Molecular Dynamics Simulations of Fullerenes and Carbon Nanotubes in Water

R. L. Jaffe
NASA Ames Research Center
Moffett Field, CA 94035

J. H. Walther, E. Kotsalis, T. Werder and P. Koumoutsakos
Institute for Computational Sciences
ETH Zentrum
Zurich, Switzerland

T. Halicioglu
ELORET, Inc. 690 W. Fremont Ave.
Sunnyvale, CA 94087

Recently carbon nanotube probes and functionalized fullerenes have been proposed for biomedical applications. Nanotubes are attractive candidates for biosensors owing to their mechanical and electronic properties and chemical inertness. Fullerenes can be used as drug delivery agents and sensors because they are readily functionalized and generally do not trigger response from the body's immune system. For these biomedical applications the modified nanotube and fullerene probes must operate in liquid water or in aqueous solutions. In this presentation we discuss the use of molecular dynamics (MD) simulations to characterize the interactions of single walled nanotubes (SWNT) and C_{60} molecules with liquid water and aqueous salt solutions.

We have characterized structure and properties of ensembles of 1, 2 and 16 nanotubes with chirality (16,0) and diameter 12.5 Å, and 1 and 2 C_{60} molecules in water and in NaCl and KCl solutions (initial results have been published in (1)). We have also studied the characteristics of water droplets inside larger-diameter SWNTs(2). Over 12000 water molecules are included in the largest calculations. The MD simulations were carried out on serial and parallel computer systems and subject to periodic boundary conditions using the computer code FASTTUBE written at ETH. The water is modeled using a flexible SPC potential and the carbon-carbon and carbon-water interactions are modeled using a new potential described in (1).

The strength carbon-water interaction potential has been calibrated to match quantum chemistry calculations and also adjusted so results of MD simulations of water droplets on graphite surfaces match experimental data. The extension of the potential energy model to include Na^+, K^+ and Cl^- has been based on the results of quantum chemistry calculations.

The water-nanotube (or fullerene) interface is characteristic of a hydrophobic interaction. The closest water molecules are 3.2-3.4 Å from the carbon surface and the dipole moments of the interfacial waters are oriented parallel to that surface. A value of 127 ± 25 dynes/cm is obtained for the surface energy of the water at the interface (for comparison the surface energy for the water liquid-vapor interface is 124 in our simulations). Thus the effect of surface curvature of the nanotube or fullerene is small.

Simulations of two nanotubes or C_{60} molecules in water display a drying transition. In these calculations the nanotubes are initially positioned 10-15 Å apart with parallel axes as shown in Figure 1. During the calculation the thin layer of water between the nanotubes is expelled and the tubes end up approximately 3.3 Å apart (figure 2). This drying transition has been fully characterized by analysis of MD trajectories and calculation of the potential of mean force. It has also been observed in a simulation of 16 nanotubes starting from a 4x4 array and ending in the formation of a nanotube rope.

Similar simulations have been carried out for aqueous NaCl and KCl solutions to determine the effect of ionic impurities on the water-carbon interface and the hydrophobic interactions observed for pure water.

References
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2. T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, F. Noca and P. Koumoutsakos, Nano Letters 2001, 1, 697.

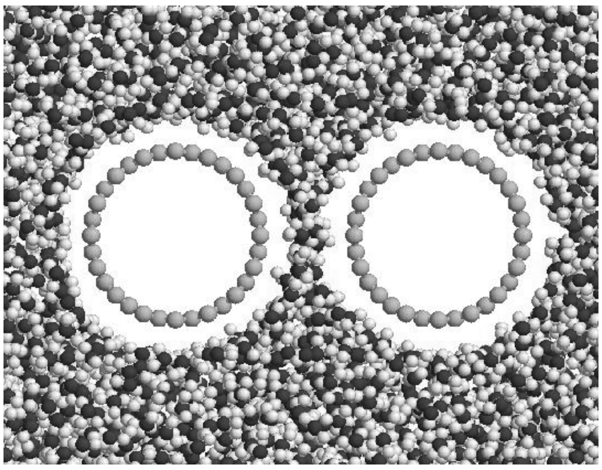

Figure 1. Cross section of simulation cell for two nanotubes in water: initial configuration (before drying).

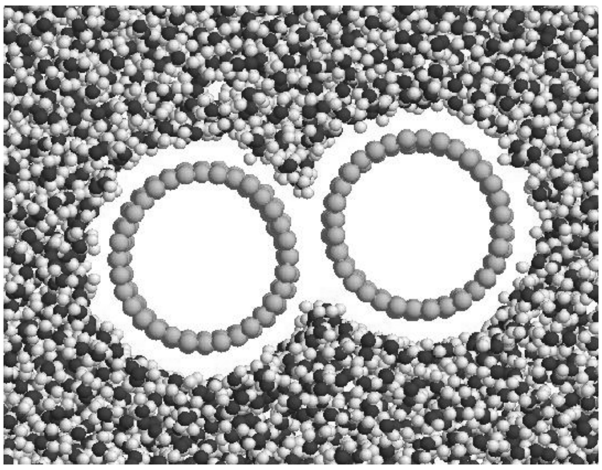

Figure 2. Cross section of simulation cell for two nanotubes in water: final configuration (after drying transition).