

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, bio-polymers 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 [3–7]. 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 [8–10], 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 co-workers [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. [9] 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 positive transfer 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 quite recently by Dill and co-workers by means of several different methods, such as constant pressure Monte Carlo simulations [19,20], entropy expansion [21], and integral equation theory [22–24]. A coherent picture of the hydrophobic effect phenomenology has been worked out, allowing to obtain a microscopic view of several anomalous properties of water both as a pure substance and as a solvent. The latter studies follow the previ-

ously mentioned idea of simplified models, that nevertheless are based on well defined microscopic interactions, that is, on an energy function, without previous knowledge of water properties. One important reason to do so is the need of modeling water in a computationally convenient way, in order to investigations on complex systems such as biomolecules, for which water plays a key role.

According to the same idea, we have recently investigated [25] 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 modeling 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 [26], but the weakening criterion is different, that is, equivalent to the one employed in quite a recent investigation by Patrykiewicz and co-workers [27,28]. 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. [25] 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 [25].

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. Section V contains some concluding remarks.

TABLE I. Possible site configurations, with corresponding labels (i), multiplicities (w_i), and occupation numbers for water ($n_{w,i}$) and solute ($n_{s,i}$).

Config.	Empty				
i	0	1	2	3	4
w_i	1	1	1	w	1
$n_{w,i}$	0	1	1	1	0
$n_{s,i}$	0	0	0	0	1

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 $c_x \eta/2$ ($c_x \in [0,1]$) 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 $-(1-c_x)\eta$. The resulting water-solute interaction has two components: The nonorientational Van der Waals term $-\epsilon_{ws}$ 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:

$$\mathcal{H} = \frac{1}{2} \sum_{\langle r,r',r'' \rangle} \mathcal{H}_{i_r i_{r'} i_{r''}}, \quad (1)$$

where \mathcal{H}_{ijk} is a contribution which will be referred to as triangle Hamiltonian, and $i_r, i_{r'}, i_{r''}$ label site configurations for the 3 vertices r, r', r'' , respectively. Possible site configurations are (see Table I): “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 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 Table I. The triangle Hamiltonian can be written as

$$\mathcal{H}_{ijk} = H_{ijk} + H_{jki} + H_{kij}, \quad (2)$$

where

$$H_{ijk} = -\epsilon_{xy}n_{x,i}n_{y,j} - \eta h_{ij}(1 - c_x n_{x,k}), \quad (3)$$

$n_{x,i}$ is an occupation variable for the x species, defined as in Table 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 ($-\eta h_{ij}$), 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 ($\eta h_{ij}c_x n_{x,k}/2$) 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

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

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 $\omega = u - \mu_x \rho_x - Ts$ (μ_x and ρ_x 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

$$\omega = \sum_{i=0}^4 \sum_{j=0}^4 \sum_{k=0}^4 w_i w_j w_k p_{ijk} (\tilde{\mathcal{H}}_{ijk} + T \ln p_{ijk}) - 2T \sum_{i=0}^4 w_i p_i \ln p_i, \quad (5)$$

where T is expressed in energy units (whence entropy in natural units). It is noteworthy that the only variational parameter in ω 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. (5) is given by the modified Hamiltonian $\tilde{\mathcal{H}}_{ijk}$, defined as

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

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

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

where ξ is a normalization constant. Such equations can be solved numerically by simple iteration (natural iteration method [29]). 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. (4) and (5) 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 pseudochemical potential μ_x^* , related to the ordinary chemical potential μ_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 Δg_x^* is defined as the difference between pseudochemical 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 pseudochemical 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

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

the solvation enthalpy

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

and the solvation heat capacity

$$\Delta c_{PX}^* = \left. \frac{\partial \Delta h_x^*}{\partial T} \right|_P. \quad (15)$$

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, we have computed numerically both kinds of derivatives, and verified that the difference between the two sets of results cannot even be appreciated at the scale of the graphs reported in the following. This point is in agreement with the experimental observations of Ref. [30]. Let us notice that the difference increases upon approaching the critical point, but this region is generally out of the experimentally interesting range, so we do not report the corresponding results.

Let us start studying solvation of an inert molecule in water. We set water parameters as follows: $\eta/\epsilon_{\text{ww}}=3$, $c_w=0.8$, and $w=20$. As shown in our previous analysis [25], this choice corresponds to a waterlike behavior, with a liquid-vapor critical point at $T/\epsilon_{\text{ww}} \approx 1.18$, and with a temperature of maximum density for the liquid around $T/\epsilon_{\text{ww}} \approx 0.67$ 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 (ϵ_{ss}) and water-solute (ϵ_{ws}) Van der Waals interaction energies. At the moment, we also set the weakening parameter c_s 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. 1(a); the transfer heat capacity in Fig. 1(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 $T/\epsilon_{\text{ww}}=0.65$ (just below the

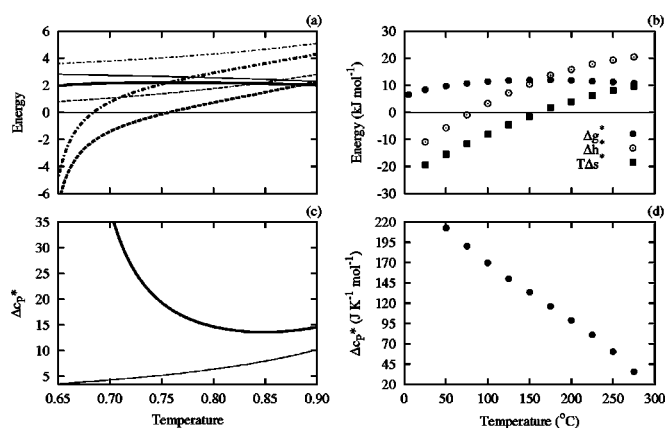


FIG. 1. (a) Solvation energies (E/ϵ_{ww}) vs temperature (T/ϵ_{ww}) for an ideal inert molecule in water at liquid-vapor coexistence: $E = \Delta g_s^*$ (solid line), $E = T \Delta s_s^*$ (dashed line), and $E = \Delta h_s^*$ (dashed-dotted line). (b) Corresponding experimental data for transfer of argon into water [30]. (c) Solvation heat capacity (Δc_p^*) vs temperature (T/ϵ_{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 quantities in nonbonding water ($\eta=0$).

temperature of maximum density for pure liquid water) and $T/\epsilon_{\text{ww}}=0.90$ (about half way between the previous temperature and the critical temperature). Remarkably, it turns out that the model, despite its simplicity, displays the defining features of the hydrophobic effect: the solvation free energy is positive and large, while the solvation entropy is negative at low temperatures and becomes positive upon increasing temperature; the heat capacity is positive and large, and also the decreasing trend with temperature is essentially reproduced. The increasing trend at high temperature is related to the fact that we are approaching the liquid-vapor critical point. Negative solvation entropy at low (room) temperature is a clear indication that solute insertion into the mixture orders the system. The corresponding positive (unfavorable) 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 compensating trend. 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. 1(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 Figs. 1(a) and 1(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. These 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

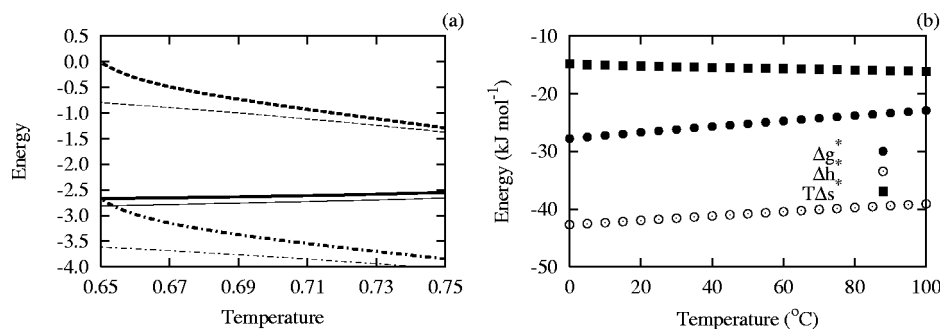


FIG. 2. (a) Solvation energies (E/ϵ_{ww}) vs temperature (T/ϵ_{ww}) for a water molecule into pure liquid water at liquid-vapor coexistence: $E = \Delta g_s^*$ (solid line), $E = T\Delta s_s^*$ (dashed line), and $E = \Delta h_s^*$ (dashed-dotted line). (b) Corresponding experimental data [30]. Thin lines in (a) denote solvation energies for nonbonding water ($\eta=0$).

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. In fact, with $\eta=0$, a water molecule can be viewed as a nonpolar molecule with Van der Waals interaction energy ϵ_{ww} .

Let us now consider also the solvation of water in its own pure liquid. The corresponding transfer energies obtained by the model are displayed in Fig. 2(a), where we have reduced the temperature interval, in order to compare with available experimental results [30], reported in Fig. 2(b). In contrast to the inert molecule case, here 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 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 suggests 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 (ϵ_{ws}, c_s) and with itself (ϵ_{ss}). Now we investigate the role of the c_s parameter, representing the fact that also a solute molecule may have a weakening effect on H bonds in its neighborhood. 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 bonding. On the contrary, a different (lower) weakening parameter for the solute, might represent a different perturbation of H bonds, related for instance to excluded volume. 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 c_s , let us investigate H bond coordination, that is, the average number of hydrogen bonds per molecule. In quite recent papers, Dill and co-workers [19] 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. In particular, they distinguished between H bond coordination for molecules in bulk water and in a hydration shell. We can evaluate analogous parameters also for our model, in the framework of the first order approximation. Each water molecule can form bonds with NN molecules only, therefore it is necessary to compute the joint probability distributions of a given site with its 6 NNs (hexagon probability distribution). According to the Husimi lattice formulation of the first order approximation, it is easy to see that only certain triangle correlations are taken into account, as shown schematically in Fig. 3. Therefore, i_0 being the central site configurations and $i_1 \dots i_6$ the NNs configurations, the hexagon probability distribution reads

$$P_{i_0 i_1 \dots i_6} = \frac{P_{i_0 i_1 i_2} P_{i_0 i_3 i_4} P_{i_0 i_5 i_6}}{P_{i_0}^2}. \quad (16)$$

We shall evaluate bond coordinations according to this factorization, which, let us notice, is perfectly consistent with our approximation scheme [32]. Let us consider a water molecule in a bonding configuration, for example $i=1$. It is not

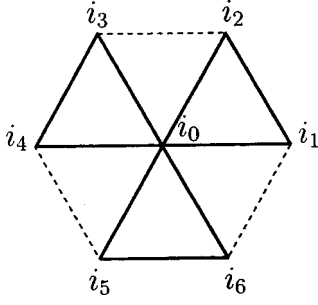


FIG. 3. Site labels for the hexagon probability distribution. Thick lines denote triangles for which correlations are taken into account.

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. 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 correction 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 the NNs host no solute molecules. 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 (16). 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. (16). 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

$$P_{q,B} = \binom{3}{q} \frac{\tilde{p}_{12}^q (\tilde{p}_1 - \tilde{p}_{12})^{3-q}}{p_1^3}, \quad (24)$$

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

$$\tilde{p}_1 = \sum_{j=0}^3 \sum_{k=0}^3 w_j w_k p_{1jk}, \quad (25)$$

$$\tilde{p}_{12} = \sum_{k=0}^3 w_k p_{12k} = p_{12} - p_{124}. \quad (26)$$

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

$$P_B = \frac{\tilde{p}_1^3}{p_1^3}. \quad (27)$$

In the work by Dill and co-workers [19], at low temperatures, H bond coordination for shell water $\langle q \rangle_S$ is greater than H bond coordination for bulk water $\langle q \rangle_B$. Such a behavior is reversed at high temperatures, where H bonds are preferably formed by bulk water, and a ‘‘crossing temperature’’ T_q is observed, at which $\langle q \rangle_S = \langle q \rangle_B$. Such temperature turns out to be approximately equal to the zero entropy temperature T_S^* (at which $\Delta s_S^* = 0$), so that quite a general relationship between H bond coordination and transfer entropy is conjectured. Let us analyze what happens in our model. First of all, let us 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). Maybe this fact is a peculiarity of the lattice model, in which H bonds can be formed just along given directions. As far as temperature dependence is concerned, we can have in principle four different behaviors, upon varying the weakening parameter c_s . At low c_s values, we have $\langle q \rangle_S > \langle q \rangle_B$ at all temperatures [Fig. 4(a)]. Upon increasing c_s , the difference between bulk and shell coordination is progressively reduced and, for sufficiently large c_s values, we can observe

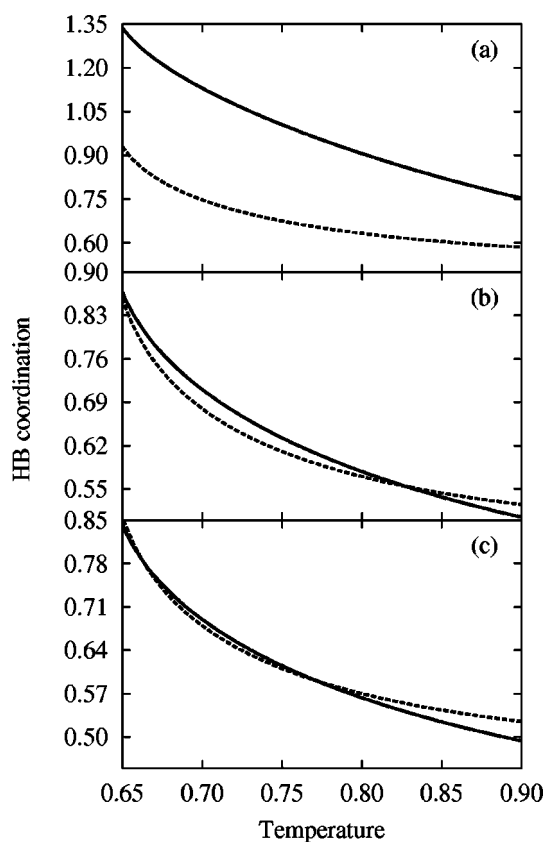


FIG. 4. H bond coordination for a shell water molecule (solid line) and a bulk water molecule (dashed line) vs temperature. (a) $c_s=0$, (b) $c_s=0.37$, and (c) $c_s=0.405$.

a crossing temperature T_q , such that $\langle q \rangle_S > \langle q \rangle_B$ for $T < T_q$ and $\langle q \rangle_S < \langle q \rangle_B$ for $T > T_q$ [Fig 4(b)]. This behavior is similar to the one found by Dill and co-workers. Increasing c_s further, we can also observe a more complicated behavior, in which a second crossing temperature $T'_q < T_q$ appears, such that the condition $\langle q \rangle_S < \langle q \rangle_B$, previously observed at high temperature, is restored for $T < T'_q$ [Fig. 4(c)]. Nevertheless, the latter region is 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 c_s values, a fourth different behavior is observed, in which $\langle q \rangle_S < \langle q \rangle_B$ at all temperatures. All possible scenarios are summarized in Fig. 5, where the crossing temperatures T_q, T'_q are displayed as a function of the weakening parameter c_s . As a comparison, in the same figure, we have also reported the zero entropy temperature T_S . It can be easily observed that, while H bond coordination is strongly dependent on c_s , 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, which we had previously shown to reproduce thermodynamic anomalies of pure water, and ex-

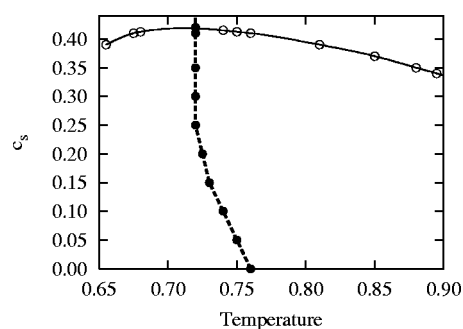


FIG. 5. Weakening parameter c_s vs crossing temperature T_q , at which $\langle q \rangle_S = \langle q \rangle_B$ (empty circles, solid line) and vs zero entropy temperature T_S , at which $\Delta s_s^* = 0$ (filled circles, dashed line).

tended the model to describe aqueous solutions. 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 small computational effort, and had been shown to be quite accurate for the pure water model. 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 peculiar features that are believed to be the fingerprints of hydrophobicity. The solvation free energy is positive (unfavorable solvation), while entropy and enthalpy are negative at low temperatures and positive at high 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. 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 temperature, that is, in the region where H bonds begin to dominate. In particular, we have observed that, while disaffinity between solute and solvent remains (the solvation free energy is still positive), such disaffinity is mainly of enthalpic nature. Both the enthalpy and entropy of solvation remain positive at all temperatures, so that also the typical strong temperature dependence, observed on hydrophobic solvation, disappears.

In order to check 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 disagreement 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 or 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

can be observed in the case of zero H bond energy, that is, for an ordinary (Ising) lattice gas. Therefore, we suggest 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 computed the average number of H bonds formed by a single water molecule (H bond coordination), both 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 seem to be closely related to the solvation entropy. In particular, negative solvation entropies (low temperatures) correspond to higher shell coordination, while positive solvation entropies correspond to higher bulk coordination. We have tried to verify whether the same effect could be observed in our model. The answer is basically 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 "crossing temperature" T_q , at which shell and bulk coordinations become equal. On the contrary, the zero entropy temperature T_S , which is actually one of the striking features of the hydrophobic effect, is quite "robust" and relatively independent of the weakening parameter. Two questions arise from the observed behavior. On the one hand, we might suspect either that the lattice model is definitely too simple to capture the microscopic physics of the hydrophobic effect, or that the approximation level is insufficient. On the other hand, the "robustness" of the zero entropy effect might 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 co-workers, could be model-dependent, and ought to be verified more carefully. We plan to investigate such issues in future works.

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