Water distribution confined in the nanochannel: the impact of the thermal motion of silicon atoms

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Abstract. Using molecular dynamics simulations, the impact of the thermal motion of atoms in silicon walls on the water distribution confined in nanochannel has been investigated. The results show that thermal motion of silicon atoms has marginal effect on water distribution when the surface was not charged. However, when the surface is charged, the thermal motion of silicon atoms decreases the adsorbed peak of water molecular, and moves the position of the Na$^+$ ion concentration peak far away from the surface.

1. Introduction
At the solid-liquid interface, due to the electrostatic attraction by surface charges, counter-ions accumulate in the vicinity of the interface to form an electrical double layer (EDL). It has been widely recognized that the distribution of ion and water near the charged surface is critical to many applications, such as colloid stabilization, biological systems and surface chemistry [1,2]. The structure of the EDL is generally modeled by the Poisson-Boltzmann (PB) theory. However, the PB theory ignores many details, such as neglecting the charged particles finite size [3,4]. Furthermore, in nanofluidic systems, the channel dimensions are comparable to the thickness of EDLs, thus the EDLs may overlap in nanochannels, and the classical PB equation may not be applicable since the Boltzmann equation cannot be used to describe the ion and water distribution in nanochannels [5].

Due to the tiny scale of the channel, it is difficult to direct observe the ion and water distribution of the channel. Molecular dynamics (MD) simulations have been demonstrated a promising tool to study the ion distribution and electro-osmotic flow inside the nanochannels and offer an effective method to discover the mysteries of the EDL. Qiao and Aluru used MD simulations to investigate the ion distribution in sodium chloride solution confined in two parallel slabs with negatively charged surfaces, and their results showed that the nonelectrostatic ion-water interactions contributed significantly to the accumulation of Na$^+$ ions near the wall [6]. Mattke et al. modeled the ion and potential distribution in electric double layers for single, overlapped and sheared double layers formed with different concentration electrolytes between two aluminosilicate kaolinite surfaces, and they found that the overlap of electric double layers could lead to significant changes to the ion and potential distribution.
[7,8]. Cui et al. studied the water distribution and confirmed the layer distribution of water molecules at the solid-liquid interface using MD simulations [9]. Qiu et al. and Xu et al. found that the orientation and concentration distribution profile of water molecules depend on the surface crystal direction and charge property [5,10]. Qiao and Aluru further examined the ion distribution under different surface charge densities and found that the ion distribution of the near channel wall could be significant different from the prediction of the classical theory [11,12]. He et al. measured the ionic current in charged conical nanopores and found that the surface charges can cause current rectification when the direction of the electric field in pore reverses [13]. However, although significant progress has been made in the past few years, the impact of thermal motion of wall atoms on the ion and water distribution has not been studied and the surface charge was assumed uniformly distributed in previous studies, which might not be the best representation of the real systems [14]. Therefore, to facilitate the development of nanofluidic devices, it is important to model the ion and water in nanochannels more accurately.

In this paper, we investigate the impact of thermal motion of wall atoms on water density distribution confined in the nanochannel. A model composed of a nanochannel and two bulk reservoirs is used to simulate the ion and water distribution in nanoconfined space between two silicon surfaces. To make the charged properties of the silicon walls more realistic, the system is not artificially electro-neutralized, but reaches its electrical neutrality through the ion migration among the bulk reservoir and the nanochannel region. The discrete surface charges were places on the inner walls. Furthermore, in this study, the silicon atoms are allowed to have thermal motion around their equilibrium positions, which was ignored in previous simulations [15].

2. Methods
The schematic diagram of the MD model used in the paper is given in figure 1. Periodic boundary condition is applied in y direction. The middle part of the model is the nanochannel where we investigate the impact of the thermal motion of silicon atoms on water density distribution. Both the upper and down walls are composed of four layers of silicon atoms oriented in the <100> direction, and atoms in the three layers neighboring to the solution are allowed to have thermal motion around their equilibrium positions, while the outmost layer and other silicon atoms are frozen during the simulation. The nanochannel height is defined as the distance between the two innermost wall layers. Two reservoirs are connected to the channel at the two ends, which working as the bulk region. Each reservoir is divided into two parts: bath and buffer. The bath regions 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 bulk regions, there is a layer of sparse atoms constructed as a solid boundary to the aqueous solution. At the beginning of our simulation, the system is equilibrated until the salt concentration in the buffer region does not change and kept at a predefined concentration. After equilibration, data is collected to get the final results for analysis.

At the beginning of each simulation, pure water is filled in the buffer and nanochannel regions and the two bath regions is filled with 1.0 mol/L aqueous NaCl solution. Once the simulation starts, ions will diffuse freely from the bath to the nanochannel through the buffer regions until the concentration gradients disappear. The solution of the two bath regions is replaced periodically by the 1.0 mol/L aqueous NaCl solution to provide enough ions during the equilibration period. With the periodically updating the solutions of the bath regions, more ions can be supplied and system could reach equilibrium quickly.
Figure 1. Schematic diagram of the MD model. (unit: nm)

Our simulations are conducted using the codes developed by our lab [16,17]. In our simulations, the water molecules are simulated by the TIP4P model and the water geometry is maintained by the SETTLE algorithm [18]. 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 are described by the Lennard-Jones (LJ) potential [11]. The LJ potential is defined as:

$$u_{LJ}(r_{ij}) = 4\varepsilon [\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6]$$

where $r_{ij}$ is the intermolecular distance between two interacting particles, $\sigma$ and $\varepsilon$ are length scale and energy parameter, respectively. The parameters for the LJ potential are listed in Table 1. The electrostatic interactions among ions, water molecules, and surface charges are modeled by the Ewald summation algorithm [19]. The motion equations for atoms are integrated with the timestep of 2.0 fs by the Leap-Frog algorithm. The interactions among the silicon atoms are described by the Stillinger-Webber (SW) potential [20]. The solution system is maintained by Berendsen thermostat [21] at a constant temperature of 298.0 K, and silicon walls are maintained at the same temperature by the Damp force method [22]. The short-range interaction of cutoff is 1.2 nm, and the relaxation time of the thermostat is 120 fs. The total simulation time is 16 ns with the first 8 ns for equilibration and 8 ns for data collection.

Table 1. LJ potential parameters without consideration of the interactions involving hydrogen atoms.

| Atom pair   | (Å)   | (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 distribution of water molecular in nanochannel

In order to investigate the effect of the thermal motion of silicon atoms on water density distributions in the confined space with different surface charge densities, simulations with/without thermal motion of silicon atoms were conducted with 0 C/m$^2$, -0.1496 C/m$^2$ and -0.2991 C/m$^2$ surface charge density, and 2.5 nm and 3.0 nm height of the nanochannel.
Figure 2 gives the water density distribution in the nanochannels with different surface charge densities. From figure 2, we can find that the water layering structure is close to the silicon wall in the region, that is, water density distribution displays oscillatory profiles. In the vicinity to the solid surface, the water layering structure is due to the phase discontinuity and interface effect, which has been confirmed by the simulations and experiments [10,23]. In the region far away from the silicon wall, the water density congregates slowly to 1.0 g/cm$^3$, it is the bulk density of water. From the figure 2, an interesting feature can be found from the water density profiles. When the surface is not charged, thermal motion of the silicon atoms has hardly effect on the water molecular distribution. But, when the surface charge density is -0.1496 C/m$^2$, two different concentration peaks can be found within 0.5 nm away from channel surface, and the first peak is usually named as the adsorbed water layer because it has the closest distance to the channel surface, the second peak is believed to be the hydration layer. When the thermal motion of wall atoms is considered, the amplitude of these two peaks is lower, and the first peak locates at 0.28 nm from the charge surface, while the first peak without thermal motion is only 0.20 nm from the channel surface. The distance between the second peak and the channel surfaces is the same whether the silicon atoms have thermal motion or not. When the surface charge density value increases to -0.2991 C/m$^2$, the peak of the adsorbed layer is reduced by the thermal motion of the silicon atoms, but the rest peaks have the same amplitude. When the surface is not charged, the peaks decrease as the distance from the wall increases and the maximum peak is about 2.0 g/cm$^3$ whether the silicon walls atoms have thermal motion or not. However, apparent discrepancy appears at silicon atoms have the high surface charge density and thermal motion, which mainly locate within 0.30 nm near the surface. This difference is very attractive to us, which may give some useful information about the hydration force. So, we further calculate the electrical property of EDL and the Na$^+$ ion distribution in the channel in order to investigate the mechanism that affects the water distribution.
Figure 2. Water density distribution in NaCl solution confined in 2.5 nm and 3.0 nm height nanochannels along z direction in the EDL region with different surface charge densities.

3.2 The distribution of Na\(^+\) ion in nanochannel

The Na\(^+\) ion distribution changes significantly when the thermal motion silicon atoms are considered from figure 3. When the silicon atoms are fixed, there are three distinct layers of the Na\(^+\) ion within 0.30 nm from the channel surface, and the first peak locates at 0.10 nm. But when the silicon wall atoms are allowed to have thermal motion, there is only one peak near the channel surface, and the position of the Na\(^+\) ion concentration peak locates at 0.30 nm away from the surface, which is farther away from the surface than the first peak without thermal motion. Compared figure 2 with figure 3, we can find that the thermal motion of the silicon wall atoms influences the water density distribution within 0.35 nm near the channel wall, this is almost the hydrated diameter of Na\(^+\) ion [24]. This is due to the thermal motion of the charged silicon atoms around their equilibrium positions, which weakens the interaction between Na\(^+\) ion the charged silicon atom, and water molecular are absorbed by the Na\(^+\) ions. The hydrated Na\(^+\) has an inherent size, so they locate far away from the charged silicon walls, which results in the difference of the water density distribution between the cases with and without thermal motion. Another interesting finding is that there are no ions close to the surface. This is because each ion has an inherent size so that it cannot approach too close to the smooth wall [15], and the ions tend to stay away from the wall so as not to disturb the order of the packed water molecules.

Figure 3. Na\(^+\) ion distribution in NaCl solution confined in 2.5 nm and 3.0 nm height nanochannels along z direction in the EDL region with different surface charge densities.

3.3 The electric property of EDL with different heights of nanochannel

In order to investigate the mechanism of the difference in water distribution between the cases with and without thermal motion in the EDL, the electric property of EDL is calculated. The statistical numbers of counter-ions (Na\(^+\)) and co-ions (Cl\(^-\)) of the EDL in nanochannels of different height is shown in Figure 4, and the surface charge density is -0.2991 C/m\(^2\). From figure 4, we can find that the number of the counter-ions is higher than that of co-ions in the EDL region, which has nothing to do with whether the silicon atoms have thermal motion or not. The interaction between the charged surfaces and ions in the
channel, which results in the exclusion of co-ions and enrichment of counter-ions in the EDL region. When the silicon atoms have thermal motion, the number of the counter-ions (Na\(^+\)) is lower than the still ones. Because every Na\(^+\) ion absorbs a water molecule, so the number of the Na\(^+\) ions and water molecules are few in the EDL region, and these results in the amplitude of the water density peak is lower when thermal motion is introduced, as shown in the case 2 and 3 of figure 2. This is may be the explanation the difference of water density distribution between the cases with and without thermal motion in the EDL. However, no matter the heights of the nanochannel, the electric property of EDL remains negative. Therefore, the EDL region is not neutral, so the assumption in the previous models of MD simulations seems to be inaccurate [25,26].

![Figure 4.](image)

**Figure 4.** The numbers of counter-ions (Na\(^+\)) and co-ions (Cl\(^-\)) and the net charges in the EDL region in nanochannels of different height.

### 4. Conclusions

The water distribution confined in the nanochannel was studied using molecular dynamics simulation. It was found that the thermal motion of wall atoms can change the water distribution and Na\(^+\) ion distribution in the EDL region when the surface charged. Due to the thermal motion of the wall atoms, in nanochannel with surface charged, the adsorbed layer peak of water distribution was lower, and the position of the Na\(^+\) ion concentration peak locates farther away from the surface. In the EDL region, the electric property of EDL remains negative, not neutral.

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### References

[1] Schneider C, Hanisch M, Wedel B, Jusufi A and Ballauff M 2011 *Journal of Colloid and Interface Science* 358 62-67
[2] Wang J Y and Xu Z 2016 *AIP Adv.* 6 075025
[3] Lee J W, Nilson R H, Templeton J A, Griffiths S K, Kung A and Wong B M 2012 *J. Chem. Theo. Comput.* 8 2012-2022
[4] Guerrero-Garcia G I, Gonzalez-Tovar E and Cruz M O 2011 *J. Chem. Phys.* 135 054701
[5] Qiu Y H, Tan Q Y, Si W and Chen Y F 2014 *China-Technological Sciences* 57 230-238
[6] Qiao R and Aluru N R 2004 *Phys. Rev. Lett.* 92 198301
[7] Mattke T and Kecke H J 1998 *J. Colloid Interf. Sci.* 208 555-561
[8] Mattke T and Kecke H J 1998 *J. Colloid Interf. Sci.* 208 562-569
[9] Cui S T and Cochran H D 2002 *J. Chem. Phys.* 1117 5850-5854
[10] Xu D Y, Leng Y S, Chen Y F and Li D Y 2009 Appl. Phys. Lett. 94 201901
[11] Qiao R and Aluru N R 2003 J. Chem. Phys. 118 4692-4701
[12] Qiao R and Aluru N R 2005 Colloid Surface A 267 103-109
[13] Gillespie Y H D, Boda D, Vlassiouk I, Eisenberg R S and Siwy Z S 2009 J. Am. Chem. Soc. 131 5194-5202
[14] Xu D Y, Li D Y, Leng Y S and Chen Y F 2007 Molecular Simulation 33 959-963
[15] Chen Y F, Ni Z H, Wang G M, Xu D Y and Li D Y 2008 Nano Lett. 8 42-48
[16] Li J P, Zhang Y, Yang J K, Bi K D, Ni Z H, Li D Y and Chen Y F 2013 Phys. Rev. E 87 062707
[17] Li J P, Wang H C, Li Y S and Han K Z 2017 Molecular Simulation 43 320-325
[18] Miyamoto S and Kollman P A 1992 J. Comput. Chem. 13 952-962
[19] Yeh I C and Berkowitz M L 1999 J. Chem. Phys. 111 3155-3162
[20] Stillinger F H and Weber T A 1985 Phys. Rev. B 31 5262-527
[21] Berendsen H J C, Postma J P M, Vangunsteren W F, Dinola A and Haak J R 1984 J. Chem. Phys. 81 3684-3690
[22] Allen M P and Tildesley D J 1987 Oxford (New York) pp 152-154
[23] Cheng L, Fenter P, Nagy K L, Schlegel M L and Sturchio N C 2001 Phys. Rev. Lett. 87 156103
[24] Kiriukhin M Y and Collins K D 2002 Biophys. Chem. 99 155-168
[25] Freund J B 2002 J. Chem. Phys. 116 2194-2200
[26] Leng Y S and Cummings P T 2006 J. Chem. Phys. 125 104701