

# Mechanical properties of nanosheets by AFM

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# Outline

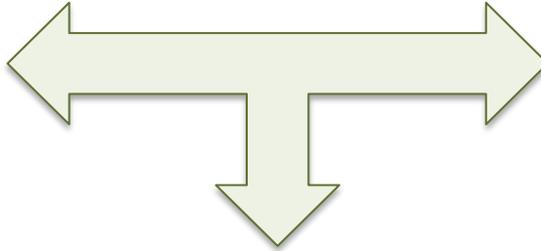
- Why mechanical properties of 2D materials ?
- Introduction
- Nano- indentation Vs Peak Force QNM
- Conclusions

# Why mechanical properties of 2D materials are important ?

- Macroscopic materials fracture are dominated by grain boundary defect and defects
- Uncertainty in sample geometry , stress concentration and distribution , structural defects for example Nano tubes
- Applicability in flexible electronic applications ex.  $\text{MoS}_2$  nanosheets
- Nanoelectromechanical systems(NEMS) –as resonators
- 2 D sheets geometry are precisely are defined and less sensitive to defects

# Mechanical properties- Different AFM modes

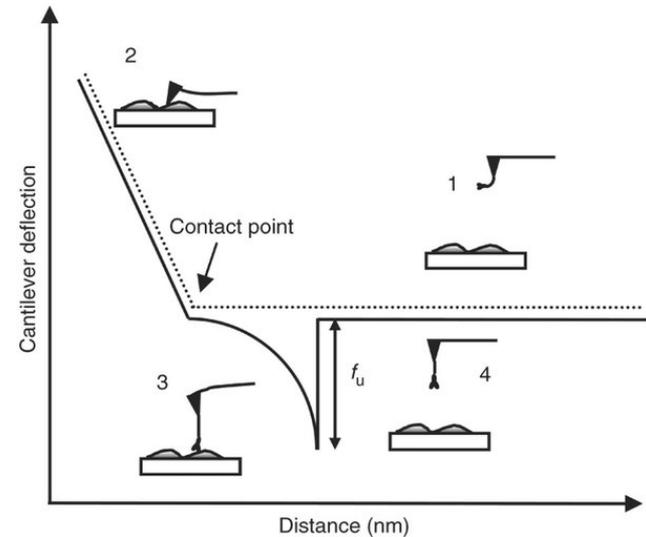
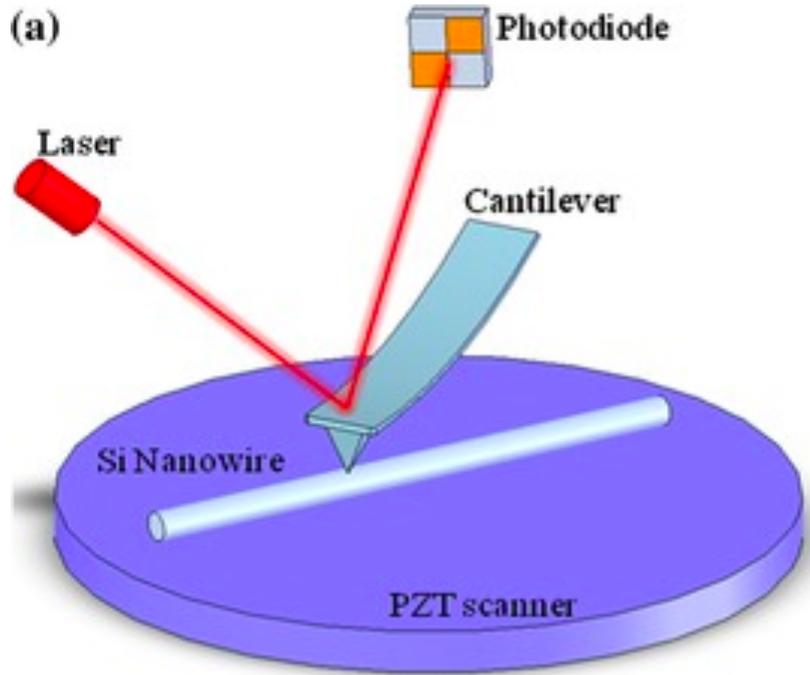
Nano-Indentation



Peak force-Quantative  
nanomechanical mapping

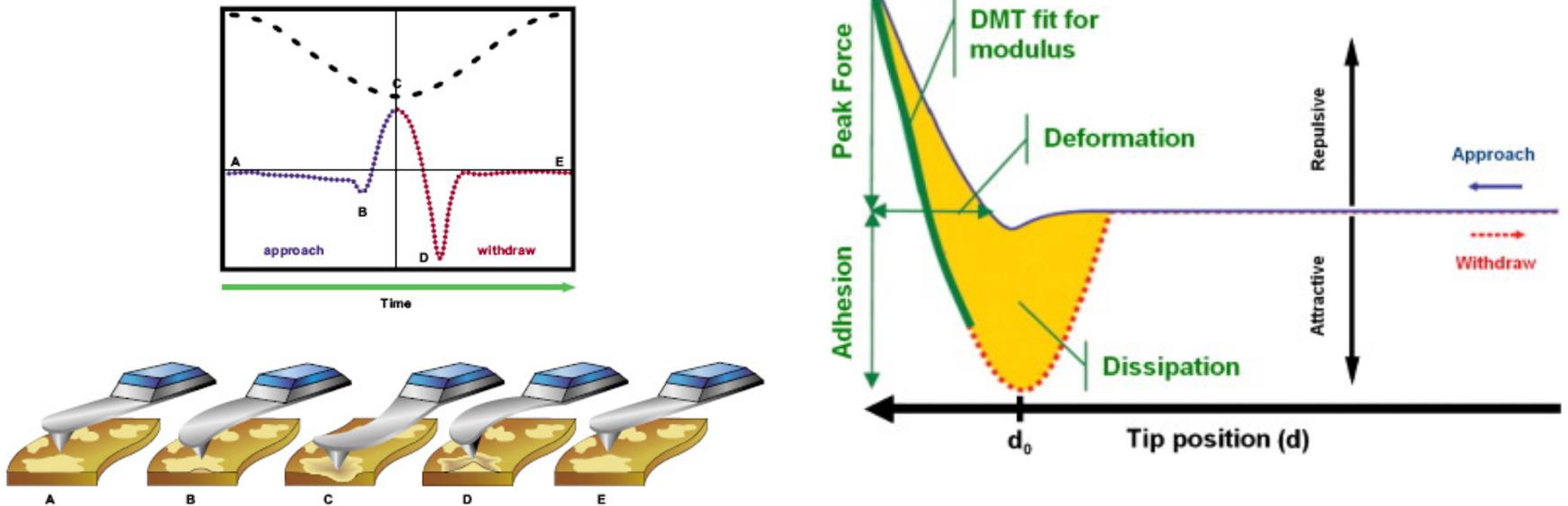
Harmonic force Microscopy

# Nano-indentation



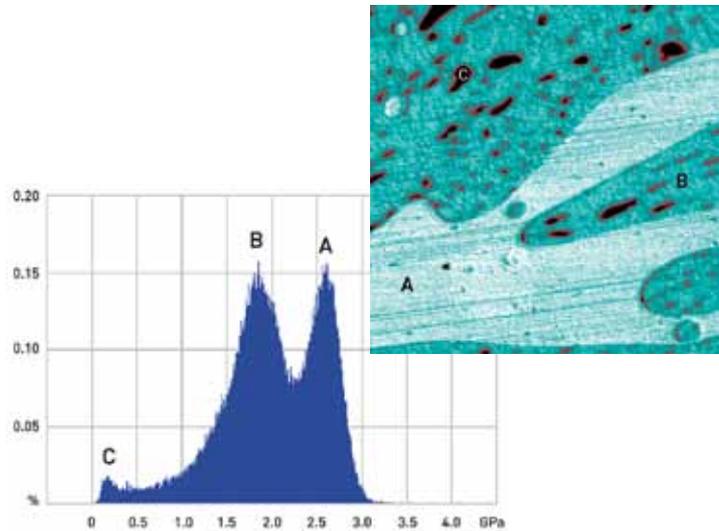
- Hertz model- Approach-retract cycle at the rate of 0.5 to 1 Hz (Very slow)
- Every pixel in an image – force Vs piezo displacement curve is obtained
- Samples :Insulin fibrils, biological substrates ,polymeric materials

# Peak Force QNM



- Derjaguin–Muller–Toporov (DMT) in-built model -includes visco-elasticity and adhesion between tip and the surface
- High-Resolution Mapping of Modulus and Adhesion
- Direct Force Control Keeps Indentations Small for higher Resolution and Non-Destructive Imaging
- Widest Operating Range for Samples from Soft Gels (~1 MPa) to Rigid Polymers (>20 GPa)

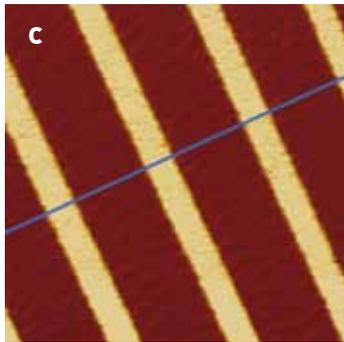
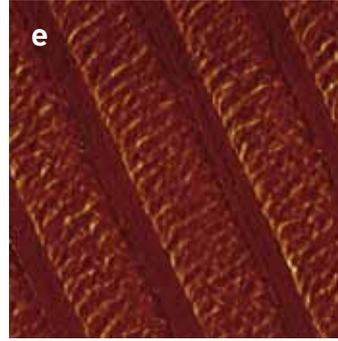
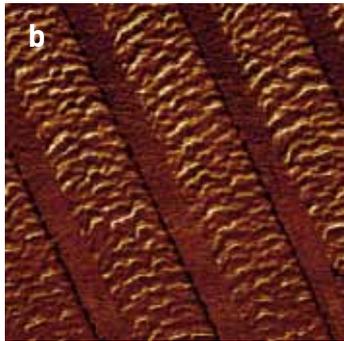
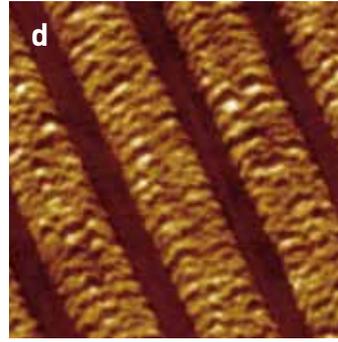
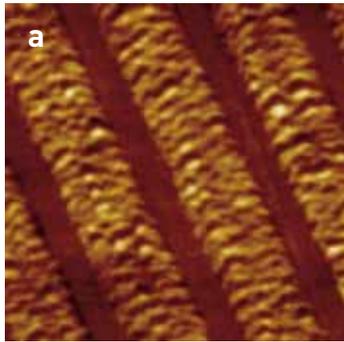
# Peak Force QNM



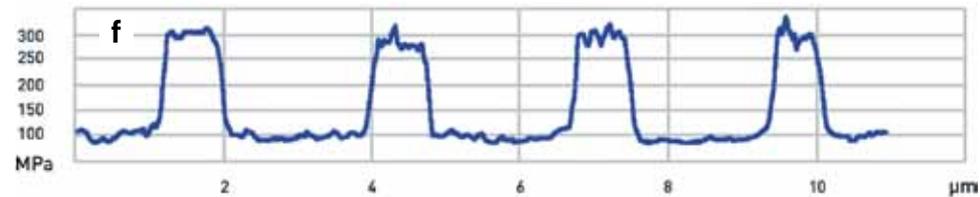
For example. Mixture of polymer blends

# Peak Force QNM

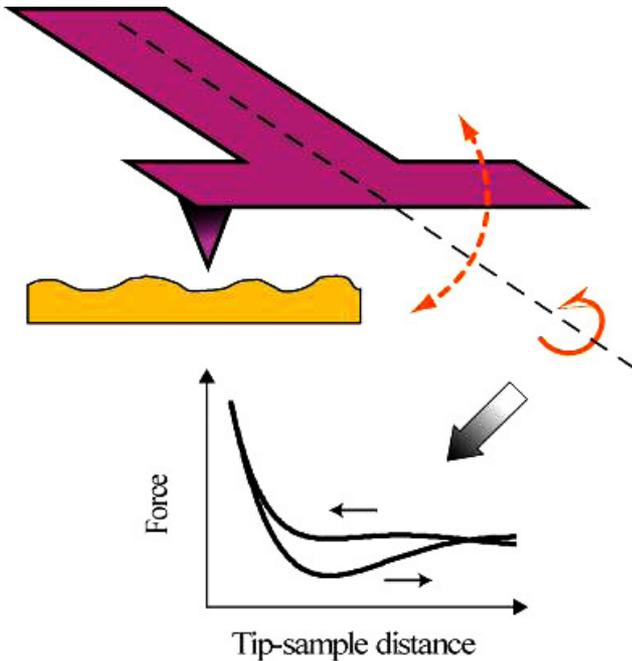
Multi-layer polymer films



- a) Height
- b) Adhesion
- c) Modulus
- d) Height
- e) phase



# Harmonic Force Microscopy



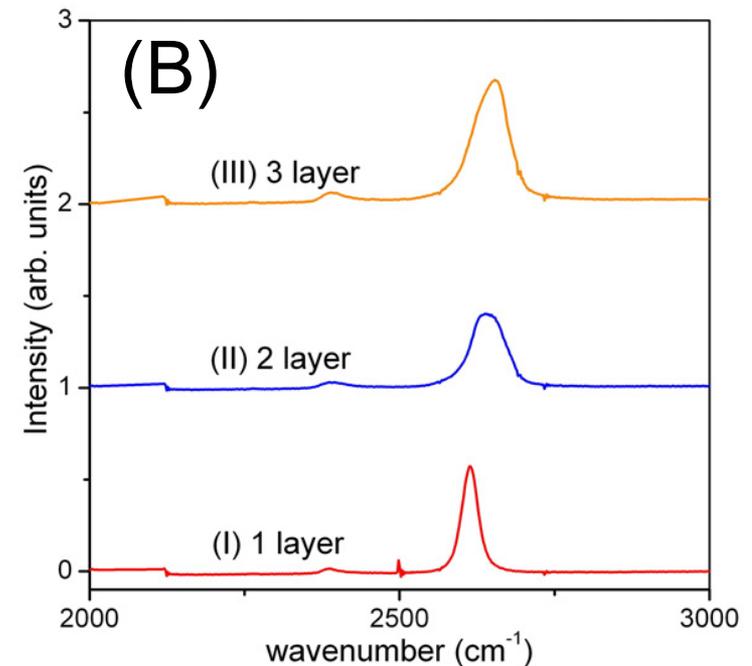
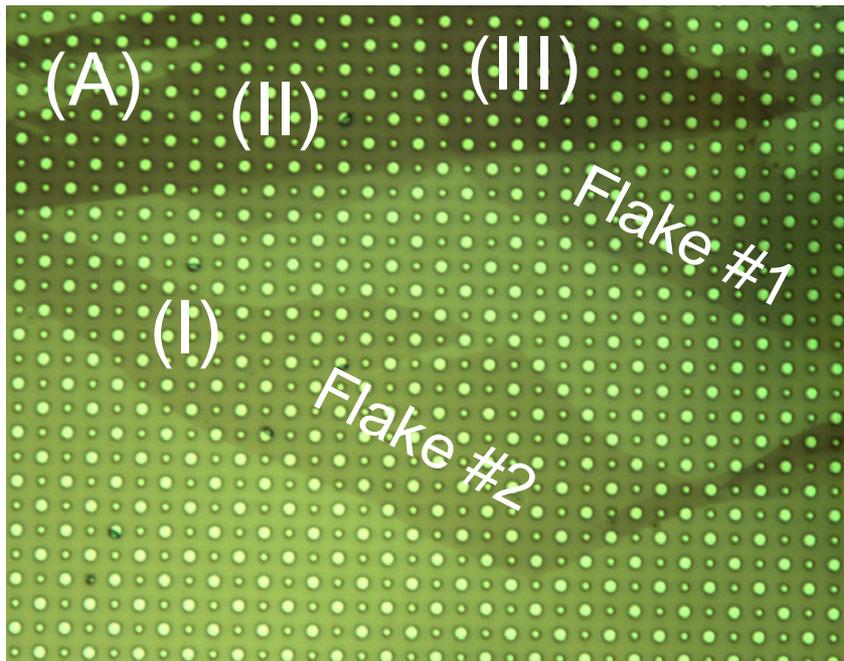
- T-shaped AFM cantilevers have enabled the measurement of time-varying tip–sample forces with good signal to noise ratio
- Torsional harmonic cantilevers (THC)
- Detected torsional motion is used to generate high-speed force–distance curves.

# Harmonic Force Microscopy

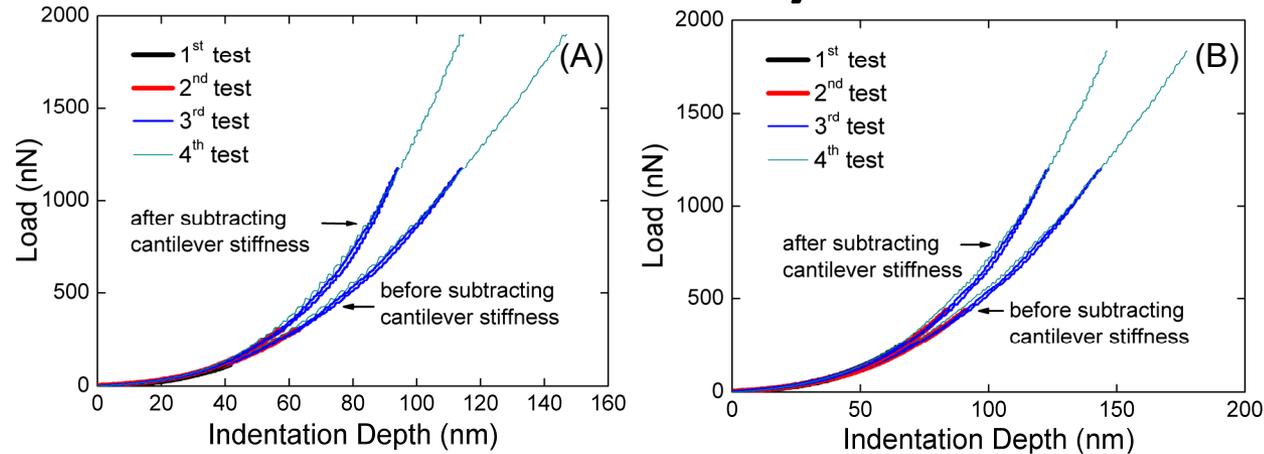


<http://www.rowland.harvard.edu/rjf/sahin/pubs.html>

# Nano-indentation of graphene monolayer



# Nano-indentation of graphene monolayer



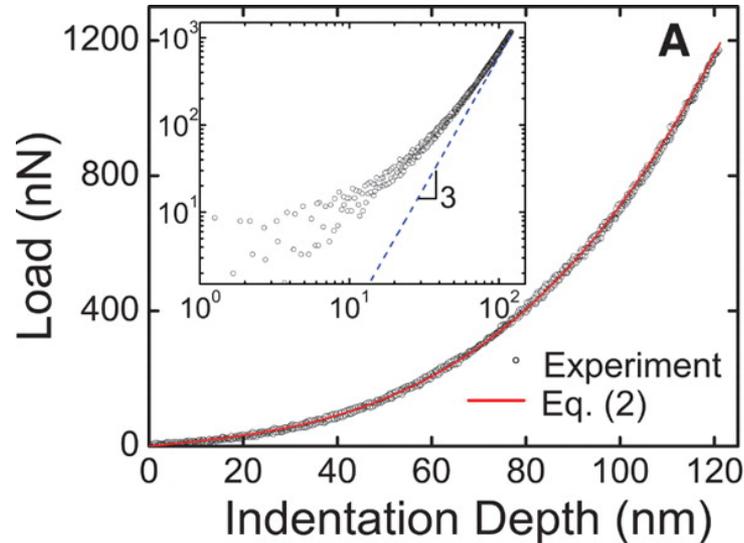
$$F = \sigma_0^{2D} (\pi a) \left( \frac{\delta}{a} \right) + E^{2D} (q^3 a) \left( \frac{\delta}{a} \right)^3 .$$

Assumptions:

- Bending stiffness and load of free standing film is negligible
- 

Channggu Lee et al. "**Measurement of the elastic properties and Intrinsic strength of Monolayer graphene**", Science ,vol 321,385-388,2008

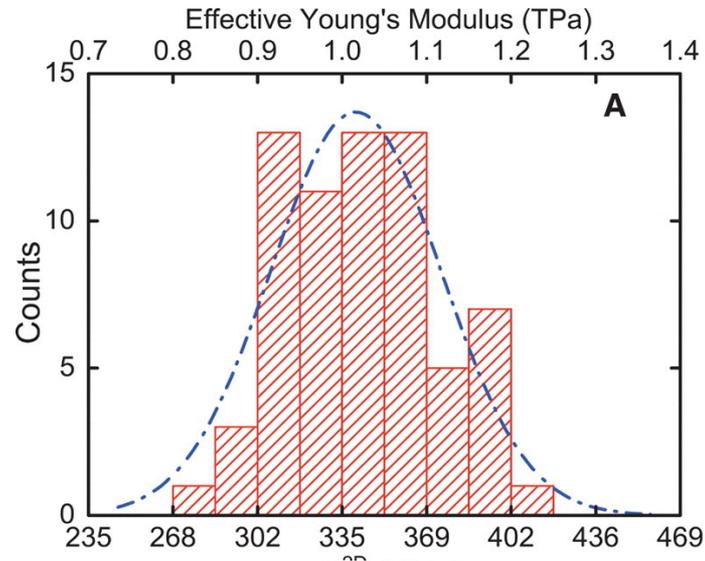
# Nano-indentation of graphene monolayer



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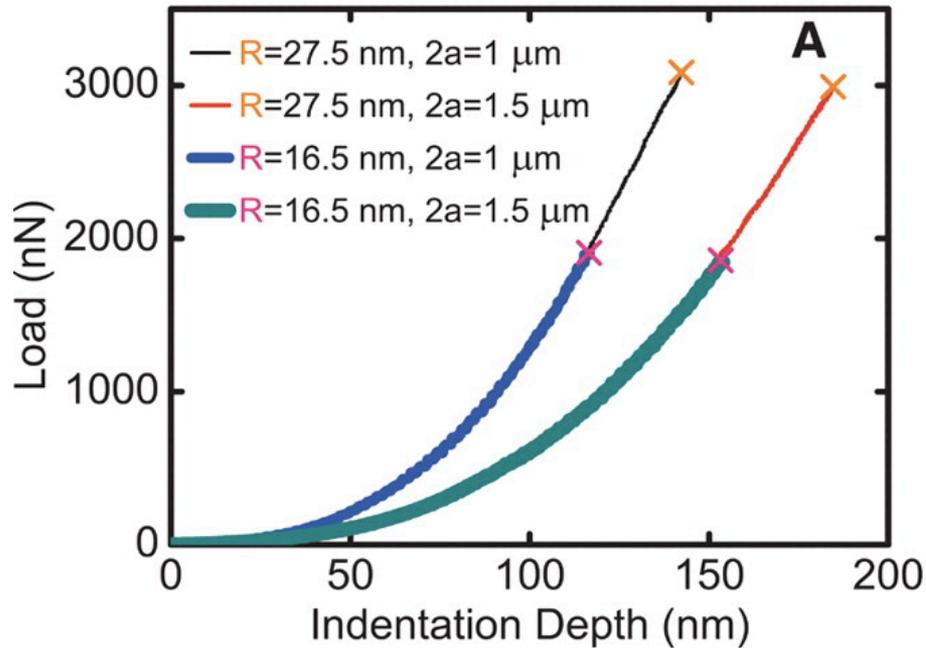
# Nano-indentation of graphene monolayer



Mean value of  $E^{2D}$  is 342 N/m with the standard deviation of 30 N/m

Channggu Lee et al. "**Measurement of the elastic properties and Intrinsic strength of Monolayer graphene**", Science, vol 321,385-388,2008

# Nano-indentation of graphene monolayer



$$\sigma_m^{2D} = \left( \frac{F E^{2D}}{4\pi R} \right)^{\frac{1}{2}}$$

Elastic stiffness for monolayer graphene are  $E^{2D} = 340 \pm 50 \text{ N/m}$

$$D^{2D} = -690 \pm 120 \text{ N/m}$$

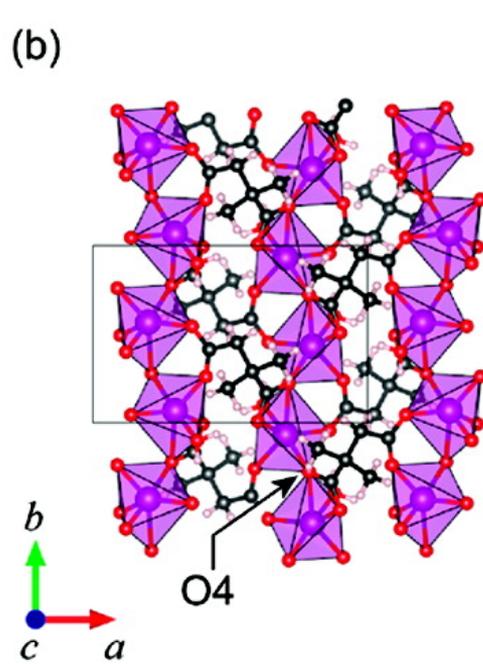
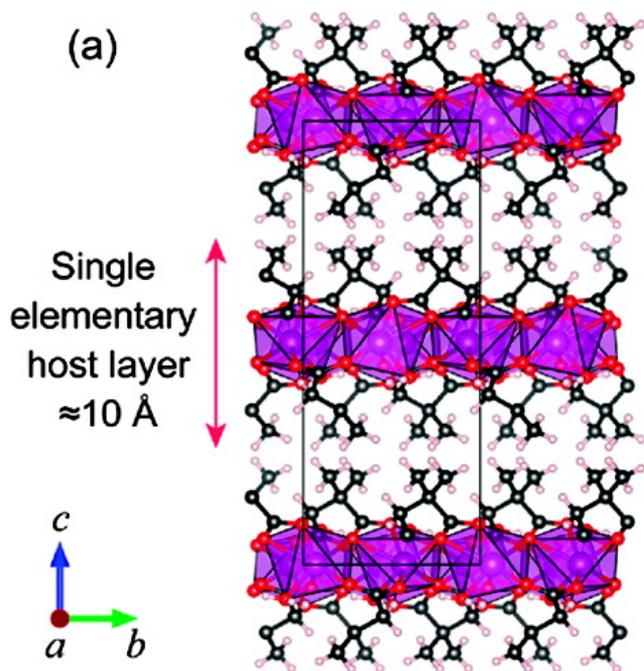
Intrinsic strength is  $\sigma_{int}^{2D} = 42 \pm 4 \text{ N/m}$

Young's modulus  $E = 1.0 \pm 0.1 \text{ Tpa}$ ,

Intrinsic stress is  $\sigma_{int} = 130 \pm 10 \text{ GPa}$  at a strain of  $\epsilon_{int} = 0.25$ .

Channggu Lee et al. "**Measurement of the elastic properties and Intrinsic strength of Monolayer graphene**", Science, vol 321,385-388,2008

# Peak Force QNM of Inorganic –organic hybrid nanosheets

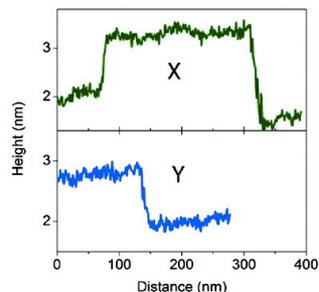
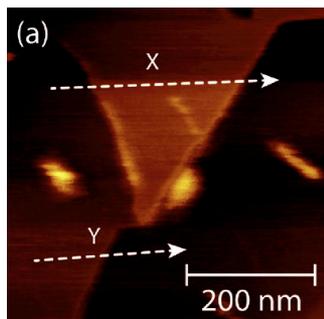


➤ MnDMS [ $\text{Mn}(\text{C}_6\text{H}_8\text{O}_4)$  ( $\text{H}_2\text{O}$ )] Mn 2,2-dimethylsuccinate

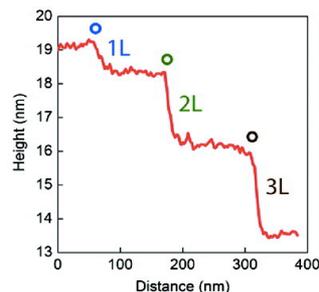
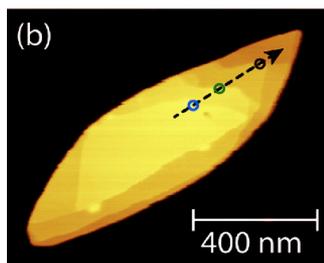
➤ Inorganic and organic building blocks covalently bonded together having distorted  $\text{MnO}_6$  octahedra

Jin-Chong Tan et al, "Hybrid nanosheets of an inorganic –Organic framework *Material*", ACS Nano , Vol 6, No.1, 615-621, 2012

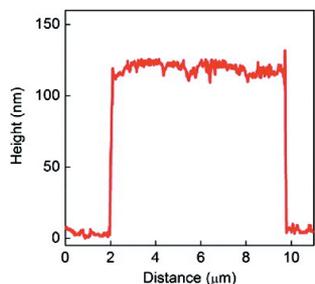
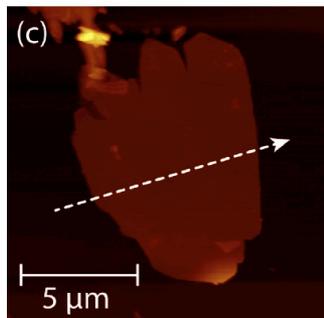
# Peak Force QNM of Inorganic –organic hybrid nanosheets



Two fully exfoliated nanosheets

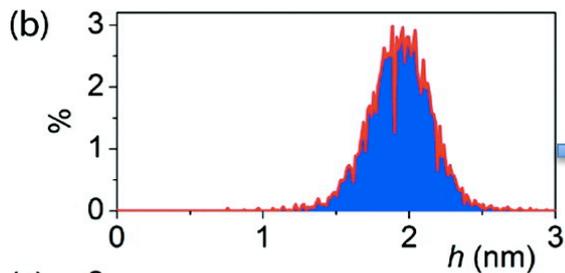
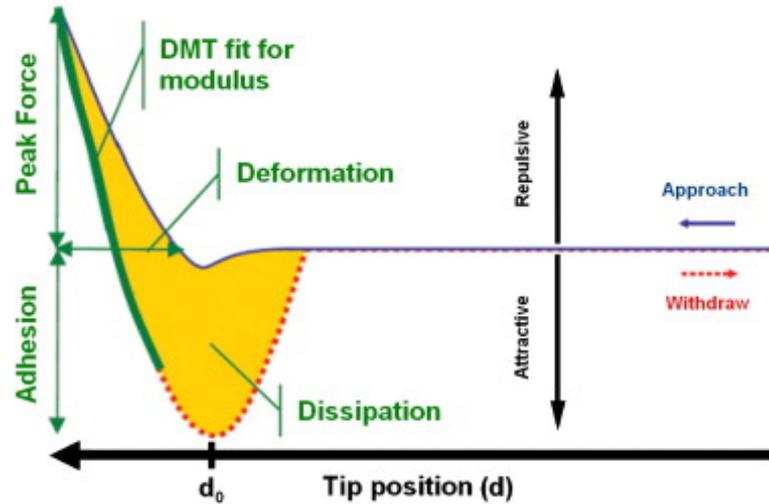
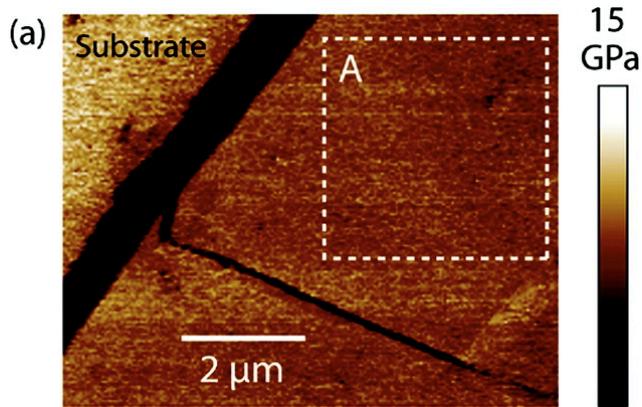


Partially exfoliated nanosheets

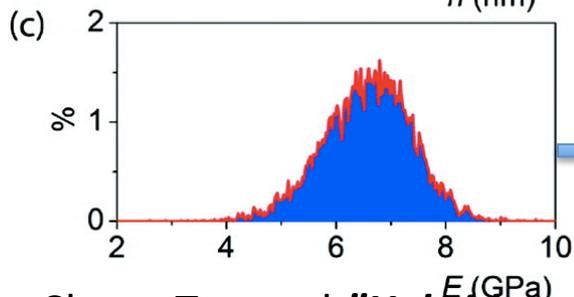


Multi-layer films

# Peak Force QNM of Inorganic –organic hybrid nanosheets



Deformation of the tip (Vertical displacement) 2,5 nm



Elastic or young's modulus- 6-7 GPa from the histogram

# Nano-Indentation Vs Peak force QNM-comparison

	Nano indentation	Peak force QNM
Model	Model varies for each system	In built model
Data analysis	Time consuming	Less time
Measured value	More precise	quantative
Sample preparation	Tedious	Flat substrate should be sufficient
Probe tip	Investigate before and after the measurement	Proper selection of the tip according to the system
Speedy of the experiement	Time consumption	Not as Nano-indentation

# Conclusions

**Nanoindentation** by AFM technique is very useful technique to precisely measure the mechanical properties of 2D structures compared to conventional test where their values are dominated by the defects, stacking faults and grain boundary in the 3D structures or nano tubes

**Peak Force QNM** is an useful technique for samples where there are two or three mixtures of components for example a bio-molecule between two nanosheets, mixtures of nanosheets , multi-layer films or surface termination in pervoskites etc