

NANOMECHANICS

Bending with slip

Bending of few-layer graphene leads to interlayer slip, and slipping lowers the bending stiffness. Beyond a critical bending angle, the graphene layers bend like a stack of paper, with a state of superlubricity for interlayer slip.

Rui Huang

A stack of paper sheets can be bent easily unless they are all stuck together — for example, by sticky glue in between the sheets. One can imagine that a stack of atomic sheets, such as graphene (a monolayer of carbon atoms), would bend similarly — easy to bend if the atomic sheets can slide against each other but much harder to bend if the sheets are bonded together to prohibit sliding. As graphene and other two-dimensional (2D) crystal sheets continue their run as wonder materials that show ever intriguing properties (with mechanical behaviour being important for their practical applications), it has remained a puzzle about how they would bend, depending on how they would slide as they are stacked in atomically close proximity. Now in a work published in *Nature Materials*, Edmund Han and co-workers¹ offer a convincing argument, by unifying continuum and atomic models based on experiments and computations, which could essentially solve this puzzle. They find that the bending stiffness of few-layer graphene (FLG) decreases as a function of the bending angle, resulting from increasing atomic interlayer slip. Beyond a critical bending angle, the graphene layers bend like a stack of paper, with superlubricity (frictionless) between the layers.

In fact, even for monolayer graphene, the bending stiffness has been a topic of debate for years. Theoretical predictions based on atomic models often give a value of $\sim 1\text{--}1.5\text{ eV}$ (ref. ²), or in the order of 10^{-19} J , a tiny bending stiffness as expected for an atomically thin sheet. However, much larger values of bending stiffness have been reported, up to 10^4 eV (ref. ³). For a bilayer graphene, a bending stiffness of $\sim 35.5\text{ eV}$ was reported⁴ based on measurements, which lies in between of two theoretical limits, $\sim 3\text{ eV}$ and 160 eV . The theoretical limits assume that the graphene layers are either lubricated with no resistance to sliding or perfectly bonded with no sliding. The former predicts a linear scaling of the bending stiffness with respect to the number of layers, whereas the latter predicts a cubic scaling as in the classic theory of elastic

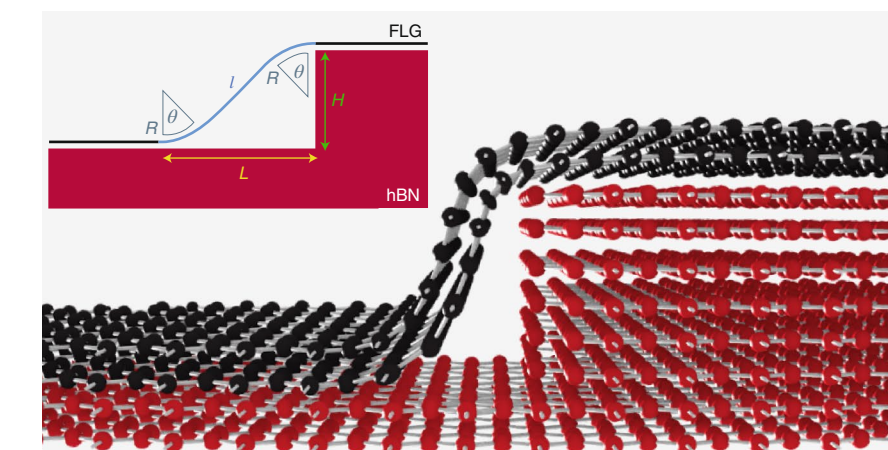


Fig. 1 | Schematic of the heterostructure, showing a graphene bilayer (black) on top of an hBN step (red), with a radius of curvature (R), and a bending angle (θ) for the two bending sections. H is the step height, l is the detached FLG length and L is detached hBN length. Figure adapted with permission from ref. ¹, Springer Nature Ltd.

plates. As the layer number increases, the gap between the two limits increases rapidly. For graphene and other 2D materials, the atomic layers are held together by relatively weak van der Waals forces between the layers, neither perfectly bonded nor ideally lubricated. It is thus expected that the bending stiffness of such layered materials should be somewhere in between of the two limits, but it is no easy task to accurately measure the bending stiffness of these atomically thin layers.

The study by Han and colleagues tackles the experimental challenge by draping graphene over atomically sharp steps of hexagonal boron nitride (hBN, another 2D material) and measuring the bending deformation of graphene (Fig. 1) by cross-sectional imaging with high-resolution aberration-corrected scanning transmission electron microscopy (STEM). Then, a simple analysis based on energy minimization yields the value of the bending stiffness from the measured radius of curvature, bending angle, step height and the adhesion energy between graphene and hBN obtained from a previous work⁵. The first important result from this measurement is the bending stiffness of monolayer graphene, 1.2 eV

and 1.7 eV , well in line with the theoretical predictions² but significantly lower than that measured by photon pressure bending and thermal fluctuations of suspended graphene cantilevers³. A possible explanation for the difference is that the bending stiffness of monolayer graphene is size dependent, predicted by considering the effect of thermal fluctuations⁶, although more measurements are needed to confirm such effect and fill in the huge gap between the nano- and microscale data.

The measured bending stiffness values for few-layer graphene (up to 12 layers) are all between the two theoretical limits but close to the lower limit with linear scaling. This result is consistent with another recent study⁷ that reported measurements of bending stiffness for multilayered graphene, hBN and MoS_2 by pressurized bubbles with 7–70 layers. More importantly, Han and colleagues revealed that the bending stiffness of FLG depends on the bending angle, defined as the angle subtending the two lines perpendicular to the straight sections joined by the bending section (Fig. 1). This may appear surprising at first but becomes clear, as explained by the authors, when considering the

discrete atomic structures of graphene. As the bending angle increases, the graphene layers become more likely to slide against each other, leading to reduced bending stiffness. In addition to the direct experimental evidence, the authors conducted computations based on first-principle density functional theory (DFT) and classical molecular dynamics (MD) simulations, to show that the thickness scaling of bending stiffness changes from cubic for a small bending angle ($\sim 1^\circ$) to linear for large bending angles (greater than $\sim 40^\circ$ for bending along the zig-zag direction of graphene). The linear scaling is an indication of superlubricity between the layers, where the bending stiffness reaches the lower theoretical limit. Therefore, with the effect of the bending angle and interlayer slip, a fundamentally consistent understanding of the bending stiffness emerges, unifying the different scaling laws based on continuum plate theory and discrete atomic

models. Additional insights on the interlayer slip are drawn from a dislocation model and a one-dimensional friction model. With further developments, the models could predict quantitatively how the interlayer slip depends on the bending angle and thus bending-induced superlubricity.

The significance of this work is not limited to monolayer and few-layer graphene. Other 2D materials, such as hBN, MoS₂ and phosphorene, share similar layered structures with van der Waals forces between the atomically thin layers⁸. As noted in another study⁷, the effect of interlayer slip on bending varies among the 2D materials with different atomic structures and interlayer interactions. Therefore, the flexibility of multilayered 2D materials depends on the interlayer slip, and the amount of interlayer slip depends on the bending angle. Such an intimate coupling between bending and interlayer slip could lead to the most flexible electronic materials

and also highly tunable flexibility in terms of the bending angle and the atomic structures including heterostructures with different 2D materials stacked together. □

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COLLOIDAL QUANTUM DOTS

Confined yet free to go

Electrons are shown to move quickly while still presenting features typical of quantum confinement in films of mercury telluride quantum dots.

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Quantum dots, which recently gained prominence in high-end televisions and displays, are nanometre-scale crystals of semiconductor materials. They derive their unique properties, such as size-tunable optical emission, from spatial confinement of the quantum-mechanical wavefunctions of electrons and holes. Quantum dots are produced by both colloidal and gas phase synthesis routes, and can be assembled into ‘quantum dot solids’. Key goals include manufacturing these at low cost and on flexible substrates, and enabling advances in opto-electronic devices such as solar cells, light-emitting devices and photodetectors. For such applications, quantum dot solids must offer good transport of charge carriers, as indicated, for example, by high mobilities; preservation of the confinement-based properties of

their building blocks would also enable a unique behaviour not achievable with other semiconductors. However, whether quantum confinement of charge carriers and high carrier mobilities can coexist in quantum dot solids is an open question. Does achieving high mobilities require abandoning confinement? This question has been debated for the past decade but has not been conclusively resolved. The study by Xinzheng Lan and colleagues reported in *Nature Materials* provides an important piece of evidence in this ongoing discussion¹.

The fundamental challenge for achieving good electrical transport in quantum dot solids is overcoming the transport barrier that exists at the interface between adjacent dots. Even a small inter-dot separation, such as that caused by the presence of surface

ligands, reduces the electronic coupling between quantum states of adjacent dots, resulting in poor carrier mobilities. Prior success in achieving transport with high carrier mobilities ($> 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) — also termed band-like when associated with decreasing mobilities at increasing temperature — involved the reduction of the inter-dot separation by exchanging the original ligands used during colloidal synthesis with very short ones, and often involved annealing that may have further or completely removed ligands^{2–4}. These studies succeeded in enhancing electronic transport but exhibited at least partial loss of optical confinement. Another strategy proposed for achieving good electronic transport across the inter-dot interface relies on a high level of doping⁵, which increases the energy of carriers at the Fermi level and enables them