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Tailoring fracture strength of graphene

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ABSTRACT

We conducted molecular dynamics simulations to investigate the atomistic edge crack–vacancy interactions in graphene. We demonstrate that the crack–tip stress field of an existing crack in graphene can be effectively tailored (reduced by over 50% or increased by over 70%) by the strategic placement of atomic vacancies of varied shapes, locations, and orientations near its tip. The crack–vacancy interactions result in a remarkable improvement (over 65%) in the fracture strength of graphene. Moreover, at reduced stiffness of graphene, due to a distribution of atomic vacancies, a drastic difference (~60%) was observed between the fracture strengths of two principal crack configurations (i.e. armchair and zigzag). Our numerical simulations provide a remarkable insight into the applicability of the well-established continuum models of crack–microdefect interactions for the corresponding atomic scale problems. Furthermore, we demonstrate that the presence of atomic vacancies in close proximity to the crack–tip leads to a multiple–stage crack growth and, more interestingly, the propagating cracks can be completely healed even under a significantly high applied tensile stress level (~5 GPa). Our numerical experiments offer a substantial contribution to the existing literature on the fracture behavior of two–dimensional nanomaterials.

1. Introduction

The extraordinary stiffness, fracture strength, and flexibility of graphene [1], a two-dimensional (2D) hexagonal lattice of sp^2 bonded carbon, demonstrate great potentials in a rich variety of applications such as flexible electronics [2–4], nanoelectromechanical systems [5–7], and nanocomposites [8–12]. Even though an atomically perfect graphene sample has an extraordinary fracture strength of 130 GPa [1], pristine graphene samples of large area are yet to be developed for the proposed applications. Even with a pristine graphene sample, atomic flaws such as vacancies and adatoms are difficult to avoid in real engineering fabrication of graphene-based nanodevices [5,13–18]. A recent experiment revealed that the fracture toughness of graphene is $\sim 4\,\mathrm{MPa}\sqrt{\mathrm{m}}$ [19], which is significantly lower than conventional engineering materials [20]. This relatively small fracture toughness poses serious limitations in the use of graphene for numerous structural applications [21]. Therefore, it is important to study the effect of the presence of and interactions between atomistic cracks and defects upon the fracture behavior of graphene. In addition, investigating potential toughening mechanisms for graphene is highly desirable in its commercialization for real life engineering applications.

In continuum fracture mechanics, it has been well established that the interaction between crack and a micro defect in close proximity plays an important role in the overall failure mechanism of quasi-brittle materials [22–28]. It has also been demonstrated that the crack-tip stress field in a linear elastic continuum can be controlled by strategically placing a microdefect near the crack-tip [29,30]. Recent nanoindentation tests of graphene containing vacancies have revealed that the catastrophic failure of graphene can be transformed into a local failure by controlling its defect concentration [31]. This observation suggests that existing cracks in graphene can be arrested by introducing a controlled distribution of topological defects, which has been realized for some other nanomaterials [32,33].

Most of the recent efforts have been focused on enhancing the fracture strength of graphene by introducing topological defects such as pentagon-heptagons [34–38] and grain boundaries [39,40] without paying attention to the complex stress state surrounding crack-defect interactions, which could unveil rich atomistic mechanisms of 2D materials. In fact, many existing molecular dynamics (MD) studies on fracture properties of graphene have focused on the central crack problem partly due to the convenience of using periodic boundary conditions in MD. In addition, advanced continuum-based design tools for characterizing crack-defect interaction [22–30] have not been tested at the atomic scale, which is critically important considering the limited applicability of continuum concepts at the nanoscale [41–47]. If

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applicable, the continuum tools such as design envelopes to ascertain crack-tip stress shielding and amplification zones due to the crack-defect interactions [29,30] can be very useful for nanoscale design of 2D materials [48].

In this work, we focus our attention on exploring the influence of interactions between existing edge nanocracks in graphene and arbitrarily located atomic vacancies at the crack-tip. Our atomistic simulations demonstrate that vacancies of varied shapes, locations, and orientations can be effectively used to shield the existing cracks from high stress levels leading to crack arrest. Moreover, our numerical uniaxial tensile tests reveal that the crack-vacancy interactions in graphene lead to a multiple-stage crack growth and crack healing under remarkably high applied tensile stress levels (~5 GPa), providing a new route for strain engineering of graphene-based devices.

2. Molecular dynamics simulations

We conducted numerical uniaxial tensile tests of graphene samples using LAMMPS MD simulator [49] with AIREBO potential [50], where the cutoff distance was modified to be 2 Å [35,37,51,52]. At the beginning of all MD simulations, energy of the graphene samples was minimized using the conjugate gradient algorithm. Then, before applying strain, the samples were allowed to relax over 25 ps and the time step was selected to be 0.5 fs. Canonical (NVT) ensemble was used for the simulations, where temperature was maintained at 300 K using Nośe-Hoover thermostat. An initial random displacement perturbation (maximum of 0.01 Å) along x, y, and z directions was imposed on carbon atoms to facilitate reaching the equilibrium configuration. In fact, inducing out-of-plane displacement perturbations is essential in these simulations because the Nośe-Hoover thermostat induces artificial thermal expansion in the absence of out-of-plane deformation [53]. After the graphene samples reached equilibrium, strain was applied to the samples along the y-direction (ε_{yy}) at a rate of 0.001 ps^{-1}. The planar dimensions of the simulated samples were selected to be 60 nm × 60 nm, and the length of edge crack was 10 nm. The selected simulation domain ensures that its boundaries do not fall within the *K*-dominant region which is at and near the crack-tip region, where the stress field decays quite rapidly. It has been previously demonstrated that the size dependency is significant when the crack length is less than 10 nm [44,54]; we used the limiting crack length of 10 nm in order to minimize the crack length dependency of the results. Virial stress [55] was used for fracture characterization. Visual Molecular Dynamics package [56] was used to visualize deformations and fracture of graphene.

Fig. 1 shows a typical MD simulation sample of graphene containing an atomic vacancy interacting with an edge crack. The origins of the two rectangular coordinate systems xy and x_0y_0 are taken at the tip of the edge crack and at the center of the vacancy, respectively. The orientation angle of the vacancy is ϕ, and its major and minor diameters are 2*c* and 2*b*, respectively. The distance between the tip of the crack and the center of the vacancy is taken to be *r*. The inclination angle between the x-axis and the line joining the tip of the crack and the center of the vacancy is θ. The value of 2*c* is selected to be 3.6 nm (see Fig. 1).

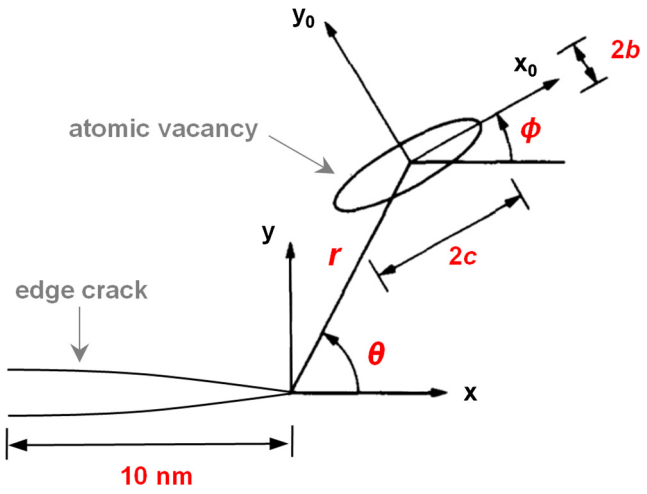

Fig. 1. A typical MD simulation sample of graphene containing an edge crack and an interacting atomic vacancy.

3. Results and discussion

3.1. Crack-tip stress distribution

The stress distribution of individual carbon atoms at the crack-tip can be very informative in characterizing the fracture behavior of graphene. In order to obtain the time averaged stress of atoms at the incipient crack propagation, we conducted two sequential MD simulations as outlined in one of our earlier publications [57]. Fig. 2a and b show the stress distributions at the armchair and zigzag crack-tips, respectively. These stress distributions resemble the ones predicted by the continuum linear elastic fracture mechanics (LEFM) [44]. The peak stress at the tip of the armchair crack at the incipient crack propagation is 17% higher than the corresponding stress of the zigzag crack. This is due to the high far field (or applied) stress σ_0 level of the armchair crack configuration and, more importantly, the different bond arrangements at the crack-tips. In contrast to the isolated bond perpendicular to the crack at the zigzag crack-tip (see inset of Fig. 2a), the two inclined bonds at the armchair crack-tip (inset of Fig. 2b) accommodate part of the applied tensile strain by adjusting the bond angles, which allows the atom at the crack-tip to carry a higher strain prior crack growth leading to a higher atomic stress.

According to LEFM, the critical stress intensity factor (SIF) of a single edge-cracked sample under mode-I loading (where the crack surfaces are displaced directly apart) K_{IC} can be defined as follows [20]:

$$K_{IC} = 1.12\sigma_f\sqrt{\pi a} \tag{1}$$

where *a* is the initial crack length, and σ_f is the fracture stress, i.e. the critical far field stress at the incipient crack propagation. The computed K_{IC} for armchair and zigzag cracks are 4.04 and 3.97 MPa$\sqrt{}$m, respectively, which are in excellent agreement with the experimentally measured value 4 MPa$\sqrt{}$m [19].

Earlier, Gong and Meguid studied the interaction between a semi-infinite crack and an elliptical vacancy located near its tip (see Fig. 1) under mode I loading [29]. In the absence of the vacancy, the singular stress field near the crack-tip can be described by using the corresponding SIF $K_I = 1.12\sigma_0\sqrt{\pi a}$. However, the presence of the elliptical vacancy in close proximity to the crack-tip influences the crack-tip stress field and leads to a modified SIF; we will call $K_I^{(c-v)}$. When a collinear elliptical vacancy is located ahead of the crack, i.e. $\theta = 0$ and $\phi = 0$, the solution for the normalized SIF under mode I loading $K_I^{(c-v)}/K_I$ can be explicitly expressed up to the order $(c/r)^4$ as follows [29]:

$$\frac{K_I^{(c-v)}}{K_I} = 1 + \left(\frac{1}{4}\right)^2(1+\beta^2)\left(\frac{c}{r}\right)^2 + \left(\frac{1}{128}\right)^2(23+46\beta^2+12\beta^3-49\beta^4)\left(\frac{c}{r}\right)^2 + \ldots \tag{2}$$