Crack Propagation Morphologies of Single-Layered Graphene under Various Low Temperatures

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The fracture behavior of single layer graphene sheet (SLGS) has been a subject of intensive research in recent years. Understanding the fracture mechanism of graphene under low temperature conditions is crucial for engineering applications of graphene. In this paper, a molecular dynamics (MD) simulation is employed to assess the effect of temperature on fracture properties of SLGS. The evolution of atomically cleaving of graphene is also discussed. A finite area of SLGS is subject to uniaxial tensile load in zigzag direction under various environmental temperatures between 1K and 77K. The effects of temperature on fracture properties as well as cracked morphology of SLGS are investigated. While our simulated results of fracture strength of SLGS agree with reported datum, simulated cracks are nucleated spontaneously instead of artificially inserted. The findings presented herein would help understand the morphology of a single layer pristine graphene sheet subjected to crack propagation at ultralow temperature.

Keywords: Graphene, Fracture, Crack Propagation, Molecular Dynamic Simulation

Introduction

Owing to its remarkable physical properties graphene is emerging as next generation material in engineering applications1-3. Graphene is the strongest material ever tested, with an intrinsic tensile strength of 130 GPa and a Young's modulus of 1 TPa4. However, despite its strength graphene is also relatively brittle, with a fracture toughness of around 4 MPa\(\sqrt{m}\)5. Low fracture toughness means that an imperfect material is likely to crack in a brittle manner. Large-area sheets of graphene with imperfection are subjected to crack initiation hence fracture. A two-dimensional sheet-like material such as free-standing graphene sheet can expose itself to out-of-plane forces which can further cause the graphene to fracture. Although the specific fracture behaviors, particularly fracture toughness of and crack propagation in graphene, have remained largely unknown, some previous studies have provided instructive insights into the fracture behaviors of graphene with defective lattice structures. For example, Wang et al.6 studied the effect of vacancy defects on the fracture strength of graphene sheets. Their results indicated that significant strength loss in graphene can be caused by vacancies. Besides, the fracture strength of graphene is dependent on temperature and loading directions. Kim, et al.7 presented both experimental and theoretical work on cracks (tears) in suspended monolayer graphene membranes. The study showed that tears in the graphene predominantly align with the armchair or zigzag direction and occasionally change directions by 30° (or multiples of 30°). Moura8 evaluated the propagation of cracks in clamped, free-standing graphene as a function of the out-of-plane force. The simulations showed that initial cracks in the middle of the sheet always run straight, while initial cracks at the edge do not. The study by Zhang, et al.9 indicated that under mode I prevailing condition, an armchair crack alternatively changes direction of growth and a zigzag edge crack grows self-similarly. It is perhaps the first study by Zhang, et al.10 who conducted an in situ nanomechanical testing of fracture in suspended graphene with controlled pre-crack sizes and the results suggested that the useful strength of large-area graphene be determined by its fracture toughness rather than its intrinsic strength. Since the experimental characterization at nanoscale is considerably complex, molecular dynamics (MD)
Simulations have become a versatile technique for assessment of large deformations, failure mechanism and temperature effects for graphene. In the present study, we investigated the crack propagation morphology of a single layer pristine graphene (SLG) under the influence of various temperatures from 1K to 77K. A series of MD simulations were conducted to investigate the crack progressions of zigzag graphene under longitudinal tensile load. Different from most previous studies, cracks were simulated spontaneously instead of being manually created. The system contains a graphene sheet which is rectangular in shape with a strain-free size of 59.7Å×36.4Å.

The thickness of graphene is assumed to be 3.335Å. Before each simulation, the graphene sheet is fully relaxed to acquire the equilibrium at the ground state with zero strain. A uniaxial displacement is then applied. The evolution of fractured morphology and strain energy distributions are taken for fracture investigation.

Simulation models

In this study, a zigzag rectangular pristine graphene sheet with single layer is considered. The graphene is subjected to tensile loading in a form of symmetrical straining in longitudinal direction. In performing the simulations, the atomic interactions were modeled using the Tersoff-Brenner potential, which takes proper account of the lattice constants, binding energies and elastic constants of graphite and diamond atoms. Meanwhile, the long range van der Waals interaction forces are calculated using the Lennard-Jones 12-6 potential with a well-depth energy of $e = 4.7483 \times 10^{-22} \text{J}$ and an equilibrium distance of $\sigma = 0.3407 \text{nm}$ which is based on the compressibility and graphene layer spacing satisfying graphite density (2.2g/cm$^3$). Various temperature levels, i.e. 1K, 5K, 10K, 20K, 30K, and 77K, were selected for the simulations. These temperatures are arbitrarily chosen to study the fracture behaviors of the SLG in extreme low temperature environment such as outer space. Each temperature was maintained using the Nosé-Hoover thermostat method. The use of this thermostat leads to less fluctuations in the temperature. Moreover, the simulations were performed using a time step of 1 fs that guaranteed good conservation of energy. It is discerned that the initial configuration of the graphene sheet in the MD simulation may not correspond to an equilibrium state of the system. Therefore, prior to applying the tensile load, a relaxation process was implemented to relax the SLGS at the selected temperature by minimizing the total potential energy of the entire graphene. A constant increment of the tension strain of $\Delta \varepsilon = 10^{-4}$ was also used to accurately account for the deformations at high applying strain rate of 0.1 ps$^{-1}$. It is noted that the system was initially relaxed for 5000 steps (5ps) which sufficed the energy of the system to be fully minimized for a specified temperature. No relaxation time was taken after imposing each incremental displacement. The tensile load was symmetrically exerted on the atoms in the outermost rows of the sheet. With the strain rate considered, the total strain energy was calculated with the form

$$E(\varepsilon) = (E^* \varepsilon^2) / 2$$

where $E^* = 59eV/atom$

Results and Discussion

Effects of temperature on the out-of-plane deformation of SLGs

As stated in Sec. 2, the system was initially relaxed before each incremental displacement was imposed longitudinally. The simulation results show that with increasing temperature there are more and more atoms possessing higher strain energy. The atoms on the relaxing graphene were seen to oscillate from their neutral position in both in-plane and out-of-plane directions. The curved free edges revealed that oscillation of atoms along the side edges caused in-plane deformation. This phenomenon is perceivable since, as it is true of all materials, regions of graphene are subject to thermal and quantum fluctuations in relative displacement. Presented in Table 1 are the variations of oscillation amplitudes of atoms along the side edges of the SLGs at different temperatures. It can be seen from the calculated $\Delta_{max}$, the out-of-plane deformation of the graphene becomes larger at elevated temperature. The out-of-plane oscillation generates compressive forces that break the weakly

<table>
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<tr>
<th>Temperature (K)</th>
<th>$\Delta_{max}$ (Å)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.410</td>
</tr>
<tr>
<td>5</td>
<td>0.522</td>
</tr>
<tr>
<td>10</td>
<td>0.959</td>
</tr>
<tr>
<td>20</td>
<td>1.097</td>
</tr>
<tr>
<td>30</td>
<td>1.320</td>
</tr>
<tr>
<td>77</td>
<td>1.393</td>
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Table 1 — Amplitudes of atoms oscillating in out-of-plane direction as SLGs are relaxed at temperatures. The peak oscillating amplitude ($\Delta_{max}$) increases with the increase in temperature.
bonded atoms in graphene, which triggers subsequent fracture to graphene.

**Effects of temperature on the strength of SLGs**

The stress-strain relations for various temperatures ranging from 1K to 77K are shown in Figure 1. In Figure 1(a) we present the stress-strain curves vs. temperature, in Figure 1(b) and (c) the variation of fracture strength and fracture strain, respectively, against temperature. As revealed in Figure 1(a), a non-linear elastic behavior is observed for graphene when it is strained over 5%. Each curve corresponding to a specific temperature ends at a sudden stress drop which manifests brittle fracture of fast crack propagation through the entire graphene sheet. Both the fracture strength and fracture strain decrease with the increase in temperature. Notice that the fracture strength was obtained when the first rupture occurred. Our simulation showed that, for the cases of 1K, 5K, 30 K, and 77k, the first rupture was followed by succeeding ruptures due to cracks which were resulted from bond breaking. This phenomenon reflects the steps on the stress cliffs in Figure 1(a). For example, the morphology progression simulation showed that there were three other ruptures following the first rupture at 1K, then it can be seen that there are three steps during the stress falls. On the other hand, at 10K the SLG was broken by one rupture so that the stress falls directly. Further examinations on the results disclose that the fracture strength can be mediated by temperature. In the low temperature regime, i.e. between 1K and 5K, the fracture strength varies from 190GPa to 188GPa, a 1% minor deviation. In the medium temperature regime, ranging from 10K to 20K, the fracture strength decreases by 1.2%, from 190GPa to 188GPa. At temperatures of 30K and 77K, there is an insignificant change on the fracture strength (only reduced by 0.8%). However, a distinct variation is noted in Figure 1(b) showing that in the transition of temperature from 20K to 30K, the fracture strength decreases from 179GPa to 149GPa, a drop of around 17%. A similar trend can also be observed for the fracture strain shown in Figure 1(c). The effect of temperature on Young’s modulus was obtained and is summarized in Table 2. As revealed, Young’s modulus decreases from 1.4 TPa as the temperature increases up to 30K beyond which it converges close to 0.93~0.96TPa. This trend of variation is in fair agreement with previous findings. In the low temperature regime, the difference in Young’s modulus value is possibly due to the use of different molecular potential.

**Effects of temperature on fracture morphology of SLGS**

From the descriptions in preceding sections, it is discerned that the temperature has significant influences on the fracture evolution of SLGS.

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**Table 2 — Variation in Young’s modulus of graphene with temperature under uniaxial tensile test along the zigzag direction**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Young’s modulus (TPa)</th>
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<tbody>
<tr>
<td>1</td>
<td>1.40</td>
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<tr>
<td>5</td>
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<td>10</td>
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<tr>
<td>30</td>
<td>0.96</td>
</tr>
<tr>
<td>77</td>
<td>0.93</td>
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**Fig. 1 —** (a) Nominal stress-strain curves of graphene under uniaxial tensile load along the zigzag direction at various temperatures. (b) Variation in fracture strength vs. temperature. (c) Variation in fracture strain vs. temperature.
Presented in Figure 2 is the progression of fractured graphene sheet at various temperatures. Each progression associated with a specific temperature comprises 7 frames in time of morphology indicating the start (the left morphology) to the end (the right morphology) of the fracture of SLGS. From Figure 2 it is seen that fracture starts from a bond breaking on the bottom right free edge of the SLG. This phenomenon is similar to what was described previously in the work of Dewapriya, et al.\textsuperscript{20} The edge atoms have two bonds while the interior atoms have three bonds. The out-of-plane oscillation generates compressive forces that break the weakly bonded atoms on the free edges. Moreover, the tensile load is applied along both upper and bottom edges. These two facts result in bond breaking on one of the four corners of the sheet instead of in the middle. Besides, the C-C bond length in graphene linearly increases with temperature using Brenner type potential\textsuperscript{21} which is related to the elongation of the C-C bonds at elevated temperature. Thus, the C-C bonds can be broken under a lower applied load. Also revealed in Figure 2 is that bond breaking triggers subsequent breakings to form a crack path. For all cases except for 10K, the crack runs along the armchair direction in its infant age, and only for 1K does the crack remain in the armchair direction while other crack paths turn to the zigzag direction. The simulated results fall in good agreement with previous study\textsuperscript{22} indicating that an armchair crack under mode I prevailing condition changes its propagating direction to zigzag. For the case of 10K, the crack propagates all the way along a 30° zigzag direction until the graphene falls apart. It is interpretable that complex mechanical stresses around the crack tip can alter the direction of crack path from its line by 30° or multiples of 30°. At lower temperature regime, e.g. 1K and 5K, more cracks are created due to new bond breakings on the other three corners. These lately created cracks run in the armchair direction until the sheet is broken through. Interestingly the simulation shows that, for the cases of 1K and 5K, after the occurrence of the second crack which was created on the bottom left free edge, the third crack was initiated on the diagonal corner, i.e., on the top right free edge. This phenomenon might be considered as crack

Fig. 2 — Morphologies of crack progression of SLGS at various temperatures. Each Crack progression comprises 7 morphologies in time frame (in fs) from left to right
induced by wave-transition of energy. Notice that the SLGS is 59.7Å×36.4Å or 5.97nm×3.64nm in size; the diagonal distance is 6.99nm. This distance is close to the wavelength as reported previously\(^2\) claiming that free edge effect induces out-of-plane deformation predicting an intrinsic wavelength for edge buckling to be 6.2nm. At higher temperature regime there is no occurrence of crack on the other loaded edge of the graphene. It is interesting to note that only for the case of 30K is there a second crack created on the bottom left corner due to bond breaking; nevertheless, the crack runs along the armchair direction. Further observations on the results shown in Figure 2 reveal that voids or vacancies are formed around the crack tip and surfaces in the course of propagation. Voids and/or defects around the crack advance dislocations nearby the crack and increase crack tip stresses. Therefore, a smaller applied load is sufficient to break C-C bonds which are located in front of the crack tip. In addition, the vacancies affect the trajectory of the crack propagation. Figure 2 also discloses that at all temperatures the faces of the cracks are symmetric with respect to the crack line hence it may suggest that the cracks are under mode I loading. This is of expectance since the graphene is subjected to uniaxial tensile loading; moreover, the linear elastic solutions of dynamic crack tip field predict that under mode I loading, the opening displacements along the crack face are symmetric with respect to the crack line \(^{24, 25}\). There is an apparent effect of temperature on the distribution of the strain energy. In this study the strain energy of the atoms is calculated based on Eq. (1). The strain energy is a quadratic function of the strain and is equivalent to work required to displace an atom from its neutral position. A highly displaced atom possesses high strain energy. For the strain energy level of an atom, we express it in term of colors. It can be seen from the morphologies that the strain energy is influenced by the temperature. At low temperatures of 1K and 5K, there are very few atoms showing higher energy. At high temperature regime, a considerable number of atoms in a zone near the crack are at higher strain energy level. Observations of the results imply that the potential of atom increases with the increase in temperature; hence, the atoms are prone to being disturbed. Once bond breaking occurs, the carbon atoms bounce off each other and then form clusters as seen in Figure 2 (10K~77K), which accelerates crack extension leading to both in-plane and out-of-plane displacements.

Moreover, the thermal energy flows into SLGS increases the crack-tip speed, where local cracks spread out to facilitate the dissipation of energy as seen in Figure 2 where the zone of elevated strain energy move along with progression of the crack. Presented in Figure 3 is the time history of the averaged strain energy of the system at various temperatures. As revealed the energy of the system increases with the temperature; the kinetic energy at higher temperatures makes graphene sheets have higher energy. When fracture occurs, the strain energy fluctuates to account for the formation of cracks and energy variation around the crack tip and faces. It can be seen that the energy fluctuation becomes significant with the increase in temperature; an indication of thermal energy flowing into the system leading crack extension to both in-plane and out-of-plane displacements. The secondary insets shown for 30K as well as 77K are the side views of the specific cracked morphology.

**Conclusion**

SLGS shows out-of-plane deformations at equilibrium configuration. The out-of-plane deformation
generates compressive forces that break the weakly bonded atoms, which triggers subsequent fracture to graphene. In the temperature range consider herein, a non-linear elastic behavior is observed from the stress-strain curve when SLGS is strained over 5%. The stress-strain curve ends at a sudden stress drop indicating brittle fracture of fast crack propagation through the entire SLGS. Both the fracture strength and fracture strain decrease with the increase in temperature. The fracture strength can be mediated by temperature. There is insignificant variation of the fracture strength of SLGS in temperature regions of 1K–5K, 10K–20K, and 30K–77K; however, the fracture strength reduced by about 17% in the transition of temperature from 20K to 30K. Young’s modulus decreases from 1.4 TPa as the temperature increases up to 30K and reaches an asymptotic value of 0.93–0.96 TPa. Fracture in SLGS is triggered by bond breaking as a result of out-of-plane deformation. The out-of-plane deformation generates compressive forces that break the weakly bonded atoms on the free edges. Bond breaking is followed by the formation of armchair crack which turns to zigzag direction as it propagates except for 10K case where the crack propagates all the way along a zigzag direction until the graphene falls apart. However, in the cases of 1K and 5K, fracture is dominated by armchair crack. Also in the cases of 1K and 5K, crack is created due to wave-transition of energy; the third crack occurs on the diagonal corner to the second crack. When a SLGS is fractured, the strain energy of graphene fluctuates; the fluctuations can be mapped on stress falls in the stress-strain curve as well as registered in the time history of the simulation results.

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Reference


