THE UNIVERSITY OF TEXAS AT AUSTIN

Mechanical Interactions at the Interfaces of Atomically Thin Materials (Graphene)

Rui Huang

Center for Mechanics of Solids, Structures and Materials
Department of Aerospace Engineering and Engineering Mechanics
The University of Texas at Austin

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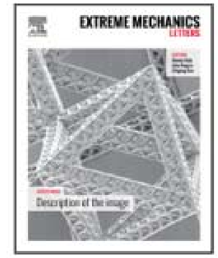


A review on mechanics and mechanical properties of 2D materials—Graphene and beyond

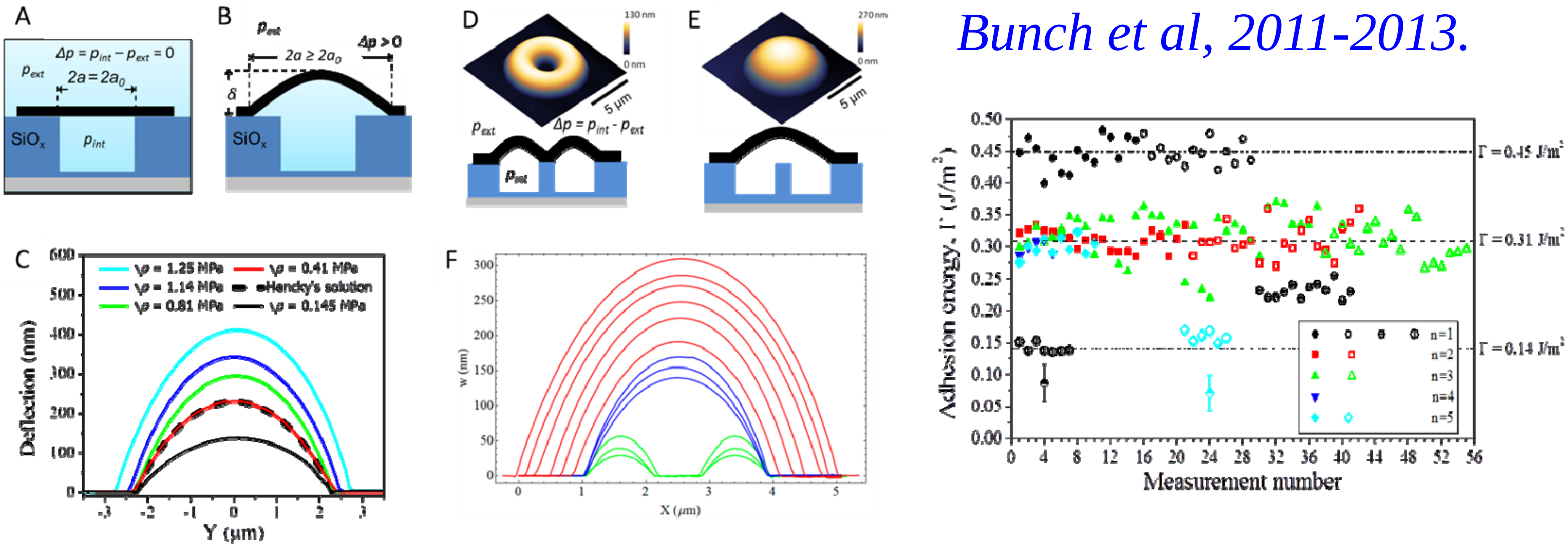
CrossMark

Deji Akinwande [a], Christopher J. Brennan [a], J. Scott Bunch [b], Philip Egberts [c], Jonathan R. Felts [d], Huajian Gao [e], Rui Huang [f,*], Joon-Seok Kim [a], Teng Li [g], Yao Li [h], Kenneth M. Liechti [f,*], Nanshu Lu [f], Harold S. Park [b], Evan J. Reed [i], Peng Wang [f], Boris I. Yakobson [j,k,l], Teng Zhang [m], Yong-Wei Zhang [n], Yao Zhou [i], Yong Zhu [o]

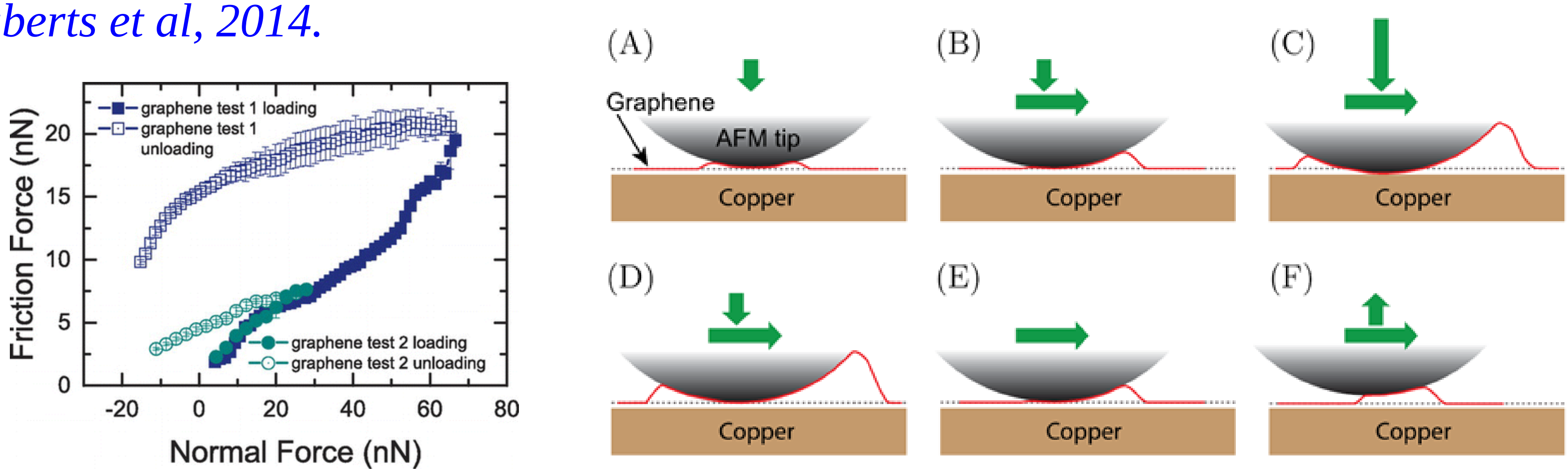
- Mechanical properties: elastic and inelastic
- Electromechanical coupling
- Interfacial properties: adhesion and friction
- Applications (synthesis, origami/kirigami, devices)

Mechanics of 2D Interfaces: Adhesion and Friction

Bunch et al, 2011-2013.

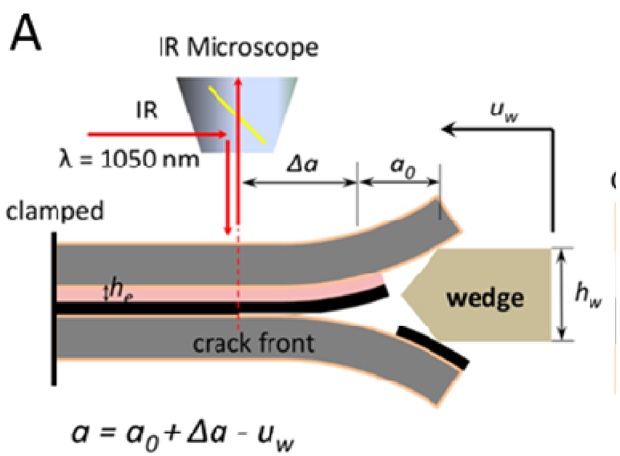


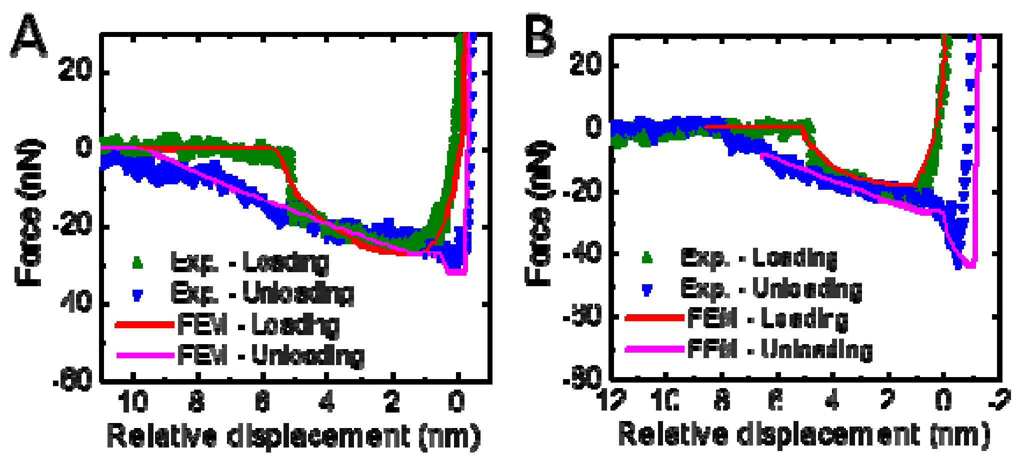
Egberts et al, 2014.



Adhesion experiments

- Micro-blister tests (Bunch et al., 2011-2013)
- Large-scale blister tests (Liechti et al., 2014-2016)
- DCB tests (Yoon et al., 2012; Na et al., 2014-2015)
- Nanoindentation experiments (Jiang and Zhu, 2015; Suk et al., 2016)

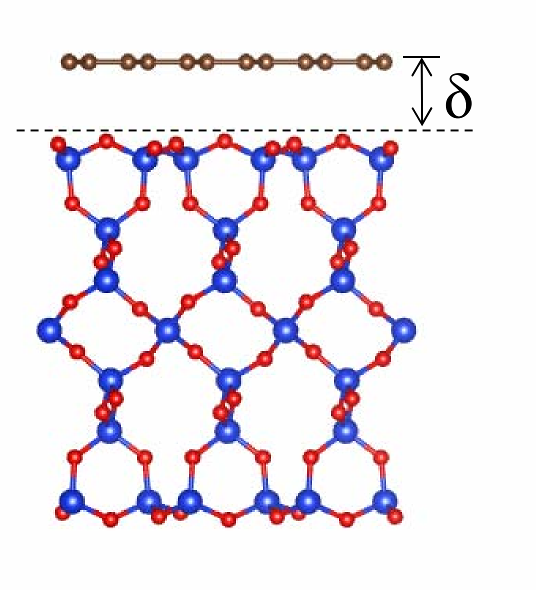


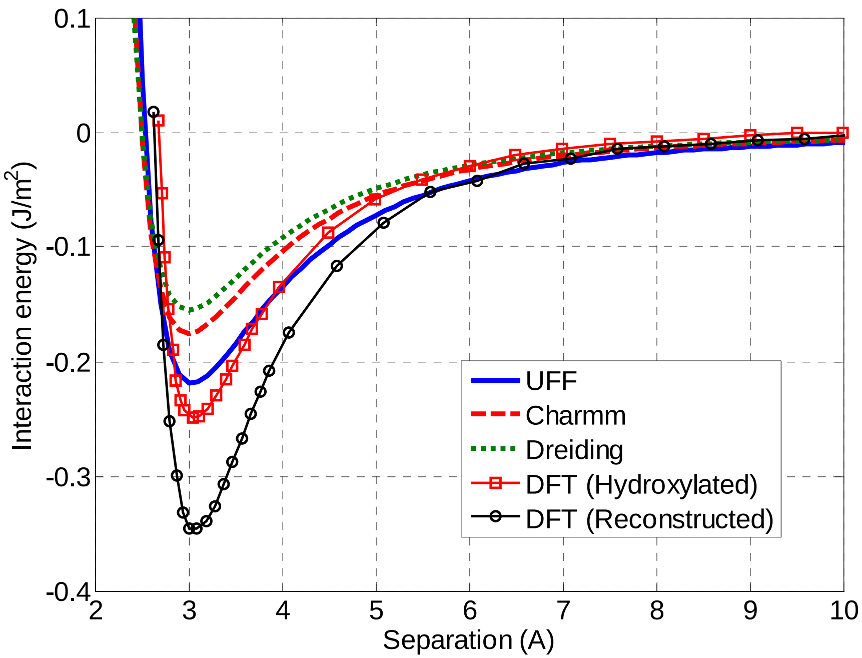


In addition to the adhesion energy, measurements of the traction-separation relations for the adhesive interactions provided more information as to the interaction mechanisms.

van der Waals Interactions

DFT (DFT-D2, vdW-TS, vdW-DF)





MD (LJ potential):

$$V_{ij}(R_{ij}) = \varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right]$$

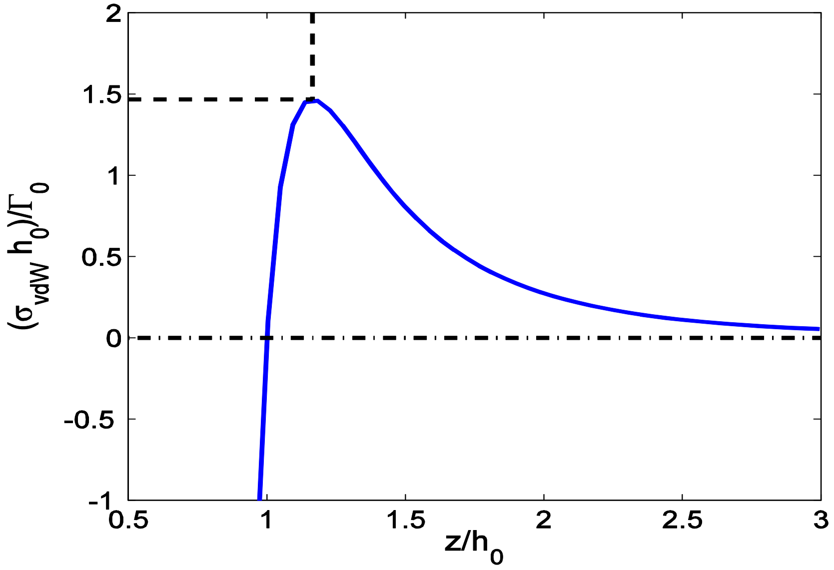
Continuum approximation:

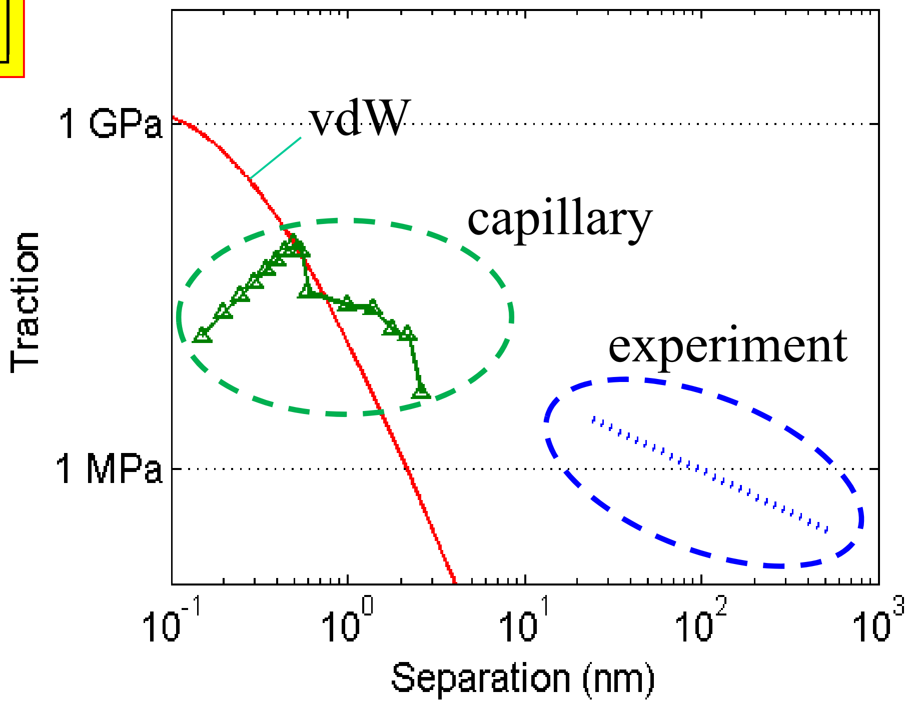
$$U_{vdW}(\delta) = -\Gamma_0\left[\frac{3}{2}\left(\frac{\delta_0}{\delta}\right)^{3} - \frac{1}{2}\left(\frac{\delta_0}{\delta}\right)^{9}\right]$$

Gao et al., J. Phys. D 47, 255301 (2014).

Traction-Separation Relations

$$\sigma_{vdW}(\delta) = \frac{dU_{vdW}}{d\delta} = \frac{9\Gamma_0}{2h_0}\left[\left(\frac{h_0}{\delta}\right)^4 - \left(\frac{h_0}{\delta}\right)^{10}\right]$$





	vdW (DFT)	Capillary (MD)	Experiments
Strength (MPa)	~1000	~90	~5
Range (nm)	~1	~3	100-600
Toughness (J/m^2)	~0.3	~0.1	~0.3

Low strength

Long range

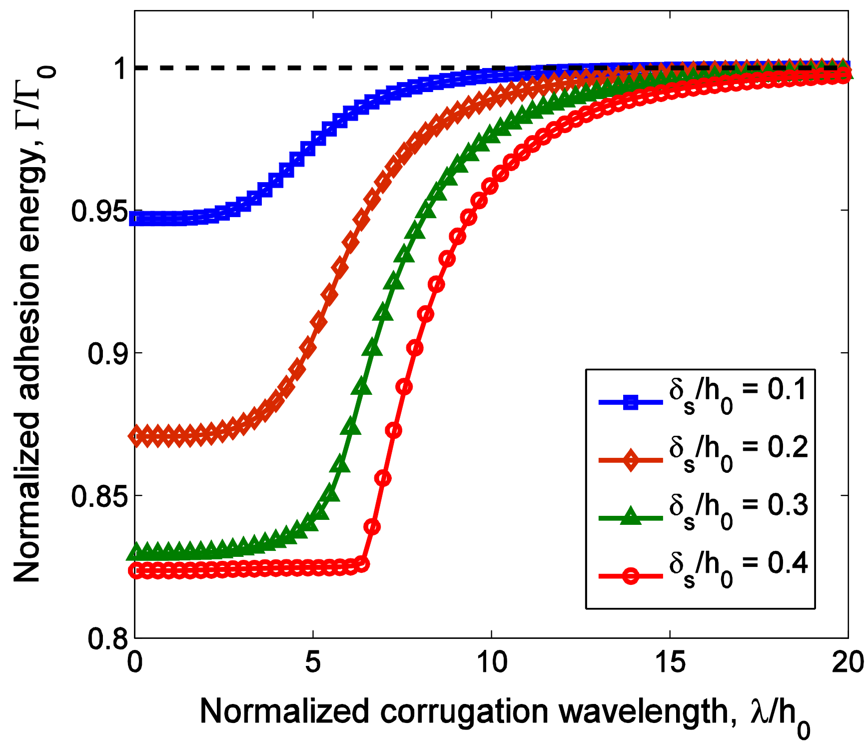
Adhesion Energy of Graphene

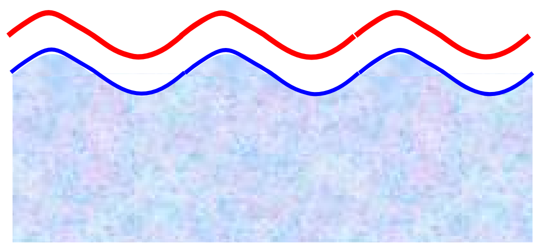
Substrate	Si/SiO_x	Cu film	Cu foil	Cu transfer
Γ (J/m^2)	0.1-0.45	0.7-1.74	~6.0	~0.34

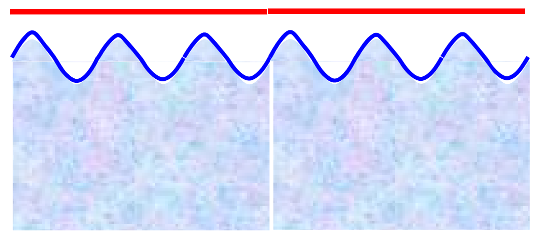
- The adhesion energy of graphene on Si/SiO_x compares closely with the predictions by DFT for van der Waals interactions.
- More complicated for copper substrates, depending on the surface roughness and Cu grain structures
- Relatively scarce data for adhesion on polymer substrates (epoxy, PDMS, PET)

- Other effects:
  - Effect of surface roughness (across many length scales)
  - Effect of temperature (thermal rippling)
  - Effect of moisture (wet adhesion)
  - Effect of mode mix (normal and shear interactions)

Effect of Surface Roughness on Adhesion



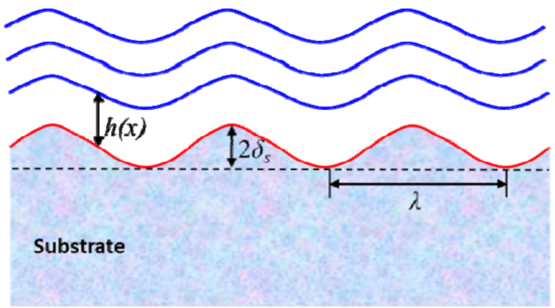




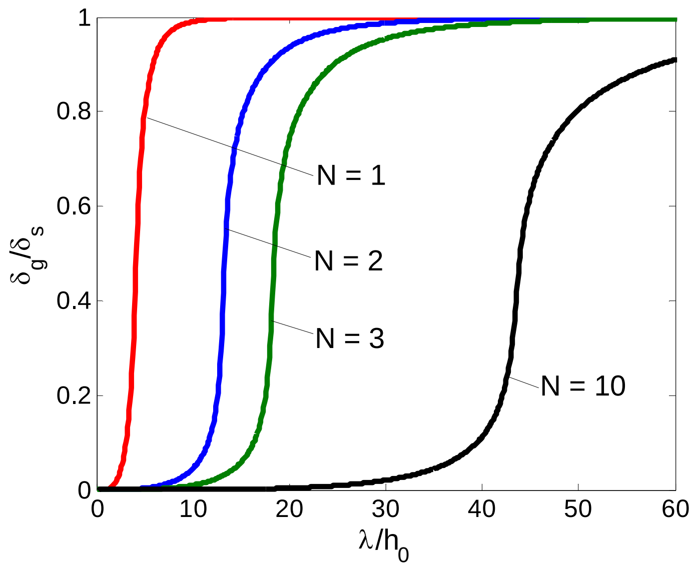
- **Long-wave limit**: conformal graphene, with the adhesion energy same as the flat surface
- **Short-wave limit**: suspended graphene, with effectively lower adhesion energy, depending on the amplitude of surface waviness

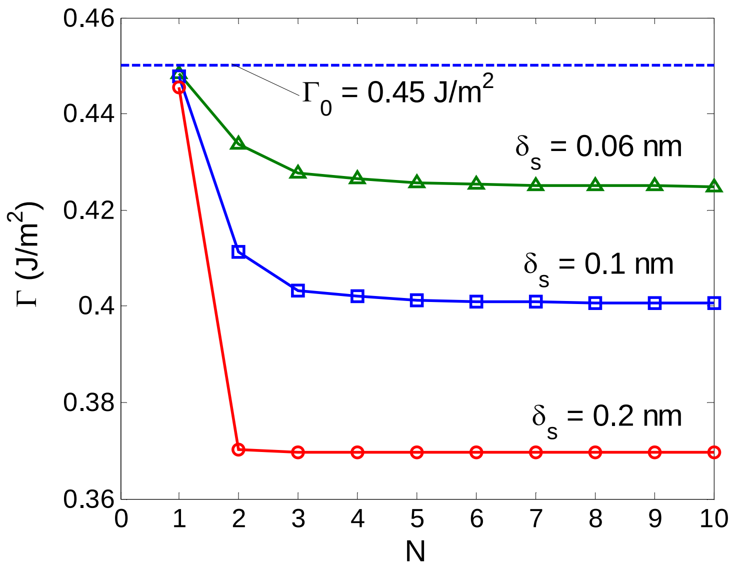
Gao and Huang, J. Phys. D 44, 452001 (2011).

Multilayered Graphene



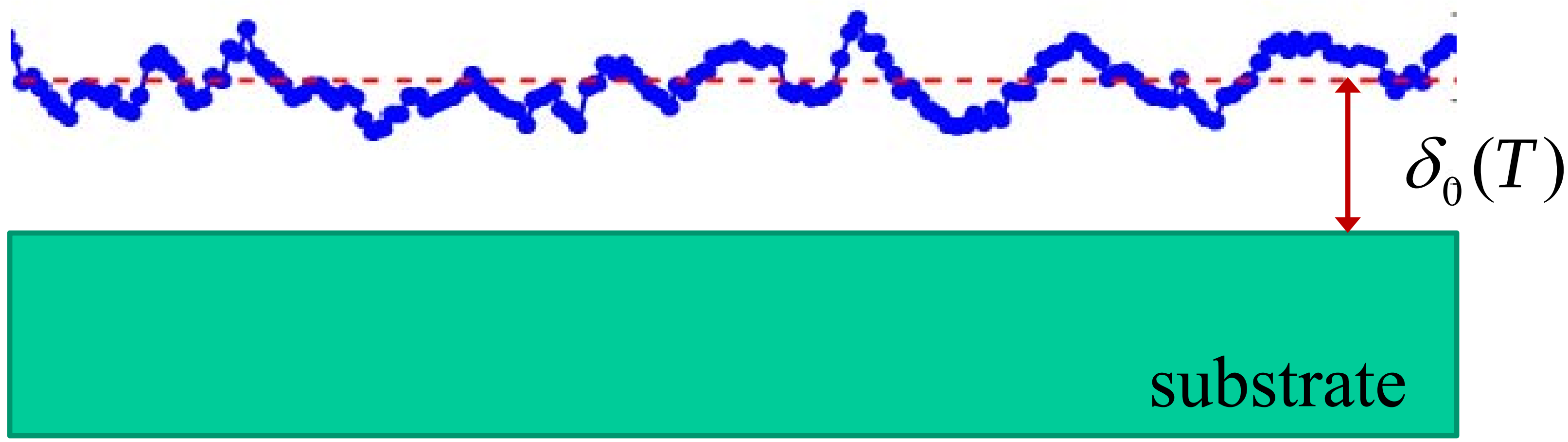
Higher bending stiffness → less conformal → lower adhesion energy





Gao and Huang, J. Phys. D 44, 452001 (2011).

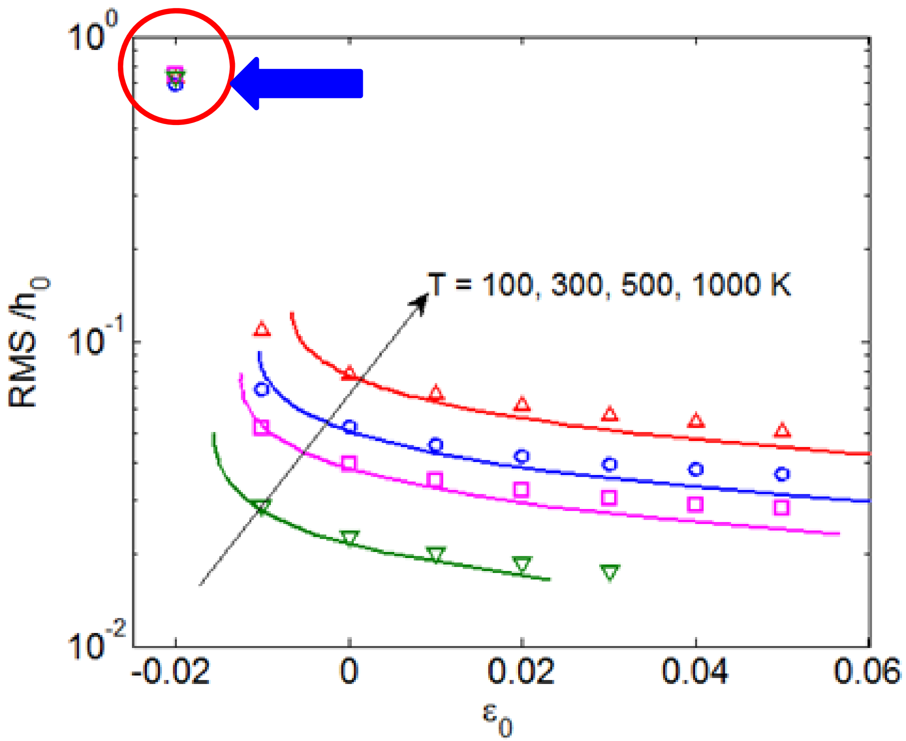
Thermal Rippling of Graphene on Substrate

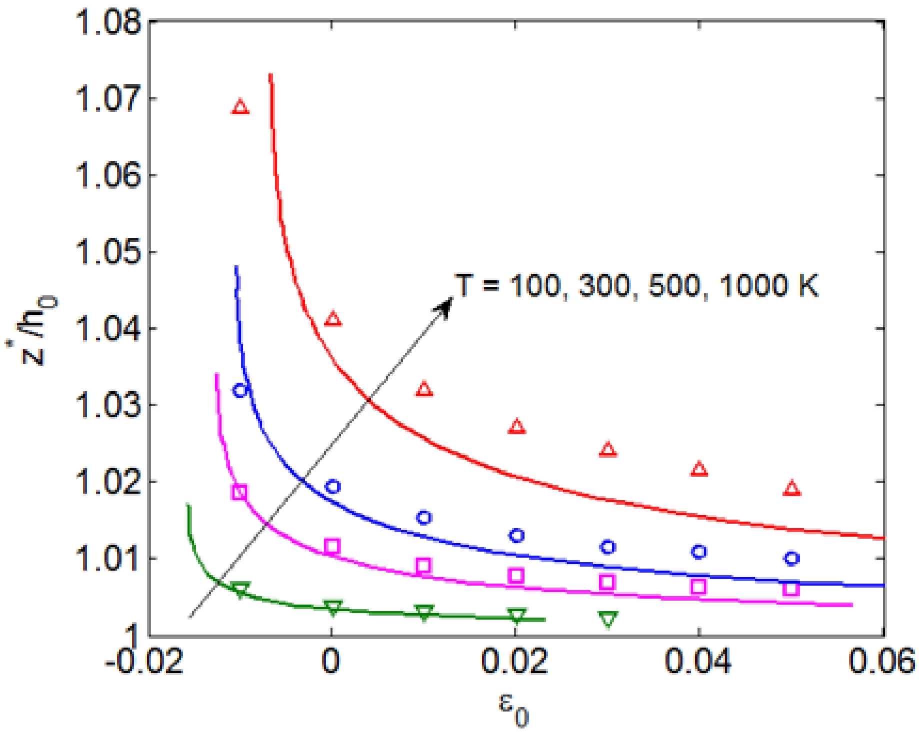


- Compared to freestanding graphene, rippling amplitude of a supported graphene is considerably lower and independent of the membrane size.
- Thermal rippling leads to an entropic repulsion, and hence the equilibrium separation increases (out-of-plane thermal expansion) and effective adhesion energy decreases with increasing temperature.

Wang et al., JAP 119, 074305 (2016).

Biaxially strained graphene



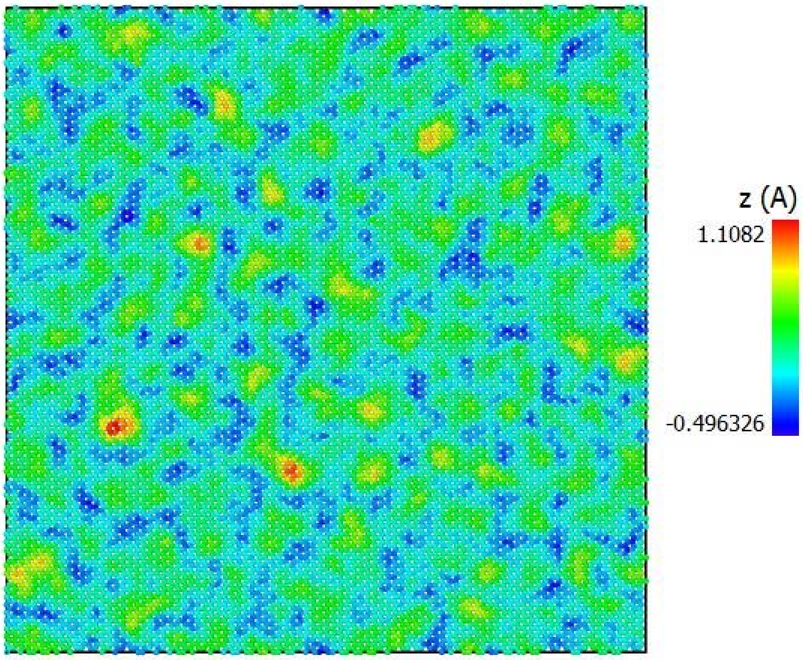


- Tension reduces rippling amplitude and the entropic repulsion.
- Compression amplifies rippling amplitude significantly, resembling a buckling instability.

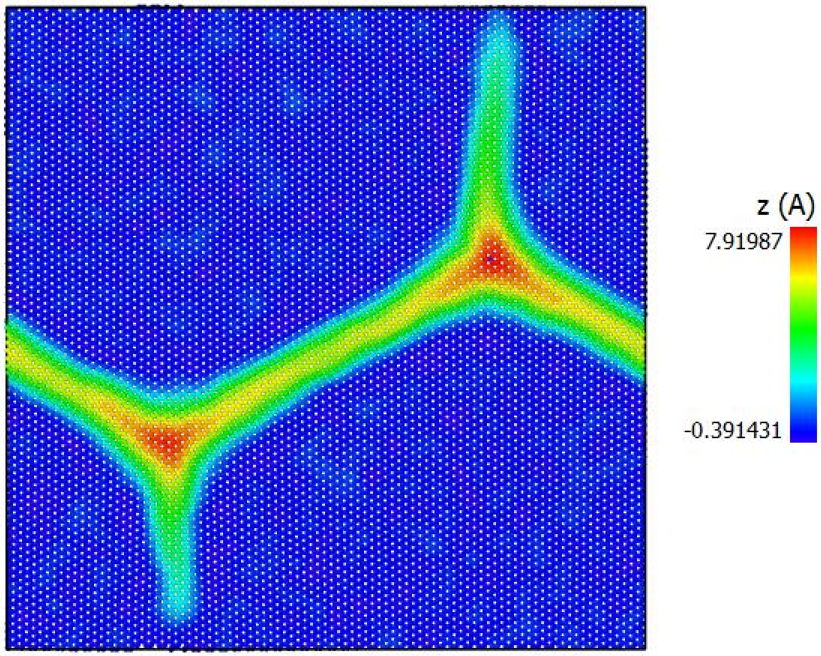
Wang et al., JAP 119, 074305 (2016).

Rippling to Buckling Transition

T = 300 K



$\varepsilon_0 = -0.013$

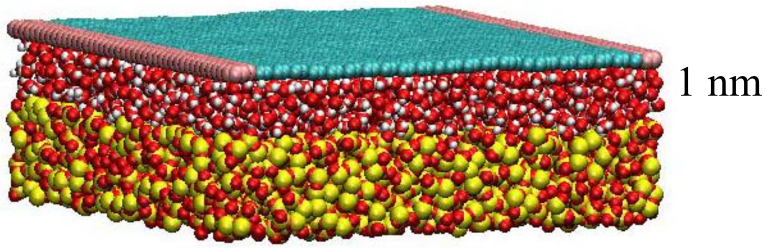


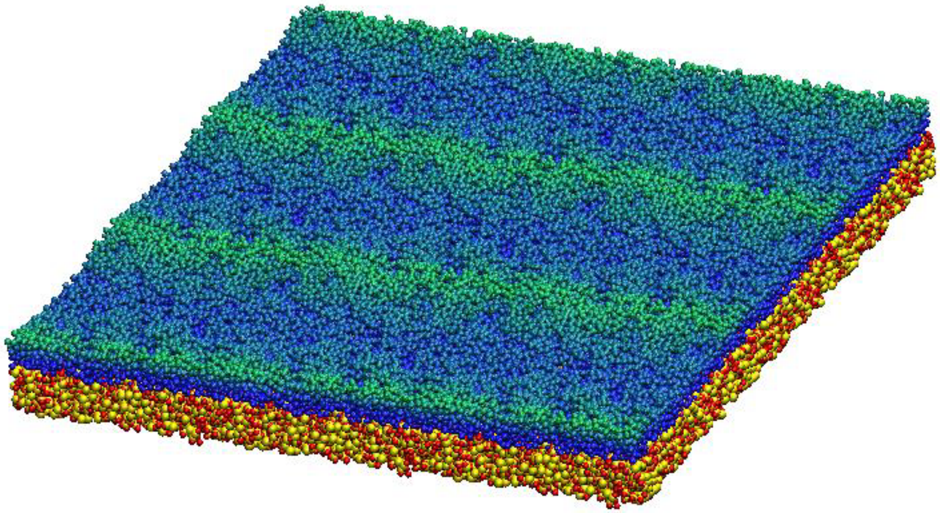
$\varepsilon_0 = -0.014$

- Beyond a critical compressive strain, localized buckling is observed, with possible delamination.

Wang et al., JAP 119, 074305 (2016).

Wet Adhesion: Graphene/water separation





Continuous water film

↓

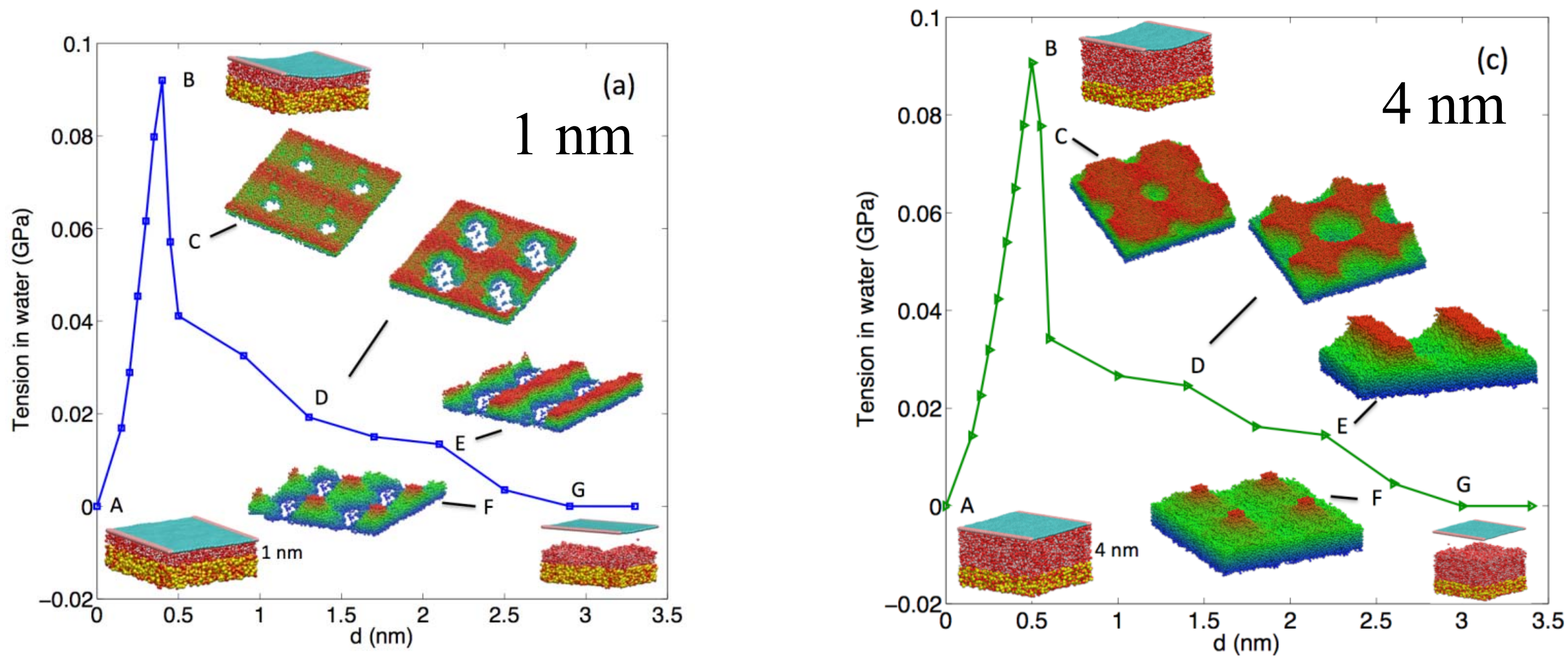
Water cavitation

↓

Water bridging

Gao et al., EML 3, 130-140 (*2015).*

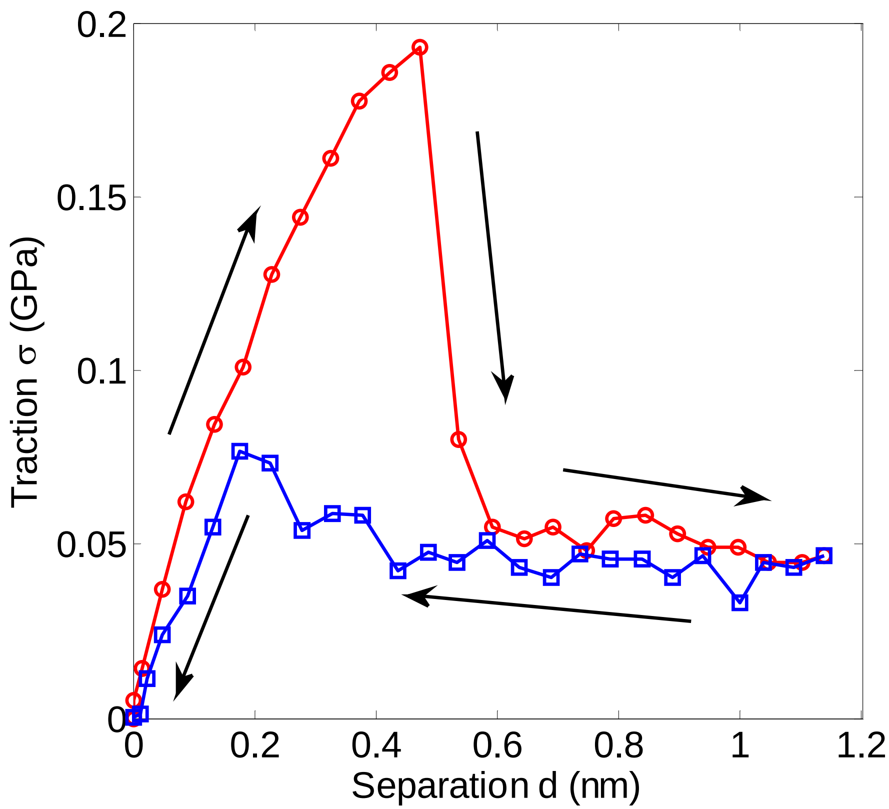
Traction-separation relations

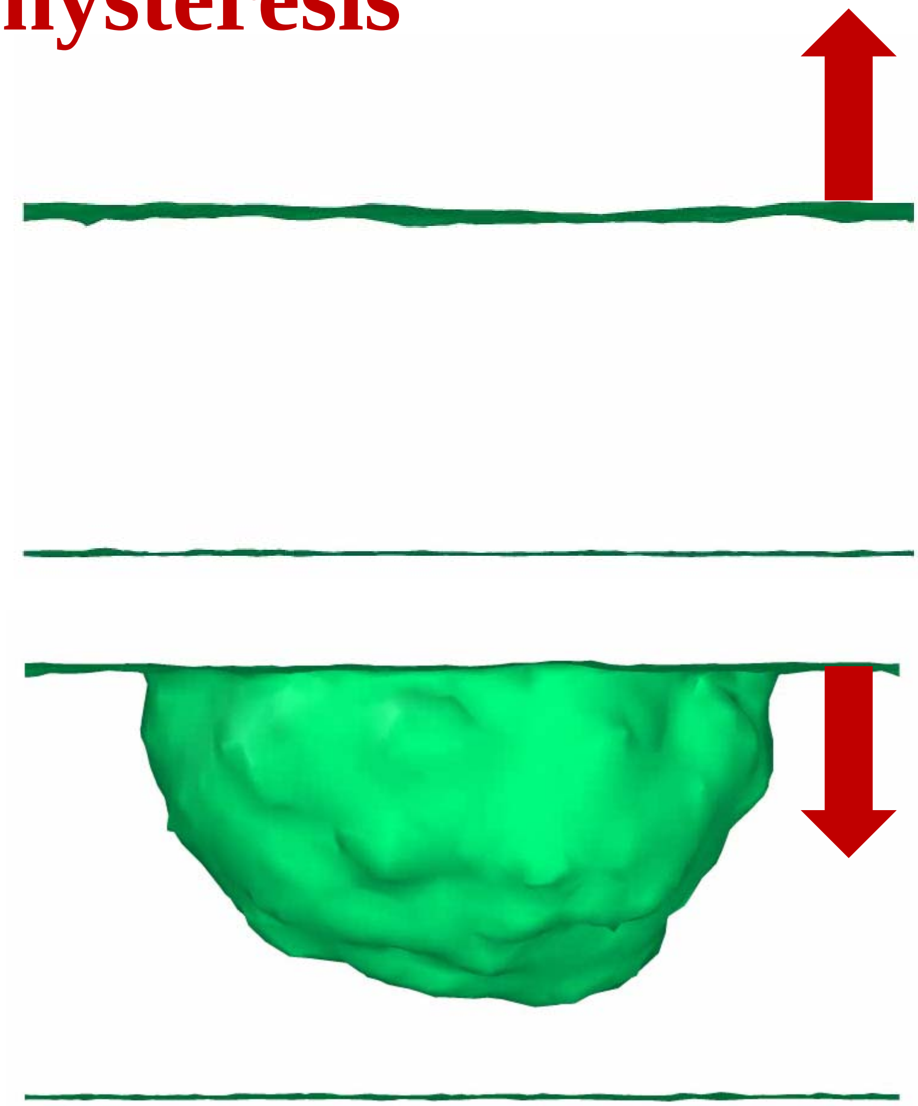


- Three stages of separation.
- Cavitation at the water/graphene interface sets the critical tension, which is considerably lower than that for bulk water (~140 MPa).
- Subsequent transitions of water morphology (cavitation to ridges to islands) depend on water thickness.

Gao et al., *EML* 3, 130-140 (*2015*).

Adhesion hysteresis

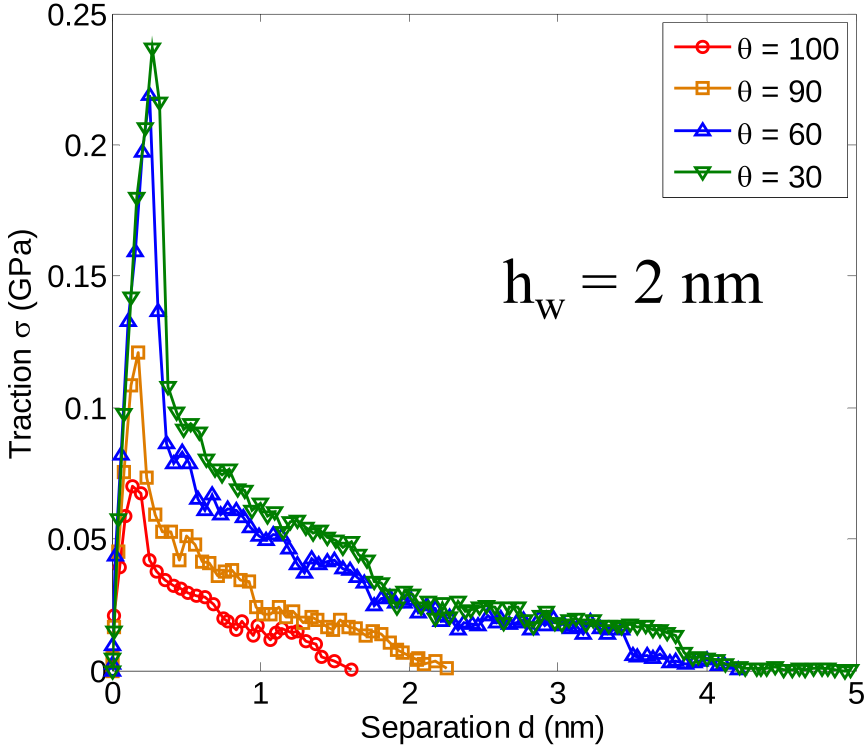


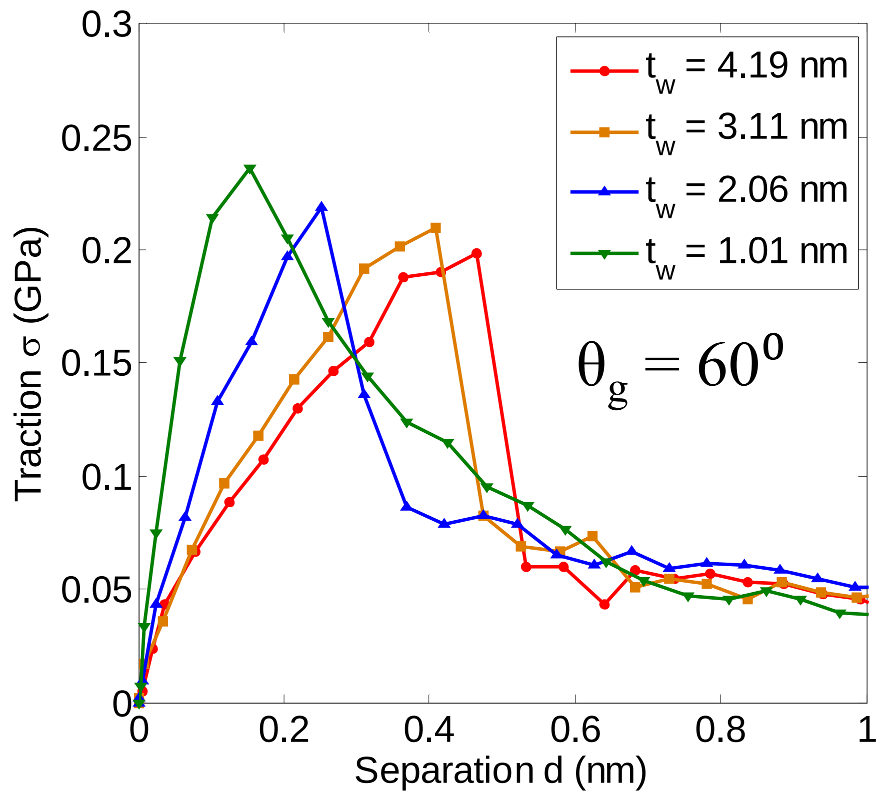


The snap transitions of cavitation leads to adhesion hysteresis.

Wang et al., unpublished.

Effect of graphene/water contact angle

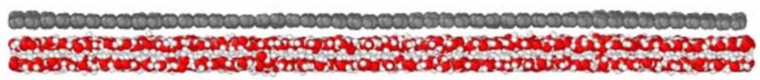


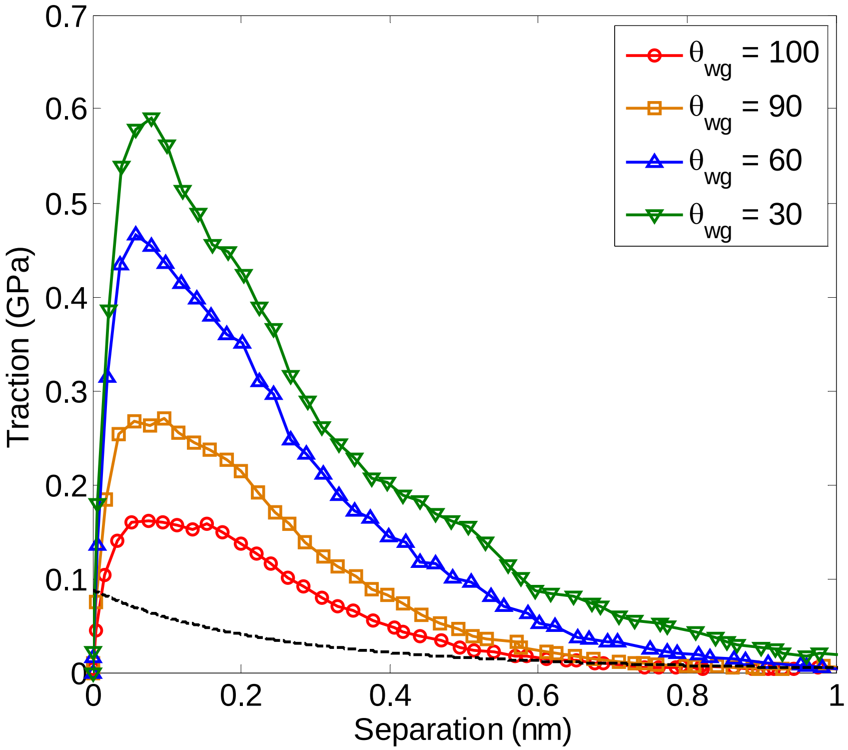


- The traction-separation relation depends on the water contact angle of graphene and the water thickness.
- Stronger graphene-water interactions lead to lower contact angle and stronger wet adhesion.
- Thinner water leads to higher initial stiffness and strength.

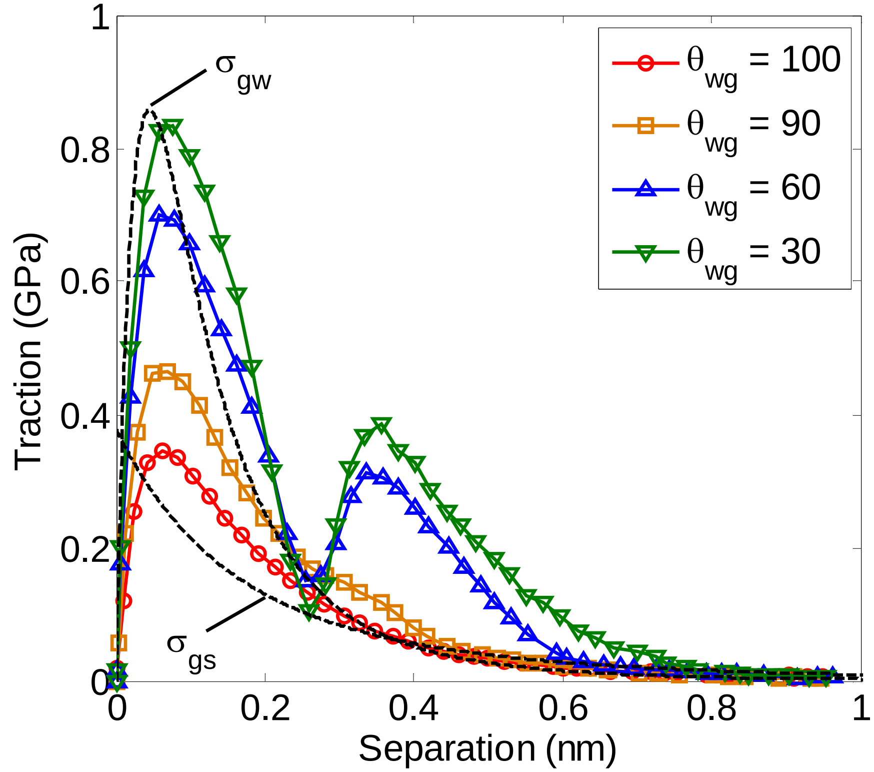
Ultrathin water (< 1 nm)

Bilayer of water molecules (~0.6 nm)



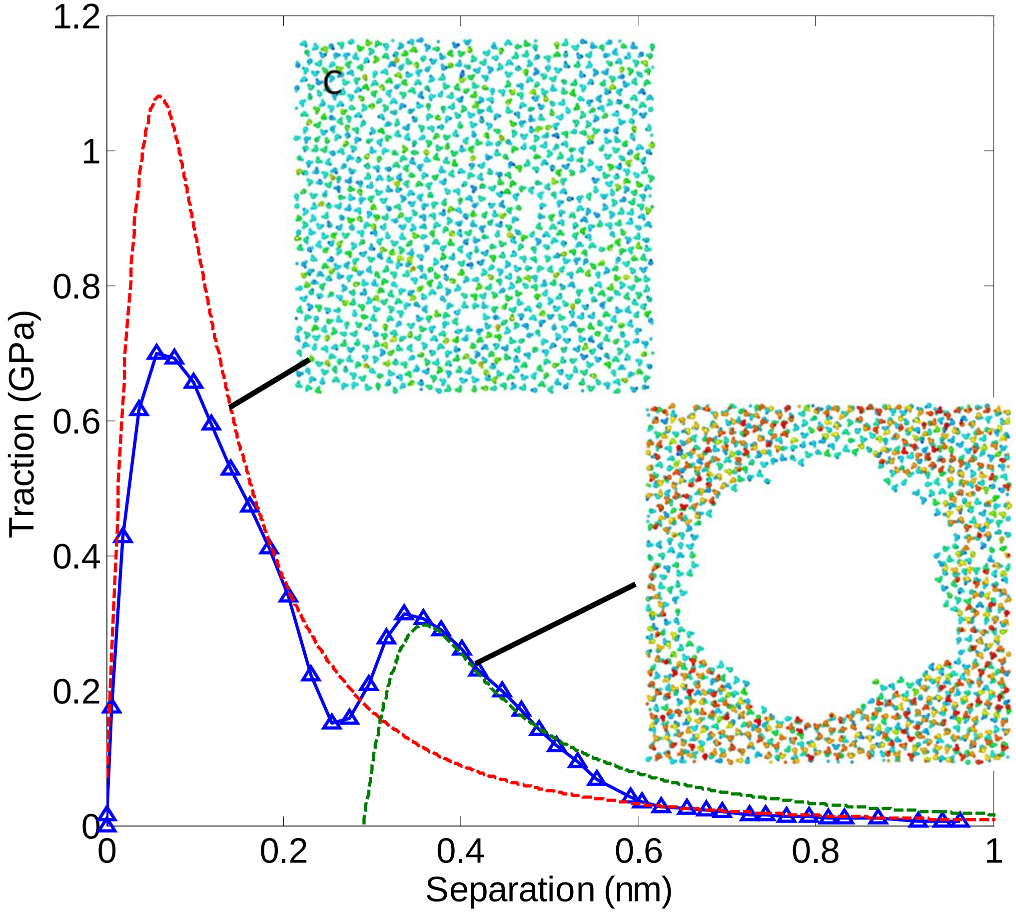


Monolayer water (~0.3 nm)



Wang et al., unpublished.

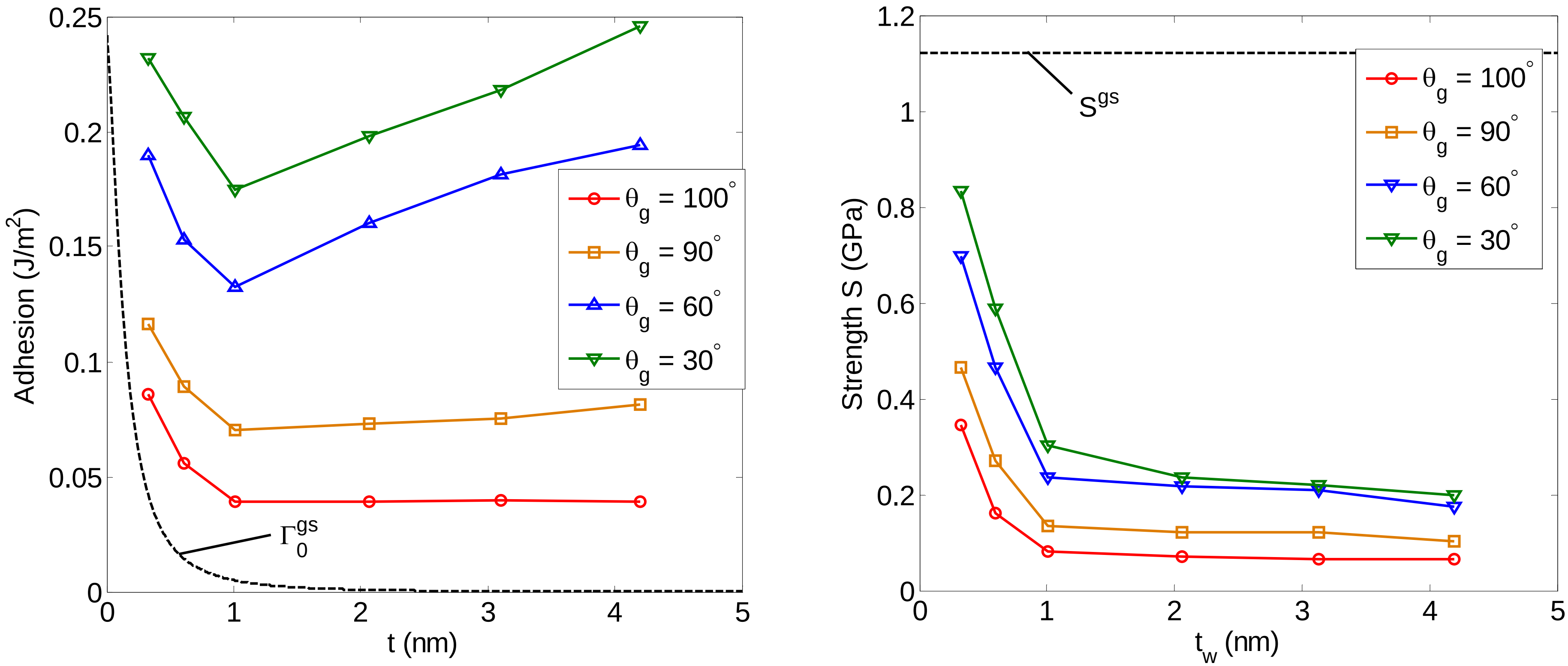
Double-peak traction-separation relation



- First peak: graphene interacting with a water monolayer
- Second peak: graphene interacting with two half-monolayers
- Only one peak for weak graphene/water interactions as water remains a monolayer

Wang et al., unpublished.

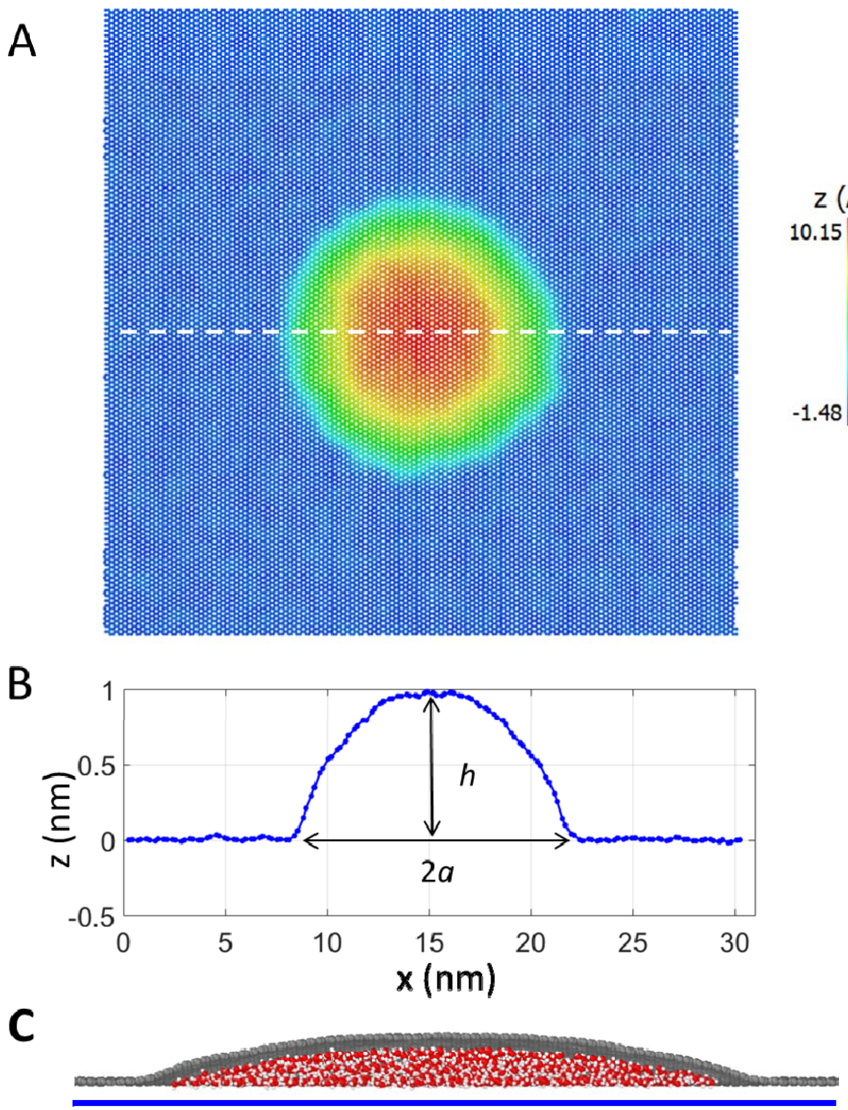
Wet adhesion of graphene (summary)

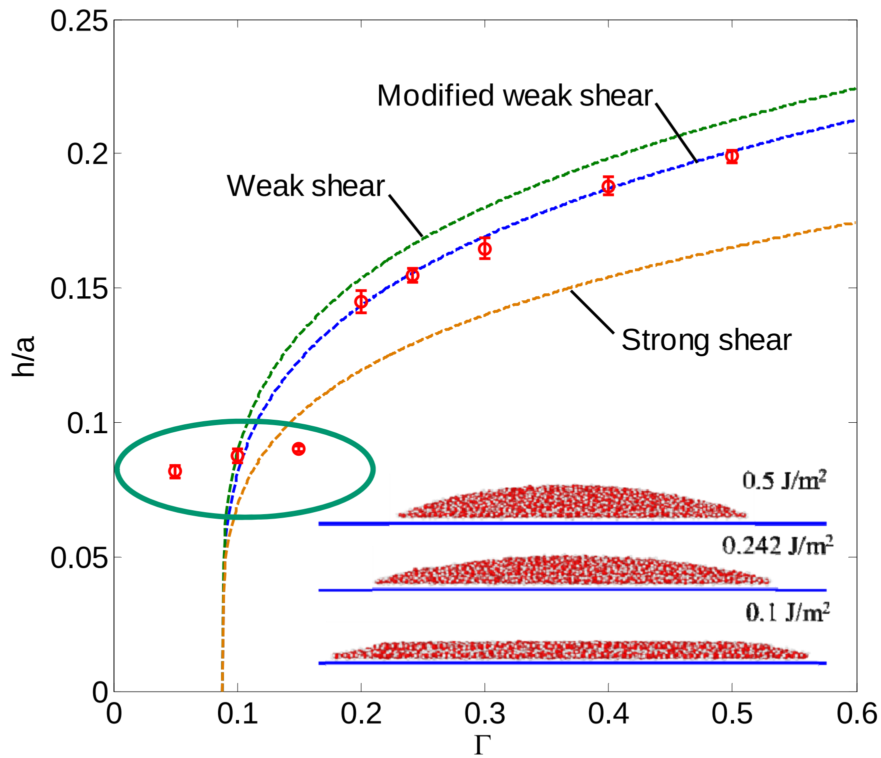


- Both the adhesion energy and strength depend on the water contact angle and water thickness.
- Discrete water layers at sub-nm thickness lead to higher adhesion energy and strength (but shorter ranged).

Wang et al., unpublished.

Water-filled graphene blisters

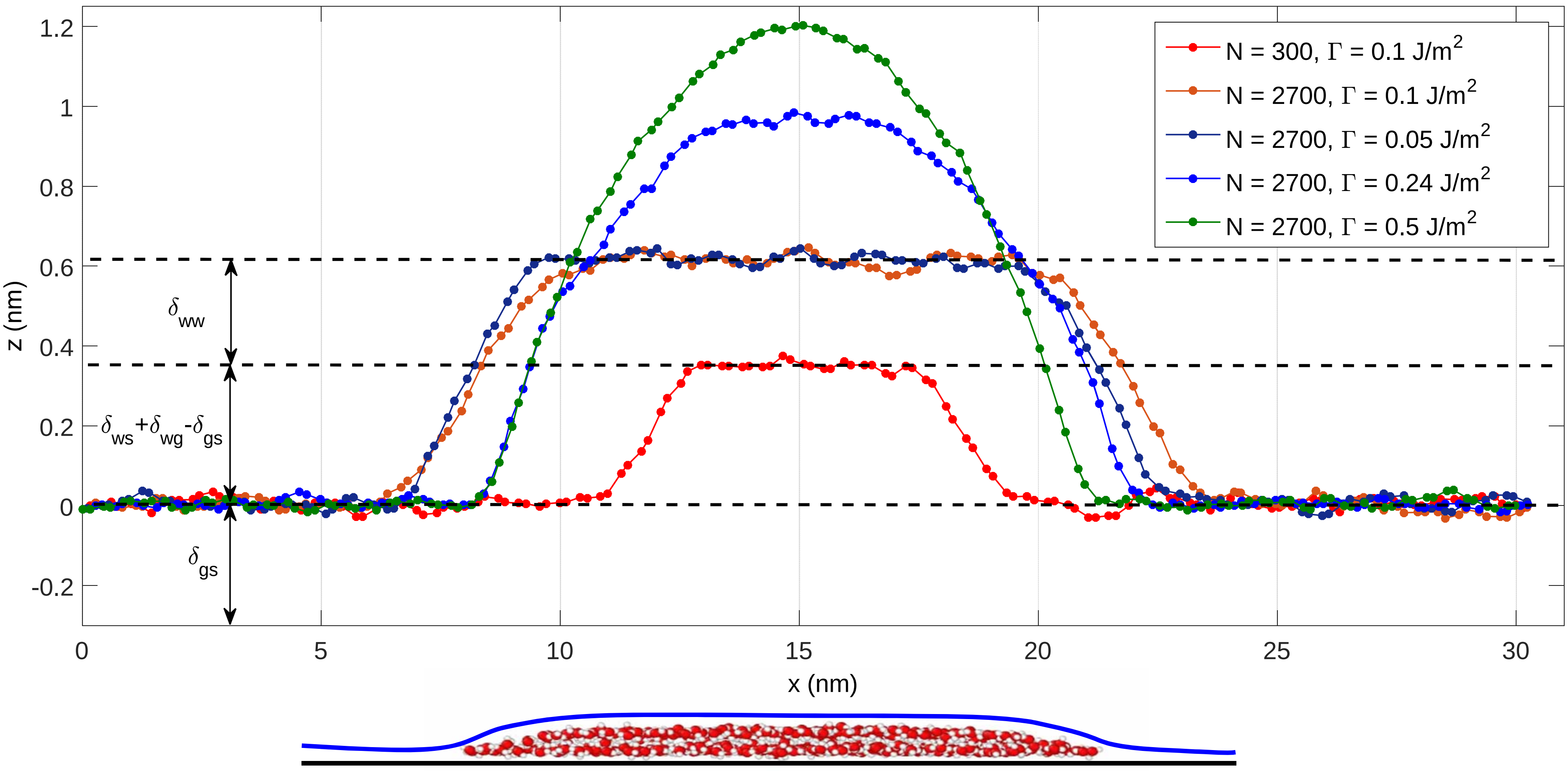




A continuum model predicts the aspect ratio as a function of the adhesion energy, independent of the number of water molecules.

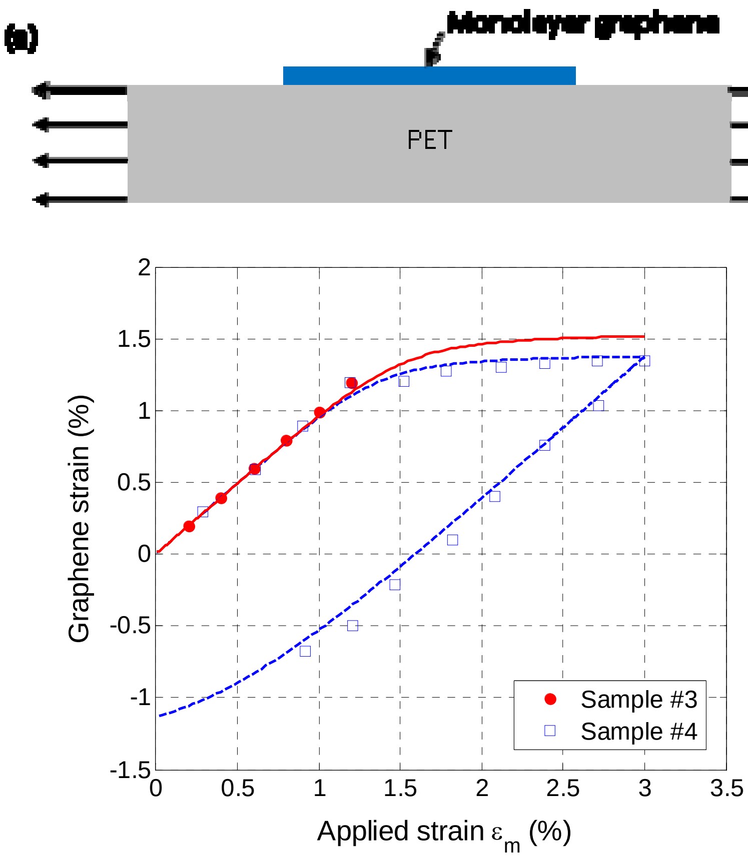
Sanchez et al., in review.

However, the continuum model breaks down when the adhesion is too weak or the number of water molecules is too small.



Sanchez et al., in review.

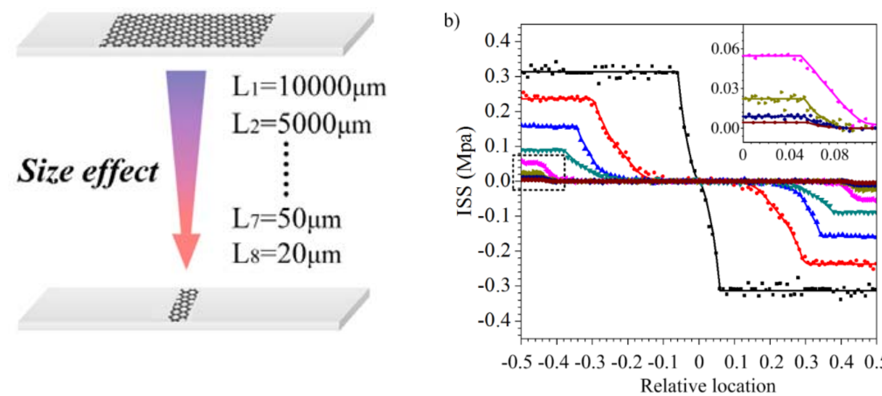
Shear interactions: sliding friction and stress transfer

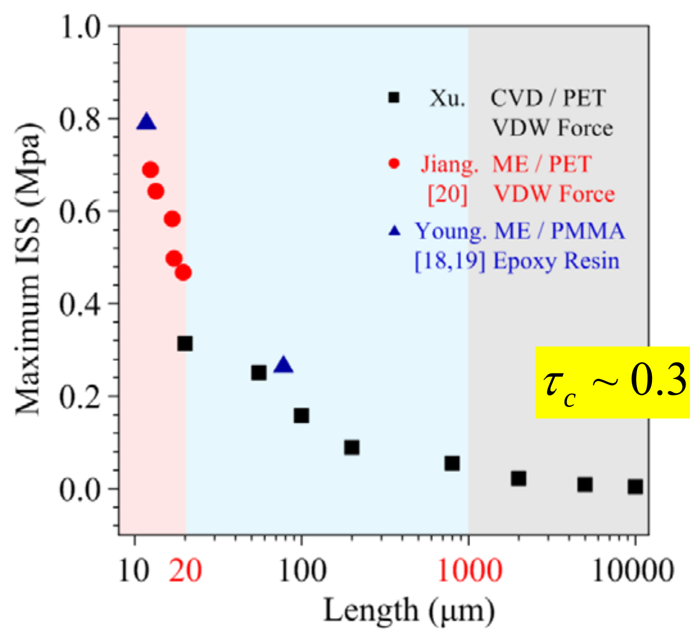


$$\varepsilon_p = \frac{\tau_c L}{2E_{2D}}$$

$\tau_c \sim 0.5\,\mathbf{MPa}$

Jiang et al., 2014.



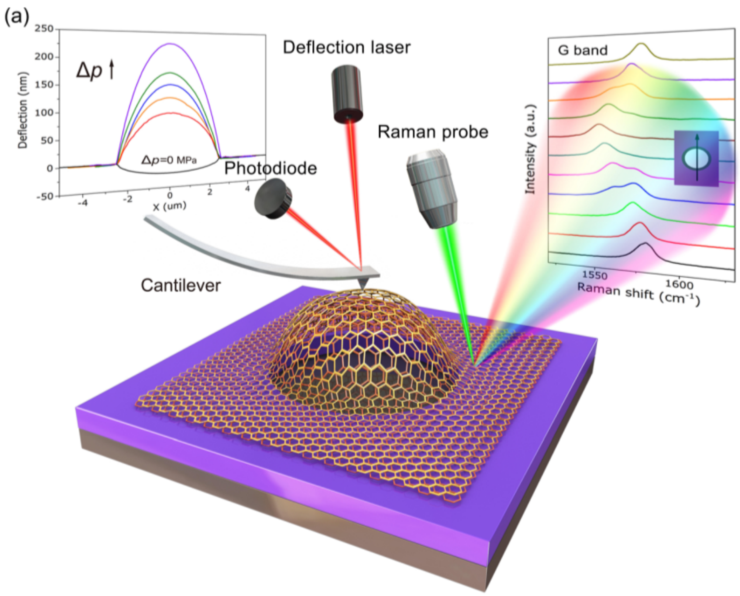


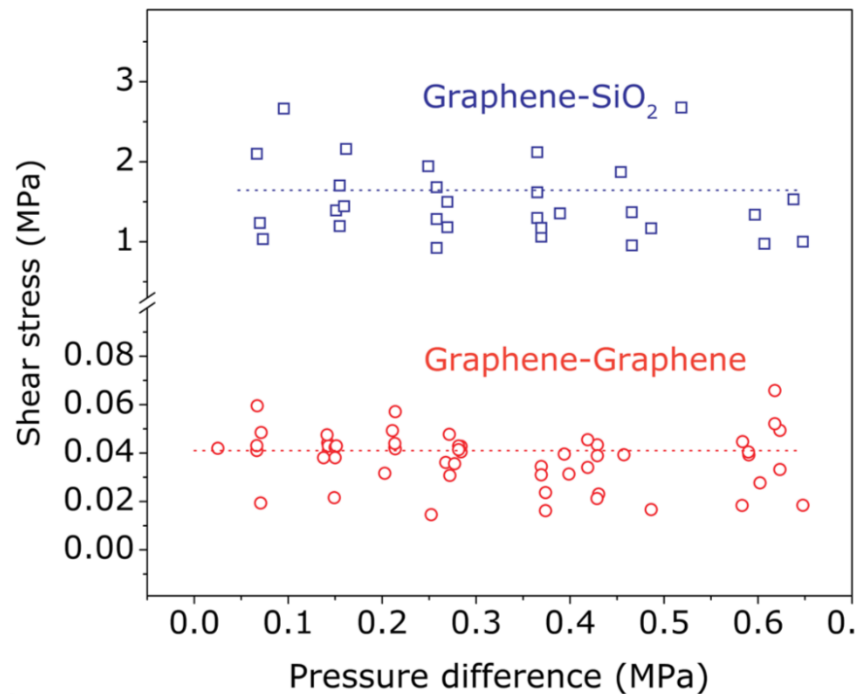
Why?

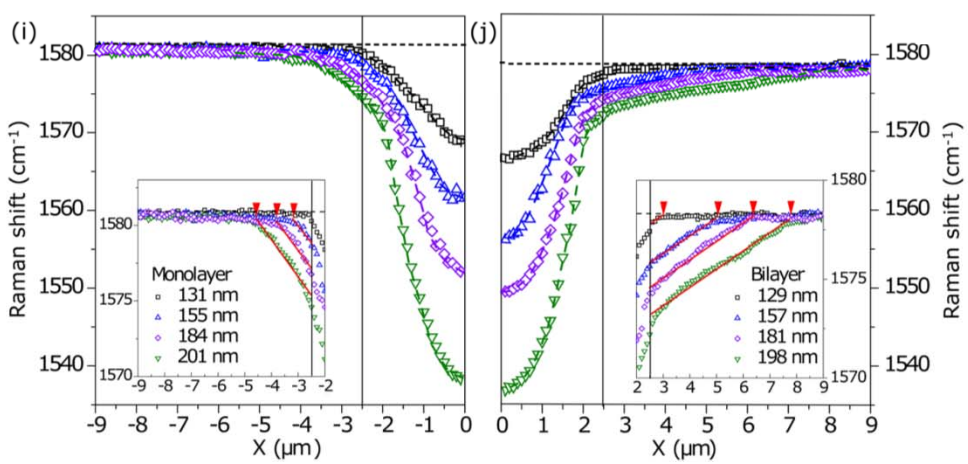
$\tau_c \sim 0.3 - 0.004\,\mathbf{MPa}$

Xu et al., 2016.

Interlayer shear interactions of bilayer graphene



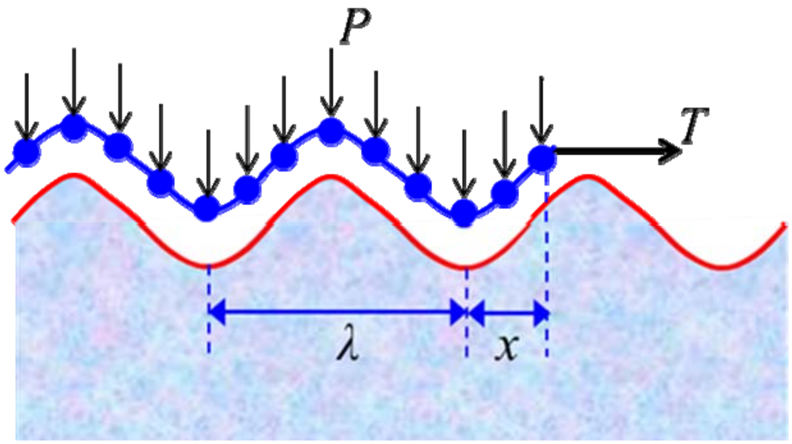




Sliding before delamination

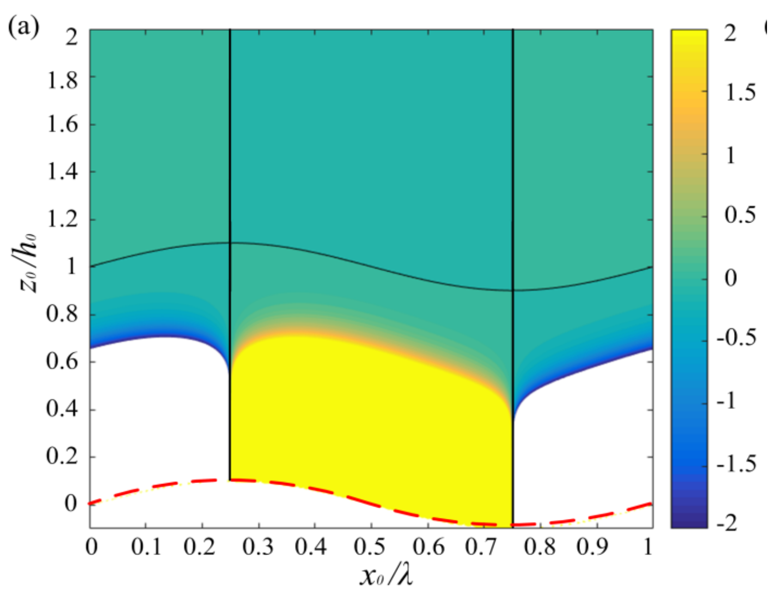
Wang et al., PRL 119, 036101 (2017).

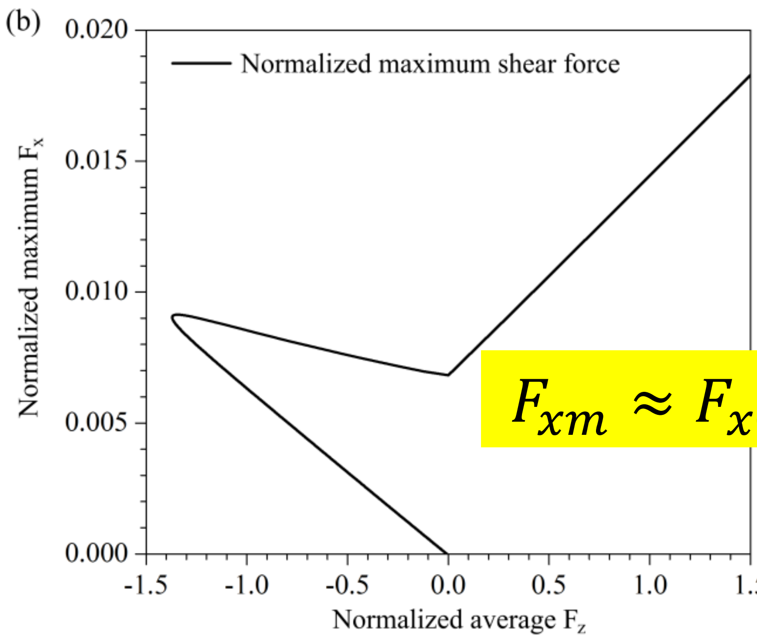
Graphene sliding on a wavy surface



Calculate the shear force on each carbon atom:

$$F_x(x_0, z_0) = -\frac{\partial W}{\partial x_0} \approx \frac{\Gamma}{\rho_g h_0} \bar{F}_x(\ldots)$$





$$F_{xm} \approx F_{x0} + \mu F_{za}$$

Xu et al., unpublished.

Relation between Adhesion and Shear (Friction)

$$F_{xm} \approx F_{x0} + \mu F_{za}$$

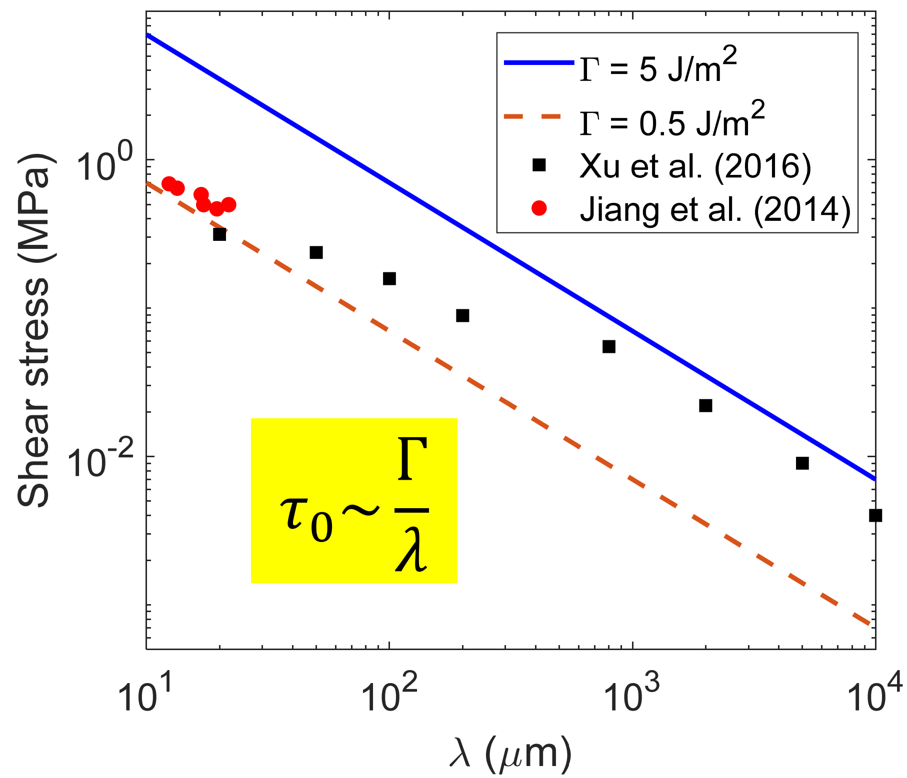
$$F_{x0} = 7.0\frac{\delta_s}{\lambda}\frac{\Gamma}{\rho_g h_0}$$

$$\mu = 8.2\frac{\delta_s}{\lambda}$$

$$\tau_m = \rho_g F_{xm} \approx \tau_0 + \mu\sigma$$

$$\tau_0 = \rho_g F_{x0} = 7.0\frac{\delta_s}{\lambda}\frac{\Gamma}{h_0}$$

$$\mu = 8.2\frac{\delta_s}{\lambda}$$



Take $\delta_s \sim 1$ nm and $h_0 \sim 0.5$ nm

Xu et al., unpublished.

Summary

- Despite extensive effort in experiments and modeling, understanding the mechanical interactions of atomically thin materials (graphene and others) remains a great challenge due to complex physics, chemistry and mechanics.

Wolfgang Pauli: "*God made the bulk; surfaces (interfaces) were invented by the devil*."

… *and as we all know, the devil is in the details.*