Molecular Dynamics Simulation of Phase-Change of Water inside a SWNT

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The phase change of liquid water to ice crystal inside a single-walled carbon nanotube (SWNT) [1] was studied with the molecular dynamics method. Water molecules were modeled with SPC/E potential [2] and carbon-carbon interaction was expressed by Brenner potential [3]. The carbon-water interaction was expressed with the Lennard-Jones function with the quadrupole interaction term [4].

We have calculated a SWNT of 20 nm length with 192 water molecules inside. In the first 50 ps of the calculation, the whole system was set to 300 K using the velocity scaling method. After reaching the equilibrium, the carbon atoms were cooled at the constant heat-removal rate. The phase change phenomena with various rates of heat-removal in a SWNT with various chiralities were examined.

In order to investigate the effect of the cooling rate, the cooling rate was set as 2.5×10^{-9} W (Case 1: Slow Cooling) and 5.0×10^{-9} W (Case 2: Fast Cooling) for a fixed chirality SWNT of (10, 10). In both cases, the phase change was observed in the range of 200K-220K, and water molecules started to form the crystalline structure as shown in Fig. 1. For the case of slower cooling rate, ice crystal forms a hollow octagonal tube. On the other hand, there are many defects on the ice tube for the faster cooling case.

Then, we calculated for several host SWNTs with different chiralities. We used (8, 8), (9, 9), (11, 11), (3, 14) and (14, 3) SWNTs. Fig. 2 shows the ice crystal for armchair SWNTs with diameters of (a) 1.11 nm , (b) 1.25 nm, and (c) 1.52 nm. It turned out that for thinner SWNTs the ice crystal favored the hollow tube structure such as pentagonal and hexagonal depending on the diameter. On the other hand, for thicker nanotube the ice tube larger than octagonal structure was not obtained as in Fig. 2(c). Depending on the diameter of SWNT, the chiral water tube structure was also observed. The diameters of the (14, 3) and (3, 14) SWNTs are very close to that of (9, 9) tube. In these SWNTs, the ice tubes become hexagonal as for the case in (9, 9) tube. Hence, it is suggested that the ice tube structure formed inside a SWNT is determined only by the diameter of the diameter of the SWNT.

[1] Maniwa, Y., et al., *J. Phys. Soc. Jpn.*, **71** (2002), 2863. [2] Berendsen, H. J. C., et al., *J. Phys. Chem.*, **91**-24 (1987), 6269. [3] Brenner, D. W., *Phys. Rev. B*, **42** (1990) 9458. [4] Walther, J. H., et al., *J. Phys. Chem. B*, **105** (2001), 9980.

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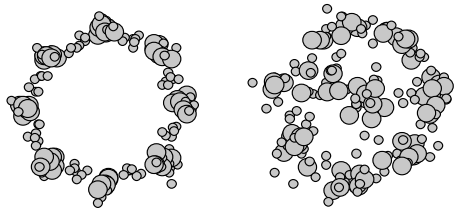
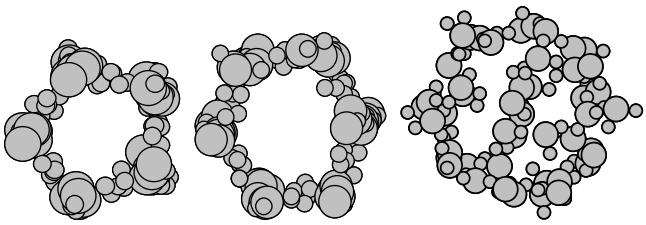


(a) Slower Cooling (b) Faster Cooling
Fig. 1 Effect of cooling rate



(a) (8,8) (b) (9,9) (c) (11,11)
Fig. 2 Effect of diameter of host SWNT