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Molecular dynamics simulations of polarizable nanotubes interacting with water

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In the present paper, we use molecular dynamics simulations to quantify the response of a finite size polarizable nanotube to the electric field created by a water environment. This response is calculated in a self-consistent way at each step of the simulation, leading to the evaluation of the energy and forces coming from the electrostatic interaction between the dipoles induced on the nanotube by the water surrounding and the set of charges accounting for the permanent electric moments of these water molecules. Our results show that the polarization of the nanotube is negligible when it is completely immersed in liquid water at 298 K due to the global symmetry of the environment. The polarization effects are slightly more important when considering the case of small water aggregates located outside the nanotube, and they are maximum when the water molecules are located inside the nanotube. However, these polarization effects never account for more than 8% of the total interaction energy and the simulations show that they depend on the geometrical arrangement of the water surrounding.

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I. INTRODUCTION

Because of their unique electrical, mechanical and thermal properties,[1,2] carbon nanotubes (CNT) have been extensively studied during the last decade. More specially, their potential applications in nanoelectronics, gas storage, fiber reinforcement, field emission display, nanoscale sensors or actuators have aroused a growing interest these last years.[3,4] Recently, other applications include the use of carbon nanotubes in biological environment (cell manipulators, nanopipets, DNA sequencing).[5,6] A common aspect of these applications is the interaction of the nanotubes with its environment, and more specially the surrounding water molecules.

From a theoretical point of view, molecular dynamics (MD) simulations have been widely used for studying the behavior of CNT in water environment, because the atomically detailed level of description in MD allows characterization of properties such as, for example, the modification of the hydrogen bond network inside[7] or around the nanotube,[8] the contact angle,[9] or the dynamical behavior of the water molecules confined inside the nanotube.[10] However, the prerequisite for using MD is the availability of accurate interaction potentials between water and CNT. Up to now, the models used in MD simulations to describe the water-CNT interactions are all based on a pairwise additive Lennard-Jones potential between the O, H, and C atoms of the water-CNT system.[11] A more sophisticated model was proposed that includes an electrostatic interaction between the partial charge sites on the water molecules and point quadrupole moments on the carbons.[8,12] However, the contribution of the quadrupolar terms to the water-CNT interaction was found to be negligible.[8]

Carbon nanotubes have been predicted to have a very large polarizability along their axis, scaling with the number of carbon atoms with a power greater than 1 for metallic tubes.[13] In a recent work, Arab *et al.*[14] have included in their calculations the polarization of the CNT to minimize at 0 K the interaction potential energy between a perfect bundle of three nanotubes and one single polar molecule such as CO, CO_2, HF, and H_2O. This study showed that the electric field created on the nanotubes by the adsorbed molecule is sufficiently large to polarize these nanotubes in a significant way. The resulting electric field thus created by the polarized nanotube interact with the permanent electric multipoles of the adsorbed molecules and the corresponding contribution to the total energy is far from being negligible, accounting for up to about 45% of the total energy when considering water adsorption. However, the results strongly depend on the adsorbed molecule and on the adsorption site.

In the present paper, we use a similar interaction potential to quantify, for the first time in MD simulations, the polarization of a carbon nanotube of finite size in contact with water at ambient temperature.

The outline of the paper is as follows: In Sec. II we present the theoretical backgrounds. The results for a finite size polarizable nanotube immersed in liquid water are presented in Sec. III, together with the results corresponding to the characterization of small water aggregates adsorbed on and in the polarizable nanotubes.

II. THEORETICAL BACKGROUND

A. Simulation setup

The "water-polarizable carbon nanotube" system is modelled using classical molecular dynamics simulations in the (NVT) ensemble. The MD simulation box is a parallelepiped of sizes 44.0 Å × 45.6 Å × 43.14 Å along the x, y, and z directions, respectively, that contains one open nanotube of finite size surrounded by a certain amount of water molecules. The nanotube is considered as a rigid fixed body located at the center of the MD box, its axis being the z axis of the MD box. Two different nanotubes have been considered in the present simulations: a (10,0) tube of 18.0 Å length and of 7.94 Å diameter that contains 180 C atoms, and a (8,4) tube of 19.0 Å length and of 8.40 Å diameter, that contains 192 C atoms. These two nanotubes are predicted to be semiconductors for infinite length. By contrast with the (10,0) nanotube, the (8,4) nanotube has a chiral geometry.

To characterize the polarization response of a nanotube immersed in a liquid medium, the (10,0) and (8,4) tubes are surrounded by $N_w = 2760$ and 2755 moving water molecules, respectively, that are initially placed on an hexagonal lattice similar to ice. The density for the corresponding nanotube + water system is equal to 995 kg m^{-3}, and the simulations are performed at 298 K. To simulate an infinite system, periodic boundary conditions are imposed by replicating the simulation box along the three directions. Note that due to the open-ends of the nanotube, a few molecules (between 5 and 7 depending on the nanotube length) enter inside the nanotube during the course of the simulations.

The equations of motions are solved by using standard MD based on the Verlet algorithm and on the quaternion representation of the molecular orientations.[15] A time step of 2.0 fs is used, and the total duration of each run involves 90 000 steps (180 ps), 60 000 of which being devoted to the equilibration of the system (i.e., 120 ps). The initial velocities for each moving molecule are taken from a Boltzmann distribution corresponding to the desired simulation temperature. During the production run, the temperature is held constant by scaling the velocities every 20 steps.

B. Interaction potentials

1. Water-water interaction

The TIP4P potential[16] is used to model water-water interactions. It consists of a Lennard-Jones term between the oxygen atoms and a Coulomb potential between partial charges q_i located on the hydrogen atoms and on an additional site displaced by 0.15 Å with respect to the oxygen atom. Thus the interaction between two water molecules w_a and w_b is written as

$$U_{w_a,w_b} = 4\epsilon_{\mathrm{OO}}\left[\left(\frac{\sigma_{\mathrm{OO}}}{r_{\mathrm{O}_a,\mathrm{O}_b}}\right)^{12} - \left(\frac{\sigma_{\mathrm{OO}}}{r_{\mathrm{O}_a,\mathrm{O}_b}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\sum_{ij}\frac{q_{i_a}q_{j_b}}{r_{i_a,j_b}}, \tag{1}$$

where ϵ_{OO} and σ_{OO} are the Lennard-Jones parameters for the O—O interaction. $r_{\mathrm{O}_a,\mathrm{O}_b}$ is the distance between the oxygen pertaining to molecules w_a and w_b, respectively, and r_{i_a,j_b} represents the distance between electric sites of the two interacting molecules.

2. Water-nanotube interaction

The interaction between the carbon nanotube and the water molecules consists of the sum of a Lennard-Jones term $U^{\mathrm{LJ}}_{w,\mathrm{C}}$ between the carbon and the oxygen and hydrogen atoms of water, and of an electrostatic term $U^{E}_{w,\mathrm{C}}$ coming from the interaction between charges on water and the induced dipoles created by the water molecules on the polarizable nanotube.

$U^{\mathrm{LJ}}_{w,\mathrm{C}}$ is based on parameters obtained from Marti and Gordillo,[17] and it is defined as

$$U^{\mathrm{LJ}}_{w,\mathrm{C}} = 4\sum_{a=1}^{N_w}\sum_{i=1}^{3}\sum_{\alpha=1}^{N_\mathrm{C}} \epsilon_{i_a,\alpha}\left[\left(\frac{\sigma_{i_a,\alpha}}{r_{i_a,\alpha}}\right)^{12} - \left(\frac{\sigma_{i_a,\alpha}}{r_{i_a,\alpha}}\right)^{6}\right], \tag{2}$$

where $r_{i_a,\alpha}$ represents the interatomic distance between the ith site of the water molecule a and the αth carbon atom.

Moreover, because it has been recently shown that polarization effects of carbon nanotubes can significantly influence the adsorption of a single polar molecules such as water,[14] we add on each carbon atom either an isotropic polarizability with the standard vacuum electrostatic propagators ($\alpha_\mathrm{C} = 0.955$ Å^3) (Ref. 18) or a local anisotropic polarizability tensor of components $\alpha_\parallel = 2.45$ Å^3 and $\alpha_\perp = 0.86$ Å^3 (where $\alpha_\parallel$ defines the polarizability along the hexagonal plane, and $\alpha_\perp$ the component perpendicular to this plane) with a renormalized propagator.[19] These values have been fitted[20] in order to recover the measured polarizability for the C_{60} and C_{70} molecules and the results issued from tight-binding studies for single wall nanotubes (SWNT) polarizabilities.[13] The local tensors are then transformed by an appropriate rotation to get their global expression in the nanotube frame.

Using a method based on a Lippmann-Schwinger-type equation for the description of the propagation of the induction in a mesoscopic tube,[18] the local electric field at the location of the αth C atom can be written as

$$\mathbf{E}(\mathbf{r}_\alpha) = \mathbf{E}_0(\mathbf{r}_\alpha) + \sum_{\beta=1}^{N_\mathrm{C}} \mathbf{T}^{(2)}(\mathbf{r}_\alpha,\mathbf{r}_\beta)\alpha_\mathrm{C}(\mathbf{r}_\beta)\mathbf{E}(\mathbf{r}_\beta) \tag{3}$$

where $\mathbf{E}_0(\mathbf{r}_\alpha)$ represents the electric field created by the water molecules on the αth C atom and where the sum describes the effect at $\mathbf{r}_\alpha$ of the dipoles induced on the other carbon atoms by the water molecules. N_C is the total number of carbon atoms, $\alpha_\mathrm{C}(\mathbf{r}_\beta)$ is the polarizability tensor of the C atoms located at position $\mathbf{r}_\beta$, and $\mathbf{T}^{(2)}$ is the electrostatic field propagator usually defined as

$$\mathbf{T}^{(2)}(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi\epsilon_0}\left(\nabla\nabla'\left(-\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right)\right). \tag{4}$$

However, if one wants to avoid polarization catastrophe it can be shown[20] that one must use a "renormalization" scheme such as the linear one proposed by Thole,[21] recently used by Torrens for carbon nanotubes,[22] and improved by Jensen *et al.*,[23] or the Gaussian scheme proposed by Mahanty and Ninham.[24] Here, we use the Mahanty-Ninham scheme which accounts for a nonpointlike distribution of charges or induced dipoles in the atom by convoluting the classical propagator with a Gaussian. In our case, this leads to[19]

$$\begin{aligned}\mathbf{T}_R^{(2)}(\mathbf{r},\mathbf{r}') = \mathbf{T}^{(2)}(\mathbf{r},\mathbf{r}')\Bigg[&\mathrm{erf}\left(\frac{|\mathbf{r}-\mathbf{r}'|}{a}\right) \\ &- \frac{2}{\pi^{1/2}a}|\mathbf{r}-\mathbf{r}'|e^{-(|\mathbf{r}-\mathbf{r}'|/a)^2}\Bigg] \\ &- \frac{1}{\pi^{3/2}\epsilon_0 a^3}\frac{(\mathbf{r}-\mathbf{r}')\otimes(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^2}e^{-(|\mathbf{r}-\mathbf{r}'|/a)^2},\end{aligned} \tag{5}$$

where erf is the conventional error function and the parameter a characterizes the size of the σ orbital. Here $a = 1.21$ Å.[20]

Equation (3) is in fact a linear system of N_C vectorial equations, i.e. $3N_C$ scalar equations with $3N_C$ unknowns, namely the $3N_C$ components of the N_C $\mathbf{E}(\mathbf{r}_\alpha)$ fields. This system can be LU factorized once for all at the beginning of the simulation, and then solved at each step of the simulation when the N_C fields $\mathbf{E}_0(\mathbf{r}_\alpha)$ can be computed from the new water molecules coordinates. Then, the electric potential on the ith site of a water molecule located at the position $\mathbf{r}_i$ can be calculated at each step of the simulation using

$$\Phi(\mathbf{r}_i) = \Phi_0(\mathbf{r}_i) + \sum_{\alpha=1}^{N_C} \mathbf{T}^{(1)}(\mathbf{r}_i,\mathbf{r}_\alpha)\alpha_C(\mathbf{r}_\alpha)\mathbf{E}(\mathbf{r}_\alpha), \tag{6}$$

where $\Phi_0(\mathbf{r}_i)$ is the electric potential created on the ith site of a water molecules by the other water molecules. The term $\alpha_C(\mathbf{r}_\alpha)\mathbf{E}(\mathbf{r}_\alpha)$ represents the dipole induced on the αth C atoms by its surrounding and $\mathbf{T}^{(1)}$ is the action tensor of rank 1, classically defined as

$$\mathbf{T}^{(1)}(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi\epsilon_0}\left(\nabla'\left(-\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right)\right) \tag{7}$$

and after “renormalization” as

$$\mathbf{T}_R^{(1)}(\mathbf{r},\mathbf{r}') = \mathbf{T}^{(1)}(\mathbf{r},\mathbf{r}')\left[\operatorname{erf}\left(\frac{|\mathbf{r}-\mathbf{r}'|}{a}\right) - \frac{2}{\pi^{1/2}a}|\mathbf{r}-\mathbf{r}'|e^{-(|\mathbf{r}-\mathbf{r}'|/a)^2}\right]. \tag{8}$$

Note that it can be demonstrated that the renormalized propagator of order n can also be calculated as the derivative of the $n-1$ renormalized propagator as in the classical case, as can be seen by replacing $1/|\mathbf{r}-\mathbf{r}'|$ by $[\operatorname{erf}(|\mathbf{r}-\mathbf{r}'|/a)/|\mathbf{r}-\mathbf{r}'|]$ in Eqs. (4) and (7).

Then, the interaction between the electric charge located on the ith site of a water molecule and the electric potential created at this position by the polarized carbon nanotube is expressed at each step of the simulation as

$$U_{w,C}^{E}(\mathbf{r}_i) = q_i\Phi(\mathbf{r}_i). \tag{9}$$

Note that we have disregarded in this work the possible polarization of the water molecules due to their interaction with the dipoles induced on the nanotube.

All the interactions have been calculated in the direct space with a radial cutoff (19 Å) that is sufficiently large for an accurate calculations of the electrostatic interactions without using the much more time consuming Ewald method. The parameters of these potentials are summarized in Table I.

TABLE I. Parameters for the water-water and water-nanotube interactions.

	Site	ϵ (kJ mol^{-1})	σ (Å)	q (atomic unit)
H_2O	O	0.647	3.154	
	H			0.52
	m[a]			−1.04
	pair	ϵ (kJ mol^{-1})	σ (Å)	
H_2O—C	O—C	0.389	3.28	
	H—C	0.129	2.81	

[a] Additional electric sites displaced by 0.15 Å from the oxygen, along the C_{2v} axis of H_2O.

III. RESULTS

A. Molecular dynamics of a nanotube immersed in a liquid medium

Molecular dynamics trajectories were first computed for a (10,0) rigid nanotube immersed in water. Three cases were considered: case 1, without including polarization effects in the potential; case 2, including isotropic polarizabilities on the C atoms of the nanotube and standard propagators; and case 3, by considering anisotropic polarizabilities on these C atoms and “renormalized” propagators. The corresponding results were analyzed in terms of total energy, water radial density profile, and the probability profile of the water orientations, especially at the water/nanotube interface.

The results of the simulations show that the total energy mainly comes from the water-water interactions, and is equal to about −41.7 kJ/mol in average per molecule, for both (10,0) and (8,4) nanotubes. The contribution coming from the interaction with the nanotube is quite small (about −0.6 kJ/mol) and, more interesting, the polarization effects are totally negligible (the electrostatic interactions account for less than 5% of the water-nanotube interaction). No significant difference is obtained when using anisotropic rather than isotropic polarizability in the description of the carbon atoms. Note that these energy values are averaged over the total number of water molecules in the simulation box, and due to this division, the molecule-nanotube interaction per water molecule appears rather weak because the large contribution corresponding to the molecules located close to the nanotube is counterbalanced by the very weak contribution of the molecules located far away from the nanotube.

Although inclusion of polarization effects has negligible impact on the total energy, we have however investigated the effects of the nanotube polarization on the structural properties of the water molecules around the CNT. For example, the radial density profiles $g(r')$ for oxygen and hydrogen atoms are shown in Fig. 1 for the simulation of the (10,0) carbon nanotube in water, including the polarization of the carbon atoms (case 3). These curves are presented as a function of the distance r' between the O or H atom and the nanotube wall, and the statistics only includes water molecules that are located in a slab defined by the nanotube length (i.e., the molecules located above or under the nanotube are disregarded). The maxima of the O and H profiles nearly coincide at 3.4 Å indicating that the plane of the water molecules is approximately tangential to the water/nanotube interface. This information is confirmed by the study of the angular distribution functions (not shown) which show that the water molecules axes are only slightly tilted with respect to the nanotube axis. Very similar features are found when

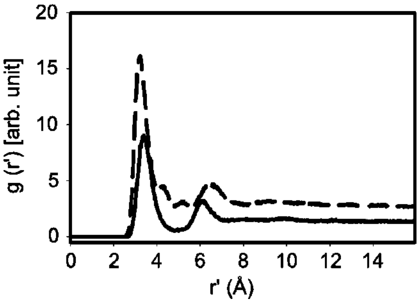

FIG. 1. Oxygen (full curve) and hydrogen (dashed curve) radial density profiles for the simulations of the (10,0) carbon nanotube immersed in liquid water at 298 K, including the polarization of the carbon atoms (anisotropic polarizability tensor). r' characterizes the distance to the nanotube wall.

considering the (8,4) chiral nanotube. As an illustration of the water arrangement around a nanotube, a snapshot issued from the simulation of the (8,4) nanotube in water at 298 K is given in Fig. 2, showing the cylindrical symmetry of the water environment close to the nanotube. These results are in fair agreement with those previously published in the literature for an infinitely long nanotube and based on different interaction potential approaches.[8]

In order to have additional information specific to the water-nanotube interaction, we have also calculated separately the average value of this interaction for the different water layers evidenced in the radial density profiles. For the first layer, corresponding to the first peak in $g(r')$ (Fig. 1), the water-nanotube interaction is equal to about -12.8 kJ/mol whereas it is much smaller for the second layer, located at about 6.0 Å from the nanotubes walls ($U_{w,\mathrm{C}}=-1.2$ kJ/mol). This interaction is negligible for the water molecules located far from the nanotube. Inside the nanotube, the water nanotube interaction energy is quite large due to confinement effects and reaches -42.0 kJ/mol. However, whatever the location of the water molecules, $U_{w,\mathrm{C}}$ mainly comes from the Lennard-Jones contribution with a vanishingly small contribution of the electrostatic interaction.

Since the polarization of the nanotube is related to the dipole moment of the water molecules through the electric field $\mathbf{E}_0$ in Eq. (3), we have characterized the time evolution of the total dipole moment μ_{total} of the water molecules in the MD box. The results (not shown) indicate that this total dipole moment remains vanishingly small ($\leqslant 0.01$ D) during the whole duration of the simulation, demonstrating that liquid water around the nanotube is in fact a quasinonpolar environment, leading to a very weak polarization response of the nanotube.

B. Molecular dynamics of small water aggregates interacting with the carbon nanotube

The present MD simulations of a nanotube immersed in a liquid water environment at ambient temperature show that the polarization of the nanotube is almost negligible and has no significant influence on the adsorption energy or on the structural arrangement of the water molecules. These conclusions are different from those recently obtained when considering the adsorption of a single water molecule in the vicinity of a perfect bundle of polarizable nanotubes,[14] that show that the induction contribution due to polarization effects can account for up to 45% of the total adsorption energy at 0 K. Because it is not realistic to simulate the adsorption of only one single water molecule on a nanotube (from the statistical point of view of molecular dynamics), we have rather investigated the adsorption of small water aggregates (5 and 7 molecules) located outside or inside the (10,0) and the (8,4) nanotubes, at low (100 K) and ambient temperatures in order to characterize also the influence of temperature effects. These small aggregate sizes correspond in fact to the maximum number of molecules that enter into the nano-

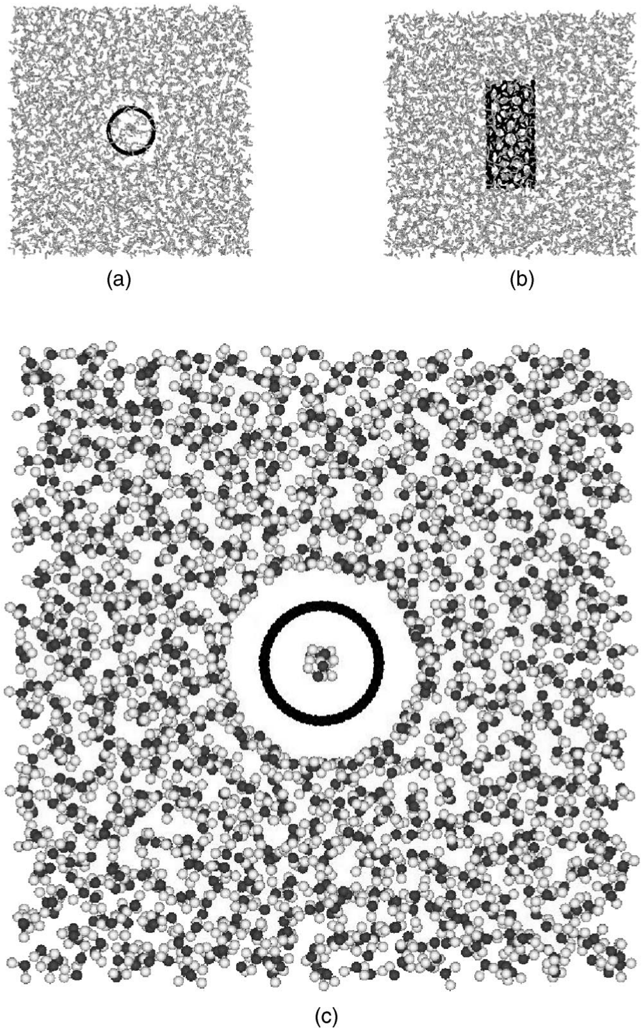

FIG. 2. Snapshot of the atoms issued from the simulation of the (8,4) nanotube in water at 298 K: (a) top and (b) side views of the simulation box (the C atoms are represented by black circles and the water molecules are schematized as small grey sticks); (c) top view of a slab (delimited by the nanotube length) of water molecules around the nanotube. This latter picture clearly shows the cylindrical arrangement of the first, and in a less extent of the second, layers of water molecules around the nanotube walls. In this simulation, the interaction potential takes into account the anisotropic polarization of the carbon atoms.

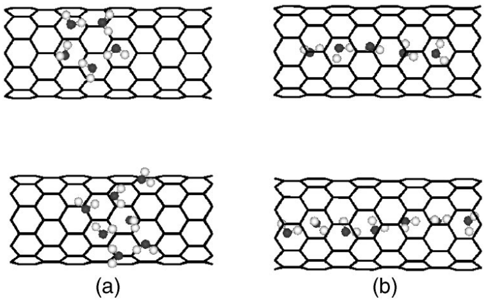

FIG. 3. Snapshots of the water molecules and C atoms issued from the simulations at 100 K for the different situations considered in our calculations: 5 (top) and 7 (bottom) water molecules (a) outside or (b) inside the (10,0) nanotube. The potential interaction takes into account the anisotropic polarization of the carbon atoms.

tube during the simulation in liquid water. Note that very long runs were performed to simulate the adsorption of these water aggregates, involving 600 000 steps (1.2 ns) of equilibration followed by 400 000 steps (800 ps) of production, to avoid artifacts due to trapping of the system in local energy minima, especially at 100 K.

As an illustration of the MD results, Fig. 3 shows snapshots issued from the simulations at 100 K of some situations considered in our calculations. For each case, the geometry of the corresponding water aggregate is clearly governed by the formation of hydrogen bonds between the water molecules, leading to compact water aggregates on the external surface of the nanotube, and to hydrogen-bonded chains of water molecules inside the nanotube. The adsorption energies (Table II) are very similar for water interacting with (10,0) and (8,4) nanotubes, and they are much more important inside (around −65 kJ/mol) than outside (∼−42 kJ/mol) the nanotubes due to confinement effects. Note that these energy values indicate that the formation of compact water aggregates outside the nanotube corresponds in fact to trapping into a local energy minimum in which our system has been "stuck" during the entire simulation. This indirectly evidences the presence of an energy barrier to enter the nanotube, that is too high to be overpassed by the water molecules at the low temperature of the simulations (100 K), at least during the long duration of our runs. At 298 K, the most stable configuration corresponds to water molecules located inside the nanotube, where they form hydrogen-bonded chains, whatever the nanotube and the initial configurations (i.e., water molecules initially located inside or outside the nanotube) under consideration. This indicates that, at room temperature, the thermal agitation is large enough to allow the water molecules to overpass the energy barrier and to enter the nanotube. At this temperature, the mean total energy per water molecule ranges from about −64 kJ/mol in the case of a $(H_2O)_5$ aggregate adsorbed in a polarizable (10,0) nanotube (anisotropic polarization) to about −58 kJ/mol in the case of a $(H_2O)_7$ aggregate adsorbed in a polarizable (8,4) nanotube (isotropic polarization).

Anyway, the main results of these simulations is that the electrostatic interactions coming from the nanotube polarization are rather weak, whatever the situation considered in the calculations. The largest polarization effects are obtained when considering water adsorbed into the nanotube and by using anisotropic polarizability tensors on the C atoms. In

TABLE II. Different contributions (in kJ/mol) to the potential energy for small water aggregates interacting with a nanotube at 100 K. *N* is the number of molecules in the aggregate, located either outside (out) or inside (in) the nanotube. The values given are average contributions per molecule. $U_{w,w}$ represents the water-water interactions, $U_{w,\mathrm{C}}^{\mathrm{LJ}}$ and $U_{w,\mathrm{C}}^{E}$ are the Lennard-Jones and electrostatic contributions to the water-nanotube interaction, respectively, and U_{total} is the sum of these three interaction potentials.

		N	$U_{w,w}$	$U_{w,\mathrm{C}}^{\mathrm{LJ}}$	$U_{w,\mathrm{C}}^{E}$	U_{total}
nanotube (10,0)	isotropic polarization	5 (out)	−28.5	−12.5	−0.7	−41.7
		7 (out)	−30.6	−12.3	−0.7	−43.6
		5 (in)	−17.8	−47.3	−3.0	−68.1
		7 (in)	−18.9	−43.9	−2.7	−65.5
	anisotropic polarization	5 (out)	−28.5	−12.4	−1.1	−42.0
		7 (out)	−28.8	−12.1	−1.5	−42.4
		5 (in)	−17.7	−45.9	−5.4	−69.0
		7 (in)	−18.7	−40.6	−5.2	−64.5
nanotube (8,4)	isotropic polarization	5 (out)	−28.4	−12.6	−0.7	−41.7
		7 (out)	−29.8	−12.4	−0.5	−42.7
		5 (in)	−19.2	−42.6	−2.9	−64.7
		7 (in)	−20.6	−40.0	−2.9	−63.5
	anisotropic polarization	5 (out)	−28.5	−12.5	−1.2	−42.2
		7 (out)	−29.8	−12.2	−0.9	−42.9
		5 (in)	−19.1	−41.4	−5.2	−65.7
		7 (in)	−20.2	−37.7	−5.3	−63.2

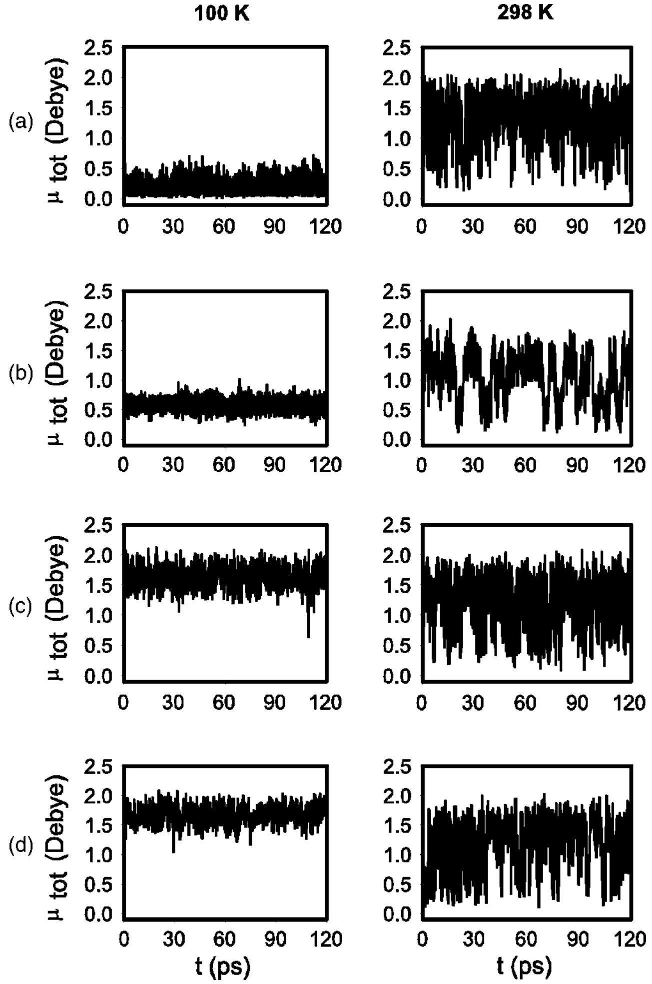

FIG. 4. Time evolution (in ps) of the average dipole moment per molecule (in Debye) engaged in a water aggregates adsorbed in or on a (10,0) nanotube. The C atoms of the nanotube are characterized by an anisotropic polarizability tensor. The water aggregate is made of 5 or 7 molecules adsorbed outside [(a) and (b), respectively] or located inside [(c) and (d)] the nanotube (at the beginning of the simulation). The simulations have been performed at 100 K (left-hand side) and 298 K (right-hand side). Note that at this latter temperature, all the molecules are located inside the nanotube during the production phase of the simulation whatever the initial configuration.

such a situation, the polarization contribution to the total energy per molecule reaches up to 8%.

These conclusions are supported by the calculations of the average dipole moment per molecule engaged in the water aggregates (μ_{tot}) adsorbed in or on the nanotube, and shown in Fig. 4. Indeed, when the water molecules are trapped on the surface of the (10,0) nanotube (for example) at 100 K, μ_{tot} is equal to about 0.5 D [left-hand side of Figs. 4(a) and 4(b)]. By contrast, inside the nanotube, μ_{tot} reaches a value equal to about 1.5 D [left-hand side of Figs. 4(c) and 4(d)]. At 298 K, the stable configurations corresponds to molecules adsorbed into the nanotube (even when starting from molecules adsorbed on the outside of the nanotube) and the corresponding value of μ_{tot} is equal to about 1.3 D, with large fluctuations between roughly 0.5 and 2.0 D, due to thermal agitation at room temperature. Indeed, the molecules inside the nanotube can fluctuate between different orientational states corresponding to similar energies but different total dipole moments. For example, the distribution function (not shown) of the tilt angle made by the water dipole moment and the *z* axis of the nanotube shows two different orientations for the water molecules inside the nanotube, around 45° and 135°. These orientations characterize the different ways to form hydrogen bonds between the water molecules inside the nanotube. Thus, the total dipole moment value of 2.0 D corresponds to a situation where the molecules have nearly all the same orientation (either all 45° or all 135°), whereas the minimum value (0.5 D) corresponds to a situation where two molecules are oriented at 45° and the three other at 135° (or the reverse situation). Note that the third situation with four molecules in a direction and the fifth molecule in the other direction seems also to occur for a dipole value around 1.0 D in Fig. 4(b) (right). Very similar results are obtained with the (8,4) nanotube.

Finally, note that the weak polarization of the nanotube leads to the existence of weak electric field around it that would not significantly polarize the surrounding water molecules. To better assess these additional polarization effects, single point energy calculations have thus been performed on the water aggregates in their most stable configurations inside or outside the nanotube, by adding a polarizability tensor at the center of mass of the water molecules. The resulting interaction energy contribution coming from the water polarization accounts for less than 0.2% of the total energy (and less than 3% of the electrostatic contribution) in each case, demonstrating that the polarization of the water molecules have a vanishingly small influence on our results. Note that we have also performed such potential energy calculations with only one single water molecule adsorbed in the nanotube, i.e., a situation that would correspond to a large polarization of the nanotube, as demonstrated in Ref. 14. The corresponding potential energy contributions due to the nanotube polarization is actually large (about 35% of the total adsorption energy) as in Ref. 14, but the water molecule polarization effects are still negligible, accounting for only 2% of the total adsorption energy.

IV. SUMMARY AND CONCLUSIONS

In this paper, we have performed the first molecular dynamics simulations of a polarizable nanotube immersed in liquid water. The results show that the influence of the nanotube polarization is clearly negligible on both the water molecules arrangement around the nanotube and on their adsorption energy. We have also characterized the adsorption of small water aggregates on and in a polarizable nanotube at low (100 K) and room (298 K) temperatures. The simulations evidence that the electrostatic interactions coming from the nanotube polarization are again rather weak although they are slightly larger when the water molecules are located inside the nanotube and when using anisotropic polarization to describe the polarizability of the carbon atoms. In such a situation, the polarization contribution to the total energy per molecule reaches at most 8%.

These conclusions seem in contradiction to those of Arab *et al.*[14] that have calculated induction contribution due to polarization effects accounting for up to 45% of the total adsorption energy at 0 K. However, the situations are far from being comparable. Indeed, Arab *et al.*[14] considered the adsorption of a single water molecule in its most stable site inside a bundle made of three adjacent long polarizable nanotubes (several hundreds of C atoms), whereas our simulations consider a larger number of water molecules adsorbed in or on a single short-length nanotube. Our results show that the strong water-water interactions lead to adsorption geometries that are governed by the formation of hydrogen bonds between water, and that the resulting aggregates are characterized by rather weak dipole moments that do not significantly polarize small nanotubes.

Note that experimentally used nanotubes are much longer than those considered in the present simulations. This can lead to larger polarization effects in experiments, because the effective polarizability per carbon atom in the nanotube increases with the number of C atoms up to some coherence length that is much larger than the lengths considered in this work and in the work of Arab *et al.* (and more generally in all the MD simulations of finite size nanotubes published in the literature). Simulations of such longer nanotubes would however require very large simulation boxes, and thus would be very time consuming. However the conclusions obtained in the present work for nanotubes immersed in liquid water would not change with the size of the nanotube because the total net dipole moment of the environment would remain close to zero.

The results of these works point out that the polarization of a nanotube interacting with polar molecules such as water strongly depends on the geometry of the adsorbate under consideration (i.e., on their net dipole moment) and, in a less significant extent, on temperature (through possible geometrical modifications). As a consequence, preliminary calculations of the net permanent dipole are necessary to characterize the polarization effects before assuming that such effects are negligible.

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