

Graphene Nano-Ribbons Under Tension

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The mechanical response of graphene nano-ribbon under tensile loading has been investigated in this paper. Lattice symmetry dependence of the elastic response is found through molecular dynamics simulation, which fits prediction from Cauchy-Born rule very well. Concurrent brittle and ductile behaviors are observed during the failure process at elastic limit, which dominate the low and high temperature behavior respectively. The free edges in finite width ribbon help to activate bond-flip events and initialize ductile behavior, which can be explained by formation energy analysis for the Stone-Wales rotations.

Keywords: Graphene Nano-Ribbons, Elastic Properties, Fracture.

Graphene, a new allotrope of carbon, has been obtained experimentally very recently.¹ The two-dimensional nature of this monolayer crystalline material leads to intriguing physical properties, such as a linear dispersion relation of Dirac fermions, anomalous quantum Hall effects and the absence of localization.¹ Besides, the strong sp^2 bonding inside the single atomic layer leads to great Young's modulus and tensile stress,² which opens new perspectives for structural or functional phase in nano-composites^{3,4} and building blocks in nano-electromechanical devices.⁵ Recent experiments also show single layer graphene materials possess extremely high thermal conductivity of 5×10^3 W/mK.⁶ Especially, finite width graphene nano-ribbons (GNRs), tailored from the 2D graphene lattice, has been found to possess interesting electronic structures with dependence on its width and edge shapes.^{7,8} To find potential applications for graphene materials such as reinforcement agents to strengthen and toughen in composites or structural parts in electromechanical devices, the mechanical response of the graphene nano-ribbons under tensile loading should be well understood. For instance, the orientation dependence of Young's modulus, Poisson's ratio and the bond breaking pattern at breaking strain. To this aim, we performed molecular dynamics simulation with focus on the elastic properties and its fracture mechanisms.

In our simulation, to describe the inter-atomic interaction in graphene, the second-generation reactive empirical bond order potential (REBO)⁹ was implemented. This potential functional and parameters was proven to give quantitatively accurate results for mechanical properties of carbon nano-structures. During the molecular dynamics

simulation for fracture process, we set the cut-off parameters to be 2.0 Å as suggested by previous studies on carbon nanotubes,¹⁰ to avoid the unphysical force enhancement caused by the artificial cut-off function in the potential function. To simulate the tensile process, graphene ribbons of length $L = 20$ nm and width $W = 10$ nm are strained at a constant rate of 0.005% per femtosecond along the direction of length L , with both ends constrained axially to maintain the load at each time step. We also performed simulations using periodic boundary conduction in the tensile direction and width varies from 5 nm to 20 nm (in this range the graphene nanoribbon possesses fascinating electronic properties such as half-metallicity or width dependent semiconducting gap^{7,8}), the results (Young's modulus, cracking pattern) are very close and here only this representative result is shown. The loading rate was chosen to be much slower than the sound velocity in graphene to reduce the effects of unphysically high strain rate.

Following previous studies on graphene,⁸ the graphene nano-ribbons are classified into armchair (AGNR), zigzag (ZGNR) and chiral graphene nano-ribbon (CGNR) based on their edge shape (transverse to electronic transport direction or tensile loading direction here). As in the carbon nanotube structures,¹¹ the key feature of the fracture path at low temperature in graphene lattice is the forces distributed in the sp^2 bonds. Following the Cauchy-Born rule¹⁰ for lattice deformation, the bonds A, Z1 and Z2 shown in Figure 1 bears the maximum loads in AGNR and ZGNR. By relating the gross elastic deformation with the individual bond elongation δl_{C-C} , the brittle-breaking strain of GNR is estimated as¹¹

$$\varepsilon_c = 2 \frac{\delta l_{C-C}}{l_{C-C}} \Big|_c [(1 - \nu) + (1 + \nu) \cos 2\theta]^{-1} \quad (1)$$

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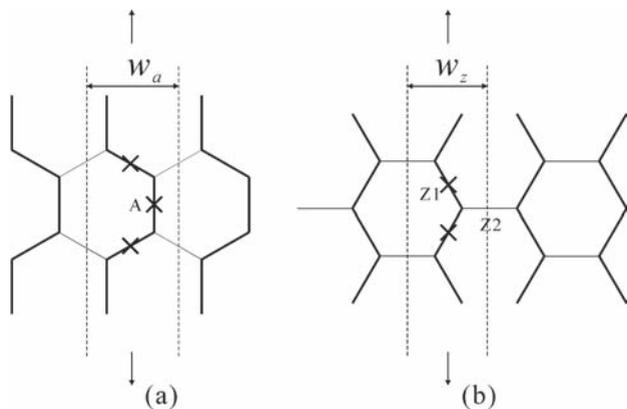


Fig. 1. Graphene nano-ribbon under tension. The bond marked with crossing bears the maximum load; w_a and w_z are the widths of unit area perpendicularly to the ribbon axis. (a) AGNR; (b) ZGNR.

where l_{C-C} is the length of carbon-carbon bond and the chiral angle θ is 0 for AGNR and $\pi/6$ for ZGNR ($\theta = \pi/12$ used in this work) respectively. Thus ZGNR (AGNR) can sustain the largest (smallest) strain before bond breaking in a brittle manner. Using the Poisson's ratio of graphite $\nu = 0.416$,² we estimate $\varepsilon_{cAGNR}:\varepsilon_{cCGNR}:\varepsilon_{cZGNR} = 0.65:0.71:1$, which is consistent with our simulation result 0.67:0.74:1 at $T = 300$ K (see Table I). The results here remind us the chirality dependence of the axial stress-strain relationship found in carbon nanotubes,¹² which can also be explained by Cauchy-Born rule. This consistency also indicates the brittle behavior of the fracture process at low temperature, which can also be revealed in the fracture pattern shown in Figure 3. As the Cauchy-Born analysis predicts, the bonds A, Z1 and Z2 under maximum loads have been found to break at first and result in a straight or zigzag crack pattern inside AGNR or ZGNR. Thus the open edges of graphene after fracture are predominately zigzag-shaped, which provide metallicity of graphene ribbons. We have also calculated the equilibrium elastic properties of GNRs through the stress-strain relation at low strain, which are shown in Table I and correspond well to the results reported by Reddy et al.²

The fracture mechanism of graphene lattice, as revealed by Dumitrica et al.¹¹ in their studies on carbon nanotubes, is dominated by the co-existing ductile flip and brittle breaking of the carbon bonds. At low temperature, the fluctuation of atomic position is prohibited and the bond breaks at elongation limit, thus the behavior can be described well by (1). At high temperature the plastic deformation such as SW bond rotation will play a significant

Table I. The mechanical properties of GNRs at 300 K.

	Young's modulus (GPa)	Yielding strength (GPa)	Breaking strain
AGNR ($\theta = 0$)	720	83	0.16
CGNR ($\theta = \pi/12$)	714	85	0.175
ZGNR ($\theta = \pi/6$)	710	98	0.24

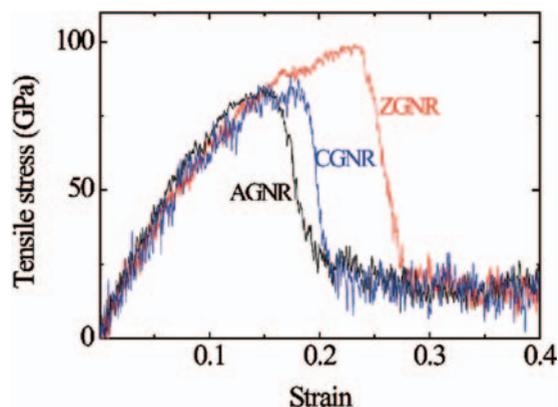


Fig. 2. The stress-strain relation of GNRs with different edge shapes at temperature $T = 300$ K.

role in the fracture process. In our simulation at $T = 2000$ and 3000 K, we have observed frequent bond-flip events (Fig. 4(a)) initialized at the free edge of graphene. The SW defects formed after the bond flipping will propagate inside the ribbon subsequently, and finally induce an edge-localized fracture pattern (Fig. 4(b)). We noticed that the brittle-ductile transition phenomenon presented here

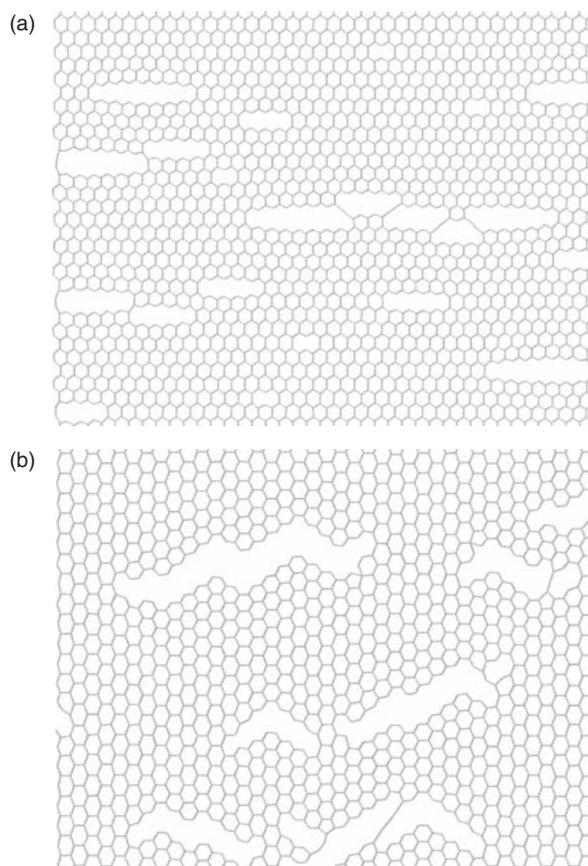


Fig. 3. The fracture pattern of AGNR (a) and ZGNR (b) at $T = 300$ K. The ribbon is strained vertically. There are several atomic chains formed in the crack region. Reprinted with permission from [15], M. A. L. Marques et al., *Nano Lett.* 4, 811 (2004). © 2004.

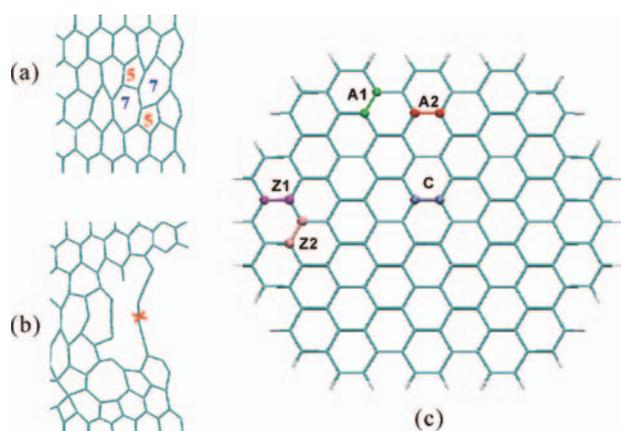


Fig. 4. The Stone-Wales 5/7/7/5 defect (a) and bond breaking event (b) initialized at the free edges of graphene nano-ribbon; (c) different sites of available 5/7 bond-flip events: bonds inside the ribbon (C), bonds close to the armchair edges (A1, A2) and zigzag edges (Z1, Z2).

is similar as observed in carbon nanotubes,¹³ except for that in the carbon nanotubes, there are no open edges. Also the finite curvature in small-diameter carbon nanotubes can assist the ductile deformation. This elasto-plastic deformation observed includes defects diffusion, coalescence and reconstruction in a rather complicate manner, and molecular dynamics simulation can only give qualitatively description of the phenomena because of the limitation of reachable time scale. Rather than full-atomistic simulation, an energetic analysis becomes more reasonable in comparison with real-time experiments at room temperature.

To explain why the bond-flip events start from the free edge, we present a formation energy analysis on the SW dislocation at different position in the ribbon through PM3 parameterized semi-empirical quantum chemical calculations.¹⁴ As shown in Figure 4(c), in a finite size graphene ribbon, we investigated five representative bond sites: bond in the central ribbon (C) approximating the bond under bulk environment, bonds near the armchair edges (A1, A2) and bonds close to the zigzag edges (Z1, Z2). To calculate the energy of SW defects, we flip these bonds by $\pi/2$ and optimize the structure to a local minimum of potential energy E_{SW} . Define as the difference between E_{SW} and the energy of defect-free ribbon E , the dislocation formation energies E_C , E_{A1} , E_{A2} , E_{Z1} and E_{Z2} are calculated and depicted in Figure 5. The dislocation energy is lowered up to 1.46 eV at A1, A2, Z1 and Z2. The decreasing of dislocation energy on the order of 1 eV should be responsible to activation of ductile fracture behavior at the free edges.

In conclusion, the mechanical properties and fracture mechanisms of graphene nano-ribbon have been investigated through atomistic simulations. Brittle bond breakings have been found to dominate at low temperature,

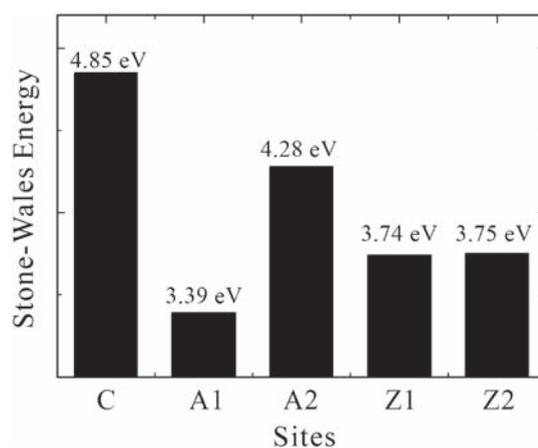


Fig. 5. The Stone-Wales dislocation energy at different bond sites shown in Figure 4(c).

and the mechanical response of GNRs in this manner can be described through the Cauchy-Born approach. The open edges after fracture are predominately zigzag-shaped, which is metallic and thus provide possibilities to fabricate half-metallic devices through mechanical cleavage. At higher temperature, the plastic deformation assisted by bond-flip events becomes significant. The free edges have been found to lower the SW dislocation energy and help to initialize ductile fracture processes.

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