Graphene confinement effects on melting/freezing point and structure and dynamics behavior of water

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ABSTRACT

In this work, the melting/freezing point of confined water between two graphene sheets was calculated from the direct coexistence of the solid-liquid interface. Also, molecular dynamics simulation of confined liquid water-ice between two graphene sheets was applied. The phase transition temperature of the confined ice-water mixture was calculated as 240 K that was 29 K less than the non-confined ice-water system. In order to study the behavior of water molecules at different distances from the graphene sheets, 5 regions were provided using some imaginary planes, located between two graphene sheets. The obtained simulation results showed that water molecules located in the region near each graphene sheet with the thickness of 2 nm had a different behavior from other water molecules located in other regions. The results demonstrated that water molecules in the vicinity of graphene sheets had more mean square displacements than those in the middle regions.

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1. Introduction

Confinement of molecules at nanometric scale provides the possibility of exploring the behavior of fluids under special conditions that are not encountered in bulk systems [1–5]. Studying the unusual properties of confined water is important for designing novel nanofluidic applications [6]. The water confined in different structures like graphite channels [7], carbon nanotubes [8,9], silica pores [10], mica surfaces [11], metal oxide-based nanocapsules [12] and reverse micelles [13] has motivated intense investigations both theoretically [14,15] and experimentally [16,17]. Recent studies have demonstrated that the confinement of matters at nanometric scale induces a phase transition or a supercooling [18–23]. It has been shown that confinement in cylindrical nanopores decreases the equilibrium melting temperature of water [23]. Many studies have shown that the phase diagram of confined water is much more complicated than that of bulk water [24–32]. It has been shown that pores with the radius of larger than 50 nm have essentially the same melting temperature as water in bulk, while pores with the radius of 1 nm or less do not exhibit first order melting transition [33,34]. A similar relationship is held for the boiling-point elevation in pores [35,36]. Recently, the rate of capillary evaporation of water confined between two hydrophobic surfaces separated by

nanoscopic gaps, as a function of gap, surface size, and temperature has been computed [37]. Emily et al. [38] used molecular dynamics simulations to study the melting temperatures and coexistence of ice and a premelted liquid layer in nanopores with the radius of 2 nm with a wide range of water—surface interactions, ranging from strongly hydrophobic to very hydrophilic. They showed that the melting temperatures of ice confined in the pores were strongly depressed with respect to melting temperature of bulk ice, 274 K in the MW water model [39]. It should be reminded that some simulations have shown that the melting temperature of confined water increases with confinement. Of course, the increase or decrease of the melting temperature may depend on the model and the hydrophobicity. Performing a simulation for a single model does not provide information about this important issue. Studies on the structure of the confined water have been ravealed that nine additional ice phases have been obtained in molecular simulation of the water confined within carbon nanotubes with unusual structures such as the bilayer ices firstly described by Koga et al. [24]. Also dynamics of water confined between two hydrophilic surfaces has been also investigated [40–42]. The obtained results have demonstrated that water molecules in the outermost layer have slower dynamics and the displayed structures are strongly influenced by the surface, as a consequence of strong hydrogen bonds established between water and hydrophilic sites of the latter [41]. Although recent studies have shown that water properties can strongly depend on confinement [43–47], effects of distance from

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confinement sheets on the behavior of water molecules have not been understood yet.

Recently, we investigated the liquid-solid phase transition temperature of the water confined between two graphene oxide (GO) sheets. The results demonstrated that, due to the presence of functional groups of the GO sheets, at temperatures below liquid-solid phase transition temperature, the water molecules near the confining sheets are not structured like ice and remained in the liquid form. The results also revealed the confinement effects on the melting and freezing rate of the water molecules. Also, the liquid-solid phase transition temperature of water in the presence of GO sheets was calculated as 236 K, which was 34 K less than the temperature of the bulk water [48]. In this work, at first, phase equilibrium of water and ice mixtures confined between two graphene sheets was examined using MD simulations. Then, in order to study the effects of graphene sheets on confined water behavior, using some imaginary planes, the distance between two graphene sheets was divided into 5 layers. The behavior of water molecules in each layer was separately investigated.

2. Simulation details

The simulations were performed using LAMMPS [49] and TIP4P/Ice model [50] as a new water model specifically designed to cope with solid-phase properties. Predictions of this model for both densities and coexistence curves of ice have been demonstrated to be better than those for other water models. TIP4P/Ice model was used here for both systems: bulk water and confined water between two graphene sheets. Bulk water was considered as the reference system. Recently, Fernández et al. [51] implemented the calculation of the melting point of ice Ih from the direct coexistence of the solid-liquid interface and that of the melting point of ice Ih at 1 bar for seven water models including SPC/E, TIP4P, TIP4P-Ew, TIP4P/ice, TIP4P/2005, TIP5P, and TIP5P-E. They demonstrated that the melting temperature from the direct coexistence simulations was in agreement with the statistical uncertainty obtained from free energy calculations. In this study, direct coexistence of the solid-liquid interface was applied for studying the properties of bulk water and confined water. For water molecules, ε parameters used for oxygen and hydrogen atoms were 0,155, and 0.0 kcal/mol. Also, σ parameters used for oxygen and hydrogen atoms were 3.16435 and 0.0 Å. Partial charge (q) parameters applied for oxygen and hydrogen atoms were -1.1794 and 0.5897 e, respectively. Also, values of ε_{OH} and σ_{OH} were calculated using Lorentz-Berthelot mixing rules [52]. All the interatomic interactions were modeled by the well-known Lennard-Jones potential. The Ewald method [53] was implemented to compute electrostatic interactions. Velocity form of the Verlet algorithm method and the Nosé-Hoover barostat and thermostat [54] were also applied with damping coefficients 1 and 0.1 ps^{-1}, respectively and time step of 3 fs was employed. Moreover, the cutoff distance of 10 Å was utilized for the van der Waals potentials. Computer simulations were carried out using a $(30 \times 20 \times 68)$ Å^3 computational cell with the periodic boundary conditions applied in all three principal directions. For the confined system, two open-ended finite-length graphene sheets with the length of 63.9 Å were considered. The distance between these two graphene sheets was 20 Å and the number of their carbon atoms was 1584. Fig. 1(a) shows the initial configuration of the simulation system. All MD simulations were performed in the NVT ensemble. Atoms of the graphene sheets were fixed at their initial positions and 1000 water molecules in liquid and ice Ih halves were placed between two graphene sheets. The Lennard-Jones potential of σC—C (ε C—C), σC—O (ε C—O), and σC—H (ε C—H) used in the simulation was 3.4 Å (0.23Åkcal/mol), 3.19 Å (0.1889 kcal/mol), and 0.0 Å (0.0 kcal/ mol), respectively. After the energy
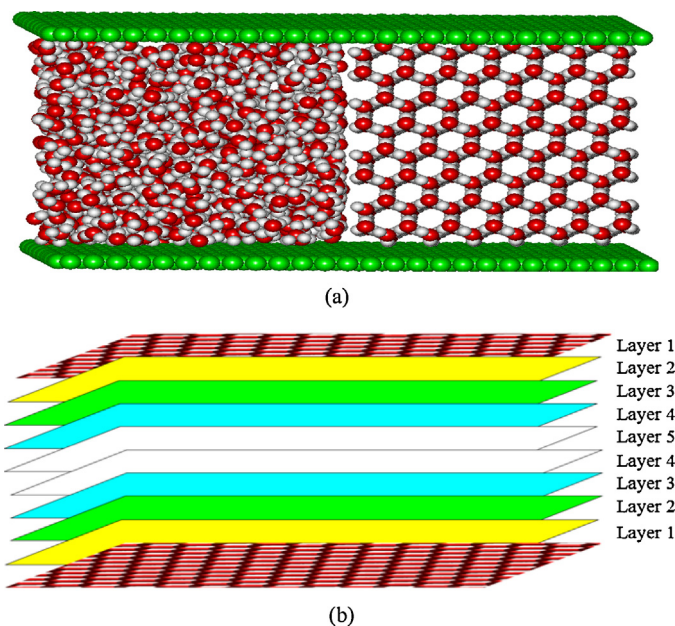

(a)

(b)

Fig. 1. (a) - Initial configuration of the simulation for confined water between two graphene sheets, green, white and red colors are carbon, hydrogen and oxygen respectively. (b) Two graphene sheets are presented in red color, layers 1 are located between two red and yellow planes. Similarly, layers 2 are located between two yellow and green planes and so on. One layer 5 is located between two white planes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

minimization step, the simulations were continued for 50 ns to obtain enough statistical sampling for the calculations. Furthermore, to determine the maximum diameter of water molecules influenced by graphene sheets, water molecules were classified into 5 layers. Two graphene molecules were fixed along the x-axis at the distance of -10 to $+10$ Å. The first layer contained the molecules, which were within -8 to -10 Å and 8–10 Å. For the second layer, the values were equal to -8 to -6 Å and 6–8 Å. Other layers were similarly defined in the range of 4 Å. Fig. 1(b) shows the schematic representation of the regions located between two graphene sheets.

3. Results and discussion

In this section, plots of total energy and phase transition temperature water are analyzed. In the following, plots of temperature versus density, radial distribution functions, density profiles, and mean-squared displacement is investigated.

3.1. Total energy diagrams

Finding a method which can present more precise melting and freezing points for fluids is of high importance. One of these methods is the coexistence of solid-liquid phases, which was first proposed by Ladd and Woodcock [55] and has been recently discussed by Fernández et al. [51]. In this method, the ice-water mixture is used, instead of pure water or pure ice, as the primary system. Although in studying melting and freezing points, the systems which consist of pure water and pure ice provide more precise results, coexistence of the solid-liquid phases removes the phenomenon of water superheating and supercooling. So, it would accelerate the system's equilibrium during water freezing and ice melting. For investigating phase transition temperature of water confined between two graphene sheets, the mentioned method was applied. For the water-ice mixture, decrease and increase of total energy indicated freezing and melting of the existing water