Breakdown of the Stokes–Einstein water transport through narrow hydrophobic nanotubes

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In this paper the transport properties of water confined inside hydrophobic and hydrophilic nanotubes are compared for different nanotube radii and densities. While for wider nanotubes the nature of the wall plays no relevant role in the water mobility, for small nanotubes the hydrophobic confinement presents a peculiar behavior. As the density is increased the viscosity shows a huge increase associated with a small increase in the diffusion coefficient. This breakdown in the Stokes–Einstein relation for diffusion and viscosity was observed in the hydrophobic, but not in the hydrophilic nanotubes. The mechanism underlying this behavior is explained in terms of the structure of water under confinement. This result indicates that some of the features observed for water inside hydrophobic carbon nanotubes cannot be observed in other nanopores.

1 Introduction

Carbon nanotubes (CNTs) have been shown to facilitate ultra-fast diffusion of water, which is a viable strategy for desalination, water treatment, photoredox catalysis and the development of biochemical nanosensors. The applications utilizing water transport through CNTs are of particular interest due to the fast water transport predicted by molecular dynamics (MD) simulations and later observed in experiments.

In principle in the processes with CNTs the wall can be considered as a hydrophobic material. However, for many applications the functionalization of the confining geometry is needed. One case is the gas storage capacity of nanomaterials. In other cases, the functionalization of CNTs is often either a prerequisite for their processing, or desirable for sensitivity and selectivity in molecular detection. Moreover, nanotubes with similar structural features to CNTs, but different atomic composition (such as Boron–Nitride), can now be routinely synthesized.

In the context of biological nanochannels, the water–surface interactions can vary depending on the hydrophobicity of the amino acids involved. Also, silica nanopores in porous rocks have hydrophobic or hydrophilic interactions. In all of these cases, the interaction between water and the nanotube atoms changes depending on its functionalization and composition, the dynamic behavior of water molecules will also be influenced. Despite the large number of studies on the water flow through CNTs, the water properties inside functionalized nanotubes are still not clear. Simple models that incorporate the details of nanotube functionalization may enable important progress in the overall understanding of fluid flow through nanopipes.

For instance, Hummer et al. have shown that very small changes in the water–carbon interaction can have an impact on whether water enters a CNT or not. Melillo also demonstrated, by varying the interaction strength, that the hydrophilicity of nanotubes is the key factor for water occupancy and can determine their structure and dynamics. The water shear viscosity has been revealed as being very sensitive to the nanoscale confinement. Moreover, the connection between water dynamics and the structure of the confined water still remains an open subject, the answer to which may require deeper physical–chemical insights.

In this work we are interested in studying the transport behavior of water inside hydrophilic and hydrophobic nanotubes. Our focus is on nanopores with radii large enough to accommodate more than a single file of water, and we study water at distinct densities. In this way, we perform molecular dynamics (MD) simulations of TIP4P/2005 water confined inside (10,10), (16,16) and (30,30) nanotubes. The interaction strength between water molecules and the wall material of the pore, characterized by the Lennard-Jones potential well depth, was tuned to represent hydrophobic and hydrophilic behavior. The paper is organized as follows. In Section 2, the computational details and the methods are described, and in Section 3 the main results of the dynamic and structural properties of the confined water are discussed. Conclusions are presented in Section 4.
2 Computational details and methods

2.1 Water and nanotube models

Molecular dynamics were performed using the LAMMPS package\textsuperscript{10} for simulations of TIP4P/2005 water\textsuperscript{29} confined inside nanotubes. The nanotube atoms are arranged on a honeycomb lattice. Two atom types that differ only in their Lennard–Jones (LJ) parameters of interaction with water were used. They correspond to sp\textsuperscript{2}-hybridized carbon with \( \varepsilon_{\text{CO}} = 0.478\ \text{kJ mol}^{-1}\) and \( \sigma_{\text{CO}} = 0.328\ \text{nm}\) (labeled hydrophilic due to its water attractive character) and reduced carbon–water interaction strength with \( \varepsilon_{\text{CO}} = 0.27\ \text{kJ mol}^{-1}\) and \( \sigma_{\text{CO}} = 0.341\) (namely hydrophobic), as done in previous works.\textsuperscript{11,23,31,32} We considered \((n,n)\) nanotubes, with \( n = 10, 16, \) and 30. The choice of TIP4P/2005 over many other models available in the literature was due to its accuracy in calculating transport properties of water under ambient conditions.\textsuperscript{29,33} We found the bulk viscosity to be 0.83 mPa s, and the diffusion coefficient was found to be 2.32 \( \times 10^7\ \text{m}^2\ \text{s}^{-1}\), in good agreement with previous studies.\textsuperscript{34–37}

Periodic boundary conditions were applied to simulate isolated infinite nanotubes. Cutoff distances for LJ and coulomb interactions are 1.0 and 1.2 nm, respectively. Long-range coulomb interactions were handled using the particle–particle particle–mesh method.\textsuperscript{38} The simulations were conducted in the NVT ensemble at a temperature of 300 K fixed by a Nosé–Hoover thermostat.\textsuperscript{29,40} The system was equilibrated with a 15 ns simulation, followed by 15 ns of data accumulation. The timestep is 1 fs. In all simulations the geometry of water molecules was constrained by the SHAKE algorithm.\textsuperscript{41} For simplicity, the positions of the carbon atoms are fixed, i.e., not integrated. For each data point five independent simulations were carried out for average and standard deviation computation.

2.2 Simulation details

In order to properly evaluate the water density inside the nanotube, we define the effective diameter \( d_{\text{eff}} = d - \sigma_{\text{CO}} \), where \( d \) is the nominal diameter and \( \sigma_{\text{CO}} \) is the Lennard–Jones (LJ) parameter for the carbon–oxygen interaction. In terms of \( d_{\text{eff}} \), the effective density is then given by

\[
\rho_{\text{eff}} = \frac{M}{\pi \cdot \ell \cdot (d_{\text{eff}})^2},
\]

where \( M \) is the total water mass in the pore and \( \ell \) is the nanotube length. Fig. 1(a) shows a schematic depiction of the nominal and effective diameters of nanotube samples, while Fig. 1(b)–(d) shows the frontal view of the \((10,10), (16,16)\) and \((30,30)\) nanotubes, respectively, filled with water molecules.

We studied the dynamical and structural properties of water inside nanotubes with \( \rho_{\text{eff}} \) varying from 0.8 to 1.4 g cm\textsuperscript{-3}. In Table 1 the nanotube dimensions as well as the water filling details are presented.

2.3 Green–Kubo relations for shear viscosity

Thermal transport coefficients represent some of the most important properties of liquids. The large statistical uncertainties that accompany transport coefficient calculations and the long computational time necessary to reasonably reproduce the experimental results have been an obstacle for such simulations with liquids, especially in confinement. The most common method for calculating the shear viscosity \( \eta \) involves the Green–Kubo (G–K) relations:\textsuperscript{44}

\[
\eta = \frac{V}{k_B T} \int_0^\infty \! dt \langle P_{xy}(t) P_{xy}(0) \rangle,
\]

\[
P_{ab} = \frac{1}{V} \sum_{i=1}^N \sum_{j=1}^N \frac{p_{ai} p_{bj}}{m} + \sum_{i=1}^N \sum_{j>1} r_{ij} f_{ai} f_{bj},
\]

where \( P_{ab} \) is the stress tensor, \( r_{ij} = |\vec{r}_i - \vec{r}_j|, f_{ij} = -\partial U(\vec{r}_j)/\partial \vec{r}_i \) denotes Cartesian components. The stress tensor can be calculated inside the force calculation subroutine.

Viscosity is a collective property of the whole sample rather than of the individual molecules, so it cannot be calculated with the same accuracy as the diffusion coefficient. For a homogeneous fluid, the statistical error could be reduced by averaging over all the viscosity components. But the nanconfinement (in our case, in \( x \) and \( y \) directions) hinders the glide of molecular layers, a necessary requirement for a shearing flow.\textsuperscript{45} To analyze the behavior of these components, we consider the radial viscosity (coming from \( P_{xy} \) and \( P_{xz} \)) and the axial viscosity (from \( P_{yz} \)), which are related to the shear in the radial and axial directions, respectively. In nanotubes, due to the confinement in \( x \) and \( y \) directions, the radial components are shown to be almost zero,\textsuperscript{46} while the axial component is shown to decrease.

Fig. 1  (a) Definition of \( d_{\text{eff}} \) and \( d \). Frontal view of a (b) (10,10), (c) (16,16) and (d) (30,30) nanotube filled with water.
with the decrease of the nanotube diameter.\(^4^2\) In particular, the viscosity dramatically decreases in very narrow tubes.\(^4^7,4^8\) In fact, in very small-sized pores the radial components do not make sense, as the space is dimensionally restricted and the molecules hardly move in the \(x-y\) direction. The axial component, however, is the only sensible definition due to the obvious displacement, and the consequent shearing flow, in the axial direction. Therefore, in this work, the axial component \(P_{yy}\) was averaged to describe the viscosity of the fluids inside the nanopores. We have collected the stress tensor components at each timestep, in order to ensure maximum accuracy, with the upper limit of 40 ps. Following this, the converged auto-correlation functions (ACF) were integrated, as shown in Fig. 3.

### 2.4 Diffusion coefficient

The diffusion mechanism of a fluid can be analyzed by the scaling behavior between the mean squared displacement (MSD) and time:\(^4^4\)

\[
\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle \propto D t^z
\]

where \(\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle\) is referred as the MSD, 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 \(t\) and \(D\) stands for the diffusion coefficient. The \(z\) exponent refers to the diffusion regime: \(z = 1\) for the linear Fickian diffusion, \(z > 1\) for superdiffusive and \(z < 1\) for subdiffusive regime. In the bulk phase, the water molecules diffuse as the Fickian type while for the water confined in CNTs, the diffusion behavior becomes extraordinary due to the nanoscale confinement.\(^4^9\) An alternative method for computing the diffusion coefficient involves the integration of the velocity auto-correlation functions (VACF); however, the Einstein relation, presented above, significantly reduces the computational time necessary for convergence.

As in the case of the viscosity calculations, the statistical error in the diffusion measurements could be reduced by averaging over all the MSD components. But the nanopore confinement in the \(x\) and \(y\) directions hinders the radial displacement of the molecules.\(^5^1\) Therefore, the radial MSD is almost zero for all cases studied here and only the axial MSD will be considered. This component has been computed in the last 15 ns of simulation, and the diffusion \(D\) was obtained by a linear fit of MSD versus \(t\).

### 3 Results and discussion

#### 3.1 Stress tensor auto-correlation function

We have calculated water viscosity trough the equilibrium G–K relations. In this method, the main contribution comes from the tail of the stress tensor auto-correlation function (ACF), but an accurate computation of the shear viscosity also requires a precise calculation of the short time ACF. Fig. 2 shows the normalized ACFs of the non-diagonal components of the pressure tensor for confined water at 300 K. Five independent runs for each system were implemented in order to increase the statistics. We can notice two decay regimes, one for short times (fast scale), and another for higher times (slow scale of time). For each case, the fast scale part is monotonically decreasing, with an ACF decay faster than \(1/t\). On the other hand, at larger times the ACF oscillates slowly while decreasing, except for the higher density case of water confined inside \((10,10)\) hydrophobic nanotubes, that presents a large oscillation decrease with time. This behavior will, in turn, lead to several consequences related to the viscosity determination, as will be discussed throughout the paper.

A careful analysis of the case of SPC/E water model in bulk was made by Guo and Zhang.\(^5^0\) Their results showed that the G–K relation leads to reliable results using an upper limit of the order of 3 ps in the integral of eqn (2). However, as Fig. 2 shows, depending on the water density for confined water, the calculations could require a higher correlation time. Particularly, for \(\rho_{eff} > 1.2 \text{ g cm}^{-3}\) the ACF goes to zero only for correlation times higher than 10 ps. Density is not the only variable which leads to the requirement for higher integration times. When calculating viscosity for bulk water at different pressure conditions, Gonzalez and Abascal\(^5^5\) also used higher time values for the integral of the ACFs. This indicates that thermodynamic parameters play an important role in the ACF calculations and,
consequently, on the precise determination of transport properties. We can also say that as the nanotube diameter increases the time required to the ACF convergence is shortened. It means that the confinement level is another important factor in calculating viscosity and should be handled carefully.

For the whole set of curves, the ACF is smaller as the density decreases, mainly in the fast time scale, with important contributions to the ACF integral. For all cases, as the density is increased the peaks become more pronounced and the oscillations are more persistent. We can also notice that as the nanotube diameter is decreased (higher confinement), the effect of density is enhanced, leading to larger oscillations for higher densities in the smaller (10,10) nanotube. The stressed situation in which more water molecules are enclosed in the nanopore leads to longer correlation between the stress components, and this is enhanced by the confinement level.

Regarding the water–wall interaction, the ACF of the water confined in hydrophobic nanotube is close to the hydrophilic case for the larger nanotubes. Only for the smaller (10,10) nanotube, the difference is enhanced at the higher density, $\rho_{\text{eff}} \sim 1.2 \text{ g cm}^{-3}$, and the hydrophobic confinement leads to a completely different behavior compared to the hydrophilic, leading the ACF to reach the convergence at times higher than 10 ps.

### 3.2 Shear viscosity of nanoconfined water

Fig. 3 shows the running values of the viscosities obtained by the integration of the normalized ACFs displayed in Fig. 2, for both water densities and for the hydrophilic and hydrophobic nanotubes. The upper limit in the integration to calculate the final values of viscosity is taken at the beginning of the plateau shown in Fig. 3(a)–(f). Despite the noise imposed by the hard convergence of the ACF tail, we can notice the convergence of the running viscosities at larger correlation times ($\sim 10–20$ ps). This time is higher than the reported for bulk water ($\sim 1–5$ ps).

When confined in nanopores, water experiences an additional shear component with the wall, which is expected to play a significant role in the viscosity prediction. Besides this, since we compute only the axial component of the viscosity, the statistical accuracy is affected and longer simulations are required to achieve the equilibrium condition necessary to the use of G–K relations. All the panels in Fig. 3 shows that the convergence is clearly affected by the density: higher is the density, larger correlation times are required. In fact, as the number of water molecules inside the pore is increased, the shear between water layers is increased, which in turn leads to a higher perturbation regime and longer simulations are necessary to obtain accurate values of viscosity.

### 3.3 The Stokes–Einstein relation

In the Fig. 4, we show the behavior of the viscosity, $\eta$, and of the diffusion coefficient, $D_z$, as a function of the density for (10,10), (16,16) and (30,30) hydrophobic and hydrophilic nanotubes. As discussed in the Section 2, the radial MSD is almost zero and only the axial diffusion $D_z$ is shown in Fig. 4(b), (d) and (f).

In principle, the Stokes–Einstein relation for translational diffusion from the kinetic theory

$$D = \frac{k_B T}{6\pi \eta \sigma^2},$$

has no grounds to be valid in confined systems. However, one could expect intuitively that the increase in the viscosity would imply a slowing down of the diffusion. The comparison

![Fig. 3 Viscosity, $\eta$, versus time for (a) and (b) (10,10), (c) and (d) (16,16) and (e) and (f) (30,30) nanotubes.](image)

![Fig. 4 Left panel: Viscosity, $\eta$, as a function of the density, effective density. Right panel: Axial diffusion $D_z$ as a function of density. Both panels are for (a) and (b) (10,10), (c) and (d) (16,16), and (e) and (f) (30,30) nanotubes.](image)
between the viscosity and the diffusion illustrated in Fig. 4 indicates that the Stokes–Einstein relation and the intuitive assumption that the diffusion decorrelates with the viscosity are valid for all the systems with the exception of the (10,10) hydrophobic nanotubes. This decorrelation have been observed in supercooled liquids confined water and methanol-diluted bulk water. Now, we extend the understanding of this decorrelation for distinct nanopores.

For the larger nanotube diameters, (16,16) and (30,30), whether the pore is hydrophobic or hydrophilic does not affect the water viscosity or diffusion, which is consistent with a previous analysis. However, for the narrow (10,10) nanotube, the viscosity shows an increase for hydrophobic nanotubes that is 4 times larger than in the hydrophilic case. This difference means that the shear between layers of water molecules is strongly dependent on the pore hydrophobicity, and this dependence is activated with increasing density. For this narrow tube, Fig. 4 also shows that the increase in the diffusion coefficient while it increases the viscosity of the system, violating the Stokes–Einstein relation.

In all the three nanotube diameters the viscosity changes its slope at densities between 1.1–1.2 g cm⁻³, as shown in Fig. 4. As we will see next, the mechanism behind this change of slope is related to the structure adopted by the water molecules inside the tubes.

3.4 Structure of nanoconfined water

The transport properties of fluids inside nanopores have a strong dependence on the molecules’ structure. The Fig. 5 illustrates the radial density profiles of the water molecules inside the hydrophobic (blue lines) and the hydrophilic nanotubes (red lines). Two densities were selected, one below the change of the slope in the viscosity and one above. Fig. 5 shows that the change in the increase of the viscosity with the density is connected to the change in the number of layers inside the tube. While for low densities one contact layer and a large central layer are formed, at high densities the system forms a number of layers. This transition between one central layer to many layers occurs at some point between \( \rho_{\text{eff}} \sim 1-1.2 \text{ g cm}^{-3} \), which coincides with the density of the change of slope in Fig. 4.

Fig. 5 also shows that, regardless of whether it is hydrophobic or hydrophilic, the smaller (10,10) nanotube leads to the formation of two concentric layers at higher densities. This change in the number of layers as the density increases results in very different effects in the viscosity and in the diffusion coefficient.

For the hydrophobic nanotube, illustrated in the Fig. 6(a), the water forms a disordered central layer which maximizes the number of hydrogen bonds already for a density that is not too high. This nonstructured layer allows for an increase in the viscosity. However, since the water–wall interaction is repulsive, the two layers move as a global structure and the diffusion coefficient is non-zero even for high densities. Therefore, the decoupling between the viscosity and the diffusion, as well as
the violation of the Stokes–Einstein relation for the hydrophobic (10,10) nanotube at high densities is related to the high connectivity of water inside this tube and to the unbinding of the molecules with the wall, which defines a viscous internal dynamics and the diffusion of the whole structure.

In the case of the hydrophilic nanotube, shown in Fig. 6(b), water forms two very ordered concentric tubes with the number of bonds increasing with the increase of the density, while the mobility decreases. Since the system exhibits only two well defined layers, the viscosity increases smoothly. The diffusion coefficient, in this case, has two dynamics. The central layer moves at distinct velocity than the contact layer. At high densities, the contact layer forms an ice-like structure and the overall mobility goes to zero.

4 Conclusions

In summary, we have calculated the viscosity and diffusion for water confined in nanotubes of different sizes. The interaction strength between water molecules and the wall material of the pore, characterized by the Lennard–Jones potential well depth, was tuned to represent the hydrophobic and hydrophilic behaviors. The viscosity calculations have been shown to depend on factors such as density, confinement size, and the water–wall interaction. A transition in the viscosity dependence with density has been found for both hydrophobic and hydrophilic nanotubes. Nevertheless, a dramatic increase in viscosity takes place for the narrow hydrophobic pore, reaching 4 times the viscosity of the hydrophilic case.

We have also identified a violation of the Stokes–Einstein relation for water confined in narrow hydrophobic nanotubes. Our findings show that the transport properties of water will only be affected by the wall properties inside narrow nanopores, where there is no space for a central liquid layer.

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