To the Graduate Council:

I am submitting herewith a thesis written by Jiandong Zhou entitled "Molecular simulation of aqueous electrolytes in silica nanochannels." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

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(Original signatures are on file with official student records.)

Molecular simulation of aqueous electrolytes in silica nanochannels

A Thesis Presented for

The Master of Science Degree

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Jiandong Zhou

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ABSTRACT

Aqueous electrolytes, NaCl and $CaCl_2$, in silica nanochannels with radius ranging from 0.67 nm to 1.5 nm were simulated with the molecular dynamics technique. An atomistic wall model and the SPC/E water model were used in the simulations. The effects of radius and charge on the wall surface of the nanochannel were studied. The self-diffusivity of water molecules and ions along the axial direction of nanochannel was calculated. It was shown that water molecules form different layers when the radius of the nanochannel changes. The effects of the wall on the movement of water molecules and ions are related to the radius of the nanochannel. The charges on the wall surface exert little influence on water molecules and chloride ions while effect positive ions greatly. Surface charges were neutralized by positive ions, which were essentially immobilized at the surface charge sites.

TABLE OF CONTENTS

LIST OF FIGURES

FIGURE **PAGE**

LIST OF TABLES

TABLE **PAGE**

1. Introduction

The current DNA sequencing methods [1] are too slow for effective and economical genotyping and drug development [2]. The speed needs to be increased by many orders of magnitude so that DNA techniques can enable more practical genome-based medicine.

With the rapid development of nanometer-scale science and technology, the use of a nanopore to characterize DNA molecules has a promising future. In concept, when single-stranded DNA is stimulated to pass through the nanopore by the electrical field exerted across the nanopore, each kind of nucleic acid will generate a distinctive electrical signal in transverse electrodes. By recording and decoding the signals, it may be possible to sequence DNA. The speed is projected to be between 1,000 and 10,000 bases per second or between 30 and 300 million bases per 8-hour day, which will be 1,000 to 10,000 times faster than the current sequencing speed. As a prerequisite condition, nanopore with ~ 2 nm diameter is required.

In 2001, using ion-beam technology, Li *et al.* [3] sculpted a 5 nm-diameter nanopore in Si_3N_4. When they imposed a voltage across the nanopore and drew double-stranded DNA with negative charge through it, diminutions of the ionic current were observed as a result of the DNA blockades due to the interactions of individual DNA molecules with the nanopore. This experiment reduced the diameter of the man-made pore to 5 nm, which is a big improvement, although it still cannot be applied to distinguish different nucleic acids.

As an alternate way to obtain a nanopore, Kasicimowicz [4] used single ion channels with ~ 1.4 nm limiting apertures in biological membranes to test DNA. He found that a single purine or pyrimidine nucleotide passing through the limiting aperture of a channel would block the ionic current in a manner that reflects the molecular size and chemical properties of each nucleotide in a polynucleotide. This result promises that it may be possible to sequence DNA practically by measuring the variation of electrical current and translation speed when DNA passes through a single pore.

However, this method has not achieved single base resolution either. There are several other problems with this technique. One is the nanopore itself [5]. The instability of a pore composed of proteins restricts the optimization of the experimental conditions and limits the standardization of this testing technique. Nanoscopic channels manufactured from more robust materials such as silica might circumvent these problems. Another problem is the lack of molecular level information when DNA in ionic solution passes through a single channel. How and to what extent different nucleotides block the aperture of the pore and affect the electrical current as well as translocation rate need to be investigated.

By means of molecular simulation, our group is modeling DNA in aqueous ionic solutions passing through artificial nanoscopic channels (nanochannels) constructed in silica. As a part of the group's work, aqueous electrolyte solutions in nanochannels with 1.3-3 nm diameter have been simulated and studied in this research.

2. Background

For molecular dynamics simulation, potential models of the system studied are necessary. For this research, potential models of H_2O and ions as well as the nanochannel are needed.

Because of its indispensability to life and importance to industry, bulk water has been extensively studied under various conditions by means of molecular dynamics simulation. A number of water potential models have been developed, tested, and modified, such as the SPC/E [6], the TIP series [7], the POL [8], the SW [9], and other models. Among these models, the SPC/E model has been widely used to simulate water and can adequately describe many of the thermodynamic properties of water [10]. It will be used in this study. Besides pure bulk water, bulk water with ions, such as sodium, calcium, chloride ions etc., has also been widely studied (for example, [11] [12]).

With growing emphasis on nanoscale science and technology, people began to study liquids in nanoscale pores. Marti *et al.* [13] studied temperature effects on the static and dynamic properties of water inside carbon nanotubes. Brodka [14] published the properties of acetone in silica nanopores. Because of the small size of nanotubes, the wall may exert force upon the all of the liquid inside; that is, the interfacial region may extend entirely across the nanotube, resulting in large differences in the behavior of the liquid under some conditions. Koga *et al.* published results of simulations of the behavior of water in carbon nanopores that suggest the existence of a variety of new ice phases not seen in bulk, and of a solid-liquid critical point [15].

However, little attention has been paid to water with ions inside nanotubes, especially nanochannels in silica. There are only a few papers on water inside nanochannels in silica. Lo *et al.* [16] simulated ions in a charged capillary, using a softly repulsive Lennard-Jones interaction (L-J) for the ion-wall interaction. Lyden-Bell studied the mobility and solvation of ions in smooth nanochannels (not silica, and smooth wall)[17].

The properties of water with ions inside charged and uncharged silica nanochannels have been investigated in this study. The objective was to understand the mechanism of ion transport as well as ion distribution in silica nanochannels with 1.3-3 nm diameter. The effect of charge on the wall upon the behavior of ions and water molecules was also investigated since ions will be used to buffer and disentangle DNA, and a charged wall will probably enable a single DNA to move electrokinetically through the channel in future studies with an imposed external field.

2.1 SPC/E water potential model

The SPC/E (extended simple point charge) model [6] is a modification of the SPC (simple point charge) model [18]. The SPC/E model has geometry with an OH distance 0.1 nm, with the HOH angle equal to the tetrahedral angle 109.47°, and with charges on the oxygen and hydrogen equal to –0.8476 *e* (electronic charge) and +0.4238 *e*, respectively. The total potential between water molecule pairs includes the Coulombic potential between these charges and a L-J potential between the oxygen centers on different water molecules. The latter is given by

$$U_{L-J}(i,j) = 4e[(\frac{s}{r})^{12} - (\frac{s}{r})^{6}] \qquad (1)$$

where the L-J well depth and core diameter are respectively, e_o/k_B = 78.168 K and s = 0.3166 Å, where k_B is Boltzmann's constant.

2.2 SiO_2 potential model

Because of the wide use of silica in life and industry, a lot of work has been done concerning the simulation of silica itself and systems including silica. A few potential models of silica have been developed. There are three important models used to model silica itself, including the Tsuneynki potential model [19], the BMH model [20], and the BKS model [21]. However, when there are other substances studied with silica, an L-J interaction site model with partial charges for SiO_2 has been used to study the effect of the silica surface on the liquids or gases in contact with the wall. Using such a potential to calculate the wall force, Brodka [14] simulated liquid acetone in a silica pore.

A simplified L-J model with s = 0.3 nm and e/k_B = 230K with and without discretely charged sites has been tailored to current system by Shengting Cui [22] and has been used in this study. In this model, a single layer of close-packed L-J sites, each representing a SiO_2 unit, is wrapped into a cylinder as shown in Figure 1. The parameters had been fitted to reproduce the surface energy of SiO_2.

Radhakrishnan *et al.* [23] modeled the pore wall even more simply as a continuum of L-J sites using the 10-4-3 Steele potential [24][25], given by:

$$f_{fw}(z) = 2p r_w e_{fw} s_{fw}^2 \Delta[\frac{2}{5}(\frac{s_{fw}}{z})^{10} - (\frac{s_{fw}}{z})^4 - (\frac{s_{fw}^4}{3\Delta(z+0.61\Delta)^3})] \qquad (2)$$

Where, the *s*'s and *e*'s are the size and energy parameters in the L-J potential, the subscripts f and w denote fluid and wall, respectively, *D* is the distance between two successive lattice planes of the solid, *z* is the coordinate perpendicular to the pore wall, and k_B is the Boltzmann's constant. This model has also been used in this study. The cross parameters of Rhadakrishnan's model are calculated using the Lorentz-Berthelot combining rules:

$$\sigma_{H2O\text{-}wall} = (\sigma_{H2O}+\sigma_{wall})/2 = (0.3166+0.3)/2 = 0.3083 \text{ nm}$$

$$\varepsilon_{H2O\text{-}wall}/k_B = (\varepsilon_{H2O}/k_B \times \varepsilon_{wall}/k_B)^{1/2} = (78.168 \times 230)^{1/2} = 134.1\text{K}$$

The other cross parameters among H_2O, ions, and wall were estimated similarly and the results are listed in Tables 1,2 and 3 which are shown in chapter 3.

3. Methods

The molecular dynamics simulation technique numerically solves Hamilton's equations of motion for each particle, that is

$$\bar{v}_i = \frac{\partial H}{\partial \bar{p}_i} = \bar{p}_i / m_i \qquad (3)$$

$$\bar{p}_i = \frac{\partial H}{\partial \bar{r}_i} = \bar{F}_i = -\frac{\partial U}{\partial \bar{r}_i} \qquad (4)$$

where H is the Hamiltonian; F_i is the force on molecule i; p_i is the molecular momentum; m_i is the mass of molecule i; r_i is the position of molecule i; U is the total potential energy of molecule i; v_i is the velocity of molecule i; and the bar, $\bar{}$, above a symbol indicates a vector.

The total potential energy, U, consists of Lennard-Jones and Coulombic energies. For water molecules and ions i, U is given as:

$$U_i = \sum_{\substack{j \\ (j \neq i)}} U_{L-J}(i,j) + \sum_{\substack{j \\ (j \neq i)}} U_{Coulombic}(i,j) + U(i, wall) \qquad (5)$$

where U_{L-J} is given by Equation(1), and

$$U_{Coulombic}(i,j) = \frac{q_i q_j e^2}{4\pi\varepsilon r} \qquad (6)$$

where q_i and q_j are the ion charges, r is the distance between two ions, ε is the dielectric constant, and e is the unit charge. $U(i, wall)$ is the total energy the wall exerts on particle i.

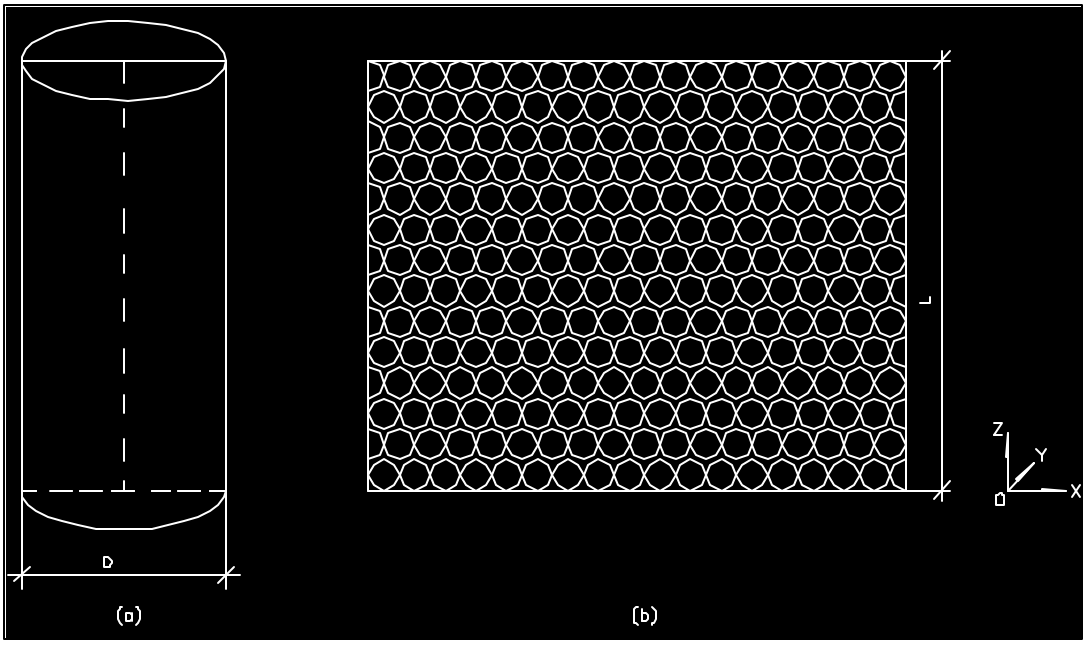

Figure 1. The stucture of the surface layer of nanochannel. a) The SiO_2 nanochannel. b) Its surface. Each site represent a SiO_2 molecule.

For the smooth-wall model, the energy between a particle in the nanochannel and the wall of the nanochannel is given by equation (2), which is a function of the distance, *z*, between particle and wall. In contrast, for atomistic wall, the structure of the wall is shown in Figure 1.

The atomistic wall is made of one layer of SiO_2 molecules which are represented by spherical sites. The distance between two centers is 0.3 nm, which is the L-J *s* parameter. The force exerted on a particle inside the nanochannel by the wall is the summation of the forces exerted by every wall site on the particle, including L-J and Coulombic forces.

For the charged wall, the charges were evenly distributed along the axial direction and around the radius of the nanotube. The parameters used in the simulation are listed in Tables 1-3, among which ion-wall parameters are calculated with Lorentz-Berthelot combining rules.

All the systems simulated comprise a cylindrical nanochannel with either smooth or atomistic walls containing water molecules, positive ions (sodium or calcium ions) and negative chloride ions. Periodic boundary conditions have been applied in the axial direction. The diameter of the nanochannel has been varied from 1.3 nm to 3 nm. Correspondingly, it has been filled with water molecules and ions so that the density of the fluid is close to 1 g/cm^3. Canonical ensembles (N,V,T) were simulated. The temperature was held constant, 298 K, by rescaling the total kinetic energy of the fluid to

Table 1. L-J parameters for NaCl-H_2O

	s (nm)	e/k_B(K)
Na – Na[a]	0.273	43.00
Cl - Cl	0.486	20.19
Na - Cl	0.387	20.51
Na - O	0.2876	62.72
Cl - O	0.378	62.72
O – O[b]	0.3166	78.168
Na - wall	0.2865	99.45
Cl - wall	0.393	68.14
Wall - wall	0.3	230

[a]Reference 26.

[b]Reference 6.

Table 2. L-J parameters for $CaCl_2$-H_2O [27]

	s(nm)	e/k_B(K)
Ca-Ca	0.2895	50.32
Ca-Cl	0.3648	50.32
Ca-O	0.303	62.72
O-O	0.3166	78.168
Cl-Cl	0.4401	50.32
Cl-O	0.3784	62.72
Ca-wall	0.2948	107.6
Cl-wall	0.3701	107.6
wall-wall	0.3	230

Table 3. Site charges

	Na^+	Cl^-	Ca^{++}	O	H
Charge(e)[a]	+1	-1	+2	-0.8476	+0.4238

a) e -- electronic charge.

be constant after each time step. The Rattle method [28] was chosen to numerically solve Hamiltonian equations of motion with the time step equal to 2.5fs. Equilibration runs were between 7,000 and 12,500ps in time length. The radial density distributions of water and ions were studied. This density, $r(r)$, is a function of the distance r from the axis of nanochannel and is defined by [14]:

$$r(r) = \frac{< n(r + \Delta r, r) >}{p\, l[(r + \Delta r)^2 - r^2]} \qquad (7)$$

where $<n(r_1,r_2)>$ is the average number of molecules between two cylinders of radii r_1 and r_2; l is the cylinder length.

The self-diffusion coefficients in the axial direction were calculated. The Einstein relation [29] was used tocalculated the self-diffusion coefficient :

$$2tD = \frac{1}{3} < (\bar{r}(t) - \bar{r}(0))^2 > \qquad (8)$$

where D is the diffusion coefficient, t is the time, and $\bar{r}$ is the position vector.

4. Results and Discussion

The specific details of each simulation case are tabulated in the Appendix.

4.1 Wall Models

In this research, two kinds of wall models were tested to calculate the wall force on water molecules and ions inside the nanochannel, a smooth wall model and an atomstic wall model. The force simulated by smooth wall is given by equation (2), which is only a function of the distance between wall and particles. The force is perpendicular to the surface of the wall and there is no shear force between wall and fluid. Velocity components in Cartesian coordinates were used to calculate temperature and rescaled to control temperature. It was, therefore possible for the cylinder of fluid to rotate as a whole. The Cartesian coordinates of this rotation were taken as excess kinetic energy and were rescaled to lower velocities. As a result, the actual thermal motion of the fluid particles was decreased, eventually producing a glass-like state. This artifact was aggravated when the cutoff distance was increased. After this result was observed, the smooth wall model was replaced by an atomistic wall model. The smooth wall model will not be discussed any further.

4.2 Potential Cutoff

The potential cutoff, r_c, refers to the distance beyond which intermolecular potential is set to zero. When r_c is up to some value, the energy beyond r_c is so trivial that it was neglected. It is so time-consuming as to be infeasible to calculate all of the interactions between a particle i and all the other particles at every timestep. It may not be necessary since the Lennard-Jones potential is short-ranged, inversely proportional to the sixth power of distance. In this research, because of the confinement of the wall of the

nanochannel, the value of cutoff was set so large that it spanned the diameter of the nanochannel. Thus, the potential cutoff only works along the axial direction of the nanochannel. However, Coulombic force is inversely proportional to the second power of the distance. It decreases much more slowly than the Lennard-Jone potential with increasing distance. So r_c should be larger when Coulombic force is considered.

In this section, the effect of r_c is discussed. The final value selected was 5.0 $s_{o\text{-}o}$, where $s_{o\text{-}o}$ = 0.3166 nm is the Lennard-Jones parameter of the oxygen atom. The same system, consisting of 709 H_2O molecules, 7 Na^+ and 3 Cl^-, was simulated with r_c set to 4.0, 4.5 and 5.0 $s_{o\text{-}o}$. The radial density distributions of O, H, Na^+ and Cl^- are shown in Figures 2 through 5. At different r_c, the radial density distributions of the oxygen atoms (water centers) are very similar. So are radial density distributions of the hydrogen atoms. For sodium ions, the shapes of the radial density distributions are qualitatively alike, but more sodium ions are attracted to the wall of the nanochannel when r_c increases. For chloride ions, the radial density distributions have the same tendency except that more chloride ions were repelled farther from the wall by the negative charge on the wall. Considering computation time and the accuracy of the calculation, it was decided to set r_c = 5.0 $s_{o\text{-}o}$ in subsequent simulations. Even though there were changes to the ion distribution when the cutoff was increased from 4.5 $s_{o\text{-}o}$ to 5.0 $s_{o\text{-}o}$, the 5.0 $s_{o\text{-}o}$ cutoff spanned the whole diameter, and it was presumed further increases would have little effect.

4.3 Charged *vs.* Uncharged Wall

One system containing 243 water molecules, 7 sodium ions, and 3 chloride ions

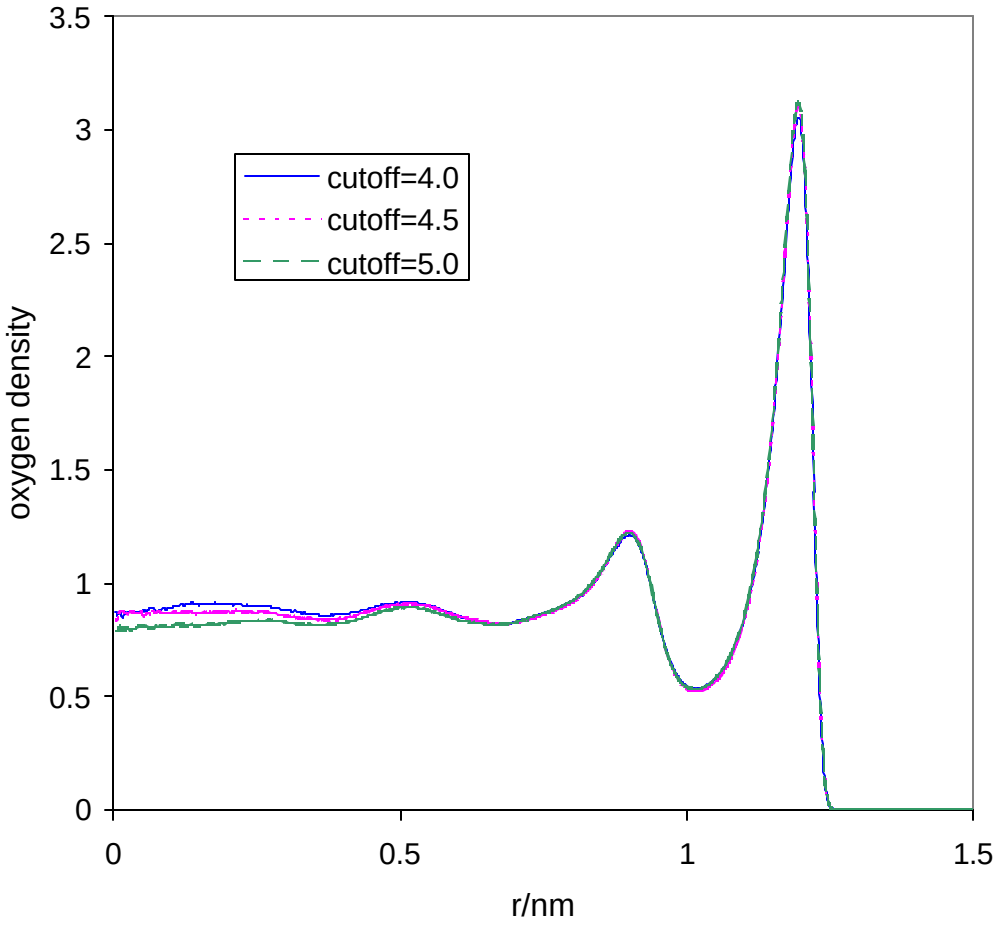

Figure 2. The radial density distribution of oxygen atoms. The radius of the nanochannel is 1.5 nm and the cell length is 4.434 nm. The fluid consisted of 709 water molecules, 7 sodium ions, and 3 chloride ions. On the surface of the wall of the nanochannel are distributed 4 negative charges. The unit of the *y*-axis is 31.51/nm^3.

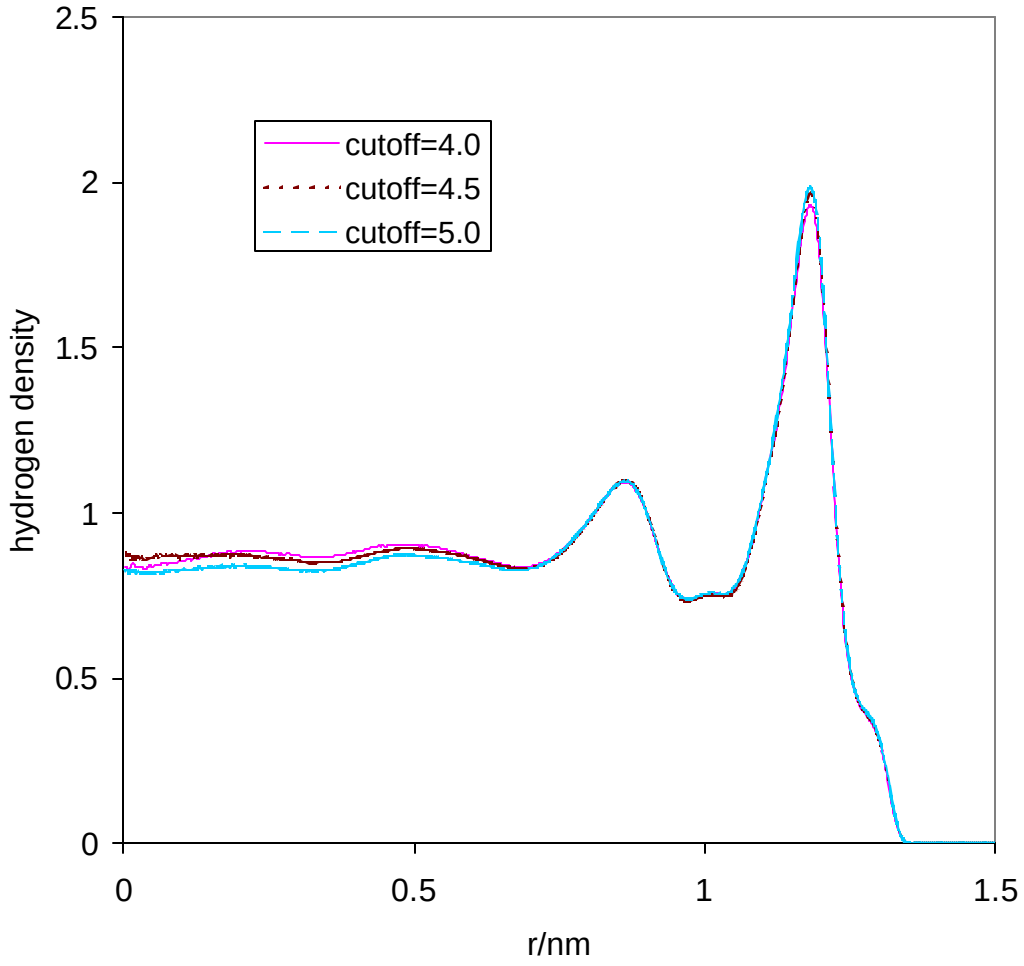

Figure 3. The radial density distribution of hydrogen atoms. The radius of the nanochannel is 1.5 nm and the cell length is 4.434 nm. The fluid consisted of 709 water molecules, 7 sodium ions, and 3 chloride ions. On the surface of the wall of the nanochannel are distributed 4 negative charges. The unit of the *y*-axis is 31.51/nm^3.

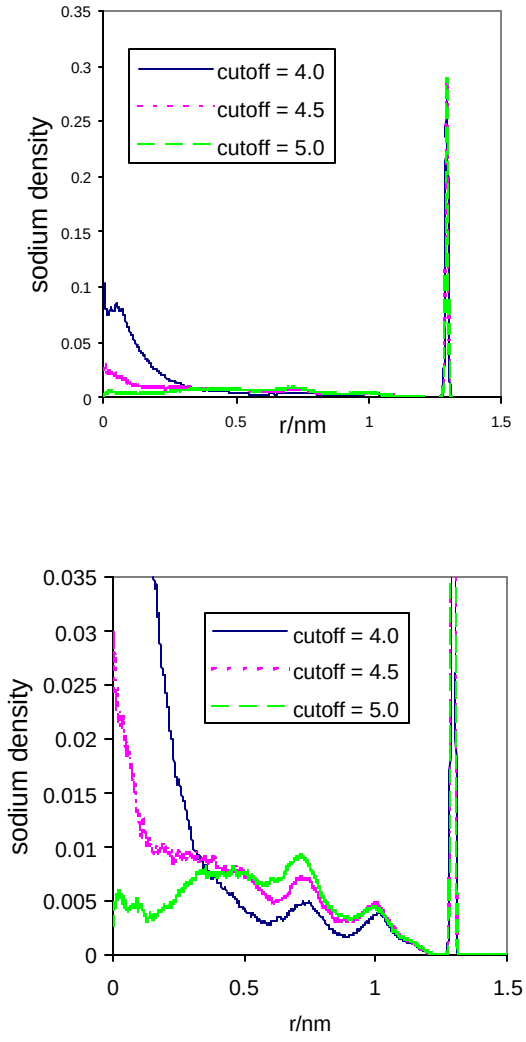

Figure 4. The radial density distribution of sodium ions. The radius of the nanochannel is 1.5 nm and the cell length is 4.434 nm. The fluid consisted of 709 water molecules, 7 sodium ions, and 3 chloride ions. On the surface of the wall of the nanochannel are distributed 4 negative charges. The unit of the *y*-axis is 31.51/nm^3. The lower plot is an expansion of the *y*-axis of the upper plot.

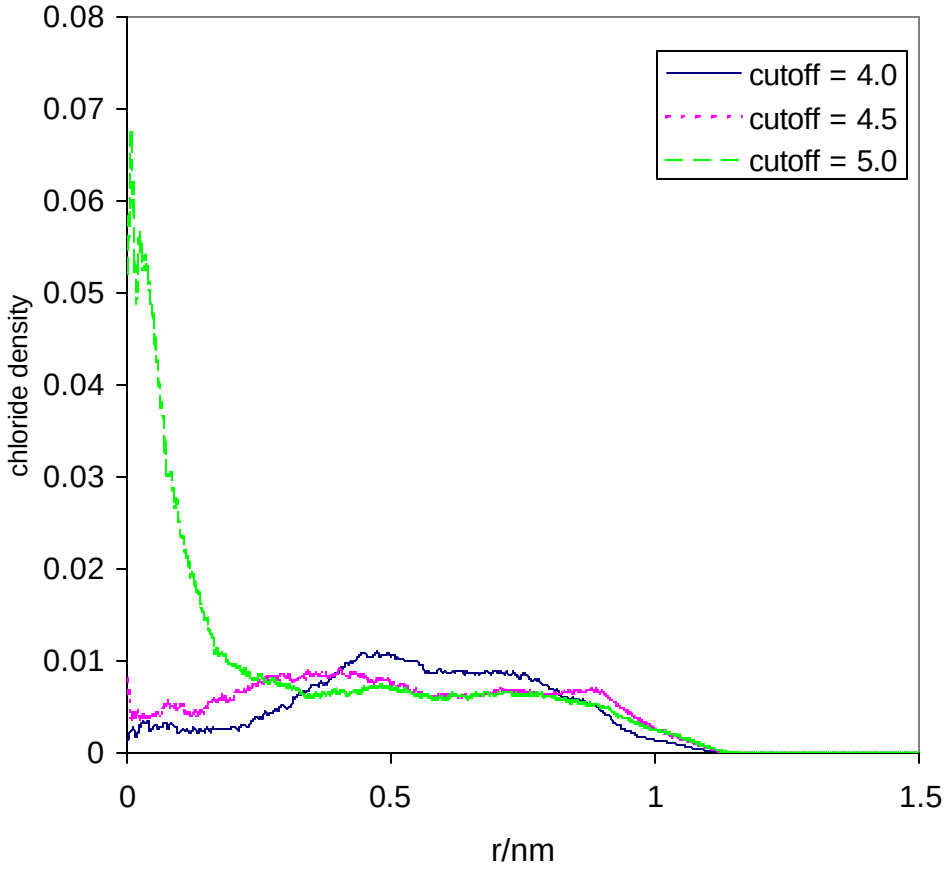

Figure 5. The radial density distribution of chloride ions. The radius of the nanochannel is 1.5 nm and the cell length is 4.434 nm. The fluid consisted of 709 water molecules, 7 sodium ions, and 3 chloride ions. On the surface of the wall of the nanochannel are distributed 4 negative charges. The unit of the *y*-axis is 31.51/nm^3.

was simulated in a nanochannel with 1 nm radius, 4.43 nm cell length, and 4 negative unit charges on its surface. Another system containing 243 water molecules, 3 sodium ions, and 3 chloride ions was simulated in the same size of nanochannel without charges on its surface. The results were compared in Figures 6 and 7.

The charges on the wall of the nanochannel set up a static electrical field. The movements of particles in the nanochannel were affected to different extent. By tracing the movements of sodium ions, it was found that 4 sodium ions were attracted and remained very close to the point where wall charges were set. These sodium ions do not move freely and just vibrate, as shown in Figure 8. In comparison, the other 3 sodium ions move randomly in the nanochannel. The attachment of the sodium ions on the wall neutralizes the charges on the wall so that the radial density distributions of other ions were hardly affected by the charge on the wall as seen in Figure 7. Except the highest peak of radial density of sodium ions (around 0.8 nm radial distance) in the charged nanochannel, the rest of the distribution is very similar to the one in the uncharged nanochannel. Both have peaks around 0.50 nm and 0.23n m, and the distance between these two peaks is close to the diameter of sodium ions. As for the chloride ions, they distribute quite similarly in the charged and uncharged nanochannels.

The radial density distribution of oxygen atom differs a little in charged and uncharged nanochannels. The density of the outside layer of oxygen atoms, which is close to the wall, was ~0.1 higher for uncharged wall than for the charged wall. Since the charge of oxygen is negative, they were repelled a little farther from the wall when they were close to the wall charge position.

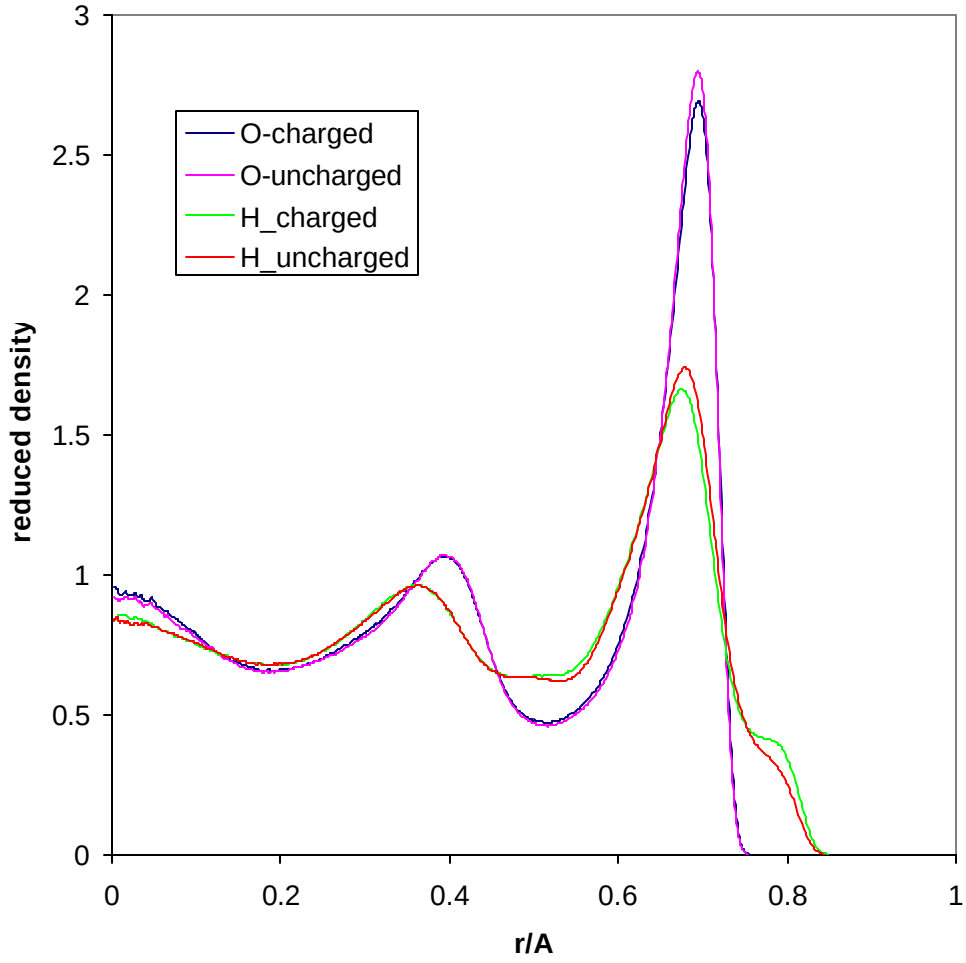

Figure 6. The radial density distribution of oxygen and hydrogen atoms. The radius of the nanochannel is 1.0 nm and the cell length is 4.434 nm. The fluid in the channel with the charged wall consisted of 243 water molecules, 3 chlorides, and 6 sodium ions. On the surface of the wall of the nanochannel are distributed 3 negative charges. The fluid in the channel with the uncharged wall included 243 water molecules, 3 chloride ions, and 3 sodium ions. There is no charge on the wall of the nanochannel. The unit of the *y*-axis is 31.51/nm^3.

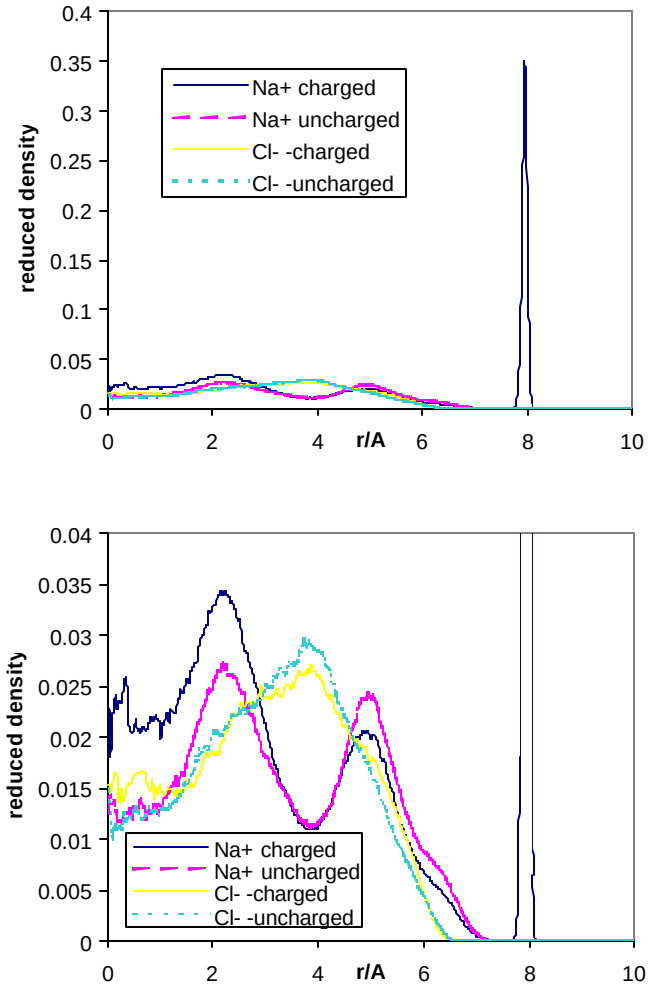

Figure 7. The radial density distribution of ions. The radius of the nanochannel is 1.0 nm and the cell length is 4.434 nm. The fluid in the nanochannle with the charged wall consisted of 243 water molecules, 3 chloride ions, and 6 sodium ions. On the surface of the wall of the nanochannel are distributed 3 negative charges. The fluid in the nanochannel with the uncharged wall included 243 water molecules, 3 chloride ions, and 3 sodium ions. There is no charge on the wall of the nanochannel. The unit of the *y*-axis is 31.51/nm^3. The lower plot is an expansion of the *y*-axis of the upper plot.

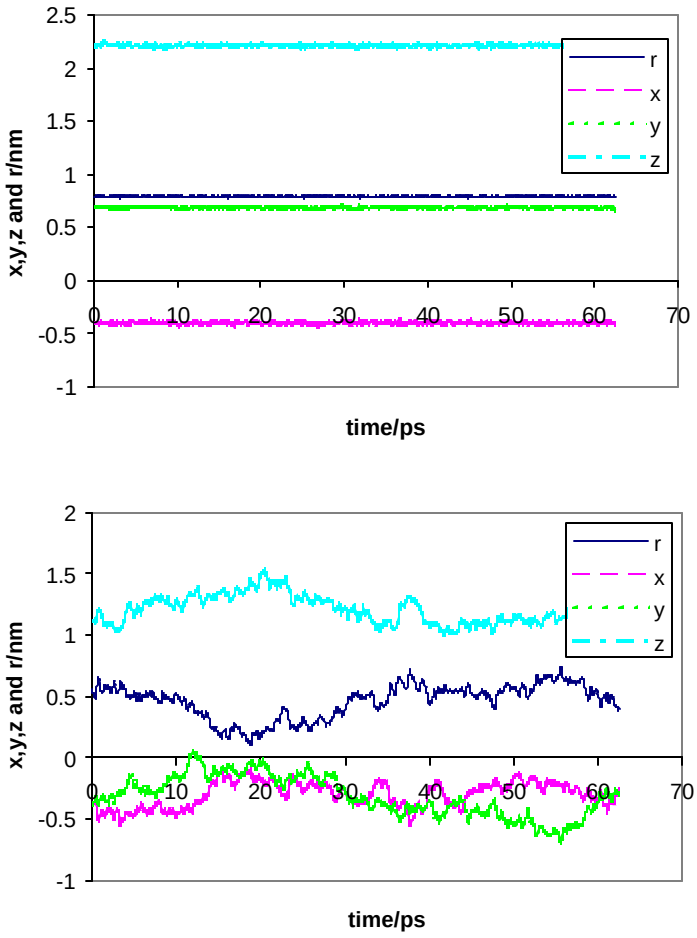

Figure 8 The coordinates of one sodium ion *vs*. time. The system consisted of 243 water molecules, 6 sodium ions, and 3 chloride ions. 3 negative charges were distributed on the surface of the wall of the nanochannel. The radius of the nanochannel is 1 nm and the cell length in axial direction is 4.434 nm. The upper part is the trajectory of a sodium ion attracted and fixed by the charge on the surface of the wall of the nanochannel. 3 of 6 sodium ions behave like this. The lower part is the behavior of a sodium ion unfixed by the charge on the wall. 3 of 6 sodium ions move in this similar manner.

Due to a similar mechanism, hydrogen atoms were attracted close to the wall. This is shown in Figure 7. Finally, the water molecules are oriented in such a way that the oxygen atom is far from the wall while hydrogen close to the wall when they are close to a wall charge.

The self-diffusivity of particles of two systems along the axial direction of the nanochannel were calculated and are listed in Table 4. The self-diffusivity of sodium ions is lower in the charged nanochannel than in the uncharged nanochannel due to the attraction of the wall charge. The axial self-diffusivity of water molecules and chloride ions also decrease in the charged nanochannel. Probably, this is attributable to the obstacle of sodium ions attached to the wall by the wall charge.

4.4 Channel Radius

The effect of radius of the nanaochannel on the movement of water molecules, sodium ions, and chloride ions was studied. Radius was varied from 0.67 nm to 0.8 nm, 1.0 nm, 1.2 nm and 1.5 nm while the other parameters were kept constant such as the concentration of chloride ions in the nanochannel, the density of charge on the wall. The radial density distributions of water molecules are displayed in Figures 9 through 13. The

Table 4. The Self-Diffusivity in Charged and Uncharged Nanochannel

	Uncharged Wall ($1\times10^{-5}cm^2/s$)	Charged Wall ($1\times10^{-5}cm^2/s$)
H_2O	6.06	3.97
Na^+	3.05	0.51
Cl^-	3.03	0.69

number of layers of water molecules varies when r changes. The number of layers and corresponding radial position at 5 different values of nanochannel radius are listed in Table 5.

Water molecules in different layers continually exchange their positions and do not stay in the same layer all the time. After moving from one layer to another, they stay for a while and then change layers again.

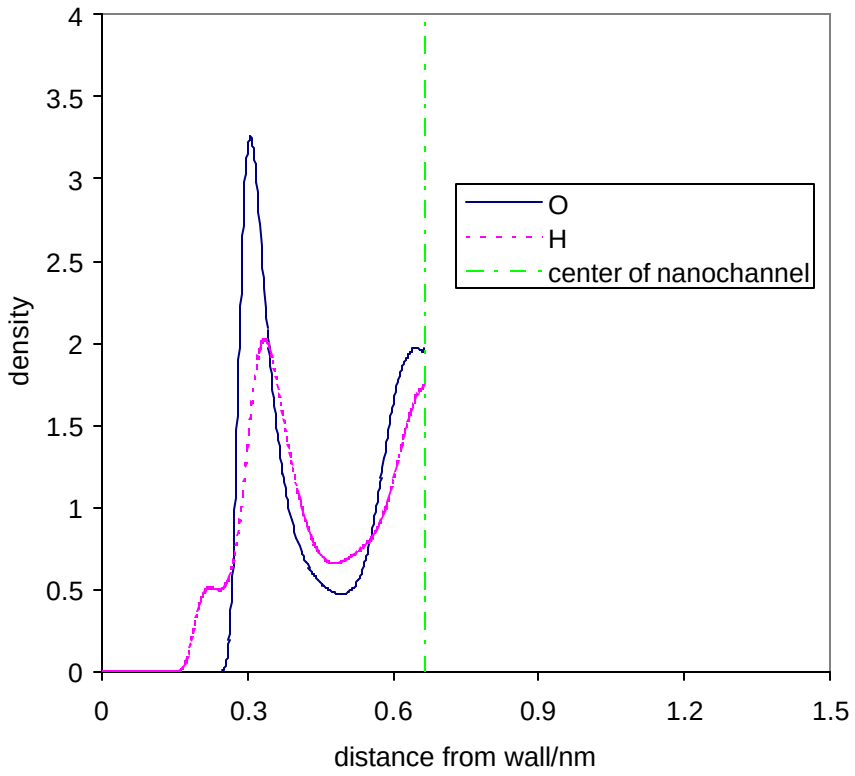

Figure 9. Radial density distributions of oxygen atoms and hydrogen atoms when the radius of the nanochannel is 0.67 nm. The system consisted of 160 water molecules, 4 sodium ions, and one chloride ion. 3 negative charges were distributed on the surface. The cell length in the axial direction is 7.063 nm. The unit of the radial density is $31.51/nm^3$.

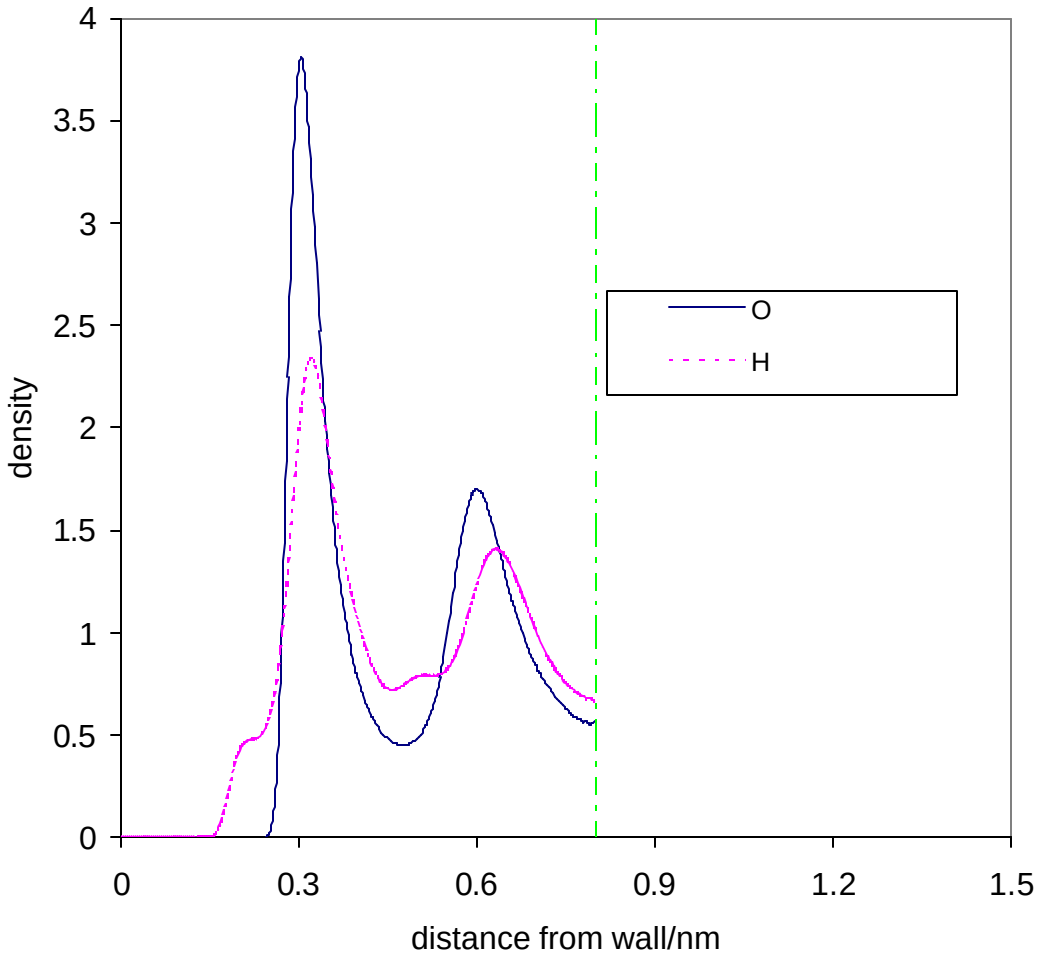

Figure 10. Radial density distributions of oxygen atoms and hydrogen atoms when the radius of the nanochannel is 0.8 nm. The system consisted of 398 water molecules, 7 sodium ions, and 2 chloride ions. 5 negative charges were distributed on the surface. The cell length in the axial direction is 9.811 nm. The unit of the radial density is 31.51/nm^3.

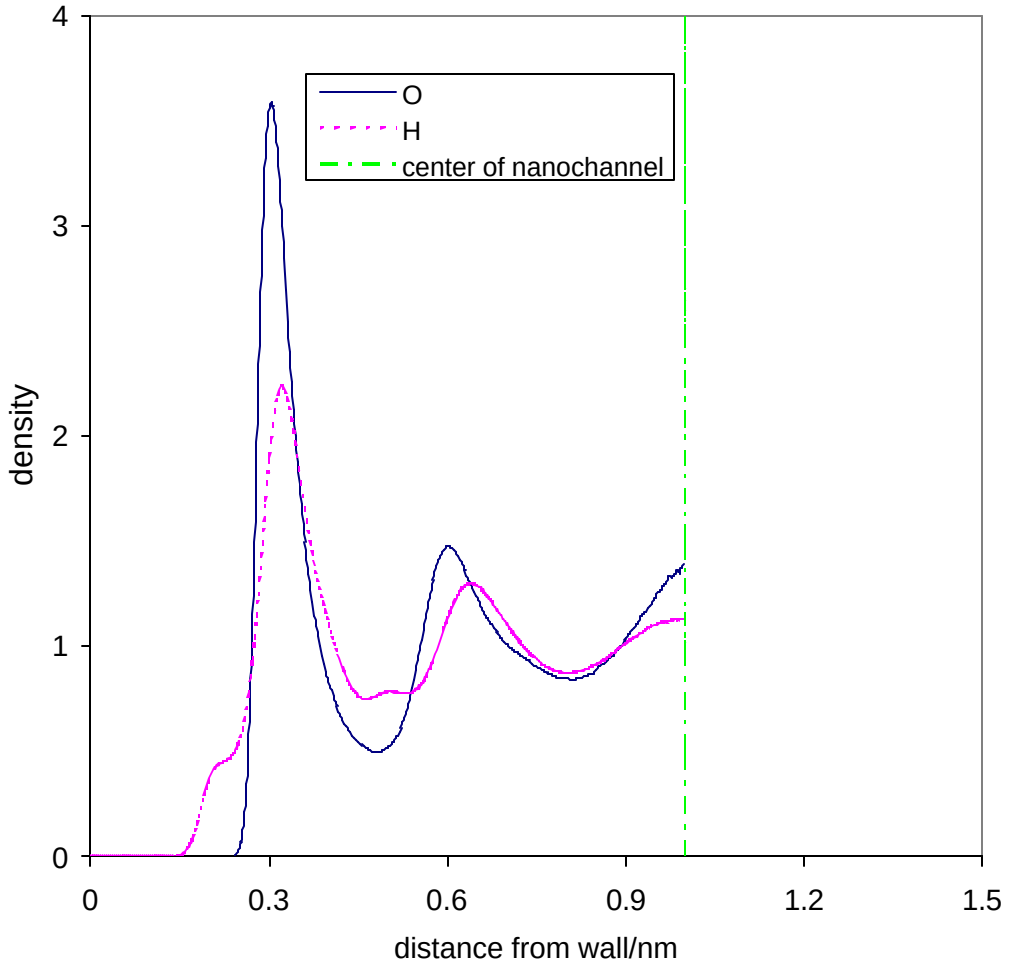

Figure 11. Radial density distributions of oxygen atoms and hydrogen atoms when the radius of the nanochannel equals 1 nm. The system consisted of 436 water molecules, 6 sodium ions, and 2 chloride ions. 4 negative charges were distributed on the surface. The cell length in the axial direction is 6.279 nm. The unit of the radial density is 31.51/nm^3.

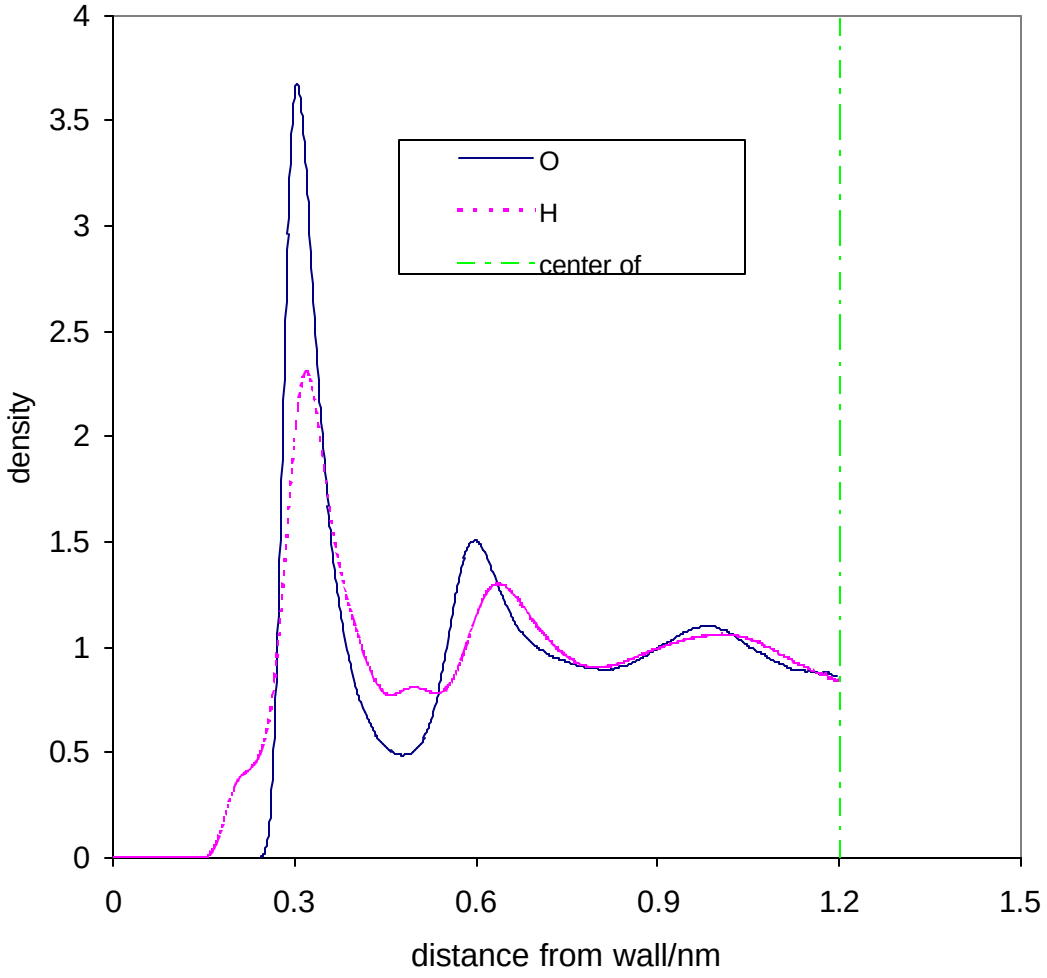

Figure 12. Radial density distributions of oxygen atoms and hydrogen atoms when the radius of the nanochannel is 1.2 nm. The system consisted of 707 water molecules, 8 sodium ions, and 3 chloride ions. 5 negative charges were distributed on the surface. The cell length in the axial direction is 6.540 nm. The unit of the radial density is 31.51/nm^3.

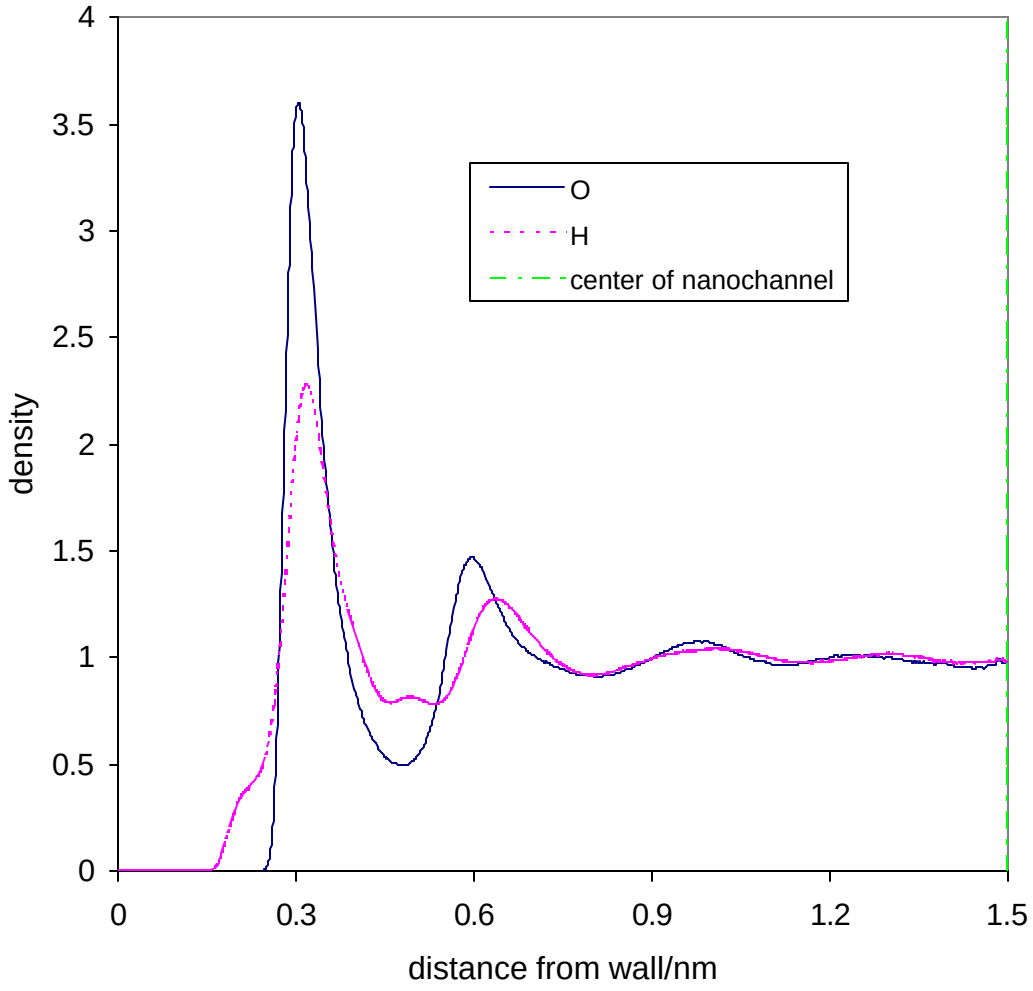

Figure 13. Radial density distributions of oxygen atoms and hydrogen atoms when the radius of the nanochannel is 1.5 nm. The system consisted of 751 water molecules, 7 sodium ions, and 3 chloride ions. 4 negative charges were distributed on the surface. The cell length in the axial direction is 4.186 nm. The unit of the radial density is 31.51/nm^3.

Table 5. The Number of Layers of Water Molecules and Their Radial Position

Radius of nanochannel/nm	Number of layers of water molecules	Radial position/nm
0.67	2	0.36, 0
0.8	2	0.5, 0.2
1.0	3	0.7, 0.4, 0
1.2	3	0.9, 0.6, 0.22
1.5	4	1.2, 0.9, 0.53, 0.24

The radial density distribution of sodium ions and chloride ions are shown in Figures 14 through 18. For sodium ion, the highest peak occurs about 0.2 nm inside the nanochannel radius.

The self-diffusivity of water molecules, sodium ions, and chloride ions in the axial direction was calculated, as shown in Figures 19, 20, 21 and Table 6.

In general, self-diffusivity of water molecules, sodium ions, and chloride ions tends to decrease when the radius of the nanochannel decreases, as shown in Figure 22. When radius is small, for example, r = 0.8 nm, if the increase of the radius can accommodate one new layer of water molecules, the self-diffusivity of water molecule increases. Otherwise, if the increase of radius is about half or one-and-a-half of the diameter of a water molecule, self-diffusivity decreases. These results were calculated for water density in the core of the nanochannel constant at about 1.0. Self-diffusivity is also affected by pressure of the fluid in the nanochannel. The pressure is not a constant when the radius varies at constant density. The effects of nanochannel radius at constant pressure will be the focus of a future study.

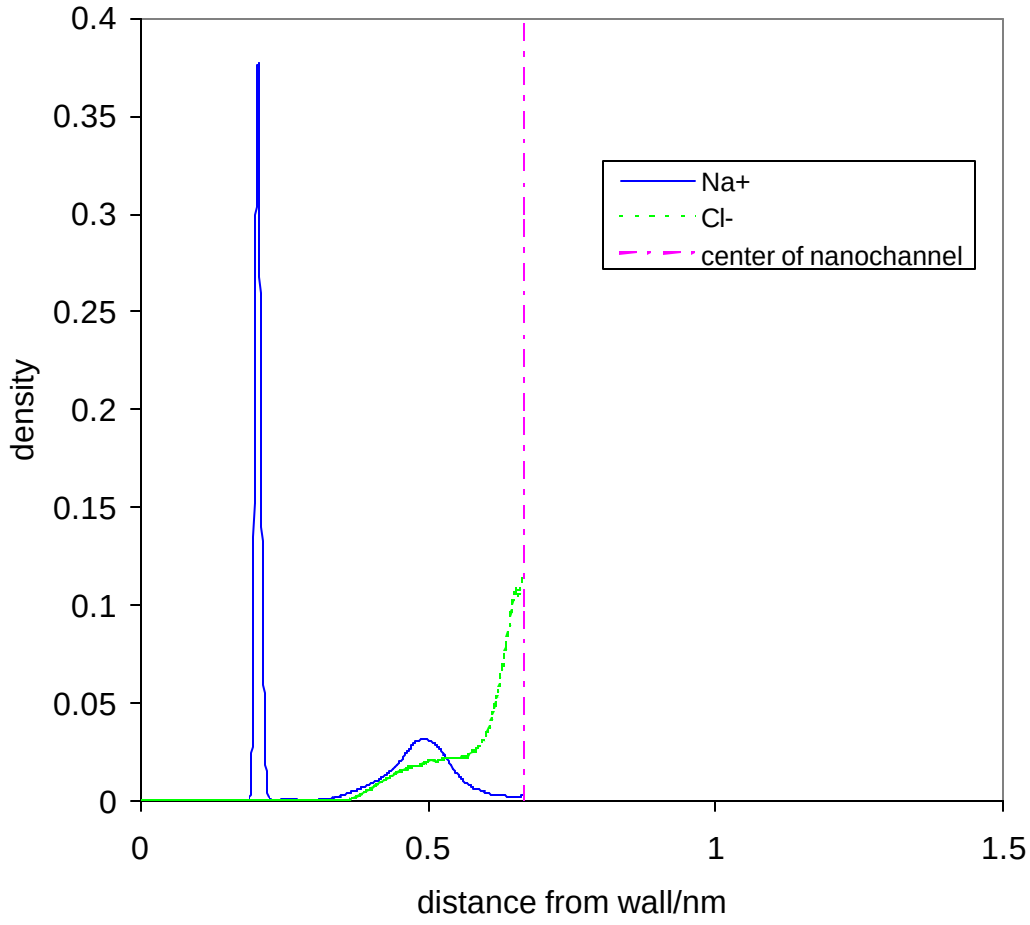

Figure 14. Radial density distributions of sodium and chloride ions when the radius of the nanochannel is 0.67 nm. The system consisted of 160 water molecules, 4 sodium ions, and one chloride ion. 3 negative charges were distributed on the surface. The cell length in the axial direction is 7.063 nm. The unit of the radial density is 31.51/nm^3.

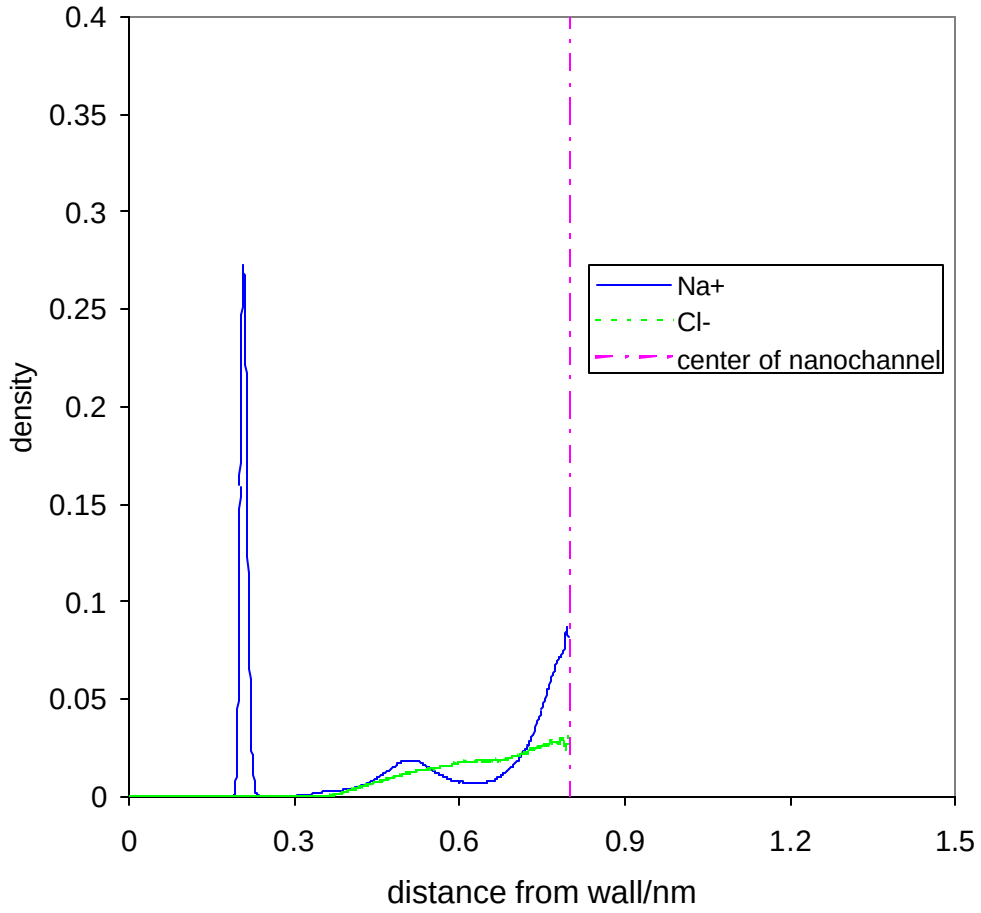

Figure 15. Radial density distributions of sodium and chloride ions when the radius of the nanochannel is 0.8 nm. The system consisted of 398 water molecules, 7 sodium ions, and 2 chloride ions. 5 negative charges were distributed on the surface. The cell length in the axial direction is 9.811 nm. The unit of the radial density is 31.51/nm^3.

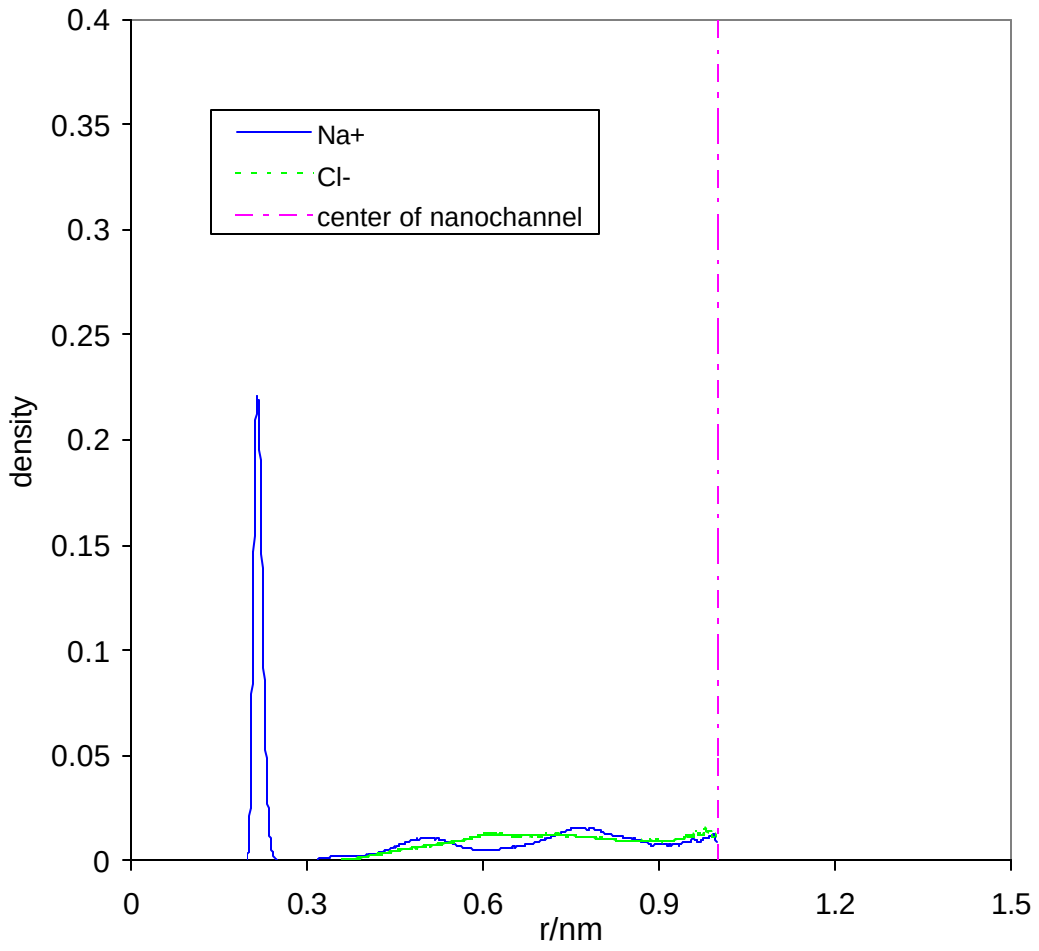

Figure 16. Radial density distributions of sodium and chloride ions when the radius of the nanochannel is 1 nm. The system consisted of 436 water molecules, 6 sodium ions and 2 chloride ions and 4 negative charges were distributed on the surface of the wall. The cell length in the axial direction is 6.279 nm. The unit of the radial density is $31.51/nm^3$.

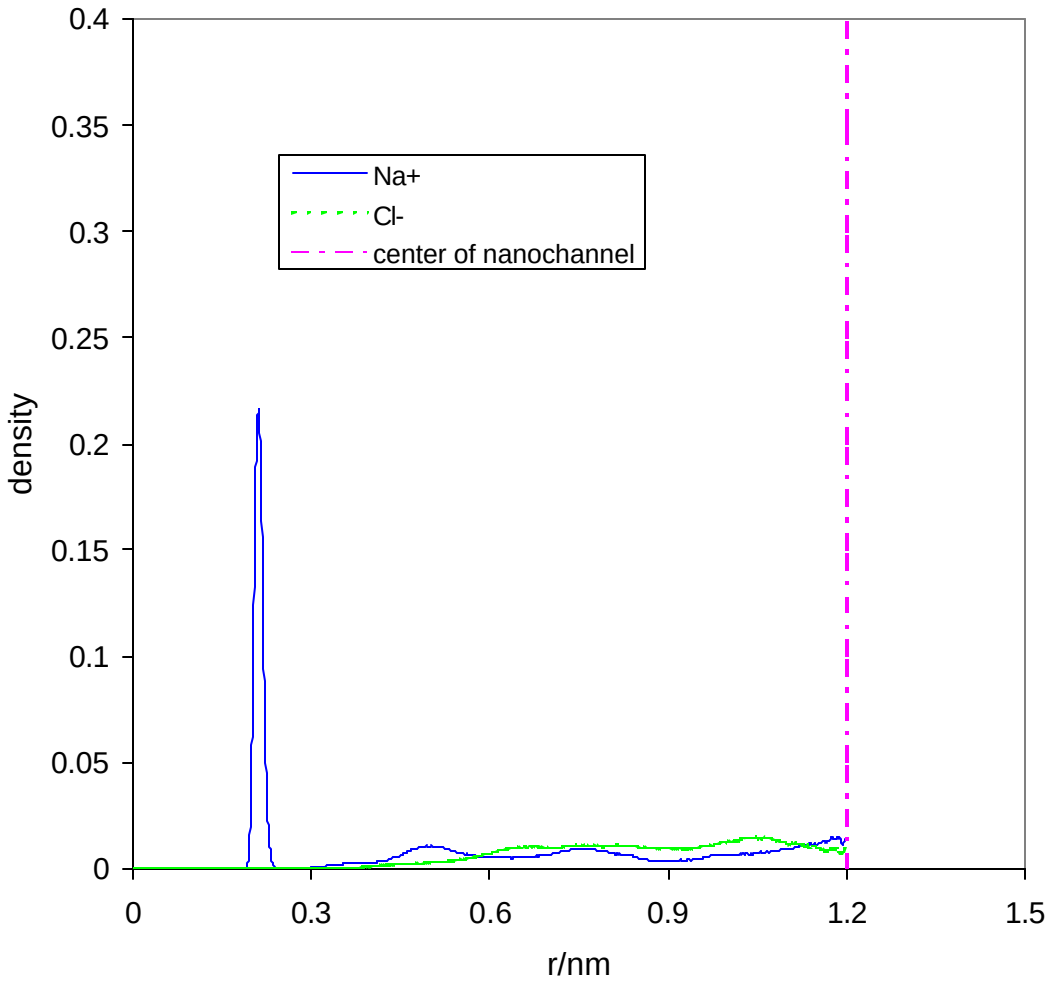

Figure 17. Radial density distributions of sodium and chloride ions when the radius of the nanochannel is 1.2 nm. The system consisted of 707 water molecules, 8 sodium ions and 3 chloride ions and 5 negative charges were distributed on the surface of the wall. The cell length in the axial direction is 6.540 nm. The unit of the radial density is $31.51/nm^3$.

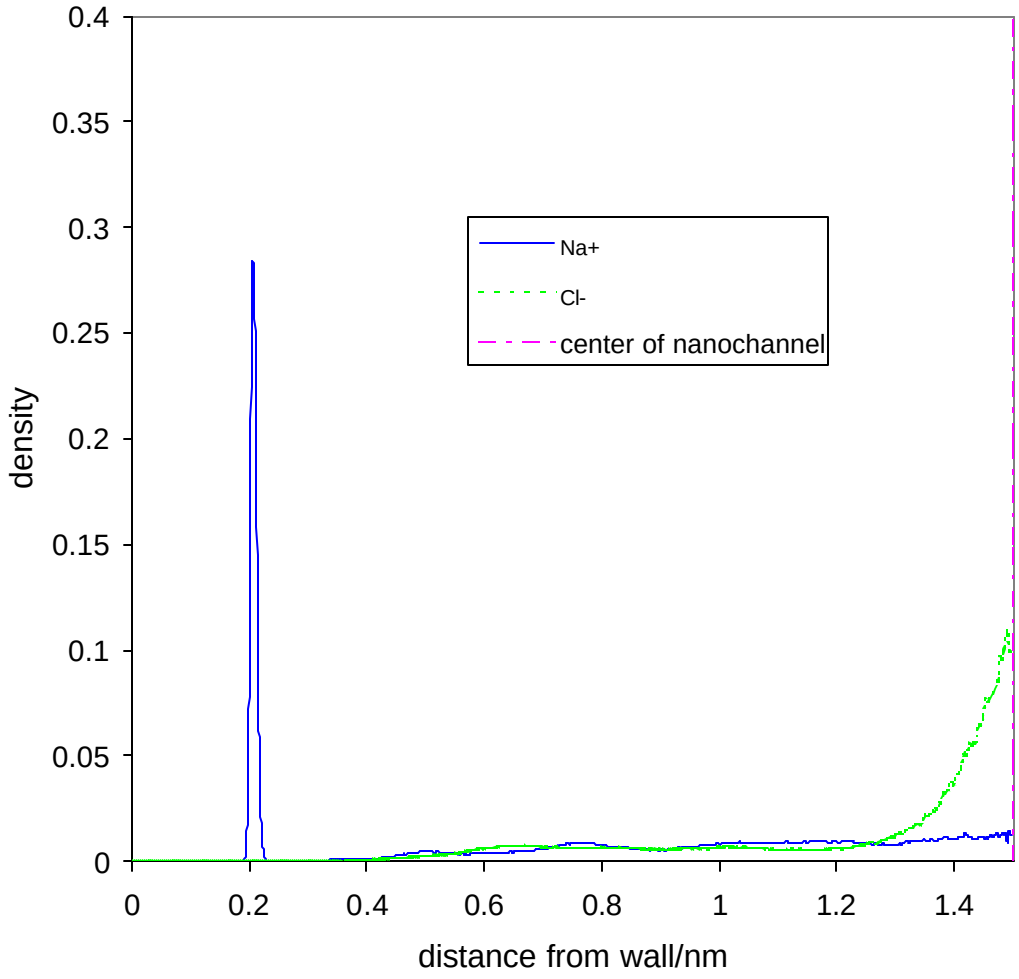

Figure 18 Radial density distributions of sodium and chloride ions when the radius of the nanochannel is 1.5 nm. The system consisted of 751 water molecules, 7 sodium ions and 3 chloride ions and 4 negative charges were distributed on the surface of the wall. The cell length in the axial direction is 4.186 nm. The unit of the radial density is 31.51/nm^3.

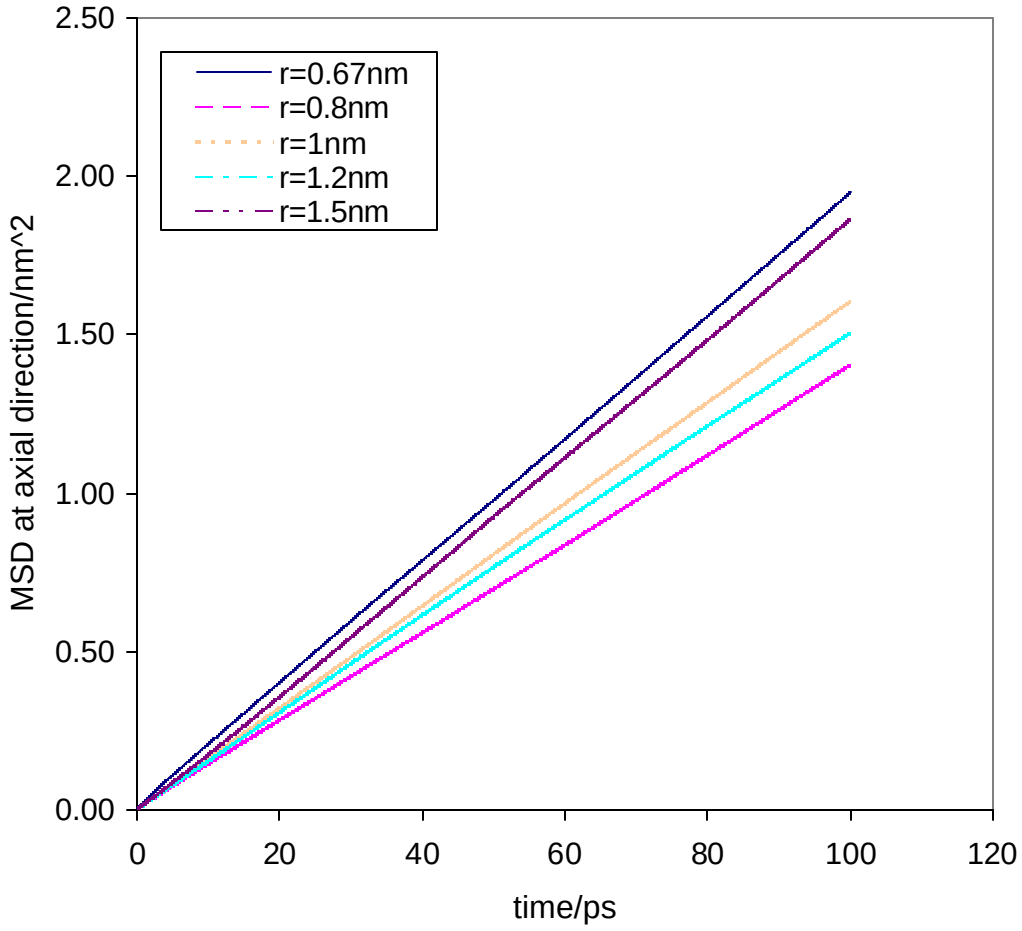

Figure 19. The mean square displacement (MSD) of water molecules in nanochannel with different radius versus time.

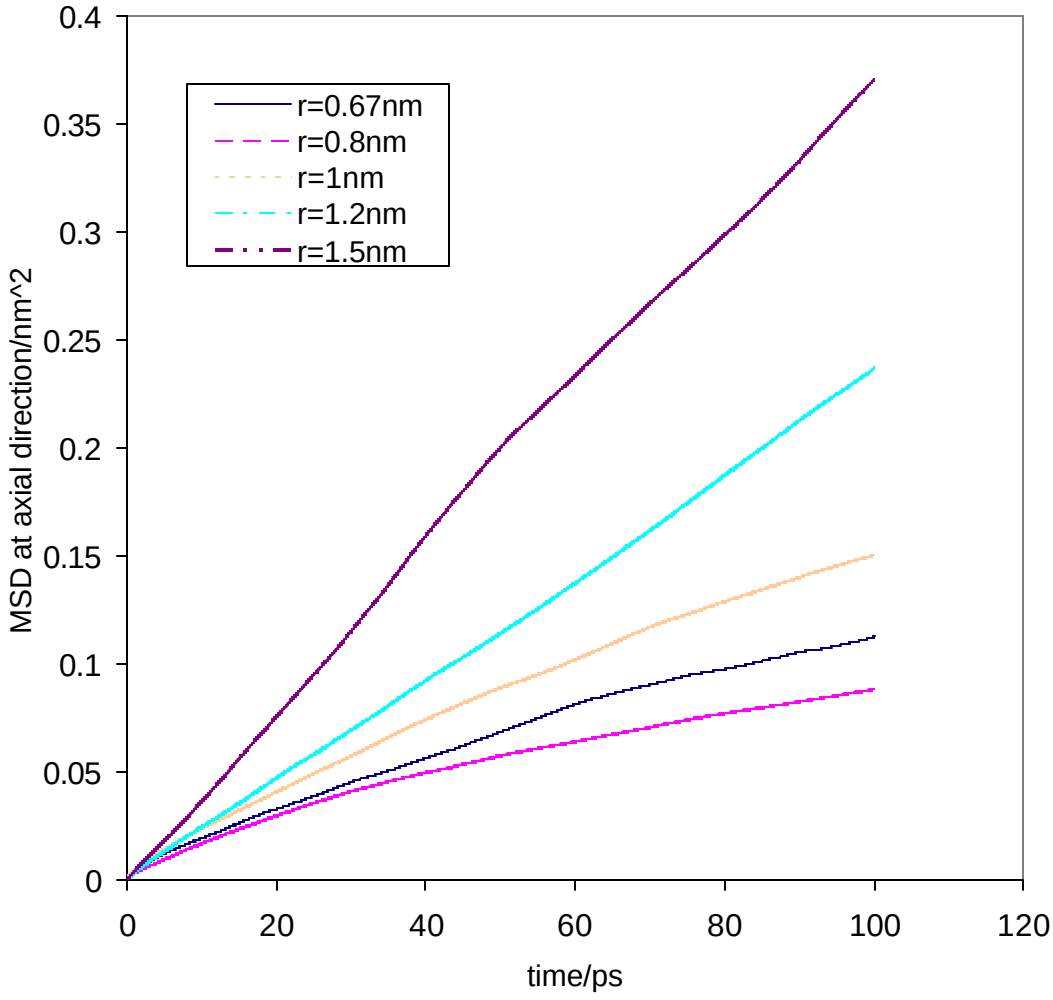

Figure 20. The mean square displacement (MSD) of sodium ions in aqueous solution in nanochannel with different radius versus time.

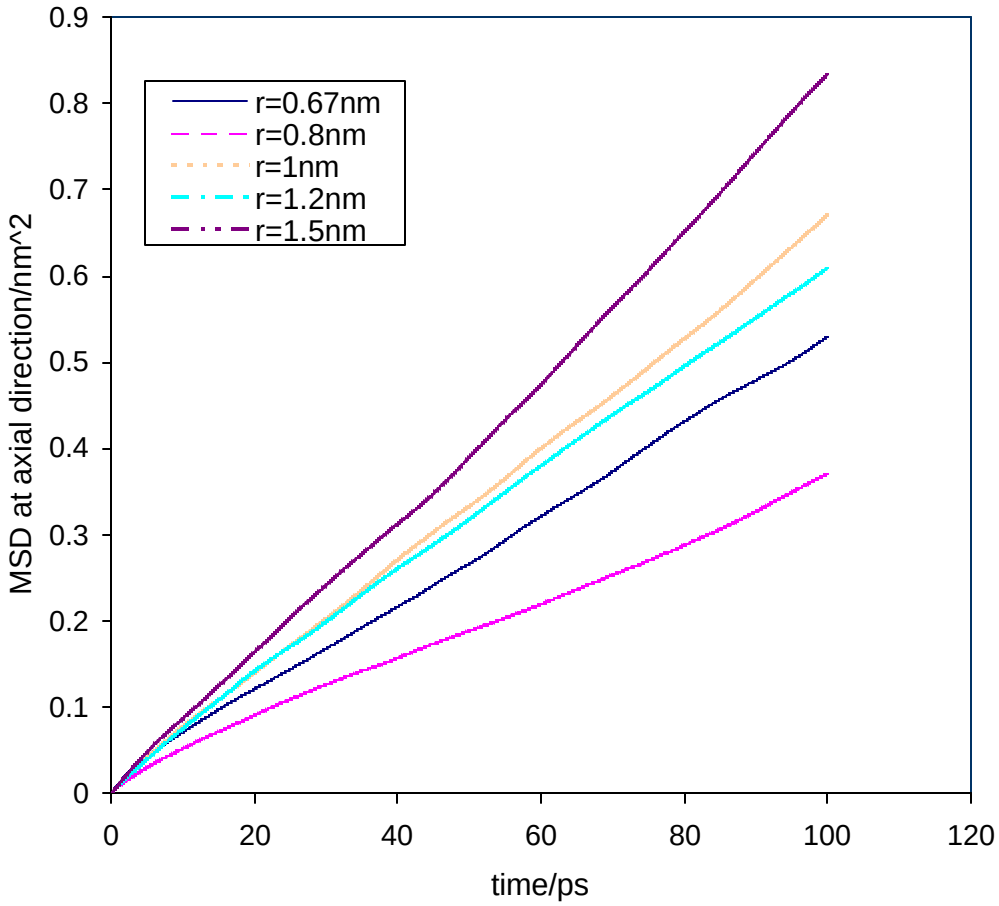

Figure 21 The mean square displacement (MSD) of chloride ions in aqueous solution in nanochannel with different radius versus time.

Table 6. Self-diffusivities along axial direction of nanochannel with different radius.

Radius/nm	H_2O ($1\times10^{-5}cm^2/s$)	Na+ ($1\times10^{-5}cm^2/s$)	Cl- ($1\times10^{-5}cm^2/s$)
0.67	3.92 ± 0.07	0.22 ± 0.02	0.66 ± 0.06
0.8	2.83 ± 0.01	0.18 ± 0.01	0.85 ± 0.09
1	3.17 ± 0.04	0.37 ± 0.06	0.69 ± 0.16
1.2	2.95 ± 0.05	0.41 ± 0.06	1.00 ± 0.13
1.5	3.68 ± 0.01	1.05 ± 0.06	1.21 ± 0.06

The self-diffusivity of water molecules in the axial direction is close to that of bulk water at ambient conditions. The self-diffusivity of sodium ions is smaller than that of chloride ions, which is contrary to behavior in bulk water at ambient conditions. Some sodium ions are attracted by the charge on the wall so that they move little. When self-diffusivity of sodium ions is calculated only for the sodium ions that are free to move, as shown in Figure 22 and Table 7, the relative behavior of sodium and chloride ions is more consistent with their behavior in bulk water at ambient conditions.

Examination of Figure 19 indicates the excellent linearity of the mean square displacement curves for water at each of the different values of radius studied. This linearity and the excellent statistics for the large number of water molecules support the possibility that the non-monotonic variation of water self-diffusivity *vs*. radius seen in Figure 23 may be real. One can speculate that this non-monotonic variation with radius may be a result of the quantized layering of the water in the nanochannels. If the non-monotonic variation of water self-diffusivity is postulated as real, then the qualitatively similar non-monotonic variation of diffusivity of the sodium and chloride ions seen in Figures 22 and 23 could also be taken as real. The hypothesized reason for the non-monotonic variation of the self-diffusivity of the ions is also the quantized layering of the water in the nanochannels. However, one cannot, at present refute, the possibility that the non-monotonic variation may only be the result of the constant-density rather than constant-pressure simulations.

4.5 $CaCl_2$ *vs.* NaCl

$CaCl_2$ and NaCl aqueous solutions were simulated separately with the same concentration of chloride ions in the nanochannel and charge density on the surface.

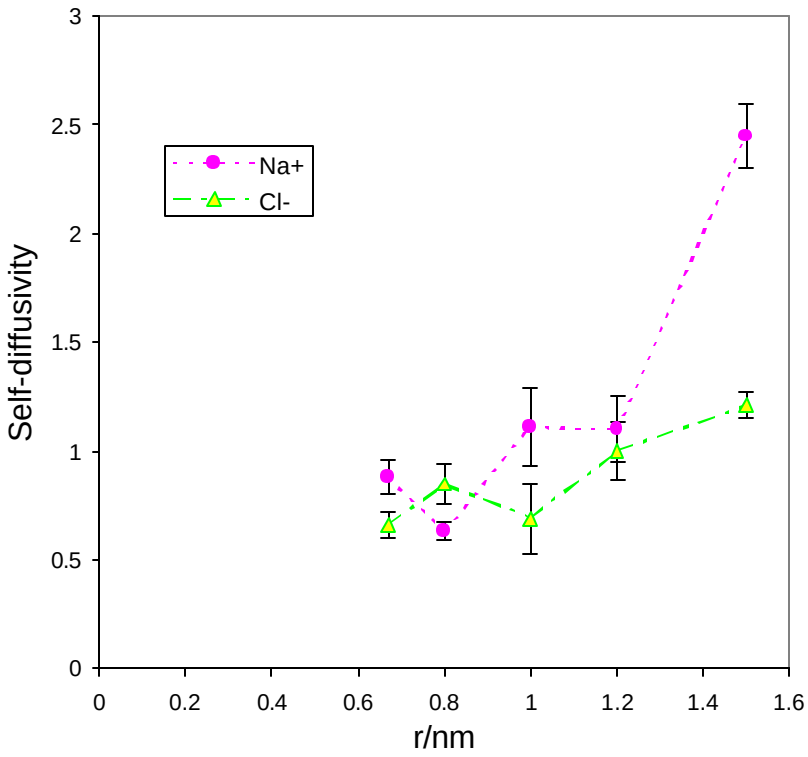

Figure 22. The self-diffusivity of chloride ions and freely moving sodium ions along the axial direction of the nanochannle *vs.* radius of the nanochannel. The unit of the *y*-axis is $1\times10^{-5}cm^2/s$.

Table 7. Self-diffusivities of chloride ions and free sodium ions along axial direction of nanochannels with different radius.

Radius/nm	Na+ ($1\times10^{-5}cm^2/s$)	Cl- ($1\times10^{-5}cm^2/s$)
0.67	0.88 ± 0.08	0.66 ± 0.06
0.8	0.63 ± 0.04	0.85 ± 0.09
1	1.11 ± 0.18	0.69 ± 0.16
1.2	1.10 ± 0.15	1.00 ± 0.13
1.5	2.45 ± 0.15	1.21 ± 0.06

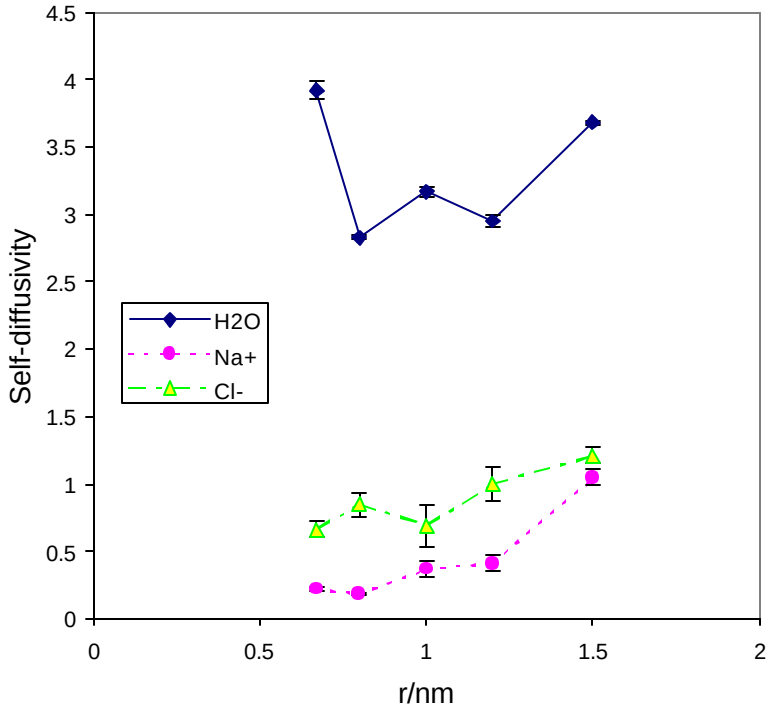

Figure 23. The self-diffusivity of water molecules, sodium ions and chloride ions along the axial direction of the nanochannel *vs*. radius of the nanochannel. The unit of the *y*-axis is $1\times10^{-5}cm^2/s$.

The radial density distributions are shown in Figures 24 through 27. In Figure 24, the highest peak of sodium ions is about 0.2 nm inside the wall while the one of calcium ions occurs about 0.45 nm inside the wall. Through tracing the movement of ions in the nanochannel, it was observed that calcium ions move freely and do not fix at the place where negative charge was distributed on the surface of the wall, in contrast to the behavior of sodium ions. Because one calcium ion has two positive unit charges, one negative unit charge on the surface is not strong enough to capture calcium ion. The radial distribution of chloride ions is similar for the two cases; so are the distributions of oxygen atoms and hydrogen atoms.

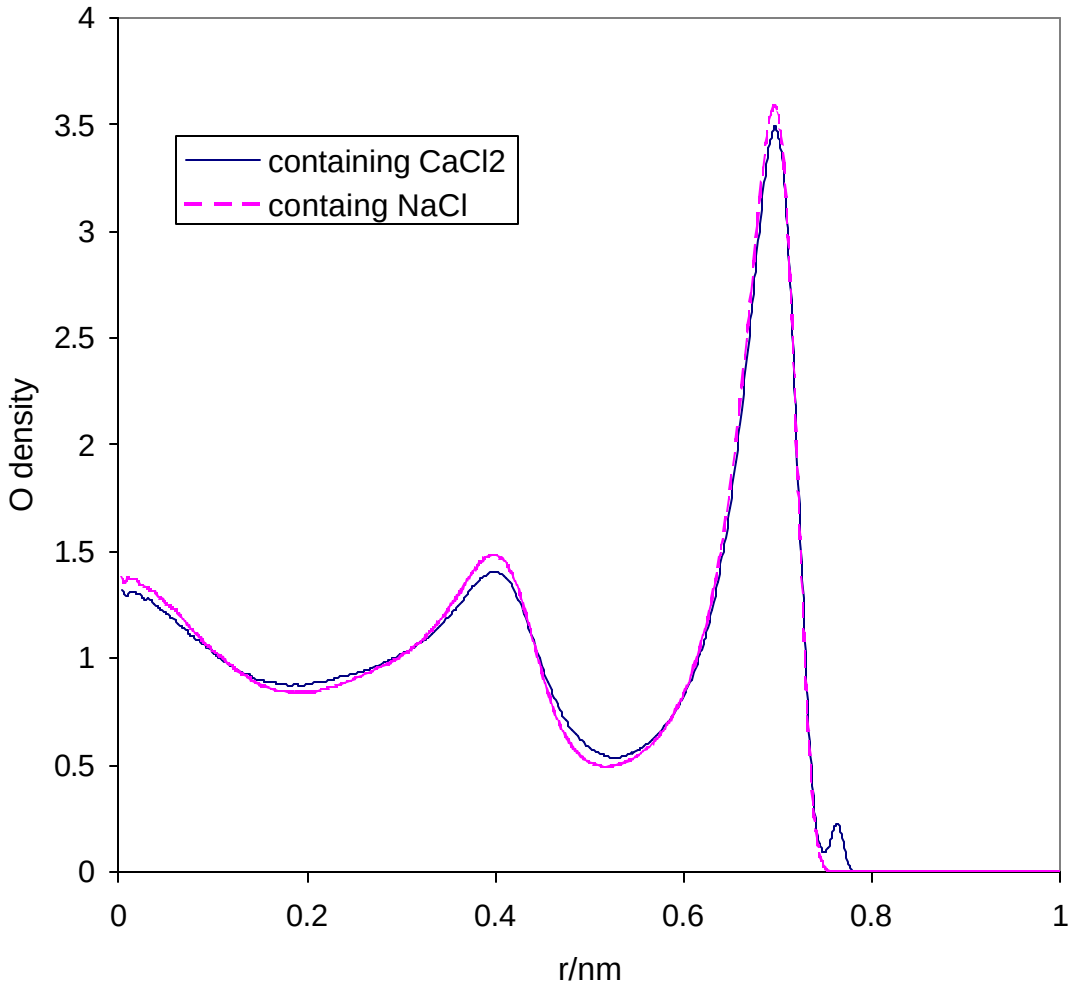

Figure 24. The radial density distributions of oxygen atoms in two aqueous solutions. One contains 462 water molecules, 3 calcium ions, and 2 chloride ions and another contains 462 water molecules, 6 sodium ions, and 2 chloride ions in the same size of nanochannel with 1 nm radius and cell length 6.651 nm in the axial direction. 4 negative charges were distributed on each surface. The unit of the *y*-axis is 31.51/nm^3.

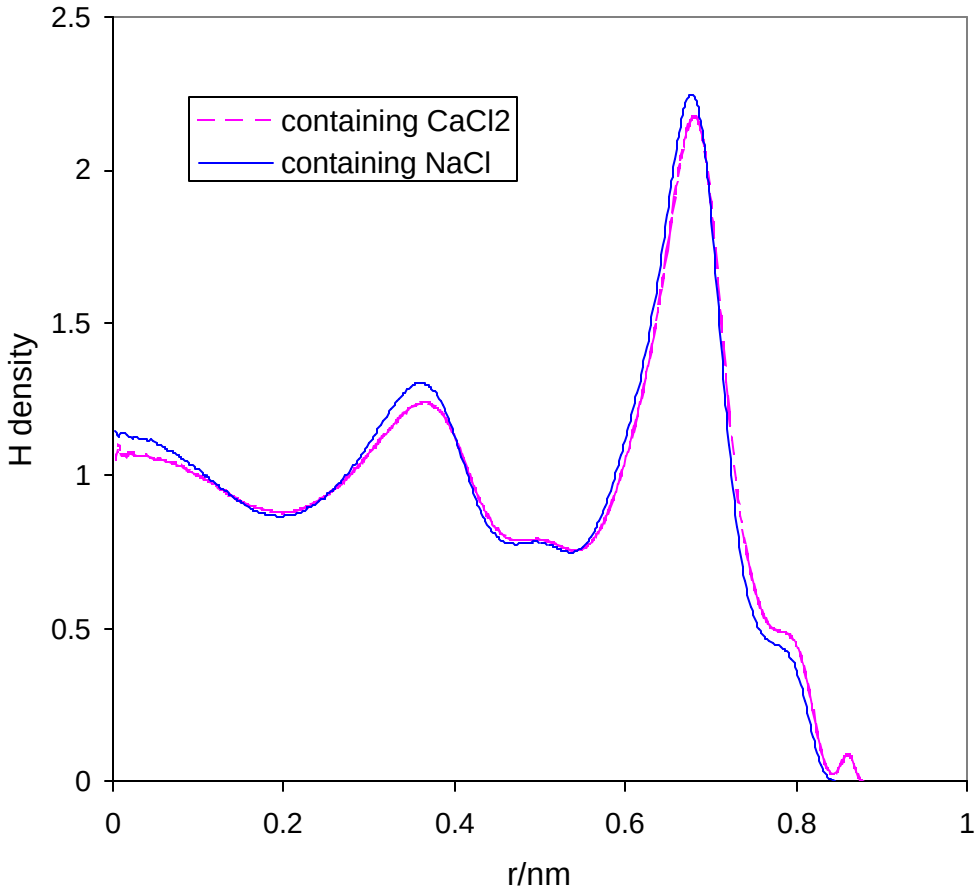

Figure 25. The radial density distribution of hydrogen atoms in two aqueous solutions. One contains 462 water molecules, 3 calcium ions, and 2 chloride ions and another contains 462 water molecules, 6 sodium ions and 2 chloride ions in the same size nanochannels with 1 nm radius and cell length 6.651 nm in the axial direction. 4 negative charges were distributed on each surface. The unit of the *y*-axis is 31.51/nm^3.

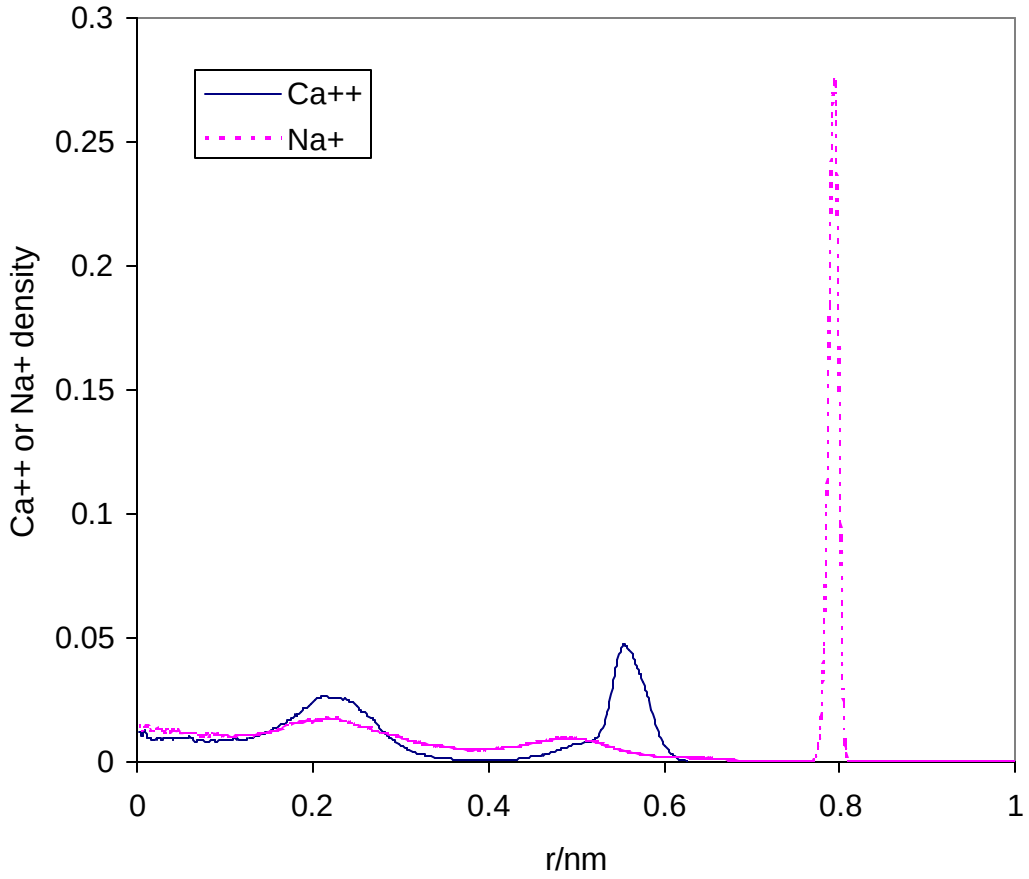

Figure 26. The radial density distribution of positive ions in two aqueous solutions. One contains 462 water molecules, 3 calcium ions, and 2 chloride ions and another contains 462 water molecules, 6 sodium ions, and 2 chloride ions in the same size of nanochannel with 1 nm radius and cell length 6.651 nm in the axial direction. 4 negative charges were distributed on each surface. The unit of the *y*-axis is 31.51/nm^3.

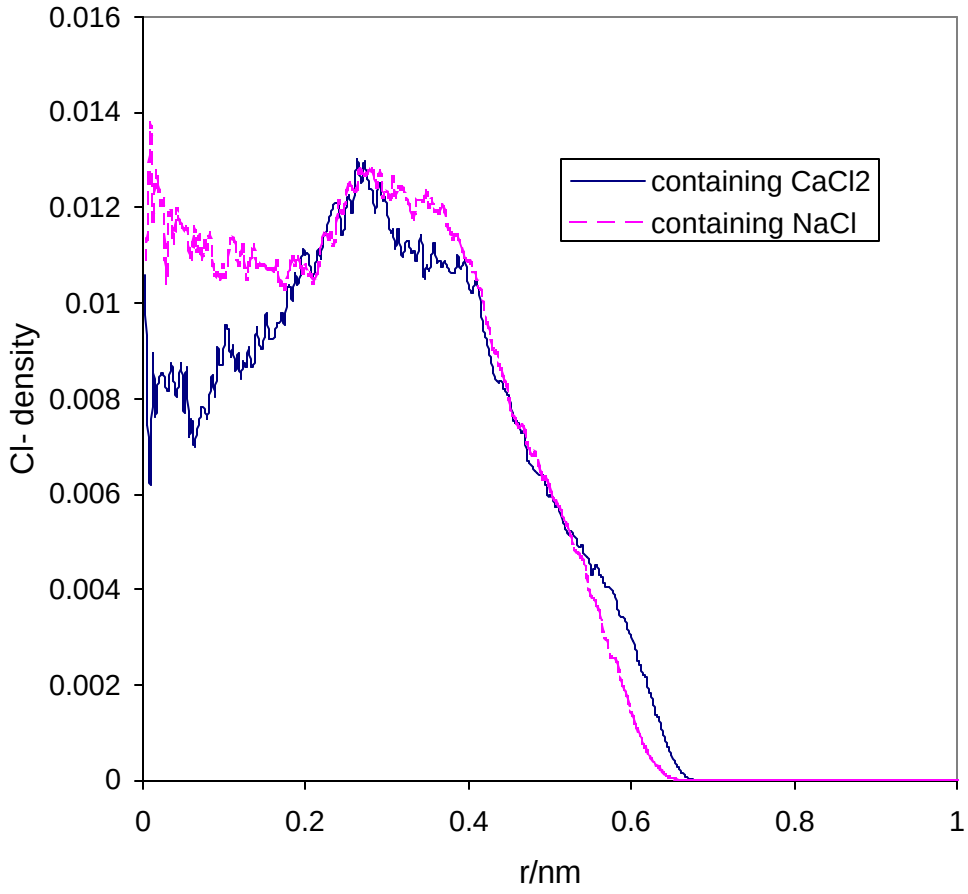

Figure 27. The radial density distribution of chloride ions in two aqueous solutions. One contains 462 water molecules, 3 calcium ions, and 2 chloride ions and another contains 462 water molecules, 6 sodium ions, and 2 chloride ions in the same size nanochannel with 1 nm radius and cell length 6.651 nm in the axial direction. 4 negative charges were distributed on each surface. The unit of the *y*-axis is 31.51/nm^3.

The self-diffusivity value of each kind of particle in the axial direction was calculated and is shown in Table 8. The self-diffusivity of calcium is much lower than that of sodium. Water molecules and chloride ions also move a little more slowly in calcium aqueous solution than in sodium aqueous solution. The obstacle presented by a calcium ion moves more slowly and has a larger diameter than the obstacle represented by a sodium ion. Movement of one ion past another of the same charge was not observed in these runs. The possible existence of a barrier to passing and its magnitude should be explored in future studies.

Table 8. Self-Diffusivity of Water Molecules and Ions in the Axial Direction in one Aqueous Solutions Containing $CaCl_2$ and in Another One Containing NaCl in Nanochannels with 1 nm Radius and 6.651 nm Cell Length in the Axial Direction.

System	H_2O ($1\times10^{-5}cm^2/s$)	Positive ions ($1\times10^{-5}cm^2/s$)	Cl^- ($1\times10^{-5}cm^2/s$)
$CaCl_2$	3.13	0.02	0.43
NaCl	3.43	0.35	0.70

5. Conclusions

The atomistic wall model is more reasonable than smooth wall model to simulate walls of SiO_2.

The radial density distributions of oxygen atoms and hydrogen atoms in the nanochannel were hardly affected by the value of the potential cutoff when it is bigger than 1.2664 nm ($4s_{o\text{-}o}$). However, those of ions are quantitatively different but qualitatively similar. Taking into account the required computer time and the accuracy of the simulation, 1.583 nm ($5\ s_{o\text{-}o}$) is a good choice.

In nanochannels with radius ranging from 0.67 nm to 1.5 nm, water molecules form different layers. In general, with the radius increasing, the particles' self-diffusivities in the axial direction of the nanochannel tend to increase. However, when the increase of radius cannot hold a new layer of molecules, the corresponding value of self-diffusivity may decrease.

The negative charges on the wall of the nanochannel have little effect on the density distribution of oxygen atoms, hydrogen atoms, and chloride ions. Negative charges on the wall attract sodium ions close to the wall so that the radial density distribution has a maximum peak about 0.2 nm inside the wall. This maximum does not exist in the nanochannel without any charge on its wall.

The sodium ions attracted by the wall charges do not move freely and just stay at the charge location, retarding the movement of water molecules and chloride ions and lowering the self-diffusivity of sodium ions themselves.

The calcium ions were not captured and fixed by one negative charge on the wall of the nanochannel since it has two positive electrical charges. Its self-diffusivity value is smaller than that of sodium ions, as is true in bulk water. The self-diffusivity of ions in aqueous solution in nanochannels is smaller than in bulk water.

5.1 Further Research

The effect of pressure has not been studied quantitatively. In future, pressure and temperature as well as charge density on the wall of the nacochannel are all parameters that should be studied.

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Appendix

The specific details of each simulation case

case	Radius of nanochannel (nm)	Length of Nanochannel (nm)	H_2O	Cl-	Na+	Ca++	Surface charge	Cutoff (σ_{o-o})
1	1.5	4.434	709	3	7	0	4	4.0
2	1.5	4.434	709	3	7	0	4	4.5
3	1.5	4.434	709	3	7	0	4	5.0
4	1	4.434	243	3	6	0	3	5.0
5	1	4.434	243	3	3	0	0	5.0
6	0.67	7.063	160	1	4	0	3	5.0
7	0.8	9.811	398	2	7	0	5	5.0
8	1	6.279	436	2	6	0	4	5.0
9	1.2	6.540	707	3	8	0	5	5.0
10	1.5	4.186	751	3	7	0	4	5.0
11	1	6.651	462	2	6	0	4	5.0
12	1	6.651	462	2	0	3	4	5.0

Vita

Jiandong Zhou graduated in July of 1992 with a B. S. in Polymer Science in the College of Chemical Engineering and Materials Science in Beijing Institute Technology (BIT). He obtained his first Mater's degree on Materials Science in BIT in March of 1995. He spent 5 years on chemical process design, simulation and optimization in WUZHOU Engineering Design & Research Institute in Beijing from April, 1995 to April, 2000. Jiandong Zhou graduated in May of 2002 with his 2nd M.S. in Chemical Engineering.