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Structural and dynamic properties of water confined inside a single-walled carbon nanotube
Molecular dynamics study

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Atomically detailed molecular dynamics simulation has been performed to study structural and dynamical properties of the cluster of water molecules $(H_2O)_{80}$ confined inside an open-ended single-walled (10,10) carbon nanotube (SWNT). The structural and dynamical properties of the confined cluster have been compared with the analogous results for an unconfined cluster of water molecules.

Key words: *nanotube; water cluster; molecular dynamics; structural properties; dynamic properties*

1. Introduction

Since Ijima [1] discovered the nanotube, this new material has been studied intensively by many researchers, because of its unique mechanical and electrical properties and also because of its potential as a medium for storing hydrogen and other gases [2–5].

During the last decade, the structural and thermodynamic properties of atoms and molecules adsorbed in the interior end exterior of single nanotubes and nanotube bundles have been widely studied both theoretically [6–8] and experimentally [9–10]. The interior of a SWNT gives new possibilities for investigating the properties of confined fluids which are not seen in the bulk system [11–19]. The behaviour of confined water plays a crucial role in many relevant biological and geological systems. Molecular dynamics simulations [14] show that water confined in CNT formed a new ice phase, not seen in bulk ice. Hummer et al. [15] have observed, in their molecular simulation studies, pulse-like transmission of water through the nanotube. Recently, Kolesnikov et al. [16] have studied the water molecule confined inside an open-ended SWNT. They reported that water molecules form a cylindrical square ice-sheet with a central water chain.

This paper presents the results of fully atomistic molecular dynamics simulation of water deposited inside a (10,10), open-ended carbon nanotube at four different temperatures.

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2. Simulation details

The simulated system consists of 80 water molecules confined inside a (10,10) open-ended SWNT. The temperature was controlled by velocity scaling during the equilibration. The thermostat was turned off after the equilibration phase. The same procedure was applied to study a free cluster of water molecules, i.e without the nanotube. The classical equations of motion have been integrated using the velocity Verlet algorithm with the integration time step of 0.2 fs, which ensures sufficient energy conservation. Water molecules were described by the flexible SPC model [20]. This model is described by an intramolecular O–H harmonic stretching and a H–O–H bending term:

$$V\left(r_{ij},\Theta_{ijk}\right)=\frac{1}{2}K_{Wr}\left(r_{ij}-r_{W}\right)^{2}+\frac{1}{2}K_{W\Theta}\left(\Theta_{ijk}-\Theta_{W}\right)^{2} \tag{1}$$

where r_{ij} is the O–H distance and Θ_{ijk} is the H–O–H angle. The nonbonding interaction between water molecule consists of two terms: the Lennard–Jones potential between oxygen atoms:

$$V(r_{ij})=4\varepsilon\left(\frac{\sigma^{12}}{r_{ij}^{12}}-\frac{\sigma^{6}}{r_{ij}^{6}}\right) \tag{2}$$

where r_{ij} is the O–O distance, and the Coulomb potential:

$$V\left(r_{ij}\right)=\frac{1}{4\pi\varepsilon_{o}}\frac{q_{i}q_{j}}{r_{ij}} \tag{3}$$

where r_{ij} is the distance between all pair of charges. All constants are listed in Table 1. The intramolecular interactions between the carbon atoms of the nanotubes have been modelled using the potential composed of the components representing the energy of the bonded C atoms and the energy of the van der Waals interaction between the non-bonded C atoms [21, 22] $V = V_{\text{bond}} + V_{\text{vdW}}$. The V_{bond} component is composed of terms representing the energies of the stretching (Morse), bending (harmonic cosine) and twisting (2-fold torsion angle) of the C–C bond:

$$\begin{aligned}V_{\text{bond}}\left(r_{ij},\Theta_{ijk},\varphi_{ijkl}\right)&=K_{r}\,(\mathrm{e}^{-\gamma(r_{ij}-r_{C})}-1)^{2}+\frac{1}{2}K_{\Theta}\,(\cos\Theta_{ijk}-\cos\Theta_{C})^{2}\\&+\frac{1}{2}K_{\varphi}\,(1-\cos2\varphi_{ijkl})^{2}\end{aligned} \tag{4}$$

where r_{ij} is the distance between a given pair of bonded atoms, Θ_{ijk} is the bending angle between a given three atoms and φ_{ijkl} is the torsional angle between a given four atoms. The values of the K_γ, K_Θ, K_φ, γ, r_C, Θ_C and φ_C parameters [22] are collected in

Table 1. The Van der Waals interaction V_{vdW} between the non-bonded atoms is modelled as a pairwise additive Lennard–Jones (L–J) potential over all pairs of atoms except 1–2 and 1–3 pairs. The values of the ε_{CC} and σ_{CC} parameters are also given in Table 1.

Table 1. Parameters of the H_2O potential

Parameter	Value	Parameter	Value
$K_{W\gamma}$	4637 kJ/mol Å^{-2}	q_{H}	–0.41 e
$K_{W\Theta}$	382 kJ/mol rad^{-2}	K_γ	478.9 kJ/mol
r_W	1.0 Å	K_Θ	562.2 kJ/mol
Θ_W	109.47°	K_φ	25.12 kJ/mol
$\varepsilon_{\mathrm{OO}}$	0.6502 kJ/mol	R_C	1.418 Å
σ_{OO}	3.166 Å	Θ_C	120°
σ_{OC}[a]	0.3126 kJ/mol	γ	2.1867 Å^{-1}
$\varepsilon_{\mathrm{OC}}$	3.19 Å	ε_{CC}	0.4396 kJ/mol
q_{O}	–0.82 e	σ_{CC}	3.851 Å

[a] Ref. [23], and the carbon interactions potentials.

The nanotube–water interaction has been modelled using the L–J potential between oxygen atoms and host C atoms. The parameters for the oxygen–carbon interaction are listed in Table 1.

3. Results and discussion

The nanotube–water interaction in NVE ensemble has been studied. The modelled system was studied at three temperatures: T_1 = 233 K, T_2 = 309 K, and T_3 = 344 K. In all cases 80 water molecules were deposited inside (10,10) a SWNT. For comparison, the properties of the water cluster was studied at T_1 = 233 K, T_2 = 309 K because, in the case of T_3 = 344 K, the free cluster starts to evaporate. Figure 1 gives a snapshot of the simulated system.

The structure of water was analyzed in terms of the radial distribution function, which was computed for all three atomic pairs: oxygen–oxygen $g_{\mathrm{OO}}(r)$, oxygen–hydrogen $g_{\mathrm{OH}}(r)$, and hydrogen–hydrogen $g_{\mathrm{HH}}(r)$. Figure 2a shows the radial distribution function of oxygen–oxygen in studied temperatures for confined water (solid line) and water cluster (dotted line). Figure 2b shows an analogous figure for the oxygen–hydrogen radial distribution function. Two characteristic maxima and one minimum can be discerned. In the case of $g_{\mathrm{HH}}(r)$ (Fig. 2c) one characteristic maximum is observed for studied temperatures and small second maximum for T_1 = 233 K.

The calculated positions of peaks for all studied cases are listed in Table 2. The confinement of water inside nanotube does not significantly change the structure of water compared to free water cluster.

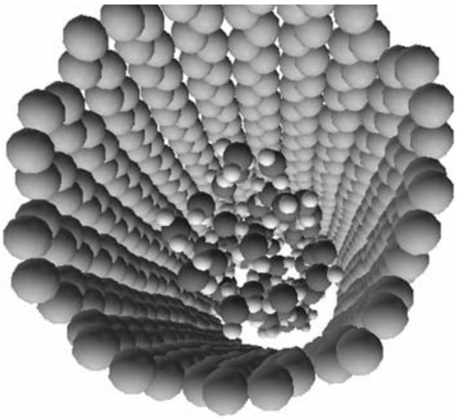

Fig. 1. A snapshot of water cluster deposited inside (10,10) SWNT at the temperature of 298 K

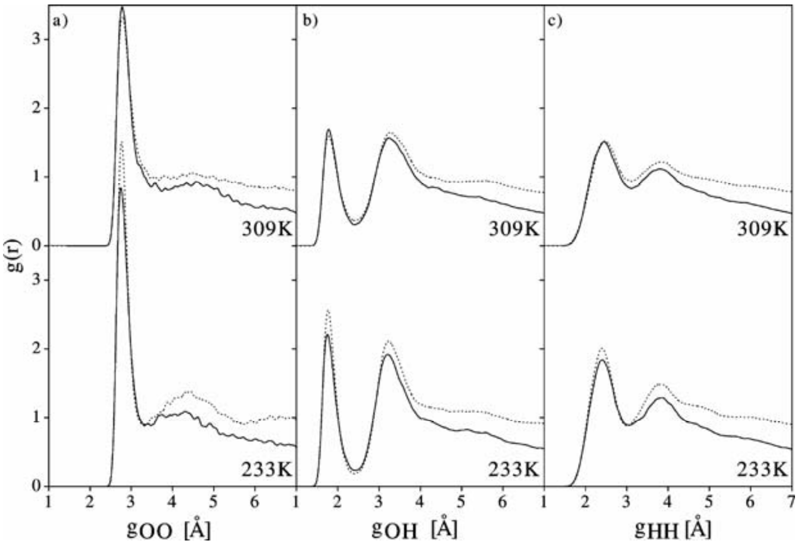

Fig. 2. The oxygen–oxygen (a), oxygen–hydrogen (b) and hydrogen–hydrogen (c) radial distribution functions of water deposited inside carbon nanotube (solid line), and not confined water cluster (dotted line), both at two different temperatures $T_1 = 233$ K and $T_2 = 309$ K

Table 2. The displacement of characteristic peaks in the oxygen–oxygen ($g_{OO}(r)$), oxygen–hydrogen ($g_{OH}(r)$) and hydrogen–hydrogen ($g_{HH}(r)$) radial distribution functions of water deposited inside carbon nanotube (SWNT) and not confined water cluster (H_2O)

SWNT	T [K]	R_1 [Å]	r_1 [Å]	R_2 [Å]	R_1 [Å]	r_1 [Å]	R_2 [Å]
$g_{OO}(r)$	233	2.78	–	–	2.78	3.32	4.39
	309	2.80	–	–	2.80	–	–
$g_{OH}(r)$	233	1.78	2.43	3.23	1.78	2.43	3.24
	309	1.80	2.46	3.28	1.80	2.45	3.28
$g_{HH}(r)$	233	2.41	3.03	3.82	2.41	3.03	3.82
	309	2.46	3.13	3.83	2.46	3.13	3.85

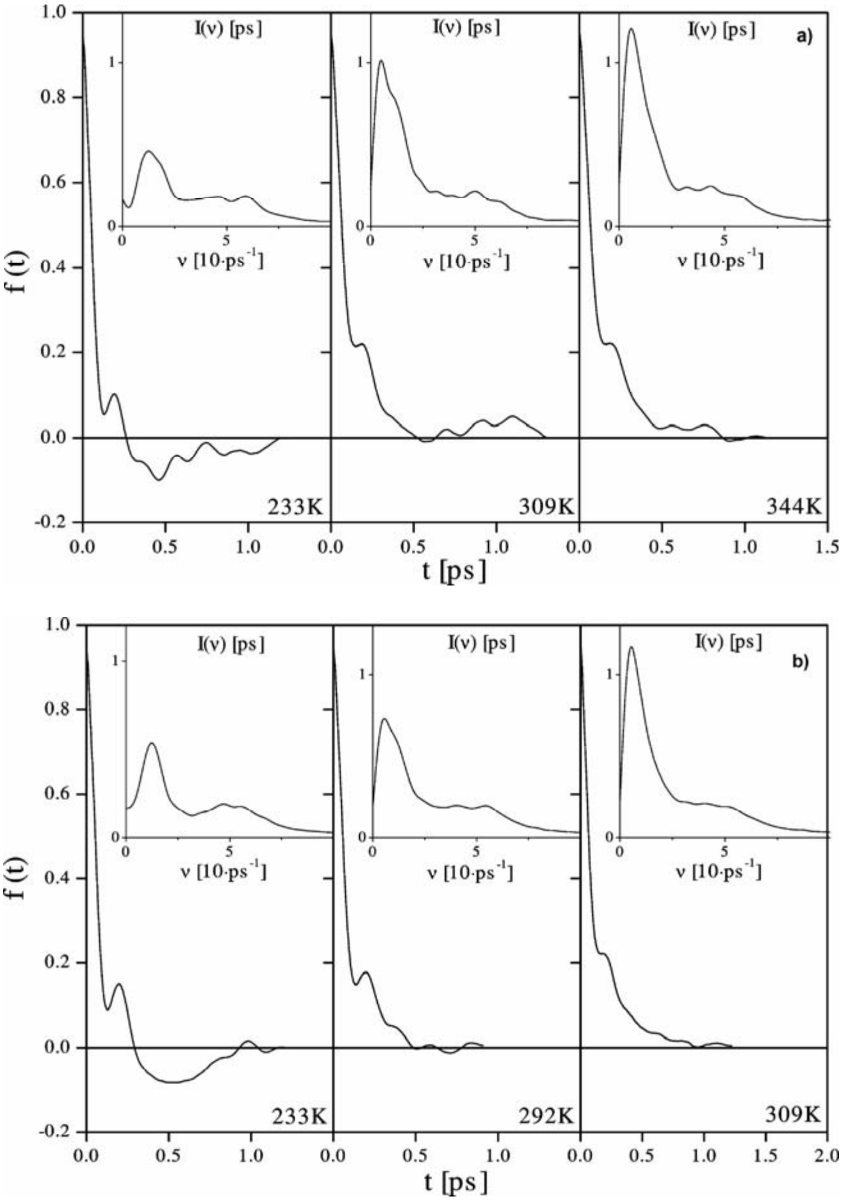

Fig. 3. The normalized centre-of-mass velocity autocorrelation function of water deposited inside carbon nanotube at three different temperatures $T_1 = 233$ K, $T_2 = 309$ K and $T_3 = 344$ K (a), and the normalized centre-of-mass velocity autocorrelation function of not confined water cluster at three different temperatures $T_1 = 233$ K, $T_2 = 292$ K and $T_3 = 309$ K (b)

In contrast to the structural properties, the dynamic properties of confined water significantly differ from those of the free water cluster. The dynamic properties have been studied in terms of the normalized velocity autocorrelation function $C_v(t)$

$$C_v(t) = \frac{\left\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\right\rangle}{\left\langle \mathbf{v}(0)\cdot\mathbf{v}(0)\right\rangle} \tag{5}$$

and spectral density $I(\nu)$, computed as the cosine Fourier transform of C_v, which is related to the phonon density of states:

$$I(\nu) = \int_0^\infty C_v \cos(2\pi\nu t)\,dt \tag{6}$$

Figure 3a shows the normalized centre-of-mass velocity autocorrelation function for water confinement in SWNT for the considered temperatures. The insets show characteristic frequency of water molecule movements. The same functions are plotted in Fig. 3b for a free water cluster.

To gain deeper insight into the temperature dependencies of dynamic properties, a free water cluster at $T_2 = 292$ K was simulated. The spectral density shows that in the case of water deposited inside a SWNT, the second characteristic frequency strongly depends on temperature. The frequency shifts toward lower values as the temperature is increased. This behaviour is not observed in the case of a free water cluster where the second peak diminishes with increasing temperature. The diminishing of the second peak with increasing temperature in bulk water is also observed experimentally [24, 25].

The diffusion coefficient is also an indicator of differences between the translational mobility of confined water molecule and the free cluster water molecules. The diffusion coefficient has been calculated from the velocity autocorrelation function:

$$D \cong \frac{1}{3}\int_0^t \left\langle \mathbf{v}_j(0)\,\mathbf{v}_j(t')\right\rangle dt' \tag{7}$$

As anticipated, in all cases studied, it was observed that the diffusion coefficients were lower for the confined water. The calculated diffusion coefficients are given in Table 3.

Table 3. Self-diffusion coefficient D calculated from the present study for water deposited inside a carbon nanotube (SWNT), and not confined water cluster (H_2O) [24, 25]

T [K]	$D\cdot 10^5$ [cm^2/s]		
	SWNT	H_2O	Exper. (T [K])
233	0.77	1.06	0.74 (265)
292	–	3.18	1.80 (289)
309	4.08	5.13	2.90 (308)
344	5.23	–	4.80 (335)

4. Conclusions

In this work, a cluster of water molecules confined inside an open-ended carbon nanotube was studied focusing on the question, of how the geometrical confinement changes the structural and dynamic properties of water. It was observed that the water–nanotube interaction does not significantly change the structural properties of the confined water in contrast to the dynamic properties. In the case of water deposited inside a SWNT, the second frequency in the spectral density shifts considerably towards lower values with increasing temperature. This behaviour is not observed, either in the free water cluster or in bulk water. The determined diffusion coefficients also indicate that both interactions between water and a nanotube, as well as the geometrical confinement, significantly influence the dynamic properties of water.

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