

Diffusion at the Liquid–Vapor Interface of an Aqueous Ionic Solution Utilizing a Dual Simulation Technique

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The recently proposed dual simulation technique [*J. Phys. Chem. B* 2004, 108, 6595.], with slight modification, was used to determine the diffusion coefficients for a variety of regions of a 2.2 M sodium chloride aqueous solution with a vapor–liquid interface. The diffusion of all species was shown to be isotropic far away from the interface, but at different regions in the interface, the diffusion coefficients parallel and perpendicular to the interface did not agree for water and chloride. Specifically, interfacial water diffusion parallel to the interface was significantly higher than diffusion perpendicular to the interface. Chloride ions showed even larger anisotropy in its diffusion coefficient at the interface, with its perpendicular diffusion being similar to its bulk value, but parallel diffusion being much higher, corresponding to the region of highest chloride ion concentration. The origin for this was found to be hydrogen bonds with waters which are highly oriented perpendicular to the interface, somewhat impeding chloride ion diffusion perpendicular to the interface. While sodium ion diffusion increased at the interface, its interfacial concentration is low in that region, and its diffusion was fairly isotropic throughout all regions.

I. Introduction

A large amount of interesting and important chemistry occurs at the interfaces between different phases, and the strong push for more nanotechnology attempts to take advantage of unique interfacial properties. Diffusion is a fundamental property for chemical systems, and the ability to calculate it in a confined region is necessary for a complete understanding of the dynamics in an interfacial region. The fundamental process of ion transport in vapor–liquid interfacial regions is very important for a variety of biological and chemical systems,^{1–3} including atmospheric processes⁴ and environmental problems.⁵ A considerable amount of work has been done to further understand equilibrium and dynamic properties of ions at aqueous interfaces, including experimental methods such as second-harmonic and sum-frequency generation techniques.^{6,7} Computational techniques provide the advantage that many properties can be studied from a single simulation, and many of their specific aspects can be selectively probed. Some computational studies of aqueous ionic interfacial properties include work by Wilson and Phorolle comparing monovalent ions transferring across a water vapor–liquid interface.⁸ In addition, Benjamin and co-workers have studied ion transfer between liquid–liquid interfaces,⁹ and Tobias and co-workers have found good agreement with experiment for equilibrium properties of ion pairs at the air–liquid interface.¹⁰

Determining the diffusion coefficient (D) in a uniform region is a common procedure in molecular simulation, in which either the Einstein or the Green–Kubo relations are used. For the Einstein relation, the mean squared displacement (MSD) of molecules is determined over a long time period (τ), leading to the limit

$$\langle \Delta r(\tau)^2 \rangle \rightarrow 2dD\tau \quad (1)$$

where $\langle \Delta r(\tau)^2 \rangle$ is the MSD for the time period τ , and d is the

dimensionality. The Green–Kubo relation is calculated from the velocity autocorrelation function for a long time (τ) period

$$D = \frac{1}{d} \int_0^\tau dt \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \quad (2)$$

When the determination of diffusion coefficients is desired for an interfacial system, they have to be calculated for confined regions. The fact that long time periods are required to determine diffusion coefficients makes this a significant challenge, since molecules are likely to leave the area of interest while the calculation is taking place. For diffusion coefficients parallel to an interface, their calculation is relatively straightforward.¹¹ If one is interested in the calculation of the diffusion coefficient perpendicular to region boundaries, this is no longer the case, and special methods have to be used to accurately calculate them.

This paper presents the use of a previously defined method¹¹ to calculate diffusion coefficients parallel to a vapor–liquid interface, and suggests modest improvements to it for the calculation of values perpendicular to an interface. Tests were performed to show that the modifications provide a self-consistent, well-defined method for the determination of the diffusion coefficient perpendicular to the interface. The system studied consists of a 2.2 M sodium chloride aqueous solution with a vapor–liquid interface. The diffusion coefficients for individual sodium and chloride ions were calculated, along with water, in 2.5 Å regions defined by their distance from the liquid center of mass.

II. Methodology

For the determination of a diffusion coefficient with respect to an interface, the system was split up into multiple regions. The particular system of interest, an aqueous sodium chloride solution with a vapor–liquid interface, was made up of 1000 water molecules, using the polarizable Dang–Chang water model,¹² and 40 polarizable sodium and chloride ions¹³ corre-

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sponding to a sodium chloride mole fraction of 0.038 in water. The molarity of the system without an interface would be 2.2 M. A self-consistent-field procedure was used to evaluate the induced dipoles, and a particle mesh ewald summation technique was used to calculate the electrostatic interactions. The water molecular geometry was kept fixed by using the SHAKE algorithm.¹⁴ The vapor–liquid interfaces existed along the z axis, while the x and y axis were periodic liquid with 26 Å box lengths. The system was split up into 2.5 Å regions along the z axis, originating from the center of mass of the system. An equilibration using NVT molecular dynamics (MD) in which the Berendsen thermostat¹⁵ was used was followed by a series of NVE MD simulations to determine the diffusion coefficients. The diffusion coefficients were determined from 4 ps intervals, and a total of 3.2 ns of simulation time was carried out for their production, with error bars calculated from standard errors from 400 ps blocks.

A. Diffusion Parallel to an Interface. For the determination of diffusion coefficients parallel to an interface, a recently defined method¹¹ was used of which a brief overview is presented here. The first step is to define the number of molecules which originate in a certain region at the beginning of a time interval ($N(0)$), and the number of molecules which stay within that region (\mathbf{R}_k) for the *entirety* of the time interval ($N(0, \tau)$) (i.e., if it leaves the region for even one time step, it is not counted). From these, a survival probability can be determined for a molecule to stay within this region for the entirety of the time interval

$$P(\tau) = \frac{N(0, \tau)}{N(0)} \quad (3)$$

Next, it is necessary to determine the MSDs of molecules that stay within a specified region for the entirety of the time interval

$$\langle \Delta r(\tau)^2 \rangle_{\mathbf{R}_k} = \frac{1}{N(0)} \sum_{i \in \mathbf{R}_k} (x_i(\tau) - x_i(0))^2 \quad (4)$$

With these properties, it is possible to calculate the value for a diffusion coefficient parallel to an interface by using the Einstein relation for sufficiently long time intervals ($\tau \rightarrow \infty$)

$$D_{xy}(\mathbf{R}_k) = \frac{\langle \Delta r(\tau)^2 \rangle_{\mathbf{R}_k}}{4\tau P(\tau)} \quad (5)$$

This formula is valid for the motion of molecules in the two dimensions (x and y) parallel to the interface ($d = 2$). The time interval used to determine diffusion coefficients is 4 ps. Longer times would be desired, but would correspond with a lower $N(0, \tau)$, and far fewer particles being included in the calculation of $\langle \Delta r(\tau)^2 \rangle_{\mathbf{R}_k}$. There has to be a balance between calculation time, region size (larger regions would obviously allow longer times with reasonable sampling), and desired precision. Unfortunately, the use of this technique for diffusion along the z direction would bias the results toward slower diffusion coefficients, since faster moving particles would be less likely to stay within the desired region throughout the time interval.

B. Diffusion Perpendicular to the Interface.

Background. The determination of diffusion coefficients perpendicular to an interface is not straightforward, with the most recently proposed method using a dual simulation technique.¹¹ This dual simulation technique compares results from MD simulations with those of Langevin Dynamics (LD). MD

simulations are carried out for interacting particles with trajectories following Newton's equations of motion, but unlike MD, LD simulations consist of noninteracting particles, which follow a stochastic trajectory. The LD simulations utilized for this work were carried out in one dimension (z) following the Langevin equation of motion¹⁶

$$m\ddot{z} = -\frac{\partial W(z)}{\partial z} - \zeta_{zz}\dot{z} + R(t) \quad (6)$$

where $W(z)$ is a potential of mean force, $R(t)$ is a Gaussian random force, and ζ_{zz} is the static friction coefficient, which is given by

$$\zeta_{zz} = \frac{k_B T}{D_{zz}} \quad (7)$$

where, k_B , T , and D_{zz} are the Boltzmann constant, temperature, and diffusion coefficient, respectively. The diffusion coefficient is user-defined, and $W(z)$ is chosen to mimic the potential of mean force derived from density distributions from MD simulations

$$W(z) = -kT \ln \frac{\rho(z)}{\rho_l} \quad (8)$$

where $\rho(z)$ is the z dependent density, and ρ_l is the bulk liquid density. For all molecules in this work, the z dependent density is derived from a spline fit potential from the average densities in individual slabs along the z direction of 0.5 and 1 Å for water and the individual ions, respectively, with respect to the center of mass of the liquid.

The way in which one determines D_{zz} begins by performing MD simulations, recording the z -dependent density distributions and the survival probabilities ($P(\tau)$) for each of the described regions (2.5 Å intervals from the liquid center of mass). This is followed by a set of LD simulations based upon the $W(z)$ values derived from the MD simulation densities. For each region in the LD simulations, the user-defined diffusion coefficient (D_{zz}) is modified, starting from an initial guess, until the $P(\tau)$ values for the defined region agree with $P(\tau)$ for the same region from MD.

The results need to be corrected, though, since it has been shown that MD simulations have faster translational motion at shorter time scales than LD simulations for the same value of the diffusion coefficient.^{11,17–19} This has been described as a “jump distance” (ω) that arises early in the calculation, after which the increases in MSDs are similar between the two simulation methods. To make the results of LD comparable with those of MD, a correction was proposed^{11,17} for the LD boundary length

$$l_{LD} = l_{MD} - 2\omega \quad (9)$$

The value for ω was shown to be similar to the maximum difference of $\sqrt{\langle z^2(t) \rangle}$ between LD and MD.¹¹ For the final determination of the diffusion coefficient perpendicular to the interface, an iterative procedure is used. First, D_{zz} is determined by fitting $P(\tau)$ from LD to those determined from MD. Then, l_{LD} is modified by comparing the MSD curves between MD and LD, and corrected for the maximum difference in $\sqrt{\langle z^2(t) \rangle}$. After the new boundary is determined, the procedure is repeated until the difference in D_{zz} values of subsequent boundary modification runs are less than 0.01 Å²/ps.¹¹ This method has been shown to provide D_{zz} values that agree with D_{xy} in bulk water, along with agreement shown for a plot of $P(\tau)$ versus

time between MD and LD (with its modified l_{LD}) over a long time period.¹¹

The implementation of this method for the current study varies slightly with the defined technique in the determination of l_{LD} . The defined technique compares MSDs between MD and LD to determine l_{LD} , but as has been stated earlier, MSDs are not well defined for a confined region along vectors which bisect its borders. This is similar to the reasons why the Einstein relation (see eq 1) has difficulties in determining D_{zz} in a confined region. Specifically, particles will leave the desired region during the calculation, and only including particles that stay within the region throughout the time of the MSD comparisons would bias the results to lower MSD or D_{zz} values. It should be noted, as will be described below, though, that for the diffusion coefficients of water in this study, comparing MSDs which spend some time in a certain interfacial region to determine l_{LD} would most likely not significantly influence the calculated D_{zz} values, but still would lack self-consistency.

Modified Technique. It has been shown that MSD increases faster for MD than LD at short times, but that the increases are the same for moderate to long times.¹¹ This fact makes evident that any comparisons between the two simulation methods should take place in moderate to long time scales, and any comparisons made at short times would most likely be invalid. In addition, using the dual simulation technique, two properties of the LD simulations need to be determined: the diffusion coefficient (D_{zz}) and the boundary lengths (l_{LD}). Since the dual simulation method already compares the $P(\tau)$ values of MD with LD at one time, a simple way to provide a self-consistent method for determining both D_{zz} and l_{LD} would be to compare $P(\tau)$ at two different times. $P(\tau)$ values, unlike MSD values, are completely defined within its region boundaries. These comparisons should be made after enough time has passed such that the increases of MSDs for MD and LD are similar.

The method proposed here is to carry out MD simulations, determining $P(\tau)$ values at both $\tau = 2$ and 4 ps. The potential of mean force taken from the MD simulations is then input into LD simulations with an initial guess for the diffusion coefficient and l_{LD} values for each region. LD simulations are then run comparing one region at a time in an iterative fashion. First, the diffusion coefficient is determined by fitting $P(\tau)$ at 2 ps between LD and MD until their agreement is better than 0.005. Then, a comparison is made between $P(\tau)$ at 4 ps, in which, if they do not agree within 0.005, the l_{LD} values are adjusted, followed by another determination of the diffusion coefficient. After the $P(\tau)$ values at both times agree, the procedure is repeated for the next region, until the diffusion coefficients are fit in all desired regions.

III. Results and Discussion

A. Testing the Method. To test the validity of the method used, 200 ps MD simulations were carried out tracking water molecules which *originated* in the region closest to the center of mass of the system at the beginning of 4 ps time intervals. The survival probabilities and MSDs in the z direction for these waters were recorded as a function of time, ensuring that nearly all water molecules stayed within the bulklike region (within 14 Å of their original position) of the aqueous system. Following the MD simulations, LD simulations were carried out to fit $P(\tau)$ values to the MD values for the innermost region, adjusting D_{zz} and l_{LD} .

Figure 1 shows a comparison of the $P(\tau)$ values between MD and LD after modifying the LD l_{LD} and D_{zz} to form agreement with the MD $P(\tau)$ values at 2 and 4 ps. For this case, an LD

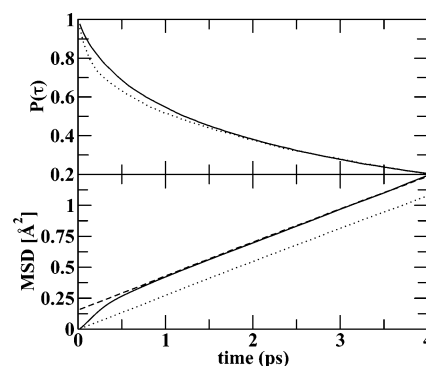


Figure 1. Comparison of $P(\tau)$ values (top) and MSDs (bottom) between MD (solid lines), raw LD results (dotted lines), and displaced LD results (dashed line). The LD simulation parameters were fit to reproduce the MD $P(\tau)$ values at 2 and 4 ps.

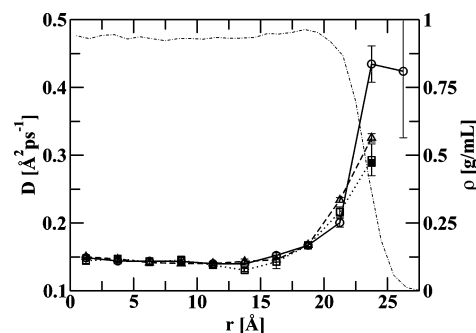


Figure 2. Water D_{xy} (circles and solid line), D_{zz} (open squares and dotted line) generated from this work comparing $P(\tau)$ at 2 and 4 ps, and D_{zz} (triangles and dashed line) generated with one LD region boundary length. The filled square point corresponds with comparing $P(\tau)$ at 3 and 6 ps. Water specific density is depicted as a dot-dashed line.

diffusion coefficient of 0.1383 Å²/ps and an l_{LD} value of 2.0 Å (compared to 2.5 Å for l_{MD}) provided the best fit. The curve shows that while the $P(\tau)$ values agree quite well between 2 and 4 ps, the LD $P(\tau)$ value is lower than MD for most of the time before 2 ps. This reinforces the point that any comparisons made between the dynamics of MD and LD at early times are not valid, but good agreement can be found at longer times. A comparison of MSDs in the z direction between MD and LD taken from the same simulations that provided the $P(\tau)$ values is given in Figure 1. It is assumed that additional regions near the innermost one of the liquid have the same MSDs, which should be the case, since the density is uniform in that region. The figure shows that after the initial increase in MSD of MD compared to LD, their MSDs increase at the same rate, which can be observed by the good agreement between the displaced line from the LD simulations and the MD line for moderate to late times. This good agreement was obtained without any direct comparisons between MD and LD MSDs, and provides strong justification for the method used. It is possible that longer times may be needed for different systems or regions, but, as with the determination of D_{xy} , longer times used would represent comparisons between fewer molecules, increasing the fluctuations (and decreasing the precision) in the calculated values.

B. Water Diffusion Comparisons. The values obtained for the diffusion coefficient both parallel and perpendicular to the interface for water are given in Figure 2. It can clearly be observed that for the bulklike region, all diffusion coefficients are very similar, further validating the techniques used to calculate the diffusion coefficients perpendicular to the interface. As has been observed previously,^{11,20} the diffusion is generally higher at the vapor–liquid interface than in the bulk, which

has also been observed for liquid argon.¹¹ This can be attributed to the lower density at the interface, resulting in waters having fewer nearest neighbors (and hydrogen bonds) at the interface.^{11,21} Using a vacancy model, diffusion is less hindered with fewer nearest neighbors, since there is more unoccupied space and vacancies for a molecule to diffuse to.

D_{zz} is slightly higher than D_{xy} at the liquid edge of the interface, which has not been observed previously. In the middle of the interface, though, D_{zz} is lower than D_{xy} , in agreement with previous observations.^{11,20} Only D_{xy} is shown at the vapor edge of the interface, since the uncertainties of D_{zz} were too high to make any definite conclusions. It is interesting to note that D_{xy} appears to be similar in magnitude at the vapor edge of the interface as in the middle of the interface. More study would be needed to be assured of this conclusion, though, because of its high uncertainty. The diffusion discrepancies can be realized by using a vacancy model. The D_{xy} value is dependent on vacancies parallel to the interface, which depends on the density of the z position in which a molecule is located. Interfacial D_{zz} values, though, are dependent on vacancies in two directions, toward the vapor phase and toward the liquid bulk. In the region between 20 and 22.5 Å in Figure 2, D_{zz} and D_{xy} are very close, but D_{zz} is slightly higher than D_{xy} , just outside the calculated error bars. This small increase of D_{zz} with respect to D_{xy} can be attributed to the fact that D_{zz} is somewhat influenced by the middle of the interface. This region is much lower in density and higher in vacancies, which should lead to faster diffusion. This is reinforced by the very high D_{xy} value in the middle of the interface, while D_{xy} in the region toward the bulk is only slightly lower. D_{zz} in the middle of the interface is influenced by both the liquid and vapor edges of the interface. It can be observed that D_{xy} does not appear to increase significantly at the vapor edge of the interface, but is much lower at the liquid edge of the interface. If D_{xy} is used as a qualitative probe for the environment perpendicular to water molecules, this sheds light onto why D_{zz} is lower in the middle of the interface than D_{xy} , since it is influenced by the fewer vacancies toward the bulk liquid.

A dual simulation method which compares the MSDs of MD and LD was carried out in which one l_{LD} value was determined, fitted to the average of the inner four regions of the simulation box. The LD simulations were carried out for one region at a time, in which $P(\tau)$ was fit in the usual way at 4 ps to determine a diffusion coefficient, and the boundary lengths were changed until the MSDs in the z direction of molecules *originating* in the region of interest agreed between MD and LD. The results from these simulations are given in Figure 2, showing agreement with the D_{zz} values obtained strictly from $P(\tau)$ for the bulklike region, but at the interface the D_{zz} values taken using the single boundary length are slightly higher than those taken from $P(\tau)$. This small disagreement can be attributed to the fact that at the interface, the diffusion is higher, which would likely result in a larger jump distance comparing MD and LD MSDs. The higher jump distance results in slightly shorter l_{LD} values (1.95 Å at the interface and 2.03 Å at the bulk) at the interface for LD simulations, resulting in a smaller LD D_{zz} value to reproduce the MD $P(\tau)$.

There are other means to compare MSDs between MD and LD. One would be to compare MSDs separately for each region, determining the MSD values for molecules either originating or spending some amount of time in the region of interest. This method would not be self-consistent within its own region, though, and possibly could result in values dominated by adjacent regions. Nevertheless, D_{zz} values calculated by deter-

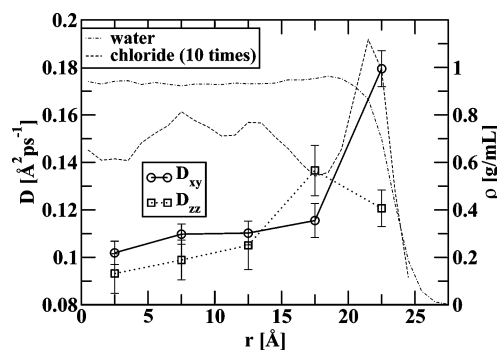


Figure 3. Chloride D_{xy} (circles and solid line) and D_{zz} (squares and dotted line) values along with the water specific density (dot-dashed line), and 10 times the chloride specific density (dashed line).

mining l_{LD} from this method would be expected to give results within the calculated error bars of the results presented here. This is because utilizing the same l_{LD} value for the interface as for the bulk was shown to result in a calculated D_{zz} value just outside the error bars if using $P(\tau)$ alone to determine l_{LD} , and any improvement in the value for l_{LD} at the interface would result in agreement for D_{zz} within the calculated error bars. This may not be the case for other systems with much sharper changes in the diffusion between different accessible regions.

Another possibility would be to compare MSDs between MD and LD for molecules which stay within one region for a set time interval. One could argue that while this would represent a flawed method for determining MSDs (since it would bias the results toward smaller values), that it would still be consistent between the two simulation methods. This technique was attempted for the current study, comparing MSDs at the end of 4 ps time intervals and $P(\tau)$ s at 2 ps intervals, and resulted in D_{zz} values in the bulklike region that were well over twice as high as D_{xy} (results not shown), which clearly would not be correct.

While the parameters used for calculating D_{zz} for this work appear to be validated for calculations in the bulk, the times used for comparisons of $P(\tau)$ may be too short for the interface, which has a lower density, which would result in fewer collisions for the same diffusion rate. This would be somewhat offset for this study, though, by the fact that diffusion rates are faster at the interface. A test was performed in which a 400 ps MD simulation was carried out recording survival probabilities at 3 and 6 ps, followed by LD simulations to determine the D_{zz} associated with these times. The D_{zz} value calculated at the interface is given in Figure 2, showing reasonable agreement with the D_{zz} results calculated comparing $P(\tau)$ at 2 and 4 ps.

C. Comparisons of Ion Diffusion. Figure 3 compares the diffusion for chloride ions calculated utilizing the dual simulation technique. The values shown for both ions are averages calculated from two adjacent regions. This was done to lower the errors, which were much higher for the ions than for water. The chloride diffusion values overlap below 15 Å, but D_{zz} is higher than D_{xy} at 17.5 Å from the liquid center of mass, in which the chloride ion concentration is very low. At 22.5 Å from the center of mass, D_{xy} is much higher than both D_{zz} at the interface and D_{xy} in the bulklike region, and D_{zz} is similar in magnitude at the interface as in the bulk. The high D_{xy} value at the interface is significant since it is where the density of the chloride ion is at its highest, even though the overall liquid density (which is dominated by water) is lower. This would make the faster diffusion of high importance in understanding dynamical properties associated with the chloride ions in highly interfacial systems such as aerosols.⁴

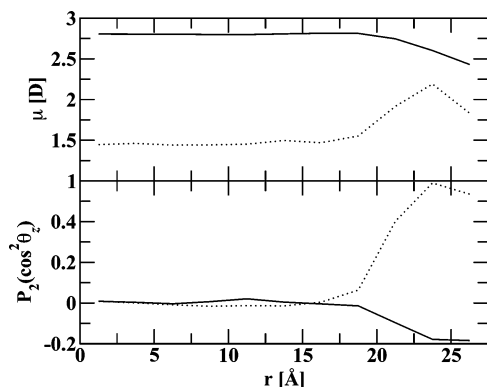


Figure 4. The top figure gives the total dipole strength for water (solid line) and chloride (dotted line) with respect to the liquid center of mass. The bottom figure gives P_2 calculated from the angle from the total dipole moment with the z axis, using the same line types as the top.

The discrepancy between D_{zz} and D_{xy} is much stronger for the chloride ion than for water. To provide a further framework for the origin for this, Figure 3 gives the dipole strength for water and chloride as a function of distance from the liquid center of mass. Sodium was not shown, since its dipole strength ranged between 0.04 and 0.05 D, being much weaker than water and chloride (and would strongly increase the graphic scale), and did not significantly change at the interface. While the dipole moment for water decreases somewhat at the interface, which occurs for pure water,¹² the chloride ion dipole moment increases significantly, which was shown to contribute to increased anion concentration at the interface.^{10,13} To gain an understanding of the orientation of the dipole vector with respect to the interface, the second moment of the orientational distribution function was calculated with respect to the interface²²

$$P_2 = \frac{1}{2} [3 \cos^2 \theta_z - 1] \quad (10)$$

where θ_z represents the angle between an individual molecular dipole with the z axis of the system. A value of zero represents unoriented dipoles, positive values represent dipoles oriented perpendicular to the interface, and negative values represents dipoles oriented parallel to the interface. Figure 4 gives P_2 as a function of distance from the liquid center of mass. What is clear is that while the water dipole orients somewhat parallel to the interface at the interface, the chloride ion strongly orients perpendicular to the interface. To determine the consequences of this, P_2 values were calculated from the angle between hydrogen bonding species. The vector representing a hydrogen bond is defined as the vector between a water hydrogen and the heavy atom (oxygen or chloride) it is hydrogen bonding to. Figure 5 gives P_2 for hydrogen bonds with waters and chloride ions, showing highly oriented hydrogen bonds with chloride ions perpendicular to the interface in the interfacial region. Water–water hydrogen bonding shows no significant orientation at the interface. This sheds light onto the large discrepancy between D_{xy} and D_{zz} at the interface for chloride ions. The oriented hydrogen bonds represent water molecules adjacent and along the z axis to interfacial chloride ions. Using a vacancy model, the increased probability for water molecules to be in this region would impede diffusion perpendicular to the interface.

Figure 6 compares the diffusion for sodium ions, showing that D_{xy} and D_{zz} mostly agree for the whole range along the z direction. D_{xy} is slightly higher than D_{zz} at 17.5 Å from the center of mass, corresponding with the region where sodium

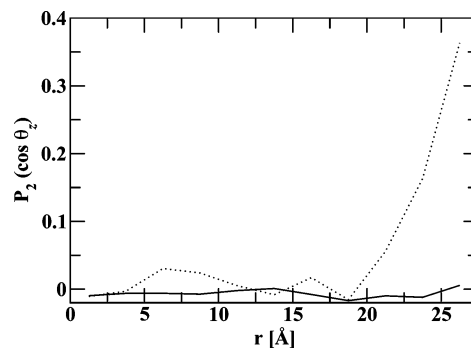


Figure 5. P_2 formed from the angle between the z axis and the vector between water hydrogens and the heavy atom to which it is hydrogen bonded, with solid and dotted lines representing water oxygens and chloride, respectively.

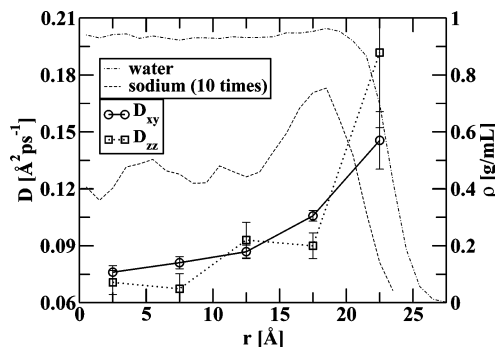


Figure 6. Sodium D_{xy} (circles and solid line) and D_{zz} (squares and dotted line) values along with the water specific density (dot-dashed line), and 10 times the sodium specific density (dashed line).

has its highest concentration, but generally are similar throughout the whole range. Also, as with all species sampled, the sodium diffusion is higher at the vapor–liquid interface, but would be less significant than for the chloride ion, since the density of sodium ion in this region is very low.

IV. Conclusions

The recently proposed dual simulation method,¹¹ with a modest modification, was used to determine the diffusion of water, chloride ions, and sodium ions at the vapor–liquid interface of a 2.2 M sodium chloride aqueous ionic solution. The method required the $P(\tau)$ values to be compared at two different times (2 and 4 ps), where the increase in MSDs for MD and LD was shown to agree for bulk water. Results showed that this method gives consistent results, and provides for a well-defined self-consistent method to determine diffusion perpendicular to an interface.

The D_{zz} values for water were shown to be higher than D_{xy} at the liquid edge of the vapor–liquid interface, but lower in the middle of the interface. For the chloride ion, a strong anisotropy of its diffusion coefficient was observed at the interface, with D_{zz} similar to bulk diffusion, but D_{xy} being much higher in value, corresponding to the region where the chloride ion density was highest. Examination of the dipole and hydrogen bond orientation showed that water molecules formed hydrogen bonds with chloride ions, oriented perpendicular to the interface, impeding chloride ion diffusion perpendicular to the interface. While sodium ions showed an increase in diffusion at the interface, its concentration was quite low, and no large differences were observed between D_{xy} and D_{zz} .

While it is not investigated here, the described method of comparing $P(\tau)$ values at two different times for MD and LD

could most likely be used to fit a memory correction to the friction coefficient $\zeta_{zz}(t)^{23}$ instead of l_{LD} , and generalized LD could be carried out that would probably give similar results for D_{zz} , but more closely model the dynamics observed from MD. This could be useful if closer modeling of MD dynamics would be desired, and may allow for comparisons between $P(\tau)$ values to be made at shorter times, which could increase the precision of the results.

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