



Wetting transition of water on graphite and boron-nitride surfaces: A molecular dynamics study

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ABSTRACT

Wetting transition of water on graphite and boron-nitride (BN) surfaces is investigated by molecular dynamics simulation. In particular, we report the effect of temperature and system size on the contact angle of water droplet on the two surfaces. Wetting temperature of water on graphite is found to be 470 ± 5 K, which is in good agreement with the estimate of Zhao (Phys. Rev. B 76 (2007) 041402) using grand-canonical Monte Carlo simulations. On the other hand, wetting temperature of water on BN surface is estimated to be lower, 438 ± 5 K. Temperature dependence of line tension of water droplet on both the surfaces is also studied, and found to vary between 10^{-10} and 10^{-9} N for temperature in the range of 300–420 K. In this work, line tension for water on graphite and BN surfaces is observed to have a logarithmic proportional behavior with the contact angle.

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1. Introduction

Wetting behavior of fluid–solid interfaces is of practical interest to technological important areas such as sensors [1] and coatings [2]. Wetting of patterned surfaces by liquids plays a key role in the fields of nanofluidics [3,4] and biophysics [5]. Increase in demand of nano-based technologies requires having a clear picture of wetting behavior on functional surfaces. Despite the potential of controlling the wettability to transform the nano-based device radically, we are yet to devise a practical way to make smart surfaces.

Wettability of solid surface is a characteristic property of materials. It strongly depends on both surface energy and surface roughness and is characterized invariably by the contact angle, θ , which is given by the following Young's relation [6]:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}, \quad (1)$$

where γ_{SL} , γ_{LV} and γ_{SV} are interfacial free energies per unit area of the solid–liquid, liquid–vapor and solid–vapor, respectively.

Wetting transition is characterized usually by the wetting temperature at which drop vanishes and wets the surfaces completely. Various works have been done in order to understand the wetting transition by experiments [7,8]. Previous theoretical studies reveal that variety of simple and associating fluids undergoes the first-order wetting transition [9–11]. Surprisingly, the experimental evidence is very limited [12–14], due to sensitivity of contact

angle to impurities/defects on the surface. Experimental observation of the contact angle of water on a graphite surface [15] at the room temperature ranges from 60° to 80° , which illustrates experimental difficulties to study such phenomena. In addition, impurities and defects of surface are unavoidable in experiment [16], which essentially changes the interfacial water behavior.

On the other hand, molecular simulation, based on molecular interaction model, can explore the behavior of fluid near the surface systematically. Various workers have done some work in this direction. For example, Pertsin and Grunze [17] studied the behavior of water confined between two graphite sheets, while Muller et al. [18] performed a Monte Carlo study on adsorption of water on activated carbons. Zhao [19] recently studied the prewetting transition of water on a graphite surface. A number of MD studies are also performed to understand the droplet dynamics on solid surfaces. For instance, Hautman and Klein [20] investigated the microscopic wetting of hydrophilic and hydrophobic surfaces with terminal function groups. Lundgren et al. [21] studied the wetting behavior of water and water/ethanol mixture on graphite surface, without considering system size effects and obtained a microscopic contact angle of 83° for water on graphite surface; while Werder et al. [22] studied contact angle of water on a graphite surface by varying interaction parameters. On the other hand, Zangi and Berne [23] investigated the dependency of temperature on contact angle of water droplet on a graphite surface. Subsequently, number of molecular dynamics studies are performed on the contact angle of water droplet on different surfaces such as TiO_2 surface [24] and amorphous silica surface [25]. Similar wetting studies have been done for silver on nickel surface [26] and aqueous trisilox-

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Table 1
Lennard–Jones parameters.

Pair	σ (Å)	ε (kJ/mol)	q (e)
OW–OW [41]	3.1666	0.6502	−0.8476
HW–HW [41]	0	0	+0.4238
C–OW [22]	3.190	0.392	0
B–B [61]	3.453	0.3971	0
N–N [61]	3.365	0.6060	0

ane and alkyl polyethoxylate surfactant solutions on a graphite substrate [27]. In all the above studies, investigation related to wetting temperature and line tension is missing. This is, in fact, the main objective of the current study. In this work, we present a systematic study of wetting transition and line tension of water droplet on graphite and boron–nitride surfaces. Such materials in different shapes such as nanotubes and fullerenes, have shown substantial evidence of extraordinary hydrodynamic behavior of water [28–37]. We expect that the current work will find use in future studies pertinent to the field of biosensors and nanofluidics.

The rest of the paper is organized as follows: in the next section, we describe the model and methods employed in this work. Section 3 presents the results on the effect of system size and temperature on the contact angle of water on graphite and BN surfaces. In addition, we report the line tension, which for the first time, to our best knowledge, is investigated systematically using molecular dynamics. Section 4 summarizes the work.

2. Computational model and method

2.1. Model

Molecular dynamic simulations are carried out under constant number of particles N , volume V , and the temperature T (NVT ensemble). In this work, we have used DLPOLY [38]. Graphite and BN surfaces are constructed by periodically replicating the unit cell in lateral directions. The graphite surface consists of two layers of carbon atoms separated by 1.53 Å and the distance between the layers is 3.4 Å. Cutoff radius of 10 Å is used to omit the effect of additional number of surface layers. The BN surface consists of alternating boron and nitrogen atoms in a graphite like sheet with almost no change in atomic spacing [39]. The surface atoms are kept frozen during simulations. The dimensions of the box varied from 150×150 to 200×200 Å² depending on the size of the droplet. The substrate size is sufficiently large to remove the effect of periodic images of the droplet in lateral directions. The height of the simulation box is taken as 270 Å to avoid any interaction of periodic image of the droplet [40].

Water–water interaction is described by the SPC/E [41] model in which the hydrogen's are located at 1 Å from the oxygen with an H–O–H angle of 109.47°. Bond distance and bond angle are fixed throughout the simulation with the SHAKE algorithm [42]. The intermolecular interaction in the SPC/E model is defined as:

$$U_{ij}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{i=1}^3 \sum_{j=1}^3 \frac{q_i q_j}{r_{ij}}, \quad (2)$$

where r_{ij} is the distance between any pair of atoms i and j , σ represents the atom size, ε is the interaction energy depth between two atoms and q_i and q_j are the charges centered on the individual atoms of different water molecules. Surface–water interaction is represented by Lennard–Jones potential and the corresponding interaction parameters are calculated using the Lorentz–Berthelot mixing rules as shown in Table 1: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$.

Initial configuration is generated by placing water molecules, in the range 2000–7000 particles, on a cubic lattice. Subsequently,

water cubic structure is kept on the surface at the bottom of the simulation box. The lateral dimension of box is the same as that of the surface. Each simulation is carried out for 1.2 ns with an integration time of 2 fs with 0.6 ns as equilibration run length and equal amount for the production run. The Nose–Hoover thermostat is used to maintain the system temperature with relaxation constant of 1.0 ps. Electrostatic interactions are incorporated using the single particle mesh Ewald method [43].

2.2. Methodology

Graphical binning approach is considered to calculate various properties such as vapor–liquid densities and contact angles. In this approach, we assume azimuthal symmetry in the droplet and introduce the cylindrical coordinate system (r, z) , where r is the distance from the z -axis. Such approach was earlier used by Werder et al. [22] and Aluru and co-worker [24]. We have considered the top most surface layer for the zero reference level and the surface normal through the center of mass of the droplet as the reference axis. The bins have a height of 1 Å and are of equal volume, i.e., the radial bin boundaries are located at $r_i = \sqrt{(i\delta A/\pi)}$ for $i = 1, \dots, N$ bins with a base area per bin of $\delta A = 95$ Å². Contact angle is extracted from a two-step procedure from the profiles as described by de Ruijter et al. [44]. First, the location of the equimolar dividing surface is determined within every single horizontal layer of the binned drop. Second, a circular best fit through these points is extrapolated to the surface where the contact angle θ is measured. The boundary between equilibrated liquid and vapor interface for a given droplet is determined at the position where the density is half of bulk water density and is modeled using the relation for liquid–gas interface:

$$\rho(r) = \frac{1}{2} (\rho^L + \rho^V) - \frac{1}{2} (\rho^L - \rho^V) \tanh \left(\frac{2(r - r_e)}{d} \right), \quad (3)$$

where ρ^L and ρ^V are liquid and vapor densities, respectively, r is the distance from origin to the droplet surface, r_e is the center of the interface region, and d is the interface thickness. The points of the equimolar surface below a height of 8 Å from the graphite or BN surface are not taken into account for the fit, to avoid the influence of density fluctuations at the liquid–solid interface.

The size of the droplet influences the wetting behavior when used as nanoscale droplets such as in microelectronic systems and microfluidic devices [45]. To determine the effect of droplet size on the microscopic contact angle we have utilized the following modified Young's equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta + \left(\frac{\tau}{r_B} \right), \quad (4)$$

where τ and r_B are line tension and radius of the droplet, respectively.

Macroscopic contact angle can be derived for infinitely large drop, i.e., $1/r_B \rightarrow 0$, which yields a well known Young's equation (Eq. (1)):

$$\cos \theta_\infty = \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right).$$

Eq. (4) can be rewritten in terms of macroscopic contact angle and line tension as shown below:

$$\cos \theta = \cos \theta_\infty - \left(\frac{\tau}{\gamma_{LV}} \right) \frac{1}{r_B}. \quad (5)$$

A series of finite size contact angles can be used along with Eq. (5) to obtain the macroscopic contact angle.

Hydrogen bond (HB) plays a crucial role in the behavior of water as their spatial patterns and fluctuations characterize the structure and dynamics of the liquid [46]. In this work, we perform HB analysis, using the geometrical criteria as described by Swiatla-Wojcik

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