Supporting Information for

Critical length scales and strain localization govern the mechanical performance of multi-layer graphene assemblies

Wenjie Xia, Luis Ruiz, Nicola M. Pugno, Sinan Keten*

Department of Civil and Environmental Engineering and Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL, 60208

*Corresponding Author: s-keten@northwestern.edu

Overview of coarse-grained (CG) graphene model

The coarse-grained (CG) model follows a 4-to-1 mapping scheme, where 4 carbon atoms are represented by 1 CG bead. The hexagonal symmetry of the atomic lattice is conserved to capture the interlayer shear response, including superlubricity effects. The CG force-field was developed based on a strain energy conservation approach, and it includes bonded contributions from bonds V_b, angles V_a, and dihedrals V_d, and nonbonded contributions from the interlayer interactions V_{nb}. There is no nonbonded interaction between CG atoms within each sheet. The force-field parameters (Table S1) are calibrated using mechanical properties obtained from density functional theory and experiments, such as elastic tensile and shear modulus, and the failure properties. The developed CG model allows us to simulate large multi-layer grapheme (MLG) systems with a ~200 fold increase in computational speed in comparison with all-atomistic simulations. The detailed derivation of the force field parameters can be found in our earlier work [1].

It should be noted that the interlayer shear modulus G determined from the bilayer shear test in our previous work is reported to be ~2 GPa, which is determined from the maximum slop in the shear force-displacement curve [1]. However, the actual shear response is not perfectly linear

due to the van der Waals interlayer interactions. In our current study, we use G ~1 GPa by linearizing the force-displacement response, which can be considered as the averaged shear modulus. Additionally, it has been well accepted that the Young's modulus of monolayer graphene sheet E_g is derived based on the definition of monolayer graphene thickness of h = 3.35 Å, which is equivalent to the 2D modulus (D) defined as $\mathrm{D} = E_g h$ [2]. We choose the former modulus definition in this study. Also note that the exact form of conventional shear-lag equation used to predict the "mortar-brick" system is slightly different from Eq. (1) due to the thickness definition of monolayer graphene. To apply the shear-lag model to MLGs, the 2D modulus (D) as $\mathrm{D} = E_g h$ is usually employed to avoid the issue of thickness definition of each graphene sheet.

Table S1. Summary of Functional Forms and Calibrated Parameters of the Coarse-grain Graphene Model Force Field.

Interaction	Functional Form	Parameters
Bond	$V_b(d) = D_0\left[1-e^{-\alpha(d-d_0)}\right]^2$ for $d < d_{cut}$	$d_0 = 2.8\ \mathring{A}$ $D_0 = 196.38\ kcal/mol$ $\alpha = 1.55\ \mathring{A}^{-1}$ $d_{cut} = 3.49\ \mathring{A}$
Angle	$V_a(\theta) = k_\theta(\theta-\theta_0)^2$	$\theta_0 = 120^o$ $k_\theta = 409.40\ kcal/mol$
Dihedral	$V_d(\varphi) = k_\varphi\left[1-\cos(2\varphi)\right]$	$k_\varphi = 4.15\ kcal/mol$
Non-bonded	$V_{nb}(r) = 4\varepsilon_g\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$ for $r < r_{cut}$	$\sigma = 3.46\ \mathring{A}$ $\varepsilon_g = 0.82\ kcal/mol$ $r_{cut} = 12\ \mathring{A}$

Characterization of single interface in a bilayer system

To understand the interlayer shear response in detail, we study a single interface (illustrated in Fig. 2(a)). This system is often considered as a basic representative volume element (RVE) in the shear-lag model based on continuum analysis [3-5]. The interlayer shear behavior of graphene

sheets is investigated by means of steered molecular dynamics (SMD) simulations [6] using the LAMMPS package [7].

In the SMD simulations, the left end of the bottom sheet is fixed, and the right end of the top one is pulled in the longitudinal direction by applying a force f generated by a stiff harmonic spring:

$$f = k_{SMD}(vt - x(t)) \tag{S1}$$

where k_{SMD} is the spring constant and v is the pulling velocity. A relatively stiff spring constant of 1000 kcal/mol Å^2 and a pulling velocity of 0.0005 Å/fs that is the same with the displacement rate of multi-layer graphene are chosen for the SMD simulations. The spring constant adopted herein has been shown in previous studies to be a reasonable choice leading to independence of the measured mechanical properties from the spring constant [1,8]. The pulling velocity also lies in the conventional strain rate regime (~10^7 to 10^9 s^{-1}) as commonly used in molecular dynamics studies [9-11]. The sheet length (or overlap length) is ~116 nm, which is well beyond the critical lengths identified from the strength and plastic stress of multi-layer graphene (L_c^s and L_c^p shown in Fig. 1(d)). The system is first relaxed through the energy minimization and dynamics run for 5000 time steps with a time step of 4 fs. After equilibration, the SMD simulation is performed at 10 K under an NVT ensemble (thermodynamic ensemble with constant number of particles, volume, and temperature). The resultant force-displacement curve can be simply described by the bilinear curves that consist of a plateau force f_p region and a linear decay region (as shown in Fig. 2(b)). The length of the linear stress decay region coincides with the critical length of L_c^p from the plastic stress measurement.

Description of the kinetic model used to characterize strain localization

To understand the failure behavior and strain localization mechanism of MLG, we employ the kinetic model on the basis of thermally activated process as observed in the atomic friction phenomenon. The representative volume element (RVE) system that we numerically simulate is equivalent to a MLG with 2 layers and 1 flake per layer ($n_l = 2$ and $n_s = 1$) with periodic boundary conditions in the longitudinal direction (x-direction). The simplification process that we follow to model the system for the kinetic model is illustrated in Fig. S1. The system is composed of two 1D energy landscapes, each representing one of the graphene-graphene interfaces. The energy landscape of each interface consists of a series of energy barriers, where the distance between two neighboring energy barriers is d_b, which is taken as the hexagonal lattice spacing of ~ 0.4 nm, and the distance from the well to the barrier is $x_b = d_b/2$. The shape of the energy landscape is constructed based on the constitutive shear responses of single interface characterized by the SMD simulations (force-displacement curve shown in Fig. 2(b) in main text). The height of the energy barriers E_b from $x = 0$ to $x = L_o - L_c^p$ is constant and can be approximated as $E_b \approx f_p \cdot x_b \approx 800$ kcal/mol. From the downturn point ($x = L_o - L_c^p$), the magnitude of the barriers decays linearly up to $x = L_o$.

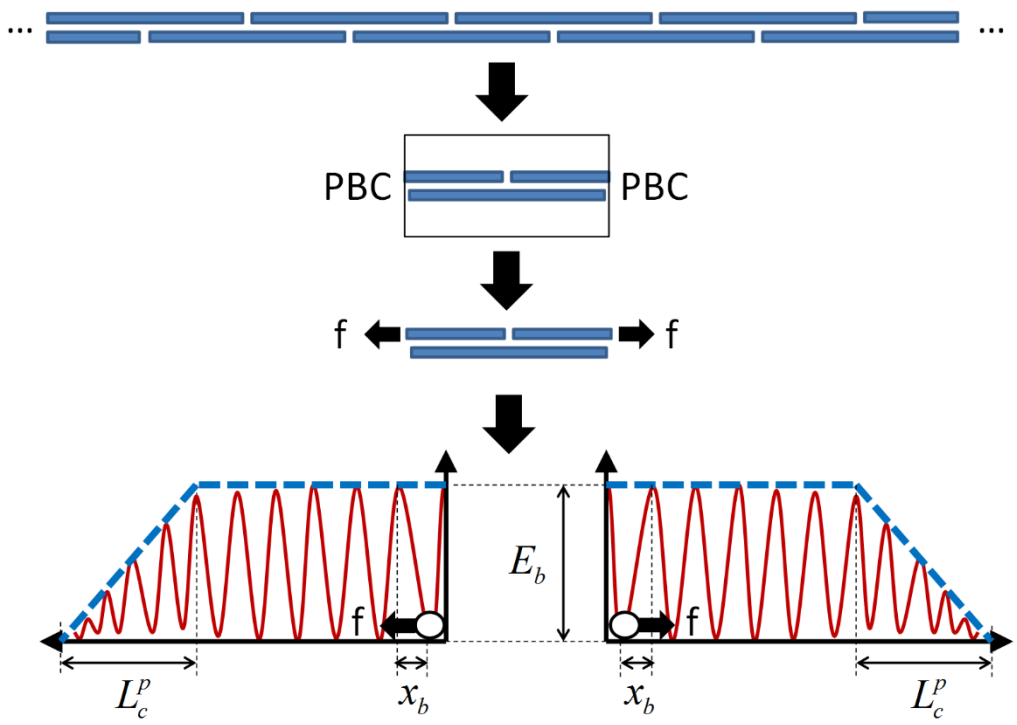

Figure S1. Illustration of the kinetic model in the representative volume element (RVE) bilayer system with two interfaces. The energy landscape of each interface is illustrated on the bottom, in which E_b is the energy barrier and x_b is half of the distance between the two neighboring barriers.

The inputs for the model are the overlap length L_o (i.e. length of each interface), the critical length L_c^p, the distance between energy barriers d_b, the thermal energy k_BT, the magnitude of the energy barriers E_b, and the vibrational frequency of the interface in the energy well ω_0. The output of each simulation is the failure strain of the system ε_f.

The numerical simulation proceeds as follows. At a given step, we apply a force f to both interfaces and calculate the probability of each one overcoming the energy barrier. According to

Bell's theory [12], the life time τ of each jump between equilibrium states under an applied force can be calculated as:

$$\tau = \exp(\frac{E_b - x_b f}{k_B T}) / \omega_0 \tag{S2}$$

The probability of the graphene sheet at each interface overcoming the energy barrier within a time interval Δt can therefore be approximated by:

$$P_{over}^{i} = 1 - \exp(-\frac{\Delta t}{\tau}) \tag{S3}$$

$$P_{over}^{i} = 1 - \exp\left[-\omega_0 \Delta t \exp(-\left(E_b^j - x_b f\right) / k_B T)\right] \tag{S4}$$

The superscript i = 1, 2 stands for each of the two interfaces. The superscript j denotes the energy barrier number in the landscape that the interface is attempting to overcome. To decide if an interface jumps over the barrier to the next equilibrium state, we compare P_{over} to a random number with a uniform probability distribution between 0 and 1, and if $rand < P_{over}$, then that interface advances to the next equilibrium energy state. If neither of the interfaces overcomes the barrier, then the force is increased by Δf and whether the interfaces advance or not is checked again. If at least one of the interfaces advances to the next equilibrium state, then the position of that interface is updated and the previous steps are iterated. The simulation stops when one of the interfaces overcomes the last energy barrier at the fully separated state. For each set of input parameters, 1000 simulations are performed. The failure strain that we report (Fig. 4(c) in the main text) is calculated as the average of the results from those 1000 numerical simulations, and the standard deviations are within the data symbol size. The calculation protocol of the kinetic model used to characterize the failure of the MLG is summarized in the flowchart in Fig. S2.

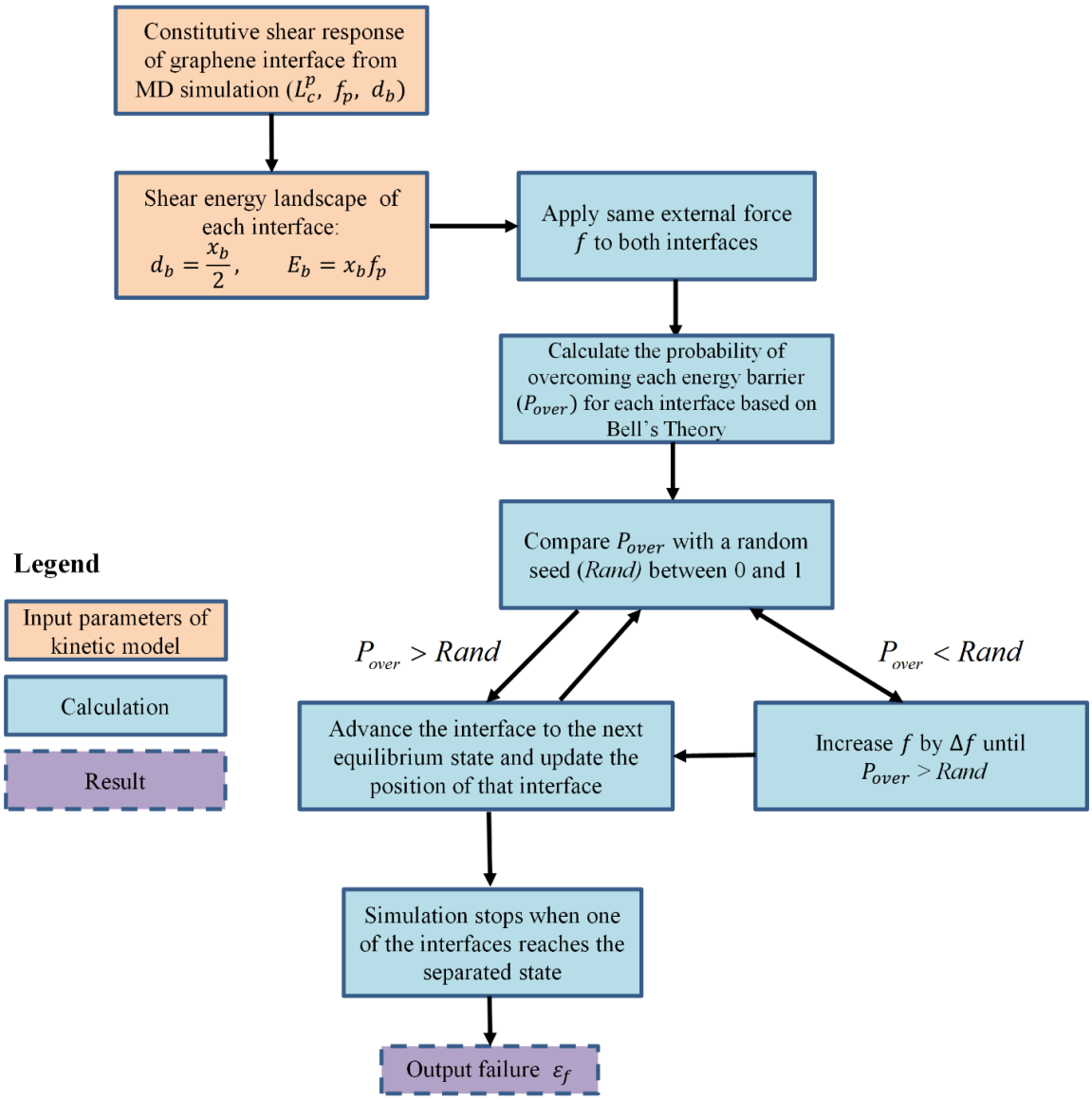

Figure S2. Flowchart that summarizes the calculation protocol of the kinetic model used to characterize the failure of the MLG.

In the model, we use $\omega_0 \sim 1\times10^{13}$ 1/s that is the typical natural frequency of oscillation of atoms in solids [12-14]. The time interval Δt to calculate P_{over} can be approximated as: $\Delta t \sim \frac{d_b}{v} \sim 1\times10^{-11}$ s. All the parameters used in the kinetic model prediction as reported in the main manuscript are summarized in Table S2. To make sure that the kinetic model makes

physical sense, we also perform sensitivity analysis of the failure strain as a function of parameters E_b and $\omega_0 \Delta t$ in the kinetic model. The result of the sensitivity analysis as shown in Fig. S3 indicates that the predicted failure stain from the kinetic model is nearly independent of these system parameters within the reasonable range. Note that changing d_b~0.4 nm to ~0.2 nm based on the atomistic graphene lattice spacing will not change the kinetic model predictions.

Table S2. Summary of the Parameters of the Kinetic Model used in the Main Manuscript.

Variable/symbol	**Parameters**
$\boldsymbol{E_b}$	800 kcal/mol
$\boldsymbol{d_b}$	0.4 nm
$\boldsymbol{\omega_0}$	1×10^{13} s^{-1}
$\boldsymbol{\Delta t}$	1×10^{-11} s
$\boldsymbol{k_B T}$	0.593 kcal/mol
$\boldsymbol{L_c^p}$	50 nm

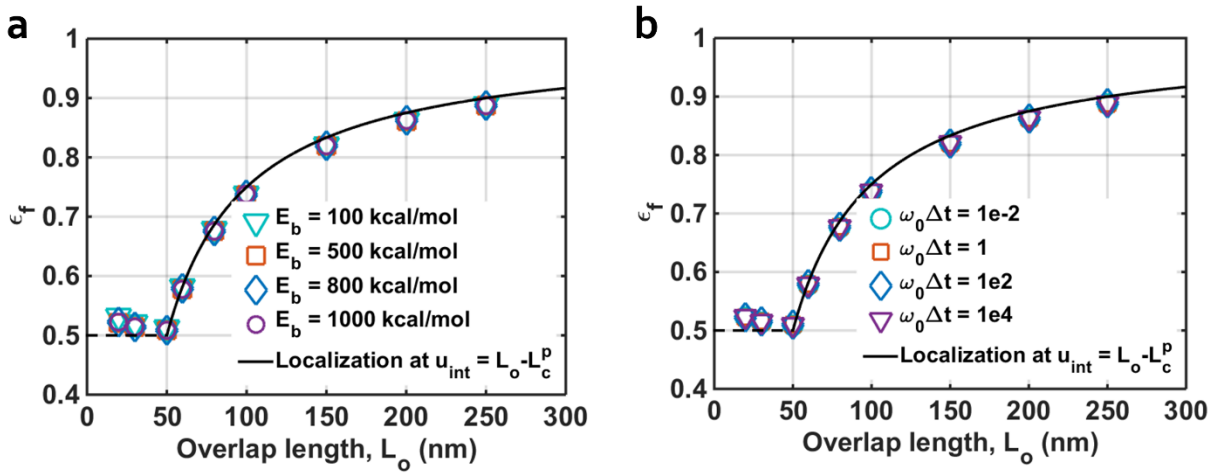

Figure S3. Sensitivity analysis for failure stain ε_f prediction as a function of the parameters **(a)** E_b and **(b)** $\omega_0\Delta t$ used in the kinetic model. The result indicates that predicted failure stain from the kinetic model is nearly independent of these system parameters within the reasonable range.

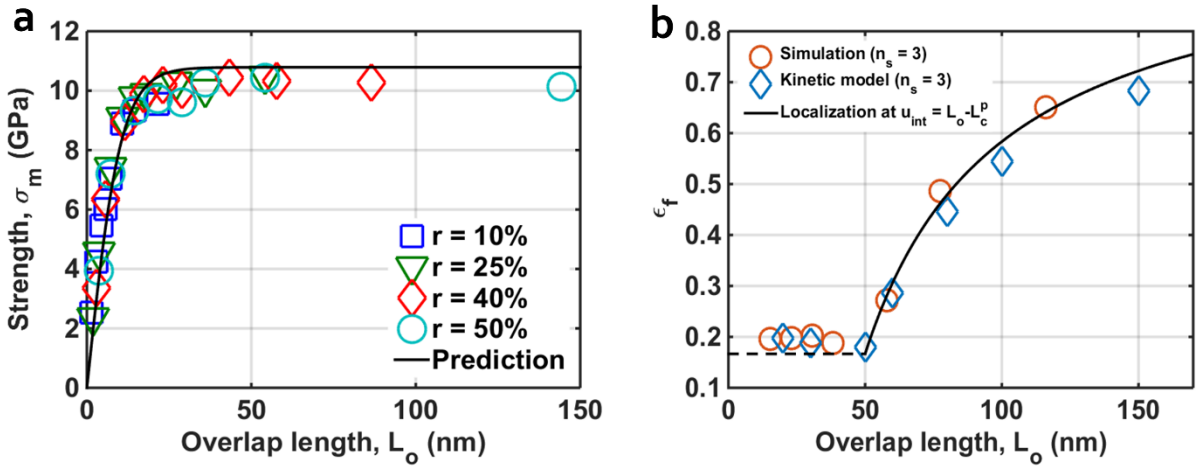

Figure S4. (a) The tensile strength σ_m with different overlap ratio r and **(b)** failure stain ε_f as a function of overlap length for the MLG with 3 sheets per layer ($n_s = 3$)**.**

The analysis of kinetic model indicates that the strain localization always initiates at the displacement around $u_{int} = L_o - L_c^p$, when $L_o > L_c^p$, leading to the failure strain $\varepsilon_f = 1 - \frac{L_c^p}{2L_o}$. We perform additional simulations and kinetic analysis for the case with three sheets per layer ($n_s =$

3) to verify our results. The tensile strength σ_m for the MLG with $n_s = 3$ and different overlap ratio r shows indistinguishable difference from the case $n_s = 1$ (Fig. S4(a)). The prediction of ε_f from the kinetic model agrees well with our CG-MD simulations as shown in Fig. S4(b).

Knowing the failure strain, the toughness T of the bilayer system with two interfaces ($n_s = 1$) can be directly approximated by integrating the stress-strain curve:

$$T = \int_0^{\varepsilon_f} \sigma d\varepsilon = \sigma_p\left(\frac{2L_o - 2L_c^p}{2L_o}\right) + \frac{1}{2}\frac{\sigma_p L_c^p}{2L_o} = \sigma_p\left(1 - \frac{L_c^p}{L_o}\right) + \frac{\sigma_p L_c^p}{4L_o} \quad \text{(S5)}$$

The above equation can be generalized for n_s number of flakes per layer, leading to Eq. (S6) (corresponding to the Eq. (5) in the main manuscript):

$$T = \sigma_p\left(\frac{2n_s L_o - 2n_s L_c^p}{2n_s L_o}\right) + \frac{1}{2}\frac{\sigma_p L_c^p}{2n_s L_o} = \sigma_p\left(1 - \frac{L_c^p}{L_o}\right) + \frac{\sigma_p L_c^p}{4n_s L_o} \quad \text{(S6)}$$

REFERENCES

[1] L. Ruiz, W. J. Xia, Z. X. Meng, and S. Keten, Carbon **82**, 103 (2015).
[2] C. Lee, X. D. Wei, J. W. Kysar, and J. Hone, Science **321**, 385 (2008).
[3] H. L. Cox, Brit J Appl Phys **3**, 72 (1952).
[4] Y. Liu, B. Xie, Z. Zhang, Q. Zheng, and Z. Xu, J. Mech. Phys. Solids **60**, 591 (2012).
[5] B. Chen, P. D. Wu, and H. Gao, Compos. Sci. Technol. **69**, 1160 (2009).
[6] S. Park and K. Schulten, J. Chem. Phys. **120**, 5946 (2004).
[7] S. Plimpton, J. Comput. Phys. **117**, 1 (1995).
[8] S. Park, F. Khalili-Araghi, E. Tajkhorshid, and K. Schulten, J. Chem. Phys. **119**, 3559 (2003).
[9] T. Zhang, X. Y. Li, S. Kadkhodaei, and H. J. Gao, Nano Lett. **12**, 4605 (2012).
[10] W. Xia and S. Keten, J. Mater. Res. **30**, 36 (2015).
[11] G. Jung, Z. Qin, and M. J. Buehler, Extreme Mech. Lett. **2**, 52 (2015).
[12] G. Bell, Science **200**, 618 (1978).
[13] S. Keten and M. J. Buehler, Nano Lett. **8**, 743 (2008).
[14] S. Keten and M. J. Buehler, Phys. Rev. E **78,** 061913 (2008).