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Molecular simulation study of temperature effect on ionic hydration in carbon nanotubes†

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Molecular dynamics simulations have been performed to investigate the hydration of Li^+ , Na^+ , K^+ , F^- , and Cl^- inside the carbon nanotubes at temperatures ranging from 298 to 683 K. The structural characteristics of the coordination shells of ions are studied, including the ion-oxygen radial distribution functions, the coordination numbers, and the orientation distributions of the water molecules. Simulation results show that the first coordination shells of the five ions still exist in the nanoscale confinement. Nevertheless, the first coordination shell structures of cations change more significantly than those of anions because of the preferential orientation of the water molecules induced by the carbon nanotube. The first coordination shells of cations are considerably less ordered in the nanotube than in the bulk solution, whereas the change of the first coordination shell structures of the anions is minor. Furthermore, the confinement induces the anomalous behavior of the coordination shells of the ions with temperature. The first coordination shell of K^+ are found to be more ordered as the temperature increases only in the carbon nanotube with the effective diameter of 1.0 nm, implying the enhancement of the ionic hydration with temperature. This is contrary to that in the bulk solution. The coordination shells of the other four ions do not have such behavior in the carbon nanotube with the effective diameter ranging from 0.73 to 1.00 nm. The easier distortion of the coordination shell of K^+ and the match of the shell size and the nanotube size may play roles in this phenomenon. The exchange of water molecules in the first coordination shells of the ions with the solution and the ion diffusion along the axial direction of the nanotube are also investigated. The mobility of the ions and the stability of the coordination shells are greatly affected by the temperature in the nanotube as in the bulk solutions. These results help to understand the biological and chemical processes at the high temperature.

I. Introduction

The hydration of ions in the nanometer scale confinement is ubiquitous and important in many biological and chemical processes.^{1–6} Ionic hydration in nanoscale channels is determinant to the functions of various ion channels. For instance, the high selectivity of K^+ to Na^+ for the KcsA channel was suggested to relate to the different hydration energy of the two ions caused by the nanoscale confinement.⁷ The lack of selectivity of K^+ to Na^+ for the NaK channel,⁸ which has a

similar structure to the of KcsA channel, was also suggested to relate to the hydration of the two cations in the channels.⁹ Additionally, the selective rate and flux of the ions in the nanoporous material is central to the purification or desalination of sea and brackish water, and the ionic hydration in the nanopore is one of the key factors in the processes' performance.

It is well known that the substance in the nanopore has a behavior different from its bulk counterpart, mainly due to geometric constraints and anisotropic interactions.^{10–16} Therefore, the ionic hydration in the nanopore may have its own characteristics and considerable efforts have been done to investigate the confinement-induced behavior of ionic hydration theoretically. Lynden-Bell and Rasaiah¹⁷ studied the hydration and mobility of the electrolyte solutions inside a channel consisted with repulsive walls using molecular dynamics (MD) simulations. Their studies showed that the ionic hydration in a narrow nanopore is incomplete, with less coordination number. The diffusion of the ion in the narrow nanopore is considerably slower than in the bulk solution. Chan and his co-workers^{18–20} also found the incomplete hydration of the ions in the nanopores by the equilibrium MD and non-equilibrium MD simulations. The simulation

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studies showed that the energy cost of constraining a hydrated K^+ within a nanopore is smaller than the cost of constraining the hydrated Na^+ .^{21,22} It may be in this way that the larger ions could pass the narrow pores more easily. The incomplete hydration of the ions also induces the cations and the anions form ion pairs more easily in the nanopore than in the bulk solution²³ and the solubility of electrolyte solution decreases monotonically as the pore size decreases.²⁴ Furthermore, recent studies showed that the confinement effects to the hydration of the cations and anions are different. For instance, the MD simulation studies of Liu *et al.*²⁵ showed that the coordination number of Na^+ in the carbon nanotube (CNT) is reduced as the diameter of CNT decreases, whereas that of Cl^- inside is similar to the bulk counterpart. However, Tanimura *et al.*²⁶ studied the structure of electrolyte solutions sorbed in carbonized polyvinylidene chloride with replica RISM theory and gained the different results. Their studies suggested that a cation adsorbed at the non-polar carbon surfaces is fully surrounded by the hydration shell of water molecules, whereas an anion adsorbed at the surface has a part of water molecules in its hydration shell squeezed out. These studies help us get more insight into the ionic hydration in the nanoscale confinement.

Nevertheless, several critical issues on the ionic hydration in the nanopore are not well elucidated yet. One is the temperature effect. According to the theoretical study on the ionic hydration in the bulk solution, the water molecules in the hydration shells of the ions have a certain preferential orientation mainly because of the electrostatic interactions between the water molecules and ions.^{27,28} This orientation distribution of water molecules is important to assess the hydration of the ions, and acts as a key role in the relationship between the coordination number of the ions and the thermodynamic properties of the ionic hydration.²⁸ The orientation structure of water molecules in the hydration shell of the ions is greatly dependent on the temperature. For instance, as shown in Rasaiah *et al.*'s study,²⁷ the highly ordered structure of water molecules in the first coordination shell of Li^+ turns to be random at high temperature, though the change of the coordination number is minor. Besides the ionic hydration, the temperature also influences the confinement effect of the nanopore.^{29–32} Under the synergistic effect of the temperature and the confinement, the ionic hydration in a nanopore may have its own characteristics, especially the structure of its coordination shell. The well elucidation of this topic is not only necessary for the better understanding of the ionic hydration in the nanopore, but also important to the partition and transport of the hydrated ions in the nanochannels and the related biological and chemical processes at high temperature.

In this work, we performed a series of MD simulations to investigate the hydration of the ions with different charges and sizes in the nanopores from 298 to 683 K. The main focus is the temperature effect on the structure order of the water molecules in the shells of the various ions. The real pores, such as those of biological channels or polymeric membranes, are complicated with irregular surface and highly inhomogeneous charge distributions, making the investigation difficult. Therefore, we pursue a different strategy to avoid the complexity of biological and industrial systems. We employ CNT as the

model because recent theoretical studies³³ suggested it as a prototype for the complicated 1-dimensional (1D) nanopores. The effective diameters of the CNT in this work are from 0.73 to 1.0 nm, similar to the size of ion channels. The rest paper is organized as follows: section II describes the details of the simulations and section III is the results and the discussions. On the basis of the discussions in section III, the main conclusions are given in section IV.

II. Simulation model and method

II.A Simulation model

We use the extended simple point charge model (SPC/E) for water molecule³⁴ because of its well representation for water molecule. The ions are treated as charged Lennard-Jones (L-J) sites, the in the way same as the literature work.^{27,28,35,36} The single-walled CNT is formed by folding a graphite sheet to a cylinder. In the same way as the study of Hummer *et al.*,³³ each carbon atom of the nanotube is treated as a neutral L-J interaction site. The CNTs used in this work are armchair series ((8,8), (9,9), (10,10)). The effective diameters of these CNTs are 0.73, 0.86 and 1.00 nm, respectively.

The potential energy of intermolecular interactions is described as a combination of L-J 12-6 potential and a Coulombic potential:

$$U(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (1)$$

where r_{ij} is the distance between atoms i and j ; q_i is the partial charge assigned to atom i , and ϵ_{ij} and σ_{ij} are energy and size parameters obtained by Lorentz–Berthelot combining rules, where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. Table 1 lists the L-J parameters and the partial charges used in this study.

II.B Simulation method

Fig. 1 schematically illustrates the electrolyte solution confined in the CNT. To avoid the disturbance from the water molecules outside the nanopore, the whole simulated system, including the CNT and the confined electrolyte solution, was placed in a vacuum. The corresponding lengths of z dimension of the simulation cell for the CNTs of the effective diameters of 0.73, 0.86 and 1.0 nm are 14.2, 20.0 and 27.5 nm. The solvent density in the CNT is an important issue in the simulation. Because of the confinement effect, the density of water inside

Table 1 The Lennard-Jones parameters and partial charges for the ions,⁴⁵ water molecules (SPC/E)³⁴ and carbon atom of CNT^{44,46,47}

	Site	σ/nm	$\epsilon/\text{kJ mol}^{-1}$	q/e
Ions	Li^+	0.213	0.0765	1.000
	Na^+	0.333	0.0116	1.000
	K^+	0.493	0.00137	1.000
	F^-	0.274	3.01248	−1.000
	Cl^-	0.442	0.493	−1.000
Water	OW	0.317	0.650	−0.8476
	HW	0.000	0.000	0.4238
CNT	C	0.355	0.293	0.000

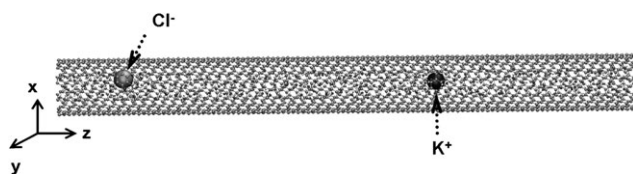


Fig. 1 Schematic of the simulation system for KCl solution in the carbon nanotube with effective diameter of 1.0 nm at solvent density of 0.71 g cm^{-3} .

CNTs can be different from the bulk solution, and influences the results considerably. We gained the equilibrium solvent densities in various CNTs at 298 K from our previous study¹³ because the study of Lakatos *et al.*³⁷ suggested that the adsorption amount of water molecules inside the CNT is not significantly affected by the ions at infinite dilution. Besides the equilibrium solvent density, we also investigate the ionic hydration in the CNT with the effective diameter of 1.0 nm at the bulk solvent density (1.0 g cm^{-3}) and half of the equilibrium solvent density (low density) for the comparison. Table 2 lists the properties of CNTs and the equilibrium densities of water inside.

The simulation system was built in the following process. First, certain water molecules were placed in the CNT randomly. After the energy minimization, two water molecules were chosen randomly to be replaced by a cation and an anion. The initial distance of the cation and the anion was at least 5.0. The details of all the simulation cases were listed in Table S1. For every case, three individual MD simulations with different initial positions and velocities for the water molecules and the ions were carried out.

MD simulations were performed in a NVT ensemble with GROMACS (version 3.3.1).³⁸ For all simulated systems, after the energy minimization and 1.0 ns MD run with integral step of 1.0 fs for equilibrium, another 1.0 ns MD run was carried out with integral step of 2.0 fs and the coordinates were saved every 0.1 ps for the further analysis. With periodic boundary conditions only in the z dimension (axial direction), the long-range electrostatic interactions were computed with a cutoff distance of 1.5 nm. The simulations with a cutoff distance of 2.5 nm were also carried out and the results were quantitatively same to that with a cutoff distance of 1.5 nm. The short-range van der Waals forces were calculated within a cutoff distance of 1.0 nm. The overall system was maintained at certain temperature with Berendsen algorithm (time constant 0.1 ps).³⁹ Intramolecular bonds of water molecules were kept rigid with shake algorithm.⁴⁰ In order to keep the diameter of the carbon nanotube steady, the carbon atoms of the nanotube were kept at their initial positions during the MD run. During the production stage, the fluctuation of the potential energy of the ensemble is around 1%.

Table 2 Properties of CNTs and equilibrium density of water within

(m,m)	D/nm	L/nm	Equilibrium density/ g cm^{-3}
(8,8)	0.73	27.5	0.72
(9,9)	0.86	20.0	0.70
(10,10)	1.00	14.2	0.73

III. Results and discussions

III.A Radial distribution functions of ion-water in CNTs

The structures of water molecules around the ions in the CNTs are studied first through the ion-solvent radial distribution functions (RDFs). Fig. 2 shows the ion-oxygen RDFs of the five ions in the CNT with the effective diameter of 1.0 nm at the equilibrium solvent density from 298 to 683 K. Because of the constraint of CNT, the values of the RDFs turn to zero as r increases, consistent with the previous observations.^{20,25,41,42} We observe a sharp peak corresponding to the first coordination shell for all the five ions, same to the reported simulation results on the confined ions.^{20,25,41,42} The second peaks of RDFs are not very significant in the CNT, indicating that the second coordination shells of the ions may be unstable in the CNT with the effective diameter of 1.0 nm, probably due to the geometric constraint.

To better study the structure of the shell, we list the positions and the heights of the first peaks and the first minima of RDFs for the five ions in the CNTs in Table 3. The corresponding values for the bulk electrolyte solutions at infinite dilution are also presented in Table 3, and we find that they agree well with the literature values for bulk solutions.^{27,28,35,43} Generally, the peak height decreases as the temperature increases, same to the tendency in the bulk solutions.²⁷ However, we find that the reduction of the peak height for K^+ is less than those for the other ions. For instance, at equilibrium density, the increase of temperature from 298 K to 683 K results in the peak height of K^+ reduce only around 22.7%, whereas it is 50.0%, 49.4%, 57.6%, and 35.0% for those of Li^+ , Na^+ , F^- , and Cl^- ions, respectively. This implies that the temperature may have special effect on the hydration of K^+ in the CNT. The peak heights at the low solvent density at 493 or 683 K are remarkably higher than the corresponding ones at the equilibrium density and the bulk density. The similar feature has been observed for the infinite dilute electrolyte in bulk phase at 683 K by Rasaiah and his co-workers.²⁷

Unlike the peak heights, the peak positions of the RDFs of the confined ions are generally unchanged during the variations of temperatures and solvent densities, same to the bulk counterparts.²⁷ This indicates that the size of the first coordination shells for the five investigated ions do not change in the CNT with the effective diameter of 1.0 nm at the investigated temperatures and densities.

III.B Coordination numbers of ions in CNTs

The coordination number N of an ions is calculated in the way as an integral of the ion-oxygen RDFs, which is shown in eqn (2).

$$N = 4\pi \int_0^R r^2 \rho g_{io}(r) dr \quad (2)$$

where ρ is the solvent density, R is the position of the first minimum and $g_{io}(r)$ is the RDF. It should be noted that the integral for the RDFs of confined ions is different from that of the bulk ones because of the remarkable density fluctuations caused by the wall of the nanotube.

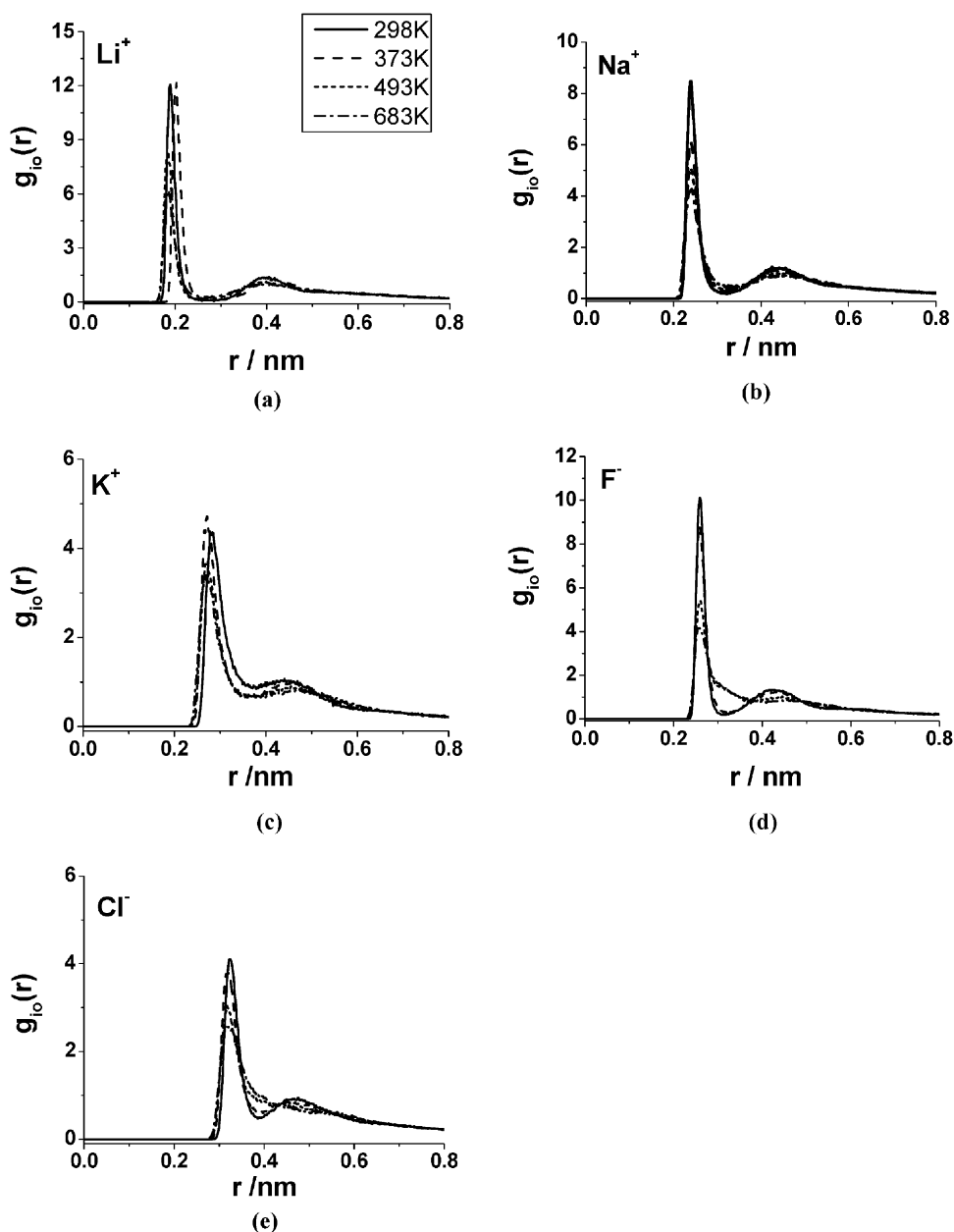


Fig. 2 Radial distribution functions of ion-oxygen in the carbon nanotube with the effective diameter of 1.0 nm at the equilibrium density and the various temperatures for (a) Li^+ , (b) Na^+ , (c) K^+ , (d) F^- and (e) Cl^- .

The coordination number of the ions could significantly decrease in a narrow nanopore, as observed by the previous simulation studies.^{17,20,24,25} Nevertheless, this effect may be only significant in the narrow pores and seems to disappear in a CNT with the effective diameter of 1.0 nm. Table 4 lists the coordination number N of the first coordination shells of the five ions in the CNT with the effective diameter of 1.0 nm at equilibrium density and 298 K and in the bulk solution at 298 K. It could be found that the values of N in the nanotube are similar to the corresponding ones in the bulk solution for Li^+ , Na^+ , F^- , Cl^- . As to K^+ , we find that N in the nanotube is around two larger than in the bulk solution, indicating that two more water molecules are in its first coordination shell in the nanotube. In other words, in a CNT with the effective

diameter of 1.0 nm, none of the five ions have incomplete hydration observed for the ions in the narrow pores.^{17,20,25}

Fig. 3 shows N of the first coordination shells of the five ions in the CNT with the effective diameter of 1.0 nm at the equilibrium and bulk densities from 298 to 683 K. We can find that the change of N with temperature is minor for the five ions at both densities. For instance, with temperature rises from 298 to 683 K, N of K^+ decreases from 8.07 to around 7.0, only around 12%, at equilibrium density. This indicates that the feature that the little change of N with temperature for the small ions²⁷ is still valid for the ions in the CNT with the effective diameter of 1.0 nm.

Table 5 lists N of the first coordination shells of the five ions in the CNT with the effective diameter of 1.0 nm at 493 and

Table 3 Positions and magnitudes at maxima and minima of ion-oxygen distribution functions in the CNT with the effective diameter of 1.0 nm and in the bulk solution at different temperatures

		298 K		373 K		493 K		683 K	
Solvent density		$r_{io}(\text{\AA})$	g_{io}	$r_{io}(\text{\AA})$	g_{io}	$r_{io}(\text{\AA})$	g_{io}	$r_{io}(\text{\AA})$	g_{io}
First maximum									
Li ⁺	Low	—	—	—	—	1.9	14.2	1.8	10.6
	Equilibrium	1.9	12.1	2.0	12.1	1.8	8.0	1.9	6.1
	Bulk in tube	1.9	11.1	2.0	10.1	1.9	8.7	1.8	7.6
	Bulk ²⁷	2.0	16	—	—	—	—	2.0	12.0
	Confined ⁴⁸	2.0	14	—	—	—	—	2.0	7.8 ~ 23.0
Na ⁺	Low	—	—	—	—	2.4	9.0	2.4	7.2
	Equilibrium	2.4	8.5	2.4	6.2	2.4	5.1	2.4	4.3
	Bulk in tube	2.4	7.0	2.4	5.6	2.4	5.6	2.4	4.5
	Bulk	2.4	8.9	—	—	—	—	2.3	8.1
	Bulk ²⁷	2.5	7.2	—	—	—	—	2.4	4.6 ~ 11.0
K ⁺	Confined ⁴¹	2.4	7.5	—	—	—	—	—	—
	Low	—	—	—	—	2.7	6.0	2.7	5.0
	Equilibrium	2.8	4.4	2.7	4.5	2.7	3.7	2.7	3.4
	Bulk in tube	2.7	4.7	2.7	4.5	2.7	4.2	2.7	4.1
	Bulk	2.8	4.0	—	—	—	—	2.8	5.0
F [−]	Bulk ^{28,35}	2.9	4.02	—	—	—	—	2.8	2.2
	Confined ⁴³	2.8	4.5	—	—	—	—	—	—
	Low	—	—	—	—	2.6	9.4	3.4	3.7
	Equilibrium	2.6	9.9	2.6	8.7	2.6	5.3	2.6	4.2
	Bulk in tube	2.6	8.3	2.6	8.3	2.6	6.7	2.6	6.1
Cl [−]	Bulk	2.6	11.4	—	—	—	—	2.6	7.2
	Bulk ²⁷	2.6	7.9	—	—	—	—	2.6	4.6 ~ 11.0
	Low	—	—	—	—	3.2	4.8	3.2	3.9
	Equilibrium	3.2	4.0	3.2	2.8	3.2	3.0	3.2	2.6
	Bulk in tube	3.2	4.1	3.1	3.8	3.1	3.3	3.1	3.2
First minimum	Bulk	3.2	4.1	—	—	—	—	3.2	4.1
	Bulk ²⁷	3.2	4.1	—	—	—	—	3.2	2.6 ~ 5.0
	Confined ⁴³	3.1	5.6	—	—	—	—	—	—
	Low	—	—	—	—	2.6	0	2.8	0
	Equilibrium	2.8	0	2.7	0	2.7	0	2.8	0
Li ⁺	Bulk in tube	2.9	0	2.9	0	2.8	0	2.8	0
	Bulk	2.7	0.0	—	—	—	—	2.8	0.50
	Bulk ²⁷	2.7	0.02	—	—	—	—	2.9	0.32
	Confined ⁴⁸	2.5	—	—	—	—	—	—	—
	Low	—	—	—	—	3.2	0.7	3.2	0.7
Na ⁺	Equilibrium	3.2	0.4	3.2	0.4	3.2	0.4	3.2	0.4
	Bulk in tube	3.2	0.5	3.2	0.5	3.2	0.5	3.2	0.6
	Bulk	3.2	0.17	—	—	—	—	3.3	0.58
	Bulk ²⁷	3.3	0.16	—	—	—	—	3.5	0.74
	Confined ⁴¹	3.2	0.1	—	—	—	—	—	—
K ⁺	Low	—	—	—	—	3.6	0.9	3.6	0.9
	Equilibrium	3.7	0.89	3.6	0.70	3.6	0.70	3.6	0.70
	Bulk in tube	3.6	0.7	3.6	0.7	3.6	0.7	3.6	0.7
	Bulk	3.7	0.47	—	—	—	—	3.8	0.74
	Bulk ^{28,35}	3.7	0.25	—	—	—	—	3.6	0.5
F [−]	Confined ⁴³	3.7	0.8	—	—	—	—	—	—
	Low	—	—	—	—	3.9	1.2	4.3	0.90
	Equilibrium	3.1	0.30	3.1	0.30	3.7	0.80	3.8	0.80
	Bulk in tube	3.0	0.18	3.1	0.37	3.1	0.55	3.4	0.64
	Bulk ²⁷	3.2	0.12	—	—	—	—	3.8	1.3
Cl [−]	Bulk	3.2	0.17	—	—	—	—	3.7	1.1
	Low	—	—	—	—	3.9	1.39	3.9	1.39
	Equilibrium	3.9	0.50	3.9	0.62	3.9	0.86	3.9	0.86
	Bulk in tube	3.7	0.59	3.7	0.76	3.7	0.94	3.8	0.94
	Bulk	3.8	0.66	—	—	—	—	3.9	1.2
First minimum	Bulk ²⁷	3.8	0.49	—	—	—	—	4.7	1.2
	Confined ⁴³	3.5	0.5	—	—	—	—	—	—

^a The absence of an entry, denoted by (—), implies that no simulation were performed at this state point. “Low” means the solvent density in the CNT is half of the equilibrium density, “equilibrium” means that the solvent density in the CNT is that gained from the previous studies; “bulk in tube” means that the solvent density in the CNT is assumed to be the same to the bulk solution.

683 K. From Fig. 3 and Table 5, we can find that N of the five ions decrease as the solvent density decreases, and this ten-

dency is more significant at higher temperature. In addition, the number of water molecules leaving the first coordination

Table 4 Coordination number N of the first coordination shells of the five ions in the carbon nanotube with effective diameter of 1.0 nm at equilibrium density and 298 K and in the bulk solution at 298 K

	Li^+	Na^+	K^+	F^-	Cl^-
Nanotube	4.72	4.85	8.06	6.26	7.17
Bulk	4.00	5.16	6.15	6.05	7.05

shell of the ions is more for the larger ions than that for the smaller ions. For example, with the solvent density decreases from the equilibrium density to half of the equilibrium density, K^+ nearly loses one and half coordinated water molecules in its first coordination shell at 493 K in the CNT with the effective diameter of 1.0 nm, as shown in Table 5. The number of water molecules leaving the first coordination shell of Li^+ is less than one. The variation of N with the solvent density for Cl^- is also much more significant than that for F^- , as listed in Table 5. This is probably due to the stronger electrostatic attraction between the small ions and the water molecules, and the relative small size of its coordination shell.

III.C Orientation structure of water molecules in the first coordination shells of the ions in CNTs

To investigate the orientation structure of water molecules in the shells of the confined ions, we define an angle α between the ion and the dipole moment of the water molecules, as illustrated in Fig. 4.

Fig. 5 shows the distributions of $\cos\alpha$ of the water molecules in the first coordination shells of Li^+ and Cl^- in the CNT with the effective diameter of 1.0 nm at the equilibrium density in the range of 298 to 683 K. The orientation distributions for the water molecules in the first coordination shells of the two ions in the bulk solution at 298 K are also plotted in Fig. 5 for comparison. We can find in Fig. 5 that the distribution profiles for Li^+ have peaks around -1 , while the profiles for Cl^- have peaks around 0.6. This feature agrees well with the previous results for the cations and anions in the bulk phase.^{27,28} It is interesting to find out in Fig. 5 that the distribution profile for Cl^- in the CNT agrees well with the bulk counterpart, whereas that for Li^+ in the CNT has peak height considerable lower than the bulk one. This indicates the confinement offered by the CNT has different influences on the orientation of water

molecules around Li^+ and Cl^- . With the increase of temperature, both the distribution profiles of Li^+ and Cl^- become broader, implying that the orientation of the water molecules in the first coordination shells for these two ions become more random.

To better investigate the orientation of water molecules in the coordination shell of the various ions in the CNT, we apply a parameter named the hydration factor proposed by Zhou *et al.*²⁸ The hydration factor of the first coordination shell of a cation is defined as the ratio of the number of water molecules in the first coordination shell with $\cos\alpha$ is less than -0.72 to the amount of water molecules in the first shell. The hydration factor of an anion is defined as the ratio of the number of water molecules in the first coordination shell with $\cos\alpha$ is larger than 0.43 and smaller than 0.76 to the total number of water molecules in the first coordination shell. The criterion for the cations is based on the distribution probability of $\cos\alpha$ of water molecules in the first coordination shell of Li^+ larger than the probability of a random distribution in the bulk phase, whereas the criterion for anions is based on that of F^- in the bulk solution. Larger hydration factor indicates the more ordered structure of the water molecules in the shell.

The hydration factors for the five ions in the CNT with the effective diameter of 1.0 nm at different temperatures and densities are shown in Fig. 6. The hydration factors for the five ions in the bulk solution at 298 K and 683 K are also shown in Fig. 6 for the comparison. The first interesting thing found in Fig. 6 is that the change of the hydration factors for the confined cations regarding to their bulk counterparts is different from those of the confined anions. This is consistent with the different changes of the distribute profiles of $\cos\alpha$ for Li^+ and Cl^- shown in Fig. 5. The hydration factors for the first coordination shells of Li^+ , Na^+ and K^+ in the CNT at 298 K are considerably less than their bulk counterparts. For instance, the hydration factor for K^+ in the nanotube at the equilibrium density and 298 K is around 0.28, only 50% of that in the bulk. The hydration factors for Li^+ and Na^+ in the CNT are about 86% and 87% of their respective bulk values. The changes of the hydration factors of the confined anions are minor. The hydration factor of F^- in the CNT is same to that in the bulk solution at 298 K. As to the larger anion, Cl^- , we find that its hydration factor in the CNT at the equilibrium

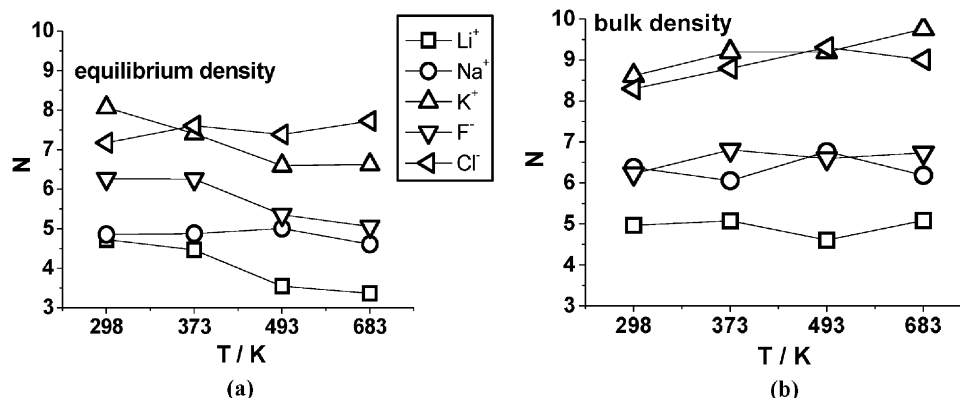


Fig. 3 Coordination number N of the first coordination shells of the ions inside the CNT with the effective diameter of 1.0 nm as a function of temperature at (a) equilibrium density and (b) bulk density.

Table 5 Coordination number N of the first coordination shells of the five ions in the carbon nanotube with the effective diameter of 1.0 nm at 493 and 683 K with the different solvent densities

	493 K			683 K		
	Low density	Equilibrium density	Bulk density	Low density	Equilibrium density	Bulk density
Li^+	3.0	3.5	4.6	3.0	3.4	5.1
Na^+	4	5	6.76	3.8	4.6	6.2
K^+	5.3	6.6	9.2	4.8	6.6	9.8
F^-	5.0	5.4	6.6	5.0	5.1	6.7
Cl^-	5.84	7.38	9.3	5.18	7.72	9.0

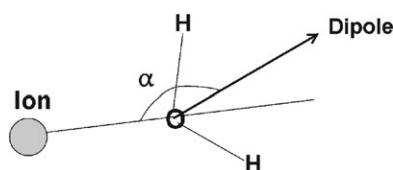


Fig. 4 Definition of angle α of an ion and the dipole moment of the water molecule.

density and 298 K also agrees well with the corresponding bulk one at the ambient condition.

The different changes of the hydration factors for the cations and anions in the nanotube may be related to the effects of CNT to the orientation of water molecules. As shown in previous studies,^{13,44} the water molecules within the nanotube would avoid their hydrogen atoms point to the non-polar wall of the nanotube in the aim to form hydrogen bonds between them. This has little effect on the original orientation of water molecules in the first coordination shells of the anions probably because the anion attracts the hydrogen atoms of water molecules in its shells to it^{27,28} and away from the wall of nanotube. However, when it comes to the water molecules in the first coordination shells of the cations, their orientation induced by the cations is characterized with the hydrogen atoms of the water molecules pointing away from the cations,^{27,28} increasing the possibility of the hydrogen atoms to point to the wall. This is opposed to the orientation of water molecules induced by the nanotube and greatly influenced by latter.

Another interesting thing shown in Fig. 6 is the temperature effect on the hydration factors of the ions. Anomalously, we find in Fig. 6c that the hydration factor of the first coordina-

tion shell of K^+ increases as the temperature increases. As shown in Fig. 6c, the hydration factor of the first shell of K^+ increases from 0.28 to around 0.48 in the nanotube at equilibrium density as the temperature increases from 298 K to 683 K. This implies that the hydration of K^+ inside a CNT with the effective diameter of 1.0 nm is enhanced with the increase of temperature, contrary to those of the other ions in the CNT of the same effective diameter (1.0 nm) and those of the five ions in the bulk solution. From Fig. 6, we can find that the hydration factors of the other four ions (Li^+ , Na^+ , F^- and Cl^-) in the CNT with the effective diameter of 1.0 nm all decrease as the temperature increases. And the five investigated ions have their hydration factors lower at the high temperature in the bulk solution, as shown in Fig. 6.

It is known that the water molecules form distinct layers at the radial direction in the CNT.^{11,13} As shown in Fig. 7, the radial density distribution of water molecules in the CNT with the effective diameter of 1.0 nm has a peak around 0.35 nm from the axial center of the tube. And as shown in Fig. 7, the size of the first coordination shell of K^+ is around 0.37 nm, larger than the value of the peak position. This indicates that the water molecules in the shell of K^+ are very close to the wall of the CNT and their orientation may be determined mainly by the wall–fluid interactions that destroy the orientation order of the shell. The effect of the CNT turns weaker as the temperature increases and the order of the first coordination shell of K^+ increases. It is noted that the structure order of the shell of K^+ in the CNT is still less than that in the bulk solution at 683 K, as shown in Fig. 7, indicating the effect of the CNT does not vanish, just becomes minor at the high temperature.

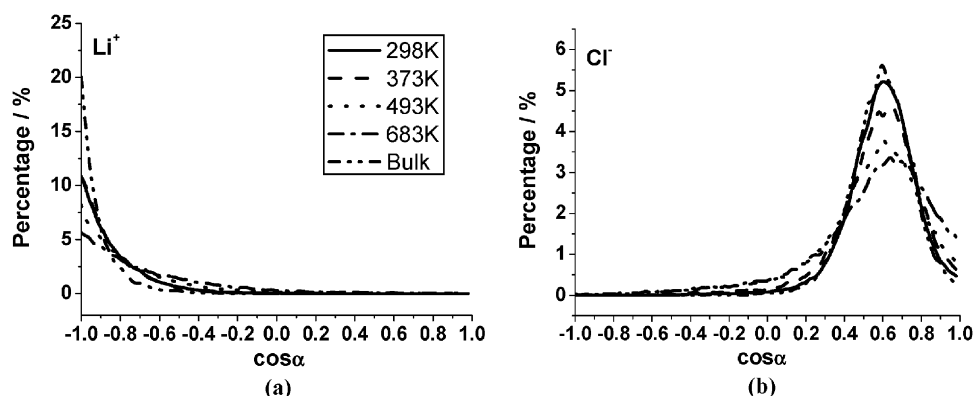


Fig. 5 Distributions of $\cos \alpha$ of the water molecules in the first coordination shells of (a) Li^+ and (b) Cl^- in the CNT with the effective diameter of 1.0 nm at the equilibrium density with the various temperatures.

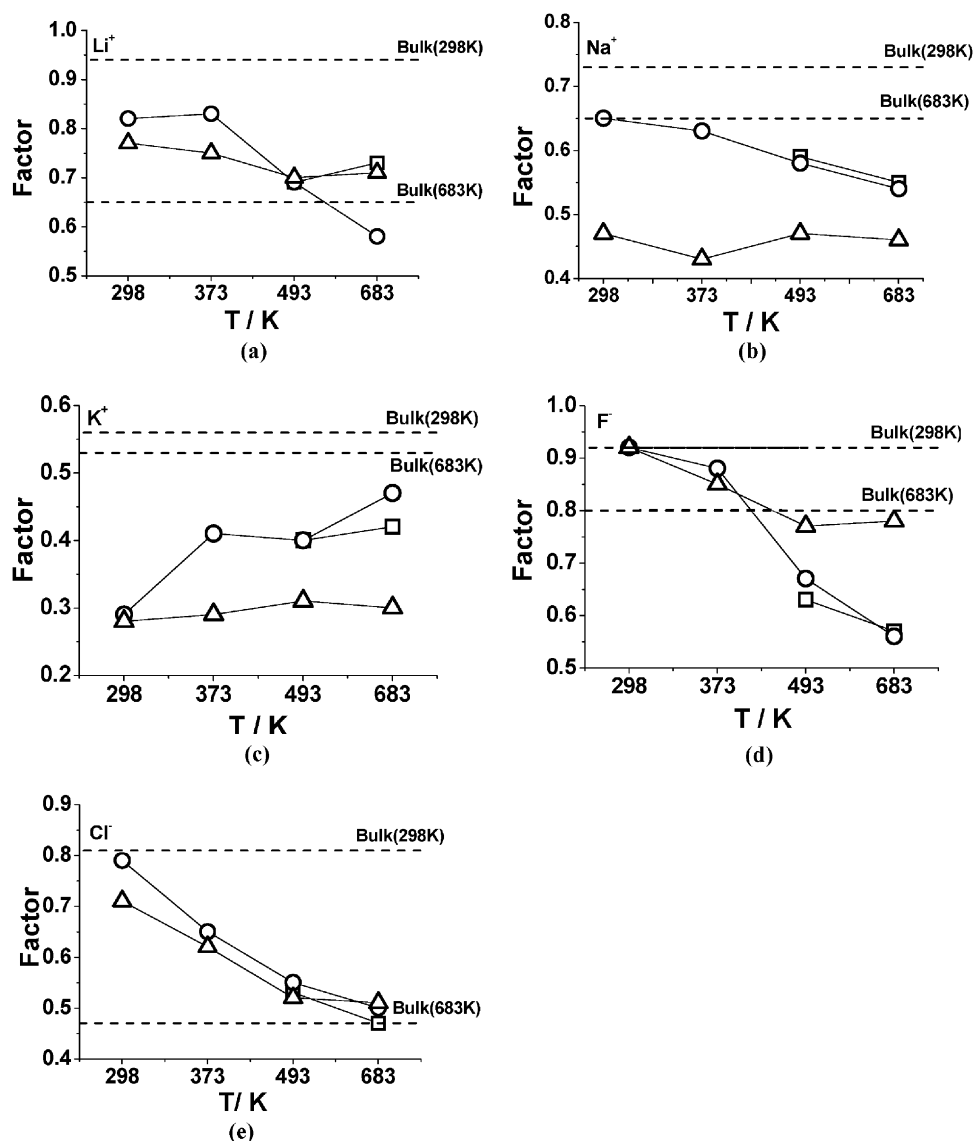


Fig. 6 Hydration factors of the five ions in the carbon nanotube at different temperatures and solvent densities. (a) Li^+ , (b) Na^+ , (c) K^+ , (d) F^- and (e) Cl^- . The square represents those with half of the equilibrium density, the circle represents those with the equilibrium density, and the triangle represents those with bulk density.

As to the other ions, the sizes of the first coordination shells of Li^+ or Na^+ are less than the value of the peak position, as shown in Fig. 7. The water molecules in their shells mainly distribute in the inner layer where the ion–fluid interactions may dominate instead of the fluid–wall interactions. The temperature increase may decrease the effect of the cations and the structure order of the shell turns to loose, same to the tendency of their bulk counterparts. It is same to the water molecules in the first coordination shells of the anions.

To better understand the temperature dependence of the structure order of water molecules in the shells of the ions in the CNTs, we further investigate the hydration factors of the first coordination shells of the five ions (Li^+ , Na^+ , K^+ , F^- and Cl^-) in the CNTs with the effective diameters of 0.73 and 0.86 nm at 298 and 683 K and the respective equilibrium densities. Table 6 lists the hydration factors of the five ions in the CNTs with the effective diameters of 0.73, 0.86 and

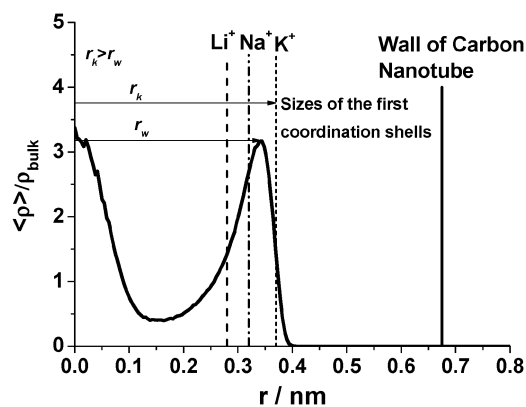


Fig. 7 Radial density distribution of the water molecules inside the CNT with the effective diameter of 1.0 nm and the sizes of the first coordination shells of Li^+ , Na^+ and K^+ .

Table 6 Hydration factors of the first coordination shells of the five ions inside the carbon nanotubes with the different effective diameters at the equilibrium densities with 298 and 683 K

	$D = 0.73$ nm		$D = 0.86$ nm		$D = 1.0$ nm	
	298 K	683 K	298 K	683 K	298 K	683 K
Li^+	0.83	0.66	0.89	0.70	0.82	0.58
Na^+	0.78	0.46	0.72	0.54	0.65	0.54
K^+	0.65	0.41	0.38	0.34	0.28	0.48
F^-	0.92	0.53	0.71	0.53	0.92	0.56
Cl^-	0.69	0.27	0.71	0.32	0.79	0.50

1.00 nm at 298 and 683 K. We find that only K^+ in the CNT with the effective diameter of 1.0 nm has its hydration factor increase with the increase of temperature. This implies that only the hydration of K^+ in the carbon nanotube with the certain effective diameter (1.0 nm) may be stronger as the temperature increases. The other four ions do not have similar feature to that for K^+ in the CNT with the effective diameter of 1.0 nm, even though the water molecules in their coordination shells are quite close to the wall of the CNT. This indicates that the easier distortion of the coordination shell of K^+ may be substantial for such anomalous behavior, as well as the proper match between the pore size and the size of the coordination shell.

As to the influence of the solvent density, we can observe in Fig. 6 that the hydration factors of the five ions in the CNT at half of the equilibrium density are similar to the corresponding ones at the equilibrium density. However, if the solvent density is assumed as the bulk solvent density, as shown in Fig. 6, the hydration factors of the first coordination shells of the cations change little with the temperature. This indicates that the assumption of the bulk density should be carefully considered to use in the study of the confined fluids. The change of the hydration factors of the first coordination shells of anions in the nanotube with the bulk solvent density is similar to that with equilibrium density.

III.D Dynamic properties of ionic hydration in CNTs

Besides the structure of the ion hydration, the confinement of the CNT can also induce the change for the dynamic properties of the ionic hydration inside. To investigate the dynamic properties of the ionic hydration in the CNT, we consider two dynamic properties: the residual time of water in the shells of the ions and the diffusion of the ions themselves along the axial direction of the CNT.

We first consider the residual times of water molecules in the coordination shells. The residual time (τ) of the first coordination shells of the five ions in the CNT are calculated from the residence time correlation function as eqn (3)

$$R(t) = \frac{1}{N_h(t)} \sum_{i=1}^{N_h(t)} \langle \theta_i(t) \theta_i(t_0) \rangle \quad (3)$$

where $\theta_i(t)$ is 1 if a water molecule i is in the coordination shell of the ion at time t and t_0 , zero otherwise. $N_h(t)$ is the coordination number of this shell at time t . The residual time

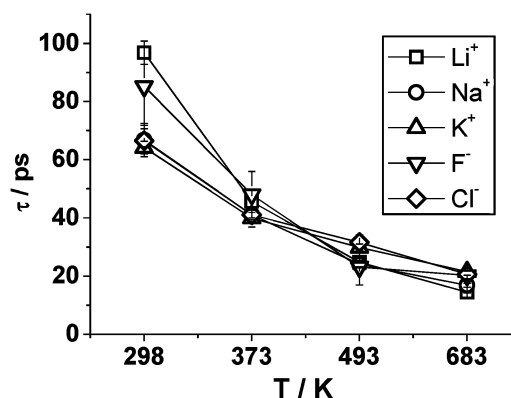


Fig. 8 Residual times of the first coordination shells of the five ions in the carbon nanotube at equilibrium density and various temperatures. The residual times for the first coordination shells in the bulk solution at 298 K are 80.5 ps (Li^+), 29.2 ps (Na^+), 15.0 ps (K^+), 26.0 ps (F^-) and 17.8 ps (Cl^-), respectively.

is given by

$$\tau_{\text{res}} = \int_0^{\infty} R(t) dt \quad (4)$$

Same as the literature,³⁶ the integration of the correlation function $R(t)$ was carried out numerically from 0 to 10 ps, and the remainder was determined analytically by fitting the tail end to an exponential function. In our definition of $R(t)$, we allow for the temporary excursions of water. In other words, the water molecules are thought in the shell only if it is in the shell at time t_0 and t . Fig. 8 shows the residual times of the first coordination shells of the five ions in the carbon nanotube with the effective diameter of 1.0 nm at the equilibrium density and the different temperatures.

The residual time in the nanotube is considerably larger than that in the bulk solution, same to Liu *et al.*'s simulation results.²⁵ This indicates that the water molecules in the shells change less frequently with the solutions in the nanotube than in the bulk phase, probably due to the constraint of the CNT. As shown in Fig. 8, the residual time decreases significantly as the temperature increases, implying that the temperature increase can also make the shells of the ions more unstable in the nanotube as to their bulk counterparts. In addition, the residual time for the five ions turns to be similar at 373, 493 and 683 K, despite the differences of the ion size and the shell size. This implies that the main constraint for the shells in the nanotube may be the wall of the CNT at high temperature.

Diffusion is another dynamic property greatly influenced by the confinement. We calculated the diffusion coefficients of the ions along the axial direction of the CNT by the mean-square displacement method shown in eqn (5)

$$D_z = \frac{1}{2} \lim_{t \rightarrow \infty} \frac{\langle |z_i(t) - z_i(0)|^2 \rangle}{t} \quad (5)$$

where the broken brackets $\langle \rangle$ denote the ensemble average of the mean axial displacement of each ion species.

Fig. 9 shows the axial diffusion coefficients of the five ions inside the CNT with the effective diameter of 1.0 nm at the equilibrium density and the bulk density with the temperatures ranging from 298 to 683 K. The diffusion coefficient of K^+ in

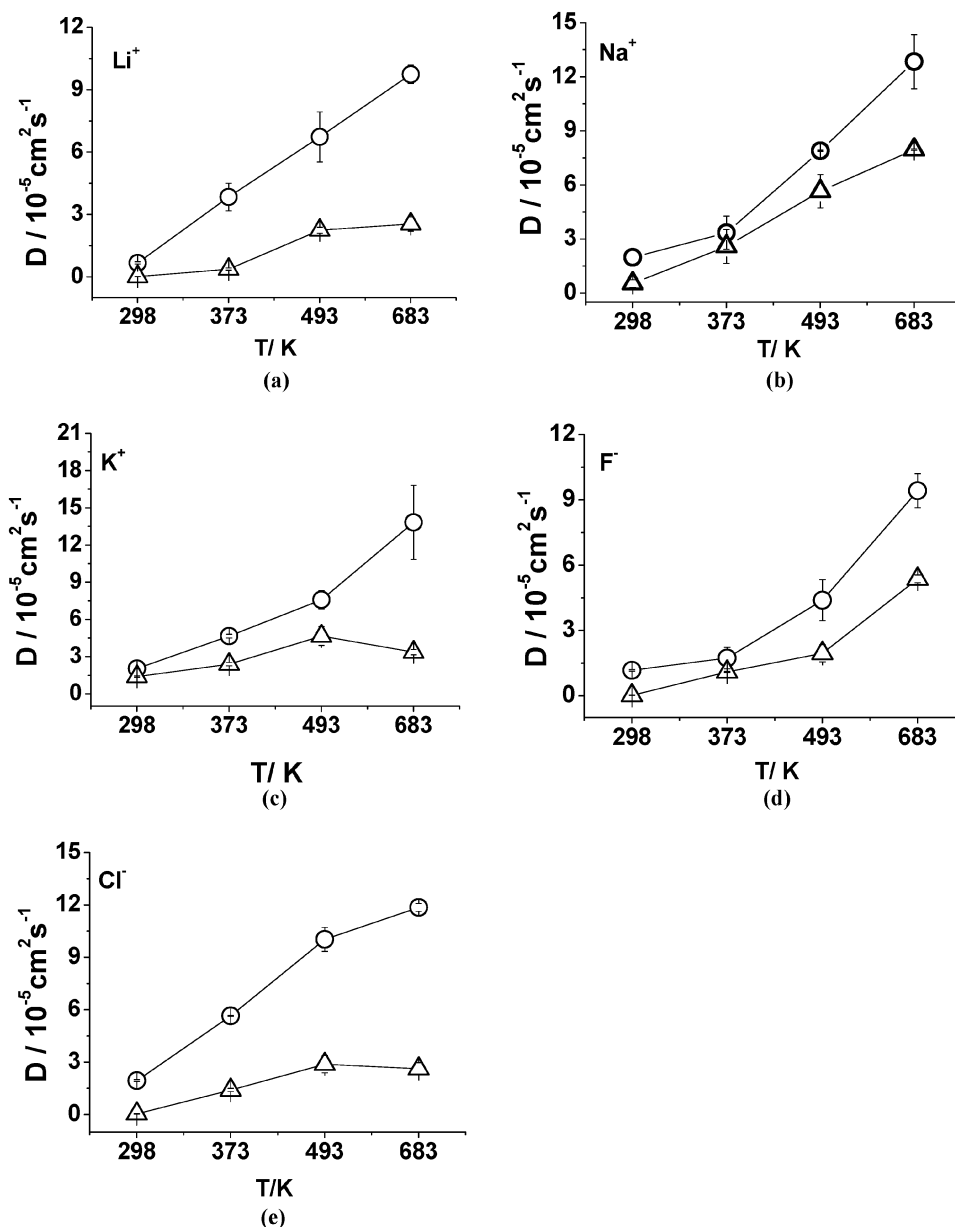


Fig. 9 Axial diffusion coefficients of the five ions inside the CNT with the effective diameter of 1.0 nm at the different temperatures and densities. (a) Li^+ , (b) Na^+ , (c) K^+ , (d) F^- and (e) Cl^- . The circle represents those with the equilibrium density and the triangle represents those with bulk density. The diffusion coefficients of the five ions in the bulk solution at 298 K are $1.53 \text{ cm}^2 \text{ s}^{-1}$ (Li^+), $1.12 \text{ cm}^2 \text{ s}^{-1}$ (Na^+), $0.90 \text{ cm}^2 \text{ s}^{-1}$ (K^+), $1.54 \text{ cm}^2 \text{ s}^{-1}$ (F^-) and $2.23 \text{ cm}^2 \text{ s}^{-1}$ (Cl^-), respectively.

CNT at bulk density and 298 K is found to agree well with the result of K^+ confined in a nanopore with the diameter around 1.0 nm gained in the simulation work of Chan and his co-workers,²⁰ which assumed the bulk density in the nanopore. We can observe from Fig. 9 that the diffusion coefficients of the ions in the CNT with the equilibrium density are around $1\text{--}2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 298 K, comparable to those in the bulk solution. With the temperature increase, the diffusion coefficients of the ions along the axial direction of the CNT increase monotonically and significantly.

From Fig. 9, we can also find that the change of the diffusion coefficients of the ions with bulk density is considerable minute compare to that with equilibrium density. The

obstacle from the water molecules may take the responsibility for this.

Conclusions

We have performed a series of MD simulations to investigate the hydration of Li^+ , Na^+ , K^+ , F^- and Cl^- inside the CNTs with the effective diameter of 0.73 to 1.0 nm from 298 to 683 K. The radial distribution functions of ion–water, the coordination numbers, the orientation structure and the residual time of the first coordination shells of the ions and the ion diffusion along the axial direction of the CNTs were analyzed to investigate the ionic hydration in the nanoscale confinement

at various temperatures. Both the exchange frequency of water molecules in the first coordination shells of the ions and the ion diffusion along the axial direction of the CNT significantly increase as the temperature increases in the CNT, same to the bulk solution. This indicates that the ionic hydration in the nanopore is still temperature dependence.

The simulation results show that the first coordination shells of Li^+ , Na^+ , K^+ , F^- and Cl^- are stable in the non-polar nanopore of the CNT with the effective diameter of 1.0 nm and their sizes and the coordination numbers in the CNT are similar to those in the bulk solution. Nevertheless, the orientation of the water molecules in the coordination shells of the cations change different from that of the water molecules in the shells of the anions. The water molecules in the first coordination shells of the cations are significantly less ordered in the nanotube than in the bulk solution, whereas the order of the water molecules in the shells of the anions is similar to that in the bulk solution. The order of the water molecules in the first coordination shell of K^+ decreases mostly.

Remarkably, we observe that the structure of the water molecules in the first coordination shell of K^+ turns to be more ordered as temperature increase in a CNT with the effective diameter of 1.0 nm, whereas become less ordered with the increase of the temperature in the carbon nanotube with effective diameter of 0.73 and 0.86 nm. In the CNT, the other four ions (Li^+ , Na^+ , F^- , Cl^-) have the structure of the water molecules in their first coordination shells less ordered as temperature increase as temperature increases. The easier distortion of the coordination shell of K^+ and the match between the shell size and the pore size may be substantial to such behavior.

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