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Nanoscratching of multi-layer graphene by molecular dynamics simulations

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ABSTRACT

Graphene or graphene-based materials are becoming a glowing material to be expected to control a frictional behavior at contact interface. However, due to its atomic layer to layer structure, it is difficult to clarify its frictional mechanism through experimental observation. Therefore, in this paper the frictional behavior of diamond tip nanoscratching on multi-layer graphene was investigated by Molecular Dynamics (MD) simulation. Results show superlow frictional behavior of graphene layers when the scratch depth is less than 5.3 Å, when the scratch depth is over this value, the friction coefficient increases at least 10 times which is caused by phase transition of graphene layers. Besides, we discussed the sensitivity of friction coefficient to the shapes of scratch tip and its anisotropy.

1. Introduction

Since graphene has been experimentally demonstrated to be one of the strongest materials so far [1–3], it is motivated to play a wider role in physical, chemical and mechanical applications. In these applications, the contact phenomena are generally inevitable. Therefore, the frictional behaviors of graphene should be better understood. Nanoscratching is an essential method to characterize the material's frictional behaviors at nanoscale. By AFM scratching, Choi et al. revealed the exfoliated graphene friction anisotropy due to the domains produced during the manufacturing process [4]. The friction force of graphene was found much smaller than that on the Si/SiO_2 substrates, and the bound strength to the substrate had influences on friction [5]. Graphene also exhibited lattice stick–slip motion with friction coefficient of 0.03, which increased as the number of layers decreased [6]. The hydrogenated carbon film with dispersed multilayer graphene demonstrated ultra-elastic recovery and low friction coefficient contrast with film that did not contain graphene [7]. By now, these scratching experiments got important progress and revealed the in-situ tribological responses of graphene in terms of friction forces and coefficients. Due to the special atomic-scale layered structure and the limitation of instrument precision, it is difficult to figure out the fundamental frictional mechanisms of graphene by experiments. On the other hand, computational calculation is accessible to the detailed atomic-scale behavior [8–10]. Numerical calculation including molecular dynamics (MD) avoids the noise and turbulence easily introduced into the nanometer scale experiments, having become indispensable methods to investigate the atomic dynamics and mechanical characteristics [11,12]. Various reports investigated the strength and defect energy of graphene or functional graphene materials. By Density Functional Theory (DFT)-based calculations, Kotakoski et al. demonstrated the electron beam energy below 50 keV could minimize the knock-on damage of graphene edges during a transmission electron microscope analysis [13]. 2D single layer fluorinated graphene exhibits more friction with less compliance and indicates the flexural phonons could be a main source for friction energy dissipation [14]. These works mainly studied the single layer graphene properties. However, in multilayer graphene, the phase transformation or defects have great influence on the mechanical properties of graphene [15]. In our previous work, we also proposed that phase transformation of four-layer graphene affects its scratch hardness [16]. Reguzzoni et al. calculated friction as a function of the film thickness during the a tip sliding against graphene film; it was found that the out-of-plane deformation of the graphene sheets increased when the number of graphene layers increased, both the vertical and the lateral contact stiffnesses increased by decreasing the number of layers [17]. Smolyanitsky et al. simulated a capped SWCNT sliding over a suspended graphene sheet; the relationship between the friction of graphene and the normal force

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was clarified [18]. However, until now, few studies took attention to the phase transformation's effect on the frictional behavior of graphene. In this paper, we clarified the frictional mechanism of graphene by analyzing the relationship between graphene phase transformations and the frictional behaviors by MD study. Furthermore, we investigated the dependence of friction coefficient on scratch depth, tip shape, and scratch direction.

2. Molecular dynamics model

In the simulation, the second generation of reactive empirical bond order (REBO) potential [19] was adopted to describe the intralayer graphene interactions as well as the interactions in the diamond tip via LAMMPS software [20]. This potential is derived from ab initio calculation, and is well suitable to classical molecular dynamics simulation of carbon system. It is in the formation similar to a pairwise dispersion-repulsion potential.

$$U = \sum_i \sum_{j(>i)} [V^R(r_{ij}) - b_{ij} V^A(r_{ij})] \quad (1)$$

$V^R(r_{ij})$ is the function of all interactomic repulsive interactions while $V^A(r_{ij})$ represents the attractive interactions. The distance between pairs of nearest–neighbor atoms i and j is expressed by r_{ij}. The bond-order function b_{ij} can deal with many-body effects and is capable to calculate the formation and cracking of covalent bonds [8]. Because the bond-order function b_{ij} not only contains dihedral angle interaction weighing the bond strength, but also describes radicals and conjugate or non-conjugate structure of carbon, as well as rotation barrier which prevents unrealistic bond rotation from occurring. The forces between the tip and graphene atoms are determined by the Lennard-Jones (LJ) potential [21], in which the equilibrium distance is 3.4 Å [22].

Fig. 1 is the MD nanoscratching simulation model of graphene. A hemispherical diamond tip with radius of 25 Å is initially indented four-layer graphene at a certain depth. After 50,000 steps relaxation, the tip scratches graphene with a speed of 5 m/s. Each graphene layer contains 3200 atoms with the size of 98 Å × 98 Å. The two boundary atoms around each graphene layer are fixed. The diamond tip is also rigid to avoid atom transferring between the tip and graphene layers. The other part of graphene is free atoms. The system is consistent with NVE microcanonical ensemble. Within this ensemble, the number of atoms N, the system volume V, and the energy E are conserved to ensure that the total energy is constant. The initial velocity was generated randomly. The equations of particles motion were solved using the Verlet algorithm, and the simulation time step is 1 fs, which is adequate for system relaxation by examining the stability through the root mean square deviations of the atoms.

In order to validate the model, the hardnesses of the four-layer graphene as a function of the indentation depth were calculated. Fig. 2 shows the hardness versus indentation depth curves of the four-layer graphene simulated by our model and Guo et al.'s model [23]. It can be seen the two results coincide quite well. Here, we need to mention that, in Guo et al.'s model, the intermolecular interactions was considered, which was not included in the REBO potential in our model. But the coincidence of the two results suggests the intermolecular interactions may be neglected in our model. In addition, it can be seen in Fig. 2 that the hardness of the graphene reaches a peak value when the indentation depth increases to 5.8 Å, and after the depth, the hardness presents an unstable behavior, showing a declining trend, this implies that the effect of outermost rigid layer on the hardness is not large. Furthermore, for the cases of horizontal force study, the influence of the rigid layer may be smaller. Therefore, we used the model as shown in Fig. 1 for studying the nanoscratching of multi-layer graphene.

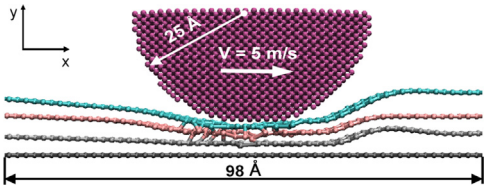

Fig. 1. MD nanoscratching model of graphene.

3. Results and discussion

Fig. 3(a) shows the variation of friction coefficient with the sliding distance under different scratch depths. When the depth are 4.48 Å and 5 Å, shown as the black and red curve, both the average friction coefficients are around zero, and the curve is very

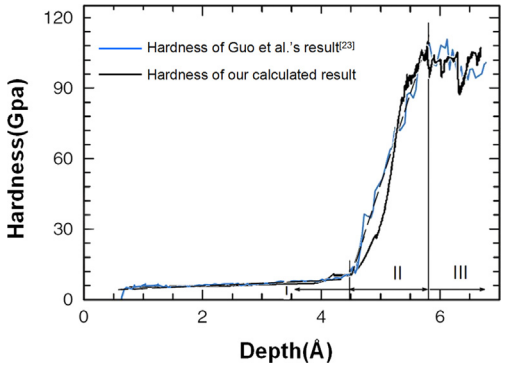

Fig. 2. Comparison of the hardness versus indentation depth curves of the four-layer graphene simulated by our model and Guo et al.'s model.

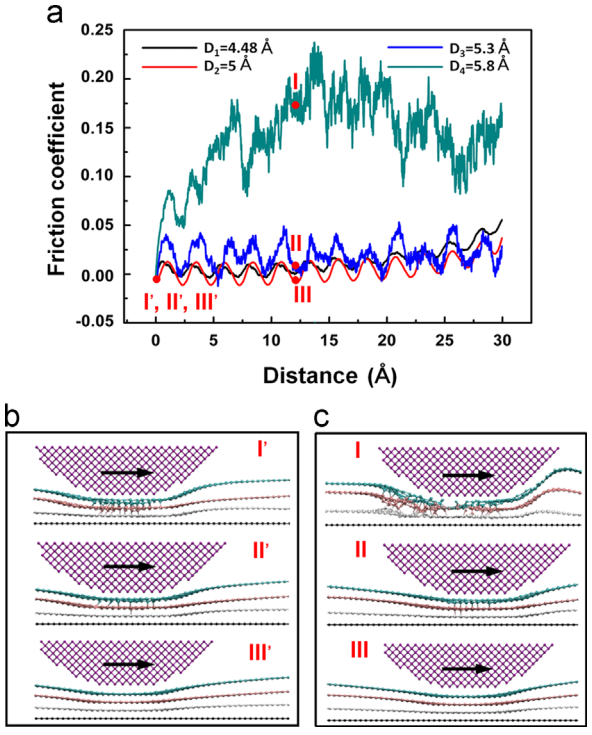

Fig. 3. (a) Under four scratch depths, the friction coefficient of the tip varying with the sliding distance. (b) and (c) The structure of graphene corresponding to scratch depth of 4.48 Å, 5.3 Å and 5.8 Å before scratch and at scratch distance of 13 Å respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)