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Enhancement of fracture toughness of graphene via crack bridging with stone-thrower-wales defects

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ABSTRACT

Ever increasing applications of graphene motivates researchers to synthesize large scale graphene sheets. In general, large scale graphene sheets are synthesized with some inherent topological defects such as vacancies, Stone Thrower Wales (STW) and grain boundaries. In this article, effect of STW defects on the fracture toughness of graphene was studied with the help of molecular dynamics based simulations. In this numerical study, different atomistic configurations of graphene containing a centrally embedded crack with or without STW defects were modelled. It can be predicted from the simulations that STW defects could be used for tailoring the fracture toughness as well as fracture behaviour of graphene. Significant improvement in the fracture toughness of graphene has been observed while applying load in zig-zag direction with STW defects were positioned next to the crack faces. Interaction of stress fields generated from crack tip as well as from STW defects helps in tailoring the fracture behaviour of graphene.

1. Introduction

Graphene is a two-dimensional (2D) monolayer of honeycomb lattice packed carbon structure that was discovered and successfully isolated from bulk graphite [1]. Owing to its outstanding physical properties [2], graphene is a promising candidate in a number of mechanical, thermal and electrical applications [2–6]. In addition to various nano-technological applications, graphene also attracts prodigious attention as reinforcing element in nanocomposites [7–10]. Characterization of graphene in terms of mechanical strength or fracture toughness is essential for its reliable applications as well as to understand its failure morphology under different boundary conditions [11–13].

Defect engineering has been widely employed by researchers to alter properties of several materials such as metals [14–15], ceramics [16] and diamonds [17]. Similarly, defects have also opened up possibilities to tailor properties of graphene for applications in diversified field such as molecule capacitors [18], ion separation and water desalination [19–20]. Due to application of graphene in diversified fields, researchers are focusing more on synthesizing large scale graphene sheets. Synthesizing of large scale graphene sheets by methods such as chemical vapour deposition usually results in a defective graphene, and these topological defects includes vacancies [2], 5-7 defects [21–24], pentagon-octagon-pentagon (5-8-5) defects [25], Stone-Thrower-Wales (STW) defects [2], adatoms, substitution atoms, impurities [26] and crack-like flaws such as slits, holes [27–28].

So far, several investigations have been carried out to investigate the effect of topological defects on the intrinsic properties of graphene. A recetly published work on 5-7 defects [29] has predicted that higher percentage of grain boundary (GB) defects could intuitively give rise to higher strength in tilt GBs. Wei et al. [30] predicted with the help of their atomsitic models that strength of GB in graphene can either increase or decrease with tilt angle. Rajasekaran and Parashar [31] has predicted a shift in the mechanical behaviour of graphene with the help of STW defects. In addition to numerical simulations, the fundamental importance of the effect of defects on the mechanical properties of graphene has also been studied by means of experimental methods [32–33].

Eventough many research have been carried out to understand the physics of defects on intrinsic properties of graphene, very limited research have been carried out to investigate the effect of topological defects on the fracture behaviour of graphene with existing cracks. Recently in 2015, Meng et al. [34] studied dislocation shielding of a nanocrack in graphene using atomistic as well as continuum scale models. It can be inferred from their work that dislocation shielding mechanism can help in enhancing the fracture toughness of graphene. Jung et al. [35] also employed classical mechanics based approach to predict 50% improvement in the fracture toughness of polycrystalline graphene with randomly distributed GB as compared to its pristine form. Zhang et al. [36–37] also studied fracture behaviour of a sinusoidal graphene ruga [38] containing periodically distributed disclination quadrupoles. In their atomistic smulations mode-I fracture toughness of sinusoidal graphene was predicted as 25.0 J/m^2, which is twice that of pristine graphene [36]. Recently in 2016, Wang et al. [39] investigated

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the effect of GB and its different misorientation angles on fracture toughness of bi-crystal graphene and also they studied the interactions between cracks and GB's using molecular dynamics. Similar to the the above studies recently Li et al. [40] studied the role of functional groups on graphene oxide in epoxy nanocomposites and Bortz et al. [41] improved the fracture toughness of epoxy composites by considering graphene oxide as a reinforcement candidate.

Despite the fact that several efforts has been directed towards developing an understanding for the fracture and failure in graphene sheet, the effect of STW defects on the fracture behaviour of graphene with excisting cracks remains largely elusive. STW defects are particularly important because it has been estabilished that interfacial bonding in graphene based nanocomposites preferebly takes place at STW defected regions [42]. It has also been predicted by Dumitrica and Yakobson [43–44] that while, subjecting carbon based nanofillers such as carbon nanotubes (CNT's) to an increasing logitudinal strain, STW formation energy decreases rapidly and causes massive generation of STW defects. This further motivates the authors to study the interaction of STW defects with the pre-existing embedded crack in a graphene sheet. In the literature, it has been reported that there exists at least three mechanisms contributing towards the toughness enhancement in graphene such as dislocation shielding, stress reduction by out-of-plane deformation and atomic-scale crack bridging [27]. Thus, concise knowledge of crack-STW defect interactions is key in understanding the structural evoluation and ripping of graphene. In this article, molecular dynamics based atomistic modelling was performed to study the effect of STW defects on threshold stress intensity factor and fracture morphology of graphene.

2. Modelling details and methodology

In this article, large-scale atomistic models of graphene were developed in the environment of molecular dynamics. All the simulations were performed in open source code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package [45]. In the proposed atomistic models, interatomic interactions between carbon atoms were simulated with the help of adaptive intermolecular reactive empirical bond order (AIREBO) potential [46]. AIREBO potential consists of three sub components, which are the reactive empirical bond order (REBO) potential [47], the Lennard-Jones (LJ) potential and the torsional component. REBO potential evaluates energy stored in atomic bonds, LJ potential accounts for the non-bonded interactions and the torsional component includes the energy due to torsional interactions between atoms. In order to avoid spurious behaviour of interatomic potential in predicting the failure properties, a single cut-off value of 1.95 Å was used in the simulations [31–32,48–49]. In order to avoid finite size effect [50–51], all the simulations performed either with pristine or with defective graphene, dimensions of the graphene were kept fixed at 27 nm, for length as well as for width, which constitutes 27,468 carbon atoms. All the simulations were performed at 300 K with an integration time step of 0.5 fs. In order to eliminate the effect of free edges, periodic boundary conditions (PBCs) were imposed along in-plane directions. After finishing relaxation of atoms for a sufficiently long period of time (30 ps), tensile strain was applied by pulling the sheet along x-direction (zig-zag) or along y-direction (armchair) at a strain rate of 0.001/ps. In order to maintain the desired boundary conditions, isothermal-isobaric (NPT) ensemble was enforced in all the simulations. Stress in the graphene sheet was computed by averaging over 100 time-steps of all the carbon atoms in the model. Atomic stress of individual carbon atoms in the graphene sheet was calculated using virial stress [2,52–55], which is defined as

$$\sigma_{ij}^{a} = \frac{1}{\Omega^{a}}\left(\frac{1}{2}m^{a}v_{i}^{a}v_{j}^{a} + \sum_{\beta=1,n} r_{a\beta}^{j} f_{a\beta}^{i}\right) \tag{1}$$

where i and j denote indices in Cartesian coordinate system; α and β are the atomic indices; m^{α} and v^{α} are mass and velocity of atom α; $r_{\alpha\beta}$ is the distance between atoms α and β; $f_{\alpha\beta}^{i}$ is the force along direction i on atom α due to atom β; Ω^{α} is the atomic volume of atom α. The atomic volume can be taken from the relaxed graphene sheet with a thickness of 0.34 nm [2]. In the current study, authors have followed the approach taken by Pei et al. [56] and Grantab et al. [29], i.e. the strength of the graphene sheet is computed by averaging the stress over all the carbon atoms in the sheet at failure. Authors have further verified that stress computed with this approach is in good agreement with the experimental data [57]. Because of the brittle nature of graphene, its useful strength with engineering relevance should be dictated by fracture toughness, which is conventionally characterized by the critical stress intensity factor (SIF), which was evaluated as,

$$K_I = Y\sigma_n\sqrt{\pi a_0} \tag{2}$$

where, Y is the dimensionless parameter [34] ($Y \approx 1$ in our model systems) and σ_n is the far field (or near the boundary) normal stress values at the instant of first bond rupture and a_0 is half of the central crack length. They have been calculated by averaging the normal stress over all the carbon atoms in the graphene sheet at failure. The fracture toughness is also often given by the critical strain energy (Γ_c) release rate of fracture, which was evaluated as,

$$\Gamma_c = \sigma_n^2\pi a_0/E \tag{3}$$

where, E is the Young's modulus of graphene.

3. Results and discussion

Stone-Thrower-Wales (STW) defect also referred as pentagon-heptagon-heptagon-pentagon (5-7-7-5) defect is formed by rotating a C—C bond by 90°, which transforms 4 hexagons into 2 pentagons and 2 heptagons, as illustrated in Fig. 1. Due to hexagonal and symmetric atomic

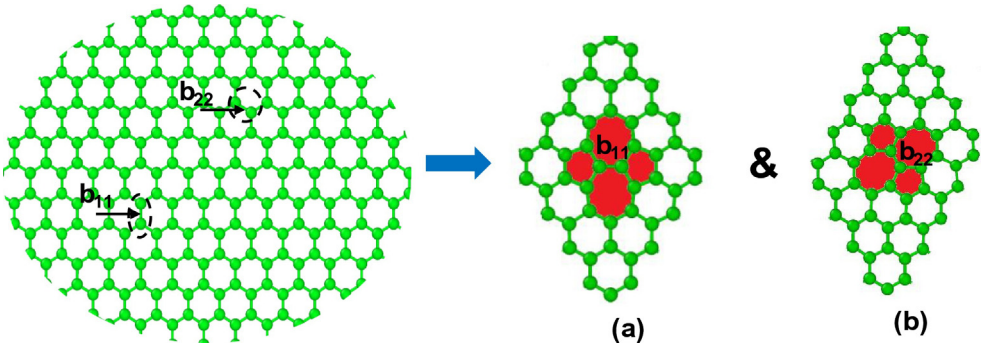

Fig. 1. Structure of STW defects. (**a**) Encircled vertical C—C bond b_{11} rotates by 90° to form STW1 defect. (**b**) Encircled inclined C—C bond b_{22} rotates by 90° to form STW2 defect.