MODELLING ADHESION OF DEFECTIVE GRAPHENE INTERFACES

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Summary We present development of a homogenous spring model to characterize the influence of surface defects on the adhesion properties of graphene interfaces. We compared the cohesive energy of the graphene silicon-dioxide interface given by the proposed model with molecular dynamics simulations, and the results are in good agreement.

The exceptional electromechanical properties of graphene have facilitated the development of the next generation of nanodevices. These state-of-the-art nanodevices, such as sensors and transistors, have profound impacts in numerous engineering disciplines, ranging from biomedicine to aerospace [1]. Recent experiments show that graphene could also be used as an ultra-strong reinforcement for composite materials. Using graphene as reinforcement provides an excellent opportunity to transfer the superior electromechanical properties of graphene, across multiple length scales, up to the macroscopic level. In both graphene-based nanodevices and composite materials, graphene is in contact with adjoining materials, creating mechanically weak interfaces between graphene and the other materials. On the other hand, defects such as surface impurities are unavoidable during fabrication of graphene-based systems. These defects could highly deteriorate the mechanical properties of graphene [2-5], which will ultimately influence the performance of graphene-based systems. Therefore, understanding the effects of defects on the mechanical properties of both graphene and graphene interfaces is critically important in designing reliable graphene-based systems.

In this paper, we develop a homogenous spring model to characterize the influence of surface defects (e.g., vacancies, adatoms) on the adhesion properties of graphene interfaces. Discrete nature of this interface model allows us to investigate the influence of point defects such as vacancies and adatoms, which breaks the continuity of the interface; therefore, the continuum-based models (e.g., [6-8]) cannot be employed. We use the adhesion properties of graphene-silicon-dioxide (SiO$_2$) interface, which is one of the most widely studied interfaces [8,9], obtained using molecular dynamics (MD) simulations to validate the proposed model. The model is a computationally efficient tool to analyze the interfacial properties of advanced graphene-based systems, and the model can also be parameterized to investigate the properties of any material interface at the atomic scale.

We modelled the interfacial adhesion of graphene-SiO$_2$ system using Lennard-Jones (LJ) potential, and the adhesion between carbon atoms of graphene and the SiO$_2$ substrate is represented by nonlinear springs. Fig. 1(a) graphically demonstrates the graphene-SiO$_2$ system, and Fig. 1(b) shows the proposed nonlinear spring model characterizing the interaction between graphene and SiO$_2$ substrate. One end of the springs are attached to carbon atoms of graphene and the other ends are connected to the substrate, which is assumed infinitely rigid considering the magnitude of van der Waals force and the stiffness of SiO$_2$ and other typical substrate materials. During the delamination process, graphene sheet is assumed to be conforming completely to a flat SiO$_2$ substrate. The separation distance between graphene and SiO$_2$ substrate is $l$, and the dimensions of the SiO$_2$ substrate are considered infinitely large. Energy stored in a nonlinear spring, $U(l)$, can be expressed in terms of the van der Waals energy between a carbon atom and the SiO$_2$ substrate as

$$U(l) = \sum_j 4\pi \rho_j \sigma_j^6 \left( \frac{\sigma_j^9}{45l^6} - \frac{\sigma_j^6}{6l^3} \right), \quad (1)$$

where, $\epsilon_j$ and $\sigma_j$ are LJ constants, and $j$ represents substrate atoms, which are silicon and oxygen in SiO$_2$; $\rho_j$ is the atomic density of the atom type $j$. Detailed information on the development of the spring model is given in [10].

![Fig. 1](Image)

Fig. 1 (a) Three-dimensional view of the graphene-SiO$_2$ system. (b) The proposed spring model characterizing interfacial adhesion between graphene and SiO$_2$ substrate.

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Figure 2(a) shows the theoretical model characterizing the interfacial adhesion of a defective graphene-SiO$_2$ interface. The hydrogen adatom is assumed to be on the side of SiO$_2$ substrate, inducing a higher influence on the adhesive properties. As demonstrated in Fig. 2(a), $l_1$ is the out-of-plane deformation of the carbon atom attached to an adatom relative to plane of graphene, and the distance between the plane of graphene and the hydrogen adatom is $l_2$. Using MD simulations, we found the values of $l_1$ and $l_2$ are 0.5 Å and 1.58 Å, respectively; these values are independent of the interfacial separation $d$ and the concentration of adatoms. The spring $S_d$ in Fig. 2(a) models a carbon atom with an adatom, and this spring has an energy contribution from the adatom as well. Therefore, energy stored in the spring ($U_d$) can be expressed as

$$U_d(l) = 4\pi \sum \rho \phi \sigma^4 \left[ \frac{\sigma^4}{45(l-l_1)} - \frac{\sigma_0^4}{6(l-l_1)} \right] + \rho \phi \sigma^4 \left[ \frac{\sigma^4}{45(l-l_2)} - \frac{\sigma_0^4}{6(l-l_2)} \right].$$

(2)

**Fig. 2** (a) Theoretical spring model characterizing graphene-SiO$_2$ interface in the presence of hydrogen adatoms. (b) Comparison of the proposed model with MD simulations.

Figure 2(b) compares the MD simulation results with the developed homogenous spring model. MD simulation results show that as the hydrogen adatom concentration increases, initially the equilibrium cohesive energy of graphene-SiO$_2$ system (i.e. $|\phi_{\text{max}}|$) rapidly decreases, however, after a certain concentration of hydrogen adatoms (~10%), the cohesive energy starts to increase again; whereas, the equilibrium separation continually increases with the adatom concentration. The proposed spring model captures these variations of cohesive energy quite accurately, and the model is accurate even at a concentration of 20%. According to the model, equilibrium cohesive energy of a pristine interface is 162.8 mJ/m$^2$, which is in between the experimentally measured values: 96 mJ/m$^2$ [11] and 450 mJ/m$^2$ [12].

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**References**


