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Effects of morphology, tension and vibration on wettability of graphene: A molecular dynamics study

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ABSTRACT

In the present study, we investigated the effects of morphology, tension and vibration on the wettability of graphene by performing classical molecular dynamics simulations. The contact angle of water droplet on ideal graphene is calculated to be 88.27° using the density profile method, which is in good agreement with the experimental data. The wrinkled morphology slightly decreases the wettability of graphene in most cases, and the droplet contact line always prefers to stay at the crest of wrinkles. The wrinkled morphology also brings extra barrier energy which leads to the pinning effect and discretized wetting effect with the droplet contact angle fluctuating up and down when the droplet volume increases. Tension and vibration strongly influence the wettability of graphene. The droplet contact angle linearly increases with increasing of biaxial tensile strain when the stain is lower than 10%, then remains at about 110°. The graphene becomes more and more hydrophobic with increasing of vibrational amplitude and decreasing of vibrational period. The contact angle of droplet on vibrational graphene and corresponding vibrational energy of graphene can be described by a logarithmic function.

1. Introduction

Graphene is a rapidly rising two-dimensional material [1,2]. Vast research efforts have been focused on its extraordinary mechanical [3], electrical [4], thermal [5], and optical [6] properties. The wettability of graphene is also an important property regarding to its huge applications in self-cleaning [7], coating [8], anti-corrosion [9], anti-icing [10,11], and water purification [12]. Wang et al. [13] experimentally measured the contact angle of water droplets on graphite, graphene and graphene oxide, respectively, and the results show that the droplet contact angle is 98.3° on graphite, 127° on graphene, and 67.4° on graphene oxide. Shin et al. [14] conducted experiment to study the wettability of graphene grown on SiC and revealed the contact angle of water droplets on monolayer, bilayer, multilayer graphene and highly oriented pyrolytic graphite are all around 92°. What's more, the contact angle of droplet decreased significantly after oxygen plasma treatment. Shih et al. [15] developed a theory to model the van der Waals interactions between liquid and graphene and tested the theory by conducting molecular dynamics simulations and experimental measurements of contact angles. Their results showed the predicted highest attainable contact angle of water droplet on a graphene-coated surface is 96°. Li et al. [16] argued that the adsorption of organic matters in the air greatly affects the wetting property of graphene and increase the water contact angle from intrinsic 50° to about 90°. Li et al. [17] simulated the wetting phenomenon of water on graphene using the van der Waals modified DFT method (DFT + D), and obtained the contact angle of water droplet on graphene is 87°.

Previous studies revealed that graphene is a weekly hydrophobic material with a water contact angle measured within the range of 87°–127°. Actually, the properties of graphene can be modified by lots of possible treatments, such as chemical functionalization [18], microstructure modulating [19], mechanical loading [20], thermal [21] or electrochemical methods [22]. By modifying the wettability of graphene, we can design and optimize different kinds of graphene-based materials. Due to the thermodynamically unstable status of graphene, and the irregularity of the graphene substrate, the surface morphology of graphene is always wrinkled [23,24]. What's more, the wrinkled graphene can be precisely engineered. It has shown that thermal expansion and substrate regulation can induce reversible wrinkling of graphene [25,26]. Zang [27] has conducted an experiment to precisely control the wrinkling of graphene. In the experiment, the graphene was transferred to a polydimethylsiloxane (PDMS) substrate, and the tunable wrinkling of the graphene can be achieved by stretching or shrinking the sub-

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strate with different levels. Moreover, tension and vibration are the most common and possible load to the graphene in its service life cycle. Thus, it has great significance to understand the wetting behavior of water on graphene that is wrinkled or under tensile or vibrational loading, which may have potential applications in novel graphene-based conductive coatings, electrodes, energy storage, composites and biomedicine that are superhydrophobic and tunable wettability [1,28].

In this study, we focus on the wetting properties of graphene by considering the effects of wrinkled morphology, biaxial tension, and sinusoidal vibration using MD simulations. First, the ideal graphene model and water droplet model are constructed, and the wetting characteristics of ideal graphene are studied. The density profile method is developed for the problem of inaccurate measurement of contact angle of water droplet at molecular scale. Then, a series of wrinkled graphene models of sinusoidal morphologies with different parameters are established, and their wetting properties are studied. Finally, the wettability of graphene under biaxial tensile loading and vibrational loading are studied respectively.

2. Methods

We perform molecular dynamics (MD) simulations to explore the wettability of graphene and influence factors based on the large-scale atomic/molecular massively parallel simulator (LAMMPS) [29]. The CHARMM (Chemistry at Harvard Macromolecular Mechanics) force field is employed in our simulations. It can be described as below:

$$U_{total} = \sum U_{bond} + \sum U_{angle} + \sum U_{LJ} + \sum U_{coulomb} \tag{1}$$

$$U_{bond} = k(r_{ij} - r_0)^2 \tag{2}$$

$$U_{angle} = k_\theta(\theta - \theta_0)^2 \tag{3}$$

$$U_{LJ} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{4}$$

$$U_{coulomb} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{5}$$

The first two terms on the right side of Eq. (1) denote bonded potential energy, including the two-body spring bond potential U_{bond} and three-body angular bond potential U_{angle}, described in Eqs. (2) and (3), respectively. In Eq. (2), k is the spring constant, $r_{ij} = \|\boldsymbol{r}_i - \boldsymbol{r}_j\|$ is the distance between atom i an atom j, r_0 is the equilibrium distance. In Eq. (3), k_θ is the angle constant, θ is the angle between vectors $\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$ and $\boldsymbol{r}_{kj} = \boldsymbol{r}_j - \boldsymbol{r}_k$, θ_0 is the equilibrium angle. The last two terms on the right side of Eq. (1) denote nonbonded potential energy, including the 12–6 Lennard-Jones (LJ) potential U_{LJ} and electrostatic potential $U_{coulomb}$, described in Eqs. (4) and (5), respectively. In these two equations, $r_{ij} = \|\boldsymbol{r}_i - \boldsymbol{r}_j\|$ is the distance between a pair of atoms, i and j, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ is the characteristic length between a pair of atoms, i and j, $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ is the characteristic energy. q_i and q_j are the charges on the on atom i and j, respectively. ε_0 is the vacuum permittivity.

Fig. 1 shows the initial configuration of the MD simulation box. As we can see, an ideal graphene of dimensions 120 Å × 120 Å and an initial water cube with 2197 water molecules are built. The graphene is modeled with orthohexagonal arranged carbons. The C—C bond length is 1.42 Å, and the bond angle is 120°. The water is modeled using the extended simple point charge (SPC/E) model [30]. In SPC/E model, the water molecular is regard as rigid structure, consisting of three point charges located at the oxygen (−0.8476e) and hydrogen (+0.4238e) positions. The O—H bond length is 1 Å, and the H—O—H angle is 109.47°. The SHAKE algorithm [31] is employed to keep the rigidity of the structure. The long-range charge-charge electrostatic interactions between water molecules are calculated using the PPPM (partical-partical partical-mesh) algorithm [32] with an accuracy of 10^{-6}. The van der Waals interaction between water molecules (oxygen atoms) described by a truncated 12–6 LJ potential with parameters $\sigma_{OO} = 3.166$ Å and $\varepsilon_{OO} = 0.65$ kJ/mol. The interaction between graphene and water droplet also described by the truncated 12–6 LJ potential with parameters $\sigma_{CO} = 3.19$ Å and $\varepsilon_{CO} = 0.392$ kJ/mol. The cutoff radius for both the electrostatic and LJ potential are 15 Å. The periodic boundary condition is applied for the simulation box of dimensions 120 Å × 120 Å × 90 Å in the x, y, and z directions, respectively. Newton's equation of motion is integrated numerically using the velocity Verlet algorithm [33] with a time step of 2.0 fs. The neighbor lists are updated every time step.

The simulations are performed as below. First, the energy minimization of the initial configuration is carried out to eliminate any excess potential energy from the initial structure. Then the system is relaxed in the NVT ensemble for 200 ps. The Nosé-Hoover thermostat [34] is used to keep the temperature at 300 K. After that, run another 200 ps in the NVE ensemble. We collect the snapshots of the water molecules of the finial 100 ps every 0.2 ps.

Our MD simulations include three stages. First, the initial water cube reached equilibrium on the ideal graphene. Second, the morphology of graphene is changed from flat to wrinkled, and the wettability change is focused. Third, the tensile and vibrational loading are applied to the graphene, respectively, and the influences of these two factor to the wetting property of graphene are investigated.

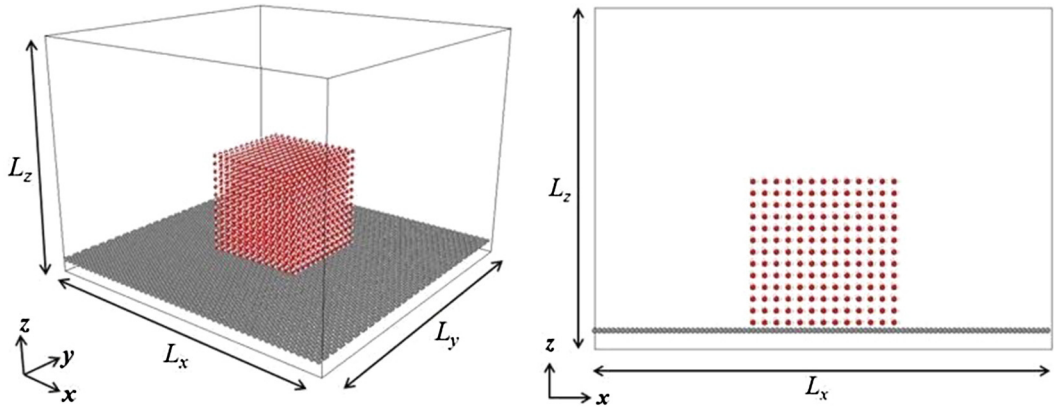

Fig. 1. Initial molecular configuration of a ideal graphene and water cube.