Supporting Information for

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

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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 graphene (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 $G \sim 1$ 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 $D = E_g h$ [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 $D = E_g h$ 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.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Functional Form</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond</td>
<td>$V_b(d) = D_0 \left[1 - e^{-\alpha(d - d_0)}\right]^2$</td>
<td>$d_0 = 2.8 \text{ Å}$, $D_0 = 196.38 \text{ kcal/mol}$, $\alpha = 1.55 \text{ Å}^{-1}$, $d_{cut} = 3.49 \text{ Å}$</td>
</tr>
<tr>
<td>Angle</td>
<td>$V_a(\theta) = k_\theta (\theta - \theta_0)^2$</td>
<td>$\theta_0 = 120^\circ$, $k_\theta = 409.40 \text{ kcal/mol}$</td>
</tr>
<tr>
<td>Dihedral</td>
<td>$V_d(\phi) = k_\phi \left[1 - \cos(2\phi)\right]$</td>
<td>$k_\phi = 4.15 \text{ kcal/mol}$</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>$V_{nb}(r) = 4\varepsilon_g \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$</td>
<td>$\sigma = 3.46 \text{ Å}$, $\varepsilon_g = 0.82 \text{ kcal/mol}$, $r_{cut} = 12 \text{ Å}$</td>
</tr>
</tbody>
</table>

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:

$$ f = k_{SMD} (vt - x(t)) $$  \hspace{1cm} (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 ($\sim 10^7$ 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 $L^p_c$ 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 $L^p_c$ 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 \((n_l = 2 \text{ and } n_s = 1)\) 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 \(\sim 0.4\) 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 $k_B T$, the magnitude of the energy barriers $E_b$, and the vibrational frequency of the interface in the energy well $\omega_0$. The output of each simulation is the failure strain of the system $\varepsilon_f$.

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 \( \tau \) of each jump between equilibrium states under an applied force can be calculated as:

\[
\tau = \exp\left(\frac{E_b - x_b f}{k_b T}\right) / \omega_b
\]

(S2)

The probability of the graphene sheet at each interface overcoming the energy barrier within a time interval \( \Delta t \) can therefore be approximated by:

\[
P^i_{\text{over}} = 1 - \exp\left(-\frac{\Delta t}{\tau}\right)
\]

(S3)

\[
P^j_{\text{over}} = 1 - \exp\left[-\omega_b \Delta t \exp\left(-\left(\frac{E^j_b - x_b f}{k_b T}\right)\right)\right]
\]

(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 \( P_{\text{over}} \) to a random number with a uniform probability distribution between 0 and 1, and if \( \text{rand} < P_{\text{over}} \), then that interface advances to the next equilibrium energy state. If neither of the interfaces overcomes the barrier, then the force is increased by \( \Delta f \) 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 $\omega_0 \sim 1 \times 10^{13}$ 1/s that is the typical natural frequency of oscillation of atoms in solids [12-14]. The time interval $\Delta t$ to calculate $P_{over}$ can be approximated as: $\Delta t \sim \frac{d_b}{v} \sim 1 \times 10^{-11}$ 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.

<table>
<thead>
<tr>
<th>Variable/symbol</th>
<th>Parameters</th>
</tr>
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<tbody>
<tr>
<td>$E_b$</td>
<td>800 kcal/mol</td>
</tr>
<tr>
<td>$d_b$</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>$1 \times 10^{13}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>$1 \times 10^{-11}$ s</td>
</tr>
<tr>
<td>$k_B T$</td>
<td>0.593 kcal/mol</td>
</tr>
<tr>
<td>$L_c^p$</td>
<td>50 nm</td>
</tr>
</tbody>
</table>
Figure S3. Sensitivity analysis for failure stain $\varepsilon_f$ 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 $\sigma_m$ with different overlap ratio $r$ and (b) failure stain $\varepsilon_f$ 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 $u_{\text{int}} = L_o - L^P_c$, when $L_o > L^P_c$, leading to the failure strain $\varepsilon_f = 1 - \frac{L^P_c}{2L_o}$. 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 $\sigma_m$ 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 $\varepsilon_f$ 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:

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

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):

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

REFERENCES