Supplementary Information for

Defect-Detriment to Graphene Strength is Concealed by Local Probe: The Topological and Geometrical Effects

Zhigong Song[1], Vasilii I. Artyukhov[2], Jian Wu[1], Boris I. Yakobson[2,*], and Zhiping Xu[1,*]

[1]Applied Mechanics Laboratory, Department of Engineering Mechanics and Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China

[2]Department of Materials Science and Nano-Engineering, Department of Chemistry, and the Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, United States

[*]Corresponding author, Email: xuzp@tsinghua.edu.cn, biy@rice.edu

This supplementary Information Material contains details of theoretical analysis for the local strength of semi-infinite and embedded GBs in graphene membrane.

Content:

1. Atomic structures of GBs in graphene

The atomic structures of graphene with aGB and zGB constructed from pileups of 5|7 pairs are illustrated in **Figure S1**, where *a* and *b* are the lattice constants in perpendicular and along the GB in the hexagonal lattice.

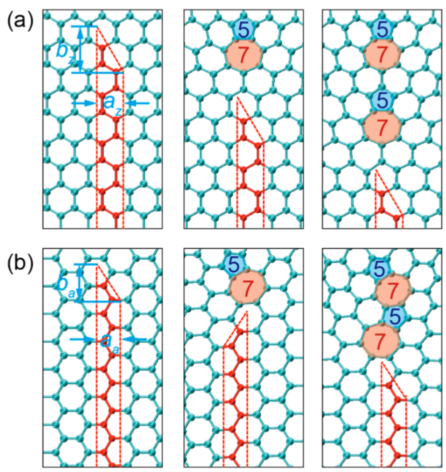

Figure S1. Illustration of the edge dislocation pileups and grain boundary (GB) structures in graphene. (a) aGB. (b) zGB. The area enclosed by red dash lines is removed to extend the GB in graphene.

2. Graphene with semi-infinite GBs

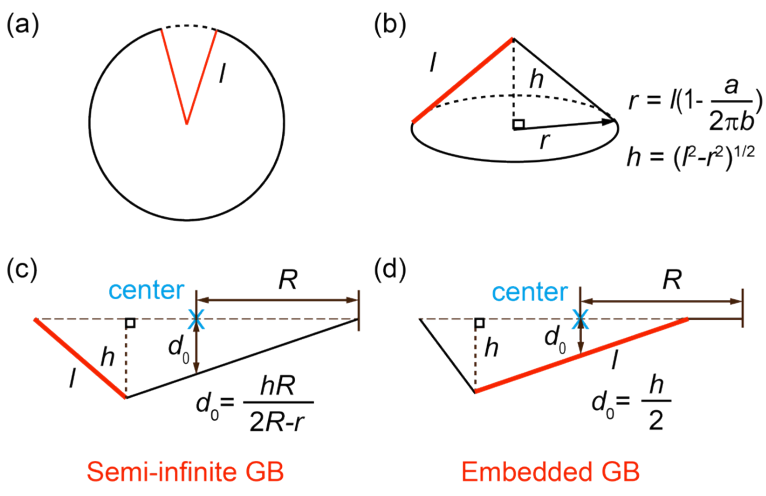

Figure S2. (a) and (b) Illustration of the cone formation by dislocation pileup in the GB for a supported circular graphene membrane. (c) and (d) Distorted geometries with the presence of semi-infinite and embedded GBs. The mechanical response is measured at the center of membrane (the cross).

In a circular graphene membrane with boundaries constrained, as illustrated in **Figure S2a** and **2b**, a semi-infinite GB corresponds to the deletion of a wedge and thus formation of a cone. For GB length $l < R$, i.e. the indentation is applied to pristine graphene lattice away from the tip of GB, the width of graphene to be removed is al/b. The geometrical distortion can be described by a cone with tip at the pentagon, base radius $r = (1 - a/2\pi b) l$, and height $h = \sqrt{(l^2 - r^2)} = \alpha l$, where $\alpha^2 = 1 - (1 - a/2\pi b)^2$. Accordingly, the initial out-of-plane displacement under indentation is

$$d_0 = h \approx hR/(2R - l) = \alpha lR/(2R - l) \tag{S1}$$

and the fracture force can be calculated from this geometrical effect as

$$f = 2\pi r_c \sigma_{2D} \sin\varphi = 2\pi r_c \sigma_{2D} (d + d_0)/\sqrt{[(d + d_0)^2 + R^2]} \approx 2\pi r_c \sigma_{2D}(d + d_0)/\sqrt{(d^2 + R^2)} \tag{S2}$$

Details:

$$f = 2\pi r_c \sigma_{2D} \sin\varphi = 2\pi r_c \sigma_{2D} \frac{d + d_0}{\sqrt{(d + d_0)^2 + R^2}}$$

$$= 2\pi r_c \left(\sigma_0 + \beta \frac{\log l}{R - l}\right) \frac{d + d_0}{\sqrt{(d + d_0)^2 + R^2}}$$

$$\approx 2\pi r_c \left(\sigma_0 + \beta \frac{\log l}{R - l}\right) \frac{d_0}{\sqrt{d^2 + R^2}} + 2\pi r_c \left(\sigma_0 + \beta \frac{\log l}{R - l}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

$$= 2\pi r_c \left(\sigma_0 + \beta \frac{\log l}{R - l}\right) \frac{1}{\sqrt{d^2 + R^2}} \times \frac{\alpha l R}{2R - l} + 2\pi r_c \left(\sigma_0 + \beta \frac{\log l}{R - l}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

$$= \left(\frac{2\alpha\pi r_c R \sigma_0}{\sqrt{d^2 + R^2}} + \frac{\alpha\beta R}{\sqrt{d^2 + R^2}} \times \frac{\log l}{R - l}\right) \times \frac{l}{2R - l} + 2\pi r_c \left(\sigma_0 + \beta \frac{\log l}{R - l}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

$$A_1 = \frac{2\alpha\pi r_c R \sigma_0}{\sqrt{d^2 + R^2}}, B_1 = \frac{\alpha\beta R}{\sqrt{d^2 + R^2}}, f_0 = 2\pi r_c \left(\sigma_0 + \beta \frac{\log l}{R - l}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

Here r_c is the contact radius between graphene and indenter, and σ_{2D} is the in-plane strength of graphene by considering local stress buildup by the dislocations, i.e.

$$\sigma_{2D} = \sigma_0 + \beta \log l/(R - l) \tag{S3}$$

where the intrinsic strength σ_0 is σ_{pristine} for $l < R$ or σ_{GB} for $l > R$. The stress buildup will decay inversely with the distance r as $1/r$. Thus by combining the stress buildup by dislocation pileup and the geometrical effect (**Eq. S1**, **Figure S2c**) we have

$$f = [A_1 + B_1 \log l/(R - l)]l/(2R - l) + f_0 \tag{S4}$$

where f_0 is the indentation fracture force for pristine graphene, A_1 and B_1 are parameters that can be tuned to fit simulation results.

For $l > R$, i.e. the mechanical response is measured on the GB, we can substitute l in the previous discussion by $2R - l$, and obtain

$$f = [A_1 + B_1 \log(2R - l)] / (l - R)](2R - l) / l + f_{\text{GB}} \tag{S5}$$

Details:

$$f = 2\pi r_c \sigma_{2D} \sin\varphi = 2\pi r_c \sigma_{2D} \frac{d + d_0}{\sqrt{(d + d_0)^2 + R^2}}$$

$$= 2\pi r_c \left(\sigma_0 + \beta \frac{\log(2R - l)}{l - R}\right) \frac{d + d_0}{\sqrt{(d + d_0)^2 + R^2}}$$

$$\approx 2\pi r_c \left(\sigma_0 + \beta \frac{\log(2R - l)}{l - R}\right) \frac{d_0}{\sqrt{d^2 + R^2}} + 2\pi r_c \left(\sigma_0 + \beta \frac{\log(2R - l)}{l - R}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

$$= 2\pi r_c \left(\sigma_0 + \beta \frac{\log(2R - l)}{l - R}\right) \frac{1}{\sqrt{d^2 + R^2}} \times \frac{\alpha l(2R - l)}{l} + 2\pi r_c \left(\sigma_0 + \beta \frac{\log(2R - l)}{l - R}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

$$= \left(\frac{2\alpha\pi r_c R\sigma_0}{\sqrt{d^2 + R^2}} + \frac{\alpha\beta R}{\sqrt{d^2 + R^2}} \times \beta \frac{\log(2R - l)}{l - R}\right) \times \frac{2R - l}{l} + 2\pi r_c \left(\sigma_0 + \beta \frac{\log(2R - l)}{l - R}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

$$A_1 = \frac{2\alpha\pi r_c R\sigma_0}{\sqrt{d^2 + R^2}}, B_1 = \frac{\alpha\beta R}{\sqrt{d^2 + R^2}}, f_{GB} = 2\pi r_c \left(\sigma_0 + \beta \frac{\log(2R - l)}{l - R}\right) \frac{d}{\sqrt{(d + d_0)^2 + R^2}}$$

where f_{GB} is the indentation fracture force for graphene with infinite GBs as discussed in the main text. **Eq. S5** is used to fit our MD simulation results in **Figure 2**.

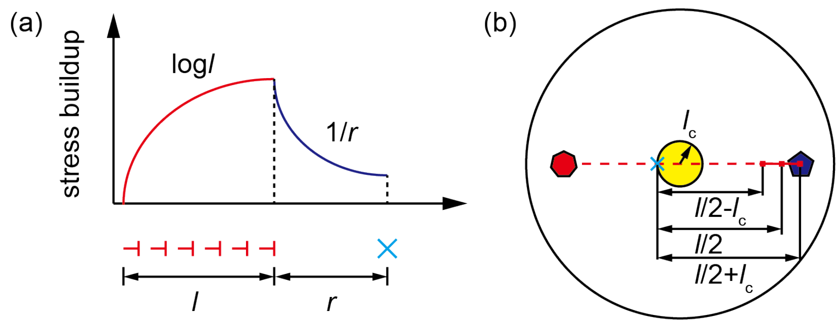

Figure S3. (a) Illustration of the stress buildup by the semi-infinite GB and its effect at the center of graphene membrane where the indentation force is applied. (b) Illustration of the stress built up at the boundary of contact between indentation tip and graphene membrane with an embedded GB, where crack nucleates. The finite contact size l_c is considered.

3. Graphene with embedded GBs

For embedded GBs, as the indentation is applied to the GBs and the contact length between the GB and indenter $2l_c \sim 1$ nm should be considered (**Figure S2d** and **S3b**). The stress buildups from two sides of the GBs outside of this contact region cancel out. The remaining asymmetric part of GB and the geometrical effect define the mechanical response at membrane center. From our MD simulation results, we find the fracture nucleate at the edge of indenter-membrane contact close to the heptagon end. The asymmetric part thus can be approximated by considered as ~three 5|7 pairs close to the heptagon end (**Figure S3b**). According to previous discussion, the stress buildup at the center of membrane is

$$\sigma = \sigma_0 + \beta[1/(l - 1) + 1/l + 1/(l + 1)] \quad \text{(S6)}$$

Assuming a conic distortion with height of $h = \alpha(2R - l)$ and the initial out-of-plane displacement at indentation center $d_0 = h/2 = \alpha(2R - l)/2$, the geometrical contribution is calculated to be

$$f = 2\pi r_c\sigma_{2D}\sin\varphi = 2\pi r_c\sigma_{2D}(d + d_0) / \sqrt{[(d + d_0)^2 + R^2]} \approx 2\pi r_c\sigma_{2D}(d + d_0) / \sqrt{(d^2 + R^2)} \quad \text{(S7)}$$

where σ_{2D} is the stress buildup following **Eq. S6**, or simply

$$f = [A_2 + 1/(l - 1) + 1/l + 1/(l + 1)](B_2 l + C_2) \quad \text{(S8)}$$

Details:

$$f = 2\pi r_c \sigma_{2D} \sin\varphi = 2\pi r_c \sigma_{2D} \frac{d+d_0}{\sqrt{(d+d_0)^2 + R^2}}$$

$$= 2\pi r_c \left(\sigma_0 - \beta \left(\frac{1}{l} + \frac{1}{l-1} + \frac{1}{l+1} \right) \right) \frac{d+d_0}{\sqrt{d^2+R^2}}$$

$$= \left(\frac{\sigma_0}{\beta} - \left(\frac{1}{l} + \frac{1}{l-1} + \frac{1}{l+1} \right) \right) \frac{2\pi r_c \beta}{\sqrt{d^2+R^2}} \left(d + \alpha \frac{2R-l}{2} \right)$$

$$= \left(\frac{\sigma_0}{\beta} - \left(\frac{1}{l} + \frac{1}{l-1} + \frac{1}{l+1} \right) \right) \times \left(-\frac{\alpha \pi r_c \beta}{\sqrt{d^2+R^2}} l + \frac{2\pi r_c \beta (d+\alpha R)}{\sqrt{d^2+R^2}} \right)$$

$$A_2 = \frac{\sigma_0}{\beta}, B_2 = -\frac{\alpha \pi r_c \beta}{\sqrt{d^2+R^2}}, C_2 = \frac{2\pi r_c \beta (d+\alpha R)}{\sqrt{d^2+R^2}}$$

with fitting parameters A_2, B_2 and C_2. **Eq. S8** is used to fit our MD simulation results in **Figure 2**.

4. Fitting parameters for Figure 2

The fitting formula and parameters for MD simulation results in **Figure 2** are summarized below.

(1) Semi-infinite aGB

$$f = \begin{cases} \left(1.055 + 2.080 \frac{\log l}{5.5 - l}\right) \frac{l}{11 - l} + 56.8695, \; l < R \\ \left[1.055 + 2.080 \frac{\log(11-l)}{l - 5.5}\right] \frac{11-l}{l} + 48.402, \; l > R \end{cases}$$

(2) Semi-infinite zGB

$$f = \begin{cases} \left(4.616 + 9.777 \frac{\log l}{5.5 - l}\right) \frac{l}{11 - l} + 58.4305, \; l < R \\ \left[4.616 + 9.777 \frac{\log(11-l)}{l - 5.5}\right] \frac{11-l}{l} + 38.3974, \; l > R \end{cases}$$

(3) Embedded aGB

$$f = \left[0.08098 - \left(\frac{1}{l} + \frac{1}{l-1} + \frac{1}{l+1} \right) \right] (21.32 - 21.12 \times l)$$

(4) Embedded zGB

$$f = \left[0.05882 - \left(\frac{1}{l} + \frac{1}{l-1} + \frac{1}{l+1}\right)\right](30.09 - 24.34 \times l)$$

5. Formation energy of finite-length GBs in graphene

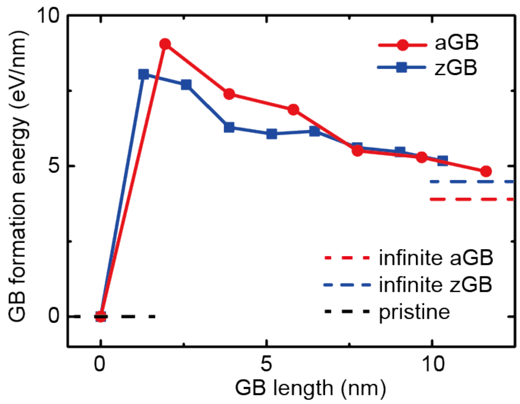

Figure S4. Formation energy of finite-length GBs that is defined as its energy difference with pristine graphene for unit length of GB. The formation energy is higher than that for pristine graphene, or graphene with infinite GBs because of the termination. For a finite sample of ~12 nm, the value converges to that for infinite GBs as the GB length increases.

6. The mechanical response of graphene with semi-infinite GBs under biaxial tensile tests

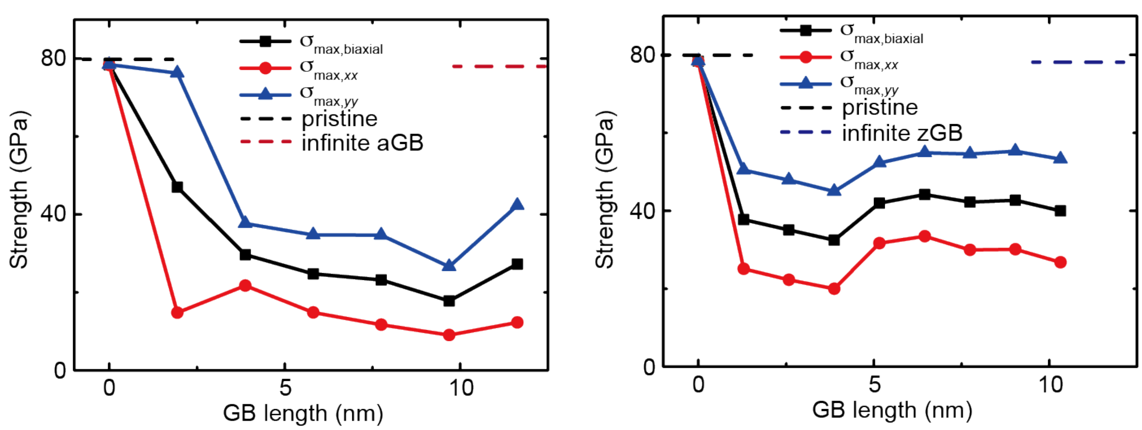

Figure S5. Strength of graphene with semi-infinite GBs under biaxial tensile tests. The results suggest that the strength is reduced compared to pristine graphene, and the reduction for graphene with armchair GBs is more significant in general because of its higher concentration of defects. The out-of-plane buckling of the lattice also modulates the length-dependence in the strength-GB length relationship as it introduces bending stresses.

7. The mechanical response of graphene with embedded GBs under uniaxial tensile tests

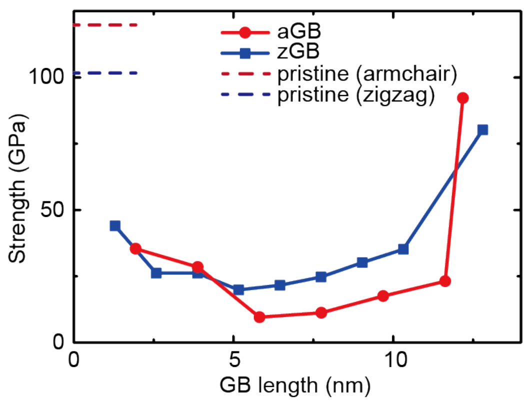

Figure S6. Strength of graphene with embedded GBs under uniaxial tensile tests. The results show that both the concentration of defects and geometrical distortion affect the strength-GB length dependence. As the length of GB approaches the sample size ~12 nm, the strength becomes that of graphene consisting of infinite GBs and is close to the pristine graphene (along armchair or zigzag directions).