Molecular dynamics simulations of ionic hydration of $\text{Na}^+$ inside the nanochannel

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Abstract. Molecular dynamics simulations were carried out to investigate the hydration of $\text{Na}^+$ ion in the nanochannels. The height of the channels varies from 0.65 nm to 3.0 nm, and the surface charge density varies from 0 to -0.2991 C/m². The simulation results showed that the channel height and surface charge had special effect on the hydration of $\text{Na}^+$ ion, and the peak height of radial distribution functions and coordination number increased as the channel height and surface charge density decreased. In the region of electrical double layer, hydration radius increased with the decreased of the channel height and the surface charge density, but the hydration radius of the $\text{Na}^+$ ion of the bulk region was kept at a constant.

1. Introduction
The ion in aqueous solution is surrounded by a layer of water molecules and these molecules are strongly oriented by the ion moved through the solution, and this phenomenon is called as ionic hydration [1]. Understanding the role of ionic hydration in aqueous salt solutions is of paramount importance for the comprehending of many chemical, biological, and environmental processes, including ion transport, charge transfer and osmosis [2-5], and the ionic hydration inside the nanochannel is critically important because of its essential role in sea water desalination process and biological ion channel [6, 7].

A variety of experimental techniques such as infrared, Raman, neutron diffraction, X-ray emission spectroscopy have been used to study the ionic hydration [8-13]. Zharnikov et al. used soft X-ray emission spectroscopy to investigate the ionic hydration in aqueous salt solutions and found a concentration-dependent suppression of ultrafast dissociation in salt solutions, associated with a significant distortion of intact hydrogen bond configurations of water molecules facilitating such a dissociation [14]. Nobuyuki's group through the spatial-decomposition analysis of energetics of hydration for a series of ionic solutions and found that the excess energy is not quantitatively localized within the first and second hydration layers, while its correlations over the variation of ions are good against the first layer contribution [15].

Due to the tiny scale, directly obtaining the contribution of each ion to hydration is difficult. Therefore, molecular dynamics (MD) simulations were widely used in ionic hydration investigation.
Previous studies have shown that MD simulation results can be in good agreement with that of experiments, which confirms the validity of using MD technique to simulate ionic hydration [16]. Xiaohua Lu et al. investigated the effect of inner wall modified groups on ionic hydration confined in carbon nanotube via MD simulations, and their results showed that the surface charge and chemical groups can change the interaction energy and water orientation distribution of ionic hydration [17, 18]. Qing Shao et al. performed MD simulations of the hydration of Na\(^+\) and K\(^+\) in infinitely long single-walled armchair carbon nanotubes (CNT). Their results indicated that the preferential orientation of water molecules in coordination shells of these two cations presents an anomalous change in the CNTs and causes a diameter-dependent variation for the interaction energy between the cation and water molecules in its coordination shell [19, 20]. Ximing Wu et al. examined the electric fields on the ionic hydration of Na\(^+\) inside carbon nanotubes, and found that the hydration of Na\(^+\) ion varies with the electric filed intensity [21]. However, despite the increasing number of experiment, theoretical, and molecular simulation studies on the electronic structure of the salt solutions and the geometrical structure of the hydration shells [4, 5, 8, 22-24], the effect of surface charge density and nanochannel height on the ionic hydration of Na\(^+\) ion still remains to be clarified.

In this paper, molecular dynamics simulations were carried out to investigate the impact of the surface charge density and height of the nanochannel on the ionic hydration of Na\(^+\) ion. Here, the model composed of a nanochannel and two bulk reservoirs was used to simulate the radial distribution function, coordination number and hydration radius of Na\(^+\) ions in confined space between two silicon surfaces. To emulate the real charged properties of the nanochannel, the systems were not artificially electro-neutral, but reached its electrical neutrality through the ion migration among the bulk and channel, and the silicon atoms were allowed to have thermal motion around their equilibrium positions, which was ignored in previous simulation [25, 26]. The simulation results showed that the channel height and surface charge had special effect on the hydration of Na\(^+\) ion, and the peak height of radial distribution functions and coordination number increased as the channel height and surface charge density decreased.

2. Methods
The schematic diagram of the model used in the simulations is shown in figure 1. The middle part of the model is the nanochannel where we investigate the impact of the surface charge density and nanochannel height on the hydration of Na\(^+\) ion. Two reservoirs are connected to the channel at the two ends in x direction, which serve as the bulk regions. Each bulk region is divided into two segments: bath and buffer. The bath segments are used to provide enough ions and water molecules by filling with a predefined salt solution during the simulations and the buffer regions are used to judge whether the system achieves equilibrium. Outside the bath segments, a layer of sparse silicon atoms constitutes a solid boundary to the aqueous solution. Both the upper and down walls of nanochannel are composed of four layers of silicon atoms oriented in the \(<100>\) direction, of which three layers silicon atoms neighboring to the solution are allowed to have thermal motion around their equilibrium positions, while the outer layer and other silicon atoms are frozen without thermal motion during the simulation. In our MD model, the nanochannel height is defined as the distance between the two innermost wall layers, and the upper wall can move up and down to achieve different heights of the nanochannel. Compared with the traditional method which set the height of the nanochannel arbitrarily and artificially [27-29], this approach can set the height of the nanochannel continuously. The surface charge density is set by artificially distributing a certain number of charges to the silicon atoms on the channel inner surface uniformly.
At the beginning of each simulation, pure water was filled in the buffer and nanochannel regions and the two bath regions was filled with 1.0 mol/L aqueous NaCl solution. Once the simulation started, ions would diffuse freely from the bath to the nanochannel through the buffer regions until the concentration gradients disappeared. Before the system reached equilibrium, the solution of the two bath regions was replaced periodically with 1.0 mol/L aqueous NaCl solution to provide enough ions. Once the salt concentration in the buffer region was not changed with the simulation time and kept at a predefined concentration for enough time, the system is considered as reaching equilibrium, and the following simulations after the system reaching equilibrium are used to get the final results for analysis. In this paper, the TIP4P model [30] was selected to simulate the water molecules and the SETTLE algorithm [31] was used to maintain the water geometry. The Lennard-Jones (LJ) potentials [32] was used to describe the interactions between different atoms except hydrogen-X pairs (X is an atom species of the aqueous NaCl solution) and silicon-silicon (Si-Si) pairs, and the parameters for the LJ potential were listed in Table 1. The electrostatic interactions among ions, water molecules, and surface charges were modeled by the Ewald summation algorithm [33]. The Stillinger-Webber (SW) potential [34] was used to describe the interactions among the silicon atoms. The cross parameters for the interactions between different atoms were calculated using the Lorentz-Berthelot combination rule [35]. For the Coulomb potential, all the charges in the system were considered, including mobile ions, charged sites in TIP4P water molecules, and surface charges. The motion equations for atoms were integrated by the Leap-Frog algorithm [35] with a time of 2.0 fs. The solution system used the Berendsen thermostat [36] to maintain a constant temperature of 298.0 K and the silicon walls maintained at that constant temperature by using the Damp force method [35].

### Table 1. LJ potential parameters $U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right]$ without consideration of the interactions involving hydrogen atoms.

| Atom pair | $\overline{(\AA)}$ | $(\text{kJ/mol})$ |
|-----------|------------------|-----------------|
| O-O       | 3.169            | 0.6502          |
| O-Na$^+$  | 2.876            | 0.5216          |
| O-Cl$^-$  | 3.785            | 0.5216          |
| O-Si      | 3.278            | 0.3278          |
| Na$^+$-Na$^+$ | 2.583    | 0.4184          |
| Na$^+$-Cl$^-$ | 3.492    | 0.4184          |
| Na$^+$-Si  | 2.985            | 1.0118          |
| Cl$^-$-Cl$^-$ | 4.401    | 0.4184          |
| Cl$^-$-Si  | 3.894            | 1.0118          |

### 3. Results and Discussion
3.1 The radial distribution functions of Na\(^+\)-water in the nanochannels

The structures of water molecules around the Na\(^+\) ion in the nanochannel with different surface charge densities and heights of the channel are studied through the ion-solvent radial distribution functions (RDFs). Figure 2 display the Na\(^+\)-oxygen RDFs (g(z)) in nanochannels of different height and with different surface charge density, where the z is the distance away from the channel surface. As shown in figure 2, the values of the Na\(^+\)-oxygen RDFs will slowly converge to a constant value as z increases, which is contrary to the observations of previous simulations of RDFs in carbon nanotubes (CNTs) [18-20]. In CNTs, RDFs converge to zero as radius increase. This is because in the previous studies [18-20], the Na\(^+\) ion was fixed in the center of CNT, but in this work, the Na\(^+\) ions can move freely. From figure 2, we can find that there is a sharp peak locating at 0.27 nm from the channel surface, corresponding to the first coordination shell for all the simulations results and this is same to the reported simulation results on the confined ions [15, 28, 37]. However, the second peaks of RDFs are not significant in the nanochannel, indicating that the second coordination shells of the ions may be unstable, probably due to the geometric constraint. Under the same surface charge density, the peak increases as the nanochannel height decreases. And in the nanochannel of the same height, the peak increases as the surface charge density decreases. This implies that the nanochannel height and surface charge may have special effects on the hydration of Na\(^+\) ion. Unlike the peak heights, the peak positions of the RDFs of the confined ions are generally unchanged with the surface charge density and height of the nanochannel, which is same to the bulk counterparts.

Figure 2. Radial distribution functions of Na\(^+\)-oxygen with different surface densities and nanochannel heights.
### 3.2 The coordination number of Na\(^+\) ion in the nanochannels

The coordination number is another characteristic variable to represent the structure of liquids, which is expressed as [38]:

\[
n(z) = 4\pi \rho \int_0^z z^2 g(z) \, dz
\]

where, \(\rho\) is the density, \(z\) is the distance away from the channel surface. The coordination number of the Na\(^+\) ion with different surface densities and heights of nanochannel is shown in figure 3. As shown in figure 3, the coordination number is zero when the distance is less than 0.24 nm away from the channel surface, and this means that there is no water molecules in this region surrounding the Na\(^+\) ions, which is consistent with the previous observations [20, 38]. Out of this region, the coordination number increases with the channel height and surface charge density decrease. The coordination number curve rises steeply when the \(z\) is in the range of 0.24 nm to 0.3 nm, where the sharp peak of the radial distribution functions occurs as shown in figure 2, corresponding to the first coordination shell. When the distance is 0.3~0.4 nm away from the channel surface, the curve of the coordination number is flat, because this range locates in the valley of the radial distribution function, and there is few water molecules surrounding Na\(^+\) ions. When the distance away from the surface large than 0.4 nm, the coordination number curve rises straightly, and the water molecules around Na\(^+\) ions are in disorder and the Na\(^+\) ions distribute randomly according to the radial distribution functions.

![Figure 3](image)

**Figure 3.** Coordination number of Na\(^+\) ions with different surface densities and nanochannel heights.

### 3.3 The hydration radius of Na\(^+\) ions in the nanochannels

In this paper, the effective ionic radius is defined as the difference between the peak position of the Na\(^+\)-oxygen radial distribution function and the effective radius of a water molecule [38]. The effective radius
of a water molecule is 0.138 nm [38]. The hydration ionic radius can be calculated from [39]:

\[ \frac{4}{3} \pi r_{\text{hyd}}^3 = v_w h_{\text{hyd}} + \frac{4}{3} \pi r_{\text{eff}}^3 \]  

(2)

where, \( r_{\text{hyd}} \) is the hydrated ionic radius, \( v_w \) is the volume of water molecule (\( v_w = 2.991 \times 10^{-29} \text{m}^3 \)), \( h_{\text{hyd}} \) is the hydration number and \( r_{\text{eff}} \) is the effective ionic radius. The calculated hydration radius of the Na\(^+\) ion in the electrical double layer (EDL) and bulk regions with different surface densities and nanochannel heights is shown in figure 4. It can be seen that in the EDL region, the hydration radius decreases as the nanochannel height increases regardless of whether the channel wall charged or not. The hydration radius also decreases as the surface charge density increases. But when the surface charge is -0.2991 C/m\(^2\), the hydration radius of the Na\(^+\) ion in the EDL region is smaller than the bulk value, this is because the high charged channel surface attracts more Na\(^+\) ion and leads to almost no water molecular distribution. In addition, the hydration radius of the Na\(^+\) ion of the bulk value is kept at \(~0.34\) nm, which is consistent with the observations of previous studies [38].

![Figure 4. Hydration radius of Na\(^+\) ion in the EDL and bulk regions with different surface densities and nanochannel heights.](image)

4. Conclusions

Molecular dynamics simulations were performed to investigate the hydration of Na\(^+\) ion in the nanochannel with the surface charge density ranging from 0 to -0.2991 C/m\(^2\) and channel height ranging from 0.65 nm to 3.0 nm, respectively. The simulation results showed that the channel height and surface charge may have special effects on the hydration of Na\(^+\) ion, and the peak height of RDFs. The coordination number increased as the nanochannel height and surface charge density decreased. The values of the RDFs converged slowly to constant value as distance \( z \) increased, which was contrary to the observations of previous simulations of RDFs in carbon nanotubes (CNTs). The peak positions of the RDFs of the confined ions were generally unchanged during the variations of the surface charge density and height of the nanochannel, which was same to the bulk counterparts. In the EDL region, hydration radius decreased with the increased in the nanochannel height and the surface charge density, but the hydration radius of the Na\(^+\) ion of the bulk region was almost constant and was \(~0.34\) nm.

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