representing ordinary Van der Waals forces. Moreover, if two arms of two NN water molecules point to each other, an energy term \( -\eta < 0 \) is added, to mimic the formation of a hydrogen (H) bond. Due to the lattice structure, a water molecule can form 3 bonds at most, and has only 2 bonding orientations, when its arms are aligned with the lattice. We also assume that \( w \) nonbonding configurations exist, where \( w \) is a model parameter, related to the H bond breaking entropy. The H bond is weakened by an energy term \( c_s \eta / 2 \) when a third molecule of \( x \) species is on a site near a formed bond. In the triangular lattice there are 2 such weakening sites per bond, so that, when both are occupied by \( x \) molecules, the H bond contributes an energy \( -(1 - c_s)\eta \). The resulting water-solute interaction has two components: The nonorientational Van der Waals term \( -\epsilon_{os} \) and the weakening term \( c_s \eta / 2 \). The latter, which is an effective 3 body interaction, can be viewed as a perturbation effect of the solute on a H bond between two water molecules.

Let us write the model hamiltonian. In order to introduce the first order approximation, it is convenient to express it as a sum over elementary triangles:

\[
\mathcal{H} = \frac{1}{2} \sum_{\langle r, r', r'' \rangle} \mathcal{H}_{i, i, i, i' i' i''},
\]

where \( \mathcal{H}_{ijk} \) is a contribution which will be referred to as triangle hamiltonian, and \( i, i', i'' \) label site configurations for the 3 vertices \( r, r', r'' \), respectively. Possible site configurations are (see Tab. B): “empty” \( (i = 0) \), “bonding water” (site occupied by a water molecule in one of the 2 orientations which can form bonds: \( i = 1, 2 \)), “nonbonding water” (site occupied by a water molecule in one

According to the same idea, we have recently investigated a lattice-fluid model of MB type on a (two-dimensional) triangular lattice, with the aim of reproducing qualitatively the thermodynamic anomalies of pure water. Of course, the lattice allows important simplifications, so that a sufficiently accurate modelling of water on a lattice may be quite an interesting issue. Our model hamiltonian includes Van der Waals interaction and hydrogen bonding, when two nearest neighbor MB water molecules point an arm to each other. Bonds can be weakened by the presence of a third competing molecule, close to the formed bond, to mimic the fact that, if water molecules are too close to one another, hydrogen bonds may be perturbed or broken. As far as bonding properties are concerned, the model is equivalent to an early model proposed by Bell and Lavis, but the weakening criterion is different, that is, equivalent to the one employed in quite a recent investigation by Patrykiejew and coworkers. Nevertheless, in the latter analysis the possibility of nonbonding orientations for water molecules is neglected, and resemblance with real water behavior is poor. In Ref. we observed that, introducing such additional orientations, which account for directionality of hydrogen bonds, the lattice model describes several anomalous properties of pure water in a qualitatively correct way. Here we extend the model to the case of an aqueous solution, working out solvation thermodynamics for an inert (apolar) solute. The analysis is also extended to transfer properties of water in its own pure liquid. Our purpose is to verify whether this simple model, which nevertheless accounts for the competition between Van der Waals interactions and hydrogen bonding in almost the same way as the off-lattice MB model, may be able to reproduce at least the main features of hydrophobicity. In particular, we also investigate how the model describes the solvation process at a microscopic level, by comparing the average number of hydrogen bonds formed by water molecules (hydrogen bond coordination) in the bulk or in the hydration shell. We shall carry out the analysis by means of a generalized first-order approximation on a triangle cluster, which has been verified to be quite accurate for the pure water model.
of the $w$ orientations which cannot form bonds: $i = 3$, “solute” (site occupied by a solute molecule: $i = 4$). Even if all configurations have unit multiplicity, except $i = 3$, it is convenient to introduce a generic multiplicity parameter $w_i$, defined as in Tab. I. The triangle Hamiltonian can be written as

$$H_{ijk} = H_{ij} + H_{ki} + H_{kj}, \quad (2)$$

where

$$H_{ij} = -\epsilon_{xy} n_{x,i} n_{y,j} - \eta_{hi} (1 - \epsilon_{xy} n_{x,k}) , \quad (3)$$

$n_{x,i}$ is an occupation variable for the $x$ species, defined as in Tab. I while $h_{ij} = 1$ if the pair configuration $(i, j)$ forms a H bond, and $h_{ij} = 0$ otherwise. Conventionally, repeated $x$ and $y$ indices are summed over their possible values $w, s$. Let us notice that triangle vertices are set on three triangular sublattices, say $A, B, C$, and $i, j, k$ are assumed to denote configurations of sites placed on $A, B, C$ sublattices respectively. Assuming also that $A, B, C$ are ordered counterclockwise on up-pointing triangles (whence clockwise on down-pointing triangles), we can define $h_{ij} = 1$ if $i = 1$ and $j = 2$ and $h_{ij} = 0$ otherwise. Let us also notice that both Van der Waals ($-\epsilon_{xy} n_{x,i} n_{y,j}$) and H bond energies ($-\eta_{hi}$), that are 2-body terms, are split between two triangles, whence the $1/2$ prefactor in Eq. (1). On the contrary the 3-body weakening terms ($\eta_{hi} \epsilon_{xy} n_{x,k}/2$) are associated each one to a given triangle, and the $1/2$ factor is absorbed in the prefactor. Let us denote the triangle configuration probability by $p_{ijk}$, and assume that the probability distribution is equal for every triangle (no distinction between up- or down-pointing triangles). Taking into account that there are 2 triangles per site, we can write the following expression for the internal energy per site of an infinite lattice

$$u = \sum_{i=0}^{4} \sum_{j=0}^{4} \sum_{k=0}^{4} w_i w_j w_k p_{ijk} H_{ijk}. \quad (4)$$

The multiplicity for the triangle configuration $(i, j, k)$ is given by $w_i w_j w_k$, where $w_i$ is the previously mentioned multiplicity parameter.

The details of the finite temperature analysis of the model, by a generalized first order approximation on a triangle cluster, follow the previous paper [25]. Not being interested in symmetry broken phases (ice), we introduce a homogeneity condition since the beginning, after which generalization is trivial. The grand-canonical free energy per site $\omega = u - \mu_s \rho_s - T s \left( \mu_p \text{ and } \rho_p \right)$ being respectively the chemical potential and the density, or site occupation probability, for the $x$ species, $T$ and $s$ being respectively the temperature and the entropy per site), can be written as a functional in the triangle probability distribution as

$$\omega = \sum_{i=0}^{4} \sum_{j=0}^{4} \sum_{k=0}^{4} w_i w_j w_k p_{ijk} \left( \hat{H}_{ijk} + T \ln p_{ijk} \right)$$

$$- 2T \sum_{i=0}^{4} w_i p_i \ln p_i,$$

where $T$ is expressed in energy units (whence entropy in natural units). It is noteworthy that the only variational parameter in $\omega$ is the triangle probability distribution, that is the 125 variables $\{p_{ijk}\}$, because $p_i$ (the site probability) can be expressed as a marginal. According to the homogeneity hypothesis, we can use the symmetrized expression

$$p_i = \sum_{j=0}^{4} \sum_{k=0}^{4} w_j w_k \frac{p_{ijk} + p_{jki} + p_{kij}}{3}. \quad (6)$$

The latter turns out to be convenient, in that it gives rise to iterative (fixed point) equations which preserve homogeneity. The energy part in Eq. 3 is given by the modified hamiltonian $\hat{H}_{ijk}$, defined as

$$\hat{H}_{ijk} = H_{ijk} - \mu_x \frac{n_{x,i} + n_{x,j} + n_{x,k}}{3}. \quad (7)$$

The minimization of $\omega$ with respect to $\{p_{ijk}\}$, with the normalization constraint, yields the equations

$$p_{ijk} = \xi^{-1} e^{-\hat{H}_{ijk}/T \left(p_i p_j p_k\right)^{2/3}}, \quad (8)$$

where $\xi$ is a normalization constant. Such equations can be solved numerically by simple iteration (natural iteration method [24]). As a result, we obtain the triangle probability values at equilibrium, from which one can compute the thermal average of every observable. The substitution into Eqs. 1 and 2 gives respectively the equilibrium internal energy and free energy, and, by the way, it is possible to show that

$$\omega = -T \ln \xi. \quad (9)$$

III. SOLVATION THERMODYNAMICS

Let us first introduce the thermodynamic quantities, generally used to describe solvation from a macroscopic point of view, which we shall evaluate for our model in
the following. The physical process we are interested in is the transfer of a component ($x = w, s$) into a water-solute mixture, with solute density tending to zero. According to the Ben-Naim standard [30], this process is well characterized by variation of the pseudo-chemical potential $\mu_s^*$, related to the ordinary chemical potential $\mu_x$ of the given component by

$$\mu_x = \mu_x^* + T \log \rho_x. \quad (10)$$

Let us notice that, in the latter term on the right hand side, the momentum partition function is missing, due to the fact that we are dealing with a lattice model [30].

The solvation free energy per molecule $\Delta g_x^*$ is defined as the difference between pseudo-chemical potential values of a molecule $x$ in the ideal gas phase ($g$) and in the liquid phase ($l$). For practical purposes, the differences between ideal and real gas can be generally neglected [30]. For a molecule of species $x$ we then have

$$\Delta g_x^* = \mu_x^{*(l)} - \mu_x^{*(g)} \quad (11)$$

where $\mu_x^{*(l)}$ and $\mu_x^{*(g)}$ are pseudo-chemical potentials of $x$ in the liquid and gas phases, respectively. Now, if liquid and gas phase coexist in equilibrium, as usual in experiments, the ordinary chemical potentials of $x$ in both phases must be equal, and by simple algebra we obtain

$$\Delta g_x^* = -T \ln \frac{\rho_x^{*(l)}}{\rho_x^{*(g)}}. \quad (12)$$

where $\rho_x^{*(l)}$ and $\rho_x^{*(g)}$ are respectively the $x$ species densities in the liquid and in the gas. Derived quantities, of interest in experiments, are the solvation entropy

$$\Delta s_x^* = -\frac{\partial \Delta g_x^*}{\partial T} \bigg|_P, \quad (13)$$

the solvation enthalpy

$$\Delta h_x^* = \Delta g_x^* + T \Delta s_x^*, \quad (14)$$

and the solvation heat-capacity

$$\Delta c_p x^* = \frac{\partial \Delta h_x^*}{\partial T} \bigg|_P. \quad (15)$$

Let us notice that, in principle, we should distinguish between a constant pressure derivative (as stated by definition) and a temperature derivative taken along the liquid-vapor equilibrium curve. In particular, we could not even use Eq. (12) because we would move out of the equilibrium curve, at which the ordinary chemical potentials are equal. Nevertheless, numerical results [30] show that the difference is negligible, definitely from a qualitative point of view. Therefore, we shall always use the latter temperature derivative definition in our calculations.

Let us start studying solvation of an inert molecule in water. We set water parameters as follows: $\eta/\epsilon_{ww} = 3$, $c_w = 0.8$, and $w = 20$. As shown in our previous analysis [25], this choice corresponds to a waterlike behavior, with a liquid-vapor critical point at $T/\epsilon_{ww} \approx 1.18$, and with a temperature of maximum density for the liquid around $T/\epsilon_{ww} \approx 0.67$ at low pressure. Solvation thermodynamics concepts introduced above are independent of density of components in the mixture. We choose to let solute density assume very low values with respect to water density (dilute solution limit), in order to compare with experiments. The “inert” nature of the solute is described, in the model framework, by setting to zero the solute-solute ($\epsilon_{sw}$) and water-solute ($\epsilon_{ws}$) Van der Waals interaction energies. At the moment, we also set the weakening parameter $c_w$ to zero, assuming that the ideally inert solute does not weaken H bonds in its neighborhood. The effect of nonzero values for this parameter, which may describe for instance a volume interaction, resulting in a perturbation of the geometry (and hence of the energy) of H bonds, will be taken into account later. The temperature trends of the free energy, entropy, and enthalpy of transfer are given in Fig. 11(a); the transfer heat capacity in Fig. 11(c). In order to compare with experimental data [30], all quantities are evaluated at liquid-vapor coexistence. For the perfectly inert solute, we have verified that concentration does not affect the results at all. To represent roughly the experimental temperature range (between 0°C and 300°C) we report model results between $T/\epsilon_{ww} = 0.65$ (just below the temperature of maximum density for pure liquid water) and $T/\epsilon_{ww} = 0.90$ (about half way between the previous temperature and the critical temperature). Remarkably, it turns out that the model, despite its simplicity, displays a clear indication that solute insertion into the mixture orders the system. The corresponding positive (unfavorable) contribution to free energy compensates a negative (favorable) enthalpic contribution, giving rise to a positive solvation free energy. At higher temperature, enthalpic and entropic contributions change sign, but they still have the same trend of compensating each other. As observed in experiments, the model predicts two different temperatures $T_H$ and $T_S$ at which the transfer enthalpy and entropy vanish, respectively [see Fig. 11(b)]. This behavior is to be ascribed to the thermodynamics of H bonding and, in order to rationalize this fact in the model framework, let us also analyze transfer quantities for the case $\eta = 0$, i.e., turning off H bond interactions [see Fig. 11(a),(c)]. As expected, the results are similar in the high temperature regime, where there is a high probability that hydrogen bonds are broken by thermal
fluctuations, whereas they change more and more dramatically upon decreasing temperature, and in particular the regions of negative transfer entropy and enthalpy completely disappear. This facts confirm that H bonding is the key element for system ordering, upon insertion of an inert molecule. Accordingly, also the divergentlike trend of the heat capacity upon decreasing temperature (related to the fact that the liquid phase is approaching a stability limit [25]) is suppressed. The process is now completely dominated by the transfer enthalpy, with a large and positive transfer free energy, and a positive transfer entropy. The transfer quantities behave qualitatively as those observed in solvation experiments of noble gas molecules in ordinary liquids [30, 31], and are relatively independent of temperature. These features characterize a regular transfer process, like the solvation of an ordinary fluid molecule from a gas phase into its pure liquid phase. In this case, upon removing H bond interactions [thin lines in Fig. 2(a)], very little changes are observed in the solvation energies, except at very low temperature, where we are approaching the stability limit for liquid water [25]. Let us discuss two issues about these results. First, the fact that so little changes are caused by turning on or off H bonds can be rationalized on the basis of the microscopic model interactions. The insertion of a water molecule into pure liquid water should imply in principle the formation of new H bonds, but the model is such that insertion of a new water molecule also weakens other H bonds in its neighborhood, and the two effects nearly compensate each other. Second, let us notice that solvation enthalpy decreases upon increasing temperature, that is, the solvation heat capacity is negative, in contrast with experiments. We do not have an explanation for this fact, but we can observe the absolute values of solvation free energy and entropy are considerably lower and the enthalpy, rather than the entropy, dominates the solvation process, and all quantities are relatively independent of temperature. These features characterize a regular transfer process, like the solvation of an ordinary fluid molecule from a gas phase into its pure liquid phase. In this case, upon removing H bond interactions [thin lines in Fig. 2(a)], very little changes are observed in the solvation energies, except at very low temperature, where we are approaching the stability limit for liquid water [25]. Let us discuss two issues about these results. First, the fact that so little changes are caused by turning on or off H bonds can be rationalized on the basis of the microscopic model interactions. The insertion of a water molecule into pure liquid water should imply in principle the formation of new H bonds, but the model is such that insertion of a new water molecule also weakens other H bonds in its neighborhood, and the two effects nearly compensate each other. Second, let us notice that solvation enthalpy decreases upon increasing temperature, that is, the solvation heat capacity is negative, in contrast with experiments. We do not have an explanation for this fact, but we can observe

**FIG. 1:** (a) Solvation energies ($E/\epsilon_{\text{ww}}$) vs temperature ($T/\epsilon_{\text{ww}}$) for an ideal inert molecule in water at liquid-vapor coexistence: $E = \Delta g^*_s$ (solid line), $E = T \Delta s^*_s$ (dashed line), and $E = \Delta h^*_s$ (dashed-dotted line). (b) Corresponding experimental data for transfer of argon into water [30]. (c) Solvation heat capacity ($\Delta c_P^*$) vs temperature ($T/\epsilon_{\text{ww}}$) for an ideal inert molecule in water. (d) Corresponding experimental data for transfer of argon into water [30]. Thin lines in (a) and (c) denote solvation energies in nonbonding water ($\eta = 0$).
that an analogous effect is observed when the model is reduced to describe a regular solvation process, that is when H bonds are turned off. This suggest that there is probably a limitation of the lattice description, that anyway has nothing to do with the peculiarities of water. The effect is quantitatively small, so that it is hidden by other large enthalpic and entropic effects observed in the case of hydrophobic solvation.

IV. HYDROGEN BOND COORDINATION

So far, we have always considered an ideal, perfectly inert solute, setting to zero all interactions with water ($\epsilon_{ws}$, $c_s$) and with itself ($\epsilon_{ss}$). Now we investigate the role of the $c_s$ parameter, which represents a weakening of H bonds, induced by the presence of a solute molecule. Let us recall that, in our model, the presence of too many water molecules close to one another weakens the H bond strength, through the $c_w$ parameter, to mimic the fact that too low average distance is unfavorable for H bonds. On the contrary, a different (lower) weakening parameter $c_s$ for a solute molecule, can represent a perturbation of H bonds, due to an excluded volume effect. Anyway, the solute weakening parameter $c_s$ is a way of tuning the degree of water ordering induced by the solute. In order to characterize this effect, together with the role of the $c_s$ parameter, let us investigate the H bond coordination, that is, the average number of hydrogen bonds per molecule. In quite recent papers, Dill and coworkers suggested, on the basis of their off-lattice MB model, that this parameter is the appropriate one to rationalize the temperature $T_S$ at which the transfer entropy vanishes. Therefore, $i_0$ being the central site configurations and $i_1 \ldots i_6$ the NNs configurations, the hexagon probability distribution reads

$$p_{i_0i_1\ldots i_6} = \frac{p_{i_0i_1i_2}p_{i_0i_1i_4}p_{i_0i_1i_6}}{p_{i_0}^2}. \quad (16)$$

We shall evaluate bond coordinations according to this factorization, which, let us notice, is perfectly consistent with our approximation scheme. Let us consider a water molecule in a bonding configuration, for example $i = 1$. It is not necessary to consider also the other ($i = 2$) bonding configuration, due to the fact that the liquid phase is isotropic, whereas we do not take into account nonbonding configurations ($i = 3$), because in that case the probability of forming a bond is zero. The bulk and shell coordinations can be written respectively
as

\[ \langle q \rangle_B = \sum_{q=1}^{3} q P_{q|B} \quad (17) \]

\[ \langle q \rangle_S = \sum_{q=1}^{3} q P_{q|S} \quad (18) \]

where \( P_{q|B} \), or \( P_{q|S} \) respectively, is the probability that the given molecule forms \( q \) bonds, given that its NN sites host no solute molecules (bulk water) or at least one solute molecule (hydration shell). Working in the infinite dilution limit, the probability of configurations with more than one NN solute is actually a small corrections over the probability of having just one solute molecule. Making use of the Bayes theorem, the bulk conditional probability can be rewritten as

\[ P_{q|B} = \frac{P_{q,B}}{P_B} \quad (19) \]

where \( P_{q,B} \) is the probability that the central molecule forms \( q \) bonds, and that its NN sites host no solute molecules, while \( P_B \) is simply the probability that NNs host no solute molecules. Moreover, making use also of the total probability theorem, the shell conditional probability can be rewritten as

\[ P_{q|S} = \frac{P_{q,S}}{P_S} = \frac{P_q - P_{q,B}}{1 - P_B} \quad (20) \]

where \( P_q \) is the total probability that the central molecule forms \( q \) bonds.

We can now evaluate the required probabilities, making use of the factorization [10]. First of all, it is easy to see that

\[ P_q = \binom{3}{q} \frac{p_{12}^q (p_1 - p_{12})^{3-q}}{p_1^3} \quad (21) \]

where

\[ p_1 = \sum_{j=0}^{4} \sum_{k=0}^{4} w_j w_k p_{1jk} \quad (22) \]

\[ p_{12} = \sum_{k=0}^{4} w_k p_{12k} \quad (23) \]

In fact, the central molecule, in the given \( i = 1 \) configuration, can form bonds along its 3 arms. Therefore, \( p_{12}^q \) is the probability that a bond is formed along \( q \) given arms, while \( (p_1 - p_{12})^{3-q} \) is the probability that bond is not formed along the remaining \( 3 - q \) arms. The probability factorizes, because arms lie on different triangles, which are uncorrelated, according to Eq. [10]. The binomial coefficient accounts for different choices of \( q \) bonds along 3 arms, while the denominator is due to the fact that \( P_q \), though not specified by the notation, is a conditional probability, with respect to the presence of a central water molecule in the \( i = 1 \) configuration. The joint probability \( P_{q,B} \) can be evaluated in similar way

\[ P_{q,B} = \binom{3}{q} \frac{\tilde{p}_{12}^q (\tilde{p}_1 - \tilde{p}_{12})^{3-q}}{\tilde{p}_1^3} \quad (24) \]

where we have to assume that no solute molecule is present in the neighborhood, that is

\[ \tilde{p}_1 = \sum_{j=0}^{4} \sum_{k=0}^{4} w_j w_k p_{1jk} \quad (25) \]

\[ \tilde{p}_{12} = \sum_{k=0}^{4} w_k p_{12k} = p_{12} - p_{124} \quad (26) \]

Finally, the probability that no solute molecule is in the neighborhood (bulk condition) can be written as

\[ P_B = \frac{\tilde{p}_1^3}{\tilde{p}_1^3} \quad (27) \]

In the work of Dill and coworkers [12], at low temperatures H bond coordination for shell water \( \langle q \rangle_S \) is greater...
than H bond coordination for bulk water \( \langle q \rangle_B \). This behavior is reversed in the high temperature region, where H bonds are preferably formed by bulk water. In this model, the crossing temperature \( T'_S \) (where \( \langle q \rangle_S = \langle q \rangle_B \)) is approximately equal to \( T_S \) (where \( \Delta s^*_S = 0 \)). As a consequence, average H bond coordination seems to be strictly related to the transfer entropy. Let us analyze what happens in our model. First of all, we observe that the range of values of H bond coordination is generally much lower than the maximum value of 3 H bonds, which can be formed by a single water molecule (see Fig. 4).

This fact may be related to a peculiarity of the lattice model, in which H bonds can be formed just along given directions. Moreover, as far as the temperature behavior is concerned, upon varying the weakening parameter \( c_s \), we can have in principle four different scenarios. As shown in Fig. 4(a), at low values of \( c_s \) (low H bond weakening near a solute molecule), shell coordination \( \langle q \rangle_S \) is greater than bulk coordination \( \langle q \rangle_B \) for all temperatures. Increasing the parameter, it is possible to observe a scenario similar to the one found by Dill and coworkers: a crossing temperature \( T'_S \) between a low temperature region dominated by \( \langle q \rangle_S \) and a high temperature one dominated by \( \langle q \rangle_B \) [Fig 4(b)]. Increasing \( c_s \) further, a more complicated scenario, involving two crossing temperatures, can be observed. The region where \( \langle q \rangle_S \) is greater than \( \langle q \rangle_B \) is upper-bounded by \( T'_S \), as in the previous scenario, and lower-bounded by a different crossing temperature [Fig. 4(c)]. This means that the high temperature behavior is restored at low temperature, though in a region very close to the stability limit for the liquid phase, which would be very difficult to reach in a real system. Finally, for very high values of \( c_s \) (high weakening of H bonds near a solute molecule) a fourth scenario is observed, reversing the behavior of the first scenario, that is, \( \langle q \rangle_B > \langle q \rangle_S \) for all temperatures. All possible behaviors are summarized in Fig. 4 where the crossing temperatures \( T_S \) and \( T'_S \) are displayed as functions of the weakening parameter \( c_s \). As a comparison, in the same figure, we have reported the zero entropy temperature \( T_S \) as a function of the same weakening parameter \( c_s \). It can be easily observed that, while H bond coordination is strongly dependent on the weakening parameter, the transfer entropy turns out to be a much more “robust” effect, and the \( T_S \) temperature has only a relatively slight dependence on the weakening parameter.

V. CONCLUSIONS

In this paper we have considered a two-dimensional waterlike lattice model, defined on the triangular lattice, which we had previously shown to reproduce qualitatively typical thermodynamic anomalies of pure water, and extended the model to the case of an aqueous solution. Water molecules are of the Mercedes Benz type, with three equivalent bonding arms, while solute molecules have no internal degrees of freedom. We have performed our calculations by means of a generalized first order approximation on a triangle cluster, which requires quite a small computational effort, and had been shown to behave quite accurately for the pure water model. In particular, in this paper we have addressed the issue of dilute solutions of inert (apolar) solutes, that is, the hydrophobic effect, and we have investigated thermodynamic equilibrium between liquid and vapor, working out solvation quantities in this case. It turns out that the model qualitatively reproduces the peculiar features that are usually believed to be the fingerprints of hydrophobicity. The solvation free energy is positive, meaning that solvation is unfavorable, while the entropy and enthalpy display an increasing trend and cross zero at two different temperatures. The solvation heat capacity is large and decreases upon increasing temperature. The model results compare qualitatively well with experimental results about solvation of noble gases into water. We have investigated the effect of H bonding, by comparing the previously mentioned results with those obtained by setting to zero the H bond energy parameter. In this case, we have obtained transfer quantities that approach the ones computed with H bonds at high temperatures, but that largely deviates from them upon decreasing temperatures, in the region were H bonding begins to dominate. In particular, we have observed that, while the disaffinity of the solute for the solvent remains, and is signaled by the positive large value of the solvation free energy, such a disaffinity is mainly of enthalpic nature, and both the enthalpy and entropy of solvation remain positive at all observed temperatures, so that the strong temperature dependence, which is typical of the hydrophobic effect, disappears.

In order to a check of the model, we have also investigated solvation of water into water at liquid-vapor equilibrium, for which experimental data are available. We have found qualitative agreement in the values of solvation free energy, entropy and enthalpy, though there is
some discrepancy in the temperature dependence of enthalpy, which indicates a negative solvation heat capacity, in contrast with experiments. Though not reporting details in the paper, we have verified that this fact is neither to be related to the approximation of the ideal/real gas phase, nor with the temperature derivative approximation, mentioned in Sec. III. On the contrary, we have observed that the same kind of discrepancy may be observed in the case of zero H bond energy, that is, for a regular solution. Therefore, we suspect that the discrepancy is to be related to an intrinsic limitation of lattice modelling. The effect is relatively small, so that it is completely invisible, when the dominant effect of H bonding is turned on.

Finally, we have performed a calculation of the average number of H bonds formed by a single water molecule (H bond coordination, in short), in two different cases, namely when the molecule is placed in the first hydration shell of a solute molecule (shell coordination), and when it is not (bulk coordination). According to Dill’s Mercedes Benz model, these two parameters are clearly related to the solvation entropy behavior, namely, negative solvation entropies (low temperature) correspond to higher shell coordination, while positive solvation entropies (high temperature) correspond to higher bulk coordination. Due to the fact that our purpose was to obtain a kind of lattice version of the MB model, describing essentially the same physics underlying the observed phenomenology, we have tried to verify whether the same effect could be observed in our model or not. The answer is essentially no, but some interesting observations can be done. We have performed the investigation, upon varying the solute weakening parameter, which, in our model, is a way of tuning the degree of water ordering induced by the solute. We have observed that such parameter strongly affects the behavior of H bond coordination, and in particular the temperature at which shell and bulk coordinations become equal. On the contrary the temperature of zero entropy $T_S$, which is actually one of the striking features of the hydrophobic effect, is quite “robust” and relatively independent of variations of the weakening parameter. Two questions arise from the discussed behavior. On the one hand, we may suspect that the lattice model is definitely too simple to capture the microscopic physics of the hydrophobic effect in a correct way, or that the approximation level is insufficient. But the robustness of the zero entropy temperature may also suggest that the simple relationship between the balance of bulk and shell H bonds and the zero of transfer entropy, proposed by Dill and coworkers, may be model-dependent, and ought to be verified more carefully. We plan to investigate on such issues in future works.

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