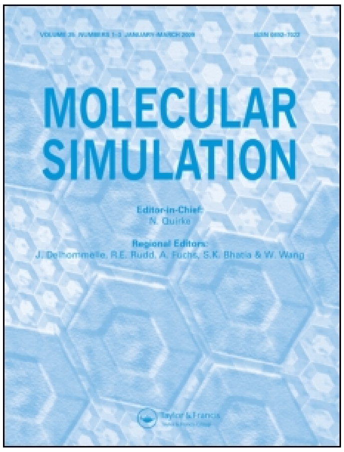

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Molecular dynamics simulations of ion distribution in nanochannels

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Molecular dynamics simulations of ion distribution in nanochannels

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Molecular dynamics simulations of ion distribution in a nanochannel were performed using a three region simulation domain including two bulk regions on each side of the nanochannel. This scheme allows the study of ion concentration and distribution inside the nanochannel under a given bulk electrolyte concentration, i.e. when the molecular system reaches equilibrium, the concentrations of the counter- and co-ions inside the nanochannel corresponding to a bulk electrolyte will emerge naturally. Our approach is in sharp contrast to the common practice in modeling electric double layers where the number of ions in the nanochannel is assigned somewhat arbitrarily, corresponding to an unknown bulk concentration.

Keywords: Molecular dynamics; Ion distribution; Nanochannels; Electric double layer

1. Introduction

Microfluidic lab-on-a-chip technology has been a focus of research over the past two decades with great impacts on rapid diagnosis, drug discovery and drug delivery. Introducing nanoscale channels into lab-on-a-chip devices represents a breakthrough in the sense of new functions such as detecting and manipulating single molecules. The success of nanofluidic devices depends on a thorough understanding of the fluid, ion and molecule behaviour in highly-confined nanochannels. For example, in recent experiments of using nanopores and nanochannels as biosensors, where the modulation of the ion current through nanopores/nanochannels was used as an indication of DNA molecules being translocated through the nanopores/nanochannels, both enhancement and blockade of the ion current were observed, depending on the ion concentrations used in the experiments [1–4]. It is believed that the opposite current modulations are the results of two competing effects, i.e. channel conductance decrease because of the volume occupied by the DNA molecule and its low mobility and channel conductance enhancement because of the additional ions adsorbed on the DNA to shield the charge of the DNA backbone. Different experiments showed different ion concentrations for the transition from current blockade to current enhancement, indicating that there could be complex interactions between the DNA molecules, surface charges and mobile ions in the nanochannel. In addition, it has been experimentally shown that the ion conductance in nanochannels could be very different from the prediction based on the bulk ion concentration and can be tuned with a gate voltage [5,6], which is due to the comparable size of the nanochannel and the Debye screening length. Therefore, understanding the ion concentration and distribution inside a nanochannel corresponding to a bulk electrolyte of certain given concentration is critical to the design and application of nanofluidic devices.

The ion concentration and distribution in nanochannels depend on the surface chemistry and the structure of the electric double layers. In nanochannels, the electric double layer may overlap, and the classical Poisson–Boltzmann

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equation may not be applicable since the Boltzmann equation can not be used to describe the ion distribution in the channel. However, an accurate and well-accepted model has not been developed. In the past decade, molecular dynamics (MD) simulations demonstrated a promising tool to study the ion distribution and electroosmotic flow inside nanochannels. Quite a few MD simulations [7–16] have been performed to study the ion and potential distributions for different ion concentrations, different surface charge densities and with separated or overlapped electric double layers. Spohr [7–9] modeled a single electric double layer formed with 2.2 mol/kg aqueous NaCl and CsF solutions near a metallic electrode that is either uncharged, positively or negatively charged with a surface charge density of 9.9 $\mu C/cm^2$. Even though the total simulation system is relatively small (400 water molecules and a total of 32 ions), the obtained water and ion profiles in the electric double layer fit the expectation based on the classical theory. In the simulation, he first assigned the numbers of mobile cations and anions and then calculated the surface charge as the difference between these two kinds of ions. The solution concentration used (2.2 mol/kg) was based on the neutral solution when there was no surface charge and it was assumed to be the same even when the number of cations and anions changed to be non-equal to each other. Mattke and Kecke [10,11] 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. It was shown that the overlap of electric double layers could lead to significant changes to the ion and potential distribution. In their simulation, the local anion concentration was taken as the electrolyte concentration. Freund [12] modeled the electroosmotic flow of a 0.01 M Cl^- solution and found that the viscosity near the wall could be six times higher than the bulk viscosity. Only Cl^- ions were considered in the simulation without justification, even though the Debye length was only 3.04 nm, less than half of the channel width (6.5 nm) of the simulation domain. Zhu *et al.* [13] studied the electroosmotic flow of a simplified electrolyte model (non-polar solvent) in nanochannels and found that the continuum theories had to be corrected to agree with the MD simulation results. The cation and anion numbers in the simulation were 31 and 12, respectively, but no discussion was presented about why these numbers were selected. Qiao and Aluru [14,15] further examined the ion distribution under different surface charge densities and found that the near-wall ion distribution could be significantly different from the prediction of the classical theory. More interestingly, in another simulation performed by Qiao and Aluru [16], it was found that under high surface charge density, the charge distribution in nanochannels could show an inversion, i.e. a higher co-ion concentration than the counter-ion concentration, in the region of 0.53 nm away from the channel wall, which is totally contradictory to the classical theory. In these simulations, either only counter-ions [14] were considered or the concentration of co-ions was assumed to be the electrolyte concentration and the number of counter-ions was taken as the sum of co-ions and the surface charges [15,16].

It can be seen from the literature that even though significant progress has been made, one important and fundamental issue remains unsolved, i.e. the assignment of the numbers of counter- and co-ions in the simulation domain seems arbitrary. So far, attention has been paid to meet the requirement of overall charge neutrality among surface charges and mobile ions in the electrolyte. However, since both counter- and co-ions may exist in the electrolyte and neither the concentration of the counter-ions nor that of the co-ions is the same as that of the bulk, the number of counter- and co-ions cannot be derived solely from the requirement of charge neutrality. In the literature, it is not uncommon that the concentration of the co-ions is taken as the bulk value, whereas the number of the counter-ions is determined to balance the sum of the surface charges and co-ions, which might not be accurate. For the cases of high electrolyte concentrations, which have small Debye lengths, only considering counter-ions in the simulation domain does not correspond to any real situation. For the development of nanofluidic devices, it is important to model more accurately the ion concentrations inside nanochannels corresponding to a certain bulk concentration to elucidate experimental phenomena such as different current modulations under different electrolyte concentrations for the experiments of DNA detection [3,4,4]. In this paper, we attempt to investigate this fundamental problem by extending the MD simulation domain to include two bulk regions sandwiching the nanochannel region of interest. Using this approach, when the system reaches equilibrium, the concentration of the electrolyte in the bulk region and the number of both counter- and co-ions in the nanochannel region emerge naturally.

2. Details of MD simulations

The simulation domain (as shown in figure 1) consists of a slab of NaCl solution confined between two parallel silicon plates. The simulation domain is divided into three regions and for regions I and III, no surface charge is assigned to the silicon wall. Therefore, there are no electric double layers in these two regions and the solution can be treated as "bulk" as long as our interest is the structure of the electric double layer, which is induced by the surface charge. In region II, however, the silicon atoms on the innermost layers of the top and bottom plates are partially charged with a given surface charge density, leading to electric double layers in this region. The overall electrical neutrality is satisfied by keeping a balance of cations, anions and surface charges in the whole simulation system. In this way, the concentrations of the counter- and co-ions in the central nanochannel region, as well as the concentration of the bulk region emerges naturally.

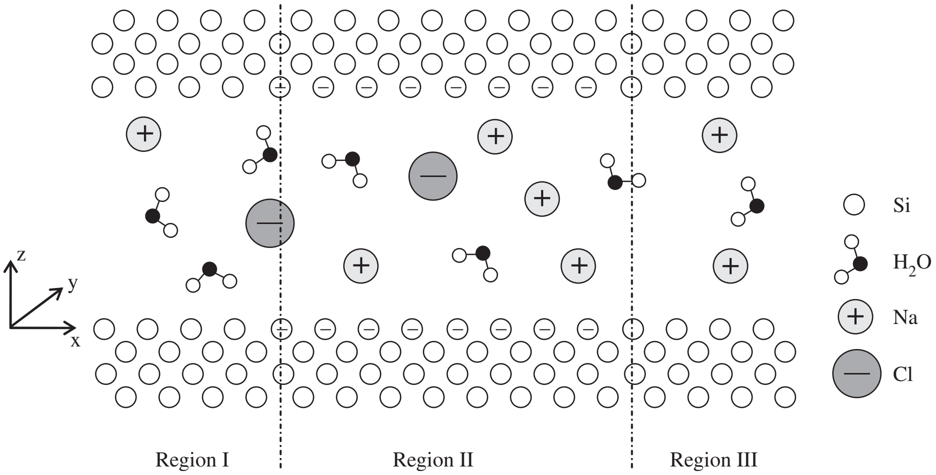

Figure 1. A schematic diagram of the simulation domain, which includes three regions: no surface charge and electric double layer in Regions I and III so the electrolyte in these regions represent bulk electrolyte. Negative surface charges are presented in Region II, leading to electric double layers in this region.

Each silicon plate is composed of four layers of silicon atoms (totally 1024) oriented in the <100> direction. The positions of the silicon atoms are given according to the Si crystal structure. The Si atoms in the lower plate are kept fixed during the simulation and the upper silicon plate can move in the z-direction to guarantee that the water density in the simulation system is 1 g/cm^3 at a pressure of 1 bar and a temperature of 298 K. For the coordinate system chosen in figure 1, $z = 0$ corresponds to the innermost layer of the lower plate. Periodic boundary conditions are applied in x- and y-directions. The dimensions of the simulation box are $L_x = 8.69$ nm, $L_y = 4.34$ nm and $L_z = 4.34$ nm, respectively.

Equilibrium MD simulations were performed with a parallel MD code modified from a code that has been used to model the hydration structure of water and ions confined between mica surfaces [17,18]. Water was modeled with the SPC/E model [19]. A SETTLE algorithm [20] was used to maintain the rigid water geometry. The intermolecular interactions were expressed as the sum of the Lennard-Jones potential and the electrostatic potential. The parameters for the Lennard-Jones potential were taken the same as those used by Qiao and Aluru [14] and the electrostatic interactions between all charges in the system (including mobile ions, O and H atoms in water molecules, and surface charges) were calculated using the Ewald summation algorithm with the slab correction [21]. The equations of motion were integrated using a leap-frog algorithm with a time step of 2.0 fs. The temperature of the system was maintained at 298 K using a Berendsen thermostat [22] with a time constant of 0.1 ps. Starting from a random configuration, the molecular system was allowed to equilibrate for 1 ns and a production run of 2 ns was followed to gather the statistically converged results. Table 1 summarizes the two cases examined in this study for the ion concentration and profile in nanochannels with two different surface charge densities.

3. Results and discussion

3.1 Ion and water distribution in bulk region

The ion and water concentration profiles in the bulk region for case 1 are shown in figure 2, which is representative for both cases in the bulk region. The layering of water near the solid wall is well-known as described in the literature [23], which is due to the interactions between water molecules and solid surfaces and exists no matter if the surface is charged or not. The concentration profiles of Na^+ and Cl^- ions in the bulk region almost coincide with each other, indicating the same concentration everywhere, as expected for bulk electrolyte.

3.2 Ion distribution in central nanochannel

Figure 3(a) shows the ion concentration profiles in the central nanochannel region with a surface charge density of -0.2034 C/m^2 (case 1). The concentration profile of the co-ions (Cl^-) in this region is similar to that in the bulk region (figure 2), while the concentration profile of the counter-ions (Na^+) is significantly different from the bulk result because of the electric double layer. A pronounced peak of Na^+ occurs at a position of 3.80 Å away from the channel wall and a very weak second peak of Na^+ concentration is observed at a position of 5.70 Å away from the channel wall.

Figure 3(b) shows the ion concentration profiles in the central nanochannel region with a surface charge density of -0.2882 C/m^2 (case 2). Different from case 1, two distinct peaks are observed for Na^+, i.e. a first peak at

Table 1. List of the simulated cases.

Case #	σ_s (C/m^2)	# of water	# of Na^+	# of Cl^-
1	-0.2034	4016	140	92
2	-0.2882	4016	152	84

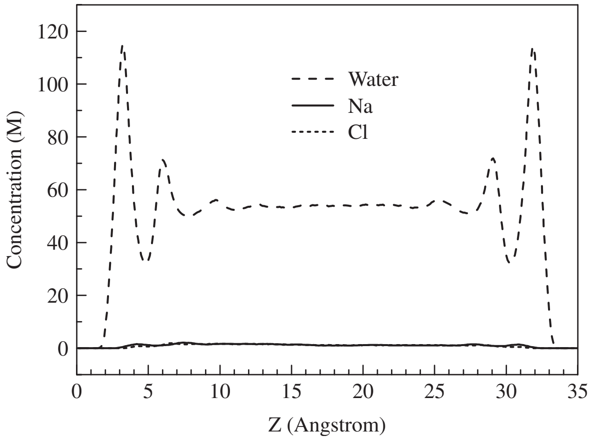

Figure 2. Ion and water concentration profiles in the bulk region for case 1.

2.10 Å and a second peak at 3.50 Å away from the channel wall. The double peak phenomenon is not predicted by the classical electric double layer theory, but has been observed in several molecular dynamic simulations [8,10,14–16]. We believe that it is due to the fact that under high surface charge density, one layer of Na^+ ions are dehydrated and adsorbed onto the negatively charged solid wall, which forms the inner Helmholtz plane. The second peak is formed by hydrated Na^+ ions, which corresponds to the outer Helmholtz plane.

3.3 Average ion concentrations in bulk and nanochannel regions

While the ion concentration profiles in the nanochannel with charged surface is similar to that reported in the literature, the overall ion concentrations in the central nanochannel region and the bulk region reveal more interesting information. The statistical numbers of counter-ions and co-ions and water molecules in the bulk and central nanochannel regions are given in table 2. While the numbers of the Na^+ and Cl^- ions in the bulk region are very close to each other, it is interesting to note that for both cases the number of Na^+ ions in the bulk region (region I + III) is slightly (less than 10%) larger than the number of Cl^- ions. This may be due to statistical error or it may be related to some other factors, which needs further investigation. In the central nanochannel region, neither the number of Na^+ ions nor that of Cl^- ions is close to those in the bulk region. Using the dimensions of the simulation box, the average ion concentrations in the bulk and central nanochannel regions were calculated as shown in table 3. The bulk concentrations were calculated with the average numbers of the Na^+ and Cl^- ions in regions I and III. Table 3 clearly shows that because of the presence of electric double layers, the concentrations of both counter- and co-ions in nanochannels can be greatly different from the bulk electrolyte, which indicates that it might not be correct to take the co-ion concentration as the bulk electrolyte concentration, as practiced in some literatures. A three region simulation domain including bulk electrolyte on each side of the nanochannel can provide the ion concentration in nanochannels with charged surfaces corresponding to a certain bulk concentration. This addresses the fundamental issue of ion number selection in MD simulations of electric double layers, which can be important for modeling electroosmotic flow and macromolecule translocation through nanochannels.

Table 2. Numbers of ions and water molecules in the three regions.

Case #	*Regions*	*# of water*	*# of Na*$^+$	*# of Cl*$^-$
1	I+III	1946.76	56.16	52.68
	II	2069.24	83.84	39.32
2	I+III	1929.81	51.00	46.95
	II	2086.19	101.00	37.05

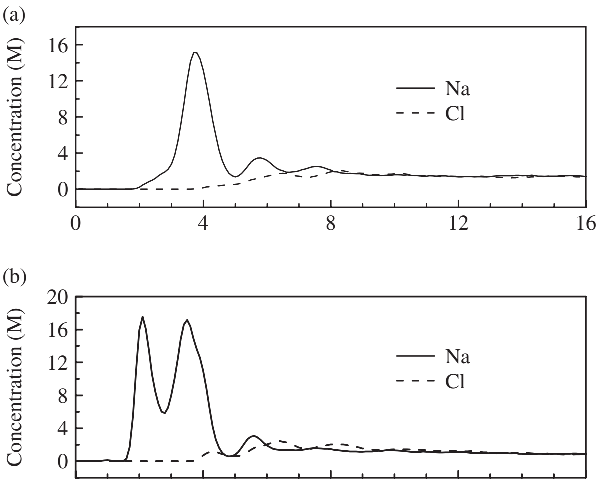

Figure 3. Ion concentration profiles in the nanochannel for case 1 (a) and 2 (b).

4. Conclusions

Equilibrium MD simulations have been performed to investigate the ion concentration and distribution in nanochannels of charged surfaces with a three region simulation domain. The counter-ion and co-ion concentrations and distributions in the nanochannel with electric double layers were obtained corresponding to a bulk electrolyte of known concentration. It was shown that both

Table 3. Average ion concentration in the bulk and the nanochannel regions.

Case #	C_{bulk} *(M)*	C_{Na+} *(M)*	C_{Cl-} *(M)*
1	1.37	2.11	0.99
2	1.23	2.54	0.93

C_{Na+} and C_{Cl-} represent the concentrations of Na^+ and Cl^- ions in the nanochannel.

the counter- and co-ion concentrations in the nanochannel could be significantly different from that of the bulk electrolyte. This approach is in contrast to the common practice in the literature where the ion numbers in the nanochannel are assigned somewhat arbitrarily and corresponding to an unknown bulk concentration.

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