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The effects of charge transfer on the aqueous solvation of ions

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Ab initio-based charge partitioning of ionic systems results in ions with non-integer charges. This charge-transfer (CT) effect alters both short- and long-range interactions. Until recently, the effects of CT have been mostly neglected in molecular dynamics (MD) simulations. The method presented in this paper for including charge transfer between ions and water is consistent with *ab initio* charge partitioning and does not add significant time to the simulation. The ions of sodium, potassium, and chloride are parameterized to reproduce dimer properties and aqueous structures. The average charges of the ions from MD simulations (0.900, 0.919, and -0.775 for Na^+ , K^+ , and Cl^- , respectively) are consistent with quantum calculations. The hydration free energies calculated for these ions are in agreement with experimental estimates, which shows that the interactions are described accurately. The ions also have diffusion constants in good agreement with experiment. Inclusion of CT results in interesting properties for the waters in the first solvation shell of the ions. For all ions studied, the first shell waters acquire a partial negative charge, due to the difference between water-water and water-ion charge-transfer amounts. CT also reduces asymmetry in the solvation shell of the chloride anion, which could have important consequences for the behavior of chloride near the air-water interface. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4736851>]

I. INTRODUCTION

When developing potential models for molecular simulations, assigning an integer charge to an ion is a choice, made for convenience or based on intuition. It is more physically realistic to assign charges based on the electron density, resulting in molecular or ionic charges which depend upon their environment. Intermolecular charge transfer (CT) is the shifting of small amounts of electron density (less than a tenth of an electron) between participants in non-bonded interactions, resulting in ionic charges which deviate from integer values and in the acquisition of charge by neutral molecules.^{1,2} The local rearrangement of charge affects both short- and long-range interactions. Electronic structure calculations have indicated the importance of CT between ions and water,^{3–7} for ions in biological ion channels,^{6,8–10} and ionic liquids.² The importance of CT between ions and water is also indicated experimentally in vibrational^{11–14} and x-ray absorption spectroscopy.¹⁵

The inclusion of multi-body effects in molecular dynamics (MD) force fields is usually accomplished by adding polarizability.^{16,17} Dipole-polarizable force fields have been developed both for neutral molecules and ions.^{18–23} Some potentials also include polarizable quadrupoles.^{24,25} A few models have been developed which include charge-transfer effects,^{11,24,26–32} often by including a charge-transfer contribution to the energy but not actually changing the particles' charges.^{24,28,31,32} Charge-transfer models are largely derived from *ab initio* calculations. They have been primarily applied to dimers and small clusters but are fairly complex.^{11,24,29–31} In a simpler technique used for ionic liquids, charge transfer has been added by assigning non-integer, but geometry independent, charges to the ions.³³

A new method for treating charge transfer has been developed recently for liquid water.³⁴ The discrete charge-transfer (DCT) method transfers a fixed amount of charge from one particle to another, if the two particles are within a prescribed distance. A switching function is used so that the amount of charge transferred goes smoothly to zero. The DCT model avoids the problems which have plagued other attempts at creating charge-transfer models,^{30,35–37} such as systems becoming conductive, and charge transfer at large distances and in the wrong direction. The DCT model is also an efficient method to treat charge transfer when simulating large systems.

In this paper, we use the DCT approach to develop a new model for ions, which includes both polarizability and charge transfer. The ions are parameterized for use with the TIP4P-FQ+DCT water model, which also incorporates polarizability and charge transfer.³⁴ Parameters for three ions (chloride, potassium, and sodium) are fit to reproduce results from experiment and electronic structure calculations. Using these models, we examine the effects of charge transfer on aqueous ions.

II. METHODS

A. Potentials

The model for ions described here expands on the basic model of ions, which includes only charge, dispersion, and repulsion interaction. Multi-body effects are incorporated via polarizability and charge transfer for both ions and water. Polarizability for the ions is treated using the Drude oscillator model.^{20,23} The total energy for the system is described by Eq. (2), below, which includes a Lennard-Jones (LJ) potential for dispersion and repulsion energies, the Coulombic energy

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between charge sites, the CT energy, and the polarization energy

$$\begin{aligned}
 U_{total} &= U_{LJ} + U_{Coulomb} + U_{CT} + U_{self,Drude} + U_{self,FQ} \\
 &= \sum_{i=1}^{N+M-1} \sum_{j<i} \left(4\epsilon \left[\left(\frac{\sigma}{r_{i\gamma j\delta}} \right)^{12} - \left(\frac{\sigma}{r_{i\gamma j\delta}} \right)^6 \right] \right. \\
 &\quad \left. + \sum_{\alpha\beta} \frac{q_{i\alpha} q_{j\beta}}{r_{i\alpha j\beta}} S_{ij}(r_{i\alpha j\beta}) \right) \\
 &\quad + \sum_{i=1}^{N+M-1} \sum_{j<i} \left(-\mu_{ij}^{CT} |q_{ij}^{CT}| + \frac{1}{2} \eta_{ij}^{CT} (q_{ij}^{CT})^2 \right) \\
 &\quad + \sum_{m=1}^M \frac{1}{2} k_D x_{mD}^2 + \sum_{l=1}^N \left(\sum_{\alpha} \tilde{\chi}_{\alpha}^0 q_{l\alpha} \right. \\
 &\quad \left. + \frac{1}{2} \sum_{\alpha} \sum_{\beta} q_{l\alpha} q_{l\beta} J_{\alpha\beta}(r_{l\alpha l\beta}) - E_l^{gp} \right), \quad (2)
 \end{aligned}$$

where N is the total number of water molecules, and M is the number of ions. The indices i and j denote separate particles, either ions or water. The indices γ and δ denote the LJ interaction sites, which are located at ion centers and on the oxygen atom of the water molecules. The indices α and β denote charge sites, either atom sites on water, ion centers, or Drude charge sites. In the Drude model, both the monopole and dipole intermolecular interactions are handled in the normal Coulomb summation. Sums over m are over ions only, and sums over l are over waters only. Distances between charge sites are given by $r_{i\alpha j\beta}$, and distances between LJ sites are given by $r_{i\gamma j\delta}$.

The electrostatic interactions are damped using the function S_{ij} , which acts only at short range and does not disturb the long-range interactions. We use the full gas-phase polarizability for all ions with Thole-type damping, suggested by the work of Masia *et al.*^{38,39} The damping is applied to all electrostatic interactions of ions (mono- and dipole) via Eq. (3)

$$S_{ij} = 1 - \left(1 + \frac{r_{ij}}{2a_{ij}} \right) e^{-r_{ij}/a_{ij}}, \quad (3)$$

where a_{ij} is a user-defined constant, which controls the strength of damping. As in previous work,^{34,35} we set $S_{ij} = 1$ for water-water interactions. Previous work using the TIP4P-FQ model with a Drude model for chloride also damped all electrostatic interactions. We find, like Stuart and Berne, that using an unscreened Coulombic interaction between the ions and water leads to poor prediction of many properties, including the water structure around the ion.²⁰

In the charge-transfer part of the equation for the total energy (Eq. (2), above), the negative of the Mulliken electronegativity, μ_{ij}^{CT} , represents the tendency of an atom to attract electrons in intermolecular CT. The hardness, η_{ij}^{CT} , represents the atoms' resistance to losing electrons in intermolecular CT.³⁵ The charge-transfer energy, which contains these two parameters, partially compensates for the loss of electrostatic energy upon charge transfer. The amount of charge

transferred, q_{CT} , which depends on the pair type and the distance, is given by the switching function

$$q_{CT} = \begin{cases} Q_{ij}^{CT} & \text{if } r_{ij} < R_1^{CT}, \\ \frac{1}{2} Q_{ij}^{CT} [1 + \cos(\pi \frac{r_{ij} - R_1^{CT}}{R_2^{CT} - R_1^{CT}})] & \text{if } R_1^{CT} \leq r_{ij} \leq R_2^{CT}, \\ 0 & \text{if } r_{ij} > R_2^{CT}, \end{cases} \quad (4)$$

where Q_{ij}^{CT} is the maximum amount of CT for each pair and depends on the pair type. The distances R_1^{CT} and R_2^{CT} define where the switching function starts and ends, respectively, for each pair type. In our potential, CT is treated in a purely distance-dependent fashion. Charges of solvated ions are not required to be integers and water molecules can become charged, either through charge transfer with ions or other water molecules.³⁴ Assigning a maximum amount of charge transfer, Q^{CT} , prevents q_{CT} from becoming extremely large at short distances. The combination of R_1 , R_2 , and Q^{CT} is chosen so that $q_{CT}^{MD} = q_{CT}^{QM}$ at the equilibrium separation of the dimers. As the distance increases, the switching function ensures a smooth approach to zero and prevents long-range CT. It also prevents the CT model from becoming conductive. The switching function is the same as that used for TIP4P-FQ+DCT and was chosen to be consistent with that model.

In the Drude model, the dipole-dipole and dipole-charge interactions are handled in the Coulomb sums. The Drude model has an additional energy contribution based on the polarizability of the ion, denoted at $U_{self,Drude}$ in Eq. (1), above. The displacement of the Drude oscillator from equilibrium is x_{mD} . The Drude spring constant k_D was set to 1000 kcal/mol/Å², and the Drude charge q_D is determined by the equation

$$q_D = -\sqrt{\alpha k_D}, \quad (5)$$

where α is the polarizability. This is the same method used by Yu *et al.*²³ Drude oscillators avoid the instabilities in point-inducible dipoles, and long-range effects are easily incorporated into Ewald sums.

The remaining terms are related to the polarizability of the water, which is handled by the fluctuating charge (FQ) method.^{34,35} The parameters χ_{α}^0 and $J_{\alpha\beta}$ correspond to μ_{ij}^{CT} and η_{ij}^{CT} , respectively, but here refer to intramolecular charge transfer. The intramolecular charge interactions are described by the Coulomb overlap integral

$$J_{\alpha\beta}(r_{l\alpha l\beta}) = \int dr_{l\alpha} dr_{l\beta} |\phi_{n_{\alpha}}(r_{l\alpha})|^2 \frac{1}{|r_{l\alpha} - r_{l\beta} - r|} |\phi_{n_{\beta}}(r_{l\beta})|^2 \quad (6)$$

of Slater functions

$$\phi_{\alpha}(r) = A_{n_{\alpha}} r^{n_{\alpha}-1} e^{-\zeta_{\alpha} r}, \quad (7)$$

where $A_{n_{\alpha}}$ is a normalization constant, n_{α} is the principal quantum number of charge site α , and ζ_{α} is considered an adjustable parameter.

The adjustable parameters in this model are:

1. LJ parameters for each ion (well-depth, ϵ , and LJ equilibrium distance, σ),
2. CT energy parameters between each pair (chemical potential, μ^{CT} , and hardness, η^{CT}),

TABLE I. Lennard-Jones and Drude parameters. The Lennard-Jones well depth, ϵ , and distance, σ , for interactions of ions with water are listed. The Drude charge and polarizabilities of ions are shown. Also included are the Lennard-Jones parameters for the TIP4P-FQ+DCT water model.³⁴ LJ parameters for ion-ion interactions are determined by Lorentz-Berthelot rules.

	ϵ (kcal/mol)	σ (Å)	q_D (e)	α (Å ³)
Na ⁺	0.0407	2.320	−0.687597	0.157
K ⁺	0.0497	3.030	−1.580968	0.830
Cl [−]	0.1490	3.720	−4.062989	5.482
H ₂ O	0.2633	3.171		

3. CT cut-off distances for each pair (R_1^{CT} and R_2^{CT}),
4. amount of charge transfer for each pair (Q_{CT}),
5. Drude charge for each ion (q_D), and
6. the damping constant for pairs (a_{ij}).

Each ion has a single Drude charge parameter and a single set of Lennard-Jones parameters. The Lennard-Jones interactions between unlike atoms use parameters from the Lorentz-Berthelot combining rules. Charge is transferred from the ion center, so the Drude charge is not affected by CT. The charge-transfer parameter, Q_{CT} , and the cut-off parameters are chosen to best fit the switching function to our electronic structure calculations. For ion-water interactions, the damping constant, a_{ij} , is chosen as the minimum amount needed to prevent overpolarization. The remaining parameters (ϵ , σ , μ^{CT} , η^{CT}) are adjusted to fit the dimer and aqueous properties. The parameters used in the simulations are listed in Tables I and II.

Ion-water parameters are fit with respect to:

1. dimer energy minimum,
2. distance at the energy minimum of dimer,
3. amount of charge transfer at the dimer minimum,
4. location of the first maximum and first minimum of the radial distribution function (RDF), and
5. the average dipole in the liquid phase (for chloride).

The height of $g(r)$ at the maximum and minimum and single-ion hydration free energies were also considered in order to differentiate between parameter sets that had very similar aqueous structure otherwise.

Once parameters were established for the ion-water interactions, additional parameters for the ion-ion interactions were determined using only the properties of the ion dimers. For ion-ion interactions, the damping constant, a_{ij} , is chosen

TABLE II. Charge-transfer parameters. The maximum amount of CT, the CT cutoffs, and the energy parameters are listed for each pair. The damping for each pair is also shown.

Pair	Q_{CT} (e)	r_{CT1} (Å)	r_{CT2} (Å)	μ_{CT} (kcal/mol/ e)	η_{CT} (kcal/mol/ e^2)	a (Å)
Na ⁺ –H ₂ O	0.033	1.7	3.3	275.33	1602.6	0.10
K ⁺ –H ₂ O	0.024	2.0	3.7	304.57	6306.7	0.10
Cl [−] –H ₂ O	0.057	1.9	3.1	95.51	995.8	0.60
NaCl	0.090	1.8	5.0	535.35	232.4	1.175
KCl	0.085	2.0	5.5	468.63	663.9	1.164

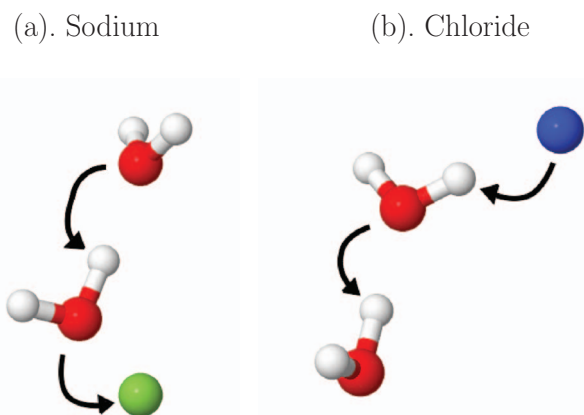


FIG. 1. Direction of charge transfer. (a) The cation receives charge from the first shell water, which in turn receives charge from the second shell water. (b) The anion transfers charge to the first shell water, which donates charge to the second shell water.

so that the dipole moment of the ion pair is in agreement with experiment.

B. Quantum calculations

Quantum mechanical studies have found that the total CT to/from an ion increases linearly with the number of ligands, implying that (approximately) the same amount of charge is transferred per hydrogen bond. The amount of CT depends on the chemical identity of the ion.^{6–8,40} These findings support a model using discrete amounts of charge transfer based on pairs.

Quantum calculations are performed on several systems using the program NWChem version 5.1 (Ref. 41) at the MP2 level⁴² with the aug-cc-pVTZ basis set⁴³ for all atoms, except potassium. Because the aug-cc-pVTZ basis set is not available for potassium, the 6-311++G(2d,2p) basis set is used instead. For each ion, the ion-water dimer and an ion-water-trimer are studied. The trimer (Figure 1) has the waters arranged to represent a water from the first and second solvation shells of the ion, in order to determine how the presence of a second water, not coordinated to the ion, affects CT between the ion and the first water. For each ion pair (NaCl and KCl), the amount of CT is calculated over a range of distances (Figure 2). The charge was partitioned according to Bader's quantum theory of atoms in molecules (QTAIM),⁴⁴ using the algorithm developed by Henkelman and co-workers.⁴⁵ QTAIM partitions the charge based on the physically meaningful zero-flux boundaries of the electron density.¹ QTAIM has been shown to have less dependence on basis sets and level of theory than other methods of charge partitioning.^{1,7} We also investigate charge partitioning based on the electrostatic potential (ESP), but it results in a large amount of charge transfer and extremely long-range CT. In another study, ChelpG, an ESP-based method, is found to be overly simple for representing a molecule with a large dipole. Inclusion of a dipole with ChelpG results in the amount of CT becoming closer to that of QTAIM results, though still higher.⁷

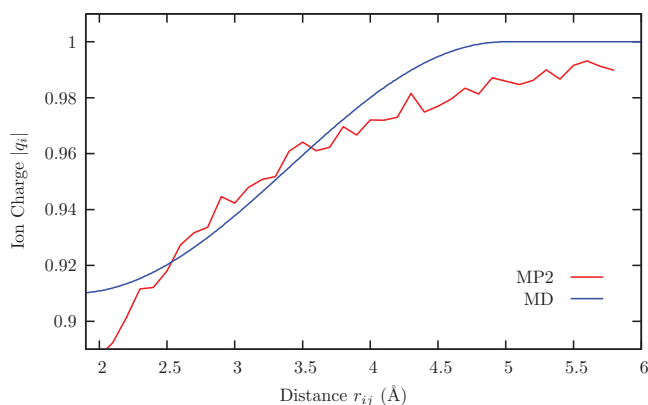


FIG. 2. Comparison of the ion charge from the QM calculations to the MD switching function. The curves pictured are for NaCl; the other dimers are qualitatively similar. The red line shows the absolute value of QTAIM ion charges, which are calculated at intervals of 0.1 Å. The blue line represents absolute values of the charges of the ions from our switching function.

C. Simulation details

Calculations of thermodynamic properties were done using a system of a single ion with 256 water molecules in the TPN ensemble with periodic boundary conditions, using our own code. All simulations used the TIP4P-FQ+DCT water model.³⁴ This model is polarizable using the fluctuating charge scheme, as discussed in the original work by Rick *et al.*³⁵ The temperature is kept at 298 K using a Nosé-Hoover thermostat, and the pressure is kept at 1 atm using an Anderson barostat.⁴⁶ The charge equilibration for the fluctuating charges is handled via an extended Lagrangian approach³⁵ using charge normal modes.^{34,47} The Drude variables are given a mass equal to 0.4 amu, which is subtracted from the mass of the ion center. The positions of the ion are propagated as described by Lamoureux and Roux.⁴⁸ The simulations use a 1 fs time step and Ewald summation for the long-range electrostatics.⁴⁶ The bonds were constrained using the SHAKE algorithm.⁴⁶ The charge degrees of freedom (Drude and charges on atom sites of water) were kept at 1 K. The diffusion constants were determined using the Stokes-Einstein equation. Diffusion simulations of single ions were performed in the EVN ensemble using systems of 256, 512, and 1024 waters, to check for system-size dependence.

Free energies are calculated relative to the hydration free energy values calculated by Warren and Patel for a non-polarizable ion in TIP4P-FQ.⁴⁹ (We use Set A of their ion parameter sets.) Warren and Patel applied several corrections to their absolute hydration free energies which allowed for calculation of real hydration free energies.⁴⁹ Therefore, our results are also real hydration free energies. Free energy perturbation theory is performed in which the ions from Warren and Patel are morphed into our ions, and the water is morphed from TIP4P-FQ³⁵ to TIP4P-FQ+DCT. The transition is done in twenty steps, with 50 ps of simulation time for each step. Double-wide sampling is used. Free energy calculations for neutral ion pairs are also performed, using thermodynamic integration in 16 steps, with 500 ps of simulation time for each. Both the single-ion and ion-pair simulations include 512 water molecules.

TABLE III. Dimer properties. The results of the present MD model are compared with quantum mechanical calculations. Note that q^{CT} in Table II is greater than q^{CT} here because the equilibrium distances are within the range of the switching function in Eq. (4) (i.e., $R_1 < r_{eq} < R_2$).

Pair		E_{min} (kcal/mol)	r_{min} (Å)	q^{CT} (e)	Reference
Na ⁺ -H ₂ O	MD	-23.72	2.25	0.024	
	QM		2.17	0.028	
	Exp.	-24.0	2.26		65
K ⁺ -H ₂ O	MD	-17.82	2.60	0.0241	
	QM		2.67	0.021	
	Exp.	-17.9	2.60		65
Cl ⁻ -H ₂ O	MD	-15.00	3.10	0.051	
	QM		3.08	0.069	
	QM	-13.6	3.09		66
NaCl	MD	-128.98	2.37	0.083	
	QM		2.35	0.082	
	QM	-131.9	2.36		67
KCl	MD	-117.39	2.70	0.083	
	QM		2.71	0.104	
	QM	-115.8	2.67		67

III. RESULTS

A. Quantum calculations and dimer properties

The equilibrium dimer distance and charge transfer at equilibrium are shown in Table III, where these values are compared to experiment and to other *ab initio* calculations. The binding energies and distance at equilibrium agree with experiment, though MP2 results in distances slightly longer than those from experiment. Figure 2 compares QM calculations to our CT (MD) model (Eq. (4)). From the QM calculations, the amount of charge transferred is found to be distance dependent, as shown in Figure 2. This compares well with previous studies.^{50,51}

Experimental data show that the NaCl dimer has a dipole moment equal to 9.0 D,⁵² and the dimer bond distance is 2.36 Å.⁵³ Assigning the ions charge of plus or minus one would give the pair a dipole moment equal to 11.3 D. Our model transfers 0.083e of charge from Cl⁻ to Na⁺, which reduces the dipole moment to 10.4 D. Choosing a_{ij} equal to 1.175 Å gives induced dipoles of 1.42 D for Cl⁻ and 0.04 D for Na⁺, reducing the total dipole to 9.0 D. A similar effect is found for KCl, where the charge transfer and polarizability both reduce the dipole of the pair.

B. Equilibrium aqueous structure

The structural properties of charge-transfer ions in water are listed in Table IV and are illustrated in Figure 3. The cations are parameterized to have RDF consistent with Tongraar *et al.*⁵⁴ The current best theoretical estimates for coordination numbers of alkali metals are from Varma and Remppe.⁵⁵ The alkali metals, Na⁺ and K⁺, are strongly coordinated by four water molecules. As the atomic number increases, loosely coordinated waters are added – one for Na⁺ and two for K⁺. Thus, the total hydration numbers are 5 for Na⁺ and 6 for K⁺.⁵⁵ Our coordination number is determined by

TABLE IV. Equilibrium properties of single ions in water. The radial distribution function is described by r_{max} , g_{max} , r_{min} , and g_{min} . The average coordination number is n_{coord} . The average charge and dipole of the ion are $\langle q_{ion} \rangle$ and $\langle \mu_{ion} \rangle$, respectively. The average charge and dipole of the waters of the first solvation shell are also listed as $\langle q_{shell} \rangle$ and $\langle \mu_{shell} \rangle$, respectively.

Ion	r_{max} (Å)	g_{max}	r_{min} (Å)	g_{min}	n_{coord}	$\langle q_{ion} \rangle$ (e)	$\langle \mu_{ion} \rangle$ (D)	$\langle q_{shell} \rangle$ (e)	$\langle \mu_{shell} \rangle$ (D)	Reference
Na ⁺	2.34	6.81	3.23	0.15	5.5	0.900	0.028	−0.009	2.57	This work
	2.33	5.5	3.0	0.5	5.6					54
	2.38	7.42	3.24	0.20	5.6	1		0		23
K ⁺	2.68	4.71	3.52	0.34	6.7	0.919	0.122	−0.010	2.51	This work
	2.81	3.4	3.7	0.6	8.3					54
	2.74	4.80	3.56	0.45	6.9	1		0		23
Cl [−]	3.03	2.69	3.72	0.74	6.4	−0.775	0.888	−0.019	2.54	This work
	3.2	3.1	4.0	0.9	5.9	−0.8	0.6		2.5	7
	3.16	3.15	3.78	0.72	6.5	−1		0		23

integration of the ion-water oxygen radial distribution function to the first minimum. Compared to Varma and Rempe, our coordination number of 5.5 for Na⁺ is acceptable, but our coordination number of 6.7 for K⁺ is high. Our results are also similar to the results for the polarizable Drude model of Yu *et al.*,²³ but the coordination number for K⁺ is smaller than the QM/MM results of Tongraar *et al.*⁵⁴ The chloride ion is parameterized to have a coordination number near 6, as is indicated experimentally.⁵⁶ Our result of 6.4 is higher than that of Zhao *et al.*, who report an average coordination number of 5.9 for chloride, using the polarizable AMOEBA model.⁷

The charge distributions of the ions from our MD simulations are shown in Figure 4. Our charge distributions are supported by electronic structure calculations of ions with their first solvation shell. Zhao *et al.* find that chloride transfers 0.03–0.05 electrons to each water in its solvation shell, resulting in a total charge of about $-0.8e$ for chloride.⁷ Using Car-Parrinello MD, Dal Peraro *et al.* find that Cl[−] transfers 0.26e to water, making the chloride charge $-0.74e$.⁴ Our average chloride charge is $-0.775e$. Varma and Rempe find a charge near $0.91e$ for both sodium and potassium, when coordinated to six waters.⁶ Our average values of 0.900 and 0.919e (for Na⁺ and K⁺, respectively) are close to their values, as well as those of Dal Peraro *et al.* (0.88e for Na⁺ and 0.87e for K⁺). The cations show a sharp peak in their probability distributions. The broader peak in the chloride charge distribution is due to greater CT and thereby greater sensitivity to fluctuations as compared to the cations. The distribution of the ion dipoles is shown in Figure 5. The dipole moments of waters around the ions are also reduced compared to bulk waters' dipoles, consistent with *ab initio* MD of the chloride ion.^{7,57}

C. Charge of solvating water molecules

Water in the first solvation shell has a partial negative charge for both cations and anions (see Table IV and Figure 6). This result is explained by the arrangement of waters in the second solvation shell (Figure 1). A first solvation shell water donates negative charge to the cation, which would give it a partial positive charge in a gas-phase dimer.

In aqueous phase, the waters of the first solvation shell also accept charge from waters in the second solvation shell. Because the first shell water can donate two hydrogen bonds but accept only one hydrogen bond while bound to the cation, the charge accepted from the second shell is greater than the charge donated, resulting in an overall negative partial charge. The negative charge of the first solvation shell is compensated by a slight positive charge spread over the second solvation shell, indicating that members of the second shell must accept slightly more hydrogen bonds than they donate. (The charge transfer between water molecules is solely determined from the hydrogen bond arrangement.)

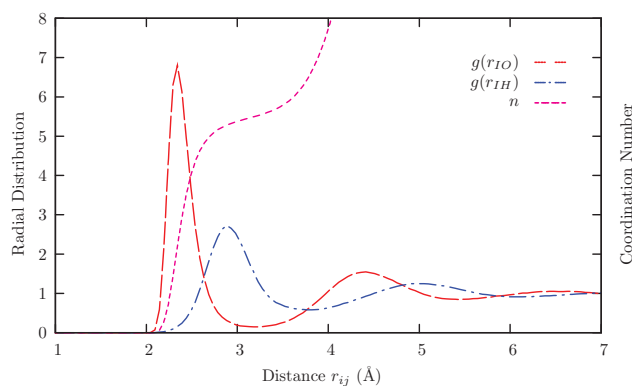
In the case of chloride, the anion is donating charge to the waters in the first solvation shell, and the waters in the first solvation shell are donating charge to waters in the second solvation shell. The amount of charge transfer between the waters is not sufficient to compensate for the charge transferred from the ion, so the first solvation shell retains a negative charge. Dal Peraro *et al.* find that waters in the first solvation shell around Cl[−] or K⁺ have a negative charge of a magnitude close to our results and that the second solvation shell of K⁺ has a small positive charge.⁴

The picture of the charge distribution among water, described above, is supported by quantum calculations on trimers (Table V and Figure 1). In the QTAIM calculations on geometry optimized trimers the water closest to the ion has a charge close to zero or negative in all cases. So, the first solvation shell water has a charge imbalance similar to that predicted by the MD CT model. The amount of charge transferred between the water molecules is 0.02e for potassium and chloride. The value 0.02e is consistent with QM calculations on water dimers at the same distance.⁵⁸ For sodium, the distance between the waters is smaller in the optimized structure, and so the charge transfer is greater.

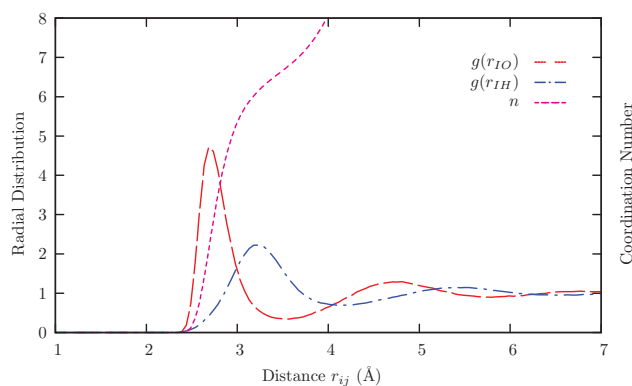
D. Asymmetry in the solvation shell of chloride

The solvation shell can be defined as all atoms that are within the first minimum of the ion-oxygen pair correlation function. For ions such as sodium, all oxygens in the first solvation shell are about the same distance from the ion. In

(a). Sodium



(b). Potassium



(c). Chloride

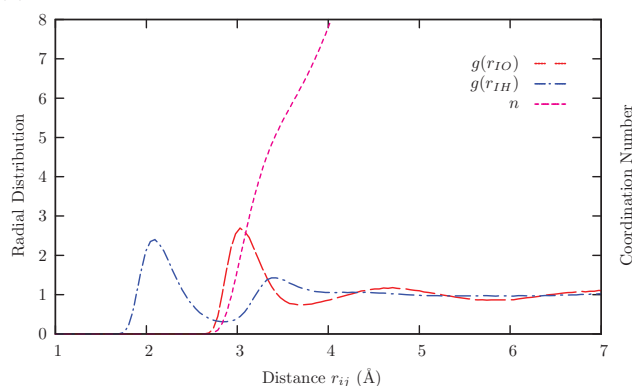


FIG. 3. Radial distribution functions. The red long dashes show the ion-oxygen distribution function. The blue dot-dash line shows the ion-hydrogen distribution functions. The magenta short dashes show the running coordination number.

contrast, several groups have reported that the first solvation shell around the chloride ion is asymmetric, both in clusters and in bulk solution.^{7,20,59,60} Asymmetry has been proposed to be a driving force for attraction of anions to the liquid-vapor interface.⁵⁹ Since non-polarizable models do not reflect experimental concentrations of anions at the liquid-vapor interface⁶¹ and asymmetry decreases when polarizability decreases,⁷ asymmetry has been attributed to the polarizability. The average of the positions of the oxygen atoms in the first solvation shell can be used to define the center of the first solvation shell. The difference between the average of the oxygens' positions and the position of the ion can be used

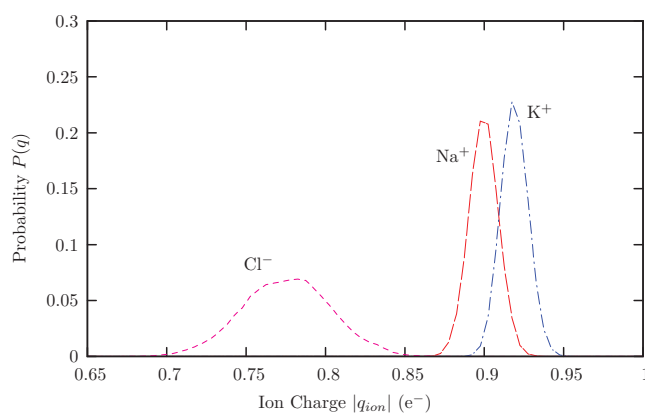


FIG. 4. Ionic charge distribution. The distribution of the ionic charge for sodium (long red dashes), potassium (blue dot-dashes), and chloride (short magenta dashes).

to determine the degree of anisotropy of the first solvation shell.

We find a slight anisotropy in the chloride solvation, whereas the cations have more symmetric hydration shells (Figure 7(a)). We find that charge transfer has a small effect on the asymmetry. Simulations of our chloride ion without charge transfer result in a more asymmetric solvation shell than when charge transfer is included. Figure 7(b) compares the results from our CT model with results for the same model without CT between the ion and water. For chloride without charge transfer, the polarizability is reduced to 4.92 \AA^3 , so that the chloride ion dipole has the same average as the CT model. (The Drude charge was reduced to $-3.850e$.) The slight negative charge in the solvation shell of the charge-transfer ion repels the negative Drude charge, thereby reducing the dipole moment of the ion. Thus, CT provides an additional damping force on the anion dipole, which results in more isotropic solvation. Furthermore, the negative charge transferred to the waters causes the first solvation shell molecules to repel each other and solvate the ion more symmetrically.

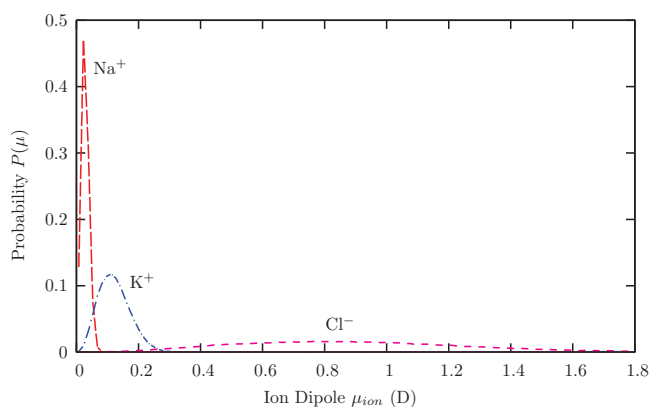


FIG. 5. Ionic dipole distribution. The distribution of the ionic dipole for sodium (long red dashes), potassium (blue dot-dashes), and chloride (short magenta dashes).

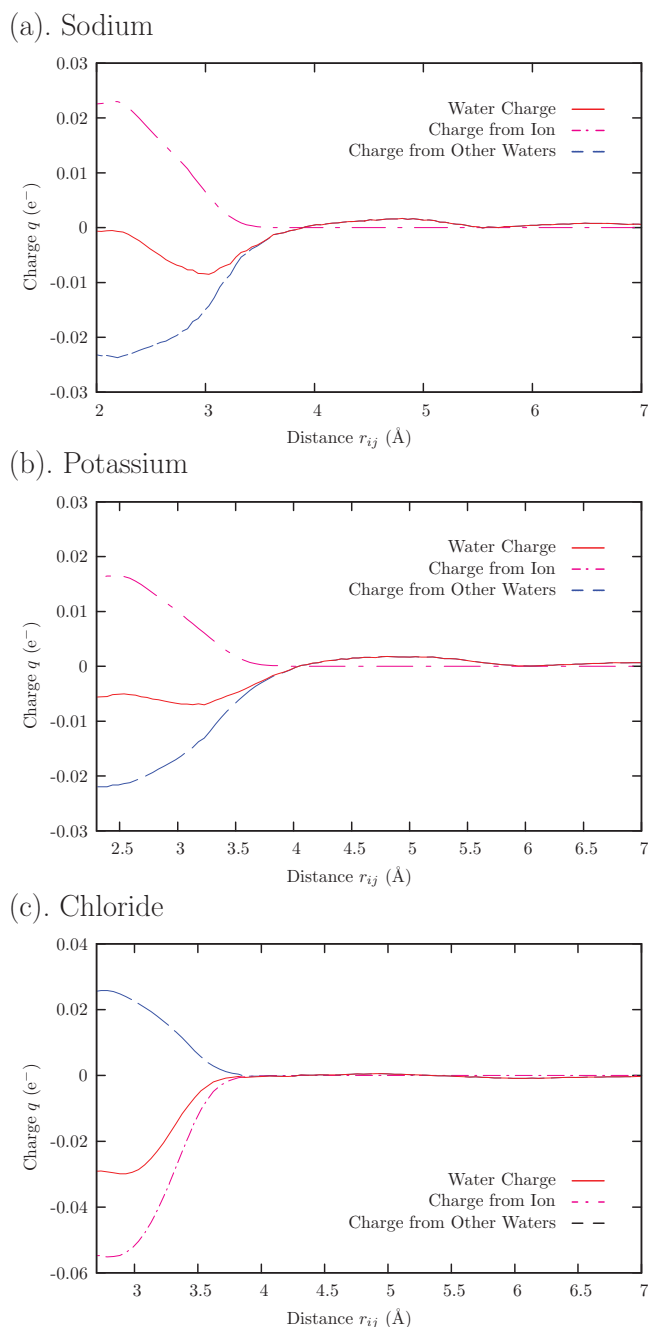


FIG. 6. The charge of water near the ion. The distribution of charge in the solvation shells near each ion is shown. The charge gained from the ion is shown as the dot-dash magenta line. The charge gained from other waters is shown as the long blue dashes. The red line shows the total charge of the water molecules, based on their distance from the ion. The distances less than those at the onset of the ion-oxygen RDF are not shown.

TABLE V. Trimers of ions with two waters. The charges of ions and waters in ion-water-water trimers, arranged as depicted in Figure 1, are listed. Units are in e .

Charge of	Ion	Closest water	Second water
Na ⁺	+0.9717	+0.0001	+0.0276
K ⁺	+0.9881	-0.0081	+0.0201
Cl ⁻	-0.9451	-0.0344	-0.0205

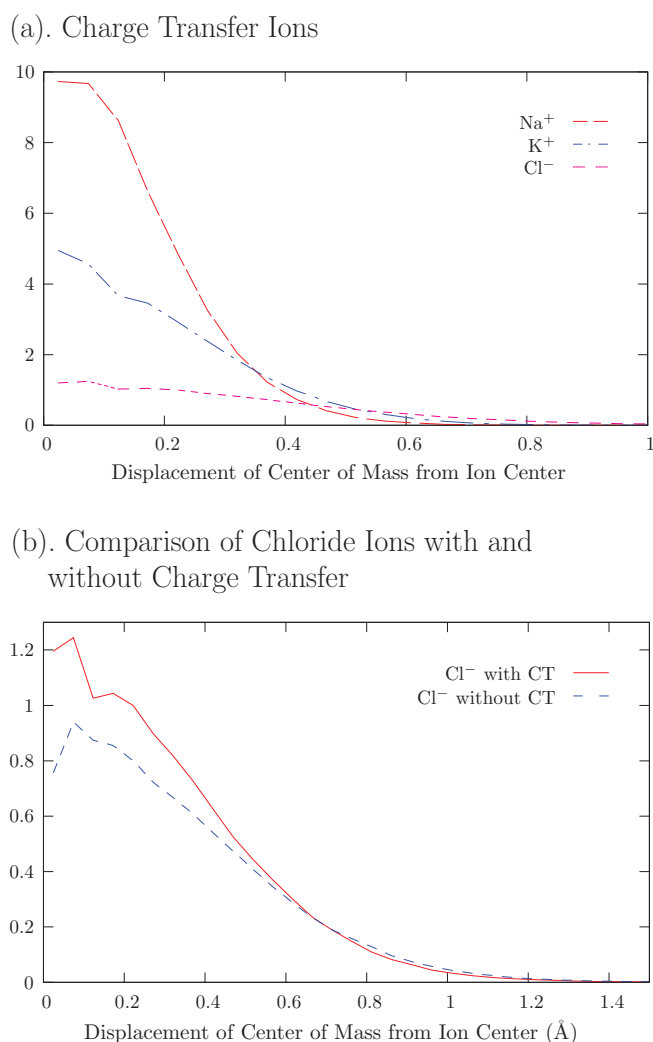


FIG. 7. Asymmetry in the first solvation shell, for (a) the three ions with charge transfer and (b) the chloride ion with (red solid line) and without (blue dashed line) charge transfer. The plots show the displacement of the center of mass of the first solvation shell from the ion's center in Å. The y-axis describes the probability corrected for a volume factor.

E. Free energies

Direct comparison of solvation free energies determined by experiment and MD simulations remains ambiguous, due to the extra-thermodynamic assumptions necessary to set experimental single-ion free energies.⁴⁹ Our hydration free energies for single ions and ion pairs compare well with

TABLE VI. Hydration free energy (ΔG_{hydr}). The single-ion hydration free energies and the ion-pair hydration free energies are compared to experimental values from Tissandier *et al.*⁶² Units are in kcal/mol.

	Calculated	Expt.
Single ions		
Na ⁺	-100.8 ± 0.6	-101 ± 2
K ⁺	-84.6 ± 0.7	-84 ± 2
Cl ⁻	-73.1 ± 0.3	-73 ± 2
Ion pairs		
NaCl	-175.2 ± 0.4	-174 ± 4
KCl	-158.6 ± 0.4	-157 ± 4

TABLE VII. Diffusion constants. The diffusion constants of single ions in 512 waters are compared to experimental values from the *Handbook of Chemistry and Physics*.⁶⁸ Units are in 10^{-5} cm²/s.

	Calculated	Expt.
Na ⁺	1.0 ± 0.2	1.33
K ⁺	1.5 ± 0.1	1.98
Cl ⁻	1.9 ± 0.1	2.03

those of Tissandier *et al.*⁶² (see Table VI). Because our ion hydration free energies are relative to those of Warren and Patel,⁴⁹ our free energies are also real hydration free energies. Our model correctly predicts the hydration free energy difference between K⁺ and Na⁺ as -17.2 kcal/mol.⁶² The calculations for the ion pairs are slightly more negative than the sum of the single-ion values, perhaps because the simulations are not at the infinite dilution limit and ion-ion interactions contribute. The ion-pair energy, found from the difference of the potential energy of ionic solution and the pure liquid, is -181 ± 6 kcal/mol for NaCl and -164 ± 7 kcal/mol for KCl. These values compare well to the experimental values: -187 ± 2 kcal/mol for NaCl and -167 ± 2 kcal/mol for KCl.⁶²

F. Diffusion constants

Our calculated diffusion constants are compared to experimental values in Table VII. The diffusion constants are in good agreement with experiment and show the correct trend among the ions ($\text{Cl}^- > \text{K}^+ > \text{Na}^+$) but are all lower than the experimental values. The water model used for these studies also has a diffusion constant less than experiment (1.9 rather than 2.3×10^{-5} cm²/s),³⁴ which may influence the results for the ion diffusion constants. The diffusion constant does not change if charge transfer is turned off and the polarizability reduced to give the same dipole, as described in Sec. III D (i.e., $Q^{CT} = 0$ and $q_d = -3.850$). For transport properties in response to an electric field or a charge gradient, charge transfer may have a larger effect. Some researchers have found a system-size dependence in the calculation of diffusion constants.⁶³ However, we do not find any difference between the simulations at different system sizes. Yu *et al.* do not observe system-size dependence of diffusion constants either.²³

IV. CONCLUSIONS

Herein, we describe a method for including charge transfer for polarizable ions in MD simulations and develop parameters for the chloride, potassium, and sodium ions. The amount of charge transfer is parameterized to be consistent with the result of electronic structure calculation for ion-water and ion-ion pairs. In the liquid, CT to the first solvation shell results in charges for the ions that average to be about $0.9e$ for the cations and $-0.77e$ for Cl⁻, in agreement with *ab initio* results for solvated ions.^{4,7,55} The charges of the ions show a distribution of values (Figure 4), representing the degree of fluctuations of the first solvation shell. Ion-ion parameters for the Lennard-Jones and charge-transfer energies are chosen to reproduce the energy and structure of the dimer pairs. The re-

sulting models properly reproduce the hydration free energies and enthalpies. Therefore, they accurately describe the interaction energies for both the dimers and in the aqueous phase (see Tables III and VI). The aqueous structures are consistent with previous MD simulations²³ and give coordination numbers consistent with experiment (Table IV). The ions also show accurate transport properties, as evidenced by the diffusion constants (Table VII). The chloride ion is parameterized to reproduce the distribution of its dipole moment in the liquid. Its value of 0.7 D compares well with quantum calculations of aqueous Cl⁻ that find the dipole moment is less than 1 D.^{7,64}

Charge transfer also affects the asymmetry of ion solvation. Comparing Cl⁻ simulations with and without CT shows that charge transfer slightly reduces the anisotropy of the first solvation shell (Figure 7). Both the reduced dipole moment of the ion and the negative charge on the solvating waters make the solvation shell more symmetric.

For all three ions, the charge of water molecules in the first solvation shell is negative (Figure 6), despite the fact that charge transfer to the cations makes the water positive in a cation-water dimer. The geometry of the solvating waters is such that molecules next to K⁺ or Na⁺ donate more hydrogen bonds with other molecules than they accept. The arrangement of the water molecules results in a transfer of negative charge to the first solvation shell, outweighing the amount of charge transferred to the ion. The first solvation shell water molecules next to Cl⁻ acquire positive charge since they accept more hydrogen bonds with other waters than they donate, but this positive charge is not large enough to outweigh the negative charge from the chloride ion and so the first solvation shell waters are negative. The second solvation shell has a compensating positive charge. Our models predict that the solvating waters are negative and the charge of water molecules near the ions is not zero.

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