diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Diffusion of Water Molecules in Narrow Carbon Nanotubes and Nanorings

Biswaroop Mukherjee, Prabal K. Maiti, Chandan Dasgupta, A. K. Sood
Department of Physics, Indian Institute of Science, Bangalore 560 012, India.
cdgupta@physics.iisc.ernet.in

Introduction: It is known that fluids confined in nanometric spaces behave very differently from their bulk counterpart [1]. Lately, the process of transport of confined water through narrow channels has attracted a lot of attention, since knowledge of these processes is important in understanding transport through ion channels [2]. Numerical studies by Lee *et al.* [3] and Mao *et al.* [4] of the diffusion of oxygen and methane molecules, respectively, through narrow carbon nanotubes suggest the occurrence of single file diffusion. However in all these simulations, the time over which the mean squared displacement (MSD) is measured is rather short (100-500 ps). Additionally, due to finite size effects (the consequences of which are elucidated in the present work), it is difficult to draw a firm conclusion about the true nature of diffusion of these molecules inside the nanotube. The goal of our study is to develop a better understanding of the nature of diffusion of water molecules in narrow carbon nanotubes.

Results: We have used [5] extensive atomistic molecular dynamics (MD) simulations to study the structure and dynamics of water molecules in narrow carbon nanotubes immersed in a bath of water [6], and in isolated carbon nanorings. The diameters of the tubes and rings are chosen to be such that only a single file of water molecules is allowed inside. The water molecules inside the nanotube show solid-like positional ordering at room temperature, which we quantify by calculating the pair correlation function. This behavior is a consequence of the formation of strong hydrogen bonds between neighboring water molecules inside the nanotube.
Our studies show that even for the longest observation times, the mode of diffusion of the water molecules inside the nanotube is Fickian (normal) and not sub-diffusive. The MSD initially increases linearly with time and then saturates at long times (see Fig.1). This is a finite-size effect, arising from the fact that the MSD is measured only for the molecules inside the finite-sized open-ended nanotube. We propose a one-dimensional random walk model for the diffusion of the water molecules inside the nanotube. Two versions of the random walk model are considered, one in which the time is treated as a continuous variable, and another, in which time is discrete, since MD observations are made at discrete times. We find good agreement between the MSD calculated from both versions of the random walk model with that obtained from MD simulations, with the discrete version faring slightly better (Fig. 1). This confirms that water molecules undergo normal-mode diffusion inside the nanotube. We attribute this behavior to strong positional correlations that cause all the water molecules inside the nanotube to move collectively as a single object. We also measure the survival probability of the water molecules inside the nanotube from MD simulations and calculate it from the random walk models. There is good agreement between the simulation results with those obtained analytically from the random walk models.

These results suggest that single file diffusion in this type of systems can be observed only when the molecules inside the channel form several clusters. In order to achieve this, we have performed simulations of water molecules inside narrow carbon rings that are partially filled with water. At intermediate fillings (between 10 to 50 %), we find that the water molecules inside the ring form two oppositely polarized clusters, each containing about twenty molecules. These clusters behave as single "particles" because of the strong hydrogen bonding discussed above and they repel each other due to electrostatic interactions. In this situation and at even lower fillings where the confined molecules form a gas-like phase, we find evidence for the occurrence of single file diffusion with the MSD scaling as the square root of time (Fig. 2). Normal diffusion is found when the molecules inside the ring form a single cluster.

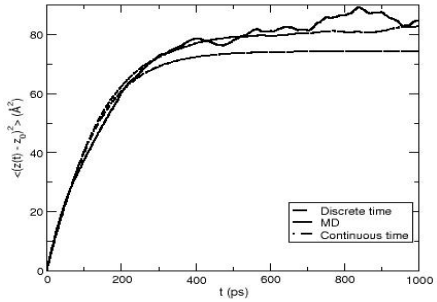

Fig.1. The MSD of water molecules inside a nanotube, from MD and random walk models.

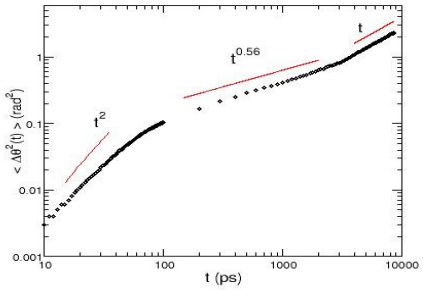

Fig.2. The MSD for bipolar water clusters inside a carbon nanoring.

Conclusions: Our results show that in order to observe single file diffusion (such as that observed, for example, in experiments [7] on confined colloidal particles) of water molecules in narrow carbon nanotubes and nanorings, the system parameters must be such that the confined molecules form several clusters. Normal (Fickian) diffusion is found when the confined water molecules form a single, tightly bound cluster due to the formation of hydrogen bonds.

References:

[1] R. Zangi, J. Phys. Condens. Matter 16 (2004) S5371.
[2] E. Tajkhorshid, P. Nollert, M. O. Jensen, L. J. W. Miercke, J. O'Connell, R. M. Stroud, K. Schulten, Science 296 (2002) 525.
[3] K. H. Lee, S. B. Sinnott, Nano Letters 5 (2005) 793.
[4] Z. Mao, S. B. Sinnott, J. Phys. Chem. B 104 (2000) 4618.
[5] B. Mukherjee, P. K. Maiti, C. Dasgupta, A. K. Sood, J. Chem. Phys. 126 (2007) 124704.
[6] G. Hummer, J. C. Rasaiah, J. P. Noworyta, Nature 414 (2001) 188.
[7] C. Lutz, M. Kollmann, C. Bechinger, Phys. Rev. Lett. 93 (2004) 026001.