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The surface tension of water calculated from a random network model

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Abstract

The surface tension (excess surface free energy) of water is an important factor in many biological and chemical systems. It is often invoked to correlate or explain the low solubility of nonpolar compounds in water as well as the so-called hydrophobic effect of nonpolar molecules aggregating in water. While water's surface tension is not easily obtained from theory, the random network model (RNM) of Henn and Kauzmann (H–K), which described water's well-known, anomalous thermodynamic properties, can be used successfully to calculate the surface tension of water at atmospheric pressure between temperatures of 0 and 100 °C. Agreement with observed values, particularly at lower temperatures, is good, although the H–K RNM is too ice-like in nature to allow for the rapid drop off of surface tension with increasing temperature. Suggestions are offered for improving the model. In addition, an alternative explanation for the preferred orientation of surface water molecules is proposed based on water's H-bonding and attendant intramolecular, zero-point distortion energy.

Keywords: Liquid water; Surface tension; Surface energy; Random network model; Interface; Distorted hydrogen bond; Surface water orientation; Zero-point distortion energy

1. Introduction

The surface tension, or excess surface free energy, of liquid water, which is much higher than that of almost all ordinary liquids, is a very important and interesting physical quantity. Interfaces involving water are of considerable importance in many biological and chemical systems such as cell membranes and industrial separations. Water's high surface tension has been invoked in correlating and explaining the very low, aqueous solubility of nonpolar compounds [1], and it has been cited as the basis for the so-called hydrophobic effect, in which nonpolar solutes and nonpolar regions of proteins, when in water, tend to minimize their surface contact with water by aggregating together [2–4].

Despite its important role in aqueous solutions, hydrophobic phenomena, and other biological processes, historically the surface tension of water has not been dealt with all that successfully from a theoretical standpoint. For instance, several groups [5–8] calculated water's surface tension using computer simulations and obtained only moderate success; and typically, the computations were limited to one or two temperatures. It wasn't until the

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Abbreviations: H-bond, hydrogen bond; RNM, random network model.

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mid-1990s molecular dynamic simulations of Tildesley and co-workers (Ref. [9] and references therein), who used an improved, extended, simple point-charge potential (SPC/E) for water, that excellent agreement with experiment was obtained. Prior to the recent simulations of Alejandre et al. [9], methods attached to specific models usually had more success in reproducing the surface tension of water. Reiss [10] used the scaled particle theory to calculate the surface tension of water, although the results, not unexpectedly, were lacking somewhat because little of water's important structural character was included in the theory. Luck [11] extended Skapski's approach [12] for calculating the excess surface energy of metals to water by combining spectroscopic data on water with a simple, two-state cluster model, consisting of free O–H groups and tridymite-like, H-bonded groups, and obtained fairly good agreement. While the significant structures theory, in its modified ice I-ice III mixture form, is no longer considered a plausible theory for water, excellent agreement with the observed surface tension of water was achieved at several temperatures by Jhon et al. [13]. Twenty years ago, Luzov et al. [14], employing a strictly geometrical approach to water's hydrogen bonding at the vapor interface and incorporating the concept of broken vs. fully formed H-bonds, calculated a surface tension that was a little more than half of the observed value at 25 °C.

In this paper, we describe how the random network model (RNM) of liquid water, as originally developed over 20 years ago by Sceats and Rice and co-workers [15–19] and later extended by Henn and Kauzmann (H–K) [20], can be used to calculate the surface tension of liquid water. The RNM of water of Sceats and Rice and co-workers had excellent success calculating the energy, entropy, and heat capacity of water as well as the liquid's radial distribution function [15–19]. Henn and Kauzmann then extended the model to include volume effects and derived an equation of state that, for example, demonstrated the unusual temperature dependence of water's coefficient of thermal expansion and isothermal compressibility [20]. More recently, Sharp and Madan had good success in utilizing the H–K RNM of water, combined with Monte Carlo simulations, to calculate the hydration heat capacities of various solutes in aqueous solutions and to investigate the attendant, solvent structural changes [21–25].

2. Review of the basic H–K RNM [20]

The main idea behind the RNM of liquid water is that, on a suitable timescale, the liquid is considered a highly distorted ice lattice consisting of all water molecules tetrahedrally engaged in four hydrogen bonds that are bent and stretched to varying degrees. With this assumption, the energy and entropy of water can be thought of consisting of two main contributions—the lattice vibrational contributions and the configurational contributions. The former arise from the oscillations of water molecules about their quasi-equilibrium positions, while the latter arise from the deformations of hydrogen bonds that help determine the quasi-equilibrium positions. The separation between these two contributions obviously is not complete, as both the intermolecular and intramolecular vibration frequencies depend on the magnitudes of the hydrogen bond distortions.

The configurational energy, as defined by Henn and Kauzmann [20], itself consists of several contributions relative to perfect ice Ih. These parts are the hydrogen bond (H-bond) bending energy, E_B, the H-bond stretching energy, E_S, the non-bonding energy, E_{NB}, and the intramolecular zero-point distortion energy, E_{ZPD}. Similar to Sceats and Rice [16,17], H–K derived the following expressions for those terms [20].

The H-bond bending and stretching variables are depicted in Fig. 1. Note that the simplifying assumption of $\langle\theta^2_{LP}\rangle = \langle\theta^2_H\rangle = \langle\theta^2\rangle$ is implicit.

$$E_B = V_0[(1-\exp(-\langle\theta^2\rangle/2)) + (1-\exp(-5.4\langle\theta^2\rangle))] \tag{1}$$

$$E_S = k_x\langle x^2\rangle(1-2\Gamma_x\langle x\rangle) \tag{2}$$

$$E_{NB} = 16\varepsilon[1-\exp(-\langle\theta^2\rangle^{1/2})][(1+\langle x\rangle)^{-12} - (1+\langle x\rangle)^{-6}] \tag{3}$$

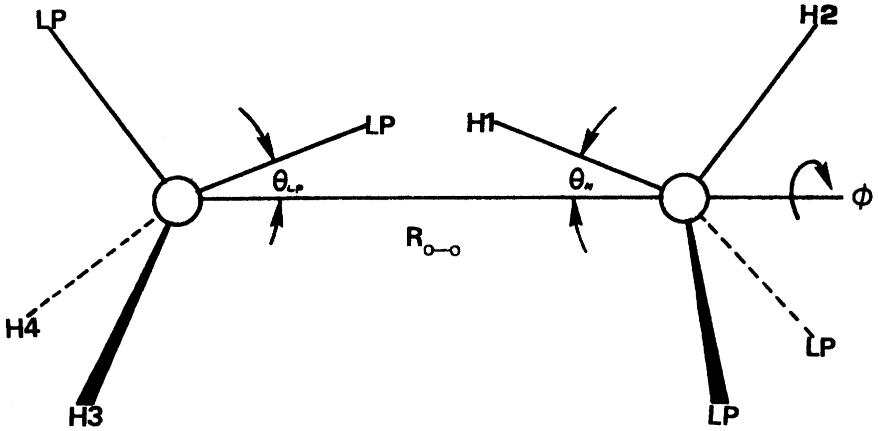

Fig. 1. Hydrogen bond distortion variables used in the H–K RNM of water. H denotes a proton and LP denotes a lone pair. Note that $\theta_{\mathrm{LP}}=\theta_{\mathrm{H}}=\theta$, $x=(R_{\mathrm{O-O}}-R_0)/R_0$, with $R_0=2.75$ Å and ϕ is ignored (see Ref. [20] for details). (Reprinted with permission from Ref. [20], © 1989 American Chemical Society.)

$$E_{\mathrm{ZPD}}=1/2N_{\mathrm{A}}hc(0.1039\nu_{1\mathrm{v}}+0.1275\nu_{3\mathrm{v}})\{1-\exp[(-1.24\langle\theta^2\rangle+1.5\Gamma_x\langle x\rangle)]\}, \qquad (4)$$

where V_0 is the height of the H-bond bending barrier; $\langle\theta^2\rangle$ is the mean squared H-bond bending angle; k_x is the relative O–O stretching constant, $\langle x\rangle$ is the average relative O–O displacement, defined as $R-R_0/R_0$, with R_0 the O–O separation in ice Ih at 0 K; $\langle x^2\rangle$ is the mean squared displacement; Γ_x is the Gruneisen constant for the O–O stretching mode in ice Ih, 1.86; ε is the potential well depth for neon's Lennard–Jones intermolecular potential; N_{A} is Avogadro's number; h is Planck's constant; c is the speed of light; and $\nu_{1\mathrm{v}}$ and $\nu_{3\mathrm{v}}$ are the frequencies of the intramolecular, symmetric and asymmetric O–H stretching modes, respectively, in vaporous (isolated) water molecules.

It should be noted that the E_{ZPD} is a positive quantity relative to ice Ih, the reference system for the H–K RNM, but negative relative to the vapor. The calculated E_{ZPD} of Ih relative to water vapor is −5.105 kJ/mole [20], which agrees well with Whalley, who determined it to be −4.98 kJ/mole from spectroscopic measurements [26]. We dwell on the zero-point distortion energy a bit here because it is important to a later discussion on the orientation of water molecules at the liquid–vapor interface.

Using the same variables, the configurational entropy, S_{conf}, is defined [18,20] as

$$S_{\mathrm{conf}}=R\ln\{1+[(\langle x^2\rangle-\langle x\rangle^2)/\langle x_0^2\rangle]\}+\mathrm{R}\ln\{1+(\langle\theta^2\rangle/(\langle\theta_0^2\rangle)\}, \qquad (5)$$

in which R is the suitable gas constant, ln indicates natural logarithm, and the 0 subscript attached to x^2 and θ^2 indicate the zero-point amplitudes of stretching and bending for ice Ih at 0 K and zero pressure. Clearly, the configurational entropy consists of two terms related to the bending and stretching of H-bonds in water and is a consequence of the increase in accessible phase space as the H-bonds are distorted [18,20].

The configurational energy is simply the sum of Eqs. (2)–(4), while the configurational Helmholtz free energy is, of course, then

$$A_{\mathrm{conf}}=E_{\mathrm{conf}}-TS_{\mathrm{conf}} \qquad (6)$$

The vibrational contributions to the free energy of water are calculated from

$$A_{\mathrm{vib}}=RT\sum_{i=1}^{6}\ln 2\sin h(h\nu_i/2kT) \qquad (7)$$

where the intermolecular vibrational density of states of the quasi, water lattice has been approximated crudely as consisting of six harmonic oscillations per molecule (three hindered translations and three hindered rotations) [17,20]. For bookkeeping purposes, the lattice energy of ice, U_L (-58.91 kJ/mole, [26]) is combined with the vibrational free energy expression to give an overall, quasi-lattice free energy expression of $A_{lat} = A_{vib} + U_L$. In Ref. [20], the lattice energy was not included in the vibrational energy expressions, but it will become obvious later why it is necessary to do so in this paper. According to the H–K model, the intermolecular vibration frequencies, ν_i, depend on the H-bond distortion variables of $\langle x \rangle$ and $\langle \theta^2 \rangle$ such that [20]

$$\nu_i = \nu_{io} \exp[-(1.24\langle \theta^2 \rangle + 1.5\Gamma_x \langle x \rangle)] \tag{8}$$

The ν_{io}'s are the intermolecular lattice frequencies for perfect ice at 0 K and zero pressure.

In addition to the configurational and vibrational entropies, we must include S_{PD}, the entropy due to proton disorder in water. Since it is assumed that all water molecules in the bulk liquid are always engaged in four hydrogen bonds (2 per molecule), the entropy of proton disorder in the liquid is taken to be the same as the residual entropy of ice, which is $R \ln(3/2)$ [18,20]. As we see later, though, the proton disorder entropy at water's surface, not unexpectedly, is shown to be higher.

The key extension by Henn and Kauzmann to the Sceats and Rice RNM of water was to define the density of water in terms of the H-bond distortion variables. By matching the density of perfect ice Ih at zero pressure and temperature, when $\langle x \rangle$ and $\langle \theta^2 \rangle$ are presumed zero, and that of a hypothetical, close-packed liquid of molecular weight 18.015 g/mole, when all the H-bonds are assumed completely distorted, they came up with an approximate expression for the molar volume, V_0, of water as a function of $\langle x \rangle$ and $\langle \theta^2 \rangle$ [20].

$$V_0 = (4\pi/3) N_A R_0^3 (1 + \langle x \rangle)^3 / \{0.905[7 - 4\exp(-\langle \theta^2 \rangle^{1/2})]\} \tag{9}$$

The square bracketed expression, $7 - 4\exp(-\langle \theta^2 \rangle^{1/2})$, is the effective number of water molecules within the so-called sample sphere used by Henn and Kauzmann [20] to calculate volumetric properties and is related obviously to the coordination number of water. The coordination number will be important later in the discussion on calculating the surface tension.

Given all the considerations above, the total Helmholtz free energy for water can be written as

$$A_{tot} = A_{conf} + A_{lat} - TS_{PD}. \tag{10}$$

One can then proceed to minimize the total free energy as a function of volume and temperature to find the average values of θ^2, x^2 and x. These three variables together determine all the thermodynamic properties of liquid water according to the H–K RNM. Typical values of the three H–K RNM variables and various thermodynamic quantities at 0 atm. and 20 °C are listed below [20].

3. Calculating the surface tension of water

The surface tension, γ, of a fluid may be defined as the work required to remove a molecule from the bulk interior and to bring it to the surface, thereby extending the surface area of the liquid [27]. This process is carried out under conditions of constant temperature and pressure. At atmos-

Table 1
Typical values of the H–K RNM variables and corresponding thermodynamic quantities of water at 0 atm. and 20°

$\langle \theta^2 \rangle$	$\langle x^2 \rangle$	$\langle x \rangle$										
0.0156	0.0024	0.0292										
E_B	E_S	E_{NB}	E_{ZPD}	E_{conf}	E_{vib}	E_{Tot}	S_B	S_S	S_{conf}	S_{vib}	S_{Tot}	A_{Tot}
2.57	2.23	-0.077	0.50	5.22	-38.70	-33.48	16.59	7.34	23.93	39.47	66.77	-53.06

$\langle \theta^2 \rangle$ in rad^2, $\langle \theta^2 \rangle^{1/2} = 7.2°$. *Notes:* All E_s' and A_{Tot} in kJ/mol, all S_s' in J/mol K; E_{vib} includes the ice Ih lattice energy, U_L; S_{Tot} includes S_{PD}. Columns 6–8 of Table IV in Ref. [20], corresponding to E_{conf}, E_{vib} and E_{Tot}, are incorrect.

pheric (near zero) pressure, the Gibbs and Helmholtz free energies are almost equal, permitting us to write

$$\gamma = [A(\mathrm{surf}) - A(\mathrm{bulk})]/\mathrm{area}. \tag{11}$$

Here $A(\mathrm{surf})$ and $A(\mathrm{bulk})$ are the total Helmholtz free energies of the surface and bulk, respectively.

During the process of bringing a molecule to the surface and extending the surface area, the total volume, V, of the system remains constant at V. Thus, in the thermodynamic limit, the pressure remains constant for the process when V is chosen such that [28]

$$\lim_{N,V \to \infty} N/V = \rho, \tag{12}$$

where N is the number of molecules in the system, and ρ is the macroscopic number density.

To determine the surface tension, we need to find the difference in free energy between the bulk and the surface. This difference arises from the dissimilar molecular interactions occurring at the surface and in the bulk. It is the excess free energy of the surface relative to the bulk that is responsible for the inward pull, or surface tension, of a liquid [27].

To simulate the interactions at the liquid surface in contact with water vapor, we have to assume something about the number and type of molecules with which a surface molecule interacts. According to the H–K RNM described above, in the bulk liquid, a given water molecule has $Z_\mathrm{b} = 2(6 - 4\exp(-\langle\theta_\mathrm{b}^2\rangle^{1/2}))$ nearest neighbor molecules surrounding it; four of these are directly H-bonded to it, and the remaining $2(4 - 4\exp(-\langle\theta_\mathrm{b}^2\rangle^{1/2}))$ molecules interact via a Lennard–Jones potential [20]. The subscript b is used here to denote bulk in order to distinguish it from surface values. Similarly for the surface region, we assume that a given molecule (strictly true only at the arbitrarily assigned Gibbs dividing surface) has a coordination number, $Z_\mathrm{s} = 2(6 - 4\exp(-\langle\theta_\mathrm{s}^2\rangle^{1/2}))$ in its sample volume. The subscript s denotes a surface value. In general, we expect $\langle\theta^2\rangle$ to be greater at the surface than in the bulk because of the weaker interactions and greater fluctuations at the surface. Likewise, $\langle x\rangle$ and $\langle x^2\rangle$ will be greater at the surface because of weaker-on-average H-bonding. Since the $\langle\theta^2\rangle$ and $\langle x\rangle$ act in opposite directions with respect to the molar volume, a constant volume can still be maintained even as the number of nearest neighbors might change slightly in going from the bulk to the surface.

From simple geometrical considerations, and following Skapski [12], we assume that, at the surface, there are only three nearest neighbors directly H-bonded to any given water molecule. The assumption that surface water molecules have only three H-bonds is lent credence by the computer simulations of Lee et al. [29], who found that water molecules near planar surfaces sacrifice a H-bond, and the theoretical work of Luzov et al. [14], who calculated that water molecules at the surface have 25% of their H-bonding reduced compared to the bulk. We assume, furthermore, that there are approximately $(3/4)[4 - 4\exp(-\langle\theta_\mathrm{s}^2\rangle^{1/2})]$ $(=6(1 - \exp(-\langle\theta_\mathrm{s}^2\rangle^{1/2})))$ molecules interacting with the given surface molecule by a L–J potential. The remaining molecules do not interact at all with the given surface molecule. Such non-interacting molecules should approximately resemble many of the vapor molecules that the liquid surface molecules might normally encounter on the vapor side of the so-called dividing surface, or surface of discontinuity.

In effect, our arbitrary (microscopic) Gibbs dividing surface [27] is taken as the plane that exactly cuts the middle of the sample volume region, centered about a given surface molecule, such that two of the three H-bonds are contained in the plane and one is directed into the bulk below. The surface sample volume is shown in Fig. 2. It is calculated as in Eq. (9), but where $\langle\theta^2\rangle$ and $\langle x\rangle$ have, of course, their surface values.

Assuming that any given surface molecule participates in three H-bonds and has only approximately three-fourths of the bulk number of nonbonded, interacting molecules permits us to write for the configurational free energy of the surface

$$\begin{aligned} A_\mathrm{conf}(\mathrm{surf}) = {} & \frac{3}{4}[E'_\mathrm{B} + E'_\mathrm{S} + E'_\mathrm{NB} - RT(S'_\mathrm{conf})] \\ & + (0.9E'_\mathrm{ZPD} + 5.1/10) \end{aligned} \tag{13}$$

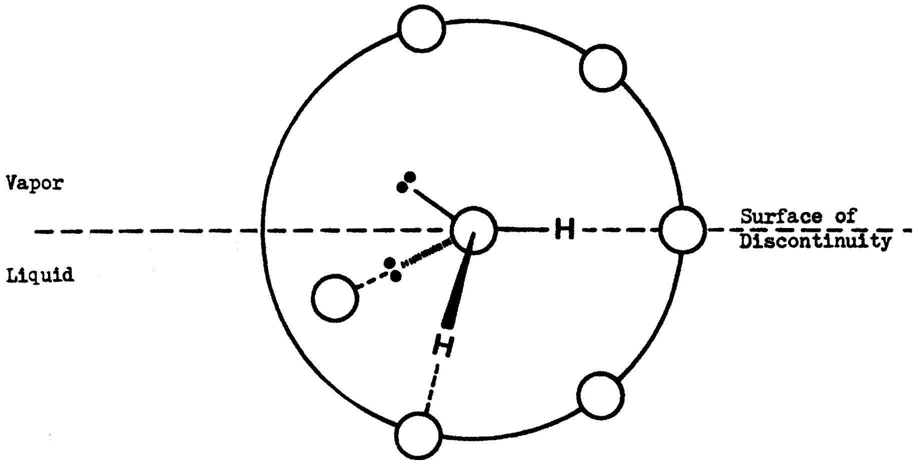

Fig. 2. H–K RNM surface sample volume sphere and Gibbs dividing surface.

Here 5.1 kJ is the maximum zero-point distortion energy, relative to ice Ih, for a water molecule not engaged in any H-bonds [20]; the primes indicate the corresponding surface quantities that are defined by the same expressions in Section 2 but with the variables $\langle\theta^2\rangle$, $\langle x^2\rangle$ and $\langle x\rangle$ having their surface values. As noted before, it is expected that all three are larger at the surface than in the bulk.

Even though it is a minor factor in the overall energy difference between surface and bulk water, E_{ZPD}, the zero-point, distortion energy contribution, to the surface free energy (last two terms in parentheses in Eq. (13)), deserves greater discussion before proceeding. Unlike the other parts of the surface configurational energy, the zero-point distortion energy of surface water molecules presents something of an awkward dilemma for the RNM because one cannot merely multiply the usual form of Eq. (4) by three-fourths. What is the E_{ZPD} if one of the hydrogens of a water molecule is sticking out above the surface, and, hence, not involved in a H-bond? We rather crudely assume that, for such a posited situation, the distortion energy is an average of the distortion energy for a water molecule having two, fully H-bonded protons (given the appropriate values of $\langle\theta^2\rangle$, $\langle x^2\rangle$ and $\langle x\rangle$) and for a molecule with two, totally non-H-bonded protons. If a lone pair is exposed to the surface, there is no difficulty, because both hydrogens of the water surface molecule are still engaged in H-bonds.

Second harmonic generation and sum frequency generation (SFG) spectroscopic examinations of the surface of water over the past 15 years indicate that at least 20% or so of surface water molecules have hydrogens dangling at the interface (manifesting as intermolecularly decoupled O–H oscillators), as most of the protons are directed slightly into the bulk interior [30–32]. Theoretical studies also suggest that, predominantly due to coupling between water's dipole and quadrupole moments, most of the surface protons point into the liquid. See, for instance, Ref. [8] and the discussion therein.

Taking the now, generally accepted orientation of surface water molecules into account, we write, as a further approximation for E_{ZPD}(surf) in Eq. (13),

$$\begin{aligned} E_{ZPD}(\text{surf}) &= 0.2[1/2(5.105+E'_{ZPD})]+0.8E'_{ZPD} \\ &= 0.9\,E'_{ZPD}+0.51 \end{aligned} \qquad (14)$$

where the prime indicates, as before, the usual distortion energy expression calculated with the structural variables found at the surface. Given that $\langle\theta^2\rangle$, $\langle x^2\rangle$ and $\langle x\rangle$ are all expected to be larger at the surface, Eq. (14) sensibly indicates that a water molecule at the surface always has a greater intramolecular, zero-point distortion energy, relative to ice Ih, than does a bulk molecule because its environment more closely resembles that of a vapor molecule.

Returning, as an aside, to possible reasons for the preferred orientation of water molecules at the liquid–vapor interface, perhaps there are other factors to consider besides coupling of the molecules' electric moments. As suggested by Matsumoto and Kataoka [8], at least one of the reasons might be related to water's hydrogen bonding, particularly since, from the RNM perspective, the zero-point distortion energy is lower when the large majority of protons are fully engaged in H-bonds at the surface than if not. In other words, it is energetically more favorable for a surface water molecule to sacrifice one of its H-bonds involving a lone pair, rather than a proton, because it gains less zero-point distortion energy.

Keeping the assumption that all the surface water molecules are engaged in three H-bonds only, and carrying out an elementary, Boltzmann statistical calculation on a two-state model using the latter obtained value of $E_{\mathrm{ZPD}}(\mathrm{surf})$ (-4.01 kJ/mole, relative now to the vapor) at 20 °C, predicts that $\sim 30\%$ of the surface water molecules have dangling protons—a result not all that far off from the experimentally estimated, lower-bound value of $\sim 20\%$ [31]. In addition, since the zero-point distortion energy changes very slowly with temperature, the preferred orientation of surface water molecules concomitantly changes very little with temperature, which again seems to agree with experiment [30,31]. Admittedly, there is a degree of circular reasoning in our analysis in that the relative weighting of hydrogens at the surface is built into the expression for the surface zero-point distortion energy, $E_{\mathrm{ZPD}}(\mathrm{surf})$ (vide supra). Nevertheless, we believe there is a valid connection between the intramolecular zero-point distortion energy and the preferred orientation of surface water molecules since a similar result is obtained if an unweighted (i.e. bulk) value of $E_{\mathrm{ZPD}}(\mathrm{surf})$ is used instead in the Boltzmann calculation.

The vibrational contribution to the free energy of the surface, $A_{\mathrm{vib}}(\mathrm{surf})$, retains the same form as for the bulk Eq. (7), as the surface molecules are still fully able to execute all the same intermolecular, quasi-lattice vibrations. According to Eq. (8), we expect the lattice frequencies to be lower at the surface because the H-bonds are more highly distorted, as reflected in larger values of $\langle \theta^2 \rangle$, $\langle x^2 \rangle$ and $\langle x \rangle$.

Similar to most of the configurational free energy expressions, the lattice energy contribution to $A(\mathrm{surf})$ is also reasonably reduced by one-fourth. A hypothetical ice crystal with only three-fourths of the usual number of interacting neighbors, including just three H-bonded nearest neighbors, would be expected to possess a lattice energy, U_{L}, approximately three-fourths of the usual ice Ih value of -58.91 kJ/mole. With 3/2 H-bonds per molecule, reducing the lattice energy of the hypothetical ice crystal by one-fourth ensures that the average H-bond strength, on which the ice lattice energy depends greatly, is the same in both reference lattices [33]. Clearly, the difference in lattice energies is a major contributor to the excess surface energy in our model.

In addition to the expressions for $A_{\mathrm{conf}}(\mathrm{surf})$ and $A_{\mathrm{lat}}(\mathrm{surf})$ stated above, we need to consider a couple of entropic factors. Because it has been assumed that there are only 3/2 H-bonds per surface molecule, the entropy of proton disorder at the surface, $S_{\mathrm{PD}}(\mathrm{surf})$, is increased relative to the bulk. Following exactly Pauling's well-known method [34] for computing the residual entropy of ice, it is easily shown that the S_{PD} for water molecules at the surface is $R \ln 6$. This result is entirely anticipated if one assumes each molecule at the surface engages in three H-bonds vs. four in the bulk. The number of ways of forming three H-bonds at four possible sites is $4!/3!1! = 4$, and, therefore, the difference in S_{PD} between the surface and bulk should be

$$\begin{aligned}\Delta S_{\mathrm{PD}} &= S_{\mathrm{PD}}(\mathrm{surf}) - S_{\mathrm{PD}}(\mathrm{bulk})\\ &= R \ln 6 - R \ln(3/2) = R \ln 4\end{aligned} \tag{15}$$

The other entropic factor we have to consider is a term, similar to that described by Skapski, which accounts for the 'unsharpness' of the surface of discontinuity resulting from the extensive thermal agitation occurring at the surface [12]. Thermal agitation causes the surface molecules to exchange sites continually with both the interacting, liquid molecules and non-interacting, vapor molecules. Assuming the surface of discontinuity remains undefined within 2–3 molecular diameter distances, which is reasonable for water [8], Skapski [12] derived an entropy of exchange term, S_{exch}

$$S_{\mathrm{exch}} = -R/(Z_s+1)[(Z_s-Z_i)\ln(Z_s-Z_i/Z_s+1)+(Z_i+1)\ln(Z_s+1/Z_s+1)] \tag{16}$$

in which Z_s is the first coordination number of any given surface molecule, and Z_i is the number of surrounding molecules that interact with the given surface molecule. Here we make no distinction between those molecules that are H-bonded to the given molecule and those that interact with it via the neon Lennard–Jones potential. Recall that $Z_s = 2(6-4\exp(-\langle\theta_s^2\rangle^{1/2}))$ and, therefore, $Z_i = \frac{3}{4}Z_s = 9-6\exp(-\langle\theta_s^2\rangle^{1/2}))$. As S_{exch} turns out to be virtually insensitive to changes in $\langle\theta_s^2\rangle$ over the temperature range examined (0 to 100 °C) at 1 atm. pressure, we use just its more or less constant value of 0.513R = 4.27 J/mol K.

Combining the previously stated forms for $A_{\mathrm{conf}}(\mathrm{surf})$ and $A_{\mathrm{lat}}(\mathrm{surf})$ and the additional entropic factors, we can now minimize the total $A(\mathrm{surf})$,

$$A(\mathrm{surf}) = A_{\mathrm{lat}}(\mathrm{surf}) + A_{\mathrm{conf}}(\mathrm{surf}) - T(S_{\mathrm{exch}} + S_{\mathrm{PD}}(\mathrm{surf})), \tag{17}$$

for a given temperature and given volume corresponding to the temperature and volume of the bulk liquid. From this procedure, $A(\mathrm{surf})$ is easily found, along with the appropriate surface values of $\langle\theta^2\rangle$, $\langle x^2\rangle$ and $\langle x\rangle$.

Except for the added S_{exch} term, $A(\mathrm{surf})$ basically describes a hypothetical fluid similar to H–K RNM bulk water but one that presumably reflects the main characteristics of liquid water found at the liquid–vapor interface. The main difference is that the hypothetical surface fluid's molecules possess overall three-fourths the number of interacting nearest neighbors as the molecules in bulk water do; and more important, they are assumed to be engaged, at any one moment, in only three, distorted H-bonds-despite having the capability to form four H-bonds, like bulk water.

Now, following from the definition of our spherical, sample volume region and the chosen, microscopic Gibbs dividing surface, the extended surface area per molecule, α, is simply

$$\alpha = \pi R_0^2(1+\langle x_s\rangle)^2 \tag{18}$$

The surface tension of water may then be calculated as

$$\gamma = [A(\mathrm{surf}) - A(\mathrm{bulk})]/\pi R_0^2(1+\langle x_s\rangle)^2 \tag{19}$$

where both $A(\mathrm{surf})$ and $A(\mathrm{bulk})$ have been minimized separately but at the same constant temperature and volume as bulk water.

4. Results and discussion

The final expressions for $A(\mathrm{bulk})$ Eq. (10) and $A(\mathrm{surf})$ Eq. (17), were each minimized with respect to the three RNM variables ($\langle\theta^2\rangle$, $\langle x^2\rangle$ and $\langle x\rangle$) every 10° over the temperature range of 0–100 °C. The constant volumes used in the calculations were the measured molar volumes of liquid water corresponding to those temperatures at 1 atm. pressure. The results show that, at the surface, $\langle\theta^2\rangle$, $\langle x^2\rangle$ and $\langle x\rangle$ all increase considerably, relative to the values found in the bulk. For instance, the values of $\langle\theta_s^2\rangle$, $\langle x_s^2\rangle$ and $\langle x_s\rangle$ at 20 °C are 0.0238, 0.0037 and 0.036, respectively. Compared to the bulk numbers in Table 1, these are increases of 53, 54 and 24%, respectively. In fact, the surface values at 20 °C are close to what the bulk values are at 100 °C, suggesting sizable thermal agitation at the surface relative to the interior. In terms of the physical quantities one can relate to directly in Fig. 1, these results translate to a mean H-bond bending angle of 8.8° at the surface vs. 7.2° in the bulk and an average O–O separation of 2.85 Å at the surface vs. 2.83 Å in the bulk. The increased H-bond bending at the surface leads to fluctuations of the O–O–O angles at the water surface that can vary by almost ±19° from the essentially tetrahedral angle found in ice Ih. The greater O–O separation at the surface leads to an extended surface area per molecule of 2.55×10^{-15} cm^2 at 20 °C.

Using the obtained values of $\langle\theta_s^2\rangle$ and $\langle x_s^2\rangle$, the symmetric and antisymmetric O–H stretching frequencies of surface water molecules are calculated to be 3323 and 3336 cm^{-1}, respectively. These frequencies fall in between the two, broad peaks, observed at 3400 and 3150 cm^{-1} in the SFG spectrum of the air–water interface [31], that are assigned, respectively, to supposed weaker and stronger surface H-bonds [32]. For the sake of completeness, we note that there is a sharp peak in the observed spectrum at 3700 cm^{-1} that identifies the 'free' O–H oscillator (dangling hydrogen) found at the surface [31].

A good exercise and test of our model is to compute the surface excess energy, ΔE_s, and surface excess entropy, ΔS_s, commonly equated to $-d\gamma/dT$, at 20 °C. Taking the differences between E_{Tot}(surf) and E_{Tot}(bulk) and S_{Tot}(surf) and S_{Tot}(bulk), as defined earlier, we find, respectively, $\Delta E_s = 121$ erg/cm^2 and $\Delta S_s = 0.15$ erg/cm^2 K. These results are to be compared to the experimentally determined values of 120 erg/cm^2 and 0.16 erg/cm^2 K [27]. The fact that both ΔE_s and ΔS_s agree so closely with the experimental values, and not just the difference, $\Delta E_s - T\Delta S_s = \Delta A_s$, suggests that we have included all the key energy and entropy factors in our analysis. By the way, as discussed in Ref. [20], ΔS_s cannot be calculated straightforwardly as $-d(\Delta A_s)/dT$ because temperature-dependent lattice frequencies are used in the H–K RNM.

As it turns out, much of the increase in the vibrational contribution to A(surf) that results from the larger values of $\langle\theta^2\rangle$, $\langle x^2\rangle$ and $\langle x\rangle$ at the surface is offset by the posited exchange entropy and enhanced proton disorder entropy at the surface. The configurational entropy, on the other hand, is actually lower at the surface than in the bulk simply because it is reduced by an overall, multiplicative factor of $^3/_4$. Thus, as noted earlier, the assumed reduction of the ice lattice energy by $^1/_4$ of its value in A_{lat}(surf) plays a prominent role in determining the overall, excess surface free energy, according to the approach presented here.

The surface tension of water at atmospheric pressure was calculated according to Eq. (19) between 0 and 100 °C, and the results are plotted in Fig. 3. As can be seen, despite all the approximations and assumptions in the model, overall agreement with water's observed surface tension [35] is quite satisfactory, particularly at the lower temperatures, where it differs by only a few mN/meter (dyn/cm) or so. More exact agreement is not expected, partly because we have approximated the Gibbs free energy with the Helmholtz free energy, and the measured values relate to a liquid water/water vapor–inert gas interface as opposed to a liquid water/pure water vapor interface. These discrepancies, however, are quite small and only account for negligible deviations from the real values.

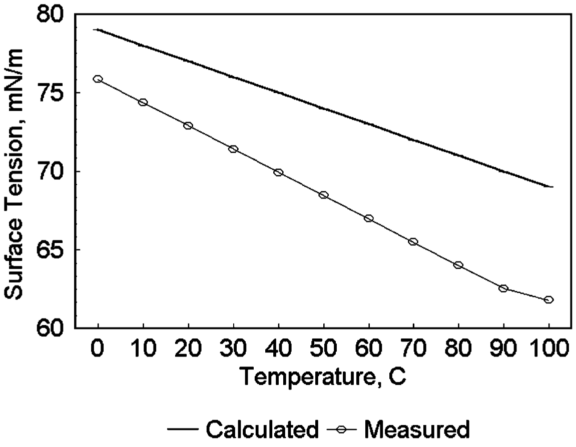

Fig. 3. Calculated (solid line) and measured (circles, Ref. [35]) surface tension of water between 0 and 100 °C.

While the temperature dependence of the calculated surface tension shows a linear decrease with increasing temperature, which is true of water in this temperature range (there is some curvature), it is clearly insufficiently steep. Only a small portion of the weak temperature dependence can be attributed to using a constant value of S_{exch}, as was done. Indeed, the predicted temperature behavior of the surface tension is not unanticipated in view of the fact that the constant pressure heat capacity calculated from the H–K RNM is lower than measured, and the calculated coefficient of thermal expansion is also lower and exhibits a weaker temperature dependence than is observed [20]. It is believed that the H–K RNM, as presently constructed, is too ice-like and rigid in nature to adequately predict water's surface tension at higher temperatures. This is especially true since the decrease in surface tension of a liquid as it is heated is closely related to the approach of the critical temperature, where ΔE_s has to go to zero. Obviously, that condition, for which we cannot talk at all about a lattice, is well beyond the applicable range of the RN model.

5. Conclusion

The RNM of liquid water, developed by Sceats and Rice and co-workers [15–19] and extended by Henn and Kauzmann [20], is used to calculate the surface tension of water by computing the difference in free energy between the fully H-bonded, bulk liquid and a similar, but hypothetical, fluid that apparently possesses the main characteristics of water at the liquid–vapor interface. In particular, the hypothetical surface fluid's molecules have the capability to form four H-bonds, like water, but are assumed to be engaged in only three H-bonds at any one time. The random network, continuum model, thus modified, is able to achieve good success in reproducing the surface tension and other excess surface quantities of liquid water, particularly at lower temperatures. Not unexpectedly, the temperature dependence of the calculated surface tension, while linear, is weaker than observed because the H–K RNM, as it presently stands, is too ice-like and rigid. Using weaker H-bond bending and stretching constants and allowing the quasi-lattice modes of hindered translations and rotations to become a mix of harmonic and free, translational and rotational degrees of freedom, as the quasi-lattice distorts, would make the RNM less ice-like and presumably more sensitive to temperature.

In addition to computing the surface tension of water, an alternative explanation for the preferred orientation of surface water molecules arises naturally from the present analysis. Due to the H-bonding and intramolecular zero-point distortion energy present in liquid water, the protons of water are more energetically disposed to point towards the bulk than dangle at the surface. The further success of the RNM in calculating the surface tension of water and in explaining the orientation of surface water molecules strengthens the case for using the RNM, perhaps expanded to include second-nearest neighbors, as a highly plausible starting point for understanding all the properties of liquid water and aqueous solutions.

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