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The fracture toughness of graphene during the tearing process

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Abstract

The fracture toughness of single-crystal graphene and bi-crystal graphene with different misorientation angles is investigated by molecular dynamics simulation. We find that the fracture toughness fluctuates when a crack propagates across the grain boundary. It indicates that the grain boundary affects the fracture toughness during the fracture process. The affected region on the graphene is limited to a small zone around the grain boundary. However, for the complete tearing-failure case, fracture toughness of bi-crystal graphene is approximate to that of single-crystal graphene, which implies that the fracture toughness is not very sensitive to the grain boundary. For comparison, the tensile fracture simulations of the single-crystal graphene and bi-crystal graphene are carried out. The results show that the grain boundaries block the crack propagation and affect fracture toughness significantly in bi-crystal graphene under tensile force. Furthermore, we analyze the fracture of a single C-C bond at the crack tip of single-crystal graphene under tearing load from the atomic view. We find that the fracture toughness of the single C-C bond occupies about half of the fracture toughness for the complete failure of the total single-crystal graphene, and the other half energy distributes in the rest of the graphene.

Keywords: graphene, tearing, fracture toughness, grain boundary

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene is a 2D material with honeycomb lattice structure, consisting of sp²-hybridized carbon atoms. It has extraordinary electronic [1–4], thermal [5, 6], and mechanical properties [7]. Actually, the properties of graphene are easily affected by the external (i.e. temperature, etc)

and internal factors (i.e. defect, size and edge, etc) [8-10]. For example, the higher temperature will soften the strength for the uniaxial stretching in both the zigzag and armchair directions [10]. Through using chemical vapor deposition (CVD) to fabricate the single and multi-layer graphene [11-13], it will unavoidably introduce different kinds of defects into the graphene, which greatly affect its properties [14-18]. The mechanical properties of graphene are sensitive to defects [19–21]. The grain boundary in bi-crystal graphene would lower the strength, depending on the density of dislocation on the grain boundary and the angle between the loading direction and the orientation of the grain boundary [22-24]. However, some other studies have shown different results, where if the grain boundary weakens or strengthens, the strength of the graphene is determined by the chirality of graphene and the detailed arrangement of the defects on the grain boundary. These construct the symmetrical or non-symmetrical grain boundaries with different misorientation angles [25, 26]. From previous study, the research work showed that the existence of point defects [27, 28] in graphene would decrease the strength of the graphene. However, the failure mechanism could be switched from the brittle fracture to ductile fracture when the vacancy defect becomes densely distributed in graphene. Therefore, the high Young's modulus of 1TPa and high strength of 130 GPa are proper parameters to describe the defect-free graphene [15, 29], while the fracture toughness is more useful to characterize the mechanical property of the defective graphene.

In continuum mechanics, there are many mechanical parameters to be used to describe the fracture toughness, such as the energy release rate [30–33], J-integral [34–36], and stress intensity factor [37, 38]. According to the simulation work of Yin et al [30], it could be found that the fracture toughness of defective single-crystal graphene under uniaxial tension force is significantly affected by the length of the initial crack and the chirality (armchair or zigzag) of graphene. The measured fracture toughness of multi-layer graphene by experiment and molecular dynamics (MD) simulation has higher value than that of single-crystal graphene [39]. The simulation results of Jung et al [40] also show that the fracture toughness of polycrystalline graphene is higher than the fracture toughness of single-crystal graphene, and it is inversely proportional to the grain size. Compared with the excellent strength and Young's modulus of perfect singlecrystal graphene [29, 41, 42], it is disadvantageous for the practical application of graphene if its fracture toughness is lowered by the various defects. Since the defects of graphene are unavoidable, many researchers in their studies [43-46] proposed making use of the defects. They found that it is effective to introduce topological defects into graphene to design its mechanical properties. In general, we can easily calculate the fracture toughness under in-plane force using the parameters of characterizing the deformation of the models. For the fracture toughness of graphene applied in the out-plane deformation case, the energy increment for creating the new crack surface is employed, which is proposed by Moura *et al* and universally accepted [47].

In the past study, the research of graphene focused on the fracture toughness of graphene under the complete-damage case, while neglecting the fracture toughness during the failure process. Furthermore, the grain boundary effect on the fracture toughness of graphene under the tearing-loading case has still not been discussed. In engineering, tearing behavior can tailor the 2D materials to the required size, so it is meaningful to study the tearing behavior for further fabrication and application of graphene in practice. In theory, during the tearing process the crack mode is mixed by the basic crack modes (opening mode/in-plane shear mode/ anti-plane shear mode) in traditional fracture theory, which shows complicated mechanical mechanism. Herein, we carry out the MD simulation by making use of the large-scale atomic/ molecular massively parallel simulator (LAMMPS) [48] to investigate the mechanical properties of graphene during the crack propagation process under tearing force. Our study reveals that the fracture toughness of bi-crystal graphene in the tearing-loading case varies slightly during the fracture process, but only when the crack propagates across the grain boundary

and just in a narrow area around the grain boundary. The fracture toughness of bi-crystal graphene in the complete-failure case is insensitive to the grain boundary, and it is almost approximate to the fracture toughness of the single-crystal graphene under tearing force, 11 J m^{-2} . However, the fracture behaviour of bi-crystal graphene under uniaxial tension is changed and transformed enormously by the grain boundary (such as from brittle fracture to ductile fracture). For single-crystal graphene, the fracture toughness is almost the same for the tensile and tearing-force-loading case, but the fracture toughness of bi-crystal graphene is more sensitive to the grain boundary under tensile force, and it increases up to about 22.46 J m^{-2} when the misorientation angle of bi-crystal graphene is 21.79°. Therefore, the graphene has distinct sensitivities to the grain boundary in different loading cases. The intrinsic cause is dependent on the difference in their deformation patterns, which is disadvantageous or advantageous to the energy accumulation when the grain boundary hinders the crack propagation and the propagating path is changed. The concentrated deformation in the tearing-loading case corresponds to the insensitivity of graphene, while the sensitivity relates to uniform deformation in the tensile-loading case. For the concentrated deformation under the tearing force, the energy mainly accumulates in a small area around the crack tip, when the crack propagation is blocked by the grain boundary. Thus, the fracture toughness is more insensitive to the grain boundary, compared with the uniform deformation under the tensile force. Furthermore, we find that the fracture toughness of a single C–C bond under the tearing force from the simulation is only half of the value of single-crystal graphene in the complete-failure case.

2. Simulation models and methods

In the present study, the dimensions of all the single-crystal and bi-crystal graphene models are 50 nm in length and 50 nm in width. The bi-crystal graphene models consist of two grains with specific orientations and a symmetric grain boundary distributed with polygon defects. The zigzag orientation of one grain is parallel to the *x*-axis, and the other has a misorientation angle (the intersection angle θ between the lattice orientations of the two grains) with the first grain. In the modeling, we generate a set of bi-crystal graphene models with various misorientation angles, including 6.01°, 13.17°, 16.43°, 21.79° and 30° (GB-575) [49, 50], as shown in figures 1(a)–(e). The initial cracks are located at the edge of the models by removing some atoms, and they have the same width of two to three atoms with length of 15 nm, as shown in figure 1(f). In the loading cases of tearing and uniaxial tension, the cracks propagate and pass through the grain boundaries. The crack paths and the grain boundaries form various angles, depending on the misorientation angles of the bi-crystal graphene grain boundaries.

In the MD simulation, the interatomic interaction between the carbon atoms of the graphene is described by the adaptive intermolecular reactive empirical bond order (AIREBO) potential [51]. The cut-off distance of the C–C bond is set as 0.2 nm [52]. The constant integration time step is 1 fs for all simulations. To minimize the thermal disturbance, the temperature is 1 K in all simulations. In the pre- and post-processes, the atomic configurations are visualized by the AtomEye package. In the tearing-loading case, the edge areas of the graphene models are driven by the tearing force and move at the velocity of 1 and -1 Å ps⁻¹ respectively, to the opposite directions in the *z*-axis, as shown in figure 1(g). For the uniaxial tensile case, a constant strain rate of 2.38×10^{-7} fs⁻¹ in the *y*-axis direction is applied to investigate the fracture behaviour of the single-crystal and bi-crystal graphene. We can calculate the virial stresses of the graphene models with the normal tensor component along the loading direction by taking the thickness of the graphene models as 0.34 nm. Both the tearing and uniaxial tensile cases apply with free boundary conditions in all directions.



Figure 1. Schematics of simulation models of graphene. The graphene grain boundary structures for different misorientation angles θ , (a) $\theta = 6.01^{\circ}$, (b) $\theta = 13.17^{\circ}$, (c) $\theta = 16.43^{\circ}$, (d) $\theta = 21.79^{\circ}$, (e) $\theta = 30^{\circ}$. (f) The top view of the partial graphene sheet with the initial crack placed along the zigzag direction (*x*-axis). The W describes the width of the initial crack. (g) Sketch map of graphene in the tearing-force case (the side view and 3D view). The edge areas in the dashed frames move to the opposite directions to realize the tearing process, pointed by the arrows. Displacement 2u describes the total displacement of the edge areas of graphene under the tearing forces.

3. Simulation results

For the tearing loading case, the critical energy release rate can characterize the fracture toughness, which represents the threshold energy dissipated for creating per unit area of new crack surface during fracture process. According to the Irwin–Orowan energy balance theory, the following parameters define the fracture toughness, i.e. the strain energy U, the kinetic energy T, the dissipation energy D for new surface, the external work W, and time t. The kinetic energy is not changeable and negligible when the crack propagation is stable at a relatively constant velocity. We assume the increment of strain energy to be negligible once the crack propagation begins, because the crack propagation is fast and the deformation of graphene is concentrated around the crack tip under the tearing force. According to Irwin–Orowan for energy-balance theory and the assumptions, the energy-balance relationship can be expressed as $\frac{dW}{dt} = \frac{dD}{dt}$. In MD simulation, the external work is almost totally stored in the system as potential energy Pe when the kinetic energy is negligible. Thus, the critical energy release rate is obtained by $G_c = dPe/dA$, where dA is the newly created surface area driven by increment

of potential energy d*Pe* during the fracture process. The relationship between the external force and external work is as follows:

$$F = \frac{\mathrm{d}Pe}{2\mathrm{d}u} \tag{1}$$

where *F* is the external tearing force, *u* is the displacement of the edge under the tearing force in graphene.

We define two expression means for critical energy release rate to investigate the fracture toughness during the whole fracture process [40].

$$G_1 = \frac{\Delta P e_1}{B \cdot \Delta a} \text{ and } G_2 = \frac{\Delta P e_2}{B \cdot \Delta L}$$
 (2)

where G_1 is defined as instantaneous energy release rate, Δa (~0.246 nm) is the distance between two nearest parallel C–C bonds along with the zigzag direction, and ΔPe_1 is the potential energy difference between two moments when the nearest parallel C–C bonds break, respectively. G_2 is defined as average energy release rate, ΔL is the total increment of crack length which increases with crack propagation, and ΔPe_2 is the potential energy difference at two moments when the model is initially relaxed and the crack length is increased by ΔL . *B* is the thickness of the single-layer graphene with a value of 0.34 nm.

We should note the following points herein. First, at the initial stage of crack propagation, the strain energy dominates the critical energy release rate calculated by equation (2), because large deformation of graphene accumulates before the crack begins to propagate. Second, the engineering fracture toughness G_c corresponding to the complete-failure state of graphene is calculated by G_2 which always contains the strain energy. Thus, the engineering fracture toughness is higher than that in the actual case, and G_1 is more accurate, but it is not convenient in practical application; the original sp² hybridization of carbon atoms is transformed into sp hybridization when the C–C bond is broken during the fracture process. Thus, the total potential energy increases when every C–C bond breaks, due to the atomic hybrid orbitals lowering the potential energy. The energy increment is also closely relative to the crack propagation path and the type of C–C bond.

We perform MD simulation to explore the fracture toughness of single-crystal and bi-crystal graphene models in the tearing-loading case. Figure 2(a) displays the curves of the fracture toughness G_1 and G_2 as functions of the crack length increment for single-crystal graphene. The results show that the G_1 and G_2 vary severely during the initial stage of the fracture process, because the strain energy has a significant effect on the fracture toughness at the initial fracture stage. The difference between the maximum value of the fracture toughness (which corresponds to the crack propagation initiation) and the value of the fracture toughness for the complete-failure case is estimated to be 23.357 J m^{-2} , revealing that the consumed external work for the crack initiation is more than that during the following fracture process. From figure 2(b), it is found that the peak fracture toughness increases with the increase in the initial crack width, and it is almost proportional to the value of $\sqrt[3]{W}$, as shown in figure 2(b). It implies that it needs more energy to start the crack propagation for a blunter initial crack in graphene. After the crack length increment increases to about 8 nm, the influence of starting the initial crack propagation is eliminated, and the fracture toughness of G_1 and G_2 are almost consistent, which is nearly equal to the fracture toughness for the complete-failure case, in which the value is approximately 11 Jm^{-2} , as shown in figure 2(a). From figure 2(c), it can be seen that the tearing force obtained from equation (1) shows a linear decrease during the stable fracture period, when the initial crack width is about 0.65nm. The crack propagation



Figure 2. (a) The curves of the instantaneous fracture toughness G_1 and average fracture toughness G_2 as functions of crack length increment ΔL for the single-crystal graphene. (b) The peak fracture toughness of single-crystal graphene relative to the initial crack propagation as a function of the widths of the initial crack W. (c) The tearing force F as a function of the total displacement (2*u*) of graphene corresponding to the two opposite tearing forces.

starts when the tearing force reaches about 2.7 nN, and then the curve of the tearing force drops sharply, when the graphene sheet is torn into two parts.

For the sake of simplicity, we define the cross carbocycle as the carbocyclic structure on the grain boundary, and it is specifically the broken structure when the crack propagates across the grain boundary. For example, 21.79°_{5} , 21.79°_{6} and 21.79°_{7} indicate that the cross carbocycles destroyed by the crack propagation are pentagon, hexagon and heptagon on the 21.79° grain boundary. The different cross carbocycles are associated with the different crack paths. Figure 3 shows the variation zone of the fracture toughness G_1 of bi-crystal graphene caused by the grain boundaries with different misorientation angles.

From figure 3, it can be seen that the zone of the fracture toughness affected by the grain boundaries with different misorientation angles, as confined in the two vertical lines, is in the narrow area near the grain boundary, and the affected crack path length is less than 4 nm. In the narrow affected crack length, the values of the fracture toughness fluctuate and the highest peak values can reach more than three times the fracture toughness for the case of complete failure. The peak points of fracture toughness G_1 of bi-crystal graphene, with misorientation angles of 13.17° and 16.43°, are much higher than the ones of bi-crystal graphene with other



Figure 3. The curves of the instantaneous fracture toughness G_1 of the bi-crystal graphene with different misorientation angles (single-crystal graphene plotted as a reference). The curves for the misorientation angles 21.79°_5 , 21.79°_6 and 21.79°_7 depict the effect of the cross carbocycles. The areas of crack length affected by the grain boundaries are included in the two vertical lines, and the unaffected areas are marked with the arrows. The maximum values of the fracture toughness G_1 , near the grain boundaries of the bi-crystal graphene with misorientation angles of 13.17° and 16.43° are higher than the values of the others.

misorientation angles. We further investigate the cross carbocycle effect on the crack propagation. From the curves of fracture toughness for the $21.79^{\circ}_{,5}$, $21.79^{\circ}_{,6}$ and $21.79^{\circ}_{,7}$ cases, it is found that the effects on the fracture toughness are distinct for the different cross carbocycles. The fracture toughness around the grain boundary varies according to the stress states for different cross carbocycles. Besides, the simulation results show that the grain boundary has negligible effect on the fracture toughness for the complete-failure case of bi-crystal graphene. From figure 3, the fracture toughness values in the areas far away from the grain boundary are hardly affected. The unaffected areas occupy the major part of the crack propagation path. Hence, the fracture toughness of the complete-failure cases for the bi-crystal graphene models with various misorientation angles is very close to that of the single-crystal graphene, approximately 11 J m⁻².

Figure 4 shows the snapshots of the accumulated potential energy zones, which represent the deformation concentration patterns during the fracture process. As shown in figure 4, the potential energy always centrally accumulates around the crack tip, rather than the widely known uniform pattern for the tensile deformation case. The concentrated deformation pattern is disadvantageous to the accumulation of a considerable amount of energy, when the crack propagates to the grain boundary and is hindered by it. Thus, the grain boundary does not dominate the fracture toughness of bi-crystal graphene for the complete-failure case. We further find that the potential energy distributes symmetrically with respect to the crack length in single-crystal graphene, but in bi-crystal graphene, the potential energy transforms to the



Figure 4. Snapshots of the accumulated potential energy zones, which represent the deformation concentration patterns during the fracture process. (a) Single-crystal graphene. (b) Bi-crystal graphene with a misorientation angle of 21.79°_7.

asymmetric pattern, because of the effect of the grain boundary, especially after the crack propagated across the grain boundary and the crack path changed to the tilted direction versus the *x*-axis. Thus, the existing grain boundary will influence the fracture toughness G_1 during the fracture process, by hindering the crack propagation and switching the potential energy distribution areas.

From the present MD simulation results (in figure 3), it clearly demonstrates the high insensitivity of the fracture toughness of the bi-crystal graphene to the grain boundary in the case of complete failure. The influence on fracture toughness only appears in a narrow crack length around the grain boundary during the fracture propagation process. To further study the effect of the grain boundary on the fracture toughness of the complete-failure case under tearing force, we also carry out the uniaxial tensile simulation for comparison. Figure 5 shows the curves of tensile stress σ_{yy} versus tensile strain ε_{yy} along the y-axis for different misorientation angles and the reference curve of single-crystal graphene under the tensile force. The results show that the different grain boundaries give rise to a large difference in fracture toughness, compared with the tearing-loading case. The fracture toughness for the completefailure case under tensile force is easily calculated by $G = EH \varepsilon_c^2$ [46], where G describes the energy release rate, E is the intrinsic Young's modulus of material (1TPa for graphene), H is half of the width of the model parallel to the y-axis (21 nm of graphene models), and ε_c is the critical strain corresponding to the critical stress σ_c . As shown in table 1, the fracture toughness G of the bi-crystal graphene characterized by the energy release rate is in the range of $11.88 - 22.46 \text{ Jm}^{-2}$. The result shows that the fracture toughness of bi-crystal graphene is always greater than that of single-crystal graphene ($G = 10.85 \text{ Jm}^{-2}$).

The results of the tensile simulation demonstrate that the fracture behaviour, whether brittle or ductile fracture, depends on the various grain boundaries. The different fracture behaviours lead to the different toughening effects. From figure 5, it can be seen that the stress–strain curves clearly reveal the plastic fractures for the misorientation angles 16.43°, 21.79°_5, 21.79°_6 and 30°. However, the tensile stress–strain curves for misorientation angles 6.01°, 13.17° and 21.79°_7 indicate that the fracture of graphene is brittle fracture. Apparently, the grain boundaries with misorientation angles 16.43°, 21.79°_5, 21.79°_6 and 30° effectively prevent the crack propagation and improve the critical strain corresponding to the rapid drop



Figure 5. Tensile stress–strain curves in the *y*-axis direction of bi-crystal graphene for different misorientation angles (a) for 0° , 6.01° , 13.17° and 21.79°_{-7} ; (b) for 16.43° , 21.79°_{-6} ; 21.79°_{-5} and 30° . The curve of single-crystal graphene is for reference.

Table 1. The critical stress, strain and energy release rate for bi-crystal graphene with different grain boundaries, corresponding to the data in figure 5.

θ (°)	0	6.01	13.17	16.43	21.79_7	21.79_6	21.79_5	30
$\sigma_{\rm c}~({\rm GPa})$	16.26	16.11	16.50	14.91	15.45	15.85	18.46	15.25
$\varepsilon_{\rm c}$ (%)	2.273	2.39	2.42	2.83	2.378	2.83	3.27	2.83
$G = EH \varepsilon_{\rm c}^2 ({\rm J} {\rm m}^{-2})$	10.85	12.0	12.3	16.82	11.88	16.82	22.46	16.82

in stress. We further examine the stress state on the crack path near the grain boundary caused by the different polygon carbocycles distributed on the grain boundary, acting as the prestress for crack propagation. Figures 6(a)-(e) present the top views for various misorientation angles. We find that the plastic fracture behaviour is relative to the compressive pre-stress along the crack path near the grain boundary, for which the misorientation angles are 21.79°_6 or 30 $^{\circ}$. In contrast, the tensile pre-stress along the crack path near the grain boundary leads to brittle fracture behaviour for the misorientation angles 6.01°, 13.17° and 21.79°_7. However, although the pre-stress state on the grain boundary shows tensile stress, the fracture behaviour for the misorientation angles of 16.43° is plastic. It is due to the sub-defect elicited by the crack propagation near the grain boundary, as shown in figure 6(f). The sub-defect neither extends nor merges with the main crack, but absorbs energy and prevents crack propagation. The plastic behaviour for the misorientation angle 21.79°_5 is more obvious, because of the simultaneously existing compressive pre-stress and sub-defect. In general, the fracture toughness for the complete-failure case under the tensile force is more sensitive to the grain boundary, and can be easily dominated by the cross carbocycles in the crack path. The reason is that the uniform deformation for the tensile-loading case is more advantageous to accumulate considerable energy when the grain boundary hinders the crack propagation.

4. Discussion of the fracture toughness of a single C-C bond

In the preceding section, we obtained the fracture toughness according to the potential energy of the total graphene model under tearing force. However, from the atomic scale point of view, the fracture of graphene only involves two carbon atoms and a C–C bond at the crack tip [53].



Figure 6. (a)–(e) Snapshots of stress (MPa) contours near the grain boundary of bicrystal graphene models for different misorientation angles. The orientation of the crack propagation after extending through the grain boundary is marked with the blue arrows. (f) Sketch map of the sub-defect caused by the crack propagation on the grain boundary.

The new crack surface appears once the C–C bond breaks. Thus, in the following, we will explore the fracture toughness at the atomistic scale in the tearing simulation of single-crystal graphene. In this study, there are two basic assumptions. The first is that the crack propagation is quasi-static, and the second is that the breakage of the C–C bond is merely relevant to the normal stress parallel to the bond length, rather than the shear stress perpendicular to the bond length.

According to the first assumption and the volume-averaging theory [54–56], the averaged Cauchy stress tensor of the two carbon atoms involved in the fracture, is obtained as $\overline{\sigma}_{ik} = \frac{1}{V} \int \sigma_{ik} dV$, where σ_{ik} represents the stress tensor of the each atom, *V* is the total volume of the two atoms. Then, combining the second assumption and the Cauchy formula, the normal stress parallel to the length of the C–C bond relative to the fracture is calculated: $\overline{\sigma}_n = \frac{1}{2}(\sigma_n^1 + \sigma_n^2)$, where $\overline{\sigma}_n$ is the average normal stress, and σ_n^1 and σ_n^2 are the contribution of the two atoms. As shown in figure 7(a), the curves represent the averaged normal stress $\overline{\sigma}_n$ and the C–C bond length b^{C-C} , as functions of the displacement of the tearing force, for different initial crack widths. It indicates that the curves of $\overline{\sigma}_n$ reveal the properties of brittle fracture, decreasing sharply when it reaches the peak point; meanwhile, the lengths of the C–C bond sincrease rapidly. Moreover, it also reveals that the breakage of the C–C bond occurs later, when the shape of the initial crack is blunter.

The definition of the average normal stress shows the same meaning to that of the C–C bond stress. The strain definition of the single C–C bond is $\varepsilon = \frac{\delta - \delta_0}{\delta_0}$, where δ is equal to b^{C-C} during the fracture process, and δ_0 is the initial bond length, 0.142 nm. Figure 7(b) shows the curves of the average normal stress as a function of the C–C bond strain. The dotted line represents the critical C–C bond strain ε_c , which corresponds to the breakage of the C–C bond. The results reveal that the initial crack width has almost no influence on the curves of $\overline{\sigma}_n(\varepsilon)$. The strength of the C–C bond is calculated as ~112 GPa by fitting the curves of $\overline{\sigma}_n(\varepsilon)$, and



Figure 7. (a) The curves of the average normal stress \overline{o}_n and the C–C bond length b^{C-C} as functions of the displacement of tearing force for different initial crack widths. The left vertical axis represents the average normal stress and the right vertical axis represents the length of the C–C bond. (b) The curves of the average normal stress as a function of the strain of the C–C bond for different initial crack widths. The dotted line corresponds to the breakage of the C–C bond. The atomic structures reveal the different widths of the initial cracks of the investigated graphene models.

the Young's modulus is ~1148.82 GPa, obtained from the derivation of the linear segment of the curves ($E = \lim_{\varepsilon=0} \frac{d\sigma_n}{d\varepsilon}$). The calculated results are very close to the intrinsic mechanical properties of graphene [29].

In order to extend the crack to forward Δa , the external work required is $\overline{\sigma}_n(B\Delta a)d\delta$ to resist the force of the covalent bond and separate the two carbon atoms by $d\delta$. The C–C bond breaks and forms the new crack surface when the C–C bond is elongated from δ_0 to δ_c . Thus, the total work for extending the Δa crack length is as follows:

$$\Delta W = \int_{\delta_0}^{\delta_c} \overline{\sigma}_n (B\Delta a) \mathrm{d}\delta = (B\Delta a) \delta_0 \int_{\varepsilon_0}^{\varepsilon_c} \overline{\sigma}_n \mathrm{d}\varepsilon$$
(3)

where the C–C bond strain ε_0 and ε_c corresponds to δ_0 and δ_c , respectively.

We should note that the external work from equation (3) is always greater than the real energy required to form the new crack surface due to the kinetic energy. The surface free energy γ_{C-C} and energy release rate G_{C-C} are approximate to $\frac{\Delta W}{2B\Delta a} = \gamma_{C-C} = \frac{G_{C-C}}{2}$, and $\Delta W =$ 2.94 eV, $G_{C-C} = 5.63$ J m⁻² are obtained by averaging the integration of figure 7(b) for different crack widths. From MD simulation results, when the graphene is in the relaxed state, the difference of the potential energy between the carbon atoms of the sp² hybridization and sp hybridization is $\Delta Pe = 2.62$ eV. Thus, the energy release rate for breaking a C–C bond and forming the new crack surface, involving two carbon atoms, is 10.03 J m⁻², which is approximately the value of G_1 and G_2 under the complete-failure case. However, the stress state of carbon atoms corresponding to just breaking the C–C bond is not fully relaxed to the low-energy state. Actually, the moment to calculate the G_1 and G_2 during the fracture process of graphene under the tearing force is when the C–C bond is just broken.

Compared with the G_1 and G_2 during the fracture process of graphene, the energy release rate calculated by the total work for breaking the single C–C bond is much lower, only about half of the fracture toughness of the graphene for complete failure. The whole graphene model and the total energy of the model are used to obtain the values of G_1 and G_2 , while only a single C–C bond is employed to obtain the value of G_{C-C} . However, during the process of breaking the single C–C bond, the energy of the atoms in the graphene becomes higher, especially near the broken bond. Thus, except the G_{C-C} for breaking the single C–C bond, another half of the G_1 and G_2 distribute in the whole graphene, especially around the crack tip.

5. Concluding remarks

In order to explore the fracture properties of graphene in the tearing-load case, we carry out MD simulations for graphene models by using LAMMPS. The results show that the fracture toughness characterized by the energy release rate fluctuates during the process of crack propagation under tearing force. The initial fracture toughness of single-crystal graphene for starting the crack propagation is much higher than the fracture toughness during the following fracture process. The initial fracture toughness increases with the widths of the initial crack, and the corresponding tearing force for the initial crack width of 0.65 nm is about 2.7 nN. The fracture toughness in the complete-failure case is approximately 11 J m^{-2} , whether for single-crystal graphene or bi-crystal graphene, i.e. the fracture toughness of graphene for the complete-failure case is insensitive to the grain boundary. However, during the fracture process, the instantaneous fracture toughness of bi-crystal graphene is affected by the grain boundary and the cross carbocycles on the grain boundary, but the affected area is limited to only a narrow area around the grain boundary. Although the grain boundary has some restraining effects for crack propagation, its effect is too tiny to affect the fracture toughness for the complete-failure case. In contrast, the grain boundary has an important impact on the fracture toughness of graphene under uniaxial tension load for the complete-failure case. Different misorientation angles and cross carbocycles of grain boundaries produce distinct toughening effects, due to the pre-stress near the grain boundary and the sub-defect effect caused by the crack propagating the grain boundary. In the tearing process, the stress and the energy increment concentrate on the area around the crack tip. Thus, the toughening effect is limited to only a smaller area. However, for graphene under uniaxial tension loading, the deformation of graphene is uniform and the grain boundary can hinder the crack propagation, because largescale energy absorption areas exist in the graphene. Thus, the toughening effect on graphene under uniaxial tension loading is stronger than that of the tearing-loading case. To investigate the energy release rate of the breakage of the C–C bond at the crack tip in the tearing-loading case, we further analyze the fracture toughness of a single C-C bond in single-crystal graphene. The results show that the fracture toughness of a single C-C bond is only half of the total fracture toughness of the graphene under complete failure, which means that the other carbon atoms consume the other half of the energy in the graphene.

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References

- [1] Geim A K and Novoselov K S 2007 The rise of graphene Nat. Mater. 6 183-91
- [2] Neto A C, Guinea F, Peres N, Novoselov K S and Geim A K 2009 The electronic properties of graphene *Rev. Mod. Phys.* 81 109
- [3] Peres N M R 2009 The electronic properties of graphene and its bilayer Vacuum 83 1248–52

- [4] Stoller M D, Park S, Zhu Y, An J and Ruoff R S 2008 Graphene-based ultracapacitors *Nano Lett.* 8 3498–502
- [5] Stankovich S, Dikin D A, Dommett G H, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 Graphene-based composite materials *Nature* 442 282–6
- [6] Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 Superior thermal conductivity of single-layer graphene *Nano Lett.* 8 902–7
- [7] Galiotis C, Frank O, Koukaras E N and Sfyris D 2015 Graphene mechanics: current status and perspectives *Annu. Rev. Chem. Biomol. Eng.* **6** 121–40
- [8] Dewapriya M A N, Phani A S and Rajapakse R K N D 2013 Influence of temperature and free edges on the mechanical properties of graphene *Modell. Simul. Mater. Sci. Eng.* 21 065017
- [9] Barnard A S and Snook I K 2011 Modelling the role of size, edge structure and terminations on the electronic properties of graphene nano-flakes *Modell. Simul. Mater. Sci. Eng.* 19 054001
- [10] Yazdani H and Hatami K 2015 Failure criterion for graphene in biaxial loading—a molecular dynamics study *Modell. Simul. Mater. Sci. Eng.* 23 065004
- [11] Li X, Cai W, An J, Kim S, Nah J, Yang D, Piner R, Velamakanni A, Jung I and Tutuc E 2009 Largearea synthesis of high-quality and uniform graphene films on copper foils *Science* 324 1312–4
- [12] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2008 Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition *Nano Lett.* 9 30–5
- [13] Li X, Magnuson C W, Venugopal A, An J, Suk J W, Han B, Borysiak M, Cai W, Velamakanni A and Zhu Y 2010 Graphene films with large domain size by a two-step chemical vapor deposition process *Nano Lett.* 10 4328–34
- [14] Liu T H, Lee S C, Pao C W and Chang C C 2014 Anomalous thermal transport along the grain boundaries of bicrystalline graphene nanoribbons from atomistic simulations *Carbon* 73 432–42
- [15] Yazyev O V and Louie S G 2010 Topological defects in graphene: dislocations and grain boundaries *Phys. Rev. B* 81 195420
- [16] Lu Y and Guo J 2012 Thermal transport in grain boundary of graphene by non-equilibrium Green's function approach Appl. Phys. Lett. 101 043112
- [17] Yazyev O V and Louie S G 2010 Electronic transport in polycrystalline graphene *Nat. Mater.* **9** 806–9
- [18] Liu X Y, Wang F C and Wu H A 2015 Anomalous twisting strength of tilt grain boundaries in armchair graphene nanoribbons *Phys. Chem. Chem. Phys.* 17 31911–6
- [19] Wang M C, Yan C, Ma L, Hu N and Chen M W 2012 Effect of defects on fracture strength of graphene sheets *Comput. Mater. Sci.* 54 236–9
- [20] Dewapriya M A N, Rajapakse R K N D and Phani A S 2014 Atomistic and continuum modelling of temperature-dependent fracture of graphene Int. J. Fract. 187 199–212
- [21] Banhart F, Kotakoski J and Krasheninnikov A V 2010 Structural defects in graphene ACS Nano 5 26–41
- [22] Jhon Y I, Jhon Y M, Yeom G Y and Jhon M S 2014 Orientation dependence of the fracture behavior of graphene Carbon 66 619–28
- [23] Liu T H, Pao C W and Chang C C 2012 Effects of dislocation densities and distributions on graphene grain boundary failure strengths from atomistic simulations *Carbon* 50 3465–72
- [24] Grantab R, Shenoy V B and Ruoff R S 2010 Anomalous strength characteristics of tilt grain boundaries in graphene Science 330 946–8
- [25] Wei Y, Wu J, Yin H, Shi X, Yang R and Dresselhaus M 2012 The nature of strength enhancement and weakening by pentagon–heptagon defects in graphene *Nat. Mater.* 11 759–63
- [26] Wu J and Wei Y 2013 Grain misorientation and grain-boundary rotation dependent mechanical properties in polycrystalline graphene J. Mech. Phys. Solids 61 1421–32
- [27] Xu L, Wei N and Zheng Y 2013 Mechanical properties of highly defective graphene: from brittle rupture to ductile fracture *Nanotechnology* 24 505703
- [28] Daly M, Reeve M and Singh C V 2015 Effects of topological point reconstructions on the fracture strength and deformation mechanisms of graphene *Comput. Mater. Sci.* 97 172–80
- [29] Lee C, Wei X, Kysar J W and Hone J 2008 Measurement of the elastic properties and intrinsic strength of monolayer graphene Science 321 385–8
- [30] Yin H, Qi H J, Fan F, Zhu T, Wang B and Wei Y 2015 Griffith criterion for brittle fracture in graphene Nano Lett. 15 1918–24
- [31] Madhukar M S and Drzal L T 1992 Fiber-matrix adhesion and its effect on composite mechanical properties: IV. Mode I and mode II fracture toughness of graphite/epoxy composites J. Compos. Mater. 26 936–68

- [32] Liao W C and Sun C T 1996 The determination of mode III fracture toughness in thick composite laminates *Compos. Sci. Technol.* 56 489–99
- [33] Marat-Mendes R and De Freitas M 2009 Characterisation of the edge crack torsion (ECT) test for the measurement of the mode III interlaminar fracture toughness *Eng. Fract. Mech.* 76 2799–809
- [34] Raghavachary S, Rosenfield A R and Hirth J P 1990 Mixed mode I/III fracture toughness of an experimental rotor steel *Metall. Trans.* A 21 2539–45
- [35] Gomoll A, Wanich T and Bellare A 2002 J-integral fracture toughness and tearing modulus measurement of radiation cross-linked UHMWPE J. Orthop. Res. 20 1152–6
- [36] Lacroix G, Pardoen T and Jacques P J 2008 The fracture toughness of TRIP-assisted multiphase steels Acta Mater. 56 3900–13
- [37] Rowcliffe A F, Robertson J P, Klueh R L, Shiba K, Alexander D J, Grossbeck M L and Jitsukawa S 1998 Fracture toughness and tensile behavior of ferritic-martensitic steels irradiated at low temperatures J. Nucl. Mater. 258 1275–9
- [38] Suresh S, Shih C F, Morrone A and O'Dowd N P 1990 Mixed-mode fracture toughness of ceramic materials J. Am. Ceram. Soc. 73 1257–67
- [39] Zhang P, Ma L, Fan F, Zeng Z, Peng C, Loya P E, Liu Z, Gong Y, Zhang J and Zhang X 2014 Fracture toughness of graphene *Nat. Commun.* 5 4782
- [40] Jung G S, Qin Z and Buehler M J 2015 Molecular mechanics of polycrystalline graphene with enhanced fracture toughness *Extreme Mech. Lett.* 2 52–9
- [41] Bi H, Yin K, Xie X, Zhou Y, Wan N, Xu F, Banhart F, Sun L and Ruoff R S 2012 Low temperature casting of graphene with high compressive strength Adv. Mater. 24 5124–9
- [42] Zheng Y, Xu L, Fan Z, Wei N and Huang Z 2012 A molecular dynamics investigation of the mechanical properties of graphene nanochains J. Mater. Chem. 22 9798–805
- [43] Bets K V, Artyukhov V I and Yakobson B I 2014 Kinetically determined shapes of grain boundaries in CVD graphene (arXiv:1412.4323)
- [44] Chakrabarty S, Wasey A A, Thapa R and Das G P 2015 First principles design of divacancy defected graphene nanoribbon based rectifying and negative differential resistance device AIP Adv. 5 087163
- [45] López-Polín G, Gómez-Navarro C, Parente V, Guinea F, Katsnelson M I, Pérez-Murano F and Gómez-Herrero J 2015 Increasing the elastic modulus of graphene by controlled defect creation *Nat. Phys.* 11 26–31
- [46] Zhang T, Li X Y and Gao H J 2014 Designing graphene structures with controlled distributions of topological defects: a case study of toughness enhancement in graphene ruga *Extreme Mech. Lett.* 1 3–8
- [47] Moura M J B and Marder M 2013 Tearing of free-standing graphene Phys. Rev. E 88 032405
- [48] Plimpton S 1995 Fast parallel algorithms for short-range molecular dynamics J. Comput. Phys. 117 1–19
- [49] Liu T H, Gajewski G, Pao C W and Chang C C 2011 Structure, energy, and structural transformations of graphene grain boundaries from atomistic simulations *Carbon* 49 2306–17
- [50] Wang B, Puzyrev Y and Pantelides S T 2011 Strain enhanced defect reactivity at grain boundaries in polycrystalline graphene *Carbon* 49 3983–8
- [51] Stuart S J, Tutein A B and Harrison J A 2000 A reactive potential for hydrocarbons with intermolecular interactions J. Chem. Phys. 112 6472–86
- [52] He L C, Guo S S, Lei J C, Sha Z D and Liu Z S 2014 The effect of Stone–Thrower–Wales defects on mechanical properties of graphene sheets—a molecular dynamics study *Carbon* 75 124–32
- [53] Gilman J J 1959 Cleavage, ductility and tenacity in crystals Fracture 193-224
- [54] Agoram B and Barocas V H 2001 Coupled macroscopic and microscopic scale modeling of fibrillar tissues and tissue equivalents J. Biomech. Eng. 123 362–9
- [55] Stylianopoulos T and Barocas V H 2007 Volume-averaging theory for the study of the mechanics of collagen networks *Comput. Methods Appl. Mech. Eng.* 196 2981–90
- [56] Howes F A and Whitaker S 1985 The spatial averaging theorem revisited Chem. Eng. Sci. 40 1387–92