Temperature-dependence of wetting properties of carbon nanotubes

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HIGHLIGHTS

- By increasing the temperature, the rate of water imbibitions into CNTs improves as well.
- CNTs are more water-wet at higher temperatures.
- The wetting transition temperature for TIP3P water inside CNTs has been estimated.

ARTICLE INFO

ABSTRACT

We have carried out molecular dynamics simulations to study the spontaneous imbibition of water into a single-wall carbon nanotube (CNT) at various temperatures, ranging from 270 K to 370 K. The simulations indicate that by increasing the temperature, the rate of mass uptake improves as well. Considering the end-loss friction as the main source of energy dissipation and ignoring the inertial effect on the nano-scale transport, we derive a simple expression that relates the CNT's wettability to the fluid viscosity and the rate of imbibition over the temperature range that we study. Our results also indicate that the increase in the wettability of the CNT, and the reduction in the viscosity of water at higher temperatures cause enhancement of water uptake into the nanotube. They also enable us to estimate the wetting transition temperature for TIP3P model of water in the CNTs.

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1. Introduction

Understanding and controlling water transport in nanoscale materials, such as nanotubes, is currently a subject of considerable interest. The interest is mostly due to water nanochannels playing a key role in transport in biological cellular channels, water desalination and other selective transport processes [1–6]. Carbon nanotubes (CNTs) are considered a good system for the study of water transport at nanoscale. Due to the many unusual properties of the CNTs, such as ultra-smooth nonpolar surfaces and nano-scale diameter, they are also a good system as a generic non-polar pore [1,7]. They are also a potential candidate for use in nanofluidic devices [8–17].

Recent experimental and numerical works have revealed that, despite their non-polar nature, the CNTs may be spontaneously invaded by water [1,7,15,18–21]. For example, Pascal et al. [19] studied the role of thermodynamics on the behavior of water in the CNTs with diameters between 0.8 and 2.7 nm and reported that water molecules inside the nanotubes have lower free energy than in the bulk and, therefore, the internal space of a CNT is wetted by water. In addition, the atomic-scale smoothness of their surface, together with the ordering of the water molecules at nanoscale resulted in fast and almost friction-less molecular transport within the CNTs [1,22].
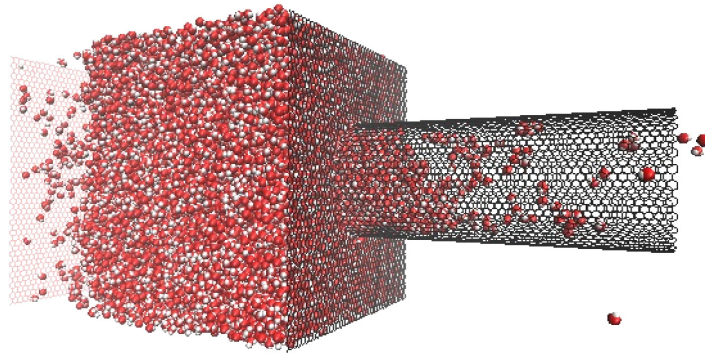

Fig. 1. A snapshot of the simulated system at $T = 520$ K.

In order to make further progress in the application of the CNTs to problems involving water, a fundamental issue that must be addressed is the wetting behavior of CNTs under various conditions. Previous studies [18,19] indicated that the behavior of water in the CNTs is strongly dependent on its structure and commensurability with the tube's size. In addition, the effect of the carbon–water van der Waals potential, which is an attractive (as opposed to repulsive) potential, on the dynamics of spontaneous imbibition of water into the CNTs has been studied previously [1,20,23,24]. The results demonstrated that even a small perturbation in the strength of the water–carbon potential remarkably changes the water distribution in the nanotube. To our knowledge, however, temperature dependence of wetting properties of the CNTs has not been explored so far. This is while we already know that, in general, wetting properties strongly change through changes in the surface energies induced by the variation in the system's temperature.

In this paper, we study the effect of temperature on the dynamics of spontaneous water imbibition into a (30, 30) CNT, where fluid transport manifests bulk-like characteristic [18]. To do so, we perform molecular dynamics (MD) simulations with a system containing a water reservoir and a pristine CNT, and study the change in the rate of frontal displacement as the temperature is varied. Then, by invoking the principle of conservation of energy, we derive a simple relation between the rate of frontal displacement, the viscosity of water, and the change in the free energy of the water column in the nanotube. This helps us to investigate the wetting property of the CNT at various temperatures and estimate the wetting transition temperature for water in the CNTs.

The rest of this paper is organized as follows. In the next section we describe the molecular models and the details of the MD simulations. Next, the results are presented and discussed. The paper is summarized in the last section.

2. Model description

We consider the spontaneous imbibition of water into an armchair (30, 30) CNT. The uncapped CNT was constructed by rolling up a graphene sheet consisting of 40×60 carbon rings into a cylinder along the z (axial) direction. The length and the radius of the channel were $H = 98.4$ Å and $R = 20.3$ Å, respectively, but the effective sizes depend on the values of the Lennard-Jones (LJ) size parameter σ of the cross-sectional atoms. Taking this into account, the effective tube radius and length were $R = 19.5$ Å and $H = 97.6$ Å. We adapted the same simulation setup and conditions as those in Refs. [21,22]. For clarity and completeness, we briefly explain the simulation procedure and conditions here.

At its left end, the CNT is in contact with a water reservoir consisting of two graphene sheets perpendicular to its axis. The schematic of the simulation system is illustrated in Fig. 1. Periodic boundary conditions were applied in all the directions, and the carbon atoms were held fixed during the simulation. The size of the simulation box was chosen so as to avoid introducing redundant interactions between the atoms. The left end of the CNT was capped at the beginning of the simulations, but the right end remained open during the entire time. At the beginning of the simulation, there were 30 720 water molecules in the reservoir, which were modeled by the TIP3P model of water molecules. They were kept at a constant temperature of 300 K using the Nose–Hoover thermostat, applied only to the degrees of freedom perpendicular to the tube axis, with a damping time of 200 fs. The density of the model water at 300 K and in liquid/vapor equilibrium coexistence was 0.98 gr/cm³. A fixed simulation time step of $\Delta t = 2$ fs was used in all the cases. As Fig. 1 indicates, after equilibrium a dense or liquid phase coexists with a vapor phase in the reservoir. The densities of both phases vary, of course, with the temperature. When liquid water reached equilibrium with its vapor, the left cap was removed to allow its molecules to penetrate the CNT.

The CNT–water interaction is usually modeled with a standard pair-wise additive LJ interaction between the carbon and the oxygen atoms of water molecule. Values of the LJ interaction parameters, ε and σ, for C and O were obtained by using the Lorentz–Berthelot mixing rules:

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]. \tag{1}$$