WATER ORDERING BY CONFINEMENT IN CARBON NANOTUBES AT 300K:

Implications for possible design of proton-conducting nano-semiconductors

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SUMMARY

In considering charge carriers for nanoscale semiconductors, electrons have the disadvantage of tunneling distances of nanometers, rendering distinction between "on" and "off" states problematic. Protons in water, on the other hand, tunnel between adjacent water molecules over the length of just a few Ångstroms. Using classical molecular dynamics simulations, we have observed ordering of water molecules at 300 K inside unmodified carbon nanotubes, providing pathways along which protons might be able to tunnel. In this ordered state the water was computed to have translational and rotational mobilities substantially reduced from those for bulk water. Our results suggest that proton conduction be considered further a possible conduction mechanism for use in nanoscale semiconductors.

Keywords: proton conduction, ordering transition, hexagonal ice, molecular dynamics simulation, biosensors.

1 BACKGROUND

The notion of carbon nanotubes as containers has existed since their discovery[1]. Several research groups over the years have succeeded in filling these containers with metal atoms. Recent experimental and theoretical work, on the other hand, has considered water as a possibility. The entry of water was suggested experimentally by the fact that the fluorescence of nanotubes is affected by the pH of external medium [2]. It was also suggested by previous molecular dynamics (MD) simulations [3,4]. Below we describe results from MD simulations in which we observe the formation of a hexagonal ice-like state at 300 K in a nanotube of critical diameter.

The simulation systems we considered consisted of single-walled, open-ended carbon nanotubes ca. 40 Å long and of various diameters, embedded in a hydrophobic slab and bathed in SPC/E water. The simulations were performed with the GROMACS simulation package using particle-mesh Ewald sums for the electrostatic interactions with the ffG50a1 parameter set describing the Lennard-Jones interactions.

2 RESULTS

Figure 1 shows representative snapshots of the disposition of the water after each system was equilibrated at 300 K. Observed here was a single-filing of the water in the narrow tube (similar to that previously observed [3]). In the widest nanotube, water is disordered in a fashion similar to bulk water. However, in a nanotube of a "critical" diameter, the water is seen to have anomalously ordered into a regular array. A magnified view of the water in this critical system reveals an ordering that is somewhat similar to that viewed along the *c*-axis of hexagonal ice.

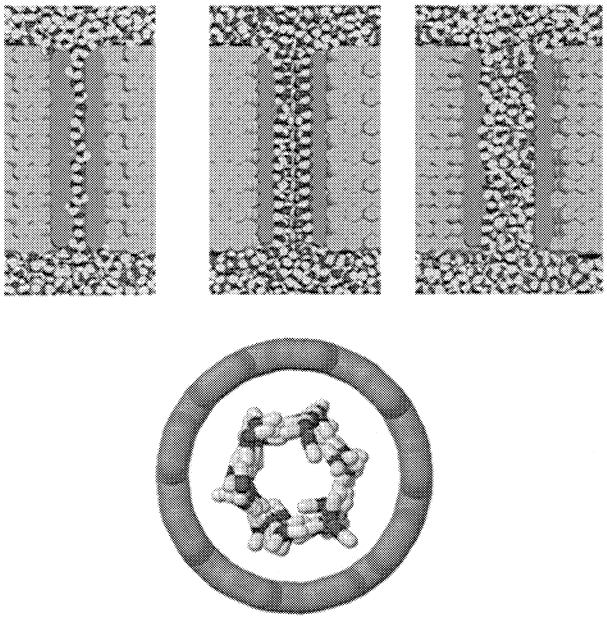

Figure 1: Snapshots from molecular dynamics simulations of water in nanotubes. (*Top series*) Slices taken at a depth of half way through the nanotubes for diameters (left to right) of 3.1, 8.6, and 18.1 Å. [Colors: slab, medium gray; nanotube, dark gray; water, the "I"-shaped region where the light and dark areas represent hydrogen and oxygen, respectively.] (*Bottom*) Magnified cross-section of the 8.6-Å diameter nanotube, showing hexagonal ice-like geometry of the confined water molecules.

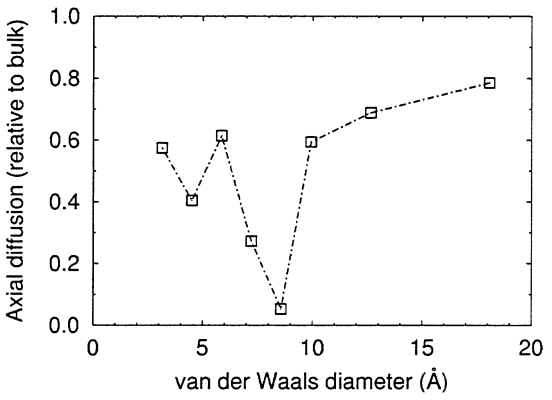

Figure 2. Axial diffusion coefficient vs. nanotube diameter for water in nanotubes at 300 K. The 8.6-Å diameter nanotube is the nanotube of critical size.

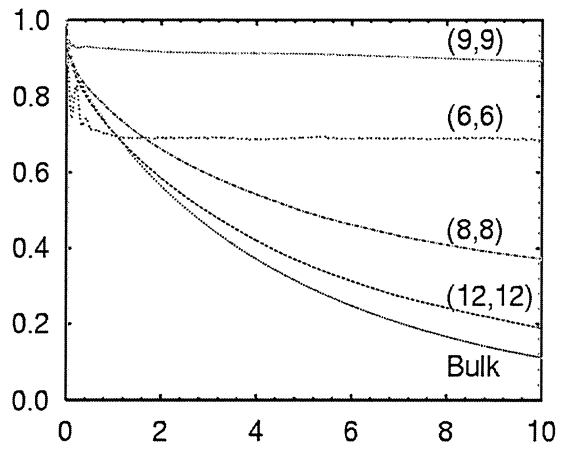

Figure 3. Normalized dipole moment vector autocorrelation function (vertical axis) vs. time lag in ps (horizontal axis) for water inside the nanotubes of various diameters, given here in terms of their graphene lattice vectors. The "critical" diameter nanotube, whose water demonstrates ice-like behavior, corresponds to the (9,9) nanotube.

Diffusion coefficients for the water inside the nanotubes as a function of nanotube diameter were derived from the mean-square distance (MSD) traversed by the center of masses of individual water molecules over the time, used in conjuction with Einstein's relation. The results in Fig. 2 (normalized to the bulk water value) show that the water diffusion coefficient inside the tubes is somewhat reduced from the bulk value in all sizes of nanotubes, with an anomalous reduction at a diameter of 8.6 Å (corresponding to the (9,9) nanotube) where the longitudinal motion is effectively eliminated.

Rotational autocorrelation functions for the water was computed for the same data. The autocorrelation function $C(t)$ for the dipole moments $\mathbf{p}_i$ of individual water molecules is $C(t) = \langle \mathbf{p}_i(0) \cdot \mathbf{p}_i(t) \rangle / \langle p^2 \rangle$, where the angle brackets denote averages over time t and molecules and p is the magnitude of the dipole moment (2.35 Debye). Figure 3 shows that the water rotational dynamics for these tubes also tends to be lowered from the bulk behavior. The behavior inside the nanotube of critical size is again seen to be anomalous.

3 CONCLUSION

We conclude that water confined inside nanotubes can generally display behavior different from that seen in bulk solvent. Confinement of water as seen here tends to reduce the flow of molecules through the nanotubes while also limiting rotational dynamics. This behavior becomes anomalously low for water in nanotubes of a "critical" diameter, in which the water symmetry bears resemblance to hexagonal ice even at temperatures of 300 K.

These results suggest that proton conduction may provide a possible mechanism for nanoscale semiconductors. Based on the present work, a device like this might operate by being "on" in the water-ordered state and turned "off" by a perturbation that disorders the water, dramatically reducing proton mobility.

4 ACKNOWLEDGMENT

Work on this project was supported by grants from the National Science Foundation, the National Institutes of Health, the Defense Advanced Research Projects Agency, and by a computer time grant from the National Center for Supercomputing Applications.

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