Hydration of ions in two-dimensional water

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We present a two-dimensional lattice model of water to study the effects of ion hydration on the properties of water. We map the water molecules as lattice particles consisting of a single oxygen atom at the center of a site and two hydrogen atoms on each side. The internal state of the system, such as the dipole moment at a site, is defined with respect to the location of the hydrogen atoms at the site depending on their role in hydrogen bonds (H bonds) being a donor or an acceptor. We study the influence of the charge and the radius of the ion on the insertion energy and on the H bonds in the first and second hydration layers around the ion and in the bulk. In particular we analyze how the competing interactions of the short-ranged H bonds and the long-ranged electrostatics influence the hydration properties. The role of the ion both as a source of the electrostatic interactions as well as a defect is also discussed. Our model also shows the well-known fact that the polarizability of the water molecules destroys the hydrogen bond network and increases the dipole moment of the molecules near the ion.

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I. INTRODUCTION

Interactions of ions with water form an important component of all biological and chemical systems [1]. Ions change the solubility of proteins and nucleic acids in water. This in turn changes their folding, permeation, and self-assembly properties [2]. In chemical systems they change the rate of reactions, and in physics they change not only the static properties but also the dynamic properties such as diffusion and transport coefficients. This in turn changes the rheology and hydrodynamics of water molecules [3]. Hydration of ions is a vast field that has been studied extensively through experiments and theories [4,5].

Ions not only modify the structure and the orientations of the water molecules through the long-ranged electrostatic forces, they help in making or breaking of the short-ranged H bonding, especially the first hydration shell [5–7]. Introducing an ion in the solution changes the existing structure of the H-bond network as the water molecules reorient themselves and break the H bonds with mostly their nearest neighbors, and sometimes with their second-nearest neighbors. Beyond the hydration layer of the ions, the electric field is screened by the dielectric constant $\epsilon$. Several experiments, such as infrared and Raman spectroscopic measurements, neutron diffraction spectroscopy, and x-ray absorption spectroscopy have been performed to investigate the effect of the ions on the H-bond network [8]. Simulations of water may be more tractable to observe the detail of the H-bond structure [9]. But the simulation results depend strongly on the water model used. Many of the results from these experiments and simulations contradict each other. Theoretical modeling of water can capture the underlying physics of the ion hydration and is essential to understand their effects on the water structure. Lynden-Bell and Rasaiah [10] developed a method to determine thermodynamic properties of hydrated solutions by treating the charge and the size of the ions as dynamical variables. Using this method they could move smoothly from hydrophilic to hydrophobic solvation conditions. Classical density functional theory (DFT) and integral equation theories have also been employed in the literature to study water properties [11,12]. However, most of these theories can not predict the details of the H-bonding structure due to the complexity of the orientation-dependent interactions. Collins [13] suggested that hydration effects on water can be described by a competition between the ion-water electrostatic interactions and the water-water H-bonding interactions. Hribar et al. [14] used a two-dimensional (2D) MB water model [15] to model ion solvation in water. They take into account the electrostatics of the ion solution by treating the water molecules as dipoles and the H bonds as short-ranged Gaussian bonds. Their model predicts that the H bonds break more easily for smaller ions than larger ones.

Indeed, to understand the ion-specific effect, we have to consider the complexity of the ionic water, in which the rather long-ranged Coulomb interaction is in a subtle balance with the short-ranged H bond attraction. The structural change due to the introduction of the ion should be fully considered in order to reflect this subtle change. The simplest way to consider the structure is to construct a lattice model of water [16]. In this work, we develop a lattice-based water model in two dimensions, with the water molecules located at the sites of a square lattice. Each oxygen at a site has four subsites, of which two are occupied by hydrogen atoms as shown in Fig. 1. We disregard the case when the hydrogen atoms are situated opposite to each other. Thus, each water molecule has a 90° structure. Since the water molecules are fixed at a given position our model has two kinds of interactions: the long-ranged electrostatic ion-water interactions and the orientational correlations caused by the H bonding. The location of the hydrogen atoms at a water site with respect to the oxygen is described using the Ising states. The short-ranged H bonds are

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then described by the nearest-neighbor interactions and the ion-water interactions by the monopole-dipole electrostatic interactions. Lattice models in one dimension have been successfully applied to water problems before in Refs. [17–20] to describe water defects in nanowires. However, in one dimension the angular structure of water is missing, and the competing effect between different interactions disappears, and hence it is not suitable for hydration shell study. Two dimensions are the minimal dimensions that contain these effects. In Sec. II, using the 2D Ising Hamiltonian, we calculate the number of H bonds, which is a good measure of network dimension. The insertion energy and the average orientation of the water molecules in each site and four sites, two of which are occupied by hydrogen atoms (blue dots) and the other two are unoccupied. Also shown are the two interactions, the repulsive $R$ interactions and the attractive H bonding interactions $\epsilon_H$.

![2D lattice model for water with an ion](image)

FIG. 1. (Color online) 2D lattice model for water with an ion at the center. Each lattice site has one oxygen atom at the center and four sites, two of which are occupied by hydrogen atoms (blue dots) and the other two are unoccupied. Also shown are the two interactions, the repulsive $R$ interactions and the attractive H bonding interactions $\epsilon_H$.

The dimensionless Hamiltonian of the system is

$$
\beta H_N = \frac{\epsilon_H}{2} \sum_{i,j} (\sigma_{i,j}^x \sigma_{i,j}^y + 1) + \frac{R}{2} \sum_{i,j} (\sigma_{i+1,j}^y \sigma_{i,j}^x - 1) + \frac{\epsilon_H}{2} \sum_{i,j} (\sigma_{i,j+1}^y \sigma_{i,j}^x + 1)
$$

$$
+ \frac{R}{2} \sum_{i,j} (\sigma_{i,j+1}^y \sigma_{i,j}^x - 1) - \sum_{i,j} \frac{\Gamma}{(i - N/2)^2 + |j - N/2|^2} \left( |i - N/2| \sigma_{i,j}^x + |j - N/2| \sigma_{i,j}^y \right)
$$

$$
= J/2 \sum_{i,j} (\sigma_{i+1,j}^x \sigma_{i,j}^y + \sigma_{i,j+1}^x \sigma_{i,j}^y) - \sum_{i,j} \Gamma (g_x(i,j) \sigma_{i,j}^x + g_y(i,j) \sigma_{i,j}^y) + N^2(\epsilon_H - R),
$$

(2)
We define an insertion energy as the energy difference to add an ion to the water with respect to the bulk water energy. The more negative the insertion energy of the ion is, the more likely it is for the ion to dissolve into the water. Close to the ion, the insertion energy at each site depends strongly on the radius of the ion, $r_0$ and the strength of the ion potential as shown in Fig. 3. At distances further from the ion, this energy goes to zero as expected. In this work we only consider dimensionless quantities. The energies are scaled with respect to $k_B T$, the distances such as the ion–water distance $r$ and the radius of the ion $r_0$ with respect to the lattice constant, which is $3$ Å in our model and the temperature is scaled with respect to the room temperature $298$ K. When the ion strength (charge) is weak and low temperatures favor the alignment of the water dipoles as shown in Figs. 3(a) and 3(b).

The number of H bonds at a given site $(i, j)$ in our model is counted by the formula

$$n_H = \frac{\sigma_{x,i,j}^x}{2} (\sigma_{i-1,j}^x + \sigma_{i+1,j}^x) + \frac{\sigma_{y,i,j}^y}{2} (\sigma_{i,j-1}^y + \sigma_{i,j+1}^y) + 2. \tag{3}$$

It is known that the number of H bonds (the extent of H bonds) has been regarded as a measure that represents the structural properties well [5]. We find from our lattice model that the nearest shell of the ion has a lower number of H bonds than that of the bulk water. While the next immediate layer has a higher number of H bonds than that of the bulk. This can be understood from the fact that we get the highest number of H bonds when the water dipoles are aligned along a specific direction. This is because of our definition of H bonds in Eq. (3) as the orientational correlations. Although the first layer has a lower number of H bonds due to the strong directional force from the ion and the deficit of bonding sites due to the presence of the ion, the H bond at the next sites can be even larger because the alignment of the hydrogens in first layer acts as a biased boundary condition to the second layer. Our simple model captures this effect as shown in Figs. 4(a) and 4(b).

Because of the excluded volume of the ion there is no H bond inside the ion radius. The second water layer has the highest number of H bonds as shown by the slight bump in the plot. From Figs. 4(a) and 4(b) we see that larger ion
charge and smaller ion size would produce more H bonds. To test our theory we perform molecular dynamics simulations in AMBER with POL3 water model. We consider three kinds of ions, sodium, potassium, and calcium, with a very dilute concentration of 1 M dissolved in 890 water molecules. We have performed NPT simulations at 300 K and pressure 1.01325 bar. After energy minimization, we ran the simulations for 10.320 ns for the system to equilibrate. We have plotted our data for the number of H bonds vs the distance from the ions (sodium, potassium, or calcium) in Figs. 4(c) and 4(d). In our simulation two water molecules are considered to be H bonded if the shortest distance between an oxygen in one molecule and a hydrogen in the other molecule is less than a cutoff distance. In Fig. 4(c), the cutoff is chosen to be 1.97 Å and in Fig. 4(d) 3.5 Å. From the simulations we find that second shell has a higher number of H bonds compared to the first shell as obtained from the theory. Na\(^+\) and K\(^+\) have the same valence but ionic radius of K\(^+\) is 1.3 times that of Na\(^+\). On the other hand Ca\(^{2+}\) and Na\(^{2+}\) have almost the same ionic radius but valence of Ca\(^{2+}\) is twice of Na\(^+\). For this reason the ion-water interaction in the first shell is weaker for K\(^+\) than Na\(^+\), which leads to the more H bonds at the first shell. But, the differences in their second or third shells are not significant. In contrast, the number of H bonds in the first shell is almost the same for Na\(^+\) and Ca\(^{2+}\) in spite of their difference in valence (their ionic radii are almost the same). However, there is a substantial difference in H bonds at their second shells. Not only is the number of the H bonds in the second shell larger for Ca\(^{2+}\), but also the shell is sharper due to the stronger H-bond network. The stronger network for the second shell is coming from the first shell configuration, which is supposed to be more biased for Ca\(^{2+}\) because of the stronger ion-water interaction at first shell. (Because the ion-water interaction decreases as fast as distance, their contribution at the second shell is much smaller than the interaction strength of the H bonds.) This behavior is also seen in Fig. 4(a) where increasing \(\Gamma\) increases the H bonds in the second shell more significantly than the first shell.

We can obtain a mean-field (MF) estimate of the number of H bonds at a given site from formula (3). Mean field involves replacing a quantity by its corresponding mean and neglecting correlations. In this way we get a contribution of \(\frac{1}{2}(\langle \sigma_i \rangle \langle \sigma_j \rangle + 1)\) to \(n_H\) for each of the nearest neighbors from Eq. (3). The MF solution of the average dipole moment at a distance \(r\) from the ion is given by the well-known mean-field solution from Ising model \(\langle \sigma(r) \rangle = \tanh[\langle \sigma(r) \rangle + g(r)]\), where \(g(r) \sim -\frac{1}{r^2}(1 - e^{-x^2/\lambda^2})\) is the ion-dipole interaction at a temperature \(T\). To first-order approximation in the MF limit the number of H bonds becomes \(n_H(r) \approx \tanh[\langle \sigma(r) \rangle + g(r)]\). Figure 5(a) shows the behavior of the H bonds in MF as a function of distance at various temperatures. At very low temperatures all the water dipoles are aligned and H bonded. The maximum number of H bonds at a given site is four. As we lower the temperature the orientation correlations become lower and the number of H bonds decreases. Figure 5(b) shows the number of H bonds in bulk at each site and as is well known it goes down with temperature. Figure 5(c) captures the mean-field limit of the orientational (dipole) order at various temperatures.
FIG. 5. (Color online) Mean-field predictions of (a) the number of H bonds, $n_H(r)$, as a function of the distances from the ion at different temperatures. (b) Number of H bonds in bulk at different temperatures. (c) The dipole moment at a site as a function of the distances from the ion at different temperatures.

IV. HYDRATION: CATION VS ANION

Unlike the classical uniform dielectric model, the hydration effect depends on the sign of the ion because the water molecule is an asymmetric dipole. In Eq. (2) the Hamiltonian cannot differentiate between the positive and negative charges of the ion as it depends on the magnitude of $\Gamma$, the strength of the ion not its sign. So we modify the ion-water interactions to consider the ion-oxygen and ion-hydrogen interactions separately. Thus the total Hamiltonian becomes

$$H_N = \frac{J}{2} \sum_{i,j} (\sigma_{i,j}^x \sigma_{i,j+1}^x + \sigma_{i,j}^y \sigma_{i,j+1}^y) + \sum_{i,j} \frac{\Gamma}{2} \sqrt{(i+\sigma_{i,j}^x b \text{ sgn}(i-N/2)-N/2)^2 + (j-N/2)^2}$$

$$+ \sum_{i,j} \frac{\Gamma}{2} \sqrt{(i-N/2)^2 + (j+\sigma_{i,j}^y b \text{ sgn}(j-N/2)-N/2)^2} - \sum_{i,j} \frac{\Gamma}{2} \sqrt{(i-N/2)^2 + (j-N/2)^2} + N^2(\epsilon_H - R)$$

with $J = \epsilon_H + R$ and $b$ is the distance between the oxygen and hydrogen atoms in each water molecule.

We see from Fig. 6(a) that anions have a higher number of H bonds and degree of orientation order than cations of same radius and charge. Also the insertion energy is lower for anions than cations; as a result anions are strongly hydrated compared to cations. The general behavior agrees with Ref. [13]. In Ref. [13] this results from the quantum-mechanical effect for which the effective interaction between the anion and hydrogen bond is stronger than between the cation and oxygen. In our model, this is because of the asymmetry between positive and negative charges within the water molecule. In this respect it is quite similar to the mechanism described in Ref. [10] where the outermost location of the positive charges in the water molecules allows them easily to be closer to the anions than the negative oxygen site to the cations.

V. HYDRATION SHELLS VS $\Gamma$ AND RADIUS OF THE ION

At a given temperature, increasing the charge on the ion has different effects on the H-bond network for smaller or larger ions. Figure 7 shows that the H bonds for the first nearest neighbors (1NN), second neighbors (2NN), and bulk are affected differently as we change the charge of the ion through $\Gamma$. For the ion of radius zero (point charge) in Fig. 7(a), the decrease in 1NN H bonds at low-$\Gamma$ values corresponds to the reorientation of the water molecules resulting in the breaking of the preexisting H bonds. As we increase $\Gamma$ further they start forming H bonds in the direction of the ions. For the next-nearest neighbors, the first layer acts like a biased boundary condition, and it is easier to establish the H bond with the first layer. As a result, the number of H bonds at this layer is larger than that in bulk. The bulk layers are not affected by the ion. Figure 7(b) shows that the influence of ions on the
first water layer is different from the second layer. There is a strong influence on the H-bond network in the first layer regardless of the strength of the Coulomb interaction \( \Gamma \). This decreases slightly on increasing \( \Gamma \) because the strong ordering due to the ion can lead to strong H bonding between the first layer and the second layer. This can be seen as an increase in the H bonds in 2NN. When \( \Gamma \) is small, which corresponds to small valency or large effective size of the ion, there is no influence to the 2NN. This is consistent with the experiments [5]. Larger \( \Gamma \), which corresponds to the larger valency of the ion or polarizability, induces stronger a H-bond network in 2NN. This is highly correlated with the increase in the number of H bonds in 1NN as we noted. Our simulation results in Fig. 4(c) agree with our findings in Fig. 7(b). For the first shell the number of H bonds for Ca\(^{2+}\) is almost the same with Na\(^{+}\), similar to the slight increase in number of 1NN H bonds with \( \Gamma \) in Fig. 7(b). The rate of increase in H bonding vs \( \Gamma \) is sharper for 2NN in Fig. 4(c), where the number of H bonds is appreciably higher in the second shell in Ca\(^{2+}\) than in Na\(^{+}\).

The insertion energy becomes more and more negative as we increase the \( \Gamma \) as shown in Fig. 8(a), thus it is easier to hydrate highly charged ions compared to weakly charged ions. The figure also shows that it harder to hydrate larger ions. Smaller ion size and larger ion charge increases the orientational order of the water molecules as shown in Fig. 8(b).

Ions affect the water properties in two different ways: as a defect to create cavity and as a source of electrostatic potential. Figure 9 shows the two effects separately. Figure 9(a) is for the case when the ion has no electrostatic interaction, i.e., it acts as a defect. A very small defect doesn’t make any difference to the H-bond structure. Larger defects decrease the number of H bonds in 1NN because of the reduction in H-bonding sites due to the defect. Interestingly, the number of H bonds for 2NN has a very weak dependence on the radius of the ion once the electrostatic interactions are switched off. This means that the overshooting of H bonds in 2NN in Fig. 4 compared to the bulk is consequence of the electrostatic interactions via modifying the configuration of the water at 1NN. Comparison with Fig. 9(b) shows that electrostatic interactions increase the number of H bonds in 2NN. On increasing the radius of the ion, the number of H bonds converges to bulk value, which confirms the idea that the larger H bond in 2NN is a combined result of the biased network in 1NN from the electrostatic interactions. Thus, for large ions the role of the ion as a defect has a stronger influence on the water properties than the electrostatic interactions. Since in our definition the number of H bonds is measured by the orientational correlations, as the ion radius increases the number of effective neighbors for the first two water layers decreases and hence \( n_H \) decreases. Simulation results for K\(^{+}\) and Na\(^{+}\) in Fig. 4(c) support this.
VI. POLARIZABILITY

One interesting property of water is the polarizability of the water molecules, which distorts the charge distribution of the water molecules in presence of ions. As reported in some references the polarization effect is crucial to the specific ion effect [21,22]. Depending on the consideration of the polarizability of the ions themselves the trend of the specific ion effect can be opposite. Here we investigate how the polarizability of water molecules influences our model. The polarization induces a dipole moment in the water molecules proportional to the electric field of the ion in addition to the permanent dipole moment of the water molecules. To include the effects of polarizability, we modify the strength of the interactions between the water molecules at site \((i,j)\) in Eq. (2) by \(J_x(i,j) = J + \alpha_x g_x(i,j)\) and \(J_y(i,j) = J + \alpha_y g_y(i,j).\) \(\alpha_x\) and \(\alpha_y\) are the polarizations along the \(x\) and \(y\) directions, respectively. For simplicity we assume isotropic polarizations \(\alpha_x = \alpha_y = \alpha.\) From Fig. 11(a) we see that the hydrogen bonds per site decrease on increasing the polarization of the water molecules. It indicates that the polarization-induced dipolar interactions are dominant over the energy of H-bond network at short distances, especially at low temperatures. At high temperatures the hydrogen bonds per site converges to the nonpolarizable model at large distance quickly. In Fig. 11(b) we plot the total dipole moment of the water molecules at different temperatures and polarizabilities. Increasing the polarizability increases the total dipole moment compared to the unpolarized case which corresponds to the bare permanent dipole moment case.

VII. CONCLUSIONS AND DISCUSSIONS

We present a simple lattice model of water based on a 2D Ising model to capture the competing interactions of the short-ranged H bonds and the long-ranged electrostatic interactions in the presence of an ion. This simple model can explain many conjectures, and experimental results about the hydration effect, especially on the stability of H bonds near the ions [5,13]. Our formalism explains qualitatively the dependence of the hydration properties of ion charge and radius, the role of the ion in breaking of the H-bond network and finally the differences between the hydration of cations and anions. We do not consider the dependence of the coordination number on the distance between the ion and the water molecules or the translational entropy of the water molecules.
The angular distribution is also discretized, and because of this the competition between H-bond and dipolar order is not well included. This can be improved in a 3D lattice model. We also omitted quantum effects, which could be important to the many-body interactions in water. In spite of these weaknesses, our model gives intuition for the very complicated effects of ion hydration. Its strength lies in its simplicity and extensibility. We can extend it to other many-body systems, or three dimensions in a straightforward way, although obtaining an analytic solution would not be easy. We also can consider the proton hopping and the ionization or deionization of water molecules, which is very important in many systems. It can be also applied to the study of the overlapping of hydration layer and their cooperativity. These are topics for future work.

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