Effect of electric field on water diffusion in carbon nanotubes

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Abstract
We investigate the diffusion and structure of TIP4P/2005 water confined in carbon nanotubes under the effect of electric field. For nanotubes with distinct diameters we vary the intensity and the direction of the electric field. We show that the nanotube diameter, the field intensity and the relative direction between field and tube axis change the water diffusion. For the (9,9) nanotube, the field along the tube axis melts the water structure increasing the water mobility. Our results suggest the use of electric field as a facilitator for filtration processes.

Keywords: Confined water, diffusion, carbon nanotubes, electric field, molecular dynamics.

1. Introduction
The characterization of the molecular transport phenomena is relevant for the study of pure liquids, mixtures and complex systems such as gels, liquid crystals and polymers. In the case of simple liquids, the diffusion coefficient, \( D \), usually increases with temperature, because the average molecular speed...
increases with temperature. This, however, is not the case of water \[1\]. The mobility of water increases with the density and it has a maximum \[1, 2\]. This diffusion anomaly is followed by a structural anomaly. Most materials become more structured as the density increases, but water has a maximum in the structural order parameter as the density is increased \[3\].

Since the anomalous bulk mobility of water is due to the hydrogen bond network, it becomes even more anomalous by nanoconfinement. For example, water flows four or five orders of magnitude faster than would be predicted from conventional fluid-flow theory \[4\]. This high flux depends on the nature of the confining structure \[5, 6\], on the number of water layers \[7, 8\], on the transition from clutter to ordered \[9, 11\] and the single \[12, 14\] or multiple \[15\] carbon walls. In addition, other factors as temperature \[16, 18\], helical form of the water flow \[19\], water-wall friction, viscosity \[20, 22\] and kinetics of the filling of the tube \[23, 24\] are relevant factors which affect the value of the enhancement of the flow.

The changes in the hydrogen bond network affects, the mobility. For bulk water it was shown that the region in the pressure versus temperature phase diagram where the the hydrogen bonds network is present coincides with the region where thermodynamic and dynamic anomalies exist \[2, 25\]. As the order of the system increases, the structural, kinetic and thermodynamic anomalies begin to appear. The relation between the bonding network and the mobility of water has new features in the confined sysem. The confined water has more unbonded water molecules \[26, 27\], flexible hydrogen bonds \[28, 29\] and the presence of this free water allows for a higher mobility which is affected by the nanotube diameter, the density and viscosity of water and the temperature \[22, 30\] what was confirmed by spectroscopy experiments \[33\]. For nanotubes with a diameter smaller than 12.2 Å, the diffusion mechanism appears in two stages reflecting the competition between the wall repulsion and the formation of the hydrogen bonds \[21, 34\].

Since the mechanism behind the high mobility of confined water is related to the hydrogen bonds which at the channel surface form a helix circulating the tube and at the center arrange in a single line, then the electric field interacting with the water polarization impacts these structures. At one hand, the electric field induces water orientation and favors the filling thin CNTs \[35\] but on the other hand it produces dipole orientation inside CNTs which results in a pumping effect \[36\]. These dipole orientation also makes the dielectric constant of water to be lower in the surface than in the center of the tube \[37\]. In some cases the field might induce phase transitions of water
molecules \cite{38, 39}. It is not clear, however, how the electric field affects the
different structures and layers produced when water is confined by nanotubes
of different diameters.

In this paper we explore the combination of the reduction of the diam-
eter of the nanotube and the presence of the field to understand how the-
setwo components affect the thermodynamic and dynamic behavior of the
nanoconfined water, in particular how they disrupt or reinforce the hydrogen
bond network. In order to evaluate the correlations between the field and
the polarization of water we analyze two cases: filed applied axial and longi-
tudinal to the nanotube axis. The remaining of the paper goes as follows. In
the section II the model and methods are presented, the results as discussed
in section III and conclusions end the paper in section IV.

2. Model and Methods

We employed molecular dynamics with the LAMMPS package \cite{40} for per-
forming simulations of TIP4P/2005 water model \cite{41} confined inside CNTs
under electric fields. The electric field was applied uniformly in all the system
charges. We varied the direction and intensity of the field. \((n, n)\) nanotubes,
with \(n=7, 9, 12, 16, 20\) and 40, were considered. The choice of TIP4P/2005
over many other models available in the literature was due to its accuracy
in calculating bulk transport properties of water at ambient conditions \cite{42}.
For the bulk diffusion coefficient we obtained the value \(2.30 \times 10^9 \text{ m}^2/\text{s}\), which
is in close agreement theory \cite{43} and experiments \cite{44}. The TIP4P/2005
water model has four points: one at the oxygen, one at each hydrogen and
one at a fictitious atom M. The interaction potential has Lennard-Jones and
Coulombic interactions namely

\[ U_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right] + \frac{1}{4\pi\epsilon_0} \frac{q_\alpha q_\beta}{r} \]  

(1)

where \(\alpha(\beta)\) represents the oxygen, hydrogen or the fictitious atom M. The
distance between the oxygen and hydrogen atoms is 0.09572 nm and each
hydrogen carries a positive charge 0.5564, the oxygen carries no charge, the
distance between the oxygen and the atom M is 0.01546 nm in the direction
between the two hydrogens. The negative charge, \(-1.1128\), which neutral-
izes the molecule is located at the M.

For the interactions between water and the nanotube, we used oxygen-
carbon Lennard-Jones parameters defined by da Silva \cite{32}: \(\epsilon_{CO} = 0.123\)
kcal/mol and $\sigma_{CO} = 0.326$ nm. The Lennard-Jones and Coulomb interaction cutoff was set to 1 nm. In all simulations the geometry of the water molecules was constrained by the SHAKE algorithm \[45\]. Long-range coulomb interactions was handled using particle-particle particle-mesh method \[46\].

The simulations were conducted as follows. Initially, the nanotubes were connected to two water reservoirs with pressure kept at 1 atm by the Parrinello-Rahman barostat \[47\] and temperature $T = 300$ K controlled by the Nosé-Hoover thermostat \[48\]. The system was equilibrated for 10 ns with timestep set as 1 fs. After system equilibration, the average number of water molecules within each nanotube were collected. This number of each CNT size is given in Table 1. Then, the reservoirs were removed and periodic boundary conditions applied in the axial direction of the tubes, as shown in figure 1, which is equivalent to an isolated infinite nanotube. Finally, 10 ns simulation for data collection was performed in the canonical (NVT) ensemble with temperature $T = 300$ K fixed by the Nosé-Hoover thermostat \[48\]. We analyzed the diffusion mechanism of a fluid by the scaling behavior between the mean squared displacement (MSD) and time \[31\]:

$$\langle ||\vec{r}(t) - \vec{r}(0)||^2 \rangle = ADt^n$$

where the angular brackets denote an average over time origins and all water molecules, $\vec{r}(t)$ is the displacement of a molecule during the time interval $t$, $A$ is a constant and $D$ stands for the diffusion coefficient. The $n$ exponent refers to the diffusion regime: $n = 1$ for the linear Fickian diffusion, $n > 1$ for superdiffusive and $n < 1$ for subdiffusive regime. The statistical error in

| CNT  | Diameter (nm) | Length (nm) | N  |
|------|---------------|-------------|----|
| (7,7) | 0.957         | 123.46      | 901|
| (9,9) | 1.22          | 50.66       | 908|
| (12,12) | 1.63       | 22.63       | 901|
| (16,16) | 2.17        | 11.07       | 911|
| (20,20) | 2.71        | 10.33       | 1440|
| (40,40) | 5.425         | 7.87        | 5221|

Table 1: Nanotube chirality, diameter, length and the average amount of water molecules (N) inside each CNT.
the diffusion measurements could be reduced by averaging over all the MSD components. The nanopore confinement in the $x$ and $y$ directions hinders the radial displacement of the molecules. Therefore, the radial diffusion is almost zero for all cases studied here and only the axial diffusion $D_z$ will be considered.

3. Results and discussions

Figures 2 (a), (c) and (e) show the diffusion coefficient as a function of the nanotube radius when water molecules are under external fields of (a) 0.5 V/nm, (c) 0.75 V/nm and (e) 1.0 V/nm. The fields are applied in three different directions: parallel to the tube axis (referred as $0^\circ$), perpendicular ($90^\circ$) and forming an angle of $45^\circ$ with the tube axis. In the case of no electric field, the diffusion is not monotonic with the nanotube radius [49] and water freezes for the 1.2 nm diameter long (9,9) nanotube, which is in accordance with the work of Farimani and Aluru [31]. The presence of a field along the tube axis as illustrated in the figures 2(a),(c) and (e) suppresses the mobility confirming previous results [39]. This decrease in the mobility is a direct consequence of the organization of the water molecules inside the tube when the field is applied. The electric field helps the water molecules to form more hydrogen bonds as illustrated in the figures 2(b),(d) and (f). In the case in which the field is applied in the orthogonal direction of the tube, as shown in the figures 2, almost no change in the mobility of water
Figure 2: Water diffusion coefficient (left) and the number of hydrogen bonds (right) as a function of the nanotube radius $r$ under external electric fields of (a) and (b) 0.5 V/nm, (c) and (d) 0.75 V/nm, (e) and (f) 1.0 V/nm.
is observed. The field does not affect the number of hydrogen bonds as the comparison with the case with no field indicates.

Comparing the behavior of the diffusion with the average number of hydrogen bonds in the figures we observe that the decrease in the diffusion is related to the increase of the average number of water-water hydrogen bonds. If the field is applied along the nanotube axis, the oxygens align forming a more rigid structure which is more distant from the nanotube wall. This distance from the wall might lead to a decrease in the dielectric constant as suggested in experiments with planar confinement [37]. If the field is applied in the radial direction, the helical structure is not strongly affected. The only exception is the (9,9) which is frozen when no field is applied and the field induces the disruption of some hydrogen bonds and the structure melts.

In order to confirm this dewetting transition, figure shows the diffusion coefficient versus the external field for various nanotubes and field directions. The figures confirm that in the case of field the parallel to the tube axis, the diffusion is suppressed by the increase of the field. For the (9,9) tube with radial field the diffusion reaches a value 3 times larger than in the absence of the field. In this case the field affects the dipole moments of water and melts the ordered structure at the nanotube wall making leading to a dewetting transition [50].

The structure assumed by the confined water dictates the fluid dynamics [21, 22]. By applying an electric field, dynamical modifications in the systems which lead to a structural transitions in the arrangement of water molecules inside the tube can appear. In order to clarify the influence of field direction over the water structure, we show in figure the radial density profile of the oxygen atoms as a function of the nanotube radius for the (9,9) case. The radial density profile is calculated by dividing the inner of the CNT in concentric cylindrical shells and averaging the number of oxygen atoms in each shell along the simulation. The parallel electric field $0^\circ$ induces water molecules to occupy positions at the center of the tube than in the case in which there is no field applied to the system or the field is perpendicular. As a result the water molecules form a highly ordered ring-like structure shown in the inset featuring a frontal snapshot of the system in the figure. This strongly packed structure forming ice-like phases lowers the water diffusion. As we apply the electric field perpendicular ($90^\circ$) to the tube axis, the water molecules are pushed closer to the hydrophobic CNT wall breaking the ring structure and increasing the mobility as shown in the figure (b).
Figure 3: Diffusion vs. Field for the six nanotubes with null field and application of three different intensities of the field in three different directions. The nanotubes: (a) (7,7), (b) (9,9), (c) (12,12), (d) (16,16), (e) (20,20), (f) (40,40).
Figure 4: Radial density profile of the water oxygen atoms inside CNT (9,9) under a 0.1 V/nm field parallel (black line) and perpendicular (red line) to the tube axis. The orange line stands for the situation when we have no field applied to the system. Here, $r = 0$ is at the center of the tube.
4. Conclusions

We studied the influence of electric fields in the diffusion, hydrogen bond network and structure of water confined in carbon nanotubes through MD simulations. We found that the diffusion depends on the hydrogen bond network.

We analyzed three different situations: the electric field parallel, transverse and perpendicular to the tube axis. We found that large fields induce the orientation of the dipole moments of water and in the case of fields applied parallel to the tube, the network becomes more organized and the diffusion decreases. For fields applied perpendicular to the nanotube axis, the water structure is not strongly affected with the exception of the (9,9) case in which the disruption of a few hydrogen bonds by the field leads to the melting of the structure.

These results open the possibility of tuning the water flux inside a CNT by only varying the direction of the applied electric field. It is particularly relevant for application in nanotube membranes, where the water moment dipole can pose as an important ingredient in the desired flux control.

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