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# Dependence of the number of hydrogen bonds per water molecule on its distance to a hydrophobic surface and a thereupon-based model for hydrophobic attraction

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A water molecule in the vicinity of a hydrophobic surface forms fewer hydrogen bonds than a bulk molecule because the surface restricts the space available for other water molecules necessary for its hydrogen-bonding. In this vicinity, the number of hydrogen bonds per water molecule depends on its distance to the surface. Considering the number of hydrogen bonds per bulk water molecule (available experimentally) as the only reference quantity, we propose an improved probabilistic approach to water hydrogen-bonding that allows one to obtain an analytic expression for this dependence. (The original version of this approach [Y. S. Djikaev and E. Ruckenstein, *J. Chem. Phys.* **130**, 124713 (2009)] provides the number of hydrogen bonds per water molecule in the vicinity of a hydrophobic surface as an average over all possible locations and orientations of the molecule.) This function (the number of hydrogen bonds per water molecule versus its distance to a hydrophobic surface) can be used to develop analytic models for the effect of hydrogen-bonding on the hydration of hydrophobic particles and their solvent-mediated interaction. Presenting a model for the latter, we also examine the temperature effect on the solvent-mediated interaction of two parallel hydrophobic plates. © 2010 American Institute of Physics. [doi:10.1063/1.3499318]

## I. INTRODUCTION

Hydrogen bonds play a crucial role in many physical, chemical, and biological phenomena of utmost scientific interest.<sup>1–3</sup> As an example, one can mention the formation, stability, and denaturation of the native structure of a biologically active protein (“protein folding” and “protein unfolding”).<sup>4–8</sup> They are also responsible for a driving force in solvent-mediated interactions between hydrophobic bodies (conventionally referred to as hydrophobic interactions). These interactions are often invoked in the biochemical literature to explain a variety of molecular processes at a fundamental level,<sup>9,10</sup> such as the conformational changes of biopolymers, in general, and protein folding/unfolding, in particular,<sup>4–8</sup> self-assembly of amphiphiles into micelles and membranes,<sup>11</sup> gating of ion channels,<sup>12</sup> etc. A major motivation for studying these interactions is to understand such processes in biosystems that cannot be explained by conventional interactions between molecules or between groups within a molecule. Hydrophobic interactions are also important in many technological and industrially significant processes (such as wetting, froth flotation, adhesion, etc.<sup>13</sup>). Understanding these interactions remains limited and the development of predictive models that are capable of estimating their temperature and pressure dependence is important.

Various mechanisms have been suggested in order to understand the nature of hydrophobic effects at a fundamental level and to explain the short-ranged attraction (less than a

few molecular diameters) of hydrophobic species.<sup>14–17</sup> It was hypothesized that hydrophobic interactions may be due to a gain in entropy due to the release of solvent molecules structured at the hydrophobic interface, disruption of the hydrogen bond network of the solvent, combinations of these, etc.<sup>14,15</sup>

Hereafter, we continue developing our probabilistic approach to the effect of water-water hydrogen bond networks around hydrophobic particles, immersed in water, on their hydration and interaction.<sup>18</sup> In that probabilistic hydrogen bond (PHB) approach, a water molecule is considered to have four hydrogen-bonding arms. The configuration of these arms is completely symmetric (tetrahedral) and rigid. Such a model for a water molecule and its hydrogen-bonding ability is similar to the Mercedes-Benz model whereof both two-dimensional<sup>19</sup> and three-dimensional<sup>20</sup> versions were extensively studied.<sup>21–24</sup> In 18(a) the PHB approach was applied to the interaction of spherical hydrophobic particles without considering temperature effects at all. The temperature effect on the solvent-mediated interaction of hydrophobic particles in the framework of the PHB approach was studied in 18(b) for the case of two identical parallel plates.

Because of the proximity to the particle surface, a water molecule in the surface hydration layer (SHL) forms a smaller number of hydrogen bonds (referred to as “boundary hydrogen bonds” in what follows) than a bulk water molecule.<sup>22,25</sup> This number depends on the molecule location and orientation.

In the original PHB model,<sup>18</sup> the vicinity of a hydrophobic surface was subdivided into two hydration shells: the first of finite thickness  $\frac{1}{2}\eta$  (with  $\eta$  being the length of a hydrogen bond) and the second of thickness  $\eta$ . Any hydrogen bond

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involving at least one water molecule from the first hydration shell was allowed to have an altered energy (enhanced compared to bulk bonds). The number of hydrogen bonds per water molecule within the first hydration shell was treated as a constant (independent of the molecule location and orientation) calculated by averaging over all possible locations and orientations of the water molecule. On the other hand, in the second hydration shell this number was the same as in the bulk.

In this paper we propose an improved version of the PHB model in which the somewhat artificial subdivision of the vicinity of a hydrophobic surface is eliminated. Instead, the number of hydrogen bonds per water molecule is considered as a location dependent quantity. At a given distance to the surface, it is determined by assuming equal probabilities for the molecule orientations and averaging with respect to them. This provides the mean number of hydrogen bonds per molecule in the vicinity of a hydrophobic surface as a function of its distance to that surface. In turn, this function allows one to give a quite natural definition of the surface hydration layer. Indeed, it can be defined as a layer that is adjacent to the hydrophobic surface and whereof the thickness equals the minimum distance between water molecule and surface at which the number of hydrogen bonds per molecule is the same as in the bulk. As in the original PHB model, the boundary bonds may be slightly (energetically) altered compared to the bulk ones. Such alteration is still a subject of contention<sup>26</sup> because different authors report opposite effects.<sup>22,27,28</sup>

Note that the PHB model was developed by considering the number of hydrogen bonds per bulk water molecule as a single reference physical quantity and by calculating the constraints that the hydrophobic surface imposes on the probability of a selected water molecule to find other water molecules to form bonds. This constitutes its principal difference from the only previously available model<sup>29</sup> for the number of hydrogen bonds in the vicinity of a hydrophobic surface which was based on two reference physical quantities—the energy of a hydrogen bond and the ratio of two subvolumes of the phase space related to broken and formed hydrogen bonds (both in the vicinity of the surface).

When two hydrophobic particles sufficiently approach each other, the overlap of boundary water-water hydrogen bond networks in their hydration layers can give rise to an additional contribution to their overall interaction potential. The PHB model suggests that this contribution usually represents additional attraction<sup>18</sup> between the particles.

The improved PHB model is also used hereafter to examine the temperature effect on the solvent-mediated interaction between two hydrophobic particles. This hydrophobic interaction is affected by the solvent (water) temperature because the density of the solvent, strength of a hydrogen bond, and number of hydrogen bonds per molecule are sensitive thereto.<sup>30–33</sup> All these characteristics that enter the PHB model<sup>18</sup> depend also on the external pressure<sup>30–32</sup> (where the solvent is subjected), but this effect will not be considered here.

The paper is structured as follows. Section II outlines a model for a single water molecule and its hydrogen-bonding

ability that is used in the probabilistic approach to water hydrogen-bonding. In Sec. III we present a detailed derivation of the mean number of hydrogen bonds per water molecule in the vicinity of a hydrophobic surface as a function of the distance between molecule and surface. The implication of this function for the solvent-mediated contribution to the interaction potential between two parallel hydrophobic plates is detailed in Sec. IV, whereas the temperature dependence of this contribution (to the potential of mean force between the two plates in water) is discussed in Sec. V. Some numerical illustrations of the analytical results are provided in Sec. VI, while Sec. VII discusses the results and summarizes the conclusions.

## II. A WATER MOLECULE AND ITS HYDROGEN-BONDING

To make our model analytically amenable, every water molecule (whereof the location is determined by its center) is considered to have four arms each capable of forming a single hydrogen bond. The configuration of four hydrogen-bonding (hb) arms is completely symmetric (tetrahedral, with the angle between any of them equal to  $\alpha = 109.47^\circ$ ) and rigid. Each hb arm can adopt a continuum of orientations subject to the constraint of tetrahedral rigidity. In order for a water molecule to form a hydrogen bond with another molecule, it is necessary (but not sufficient) that the tip of any of its hb arms coincides with the second molecule. The length of a hb arm thus equals the length of a hydrogen bond hereafter denoted by  $\eta$ . (The sufficient condition for a hydrogen bond between two water molecules to form would require that any hb arm of one molecule roughly coincide with any hb arm of the other.)

As mentioned above, the tetrahedral configuration of hb arms of a model water molecule will be assumed to be rigid independent of whether the water molecule is located in the bulk or in the vicinity of the hydrophobic surface, as well as independent of temperature (much like in the Mercedes-Benz model and its applications to hydrophobic effects<sup>21–24</sup>). These assumptions imply that the *intrinsic* hydrogen-bonding ability of each arm, i.e., the electron density distribution in a water molecule, is little sensitive (both energetically and geometrically) to the temperature and to the proximity of the hydrophobic surface.

Despite the rigidity of the hb arm configuration, the network of hydrogen bonds in liquid water is not rigid because with increasing temperature the thermal chaotic motion of water molecules becomes increasingly capable of breaking hydrogen bonds. This effect is implemented in the PHB model via the temperature dependence of the number of bonds per bulk water molecule, experimentally measurable quantity.<sup>1,2,34</sup>

Hydrogen-bonding in bulk water has been extensively studied by various (experimental, simulational, and theoretical) methods.<sup>1,2,30–34</sup> In contrast, there are many obscurities concerning boundary hydrogen-bonding, i.e., water-water hydrogen-bonding in the vicinity of a hydrophobic surface.<sup>14,15,22,25</sup>

First, the energetics of hydrogen bonds in the vicinity of a hydrophobic surface is rather controversial.<sup>26</sup> On one hand,

they are mostly believed to be slightly energetically enhanced<sup>22,27</sup> compared to the bulk bonds. On the other hand, the opposite effect (i.e., the weakening of boundary hydrogen bonds) is also suggested to take place.<sup>28</sup> Hereafter, the energy of a bulk (water-water) hydrogen bond is denoted by  $\epsilon_b < 0$ , whereas the energy of a boundary hydrogen bond (BHB), i.e., a bond involving at least one boundary water molecule, is denoted by  $\epsilon_s < 0$ . The PHB model does not impose any restriction on the latter and is valid independent of whether  $\epsilon_b < \epsilon_s$  or  $\epsilon_b = \epsilon_s$ , or  $\epsilon_b > \epsilon_s$ , although in the numerical calculations and Sec. V only  $\epsilon_s = \epsilon_b$  will be considered.

Next, a water molecule in the vicinity of a hydrophobic surface [hereafter referred to as a “boundary water molecule” (BWM)] forms a smaller number of hydrogen bonds than in bulk water. This is due to the proximity of a BWM to the surface which restricts the configurational space available to other water molecules necessary for the BWM to form hydrogen bonds. The dependence of the number of bonds that a BWM can form on its distance to the hydrophobic surface has been little studied so far. In Sec. III we obtain an analytic expression for this function (i.e., the average number of bonds that a BWM can form versus its distance to a hydrophobic surface).

### III. THE AVERAGE NUMBER OF BOUNDARY HYDROGEN BONDS PER WATER MOLECULE AS A FUNCTION OF ITS DISTANCE TO A HYDROPHOBIC SURFACE

Denote the number of hydrogen bonds per bulk water molecule by  $n_b$  and the *average* number of hydrogen bonds per BWM by  $n_s$  (averaged with respect to all possible orientations of the water molecule). The latter is a function of distance  $x'$  between the water molecule and the hydrophobic surface:  $n_s \equiv n_s(x')$ . If  $x'$  is larger than  $2\eta$ , the number of hydrogen bonds that the molecule can form is not affected by the presence of the surface because the latter does not restrict the configurational space for other water molecules necessary to form bonds with the selected one. Therefore,  $n_s(x') = n_b$  for  $x' \geq 2\eta$ . On the other hand, the function  $n_s(x')$  attains its minimum at the minimal distance between the water molecule and the plate, i.e., at  $x' = \eta$ , because at this distance the configurational space available for the neighboring water molecules (to form a bond with the selected one) is restricted (compared to the bulk water) by the plate the most. The layer of thickness  $\eta$  from  $x' = \eta$  to  $x' = 2\eta$  will be referred to as the SHL.

To find the function  $n_s(x')$ , first consider its bulk analog  $n_b$  and represent it as<sup>18</sup>

$$n_b = b_1 + b_{2(1)} + b_{3(2,1)} + b_{4(3,2,1)}, \quad (1)$$

where  $b_1$  is the probability that one of the hb arms (of a bulk water molecule) can form a hydrogen bond,  $b_{2(1)}$  is the probability that a second hb arm can form a hydrogen bond subject to the condition that one of the hb arms has already formed a bond,  $b_{3(2,1)}$  is the probability that a third hb arm can form a hydrogen bond subject to the condition that two of the hb arms have already formed bonds, and  $b_{4(3,2,1)}$  is the

probability that the fourth hb arm can form a bond subject to the condition that three of the hb arms have already formed bonds.

Note that the probability  $b_1$  can be formally represented as a product  $b_1 = P_{S \rightarrow N} P_{N \rightarrow S}$ , where  $P_{S \rightarrow N}$  is the probability that the tip of any hb arm of molecule  $S$  roughly coincides with molecule  $N$  and  $P_{N \rightarrow S}$  is the probability that the tip of any hb arm of molecule  $N$  roughly coincides with molecule  $S$ . (Similar considerations are valid for  $b_{2(1)}$ ,  $b_{3(2,1)}$ , and  $b_{4(3,2,1)}$  as well.) Neither  $P_{S \rightarrow N}$  nor  $P_{N \rightarrow S}$  can be found in the framework of our simple model, but their product (i.e.,  $b_1$ ) can be determined from readily available experimental and simulational data on  $n_b$ .

Indeed, in the chosen model of a water molecule, the events of formation of bonds by the hb arms (in bulk water) can be considered as independent of each other, so that  $b_{2(1)} = b_1^2$ ,  $b_{3(2,1)} = b_1^3$ ,  $b_{4(3,2,1)} = b_1^4$ . Thus, the probability  $b_1$  can be evaluated as the positive solution of the equation  $n_b = b_1 + b_1^2 + b_1^3 + b_1^4$  satisfying the condition  $0 < b_1 < 1$ . Clearly, the latter representation of  $n_b$  implies that the intrinsic hydrogen-bonding ability of each arm is independent of whether the other arms have been already engaged in hydrogen bonds or not. That is, when the first hb arm of a water molecule forms an actual bond, the electron density distribution in a water molecule determining the ability of the other three hb arms (that are not engaged yet) to form bonds (and their potential orientations) remains unaffected (there is no issue with the availability of water molecules necessary for the selected bulk molecule to form bonds).

For a BWM, let us represent  $n_s$  in a form analogous to Eq. (1),

$$n_s = s_1 + s_{2(1)} + s_{3(2,1)} + s_{4(3,2,1)}. \quad (2)$$

Here  $s_1 \equiv s_1(x')$ ,  $s_{2(1)} \equiv s_{2(1)}(x')$ ,  $s_{3(2,1)} \equiv s_{3(2,1)}(x')$ ,  $s_{4(3,2,1)} \equiv s_{4(3,2,1)}(x')$  are probabilities analogous to  $b_1$ ,  $b_{2(1)}$ ,  $b_{3(2,1)}$ ,  $b_{4(3,2,1)}$  subject to the constraint that some orientations of the hb arms cannot lead to the formation of hydrogen bonds because of the proximity to the hydrophobic particle. The severity of this constraint depends on the distance of the BWM to the particle, hence the  $x'$ -dependence of  $s_1$ ,  $s_{2(1)}$ ,  $s_{3(2,1)}$ ,  $s_{4(3,2,1)}$ . Again, as a first approximation the intrinsic hydrogen-bonding ability of a BWM (i.e., the tetrahedral configuration of its hb arms and their lengths and energies) can be considered to be unaffected by its proximity to the hydrophobic particle so that the latter only restricts the configurational space available to other water molecules necessary for this BWM to form hydrogen bonds. Thus, one can relate  $s_1$ ,  $s_{2(1)}$ ,  $s_{3(2,1)}$ , and  $s_{4(3,2,1)}$  to  $b_1$ ,  $b_{2(1)}$ ,  $b_{3(2,1)}$  and  $b_{4(3,2,1)}$ , respectively, as

$$s_1 = k_1 b_1, \quad s_{2(1)} = k_2 b_{2(1)}, \quad (3)$$

$$s_{3(2,1)} = k_3 b_{3(2,1)}, \quad s_{4(3,2,1)} = k_4 b_{4(3,2,1)},$$

where the coefficient-functions  $k_1 \equiv k_1(x')$ ,  $k_2 \equiv k_2(x')$ ,  $k_3 \equiv k_3(x')$ , and  $k_4 \equiv k_4(x')$  are evaluated by using geometric considerations with their dependence on the BWM orientations averaged.



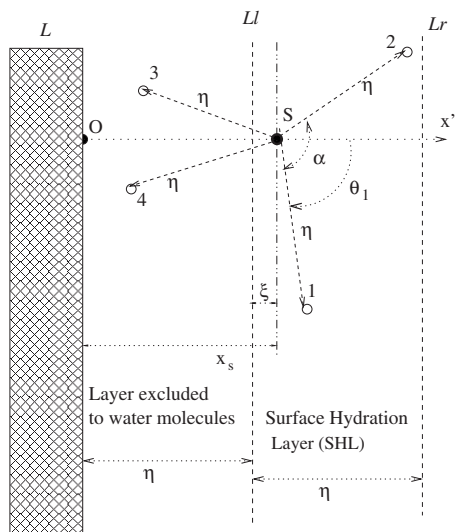


FIG. 1. A water molecule in the SHL of the plate  $L$ . The left boundary of the SHL is marked as plane  $Ll$  at the distance  $\eta$  from the plate  $L$ , while the right boundary as plane  $Lr$  at the distance  $2\eta$  from the plate. The molecule (disk  $S$ ) is at the distance  $x'$  from the plate. Two hb arms of the molecule (arms 1 and 2) are in the figure plane, while arms 3 and 4 are under and above the figure plane. The angle between any two hb arms is  $\alpha$ . The origin  $O$  of the Cartesian coordinate system (with the  $x'$ -axis normal to the plate) lies on the plate surface. The angle between hb arm and axis  $x'$  is denoted by  $\Theta$ .

The coefficient  $k_1$  is calculated by taking into account that a BWM can form a hydrogen bond “almost” like a bulk molecule except for the constraint that the tip of the hb arm (arm 1) must not be too close to the plate surface. Select an arbitrary water molecule at a distance  $\eta \leq x' \leq 2\eta$  from plate  $L$  and denote it  $S$  (Fig. 1). Any of its hb arms can form a hydrogen bond if the tip of the arm is located anywhere on a sphere of radius  $\eta$  (centered at  $S$ ) from which a spherical cap is cut out by the plane  $Ll$ , left boundary of the SHL of plate  $L$ . Denoting the corresponding solid angle by  $\Omega_s(x')$ , one can write

$$\Omega_s(x') = 2\pi \int_0^{\Theta_{1M}(x')} d\Theta_1 \sin(\Theta_1), \quad (4)$$

where  $\Theta_1$  is the angle between hb arm 1 and axis  $x'$  (Fig. 1) and  $\Theta_{1M}(x') \equiv \pi - \arccos(x'/\eta - 1)$  is the maximum value of the angle  $\Theta_1$  at which hb arm 1 can still form a bond. The probability  $s_1(x')$  that any one of hb arms of molecule  $S$  can form a hydrogen bond is related to  $b_1$  via

$$s_1(x') = \frac{\Omega_s(x')}{\Omega_b} b_1, \quad (5)$$

where  $\Omega_b = 4\pi$ . Integrating the right hand side of Eq. (4), substituting the result into Eq. (5), and taking into account Eq. (3), one obtains the coefficient  $k_1(x')$  to be a linear function of  $x'$ ,

$$k_1(x') = \frac{1}{2} \frac{x'}{\eta}. \quad (6)$$

The explicit expressions for the coefficient-functions  $k_2(x')$ ,  $k_3(x')$ , and  $k_4(x')$  are more complicated than that for  $k_1(x')$ . They are provided (along with the complete details of their derivation) in Appendix. The functions  $k_1(x')$ ,  $k_2(x')$ ,  $k_3(x')$ ,

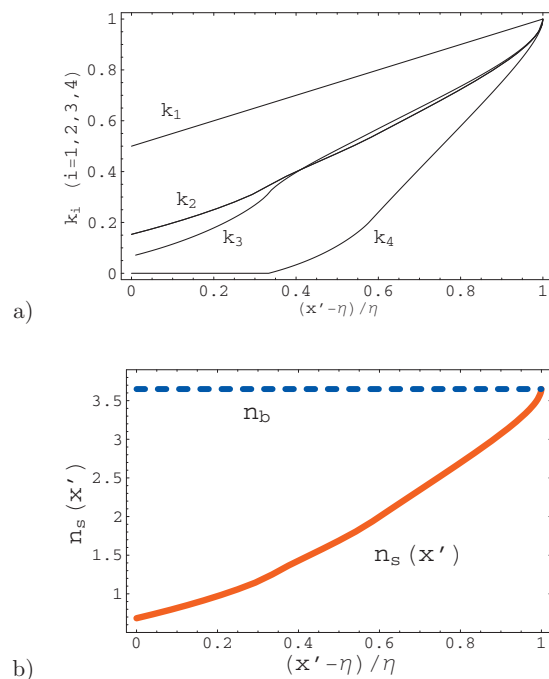


FIG. 2. (a) The functions  $k_1(x')$ ,  $k_2(x')$ ,  $k_3(x')$ , and  $k_4(x')$  for calculating the average number  $n_s$  of hydrogen bonds per water molecule as a function of its distance  $x'$  to the hydrophobic surface (curves from top to bottom, respectively). (b) The function  $n_s(x')$  itself (at  $T=293.15$  K with  $n_b=3.65$ ).

and  $k_4(x')$  are presented in Fig. 2(a). One can note the non-linearity of the dependence of  $k_2$ ,  $k_3$ , and  $k_4$  on  $x'$ .

Knowing  $k_1(x')$ ,  $k_2(x')$ ,  $k_3(x')$ ,  $k_4(x')$  as well as  $b_1$ , one can calculate  $n_s(x')$  [see Fig. 2(b)]. [Note that since  $b_1$  is uniquely determined by  $n_b$ , it is clear that  $n_s(x')$  is a single-valued function of  $n_b$ .] Knowing the function  $n_s(x')$ , one can examine the effect of water hydrogen-bonding on the hydration of hydrophobic (and even composite) particles as well as on their solvent-mediated interaction. Leaving the former phenomenon for future investigations, we will consider the latter as an example of the application of the above PHB model.

#### IV. HYDROGEN BOND CONTRIBUTION TO THE INTERACTION OF HYDROPHOBIC PLATES

Let us derive an expression for  $\Phi(x)$ , the water hydrogen bond contribution to the solvent-mediated interaction potential between two parallel hydrophobic plates  $L$  (left) and  $R$  (right) as a function of the interplate distance  $x$ . This can be neglected until the SHLs of plates  $L$  and  $R$  overlap. (This requires an approximate equality of the energy of a bond between a boundary molecule and a bulk one with the energy of a bond between two bulk molecules.) The overlap of the surface hydration layers of the plates leads to the restructuring of their boundary hydrogen bond networks and to a decrease in the number of boundary water molecules.

Choosing a Cartesian coordinate system so that the  $x'$ -axis is normal to the plates with the plate  $L$  at  $x'=0$ , the coordinate  $x'=x$  of the plate  $R$  represents the interplate distance. The largest distance between the plates at which the outermost molecules of their SHLs can interact (by forming hydrogen bonds) is equal to  $\tilde{x} \equiv 5\eta$ . At large separations be-

tween the plates ( $x > \tilde{x}$ ) their BHB networks remain intact and do not contribute to the interaction potential between the plates. Let us denote the total number of molecules in the SHLs of both plates L and R by  $N_0 = 2A \int_{\eta}^{2\eta} dx' \rho(x')$ , where  $\rho(x')$  is the number density of water molecules at a distance  $x'$  from plate L. The total energy of all hydrogen bonds in which these molecules are involved at  $x > \tilde{x}$  can be determined from

$$\Phi_{\infty}^{\text{hl}} = 2A\epsilon_s \int_{\eta}^{2\eta} dx' \left[ 1 - \frac{1}{2}\chi_s(x') \right] n_s(x') \rho(x'), \quad (7)$$

where the factor of 2 appears because there are two identical plates,  $\chi_s(x') = \eta/x'$  is the probability that a hydrogen bond, formed by a selected BWM (at a distance  $x'$  from the plate), is a bond within the corresponding SHL (see Ref. 35 for its derivation), and the factor  $1 - \frac{1}{2}\chi_s(x')$  ensures the correct counting of bonds within the SHL (requiring a factor of  $\frac{1}{2}$  to avoid the double-counting of bonds upon integration) and between a BWM and a bulk molecule (which do not require a factor of  $\frac{1}{2}$  upon integration). Indeed, the number of bonds that a BWM (at a distance  $x'$  from the plate L) forms with other BWMs is  $\chi_s(x')n_s(x')$ . Thus, in calculating the total number of boundary hydrogen bonds by integration within the whole SHL, every molecule should be assigned  $\frac{1}{2}\chi_s(x')n_s(x')$  intra-SHL bonds; upon integration, each of these bonds is counted twice, hence the necessity of the factor of  $\frac{1}{2}$ . On the other hand, a BWM forms  $(1 - \chi_s(x'))n_s(x')$  bonds with molecules *outside* the SHL. These “outside-SHL” bonds are *not* counted twice in calculating the total number of boundary hydrogen bonds by integration within the whole SHL, hence the factor of  $\frac{1}{2}$  is not required. Therefore, in calculating the total number of boundary hydrogen bonds via integration, the total number of boundary bonds (including both intra-SHL and outside-SHL bonds), that should be assigned every BWM, is equal to the sum  $\frac{1}{2}\chi_s(x')n_s(x') + [1 - \chi_s(x')]n_s(x')$  which reduces to the factor  $[1 - \frac{1}{2}\chi_s(x')]n_s(x')$  entering the integrand on the right hand side of Eq. (7).

When the plates are sufficiently but not too close to each other so that  $4\eta \leq x < \tilde{x}$ , their SHLs do not overlap yet. Still, at these distances the plates already “feel” each other because, as the distance between the plates becomes smaller than  $5\eta$ , some of the bonds between BWMs and non-BWMs are replaced by hydrogen bonds between molecules belonging to the SHLs of different plates. Upon every such a replacement two bonds of energy  $\epsilon_s$  (one between a BWM of plate L and a molecule outside its SHL and the other between a BWM of plate R and a molecule outside its SHL) are replaced by one bond (of the same energy  $\epsilon_s$ ) between a BWM of plate L and a BWM of plate R. The freed hydrogen bond is transferred to the bulk with the energy  $\epsilon_b$ . Hereafter, the contribution from this effect (to the total energy of hydrogen bonds of interest) will be denoted by  $\Phi_x^{(45)} \equiv \Phi_x^{(45)}(x)$ . With  $x$  decreasing from  $5\eta$  to  $4\eta$ , it increases from 0 to its maximum value  $\Phi_4^{(45)} \equiv \Phi_4^{(45)}(4\eta)$  and remains constant upon further decrease in  $x$ , so that  $\Phi_x^{(45)} \equiv \Phi_4^{(45)}$  for  $\eta \leq x < 4\eta$ .

With decreasing  $x$  ( $x < 4\eta$ ), the SHLs overlap and the total volume of the two hydration layers decreases which leads to a decrease in the total number of molecules therein. Some of the  $N_0$  molecules are removed from between the plates being transferred into the bulk. Upon this transfer, some of the BHBs must be broken and bulk hydrogen bonds are created instead. The number and energy of the broken bonds differ from the number and energy of the newly formed ones. The total energy  $\Phi_x^{\text{hlb}} \equiv \Phi_x^{\text{hlb}}(x)$  of the hydrogen bonds, in which these  $N_0$  molecules are involved for  $x < 4\eta$ , differs from  $\Phi_{\infty}^{\text{hl}}$ . This gives rise to a hydrogen bond contribution to the potential between plates L and R.

The energy  $\Phi_x^{\text{hlb}}$  can be represented as a sum of three terms,  $\Phi_x^{\text{hlb}} = \Phi_x^{\text{hl}} + \Phi_x^{\text{b}} + \Phi_4^{(45)}$ , where  $\Phi_x^{\text{hl}}$  is the energy of boundary hydrogen bonds of water molecules remaining between the two plates (now at a distance  $x < 4\eta$ ),  $\Phi_x^{\text{b}}$  is the energy of the new bulk hydrogen bonds formed by those water molecules that had been initially (i.e., at  $x \geq \tilde{x}$ ) BWMs but upon the overlapping of the SHLs were squeezed out from there and transferred into the bulk water.

Denoting the half-width of the SHLs overlap region by  $\Delta = (4\eta - x)/2$ , one can obtain the following expressions for these terms:

$$\Phi_x^{\text{hl}} = \frac{1}{2}\epsilon_s A \int_{\eta}^{x-\eta} dx' \hat{n}_s(x') \hat{\rho}(x'), \quad (8)$$

$$\Phi_x^{\text{b}} = \epsilon_b n_b A \int_{2\eta-\Delta}^{2\eta} dx' \rho(x') \quad (x < 4\eta),$$

and

$$\Phi_x^{(45)} = \epsilon_b A \int_{\eta}^{2\eta} dx' n_s(x') \chi_{\text{LR}}(x, x'), \quad (9)$$

where  $\chi_{\text{LR}} \equiv \chi_{\text{LR}}(x, x')$  is the probability that if a BWM of plate L forms a hydrogen bond, it will be a bond with a BWM of plate R (see Ref. 35, for details),

$$\chi_{\text{LR}} \equiv \chi_{\text{LR}}(x, x') = \begin{cases} 0 & (\eta \leq x' < x - 3\eta) \\ (x' - x + 3\eta)/x' & (x - 3\eta < x' \leq 2\eta). \end{cases}$$

The functions  $\hat{n}_s(x')$  and  $\hat{\rho}(x')$  in Eq. (8) are symmetric in the interplate space with respect to the vertical axis  $x' = x/2$  and are defined as

$$\hat{n}_s(x') = \begin{cases} n_s(x') & (x' < x/2) \\ n_s(x - x') & (x' \geq x/2), \end{cases} \quad (10)$$

$$\hat{\rho}(x') = \begin{cases} \rho(x') & (x' < x/2) \\ \rho(x - x') & (x' \geq x/2). \end{cases}$$

Clearly, using  $\hat{n}_s(x')$  and  $\hat{\rho}(x')$  defined by Eq. (10) in the expression for  $\Phi_x^{\text{hl}}$  [given in Eq. (8)] implies that the functions  $n_s(x')$  and  $\rho(x')$  for the SHL of an isolated hydrophobic surface remain unaffected even when the SHLs of two hydrophobic surfaces are so close to each other that they overlap. The inaccuracy  $\delta\Phi$  in  $\Phi_x^{\text{hl}}$  arising due to this approximation  $\tilde{n}_s(x, x') \approx n_s(x')$  in Eq. (10) can be shown to be

negligible compared to  $\Phi_x^{\text{hl}}$  (see Ref. 35, for more details).

The hydrogen bond contribution  $\Phi(x)$  to the solvent-mediated interaction of plates  $L$  and  $R$  as a function of the distance between them is then provided by

$$\Phi(x) = (\Phi_x^{\text{hl}} + \Phi_x^{\text{b}} + \Phi_4^{(45)}) - \Phi_\infty^{\text{hl}} \quad (x \leq 4\eta), \quad (11)$$

with  $\Phi_x^{\text{hl}}$ ,  $\Phi_x^{\text{b}}$ ,  $\Phi_4^{(45)}$ , and  $\Phi_\infty^{\text{hl}}$  determined by Eqs. (8), (9), and (7). The number of hydrogen bonds  $n_b$  per molecule of bulk water is a well-studied quantity and the density profile  $\rho(x')$  in the vicinity of a plate can be obtained by using the density functional theory. The function  $n_s(x')$  is now provided by the PHB model presented above.

As already mentioned, in the original version of the PHB approach,<sup>18</sup> the vicinity of a hydrophobic surface was somewhat arbitrarily subdivided into two hydration shells: the first of thickness  $\eta/2$  and the second of thickness  $\eta$ . The number of hydrogen bonds per water molecule within the first hydration shell was independent of the molecule location and orientation and was obtained via averaging over all possible locations and orientations of the water molecule. On the other hand, in the second hydration shell this number was the same as in the bulk.

Thus, as clear from Eqs. (7)–(11), the modified version of the PHB model (presented in Sec. III) constitutes a significant improvement over its original version<sup>18</sup> because it allows one to more accurately describe the effect of water hydrogen-bonding on the solvent-mediated interaction of hydrophobic particles. First, the improved PHB model implements a more detailed behavior of hydrogen-bonding ability of water molecules in the vicinity of a hydrophobic surface, as represented by the function  $n_s(x')$ . Second, the somewhat artificial subdivision of the vicinity of a hydrophobic surface into the first and second hydration shells (adopted in the original PHB model<sup>18</sup>) is also eliminated in the improved PHB model. The function  $n_s(x')$  provides a quite natural definition of the surface hydration layer as a layer that is adjacent to the hydrophobic surface and whereof the thickness equals the minimum distance between water molecule and surface at which the number of hydrogen bonds per molecule is the same as in the bulk.

## V. TEMPERATURE DEPENDENCE OF THE SOLVENT-MEDIATED CONTRIBUTION TO THE POTENTIAL OF MEAN FORCE

As clear from the above consideration, the function  $\Phi(x)$  represents a hydrogen bond (i.e., a solvent-mediated) contribution to the potential associated with (that is, whereof the negative gradient gives) the mean force<sup>36</sup> acting on any of the two hydrophobic plates  $L$  and  $R$ . Because of the statistical averaging involved in  $\Phi(x)$  (see Ref. 18 and the above equations), this potential has the nature of a free energy. Hence one can formally separate  $\Phi(x)$  into energetic and entropic components.

Indeed, consider, e.g., a thermodynamic system with constant number of molecules  $N$  under conditions of constant volume  $V$  and temperature  $T$  (i.e., a canonical ensemble). The characteristic thermodynamic potential of this (canonical) ensemble is the Helmholtz free energy  $F = E - TS$ , where

$E$  is the internal energy and  $S$  is the entropy of the system. Thus, in the canonical ensemble one can find the entropic  $F_S$  and energetic  $F_E$  contributions to  $F$  as

$$F_S \equiv -TS = -T(\partial F / \partial T)_{V,N}, \quad (12)$$

$$F_E \equiv E = (\partial(F/T) / \partial(1/T))_{V,N},$$

respectively, where the subscripts of the partial derivatives indicate the thermodynamic variables held constant upon taking the derivatives.

Thus, in order to find the energetic and entropic contributions to  $\Phi(x)$ , it is necessary to know its temperature dependence that will be hereafter indicated by introducing the second argument  $T$ , so that  $\Phi \equiv \Phi(x, T)$ . In our model, the  $T$ -dependence of the potential of mean force  $\Phi$  is due to the temperature dependence of five quantities:  $n_s$ ,  $n_b$ ,  $\epsilon_s$ ,  $\epsilon_b$ , and  $\rho_w$ . The functions  $\rho_w \equiv \rho_w(T)$ ,  $\epsilon_b \equiv \epsilon_b(T)$ , and  $n_b \equiv n_b(T)$  are either readily available or can be constructed on the basis of available data. On the other hand,  $n_s$  is unambiguously related to  $n_b$  hence its dependence on  $T$  can be considered to be known as well. Finally, it is reasonable to assume that, whether in the bulk or in the surface hydration layer, the energy of a hydrogen bond depends on temperature in such a way that the ratio  $\epsilon_s(T) / \epsilon_b(T)$  is independent of  $T$ . One can then consider the potential of mean force  $\Phi$  to be a known function of not only  $x$  but also  $T$ ,  $\Phi = \Phi(x, T)$ .

Knowing the solvent-mediated part  $\Phi$  of the potential of mean force as a function of  $x$  and  $T$ , one can also determine the energetic and entropic contributions to  $\Phi(x, T)$  from

$$\Phi_E \equiv \Phi_E(x, T) = \left( \frac{\partial \Phi / T}{\partial 1/T} \right)_{V,N} \quad (13)$$

and

$$\Phi_S \equiv \Phi_S(x, T) = -T \left( \frac{\partial \Phi}{\partial T} \right)_{V,N}, \quad (14)$$

respectively, such that  $\Phi = \Phi_E + \Phi_S$ .

Hydrophobic interactions are unambiguously determined by the properties of hydrophobic hydration. The hydration of hydrophobic solutes in water near room temperature is a process dominated by the entropy.<sup>37–40</sup> The energetic contribution to the free energy of hydration is favorable but smaller in magnitude than the unfavorable entropic contribution. Such a hydration behavior underlies the conventional understanding of pairwise hydrophobic interactions according to which the energetic component of the solvent-mediated contribution to the potential of mean force is unfavorable (i.e., leading to an increase in the free energy of the system) to the association of solutes, whereas the entropic component is favorable (i.e., leading to a decrease in the free energy of the system). Indeed, the entropy decrease upon solvating two well-separated solutes should be greater than that upon solvating a pair of associated solutes because in the latter case the total hydrophobic surface area is reduced substantially compared to the former. Similar arguments suggest that the energy of association should be positive. This leads to a net attraction between hydrophobic solutes.<sup>14,15,41–44</sup>



## VI. NUMERICAL EVALUATIONS

For numerical evaluations, we considered two identical, completely hydrophobic plates with  $A=100\eta^2$  immersed in water. Note that the surface area of a plate plays rather a trivial role in our calculations because all the potentials and their derivatives are proportional to  $A$ . The numerical results (for the potential of mean force and its components) for another pair of plates of different surface areas  $A'$  will differ from those presented below just by a factor  $A'/A$ . For the sake of simplicity, the enhancement ratio  $\epsilon_{sb}=\epsilon_s/\epsilon_b$  (independent of  $T$ ) of hydrogen bonds (in the SHL compared to the bulk) is taken to be 1.

Currently, there is some uncertainty concerning the “correct” profile of the fluid density at the interface between a hydrophobic particle and bulk water.<sup>14,15,45–48</sup> In our calculations we assumed a gradual increase of the water density from that of the vapor at the closest distance to a plate (as suggested in Ref. 45) to that of the bulk liquid,  $\rho_w \equiv \rho_w(T)$  (several molecular diameters away from the plate).<sup>45,49</sup> Thus, the number density of water molecules was assumed to vary from its “vapor” value of  $2 \times 10^{-5} \rho_w$  at  $x'=\eta$  to its bulk “liquid” value  $\rho_w$  at  $x'=3\eta$ . The function  $\rho(x')$  was thus approximated by  $\rho(x')=\rho_w\{0.499+0.349 \arctan[7(x'-2)]\}$ . [Note that this is a purely qualitative approximation for illustrative purposes only and is not meant to represent water fluid at a hydrophobic surface in any particular system. A quantitative profile can be obtained by using, e.g., the density functional theory methods if the water-water pairwise and water-substrate (either pairwise or field type) interactions are known.<sup>50–52</sup>]

The temperature dependence of the bulk water density  $\rho_w$  was approximated by the Thiesen–Scheel–Diesselhorst equation,<sup>53</sup>

$$\rho_w \equiv \rho_w(T) = \left[ 1 - \frac{T + 15.79}{508\,929.2(T - 205.02)} (T - 277.14)^2 \right] \rho_0,$$

where  $\rho_0=1 \text{ g/cm}^3$ . The dependence of  $\epsilon_b$  on  $T$  was approximated by the linear function,

$$\epsilon_b \equiv \epsilon_b(T) = a_\epsilon - b_\epsilon(T - 273.15),$$

with the constants  $a_\epsilon=3.82 \times 10^{-13} \text{ erg}$  and  $b_\epsilon=4.98 \times 10^{-16} \text{ erg/K}$  determined from the data provided in Refs. 26 and 31, respectively (the ratio  $\epsilon_{sb}$  was assumed to be temperature-independent). Likewise, the number of hydrogen bonds per bulk water molecule was approximated using a linear least-mean squares fit of the data provided in Refs. 1, 2, and 34 ( $n_b=3.69$  at  $0^\circ\text{C}$ ,  $n_b=3.59$  at  $25^\circ\text{C}$ , and  $n_b=3.24$  at  $100^\circ\text{C}$ ), resulting in

$$n_b \equiv n_b(T) = a_n - b_n(T - 273.15),$$

with  $a_n=3.695\,77$  and  $b_n=0.004\,538\,5 \text{ K}^{-1}$ . Finally, the temperature dependence of  $n_s$  is uniquely determined by the function  $n_b(T)$  because

$$n_s = k_1 b_1 + k_2 b_1^2 + k_3 b_1^3 + k_4 b_1^4,$$

where the coefficients  $k_1, k_2, k_3$ , and  $k_4$  are functions of  $x'$  (determined in Sec. III and Appendix) and  $b_1$  is unambiguously determined by the thermodynamic state of the bulk

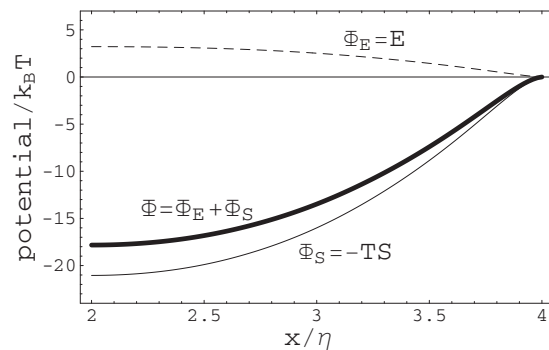


FIG. 3. The energetic and entropic contributions to the potential of mean force between two identical parallel plates as functions of interplate distance at constant temperature  $T=293.15 \text{ K}$ . The thick solid curve presents the potential of mean force  $\Phi$  itself, whereas the dashed and thin solid curves represent its energetic and entropic components,  $\Phi_E$  and  $\Phi_S$ , respectively.

water (temperature, pressure, etc.) as mentioned in Sec. III (see also Ref. 18). The temperature dependence of the potential of mean force  $\Phi$  is then obtained by substituting the functions  $\rho_w(T)$ ,  $\epsilon_b(T)$ ,  $n_b(T)$ , and  $n_s(T)$  into Eqs. (1)–(8).

In Fig. 2(a) the coefficients  $k_1, k_2, k_3$ , and  $k_4$  are plotted as functions of  $x'/\eta$ , the distance between a water molecule and the hydrophobic surface (in units of  $\eta$ ). The resulting function  $n_s=n_s(x')$ , provided by Eqs. (2) and (3), is presented in Fig. 2(b) for  $T=293.15 \text{ K}$ . As expected, the average number of hydrogen bonds per water molecule monotonically increases from its minimal value at  $x'=\eta$  (the closest possible distance to the plate) to its maximum bulk value  $n_b=3.65$  at  $x'=2\eta$ .

It is worth emphasizing that, in the PHB model, the number of hydrogen bonds per bulk water molecule,  $n_b$ , is a single physical quantity that serves as a reference. Consequently, the model predictions for the function  $n_s=n_s(x')$  and its temperature and pressure dependence are uniquely related to  $n_b$  and its temperature and pressure dependence via a unique relationship between  $n_b$  and  $b_1$ . This is a principal difference between the PHB model and the only previously available model<sup>29</sup> for the number of hydrogen bonds in the vicinity of a hydrophobic surface which was based on two physical quantities (both in the vicinity of the surface)—the energy of a hydrogen bond and the ratio of two subvolumes of the phase space related to broken and formed hydrogen bonds. The problem is that there is apparently no definitive way to distinguish between a completely intact hydrogen bond in liquid water from a completely broken one (see Ref. 32 and references therein). Moreover, these quantities and their temperature and pressure dependence are even harder for experimental and theoretical determination in the vicinity of a hydrophobic surface.

Figure 3 presents  $\Phi_E$  and  $\Phi_S$ , the energetic and entropic components of the solvent-mediated part of the potential of mean force as functions of  $x$  at  $T=293.15 \text{ K}$ . The thin solid curve represents  $\Phi_S$ , while the dashed curve is for  $\Phi_E$ . For completeness, the function  $\Phi(x)$  is also shown as a thick solid curve. All the potentials are in units of  $k_B T$  (with  $k_B$  the Boltzmann constant) and the interplate distance is in units of  $\eta$ . As clear, the entropic component of  $\Phi$  is largely negative and hence it favors the association of the two plates, while



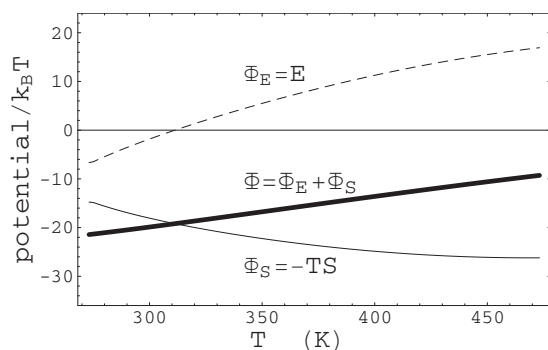


FIG. 4. The energetic and entropic contributions to the potential of mean force between two identical parallel plates as functions of temperature at a given interplate distance  $x=2\eta$ . The thick solid curve presents the potential of mean force  $\Phi$  itself, whereas the dashed and thin solid curves represent its energetic and entropic components,  $\Phi_E$  and  $\Phi_S$ , respectively.

the energetic contribution to  $\Phi$  is positive, hence it tends to prevent them from associating. The favorable entropic component of the free energy of particle association dominates the unfavorable energetic component thus leading to a net (solvent-mediated) attraction between the two hydrophobic plates. This result is consistent with the traditionally accepted mechanism underlying the effect of hydrophobic attraction.<sup>37–44</sup>

The temperature effect on the strength of solvent-mediated part of hydrophobic attraction is demonstrated by Fig. 4 that presents  $\Phi_E$  and  $\Phi_S$ , energetic and entropic components of the solvent-mediated part of the potential of mean force as functions of  $T$  at  $x=2\eta$ . The thin solid curve represents  $\Phi_S$  while the dashed curve is for  $\Phi_E$ , and the function  $\Phi(x)$  is presented as a thick solid curve. All the potentials are in units of  $k_B T$ . The range of temperatures shown in this figure extend from 0 to about 200 °C. Considering hydrogen bond networks in water at temperatures above 100 °C implies that it is under high pressure to avoid boiling and keep it in a liquid state. Note that such a wide range of temperature scale is shown not only for illustrative purposes but because even at temperatures close to 500 °C significant amounts of hydrogen bonds are evidenced by both simulations and experiments.<sup>30</sup>

As clear, the PHB model suggests that the solvent-mediated contribution to the hydrophobic attraction of two macroscopic particles should weaken with increasing temperature. Currently there are conflicting results (reported by different authors using different theoretical models or experiments) concerning the temperature dependence of the strength of the solvent-mediated contribution to the potential of mean force (see, e.g., Ref. 34 and references therein). Some studies report that the net attraction between the solute particles should decrease as the temperature increases,<sup>54</sup> the others find the opposite effect<sup>43</sup> (both predictions are for solutes of linear sizes comparable to that of a water molecule). Moreover, the comparison of the predictions of our (PHB) model for quasimacroscopic plates with the results for molecular (microscopic) size solutes might not be meaningful because it is now generally recognized that the physics underlying the phenomenon of hydrophobicity depends on the size scales of particles involved.<sup>14–16,47,55–59</sup>

## VII. CONCLUDING REMARKS

Previously,<sup>18</sup> we proposed a probabilistic approach to examining the effect of water-water hydrogen bond networks around two solute particles (immersed in water) on their interaction. Because of the proximity to the hydrophobic surface, a boundary water molecule forms a smaller (compared to a bulk molecule) number of hydrogen bonds that can be evaluated analytically in the framework of the probabilistic approach. This number depends on the molecule location and orientation. In the original PHB model,<sup>18</sup> it was calculated as a mean quantity for the whole surface hydration layer by averaging over all possible locations and orientations.

In this paper, we have improved the PHB model by obtaining the number of hydrogen bonds per molecule as a function of its distance to the hydrophobic surface. [The molecule orientations in the vicinity of the surface were assumed to be distributed uniformly (with equal probabilities) and the number of hydrogen bonds per molecule was averaged with respect to them.] This function can play a crucial role in developing new theoretical models of hydration of solute particles and their solvent-mediated interactions.

The improved PHB model has been used to examine the temperature effect on the solvent-mediated interaction of two hydrophobic solutes. The (solvent-mediated) hydrophobic interaction of solutes is affected by the solvent (water) temperature because the density of the solvent, strength of a hydrogen bonds, and number of hydrogen bonds per molecule are sensitive thereto (their dependence on the external pressure was not considered). The tetrahedral rigidity of the hydrogen-bonding arms of a model water molecule was assumed to be unaffected with changing the temperature.

The numerical calculations show that the solvent-mediated attraction of hydrophobic solutes is driven by the favorable entropy of solute association (negative entropic component of the potential of mean force) that dominates the unfavorable enthalpy of association (positive enthalpic component of the potential of mean force). This result is consistent with the conventional understanding of the nature of hydrophobic attraction.<sup>37–44</sup> Furthermore, the PHB model predicts the strength of hydrophobic attraction of macroscopic solute particles to decrease with increasing temperature. These predictions corroborate some of the previously reported results<sup>54</sup> while differ from the others for molecular-size solutes.<sup>43</sup>

It should be noted that the number of hydrogen bonds per bulk water molecule serves as a reference for the PHB model. The number of hydrogen bonds per boundary water molecule is obtained by calculating the constraints that the hydrophobic surface imposes on the ability of a water molecule to find other water molecules to form bonds. In the bulk this ability is not constrained because water molecules are everywhere around any selected molecule. Except for this constraint, the temperature and pressure dependence of the hydrogen-bonding ability of a boundary water molecule is the same as in the bulk and is determined by the corresponding dependence of the number of hydrogen bonds per bulk water molecule, a well defined physical quantity. The first (and only) previously available model<sup>29</sup> for the number

of hydrogen bonds in the vicinity of a hydrophobic surface was based on two physical quantities—the energy of a hydrogen bond and the ratio of two subvolumes of the phase space related to broken and formed hydrogen bonds. The problem is that there is apparently no definitive way to distinguish between a completely intact hydrogen bond in liquid water from a completely broken one.<sup>22</sup> For example, in Ref. 60 only 13% of ice hydrogen bonds were reported to be broken during melting (which is quite different from that assumed in Ref. 29), while the other estimates of this quantity vary widely from 7% to 60% (see Ref. 22 and references therein).

## APPENDIX: DERIVATION OF THE EXPRESSIONS FOR $k_2$ , $k_3$ , and $k_4$ as functions of $x'$

### 1. Coefficient $k_2$

By definition, the coefficient  $k_2(x')$  is equal to the ratio  $s_{2(1)}(x')/b_{2(1)}$ , where  $s_{2(1)}(x')$  is the mean probability  $s_{2(1)} = s_{2(1)}(x')$  that molecule  $S$  at a distance  $x'$  from the plate  $L$  forms a second hydrogen bond once its hb arm 1 has already formed a bond and  $b_{2(1)}$  is the analogous probability for a bulk water molecule. The independence of  $s_{2(1)}$  of  $\Theta_1$  angle between hb arm 1 and axis  $x'$  (see Fig. 1) is the result of averaging over all possible orientations  $\Theta_1$  (assumed to be distributed uniformly as if the molecules were in bulk water).

To find this coefficient, consider hb arm 1 of molecule  $S$  and assume that it has already formed a BHB in an arbitrary orientation, determined by its angle  $\Theta_1$ , and take into account the constraint that, in order for hb arm 2 to form a

bond, its tip must not lie closer to the solute than the plane  $Ll$  (Fig. 1). The angle between hb arms 1 and 2 must equal  $\alpha$ .

For a bulk water molecule the probability  $b_{2(1)}$  that the second hydrogen bond forms once the first one has formed is proportional to the full length  $L_b$  of the circle formed by the possible loci of the tip of the *engaged* second hb arm (say, arm 2). Since the radius of that circle is equal to  $\eta \sin(\alpha)$ , we have

$$L_b = 2\pi\eta \sin(\alpha). \quad (\text{A1})$$

For molecule  $S$ , however, because of its proximity to the hydrophobic surface, the possible loci of the tip of engaged hb arm 2 constitute just a part of that circle, the other part (a circular arc) being excluded by the left boundary  $Ll$  of the SHL of plate  $L$ . The length of the “available” part of this circle is a function of  $x'$  and  $\Theta_1$  and is denoted by  $L_s \equiv L_s(x', \Theta_1)$ . The probability  $s'_{2(1)} \equiv s'_{2(1)}(x', \Theta_1)$  that molecule  $S$  engages in a second hydrogen bond once its hb arm 1 has already formed a bond is proportional to  $L_s(x', \Theta_1)$ . Thus, assuming that the intrinsic hydrogen-bonding ability of a BWM is the same as that of a bulk water molecule,

$$s'_{2(1)} = \frac{L_s}{L_b} b_{2(1)}. \quad (\text{A2})$$

The length  $L_s$  can be found to be

$$L_s = 2\pi \left[ 1 - \frac{1}{\pi} \arccos \left( \frac{q(x', \Theta_1)}{\sin(\alpha)} \right) \right], \quad (\text{A3})$$

where for  $\eta(1 - \cos(\alpha)) \leq x' \leq 2\eta$  the function  $q(x', \Theta_1)$  is defined as

$$q(x', \Theta_1) = \begin{cases} \sin(\alpha) & \left( \Theta_1 \leq \pi - \alpha - \arccos \left( \frac{\xi}{\eta} \right) \text{ or } \Theta_1 \geq \pi - \alpha + \arccos \left( \frac{\xi}{\eta} \right) \right) \\ \frac{\frac{\xi}{\eta} + \cos(\alpha)\cos(\Theta_1)}{\sin(\Theta_1)} & \left( \pi - \alpha - \arccos \left( \frac{\xi}{\eta} \right) \leq \Theta_1 \leq \pi - \alpha + \arccos \left( \frac{\xi}{\eta} \right) \right), \end{cases} \quad (\text{A4})$$

with  $\xi \equiv x' - \eta$ , while for  $\eta \leq x' \leq \eta(1 - \cos(\alpha))$  it is

$$q(x', \Theta_1) = \begin{cases} -\sin(\alpha) & \left( \Theta_1 \leq \alpha - \arccos \left( -\frac{\xi}{\eta} \right) \right) \\ \frac{\xi/\eta + \cos(\alpha)\cos(\Theta_1)}{\sin(\Theta_1)} & \left( \alpha - \arccos \left( -\frac{\xi}{\eta} \right) \leq \Theta_1 \leq \pi - \alpha + \arccos \left( \frac{\xi}{\eta} \right) \right) \\ \sin(\alpha) & \left( \Theta_1 \geq \pi - \alpha + \arccos \left( \frac{\xi}{\eta} \right) \right). \end{cases} \quad (\text{A5})$$

Averaging  $s'_{2(1)}(x', \Theta_1)$  over all possible orientations  $\Theta_1$  (assumed to be distributed uniformly), one can obtain the mean probability  $s_{2(1)} = s_{2(1)}(x')$  that molecule  $S$  at a distance  $x'$  from the plate  $L$  forms a second hydrogen bond once its hb arm 1 has already formed a bond. Taking into account Eq. (3), one thus finds

$$k_2(x') = \frac{1}{\pi} \int_0^{\Theta_{1M}^{(2)}(x')} d\Theta_1 \left( 1 - \frac{1}{\pi} \arccos \left( \frac{q(x', \Theta_1)}{\sin(\alpha)} \right) \right), \quad (\text{A6})$$

with  $\Theta_{1M}^{(2)}(x') = \pi - \arccos(x'/\eta - 1)$  and the function  $q(x', \Theta_1)$  defined by Eqs. (A4) and (A5).

## 2. Coefficient $k_3$

The coefficient  $k_3$  is found by assuming that hb arms 1 and 2 of molecule  $S$  (see Fig. 1) have already formed bonds in arbitrary orientations, determined by angles  $\Theta_1$  and  $\Theta_2$  that they form with the  $x'$  axis, subject to the condition that the angle between them is equal to  $\alpha$ , and calculating the probability that the third hb arm (say, hb arm 3) can also form a bond. Clearly, it must be taken into account that in order for hb arm 3 to form a bond, its tip must not lie to the left of the plane  $Ll$  (left boundary of the SHL) and it must have angles  $\alpha$  with both arms 1 and 2. The orientations of hb arms 1 and 2 are eventually averaged assuming their uniform distributions.

The probability  $s'_{3(2,1)}$  that the third hb arm will form a bond as well is a function of  $x'$ ,  $\Theta_1$ ,  $\Theta_2$ , i.e.,  $s'_{3(2,1)} \equiv s'_{3(2,1)}(x', \Theta_1, \Theta_2)$ . Denote the angle between arm 3 and

$x'$ -axis by  $\Theta_3$  (the angle between any pair of arms themselves being  $\alpha$ ). In a Cartesian coordinate system with its origin  $O$  as shown in Fig. 1, its  $x'$ -axis perpendicular to the plane  $Ll$  and directed from molecule  $S$  into the bulk, the plane  $x'Sz'$  coinciding with the plane of the figure, the positive direction of the  $z'$ -axis upward, and the positive direction of the  $y'$ -axis away from the reader, the coordinates of the tip of arm  $i$  ( $i=1,2,3$ ) will be denoted by  $x_i$ ,  $y_i$ ,  $z_i$ . One can easily see that the location of the tip of hb arm 1 is given by  $x_1 = x' + \eta \cos(\Theta_1)$ ,  $y_1 = 0$ ,  $z_1 = -\eta \sin(\Theta_1)$ .

Clearly, hb arm 3 can form a bond with the same probability as in the bulk if the location of molecule  $S$  and orientation of its arms 1 and 2 (i.e.,  $x'$ ,  $\Theta_1$ , and  $\Theta_2$ ) are such that the tip of arm 3 is not located to the left of the plane  $Ll$ , i.e., if  $x_3 \geq \eta$ . Otherwise, hb arm 3 cannot form a bond at all. Keeping in mind that  $s'_{3(2,1)} \equiv s'_{3(2,1)}(x', \Theta_1, \Theta_2)$ , one can thus write that

$$s'_{3(2,1)} = \begin{cases} b_{3(2,1)} & (\Theta_1^{(3)}(x') \leq \Theta_1 \leq \Theta_{1M}^{(3)}(x'), \quad \Theta_{2m}^{(3)}(x', \Theta_1) \leq \Theta_2 \leq \Theta_{2M}^{(3)}(x', \Theta_1)) \\ s'_{3(2,1)} = 0 & (\text{otherwise}). \end{cases} \quad (\text{A7})$$

Here,  $\Theta_{1m}^{(3)}(x')$  and  $\Theta_{1M}^{(3)}(x')$  are the minimum and maximum angles (both greater than 0 but smaller than  $\pi$ ) that hb arm 1 can have with the  $x'$ -axis in order for three hydrogen bonds to form (for a given  $x'$ ). Further,  $\Theta_{2m}^{(3)}(x', \Theta_1)$  and  $\Theta_{2M}^{(3)}(x', \Theta_1)$  are the minimum and maximum angles (both greater than 0 but smaller than  $\pi$ ) that hb arm 2 can have with the  $x'$ -axis in order for three hydrogen bonds to form [assuming that  $\Theta_{1m}^{(3)}(x') \leq \Theta_1 \leq \Theta_{1M}^{(3)}(x')$  for a given  $x'$ ].

The mean probability  $s_{3(2,1)}$  that molecule  $S$  with a given  $x'$  forms a third hydrogen bond once its hb arms 1 and 2 have already formed bonds can be obtained by averaging  $s'_{3(2,1)}$  over all the possible orientations of its hb arms 1 and 2, i.e., over  $\Theta_1$  and  $\Theta_2$  (both angles assumed to be distributed uniformly as if they were in the bulk),

$$s_{3(2,1)} = \int_{\Theta_{1m}^{(3)}(x')}^{\Theta_{1M}^{(3)}(x')} d\Theta_1 p_1(\Theta_1) \int_{\Theta_{2m}^{(3)}(x', \Theta_1)}^{\Theta_{2M}^{(3)}(x', \Theta_1)} d\Theta_2 p_2(\Theta_2 | \Theta_1) s'_{3(2,1)}(x', \Theta_1, \Theta_2), \quad (\text{A8})$$

where  $p_1(\Theta_1)$  is the probability distribution of the angle  $\Theta_1$  in the bulk and  $p_2(\Theta_2 | \Theta_1)$  is the probability distribution of the angle  $\Theta_2$  in the bulk for a given  $\Theta_1$ .

For  $x' > \eta(1 - \cos(\alpha))$  the minimum value  $\Theta_{1m}^{(3)}(x')$  of  $\Theta_1$  is equal to 0, whereas for  $\eta \leq x' \leq \eta(1 - \cos(\alpha))$ , it is given by the expression  $\Theta_{1m}^{(3)}(x') = \pi/2 - \arccos(-\cos(\alpha)/\cos(\alpha/2)) - \arcsin(\xi/\eta \cos(\alpha/2))$  with  $\xi = x' - \eta$ . The maximum angle  $\Theta_{1M}^{(3)}(x')$  of  $\Theta_1$  is equal to  $\pi - \arccos(\xi/\eta)$  for any  $\eta \leq x' \leq 2\eta$ .

The maximum value  $\Theta_{2M}^{(3)}(x', \Theta_1)$  of the angle  $\Theta_2$  for given  $x'$  and  $\Theta_1$  can be shown to be

$$\Theta_{2M}^{(3)}(x', \Theta_1) = \begin{cases} 2\pi - \alpha - \Theta_1 & \left( \Theta_1 \geq \pi - \alpha + \arccos\left(\frac{\xi}{\eta}\right) \right) \\ \pi - \arccos\left(\frac{\xi}{\eta}\right) & (\Theta_{1nx}^{(2)}(x')) < \Theta_1 < \pi - \alpha + \arccos\left(\frac{\xi}{\eta}\right) \\ \alpha + \Theta_1 & (\Theta_1 \leq \Theta_{1nx}^{(2)}(x')), \end{cases} \quad (\text{A9})$$

where  $\Theta_{1nx}^{(2)}(x') = \max[\Theta_{1m}^{(2)}(x'), \pi - \alpha - \arccos(\frac{\xi}{\eta})]$  with  $\Theta_{1m}^{(2)}(x') = 0$  for  $x' > \eta(1 - \cos(\alpha))$  and  $\Theta_{1m}^{(2)}(x') = -\pi + \alpha + \arccos(\frac{\xi}{\eta})$  for  $\eta \leq x' < \eta(1 - \cos(\alpha))$ .

It is relatively simple to see that for a given  $x'$ , the minimum value  $\Theta_{2m}^{(3)}(x', \Theta_1)$  of the angle  $\Theta_2$  is  $\Theta_{2m}^{(3)}(x', \Theta_1) = |\alpha - \Theta_1|$  if  $\Theta_{1upp}^{(3)}(x') \leq \Theta_1 \leq \Theta_{1M}^{(3)}(x')$ , where  $\Theta_{1upp}^{(3)}(x') = \min[\Theta_{1M}^{(3)}(x'), \pi - \alpha + \arccos(\xi/\eta)]$ . On the other hand, if  $\Theta_{1M}^{(3)}(x') \leq \Theta_1 \leq \Theta_{1ypp}^{(3)}(x')$ , then the derivation of an explicit expression for  $\Theta_{2m}^{(3)}(x', \Theta_1)$  requires lengthy and tedious (although simple enough) analytical and geometric manipulations taking into account that

$$\begin{aligned} \cos \alpha &= \frac{1}{\eta^2}(x_1x_2 + y_1y_2 + z_1z_2) = \frac{1}{\eta^2}(x_1x_3 + y_1y_3 + z_1z_3) \\ &= \frac{1}{\eta^2}(x_2x_3 + y_2y_3 + z_2z_3), \end{aligned} \quad (\text{A10})$$

$$x_i^2 + y_i^2 + z_i^2 = \eta^2 \quad (i = 1, 2, 3), \quad (\text{A11})$$

and  $x_3 = -\xi$  [in addition to  $x_1 = x' + \eta \cos(\Theta_1)$ ,  $y_1 = 0$ , and  $z_1 = -\eta \sin(\Theta_1)$ ].

The solution of these equations with respect to  $x_2$  provides two roots,  $x_2^+$  and  $x_2^-$ . Out of these roots, it is necessary

to choose the one that satisfies the condition  $\eta < x_2 < 2\eta$ ; if both do, then the correct root is  $x_2 = \max[x_2^+, x_2^-]$  because it provides the minimum angle between hb arm 2 and axis  $x'$  (for given  $x'$  and  $\Theta_1$ ). One can thus find

$$\Theta_{2m}^{(3)}(x', \Theta_1) = \arccos(x_2/\eta - 1). \quad (\text{A12})$$

Taking into account Eq. (A1), the limits of integration in Eq. (A2), and the definitions in Eq. (3), one thus obtains that the coefficient-function  $k_3(x')$  is determined by

$$k_3(x') = \frac{1}{\pi} \int_{\Theta_{1m}^{(3)}(x')}^{\Theta_{1M}^{(3)}(x')} \frac{\Theta_{2M}^{(3)}(x', \Theta_1) - \Theta_{2m}^{(3)}(x', \Theta_1)}{\Theta_{2M}^{(2)}(x', \Theta_1) - \Theta_{2m}^{(2)}(x', \Theta_1)} d\Theta_1, \quad (\text{A13})$$

where

$$\Theta_{2m}^{(2)}(x', \Theta_1) = \begin{cases} |\alpha - \Theta_1| & (\Theta_1 \geq \Theta_{1m}^{(2)}(x')) \\ \pi - \arccos\left(\frac{\xi}{\eta}\right) & (\Theta_1 < \Theta_{1m}^{(2)}(x')), \end{cases} \quad (\text{A14})$$

with  $\Theta_{1m}^{(2)}(x') = 0$  for  $x' > \eta(1 - \eta \cos(\alpha))$  and  $\Theta_{1m}^{(2)}(x') = -\pi + \alpha + \arccos(\xi/\eta)$  for  $\eta \leq x' \leq \eta(1 - \cos(\alpha))$ ,

$$\Theta_{2M}^{(2)}(x', \Theta_1) = \begin{cases} 2\pi - \alpha - \Theta_1 & \left( \Theta_1 \geq \pi - \alpha + \arccos\left(\frac{\xi}{\eta}\right) \right) \\ \pi - \arccos\left(\frac{\xi}{\eta}\right) & (\Theta_{1nx}^{(2)}(x') < \Theta_1 < \pi - \alpha + \arccos\left(\frac{\xi}{\eta}\right)) \\ \alpha + \Theta_1 & (\Theta_1 \leq \Theta_{1nx}^{(2)}(x')). \end{cases} \quad (\text{A15})$$

### 3. Coefficient $k_4$

The coefficient  $k_4$  is calculated by assuming that hb arms 1, 2, and 3 have already formed bonds subject to the condition that the angle between any two of them is equal to  $\alpha$  and taking into account that, if the water molecule is far enough from the hydrophobic surface (but still in the LHS), hb arm 4 can still form a bond subject to the condition that its tip must not be too close to the plate  $L$  and it must form an angle  $\alpha$  with any of arms 1, 2, and 3. The orientations of arms 1 and 2 are arbitrary (with the angle between them equal to  $\alpha$ ), while arm 3 can have any of just two possible orientations determined by those of arms 1 and 2. The orientations of arms 1 and 2 are eventually averaged assuming their uniform distributions, choosing the Cartesian coordinate system with the origin as in the previous section [in calculating  $k_3(x')$ ].

Again, let us consider molecule  $S$  in the SHL of plate  $L$  (i.e., at a distance  $\eta \leq x' \leq 2\eta$  from plate  $L$ ), whereof hb arms 1, 2, and 3 have already formed bonds. What is the probability  $s'_{4(3,2,1)} \equiv s'_{4(3,2,1)}(x', \Theta_1, \Theta_2)$  that hb arm 4 will form a bond as well? Let us denote the angle between arm  $i$  ( $i = 1, 2, 3, 4$ ) and axis  $x'$  by  $\Theta_i$  (the angle between any pair of arms themselves being  $\alpha$ ). The Cartesian coordinates of the tip of arm  $i$  ( $i = 1, 2, 3, 4$ ) will be denoted by  $x_i, y_i, z_i$ . First of all, in order for hb arm 4 to form a bond, molecule  $S$  must be sufficiently far away from the lower boundary of the LHS. The minimum distance  $x'_{\min}$ , at which this is possible is equal to  $\eta + \Delta x_n$ , where  $\Delta x_n = -\eta \cos(\alpha)$  is the height of a regular pyramid whereof the apex coincides with molecule  $S$  and the basis is formed by the tips of three hb arms in the plane  $x' = \eta$  (i.e., in plane  $L$ ). Therefore,  $x'_{\min} = \eta(1 - \cos(\alpha))$  is the



minimum value of the distance  $x'$  between molecule  $S$  and plate  $L$  necessary for  $S$  to simultaneously form four hydrogen bonds.

Further, hb arm 4 can form a bond with the same probability as in the bulk if the location of molecule  $S$  and orien-

tation of its arms 1 and 2 (i.e.,  $x'$ ,  $\Theta_1$ , and  $\Theta_2$ ) are such that the tip of arm 4 is not located to the left of the plane  $Ll$ . Otherwise, hb arm 4 cannot form a bond at all. Keeping in mind that  $s'_{4(3,2,1)} \equiv s'_{4(3,2,1)}(x', \Theta_1, \Theta_2)$ , one can thus write that

$$s'_{4(3,2,1)} = \begin{cases} b_{3(2,1)} & (\Theta_{1m}^{(4)}(x') \leq \Theta_1 \leq \Theta_{1M}^{(4)}(x'), \Theta_{2m}^{(4)}(x', \Theta_1) \leq \Theta_2 \leq \Theta_{2M}^{(4)}(x', \Theta_1)) \\ s'_{3(2,1)} = 0 & (\text{otherwise}). \end{cases} \quad (\text{A16})$$

Here,  $\Theta_{1m}^{(4)}(x')$  and  $\Theta_{1M}^{(4)}(x')$  are the minimum and maximum angles (both greater than 0 but smaller than  $\pi$ ) that hb arm 1 can have with the  $x'$ -axis in order for four hydrogen bonds to form (for a given  $x'$ ). Further,  $\Theta_{2m}^{(4)}(x', \Theta_1)$  and  $\Theta_{2M}^{(4)}(x', \Theta_1)$  are the minimum and maximum angles (both greater than 0 but smaller than  $\pi$ ) that hb arm 2 can have with the  $x'$ -axis in order for four hydrogen bonds to form [assuming that  $\Theta_{1m}^{(4)} \times (x') \leq \Theta_1 \leq \Theta_{1M}^{(4)}(x')$  for a given  $x'$ ].

The mean probability  $s'_{4(3,2,1)}$  that a boundary molecule (i.e., molecule  $S$ ) forms a fourth hydrogen bond once its hb arms 1, 2, and 3 have already formed bonds can then be obtained by averaging  $s'_{4(3,2,1)}$  over all possible orientations of its hb arms 1 and 2,  $\Theta_1$  and  $\Theta_2$  (assumed to be distributed uniformly as they are in the bulk),

$$s_{4(3,2,1)} = \int_{\Theta_{1m}^{(4)}(\kappa)}^{\Theta_{1M}^{(4)}(\kappa)} d\Theta_1 p_1(\Theta_1) \int_{\Theta_{2m}^{(4)}(\kappa)}^{\Theta_{2M}^{(4)}(\kappa, \Theta_1)} d\Theta_2 p_2(\Theta_2 | \Theta_1) \times s'_{4(3,2,1)}(x', \Theta_1, \Theta_2), \quad (\text{A17})$$

where  $p_1(\Theta_1)$  is the probability distribution of the angle  $\Theta_1$  in the bulk and  $p_2(\Theta_2 | \Theta_1)$  is the probability distribution of the angle  $\Theta_2$  in the bulk for a given  $\Theta_1$ .

Thus, one can conclude that the coefficient  $k_4(x')$  is equal to zero for  $\eta \leq x' \leq \eta(1 - \cos(\alpha))$ . For  $\eta(1 - \cos(\alpha)) < x' \leq \eta\sqrt{0.5(1 + \cos(\alpha))}$  this coefficient is given by

$$k_4(x') = \frac{1}{\pi} \left( \int_0^{\alpha - \arccos(C_n^4(x'))} + \int_{\arccos(C_n^{(14)}(x'))}^{\pi - \arccos(\xi/\eta)} \right) \times d\Theta_1 \frac{\Theta_x^{(24)}(x', \Theta_1) - \Theta_n^{(24)}(x', \Theta_1)}{\Theta_x^{(22)}(x', \Theta_1) - \Theta_n^{(22)}(x', \Theta_1)}, \quad (\text{A18})$$

where  $\Theta_{nU}^{(14)}(x') = \min[\alpha - \text{sign}(\xi + \eta \cos(\alpha)) \times \arccos(C_p^4(x')), \pi - \arccos(\xi/\eta)]$ ,  $C_p^4(x') = (-b_4(x') + \sqrt{b_4^2(x') - 4a_4(x')c_4(x')})/2a_4(x')$ , and  $C_n^4(x') = (-b_4(x') - \sqrt{b_4^2(x') - 4a_4(x')c_4(x')})/2a_4(x')$  with  $a_4(x') = 0.5(1 + \cos(\alpha))$ ,  $b_4(x') = -(\xi/\eta)\cos(\alpha)$  and  $c_4(x') = \cos(\alpha) - 0.5(1 + \cos(\alpha) + (\xi/\eta)^2)$ . For  $\eta(1 + \sqrt{0.5(1 + \cos(\alpha))}) < x' < 2\eta$  it is determined by

$$k_4(x') = \frac{1}{\pi} \int_0^{\pi - \arccos(\xi/\eta)} d\Theta_1 \frac{\Theta_x^{(24)}(x', \Theta_1) - \Theta_n^{(24)}(x', \Theta_1)}{\Theta_x^{(22)}(x', \Theta_1) - \Theta_n^{(22)}(x', \Theta_1)} \quad (\text{A19})$$

(remind that by definition  $\xi = x' - \eta$ ).

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