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Development of a homogenous nonlinear spring model characterizing the interfacial adhesion properties of graphene with surface defects

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ABSTRACT

In graphene-based systems, the interface between graphene and other materials creates a mechanically weak region. Therefore, understanding the mechanical behaviour of graphene interfaces is critically important in designing reliable graphene-based systems. On the other hand, defects such as surface impurities are unavoidable during the fabrication of nanoscale systems. We developed a nonlinear spring model to characterize the influence of surface defects on the adhesion properties of graphene interfaces. The model was extensively validated using molecular dynamics simulations for graphene–silicon dioxide interface, and the computed cohesive energy is also in agreement with the recently measured energies. Our results indicate that low concentrations of hydrogen adatoms highly degrade the interfacial strength, whereas vacancies have a negligible effect on the interfacial strength. We also compared the influence of hydrogen adatoms on the properties of several commonly encountered graphene interfaces. In addition, we developed a novel analytical framework to compute the required graphene-substrate interfacial area to withstand an applied force during the indentation test. These findings are useful in designing graphene-based nanoelectromechanical systems and composite materials. More importantly, the developed spring model can be parameterized to investigate the mechanical behaviour of any material interface, which is vitally important in designing reliable nanodevices and nanocomposites.

1. Introduction

The extraordinary strength and stiffness, high flexibility, extremely low weight, high electrical and thermal conductivities, and superior magnetic properties of graphene [1] facilitate the development of the next generation of nanoelectromechanical systems (NEMS) such as resonators [2–4], actuators [5], sensors [6,7], nano-switches [8], transistors [9], solar cells [10], and optical modulators [11]. On the other hand, using graphene as reinforcement in composite materials provides an excellent opportunity to transfer the superior electromechanical properties of graphene, across multiple length scales, up to the macroscopic level [12–16]. In both NEMS and composite materials, graphene is in contact with an adjoining material creating an interface between graphene and the other material. This interface is a mechanically weak region of the system. Therefore, understanding the mechanical behaviour of graphene interfaces is critically important in design and development of reliable graphene-based applications such as NEMS and nanocomposites.

Graphene does not usually make covalent bonds with the adjoining material, and the interfacial interaction occurs mainly via attractive inter-surface forces such as van der Waals force [17–22]. Several recent studies measured the interfacial adhesions of graphene-silicon [17,18], graphene–silicon dioxide (SiO_2) [19,20], and graphene–copper [21,22] systems, where blister test [17,19,21] and double cantilever beam fracture test [18,22] are commonly employed in these experiments. The measured adhesion energies by different experiments, however, demonstrate a significant variation. As an example, Koeing et al. [19] reported the adhesion energy between graphene and SiO_2 as 0.45 J/m^2, whereas it is 0.096 J/m^2 according to Ishigami et al. [20]. Similarly, the adhesion energy between graphene and copper were reported to be 0.34 J/m^2 by Cao et al. [21] and 0.72 J/m^2 by Yoon et al. [22]. Discrepancies of these measured adhesion energies could be due to several factors such as rate of interfacial separation [23], uneven surfaces [20,24,25], and the presence of surface defects/impurities [20,26].

Experiments on measuring interfacial properties of graphene are challenging due to limited capabilities in manipulating

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atomically thin graphene membranes and also due to difficulties in taking required measurements and conducting necessary analysis [17–22]. Atomistic modelling and simulations are viable alternative for the challenging experiments, and these theoretical studies have provided an excellent understanding of the mechanics and interfacial properties of graphene [24–31]. Density functional theory based calculations showed that the graphene-nickel interface is stronger than graphene–copper interface [24], and the adhesion energy of graphene–SiO_2 interface is reduced by surface hydroxylation and adsorption of water molecules [25]. Continuum-based analytical models reveal that surface morphology of substrate has a significant influence on the adhesion energies of graphene-based systems [26–28]. Continuum-based models [26–31], however, have limitations when it is used to studies systems with surface defects such as vacancies (missing atoms) and adatoms (presence of foreign atoms), which are practically unavoidable during synthesis and fabrication of many graphene-based systems [1–11,32].

In this work, 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 reported continuum-based models (e.g., Refs. [26–28]) cannot be used. We use the adhesion properties of graphene–SiO_2 interface, which is one of the most widely studied interfaces [19,20,25,26], 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. In developing this model, however, we assumed that the interlocking friction between graphene and substrate is negligible (i.e. smooth substrate surface). The characterization of substrate surface roughness, which originates of the interlocking friction, is extremely challenging due to complex surface morphology at the atomic scale, although some studies use a simplified sinusoidal approximation for surface roughness to model interfacial adhesion [26,27]. Our assumption on substrate surface results in a computationally efficient and relatively simple model. In addition, neglecting interlocking fictions is a conservative approach because the interlocking friction always resists the failure by interfacial sliding.

The paper is organized as follows: Section 2 describes the MD simulations of graphene–SiO_2 interface. Section 3 presents the proposed continuum-based homogenous spring model. In Section 4, the proposed model has been used to investigate the interfacial sliding of finite graphene–SiO_2 systems. The influence of hydrogen adatoms on the properties of commonly encountered graphene interfaces are compared in Section 5, and conclusions are drawn in the final section.

2. Molecular dynamics simulations

Before developing the spring model, we conducted a comprehensive MD simulation study evaluating adhesion characteristic of graphene–SiO_2 system to gain basic understanding on the interfacial behaviours. These MD simulation results will also be used in Section 3 to validate the proposed continuum-based model.

Molecular dynamics simulations were performed using the LAMMPS package [34]. Interactions between silicon and oxygen in SiO_2 were modelled using Tersoff potential [35,36], and graphene (including hydrogen adatoms) were modelled using adaptive intermolecular reactive empirical bond order (AIREBO) potential [37].

The AIREBO potential consists of three sub-potentials, which are the Lennard–Jones (LJ) potential, the torsional potential, and the reactive empirical bond order (REBO) potential. The LJ potential incorporates the van der Waals forces, and the torsional potential includes the energy due to torsional interactions between atoms. The REBO potential evaluates energy stored in atomic bonds; the energy stored in a bond between atom *i* and atom *j* can be expressed as [38]

$$E_{ij}^{REBO} = f(r_{ij})\left[V_{ij}^{R} + b_{ij}V_{ij}^{A}\right] \quad (1)$$

where V_{ij}^{R} and V_{ij}^{A} are the repulsive and the attractive potentials, respectively; b_{ij} is the bond order term, which modifies V_{ij}^{A} according to the local bonding environment; r_{ij} is the distance between the atoms *i* and *j*; $f(r_{ij})$ is the cut-off function, which limits the interatomic interactions to the nearest neighbours. The REBO potential has been developed using the many-body concept established in the Tersoff potential [35–37].

The Tersoff potential has been used to accurately simulate amorphous silicon [39,40], and the potential consists of two-body terms depending on the local bonding environment [35]. Energy expression of Tersoff potential is equivalent to that of REBO potential given in Eq. (1). Using the first principle calculations, Tersoff parameters for modelling interactions between silicon and oxygen have been developed in Refs. [36], and we used these parameters in our MD simulations.

Interactions between SiO_2 and graphene were modelled using LJ potential, where the energy stored due to van der Waals force between atom *i* and atom *j*, separated by a distance r_{ij}, is expressed as

$$V(r_{ij}) = 4\varepsilon_{ij}\left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right), \quad (2)$$

where, ε_{ij} is the energy when the atoms are at equilibrium separation which is $\sqrt[6]{2}\sigma_{ij}$, and σ_{ij} is the distance between atoms when the energy, $V(r_{ij})$, is zero. Values of ε_{ij} and σ_{ij} depend on the type of atom, and the corresponding values for simulating graphene–SiO_2 system with hydrogen adatoms are given in Table 1. We calculated the values of ε_{ij} and σ_{ij} in Table 1 using the van der Waals interaction parameters specified in the Universal Force Field [41], and the Lorentz–Berthelot mixing rules [42] were employed in the calculations as suggested in Ref. [40]. The van der Waals energy is considered to be stored in the both interacting atoms by equal amounts (i.e. 0.5 $V(r_{ij})$ in atoms *i* and *j*).

The cut-off distance of LJ potential is expressed in terms of σ_{ij}, and we used an extended cut-off distance of $5\sigma_{ij}$ ensuring the full range of van der Waals interactions are taken into account. At a cut-off distance of $5\sigma_{ij}$, the van der Waals energy is 0.006% of the equilibrium energy. The default LJ cut-off distance of the AIREBO potential was also changed from $3\sigma_{ij}$ to $5\sigma_{ij}$. It should be noted that the LJ potential included in AIREBO potential takes into account the van der Waals interactions between hydrogen and carbon atoms only. Therefore, the LJ potential of AIREBO potential does not interfere with the LJ potential used to simulate the van der Waals interactions between graphene and SiO_2.

The simulated pristine graphene–SiO_2 system is shown in

Table 1
Required LJ parameters to model graphene–SiO_2 system.

Atom *i*	Atom *j*	σ_{ij} (Å)	ε_{ij} (meV)
C	Si	3.33	8.91
C	O	3.00	3.44
H	Si	3.20	5.77
H	O	2.85	2.23