Gordon Research Seminar on Tribology (2024)
Lewiston, Maine, June 22-23, 2024

Contact Mechanics Correction of Activation Volume in Mechanochemistry

Cangyu Qu, Lu Fang and Robert W. Carpick

Department of Mechanical Engineering and Applied Mechanics

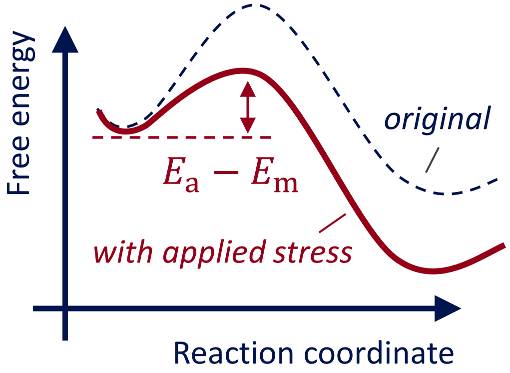
University of Pennsylvania

The Concept of Activation Volume(s)

Mechanochemistry:

controlling chemical reactions by stress

$$k = A \exp\left(-\frac{E_a - E_m}{k_B T}\right) = A \exp\left(-\frac{E_a - \sigma \Delta V}{k_B T}\right)$$



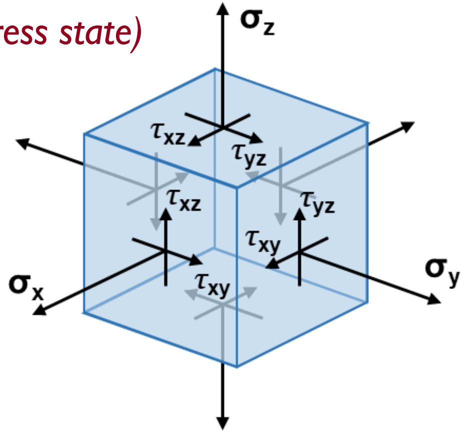
Energy diagram for a mechanochemical reaction

$E_m = \sigma \Delta V \leftarrow$ *(Hydrostatic pressure)* ΔV: volume change

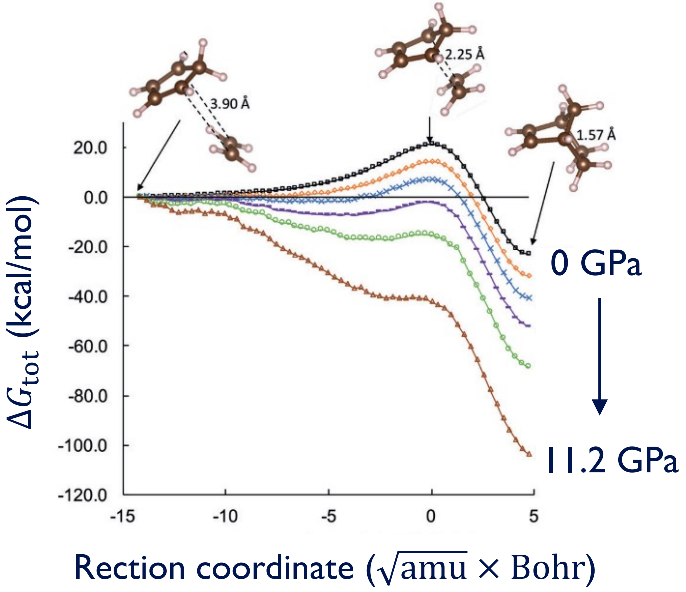
(Arbitrary stress state)

$$E_m = \sum_{i,j} \sigma_{ij} \Delta V_{ij}$$

$$\sigma_{ij} = \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \sigma_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \sigma_{zz} \end{pmatrix}$$



The Concept of Activation Volume(s)



Chen, B., Hoffmann, R., & Cammi, R. (2017). *Angewandte Chemie International Edition*, *56*(37), 11126–11142.

Mechanochemical reactions:

Stress-assisted thermal activation model

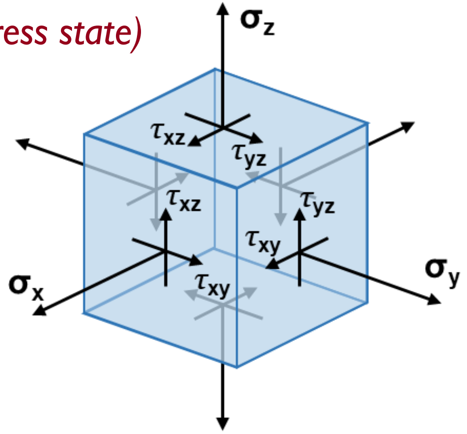
$$k = A \exp\left(-\frac{E_{\mathrm{a}} - E_{\mathrm{m}}}{k_{\mathrm{B}}T}\right) = A \exp\left(-\frac{E_{\mathrm{a}} - \sigma\Delta V}{k_{\mathrm{B}}T}\right)$$

$E_{\mathrm{m}} = \sigma\Delta V \leftarrow$ *(Hydrostatic pressure)* ΔV: volume change

(Arbitrary stress state)

$$E_{\mathrm{m}} = \sum_{i,j} \sigma_{ij}\Delta V_{ij}$$

$$\sigma_{ij} = \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \sigma_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \sigma_{zz} \end{pmatrix}$$



Penn Engineering

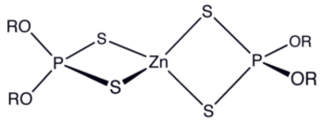
Discrepancy in Activation Volume Measurement

Experimentally-measured activation volume values vary a lot!

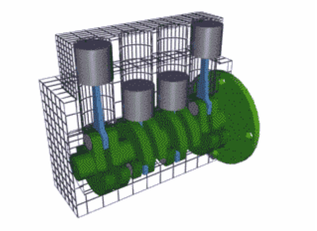
Examples:

Growth of antiwear film from ZDDP

$$\Delta V = 3.8\sim180\ \text{Å}^3$$



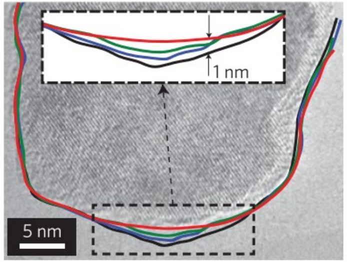
Zinc dialkyl dithiophsophate (ZDDP)



http://www.howstuffworks.com/engine2.htm

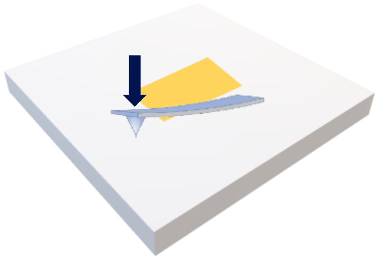
Tribochemical material removal (wear) of Si:

$$\Delta V = 6.7\sim60\ \text{Å}^3$$



- A. Martini and S. H. Kim, Tribol. Lett. **69**, 150 (2021).
- T. D. B. Jacobs and R. W. Carpick, Nat. Nanotechnol. **8**, 108 (2013).

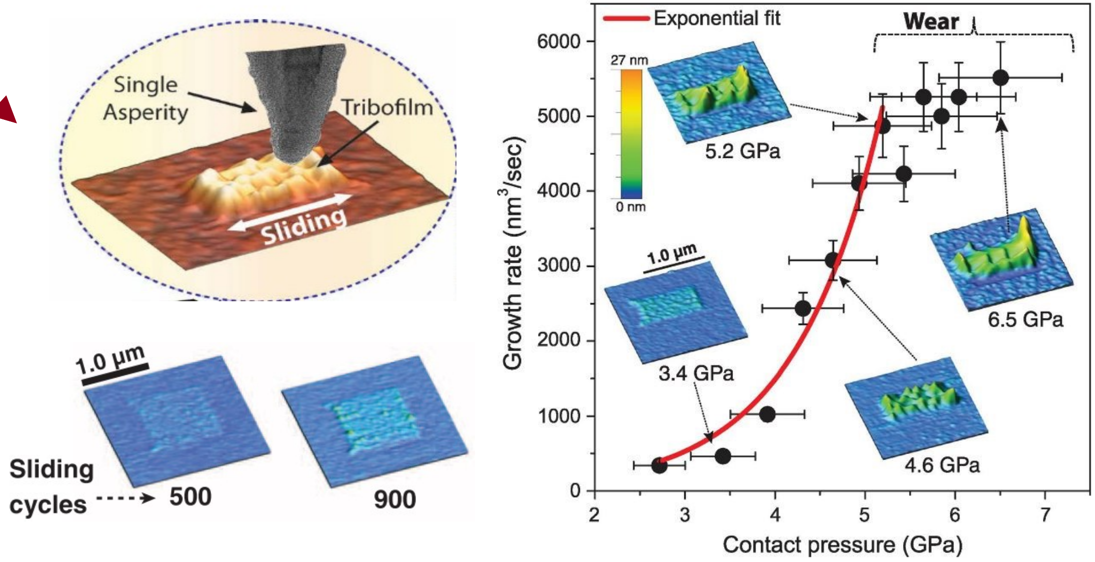
Methods of Measuring Activation Volume



Atomic force microscope (AFM) cyclic sliding

Ball-on-flat tribometer

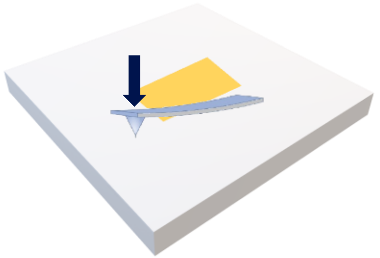
Animations: Lu Fang



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

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

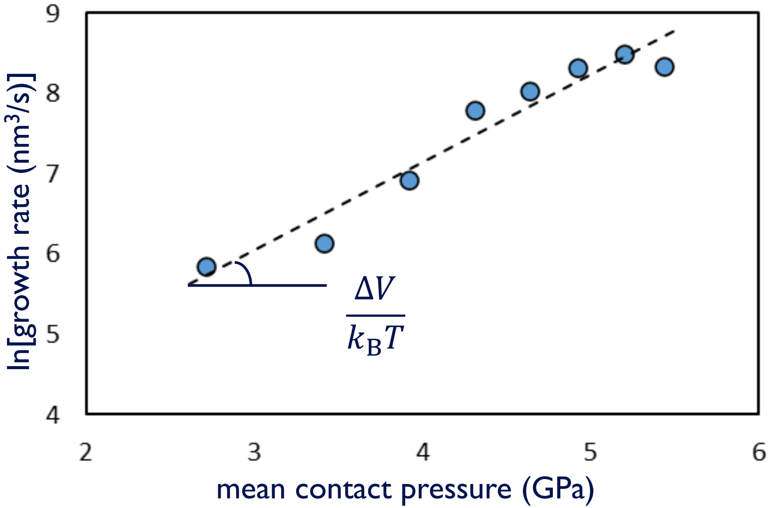
Methods of Measuring Activation Volume



Atomic force microscope (AFM) cyclic sliding

Ball-on-flat tribometer

Animations: Lu Fang



activation volume

activation energy

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

growth rate

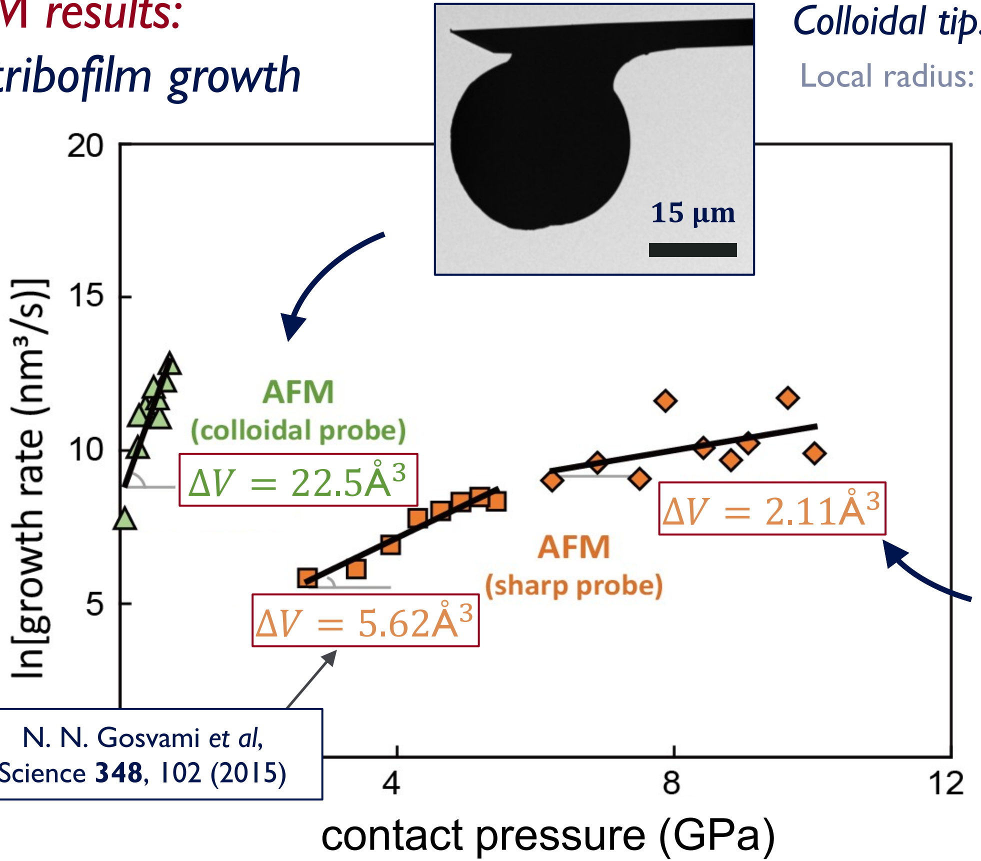
stress

ΔV is measured from the slope

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

Methods of Measuring Activation Volume

Our AFM results:
ZDDP tribofilm growth

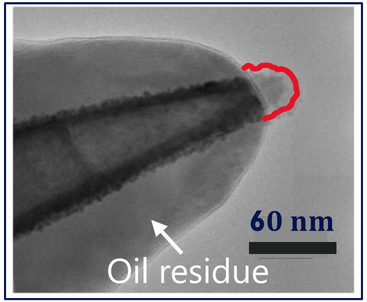


Colloidal tip: low stress

Local radius: 1.9 µm

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

x10 difference in ΔV??



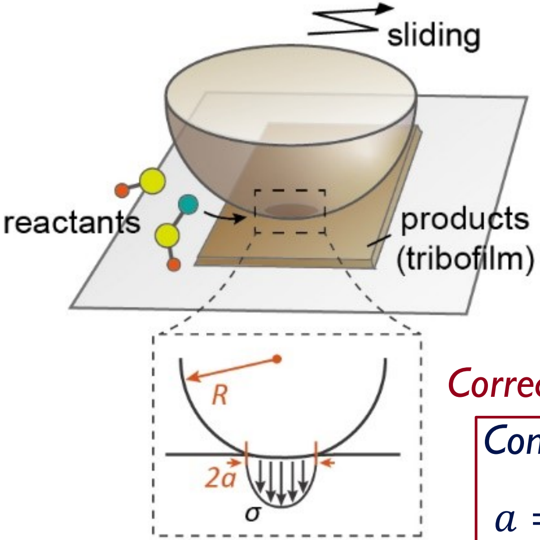
Sharp tip: high stress

8.6 GPa, 402mm sliding

Radius change:
22.9 nm → 28.2 nm

Image: Lu Fang

Considering Contact Mechanics



Correction #2

Contact radius:

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

Correction #1

Pressure distribution:

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

σ_m: *mean stress*

E^*: *contact modulus*

ρ: *reactant areal concentration*

Γ: *growth rate*

Γ_0: *pre-factor*

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

#1: Pressure distribution

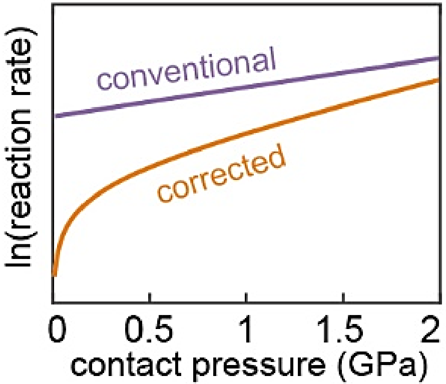
Hertz model

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

#2: Contact radius

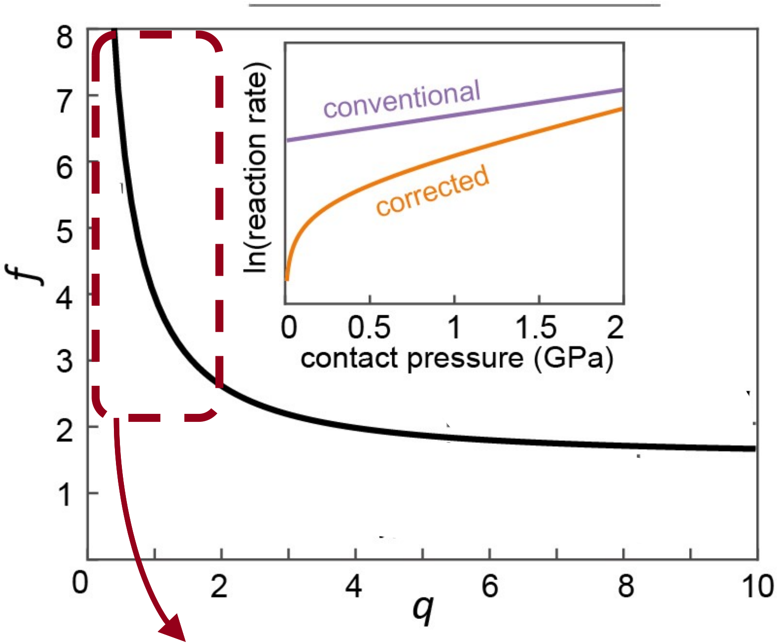
$$\longrightarrow \Gamma = \frac{\pi^3}{2}\rho\Gamma_0 e^{-\frac{E_\mathrm{a}}{k_\mathrm{B}T}}\left(\frac{Rk_\mathrm{B}T}{E^*\Delta V}\right)^2\left[1+e^{\lambda\sigma_\mathrm{m}}(\lambda\sigma_\mathrm{m}-1)\right]$$

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



predicts a very different stress-dependence!

The Correction Function



*Activation volume measurements at **low stresses** could have been wrong!*

Slope in the semi-log plot: $$\frac{d(\ln \Gamma)}{d\sigma_\mathrm{m}} = \frac{\Delta V}{k_\mathrm{B}T} f(q)$$

Correction function (Hertz): $$f(q) = \frac{3}{2} \cdot \frac{q e^q}{1 + e^q (q-1)}$$ $\left(q = \lambda \sigma_\mathrm{m} = \frac{3\Delta V \sigma_\mathrm{m}}{2k_\mathrm{B}T}\right)$

dimensionless number

Examples:

(for a hypothetical reaction of $\Delta V = 10\ \text{Å}^3$ at $T = 130°\mathrm{C}$)

- Colloidal AFM: $\sigma_\mathrm{m} = 200\ \mathrm{MPa}$ → $f = 6.61$
- Sharp AFM: $\sigma_\mathrm{m} = 2\ \mathrm{GPa}$ → $f = 1.84$
- Large-stress limit: $f = 1.5$

Removed by using σ_{max} instead of σ_m

Penn Engineering

Adding Shear Stress to the Model

*Note: sign convention

Reaction rate: $\Gamma_0 e^{-\frac{E_a - \sigma_{ij}\Delta V_{ij}}{k_B T}} = \Gamma_0 e^{-\frac{E_a - \tau\Delta V_s + \sigma\Delta V_n}{k_B T}}$

assume $\tau = \mu\sigma$ (constant μ) $\longrightarrow$

$$\Gamma_0 \exp\left(-\frac{E_a - \sigma\Delta V_{eff}}{k_B T}\right)$$

$$\Delta V_{eff} = \mu\Delta V_s - \Delta V_n$$

generally, two independent variables σ and τ

$$\Gamma = \int_0^a \rho\Gamma_0 e^{-\frac{E_a - (\Delta V_s \tau - \Delta V_n \sigma)}{k_B T}} 2\pi r dr = \cdots$$

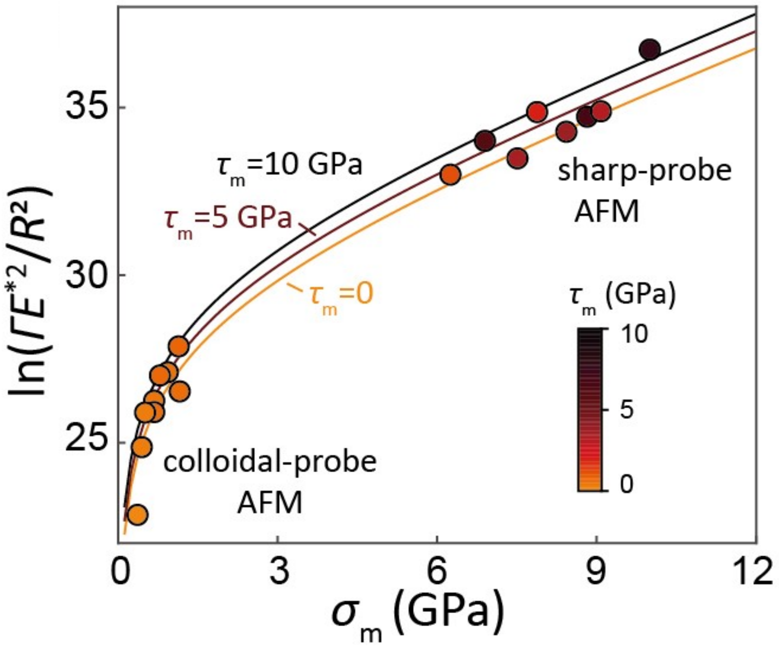
$\boxed{\text{Hertzian model}}$

- μ: friction coefficient
- ΔV_s: activation volume for shear stress
- ΔV_n: activation volume for normal stress
- ΔV_{eff}: effective activation volume
- E_a: activation energy
- σ_m: mean normal stress
- τ_m: mean shear stress
- E^*: contact modulus
- R: ball radius
- ρ: reactant areal concentration
- Γ: growth rate

$$\ln\left(\frac{\Gamma E^{*2}}{R^2}\right) = \ln\left(\frac{\pi^3 k_B^2 \rho T^2 \Gamma_0}{2}\right) - \frac{E_0}{k_B T} - 2\ln\left(\frac{\tau_m}{\sigma_m}\Delta V_s - \Delta V_n\right) + \ln\left[1 + e^{\frac{3(\Delta V_s \tau_m - \Delta V_n \sigma_m)}{2k_B T}}\left(\frac{3}{2}\cdot\frac{\Delta V_s \tau_m - \Delta V_n \sigma_m}{k_B T} - 1\right)\right]$$

A two-variable model for fitting experimental data

Fitting to Experimental Data



- Normal stress **promotes** reaction
- Shear stress has little effect

Fitting to new model:

$$\Delta V_n = -2.08 \pm 0.36\ \text{Å}^3$$
$$\Delta V_s = 0.43 \pm 0.57\ \text{Å}^3$$

$$\rightarrow \Delta V_{eff} = \mu_m \Delta V_s - \Delta V_n = \boxed{2.3\ \text{Å}^3}$$

Previous results:

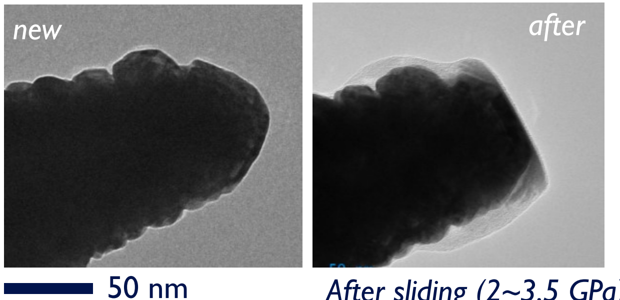
Sharp AFM: $\Delta V_{eff} = 2.1\ \text{Å}^3$

Colloidal AFM: $\boxed{\Delta V_{eff} = 22.5\ \text{Å}^3}$

over-estimated!

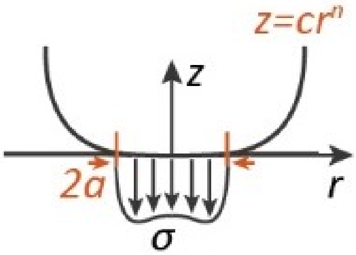
Extension to Non-Hertzian Contacts

Tip flattening: Pt-coated Si tip



50 nm

After sliding (2~3.5 GPa)

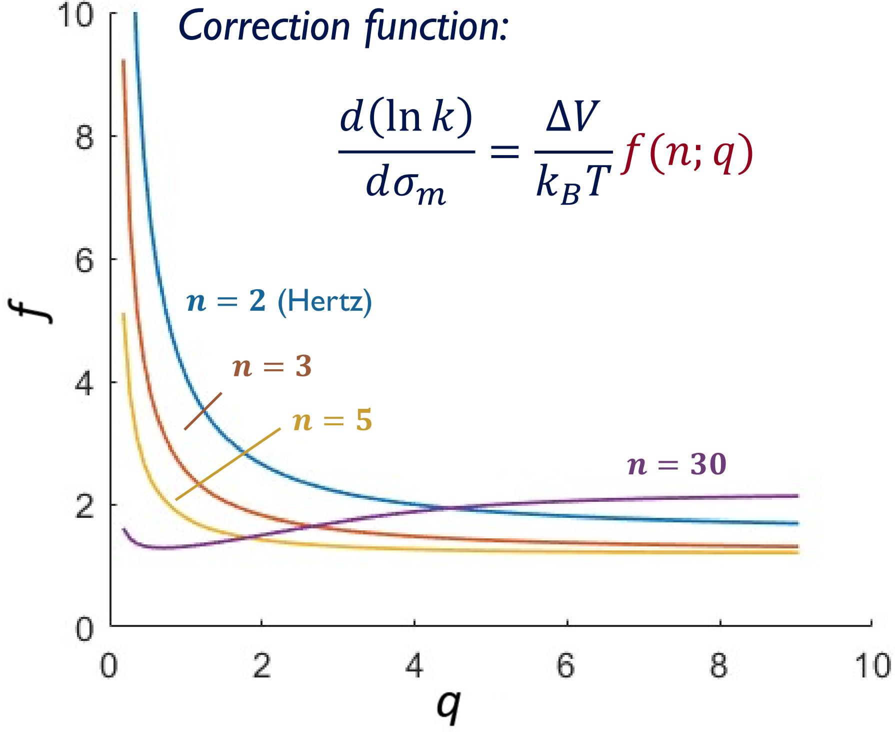


Non-Hertzian:

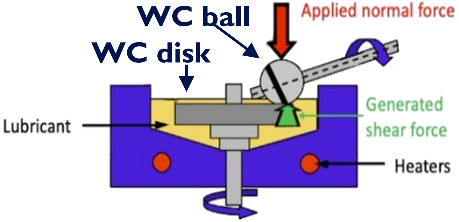
Power-law tip shape $z = cr^n$ $(n \geq 2)$

Correction function:

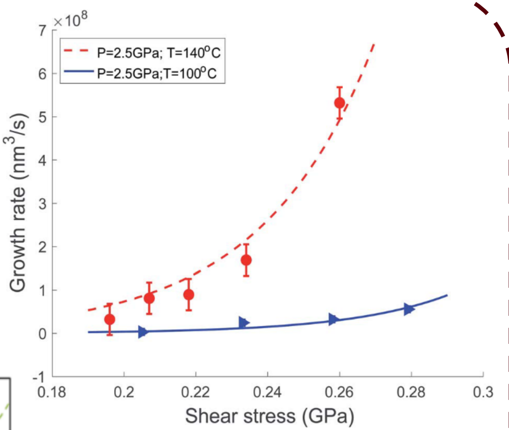
$$\frac{d(\ln k)}{d\sigma_m} = \frac{\Delta V}{k_B T} f(n;q)$$



More Questions to Ask …

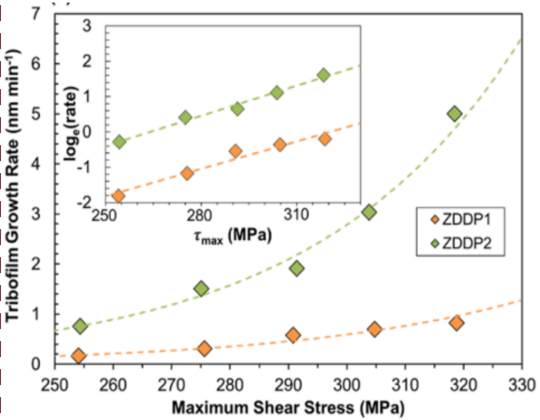


mini-traction machine (MTM)



L. Fang et al, Faraday Discuss. **241**, 394 (2023).

$\Delta V_\mathrm{s} = 180\ \text{Å}^3, \Delta V_\mathrm{n} = 10\ \text{Å}^3$

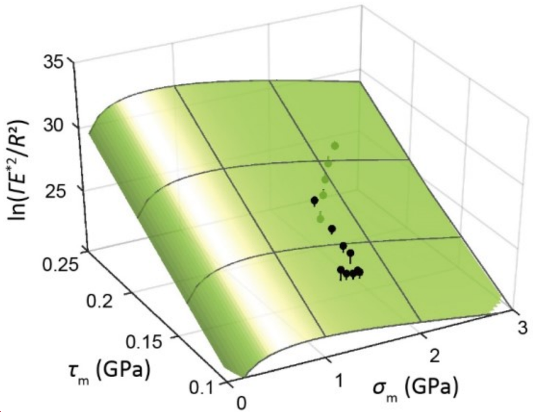


J. Zhang et al, ACS Appl. Mater. Interfaces 12, 6662 (2020).

$\Delta V = 125\ \text{Å}^3$ (for τ)

$\xrightarrow{\mu \approx 0.1}$ $\Delta V = 12.5\ \text{Å}^3$ (for σ)

contact mechanics correction



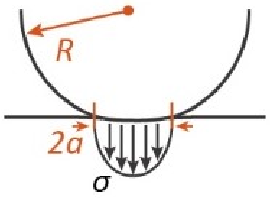
$\Delta V_\mathrm{s} = 274\text{Å}^3, \Delta V_\mathrm{n} = 9.9\text{Å}^3$

$\rightarrow \Delta V_\mathrm{eff} = \mu_\mathrm{m} \Delta V_\mathrm{s} - \Delta V_\mathrm{n} = \boxed{17.5\ \text{Å}^3}$

Contradictory to AFM results:

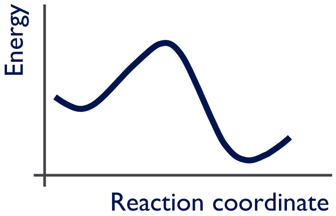
- Shear stress **promotes** reaction
- Normal stress **inhibits** reaction

Summary



Contact mechanics

+



Tribochemistry

→

$$\frac{d(\ln \Gamma)}{d\sigma_{\mathrm{m}}} = \frac{\Delta V}{k_{\mathrm{B}}T}\, \underline{f(q)}$$

Contact mechanics correction: a general framework for measuring activation volume correctly

- Hertzian contact:
  - Slope of the semi-log plot $\xleftrightarrow{\textit{Correction function}}$ activation volume
- Extension to non-Hertzian contacts
- Validation with experiments: ZDDP tribofilm growth

Acknowledgements

Thank you!

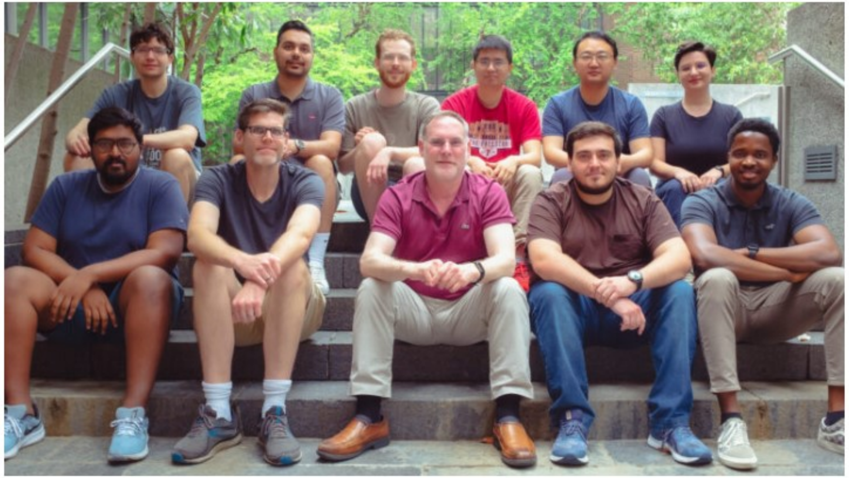
Contact: qucangyu@seas.upenn.edu

QR code:
Carpick group website

Dr. Lu Fang

Prof. Robert Carpick

Carpick group



Penn Engineering

NSF

This work was supported by NSF CMMI-1854702, and was carried out in part at the Singh Center for Nanotechnology, which is supported by the NSF National Nanotechnology Coordinated Infrastructure Program under grant NNCI-2025608.