Pairwise-additive force fields for selected aqueous monovalent ions from adaptive force matching

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Simple non-polarizable potentials were developed for Na^+ , K^+ , Cl^- , and Br^- using the adaptive force matching (AFM) method with *ab initio* MP2 method as reference. Our MP2-AFM force field predicts the solvation free energies of the four salts formed by the ions with an error of no more than 5%. Other properties such as the ion-water radial distribution functions, first solvation shell water tilt angle distributions, ion diffusion constants, concentration dependent diffusion constant of water, and concentration dependent surface tension of the solutions were calculated with this potential. Very good agreement was achieved for these properties. In particular, the diffusion constants of the ions are within 6% of experimental measurements. The model predicts bromide to be enriched at the interface in the 1.6M KBr solution but predicts the ion to be repelled for the surface at lower concentration. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935599>]

I. INTRODUCTION

Ion-water interactions play an important role in many industrial and environmental processes. Minor differences in ion sizes lead to surprising selectivity of trans-membrane ion channels in biological systems.¹ Solvation and surface specificity of ions strongly influence aerosol chemistry.² It has been argued that the Hofmeister series are strongly influenced by ion solvation structures and free energies.^{3–5}

Simulations play an indispensable role in understanding ion solvation and interactions with other molecules.^{6–8} Many potentials have been developed for modeling the solvation of ions. The majority of these models are point charge based potentials,^{9–11} although some recent models include terms describing polarization¹² and charge transfer.¹³ Although a few models were parameterized based on solid state properties of salts,^{14,15} the majority of the models are designed to reproduce the hydration free energies^{10–12,16} of the ions in a certain water model.

However, there are uncertainties in the experimental solvation free energies of single ions. These quantities cannot be measured directly in a solution and ambiguity arises when a reference, typically chosen to be the hydronium, is used. Rather than fitting hydration free energies, it will be desirable to develop ion potentials using only electronic structure information as Refs. 17 and 18. In this work, we will develop potentials for several monovalent ions, namely, Na^+ , K^+ , Cl^- , and Br^- using the adaptive force matching (AFM) procedure published previously in our group.^{19–22}

Although the importance of polarizable ion potentials has been widely accepted,^{23,24} in this work, we will restrict ourselves to pairwise additive potentials that use point charges to account for polarization effects implicitly. The creation of a polarizable potential is on our priority list; however, a point charge based model is much more computationally efficient

and allows for larger systems to be simulated on current generation computational hardware.

Solvation free energies directly influence the solubility and reactivity of salts and ions. The ability of a model potential to properly predict the solvation free energy is an important check for the usefulness of the potential. Although the experimental solvation free energy of ions has significant uncertainty, the solvation free energy of salts can be determined reliably. A substantial difference in solvation free energy of salts surely indicates a problem with the potential. It will be shown that our ion-water potentials correctly reproduce experimental solvation free energies for the salts. The error is less than one percent for both potassium salts and less than 5% for the sodium salts.

In this paper, the details of the AFM procedure for the ion force field development are reported in Section II, along with some discussions of the challenges in the application of AFM to ions. The properties of the solvated ions according to our AFM potential are reported in Section III; summary and conclusion are provided in Section IV.

II. DEVELOPMENT OF THE ION-WATER FORCE FIELD

A. Adaptive force matching

The adaptive force matching method was used to determine the ion-water and ion-ion potential parameters. Details of the AFM method have been reported previously.^{19,21,25} A brief summary of AFM will be provided below.

AFM is an iterative force field development protocol. Each iteration of AFM is composed of three steps: the sampling step, the quantum mechanics (QM) and molecular mechanics (MM) step, and the fitting step. In the sampling step, a guess force field is used to sample the region of phase space the target force field is designed to model. In the QM/MM step, electronic structure forces are calculated on the QM atoms for configurations collected in

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the sampling step; and the MM part of the QM/MM is modeled using the guess force field. In the fitting step, the force field is reparameterized using the electronic structure forces from the QM/MM calculations as reference. The force field created in the fitting step is then used as the guess force field for another iteration of AFM. Typically several AFM iterations are run until force field parameters or key properties from simulations converge. Additional iterations of AFM can be run after convergence and the reference forces from all converged iterations are fitted together in a global fit to reduce the error bar of the final parameters.

B. Choice of the water model

In this work, the BLYPSP-4F potential will be used to model water.²⁵ BLYPSP-4F was optimized with AFM to model liquid water in the temperature range from 0 to 40 °C. This model was created by fitting to coupled-cluster quality forces obtained using the density functional theory supplemental potential (DFT-SP) approach.^{26,27}

BLYPSP-4F is a flexible 4-site model with positive charges on the hydrogen atoms and the negative charge on the virtual site M. The parameters of the BLYPSP-4F model have been published previously and are summarized in Table I for convenience. Several liquid properties, such as the heat of vaporization, Radial Distribution Function (RDF), diffusion constant, and freezing temperature, have been reported previously for the BLYPSP-4F model and were found to be in very good agreement with experimental values.^{28,29} Notably at 300 K, the BLYPSP-4F model produces a surface tension of 68.6 mN/m and a dielectric constant of 76.4 in good agreement with the experimental values of 71.99 mN/m and 78.41, respectively. These properties are expected to be important for modeling the surface propensity of ions in water.

C. Ion-water model development

In this work, only the ion-water and ion-ion parameters are determined by AFM. The initial guess parameters for the ions were borrowed from the Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) force field.³⁰ The initial guess for the ion-water cross-terms was obtained using the geometric combination rules assuming water having TIP4P parameters.³¹ We note that the combination rules are only used for the initial guess and the final AFM force field does not rely on any combination rules for cross-terms.

The ion-water and ion-ion parameters were determined in separate AFM runs to minimize the computational cost of the sampling step and the QM/MM calculations. First, the ion-water parameters were determined, one separate AFM run for each ion. The ion-ion parameters were determined after all the ion-water parameters had been fit.

For the determination of the ion-water parameters, the sampling was accomplished by molecular dynamics (MD) simulations at 300 K with one ion in 1000 water molecules. The simulations were performed with the Nosé-Hoover thermostat^{32,33} and Parrinello-Rahman barostat^{34,35} with a time step of 0.5 fs. The electrostatic interactions were treated with the particle mesh Ewald method.³⁶ A total of 5 ns of sampling were performed for each generation of AFM. 100 equally spaced conformations were extracted from the final 2 ns of the MD trajectory and used as the training set.

For each configuration in the training set, a QM region is identified using the following procedure:

- The ion of interest will be the center of the QM region.
- All water molecules within an R_{cut} of the ion will be included in the QM region. They will be referred to as the first solvation shell water molecules.
- Randomly pick one molecule, W_A , from the first solvation shell water molecules. W_A and all the water molecules within 2.6 Å of W_A will be included in the QM region.

TABLE I. The parameters of the BLYPSP-4F water model.²⁵

Term	Formula	Parameters
Coulombic	$U = \frac{q_i q_j}{4\pi\epsilon r}$	$q_H = 0.6645 e$ $q_M = -1.3290 e$
Virtual site	$\vec{r}_{OM} = a(\vec{r}_{OH1} + \vec{r}_{OH2})$	$a = 0.2$
Intermolecular O-O	$U_{OO} = A_{OO}\exp(-\alpha r_{OO}) - \frac{C_{OO}}{r_{OO}^6}$	$\alpha = 4.055 \text{ \AA}^{-1}$ $A_{OO} = 210.710 \times 10^3 \text{ kcal/mol}$ $C_{OO} = 610.578 \text{ \AA}^6 \text{ kcal/mol}$
Intermolecular H-M	$U_{HM} = \begin{cases} \frac{A_4}{r_{HM}^4} - \frac{A_4}{r_c^4} + \frac{4(r-r_c)}{r_c^5} & r \leq r_c \\ 0 & r > r_c \end{cases}$	$r_c = 2.483 \text{ \AA}$ $A_4 = 81.489 \text{ \AA}^4 \text{ kcal/mol}$
O-H bond	$U = \frac{k_2}{2}(r-r_e)^2 + \frac{k_3}{3}(r-r_e)^3 + \frac{k_4}{4}(r-r_e)^4$	$r_e = 0.951 \text{ \AA}$ $k_2 = 1255.19 \text{ \AA}^{-2} \text{ kcal/mol}$ $k_3 = 4503.57 \text{ \AA}^{-3} \text{ kcal/mol}$ $k_4 = 7020.31 \text{ \AA}^{-4} \text{ kcal/mol}$
H-O-H angle	$U = \frac{1}{2}k_\theta(\theta - \theta_e)^2$	$\theta_e = 106.678^\circ$ $k_\theta = 82.658 \text{ rad}^{-2} \text{ kcal/mol}$

- (d) Randomly select a molecule, W_B , from the subset of water molecules that are within 2.6 Å of W_A but is not a first solvation shell water molecule of the ion. All the water molecules within 2.6 Å of W_B will be included in the QM region.
- (e) Include water molecules that are closest to the ion until a total of 20 water molecules are included in the QM region.

In the above procedure, 2.6 Å was determined previously to be the distance beyond which approximating quantum water as molecular mechanics point charges no longer introduces substantial errors.²¹

In AFM, only molecules sufficiently distant from the QM/MM boundary are used for fitting. These molecules are assigned a solvation factor of one according to the objective function published previously.²¹ The procedure described above will ensure the ion, one first solvation shell water molecule, W_A , and one second solvation shell water molecule, W_B , be sufficiently away from the QM/MM boundary and thus being fit. Any other water molecules that do not have a MM atom within 2.6 Å will also be fit. Water molecules that have MM atoms within 2.6 Å will be assigned a solvation factor of zero and will not contribute to the objective function being optimized at the fitting step.²¹

After step (d) above, the number of water molecules in the QM region varies from 18 to 20 depending on the configuration. The purpose of step e is to make all QM regions the same size so that all the QM/MM calculations take approximately the same amount of time.

In this work, an R_{cut} of 3.5 Å was used for all cations and 4.0 Å all anions. The QM region identification procedure is not very sensitive to the choice of R_{cut} since the thickness of each solvation shell is more than 2.0 Å by itself. In general, we anticipate the location of the first minimum of the ion-water-oxygen RDF to be a good approximation for R_{cut} .

After the QM region is identified, QM/MM calculations are performed including all the remaining water molecules in the MM region. Rather than using the periodic boundary condition, the MM region is truncated, keeping only the nearest image atoms from the ion. The truncation of an infinite periodic system to the nearest image is not expected to cause systematic errors since the same truncated MM conformations are used when performing the fit. Thus, the error introduced by the truncation cancels.

The QM/MM calculations were performed using the GAMESS code version 1 MAY 2013.³⁷ The MP2 method³⁸ was used to treat the QM region with Columbic embedding of the MM charges. The aug-cc-pVTZ-df basis set was used on all the atoms being fit, except K^+ . The aug-cc-pVDZ basis set^{39–41} was used on all the atoms at QM/MM boundary. The aug-cc-pVTZ-df basis set was constructed by removing the d functions on the hydrogen atoms and the f functions on the other atoms in the aug-cc-pVTZ basis set^{39,40} to reduce the computational cost. We had used this basis set in several of our past calculations and the error on forces introduced by removing the highest angular moment functions is negligible. The 6-311G(2df,2pd) basis set⁴² was used for K^+ since the aug-cc-pVTZ basis set is not available for this element.

The frozen core approximation was used for the MP2 calculations.⁴³ For Na^+ , only the 1s orbital is frozen; for K^+ and Cl^- , the first two principal quantum shells were frozen; the first three complete shells were frozen for Br^- . It is worth noting that GAMESS by default regards both the first and second shells of Na^+ as core levels; only valence orbitals in water are correlated for the Na^+ -water QM/MM calculations. As will be discussed below, MP2 reference forces with the larger frozen core are also used for developing parameters for Na^+ and the results are reported as $Na(lc)^+$. The difference between the two frozen core approximations is fairly large and warrants additional study.

Several possible choices for the energy expressions for the ion-water and ion-ion potentials have been explored. Any additional term in the energy expression will necessarily reduce the root mean square error (RMSE) of forces. However, if a new term only improves RMSE marginally, one would risk overfitting. We require each new term to reduce the force RMSE by at least two percent to be included in the final expression.

In this work, the interaction between the ion and each water molecule is described by

$$U_{\text{ion-water}} = q_{\text{ion}} \sum_j^{\text{water}} \frac{q_j}{r_{\text{ion},j}} + U_{\text{ion-O}}(r_{\text{ion-O}}) + \sum_{\text{oc}}^{\text{water}} U_{\text{ion-oc}}(r_{\text{ion-oc}}), \quad (1)$$

where q_{ion} is the charge of the ion, $r_{\text{ion},j}$ is the distance between the ion and site j of water with charge q_j . In Eq. (1),

$$U_{\text{ion-O}}(r) = Ae^{-\alpha r} - C_6/r^6 \quad (2)$$

is a Buckingham potential between the ion and the water oxygen separated by a distance r .

The ion and the site carrying the opposite charge in water tend to get close to each other due to electrostatic attraction. A point charge model has a singularity at zero separation and tends to over-estimate the attraction at short distances.²⁰ The last term in Eq. (1),

$$U_{\text{ion-oc}}(r) = Be^{-\beta r}, \quad (3)$$

is used to improve the representation of steric repulsion at short distances between the ion and the site in water carrying opposite charges, where $r_{\text{ion-oc}}$ is the distance. For anions, the sum in Eq. (1) is over the two positively charged hydrogen atoms; for cations, only a single term between the ion and the negatively charged M site remains.

When we fit Eq. (1) with AFM, large C_6 values were obtained suggesting a strong attraction with a distance-dependence the same as the leading term in dispersion. For example, the C_6 between Cl^- and water oxygen was 4552.7 Å⁶ kcal/mol and that for Br^- and water was 4633.2 Å⁶ kcal/mol. In order to check whether the large C_6 is physical, symmetry adapted perturbation theory (SAPT) calculations^{44,45} were performed to obtain the “exact” dispersion contribution the C_6 term is designed to model.

The SAPT E2 dispersion energies for Cl^- -water and Br^- -water in the distance range from 3 to 10 Å are shown

FIG. 1. SAPT E2 dispersion energy for Cl^- -water (a) and Br^- -water (b). The red dash and blue solid lines are fit to the short range (3-5 Å) and long range (7-10 Å) of the SAPT dispersion, respectively.

in Figure 1. Considering the presence of an anion, the E2 dispersion was confirmed to be accurate with Coupled Cluster (CC)-SAPT calculations⁴⁶ at a few selected distances. To our surprise, the E2 dispersion deviates from a simple $1/r^6$ behavior, showing stronger distance dependence at separations less than 7 Å. The stronger distance dependence most likely reflects contributions from higher order dispersion interactions.

Fitting the E2 dispersion from 3 to 5 Å to $-C_6/r^6$ results in a C_6 of 4171.2 Å⁶ kcal/mol for Cl^- -water and 5266.5 Å⁶ kcal/mol for Br^- -water. Considering the QM-region in the training set oversamples shorter ion-water separations, the AFM C_6 is actually in fair agreement with a direct fit to SAPT. It is, however, important for the C_6 term in the force field to have the correct asymptotic behavior, which is challenging to achieve without significantly increasing the size of the QM region. Therefore, in this work, we will determine the ion-oxygen C_6 by fitting to the SAPT E2 dispersion in the distance range from 7 to 10 Å where the dispersion shows approximately a $1/r^6$ dependence.

After the C_6 parameters are determined by fitting to the long-range tail of the SAPT E2 dispersion, other parameters are determined by minimizing the objective function in AFM. Of all the parameters for each ion, only the two exponents α

and β are nonlinear. The non-linear parameters were optimized with the simplex method; and the linear parameters were determined with singular value decomposition (SVD) at each vertex of the simplex.⁴⁷

In the fitting step, we used the previously published objective function,

$$\chi^2 = \sum_i w_i (F_i^{\text{ref}} - F_i^{\text{fit}})^2 + \sum_i w_i (\tau_i^{\text{ref}} - \tau_i^{\text{fit}})^2 + \lambda \sum_{\mu} \left(\sum_{\nu} n_{\nu} q_{\mu\nu} \right)^2, \quad (4)$$

where w_i are the weighting factors for net forces and torques, λ is the weighting factor for the charge constraint. Details of the choice of the weighting factor can be found in our previous publications.¹⁹

When the parameters were fitted for each ion independently, the ion charges were close but not identical. For example, when comparing only the magnitudes, the largest partial charge was $-0.822 e$ for Br^- , and the smallest is $0.753 e$ for Na^+ . If the cations and anions have different partial charges, a simulation box containing the salt will not be neutral. In order to avoid the need of a neutralizing background, the magnitude of the charges was constrained to the average of the magnitudes of all four ion charges. This results in a charge of $0.804 e$ for the cations and $-0.804 e$ for the anions. It has been argued that the atomic charges in a non-polarizable model should be scaled by $\sqrt{1/\epsilon_{el}}$, where ϵ_{el} is the high frequency optical dielectric constant.⁴⁸ For liquid water, the ϵ_{el} is 1.78,⁴⁹ which leads to an estimated ion charge of $0.75 e$. This is close to the charge magnitude obtained by AFM.

For each ion, at least 5 generations of AFM were performed without constraining charges. The final 3 generations of AFM were fit with the charge constraint and the SAPT C_6 parameter. The final parameters from the global fit are summarized in Table II.

D. Ion-ion parameters

The ion-ion parameters were determined after the ion-water terms had been fitted. Parameters for 8 different ion pairs Na^+-Na^+ , Na^+-Cl^- , Na^+-Br^- , K^+-K^+ , K^+-Cl^- , K^+-Br^- , Cl^--Cl^- , and Br^--Br^- were developed and the SAPT E2 dispersion was used for determining the C_6 parameter for Cl^--Cl^- and Br^--Br^- . Dispersion between all other pairs of ions was neglected due to the small polarizability of the cations.

The SAPT E2 dispersion energies as a function of distance from 7 to 10 Å for Cl^--Cl^- and Br^--Br^- are shown in

TABLE II. The parameters for modeling ion-water interactions.

Ion	q_I (e)	A	C_6	α	B	β
		(kcal/mol)	(Å ⁶ kcal/mol)	(Å ⁻¹)	(kcal/mol)	(Å ⁻¹)
Na^+	0.804	1 093 577.6	52.306	6.083	579 916.1	5.467
$\text{Na}(\text{lc})^+$	0.804	378 241.1	52.306	5.175	148 610.2	4.639
K^+	0.804	217 453.3	555.769	4.277	185 323.2	4.263
Cl^-	-0.804	658 006.7	2038.906	4.090	1 958.131	2.974
Br^-	-0.804	624 743.7	2750.986	3.904	2 041.254	2.791

FIG. 2. SAPT E2 dispersion energy for $\text{Cl}^- - \text{Cl}^-$ (a) and $\text{Br}^- - \text{Br}^-$ (b). The red dash and blue solid curves were fit to C_6/r^6 and $C_6/r^6 + C_8/r^8$, respectively.

Figure 2. Significant deviations from a simple $1/r^6$ behavior were observed for these ion pairs even at this separation. Rather than going to even larger distances, we decided to fit the dispersion of $\text{Cl}^- - \text{Cl}^-$ and $\text{Br}^- - \text{Br}^-$ to a sum of $-C_6/r^6$ and $-C_8/r^8$ terms. It is clear from Figure 2 that the addition of the higher order $1/r^8$ term significantly improved the agreement with the SAPT dispersion energy.

The final ion-ion energy expression is thus of the form

$$U_{\text{ion-ion}}(r) = Ae^{-\alpha r} - C_6/r^6 - C_8/r^8, \quad (5)$$

where C_6 and C_8 were determined by fitting to SAPT E2 dispersion and A and α were determined by AFM.

For each ion pair, only one generation of AFM was performed. In order to ensure good sampling of short-range configurations, a harmonic constraint potential was applied between the two ions in each pair. The force constant for the harmonic constraint was chosen to be $47.7 \text{ \AA}^{-2} \text{ kcal/mol}$, which led to a penalty energy of approximately 5 RT at a displacement of $0.25 \text{ \AA}$ at the sampling temperature of 300 K .⁵⁰ A series of constraints from 1.5 to $5.5 \text{ \AA}$ in increments of $0.5 \text{ \AA}$ were used for $\text{Na}^+ - \text{Na}^+$ and $\text{Na}^+ - \text{Cl}^-$, and from 2.5 to $5.5 \text{ \AA}$ for other ion pairs. 20 configurations from each window were used for fitting. This leads to 180 QM/MM configurations for $\text{Na}^+ - \text{Na}^+$ and $\text{Na}^+ - \text{Cl}^-$ and 140 QM/MM configurations for other ion pairs. The final ion-ion parameters were summarized in Table III.

TABLE III. The parameters for ion-ion interactions.

Ion pair	A (kcal/mol)	α ($\text{\AA}^{-1}$)	C_6 ($\text{\AA}^6 \text{ kcal/mol}$)	C_8 ($\text{\AA}^8 \text{ kcal/mol}$)
$\text{Br}^- - \text{Br}^-$	164 811.3	2.846	5938.672	107 071.903
$\text{Cl}^- - \text{Cl}^-$	179 108.5	3.146	3335.950	47 519.279
$\text{K}^+ - \text{K}^+$	1 533.2	2.078	0	0
$\text{Na}^+ - \text{Na}^+$	160 647.3	5.434	0	0
$\text{K}^+ - \text{Br}^+$	74 972.7	3.064	0	0
$\text{K}^+ - \text{Cl}^-$	90 583.8	3.297	0	0
$\text{Na}^+ - \text{Br}^-$	11 725.3	2.777	0	0
$\text{Na}^+ - \text{Cl}^-$	93 819.7	3.863	0	0

E. Removal of singularity at short inter-atomic distances

In this work, the potentials of ion-water and ion-ion are composed of an exponential term and one or more additional terms that go to negative infinity at zero distance. Such a combination leads to a singularity at short distances. In order to avoid the singularity, we invert the force at short-range using the formula

$$F_{\text{SF}}(r) = \begin{cases} F(r), & r > R^* \\ 2F^* - F(r), & r \leq R^* \end{cases}, \quad (6)$$

where R^* is the location of maximum repulsive force, $F(r)$ is the force of the original potential, and $F^* = F(R^*)$. $F_{\text{SF}}(r)$ is the force of the new singularity free potential,

$$U_{\text{SF}}(r) = \begin{cases} U(r), & r > R^* \\ 2[U(R^*) - F^* \cdot (r - R^*)] - U(r), & r \leq R^* \end{cases}. \quad (7)$$

In Eq. (7), $U(r)$ is the original potential. Both $U_{\text{SF}}(r)$ and $F_{\text{SF}}(r)$ are everywhere continuous.

III. PROPERTIES PREDICTED BY THE AFM ION-WATER POTENTIALS

A. Solvation free energy

For the determination of the solvation free energy of single ions, a cubic simulation box containing 2224 water molecules was used. Under a constant pressure of 1 bar, the box was approximately 4.05 nm on each side. Long-range electrostatics was treated using the particle mesh Ewald method. The solvation free energy was calculated with the Bennett's acceptance ratio (BAR) method⁵¹ as implemented in GROMACS.⁵² We used 21 steps (a $\Delta\lambda$ of 0.05) for determining each of the Columbic and van der Waals contributions to the free energy.

In order to compare to the experimental free energies, the solvation free energy computed with a periodic box simulation has to be corrected.^{53,54} The leading term of the correction is from the interaction between self-images in the reciprocal space in the Ewald method. For a single ion in the periodic box, Ewald will give a non-zero self energy. This correction is of the form

$$\Delta G_{\text{LS}} = \frac{N_A q_i^2 \epsilon}{8\pi \epsilon_0 L} \cdot \left(1 - \frac{1}{\epsilon_s}\right), \quad (8)$$

where ξ is -2.837297 for a cubic box;⁵⁵ the charge of the ion q_I is $0.804 e$; L is the length of the simulation cell; ϵ_s is the static dielectric constant of the water model. We used an ϵ_s value of 42, which is the static dielectric constant of BLYPSP-4F water without the high frequency correction. We note that the vacuum self energy correction has been taken account by GROMACS; thus, only the second term in Eq. (8) needs to be incorporated explicitly.

The second correction is due to the introduction of an artificial dipole layer at the cutoff sphere; this term presents even with the Ewald method, where the cutoff sphere is at infinity.⁵⁶ This is corrected by

$$\Delta G_{ODL} = -q_I \frac{1}{6\epsilon_0} \rho_n \gamma, \quad (9)$$

where ρ_n is the number density of the solvent and γ is the second multipole moment of a solute molecule.^{57,58} Since water has a finite dipole moment, the second multipole moment of water depends on the choice of origin. In this work, the center of mass of water was used to calculate this correction term. Fortunately, this correction term adds to zero for a salt.

Another correction term arises from the missing of a real liquid-vapor interface in a periodic box. This term has the form,

$$\Delta G_{\text{surf}} = q_I \phi_{\text{surf}}, \quad (10)$$

where q_I is the charge of the ion and surface potential ϕ_{surf} was chosen to be -0.527 V.⁵⁹ Although this term depends on the choice of ϕ_{surf} , it only influences the single ion solvation free energies and cancels for the salt.

Finally, there is a correction term for concentration and pressure. The experimental solvation free energy represents the free energy for solvating non-interacting ions in the gas phase at 1 bar to form an ideal solution with a molality of 1 mol/kg. If we ignore the difference between molality and molarity, a correction term of the form

$$\Delta G_{\text{cp}} = RT \ln \frac{c_0}{c_1} + RT \ln \frac{p_g}{p_0} \quad (11)$$

should be used. In Eq. (11), c_0 and c_1 are 1M and 0.025M, respectively; p_0 and p_g is 1 bar and 24.6 bars, respectively. 0.025M is the concentration of the simulation box. 24.6 bars is the ideal gas pressure of the ion removed in the BAR calculation.

The use of a non-unit charge on monovalent ions causes another complication when comparing to experiments. The experimental solvation free energy reflects the free energy of solvating an ion in the gas phase. Thus, the Born solvation free energy can be expressed as⁶⁰

$$\Delta G_{\text{slv}}^{\text{Born}} = -\frac{q^2}{8\pi\epsilon_0 r_0} \left(1 - \frac{1}{\epsilon_s}\right) = -\frac{q^2}{8\pi\epsilon_0 r_0} + \frac{q^2}{8\pi\epsilon_0 r_0} \cdot \frac{1}{\epsilon_s}, \quad (12)$$

where r_0 is the effective radius of the ion, q is the charge, and ϵ_s is the static dielectric constant of the solution.

The first term of Eq. (12) is associated with charging the ion with a radius r_0 in vacuum, and the second term is associated with charging of the ion in solution. The AFM

force field with non-unit charge is adequately reproducing the second term since the dielectric constant of the BLYPSP-4F water model without the high frequency correction is 42.²⁸ The ratio of q^2/ϵ_s is 0.0154. With the experimental dielectric constant of 78, a unit charge will give this ratio to be 0.0128, not too different from the actual ratio of 0.0154. However, in vacuum, the ion charge should be unity. Thus, the raw solvation free energy calculated with the AFM potential will grossly underestimate the first term of Eq. (12).

In order to correct for this underestimation and avoid a determination of r_0 , we will scale all the solvation free energies by

$$\frac{1 - 1/78}{0.804^2 \cdot (1 - 1/42)} = \frac{1}{0.804^2} + 0.017 = 1.564. \quad (13)$$

It can be seen from Table IV that the scaled solvation free energies for the salts are in excellent agreement with experimental estimates. The error is less than one percent for the two K^+ salts and less than 5% for the two Na^+ salts.

The agreement between the scaled single ion solvation free energies and the experimental reference is less than stellar, giving about 10% error for most ions except Na^+ . However, due to the ambiguity in experimental single ion solvation free energies and the various approximations made in our choice of correction terms, we are not concerned about the minor disagreement.

For a salt, the correction terms only arise from ΔG_{LS} and ΔG_{cp} . Both of these terms are well justified. Good agreement with experimental solvation free energies for the salts strongly suggests the superior quality of the ion potentials developed by AFM. The agreement for single ions can be improved if we incorporate a fudge factor of -35 kJ/mol to all the cations and 35 kJ/mol to all the anions. This term accounts for possible ambiguities in the correction terms, mostly in the surface energy and the ΔG_{ODL} term, and experimental uncertainty with respect to the choice of the reference free energy. We note that different experimental estimates of single ion solvation free energies differ by a comparable amount.^{61,62}

With the fudge factor, the single ion solvation free energies are in excellent agreement with experimental values

TABLE IV. The solvation free energy for the single ions and the salts (kJ/mol). The MP2-AFM solvation free energy (ΔG_{slv}) can be calculated by multiplying the solvation free energy determined with BAR (ΔG_{sim}) by 1.564 (see text) and add the correction term (ΔG_{corr}).

Ion/salt	ΔG_{sim}	ΔG_{corr}	ΔG_{slv} (MP2-AFM)	ΔG_{slv} (fudged)	ΔG_{slv} (expt.) ⁶²	Error (%)
Na^+	-228.44	-62.86	-420.14	-455.14	-423.8	7.4
$\text{Na}(\text{lc})^+$	-192.40	-62.86	-363.78	-398.78	-423.8	-5.9
K^+	-161.79	-62.86	-315.90	-350.90	-352.0	-0.3
Cl^-	-279.48	98.56	-338.54	-303.54	-304.2	-0.2
Br^-	-259.36	98.56	-307.08	-272.08	-277.4	-1.9
NaCl	-507.92	35.70	-758.69		-728.0	4.2
$\text{Na}(\text{lc})\text{Cl}$	-471.88	35.70	-702.32		-728.0	-3.5
NaBr	-487.80	35.70	-727.22		-701.2	3.7
$\text{Na}(\text{lc})\text{Br}$	-451.76	35.70	-670.85		-701.2	-4.3
KCl	-441.27	35.70	-654.45		-656.2	-0.3
KBr	-421.15	35.70	-622.98		-629.4	-1.0

with the exception of Na^+ , for which a 7% error was observed. The larger error for Na^+ is consistent with the slightly worse accuracy for the two Na^+ salts.

The larger error for Na^+ might be due to a sensitivity of the MP2 reference forces to the proper choice of the valence space in the frozen core approximation. The 2s and 2p orbitals of Na^+ have an energy of 2.7 and 1.4 hartree, respectively, which is fairly close to the energy of the valence orbitals of surrounding water molecules. Thus, the 2s and 2p orbitals were treated as valence orbitals in our MP2 calculations. With the GAMESS code, the default choice of the valence space does not include 2s and 2p of Na^+ leading to a larger core being frozen. The parameters for the Na^+ with the larger core, $\text{Na}(\text{lc})^+$, are also reported in Table II with the solvation free energies summarized in Table IV. The $\text{Na}(\text{lc})^+$ parameters lead to an underestimation of the single ion solvation free energy by about 6%.

It is quite surprising that different choices of core orbitals in our MP2 calculations lead to a fairly large difference of 56 kJ/mol in the solvation free energy. Since the small core calculations include more correlation, we use it as our preferred model for Na^+ for all subsequent calculations. However, with the aug-cc-pVTZ-df basis set, no basis functions exist to properly correlate the 2s2p electrons in our small core MP2 calculations. As has been pointed out by Taylor,⁶³ the use of valence-optimized orbitals for correlating core electrons may cause undesirable effects. It is likely that our use of valence optimized basis set with the small core led to the fairly large error in Na^+ solvation free energies. We are working on a more thorough investigation for the proper treatment of the Na^+ core correlations with core-valence basis sets.

It is worth pointing out that even considering the larger error for Na^+ , the overall agreement with experiments is excellent especially considering no experimental values were fit in the development of the potentials.

B. Solvation structures

Figure 3 reports the RDF for each of the four ions obtained from NPT simulations using the 2224 water cubic boxes with one ion. Several RDFs published previously based on either Car-Parrinello (CP) MD or QM/MM MD are shown for comparison.^{64–68} Both the location and the height of the first peak in the ion-oxygen RDF show very good agreement with CPMD or QM/MM MD for $\text{Na}(\text{lc})^+$, K^+ , Cl^- , and Br^- . With the small frozen core, the Na^+ has a tighter first solvation shell, which is consistent with its higher solvation free energy. For the second solvation shell, good agreement is shown with PBE-D CPMD simulations by Bankura *et al.* for both Na^+ and K^+ .⁶⁴ In many other previously published RDFs, the second ion-oxygen peak is not fully converged making a direct comparison impossible. We note that our simulation box has 2224 water molecules; on the other hand, most CPMD based simulations used no more than 64 water molecules;^{69,70} and the MP2 QM/MM calculations by Rowley used a 12 water QM region.⁶⁵ The influence of finite size effects on the second RDF peak is minimized in our simulations.

Figure 4 reports the tilt angle distributions of the four ions calculated with a single ion in a 343 water box. The tilt

angle is defined as the angle formed by the OH-bond bisector and the ion-oxygen vector. Previously published tilt angle distributions obtained with CPMD and MP2 through QM/MM are shown for comparison. The tilt angle distribution predicted by the AFM force field is in good agreement with previously published results for the cations with the MP2-AFM model showing stronger dipole alignment, with $(1 - \cos \phi)/2$ being one, for Na^+ . We note the MP2 QM/MM distribution showed stronger dipole alignment for K^+ than Na^+ . Intuitively, since Na^+ is smaller, one would anticipate that the charge-dipole interaction better aligns water with Na^+ . The weaker alignment for Na^+ with the MP2 QM/MM is rather counter-intuitive. We note the MP2 QM/MM used a small 12 water QM region. In addition, the aligned arrangement has a rather small solid angle that is challenging to obtain a converged distribution. Thus, it is not completely certain whether the MP2-AFM or the MP2 QM/MM distribution is more realistic. For the anions, the AFM force field provides good agreement with the peak positions but shows a wider angle distribution. The wider distribution reflects a loss of specific directionality. Although the loss of directionality may reflect a limitation of the non-polarizable AFM potential, it may also reflect an over-estimation of water structure for the DFT functionals used for the CPMD studies. It has been shown popular DFT functionals lead to over-structured water that melts at a temperature significantly higher than 273 K.^{71,72} An over-structured water may lead to sharper peaks in the tilt angle distribution.

Table V reports the average number of hydrogen bonds of the first solvation shell water molecules and the average number of hydrogen bonds between the first solvation shell water molecules. In this work, we consider a hydrogen bond to be formed when the distance between the donor and the acceptor oxygen is less than 3.5 Å and the angle formed by the hydrogen, the donor oxygen, and the acceptor oxygen is no more than 30°. With this geometric criterion, approximately 3.5 hydrogen bonds are formed at 300 K in liquid water. From Table V, it is clear that the number of hydrogen bonds formed by the first solvation shell water molecules decreases, as ionic radii decrease. This is most likely due to a balance between the need to align the water dipole moment with the field of the ion and the stabilization provided by the extra hydrogen bonds.

The total number of hydrogen bonds formed by each first solvation shell water molecule is approximately one more than the number of hydrogen bonds formed between the first solvation shell water molecules. For smaller ions, the electric field generated by the ion is stronger; water prefers to align its dipole to minimize Coulombic energy. The aligned orientation of water reduces the number of hydrogen bonds that can be formed by each first solvation shell water molecule. For larger ions, the field is weaker. The first solvation shell water molecules thus sacrifice dipole alignments in order to form more hydrogen bonds. This results in a better connected hydrogen bond network between first solvation shell water molecules. We will refer to the more ordered water orientation for smaller ions, a puckered solvation structure and the more connected hydrogen bond network for larger ions, a cage-like solvation structure. We anticipate a multi-valent ion most likely will have a puckered solvation structure.

FIG. 3. Radial distributions function between the four ions and water oxygen (left) and water hydrogen (right). The potential developed in this work is labeled as MP2-AFM. In case of $\text{Na}^+\text{-O}$ and $\text{Na}^+\text{-H}$, the MP2(lc)-AFM shows the RDF between $\text{Na}(\text{lc})^+\text{-O}$ and $\text{Na}(\text{lc})^+\text{-H}$ as described in the text. Several previous published RDFs from CPMD and QM/MM simulations are labeled as PBE-D CPMD,⁶⁴ MP2 QM/MM,⁶⁵ PBE CPMD,⁶⁵ PBE QM/MM,⁶⁶ PBE0 AIMD,⁶⁷ and BLYP CPMD.⁶⁸

C. Surface tension and surface propensity

The surface tension and the surface propensity of ions have also been investigated with slab simulations using 2224

water molecules with 16, 32, 48, and 64 ion pairs. The corresponding salt concentrations are 0.4M, 0.8M, 1.2M, and 1.6M, respectively. The surface tension is measured using the mechanical method through the formula,

FIG. 4. Tilt angle distribution of the first solvation shell water of Na^+ (a), K^+ (b), Cl^- (c), and Br^- (d). MP2-AFM is the potential developed in this work. Previously published distributions are labeled as MP2 QM/MM,⁶⁵ PBE CPMD,⁶⁵ PBE0 AIMD,⁶⁷ and BLYP CPMD.⁶⁸

$$\gamma = \frac{L_Z}{2} \left(P_Z - \frac{P_X + P_Y}{2} \right), \quad (14)$$

where L_Z is the thickness of the box, and the factor of 2 is due to the presence of two interfaces. For each slab simulation, a vacuum region of approximately 80 Å thick is added so that the final box dimension is around $41 \times 41 \times 120$ Å³. The long-range electrostatics is modeled with the particle-mesh Ewald method in three dimensions.

Figure 5 reports the surface tension as a function of salt concentration. The experimental dependence is also shown for comparison. A total of 80 ns worth of statistics were accumulated for the calculation of each surface tension point. However, the error bar remains fairly large. As has been pointed out in the literature, the surface tension is notoriously

difficult to converge.^{73,74} This is partly due to the difficulty in converging the concentration profiles especially at lower concentrations. Our results support an increase of the surface tension as the concentration of the salts increases, consistent

TABLE V. The average number of the hydrogen bonds of the first solvation shell water molecules of the ions and the average number of hydrogen bonds formed between the first solvation shell water molecules of the ions.

Ion	Of the first solvation shell water	Between the first solvation shell water
Na^+	1.11	0.10
K^+	1.37	0.39
Cl^-	1.65	0.67
Br^-	1.76	0.91

FIG. 5. Change of the surface tension relative to that of pure water as a function of concentration. The symbols are from the simulations at 0.4M, 0.8M, 1.2M, and 1.6M. The color-coded solid lines are from experiments.⁸⁶ The concentrations for NaBr, KCl, and KBr are slightly shifted to the right to improve legibility.

with experimental observations.⁷⁵ However, the calculated dependency is higher than that observed experimentally and the subtle differences between different salts are not fully captured.

Figure 6 reports the ion density profile for the salts at 0.4M and 1.6M. It is interesting that the AFM models predict a concentration dependent behavior. At 0.4M salt concentration, all ions are repelled from the surface with the cations reaching slightly closer to the interface than the anions and K^+ seems to be penetrating stronger to the surface than Na^+ . At 1.6M, an enrichment of Br^- near the interface can be observed in the KBr solution. The peak is about 8 Å below the Gibbs surface. Since the Na^+ is being repelled from the interface stronger than the K^+ , the enrichment of Br^- is not obvious in NaBr at 1.6M.

The 8 Å difference between the peak of the Br^- density and the Gibbs surface is consistent with several previous experimental work showing halide anions to be expelled from the top-most layer of the liquid-vapor interfaces.^{76,77} Our result is consistent with experiments showing Br^- enrichment at the interface at fairly high concentrations,^{76,78,79} although the low concentration density profile is somewhat surprising and worth further investigation. We are not aware of direct experimental evidence against this observation.⁸⁰

It has been argued that explicit treatment of polarization is important for the correct modeling the surface specificity of ions.^{74,81} Although the BLYPSP-4F model does not have

an explicit polarizable site, due to the flexibility in water geometry, the water dipole moment may change by varying the HOH angle. For example, the BLYPSP-4F water has a dipole moment of 2.19 D at the monomer geometry, but the average dipole in the liquid state is 2.24 D. It has been shown that BLYPSP-4F has an effective polarizability of 0.963 Å^3 along the HOH bisector.⁸² However, the ions are not polarizable. We postulate explicit treatment of polarization, especially ion polarization may be important for quantitative prediction of the surface tension of the salt solutions and may change the specific concentration, at which the Br^- starts to be enriched at the interface. We plan to investigate the effect of explicit treatment of polarization by developing a polarizable ion potential with AFM.

D. Diffusion constants

Kinetic information, such as diffusion constants and solvent exchange rates, is of significance to many fundamental questions regarding ion solvation.^{83,84} The diffusion constant of each ion is reported in Table VI along with experimental results. The diffusion constant was measured using 100 ns of MD simulations in a 343 water box containing only one ion in each simulation. The calculated diffusion constant is in excellent agreement with experimental values obtained at

FIG. 6. Z-density distribution of salt solutions at 0.4M and 1.6M concentrations. The axis on the left is the concentration of the ions; the axis on the right shows the water concentration.

TABLE VI. The diffusion constants of ions calculated with the MP2-AFM potential and the experimental references at infinite dilution.⁴⁹

Ion	$D_{\text{ion}} (10^{-5} \text{ cm}^2/\text{s})$	$D_{\text{expt.}} (10^{-5} \text{ cm}^2/\text{s})$
Na^+	1.33 ± 0.02	1.334
K^+	2.09 ± 0.03	1.957
Cl^-	2.05 ± 0.09	2.032
Br^-	2.01 ± 0.04	2.080

FIG. 7. Diffusion constant of water for salt concentrations at 1M and 2M, the experimental diffusion constant was shown for comparison.⁸⁵ The lines are only guide for the eyes.

infinite dilution further validating the quality of the potentials developed.

The concentration dependent diffusion constant of water is also calculated for NaCl and KBr at 0.5M, 1.0M, and 2.0M concentrations. The results are reported in Figure 7 along with experimental diffusion constants.⁸⁵ With the 1.75 nm cutoff for van der Waals interactions, the BLYPSP-4F water diffusion constant is $2.25 \times 10^{-5} \text{ cm}^2/\text{s}$, in good agreement with the experimental value of $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$.⁴⁹ This value is slightly smaller than that reported previously when a smaller van der Waals cutoff of 0.9 nm was used.²⁵ As shown in Figure 7, NaCl leads to a reduction in water diffusion constant while KBr leads to an increase in water diffusion constant, consistent with experimental findings.^{84,85} It is encouraging that Figure 7 shows good agreement with the absolute experimental diffusion constants rather than only relative diffusion constants. The non-polarizable salt potentials correctly reproducing the trend in water diffusion constant are consistent with the conclusion from a previous study by Kann and Skinner.⁹ It was shown in the Kann and Skinner work that the implicit treatment of polarization through charge scaling is sufficient for capturing the trend in water diffusivity. The puckered solvation structure around smaller ions most likely leads to longer residence times for water thus reducing the diffusion constant. On the other hand, the average number of hydrogen bonds in the caged solvation structure is smaller than that in the bulk water. It is possible that the reduced number of hydrogen bonds is responsible for the enhanced diffusivity in KBr.

IV. SUMMARY AND CONCLUSION

Using the MP2 method with the triple-zeta basis sets as reference, point-charge based pair-wise additive potentials were developed with AFM for Na^+ , K^+ , Cl^- , and Br^- interacting with BLYPSP-4F water. The optimal charge of the ions is less than the nominal ionic charge consistent with prior arguments based on the optical dielectric constants of the solution.⁴⁸

With simple energy expressions, the AFM potentials were able to reproduce the solvation free energies of the salts within 5% of experimental estimates. The single ion solvation free energies also agree with experimental values⁶² after a 35 kJ/mol fudge factor is incorporated. The AFM models were validated by comparing the RDF, the tilt angle distribution, and the diffusion constants with previously published CPMD and QM/MM simulations and experimental values. The AFM models predict the RDF in excellent agreement with previous theoretical modeling with the exception of Na^+ , where a slightly tighter first solvation shell is predicted when the MP2 reference calculations include excitations of the 2s2p electrons. The AFM models predict a slightly wider tilt angle distribution for anions when compared to previous DFT simulations. The calculated diffusion constants of both the ions and water as a function of salt concentration are in excellent agreement with experimental measurements. The ion diffusion constant agrees with experimental measurements with a maximum error of 6%.

The AFM model shows an increase of surface tension when the concentration of the salts increases in qualitative agreement with experimental measurements. The AFM models predict that surface specificity of ions depends on concentration. Although all the ions are repelled from the interface at low concentrations, an enrichment of Br^- at the interface can be observed at 1.6M concentration in KBr. The high concentration enrichment of Br^- is consistent with the results from many experimental and simulation work.

Our simulation suggests that the first solvation shell water molecules of an ion can either assume a cage-like structure that maximizes hydrogen bonds or a puckered structure that maximizes dipole alignment. Smaller ions such as Na^+ and possibly many divalent cations have a puckered first solvation shell structure, and larger ions such as Br^- have a cage-like solvation structure.

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