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Effects of hydrogen adsorption on the fracture properties of graphene

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ABSTRACT

Adsorption of environment molecules to graphene alters the atomic structure of graphene and impacts fracture properties of graphene. In this paper, we use molecular dynamics (MD) modeling to study the effects of hydrogen adsorption on the fracture mechanics of graphene. Both armchair and zigzag cracks under mode I and II fracture loadings are considered. Our molecular dynamics simulations predict that adsorption of hydrogen atoms to the crack tip or surface leads to a reduction in graphene toughness and can alter the crack propagation paths. Based on our MD simulations, the location of carbon atoms at which hydrogen atoms are attached is a main factor in the level of impact that hydrogen atoms have on the fracture properties of graphene.

1. Introduction

Fantastic mechanical [1], electrical [2,3] and physical [4] properties of graphene make it an ideal candidate for a wide spectrum of applications such as composite materials [5], nano-sensors and nano-devices [6], nanomedicine [7], and energy storage [8,9]. Understanding mechanical properties of graphene is essential toward reliable design and manufacturing of graphene-based nano-devices and nano-materials. Specially, it is important to predict and eventually prevent the fracture of graphene, which necessitates a thorough understanding of the fracture properties of graphene.

Due to the difficulties in designing and performing experiments at nanoscale, experimental approach for determining the physical and mechanical properties of nanomaterials is very challenging. Atomistic modeling, on the other hand, can provide valuable insights into the properties of nanomaterials [10–15]. In particular, atomistic modeling techniques have proven themselves as invaluable tools in determining fracture properties of graphene and graphen-like two-dimensional materials [16–27]. Omeltchenko et al. [21] used the first generation of reactive empirical bond order (REBO) potential to study mode I crack propagation in graphene. Khare et al. [22] used a coupled quantum mechancis/molecular mechanics model to study the effect of defects and cracks on the mechanical properties of graphene. Xu et al. [23] used a coupled quantum/continuum mechanics approach to obtain the critical stress intensity factors of graphene under quasi-static loading. Zhang et al. [24] used molecular dynamics simulations to study fracture in graphene under mixed mode I and II loading. Dewapriya et al. [25,26] used atomistic simulations to study how nanocracks impact the fracture strength of graphene sheets. Tabarraei et al. [27] used density functional theory (DFT) to study the fracture mechanism of graphene nanoribbons with different chirality. Jung et al. [28] used molecular dynamics method to show that polycrystalline graphene releases up to 50% more fracture energy than pristine graphene.

The previous studies on graphene fracture have focused on a graphene sheet with no adsorbed atoms of any kinds. In many applications, chemical functionalization [29] of graphene via attachment of atoms have been used as a mean for tuning the properties of graphene. Among different functional groups, hydrogen has attracted considerable attentions. Adsorption of hydrogen atoms can change the graphene atomic structure [30] which in turn can modify electronic and magnetic properties. For example, the adsorption of hydrogen atoms can induce a band gap around Fermi level which converts graphene from a semimetal to a semiconductor [31], or it can lead to the formation of a magnetic structure [30,32] in graphene.

In addition to deliberate functionalization of graphene sheet with hydrogen, the presence of hydrogen in many environments such as water and air provides many opportunities for its introduction to graphene. The adsorption of hydrogen atoms alter the mechanical properties of graphene. Graphene sheets with adsorbed hydrogen atoms have a lower Young's modulus, tensile strength and fracture strain than those of pristine graphene sheets [33]. Furthermore, it is shown that hydrogenation of graphene grain boundaries leads to substantial reduction in the strength

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and ductility of polycrystalline graphene sheets [34]. Recent experiments provide evidence that the attachment of hydrogen atoms to the crack tip or surface can leads to the environment assisted cracking of graphene sheets [35], as a consequence of which the graphene undergoes sub-critical crack growth.

Attachment of hydrogen atoms to the carbon atoms located in the vicinity of crack tip or edges change the morphology of crack and subsequently affect the fracture properties of graphene. The impact of hydrogen atoms on the fracture properties of graphene sheets has not yet been fully investigated. In this paper, we use molecular dynamics simulations to probe how hydrogen atoms modify the crack configuration and impact the fracture mechanism of graphene sheets.

2. Simulation models and methodology

Our molecular dynamics simulations are performed using LAMMPS (Large-Scale Atomic/Molecular Massively Paralle Simulator) package. The adaptive intermolecular reactive bond order (AIREBO) [36] potential is used to consider the interaction between atoms in the graphene sheet. AIREBO potential allows bond breaking and forming, hence it is suitable for modeling failure. The original AIREBO potential employs two cutoff distances with values of 1.7 and 2 to allow a smooth transition of cutoff function from one to zero. It has been observed that such a cutoff function generates non-physical strain hardening in the stress–strain behavior of carbon nanostructures which is due to the discontinuity in the second derivative of the cutoff function. As a remedy of this issue it is suggested to eliminate the transition zone; the cutoff function is 1.0 for distances less than R and be 0 otherwise. A value of 1.9–2.2 Å [24,34,37–39] has been used for the cutoff distance R. In this paper we use a value of 1.92 Å, as is suggested in Ref. [37] and has been used in the past to successfully capture the fracture properties of graphene [24,40].

We consider the crack propagation of zigzag and armchair cracks under mode I and II loading. For the purpose of computational efficiency, a small circular-shaped domain of radius 70 Å from the crack tip is used to model a semi-infinite crack in a graphene sheet. The size of the domain is chosen such that the whole domain falls within the K-dominant field. The initial zigzag and armchair cracks are generated by removing two or three layers of atoms, respectively. Using this geometry, our domain is composed of about 6000 carbon atoms. Mode I and II displacement field are applied as the boundary conditions to the outermost layers of atoms. The boundary atoms are shown in blue in Fig. 1. We have assumed that the far field behavior is well-represented by a linear, isotropic response because the crack-tip strain filed reduces with distance and graphene behavior is anisotropic only at large strain [41,42]. Atomic displacements on the boundary of the molecular dynamic (MD) zone are prescribed using the crack-tip asymptotic displacement field given by [43]

$$u_x = \frac{K_I}{2\mu}\sqrt{\frac{r}{2\pi}}\cos\frac{\theta}{2}[\kappa - \cos\theta] + \frac{K_{II}}{2\mu}\sqrt{\frac{r}{2\pi}}\sin\frac{\theta}{2}[\kappa + 2 + \cos\theta], \quad (1a)$$

$$u_y = \frac{K_I}{2\mu}\sqrt{\frac{r}{2\pi}}\sin\frac{\theta}{2}[\kappa - \cos\theta] - \frac{K_{II}}{2\mu}\sqrt{\frac{r}{2\pi}}\cos\frac{\theta}{2}[\kappa - 2 + \cos\theta], \quad (1b)$$

where r is the distance between a boundary atom and crack-tip, θ is the polar angle depicted in Fig. 1, K_I and K_{II} are mode I and II stress intensity factors, respectively, μ is the shear modulus, and $\kappa = \frac{3-\nu}{1+\nu}$, where ν is the graphene Poisson's ratio which is taken equal to 0.165. To apply a pure mode I or pure mode II displacement field, the values of K_{II} or K_I parameters are set equal to zero, respectively.

The displacement field is gradually applied to the boundary atoms by incrementing the stress intensity factors in increments of 0.01 MPa $\sqrt{\text{m}}$. After each load increment, by keeping the boundary atoms fixed, first the energy of the system is minimized, and then the system is equilibrated for 6000 time step at a temperature of 300 K using Nosé-Hoover thermostat [44]. The velocity-Verlet scheme with a time step of 1 fs is utilized for the purpose of time integration. The stress intensity factor at which the initial crack advances or a new crack branches off the original crack is considered as the critical stress intensity factor of the domain.

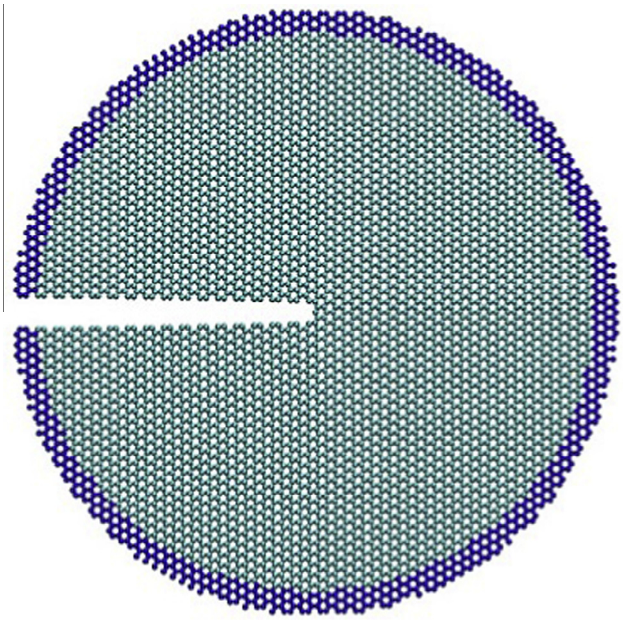

Fig. 1. An initial armchair crack in a graphene sheet. The K-field displacement field is applied to the boundary atoms (shown in blue) while the position of interior atoms (shown in green) are relaxed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To check the validity of our MD modeling approach and for the purpose of comparison, we first find mode I and II critical stress intensity factors of armchair and zigzag cracks when no hydrogen atoms is adsorbed. Our MD simulations predict a mode I critical stress intensity factor (K_I^c) of 3.22 MPa$\sqrt{\text{m}}$ for armchair cracks and 2.88 MPa$\sqrt{\text{m}}$ for zigzag crack, whereas mode II critical stress intensity factors (K_{II}^c) of armchair and zigzag cracks are 3.95 MPa$\sqrt{\text{m}}$ and 3.65 MPa$\sqrt{\text{m}}$, respectively. These values are in good agreement with the values reported previously [23,24,45].

The crack propagation path of armchair and zigzag cracks under mode I and II loading are shown in Fig. 2. These results show that zigzag and armchair cracks propagate along a zigzag path under both mode I and II loading. This is consistent with the previous results [23,24] and confirms that in graphene the surface energy of zigzag edges is smaller than that of armchair edges.

Moreover, our MD simulations predict that under mode II loading the top surface of the crack which is under a compressive load will undergo a buckling (out-of-plane) deformation, a phenomenon which has been observed in thin cracked plates under tensile and shear loading [46–48] as well. The buckling of a graphene sheet with an armchair crack under mode II loading is shown in Fig. 3. The impact of the out-of-plane deformation of graphene on fracture toughness of graphene is studied in [49] and it is shown that the out-of-plane deformation of the graphene can be used as a topological defect to increase the fracture toughness of graphene.

To investigate the impact of the domain size on the results, we have modeled the crack propagation paths and obtained the crack intensity factors using domains with 60,000 atoms. The results