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Recoverable Slippage Mechanism in Multilayer Graphene Leads to Repeatable Energy Dissipation

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ABSTRACT: Understanding the deformation mechanisms in multilayer graphene (MLG), an attractive material used in nanodevices as well as in the reinforcement of nanocomposites, is critical yet challenging due to difficulties in experimental characterization and the spatiotemporal limitations of atomistic modeling. In this study, we combine nanomechanical experiments with coarse-grained molecular dynamics (CG-MD) simulations to elucidate the mechanisms of deformation and failure of MLG sheets. Elastic properties of graphene sheets with one to three layers are measured using film deflection tests. A nonlinear behavior



in the force vs deflection curves for MLGs is observed in both experiments and simulations: during loading/unloading cycles, MLGs dissipate energy through a "recoverable slippage" mechanism. The CG-MD simulations further reveal an atomic level interlayer slippage process and suggest that the dissipated energy scales with film perimeter. Moreover, our study demonstrates that the finite shear strength between individual layers could explain the experimentally measured size-dependent strength with thickness scaling in MLG sheets.

KEYWORDS: graphene, slippage, stacking nonlinearity, energy dissipation, strength

he exceptional elastic modulus $(1.01 \pm 0.15 \text{ TPa})$ and intrinsic strength $(130 \pm 10 \text{ GPa})$ of suspended monolayer graphene have been experimentally measured using atomic force microscopy (AFM).¹ These excellent mechanical properties have made graphene an ideal reinforcement material in lightweight and high-performance composites design.^{2,3} Dispersion of graphene flakes in matrix materials has been found to effectively improve the stiffness and strength of nanocomposites.^{4,5} Likewise, it has been demonstrated that graphene oxide/polymer layered composites can achieve superior strength and damage tolerance.⁶ Nevertheless, current graphene-based composites usually achieve strengths of several hundred MPa,^{7,8} far lower than that of their single-atom-thick building blocks.

To overcome the discrepancy between the theoretically predicted and experimentally obtained strength values for graphene-based composites, a fundamental understanding of the mechanical properties of multilayer graphene (MLG) platelets (*i.e.*, the reinforcement phase) and the associated deformation mechanisms as the material scales in the thickness direction becomes crucial. By performing film deflection experiments on MLG sheets using AFM, Lee *et al.* found that graphene strength reduces as the number of layers increases from one to three.⁹ The hypothesis for the degradation of the material strength is that interactions between layers influence load distribution in the material, and thus, lead to the material weakening. Recent studies also pointed out that differences in the stacking order and relative twist between layers may result in different electronic and mechanical properties.^{10,11} However, due to the large size of these experimentally tested graphene

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Figure 1. Experimental results for the elastic properties of monolayer, bilayer, and trilayer graphene sheets. (a) Illustration of the AFM experimental setup. (b) Raman spectra of mono-, bi-, and trilayer graphene sheets. (c) Experimental loading/unloading curves for three systems and the linear-elastic model fitting. (d) Histograms of the elastic moduli for three systems.

sheets (approximately 1 μ m in diameter), directly reproducing experimental observations and explaining key mechanisms through atomistic simulations have remained major challenges. For instance, while full atomistic molecular dynamics (MD) simulations capture the in-plane elastic properties accurately for single layer graphene, modeling monolayer and MLG sheets greater than 30 nm in radius remain unrealistic due to prohibitive computational costs.¹²⁻¹⁴ While all-atom simulations and first-principles calculations do provide quantitative agreements in the elastic responses of the material, the size dependence of the large-deformation mechanisms calls for multiscale approaches that address the spatiotemporal shortcomings of high-fidelity atomistic calculations. Another obstacle in the way of computational investigations of two-dimensional nanomaterials is the necessity to capture anisotropy and key atomic features in order to accurately reproduce mechanical properties. Some of these features are not straightforward to capture with traditional continuum models.^{15–19} Specifically, accounting for the superlubricity and anisotropy in interlayer interactions between graphene basal planes remains a challenge in continuum model development due to the lack of atomic lattice structure.^{20–22}

To overcome these issues, we recently developed an atomistically informed coarse-grained molecular dynamics (CG-MD) framework that can reproduce the elasticity, strength, failure mechanisms, and anisotropy of single and multilayered graphene.²³ The dramatic increase in computational efficiency with this model allows us to conduct nanoindentation simulations at scales comparable to experiments. Built upon this capability, here we present a coupled experimental-computational study that focuses on quantifying

and interpreting the mechanical properties of MLG sheets using nanoindentation.

RESULTS AND DISCUSSION

By correlating CG-MD simulations with AFM film deflection experiments, we first evaluate the elastic properties of MLG and advance the understanding of the deformation mechanisms in MLG beyond material elasticity. Additionally, we carry out cyclic deformation tests to reveal a hysteretic energy dissipation mechanism that manifests as recoverable slippage. To our best knowledge, this is the first observation of such a deformation mechanism in these multilayered systems. Finally, we examine how interlayer interactions lead to load distribution inside MLG and, consequently, cause strength to become sizedependent as the material scales up in the thickness dimension.

In-Plane Linear and Nonlinear Elasticity. We begin by summarizing experimentally observed linear elastic properties in single- and multilayered graphene samples. In Figure 1a, the film deflection experimental configuration used in this study is shown. Raman spectroscopy (with a laser excitation of 532 nm) is used to confirm the number of graphene layers. As the graphene number of layers increases, the ratio of the integrated intensities of G and 2D peaks increases, serving as a powerful tool to verify the graphene sheet thickness. As shown in Figure 1b, the ratios of G/2D peak intensities for mono-, bi-, and trilayer graphene sheets are 0.31, 0.45, and 0.58, agreeing favorably with previous reports.^{24,25} A diamond probe, with a semispherical tip, is used to load freestanding circular films at the center using an AFM (XE-100, Park Systems). Typical force vs deflection curves for monolayer, bilayer, and trilayer graphene at small deflections (less than 30% of the deflection required to rupture the specimen) are shown in Figure 1b. No

appreciable hysteresis is observed between the loading and unloading curves, suggesting that all specimens deform purely elastically, with no slip between the deformed sheets. Because of the large ratio of film radius to tip radius in the experiments, the system is approximated as a clamped circular film, made of a linear isotropic elastic material, subjected to a central point loading. Thus, the force vs deflection behavior can be approximated as

$$F = \sigma_0 \pi t \delta + \frac{Et}{q^3 a^2} \delta^3 \tag{1}$$

where F is the applied force, δ is the central deflection or indentation depth, a is the film radius, q = 1.02 is a dimensionless constant, $t = nh_{eq}$ is the thickness of the graphene sheet, and $h_{eq} = 0.335$ nm is the equivalent graphene monolayer thickness (n = 1, 2, 3 is the number of layers).^{1,26} The prestress σ_0 and elastic modulus *E* of the material are obtained by fitting the experimental results at small deflections to the linear elastic response described by eq 1. The histograms of the elastic moduli for three systems are shown in Figure 1c. The measured monolayer graphene elastic modulus is 1.06 \pm 0.08 TPa, and the elastic moduli of bilayer and trilayer graphene sheets are 1.04 ± 0.04 and 0.98 ± 0.06 TPa, respectively. Within experimental error, the elastic moduli for graphene flakes up to three layers are identical and equal to the value for bulk graphite and clearly do not exhibit sizedependence.²

To compare these experimental measurements with predictions from CG-MD simulations, we carried out film deflection simulations on graphene sheets up to 5 layers. Multilayer graphene sheets have an in-plane area of 100×100 nm². The square sheets are suspended over a circular hole at the center, with a diameter of 50 nm. The fact that the sheet size is much larger than the suspended region makes it possible to mimic the boundary conditions in the experiments. Specifically, the area outside the suspended region of the bottom layer is fixed, and the other layers are laid on the bottom layer and held in place only by nonbonded interactions (see Methods section for additional details). In MLG, two stacking configurations were considered: commensurate stacking and noncommensurate stacking. The commensurate stacking configuration chosen in this study is similar to the socalled Bernal stacking,²⁸ corresponding to the minimum energy configuration of the sheets with no rotational stacking fault. The noncommensurate stacking configuration chosen herein is obtained by having a 90° offset angle between each pair of the adjacent layers. This noncommensurate stacking configuration, being a higher energy state and having a lower interlayer shear stiffness, is stable for the sizes of the sheets studied here, as spontaneous rotation is not a kinetically accessible pathway for large sheet overlaps.

The indentation simulation results of MLG for the commensurate stacking configuration are shown in Figure 2a, with the force normalized by the number of layers (*i.e.*, F/n). We note that while there is a finite amount of pretension in experiments, in simulations the sheets are fully relaxed and have no initial tension. Simulations reveal that the normalized force vs deflection curves are superposed with each other at small deflections. This observation indicates that the elastic modulus is nearly invariant to the number of layers, which is in good agreement with experiments. The elastic moduli extracted again by fitting eq 1 are found to be approximately 1.02 \pm 0.06 TPa for single- to five-layered graphene. Simulations were also



Figure 2. Simulation results for commensurate stacked multilayer systems. (a) Indentation force vs deflection curves for systems with different number of layers *n*. To facilitate the comparison between the different cases, the forces are normalized by *n* and all the curves are plotted up to the same indentation depth (\sim 60% of maximum indentation depth). (b) Bond energy distribution in a circular region with a radius of 10 nm in each layer of commensurate stacked trilayer system at an indentation depth of 5 nm. The average values of bond energy (in units of kcal/mol) within the circular region are labeled in each panel.

performed on MLG with the noncommensurate stacking configuration, and the results indicate that the elastic modulus is insensitive to the stacking configuration.



Figure 3. Experimental curves for bilayer (a) and trilayer (b) graphene sheets $(1.5 \ \mu m \text{ diameter})$ demonstrate the energy dissipation from a loading/unloading cycle. Insets highlight the slippage (denoted by black arrows). Three-cycle tests on bilayer (c) and trilayer (d) graphene sheets are included to show the repeated energy dissipation (origins of curves are offset by 20 nm).



Figure 4. Simulated loading/unloading curves for (a) commensurate stacked and (b) noncommensurate stacked trilayer graphene. (c) Time evolution of the slippage events responsible for the onset of hysteresis in the commensurate stacked (left column) and commensurate stacked (right column) trilayer system. Each plot shows the in-plane (x-y plane) accumulated relative displacement between the middle layer and the bottom layer. The white dash circle indicates the hole rim and the yellow arrow indicates the position where the slippage is initiated. (d) Atomic slippage between middle layer and bottom layer for commensurate stacking (left column) and noncommensurate stacking (right column). The arrows in commensurate stacking case show the slippage direction of the lattices (the blue arrows show the slippage direction during loading and the green ones show the direction during unloading). From top to bottom, it shows the sequence of the recoverable slippage: initial state, state after slippage during loading, and final recovered state during unloading.

The CG-MD modeling also captures the nonlinear elastic response in the basal plane of monolayer graphene.^{12,27,28} As shown in Figure 2a, when film deflection is large, the monolayer graphene force vs deflection curve gradually deviates from the linear elastic model. Furthermore, the CG-MD results

show that the curve deviates from the linear elastic model at smaller deflections when the number of layers increases. This observation suggests a new contribution to the nonlinearity in the mechanical response of graphene. We attribute this to the greater inhomogeneity in the strain distribution between the layers as the number of layers increases. As shown in Figure 2b, the distribution of tensile strain is more spread out in the bottom layer, indicated by the increase in the average bond energy from the top to the bottom layer. The inhomogeneous strain distribution leads to reduced elastic properties compared to the ideal system with the same strain distribution in all the layers, and thus results in an earlier and more pronounced nonlinear elastic behavior as the number of layers increases. It should be noted that we do not observe any interlayer slippage in this small deflection regime by tracking the relative interlayer displacement during the indentation loading.

Stacking Nonlinearity and Repeatable Energy Dissipation. The MLG samples show more interesting behavior as the film deflection increases. In addition to the aforementioned in-plane nonlinear elasticity, another interesting deformation mechanism is observed in the experiments through a closed hysteresis loop during a loading/unloading cycle. To distinguish this nonlinearity with the response caused by the in-plane nonlinear elasticity, we call it a "stacking nonlinearity" in MLG.

As shown in Figure 3a and b, at deflections of approximately 80 nm, kinks in the experimental force vs deflection curves can be seen for both bilayer and trilayer graphene sheets. Beyond the kink, the material behavior deviates from the linear elastic model prediction. Moreover, the unloading segment following tip retraction deviates from the loading segment on the force-displacement curve. Instead, hysteresis is clearly shown in the loading/unloading cycle, indicative of energy dissipation. Nevertheless, the unloading segment coincides with the loading segment when the film deflection is below 50 nm, suggesting the system goes back to its original energy state. We found that this energy dissipation occurs repeatedly and regardless of the number of loading/unloading cycles, as shown in Figure 3c and d.

The CG-MD simulation results provide more insight into this energy dissipation mechanism. First, the CG model reproduces the kink as the deflection increases and the hysteresis takes place during the loading/unloading cycle. Taking trilayer graphene as an example, in Figure 4a and b, the kinks are observed in the curves for both commensurate and noncommensurate stacked systems. We also notice that the activation force for the kink for the commensurate stacked trilayer (~550 nN) is higher than that for the noncommensurate stacked trilayer (~380 nN). Interestingly, in the CG-MD simulations, the unloading segments also coincide with the loading segments as the tip retracts to its original position, indicating the systems return to their original energy states when fully unloaded.

A close inspection of the CG bead trajectories during the loading/unloading process reveals that recoverable interlayer slippage is the corresponding mechanism for this repeatable energy dissipation phenomenon, where the onset of the interlayer slippage coincides with the kinks in the force vs deflection curves. Each slippage event corresponds to part of the interface overcoming energy barriers from initial energy minima state to the adjacent energy minima state, due to the shear force induced by indentation. During unloading, the whole system will return to the initial minimum energy state. Possibility of this type of mechanically activated slippage in bilayer graphene was suggested by first-principles calculations.^{29,30} Additional first-principles calculations investigated the stacking configuration change due to the presence of electric field, spin polarization, and quantum confinement

effects.^{31–33} To our best knowledge, our study is the first report on the recoverable interlayer slippage observed in experiments and MD simulations.

The fact that the indentation force required to activate the interlayer slippage is greater in commensurate stacked multilayer system can be attributed to the stronger interlayer interactions between graphene layers compared to the noncommensurate stacked systems. As confirmed by experiments and simulations, the shear strength τ_f between two commensurate stacked graphene layers is at least 2 orders of magnitude higher than that for two noncommensurate stacked graphene layers.^{20–22} This anisotropy of interlayer interactions is also known as graphite superlubricity. The CG model used in this study could reproduce the orientation-dependent shearing response as well as interlayer adhesion energy at a quantitative level,²³ which are the keys to capture the slippage event as observed in experiments.

In Figure 4c, we characterize the slippage process in simulations by measuring the accumulated relative displacements between middle layer and bottom layer projected in the basal plane (x-y plane) for both commensurate and noncommensurate stacked trilayer graphene. As film deflection increases, slippage initiates at a location near the boundary of the circular suspended region and, subsequently, propagates along the periphery. This is logical since the interlayer shear is localized at the hole periphery given that the relative displacements between adjacent layers are maximized therein. The accumulated local shear deformation eventually overcomes the energy barrier for the adjacent layers to find their next stable state (i.e., another interlayer registry), and thus, initiates slippage. Finally, the slippage propagates along the contour of the sheet. Due to the dynamic nature of the simulation and no longer conservation of perfect n-fold symmetry for the multilayer systems, the slippage initiation position is stochastic along the boundary and the propagating area varies every run. It is also interesting to notice that the slippage distance for the noncommensurate stacked case is larger than for the commensurate stacked case due to the fact that the distance between adjacent energy minima for the noncommensurate stacked case is also larger.

Figure 4d shows more detailed information about atomic slippage between the bottom and middle layers of a small region near the boundary of the circular suspended region for both commensurate stacking and noncommensurate stacking. For the commensurate stacking case (left column of Figure 4d), the interlayer shear strength is maximized, and the slippage follows a stick—slip mechanism, with sharp jumps between different states during loading and unloading. For noncommensurate stacking (right column of Figure 4d), the periodic energy barriers in the interlayer shear landscape still exist but their magnitude is significantly smaller. As a result, the slippage is observed to be more progressive, especially during the unloading process. The kinks in the force vs deflection curves are less remarkable than those in the commensurate stacking case.

These experimental and computational observations of MLG closely resemble the slippage phenomena in metals. For MLG, an orientation-dependent critical shear stress is required to activate the interlayer slippage. Similarly, metal crystals have multiple slip systems, and the slip is activated when the shear stress along the direction of slip exceeds the threshold value (i.e., the critical resolved shear stress).³⁴ Nevertheless, there is an essential difference: the interlayer slippage in MLG is

recoverable and leads to an energy dissipation mechanism, while the slip in metals is (usually) irrecoverable and results in permanent deformation. Thus, we use the term "recoverable slippage" to define the mechanism identified for the first time in MLG herein. It is worth noting that dislocation reversibility was also reported in penta-twinned silver nanowires.^{35,36} This shows that in the absence of defect trapping, reversibility upon unloading can take place in various nanosystems.

To better understand the energy dissipation (i.e., the area of the hysteresis loop) from a loading/unloading cycle, we have carried out systematic simulations by only varying the film radii for both commensurate stacked and noncommensurate stacked bilayer graphene. We find that the dissipated energy scales linearly with film radius, as shown in Figure 5. Inspired by the



Figure 5. Dissipated energy from loading/unloading cycle for commensurate stacked and noncommensurate stacked bilayer graphene with different film radii.

observation from the CG-MD simulations that the slippage initiates and propagates along the film periphery, we thus hypothesize that the dissipated energy from a loading/ unloading cycle scales with the film perimeter of a multilayer system. Normalizing the dissipated energy in the CG-MD simulation by the film perimeter yields 0.495 and 0.131 nJ/m for commensurate and noncommensurate stacked bilayer graphene and 0.523 and 0.233 nJ/m for commensurate and noncommensurate stacked trilayer graphene, respectively. By comparison, normalization of the experimentally measured dissipated energy yields 0.348 nJ/m for bilayer and 0.344 nJ/m for trilayer graphene, lying in between the extremes of the CG-MD predictions. This scaling actually coincides with the nature of the interactions between graphene layers, due to the periodic interlayer shear stress-strain constitutive law for graphene,²³ once the slippage happens along a line where the energy barrier is overcome, much lower energy is required for the slippage to propagate. Similarly, it is proposed that for large bilayer graphene the threshold force to initiate the slippage is independent of the overlap length of the layers in the direction of the force by using the framework of the Frenkel-Kontorova model.²⁹ We also expect that the dissipated energy would scale up if the slippage could be activated in multiple interfaces as the number of layers increases, even though this is not observed in the experiments due to the limited number of attainable graphene layers. This reversible energy dissipation mechanism has great potential in future applications such as enhanced acoustic damping in nanoelectronic devices. Therefore, a comprehensive understanding of the scaling of the dissipated energy is of great significance and requires more experimental and theoretical work in future studies.

Material Failure and Strength. The aforementioned inhomogeneous strain distribution and stacking nonlinearity have a prominent effect on the effective strength due to material size-scaling in the thickness direction. The interlayer slippage, once it occurs, magnifies uneven stress distributions among individual layers. The higher stress level on the bottom layer then leads to the premature failure of multilayer systems, and thus lowers the effective material strength. We note that the maximum stress formula $\sigma = \sqrt{FE/(4\pi Rt)}$ (where F is the rupture force, R is the indenter radius, and t is the film thickness) is for a linear elastic circular film under a spherical indenter,³⁷ and cannot be applied directly in this study to derive the strength of multilayer graphene due to the material nonlinearity. However, the previous work by Lee et al. suggests that the scaling relationship $\sigma \propto \sqrt{F/(Rt)}$ between the strength and the rupture force still holds for these systems.⁹ Thus, we can use the measured strength of monolayer graphene to scale the results of multilayer graphene. That is, the effective strength (measured by nanoindentation) is defined as $\sigma_{\rm eff} = \sigma_{\rm mono} \sqrt{\frac{F_{\rm f}}{F_{\rm mono}n}}$ for *n*-layered graphene, where $\sigma_{\rm mono} = 130$ GPa is the intrinsic strength of monolayer graphene,¹ and F_{mono} and $F_{\rm f}$ are the rupture force for monolayer graphene and nlayered graphene, respectively, for a given indenter radius. Table 1 lists the Weibull analysis results for the effective

Table 1. Weibull Analysis Results for MLG Effective Strength

	monolayer	bilayer	trilayer
scale factor (GPa)	130	127	109
Weibull modulus	32.6	17.8	8.4

strength values for mono-, bi-, and trilayer systems. It is clear that the effective strength decreases because of the more uneven stress distribution with increasing numbers of graphene layers. Furthermore, the probability of slippage would increase as more layers are added. This explains the drop in the Weibull modulus in Table 1, which indicates a wider variation in the probability distribution as the number of layers increase.

The experimentally observed thickness-dependent effective strength is also seen in the CG-MD simulations, as shown in Figure 6. The effective strength of both commensurate and noncommensurate stacked systems decreases with increasing



Figure 6. Comparison between the experimentally measured (solid symbols) and theoretically predicted (open symbols) effective strengths normalized by the effective strength of monolayer (*i.e.*, $\sigma_{\rm eff}/\sigma_{\rm mono}$) as graphene scales up in the thickness dimension.

numbers of layers. However, compared to the commensuratestacked systems, the noncommensurate stacked systems have a lower interlayer shear strength which enables slippage to occur earlier than in commensurate stacked systems. This leads to a faster drop in the effective strength of noncommensurate stacked systems, which agrees well with experimental measurements.

To emphasize the effect of interlayer shear behavior on effective strength, we consider two limiting hypothetical cases. First, if perfect bonding between layers is assumed (i.e., the interlayer shear strength $\tau_{\rm f} \rightarrow \infty$), the multilayer system behaves as a single sheet and there would be no interlayer slippage (i.e., no kinks and hysteresis in force vs deflection curves). Thus, the effective strength will remain close to the value of monolayer graphene regardless of the number of layers, assuming the bending contribution is negligible. Second, the individual layers are perfectly lubricated, or equivalently, surfaces are perfectly smooth with no friction, in which the interlayer shear strength $\tau_f \rightarrow 0$. In this case, the bottom layer carries most of the load ($F_{\rm f}$ is close to $F_{\rm mono}$), and thus the normalized effective strength decreases with $n^{-1/2}$. To further prove the two hypothetical cases, we simulate two systems, one with very high interlayer interaction, and the other with extremely low interaction between the sheets. We modify the shear strength accordingly. We find that for the higher interlayer shear strength case, the effective strength is higher than those in the original commensurate stacking case and approaches the limiting value of 1. For the lower shear strength case, the effective strength approaches the $\tau_f \rightarrow 0$ theoretical result. Therefore, the effective strength extracted from indentation measurement is greatly affected by the interlayer shear strength, which should be taken into account in the strength measurements of other 2D materials.

CONCLUSIONS

In this study, we utilize nanoindentation experiments combined with a novel CG-MD simulations approach to thoroughly characterize the deformation and the effective strength of MLG. Virtually identical elastic moduli are measured for MLG from both experiments and simulation with no size-dependence in the thickness dimension. An interesting stacking nonlinearity in the force vs deflection curve is identified using film cyclic deflection experiments. The CG-MD simulations provide new physical insights into the mechanical behavior of MLG during the indentation loading and unloading processes. We observe in simulations that recoverable slippage between graphene layers is the underlying mechanism for the closed hysteresis loop in a loading/unloading cycle. This enables the material to repeatedly dissipate energy, and the dissipated energy scales with the perimeter of the film. More interestingly, the interlayer slippage is activated when an orientation-dependent critical shear stress threshold is reached, which implies that the atomic scale friction of MLG is dependent on stacking properties, consistent with other studies. Finally, this orientation-dependent shear strength will lead to a difference in nanoindentation measured strength when graphene samples are scaled in the thickness dimension. The recoverable interlayer slippage and orientation-dependent degradation of strength is believed to exist in other 2D materials that have similar layered structures.

In closing, we note that the orientation-dependent shear strength of 2D materials should be considered in future material design and experimental interpretation. In addition, the repeatable energy dissipation capability observed in this study has great potential in future applications, such as acoustic damping at the nanoscale.³⁸ The methods proposed here can be extended to understand the interfaces of heterogeneous van der Waals materials, such as boron nitride + graphene, molybdenum disulfide + graphene, and so forth.

METHODS

Experimental Setup. Film deflection experiments were conducted to measure the mechanical properties of MLG. First, a Si substrate with a 300 nm SiO₂ epilayer containing an array of circular wells (diameters of 1.5 and 1 μ m, depth 500 nm) was prepared using lithography and reactive ion etching as described in detail in a previous report.¹ Monolayer, bilayer, and trilayer graphene flakes were mechanically exfoliated from a piece of highly ordered pyrolytic graphite (HOPG, from Toshiba Ceramics), and laid onto the substrate to form drum-head like specimens. Specimen thickness was confirmed by AFM contact mode imaging and Raman spectroscopy.²⁴ Two tips were used, and the tip radii, $R_1 = 16.5$ nm and $R_2 = 27.5$ nm, were measured via transmission electron microscopy (TEM). Ten monolayer and 10 bilayer systems were tested using the smaller tip, and 13 trilayer graphene sheets were tested using the larger tip. A total of 44, 52, and 50 data sets, respectively, were obtained for analyzing elastic properties. To compare the strength for three systems, the rupture forces for trilayer sheets were converted by a factor of $\sqrt{R_1/R_2}$ to obtain equivalent values to the smaller tip.^{1,9} First, each specimen was deflected up to maximum deflections below 50 nm, followed by load reversal, with force vs deflection data recorded for elastic properties analysis. Then, experiments were carried out with the maximum film deflection gradually increased to examine the inelastic behavior. Finally, each specimen was loaded monotonically until failure. In all experiments, a constant tip displacement rate of 1.3 μ m/s was used.

Overview of the Coarse-Grained Model. In this study, we use a 4-to-1 mapping scheme coarse-grained model of graphene calibrated by experimentally reported mechanical properties, in which 4 connected carbon atoms are grouped into one CG bead.²³ The CG model conserves the hexagonal lattice symmetry of graphene, allowing it to capture the anisotropic mechanical behavior and orientation dependence of interlayer shear response. The computational efficiency is about ~200 fold compared to atomistic model. Since the original CG model slightly underestimates the failure strain $(16\%)^{23}$ compared to the experimental value of 25%,¹ here we revise the Morse bond potential to match the experimental strain value. The strength of monolayer graphene computed from the modified CG model is around 125 GPa, which is consistent with the experimental value of 130 GPa. Further details of the CG graphene model have been reported in our previous study.²³

Details of the Nanoindentation Simulations. We employ the Large-scale Atomic/Molecular Massively Parallel (LAMMPS) package³⁹ to carry out all CG molecular dynamics simulations. The initial configurations of CG graphene sheets are generated with different number of layers ranging from one to five layers and different stacking orientations. A circular indentation region is defined in the center of the square sheets. To mimic the experimental boundary condition in which the strong substrate-graphene interaction prevents slippage of the bottom layer of graphene, the beads outside of the circular region in the bottom layer are fixed by a stiff harmonic spring with spring constant 10 000 kcal/mol·Å3. The beads within the circular indentation region are set freestanding without any constraints. No extra constraints are applied to beads on any other layers, if present. Nonperiodic boundary conditions are employed. To reduce thermal noise, all the simulations are performed under the canonical (NVT) ensemble at low temperature with T = 10 K. A time step of 4 fs is adopted.

The graphene sheets are first relaxed using energy minimization with the conjugate gradient algorithm and further relaxed in the NVT ensemble at temperature T = 10 K for 200 ps. During the equilibration process, the beads of the bottom graphene layer are only allowed to

move within the x-y plane in order to create a purely flat sheet. After equilibration, the MLG sheets are indented by a spherical indenter with radius of 4 nm at the center of the sheet at a constant rate. The indenter interacts with CG graphene beads via a repulsive harmonic force, $F(r) = k_{in}(r - R)^2$, where k_{in} is a force constant set to be 1000 kcal/mol·Å³ that can be treated as a rigid indenter, r is the distance between the center of the indenter and CG bead, and R is the radius of the indenter. Through the process, the forces on the indenter and the corresponding indentation depths are gathered for analysis. To examine the nonlinearity and hysteresis of the system, a cyclic load is prescribed by displacing the indenter to a moderate depth, holding the indenter for approximately 100 ps to allow the system to fully relax, and then moving the indenter back to its origin. Indentation sensitivity tests show that below an indentation rate of 5 m/s, the simulation results are insensitive to the indentation rate. Thus, a constant indentation rate of 5 m/s is chosen for all the simulations in this study.

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Notes

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