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# Molecular dynamics study on friction of polycrystalline graphene

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ABSTRACT

Graphene, as a one-atom thick 2-dimensional material, is an ideal solid lubricant for small length scale devices such as NEMS/MEMS (nano/micro-electro-mechanical systems) and is often synthesized using chemical vapor deposition (CVD). While CVD-grown graphene consists of a large number of randomly-oriented grains, the effects of this polycrystalline structure on graphene friction still remain far from completely understood. In this study, we investigate the tribological properties of the multigrain structure against a pristine (defect-free single-crystal) graphene surface using molecular dynamics (MD) simulations. The MD simulations presented here test the friction of multiple such configurations created by a novel method mimicking the natural growth of grains in two dimensions. The simulation results reveal that most multigrain configurations exhibit persistent negligible friction without transiting to high friction states. However, there also exist several configurations having relatively large friction forces compared with those from perfectly-aligned single-crystal graphene interactions. A systematic analysis of the independent effects of the grain orientation and grain boundary explains these observations. In particular, it is found that there exists a critical range in the misalignment angle of grain (0.3–1.5°, to the pristine surface) where the shear stress (friction force per unit area) is two or three times larger than the perfectly-aligned grain. Thus, configurations which contain grains with a small misalignment angle in this critical range exhibit large friction forces, despite their substantially smaller grain area. Moreover, for those configurations where all grains have misalignment angles greater than the critical angle, grain boundaries act as the primary source of friction.



## 1. Introduction

Graphene is a promising material for various applications due to its exceptional thermal, chemical, electrical/electronic, optical, and mechanical properties [1–6]. In particular, its low resistance to sliding as well as the dimensional advantage of being a one-atom thick 2-dimensional material makes graphene an ideal solid lubricant for small length scale devices such as NEMS/MEMS (nano/micro-electro-mechanical systems), to which fluid lubrication is difficult to apply [7,8]. Moreover, the chemical vapor deposition (CVD) method has opened up a new possibility for the scalable production of graphene [9,10]. Thus, many research efforts have focused on studying tribological properties of graphene through experimental and theoretical approaches.

Experimental studies of graphene friction have been conducted from nano to macro scales and found promising results in all length scales. For example, in a nanometer scale friction test using atomic force microscopy (AFM) Egberts et al. found that the friction force was lowered by a factor of 1.5–7 when graphene is coated on oxidized copper surfaces [11]. Moreover, a friction and wear experiment of multilayer graphene on a silicon substrate showed that the friction of graphene films was lower than bare Si surfaces [12]. On micrometer scales, Kim et al. showed that the friction coefficient of $SiO_2$/Si surfaces decreased from 0.68 to 0.12 ~ 0.22 with CVD-grown graphene thin films [13]. Furthermore, in a recent pin-on-disk experiment with a stainless steel ball of 9.5 mm diameter Berman et al. reported that solution-processed graphene layers reduced the friction coefficient by a factor of 6 and the wear by 4 orders of magnitude [14]. A more comprehensive review on graphene friction can be found in [15].

Theoretical and simulation studies on various factors affecting graphene friction have also been performed to elucidate the experimental observations. For example, a finite element analysis [16] and molecular dynamics (MD) studies [17] showed that the reduction in friction force with increasing number of layers, which has been reproduced in many experiments [11,16,18–20], is caused by the puckering effect (i.e. wrinkles forming at the front of a

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scanning tip). Simulations have also been used to understand fundamental atomic-scale mechanisms of graphene friction. First, the effect of the relative orientation between two graphene layers was investigated [21–23] to explain that friction force becomes large at every 60° while negligible at other angles [24]. Moreover, the role of some types of defects in graphene friction has also been studied, for example, it was shown that surface steps on graphene layers can increase the friction force [25–27] and Sun et al. showed that Stone–Wales (SW) type defects and vacancies can increase the friction force of pristine graphene depending on their location and type [28].

CVD is generally regarded as the most promising technique for producing graphene because of its incomparable scalability, flexibility, and transferability [29]. Graphene synthesized by CVD is featured with a multigrain structure in which randomly-oriented individual crystals meet at grain boundaries [30]. Since atoms at grain boundaries are not in perfectly symmetrical environments, the properties of polycrystalline graphene may significantly deviate from those of pristine graphene. Thus, a number of research efforts have been made to investigate electrical/electronic [31–38], thermal [39–42], chemical [43–45], structural [46–50] and mechanical properties [51–53] of polycrystalline graphene. As such, theoretical models based on fundamental atomistic theories, if properly verified and validated by experiments, can greatly enhance our understanding of material properties and behaviors. However, many theoretical predictions and simulation results about the mechanical strength of polycrystalline graphene do not agree with each other and are at times even contradictory [54–58]. For example, one study [54] found no relation between failure stress and grain size and others showed an increase with increasing grain size [56,57] while there are studies which had a decrease [55,58]. Moreover, a number of theoretical studies have focused on *unrealistic infinite straight grain boundaries* [59–66], which do not contain important features like grain boundary junctions. The few friction studies [67,68] in this area have concentrated on the behaviors of isolated non-hexagonal rings constituting grain boundaries. However, the tribological properties of polycrystalline graphene have rarely been studied in its entirety so they remain far from understood.

In this research, we use molecular dynamics methodology to study the role of multigrain structure in friction of polycrystalline graphene. Creating a multigrain graphene model for MD simulation we measured its friction force using multiple unique configurations. We also investigated the role of individual factors in friction such as grain orientation, size, as well as grain boundaries in connection with the observations from our simulations. We found that the friction force of the multigrain graphene can be explained by considering the area and orientation of each grain comprising the system and the total area of grain boundaries in a consistent way.

The article is structured as follows. In Section 2, we describe the simulation model and method used in this study. Section 3 presents the simulation results for friction of pristine and multigrain graphene layers. In Section 4 the role of various factors affecting the friction force is analyzed to explain the simulation results. Finally, Section 5 provides a summary.

## 2. Models and methods

### 2.1. Simulation model

Fig. 1 shows the simulation model for the friction test consisting of four graphene layers, labeled 1–4 in increasing order from the bottom. Each layer has the dimensions of 200.756 Å × 75.409 Å with periodic boundary conditions applied in the $x$ and $y$ directions

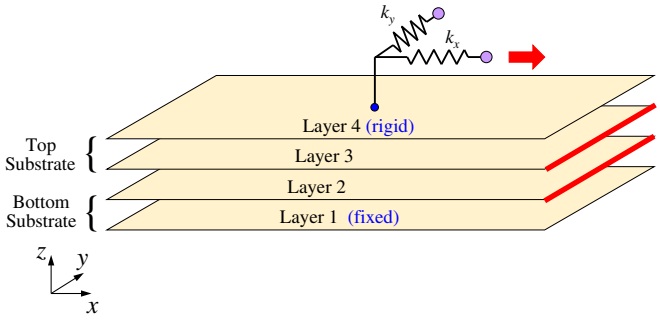


**Fig. 1.** A schematic diagram of the simulation model consisting of four graphene layers.

to create a pseudo-infinite layer. The mass center of the top layer (layer 4) is attached to two linear springs in the $x$ and $y$ directions as shown in Fig. 1, which mimic the stiffness of an AFM cantilever. Their spring constants, denoted by $k_x$ and $k_y$, respectively, are chosen as 5.75 N/m, which is obtained from the stiffness value of an AFM experiment with graphene [24]. This allows us to model the sliding of graphene layers attached to an AFM tip against the bottom substrate. The spring in the $x$ direction is connected to a slider, which moves in the $x$ direction at a constant velocity of 1 m/s during the friction simulation. The slider starts from the initial location of the mass center of the top layer and travels a distance of 25 Å in the $x$ direction. This motion of the slider provides a lateral force to the top layer, which is used to measure the friction force as in the AFM experiment. The $y$ directional fluctuation of the top layer is independently controlled through the second spring in the $y$ direction, which is connected to a point mass whose $y$ position remains unchanged to the initial $y$ position of the mass center.

The top layer remains rigid during sliding so that there is no relative motion between the atoms comprising the layer. Similarly, the atom positions of the bottom layer (layer 1) are fixed to prevent the rigid body translation caused by the moving slider. One row of atoms located at the right end of layers 2 and 3 (illustrated by thick lines in Fig. 1) are rigidly attached to layers 1 and 4, respectively, so that sliding occurs exclusively between layers 2 and 3. Hereafter, layers 1 and 2 together will be referred to as the bottom substrate and layers 3 and 4 as the top substrate.

All the intralayer interactions between carbon atoms are defined by the adaptive intermolecular reactive empirical bond order (AIREBO) potential [69] while the interlayer interactions are modeled by the Lennard-Jones (L-J) potential. The L-J parameters were chosen to reproduce an equilibrium interlayer distance of 3.35 Å [23]. While the proper modeling of interlayer interactions of multigrain graphene poses far more difficult challenges than pristine graphene, it has been known that the L-J potential provides reasonable predictions for the interlayer interaction of graphene, which are also consistent with *ab initio* calculations [70]. Another consideration for the interlayer interaction is the possibility of chemical reaction at the grain boundary due to the presence of dangling bonds [43]. Since we assume that sliding occurs under perfect vacuum conditions, the only possible chemical reaction we can expect to occur is the formation of strong covalent bonds between layers. However, due to the relatively small size of atomistic models used in MD, the existence of even a single such bond dramatically increases the shear resistance between layers preventing any sliding from occurring, which is against most experimental observations that graphene layers have very low friction. Therefore, in our MD simulations we intentionally excluded its possibility by adopting the L-J potential for interlayer interactions, which was also employed in prior friction studies of defected graphene layers [28,68].