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# Surface solvation for an ion in a water cluster

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We have used molecular dynamics simulations to study the structural, dynamical, and thermodynamical properties of ions in water clusters. Careful evaluations of the free energy, internal energy, and entropy are used to address controversial or unresolved issues, related to the underlying physical cause of surface solvation, and the basic assumptions that go with it. Our main conclusions are the following. (i) The main cause of surface solvation of a single ion in a water cluster is both *water and ion polarization*, coupled to the charge and size of the ion. Interestingly, the total energy of the ion increases near the cluster surface, while the total energy of water decreases. Also, our analysis clearly shows that the cause of surface solvation is not the size of the total water dipole (unless this is too small). (ii) The entropic contribution is the same order of magnitude as the energetic contribution, and therefore cannot be neglected for quantitative results. (iii) A pure energetic analysis can give a *qualitative* description of the ion position at room temperature. (iv) We have observed surface solvation of a large positive iodinelike ion in a polarizable water cluster, but not in a nonpolarizable water cluster. © 2005 American Institute of Physics.

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## I. INTRODUCTION

Ion solvation in finite clusters has led to an enormous body of theoretical and experimental research.<sup>1–12</sup> New experimental techniques such as cluster ion beam or electron photodetachment experiments, have proved extremely useful in the study of ion solvation in gaseous clusters. Unlike experimental bulk studies, where generally only ion-pair energetics can be probed, cluster experiments allow for the exploration of *single-ion* solvation. In this way, it is possible to obtain thermodynamic quantities for only one ionic species (and then extrapolate to “infinite cluster” or bulk, if need be). The adsorption and distribution of ions at or near interfaces is of particular interest, since this process is present in very diverse chemical and biological systems.<sup>13</sup> Ion interface solvation is very important for the structure and stability of proteins, nucleic acids, and membrane molecules, where many ions tend to sit near or at the interface between the biomolecule (with a low dielectric constant of 1–4) and water (with a high dielectric constant of  $\sim 80$ ). Ion interface solvation is also relevant for chemical reactions at the interfaces, for the atmospheric reactivity of aqueous sea-salt microparticles,<sup>14–16</sup> and other situations.

Theoretically, molecular dynamics (MD) simulations have been used to shed light into the structural, dynamical, and thermodynamical properties of ions in clusters at the atomic scale. These studies have been extremely important in elucidating the surface-versus-bulk solvation of ions (espe-

cially of halide ions), to sample trajectories, and to measure quantities inaccessible to experiments. The first MD simulations predicting surface solvation investigated fluoride, chloride, bromide, and iodide ions in small water clusters containing 20 molecules or less,<sup>17–21</sup> and larger clusters (around 255 molecules).<sup>22</sup> Perera and Berkowitz<sup>17</sup> were the first to predict that a  $\text{Cl}^-$  anion solvated in a cluster composed of up to 20 water favors surface solvation. This was subsequently confirmed experimentally by photoelectron spectroscopy.<sup>23,24</sup> At the time, the conclusion was unexpected because it had been previously assumed<sup>25,26</sup> that by adding water molecules individually, the first solvation shell would fill before the second solvation shell started to form. The new results, on the other hand, showed that the halide ion would keep its first solvation shell partially empty, even in the presence of the second shell, due to the preference of the ion for surface solvation. *Ab initio* simulations<sup>27,28</sup> have confirmed these conclusions.

The initial work of Perera and Berkowitz was later generalized<sup>17–29</sup> to include other ions. The main conclusions are that large halide anions such as  $\text{Cl}^-$ ,  $\text{I}^-$ , and  $\text{Br}^-$  prefer to reside close to the surface of the cluster, while small negative ions such as fluoride and positive ions both reside in the interior of water clusters. By comparing simulations employing polarizable or nonpolarizable force fields, it was found that the driving force for surface solvation is the polarizability of water; all simple point charge water models such as

SPC/E (Ref. 30) are unable to reproduce induced polarization and are therefore unable to predict surface solvation. Interestingly, the SPC/E model was devised to take polarizable effects in an average way (as compared to its predecessor SPC), but this is not enough to capture the true solvation behavior of ions in a cluster environment.

It is instructive to take a brief look at the predictions of dielectric theory. Continuum dielectric theory is valid for water molecules far from the ion. Although it can provide a reasonable estimate of the magnitude of solvation free energies, it cannot give quantitative results for small cluster sizes. It only provides the asymptotic functional dependence of solvation energy on cluster size, and it breaks down near the ion. The simplest approximation to the solvation free energy of an ion is given by the Born model,<sup>31,32</sup> where the solvent medium is modeled as a continuous dielectric medium with a dielectric constant  $\epsilon$ , and the ion as a sphere of radius  $R$  with a charge  $q$  uniformly distributed over the surface. Under these conditions, the solvation free energy is given by

$$F_{\text{Solv}} = - \left( 1 - \frac{1}{\epsilon} \right) \frac{q^2}{2R}. \quad (1.1)$$

This can be separated into energetic and entropic terms by taking the derivative with respect to temperature,

$$S_{\text{Solv}} = - \frac{dF_{\text{Solv}}}{dT} = - \frac{q^2}{2R} \frac{1}{\epsilon^2} \frac{d\epsilon}{dT}, \quad (1.2)$$

$$U_{\text{Solv}} = F_{\text{Solv}} + TS_{\text{Solv}} = - \frac{q^2}{2R} \left( 1 - \frac{1}{\epsilon} + \frac{T}{\epsilon^2} \frac{d\epsilon}{dT} \right). \quad (1.3)$$

Experimentally,<sup>33</sup> for water at 298 K it is measured  $\epsilon = 78.358$  and  $T \epsilon d\epsilon^{-1}/dT = -1.3679$ . These values immediately give  $F_{\text{Solv}} = -163.85q^2/R$  and  $TS_{\text{Solv}} = -0.97q^2/R$ . The model therefore predicts that the main contribution to the free energy comes from the energy contribution given by Eq. (1.3), which is independent of the sign of the charge, and that entropic contributions are negligible. What happens with more realistic, atomistic models of water? In infinite clusters of simple models of water, such as SPC/E, it has been shown<sup>34</sup> that the contribution of the entropy to the free energy is still small compared to the solvation energy. However, in atomistic water models—unlike in the Born model—the dynamics and thermodynamics of the ion depend on the sign of the ionic charge.

While studying the literature of ion solvation, we found that certain issues have been clearly resolved: mainly, the conclusions stated above, that big halide ions prefer surface solvation, while cations and small negative ions reside in the interior of *polarizable* water clusters. However, there remains a number of somewhat controversial issues, mainly related to the underlying physical cause of the observed phenomena, and—when the cause is correctly given—the lack of a rigorous explanation for it. In this work, we have reexamined the issue of ion solvation in a water cluster with extensive MD simulations to measure the changes in free energy, energy, and entropy in order to understand the driving forces involved in ion solvation. We have therefore provided answers to the issues that we enumerate below.

*a. What is the cause of surface solvation?* Perera and Berkowitz provided the key answer for this: mainly the polarization of the system, with the waters playing a major role. However, this does not seem entirely recognized by the community involved in ion solvation problems. For instance, the halide anion polarizability has been cited<sup>35,36</sup> as playing the most important role in the ion's preference for surface location, and water polarization effects have been deemed not important.<sup>20</sup> In this work, we carefully measure the effects of water polarizability and those of the ion polarizability and show that, indeed, both effects are comparable. Moreover, while the *ion total* energy increases at the surface of the cluster, the *water total* energy decreases at the surface. Another somewhat different explanation to the cause of surface solvation in an aqueous cluster was provided by Stuart and Berne.<sup>22</sup> The authors recognized that the water models with induced polarization have larger average dipole than those without it. Therefore, they reasoned, it is probably that the *total* dipole (and not necessarily the induced polarization) is responsible for the surface effects. In order to test this hypothesis, they compared three water models: a model, TIP4P/FQ,<sup>37</sup> that includes induced polarization and has large average dipole moment; a simple charge model, TIP4P,<sup>38</sup> that has a smaller dipole moment; and a modification of TIP4P, where the values of the point charges were increased so as to reproduce the larger average dipole moment of TIP4P/FQ. Their results indicated that the big average dipole moment of the water molecule is the main factor that drives the ion to the surface. However, they explained clearly that the modified large permanent dipole model did not give the right physical properties of water. In the same spirit of this hypothetical experiment, we have reduced the charges of a polarizable water model, so that the average dipole moment becomes *smaller* than that for the simple point charge SPC/E model. We find that the modified polarizable model predicts surface solvation (SPC/E does not) in spite of having an average total dipole moment smaller than that of SPC/E. In fact, all the evidence seems to indicate that—within those physical parameters that make a water model behave more or less like water—it is the polarization (coupled to the sign and size of the ion) the underlying cause of surface solvation.

*b. What is the role of entropy?* Continuum dielectric theory and studies of infinite clusters of simple models of water, such as SPC/E, predict that entropic contribution to the free energy is negligible with respect to the energy contribution. Surprisingly, the role of entropy in finite water clusters has not been addressed. The approaches generally used in the literature have been implementing MD simulations with different water models and measuring ion distributions, or studying the global energy minimum at zero temperature.<sup>17–19</sup> In general, the entropic contribution has been deemed “negligible.” In this work we show that far from negligible, the entropic contribution is of exactly the same order of magnitude as the energy contribution. Therefore, it cannot be neglected if one seeks quantitative results.

*c. What sort of information can be obtained by a pure energetic analysis at room temperature?* Although the entropic effects play a very important role, one can still make a pure internal energy analysis to understand *qualitatively* the

different physical contributions to ion solvation. The reason why this analysis is still valid at room temperature is given in Sec. III C, mainly that the probability distribution computed from the average internal energy has its maximum at the same point or very near to the maximum of the exact probability derived from the free energy. One can therefore study the changes in entropy and different components of the energy as the ion approaches the cluster surface, and find strong correlations between changes, in the particular components of the energy and the entropy.

*d. Can positive ions be surface solvated?* If the polarization is the main cause of surface solvation, one would expect that positive ions also be found on the surface. However, solvation of a positive atomic ion has not been reported in the literature. Since we know that the small fluoride ion stays inside the cluster and larger halides go to the surface, it is also possible that small positive ions stay inside the cluster and larger cations move to the surface. The asymmetry of the water could probably arise in what the “critical” ion size is for surface solvation, with positive ions requiring a much larger size (larger than the size of the simple monovalent cations). We have tested this hypothesis with a (nonexistent) large positive iodinelike monovalent ion, and found surface solvation for the polarizable water model but not for the nonpolarizable model.

The results presented here clearly indicate the need for a correct treatment of electrostatics<sup>39</sup> in water models. In fact, more accurate models are being developed using both polarizable and higher-order multipoles.<sup>40–43</sup> Simulations with these more sophisticated models are feasible due to very efficient codes developed in our group.<sup>42,44,45</sup> In particular, the calculations for the polarizable water model were performed using a Car-Parrinello scheme<sup>44</sup> for the computation of the induced polarization implemented in the SANDER molecular dynamics module of AMBER 6, 7, and 8.<sup>46,47</sup>

This paper is organized as follows. Section II presents the model used, and the descriptions of the potential energy, of the potential of mean force, and of the method of umbrella sampling, as well as details of the simulations. Section III presents results concerning the four questions enunciated above. Section IV ends the paper with a conclusion.

## II. SOLVATION OF AN ION IN A SPHERICAL CLUSTER OF ATOMISTIC WATERS

### A. Potential energy

Two existing water models were used in the simulations: the SPC/E model,<sup>30</sup> where the electronic density is simply represented by point charges localized at the atomic nuclei; and the RPOL (Ref. 48) model, where in addition to the point charges the atoms also carry a polarizability. In both representations, the ion is considered to be a point charge (with or without polarization) on a Lennard-Jones (LJ) center.

The total potential energy is the sum of three terms,

$$U_{\text{tot}} = U_c + U_{\text{LJ}} + U_{\text{pol}}, \quad (2.1)$$

where  $U_c$  is the pairwise contribution that comes from the charge-charge interaction,  $U_{\text{LJ}}$  is the Lennard-Jones interaction, and  $U_{\text{pol}}$  is a nonadditive contribution coming from the

induced dipoles (interacting with themselves and the charges). To facilitate the understanding of the ion dynamics in the cluster, we can decompose each of the first two terms in Eq. (2.1) into the contributions from the water-water and ion-water interactions. Naturally, the presence of the ion is also felt in the water-water interactions through the particular ordering of the water molecules imposed by the ion. For  $N$  water molecules, there are  $3N+1$  charges and induced dipoles. We label the ion as particle 1 and write the first two terms as

$$U_c = \sum_{i < j}^{3N+1} \frac{q_i q_j}{r_{ij}} = \sum_{j=2}^{3N+1} \frac{q_1 q_j}{r_{1j}} + \sum_{1 < i < j}^{3N+1} \frac{q_i q_j}{r_{ij}} \\ = U_c^{\text{ion}} + U_c^{\text{wat}}, \quad (2.2)$$

$$U_{\text{LJ}} = \sum_{i < j}^{3N+1} \left( \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right) \\ = \sum_{j=2}^{3N+1} \left( \frac{A_{1j}}{r_{1j}^{12}} - \frac{B_{1j}}{r_{1j}^6} \right) + \sum_{1 < i < j}^{3N+1} \left( \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right) \\ = U_{\text{LJ}}^{\text{ion}} + U_{\text{LJ}}^{\text{wat}}. \quad (2.3)$$

The superscripts *ion* and *wat* indicate the ion-water and the water-water contributions, respectively. The third term ( $U_{\text{pol}}$ ), on the other hand, is not an additive two-body potential but a many-body potential, since the induced dipoles are given by the constitutive equation  $\mu_i = \alpha_i \mathbf{E}_i$ , where  $\alpha_i$  is the polarizability and  $\mathbf{E}_i$  is the *total* electrostatic field due to both the permanent charges and induced dipoles. There are three contributions to  $U_{\text{pol}}$ : the energy of the induced dipoles in the “external” field produced by the permanent charges, the interaction energy of the induced dipoles, and the dipolar self-energy. The constitutive equation must be solved either self-consistently by some iterative scheme or by some other method such as Car-Parrinello.<sup>44</sup> Once the dipoles have completely converged, this term can be written as

$$U_{\text{pol}} = -\frac{1}{2} \sum_{i=1}^{3N+1} \mu_i \cdot \mathbf{E}_i^{(0)} \\ = -\frac{1}{2} \mu_1 \cdot \mathbf{E}_1^{(0)} - \frac{1}{2} \sum_{i=2}^{3N+1} \mu_i \cdot \mathbf{E}_i^{(0)} \\ = U_{\text{pol}}^{\text{ion}} + U_{\text{pol}}^{\text{wat}}. \quad (2.4)$$

In these equations,  $\mathbf{E}_i^{(0)}$  is the electrostatic field produced by all charges except charge  $i$ ,  $\mathbf{E}_i^{(0)} = \sum_{j \neq i}^{3N+1} (q_j \mathbf{r}_{ij} / r_{ij}^3)$ . The decomposition has not the same meaning than before. Here  $U_{\text{pol}}^{\text{ion}}$  represents the interaction of the ionic dipole with all the water permanent charges while  $U_{\text{pol}}^{\text{wat}}$  represents the interaction of the water dipoles with all the permanent charges of the system (including that of the ion). If the ion polarizability is set to zero the first term vanishes.

### B. Potential of mean force

To characterize the behavior of the ion in the water cluster, we want to evaluate the free energy, the internal energy,



and the entropy of the system as the ion moves outwards in the radial direction. Since our simulations are performed at constant volume, temperature, and number of particles the natural thermodynamic potential is the Helmholtz free energy, which can be written as

$$F(r) = -kT \ln \left[ 4\pi r^2 \int d\Gamma' \frac{\exp[-\beta U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{3N+1})]}{Z} \right] + C_1$$

$$= -kT \ln P(r) + C_2, \quad (2.5)$$

where  $Z = \int d\Gamma (e^{-\beta U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{3N+1})})$ ,  $d\Gamma = d^3r d^3r_2 \dots d^3r_{3N+1}$ ,  $d\Gamma' = d^3r_2 d^3r_3 \dots d^3r_{3N+1}$ ,  $\beta = 1/kT$ ,  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $C_1$ ,  $C_2$  are arbitrary constants. Due to the spherical symmetry of the system, ion trajectories inside a spherical shell at a given radial distance  $r$  from the center of the cluster constitute equivalent ensembles of the system, therefore, the integral above does not depend on the angular coordinates of the ion (and hence the factor  $4\pi$ ). We denote by  $P(r)$  the probability of finding the ion at a distance between  $r$  and  $r + dr$ . This probability has two contributions: one coming from the interactions (electrostatics, Lennard-Jones, etc.) and the other coming from the increase in the volume element with  $r$  that is given by the factor  $4\pi r^2$  in Eq. (2.5) (the constant shell width  $dr$  has been absorbed in the constant  $C$ ). Even when this gives the actual probability of finding the ion at a certain distance  $r$  in the cluster, to study structural changes of the system as the ion approaches the surface it is more useful to factor out the volume element  $4\pi r^2 dr$ . For this, one compares changes in free energy as the ion moves between *equal* volume elements  $d^3r$  separated by a distance  $r$ . In this case the free energy can be written as

$$\mathcal{F}(r) = -kT \ln \left[ \int d\Gamma' \frac{\exp[-\beta U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{3N+1})]}{Z} \right] + C_3$$

$$= -kT \ln \mathcal{P}(r) + C_4, \quad (2.6)$$

$\mathcal{P}(r)$  is the probability of finding the ion in a volume element  $d^3r$  located at a distance  $r$  (the constant volume element  $d^3r$  has been absorbed in the  $C$  constants). Although the angular components of  $\mathbf{r}$  have not been integrated out,  $\mathcal{F}$  and  $\mathcal{P}$  only depend on  $r = |\mathbf{r}|$  due to the rotational symmetry of the problem.

The connection between  $\mathcal{F}(r)$  and the macroscopic quantities  $\bar{U}_{\text{tot}}(r)$  and  $S(r)$ , is given by

$$d\mathcal{F}(r) = d\bar{U}_{\text{tot}}(r) - TdS(r), \quad (2.7)$$

where  $\bar{U}(r) = \int d\Gamma' [U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{3N+1}) e^{-\beta U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{3N+1})}] / \int d\Gamma' e^{-\beta U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{3N+1})}$  is the average value of the energy  $U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{3N+1})$  for the ion at a fixed distance  $r$ . With the new definition Eq. (2.6) of the free energy, the entropy in Eq. (2.7) does not consider the contribution proportional to  $\ln(4\pi r^2)$  that simply describes the increase in entropy due to the increase in accessible volume for the ion to move as  $r$  increases.

## C. WHAM method and simulation details

The molecular dynamics simulations were performed on spherical clusters consisting of a single ion and 238 water molecules. The averages on the force and potential energy were measured using the umbrella sampling method where the reaction coordinate  $r$  is the distance of the ion from the center of the cluster. The reaction coordinate was subdivided in 20 windows centered at  $r_{\text{win}} = 1, 1.5, 2, 2.5, \dots, 11, 11.5$  Å. The biased potential was chosen as

$$W_{\text{win}}(r) = \begin{cases} K_{\text{win}} r + K_{\text{restr}}(r - r_{\text{win}})^2, & |r - r_{\text{win}}| > 0.5 \text{ Å} \\ K_{\text{win}} r, & |r - r_{\text{win}}| \leq 0.5 \text{ Å} \end{cases}, \quad (2.8)$$

where  $K_{\text{win}}$  is a window-dependent value and the constant  $K_{\text{restr}} = 43 \text{ kcal mol}^{-1} \text{ Å}^{-2}$  restricts the sampling within each window to approximately 1 Å. The values of  $K_{\text{win}}$  were set so that the probability of finding the ion inside the window is approximately constant.

The set of biased probabilities distributions  $\{P_j^b(r)\}$  was obtained for each window  $j$ . The unbiased probability  $P(r)$  was obtained by applying the WHAM method<sup>49</sup> and solving iteratively the set of equations,

$$P(r) = \sum_{i=1}^{22} \frac{P_i^b(r)}{\sum_{j=1}^{22} e^{-\beta[W_j(r) - f_j]}}, \quad (2.9)$$

$$e^{(-\beta f_i)} = \int dr P(r) e^{-\beta W_i(r)}. \quad (2.10)$$

In the simulations we used the nonpolarizable water model SPC/E (Ref. 30) and the polarizable water model RPOL.<sup>48</sup> The SPC/E water model assigns point charges of  $-0.8476e$  and  $0.4238e$ , to the oxygen and hydrogen atoms, respectively. The bond length between oxygen and hydrogen is 1 Å and the bond angle is 109.47°. The RPOL water model has the same geometry as SPC/E but assigns smaller charges of  $-0.73e$  and  $0.365e$  together with an atomic polarizability to the oxygen and hydrogen atoms. The Lennard-Jones interactions between SPC/E or RPOL waters act only between water oxygens. Similarly the ion-water LJ interactions act between the water oxygen and the ion. The probe ions used in the simulations were  $\text{Cl}^-$  and  $\text{Cl}^+$  (which is of similar size to  $\text{Cs}^+$ ), that have the chloride parameters differ in the sign of the ion charge;  $\text{I}^-$  and  $\text{I}^+$ , that have the iodide parameters but with opposite charge. The parameters are summarized in Table I.

For each window 20 clusters were built with uncorrelated water and ion coordinates and each of these clusters was equilibrated for 150 ps (SPC/E) and for 250 ps (RPOL). A 300 ps simulation for data collection under biased potential was performed for each of the 400 clusters. These simulations were all performed using the SANDER module of the AMBER7 simulation<sup>47</sup> package. The water geometry was constrained throughout all simulations by using the analytic<sup>50</sup> version of SHAKE.<sup>51</sup> Simulations were performed at constant volume and temperature. The temperature was controlled by using a Berendsen thermostat<sup>52</sup> with a 400 fs relaxation time. The volume was constrained using the CAP option in the SANDER module of AMBER, which imposes a

TABLE I. Parameters for the water models and ionic species.

Species	$A_{ij}$ (kcal $\text{\AA}^{12} \text{mol}^{-1}$ )	$B_{ij}$ (kcal $\text{\AA}^6 \text{mol}^{-1}$ )	$q(e)$	$\alpha$
RPOL				
O(H <sub>2</sub> O)	$7.5182 \times 10^5$	$6.9366 \times 10^2$	-0.730	0.528
H(H <sub>2</sub> O)	...	...	+0.365	0.170
Cl <sup>-</sup>	$2.4120 \times 10^7$	$3.1061 \times 10^3$	-1	3.2
Cl <sup>+</sup>	$2.4120 \times 10^7$	$3.1061 \times 10^3$	+1	3.2
I <sup>+</sup>	$3.0214 \times 10^8$	$1.1530 \times 10^4$	+1	6.5
I <sup>-</sup>	$3.0214 \times 10^8$	$1.1530 \times 10^4$	-1	6.5
SPC/E				
O(H <sub>2</sub> O)	$6.3044 \times 10^7$	$6.2600 \times 10^2$	-0.8476	...
H(H <sub>2</sub> O)	...	...	+0.4238	...
Cl <sup>-</sup>	$2.1062 \times 10^7$	$2.9025 \times 10^3$	-1	...
I <sup>+</sup>	$3.0214 \times 10^8$	$1.1530 \times 10^4$	+1	...
I <sup>-</sup>	$3.0214 \times 10^8$	$1.1530 \times 10^4$	-1	...
Low dipole				
O(H <sub>2</sub> O)	$7.5182 \times 10^5$	$6.9366 \times 10^2$	-0.630	0.528
H(H <sub>2</sub> O)	...	...	+0.315	0.170

half harmonic restoring potential on waters outside the cluster radius defined as 12  $\text{\AA}$ . We use the default CAP force constant of  $1.5 \text{ kcal mol}^{-1} \text{\AA}^{-2}$ . Lorentz-Bertholet mixing rules<sup>53</sup> were used for the Lennard-Jones interaction coefficients. The nonbonded cutoff was set sufficiently large (999  $\text{\AA}$ ) to ensure that all nonbond interactions were correctly calculated. For the calculation of the induced dipoles, we used the Car-Parrinello method for classical induced dipoles in SANDER (Ref. 44) with a dipolar mass of 0.33.

### III. RESULTS AND DISCUSSION

#### A. Free energy, energy, and entropy

We computed as a function of radial distance the free energy  $\mathcal{F}(r)$  according to Eq. (2.6), the average value of the total energy  $\bar{U}_{\text{tot}}(r)$ , and the entropy  $TS(r)$  according to Eq. (2.7). These quantities are shown in Fig. 1 for the chloride ion. Since we are interested in the relative value of each of the quantities in Eq. (2.7), we have added arbitrary constants to facilitate comparison, so that  $TS(1 \text{ \AA}) = \bar{U}_{\text{tot}}(1 \text{ \AA}) = \mathcal{F}(1 \text{ \AA}) = 0$ . In other words, Fig. 1 shows the difference in entropy, energy, and free energy with respect to their respective values at a distance  $r = 1 \text{ \AA}$  from the ion center. The top panel of Fig. 1 shows the results for the SPC/E model and the bottom panel shows the results for the RPOL model. Two important results are immediately apparent in this figure. First, it is clear that the changes in entropy and energy are of the same order of magnitude independently of the model considered. Second, the behavior of  $TS(r)$  and  $\bar{U}_{\text{tot}}(r)$  is very different for each of the models, with the free energy predicting surface solvation for the ion in RPOL waters, but not in SPC/E waters.

It is possible to invoke the concepts of “structure breaking” and “structure making,” introduced by Frank and Evans<sup>54–57</sup> to describe the variation of the entropy and the structural changes of the solvent. The change in solvation entropy of monovalent ions is usually compared to that of the H<sup>+</sup> ion. Using this definition, most of the negative ions are considered “structure breakers,” in the sense that they

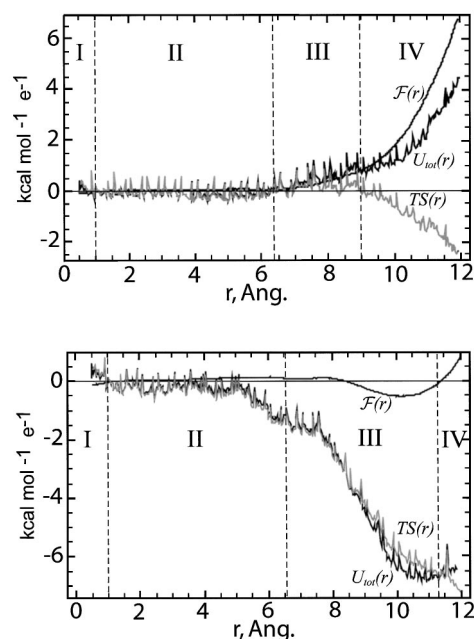


FIG. 1. Free energy  $\mathcal{F}(r)$  (smooth dark line), internal energy  $\bar{U}_{\text{tot}}(r)$  (noisy dark line), and entropic contribution  $TS(r)$  (noisy, lighter line) for the SPC/E cluster (top panel) and the RPOL cluster (bottom panel). The ion is Cl<sup>-</sup>.

create more disorder than the H<sup>+</sup> ion. Another definition involves the measurement of the change in entropy of the system with the solvated ion with respect to the entropy of the system of waters without the ion. In this sense most negative ions are “structure makers,” because they reduce the entropy of water as they get solvated.<sup>58</sup> In addition to the change in entropy due to the ion type, an ion in a *finite* cluster also produces a change in entropy due to the broken translational symmetry in the radial direction. This means that the ion not only changes the water structure relative to another ion but also relative to the position of the ion in the cluster. We are interested in this second effect. By choosing as reference the position of the ion at  $r = 1 \text{ \AA}$ , we define the ion as structure breaker if the entropy increases as the ion is displaced, or a structure maker if the entropy decreases. In this way, by measuring the relative positional entropy  $\Delta S(r) = S(r) - S(1 \text{ \AA})$ , we factor out the “ion-type” effect (change of entropy with respect to H<sup>+</sup> in an infinite cluster) and concentrate on the finite cluster effect.

According to the radial distance, we divide the two panels in Fig. 1 in four different regions. First, we analyze the behavior of the ion in the SPC/E water model. As the ion comes closer to the center of the cluster (regions I and II), the energy and entropy increase slightly. The center of the cluster, therefore, is the position in which the ion becomes more structure breaking. Perhaps the simplest way to interpret this is to consider the water molecules as permanent dipoles, with the ion located at the center of the cluster. The dipoles tend to align in the direction of the field produced by the ion, so a dipole located in the position  $\mathbf{r}$  aligns itself in the opposite direction of a dipole at a position  $-\mathbf{r}$ . Since the minimum-energy, minimum-entropy configuration of the ideal dipoles is one in which they are all parallel, both energy

and entropy must increase when the ion is placed in the center of the cluster. The difference between these quantities results in a slight decrease of the free energy, so that the free energy has its global minimum at the center of the cluster. In region II the system becomes slightly more structure making, with a minimum in the entropy around 5 Å. The free energy, on the other hand, stays constant in this region. In region III the entropy reaches a local maximum (the ion is more structure breaking) and the energy starts to increase, driving a net increase in the free energy. Finally, in region IV, the system becomes more ordered, with a net decrease in entropy and a net increase in energy resulting in a major increase in free energy: surface solvation of the ion is definitely not favored by the SPC/E waters.

Now we consider the behavior of the ion in RPOL waters shown in the bottom panel in Fig. 1. In region I there is a similar behavior to that observed in the SPC/E waters, but the effect is slightly bigger due to the induced dipoles. In region II the ion is more structure making than the ion in SPC/E waters, with a decrease in entropy slightly larger than the decrease in energy, resulting in a slightly positive free energy (in this region the ion is more “hydrophobic”—in relative terms—than it is at  $r=1$  Å). In region III both the energy and entropy decrease considerably, but the energy is dominant resulting in a net decrease of the free energy: surface solvation of the ion is favored by the RPOL waters. Finally region IV shows a net increase in the free energy as the ion starts to cross the surface of the cluster. We observe that in both models, the waters become more ordered (net decrease in entropy) as the ion moves to the surface, although this effect is much larger in the RPOL model due to the induced dipoles. Sometimes the word “freezing” has been used to describe a decrease of both energy and entropy observed in dielectrics. Using the term in this sense, one could say that the RPOL waters experience some sort of relative freezing as the ion moves across region III, due to the simultaneous reduction of energy and entropy. Note that the lower entropy associated with the solvation of hydrophobic solutes has been known for many years and has been ascribed to a local freezing of the water induced by the solute, sometimes known as the iceberg or clathrate effect. One final observation is that in RPOL the surface effects are “deeper”: the main changes in RPOL waters start around 7 Å from the surface while in SPC/E they start at around 6 Å from the surface. The reason for this difference is also an effect of the induced polarization, as will be discussed in the following section.

In Fig. 2 we show the results for  $TS(r)$ ,  $\bar{U}_{\text{tot}}(r)$ , and  $\mathcal{F}(r)$  for the Born model applied to a cluster of 12 Å and an ion radius of 3 Å, with  $T=298$  K,  $\epsilon=78.358$  and  $T\epsilon d\epsilon^{-1}/dT=-1.3679$ . The inset shows the entropy contribution in a smaller scale. Obviously, much of the phenomena described above is not observed in this simple model. The absence of structural effects in the Born model results in an entropic contribution that is way too small and that favors increasing disorder as the ion approaches the surface.

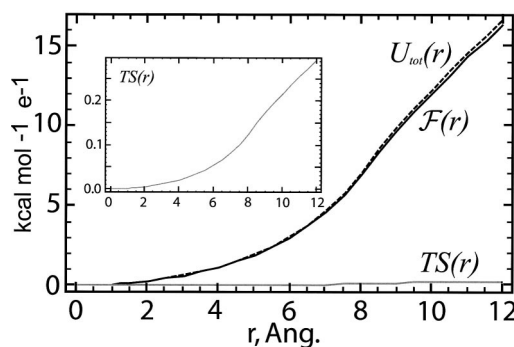


FIG. 2. Born model approximation to the free energy  $\mathcal{F}(r)$  (smooth dark line), internal energy  $\bar{U}_{\text{tot}}(r)$  (dashed line), and entropic contribution  $TS(r)$  (lighter line). The inset shows the entropic contribution in an enlarged scale. The ion is  $\text{Cl}^-$ .

## B. Energy decomposition

Decomposing the total energy into different terms allows for a physical insight into the changes in the system as the ion moves to the surface. In this process, the kinetic degrees of freedom do not change, therefore the change in total energy is equal to the change in average potential energy. In the present water models, contributions to the potential energy come from the charge-charge interactions, the Lennard-Jones, and induced dipoles interactions. An energy decomposition analysis allows for an estimate of the different weights of these contributions, as well as indirect information on structural changes that can be interpreted in terms of order or disorder, from the entropic point of view.

Figure 3 shows the decomposition of the total energy in terms of the different contributions for both RPOL and SPC/E systems. The left panels show the charge contribution  $U_c$  and the Lennard-Jones contribution  $U_{\text{LJ}}$ . The right panels show the induced polarization  $U_{\text{pol}}$  and the total energy  $U_{\text{tot}}$ . The main result of this decomposition is that the contribution of the induced polarization  $U_{\text{pol}}$  (in RPOL) is essential for the correct balance in the total energy. As the ion is displaced to the surface,  $U_{\text{pol}}$  decreases monotonically after  $\approx 5.2$  Å.

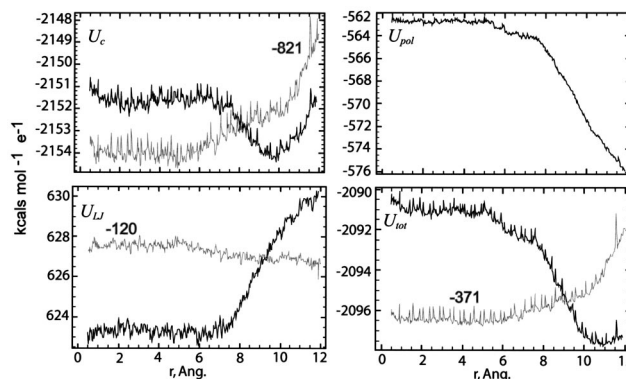


FIG. 3. Total energy components for the RPOL cluster (dark line) and the SPC/E cluster (lighter line). For ease of visualization, the lines representing the SPC/E results have been displaced; the absolute values of the energy can be obtained by adding the numbers indicated in the figures. The energy components shown are the charge-charge interaction energy  $U_c$ , the Lennard-Jones energy  $U_{\text{LJ}}$ , the polarization energy  $U_{\text{pol}}$ , and the total energy  $U_{\text{tot}}$ . The ion is  $\text{Cl}^-$ .



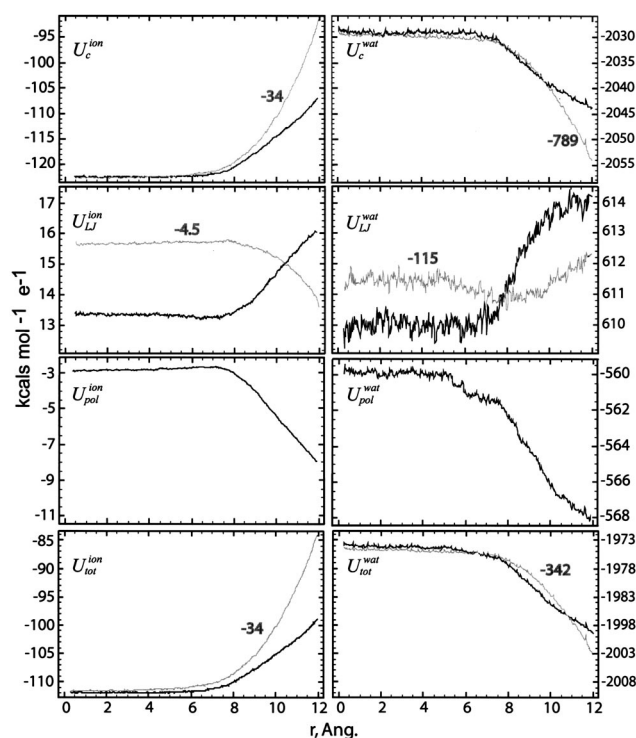


FIG. 4. Energy components for the RPOL cluster (dark line) and the SPC/E cluster (lighter line). The left column represents the “ion-water” terms (see equations and definitions in the text) while the second column represents the “water-water” terms. The ion is  $\text{Cl}^-$ . The energy components shown are the charge-charge interaction energy  $U_c$ , the Lennard-Jones energy  $U_{LJ}$ , the polarization energy  $U_{pol}$ , and the total energy  $U_{tot}$ . For ease of visualization, the lines representing the SPC/E results have been displaced; the absolute values of the energy can be obtained by adding the numbers indicated in the figures.

This means that the polarization starts to feel the effects of the surface before any of the other two contributions  $U_c$  and  $U_{LJ}$ , that only start to vary at about 7 Å. So the induced polarization is not only the main contribution to the total energy but also “feels” the surface before any other interaction. We observed that the decrease in  $U_{pol}$  is produced by both an increase in magnitude and the alignment of the induced dipoles as the ion gets closer to the surface. A comparison with the entropy in Fig. 1 shows a strong correlation between these two quantities: both  $U_{pol}$  and the entropy start to decrease monotonically at around the same distance, plunging down as the ion approaches the surface. The main change in entropy can therefore be interpreted as due to the order imposed by the alignment of the induced dipoles. The alignment results from the dipoles’ mutual interactions and from their interaction with the fixed charges. The general trends in the energies for the SPC/E models, on the other hand, agree better with those in the Born model: the Lennard-Jones contribution is almost constant and the charge electrostatic energy increases as the ion approaches the surface, becoming in this way the dominant contribution to  $U_{tot}$ .

In Fig. 4 we present the results of the energy decomposition in Eqs. (2.1)–(2.4). The left column shows the results for  $\bar{U}^{ion}$  while the right column shows the results for  $\bar{U}^{wat}$ . In all cases, the changes to the corresponding energy com-

ponent start at 6 Å or slightly less from the surface. The exception to this is given by  $\bar{U}_{pol}^{wat}$  which starts to decrease at approximately 7 Å from the surface. Although the water contribution  $\bar{U}_{pol}^{wat} \approx 8$  kcal/mol is larger than the ion polarization  $\bar{U}_{pol}^{ion} \approx 5$  kcal/mol, both contributions can be considered the same order of magnitude. It is interesting to note that the ion total energy  $\bar{U}_{tot}^{ion}$  increases at the surface of the cluster, while the water total energy  $\bar{U}_{tot}^{wat}$  decreases. For more polarizable ions (such as iodide), the ion polarization energy is more significant than for chloride, and the resulting polarization contribution  $\bar{U}_{pol}^{ion}$  may actually be larger than the water contribution  $\bar{U}_{pol}^{wat}$ . Finally, a more accurate treatment of the balance of energies would require a better description of the dispersive and repulsive interactions than that provided by the simple Lennard-Jones potential.

### C. Entropy and probability

Most of the literature results pertaining to ions near water cluster surfaces have been obtained from simulations by simply observing the probability of finding the ion at a certain distance from the interface, or by an analysis of the energy components at zero temperature. Generally, the only statements in the literature about entropy are that it is negligible (an exception to this is to be found in the work by Perera and Berkowitz,<sup>60</sup> where entropy was cited as a possible cause for bulk solvation of the  $\text{F}^-$  anion). Yet, as Fig. 1 shows, the entropic effects are exactly the same order of magnitude as the energy effects, and the claim of “negligible” effects is not right. In spite of this, conclusions based on an energetic analysis are still valid, at least for the type of ions and cluster geometries studied in this work. Here we explain why this is so.

Assume for a moment that entropic effects are indeed negligible. This means that the free energy can be expressed as

$$F(r) = -kT \ln P(r) + C \quad (3.1)$$

$$\approx \bar{U}_{Tot}(r) - kT \ln(4\pi r^2) + C', \quad (3.2)$$

where the second term is simply the entropic contribution due to the change in volume in phase space, and  $C$  and  $C'$  are arbitrary constants. From this expression the probability is obtained as

$$P(r) \approx A 4\pi r^2 \exp[-\beta \bar{U}_{Tot}(r)], \quad (3.3)$$

where  $A$  is a normalization factor.

In Fig. 5 we compare the true probability  $P(r)$  with the results for the approximation given by Eq. (3.3). These probability distributions are for the  $\text{Cl}^-$  ion in the SPC/E water cluster (top panel) and in the RPOL water cluster (bottom panel). What these graphics tell us is that even when the entropic effects are as large as the energy effects, calculating the probability with just the average potential energy gives a reasonable approximation as to where the ion is preferentially located. In other words, for an ion in a cluster a simple energetic analysis is indeed useful for a qualitative prediction of the ion location (which will be close to the minimum of energy). Quantitative results, on the other hand, necessarily



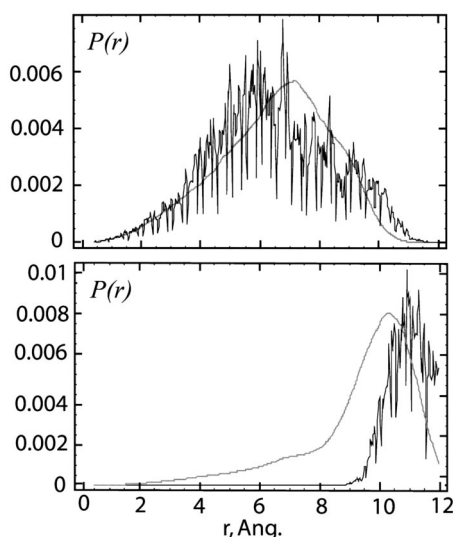


FIG. 5. Exact probability distribution (smooth line) and energy approximation [Eq. (3.3)] to the probability (noisy line) for  $\text{Cl}^-$  in an SPC/E cluster (top panel) and an RPOL cluster (bottom panel).

require to take into account the entropic contributions (which are larger in the polarizable case). The agreement between the preferential ion positions predicted by the approximation in Eq. (3.3) and by the true probability  $P(r)$  is a feature that we have seen systematically for every ion that we have studied.

There are many possible ways to achieve a full decomposition of the free energy. For instance, an analogous decomposition to the one we used for the potential energy has been given by Brady *et al.*<sup>61</sup>

$$\mathcal{F}_j(r) = \frac{1}{\beta} \int_0^\beta \bar{U}_j(r)_\beta d\beta', \quad (3.4)$$

where the index  $j$  runs over all the energy components and  $\bar{U}_j(r)_\beta$  is the average component  $j$  of the internal energy at the temperature  $T = (k\beta)^{-1}$ . In this way each component of the free energy has a natural correspondence to each term in the Hamiltonian. This component analysis can be interpreted as a special thermodynamic integration in which all terms in the interaction energy are turned on simultaneously using  $\beta$  as the coupling parameter. Clearly  $\mathcal{F}_j(r)$  as well as  $\bar{U}_j(r)$  have an implicit dependence on all the other terms of the potential energy. From this expression it is trivial to find an analogous decomposition for the entropy,

$$TS_j(r) = \bar{U}_j(r) - \mathcal{F}_j(r). \quad (3.5)$$

Thus the energy decomposition proposed in the preceding section can be interpreted as an approximation to the free energy components given in Eq. (3.4), where the entropic contributions have been neglected.

#### D. Positive ions

For both continuum dielectric theory and structureless dipolar solvents (such a Stockmayer fluid<sup>62</sup>), solvation effects are independent of the charge sign. However, it has been known for some time that solvation effects in water

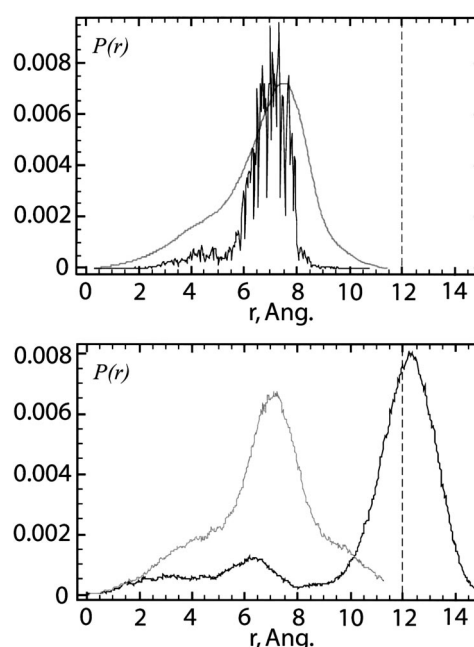


FIG. 6. Top panel: Exact probability distribution (smooth line) and energy approximation [Eq. (3.3)] to the probability (noisy line) for  $\text{Cl}^+$  in an RPOL cluster. Bottom panel: Probability distribution for  $\text{I}^+$  in an SPC/E cluster (lighter line) and an RPOL cluster (darker line).

clusters strongly depend on the charge sign. As an example, Fig. 6 shows the probability distribution  $P(r)$  (and the total energy approximation to the probability) for a positive chloride ion  $\text{Cl}^+$  in the RPOL water cluster. The probability distribution clearly predicts bulk solvation, as opposed to surface solvation of  $\text{Cl}^-$  (compare with Fig. 5). This difference is mainly due to the structure of the water, which affects both the orientation of the water molecule around the ion and the proximity of the water atoms to the ion. Thus, in the first solvation shell around a negative ion, the water molecule orients itself such that the bisector of the angle  $\text{H}-\text{O}-\text{H}$  is more or less perpendicular to the radial direction and one of the water protons can approach the negative ion closely. In the first solvation shell around a positive ion, the water molecule orients itself such that the bisector of the angle  $\text{H}-\text{O}-\text{H}$  is more or less in the radial direction and the water oxygen cannot get as close to the ion. Apart from structural changes, this also results in an interaction of negative ions with the first solvation shell that is stronger than that for positive ions. This asymmetry is reflected in many thermodynamic quantities, such as the ionic charging free energies, whether for ions in SPC/E waters<sup>63</sup> or in RPOL waters.<sup>64</sup>

Studies in the literature<sup>18,65</sup> of positive ions in water clusters have concluded that positive ions stay inside the water cluster. However, in this work we see that polarization is the main cause of surface solvation. Water polarization is present for positive ions so one would expect that some positive ions also be surface solvated. Which ones? The answer is given by studies on negative ions: the small  $\text{F}^-$  ion—unlike  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ —stays inside the cluster. Polarization effects being present, we speculate that the charge-sign asymmetry leads to a requirement of a larger size for the positive ion to be solvated on the surface. This is in fact the case. The

bottom panel of Fig. 6 shows the probability distribution for a positive iodide ion, with the same parameters—except opposite charge—as the iodide ion  $\text{I}^-$ . In the figure we also plot the results for the  $\text{I}^+$  ion in the SPC/E water cluster: again, surface solvation can only be predicted with the use of polarizabilities. For the  $\text{I}^+$  ion in the RPOL waters, the surface polarization is due to the water charge-charge interaction  $\bar{U}_c^{\text{wat}}$  and the water polarization  $\bar{U}_{\text{pol}}^{\text{wat}}$ ; the ion polarization term  $\bar{U}_{\text{pol}}^{\text{ion}}$  does not contribute. These results have practical implications for the solvation of *small* molecular ions with a positive single charge.

### E. Water molecule with small average dipole moment

Most of the water models that include induced polarization effects have a bigger average dipole moment, i.e., RPOL, TIP4P-FQ, TIP5P-FQ, etc.,<sup>37,66,67</sup> than the simple point charge models such as, i.e., SPC/E, TIP3P, TIP4P, etc.<sup>38,68</sup> The higher average dipole moments are closer to what is at present believed to be the dipole moment of water in condensed phase ( $\mu$ ) $\approx$ 2.95 D.<sup>69</sup> Guided by this fact, Stuart and Berne<sup>59</sup> compared several water models to check whether the surface solvation was due to the polarization or to a large total dipole moment. These models included the polarizable TIP4P-FQ model<sup>37</sup> with dipole moment ( $\mu$ ) $\approx$ 2.62 D, the nonpolarizable TIP4P model<sup>38</sup> with dipole moment  $\mu$  $\approx$ 2.18 D, and a “medium charge” MQ model, where the TIP4P charges were increased to the average values of those in TIP4P-FQ. In this way, the *ad hoc* MQ model became a simple-point charge model with a large dipole moment. Polarizable or nonpolarizable  $\text{Cl}^-$  ions were solvated in the different water models. The results were twofold. First, the polarization of the ion itself did not make a difference. Second, the ion was surface solvated for both TIP4P-FQ and MQ, but not for TIP4P. This led Stuart and Berne to conclude that the *large* dipole moment (and not necessarily the polarization) was responsible for surface solvation. This conclusion agrees with the results by Lu and Singer<sup>62</sup> for a Stockmayer fluid. In this fluid, the particles are described by both a Lennard-Jones parametrization and a permanent point dipole. In the present context, the authors found that surface or bulk solvation depend on the relation between the reduced charge of the ion and the reduced dipole model. If the magnitude of the latter is big enough (in relative terms) then the system will favor surface solvation.

Although in general these conclusions are true, water imposes a set of more restrictive conditions. As Stuart and Berne point out, fixed-charge models with large dipoles tend to be too strongly bound and suffer from very slow dynamics, and therefore are not appropriate for a physical description of water. Now we also ask ourselves if it is really true that a *big total* dipole is necessary for surface solvation. What would happen with a model that has *small total* dipole but includes polarization? In order to answer this, we arbitrarily reduced the permanent charges of RPOL, but kept its polarizability. The average dipole moment in this case is ( $\mu$ ) $<$ 2.35 D, smaller than that of SPC/E. Figure 7 shows the results for an  $\text{I}^-$  ion immersed in the “new” model waters. The ion is clearly surface solvated. Notably, the SPC/E

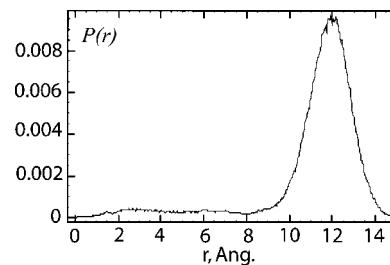


FIG. 7. Probability distribution for  $\text{I}^-$  in a polarizable water model obtained by reducing the charges of the RPOL model, so that the average total dipole moment is smaller than that of the SPC/E model.

model with a larger total average dipole predicts bulk solvation for the same ion. Of course, we do not expect this reduced-charge model to give a very physical representation of water—but neither does MQ. In other words, in the context of ion solvation in “real” water, the polarization of the water, as well as the charge, size, and polarizability of the ion, are the relevant variables to the surface-versus-bulk solvation process.

### IV. CONCLUSIONS

We have reexamined the issue of ion solvation in a water cluster with molecular dynamics simulations to study the structure, dynamic, and thermodynamic properties of ions in water clusters. Considerable attention has been paid to the evaluation of the free energy, internal energy, and entropy. This was accomplished by means of umbrella sampling: the radial coordinate of each 238 water cluster was divided in 20 windows, and for each of the windows statistical data was gathered from 20 independent clusters. All in all, simulations have run for a *cumulative* time greater than 2.2  $\mu\text{s}$ . With these careful simulations we have addressed controversial or unresolved issues, mainly related to the underlying physical cause of the observed phenomena, and the basic assumptions that go with it. Our main conclusions are the following.

(i) *The main cause of surface solvation of a single ion in a spherical water cluster is water and ion polarization, coupled to the charge and size of the ion:* In particular, the contributions of water polarization are of the same order than those from the ion polarization. For  $\text{Cl}^-$ ,  $\bar{U}_{\text{pol}}^{\text{wat}} \approx 1.6 \bar{U}_{\text{pol}}^{\text{ion}}$ ; for ions with larger polarization  $\bar{U}_{\text{pol}}^{\text{ion}}$  may be larger than  $\bar{U}_{\text{pol}}^{\text{wat}}$ . In the past, a *large* total water dipole—whether permanent or having an induced contribution—has been claimed as the physical cause of surface solvation. Although a large permanent water dipole does in fact produce surface solvation, such a representation does not reproduce water properties. Within parameters that make a water model physical it is the induced polarization the physical driving force behind surface polarization. In particular, we showed that a model with an average total dipole smaller than SPC/E but with induced polarization, presents surface solvation, while the simple point charge model does not.

(ii) *The entropic contribution is the same order of magnitude as the energetic contribution:* The role of entropy had not been addressed before or had been deemed negligible. This is perhaps due to the fact that continuum dielectric

theory and studies of infinite clusters of simple models of water, such as SPC/E, predict that the entropic contribution to the free energy is negligible with respect to the energy contribution. However our study shows without a doubt that in a finite cluster the entropic contribution is the same order of magnitude as the energy contribution, and therefore cannot be neglected if one seeks quantitative results.

(iii) *A pure energetic analysis can give a qualitative description of the ion position at room temperature:* Although the entropic effects play a very important role, one can still make a pure internal energy analysis to understand *qualitatively* the different physical contributions to ion solvation at room temperature. This is because the probability distribution computed from the average internal energy has its maximum at the same point or very near to the maximum of the exact probability derived from the free energy. One can therefore study the changes of the different components of the energy as the ion approaches the cluster surface.

(iv) *Large positive ions (larger than the monoatomic species) can also be surface solvated:* This size dependence is also found in negative ions: small fluoride stays inside the cluster and larger halides go to the surface. Much larger positive ions, however, are needed for surface solvation. This due to the asymmetry that manifests itself not only in the order of the water molecules around the ion in the first and second solvation shells but also in the fact that the water hydrogens are closer to the negative ions than the water oxygens with respect to the positive ions. Many thermodynamic quantities, such as ionic charging free energies, reflect this asymmetry.<sup>63,70,64</sup> In our work, a large positive iodinelike ion preferred surface solvation in the polarizable water cluster, but not in the nonpolarizable cluster.

## ACKNOWLEDGMENTS

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