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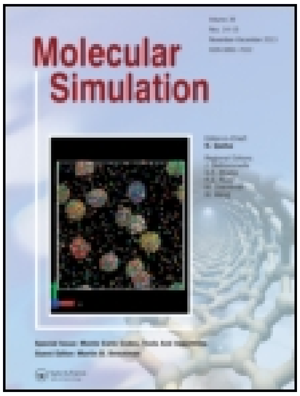

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Molecular dynamics simulation study for diffusion of Na^+ ion in water-filled carbon nanotubes at 25°C

Song Hi Lee[a]
[a] Department of Chemistry, Kyungsung University, Busan, 608-736, Republic of Korea

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Molecular dynamics simulation study for diffusion of Na^+ ion in water-filled carbon nanotubes at 25°C

Song Hi Lee*

Department of Chemistry, Kyungsung University, Busan 608-736, Republic of Korea

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We present results of molecular dynamics simulations for diffusion of Na^+ ion in water-filled carbon nanotubes (CNTs) at 25°C using the extended simple point charge water potential. Simulation results indicate the general trend that the diffusion coefficients of Na^+ ion and water molecule in CNTs decrease with an increase in water density and are larger than those in the bulk solution. The average potential energies of ion–water and water–water, the radial distribution functions, the hydration numbers and the residence times of the hydrated water molecules are discussed. The classical solventberg picture describes Na^+ ion in water adequately for systems with the small values of diffusion coefficients.

Keywords: diffusion of Na^+ ion; carbon nanotube; molecular dynamics simulation

1. Introduction

Ionic hydration in carbon nanotubes (CNTs) is ubiquitous and important in many biological and chemical processes.[1–6] It is well known that the substance in the nanopore has a behaviour different from its bulk state, mainly due to geometric constraints and anisotropic interactions.[7–14] Lynden-Bell and Rasaiah [15] reported the hydration and mobility of the electrolyte solutions inside a channel consisted with repulsive walls using molecular dynamics (MD) simulations. Their studies indicated 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 that in the bulk solution. Chan and his co-workers [16–18] also found the incomplete hydration of the ions in the nanopores by the equilibrium MD and non-equilibrium MD simulations. However, the diffusional behaviour of ions in a narrow nanopore has received relatively little attention.

In this study, we carried out a series of MD simulations to investigate the diffusion of Na^+ ion with different diameters of CNTs and different numbers of water molecules at 298.15 K. The main focus is the CNT effect on the diffusion of Na^+ surrounded by the water molecules inside a narrow nanopore. The paper is organised as follows. Section 'MD simulation' contains a brief description of molecular models and MD simulation methods. Section 'Results and discussion' presents the results of our simulations, and our conclusions are summarised in section 'Conclusion'.

2. MD simulation

We have selected 11 systems involving a single Na^+ ion in various diameters of CNT with the same length of 5.87 nm immersed in different numbers of water molecules at 298.15 K. A stationary chloride (Cl^-) counterion is introduced at the corner of CNT to maintain electroneutrality. Table 1 lists the details of all 11 simulation systems, and Figure 1 shows the schematic for the simulation cell of Na^+ ion in system 2 with the stationary Cl^- ion as an example. The SPC/E (extended simple point charge) model [19] was adopted for water and ion–water. The pair potential between water and ion has the form

$$v_{iw} = 4\varepsilon_{io}\left[\left(\frac{\sigma_{io}}{r_{io}}\right)^{12} - \left(\frac{\sigma_{io}}{r_{io}}\right)^{6}\right] + \sum\nolimits_{j\in w} \frac{q_i q_j}{r_{ij}}, \qquad (1)$$

where σ_{io} and ε_{io} are Lennard-Jones (LJ) parameters between oxygen on a water molecule and an ion i, q_j is the charge at site j in water and q_i is the charge on ion i. Also, r_{io} and r_{ij} are the distances between ion i and an oxygen site of a water molecule and between ion i and a charge site j in water. σ_{io} and ε_{io} are obtained by Lorentz–Berthelot rules, where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{1/2}$. Table 2 lists the LJ parameters and the charges used in this study.

Each MD simulation was carried out in the canonical ensemble, and the density of water was fixed at a given value in Table 1. The usual periodic boundary condition was applied only in the z-direction not the x- and y-directions, and the minimum image convention for pair potential was applied. Nosé–Hoover thermostat [20] was

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*Email: shlee@ks.ac.kr

Table 1. Details of simulated systems.

System	CNT	N_C	r_{CNT} (nm)	N_w	ρ_w (g/cc)	M (mol/l)
S1	(8,8)	768	0.5416	46	0.2544	0.3070
S2	(8,8)	768	0.5416	104	0.5752	0.3070
S3	(8,8)	768	0.5416	162	0.8959	0.3070
S4	(10,10)	960	0.6670	85	0.3099	0.2024
S5	(10,10)	960	0.6670	162	0.5907	0.2024
S6	(12,12)	1152	0.8125	162	0.3981	0.1364
S7	(12,12)	1152	0.8125	348	0.8552	0.1364
S8	(13,13)	1248	0.8802	348	0.7287	0.1162
S9	(14,14)	1344	0.9479	234	0.4225	0.1002
S10	(14,14)	1344	0.9479	348	0.6283	0.1002
S11	(16,16)	1536	1.0833	348	0.4811	0.0768

Notes: N_C and N_w are the numbers of carbon atoms and water molecules in CNTs, respectively. The length of all CNT is 5.87 nm. The geometric volume is used for ρ_w.

used to control the temperature, and a quaternion formulation [21,22] was employed to solve the equations of rotational motion about the centre of mass of rigid SPC/E water molecules. The velocity Verlet algorithm [23] with a time step of 1 fs served to integrate the equations of motion. MD runs of 2,000,000 time steps each were needed for the ion–water–CNT system to reach equilibrium. The equilibrium properties were then averaged over 10 blocks of 1,000,000 time steps (1 ns) for a total of 10,000,000 (10 ns). The configurations of molecules were stored every 10 time steps for further analysis.

The equations of rotational motion about the centre of mass for molecular fluids in a canonical (NVT: fixed) ensemble are derived using quaternions [21,22] which are as follows:

$$\mathbf{T}_i^p = A_i T_i, \tag{2a}$$

$$\dot{\mathbf{L}}_i^p = T_i^p - a_r \mathbf{L}_i^p, \tag{2b}$$

$$\omega_{ik}^p = \frac{L_{ik}^p}{I_k}, \quad k = x, \;\; y, \;\; z, \tag{2c}$$

$$\begin{bmatrix} \dot{q}_{i1} \\ \dot{q}_{i2} \\ \dot{q}_{i3} \\ \dot{q}_{i4} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -q_{i3} & -q_{i4} & q_{i2} & q_{i1} \\ q_{i4} & -q_{i3} & -q_{i1} & q_{i2} \\ q_{i1} & q_{i2} & q_{i4} & q_{i3} \\ -q_{i2} & q_{i1} & -q_{i3} & q_{i4} \end{bmatrix} \begin{bmatrix} \omega_{ix}^p \\ \omega_{iy}^p \\ \omega_{iz}^p \\ 0 \end{bmatrix}, \tag{2d}$$

$$\mathbf{A}_i = \begin{bmatrix} -q_{i1}q_{i1} + q_{i2}q_{i2} - q_{i3}q_{i3} + q_{i4}q_{i4} & 2(q_{i3}q_{i4} - q_{i1}q_{i2}) & 2(q_{i2}q_{i3} + q_{i1}q_{i4}) \\ -2(q_{i1}q_{i2} + q_{i3}q_{i4}) & q_{i1}q_{i1} - q_{i2}q_{i2} - q_{i3}q_{i3} + q_{i4}q_{i4} & 2(q_{i2}q_{i4} - q_{i1}q_{i3}) \\ 2(q_{i2}q_{i3} - q_{i1}q_{i4}) & -2(q_{i1}q_{i3} - q_{i2}q_{i4}) & -q_{i1}q_{i1} - q_{i2}q_{i2} + q_{i3}q_{i3} + q_{i4}q_{i4} \end{bmatrix}, \tag{2e}$$

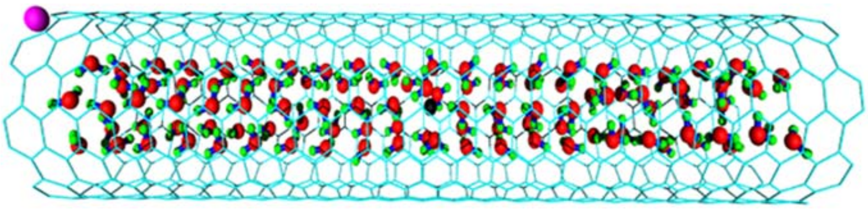

Figure 1. (Colour online) A schematic illustration of MD simulation for system 2 (purple: Cl^- and black: Na^+).

Table 2. The LJ parameters and potential charges for ions, SPC/E water molecules and carbon atom of CNT.[13,14]

Ion–water–CNT	σ (Å)	ε (kJ/mol)	Charge (q)
Na^+	3.33	0.0116	$+1$
Cl^-	4.42	0.493	-1
$O(H_2O)$	3.166	0.650	-0.8476
$H(H_2O)$	–	–	$+0.4238$
C(CNT)	3.55	0.293	0

where $\mathbf{L}_i$ is the angular momentum of molecule i, $\mathbf{T}_i$ is the torque on molecule i in the laboratory frame, $\mathbf{L}_i^p$ and $\boldsymbol{\omega}_i^p$ are, respectively, the angular momentum and angular velocities of molecule i in its principal axis frame, $\mathbf{A}_i$ is the rotation matrix which transforms vectors from the laboratory frame to the principal axis frame of molecule i, I_k is the principal axis of moment of inertia of each molecule and q_{ik}, $k = 1, 2, 3, 4$, are the quaternion parameters related to the Euler angles describing the orientation of molecule i in the laboratory frame

$$e_i = \begin{bmatrix} 2(q_{i2}q_{i2} - q_{i1}q_{i4}) \\ -2(q_{i1}q_{i3} + q_{i2}q_{i4}) \\ -q_{i1}q_{i1} - q_{i2}q_{i2} + q_{i3}q_{i3} + q_{i4}q_{i4} \end{bmatrix}, \tag{2f}$$

where $e_{i\alpha}$ ($\alpha = x, y, z$) are the components of its orientational unit vector of molecule i. Note that the quaternions satisfy the normalisation $q_{i1}^2 + q_{i2}^2 + q_{i3}^2 + q_{i4}^2 = 1$. The use of quaternions leads to singularity-free equations of motion.[21,22] The rotational temperature constraint parameter α_r is given by

$$a_r = \frac{\sum_i^N [L_i \cdot T_i]}{\sum_i^N L_i^2}. \tag{2g}$$

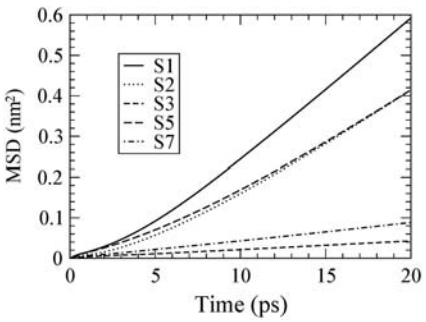

Figure 2. MSD of Na^+ ion in various CNTs.

3. Results and discussion

The diffusion coefficients D and D_w calculated from the mean square displacement (MSD, Figure 2 for Na^+) of Na^+ ion and water molecule in various CNTs and in the bulk solution are listed in Table 3 and shown in Figure 3 as a function of water density (ρ_w). D and D_w and their error bar estimates were obtained from the averaged MSDs over 10 blocks of 1,000,000 time steps. The MSDs of Na^+ in various CNTs show a straight line as a function of time in Figure 2.

Figure 3 shows the general trend that the diffusion coefficients of Na^+ ion and water molecule decrease with an increase in water density. The exceptions are for S1 and S11. In the CNTs of the same diameter, more number of water molecules prevent Na^+ ion from diffusing in the CNT. For example, in the same CNT(8,8) – S1, S2 and S3, D of Na^+ ion decreases 5.81, 4.26 and 0.36 as N_w increases 46, 104 and 146. D_w also decreases with an increase in N_w. This trend is also seen in the CNTs of (10,10) – S4 and S5, (12,12) – S6 and S7 and (14,14) – S9 and S10. The other example is for the same number of water molecules but with different diameters of CNT (S7, S8, S10 and S11) in which D of Na^+ ion and D_w increase with an increase in diameter of CNT except for S11. This exception is

Table 3. Diffusion coefficients D (10^{-5} cm^2/s) of Na^+ ion and water molecule at 25°C.

System	CNT	D_{tot}	D_z	D_{xy}	$D_{w,tot}$	$D_{w,z}$	$D_{w,xy}$
S1	(8,8)	5.81(48)	5.79(48)	0.01(0)	6.34(40)	6.12(41)	0.11(1)
S2	(8,8)	4.26(39)	4.24(39)	0.01(0)	4.28(41)	4.02(40)	0.13(2)
S3	(8,8)	0.36(7)	0.36(7)	0.00(0)	0.49(10)	0.33(7)	0.08(2)
S4	(10,10)	6.56(49)	6.39(50)	0.09(1)	7.16(46)	5.90(45)	0.63(9)
S5	(10,10)	4.21(34)	3.93(34)	0.14(2)	4.47(32)	3.21(31)	0.63(5)
S6	(12,12)	5.34(37)	4.52(36)	0.41(2)	6.26(32)	4.10(35)	1.08(7)
S7	(12,12)	0.76(6)	0.58(5)	0.09(2)	0.80(12)	0.50(6)	0.15(4)
S8	(13,13)	2.81(16)	1.99(19)	0.41(3)	2.88(14)	1.61(10)	0.63(5)
S9	(14,14)	4.70(35)	3.36(30)	0.67(5)	4.24(24)	2.46(23)	0.90(8)
S10	(14,14)	4.04(35)	2.78(20)	0.63(6)	5.10(22)	2.86(18)	1.12(4)
S11	(16,16)	3.96(20)	2.40(16)	0.78(5)	5.03(26)	2.59(15)	1.32(5)
S12	Bulk	1.96(11)	–	–	2.60(4)	–	–
S13	Bulk[a]	1.22(47)	–	–	3.03(16)	–	–

Note: Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis.
[a] Using the set of LJ parameters in Refs. [15,24].

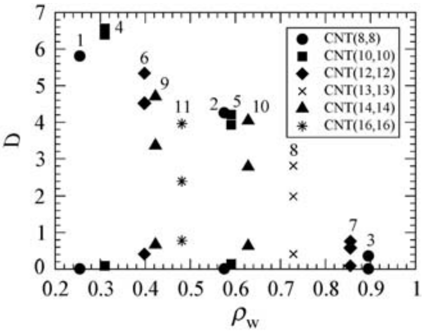

Figure 3. Diffusion coefficients D (10^{-5} cm^2/s) of Na$^+$ ion as a function of water density ρ_w (g/cc) as listed in Table 3. In each column from top, the symbols are for D_{tot}, D_z and D_{xy} except for the case of CNT(8,8) in which $D_{xy} \approx 0$ and $D_{tot} \approx D_z$. The numbers indicate the CNT systems as listed in Table 1.

attributed to that the perpendicular components D_{xy} of Na$^+$ ion and $D_{w,xy}$ along the axis of the CNT increase continually with an increase in the diameter of CNT but the parallel components D_z of Na$^+$ ion and $D_{w,z}$ decrease in S11. In general, D_w is larger than D of Na$^+$ ion except for the case of S9.

When compared with the systems of Na$^+$ ion in the bulk solution, D of Na$^+$ ion and D_w in the CNTs are larger than those in the bulk solution due to lower water density than bulk water except in the CNTs of very high water density (S3 and S7). This result is opposite to the observation by Lynden-Bell and Rasaiah.[15] Replacing the current set of LJ parameters ($\sigma_{io} = 3.25$ Å; $\varepsilon_{io} = 0.0868$ kJ/mol) for Na$^+$ by ($\sigma_{io} = 2.88$ Å; $\varepsilon_{io} = 0.522$ kJ/mol) in Refs. [15,24], D of Na$^+$ ion decreases (1.22×10^{-5} cm^2/s) but D_w increases (3.03×10^{-5} cm^2/s) at 25°C, which are compared with the experimental measurements -1.33×10^{-5} and 2.26×10^{-5} cm^2/s at 25°C.[25]

In CNT(8,8), the perpendicular diffusion coefficients D_{xy} of Na$^+$ ion is nearly zero because of the narrowest diameter of CNT in this study. Although D of Na$^+$ ion and D_w decrease except for S1 with an increase in water density, the perpendicular components D_{xy} of Na$^+$ ion and $D_{w,xy}$ increase continually with an increase in diameter of CNT (S1, S4, S6, S9 and S11) as seen in Figure 3. This trend is also seen for S2, S5, S8 and S10. The exception is S7 due to high water density. The parallel components D_z of Na$^+$ ion and $D_{w,z}$ decrease continually with an increase in water density (S4, S6, S9 and S11; S5, S10, S8 and S7), although the length of all CNT is the same.

The average potential energies of ion–water and water–water in various CNTs are listed in Table 4 in which the potential energy for water includes a polarisation correction of 5.2 kJ/mol. [19] The ion–water interactions are in the narrow range of −655 to −686 kJ/mol except S2 (−534) and S3 (−624) which are much larger than that in the bulk solution, but smaller than that using the other set of LJ parameters [15,24] due to the large value of ε_{io} (0.522 kJ/mol). The average potential energies of water–water are also in the narrow range of −34.1 to −42.3 kJ/mol except S1 (−27.8) and S3 (−28.2) which are much close to the corresponding water–water energy in bulk solutions of both set of LJ parameters. The water–water energy for bulk water using SPC/E model is −41.4 kJ/mol.[19]

The radial distribution functions, $g_{io}(r)$, for Na$^+$ ion and O atom of water molecules for systems S1, S2, S3, S5 and S7 are shown in Figure 4, and Table 4 contains the positions and magnitudes of the maxima and minima of $g_{io}(r)$ in the first shell at 25°C. The profile shapes of $g_{io}(r)$ for S4, S6 and S9 are similar to S1, S8 is similar to S7, S10

Table 4. Average ion–water and water–water potential energies, and positions and magnitudes at the first maximum and minimum of ion–oxygen $g_{io}(r)$ radial distribution functions at 25°C.

		$-U$ (kJ/mol)		First maximum		First minimum	
System	CNT	Ion–water	Water–water	r_{io} (Å)	g_{io} (r)	r_{io} (Å)	g_{io} (r)
S1	(8,8)	648(5)	27.8(2)	0.24	25.2	0.34	0.43
S2	(8,8)	534(8)	41.2(2)	0.24	10.0	0.36	0.53
S3	(8,8)	624(8)	28.2(2)	0.245	6.8	0.36	1.25
S4	(10,10)	655(5)	34.1(1)	0.24	19.6	0.32	0.79
S5	(10,10)	660(4)	38.7(1)	0.24	10.6	0.32	0.56
S6	(12,12)	670(4)	37.8(1)	0.24	15.1	0.325	0.64
S7	(12,12)	671(6)	42.3(4)	0.24	8.1	0.325	0.72
S8	(13,13)	676(6)	42.1(1)	0.24	8.8	0.32	0.53
S9	(14,14)	680(2)	39.5(2)	0.24	14.3	0.325	0.57
S10	(14,14)	684(3)	41.2(1)	0.24	9.7	0.325	0.41
S11	(16,16)	686(2)	40.8(2)	0.24	12.5	0.325	0.51
S12	Bulk	548(1)	39.5(1)	0.235	6.1	0.32	0.21
S13	Bulk[a]	745(4)	39.8(1)	0.245	7.2	0.325	0.16

Note: Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis.

[a] Using the set of LJ parameters in Refs. [15,24].

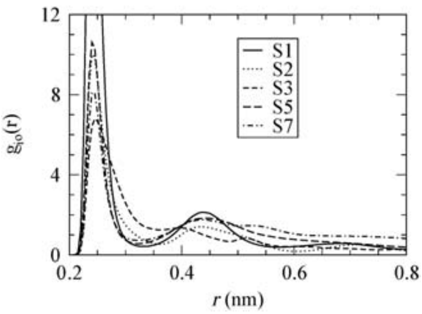

Figure 4. Radial distribution functions $g_{io}(r)$ of SPC/E water molecules in various CNTs as a function of the distance r (Å) between the Na$^+$ ion (i) and the oxygen atom (o) of a water molecule.

is similar to S2 and S11 is similar to S5. No second hydration shell is formed for the case of S3. Although $g_{io}(r)$ are different from each other in different CNTs, there exist a distinct first minimum and a nearby minimum which indicates the formation of the hydration shell around Na$^+$ ion. Some $g_{io}(r)$ do not have the asymptotic value of the unity as r goes to infinity due to less number of water molecules in the narrow CNTs which indicates an incomplete hydration reported by Lynden-Bell and Rasaiah [15]. Although the magnitudes of the first maximum and minimum in the Na$^+$ ion–oxygen radial distribution functions in various CNTs are always higher than those in the bulk solution due to lower water density in the CNTs, the positions of the first maximum and minimum in $g_{io}(r)$ do not have much changes but slightly increased due to the lower water density in CNTs.

The hydration number N_r in the first shell is calculated from the Na$^+$ ion–oxygen distribution functions $g_{io}(r)$ using

$$N_r = \rho_{\mathrm{w}} \int_0^{R_1} g_{\mathrm{io}}(r) 4\pi r^2 \, \mathrm{d}r, \tag{3}$$

where the upper limit of integration R_1 is the radius of the first hydration sphere which corresponds to the first minimum in $g_{io}(r)$. The size of hydrated ion is often measured by the first minimum in $g_{io}(r)$.

Table 5 displays the average coordination numbers of water molecules in the first solvation shell of the Na$^+$ ion, calculated from our simulations. Generally speaking, many of these numbers are not altered from the number in the bulk solution, but Na$^+$ ions with low diffusion coefficient in CNTs have much larger hydration numbers in which the hydrated water molecules prevent Na$^+$ ion from diffusing easily. This indicates the solventberg picture [26,27] with the residence time discussed below.

Table 5. Average coordination number and residence times (ps) of water molecules in hydration shells of Na$^+$ ion at 25°C.

System	CNT	Hydration number	Residence time (ps)
S1	(8,8)	5.50(3)	50.4(61)
S2	(8,8)	7.54(19)	343(39)
S3	(8,8)	13.14(11)	2870(90)
S4	(10,10)	5.60(2)	26.9(38)
S5	(10,10)	6.01(2)	34.9(30)
S6	(12,12)	5.69(4)	22.2(17)
S7	(12,12)	7.53(19)	97.3(48)
S8	(13,13)	6.40(3)	24.8(30)
S9	(14,14)	5.72(3)	20.0(14)
S10	(14,14)	5.81(3)	20.2(15)
S11	(16,16)	5.74(4)	19.5(20)
S12	Bulk	5.60(2)	22.0(12)
S13	Bulk[a]	5.9	26.4

Note: Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis.
[a] Using the set of LJ parameters in Refs. [15,24].

Finally, we discuss the residence time for the hydrated SPC/E water molecules in the hydration shells of Na$^+$ ion in various CNTs. The residence times are calculated from time correlation functions [26,28] defined by

$$R(r,t) = \frac{1}{N_r} \sum_{i=1}^{N_r} [\theta_i(r,0) \cdot \theta_i(r,t)], \tag{4}$$

where $\theta_i(t)$ is the Heaviside unit step function, which is 1 if a water molecule i is in a region r within the coordination shell of the ion at time t and zero otherwise, and N_r is the average number of water molecules in this region r at $t = 0$. Figure 5 shows the time dependence of $R(r,t)$ for water in the first hydration shell alone of Na$^+$ ion calculated for systems S1, S2, S3, S5 and S7. All the time correlation functions for the other systems are very similar to system S5. The residence time is obtained by fitting the time correlation function to an exponential decay $< R(r,t) > \approx \exp(-t/\tau)$, which is useful particularly when τ is large.

The residence times, also listed in Table 5, show the average decay times of water in the first shell alone calculated from the residence correlation functions. We note that this time increases rapidly with an increase in water density and that the decay time for water in the first

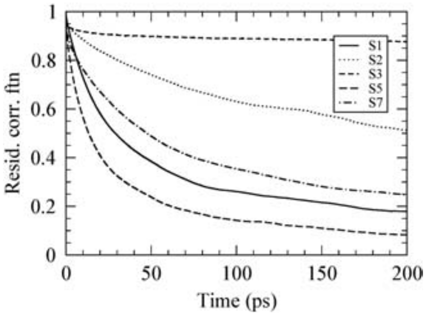

Figure 5. Residence time correlation function for the hydrated SPC/E water molecules in the first hydration shell of Na$^+$ ion in various CNTs.

shell around Na^+ ion in system S3 is abnormally large which is consistent with the smallest diffusion coefficient of Na^+ ion among various CNTs studied in this study. The solventberg picture [26,27] for Na^+ ion is most adequate for systems S2, S3 and S7. The residence times of water around Na^+ ion in the other CNTs are not much different from those in bulk solutions in which the larger value of LJ parameter (ε_{io}) reflects a longer residence time.

4. Conclusion

We have carried out a series of MD simulations of model Na^+ ion–water–CNT systems using the SPC/E water potential. Simulation results show that the diffusion coefficients of Na^+ ion and water molecule in CNTs decrease with an increase in water density, and that most of Na^+ ions and water molecules have larger diffusion coefficients than those in the bulk solution although water densities in CNTs are smaller than those in the bulk solution. The perpendicular components' diffusion coefficients D_{xy} of Na^+ ion and $D_{w,xy}$ of water molecule increase continually with an increase in the diameter of CNT. The structure of the surrounding water molecules around the Na^+ ions with smaller values of diffusion coefficients than that in the bulk solution is well described by the compact solventberg picture. That is characterised by the small sizes of the hydrated ions measured by the first minimum in $g_{io}(r)$ and the abnormally long residence times of the hydrated water molecules around the Na^+ ions.

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