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An atomistic methodology of energy release rate for graphene at nanoscale

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Graphene is a single layer of carbon atoms packed into a honeycomb architecture, serving as a fundamental building block for electric devices. Understanding the fracture mechanism of graphene under various conditions is crucial for tailoring the electrical and mechanical properties of graphene-based devices at atomic scale. Although most of the fracture mechanics concepts, such as stress intensity factors, are not applicable in molecular dynamics simulation, energy release rate still remains to be a feasible and crucial physical quantity to characterize the fracture mechanical property of materials at nanoscale. This work introduces an atomistic simulation methodology, based on the energy release rate, as a tool to unveil the fracture mechanism of graphene at nanoscale. This methodology can be easily extended to any atomistic material system. We have investigated both opening mode and mixed mode at different temperatures. Simulation results show that the critical energy release rate of graphene is independent of initial crack length at low temperature. Graphene with inclined pre-crack possesses higher fracture strength and fracture deformation but smaller critical energy release rate compared with the graphene with vertical pre-crack. Owing to its anisotropy, graphene with armchair chirality always has greater critical energy release rate than graphene with zigzag chirality. The increase of temperature leads to the reduction of fracture strength, fracture deformation, and the critical energy release rate of graphene. Also, higher temperature brings higher randomness of energy release rate of graphene under a variety of predefined crack lengths. The energy release rate is independent of the strain rate as long as the strain rate is small enough. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4869207]

I. INTRODUCTION

Graphene, a two-dimensional material system, is the building block of fullerenes, carbon nanotubes, and graphite. Since Geim and his colleagues¹ discovered a simple but novel method to isolate single atomic layers of graphene from graphite in 2004, graphene has attracted considerable interest and became the focus of extensive research due to its favorable mechanical, electronic, thermal, and optical properties.¹–⁹ Its extraordinary properties make graphene suitable for a great number of promising applications such as nanoelectromechanical systems (NEMSs),¹⁰ electronic circuitry,¹¹ and biodevice.¹² Even though atomically perfect nanoscale materials can be mechanically tested to deformations well beyond the linear regime, monolayer graphene membrane is intrinsically brittle at room temperature as catastrophic fracture is observed during the indentation.¹³ On account of the brittleness, there is a need to thoroughly understand fracture mechanics of graphene at atomic scale especially when it is used as nanostructured materials.

To give insights into the material’s behavior at the fundamental level, researchers have investigated fracture mechanics of graphene at atomic scale through molecular dynamics (MD) simulations. Jack et al.¹⁴ found specific patterns of vacancies could control fracture surface geometries of graphene under uniaxial tensile load. Zhao and Aluru¹⁵ tested the variation in fracture strength of monolayer pristine graphene with temperature by performing the uniaxial tensile test. Simulation results showed that the fracture strength of graphene decreased with the increase of temperature. Stress intensity factor and J-integral are widely used to describe the fracture mechanical behavior at continuum level. However, at atomic scale, there is no crack tip singularity. Therefore, the stress intensity factor which is closely associated with singularity is not applicable in MD simulation. Jin and Yuan¹⁶ developed an atomistic approach to evaluate the path-independent J-integral of discrete atomic system. The J-integral developed by Rice and Rosengren¹⁷ is considered as an essential parameter to evaluate fracture mechanical behavior of materials. It assumes the crack propagates self-similarly. However, crack propagation does not always follow this rule at atomic scale. Sen et al.¹⁸ found that when tearing graphene sheets from adhesive substrates, the two initially parallel crack notches propagate towards each other and finally form a non-symmetric horned edge. Brommer and Buehler¹⁹ showed that the crack propagation of graphyne deviated from the initial direction even at simplest opening mode loading. Not only that, but all other graphynes have been found similar phenomena.²⁰ These findings are in disagreement with the macroscopic continuum theory.

In fracture mechanics, Griffith introduced a fundamental physical quantity, energy release rate, to evaluate the material property in 1921.²¹ Energy release rate is defined as the energy dissipated during fracture per unit of newly created fracture surface area. This macroscopic fracture parameter is well formulated from the continuum mechanics approach.

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Different from J-integral, energy release rate does not assume crack grows self-similarly, and it is a more general and more fundamental physical quantity to characterize the fracture mechanical property of materials. Jin and Yuan\textsuperscript{22} developed two different methods, the global energy method and the local force method, to calculate the energy release rates in atomic systems. The global energy method was based on the change of total potential energy of two graphene sheets, of which the only difference is central crack length, while the local force method is based on the virtual work that is required to prohibit the crack extension. Both methods are based on a static model which is not suitable for investigating the temperature effects. In the study of flaw insensitive fracture in nanocrystalline graphene, Zhang \textit{et al.}\textsuperscript{23} first estimated the fracture surface energy of nanocrystalline graphene through the facture strength of a center-cracked strip according to the classical Griffith model. But there remains lack of the formulation of energy release rate through atomistic approach at nanoscale, which should be different from the one we are familiar with in continuum mechanics. Therefore, it is necessary and worthwhile to establish the new formulation of energy release rate when we investigate the fracture behavior at the atomic scale.

In this paper, energy release rate of a single layer graphene system with slit crack will be studied by performing MD simulations. Following Griffith’s theory, which focuses on the global energy balance during crack growth, we develop an atomistic simulation methodology to unveil the fracture mechanism of graphene at nanoscale. In our model, the energy release rate is related to the total work done externally. Since the Griffith criterion of fracture is based on the energy balance of two metastable states along the fracture path, which differs by lattice spacing in crack length at atomistic model,\textsuperscript{24} the strain rate has to be small enough to simulate a pseudo static process. Energy release rates of graphene at different small strain rates are investigated. We study both opening mode (external loading perpendicular to the slit crack) and mixed mode at nearly absolute zero temperature, room temperature (300 K), and high temperature (1000 K).

\section{II. SIMULATION MODEL AND COMPUTATIONAL}

In our MD simulations, a square-shaped single-layer graphene sheet is placed in the XY plane and the Z axis is defined normal to the graphene plane and a slit crack along the Y axis is predefined on graphene sheet (cf. Fig. 1(a)). This displacement boundary condition applies to the carbon atoms within the bounds of 0.21 nm from the two edges parallel to the X axis. The graphene sheet is set at different temperatures initially using the Nose-Hover thermostat.\textsuperscript{25} Then we perform uniaxial tension by applying a constant strain rate. The time step is set as 0.483 fs. The initial crack length is defined as distance between the edge and the last void atom (cf. Fig. 1(b)). In mixed mode cases, we examine a single-layer graphene sheet with an inclined slit crack (cf. Fig. 1(c)). The crack angle $\theta$ is defined as the angle between the crack and the X-axis. Because of the discontinuity at atomic scale and the hexagonal structure of graphene, we only consider two cases: $\theta = 60^\circ$ and $\theta = 30^\circ$. The boundary conditions and the time step in mix mode case are the same as in opening mode case.

A variety of force fields have been developed to describe the interaction of graphene system. The reactive empirical bond order (REBO) potential developed by Tersoff\textsuperscript{26} accounts for the many-body interatomic forces and well describes the bonding in a wide range of carbon nanostructures. The adaptive intermolecular reactive empirical bond order (AIREBO) potential,\textsuperscript{27} which furthermore including the long-range interaction and torsional potential, has been

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) Computational model of the armchair graphene with dimension of 11.11 nm $\times$ 10.58 nm. Slit crack locates on the edge, and the initial crack length is $a = 0.85$ nm. The external loading is applied along the X axis on atoms in green colored region; (b) illustration for definition of initial crack length; (c) computational model of the armchair graphene with an inclined crack of angle of 60$^\circ$.}
\end{figure}
performed to describe graphene fracture behavior well.\textsuperscript{28} The first-principles-based reactive force field ReaxFF\textsuperscript{29} is based on highly accurate and benchmarking density functional studies and is widely used to characterize fracture properties of graphene.\textsuperscript{18} The Tersoff potential is employed here since it is fairly enough to show the general principles of energy release rate in our methodology with high computation efficiency. We calculated the interatomic force $F_i$ acting on the $i$th atom based on the total potential energy $E$ in our previous work.\textsuperscript{30}

When stretching out the sample slowly with a constant rate, we consider that the graphene sheet reaches equilibrium state at each time step. From the Newton’s third law, the external force acting on the $i$th atom, $f_i$, is equal to the opposite of the interatomic force $F_i$, i.e., $f_i = -F_i$. To simplify the plot, we define the total external force as

$$ F = \sum_{i=1}^{N_B} f_i \cdot \vec{v}^i, $$

where $\vec{v}^i$ is the stretching velocity of the $i$th atom in the boundary region and $N_B$ is the number of atoms in that region. In our simulation, the strain rate is fixed, namely, $|\vec{v}^i| = \nu$. Besides, we define fracture strength $F_{\text{max}}$ as the maximal external loading force before the crack starts to grow; fracture deformation $U_{\text{max}}$ is the maximal displacement of atoms at boundary before the crack grows. Both of them can be found at the critical moment when the crack is about to propagate from its initial state. In order to obtain the critical energy release rate, one needs to accumulate the total external work before the crack starts to grow. Therefore, the total external work $W$ is given by

$$ W = \int \sum_{i=1}^{N_B} f_i(t) \cdot \vec{v}^i dt = \int F(t) \nu dt. $$

In this study, an interlayer separation distance of graphite, which is 0.34 nm, is defined as the effective thickness. Then the critical energy release rate is given by
where $W_{a}$ and $W_{a+\Delta a}$ are the critical values of total external work with initial crack length $a$ and $a+\Delta a$, respectively.

### III. RESULTS AND DISCUSSIONS

In our methodology, the pseudo static process requires small strain rate. We test four different strain rates on the same graphene sample; the results are depicted in Fig. 2. When the strain rate is $8.26 \times 10^{-3}$ ps$^{-1}$, the critical energy release rate $G_C$ is slightly overestimated. When it is smaller than a critical value, the strain rate barely has no effect on $G_C$. Therefore, for the purpose of illustration, we use the same strain rate $4.13 \times 10^{-3}$ ps$^{-1}$ for all the following simulations.

First, we consider opening mode case at nearly 0 K. We investigate three armchair graphene sheets with different sizes: sample A with dimension $5.82 \text{ nm} \times 5.29 \text{ nm}$, sample B with dimension $11.11 \text{ nm} \times 10.58 \text{ nm}$, and sample C with dimension $16.40 \text{ nm} \times 15.88 \text{ nm}$. The initial crack lengths range from $a = 0.58 \text{ nm}$ to $a = 2.27 \text{ nm}$, from $a = 0.85 \text{ nm}$ to $a = 4.69 \text{ nm}$, and from $a = 0.85 \text{ nm}$ to $a = 6.10 \text{ nm}$ for samples A, B, and C, respectively. The simulation results show that the crack propagates straightly along the Y axis through the graphene sheet. Even though the crack surface can be a little bit rough, the propagation direction trends to be perpendicular to the applying direction of the external force (cf. Fig. 3). The crack propagation patterns of both armchair and zigzag graphene are similar, regardless of graphene dimension or initial crack length. The total external force keeps on increasing as graphene sheet being stretched, and the curve collapses at the critical moment when the crack starts to grow, as shown in Figure 4. To hold the same deformation, a larger total external force is applied on graphene sheet with a smaller initial crack length. As depicted in Figure 4, graphene with a larger initial crack length has a tendency to break earlier than the one with a smaller initial crack length.

Follow the methodology as described in Sec. II, the critical energy release rate $G_C$ of armchair graphene can be obtained as shown in Figure 5(a). For each sample, $G_C$ barely varies with initial crack length. Besides, the sample dimension nearly has no influence on the critical energy release rate. The average values and standard deviations of sample A, sample B, and sample C are listed in Table I. Overall, $G_C$ of armchair graphene at nanoscale is $33.02 \pm 0.79 \text{ J/m}^2$, and it is independent of the sample dimension and initial crack length. From the results in Figure 5(b) and Table II, for sample B, the critical energy release rate of armchair graphene is $33.18 \text{ J/m}^2$, while that of zigzag graphene is $29.45 \text{ J/m}^2$. Therefore, when the orientation changes, the critical energy release rate varies.

**TABLE I.** Comparison of the critical energy release rate for armchair graphene sheet with different dimensions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average value ($\text{J/m}^2$)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>32.56</td>
<td>1.11</td>
</tr>
<tr>
<td>B</td>
<td>33.18</td>
<td>0.47</td>
</tr>
<tr>
<td>C</td>
<td>33.19</td>
<td>0.82</td>
</tr>
</tbody>
</table>

**FIG. 4.** Force-displacement relation for sample B under opening mode with various initial crack lengths $a$ at temperature 0 K.

**FIG. 5.** (a) Critical energy release rate vs. initial crack length for armchair graphene with different dimensions; (b) critical energy release rate vs. initial crack length for sample B at different orientations.
For mixed mode case at 0 K, all simulations are performed on graphene with dimension of 11.11 nm × 10.58 nm. The processes of crack propagation are depicted in Figure 6. No matter how large the initial angle is, the crack eventually propagates through graphene sheet perpendicular to the direction of external loading, same as in opening mode case. The opening mode case can be considered as the case that the crack angle is 90°. The simulation results tell us that when the initial crack length is the same, as the crack angle decreases, the fracture deformation and the fracture strength increase. Therefore, decreasing the angle of the initial crack can improve the ability of resisting large deformation and large external loading. The critical energy release rate still remains constant with changing initial crack length.

<table>
<thead>
<tr>
<th>Armchair direction</th>
<th>Zigzag direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value (J/m²)</td>
<td>33.18</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.47</td>
</tr>
</tbody>
</table>

TABLE II. Comparison of the critical energy release rate for graphene sheet (sample B) with different directions.

FIG. 6. Snapshots of crack propagation of armchair graphene under mixed mode at nearly 0 K. The initial crack length is a = 2.13 nm and the crack angle is 60°. (a) Initial moment; (b) before the crack begins to grow; (c) after the first chemical bond breaks near crack tip; (d) and (e) crack keeps growing; (f) at the end, the specimen breaks into two pieces.

FIG. 7. Critical energy release rate vs. initial crack length for graphene sheets with different orientations under mixed mode. (a) 60° crack angle; (b) 30° crack angle.
FIG. 8. Close-up views of crack tip of 9 different cases at 0 K. Pink color highlights the atoms and bonds which deform easily due to the voids and the horizontal external loading. (a) Opening mode case for armchair graphene type I; (b) opening mode case for armchair graphene type II; (c) opening mode case for zigzag graphene; (d) mixed mode case (30° crack) for armchair graphene type I; (e) mixed mode case (30° crack) for armchair graphene type II; (f) mixed mode case (60° crack) for armchair graphene; (g) mixed mode case (30° crack) for zigzag graphene; (h) mixed mode case (60° crack) for zigzag graphene type I; (i) mixed mode case (60° crack) for zigzag graphene type II.

FIG. 9. Snapshots of crack propagation of armchair graphene under opening mode at room temperature. The initial crack length is $a = 2.13$ nm. (a) Initial moment; (b) before the crack begins to grow; (c) after the first chemical bond breaks near crack tip; (d) and (e) crack keeps growing; (f) at the end, the specimen breaks into two pieces.
under mixed mode deformation; however, it decreases as the initial crack angle decreases, opposite to the fracture deformation and fracture strength. As stated before, $G_C$ of armchair graphene under opening mode is $33.18 \text{ J/m}^2$ (Figure 5). From Figs. 7(a) and 7(b), it can be obtained that $G_C$ of armchair graphene are $27.40 \text{ J/m}^2$ and $18.13 \text{ J/m}^2$ when crack angles are $60^\circ$ and $30^\circ$, respectively. These results indicate that under the same loading, crack grows earlier under opening mode case than mixed mode case; once the crack starts propagation, graphene under opening mode has stronger ability of resisting against crack propagation than mixed mode. Besides, with other factors being the same, armchair graphene always has larger energy release rate than zigzag graphene, which can be seen from Fig. 7.

Fig. 8 shows close-up views of the bond breaking configurations near the crack tip in opening mode and mixed mode. First of all, bond breaking always occurs at the atom close to the last void. In opening mode cases, the atom can be found along initial crack alignment, as depicted in Figs. 8(a)–8(c). In mixed mode cases, crack growth happens at the weakest bonded atom around the crack tip, on the side close to the midline of the graphene sheet, which is the left side in our simulations. On the effort of horizontal external loading, all atoms around the crack tip surface are forced to align with the horizontal direction, and bond rotation mainly serves as a cushion. Later, bond stretching bears most of the loading and finally triggers the bond breaking. Here, we can conclude that the occurrence of bond breaking depends on the interplay of bond energy, external loading, and local geometry.

Based on the opening mode case, we study on sample B before, when we increase the initial temperature to 300 K, the propagation direction is still perpendicular to the direction of the external force, as shown in Fig. 9. A similar phenomenon is observed at 1000 K. From Table III, keeping all other factors unchanged, the fracture deformation and fracture strength decrease as the temperature increases. The results demonstrate that the temperature plays an important role in determine the critical energy release rate. The higher the temperature is, the lower the energy release rate is.

Moreover, high temperature brings significant fluctuation of the value of $G_C$, as seen in Table IV and Fig. 10. It is common sense that in MD simulations the real-time temperature of the system with controlled temperature ensemble fluctuates itself around the desired temperature. Meanwhile, as the temperature increases, the mechanical rippling instability increases too. Therefore, it is reasonable that the energy release rate oscillates fiercely with high temperature.

### IV. CONCLUSION

This paper presents a new methodology to study the fracture mechanics of graphene at atomic scale. It is based on Griffith’s energy release rate, without any other assumption. Therefore, this methodology can be used for any atomic system. The findings from the simulations can be summarized as:

1. The crack path in graphene sheet does not depend on crack angle, temperature, or graphene orientation, which is mainly determined by the direction of external loading.
2. The critical energy release rate of a finite size graphene sheet is a constant for small strain rate.
3. The critical energy release rate of a finite size graphene sheet is a constant for both opening mode and mixed mode.
4. Even though decreasing crack angle can improve the ability of resisting large applied loading in comparison with the case in opening mode, the critical energy release rate of graphene in opening mode is greater than that in mixed mode.
5. Armchair graphene always has larger critical energy release rate than zigzag graphene.
6. Under the same circumstances, graphene sheet is easier to break at higher temperature; the fracture deformation, the fracture strength, and the critical energy release rate decrease as the temperature increases.

These findings lend compelling insights into the atomistic mechanism of graphene fracture and provide useful guideline for the design of graphene-based nanodevices.


