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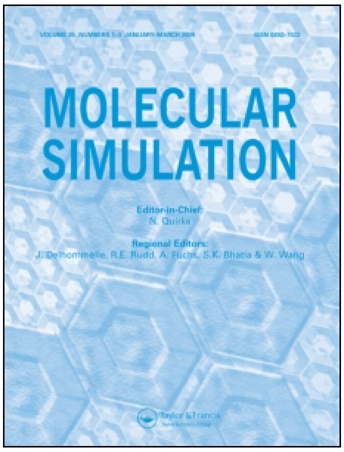

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Self-diffusivity, hydrogen bonding and density of different water models in carbon nanotubes

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Self-diffusivity, hydrogen bonding and density of different water models in carbon nanotubes

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In this paper, the density, hydrogen bonding and self-diffusivity of water confined in carbon nanotubes are investigated. Molecular dynamics is used to simulate a large variety of nanotubes with various water models. Our results produce, for the first time, the complete trend of these properties from narrow nanotubes, where water shows particularly anomalous behaviour, to large ones where its characteristics are similar to those of bulk.

Keywords: carbon nanotubes; confined water; molecular dynamics; water properties

1. Introduction

Nanotechnology will probably have an enormous impact on our future and the number of applications related to this discipline is expected to grow exponentially in the next decades. Among all the nanotechnology related materials, carbon nanotubes (CNT) play a key role in many envisaged cases and deserve the closest attention from the scientific community. Experimental evidence, for instance, suggests that CNTs can be internalised into living cells without toxic effects and shuttle various cargoes across the cellular membrane, opening a new route for medicine delivery and cancer therapy [1,2]. A key step for this novel nanomedicine technology consists in delivering small amounts of aqueous solutions through the hollow interior of CNTs. When water is confined within small nanotubes, however, its properties, structure and dynamics change dramatically and differ considerably from those of bulk (see for instance [3–7]). The goal of this work is to use molecular dynamics (MD) to gain further insights into some of the properties of water confined in CNTs. The following three aspects can be considered as the main original contributions of this work to the literature: comparison among different water models, comparison between flexible and rigid CNT and investigation of water's physical properties for a wide range of nanotube sizes.

The use of any water model available in the literature for simulating H_2O molecules in confined space is, at least in theory, not correct since these models were proposed for bulk water. Furthermore, no model can simulate correctly all the characteristics of bulk water. Even the most used and tested models, usually, give good approximations of certain properties at the expense of others [8]. For this reason, we believe that the best practice for classic MD simulations of water in CNTs is to compare the results obtained with different models since, at least until adequate experimental analysis is available, there are no means to conclude that any particular model is more reliable than the others.

Concerning the comparison between rigid and flexible CNTs, it must be noted that in the majority of articles the water–CNTs system is simulated using rigid nanotubes. Only in a few exceptions, Associated Model Building with Energy Refinement (AMBER) or, more rarely, the similar Chemistry at HARvard Molecular parameters were used. Jakobtorweihen et al. [9] found that, in the case of CH_4, the flexibility of small CNTs can affect certain physical properties of the fluid like the self-diffusion coefficient. This happens, however, only in the case of very low loadings ($P < 0.05$ bar), while, under conditions similar to the ones investigated in this paper, the results are basically identical. An analogous comparison for water in CNTs was, however, missing and, thus, it was included in this paper.

Finally, the wide range of CNTs used in this work extends considerably the previous analysis, which was in most cases based on small armchair or zigzag nanotubes. Only a few publications [5] took into account diameters up to 20 Å, but a complete trend, from small diameters to bulk-like conditions, requires larger nanotubes (up to 55 Å). Thanks to these complete trends, we could highlight the discontinuities in the behaviour of water density and self-diffusivity in CNTs as it is discussed further on.

2. Numerical method

MD simulations at 300 K (Langevin thermal bath) and 1 atm (Nosé–Hoover Langevin Piston) were carried out

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Table 1. Water models parameters.

Model	σ_{O-O} (Å)	ε_{O-O} (kJ mol^{-1})	r_{0H} (Å)	q_H (e)	q_O (e)	θ_{HOH} (°)
SPC [34]	3.166	0.650	1.0	+0.41	−0.82	109.47
SPC/E [35]	3.166	0.650	1.0	+0.4238	−0.8476	109.47
TIP3P [16]	3.15061	0.6364	0.9572	+0.4170	−0.8340	104.52

using the NAMD 2.6 software package, which was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign [10], running in parallel on a 32 processors AMD-Opteron cluster. Long range forces were modelled by a Lennard-Jones (L-J) potential with a cut-off distance of 1.0 nm. The values of σ_{C-C} and ϵ_{C-C} used in the simulations were, respectively 3.4 Å and 0.086 kcal mol^{-1} (AMBER force field). The σ_{O-O} and ϵ_{O-O} parameters, on the other hand, depend on the water model used and are reported in Table 1 (together with other model details like the OH bond distance r_{0H}, the hydrogen q_H and oxygen q_O charges and the HOH bond angle θ_{HOH}). Interatomic L-J potentials were calculated according to the Lorentz–Berthelot rule and Particle Mesh Ewald was used to compute electrostatic forces.

Simulations involving flexible water or flexible nanotubes also require the modelling of intramolecular forces. The relative potentials of these forces are approximated by NAMD on the basis of the following equation:

$$U_{\text{intramolecular}} = U_{\text{stretch}} + U_{\text{angle}} + U_{\text{dihedral}}. \qquad (1)$$

Each contribution to $U_{\text{intramolecular}}$ is further modelled according to

$$U_{\text{stretch}} = k_{\text{bond}}(r - r_0)^2, \qquad (2)$$

$$U_{\text{angle}} = k_{\text{angle}}(\theta - \theta_0)^2, \qquad (3)$$

and

$$U_{\text{dihedral}} = k_{\text{dihed.}}(1 + \cos(n\phi - \phi_0))^2. \qquad (4)$$

U_{stretch} represents the force applied when the bond is stretched from its initial position r_0 to the new position r; U_{angle} models the force exerted when the angle θ between two bonds changes with respect to its initial angle θ_0; U_{dihedral} describes the force that atoms separated by three covalent bonds exert where they are subject to a torsion angle ϕ. The values of these parameters for the CNT and the flexible water models are reported in Table 2. NAMD 2.6 uses a harmonic approximation of the bond potential, which is correct only when the displacement of the carbon atoms with respect to the equilibrium distance does not exceed a certain value [10]. When this happens, more sophisticated many-body potentials [11] must be taken into account. In a previous paper [12], we showed that in the case of H_2O–CNT systems the displacement is of the order of 0.01 Å and the harmonic approximation can be applied[1].

In all the simulations, the CNTs are surrounded by a water box in order to let the H_2O spontaneously enter the nanotubes[2]. In Table 3, the type of (n,m) CNT, the diameter d, chirality θ, length L, dimension of relative water boxes (Z_{BOX} and XY_{BOX}) and number N_{H_2O} of water molecules used in the simulations carried out with 'model 0' (see Table 4) are reported. Simulations of the nanotubes marked with an asterisk were repeated using different combinations of water model and nanotube rigidity (see Table 4, models 1–5). A time step of 2 fs was employed for simulations with rigid bonds, while in the case of flexible water the time step was reduced to 1 fs. The system was initially equilibrated for 1 ns, and then simulated for other 4–5 ns. Atoms trajectories, used in the subsequent statistical analysis of the results, were saved each 1 ps. Independence of the results from the size of the water box, length of the nanotubes, cut-off parameter and equilibration time was verified.

3. Results

In the following sections, density, hydrogen bonding and self-diffusivity are derived from the atoms trajectories calculated during the MD simulations listed in Table 3. There is a remarkable change of these properties especially for water confined within small nanotubes.

Table 2. Intramolecular forces Equations (2)–(4) parameters.

	k_{stretch} (kcal mol^{-1} Å^{-2})	r_0 (Å)	k_{angle} (kcal mol^{-1} rad^{-2})	θ_0	$k_{\text{dihedr.}}$ (kcal mol^{-1})	n	ϕ_0
CNT (AMBER)	469	1.4	63	120°	3.625	2	180°
Flexible SPC [36]	554.13	1.00	91.54	109.47°	n.a.	n.a.	n.a.
Flexible TIP3P (AMBER)	450	0.9572	55	104.5°	n.a.	n.a.	n.a.

Table 3. List of the CNT and relative water boxes used in the simulations.

(n,m)	d (Å)	θ (°)	L (Å)	Z_{BOX} (Å)	XY_{BOX} (Å)	N_{H_2O}
(5,5)	6.78	30	17.23	48	20	561
(6,6)	8.14	30	20.92	60	30	1596
(8,8)	10.86	30	28.30	85	24	1420
(10,10)	13.57	30	28.30	85	24	1339
(12,12)	16.28	30	33.23	85	20	933
(16,16)	21.71	30	39.38	85	44	4810
(20,20)	27.14	30	49.22	90	55	7964
(24,24)	32.57	30	59.07	90	40	4041
(30,30)*	40.71	30	62.76	100	60	10459
(40,40)	54.28	30	81.22	120	55	10375
(10,0)	7.83	0	21.32	60	25	1102
(14,0)	10.97	0	27.71	75	30	1978
(19,0)*	14.89	0	29.84	75	40	3529
(24,0)	18.80	0	38.37	76	40	3532
(32,0)	25.07	0	49.02	96	50	7010
(45,0)*	35.25	0	51.16	90	60	9466
(58,0)*	45.44	0	76.73	100	55	8631
(8,4)	8.29	19.11	22.56	48	24	803
(10,5)	10.36	19.11	33.84	80	30	2107
(18,9)*	18.66	19.11	39.48	80	32	2339
(22,11)	22.80	19.11	45.12	90	40	4158
(34,17)	35.24	19.11	56.39	100	50	7219
(50,25)	51.82	19.11	67.67	120	80	22622
(8,2)*	7.18	10.89	19.54	48	20	557
(12,3)	10.77	10.89	29.30	54	18	476
(20,5)	17.95	10.89	32.56	60	40	2786
(32,8)*	28.72	10.89	39.07	72	58	7098
(52,13)	46.67	10.89	58.61	100	80	18857
(7,1)	5.91	6.59	32.18	100	18	946
(5,4)	6.12	26.33	33.30	100	18	948
(10,3)	9.24	12.73	25.13	80	20	926
(11,3)*	10.00	11.74	27.21	100	24	1687
(13,5)*	12.61	15.61	34.30	100	24	1660
(18,12)*	20.49	23.41	37.16	100	40	4679

The nanotubes without asterisk were simulated only with ‘model 0’, the others with all the models reported in Table 4.

If we increase the CNT diameter, on the other hand, the numerical value of the specific property goes asymptotically towards the bulk value calculated with the corresponding water model [16–19].

3.1 Density

The modification of the density is probably the most evident effect of the confinement of water within CNTs. Both molecular simulations and experiments [20] show that water in the proximity of CNT walls assumes a stratified structure, which modifies the organisation of water molecules within the nanotube. In the majority of works [3,21–25], however, density is fixed during the simulation. This is usually done in order to calculate only water molecules located inside the nanotube, thus avoiding the simulation of the external bath. Only a few articles [7,26] provide insights into the ‘natural density’ of water by taking into account the spontaneous entrance of water molecules in small CNTs from an external bath. Hanasaki et al. [5,27,28] used an alternative method called fluidised piston model, which may provide information on the density as well; the range of their investigation, however, does not go beyond 28 Å.

Table 4. Simulations listed according to water model and nanotube rigidity.

Group	Water model	Nanotube
0	TIP3P	Rigid
1	TIP3P	Flexible
2	SPC/E	Rigid
3	TIP3P flexible	Rigid
4	SPC flexible	Rigid
5	SPC flexible	Flexible

Figure 1 shows our results (further details on density can be found in a previous paper [12]). The density is calculated on the basis of the empty nanotube volume, which is not $(\pi/6)Ld^2$, but $(\pi/6)L(d-\sigma_{CO})^2$ in order to take into account the occupancy of carbon atoms. The difference among results obtained with different

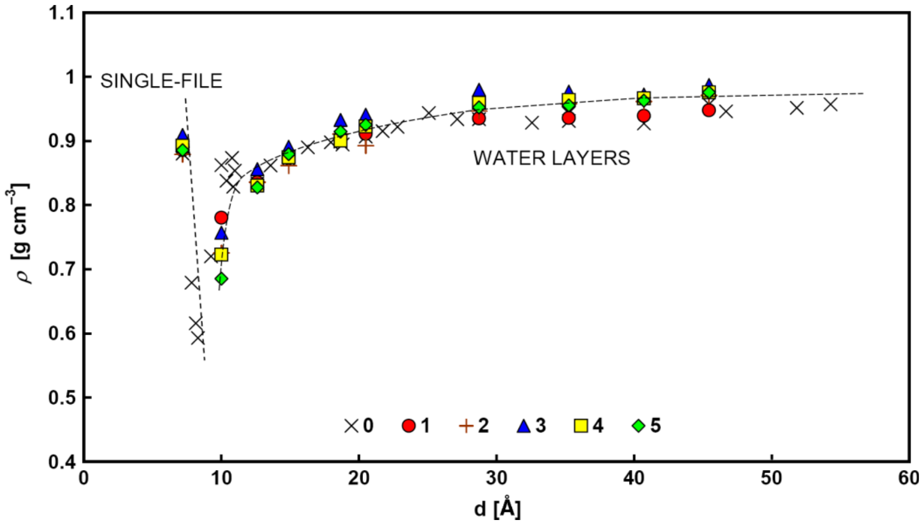

Figure 1. Density of water ρ vs. nanotube diameter calculated with various models (see Table 4).

models does not go beyond 5.3% with the only exception of the (10,3) CNT (13.5%). The use of flexible or rigid nanotubes does not change much the results as comparison between ‘model 0’ and ‘model 1’ or between ‘model 4’ and ‘model 5’ shows. Simulations with flexible water, on the other hand, produce higher densities as comparison between ‘model 0’ and ‘model 3’ illustrates. The most notable features in Figure 1 is the presence of a discontinuity in the results at small diameters. The line labelled ‘single-file’ indicates the narrowest nanotubes, which can contain only a single file of water molecules (Figure 2). In this case, if the size is reduced, for instance, from (6,6) to (8,2), the number of molecules per nanotube length does not change very much. The volume of the nanotube, however, decreases more significantly and, consequently, the density is augmented. When the diameter is in the ‘layered mode’ (region indicated with ‘waters layers’ in Figure 1), on the other hand, the arrangement of water molecules near the walls assumes the typical layered structure [3], which has a higher void fraction and, consequently, lower density. If we augment further the diameter, the distance between the walls and the core of the nanotube increases and the water molecules located at the centre of the CNT behave like in bulk. The density, consequently, grows asymptotically towards the bulk value as the diameter increases, as Figure 1 shows.

3.2 *Hydrogen bonding*

The hydrogen bond (HB) is a special type of attractive interaction that exists between an electronegative atom and a hydrogen atom bonded to another electronegative atom. Since many thermodynamical properties of water depend on the HB, it is worth investigating this

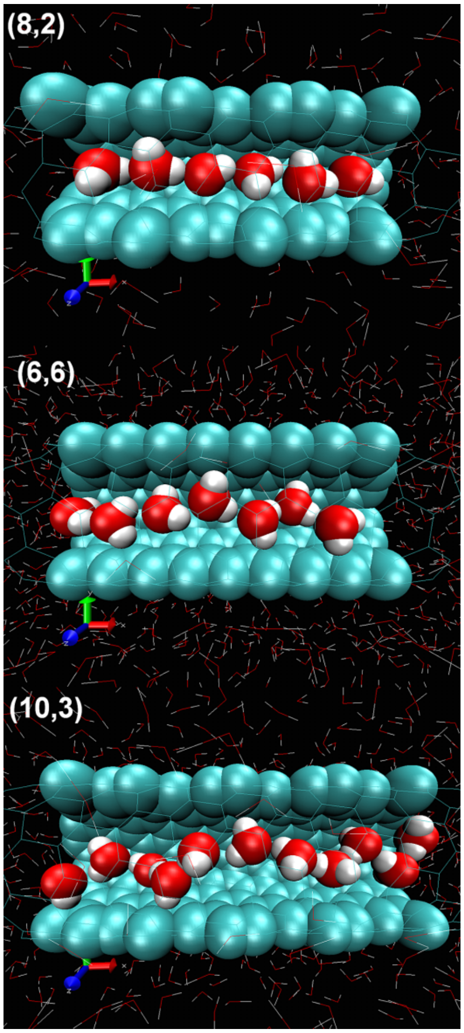

Figure 2. Single-file distribution of water molecules in a (8,2), (6,6) and (10,3) carbon nanotube.

parameter in the case of CNTs (see also [3,4,21] for a smaller range of nanotubes). The average number of HB per molecule in bulk water varies from 2.3 to 3.8 [18,29] according to the water model and the definition of HB. In this paper, the geometric definition [30] is used. The following three conditions must be satisfied in order to have a HB:

(1) the distance between the oxygens of both molecules has to be smaller than a certain threshold value R_{OO};
(2) the distance between the oxygen of the acceptor molecule and the hydrogen of the donor has to be lower than a certain threshold value R_{OH};
(3) the bond angle between the O—O direction and the molecular O—H direction of the donor, where H is the hydrogen which forms the bond, has to be lower than a certain threshold value ϕ.

Within this definition, different values of R_{OO}, R_{HO} and ϕ have been employed in the literature. We used $R_{OO} = 3.3$ Å, $R_{HO} = 2.4$ Å and $\phi = 30°$ as done in Gordillo and Martí [3], but other choices (i.e. [4] or [21]) are equally possible.

In Figure 3, the average number of HBs for water molecule (N_H) resulting from our simulations is reported. The SPC–SPC/E family gives a higher number of N_H with respect to the TIP3P family. Within the same family, however, flexible water models have higher N_H than rigid models. The differences, however, are all within 10%. The labels 'single-file' and 'water layers' were kept in Figure 3 for comparison with the analogous Figures 1, 5 and 6, although in this circumstance the separation between these two zones is not as clear as in the other cases.

3.3 *Self-diffusion*

Liu and Wang [23,24] calculated the self-diffusivity (D) of water in armchair nanotubes from (8,8) to (16,16) at fixed densities (from 0.875 to 1.25 g cm^{-3}) by means of the Einstein Equation [31]:

$$D = \lim_{t\to\infty} \frac{1}{2kt} \langle |r(t) - r(0)|^2 \rangle, \tag{5}$$

where $r(t)$ is the position of the centre of mass of water molecules at time t, k is the dimensionality of the system. Striolo et al. [32], on the other hand, studied water diffusion in long and narrow CNT at low density taking into account the possibility of non-Fickian behaviour:

$$D \propto \frac{|r(t) - r(0)|^2}{\Delta t^{\alpha}}, \tag{6}$$

with $\alpha = 1$ in case of Fickian diffusivity, $\alpha = 0.5$ in case of 'single-file' diffusivity and $\alpha = 2$ in case of 'ballistic' diffusivity. Striolo et al. [32] and later Mukherjee et al. [33] showed that water molecules initially undergo ballistic diffusion, which, at long times, changes to Fickian. In fact, water molecules exhibit strong correlations due to hydrogen bonding. Therefore, they are highly coordinated like in ballistic mode but, at the same time, in small nanotubes, they move in a mono-dimensional fashion, which would result in single-file diffusion. The compromise between these two opposite situations results in the apparent Fickian diffusivity observed. Our work differs from those previous investigations since 'natural' density instead of fixed density is assumed in the CNTs.

In Figure 4, the average square molecular displacement $\Delta r^2(t) = \langle (r(t) - r(0))^2 \rangle$ in the x-, y- and

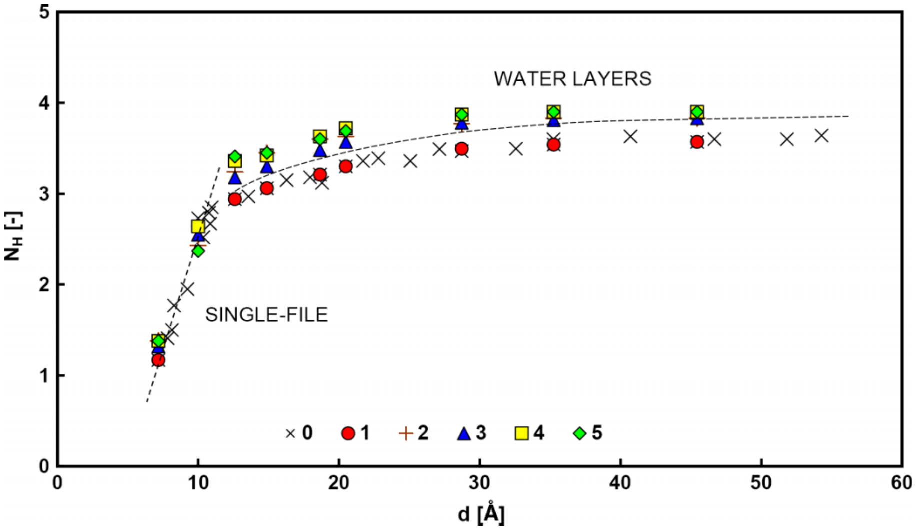

Figure 3. Average hydrogen bonds per water molecule N_H vs. nanotube diameter calculated with various models (see Table 4).

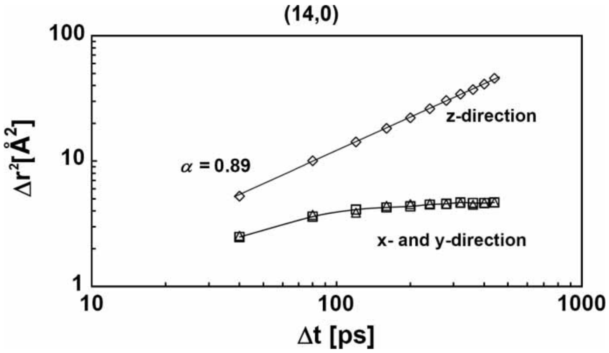

Figure 4. Mean molecular displacement $\Delta r^2(t)$ in the x-, y- and z-directions (logarithmic scale).

z-directions and for a (14,0) nanotube is shown[3]. Linear fit of $\ln(\Delta r(t))$ in the axial z-direction shows that, in the particular case of Figure 4, $\alpha = 0.89$. The radial x- and y-directions, on the other hand cannot be fitted by Equation (6) and after a certain time Δr^2 reaches a plateau. This is understandable, if we take into account the fact that the displacement is limited by the nanotube wall and that, as a consequence, water molecules cannot move beyond the value of d. In Figure 5, the parameter α is calculated from the trajectories obtained in our simulations. Also in this case, results coming from different models have a similar trend. Striolo et al. [32] reported that in long nanotubes the diffusion mechanism initially is ballistic and only after a certain time it changes to Fickian. The initial ballistic step, however, was not observed in our simulations. In our work, in fact, the concentration of water is higher and, unlike Striolo et al. [32], there is not formation of water clusters, which play an important role in the initial ballistic phase[4].

In the case of self-diffusion D, Figure 6 shows that different models yield different values of D. This fact, however, is consistent with results of bulk water diffusivity coming from comparisons among different water models[5] [17,19]. Both Figures 5 and 6 have the discontinuous behaviour already seen in Figure 1. In the single-file mode the diffusion exponent α increases when the diameter decreases, while in the layered mode the opposite happens. This circumstance is not immediately understandable since single-file arrangements tend to have $\alpha = 0.5$, if there is no additional interaction between the molecules. Water molecules form hydrogen bonds, which can enhance coordination and, consequently, the value of α, but, according to Figure 3, N_{H} decreases at low diameters. The fact that must be noted, however, is that the lower the diameter the more 'straight' the water-file (see Figure 2). This circumstance tends to favour HBs with orientation parallel to the nanotube axis and, therefore, coordination in this direction. In bulk, in fact, N_{H} is almost four, but water molecules are pulled or pushed isotropically by their HBs without any preferential direction in space. In small nanotubes, on the other hand, N_{H} is between 1 and 2, but it acts mainly on the z-axis favouring coordination, hence α, in this direction.

4. Conclusions

Water properties (i.e. density, hydrogen bonding and self-diffusivity) in CNT have been investigated by means of MD. Some of these properties were also investigated by other authors, but only for a small range of the nanotube diameters and a complete profile of their behaviour has never been presented so far. Our results

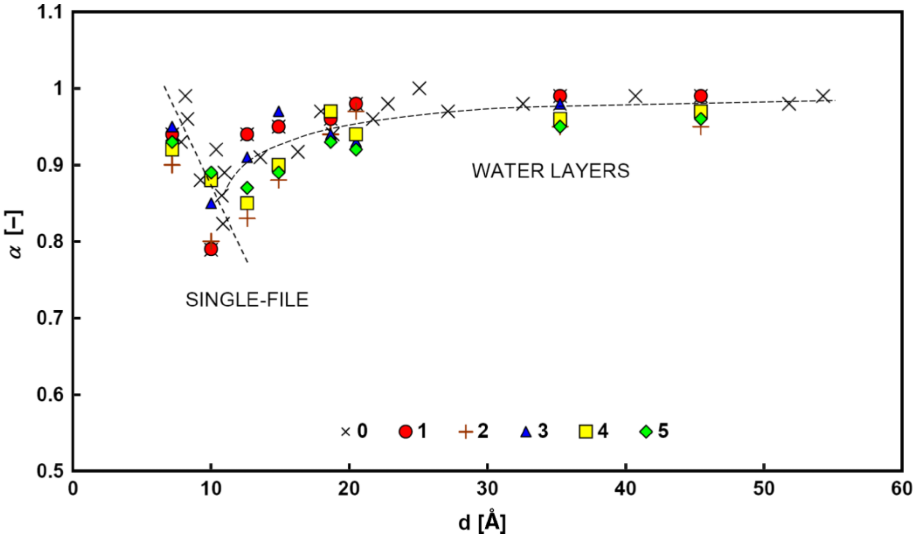

Figure 5. Self-diffusivity parameter α vs. nanotube diameter calculated with various models (see Table 4).

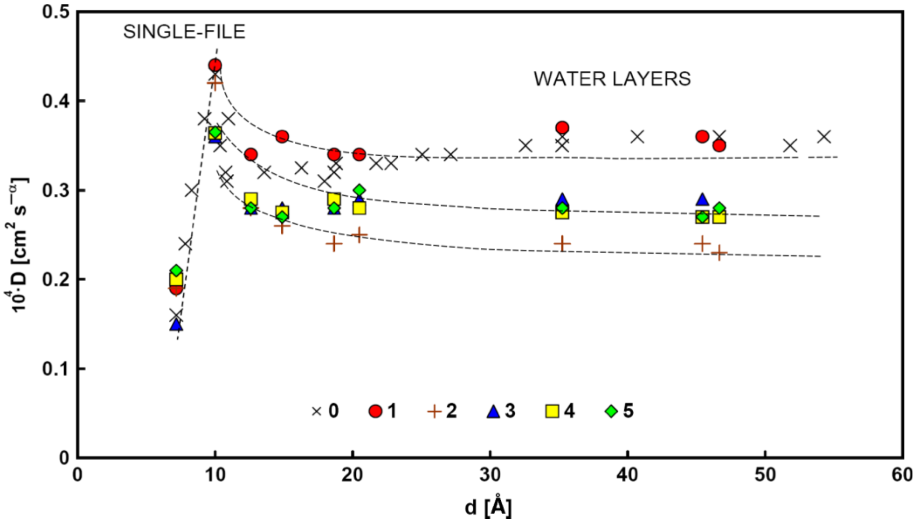

Figure 6. Self-diffusivity coefficient D vs. nanotube diameter calculated with various models (see Table 4).

show that these properties follow two different, and in certain cases opposite, trends according to the geometrical disposition of water molecules inside the nanotube. The critical diameter is found at approximately 10 Å. For $d < 10$ Å, in fact, H_2O molecules form a single-file geometry, while for $d > 10$ Å a layered water structure appears. In this work, furthermore, it was shown that various water models produce similar trends, while the use of rigid or flexible nanotubes was shown to have no practical consequences on the final results.

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Notes

1. The consequences of the use of flexible nanotubes under various pressure conditions and different bonding potentials in water/CNT systems is investigated in the works of Longhurst and Quirke [13–15].
2. In this work, properties calculated by letting water molecules enter spontaneously the nanotube are sometimes called ‘natural’ in order to distinguish from those obtained with a prescribed number of molecules in the nanotube.
3. The initial time $t = 0$ begins after the statistical steady state is achieved. The molecules, moreover, are followed until they begin to exit the nanotube (approximately 500 ps in Figure 4).
4. It must be also considered that in our case the nanotubes length and, consequently, the average residence time of a water molecule in the CNT is shorter than in Striolo et al. [32].
5. Figure 6 compares quantities with different units since the value of α is variable and therefore only a qualitative comparison can be made. Even though the variation of α is relatively small, that data in Figure 6 show higher noise with respect to the previous figures. This is due to the fact that small errors in α are reflected exponentially in D.

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