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The Role of Hydrogen Bond in Mechanism of Water Diffusion in Carbon Nanotubes

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1. Introduction

There remains much dispute over the nature of water diffusion in carbon nanotubes. Striolo, using (8,8) single-walled carbon nanotubes (SWNT), advocates that long-lasting hydrogen bonds are responsible for the ballistic diffusion of water clusters in narrow carbon nanotubes. When the trajectories of confined water are studied at time scales in excess of 500 ps, a Fickian-type diffusion mechanism prevails [1]. Mukherjee et al. [2], on the other hand, argues that the time up to which the water molecules undergo single file diffusion (SFD) is shown to be the lifetime of the water molecules inside the water chains. By simulating water in a (6,6) carbon nanotube, he conclusively proves that the diffusion is Fickian when there is a single chain of water and SFD is observed only when two or more chains are present [2]. These works suggest that water molecules are in SFD in (6,6), but diffuse by a Fickian mechanism in (8,8) SWNTS, and so it is of interest to ask what factors influence the crossover from SFD to Fickian diffusion.

One might plausibly expect that the crossover for water molecules, unlike Argon or Xenon as previously studied [3], is probably not only a matter of geometry of the host and the size of guest molecules, but is also affected by hydrogen bonding. The hydrogen bond, which connects water molecules, restrains the water molecules from passing each other, thus leading to single-file diffusion over the lifetime of the bonds.

2. Methods

Molecular dynamics (MD) simulations were performed using the NAMD simulation package to investigate the diffusion mechanism of water confined in (n,n) SWNTs. A set of carbon nanotubes was prepared. Index n of 6, 7, 8, 9, 10 corresponds to the diameter of 0.812, 0.948, 1.08, 1.22 and 1.35 nm. The TIP3P potential model was used for water-water interactions. Simulations were run in The Stochastic NVT ensemble using a Langevin thermostat with damping coefficient of 1 ps^{-1}. The Stochastic NVT ensemble seems to be immune to the size effect and it is a reasonable way for studying diffusion mechanism according to several of our previous studies. The mean-squared displacement was measured in the axial direction of the nanotubes. Periodic boundary conditions were used in the axial direction of the nanotubes.

3. Results and Conclusion

Our results indicate that the diffusion mechanism of water confined in SWNTs is not only dependent on the tube diameter, but also on the hydrogen bonding. In (6,6) and (7,7) SWNTs, where only one water molecular layer can form, the MSDs are proportional to the square root of time, indicating SFD. However, for the (8,8) and (9,9) SWNTs, although there is enough space for a second water molecular layer to form, the molecules cannot pass each other due to the hydrogen bonds over the lifetime of the bonds, and water molecules still diffuse in SFD. Thus we conclude that hydrogen bonds play a key role in the diffusion mechanism of water confined in SWNTs, especially if there are two molecular layers. Even though the space is enough for two layers of water molecules to form, hydrogen bonds restrain the water molecules, so that there is a double layer single-file diffusion in (8,8) and (9,9) tubes for short times. These H-bond effects appear to be responsible for the controversy in the literature.
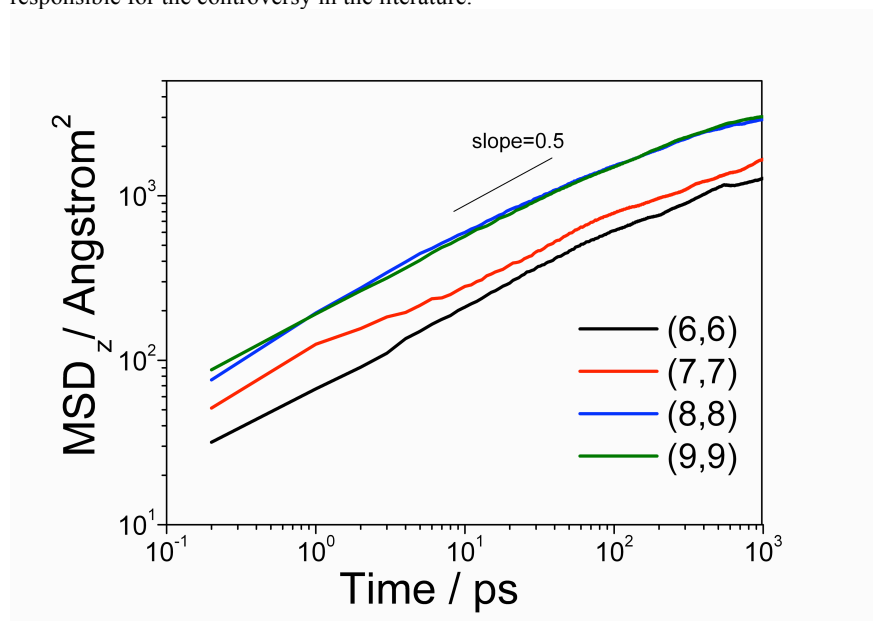
Fig. 1. Mean squared displacement with respect to the time of water confined in carbon nanotube.

References

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