Exploring the behaviour of the hydrated excess proton at hydrophobic interfaces

Revati Kumar,\textsuperscript{ab} Chris Knight\textsuperscript{ab} and Gregory A. Voth\textsuperscript{*ab}

Received 13th May 2013, Accepted 24th June 2013
DOI: 10.1039/c3fd00087g

The affinity of the excess proton for the aqueous solution–hydrophobic interface was examined for two specific examples, the air–water and hydrophobic wall–water cases, using a multiconfigurational molecular dynamics algorithm. The use of a reactive simulation method is important as it allows for a realistic description of the excess proton, namely, its propensity to hop between water molecules via the Grotthuss mechanism. The free energy profile reveals a minimum at these interfaces due to a favourable enthalpic term that outweighs the entropic penalty. The key factors that contribute to this enthalpic minimum were examined using a generalization of a scheme that decomposes the interaction energy into separate terms arising from various local environments [Otten et al., \textit{Proc. Natl. Acad. Sci. USA}, 109, 701 (2012)] (coordination shell, bulk, and interface) and the delocalization energy (which allows the proton to hop). For both systems, it was observed that the energetic penalty for loss of coordinating water molecules as the excess proton moves toward the hydrophobic interface is more than compensated by the displacement of unfavourable interfacial water molecules. In addition, the ion becomes more delocalized, more Zundel-like, and therefore possesses a larger effective radius as it moves to the interface. The fluctuations of the instantaneous interface were reduced near the vicinity of the ion, thereby giving rise to an entropic penalty. This paper will discuss the application of energy decomposition schemes to multiconfigurational simulations and the resulting consequences realized for the excess proton at hydrophobic interfaces.

1. Introduction

The presence of hydrated excess protons at the air–water interface has been the subject of intense debate with a renewed enthusiasm towards the topic in recent years.\textsuperscript{1–17} The general consensus, based on both experimental and computer simulation studies, is that common cations prefer to remain in the bulk while large “floppy” anions tend towards the interface.\textsuperscript{5} However, vibrational sum
frequency generation as well as resonance enhanced second harmonic generation spectroscopy, both surface sensitive experiments, suggest the presence of the excess protons and not hydroxide ions at these interfaces.\textsuperscript{4,7,10} These latter results have been further validated by heterodyne-detected electronic sum frequency spectroscopy, which suggests that the pH of the surface is lower than that of the bulk by around 1.7.\textsuperscript{15} This is to be contrasted with another set of experiments, electrophoretic experiments on water bubbles, which suggest the presence of a negative charge at this interface, possibly arising from the presence of the hydroxide ion.\textsuperscript{18} In a recent study Colussi \textit{et al.} looked at the deprotonation of gaseous carboxylic acid (RCOOH) on the air–water interface using electrospray ionization mass spectrometry experiments.\textsuperscript{19} The results of their limited quantum calculations on water clusters suggested that the kinetic barrier for the deprotonation is very high unless OH\textsuperscript{−} was present. They thus concluded that the detection of RCOO\textsuperscript{−} in the interfacial region was due to the presence of OH\textsuperscript{−} ions. Despite the general trends that several common ions seem to suggest, the deceptively simple hydrated proton and hydroxide ions appear to create their own set of controversies.

Computer simulations of the hydrated excess proton are complicated by the so called “Grotthuss” shuttling, wherein the proton hops between neighbouring water molecules.\textsuperscript{20,21} Conventional molecular dynamics (MD) force fields assume a constant chemical bonding topology throughout a simulation and do not allow for changes in bond topology, which automatically preclude their use in modelling proton transfer reactions and other chemical reactions without some significant modification. More advanced MD simulations, such as those calculating the electronic structure and hence the forces on the nuclei “on-the-fly” as in \textit{ab initio} molecular dynamics (AIMD),\textsuperscript{22} do not presume a molecular topology and explicitly treat the electronic degrees of freedom. Thus, they are a natural choice for modelling reactive processes and have been used to investigate the excess proton and hydroxide at the air–water interface.\textsuperscript{8,23,24} However, due to their demanding computational cost, these AIMD simulations are currently limited in the amount of statistical sampling that can be achieved with respect to both temporal and spatial scales, as well as by the accuracy of the underlying electronic underlying density functional theory (DFT) and basis sets used in these methods. At a slightly reduced computational cost, hybrid quantum mechanical/molecular mechanics (QM/MM)\textsuperscript{25,26} simulations can be used to model the reactive species within a QM region that is embedded within a larger nonreactive MM environment.\textsuperscript{14} Owing to the rather high diffusion rate of the excess proton, from the proton hopping along water hydrogen \textit{via} the Grotthuss mechanism, QM/MM methods would be difficult to apply to hydrated protons or hydroxide anions because a fixed QM region is typically assumed throughout the calculation. This limitation of QM/MM calculations has been addressed with the recent development of methods to deal with the swapping of identities of species between QM and MM subsystems, but it remains to be seen if these methods are appropriate for proton transport processes.\textsuperscript{27–29}

A computationally efficient method for treating the hydrated proton and hydroxide ions must treat the dynamic bond making and breaking within a region of interest, whilst leaving the remaining “spectator” region modelling with a simpler MM force field. The collection of multiconfigurational MD methods is one class of algorithms that possess these general features.\textsuperscript{30–42} These algorithms
model a system as a linear combination of physically relevant chemical bonding topologies. For the subset of multiconfigurational MD methods, the bonding topologies are chosen “on-the-fly” over the course of a simulation in response to changes in the environment. Voth and coworkers have successfully used these latter methods to study proton transport in a myriad of condensed phase systems, including aqueous systems and proteins. A more detailed review of this reactive simulation methodology is presented elsewhere and the reader is referred to the appropriate references for further details.

In a previous study using our multi-state empirical valence bond (MS-EVB) version of the multiconfigurational MD methods (specifically the MS-EVB model), Iuchi et al. calculated the free energy profile for bringing the hydrated excess proton to both the air–water and a hydrophobic wall–water interface. Their results showed a minimum at the interface for both cases, and the subsequent decomposition of the free energy revealed an entropic penalty compensated for by a large favourable enthalpic contribution at the interface. The preference for the hydrated proton at the interface was also observed in path integral MD simulation reported in that work where nuclear quantum effects were explicitly included. However, the underlying mechanism for the hydrated proton’s attraction to the interface remains to be analysed through a more detailed theoretical picture. Another MD study using an explicitly polarizable version of the MS-EVB model of the proton did not show a free energy minimum at the air–water interface, while an AIMD study showed a minimum of a depth of around 1.3 kcal mol⁻¹ at the interface, in general agreement with the simulations of Iuchi et al. Interestingly in the case of the polarizable model mentioned above, a minimum in the free energy was observed at the interface when the polarizability was turned off. (It should be noted that the MS-EVB model is already polarizable in the hydrated proton complex, so the addition of additional electronic polarizability runs the risk of overpolarizing the complex and thus leading to an oversolvation of it by the water solvent around it, as seen in the simulations of Wick. This behaviour affects the propensity for the hydrated proton to be near the interface relative to the bulk.)

A number of simulation studies have also been carried out to determine the presence of simple monoatomic ions at the air–water interface. Otten et al. have shown that in the case of the iodide ion the enthalpic behaviour at the interface is dominated by two competing effects – the penalty imposed by losing energetically favourable solvent molecules when the ion is brought to the surface and the gain due to the displacement of higher energy interfacial water molecules. With an appropriate and non-trivial modification, this type of local energy decomposition scheme can prove particularly useful to examine the case of hydrated excess protons at the interface, but first, the scheme requires a generalization to account for the delocalized nature of the electronic charge defect associated with the hydrated proton. The present work provides such a generalization with an application to the hydrated excess proton. In turn, it is shown to provide a deeper analysis of the origin of the thermodynamic forces driving the hydrated proton to the air–water and hydrophobic interfaces, while also unravelling the competition between enthalpy and entropy at such interfaces. Interestingly, with this generalization the simple picture of Otten et al. is still seen to hold, although key differences do exist due to the delocalized nature of the excess proton charge defect.
In the next section, the computational methods employed in this work will be discussed, including a generalization of the energy decomposition scheme to multi-state reactive MD algorithms. The results from the reactive simulations and subsequent energy decomposition will be described in section 3. This is followed by a discussion of the results before concluding with a summary in the last section.

2. Methods and computation

As stated earlier, the modelling of a delocalized charge defect, such as the excess proton, can be challenging to accurately describe in a computationally efficient manner. This is largely due to the fact that the proton can readily shuttle between water molecules that are hydrogen-bonded (H-bond) to one another. Thus, the net positive charge density of the excess proton is actually delocalized over several nearby solvating water molecules instead of being localized at a single point in space. This has the consequence that transport of the excess proton involves the coordinated rearrangement of several water molecules. Additionally, this diffusion process involves principally two components (hopping and vehicular) with separate timescales, both of which are coupled to the dynamics of the surrounding H-bond network.

Multiconfigurational MD methods have been successful in their application to proton (and hydroxide ion) solvation and transport in aqueous, biological, and materials systems. In the MS-EVB class of methods, a quantum-like Hamiltonian matrix is constructed and evaluated at each step in the simulation. The dimension of this Hamiltonian dynamically changes over the course of the simulation depending on how many reactant molecules are proximal to an initial reactive species. The initial reactive molecules and surrounding reactant molecules form the reactive complex, within which, the bonding topology is variable. Outside this reactive complex, the remainder of the system, the environment, is modelled using a single bonding topology. The diagonal elements of this Hamiltonian matrix correspond to distinct bonding topologies resulting from chemical reactions between proximal reactant molecules, such as a proton hopping to a nearby water molecule. The likelihood for a successful reaction is then a function of the off-diagonal couplings between diabatic states and environmental influences that may modulate the reaction barriers. These multistate methodologies are somewhat similar in spirit to the QM/MM class of methods. However, instead of explicitly treating the electronic degrees of freedom using an expensive QM method for the reactive portion of the system, the Hamiltonian matrix elements are typically modelled using MM-type expressions for reasons of computational efficiency. This is not a limitation of the multistate methods and in fact, if one chose to, the electronic degrees of freedom could be explicitly retained and the multi-state Hamiltonian matrix elements evaluated using QM approaches. Once the Hamiltonian matrix has been evaluated and diagonalized, the ground state eigenvector is used with the Hellmann–Feynman theorem to obtain atomic forces. Once the total forces on all atoms are known, then an MD simulation would proceed as normal and integrate Newton’s equations of motion to propagate the system. Additional details describing these methodologies can be found in ref. 32, 36, 37, and 42.
For the reactive simulations discussed here, the MS-EVB3 model\textsuperscript{37} was used to describe the hydrated proton at two types of interfaces: the air–water and the air–hydrophobic wall.\textsuperscript{11} This model for the hydrated proton was primarily chosen to facilitate the comparison with previous work, and in fact, has been shown to yield results in good agreement with a similar model explicitly derived from AIMD simulations.\textsuperscript{52} The air–water interface was modelled in these simulations as a water slab, with vacuum on either side along the z-axis, consisting of 998 water molecules and an excess proton in a periodic box of dimensions $31.07 \times 31.07 \times 100 \,\text{Å}$. Thus, the pH of the system was effectively equal to 1.3. The water molecules were modelled using the simple point charge flexible (SPC/Fw) water model,\textsuperscript{53} as utilized in the MS-EVB3 model. In a second set of simulations having the same number of water molecules, a rigid atomistic hydrophobic wall consisting of carbon atoms arranged in a graphene-like lattice was used with Lennard Jones interactions parameters $\sigma = 3.8 \,\text{Å}$ and $\varepsilon = 0.1051 \,\text{kcal mol}^{-1}$ defined between wall particles and oxygen atoms. The system dimensions for this system were $31.93 \times 31.90 \times 100 \,\text{Å}$ with the walls centred at $z = 0.0$ and $z = 36.0 \,\text{Å}$.

All MS-EVB simulations were calculated using a modified version of the LAMMPS MD code.\textsuperscript{54} Unless otherwise stated, the Particle–Particle–Particle Mesh (PPPM) method with a precision of $10^{-5}$ was used for long-range electrostatic interactions. The equations of motion were integrated with a 1.0 fs timestep in the constant NVT ensemble at 300 K using the Nose–Hoover thermostat with a relaxation time of 0.05 ps. The potential of mean force (PMF) for moving the excess proton towards the interface was calculated using the umbrella sampling\textsuperscript{55} method, with a total of 11 windows evenly spaced between 5.0 and 15.0 Å from the centre of the water slab. The harmonic force constant for each of the bias potential in each window was 5 kcal mol$^{-1}$ Å$^{-1}$. The umbrella sampling collective variable was defined to be the distance, in the z-direction, between the centre of mass of the system and the hydrated proton centre of excess charge (CEC). Since the identity of the excess proton continuously changes over the course of an MS-EVB simulation, the CEC coordinate ($r_{\text{CEC}}$)\textsuperscript{11,37} is a convenient coordinate that allows one to continuously track the reactive species (proton) during the simulation. This coordinate is defined as

$$r_{\text{CEC}} = \sum_i c_i^2 r_{i,\text{COC}}$$

where $c_i^2$ is the square of the ground state eigenvector coefficient of the $i^{th}$ diabatic state and $r_{i,\text{COC}}$ is the centre of charge coordinate for each diabatic state in the MS-EVB matrix, which mostly corresponds to the hydronium oxygen atom in each state. More specifically, the z component of this CEC coordinate was used as the definition of the collective variable. The potentials of mean force were constructed from the umbrella sampling data using the weighted histogram analysis method (WHAM).\textsuperscript{56} In order to decompose the free energy, eqn (2) below, into entropic, $-T\Delta S(z)$, and enthalpic, $\Delta U(z)$, contributions, additional PMFs were calculated at two new temperatures (280 K and 320 K for the air–water case and 320 K and 340 K for the wall–water case). The set of PMFs at three different temperatures were then used in a finite difference approach to extract the two contributions as well as estimate the statistical errors:\textsuperscript{11}

$$\Delta F(z) = \Delta U(z) - T\Delta S(z)$$
2.1 Local energy decomposition scheme (enthalpy)

For the case of a single simple monoatomic ion in a slab of water with vacuum on either side, it was recently found that the total energy of the system is well approximated by a sum of interactions that are local in their nature. Using this local decomposition scheme as proposed by Otten et al., the total energy is decomposed into contributions due to solvent molecules that are coordinating the ion, the bulk water molecules, and the interfacial water molecules. If the ion is at a distance \( z \) from the interface, the total energy can be approximated as \( U_{\text{local}}(z) \), which is defined to be

\[
U_{\text{local}}(z) = E_{c}n_{c}(z) + E_{b}n_{b}(z) + E_{i}n_{i}(z),
\]

(3)

where \( E_{c} \) is the average energy of a water molecule coordinating the ion, \( E_{b} \) is the average energy of a water molecule in the bulk (but not coordinated to the ion), and \( E_{i} \) the average energy of an interfacial water molecule (not coordinated to the ion). The three average interaction energies \( (E_{b}, E_{c}, \text{and } E_{i}) \) are calculated from molecular simulations when the ion is in the bulk. Each of these energies can be further decomposed into contributions arising from water–water and water–ion interactions. After these energies have been determined, one simply has to count the number of water molecules in the interfacial \( (n_{i}) \), bulk \( (n_{b}) \), and coordination shell \( (n_{c}) \) subsystems and then use eqn (3) to calculate the energy (enthalpy) when the ion is at a distance \( z \) from the interface. For the simple case of the iodide ion, Otten et al. obtained quantitative agreement between the local approximation to the total energy and the true enthalpy extracted from their simulations. The advantage of this local scheme is that it allows one to study the effect of various interactions on the enthalpy.

For the case of the hydrated excess proton, however, the situation is more complicated because one is no longer dealing with a monoatomic spherical species, but also because the hydrated proton is delocalized charge defect spanning several water molecules. In the original decomposition scheme, the energy quantities \( E_{x} \) were given by the relations

\[
E_{x} = \frac{1}{2} \left< E_{\text{water–water}} \right>_{x} + \left< E_{\text{water–ion}} \right>_{x},
\]

(4)

where \( E_{\text{water–water}} \) and \( E_{\text{ion–water}} \) are the average interaction energies between water–water and water–ion pairs, respectively, in the region \( x \) (bulk, coordination shell, or interface). For the case of the hydrated proton as described by MS-EVB simulations, it is necessary to recast each contribution as a weighted averaged over the diabatic states sampled in a reactive simulation so as to incorporate the delocalization of the charged defect. The generalization of these terms is given in eqn (5) as summations over MS-EVB states and the corresponding interaction energy for the \( i \)th state, given by

\[
\left< E_{\text{ion–water}} \right> = \sum_{i=1}^{m} c_{i}^{2} E_{i}^{\text{ion–water}} \quad \text{and} \quad \left< E_{\text{water–water}} \right> = \sum_{i=1}^{m} c_{i}^{2} E_{i}^{\text{water–water}}
\]

(5)

The weights in these terms are the ground state MS-EVB eigenvector coefficients, \( c_{i}^{2} \). Reasonable convergence of the quantities in eqn (5) does not require a complete summation over MS-EVB states. It was found to be satisfactory for the summation to instead be taken over only those \( m \) states with the largest amplitudes with \( m \).
chosen to be 4. In bulk water simulations with the MS-EVB3 model for the excess proton, the total number of states at any point in the simulation typically exceeds 20, although usually no more than a few at a given time dominate the behaviour. While most of these MS-EVB states are crucially important to include in the energy/force calculations to properly conserve constants of motion during the simulation, the results of this post-processing procedure are not significantly altered when additional states are included. Physically, these 4 dominant states mostly correspond to a reactive complex involving those water molecules that accept strong H-bonds from the hydronium cation when in Eigen-type (H9O4+) configurations and during proton hopping events when the structure of the proton more closely resembles that of the Zundel ion (H5O2+).

So far, the discussion has focused only on the contributions to the local energy approximation from the diagonal elements of the MS-EVB Hamiltonian matrix. Since it is only possible in this multistate reactive MD algorithm for chemical reactions to occur when the off-diagonal couplings are nonzero, eqn (3) needs to be supplemented with an appropriate contribution from the off-diagonal matrix elements. This correction takes the form of the average off-diagonal energy, $U_{\text{off-d}}(z)$, when the ion is at a particular distance $z$ from the interface and can be extracted from simulations. The resulting final expression for the local approximation to the ion total energy is

$$U_{\text{local}} = E_{c}n_{c}(z) + E_{b}n_{b}(z) + E_{i}n_{i}(z) + U_{\text{off-d}} \quad (6)$$

### 2.2 Instantaneous interface surface fluctuations (entropy)

Unlike the case of enthalpy, which can be decomposed into a series of terms accounting for different interactions, it is not possible to straightforwardly decompose the entropic contribution to the free energy in a similar manner. However, the fluctuations of the instantaneous interface can provide useful information to help elucidate the origins of the entropic behavior of ions near the interface. In order to construct this instantaneous interface, the coarse-grained density field approach of Willard and Chandler can be employed. Briefly, at every oxygen position in the simulation cell, a Gaussian function whose width is one water molecular diameter is added to give rise to a smooth “density field”. The instantaneous interfacial surface is then defined as the surface for which this coarse-grained density is equal to half of the bulk value. For a more detailed discussion, the reader is directed to the original paper. The quantity of interest to be extracted from this instantaneous surface is the average fluctuation of this surface as a function of radial distance from the ion, when the ion is at the interface, and is defined as follows

$$\partial h(r_{p}) = h(r_{p}) - \langle h(r_{p}) \rangle \quad (7)$$

where $h(r_{p})$ is the vertical height of the instantaneous surface at a radial distance, $r_{p}$, from the ion. If $\langle \partial h(0)^{2} \rangle$ (i.e., average fluctuation at the vicinity of the ion) is smaller than the corresponding value at large $r_{p}$, then it implies that the ion is pinning the nearby instantaneous interface, thus giving rise to an entropic penalty. The smaller the value at $r_{p} = 0$, the greater the pinning, and hence the entropic penalty.
Therefore, the ratio of $\langle \delta h(r_p)^2 \rangle$ to the value at large $r_p$, $\langle h(r_L)^2 \rangle$, proves to be a useful measure to study the effect of the ion on the instantaneous interface and provides information regarding entropic contributions to the free energy.

3. Results and discussion

3.1 Free energy profile

It will prove useful in later discussions to partition the water slab structure into distinct regions. Based on the equilibrium structure of the water slab, these regions can be straightforwardly identified upon examination of the average water density as a function of distance from the centre of mass (COM) of the system. This distribution is plotted in the inset of Fig. 1 with the density normalized to the density of bulk water at ambient conditions. From this plot, it is clear that the water slab is mostly bulk-like up to 12.0 Å before density-depletion is observed near the air–water interface. Based on this density profile, the interfacial region can be divided into 3 parts: an inner interface from 11.0 to 12.5 Å with water density close to that of the bulk, a middle region from 12.5 to 14.0 Å where the density first starts to decrease, and an outer region that extends beyond 14.0 Å into the vacuum.

The free energy profile (Fig. 1) for the excess proton shows a well depth of 1.8 kcal mol$^{-1}$ at a separation of around 15.0 Å from the slab COM. The minimum is located just after the onset of the outer interfacial region where the water density has already dropped to less than half of the bulk value. As expected, this result is in agreement with previous, separate reports that used MS-EVB3 to study the water–air interface. By analysing the enthalpic and entropic contributions that arise from the finite difference decomposition of the PMF at 300 K, it is revealed that the enthalpic contribution favors the interface and more than compensates for the entropic penalty. The corresponding maximum and minimum of the individual contributions are located at separations just below 15.0 Å from the slab COM, which is closer to the location at which the slab water

![Fig. 1](https://example.com/fig1.png)

Fig. 1 Free energy profile of the hydrated excess proton for the air–water case along with the decomposition into enthalpic and entropic terms from eqn (2). The inset shows the average water density for the air–water system as a function of distance from the centre of mass.
density is half of the bulk value. These results are again in good agreement with previous work on decomposing the PMF for the proton at the air–water interface,$^{11}$ thus confirming the reproducibility of results from this reactive simulation methodology produced using completely separate software packages.

Similar results are also observed for the case of the hydrophobic wall (Fig. 2). With the presence of the wall, the deviations in the water density from bulk values are more pronounced with clear evidence of water layering adjacent to the wall with the two peaks near 11.0 and 14.0 Å. The effects of the hydrophobic wall are even observed at short separations (~5–7 Å) from the slab COM, where no such deviations from the bulk density are apparent. Despite this apparent difference in the interfacial structure of the water slab near the hydrophobic wall compared to that of the air–water interface, there is still a minimum in the hydrated proton PMF located near the position of the first water layer. The depth of this free energy well is 2.0 kcal mol$^{-1}$, which is slightly larger than the value observed for the air–water interface, but the two values are still within statistical error of one another. The enthalpic and entropic contributions resulting from the decomposition of the PMF are similar in structure to the curves obtained for the air–water interface, through the magnitude of the change is smaller, despite the similarity of the well-depths of the PMFs. For example, the entropic barrier for the air–water system has a maximum near 7.5 kcal mol$^{-1}$ while the same curve for the hydrophobic interface only rises up to 1.5 kcal mol$^{-1}$. Similar to the air–water interface, there is a pronounced decrease in magnitude for both decomposed curves resulting in the PMF having a value of nearly zero only a few Angströms away from the interface.

### 3.2 Local energy decomposition

Attention now turns to the main thrust of this paper, which is to address the question of whether a complex charged defect, such as the hydrated excess proton, can be effectively modelled using a short-ranged decomposition of the
total energy. Using the results from reactive MS-EVB simulations at 300 K in which the ion was constrained to be near the centre of mass of the system, the average water–water and water–ion energies were calculated for both the air–water and wall–water systems using the multistate generalized expressions for the interaction energies, eqn (5). The resulting energy contributions (water–water and ion–water) are shown in Fig. 3 as contour plots for both systems. Along the y-axis is the vertical distance \((r_z)\) of a water molecule from the slab COM, while the x-axis for each contour plot indicates the radial distance from the ion in the plane parallel to the interface. In each plot, the hydrated excess proton is located in the middle of the slab (bulk region) with the interfaces found at the top and bottom of each plot. The water–water and ion–water energies are shown in Fig. 3a and b, respectively, for the case of the air–water interface. It is clear from these figures that there exists an obvious division of the system into a coordination shell region (of about 5 Å) surrounding the ion, a bulk region, and an interfacial region (around \(z = \pm 13\)). The wall–water interface shows a similar trend (Fig. 3c and d) with essentially the same scale of energies. The average energy in each of the three regions was determined from the MS-EVB simulation.

The average number of water molecules in each region as a function of the distance \((z)\) of the ion from the centre of mass was calculated from the different umbrella sampling simulations, as was the average off-diagonal energy. Using eqn (6) the energy of moving the ion from the bulk to the interface was constructed (Fig. 4). For both systems, a substantial drop in enthalpy is observed with the minimum located at the interface in both instances, albeit at the inner interface rather than the outer interface. For both systems, the decrease in enthalpy is roughly equivalent at 6 kcal mol\(^{-1}\), while the position of the minimum

![Fig. 3](image-url)  
*Fig. 3*  
a) Water–water interaction energy (in kcal mol\(^{-1}\)) for the air–water case as a function of radial distance from the ion \((r_p)\) which is at the origin and the vertical distance from the center of mass \((r_z)\). b) Shows the water–ion interaction energy (in kcal mol\(^{-1}\)) for the air–water case as a function of \(r_p\) and \(r_z\). c) and d) Plots of the water–water and water–ion interaction energies, respectively, for the wall–water case.
would appear to be shifted towards the inner interfacial region. While there is a steep enthalpic penalty for bringing the ion close to the hydrophobic wall near 15.0 Å, similar to the case for the PMF decomposition in Fig. 2, the same curve for the air–water interface is presumably tending towards zero.

The water molecules in the ion coordination shell are energetically more favourable by around 2.5 kcal mol$^{-1}$ compared to those water molecules in the bulk for both the wall and air cases. On the other hand, the interfacial water molecules are energetically less stable than the bulk by approximately 1.5 kcal mol$^{-1}$ for the air case and around 1.0 kcal mol$^{-1}$ for the wall case. As one moves to the interface, energetically favourable coordinating waters are removed, but so are energetically unfavourable interfacial waters. The excess proton retains a large portion of its coordination shell as it moves to the interface, while at the same displacing unfavourable interfacial waters, which then results in an enthalpic minimum (attraction) at the interface.

Interestingly, the average off-diagonal energy is more favourable by 1.5 kcal mol$^{-1}$ at the outer interface compared to bulk for the air–water case. The off-diagonal energy is a measure of the delocalization of the net positive charge defect of the hydrated proton ion and the more negative value at the interface suggests the presence of a more delocalized and hence larger effective ion. In Fig. 5, the distribution of the largest EVB state amplitude, $c_1$, obtained from the ground state MS-EVB eigenvector at each step in the simulation is plotted for the air–water interface. When this weight is close to 0.5, it indicates that the system is in a predominantly Zundel state, i.e. a state in which the excess proton is shared equally between two adjacent water molecules as opposed to the Eigen state around 0.6 in which case the proton is predominantly on the central water (hydronium cation). As the ion moves through the interface, the fraction of Zundel species increases, which is consistent with the more favourable off-diagonal energy.

For the wall–water case (see Fig. 6) the fraction of Zundel species first increases as the ion moves through the interface, but decreases at the outer interface. The comparison of the distribution at the outer interface for the air–water and

![Fig. 4](image-url) Local energy for the air and wall interfaces.
wall–water cases (see Fig. 7) shows that the fraction of Zundel species is smaller for the wall–water case implying that the hydrated excess proton ion at the wall–water interface is effectively “smaller” than in the air–water case.

The local energy scheme assumes that the radius used to define the coordination shell does not change as it moves to the interface. This is clearly not the case for the hydrated excess proton. Secondly, in the case of a complex ion like the excess proton where specific H-bonds are part of the solvation shell, spherical symmetry is a crude approximation, especially when the ion is at the interface. In addition, only intermolecular interaction energies were considered and the effect of moving the ion to the interface on the intramolecular geometry of the ion as well as the coordinating water molecules was not considered. Lastly, the repulsive effect of the hydrophobic wall on the interaction energy was ignored. Despite these approximations, the local scheme does help identify the key interactions that cause the large enthalpic minimum at the interface.
3.3 Instantaneous interface

The average fluctuation of the instantaneous interface at \( z = 14 \, \text{Å} \) as a function of radial distance from the ion and normalized to the value far away from the ion is shown in Fig. 8 for both types of interfaces. The fluctuations near the ion are much smaller for the air–water case, indicating the pinning of the interface and hence the high entropic penalty. On the other hand, for the wall case, the fluctuations near the ion are not dampened as much, which is consistent with the smaller value of the unfavourable entropic contribution. The hydrophobic wall dampens overall the fluctuations at the interface. In addition to this, the effective size of the ion in the wall case is smaller and therefore should exhibit less pinning. These two effects clearly contribute to the entropic behaviour near the wall.

![Fig. 7](image1.png)

**Fig. 7** Normalized probability distribution of the largest MS-EVB coefficient weight for the air–water and wall–water cases at the outer interface.

![Fig. 8](image2.png)

**Fig. 8** The fluctuations of the instantaneous interfacial surface as a function of radial distance away from the ion, when the ion is at the outer interface. The inset shows the instantaneous surface (blue) for the air–water case with the ion (green) and the water oxygen atoms (red).
The simple model of two competing terms, the loss of favourable coordinating water molecules versus the gain in favourable energy due to displacement of interfacial waters, does explain the overall trend in the enthalpy profile near the interface. However, this analysis is further complicated by the delocalization of the excess proton charge defect and the change in this delocalization as the ion moves to the interface. The hydrated proton ion gets effectively larger as it moves to the hydrophobic interface and this is more pronounced for the air–water case. This does suggest that rather than the sign of the charge, it is instead the ratio of the absolute value of the charge divided by the effective ion radius that governs the presence of ions at the aqueous–hydrophobic interface. The excess proton is effectively a large ion and therefore moves to the interface. This same effectively large ion pins the instantaneous surface near it, resulting in an unfavourable entropic term near the interface.

4. Conclusions

The free energy profile for moving the hydrated excess proton close to two different hydrophobic interfaces, the air–water and hydrophobic wall–water interfaces, was calculated using a reactive MD simulation methodology. For both cases, a minimum in the free energy was found with a depth of approximately 2 kcal mol$^{-1}$. The enthalpic contribution to the free energy shows a clear minimum at the interface, which more than compensates for the entropic penalty. A scheme for decomposing the total energy into a sum of short-ranged interactions was generalized for the case of MS-EVB simulations. The terms arising in this scheme from the coordination environment of the excess proton, the bulk, and the interface along with a correction for the charge defect delocalization energy yielded a minimum at both interfaces of similar depths. Through analysis of the individual terms in the energy decomposition, it was found that the minimum arises from the displacement of unfavourable interfacial water molecules as the ion moves towards the interface, and this outweighs the energy cost from the loss of favourable coordinating water molecules. In addition, the hydrated proton ion effectively gets larger as it moves towards the interface. The ion pins the water molecules near it, thereby decreasing the fluctuations of the instantaneous interfacial surface in its vicinity, which in turn contributes to the entropic penalty near the interface. This effect is significantly reduced for the hydrophobic wall interface. It will be very interesting to compare these results with those obtained from a similar analysis for the hydroxide ion near interfaces in order to rationalize the various results coming from the experimental studies.

Acknowledgements

This research was supported in part by the National Science Foundation (NSF grant CHE-1214087). The computations in this work utilized the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575, with an allocation of time on TACC computing resources. The computations were also supported in part by a grant of computer time from the DOD High Performance Computing Modernization Program at the Air Force and Navy DOD Supercomputing Resource Centres.
Notes and references


