Molecular Dynamics Simulation of Fracture Strength and Morphology of Defective Graphene

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Abstract. Different types of defects can be introduced into graphene during material synthesis, and significantly influence the properties of graphene. In this work, we investigated the effects of structural defects, edge functionalisation and reconstruction on the fracture strength and morphology of graphene by molecular dynamics simulations. The minimum energy path analysis was conducted to investigate the formation of Stone-Wales defects. We also employed out-of-plane perturbation and energy minimization principle to study the possible morphology of graphene nanoribbons with edge-termination. Our numerical results show that the fracture strength of graphene is dependent on defects and environmental temperature. However, pre-existing defects may be healed, resulting in strength recovery. Edge functionalization can induce compressive stress and ripples in the edge areas of graphene nanoribbons. On the other hand, edge reconstruction contributed to the tensile stress and curved shape in the graphene nanoribbons.

Introduction

Graphene has attracted increasing research effort since its discovery \cite{1}, largely due to its exceptional electrical, mechanical and thermal properties. For example, graphene has high electron mobility (25000 cm\textsuperscript{2}/Vs) at room temperature \cite{1}, anomalous quantum Hall effect \cite{2}, extremely high Young’s modulus (~1TPa) and fracture strength (~130 GPa) \cite{3} and superior thermal conductivity (5000 Wm\textsuperscript{-1}K\textsuperscript{-1}) \cite{4}. All these excellent properties can be attributed to its two-dimensional (2D) honeycomb lattice of sp\textsuperscript{2}-hybridized carbon atoms.

Structural defect such as Stone-Wales (S-W) defect, single or multiple vacancies, reconstructed rings, accessory chemical groups etc., plays a significant role in the structure-property relationship of graphene. Gorjizadeh et al. \cite{5} demonstrated that the conductance decreases in defective graphene sheets. Pei et al. investigated the effect of functionalized groups on mechanical properties of graphene. Liu et al. \cite{6, 7} reported structure, energy and transformations of graphene grain boundaries and their effect on failure strength. In addition, the morphology of graphene is also governing the structure-property relationship. Researchers have demonstrated that long-range order of graphene can present due to anharmonic coupling between bending and stretching modes \cite{8, 9}. As a result, the 2D membranes can exist but tend to be rippled at finite temperature. Indeed, ripples in freestanding graphene were observed in recent experiments \cite{10, 11}. Some intrinsic or extrinsic factors, including chirality, structural defects, geometry sizes and substrate-interaction can greatly influence the morphology of graphene. Recent research also reported that the curvature of graphene...
sheets can induce the change of the low energy electronic structure of graphene [12, 13]. However, the formation of structural defects and the effect of defects on the morphology have not been well understood. Further study is much required. Due to the nano-scale dimensions, it is difficult to accurately evaluate the properties of graphene sheets via experiment. Alternatively, molecular dynamics (MD) simulation has been widely utilized to investigate carbon-based nanomaterials [14-18]. In this work, we presented a MD investigation on the influence of structural defects (Stone-Wales defect, edge functionalisation and reconstruction) on the fracture strength and morphology of graphene sheets and nanoribbons. The initiation of S-W defect and the competition between the initiation of S-W defect and bond-breaking were also investigated.

**MD Simulation**

To simulate a monolayer graphene sheet, a MD model (42.6 Å × 49.2 Å) was built that consists of 800 carbon atoms. As confirmed by Zhao et al. [19], the possible model size effect on mechanical properties can be largely neglected when the diagonal length is over 5 nm. Therefore, the diagonal length of our model was chosen as 6.51 nm. The uniaxial tensile load was applied to the graphene sheet along both armchair and zigzag directions (Fig. 1(a)), at a strain rate of 0.005 ps⁻¹ and a time step of 0.001 ps. The model was firstly relaxed to a minimum energy state with the conjugate gradient energy minimization. Then, Nose-Hoover thermostat [20, 21] was employed to equilibrate the graphene sheet at a certain temperature with periodic boundary conditions (PBCs). The adaptive intermolecular reactive bond order (AIREBO) potential [22] implemented in the software package LAMMPS [23], was used to simulate covalent bond formation and bond breaking. Such AIREBO potential has successfully simulated and predicted mechanical properties of carbon-based materials, i.e. fullerene, carbon nanotube and graphene.

![Figure 1](image)

**Fig. 1** (a) Uniaxial tension along the armchair (left) and zigzag (right) directions, and (b) stress-strain curves of pristine graphene sheet under uniaxial tension along armchair and zigzag directions at different temperatures (300~900 K).

Fig. 1(b) shows corresponding stress-strain curves at different temperatures (300 K~900 K). In terms of true (Cauchy) stress, fracture strengths along armchair and zigzag directions at 300 K are 104 and 127 GPa, respectively. These values are in good agreement with experiment results $\sigma_f \approx 130$ GPa [3], as well as previous atomistic simulation results [19, 24]. Therefore, accuracy of our MD models can be confirmed.

**Fracture Strength of Defective Graphene**

**Formation of S-W Defect.** Due to the short-ranged covalent bonding between carbon atoms, bond rotation and bond breaking are two basic deformation mechanisms in graphene. They can subsequently induce either the formation of S-W defect (bond rotation by 90°) or bond-breaking, as
shown in Fig. 2(a). However, S-W defects are inaccessible by direct molecular dynamics simulations, in that the kinetic rate of defect initiation for a short time scale is quite small at low temperature. In order to overcome the time-scale constraint in simulating S-W defects, nudged elastic band (NEB) method [25] was employed to evaluate the minimum energy path (MEP). The energy barrier for defect initiation under different strain loading can be determined by the saddle points in the MEP.

![Fig. 2](a) Four types of possible defects caused by one C-C bond: S-W defect (a1→c1), S-W2 defect (a2→c2), and bond-breaking defect (a1→b1 or a2→b2). (b) A schematic description of the variation of energy landscape for S-W defects under mechanical strain.

In Fig. 2, energy barrier against transition from State A to State B represents the energy barrier for defect initiation. Energy barrier against transition from State B to State A represents the energy barrier for defect healing. Without mechanical loading, the energy barriers $E_{ch}^+$ for the generation of S-W1 (shown in c1, Fig. 2) and S-W2 (shown in c2, Fig. 2) defects are relatively high (about 60 eV and 80 eV). The defect formation rate is expected to be very low if the thermal activation energy is low at low temperatures. Our MEP analysis demonstrated that both mechanical strain and loading direction can greatly influence the energy barrier $E_{ch}^+$ for the initiation of S-W defects and energy barrier $E_{ch}^-$ for healing of S-W defects [24], as shown in Fig. 2(b). Under zigzag loading, mechanical strain can lower $E_{ch}^+$ for the formation of both S-W1 and S-W2 defects. $E_{ch}^+$ for S-W1 initiation is constantly lower than that for S-W2, regardless of strain level. This suggests that S-W1 defect is more kinetically favourable than S-W2. Under armchair loading, $E_{ch}^+$ for S-W2 initiation is lowered by increasing mechanical strain. However, $E_{ch}^-$ for S-W1 initiation is significantly increased by mechanical strain. Corresponding to the failure strain, non-zero $E_{ch}^-$ is observed, which implies that mechanical strain alone is insufficient to achieve the athermal limit for generation of S-W defects. While for bond-breaking (shown in b1 and b2, Fig. 2), they are in a meta-state, and little thermal activation can heal such defects. This can be attributed to the dangling bonds with higher energy. The MD simulation shows graphene exhibits typical feature of brittle material under 1000 K, as brittle rupture can be initiated by the initial bond breaking.

**Effect of S-W Defect on Fracture Strength.** In addition, both S-W defects and temperature can significantly deteriorate the fracture strength of graphene. Fig. 3 shows the fracture strength of graphene with S-W defects at different temperatures (300 K ~ 900 K). Under zigzag loading, the average strength loss caused by S-W1 and S-W2 is 16.26% and 41.30%, respectively. Under armchair loading, the average loss of fracture strength by S-W2 defect is about 15.75%. For S-W1, however, fracture strength increases when temperature is above 600 K (C point in Fig. 3(a)). This is attributed to the healing of S-W1 defect with increasing temperature. As shown in Fig. 3(b), at 600 K, the S-W1 defect is stable. At 700 K, however, the S-W1 defect is healed by 90° rotation of C-C
bond. As mentioned above, mechanical strain can lower the healing energy barrier $E_{hv}$. Therefore, according to the kinetic rate of the healing of S-W defects ($\nu$),

$$\nu = a f_0 \exp(-\frac{E_{hv}}{kT})$$

where $f_0$ is attempt frequency (about $10^{13}$/s); $k$ is the Boltzmann’s constant and $a$ is the lattice spacing $a = \sqrt{3}r_0$, where $r_0 = 1.42\,\text{Å}$ is the C-C bond length. From Eq. 1, the healing of S-W$_1$ defect becomes easier with increase of mechanical strain and temperature, consistent with the MD simulation.

Furthermore, the MD results of fracture strength of pristine graphene match well with the non-linear elastic (NLE) model [26], which builds the relationship between fracture strength $\sigma$, strain rate $\dot{\varepsilon}$ and temperature $T$. It can be given as

$$\sigma(\dot{\varepsilon}, T) = \frac{a kT}{\gamma a + kT} \left[ U_0 + \ln \left( \frac{b \dot{\varepsilon} \tau_0}{kT} \left( \frac{\gamma a}{kT} + 1 \right) \right) \right]$$

where $\tau_0 = 10^{-13}$ s is the average vibration period of atoms in solid; $k$ is the Boltzmann constant; $T$ is the temperature; $\gamma = qV$, where $V$ is the activation volume and $q$ is the coefficient of local over stress; $U_0$ is the interatomic bond dissociation energy; $n_s$ is the number of sites available for the state transition; $a$ and $b$ are the material constant for NLE behaviour of graphene. To fit the data in Fig.3 using Eq. 2, $a = 111$ GPa and $b = 9.69$.

![Fig. 3](image)

**Fig. 3** (a) Fracture strength of pristine, S-W$_1$ and S-W$_2$ defected graphene versus temperature under armchair and zigzag loading conditions, and (b) configuration change in the pre-existing S-W$_1$ defect from point B (at 600 K) to point C (at 700 K) highlighted in (a).

**Morphology of Graphene with Edge Functionalisation and Reconstruction**

For graphene nanoribbon (GNR), both edge functionalisation and reconstruction affect its electrical properties [27-29]. Meanwhile, they may also influence the morphology of GNR. Previous research demonstrated that edge termination can result in the variation of the bonding configuration of atoms located at the edges of GNRs, and induce the intrinsic edge stress [30, 31]. To study the effect of edge termination (hydrogen functionalisation (r-H) and pentagon-hexagon reconstruction (r-5-6)) on the morphology of GNRs, we neglected the temperature effect and evaluated the resulting morphologies by out-of-plane perturbation and energy minimization.
Different from r-H edges, r-5-6 edges are subject to tensile stress along the edge direction. The MD result of such stress is 3.495 eV/Å, much higher than the magnitude of that in r-H edges. Under the action of the tensile stress, GNRs spontaneously curl along the width direction with tapered ends, as shown in Fig. 5. In energy analysis, the free edges need shorten to lower the total potential energy. The tensile stress here serves as driving force to form the curvature of GNRs, subsequently triggering their ends arching inward. In fact, this formation process is similar to the formation of other graphene-based structures, such as fullerene and carbon cone. The existing pentagon rings in graphene cause the change of curvatures of graphene and generate those novel nano-structures. A theoretical study also reported that the formation of defects at the edge of graphene is the crucial step in the process of transformation of a graphene sheet into a fullerene [32].

Summary

In this work, the effect of structural defects (S-W defects, edge functionalisation and reconstruction) on the fracture strength and morphology of graphene was investigated using MD simulation. The results indicate that both loading level and loading direction can significantly influence the formation of Stone-Wales defects. Generally, mechanical strain can lower the energy barrier for the formation of S-W defects, except S-W₁ formation under armchair loading where mechanical strain increases energy barrier for defect initiation. This is attributed to the healing of S-W₁. The fracture strength of graphene is dependent on S-W defects and temperature. The MD simulations also show that both edge functionalisation and reconstruction can significantly influence the stress state at free edges as well as final morphologies of GNRs. Edge functionalisation can induce compressive stress which promotes the formation of ripples in the edge areas. On the other hand, edge reconstruction produces tensile stress and curved shape in the GNRs.

References


