

Article

# The Influence of Hydroxyl Groups on Friction of Graphene at Atomic Scale

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**Abstract:** Hydroxyl groups play an important role in friction of graphene oxides. In this paper, the influence of hydroxyl groups on friction of graphene is investigated by molecular dynamics simulation. The results show that the friction does not always go up with the rising of hydroxyl groups ratio, and reaches the maximum when the hydroxyl groups ratio between interfaces is about 10%. The reason is that hydrogen bonds tend to form in interlayers when the hydroxyl groups ratio is high. The formed hydrogen bonds between interfaces are closely related to the friction. However, the analysis of the component of van der Waals, Coulomb's forces and hydrogen bonds interaction between interfaces indicates that van der Waals forces are dominant in friction, which can be attributed to the influence of interface distance on friction.

**Keywords:** graphene; friction at atomic scale; hydroxyl groups

## 1. Introduction

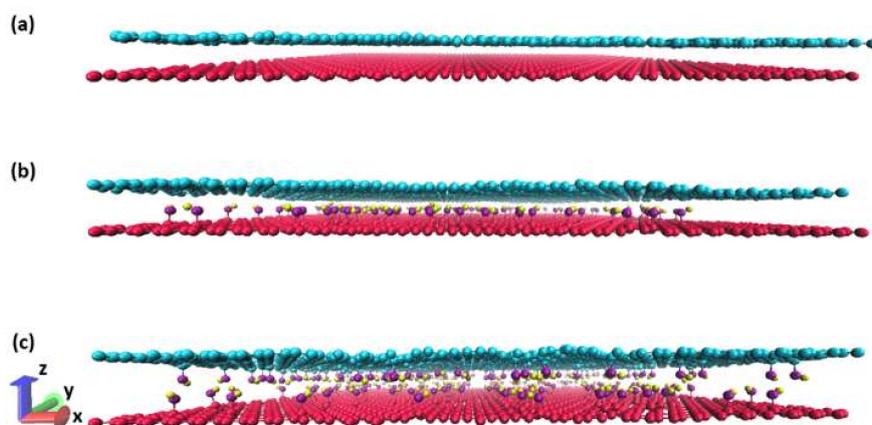
Graphene and graphene oxides have attracted a lot of attention owing to their excellent electronic and mechanical characteristics [1–3]. Friction and adhesion play significant roles in their application. Raman results have shown that graphene oxides contained large density structural defects, and the XPS results suggested that these defects were epoxy and carbonyl/hydroxyl functional groups at the basal plane and the edges of the graphene sheets, respectively [4]. The friction of graphene and graphene oxides are very different from each other because of these functional groups. The friction of graphene has been investigated sufficiently in recent years [5–9], and the influences of layer stacking and the other structural properties are clear. However, research on the friction of graphene oxides and how their related functional groups influence friction is relatively little. In a previous experimental work, graphene oxides, as lubricant additive, were found to reduce friction and wear [10]. The role of oxygen functional groups of graphene oxides for lubrication were also discussed by measuring the friction coefficient and the wear of two reduced graphene oxides terminated with hydroxyl and epoxy-hydroxyl groups and polyethylene glycol [4]. The authors indicated that the strong coupling between two graphene sheets through hydroxyl units caused the interaction of polyethylene glycol with the graphene oxides to be non-effective for lubrication. In microscale, Wei [11] and Byun [12] measured the friction of graphene, graphene oxide and reduced graphene oxides by AFM. They both indicated that graphene oxides presented much higher friction than graphene. Berman [13] confirmed that the oxidation resulted in dramatic increase of multilayer graphene friction.

Because functional groups trigger the big difference of friction between graphene and graphene oxides, researchers have started to focus on explaining why functional groups influence the friction behavior of graphene. Dong [14] revealed that atomic roughness induced by hydrogenation was the primary cause of friction enhancement. Kwon [15] and Ko [16] associated enhanced friction of chemically modified graphene with the increased out-of-plane elastic characteristics after chemical

modification. However, because carboxyl, epoxide and hydroxyl groups on graphene oxides may lead to the formation of hydrogen bonds between interfaces, interface interaction is more complicated than hydrogenation and fluorination. Medhekar [17] investigated hydrogen bond networks in graphene oxides using ReaxFF reactive force field. Wang and Ma [18] pointed out that the interlayer hydrogen bond interaction resulted in high static lateral force between two graphene oxide layers by density functional theory. Gupta et al. [4] indicated that the strong coupling between graphene sheets through hydroxyl units obviously affected their lubrication. In fact, the influence of hydrogen bonds on interface distance [19,20] and friction were also discussed in other materials; for example, silica/silica interfaces [21], and biomatter [22]. However, when hydrogen bonds form between interfaces, how several kinds of forces between interfaces influence friction, and whether hydrogen bond interactions are dominant in friction are still not clear. In this study, we build three simulation models including two-layer graphene, the lower layer of graphene grafted with hydroxyl groups and the two layers of graphene both grafted with hydroxyl groups between interfaces by molecular dynamics simulation. The contributions of hydrogen bond interaction, van der Waals forces and Coulomb's forces on friction is made clear, and the influence of hydroxyl groups ratio on friction of graphene are also investigated.

## 2. Simulation Model

The three simulation models used in this paper are illustrated in Figure 1. The ideal model a is two layers of graphene. In model b, hydroxyl groups are introduced randomly on the bottom layer. In model c, the interfaces between the two layers are both randomly grafted with hydroxyl groups. Hydroxyl groups ratio on graphene denotes the number of hydroxyl groups to the number of carbon atoms on the layer. The  $x$  and  $y$  dimensions of graphene layers are 7.38 nm and 7.46 nm, respectively.



**Figure 1.** The structures of simulation models (a–c). Blue, red, purple and yellow balls denote C atoms in the upper graphene layer, C atoms in the lower graphene layer, O atoms and H atoms, respectively. In model (b) and (c), the hydroxyl groups ratio on graphene layers is 0%/5% and 5%/5% respectively.

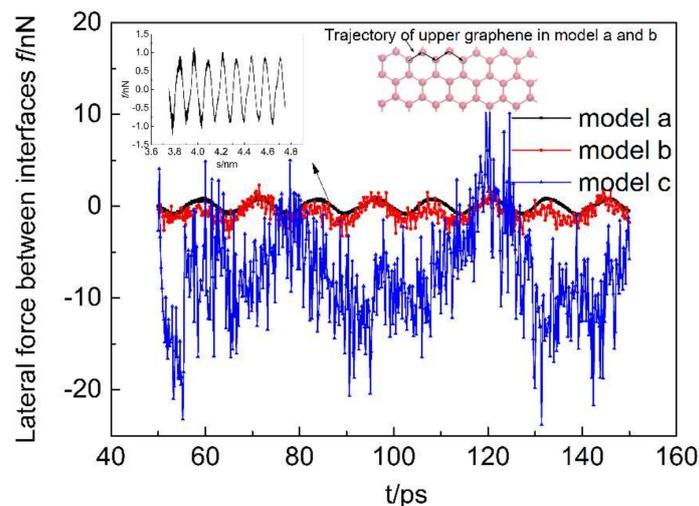
The REBO (The reactive empirical bond order) [23] potential is applied to describe the C–C bond interactions within graphene. Since the O atoms are not considered in REBO potential, Hughes [24] indicated that OPLS (Optimized potentials for liquid simulations) force field [25] could be applied to describe C–O–H interactions. The charges on the hydroxyl groups and corresponding C atoms on graphene could be found in the literature [26]. Classic 12–6 Lennard–Jones potential [27] is applied to calculate van der Waals forces between interfaces in three models. The hydrogen bond in model c is described by the DREILDING [28] force field. The bottom graphene layer is fixed. The periodic boundary conditions are applied along the  $x$  and  $y$  directions. The simulations are carried

by LAMMPS [29]. NVT ensemble with a system temperature of 300 K controlled by the Langevin thermostat method is used. Velocity–Verlet algorithm with a time step of 1 fs is adopted.

The simulation process is as follows: First, the simulation systems under load relax to reach the equilibrium. Second, the top layer of graphene slides over the bottom layer at a constant speed in  $x$  direction.

### 3. Results and Discussion

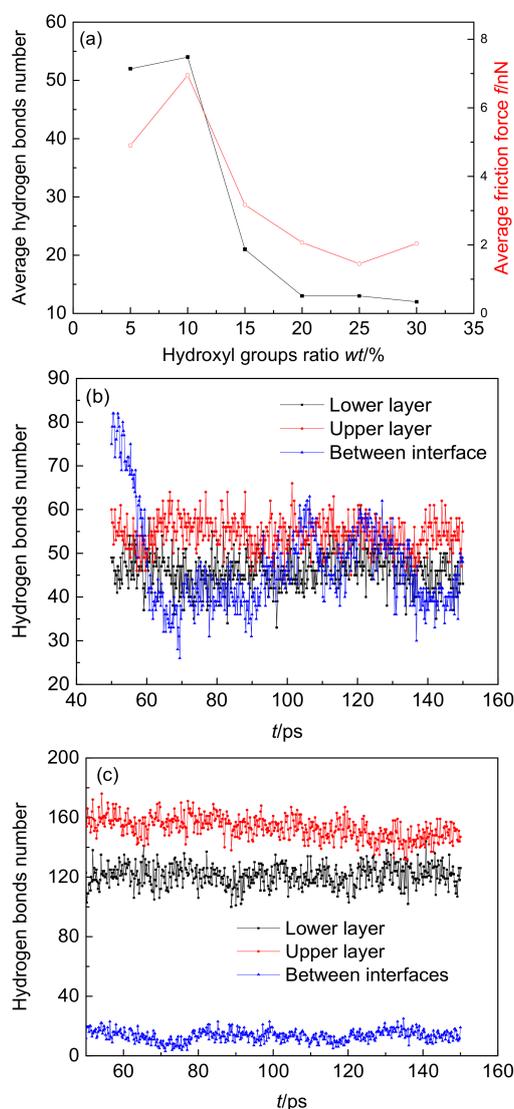
When hydroxyl groups are introduced between interfaces or only on the bottom layer, the influence of the groups on friction is apparently different. The lateral forces between interfaces in model a, b and c are shown in Figure 2. The lateral force in model b is a little larger than in model a, and they present similar periods. The inset is the lateral force with move distance in  $x$  direction in model a. The period is about 0.12 nm, which is similar to  $\sqrt{3}/2 \times A$ , where  $A$  denotes C–C bond length. The reason that causes this phenomenon is that the upper graphene layer slides over the bottom layer in a periodic zig-zag way. The trajectory of the upper graphene is as shown in the upper right corner of Figure 2. However, in model c, when hydroxyl groups are introduced between interfaces, the lateral force obviously changes. The average friction force is much higher than 0.67 nN in model b and nearly zero in model a. The lateral force in model c is not periodic any more owing to the random distribution of hydroxyl groups. The reason is that hydrogen bonds form between the hydroxyl groups when their distance and angle are in a certain domain. The formation and break of hydrogen bonds during sliding increase friction. Wang and Ma [18] indicated that hydrogen bonds formed between interfaces obviously influenced friction. Our results agree with their conclusion.



**Figure 2.** The lateral force between interfaces in models a, b and c. In model b and c, the hydrogen groups ratio on the upper and lower graphene layers is 0%/5% and 5%/5%, respectively. The inset curve shows the lateral force with move distance in  $x$  direction in model a. The trajectories of the upper graphene layer in model a and b are similar, which is illustrated in the upper right corner.

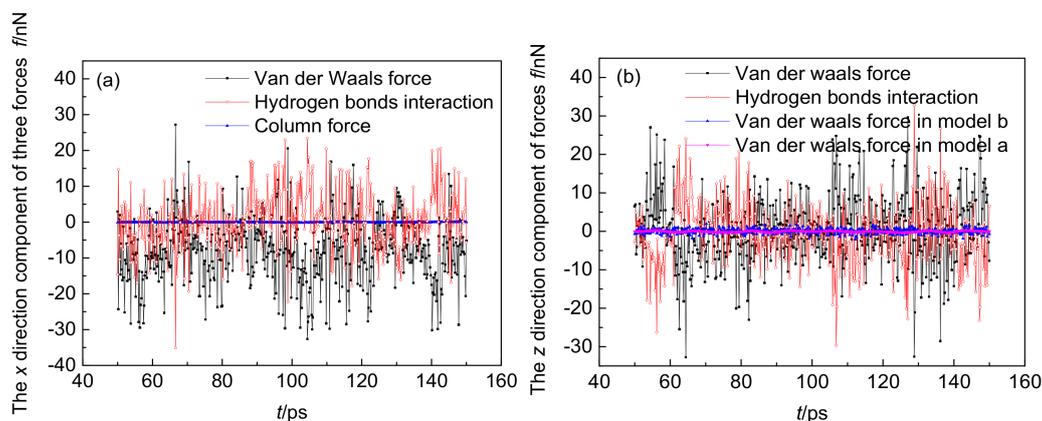
In general, it will be regarded that more hydroxyl groups will lead to more hydrogen bonds being formed, which results in higher friction. However, we find that larger hydroxyl groups ratio on graphene does not mean higher friction. Figure 3a shows the average friction force and the average hydrogen bond number between interfaces during motion stage in six cases, in which hydroxyl groups ratio varies from 5%/5% to 30%/30%. Hydrogen bonds are considered to form when the distances between the acceptor atoms and the donor atoms are smaller than 0.35 nm and the bond angles between the acceptor atoms, the hydrogen atoms and the donor atoms are larger than  $150^\circ$ . The average hydrogen bond number between interfaces shows a similar trend to friction, which implies

that friction is correlated with hydrogen bonds formed between interfaces. Friction force reaches the maximum when the ratio is about 10%/10%, then decreases with hydroxyl group ratio. To explain why the higher hydroxyl groups ratio does not lead to more hydrogen bonds between interfaces and higher friction, the numbers hydrogen bonds formed during the motion stage in the lower graphene layer, the upper graphene layer and between interfaces when hydroxyl groups ratio is 5%/5% and 20%/20%, are shown as Figure 3b,c. In the case with ratio 20%/20%, the hydrogen bonds formed between interfaces are obviously less than in the case with the ratio 5%/5%. However, the hydrogen bonds in interlayers show opposite results. It can be concluded that hydrogen bonds tend to form in interlayers in cases with high hydroxyl groups ratio, which suppresses the formation of hydrogen bonds between interfaces and causes a decrease in friction. Besides, it can be seen in Figure 3a that the average hydrogen bond number between interface is similar when hydroxyl groups ratio is between 20%/20% and 30%/30%, which implies that the formed hydrogen bonds will be stable when the hydroxyl group ratio reaches a certain value.



**Figure 3.** (a) The average hydrogen bonds number between interfaces and the average friction force during motion stage in six cases with hydroxyl groups ratios of 5%/5%, 10%/10%, 15%/15%, 20%/20%, 25%/25% and 30%/30%; (b) The hydrogen bonds number in the lower graphene layer, the upper graphene layer and between interfaces in the case with hydroxyl groups ratio 5%/5%; (c) The hydrogen bonds number in the case with hydroxyl groups ratio 20%/20%.

To further explain how the hydrogen bond influences friction, interface interaction is analyzed in details in this paper. When hydroxyl groups are introduced between interfaces, three kinds of forces including van der Waals forces, Coulomb's forces and hydrogen bond interactions appear. Figure 4a shows the  $x$  direction component of van der Waals forces, Coulomb's force and hydrogen bond interactions between interfaces when the hydroxyl groups ratio is 10%/10%, in which case the average friction is the largest. The  $x$  direction component of van der Waals forces and Coulomb's forces can be calculated directly in LAMMPS. The component of lateral force caused by hydrogen bonds is obtained through the total lateral force minus the other two parts. The results show that van der Waals forces and hydrogen bond interactions play more important roles in lateral forces. Moreover, hydrogen bond interaction is not dominant in lateral forces. In the research of frictional sliding between Cellulose  $\beta$  nanocrystals, Wu et al. [30] indicated that although the observed friction trends could be correlated with hydrogen bonding, it might not be the most significant factor in determining frictional behavior on cellulose nanocrystal surfaces. In our results, this speculation is confirmed and the dominant factor is found. In Figure 4a, it can be clearly seen that van der Waals forces are dominant in friction. Why hydrogen bond interaction between interfaces is correlated with friction but is not dominant can be explained as follows. Figure 4b shows that the  $z$  direction component of van der Waals forces in models a, b, c, and the  $z$  direction component of hydrogen bond interactions in model c. The fluctuation of  $z$  direction components of van der Waals forces in model c is obviously larger than in models a and b, which implies high van der Waals forces between interfaces owing to the introduced hydroxyl groups. Because more formed hydrogen bonds result in smaller interface distance, larger van der Waals forces and higher friction will occur, therefore, friction is correlated with hydrogen bonds, however, van der Waals forces still play the most important role.



**Figure 4.** (a) The  $x$  direction component of van der Waals forces, Coulomb's forces and hydrogen bond interactions between interfaces in model c; (b) The  $z$  direction component of van der Waals force in models a, b, c, and the  $z$  direction component of hydrogen bonds interaction in model c.

#### 4. Conclusions

In this paper, the influence of hydroxyl groups on friction of graphene at the atomic scale is investigated. The results show that the introduced hydroxyl groups between interfaces will obviously increase the friction. The friction force and hydrogen bond numbers between interfaces reach the maximum when the hydroxyl groups ratio is about 10%/10%. The reason is that the hydrogen bonds formed in interlayers suppress the formation of hydrogen bonds between interfaces. The hydrogen bonds trend with hydroxyl groups ratio is correlated with friction, however, van der Waals forces are still dominant in friction. It can be explained that more formed hydrogen bonds decrease interface distance, which leads to larger van der Waals forces, and then results in higher friction.

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**Author Contributions:** Rui Li wrote the paper. Chenggang Song conducted part of the simulations.

**Conflicts of Interest:** The authors declare no conflict of interest.

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