

Wettability of boron monolayer using molecular dynamics simulation method

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Abstract.

Over the past years, two-dimensional materials such as graphene, phosphorene, silicene, and boron-nitride have attracted the attention of many researchers. After the successful synthesis of graphene, due to its many new applications, researches began to produce nanosheets from other elements, and among these elements, boron was one of the options. In the periodic table of elements, boron is ahead of carbon and after beryllium, which exhibits metallic and non-metallic properties. The two-dimensional boron sheets called borophene are one of the allotropes of this element that reaches their stable and single-layer structure by forming triangular lattice and the carbon like SP^2 hybridization. Since boron is carbons neighbour, so it is expected that two-dimensional boron sheets would have properties close to graphene. Here, we investigate the wettability of the borophene mono-layer surface by calculating contact angle of the water and the surface of the sheet by using the molecular dynamics simulation method. According to the measurements obtained from this simulation, the contact angle is approximately 131 degrees, indicating that such a structure is hydrophobic. Also, the effect of diameter of nanodroplet on the surface contact angle has been studied.

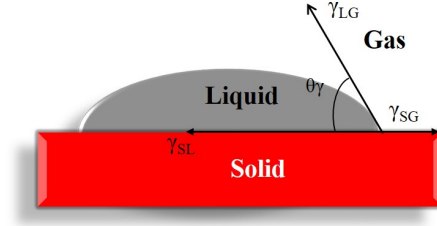
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1 Introduction

Various surfaces show different reactions when they touch water. These diverse interactions with waters surface are called wetting. Wetting is a part of the soft matter science. It studies the capability of a fluid to scatter on the surface of a solid matter. Wetting is a characteristic of the matter, greatly under the influence of chemical combination and geometric structure of the surfaces. It plays an important role in science, industry and material coating. This behavior is very important in oil recovery, greasing, anti-corrosion surfaces, self-cleaning coating and printing [1]. Surface wetting is determined by measuring the angle of the contact. Basically, contact angle is the angle that the outer contact line of the drop makes with the surface in the contact triple point. On a smooth and homogenous surface, it is called Young contact angle. As we see in Fig. 1, it is determined with θ_γ [2]. Contact angle was first explained by Thomas Young [3] in 1805. It is quantified according to equation 1:

$$\cos \theta_\gamma = \frac{(\gamma_{SG} - \gamma_{SL})}{\gamma_{LG}} \quad (1)$$

Contact angle of a liquid drop on a solid surface is defined as the mechanical balance of the drop under three interfacial tensions. Equation 1 is called Young Contact Angle in which

Figure 1: Young's contact angle θ_γ

γ_{SG} , γ_{SL} , γ_{LG} are solidvapor, solid-liquid and liquid-vapor interfacial energies. According to Young equation, if θ_γ is smaller than 90 degrees, then the surface is hydrophilic, if it is between 90 to 150 degrees, then it is hydrophobic and if it is more than 150 degrees, then the surface is super hydrophobic. Hydrophilic, hydrophobic and super hydrophobic surfaces are used to increase durability, to reduce costs and time required to clean the equipments in different industries like automobile manufacture, cooling towers, sewer treatment, railway, etc. Self-cleaning hydrophobic coatings and paints demolish surface pollutions by moving water on their surface [4]. Graphene has extraordinary properties in electrical and thermal conductivity, high density, high mobility in load carriers, optical conductivity, and mechanical properties. These properties have made it an astonishing material [4]. According to previous studies, graphenes surface is hydrophobic and its contact angle is 90 – 100 degrees [4]. Hautman and Klein studied hydrophilic and hydrophobic surfaces and discovered that the contact angle on graphite is 83 degrees and on graphene, it is between 90 to 100 percent [4]. The single-layer atom of boron, also known as borophene [5], is structurally similar to graphene. The difference is that due to the shortage of electron in its structure, it avoids the formation of honeycomb structure like graphene. This similarity led to the conduction of researches about boron and making of sheets, nanotubes, and nanotapes from boron. These sheets form triangular structures, and due to strong connections between boron atoms and similarity of structure and closeness to carbon, the bidimensional structure of boron is expected to be very firm and strong. Also, the properties are expected to be very similar. As depicted in Fig. 2, unlike graphene, borophene crystalline structure is quasi-flat. If you observe it from the opposite view, there is a lower layer and another layer above with the height of h out of the sheet. They are connected with a strong boron-boron connection. According to the results of the density function theory, this structure has two lattice vectors of $a_1 = 1.614\text{\AA}$ and $a_2 = 2.866\text{\AA}$ which are in agreement with the empirical and theoretical results [6]. Also, on the direction of b it has a height of $h = 0.911\text{\AA}$ [6]. In the current paper, we studied hydrophilia, hydrophobia and the influence of size on the single layers with dynamic molecular simulation.

2 Simulation Method

Molecular dynamic simulation was done for a borophene sheet which was 14 nm14 nm. A number of 4311 atoms (1437 molecules of water) were considered for the nanodrops of water, since the measurements were time consuming. There are different models for water simulation which include SPC/E [7], TIP4P [7], and TIP3P [7]. SHAKE algorithm was used to maintain the bond length and angle between water molecules during simulation [7]. We performed all simulations using the LAMMPS package, which is a molecular dynamics

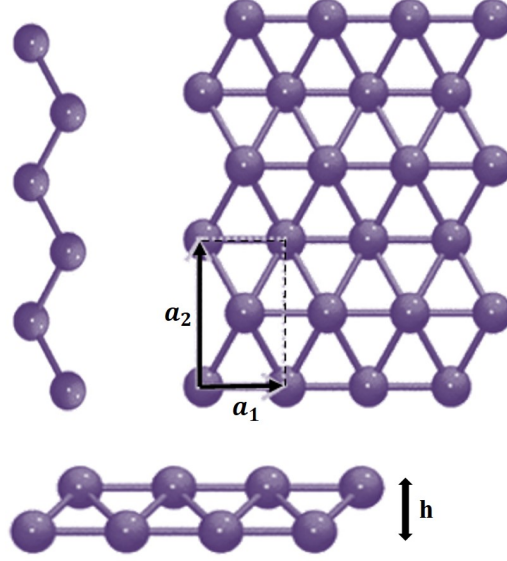


Figure 2: The borophene structure from the top and side view, where the unit cell with the a_1 and a_2 lattice constants are shown and h represents the out of plan of the boron sheet.

simulation code [8]. The ReaxFF potential was used to describe the interaction between boron and boron atoms [9]. We used P3TIP potential to simulate water. Also, to describe the interaction between atoms of water and boron molecules ReaxFF potential was used. We applied periodic boundary conditions along the surface to keep the number of particles constant and to eliminate surface effects; also, we applied a vacuum gap so that the number of particles in this direction remains constant. The equations of motion were solved using verlet algorithm with time intervals of 0.25 femtoseconds for the entire simulation system, including the nondrop and sub-layer. First, we balanced the temperature and pressure of the system with thermostat and barometric nitrogen at 300 K and at a pressure of 1 atm. A square cube volume containing water molecules was placed on the surface of the borophene, as shown in Fig. 3 (a), and after 750 picoseconds, the drop spread over the surface and, as shown in Fig. 3 (b), reached its balanced state.

Then, as we see in Fig. 3 (b), contact angle was measured using simulation and ImageJ [10] software which is a software program to process pictures. In order to study different diameters of nano droplets, we repeated the simulation for more water molecules, each of which contained 1437, 2132, 2830, 3456, 4162 and 4692 molecules of water, with an approximate diameter of each of them equal to 8.45Å, 51.2Å, 57.3Å, 61.9Å, 66.5Å and 69.1Å respectively. Finally, the corresponding charts are presented in the distribution of the results.

3 Results

In this simulation, first we balanced the lower layer in the temperature of 300 and the duration of 50 picoseconds. As shown in Fig.3, the whole system including the nondescript and sub-layers is simulated, and after 750 picoseconds, the nanodrop becomes stable and the contact angle does not change significantly afterwards. So, it is suitable for measuring

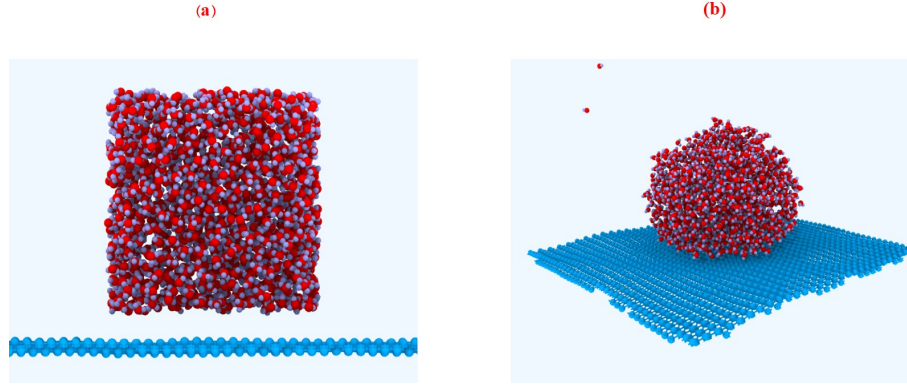


Figure 3: Diffusion of nano droplet on the surface : a) at first step of simulation which we set the box of water on the surface. b) after 750 pico seconds that the system has reached the equilibration.

the contact angle. So, we studied the hydrophobicity and hydrophilicity of the borophene and the effect of size on contact angle by checking the balanced system and the graphs that show this balance. The figures showing the system's balance were the energy potential diagram (Fig. 4) and temperature (Fig. 5) based on the simulation time. According to these diagrams, potential energy and temperature fluctuate around a steady amount over time, indicating the systems balance. After the balance of the system, the contact angle of this layer was obtained which was 131 degrees, suggesting that this layer was hydrophilic. By obtaining the contact angle, we looked for the effect of the diameter of the droplet on the contact angle, so that we could better approach the laboratory conditions. The diagram (Fig. 6) shows the diameter effect. One can state that with the increase in the diameter of the water the contact angle decreases. In the following, we examined the dependence of surface area on the contact angle (Fig. 7). As shown in Fig. 7, the contact angle decreases with increasing of the surface area between nanodroplet and borophene.

4 Discussion

In this study, molecular dynamics simulation was used as a tool to find properties that are not easily visible and measureable in the laboratory so that we can measure the properties of the borophene layer as a new form of boron structure. The results of this study may be summarized as follows:

The borophene contact angle is 131 degrees. This indicates the hydrophobicity of this sub layer, which is more hydrophobic than graphene with a contact angle of 90-100 degrees. Hydrophobic materials play an important role in life, the most important applications of which can be their resistance against freezing, which makes them useful as antifreeze in industries and cold regions. So, it is very economical to replace graphene with borophene in industries. Regarding the influence of the diameter of the water on the contact angle, we found out that the angle of contact decreases as the diameter increases.

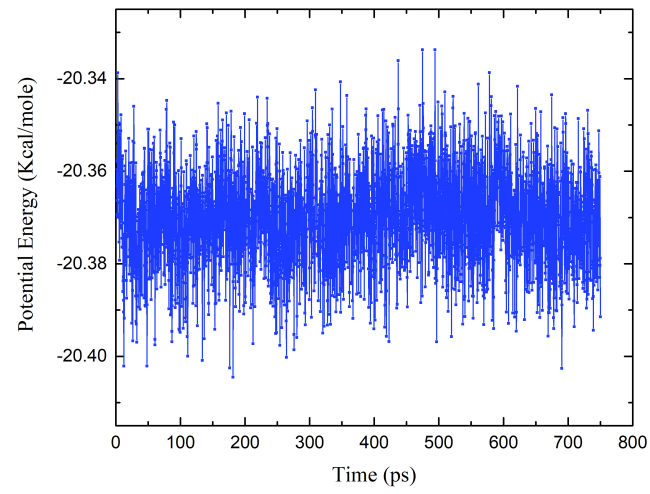


Figure 4: Water nanodroplet potential energy graph on the surface of the borophene at the equilibrium stage and at 300 K

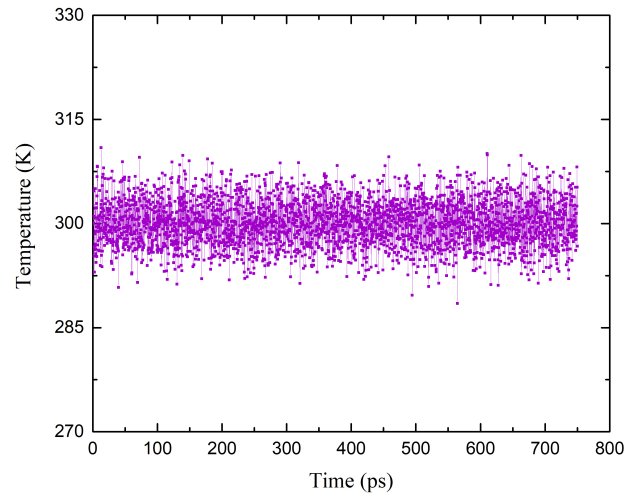


Figure 5: Water nanodroplet temperature graph on the surface of the borophene at the equilibrium stage and at 300 K

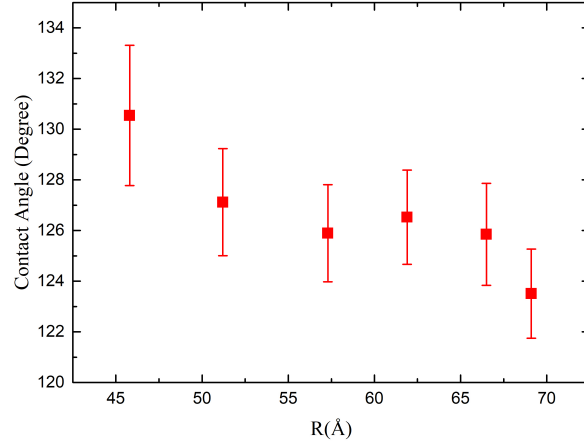


Figure 6: The dependency of the contact angle of water nanodroplet on the borophene surface to nanodroplet size at 300 K.

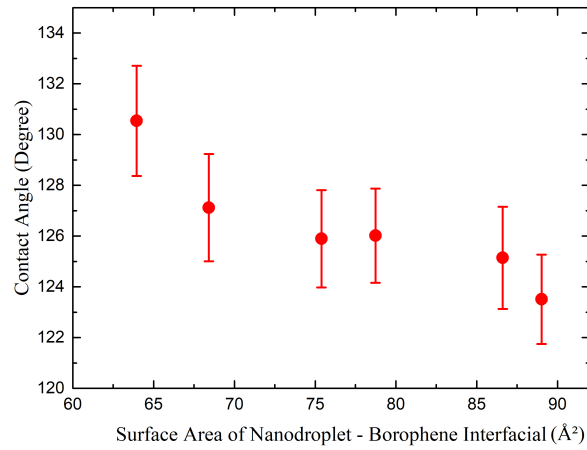


Figure 7: The dependency of the contact angle of water nanodroplet on the borophene surface to interfacial surface at 300 K.

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