The Effect of Nanoconfinement on the Structural & Transport Properties of Water Under Equilibrium Conditions

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Background

Carbon nanotubes (CNTs) are comprised of 6 ringed carbon groups that form extremely strong bonds between each other into a tube shaped structure. They are a particularly interesting area of research since they have been known to demonstrate unique properties that cannot be observed on any other scale. Due to their size being ten thousand times smaller than a human hair, however, CNTs are difficult to manufacture, making it difficult to study their unique interactions. Consequently, most of the properties of carbon nanotubes are discovered through modeling and running simulations.

When interacting with water, CNTs have been known to induce higher water flux using lower amounts of energy than current membranes. This gives way for many practical uses of CNTs. One important potential use of these tubes is in water desalination plants. Due to an increase in flux, water is able to move through a semi-permeable membrane comprised of CNT's five times faster than traditional brackish water treatment plants.

Each water molecule's properties changes as it comes in contact with the CNT that alters it's behavior from what's normally seen. Most of the time, CNT are studied while exhibiting hydrophobic behavior. However, changing the polarity (the direction of the magnetic fields) can result in different effects on the dipole moment (the measurement of separation between two charges), number of permeations (the flow of water molecules through the CNT), and the number of molecules within the CNT at different time intervals.

Purpose

Determine how changing the size and non-bonded intermolecular interactions of a single-walled carbon nanotube (SWCNT) impacts the number of water molecules enclosed within, the number of permeations through its walls, and the average dipole moment along the length of the SWCNT with respect to the its longitudinal axis.

Hypothesis

If the diameter of the SWCNT nanotube increases, then the occupancy of water molecules enclosed within and the number of permeations would both increase while the average dipole moment along the length of the SWCNT with respect to the its longitudinal axis would remain relatively unaffected. However, if the non-bonded intermolecular interactions were to change (hydrophilic → hydrophobic SWCNT), then the occupancy of water molecules enclosed within and the number of permeation would both decrease while the average dipole moment along the length of the SWCNT with respect to its longitudinal axis would experience less fluctuation.

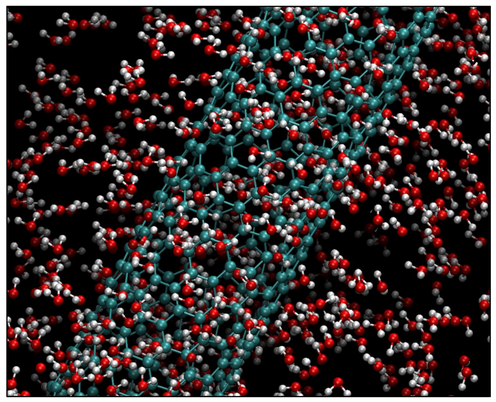


Figure 1. Partial VMD Representation Of SWCNT Submerged In TIP3P Water

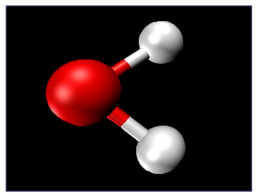


Figure 2. TIP3P Water Representation

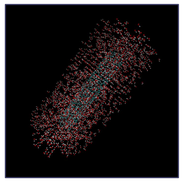


Figure 3. Full VMD Representation

Methods and Materials

1. Create three individual LAMMPS data files that each contain a SWCNT—chiral indexes of (3,6), (4,8), (5,10), length of 3 nanometers—immersed in water molecules with a density of 33.45 mol/nm^3
   - Contains information regarding bonds, angles, dihedrals, impropers
   - TIP3P Water Model
2. Create a LAMMPS input script that reads in the data file and outputs .dcd files at specified time intervals
   - Lennard-Jones Potential
   - Hydrophobic/Hydrophilic Interactions
3. Create a supercomputer job script that feeds the LAMMPS input script into LAMMPS
4. Run the supercomputer job script
5. Create Tcl scripts to log the number of water molecules within the nanotube, the number of longitudinal permeations, the associated average number of h-bonds per water molecule, and the dipole moment with respect to the longitudinal axis of the SWCNT.
6. Load the Tcl scripts into VMD and analyze the results

Supercomputer (Hercules) provided by the McCormick School of Engineering at Northwestern University

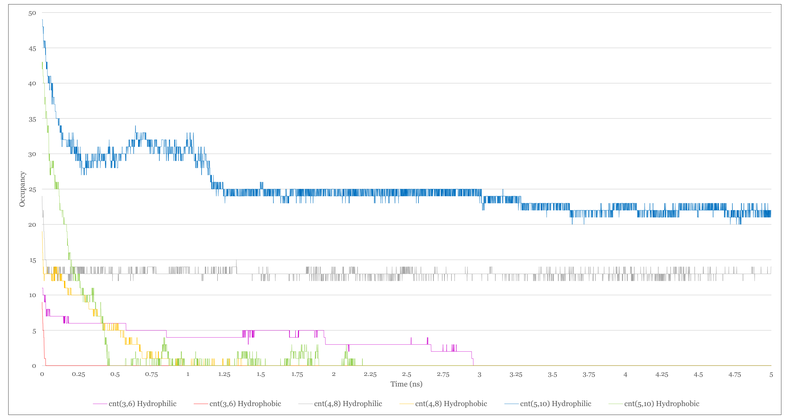


Figure 4. Effect Of Diameter on the Water Occupancy of Carbon Nanotubes

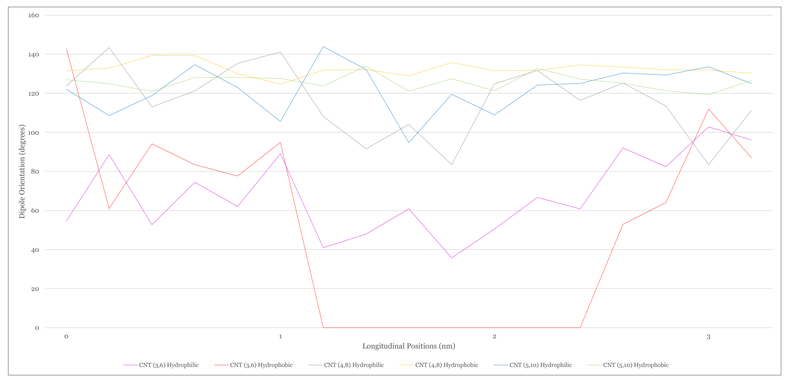
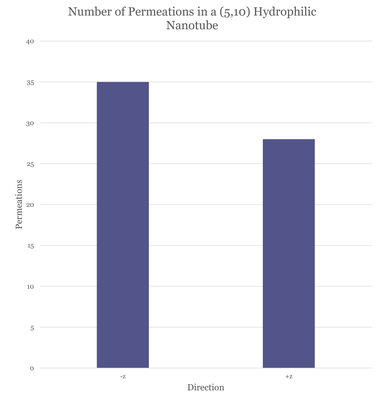
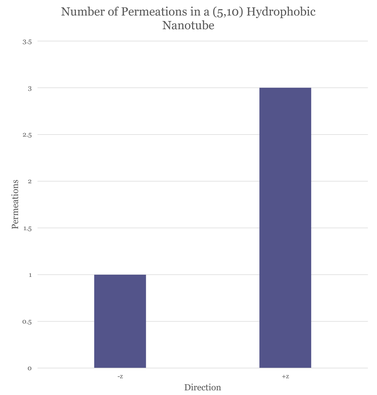


Figure 5. Effect of Non-Bonded Intermolecular Interactions on the Dipole Moment of Carbon Nanotubes





Discussion

The results obtained from the simulation regarding the impact of the changing the diameter and non-bonded intermolecular forces of a SWCNT supported the hypothesis that 1) As the diameter of the SWCNT increases, the water occupancy and the number of permeations would both increase, while the average dipole moment along the length of the SWCNT with respect to its longitudinal axis would remain relatively unaffected, and 2) As the non-bonded intermolecular forces change from being hydrophilic to hydrophobic, the occupancy of water molecules enclosed within and the number of permeations would both decrease while the average dipole moment along the length of the SWCNT with respect to its longitudinal axis would experience less fluctuation.

The maximum occupancy of the (5,10,3) SWCNT—forty-nine water molecules—was greater than the maximum occupancy of both the (3,6) SWCNT—eleven water molecules—and the (4,8) SWCNT—twenty-four water molecules. Under normal circumstances, there would have been roughly 84 water molecules occupying the space in which the (5,10) SWCNT was positioned, and the (5,10,3) SWCNT can fit a maximum of roughly ninety-seven water molecules. There were 0 permeations through both the +z and –z axis of the (3,6) and (4,8) SWCNTs, however, for the (5,10) SWCNT, there were thirty-five permeations through the –z axis and twenty-eight permeations through the +z axis when the SWCNT was hydrophilic, and one permeation through the –z axis and three permeations through the +z axis when the SWCNT was hydrophobic.

When the LJ Potential values were adjusted for the SWCNT to be more hydrophobic, the occupancy of all of the SWCNTs experienced a drastic dip. By the conclusion of three nanoseconds, the number of water molecules in the (3,6), (4,8) and (5,10) SWCNTs had all dropped to zero, and remained relatively similar for the rest of the simulation. Regarding the dipole moment, with the sole exception of the (3,6) SWCNT, the change from hydrophilic to hydrophobic resulted in less variation regarding the average dipole moment along the tube with respect to it longitudinal axis. The (3,6) SWCNT was likely an anomaly simply because the narrow width of the tube, combined with the hydrophobic nature, didn't facilitate the ability for any water molecules to flow through the tube, but rather ejected them immediately. Consequently, the dipole moment along those distances would be zero.

Future simulation analysis of the various properties regarding SWCNT's will provide a better understanding regarding the effects of outside stimulation on its transport properties. Some potential examples include extremities in relation to the Lennard-Jones Potential, length, temperature, as well as electric and magnetic fields.

Supercomputer Specifications

- Twenty-three nodes (one server node, twenty-two computer nodes)
- Each node is equipped with a two quad-core 2.0 GHz E5335 Xeon processors and 16 GB of RAM
- Roughly 14 TB of storage
- Runs on an Ubuntu 8.04 server

Acknowledgments & References

The supercomputer (Hercules) was provided by the McCormick School of Engineering at Northwestern University. Documentation can be found at: https://sites.google.com/site/herculeswiki/

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