Molecular Dynamics Simulation of Fracture of Graphene

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Abstract A molecular dynamics (MD) simulation to assess the effect of crack length on the ultimate tensile strength of infinitely large armchair and zigzag graphene sheets is presented. The strength of graphene is inversely proportional to the square-root of crack length as in continuum fracture theories. Further comparison of the strength given by MD simulations with Griffith's energy balance criterion demonstrates a reasonable agreement. Armchair and zigzag graphene sheets with 2.5 nm long crack exhibit around 55% of the strength of pristine sheets. Investigation of the influence of temperature on the strength of graphene indicates that sheets at higher temperatures fail at lower strengths, due to high kinetic energy of atoms. We also observe out-of-plane deformations of the crack tip at equilibrium configuration of both types of sheets due to compressive forces acting on the crack surface. This deformation propagates with applied strain in the direction normal to the crack and eventually generates ripples in the entire sheet.

Keywords Graphene, Fracture, Molecular Dynamics, Vacancy Defects

1. Introduction

Experimental investigations with atomic force microscope (AFM) have revealed that the ultimate tensile strength and Young's modulus of graphene are around 130 GPa and 1 TPa, respectively [1]. Researchers have found experimental evidence for the existence of defects such as the absence of carbon atoms in graphene sheets [2]. The absence of carbon atoms in graphene is known as vacancy defects. The influence of vacancy defects on the strength of graphene has not been studied experimentally. However, a number of theoretical studies have been conducted, and it has been found that vacancy defects could reduce the strength of graphene by around 50% [3-9].

Khare *et al.* [4] studied the effects of large defects and cracks on the mechanical properties of carbon nanotubes and graphene using a coupled quantum mechanical/molecular mechanical method. They found that the weakening effects of holes, slits, and cracks vary only moderately with the shape of the defect, and instead depend primarily on the cross section of the defect perpendicular to the loading direction. Ansari *et al.* [5], using MD simulations, showed that the presence of vacancy defects significantly reduces the ultimate strength and strain of graphene, while it has a minor effect on Young's modulus. They also showed that defects have a lower effect in armchair direction compared to zigzag direction. Wang *et al.* [6] studied the effect of vacancy defects on the fracture strength of graphene sheets using MD. They found that vacancies can cause significant strength loss in graphene and also concluded that temperature and loading directions affect the fracture strength. Omeltchenko *et al.* [7] estimated the fracture toughness of armchair graphene from Griffith analysis and local-stress distributions, and the toughness values are 4.7 MPa $m^{1/2}$ and 6 MPa $m^{1/2}$, respectively. The study was conducted using MD simulations. A recent work from Xu *et al.* [8] revealed that the critical stress intensity factors of graphene are 4.21 MPa $m^{1/2}$ and 3.71 MPa $m^{1/2}$ for armchair and zigzag directions, respectively. They used a coupled quantum/continuum mechanics model for the study.

Coupled quantum mechanics models are generally computationally expensive and those models cannot incorporate temperature effects. Therefore, it is useful to have a simple MD model, which can be used to investigate the fracture of nanoscale systems such as graphene. This paper presents a MD simulation of fracture of armchair and zigzag graphene at temperatures of 1 K and 300 K.

2. Molecular Dynamics Simulations

Adaptive intermolecular reactive empirical bond order (AIREBO) potential [10], implemented in LAMMPS MD simulation package [11] is used in this study. Cut-off radius of AIREBO potential is set to be 2 Å to eliminate the non-physical strain hardening of the stress-strain curve [12]. Length and width of the simulation box are selected to be greater than 10 times of the crack length in order to avoid finite-size effects [13]. Strain rate and time step are 0.001 ps^{-1} and 0.5 fs, respectively. MD simulations are performed at 1K and 300K on armchair and zigzag sheets with crack lengths ranging from 4 Å to 29 Å to investigate the effect of crack length and temperature on the tensile strength (σ_{ult}). The crack lengths are defined as shown in Fig. 1.

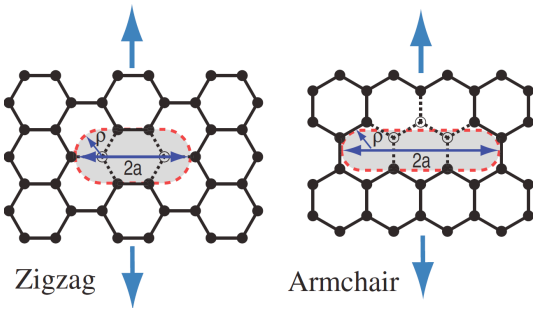


Figure 1: Crack length (2a) and crack tip radius (ρ) of armchair and zigzag graphene sheets. Arrows indicate the straining direction.

It is noticed during MD simulations that crack tips come out of the plane of graphene sheet at unstrained state. The crack tips are free edges. Deformation of free edges of graphene could be explained by considering an edge force, which arises from the difference in the energy stored in edge atoms and interior atoms [14]. As shown in Fig. 2, the out-of-plane deformation of a crack tip at equilibrium configuration is localized around the tip. However, as strain increases up to 0.018, the shape of the crack tip changes, and it acts as a localized ripple. As strain further increases up to 0.0235, this localized ripple spreads throughout the sheet.

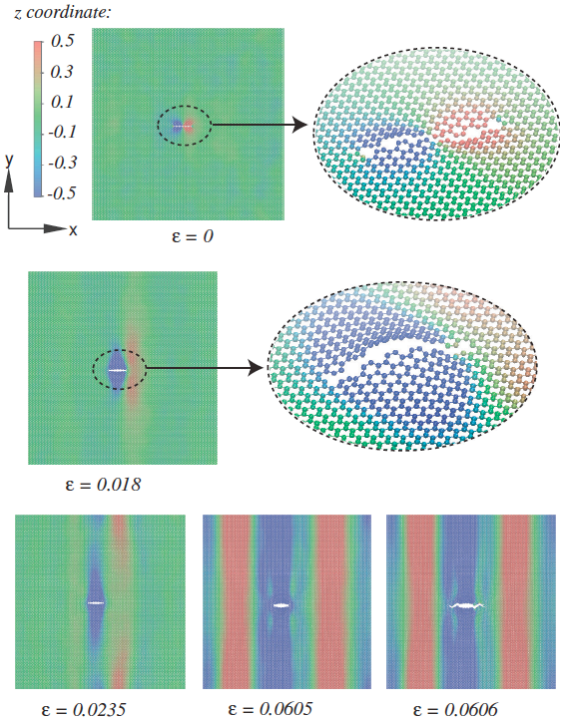


Figure 2: Ripples in 27 nm x 27 nm sheet with central crack. Strain is applied along y-direction.

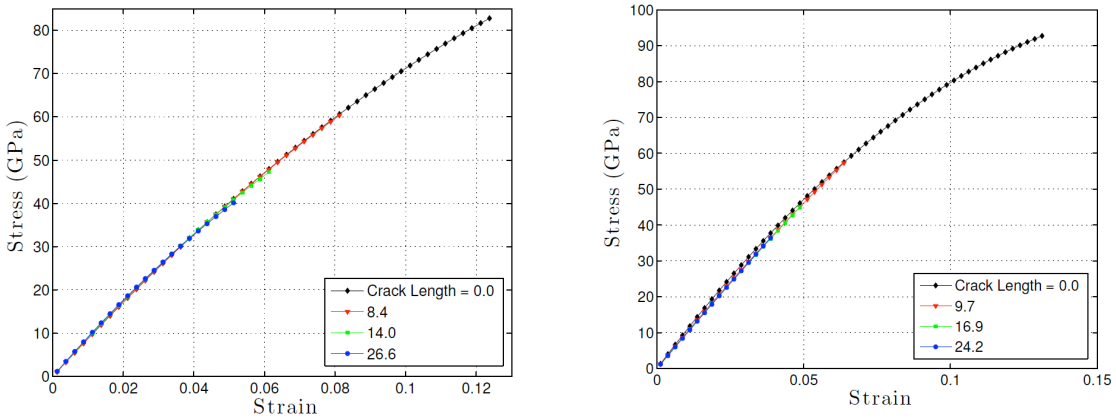
3. Strength of Graphene

Stress of a graphene sheet (σ) is obtained from the gradient of the strain energy (U) - strain (ε) curve as,

$$\sigma = \frac{1}{V}\frac{\partial U}{\partial \varepsilon} \tag{1}$$

where, V is the volume of graphene sheet and the thickness of graphene is taken as 0.34 nm.

The stress-strain curves of sheets for different crack lengths at 300 K are shown in Fig. 3. The results reveal that a single vacancy (one missing atom) reduces σ_{ult} in armchair sheets by 15.7% and in zigzag sheets by 23.3%, which indicates that graphene is very sensitive to vacancy defects. It can also be noticed in Fig. 3 that Young's modulus does not change with crack length.



(a) (b)

Figure 3. Stress - strain curve of graphene with crack length; (a) armchair and (b) zigzag at 300 K.

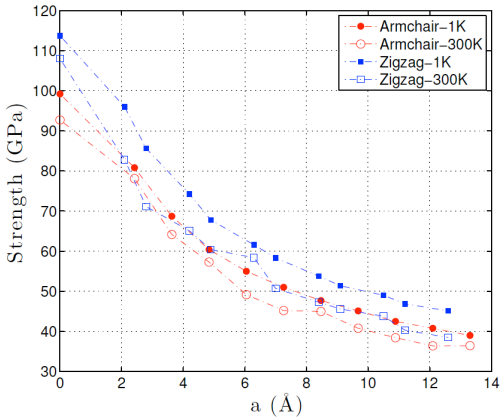


Figure 4. Effect of temperature on strength of graphene for various crack lengths.

Figure 5 shows a plot of $1/\sqrt{a}$ vs. σ_{ult}, and it clearly shows proportionality at 1 K. This indicates a formal similarity with continuum fracture mechanics. The stress intensity factor of graphene (K_I^g) can therefore be approximated as

$$K_I^g = (\sigma_f - c)\sqrt{2\pi a}, \tag{2}$$

where c is a constant (c is zero for a continuum) and a is the crack length. The values of K_I^g and c are given in Table 1 based on MD simulations. K_I^g decreases as temperature increases from 1 K to 300 K, which reflects the reduction of σ_{ult} as shown in Fig. 4. The reduction of K_I^g in zigzag sheets is greater than that of armchair. The general agreement of MD simulation results with continuum

fracture mechanics motivates further investigation of fracture of graphene using continuum concepts.

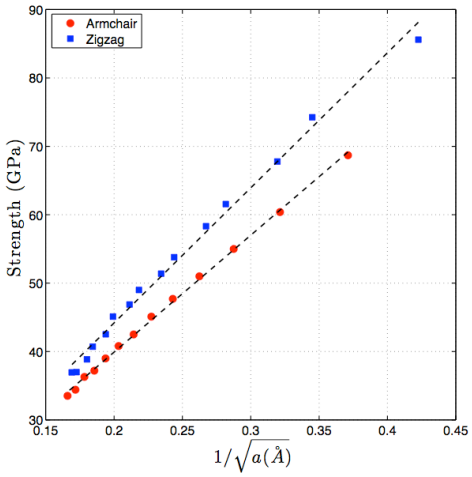


Figure 5. Variation of ultimate strength with crack length at 1 K; σ_{ult} = 120.9*(1/√a) + 5.7 and σ_{ult} = 139.7*(1/√a) + 4.7 for armchair and zigzag sheets, respectively.

Table 1: Variation of K_I^g and c with temperature.

	Temp (K)	K_I^g (MPa m$^{1/2}$)	c (GPa)
Armchair	1	4.8	5.7
	300	4.2	11
Zigzag	1	5.6	4.7
	300	4.6	4

4. Continuum Fracture Mechanics

Inglis [15] and Griffith [16] proposed two fundamental theories in fracture mechanics. Inglis derived the stress concentration due to an elliptical hole in a linearly elastic material [15]. Considering the nonlinear σ-ε relation of graphene, the remote stress at failure (σ_f) can be written as

$$\sigma_f = \sqrt{\frac{E_f \gamma_s}{4a}}, \tag{3}$$

where E_f is the tangent modulus at failure; γ_s is the surface energy and a is the crack length.

Inglis' theory was followed by Griffith's work on the fracture of brittle solids [16]. Griffith's energy balance says that failure occurs when the energy stored in the structure is sufficient to overcome the surface energy of the material. Failure stress of Griffith's model is expressed as

$$\sigma_f = \sqrt{\frac{2E_f \gamma_s}{\pi a}}. \tag{4}$$

The value of γ_s is calculated by dividing the difference in energy of a graphene sheet before and after fracture by the area of newly created surface. The value of γ_s is 5.02 J/m^2 for both armchair and zigzag graphene since the distance between two broken carbon-carbon bonds is similar in both sheets. The tangent modulus at failure is obtained from the σ-ε curves of pristine graphene sheets, and it can be expressed of as $E(\varepsilon)$ = -5.89ε + 1.08 TPa and $E(\varepsilon)$ = -3.50ε + 0.89 TPa for armchair

and zigzag sheets, respectively. The value of E_f is given by $E(\varepsilon_f)$, where ε_f is the failure strain of a sheet with a particular crack length.

A comparison of strength of graphene sheets with various crack lengths is given in Fig. 6. The strength of graphene sheets obtained from MD is between the values given by Inglis' and Griffith's approaches. The strength at 300 K shows slight fluctuations due to kinetic energy of atoms. The strength of zigzag graphene sheets given by Griffith and MD simulations agrees quite well with each other. However, both Inglis' and Griffith's theories have been derived for a flat structure, whereas graphene with a crack does not remain flat as shown in Fig. 2. The continuum theories also assume the continuity of material, which is not the case in graphene. Therefore, a perfect agreement between continuum theories and MD simulations cannot be expected.

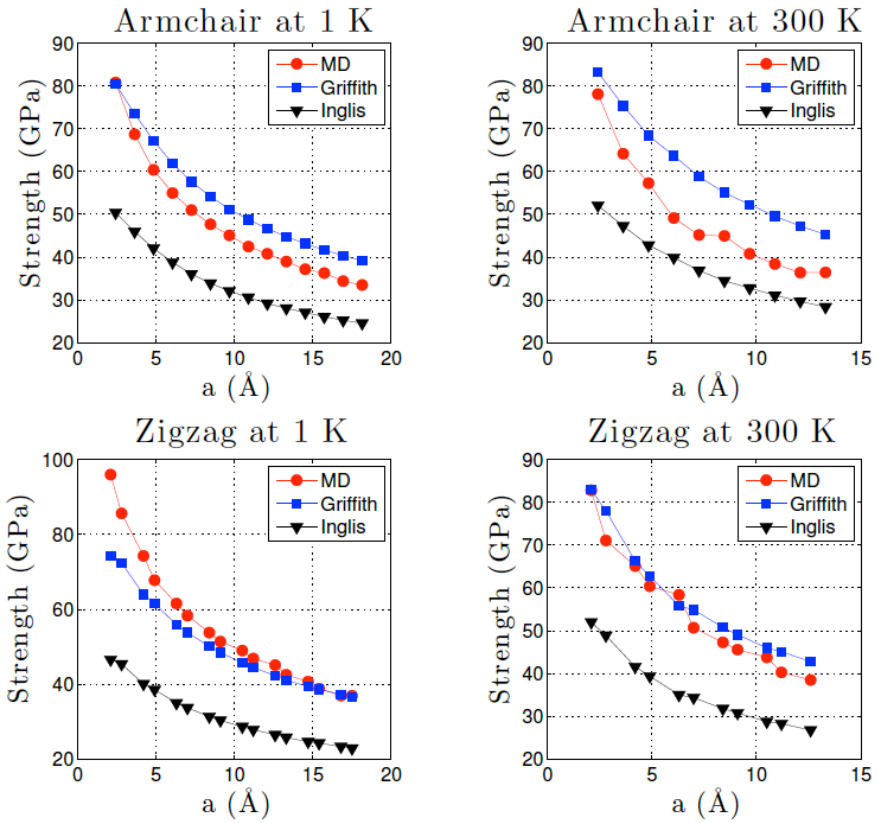


Figure 6. Comparison of Griffith's and Inglis' theories with MD simulations.

5. Conclusions

The crack tips of graphene show out-of-plane deformations at equilibrium configuration. These deformations propagate with the applied strain and eventually generate ripples in the sheet. A crack with the length of 2.5 nm reduces the strength of both armchair and zigzag graphene sheet by around 55%. Strength obtained from molecular dynamics simulations shows inverse square-root proportionality with crack length as in continuum fracture mechanics theories. Strength of graphene sheet given by Griffith's theory reasonably agrees with strength obtained from molecular dynamics simulations.

Acknowledgements

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