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Computational investigation of the temperature influence on the cleavage of a graphite surface

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ABSTRACT

Mechanical exfoliation of a graphite surface with an adhesive nanoasperity is studied under different temperatures ranging from 298 K to 2 K using classical molecular dynamics. Two types of the interlayer interaction are investigated. For a pairwise Lennard-Jones potential the complete removal of the upper graphene layer during the retraction of the nanoasperity occurs in the whole range of the temperatures considered. The results obtained using registry dependent potential, which takes into account electronic delocalization contribution besides the van der Waals one, exhibit more pronounced temperature dependence. In this case the exfoliation takes place for temperatures higher than 16 K, but beginning from 8 K down to 2 K the system behavior manifests qualitative changes with the absence of cleavage of the sample. Analytical estimates combined with the results of the simulations reveal that the contribution of the overlap of π orbitals of carbon atoms plays an important role in the exfoliation of graphite.

1. Introduction

Graphite is a lamellar material which is widely used in the experiments where an atomically flat surface is required and its fabrication is accomplished by mechanical cleavage of a graphite sample [1–4]. The cleavage of graphite is usually considered in the mentioned applied context. However, understanding the detailed physics of this process and elucidating the influence of different factors on its behavior may be valuable both from practical and theoretical viewpoints. In this context it is worth mentioning that mechanical exfoliation was the technique which allowed the discovery of graphene [5], a monolayer of carbon atoms tightly packed into a honeycomb lattice. This novel material has unusual electronic properties and it is promising for a wide variety of applications, in particular, the creation of new high-frequency electronic devices [6,7]. In spite of the development of new methods for producing graphene at high yields [8–10], micromechanical cleavage or exfoliation of bulk graphite still remains the main technique used by most experimental groups for the fabrication of high-quality graphene samples [10–12]. Comprehensive understanding of this process may assist in adjusting the conditions for production of samples with the desired characteristics. The cleavage of graphite is also closely related to the so-called superlubricity which was observed during probing a graphite surface with tungsten tip of a friction force microscope (FFM) [3,4]. This phenomenon is characterized by a reduction of friction by orders of magnitude and it is attributed to the existence of a small graphite flake attached to the tip [3,4,13,14]. Revealing the contributions of different factors to the formation of a graphitic flake, which occurs by cleavage from a graphite surface, may be valuable for the establishing the conditions of realization of the superlubricity phenomenon.

In spite of practical significance of the graphite exfoliation there is a lack of its theoretical studies. Models of superlow friction of graphite are often based on the assumption of the presence of the cleaved graphitic layers [4,13–15]. There are also theoretical investigations of nanoindentation of graphite using classical molecular dynamics (MD) [16–18] or boundary element method [19]. Diamond [16] and virtual indentors [17–19] are employed to probe the mechanical properties of graphite [16,17,19] or to explore the formation of interlayer sp^3 bonds under high pressures [18]. However, repulsive interactions between the indentor and the sample in the works mentioned above do not allow the investigation of mechanical exfoliation of graphite which could have been observed for the adhesive tips. Some theoretical analysis of graphite cleavage can be found in Ref. [20] where novel fabrication method for incorporating nanometer to micrometer scale few-layer graphene features onto substrates with electrostatic exfoliation is described. Numerical simulations represented in Ref. [20], however, are intended only to determine the field strengths needed for performing the described process and do not reveal the accompanying physics.

To fill up the gap in theoretical studies of graphite cleavage we have carried out computer experiments using classical MD. The

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considered model resembles ones described above for the graphite indentation, but it has the following two principal differences. The first one is the use of the adhesive tip. Note, that the indentation, which occurs as a consequence of a jump-to-contact, is very shallow and is not the target of the current investigation. The second difference pertains to the interlayer interaction. In the mentioned works [16–18] a pairwise Lennard-Jones potential (LJP) which takes into account only van der Waals (vdW) attraction between the layers is used. However, as studies exploiting quantum-mechanical techniques suggest, there is also a short-ranged electronic delocalization contribution to the interlayer bonding of graphite [21,22], and neglecting it may influence the exfoliation process. Thus, we performed the separate simulations using the LJ and the registry dependent potential (RDP) [22], which includes the mentioned orbital overlap contribution. The main aim of the work is to analyze the graphite cleavage under different temperatures using these two interlayer potentials. Temperature of the sample is one of the natural factors that has an impact on the interlayer cohesion in graphite, and it has been recently used in the solvothermal-assisted method of graphene production [9], hence indicating the need of its thorough exploration. The next section gives the details of the simulation setup.

2. Model

The graphitic sample consists of three graphene layers with AB stacking (Fig. 1) which reflects α form of graphite. Armchair and zigzag graphene edges lie along x and y coordinate axes, respectively, and periodical boundary conditions are applied in the xy-plane. Each layer is composed of 24×24 honeycombs thus containing 3456 carbon atoms and the lengths along x and y directions are 10.082 nm and 8.731 nm, respectively. To hold the sample in space, the bottom graphitic layer is rigid throughout the simulations.

Our model is mainly approached to the experiments pertaining to the superlubricity. The graphite surface interacts with an infinitely hard square pyramidal nanoasperity (to which we also refer as the tip) which simulates the tip of FFM. The asperity consists of five layers of atoms parallel to the xy-plane. Particles are arranged in a perfect bcc lattice with constant of 0.3165 nm and this corresponds to the crystal structure of tungsten [24]. The tapered form is provided by adding one atomic row in x and y directions per layer when moving from the bottom (which is the nearest to the sample part of the asperity) to the top of the tip. The bottom atomic layer exposes (001) crystallographic plane and has 13×13 atoms on the area $a_x \times a_y$. The nanoasperity contains 1135 atoms and the total number of particles involved in the simulations is 11,503.

It should be noted, that the hardness of the nanoasperity may influence the exfoliation and, strictly speaking, for completely realistic reproduction of the experimental conditions the tip in the model should be able to deform. This can be achieved by exploiting one of the available interatomic potentials for tungsten, e.g. based on the modified embedded atom method [25] or its new form [26]. Nevertheless, absolutely rigid surfaces are quite often used in MD simulations [27,28] and we also decided to study the system under mentioned approximation as the first step towards more realistic modeling.

Nanoasperity dimensions are chosen to satisfy the fact that accordingly to the experiments the flake is assumed to attach to asperities on the tip with sizes of several nanometers (see high-resolution transmission electron microscopy micrograph of the tungsten tip in Fig. 5.11 in Ref. [4]). The size of the nanoasperity greatly affects the exfoliation in our simulations (this is analyzed in Section 4) and its value has been chosen to provide the most suitable conditions for the demonstration of the differences in system behavior with LJP and RDP.

Covalent bonds between carbon atoms within the two upper dynamic graphene layers are described by the Brenner potential. It has the following form [29,30]

$$V_B = \sum_i \sum_{j>i} [V^R(r_{ij}) - \bar{b}_{ij} V^A(r_{ij})]. \tag{1}$$

In the current study expressions of a second-generation reactive empirical bond order (REBO2) form of the potential [30] are used for pair-additive interactions $V^R(r_{ij})$ and $V^A(r_{ij})$. Bond order function $\bar{b}_{ij}$ is chosen as in the first version of the Brenner potential (REBO1) with parameters for potential II in Ref. [29]. The code from TREMOLO software [31] is partly used in calculations of cubic splines and their derivatives in the bond order term, and the interactions from Brenner potential are computed using parallel algorithm presented in Ref. [32].

The use of pairwise interactions from REBO2 in the current model is caused by the fact that REBO1 is incapable of proper description of any short-range hard wall repulsion that might prove important under high compression [30,33]. However, more complex form of the bond order term in REBO2 and hence more intensive computations forced us to use the $\bar{b}_{ij}$ from REBO1 because of the computational restrictions. There are, however, several arguments that justify its use in the context of our problem. First, let us analyze the roles that different contributions play in the REBO potential. The energetics of each given hydrocarbon structure is defined by the pairwise terms $V^R(r_{ij})$ and $V^A(r_{ij})$ with the latter modulated by the bond order function $\bar{b}_{ij}$. The main aim of $\bar{b}_{ij}$ is to appropriately adjust the energy of the atomic

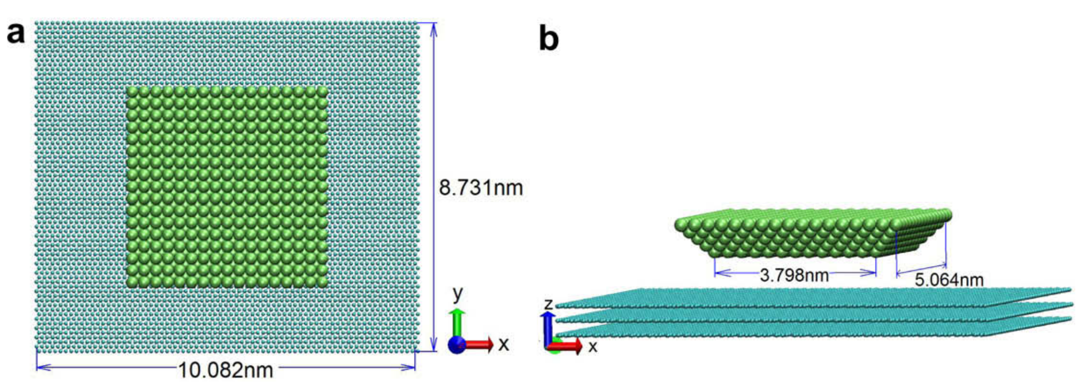

Fig. 1. Top (a) and perspective (b) views of the initial atomic configuration of the studied system. Green and cyan balls correspond to tungsten and carbon atoms respectively (all snapshots in this work are produced with Visual Molecular Dynamics software [23]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)