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Structure of Water Molecules inside Nanotubes with Varying Hydrophobicity Using Molecular Dynamics Simulation

Daejoong Kim*, Artit Wangperawong** and Eric darve***

분자동역학 기법을 이용한 나노튜브의 소수성 또는 친수성에 의한 내부 물 분자의 구조 연구

김대중* · Artit Wangperawong** Eric Darve***

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Abstract

Nanotubes fabricated with diverse materials show different hydrophobic properties. The hydrophobic property is one of key properties for possible applications to ion channels due to their affinity. This study focuses on the structures of water molecules inside nanotubes with varying hydrophobicity using molecular dynamics simulation. Hydrophobicity here is determined by varying the attraction term in Lennard-Jones potential. The number of water molecules inside hydrophilic nanotubes increase, as expected, and their mobilities also increase. This trend is rather discrete with increasing number of water molecules and this discreteness is attributed to hydrogen bond. We plan to perform energy analysis to understand these structural results.

1. Introduction

Various types of nanotube have recently gained much attention from life science societies due to their affinity with ion channels in biological entities. As pointed out by Hummer et al. [1] and Noon et al. [2], the hydrophobic nature of carbon nanotubes elicits great interest in biomedical applications since proton-conducting pores are generally hydrophobic. In addition to potential applications of these novel materials as artificial ion channels, the physics behind the confinement effect on water transport inside nanotubes is of fundamental interest. Previous works [1-4] by other groups have also shown the existence of helical water structures inside narrow carbon nanotubes and seemingly abnormal water transport phenomena through them. Water transport through carbon nanotubes is also indebted to the interplay of lost hydrogen bonds and hydrophobicity. Based on this notion, hydrophobicity is one of important factors in modeling carbon nanotubes. We therefore hypothesized that varying hydrophobicity of nanotubes would result in great changes in water transport. The molecular dynamics (MD) simulation about carbon nanotubes solvated in water have been studied with different configuration and models [1-4]. Unfortunately, we have noticed that results vary from study to study. It is partly due to the lack of a reliable force-field for carbon nanotubes in water. In this study, we would like to see the change in transport phenomena due to fine tuning of force-field.

This study may also lead to a greater understanding of nanotubes of various materials, e.g. hydrophobic carbon nanotubes versus hydrophilic silica nanotubes. Other types of nanotube also have different degree of hydrophobicity, such as boron nitride nanotubes [5]. Our studies seek to contribute to a greater understanding of nanotubes of various sizes and hydrophobic properties as well as provide a basis for comparison between differing MD simulations.

* 서강대학교 기계공학과, daejoong@sogang.ac.kr
** Stanford University, Dept. of Mechanical Engineering, artitw@stanford.edu
*** Stanford University, Dept. of Mechanical Engineering, darve@stanford.edu

2. Computational details

The computation models include water molecules and nanotubes of varying hydrophobicity. Figure 1 shows a snapshot of one model case where water molecules are transported through a (6,6) nanotube with hydrophobicity comparable with that of carbon nanotubes.

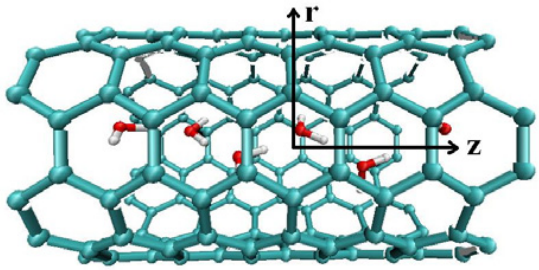

Figure 1 Snapshot of water molecules inside the (6,6) nanotube with hydrophobicity comparable with that of carbon nanotubes.

We simulate all the nanotubes as rigid structures where each atom was assigned the Lennar-Jones potentials. We varied the size of nanotubes between (6,6) and (11,11). We tuned hydrophobicity with the attraction term in the Lennard-Jones potential. We show contact angle change due to this tuning.

We used GROMACS package with the GROMOS-96 forcefield. The computational procedure is similar to that in reference 6.

3. Results and Discussion

3.1 Varying hydrophobicty tuned with Lennard-Jones potentials

We first show the contact angle variation against the tuning parameter κ (refer to the Lennard-Jones potential form: $V(r) = 4\varepsilon\left[(\sigma / r)^{12} - \kappa(\sigma / r)^{6}\right]$). For this, we used (18,18) nanotubes inside which water molecules behave similar to in the bulk [2]. We confirm that our approach of varying the Lennard-Jones potential to assimilate varying hydrophobicity works.

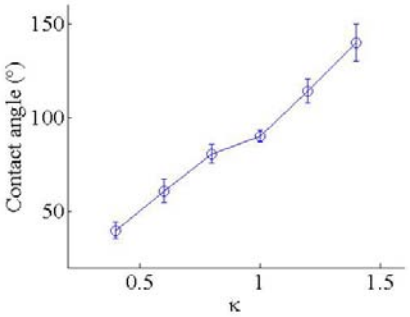

Figure 2 Contact angles against the tuning parameter in the Lennard-Jones potential.

3.2 Water transport with varying hydrophobicty

In Figure 3, we show the number of water molecules inside nanotubes of two sizes, (6,6) and (11,11), with varying hydrophobicity. As expected, its number increases with hydrophilicity. The increasing trend however is not monotonic but rather in a discrete fashion. For both sizes, water molecules are almost absent inside hydrophobic nanotubes with 40° and 61° contact angles. This is what was original expected for carbon nanotubes since graphene sheets were believed to be very hydrophobic. However, the number of water molecules suddenly changes from the nanotube with 61° contact angle to the nanotube with 81° contact angle. For (11,11) nanotubes, its number is below 5 for hydrophobic cases but becomes around 60 for 81° contact angle. We believe that this sudden change is attributed to single-file transport of water molecules, first noted by Hummer et al. [1]

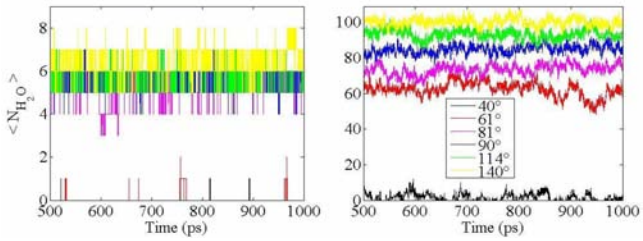

Figure 3 The number of water molecules inside (6,6) nanotubes (left) and (11,11) nanotubes (right) both with varying hydrophobicity.

Figure 4 shows water density profiles along the axis of (6,6) nanotubes with varying hydrophobicity. The distinct peaks correspond to the locations of water molecules. This is believe to be due to lost hydrogen bonds and hydrophobicity.

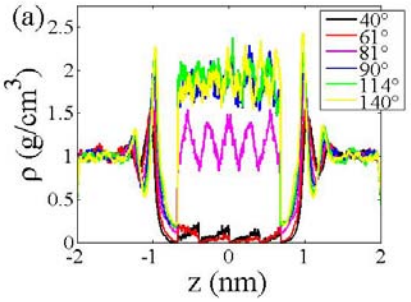

Figure 4 Water density profiles along the axis of nanotubes with varying hydrophobicity.

4. Conclusion

We report molecular dynamics simulation of water molecule transport through nanotubes with varying hydrophobicity. We found that the number of water molecules strongly depends on hydrophobic properties of nanotubes. We also found that water molecules have preferred locations inside nanotube.

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