Simulation of TIP4P/2005 water confined in hydrophobic nanotubes

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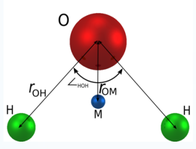
Abstract

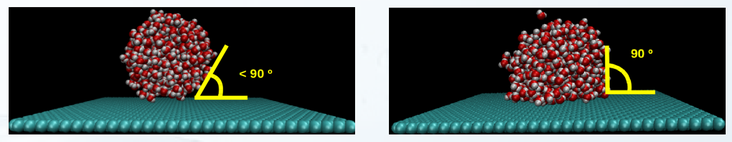
Water is the essential medium for life on our planet. In spite of being a simple molecule, water shows anomalous behavior and properties that are still unknown and are currently being under study. Under specific conditions of pressure and temperature, water suffer phase changes that lead to one of the most complex phase diagram known so far with more than 16 allotropic crystalline forms. Molecular simulation is a tool which allows us to study quantitatively the physics involved in these processes at a nanometric scale. To do that, water models have been developed [1,2] whose aim is to reproduce, as best as possible, water behavior in a wide range of pressure and temperature. In this work we study by means of simulations the transport properties (such as diffusion and viscosity) of confined water in hydrophobic nanotubes (1D) at different temperatures.The water confinement leads to new phase diagrams [3] that are currently under study. Moreover there is a great controversy in the bibliography about confinement, being not clear whether it favors [4-6] or slows down [7] water dynamics.

Water Model: TIP4P/2005[1]



r_{OH}(Å)	<HOH,deg	σ(Å)	ε/k	q(O)(e)	q(H)(e)	q(M)(e)	r_{OM}(Å)
0.9572	104.52	3.1589	93.2	0	0.5564	-2q(H)	0.1546

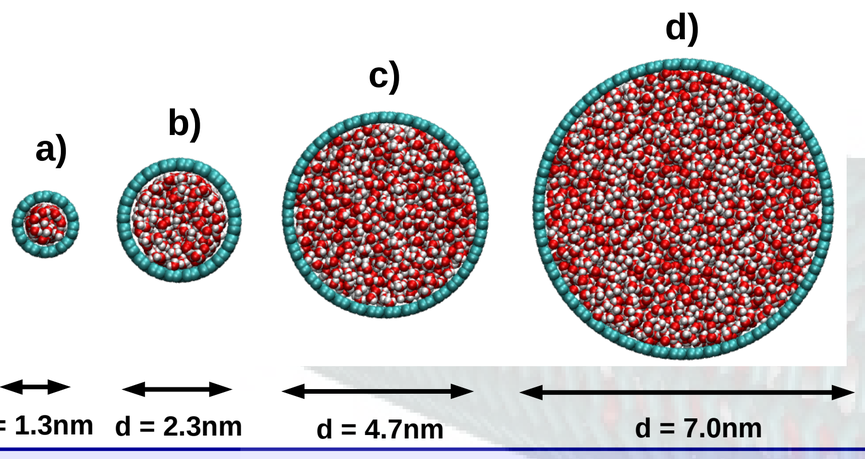
Tuning water-carbon interactions:



Previous results[8], show that a water droplet in contact to a graphene layer, forms a contact angle smaller than 90º meaning that graphene is slightly hydrophobic. Based on these results we tune carbon-water interaction.

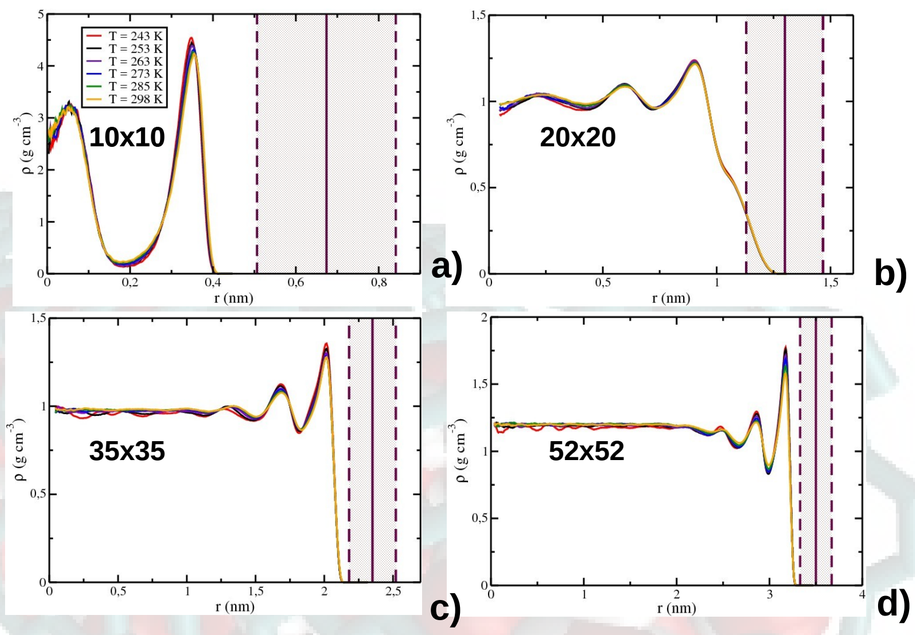
	Super-Hydrophobic	Hydrofobic
$\sigma_{O\text{-}C}$ (nm)	0.3349	0.3349
$\varepsilon_{O\text{-}C}$ (kJ/mol)	0.0476	0.2703

Systems under study:

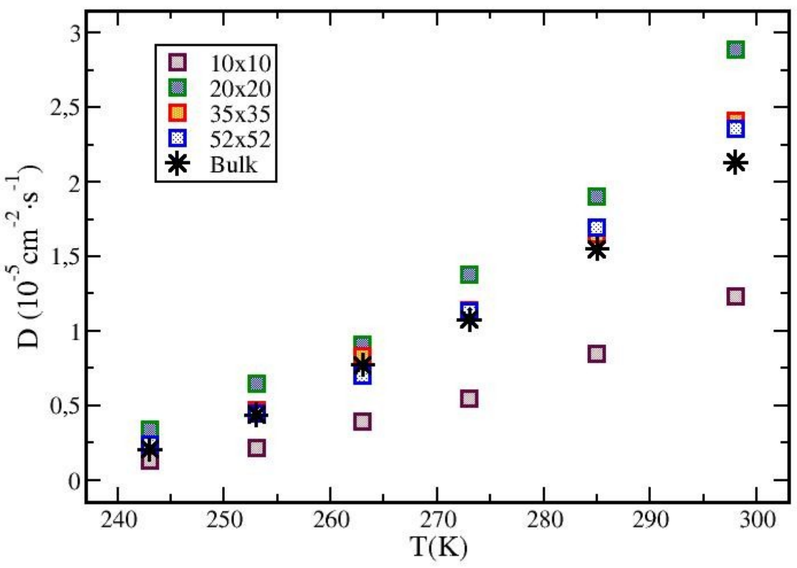


Systems under study: a) 10x10 nanotube with 141 molecules of water (N_w) , b) 20x20 nanotube where N_w = 640 , c) 35x35 nanotube with N_w = 2262 and d) 52x52 nanotube with 6407 molecules of water inside. In all cases **L** = 5 nm.

Density profiles:



Study of the Diffusion Coefficient



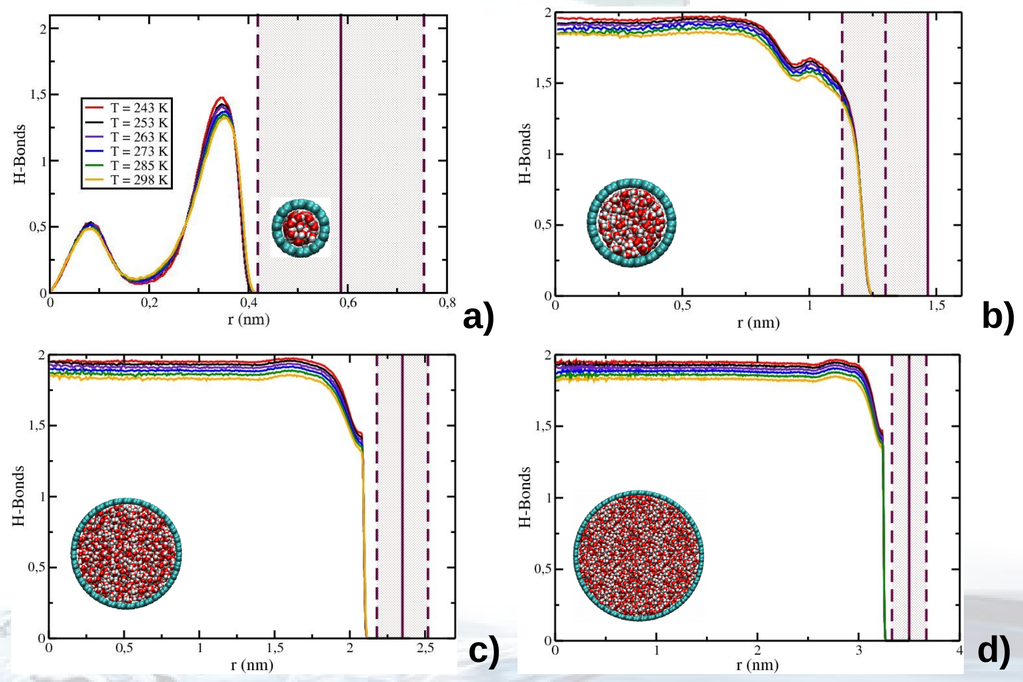
Water diffuses faster in Carbon Nanotubes but…

why?

Diffusion coefficient of water versus temperatrue for nanotubes 10x10 (brown squares), 20x20 (green squares), 35x35 (blue squares) and Bulk (black stars). It can be observed that for 20x20, 35x35 and 52x52 nanotubes water diffuses faster than Bulk at high temperatures. Due to the chain-like structures formed in nanotube 10x10 water diffuses slower than Bulk.

Study of the density profile and the Hydrogen bonds as a function of the temperature for : a) 10x10 nanotube, b) 20x20 Nanotube, c) 35x35 Nanotube and d) 52x52 nanotube. Dashed lines represent the nanotube wall. By means of these analysis we calculate the number of Hydrogen bonds dividing the nanotube in "cylindrical onion layers" starting from the center of the nanotube to its wall.

Study of the H-Bonds



Summary

By using Molecular Simulations, we have studied TIP4P/2005 water diffusion confined in hydrophobic Carbon nanotubes. The smallest nanotube studied was (nxn) = 10x10 with a diameter of 1.3 nm. This nanotube contains 141 molecules of water inside. Due to its small size, water tends to form structures which difficult the diffusion. The 20x20 nanotube with 640 molecules of water has a diameter of 2.3 nm. Water adopts bulk-like structure in this nanotube and the diffusion is the highest observed in this work. The 35x35 (d=4.7nm, N_W= 2262) and 52x52 nanotubes (d= 7.0 nm,N_W= 6407) have a very similar behavior being water diffusion faster than in bulk at higher temperatures. Hydrogen bonds study suggests that water molecules close to the nanotube wall form less Hydrogen Bonds than 1.8 (as observed in Bulk). These molecules seem to be responsible for the fact that water diffuses faster inside nanotubes making this difference higher when nanotube diameter decreases until reaches the 10x10 size which force water to adopt chain-like structure (making water to diffuse slower).

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