MAE Thematic Seminar
Jan. 21, 2025

Mechanics and Tribology of Nano-/Microscale Solid Interfaces:

From “Zero Friction” to Force-Driven Chemistry and Nanofracture

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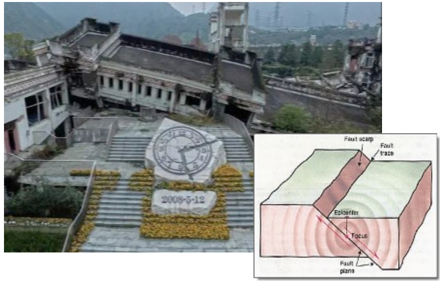
Mechanics and Tribology of Solid Interfaces

Tribology: the science and engineering of friction, adhesion, wear, and lubrication

Energy & Environment

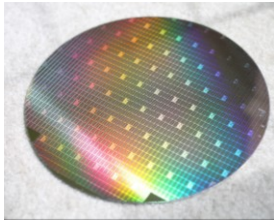
Machining & Processing

Microdevice



Natural disasters

Health care



Semiconductor manufacturing

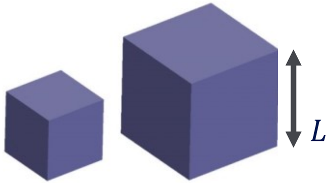
Economic impact:

- Friction consumes ~30% global primary energy;
- Wear causes ~80% machine failures;
- Economic loss: 2%~7% of GDP

H. Liu, et al, *Friction* 11, 839 (2023).

Solid Interfaces on Nano-/Microscales

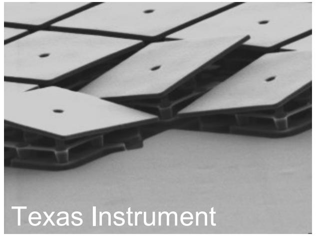
Why nano-/microscale?

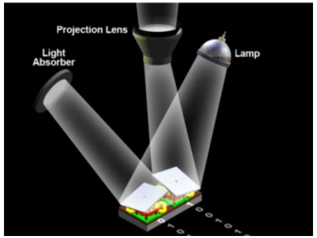


surface: $\sim L^2$

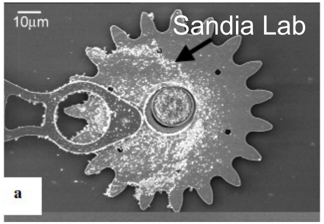
volume: $\sim L^3$

Surface-to-volume ratio

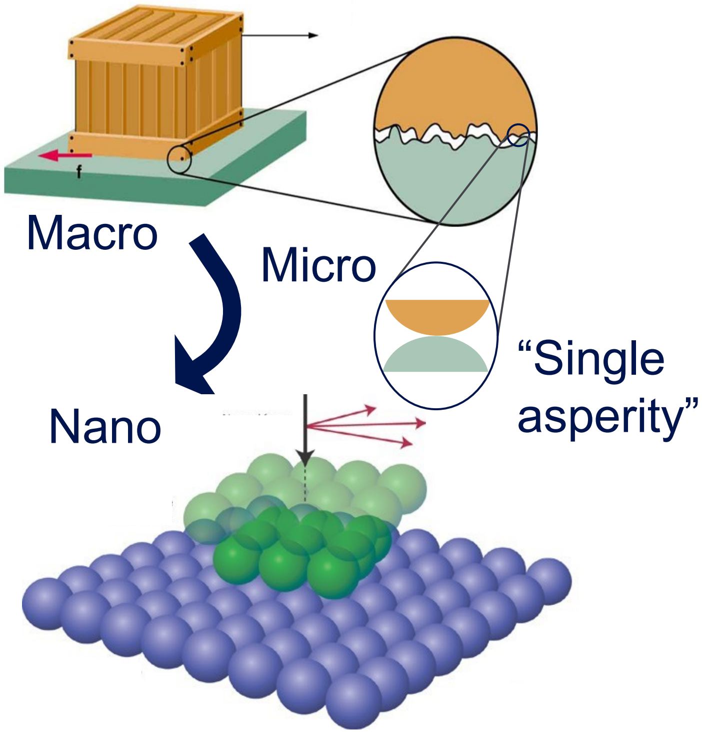




Digital micro-mirror arrays

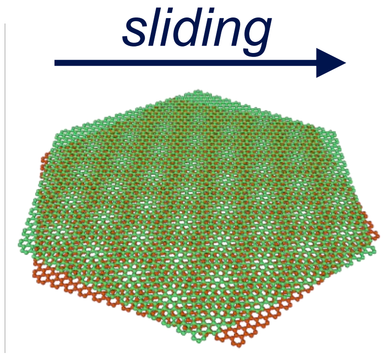


Tribology in microdevices



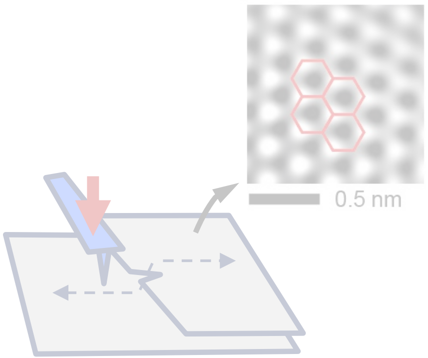
M. Urbakh & E. Meyer. *Nat. Mater.* 9, 8–10 (2010).

Outline



Structural Superlubricity

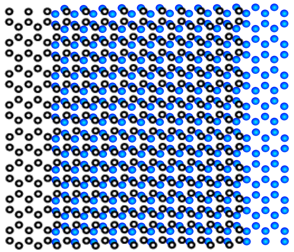
Mechano-chemistry



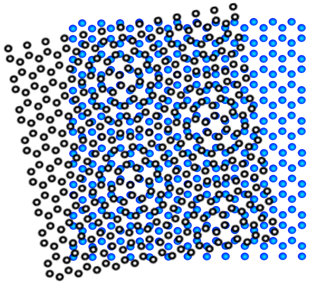
Nanofracture of 2D Materials

Structural Superlubricity: “Zero Friction” without Lubricants

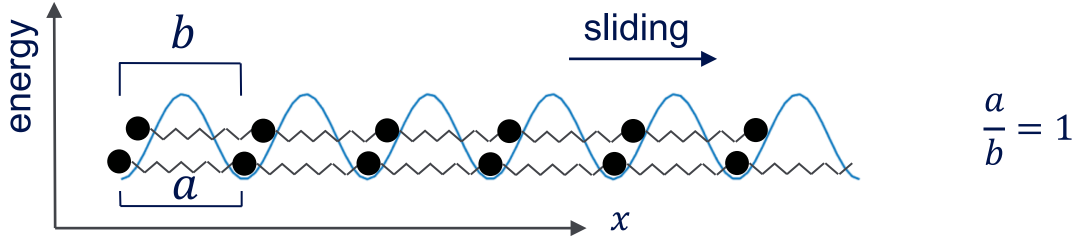
The atomic chain model:



Commensurate: high friction

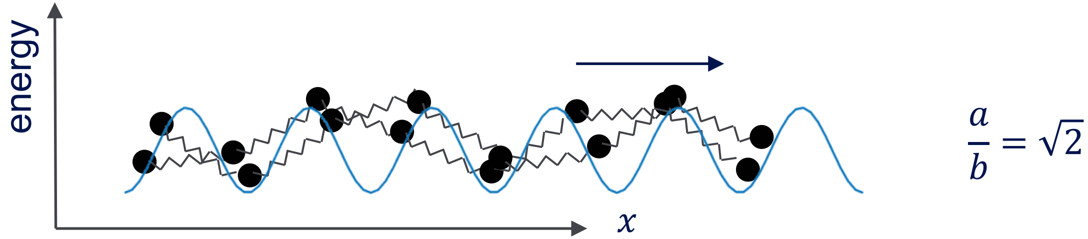


Incommensurate: superlubricity



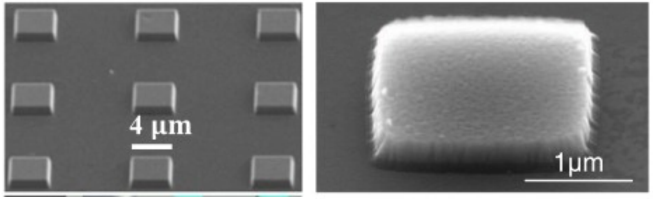
Each atom: $U(x_i) = U_0 \sin\left(\frac{x_i}{2\pi a}\right)$

Total potential: $U_{\text{tot}}(x) = NU(x_i)$ → friction ~ $-\frac{dU_{\text{tot}}}{dx}$

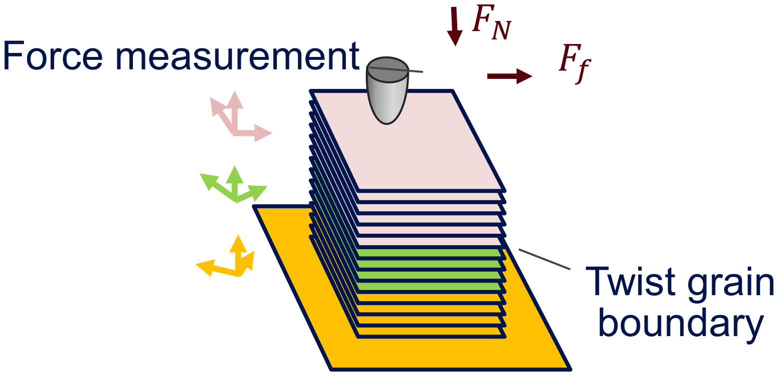


U_{tot} is **translational invariant**: no friction

The “Graphite Mesa” System



Z. Liu, et al. *Phys. Rev. Lett.* 108, 205503 (2012).

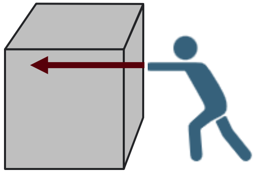


K. Wang, C. Qu*, J. Wang, B. Quan, and Q. Zheng*,
Phys. Rev. Lett. 125, 026101 (2020).

Friction measurement results:

- Superlubricity: ~0.01 MPa
- Shear strength (steel): 100~600 MPa

10 t weight, 1x1 m^2, 0.1% contact area

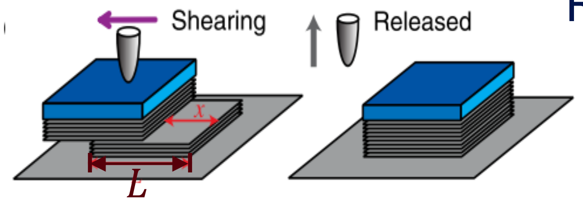


Force to move:

- Non-superlubric: 10 kN
- Superlubric:1 N

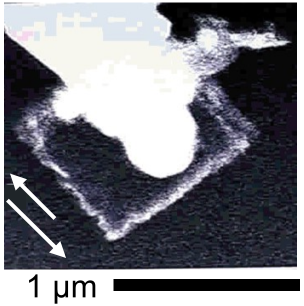
Unique Behaviors under Near-Zero Friction

The "self-retraction" motion:

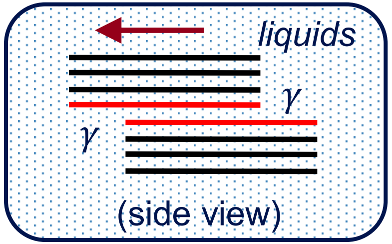


Retraction force:

$$F_{\mathrm{ret}} = -\frac{\partial U}{\partial x} \approx -2\gamma L$$



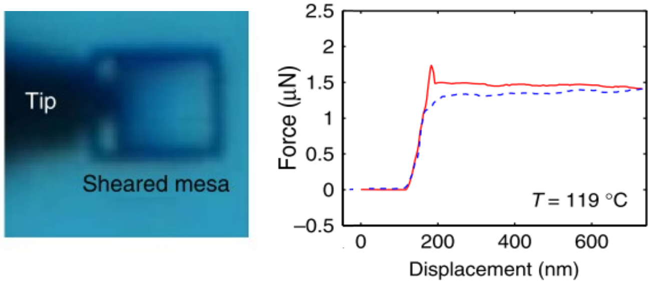
(top view)



Surface energy: γ

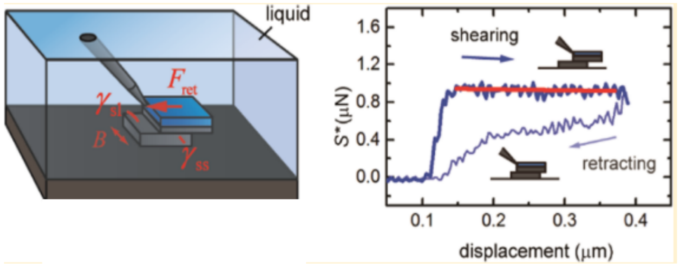
Q. Zheng, et al, *Phys. Rev. Lett.* 100, 067205 (2008).

measure **surface energy**



W. Wang, et al, *Nat. Commun.* 6, 7853 (2015).

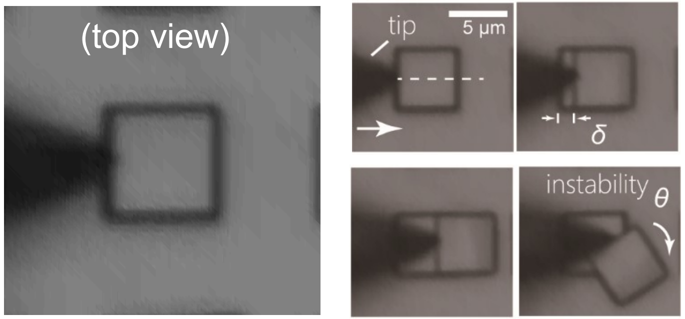
measure solid-liquid **interfacial energy**

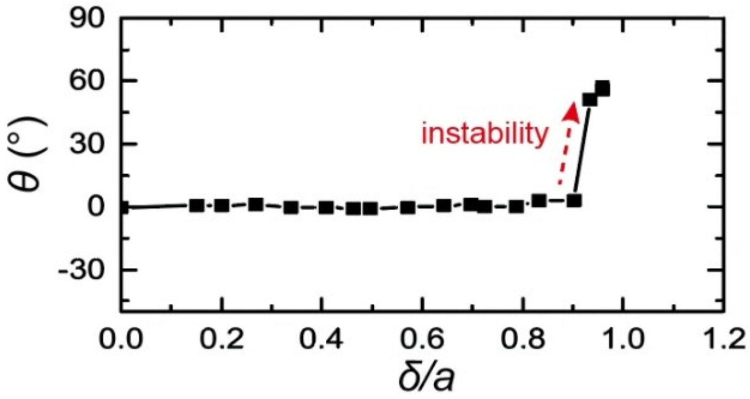


C. Qu, et al, *J. Phys. Chem. C* 123, 11671 (2019).

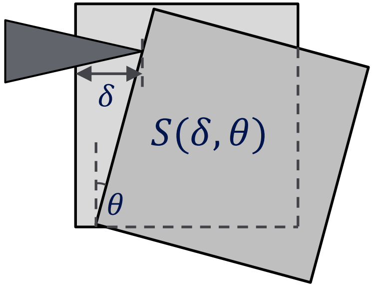
Unique Behaviors under Near-Zero Friction

The "rotational instability":



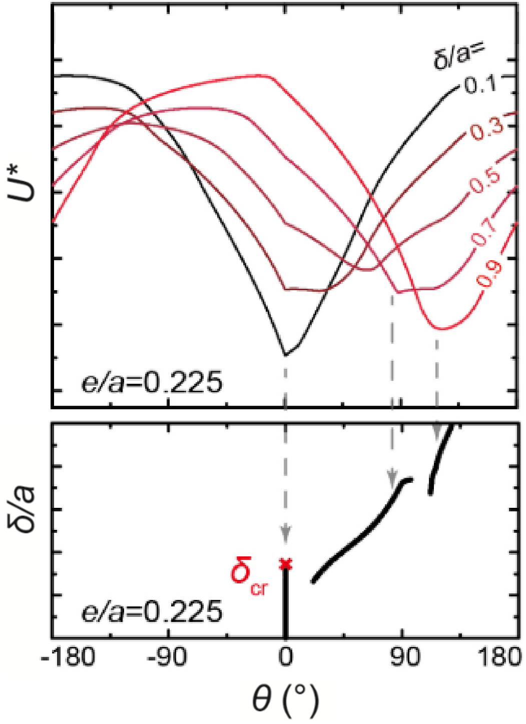


A simple mechanics model



$$U(\delta,\theta) \sim -2\gamma S(\delta,\theta)$$

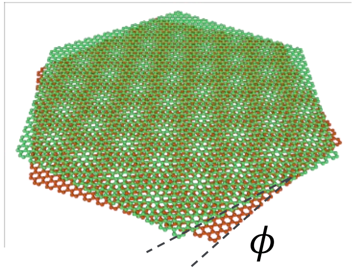
total free energy *overlapping area*



C. Qu, S. Shi, M. Ma, and Q. Zheng, *Phys. Rev. Lett.* 122, 246101 (2019).

Unique Behaviors under Near-Zero Friction

Controlling rotation is crucial:



Maintaining the misfit angle

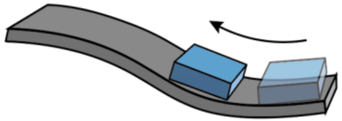
Friction force:

Commensurate

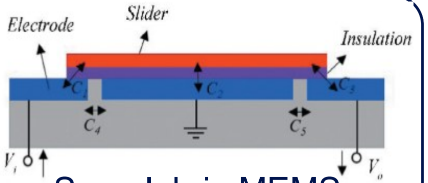
≈

10,000x incommensurate

Possible applications:



Superlubric “slider-track”



Superlubric MEMS (oscillator)

C. Qu, et al. *J. Harbin Inst. Technol.* 27, 45 (2020)

Highlighted by Nature Materials:

MATERIAL WITNESS

A new twist on superlubricity

Lubrication has traditionally relied on fluids and other additives to reduce frictional dissipation as one solid surface moves over another. But over the past decade or so it has become clear that dry sliding at the microscale can become almost frictionless when there is incommensurability in the atomic-scale structure of the two surfaces[1]. This effect was predicted in the 1980s[2], and dubbed superlubricity in 1991[3] — but only more recently have technological developments in microscale fabrication and manipulation advanced to the point where it can be seen and investigated.

so as to minimize the interfacial energy — something only possible when the frictional forces are so low that this interfacial energy becomes the dominant determinant of the structure’s configuration.

Quanshui Zheng of Tsinghua University — one of the authors of that earlier study — and co-workers have now uncovered a new aspect of this phenomenon. They find that a flake pushed in this manner may spontaneously rotate after it has moved a certain distance, in order to move into a lower-energy commensurate relationship with the lower surface[6]. Once the rotation

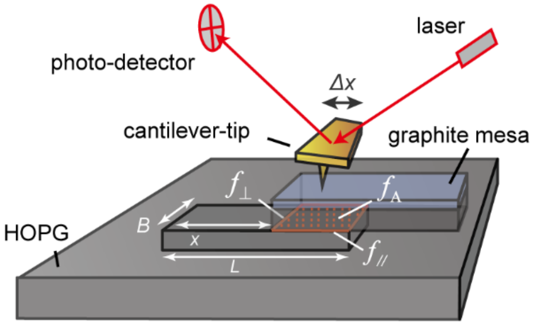
“ … *understanding this rotational effect in superlubricity should* ***enable it to be controlled****, … for a rectangular flake sliding almost friction-free along a ‘guide rail’ … the slider* ***literally stays on track****.”*

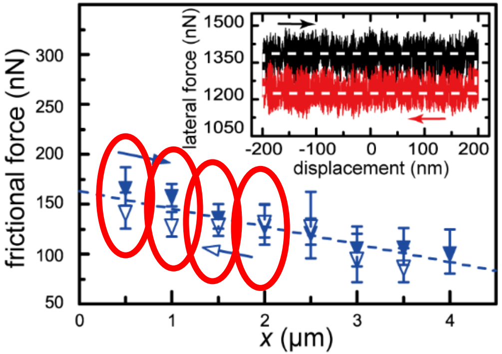
Nature Materials. 18 (8), 774-774 (2019).

Contact Edges in Superlubricity

Where does the non-zero friction come from?

Atomic force microscope (AFM)



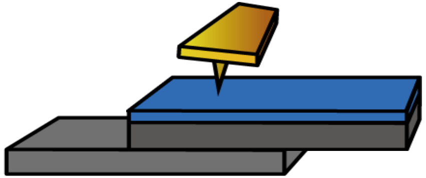


Contact area: $A = B(L - x)$

Contact edge length:

$C = 2(L - x) + 2B$

$$F_f = f_{\text{area}}A + f_{\text{edge}}C$$



Edge atom: 1.1 ± 0.1 pN/atom

Inner atom: -0.05 ± 0.05 fN/atom

≈ 0 *in current noise level*

Edge atoms:

10,000x larger friction than inner atoms

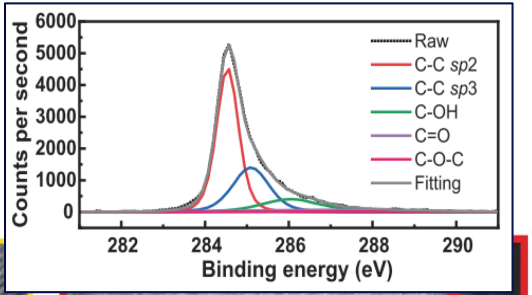
1st experiment to decouple edge- and area-induced friction

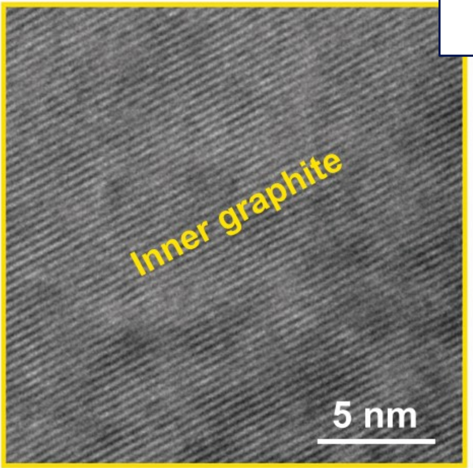
C. Qu, K. Wang, J. Wang, Y. Gongyang, R. W. Carpick, M. Urbakh, and Q. Zheng, *Phys. Rev. Lett.* 125, 126102 (2020).

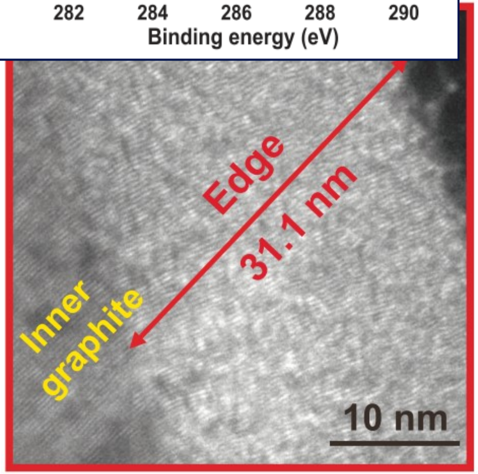
Implications of Edge-Dominated Friction

Edge characterizations

- Distorted layer
- sp^2, sp^3
- O-groups



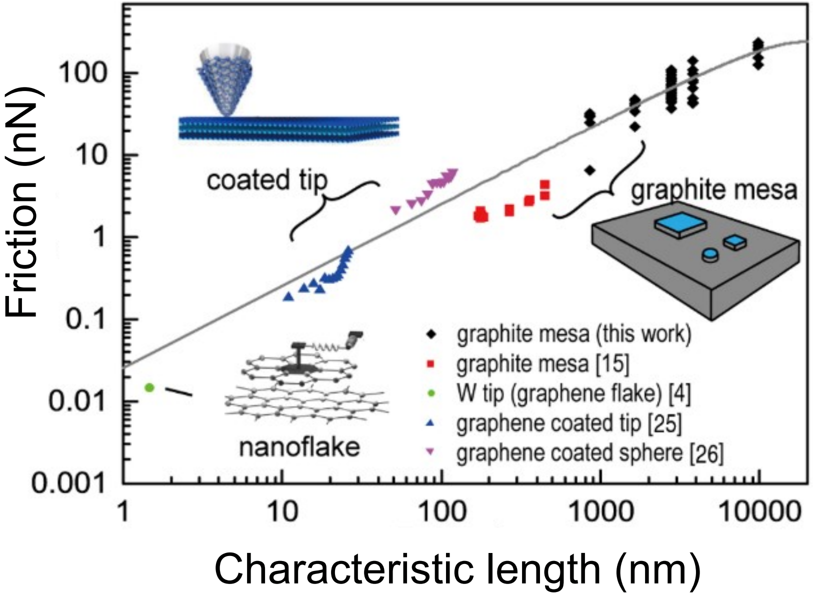




H. Hu, et al. *Nat. Commun.* 15, 1 (2024).

Scaling law of superlubricity

$$F_f = f_{\mathrm{area}} L^2 + f_{\mathrm{edge}} L$$



C. Qu, et al. *Phys. Rev. Lett.* 125, 126102 (2020).

Defects Limit the Size of Superlubricity

Superlubricity fails for large contacts !

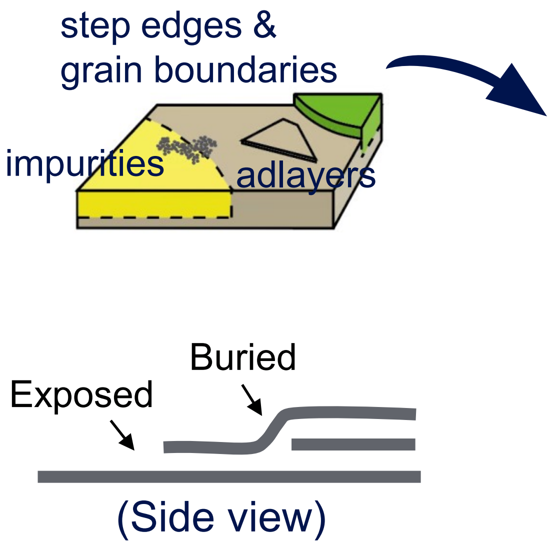
Current limit: ~20 μm

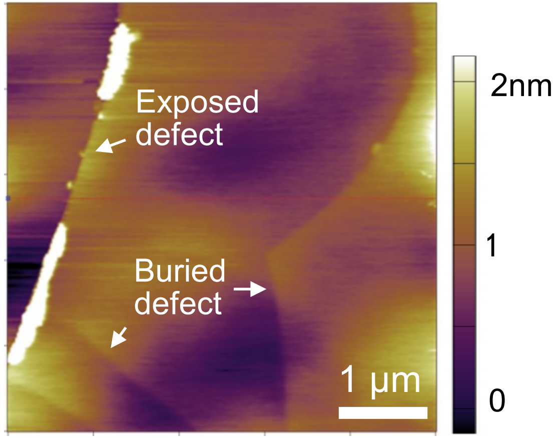
Structure-property relation:

(1). No defects → √

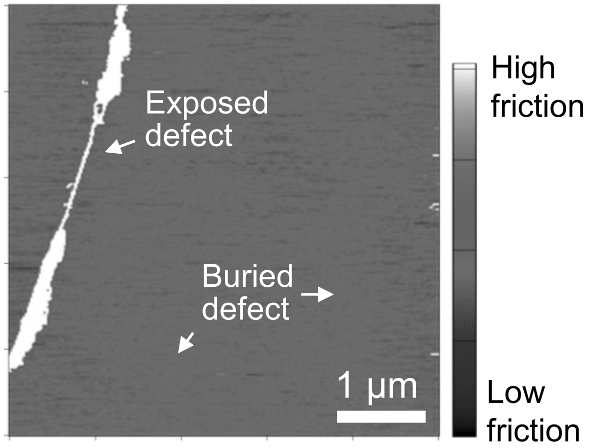
(2). Buried defects → √

(3). Exposed defects → ✕





Surface height image



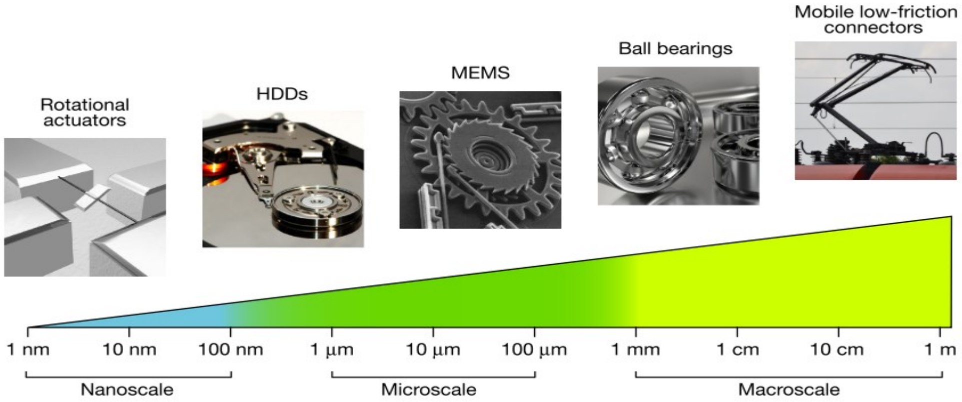
Friction image

- K. Wang, C. Qu*, J. Wang, B. Quan, and Q. Zheng*, *Phys. Rev. Lett.* 125, 026101 (2020).
- D. Yang, C. Qu*, Y. Gongyang, and Q. Zheng*, *ACS Appl. Mater. Interfaces* 15, 44563 (2023).

Opportunities and Challenges

Scaling-up of superlubricity

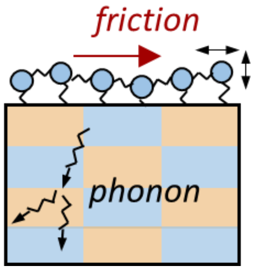
- Superlubric material fabrication
- Device development with current size constraints



O. Hod, E. Meyer, Q. Zheng & M. Urbakh *Nature* 563, 485–492 (2018).

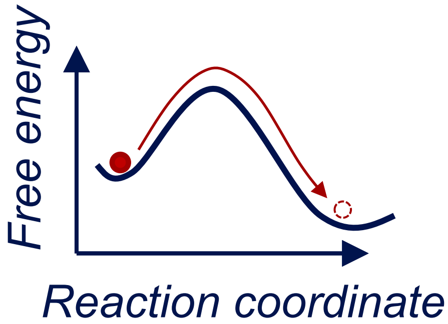
New friction control paradigms

- Energy transport & dissipation
- Overlapping classical/quantum mechanics
- Relatively unexplored, potential for new discoveries

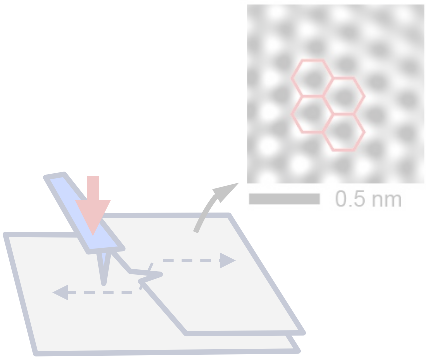


Outline

Structural Superlubricity



Mechano-chemistry



Nanofracture of 2D Materials

Mechanochemistry: Force-Driven Reactions

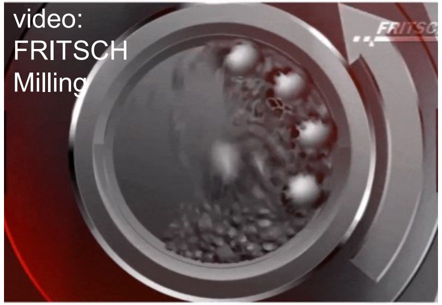
Mechanochemistry: chemical reactions modified by force and stress

- Green chemistry:
  - Environmentally friendly
  - High efficiency
- One of ten "*emerging technologies in chemistry*" (2019, IUPAC)

Chemical synthesis:

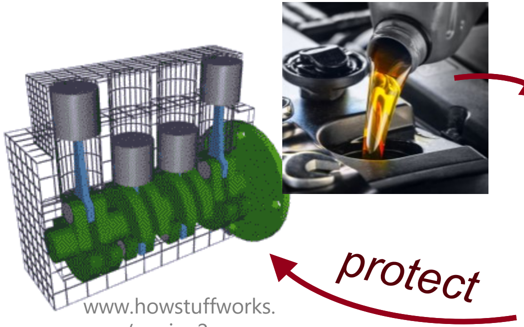
HgS+Cu→Hg+CuS

~4th century B.C.

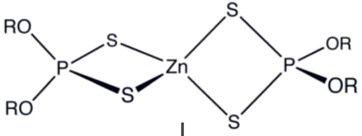


Modern reactor

Mechanical interfaces:



Zinc dialkyldithiophosphates (ZDDP)



T, σ

In-situ **anti-wear coating**

Mechanochemistry: Force-Driven Reactions

Mechanochemistry: chemical reactions modified by force and stress

- Green chemistry:
  - Environmentally friendly
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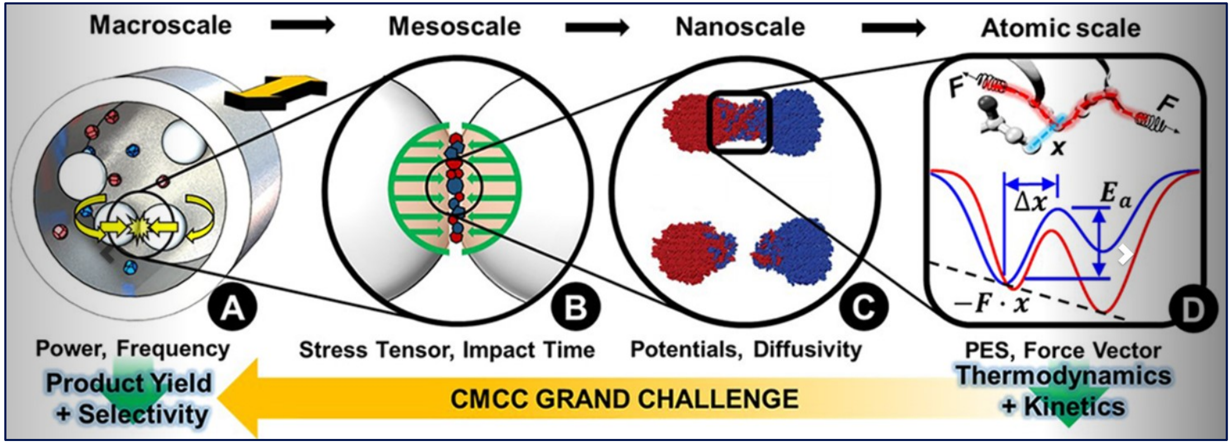
- One of ten “*emerging technologies in chemistry*” (2019, IUPAC)



https://www.chem.tamu.edu/cmcc/

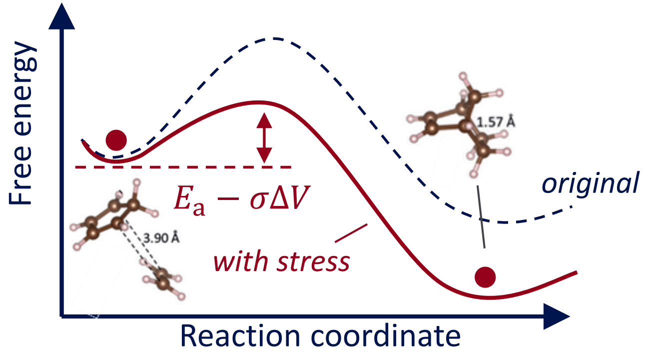
Example:

US NSF - *Center for the Mechanical Control of Chemistry*

- Collaboration: 10+ institutes
- $20+ million total funding
- 2-phase project 2020-2028

Mechanism and Knowledge Gap

Theory: thermal activation



Activation volume

Stress

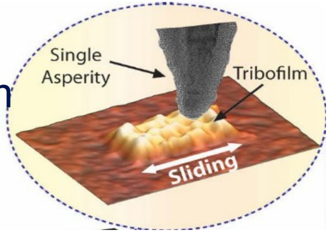
$$\Gamma = \Gamma_0 \exp\left(-\frac{E_a - \sigma\Delta V}{k_B T}\right)$$

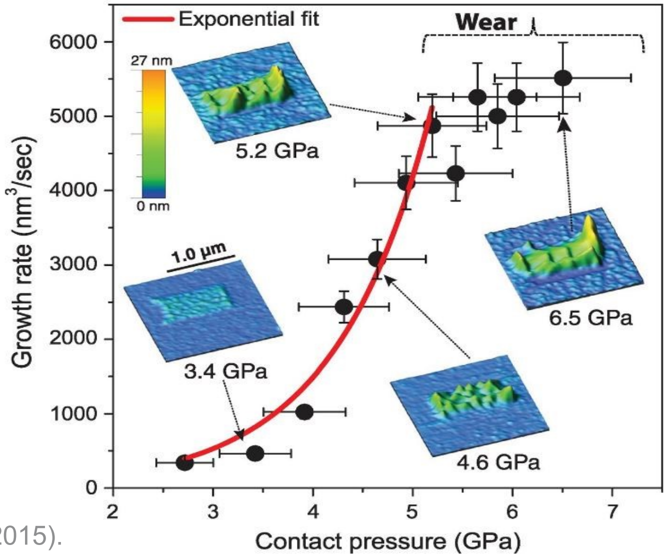
Reaction rate

Thermal energy

Nanoscale experiments

ZDDP film growth





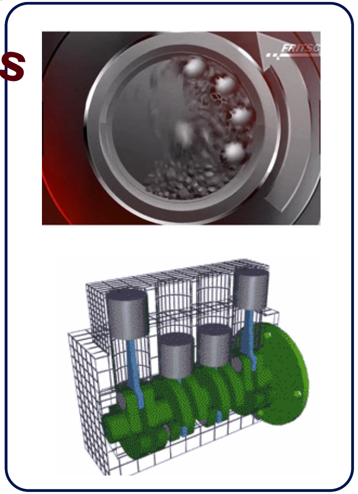
- N. N. Gosvami, et al, *Science*. 348, 102 (2015).

Contact mechanics

?

Gap

Macroscale

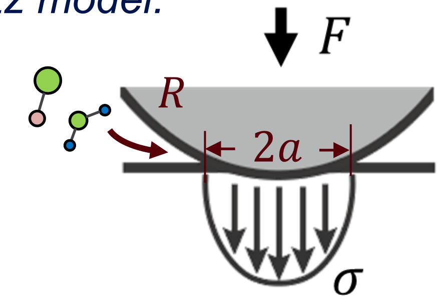


Engineering Interface:

- Geometry & deformation
- Complicated stress state
- Hard to measure/control

Adding Contact Mechanics to Mechanochemistry

Hertz model:



#1 Contact radius:

$$a = \frac{3R\pi}{4E^*}\sigma_{\mathrm{m}}$$

#2 Stress distribution:

$$\sigma(r) = \frac{3}{2}\sigma_{\mathrm{m}}\sqrt{1-\left(\frac{r}{a}\right)^2}$$

R: ball radius
a: contact radius
σ_{m}: mean stress
E^*: reduced Young's modulus
ρ: reactant areal concentration
Γ: reaction rate
Γ_0: pre-factor

Reaction rate: $\Gamma = \iint_A \rho\Gamma_0 e^{-\frac{E_{\mathrm{a}}-\sigma\Delta V}{k_B T}}\,\mathrm{d}A$

$$\longrightarrow \quad \Gamma = \boxed{\int_0^a}\rho\Gamma_0 e^{-\frac{E_{\mathrm{a}}-\Delta V\boxed{\sigma(r)}}{k_{\mathrm{B}}T}}\,2\pi r\mathrm{d}r$$

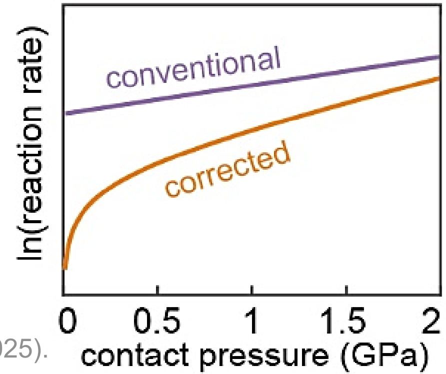
#2: Stress distribution

#1: Contact radius

$$\left(\lambda = \frac{3\Delta V}{2k_{\mathrm{B}}T}\right)$$

$$\longrightarrow \quad \Gamma = \frac{\pi^3}{2}\rho\Gamma_0 e^{-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}}\left(\frac{Rk_{\mathrm{B}}T}{E^*\Delta V}\right)^2\left[1+e^{\lambda\sigma_{\mathrm{m}}}(\lambda\sigma_{\mathrm{m}}-1)\right]$$

The "contact-mechanics-corrected" model



Compare with conventional:

$$\Gamma = \Gamma_0 \exp\left(-\frac{E_{\mathrm{a}}-\sigma_{\mathrm{m}}\Delta V}{k_{\mathrm{B}}T}\right)$$

- C. Qu, L. Fang, and R. W. Carpick, *Phys. Rev. B* 111, 195405 (2025).

Reliable Measurement of ΔV: The Problem

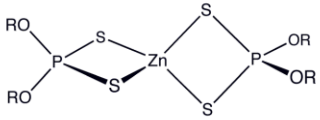
Problem: literature values of activation volume scatter by a lot!

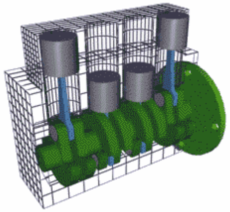
$$\ln\Gamma = \boxed{\frac{\Delta V}{k_B T}}\sigma + \ln\Gamma_0 - \frac{E_a}{k_B T}$$

Examples:

Growth of antiwear film from ZDDP

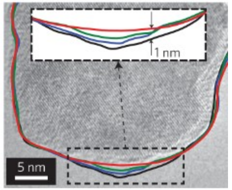
$\boldsymbol{\Delta V = 3.8\sim180\ \text{Å}^3}$

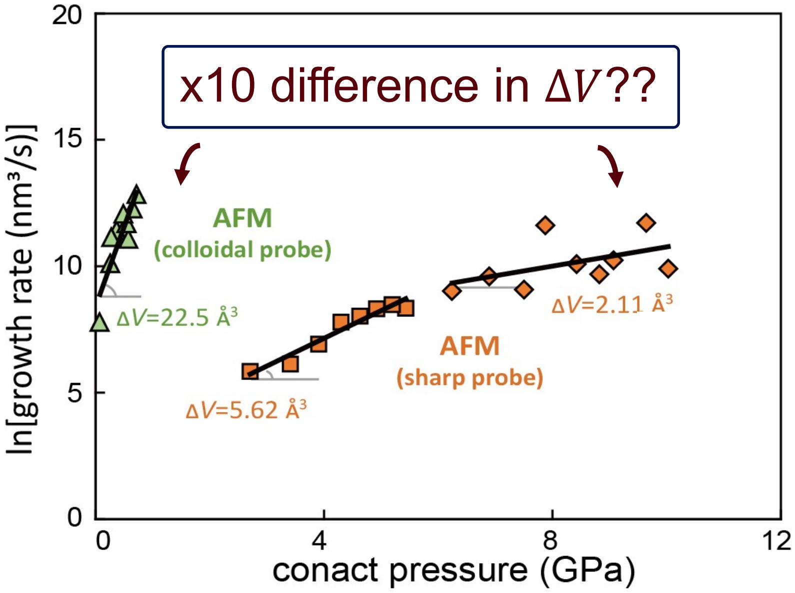




Tribochemical material removal (wear) of Si:

$\boldsymbol{\Delta V = 6.7\sim60\ \text{Å}^3}$



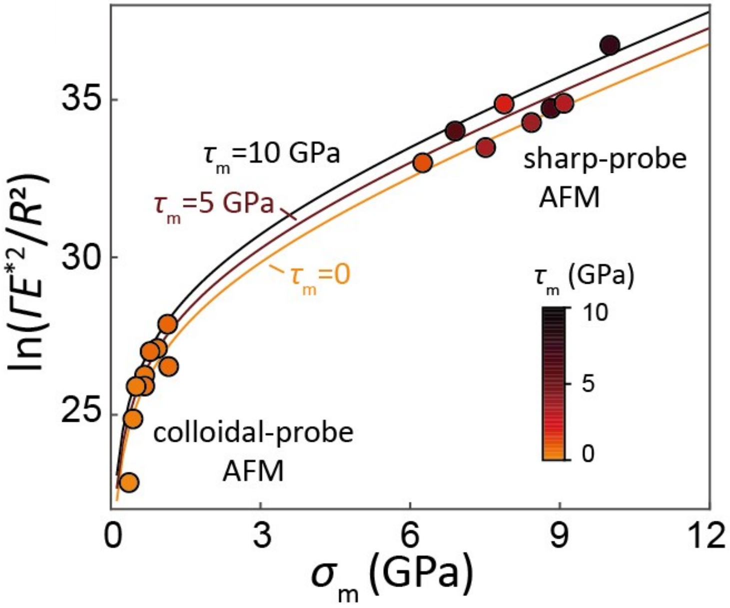


- A. Martini and S. H. Kim, *Tribol. Lett.* 69, 150 (2021).
- T. D. B. Jacobs and R. W. Carpick, *Nat. Nanotechnol.* 8, 108 (2013).
- C. Qu, L. Fang, and R. W. Carpick, *Phys. Rev. B* 111, 195405 (2025).

Reliable Measurement of ΔV: The Solution

The new "contact-mechanics-corrected" model:

$$\ln\left(\frac{\Gamma {E^*}^2}{R^2}\right) = F(\sigma_\mathrm{m}, \tau_\mathrm{m}, T; \Delta V_\mathrm{n}, \Delta V_\mathrm{s})$$



Unified values for activation volume:

Fitting to new model:

$\Delta V_\mathrm{n} = -2.08 \pm 0.36$ Å^3

$\Delta V_\mathrm{s} = 0.43 \pm 0.57$ Å^3

→ $\Delta V_\mathrm{eff} = \mu_\mathrm{m}\Delta V_\mathrm{s} - \Delta V_\mathrm{n} = \boxed{2.3 \text{ Å}^3}$

Previous results:

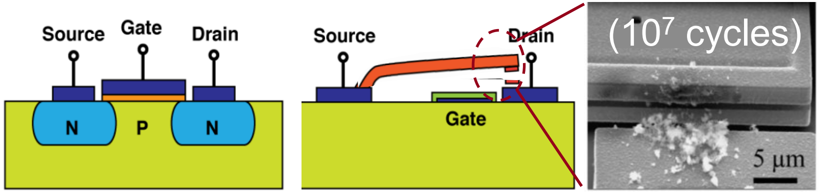
$\Delta V_\mathrm{eff} = 2.1$ Å^3~$\boxed{22.5 \text{ Å}^3}$

over-estimated!

- C. Qu, L. Fang, and R. W. Carpick, *Phys. Rev. B* 111, 195405 (2025).

Application in Nano-Electro-Mechanical Systems (NEMS)

Background:

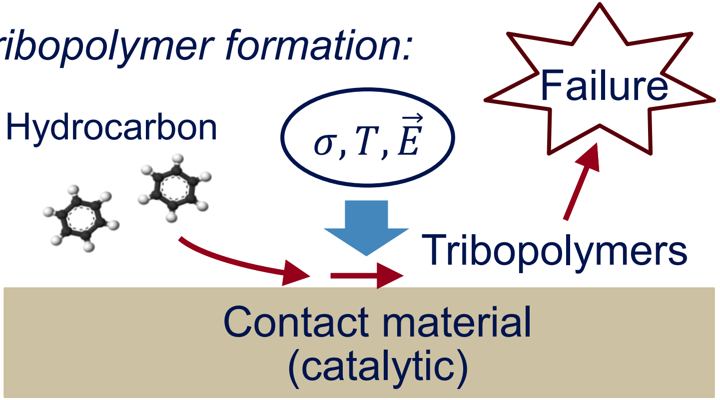


Solid-state transistor

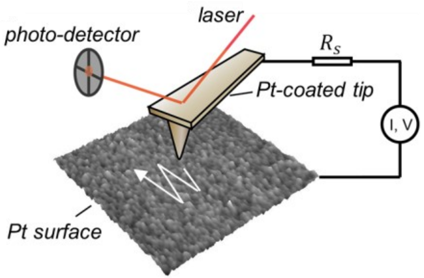
NEMS switch

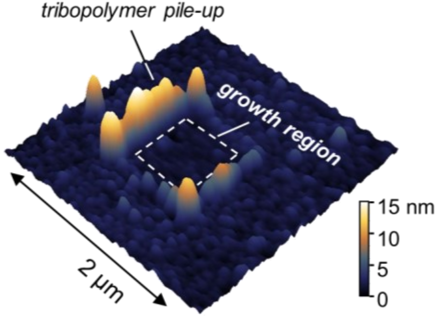
Tribol. Int. 85, 48 (2015)

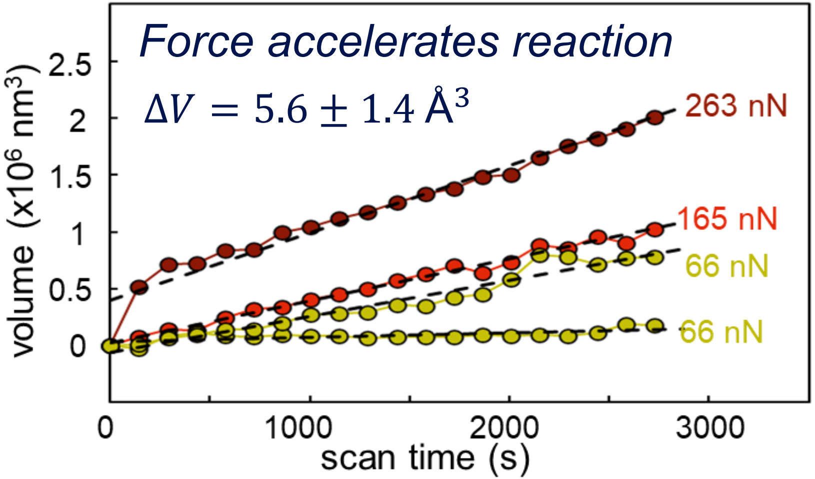
Tribopolymer formation:



AFM experiment:



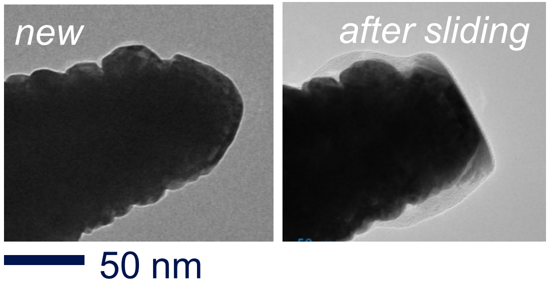


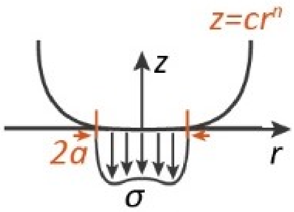


- C. Qu, R. W. Carpick (under review in *ACS Appl. Mater. Interfaces*)

Application to Nano-Electro-Mechanical Systems (NEMS)

Extending the contact-mechanics-corrected model to flattened tips:



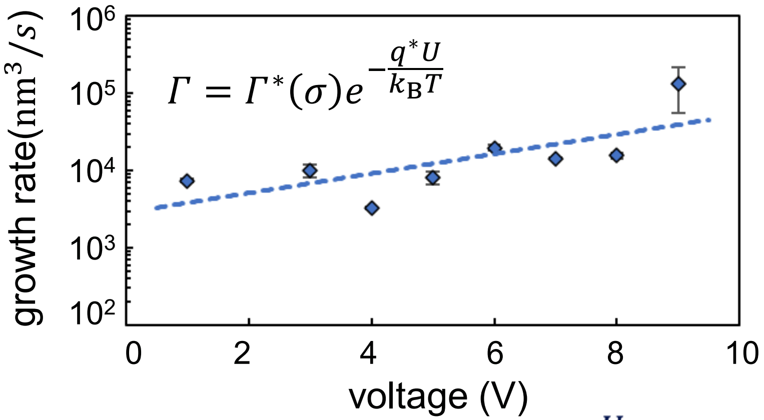


Power-law shaped tip:

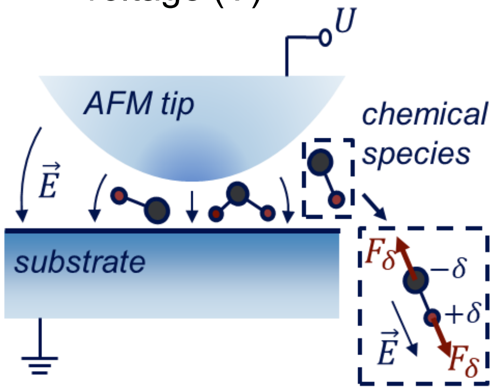
$$z = cr^n$$

$$\Gamma = \underbrace{2\pi A_0 \left(\frac{\pi}{E^*\kappa(n)c}\cdot\frac{n+1}{2n}\right)^{\frac{2}{n-1}} e^{-\frac{E_a}{k_BT}}}_{\text{constant}} \cdot \underbrace{\sigma_{\mathrm{m}}^{\frac{2}{n-1}}\int_0^1 e^{\frac{\Delta V^*\sigma_{\mathrm{m}}\cdot\Sigma(n;\xi)}{k_BT}}\xi\,\mathrm{d}\xi}_{\text{function of } \sigma_{\mathrm{m}}}$$

Effect of voltage:



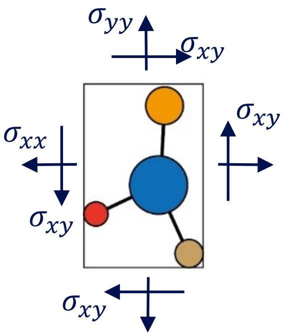
Bond-stretching model



- C. Qu, R. W. Carpick (under review in *ACS Appl. Mater. Interfaces*)

Opportunities and Challenges

The activation volume tensor:



Hydrostatic P:

(IUPAC definition, 1994)

$\Delta V = V_{\text{transition}} - V_{\text{initial}}$

General σ_{ij}:

$$\underline{\Delta V_{ij}} = \left(\frac{\partial \Delta G}{\partial \sigma_{ij}}\right)_T \underline{\sim \varepsilon_{ij}}$$

experiment simulation

Mechanochemistry of rough interface:

$$\left(\xi_{\sigma_0} = \frac{\sigma_0}{E^*\sqrt{m}}, \xi_{\sigma_Y} = \frac{\sigma_Y}{E^*\sqrt{m}}, \xi_{\Delta V} = \frac{\Delta V E^* \sqrt{m}}{k_B T}\right)$$

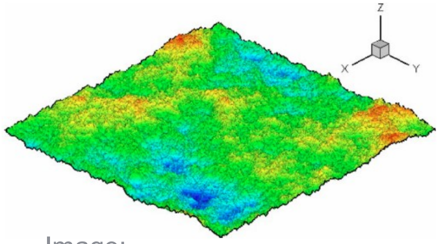


Image:
S. Hyun, et al, *Phys. Rev. E* 70, 12 (2004)

Plastic: $\Gamma \sim \frac{\xi_{\sigma_0}}{\xi_{\sigma_Y}} \cdot e^{\xi_{\Delta V}\xi_{\sigma_Y}}$

Elastic: $\Gamma \sim \frac{2}{\pi}\xi_{\sigma_0} h(\xi_{\Delta V})$

$\Gamma \sim e^{\xi_{\Delta V}\xi_{\sigma_0}}$

C. Qu, R. W. Carpick (in preparation)

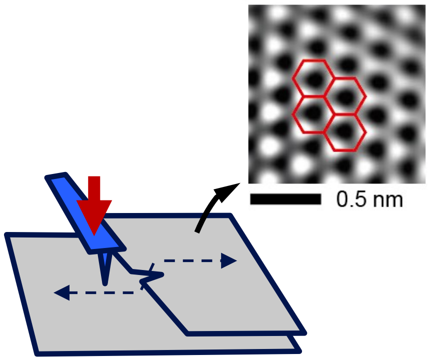
Goal:

- To make mechanochemistry understandable and predictable
- New methods, new designs, better performance

Outline

Structural Superlubricity

Mechano-chemistry



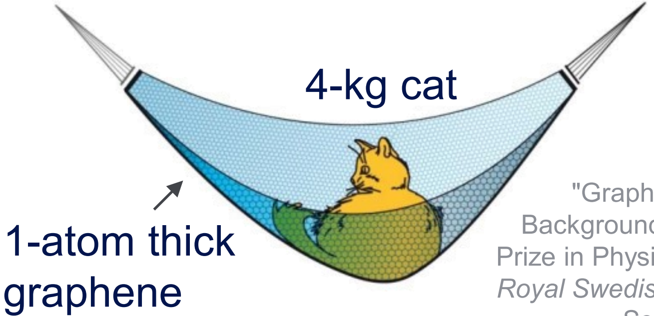
Nanofracture of 2D Materials

Nanofracture of 2D materials

Mechanical properties of graphene:

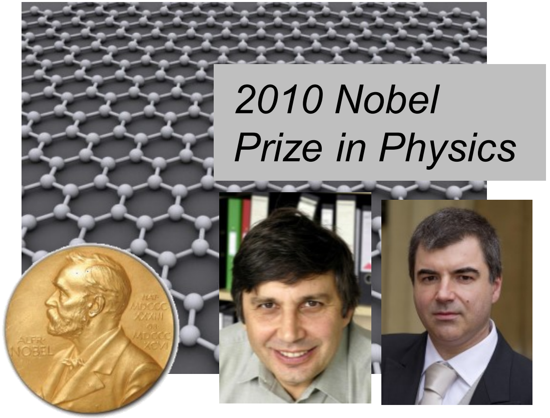
Young’s modulus: ~1 TPa (>5x steel)

Strength: ~130 GPa (>100x steel)



"Graphene: Scientific Background on the Nobel Prize in Physics 2010." *The Royal Swedish Academy of Sciences* (2010).

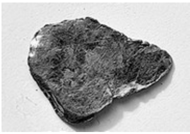
Mechanical exfoliation to fabricate graphene:



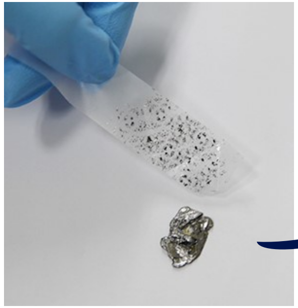
A. Geim & K. Novoselov

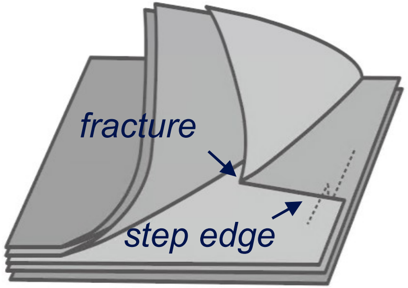
Adhesive tape

Graphite



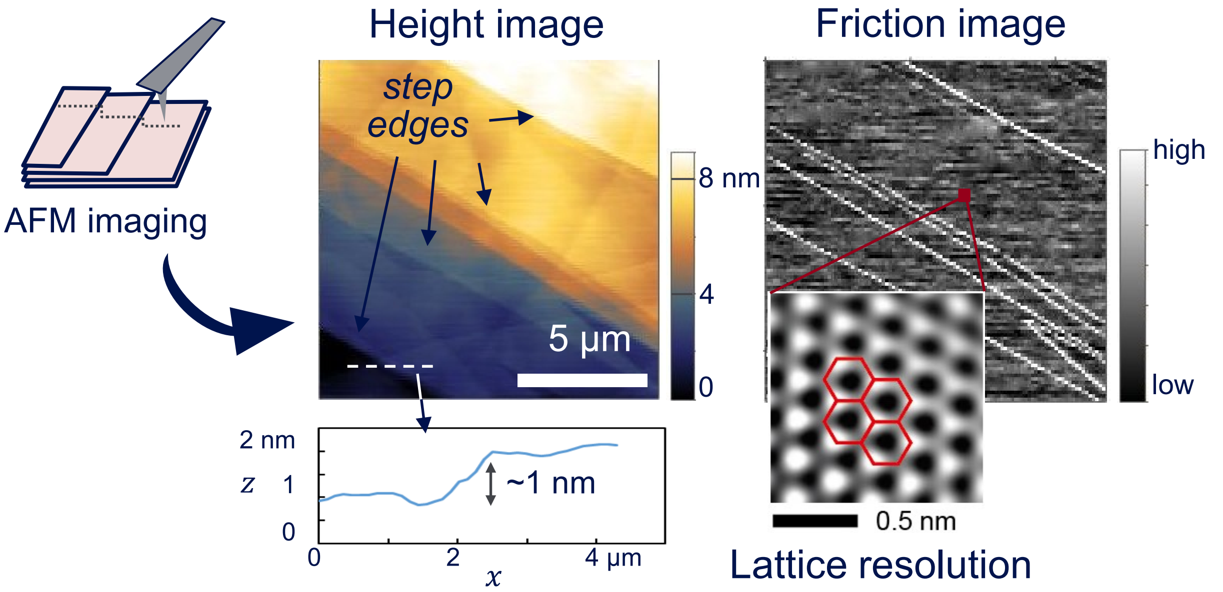
Mechanical exfoliation





A New AFM Approach

Step edges as imaged by atomic force microscopy (AFM):



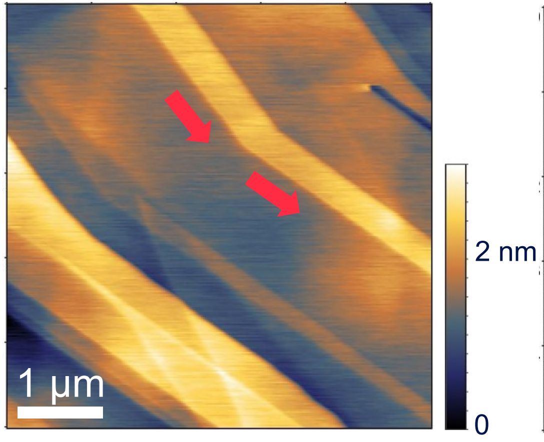
A new AFM approach:

- High-throughput
- High spatial resolution (sub-nanometer)
- Combining mechanics models

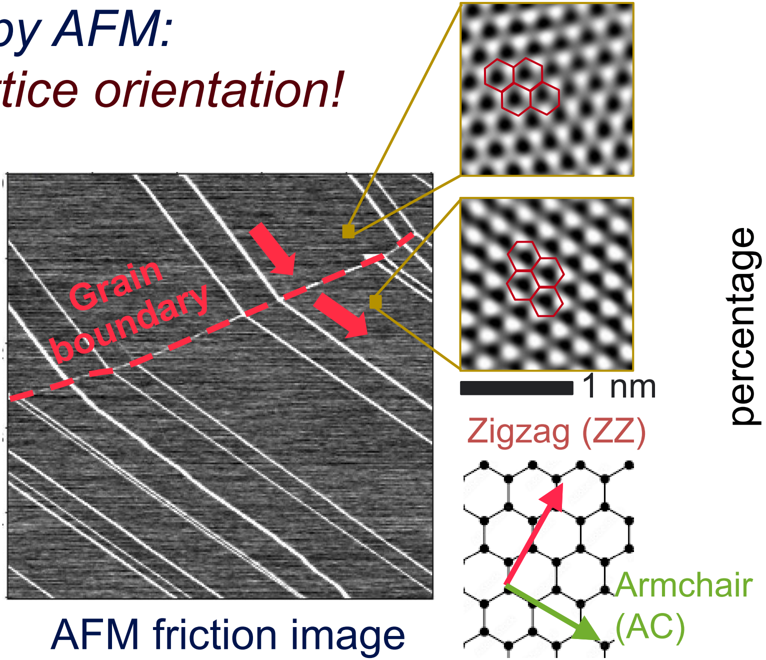
- C. Qu, et al. *Phys. Rev. Lett.* 129, 026101 (2022).

Study 1: Anisotropic Fracture of Graphene

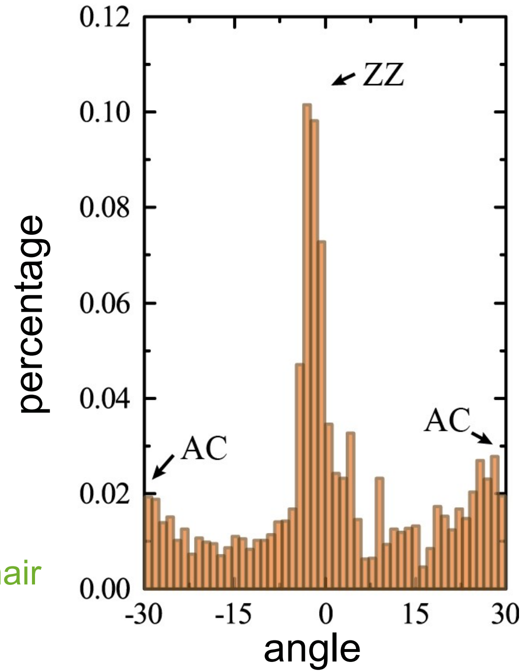
Step edges as imaged by AFM:
They follow a certain lattice orientation!



AFM height image



AFM friction image

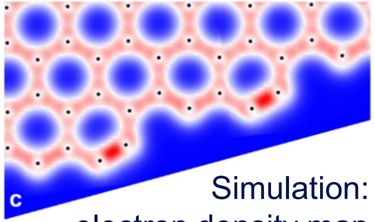


Large dataset:
~100 grains,
~3000 step edges

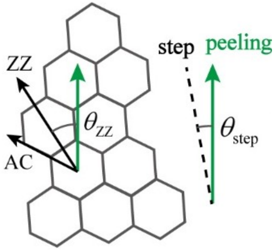
This means:
The in-plane fracture of graphene is anisotropic

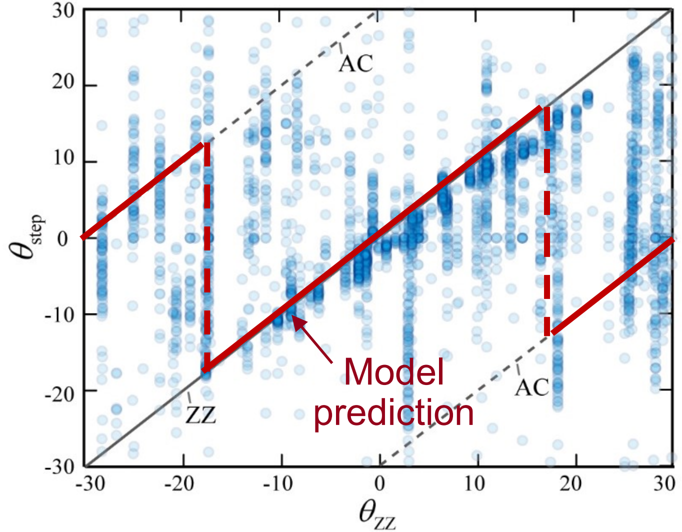
- C. Qu, et al. *Phys. Rev. Lett.* 129, 026101 (2022).

Mechanics Modelling



Simulation:
electron density map





Anisotropic fracture toughness:

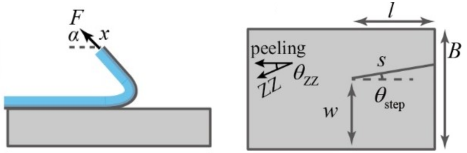
$$G_c(\theta) = 2\gamma(\theta) \sim \gamma_{AC} \sin\theta + \gamma_{ZZ} \sin(30° - \theta)$$

Y. Liu, A. Dobrinsky, and B. I. Yakobson, *Phys. Rev. Lett.* 105, 235502 (2010).

Energy analysis:

$$U = U_{\mathrm{E}} + 2\gamma ts/d + \tau Bl$$

Elastic energy *Edge energy* *Delamination energy*



Equilibrium crack extension & max energy release rate:

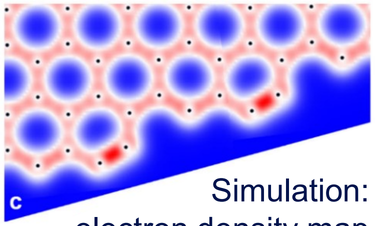
$\partial U/\partial s = 0, \ldots$ → *Criterion for crack direction:*

$$\theta_{\mathrm{peel}} - \theta_{\mathrm{ZZ}} \gtrsim \tan^{-1}\left(2\frac{\gamma_{\mathrm{AC}}}{\gamma_{\mathrm{ZZ}}} - \sqrt{3}\right)$$

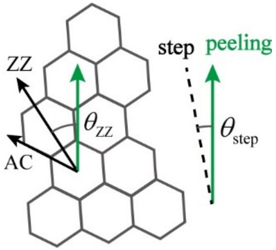
External force Lattice orientation Fracture anisotropy

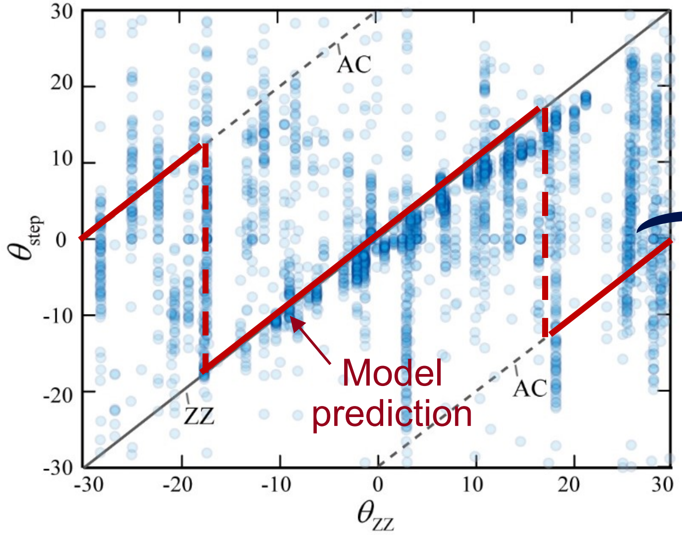
- C. Qu, et al. *Phys. Rev. Lett.* 129, 026101 (2022).

Mechanics Modelling



Simulation:
electron density map





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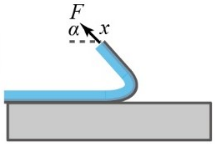
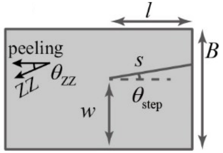
Elastic energy *Edge energy* *Delamination energy*





Equilibrium crack extension & max energy release rate:

$\partial U/\partial s = 0, \ldots$

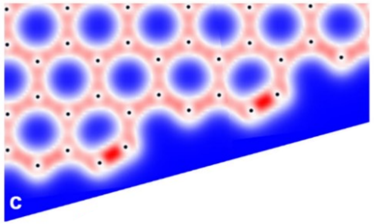
A measurement on graphene's fracture toughness anisotropic factor

$$\frac{G_{\mathrm{ZZ}}}{G_{\mathrm{AC}}} = \frac{\gamma_{\mathrm{ZZ}}}{\gamma_{\mathrm{AC}}} = 0.971$$

- C. Qu, et al. *Phys. Rev. Lett.* 129, 026101 (2022).

Implications of the Anisotropic Fracture

Edge atom density & energy



$$\frac{\rho_{ZZ}}{\rho_{AC}} = \frac{\sqrt{3}}{2} \approx 0.866$$

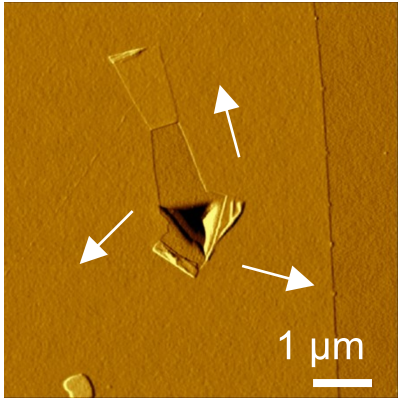
$$\frac{\gamma_{ZZ}}{\gamma_{AC}} = 0.971$$

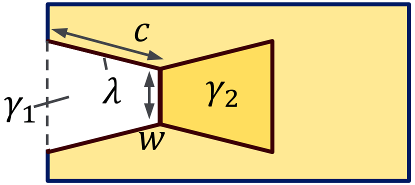
Benchmark for simulations

Method	γ_{ZZ}/γ_{AC}
Experiment (present work)	0.971
Density functional theory	0.95~1.34
Molecular dynamics	0.69~1.05

- C. Qu, et al. *Phys. Rev. Lett.* 129, 026101 (2022).
- H. Yin, et al. *Nano Lett.* 15, 1918 (2015).
- C. K. Gan and D. J. Srolovitz. *Phys. Rev. B* 81, 125445 (2010).
- Y. Liu, A. Dobrinsky, and B. I. Yakobson. *Phys. Rev. Lett.* 105, 235502 (2010).
- P. Zhang et al. *Nat. Commun.* 5, 3782 (2014).

Spontaneous self-assembly of graphene





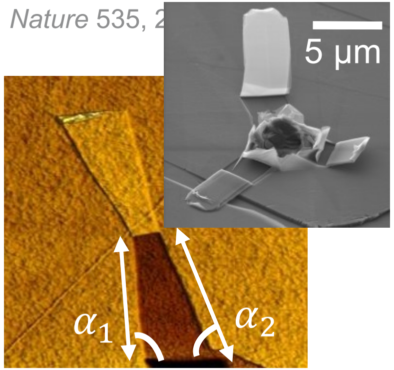
$$(\gamma_2 - \gamma_1)\frac{w\delta l}{\delta c} \geq \frac{\delta U_{\mathrm{fold}}}{\delta c} + 2\lambda$$

Surface energy *Elastic energy* *Fracture energy*

- J. Annett and G. L. W. Cross, *Nature* 535, 2

- Anisotropic fracture energy $\lambda(\alpha)$
- Controlled self-cutting

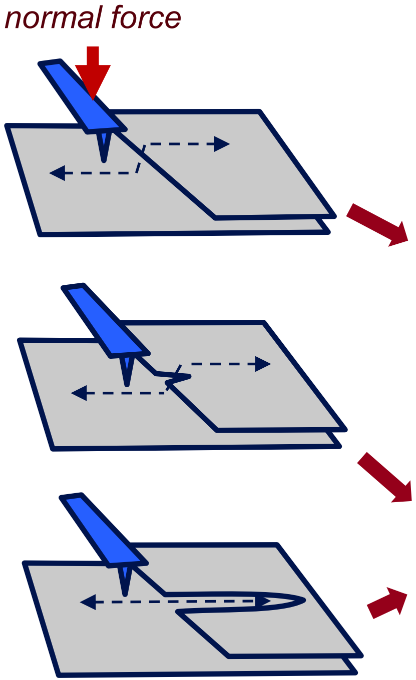
L. Capaldi, L. Yuan, C. Qu, D. Sanchez, R. Carpick, O. Tertuliano, (under review in Nano Lett.)



Study 2: Detecting Fracture Initiation with AFM

Fracture initiation in step edges:

1. Reciprocal scanning at a fixed location (cutting attempts)



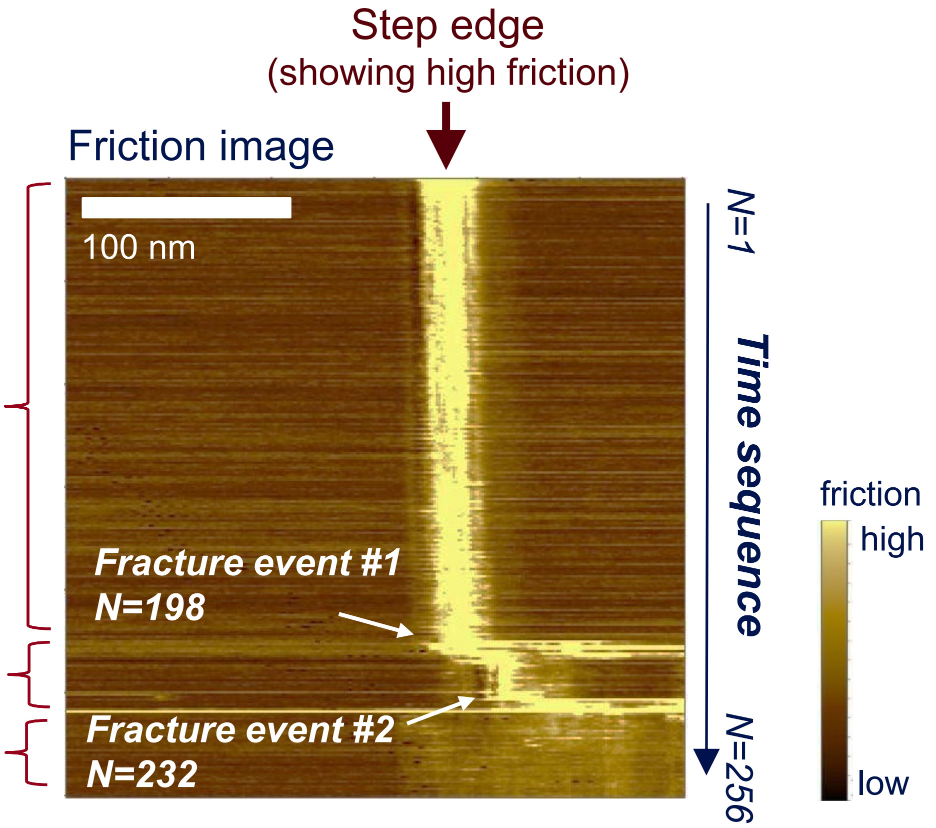
2. Fracture event detected (N=198)

fracture initiation rate:

$f \stackrel{\text{def}}{=} 1/t$

(t: time exposed to stress)

3. Further fracture events

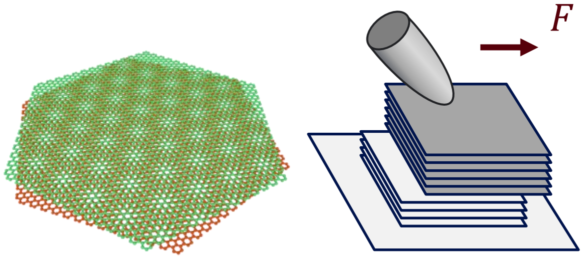


- C. Qu, E. Acosta, R.W. Carpick (in preparation)

Summary

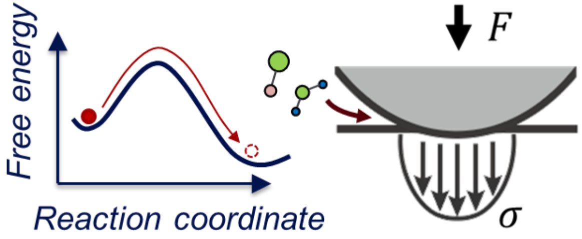
Structural superlubricity

- ❑ Achieving “zero friction” without lubricants
- ❑ Unique behaviors at “zero friction”
- ❑ Mechanisms & limitations (edge, defects, size)



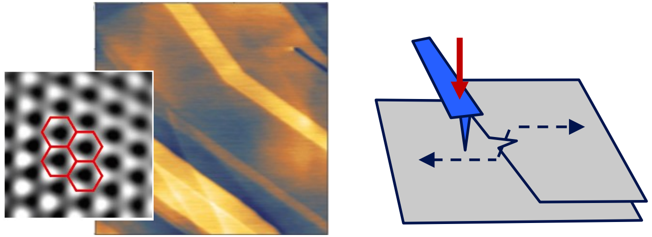
Mechanochemistry

- ❑ Green synthesis & engineering interfaces
- ❑ New insight: contact mechanics + mechanochemistry



Nanofracture of 2D Materials

- ❑ A new AFM-based experimental approach
- ❑ Fracture anisotropy ❑ Fracture initiation



Acknowledgements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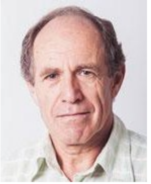
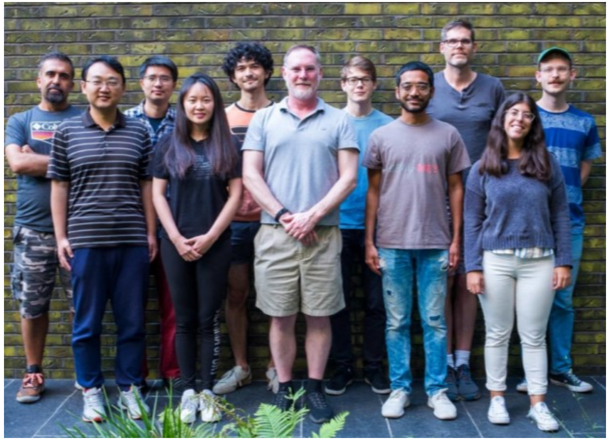
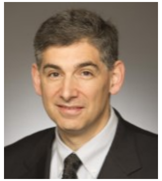

Prof. M. Urbakh (Tel Aviv Univ.)


Carpick Group @ UPenn

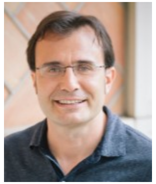

Prof. R. Carpick (UPenn)


Prof. D. Srolovitz


Prof. G. Cross (TCD Ireland)


Prof. A. Rappe (UPenn)


Prof. M. de Boer (CMU)


Prof. G. Piazza (CMU)

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NSFC
National Natural Science Foundation of China

NSF

Thank you !!

Cangyu Qu (瞿苍宇)

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- University of Pennsylvania
- E-mail: qucangyu@seas.upenn.edu