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New Insights about the Fundamental Mechanisms of Friction in MoS_2

John F. Curry[1], Adam K. Hinkle, Tomas Babuska[1,2], Michael Chandross[1], Michael T. Dugger[1], Brendan L. Nation[1], Nicolas Argibay[1], Brandon A. Krick[2]

[1]Materials Science and Engineering Center
Sandia National Laboratories
Albuquerque, NM

[2]Department of Mechanical Engineering
Lehigh University
Bethlehem, PA

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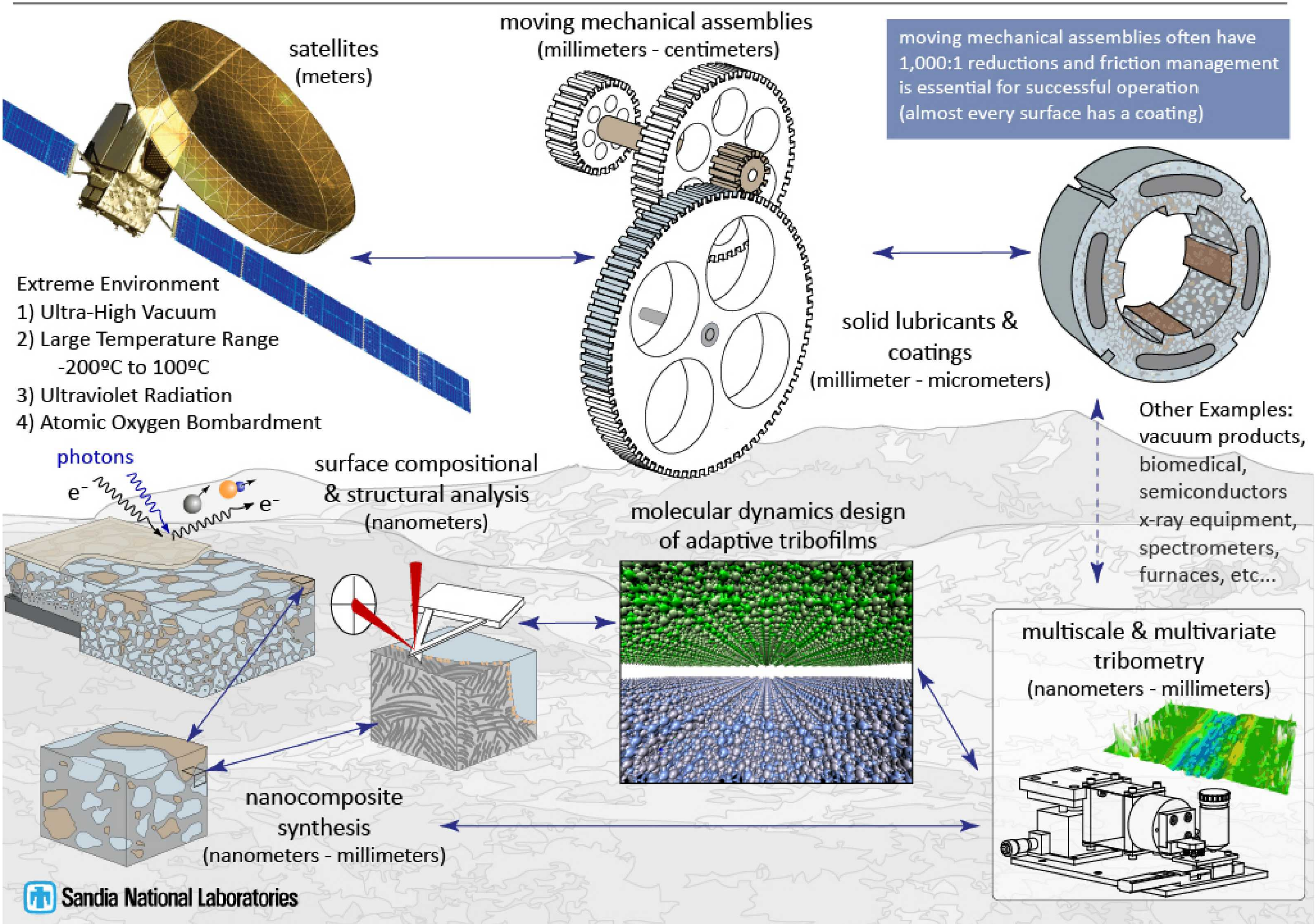
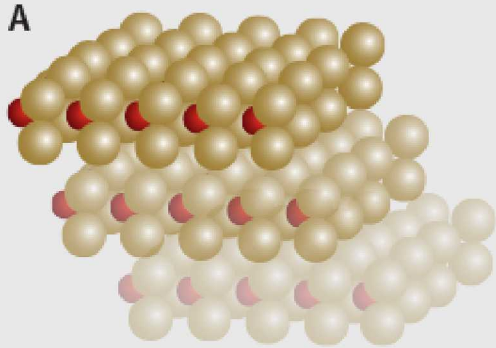
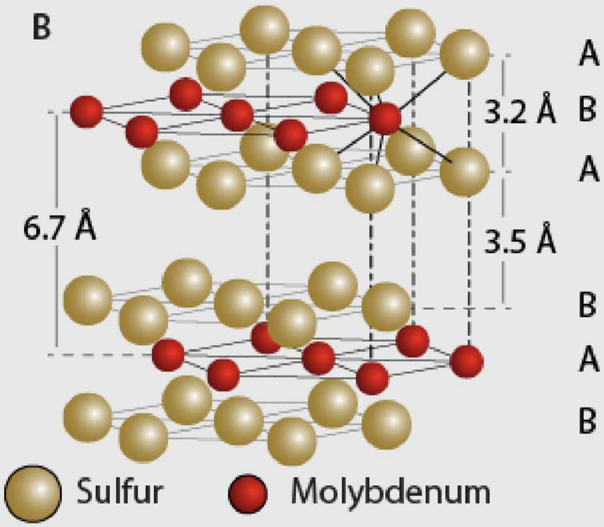
Fundamental Studies and Applied Challenges



MoS_2 Coatings

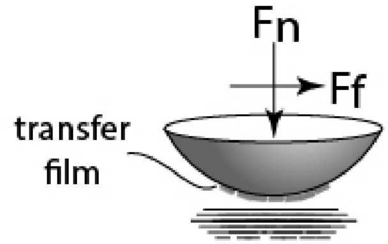
molybdenum disulphide
μ = 0.02 - 0.06 (inert @ 1N)
μ = 0.15 - 0.25 (humid air @ 1N)





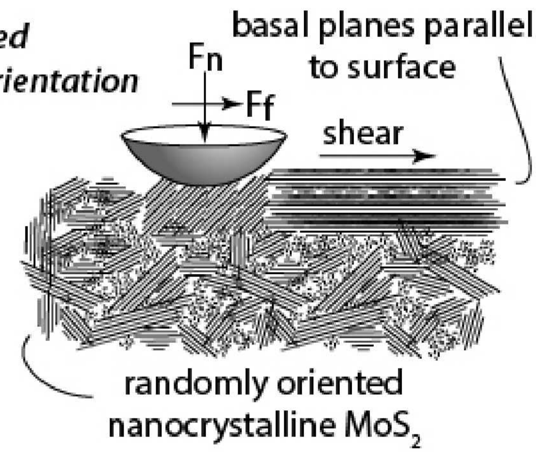
(A) Depiction of the layered structure of MoS_2 lamellae stacked upon one another. (B) Hexagonal stack lattice structure of MoS_2 with atomic spacing and sequencing.

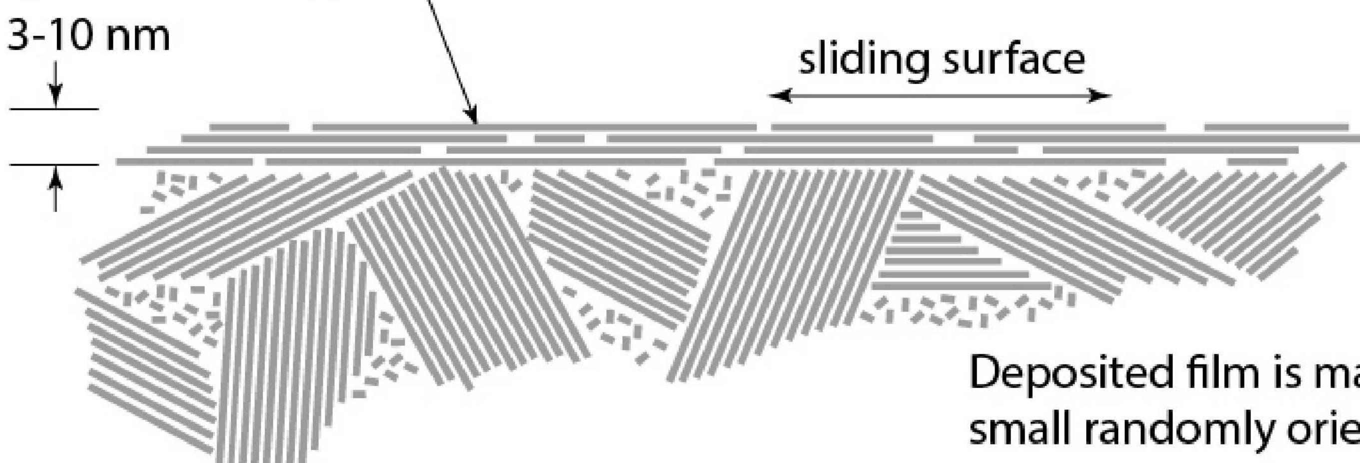
Run-In Processes



1) Transfer Film Formation

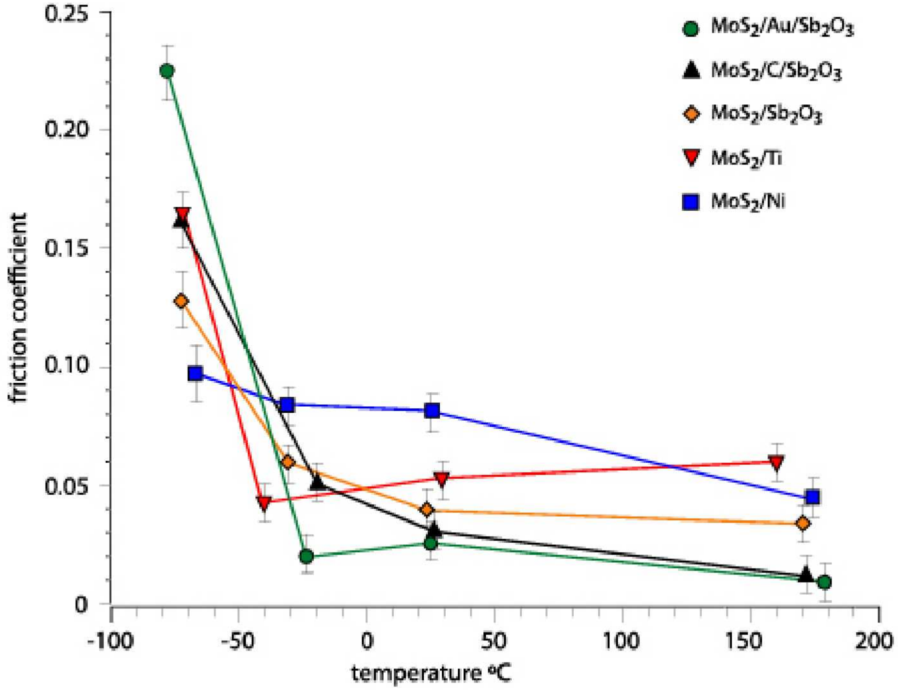
2) Shear-induced crystallite re-orientation



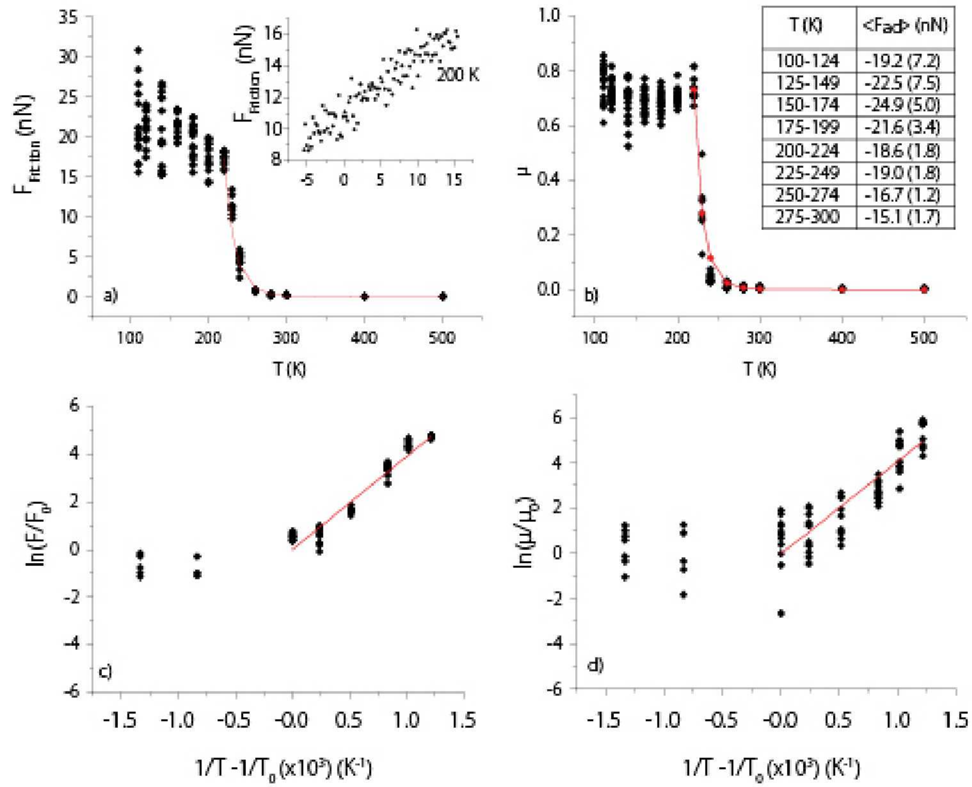


Deposited film is made of many small randomly oriented crystallites of molybdenum disulphide.

Recent Temperature Dependence in Literature



ref: Hamilton et al. Tribology Letters 2008

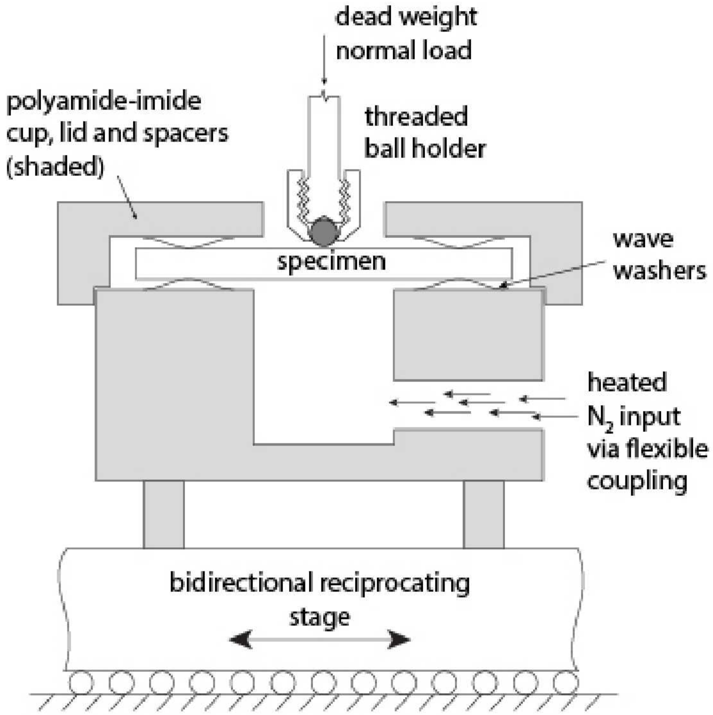


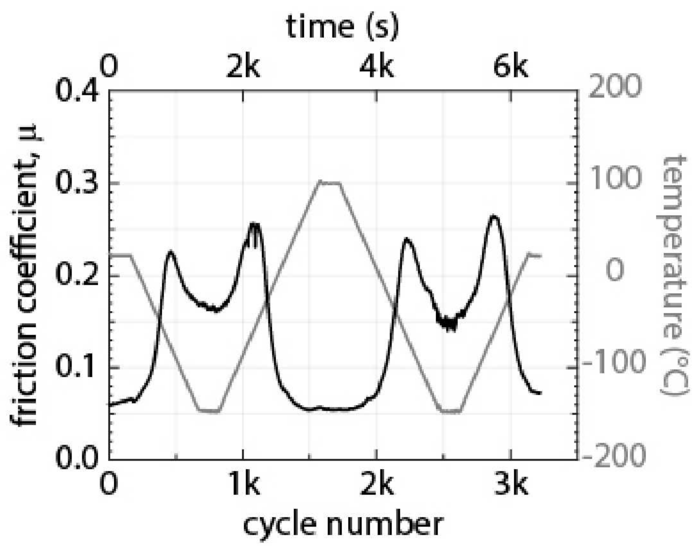
ref: Zhao et al. Phys. Rev. Lett. 2009

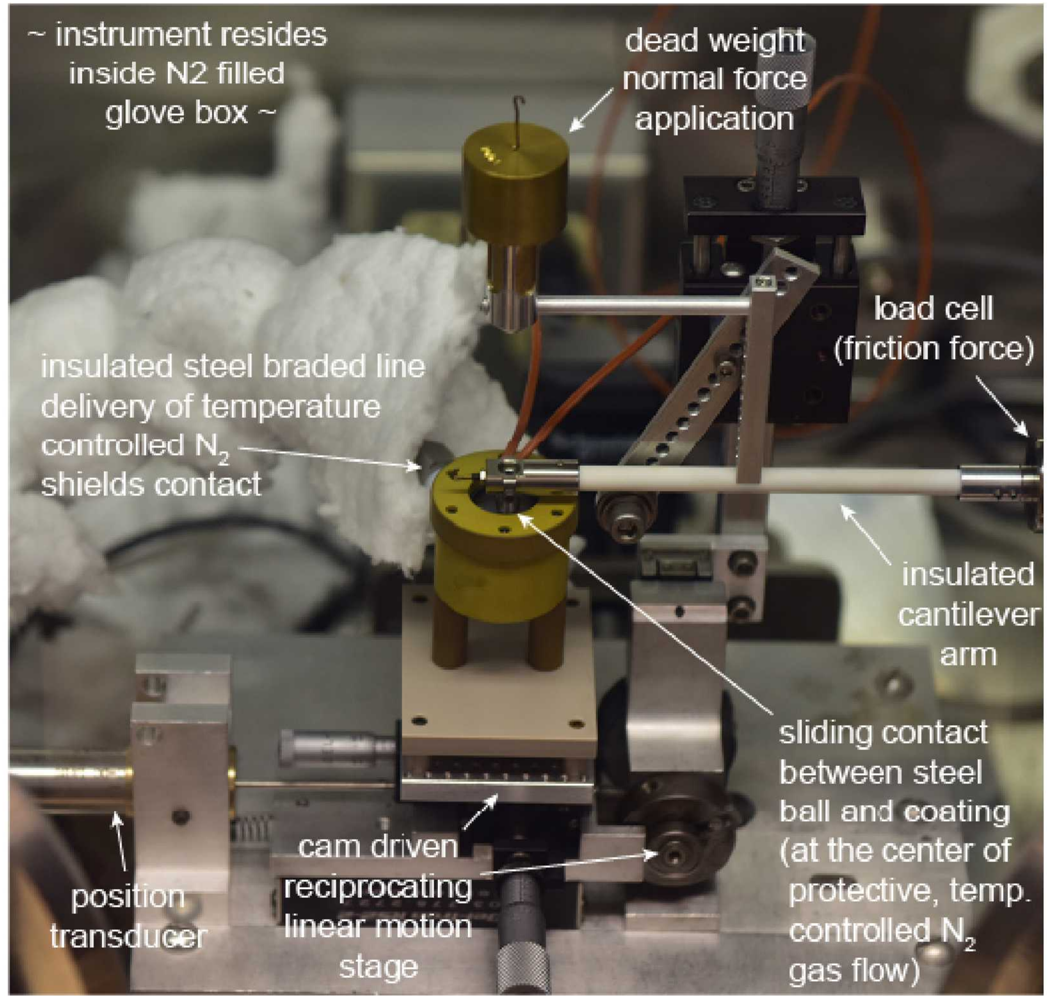
Macro-scale tests by Hamilton only tested composites - not all results agreed with findings of increased friction at reduced temperatures.

AFM studies by Zhao reported unusually high friction (μ~ 0.8); very high contact pressures & sharp silicon tip may not be representative contact conditions

High Temperature Tribometer Studies







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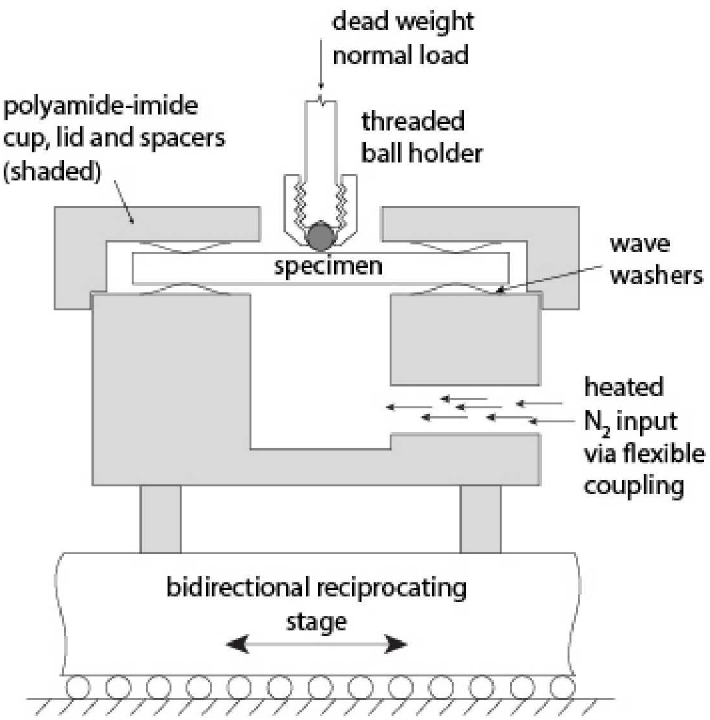
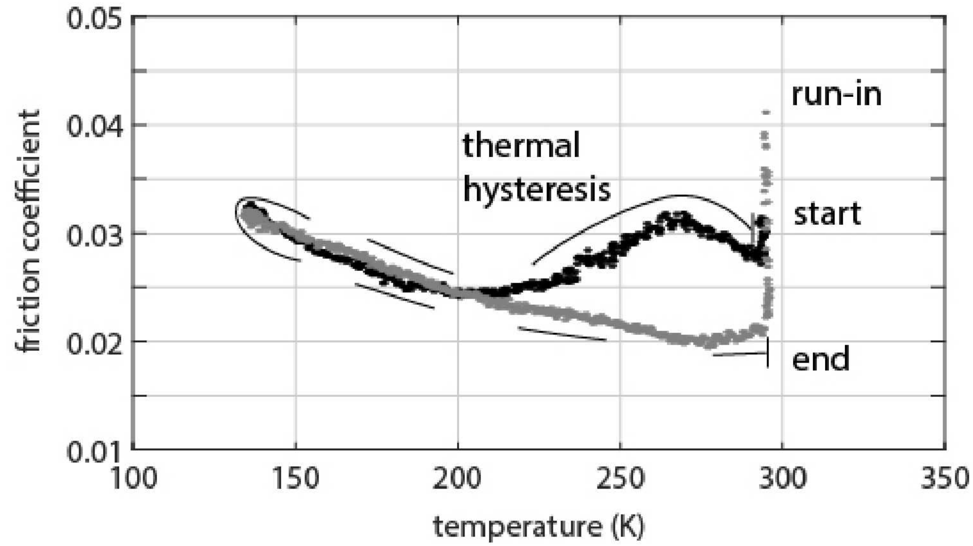
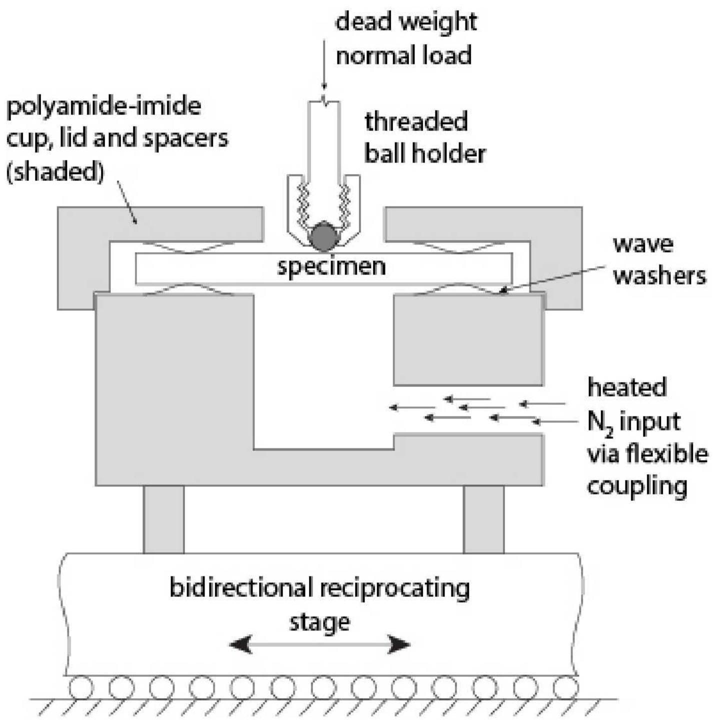


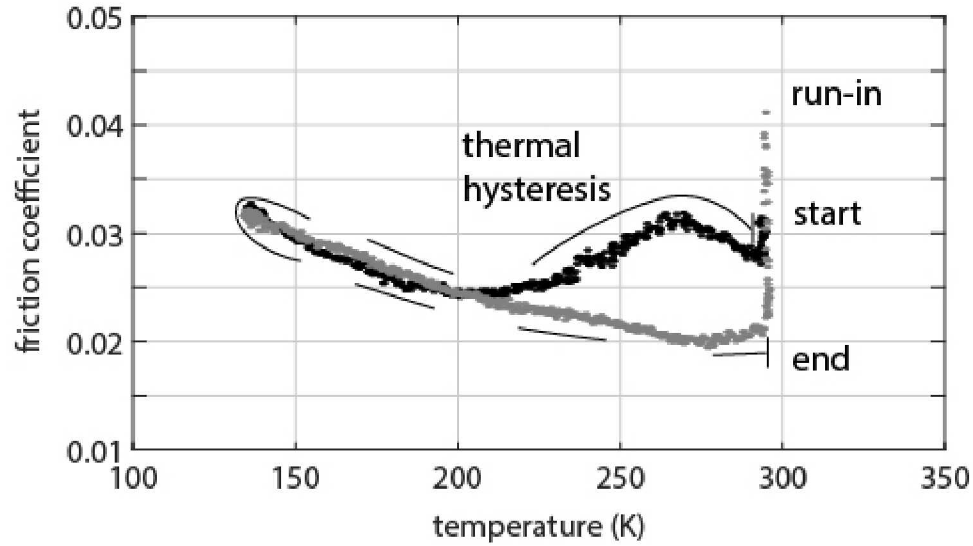


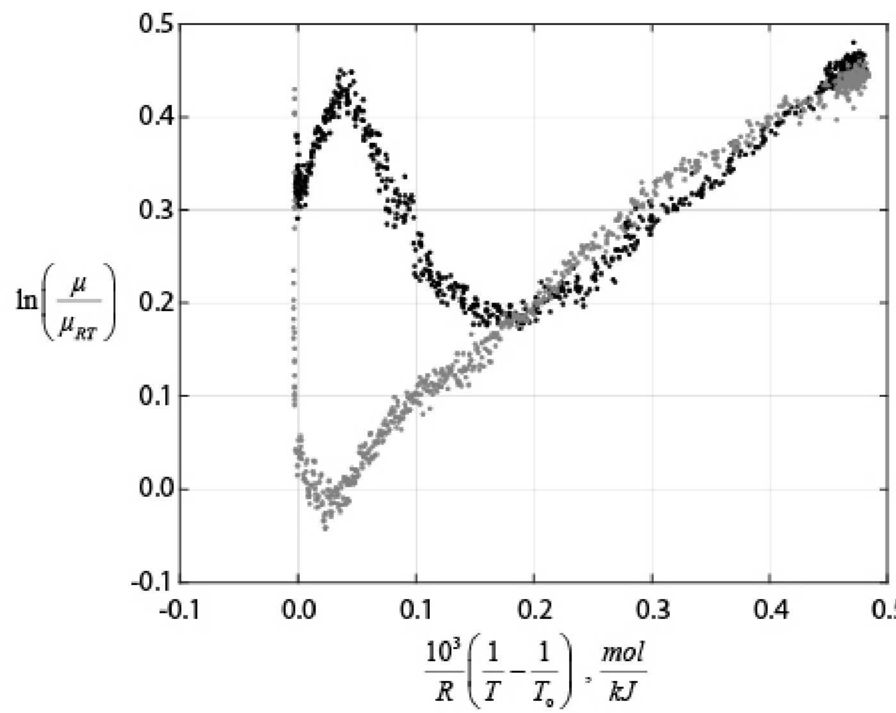
- MoS_2 exhibits a thermal to athermal transition in friction and wear at room temperature

- Hysteresis most likely due to high friction typically observed during run-in

High Temperature Tribometer Studies







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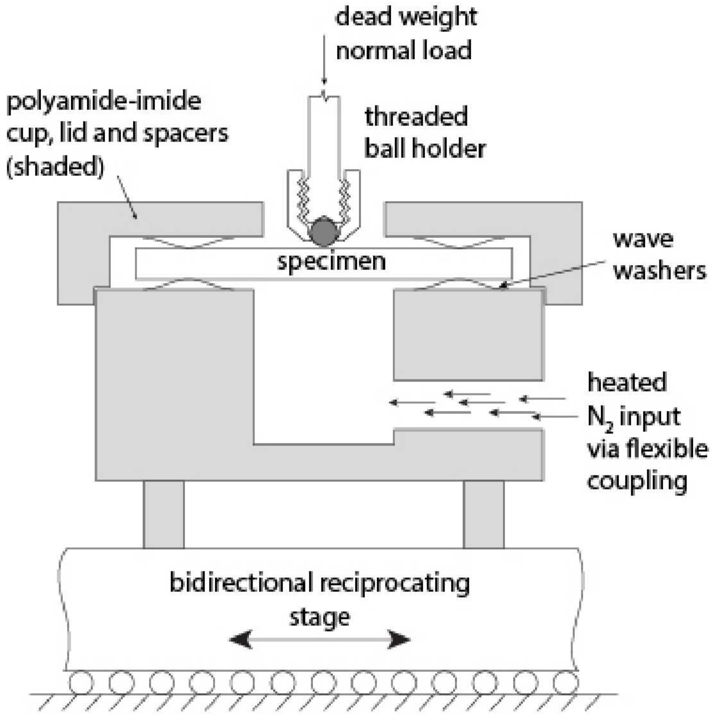
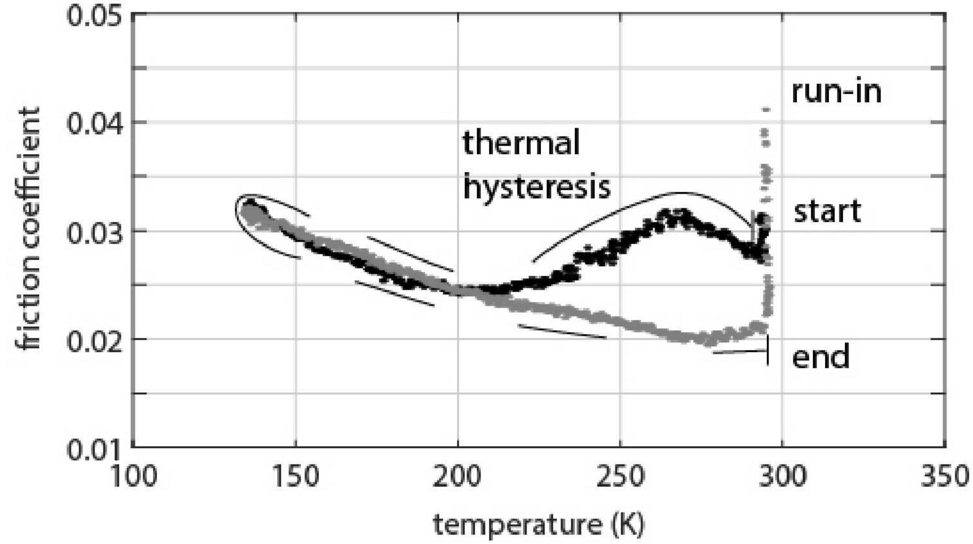
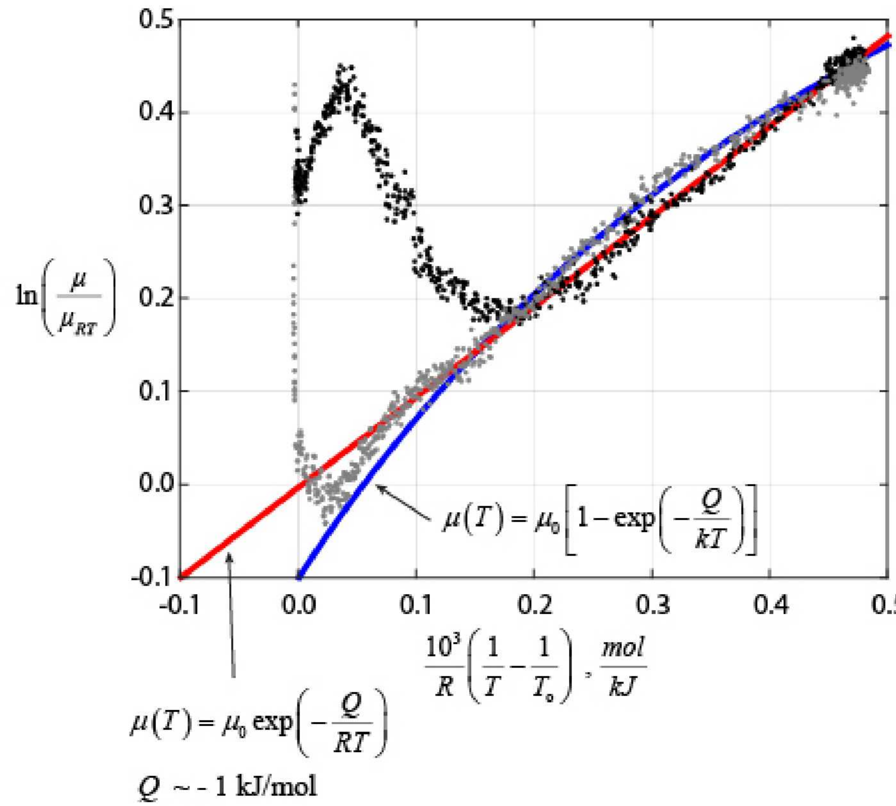
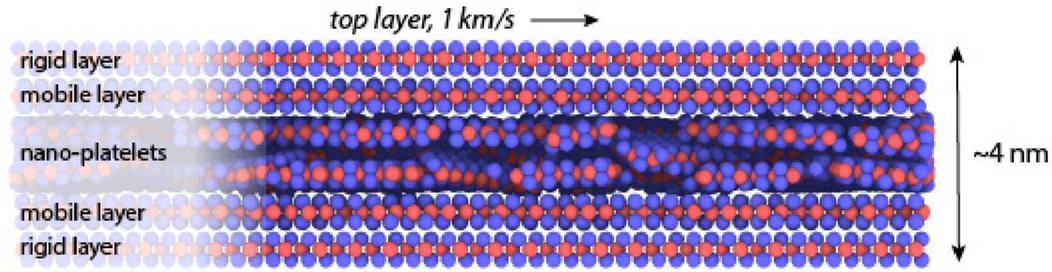


- MoS_2 exhibits a thermal to athermal transition in friction and wear at room temperature
- Hysteresis most likely due to high friction typically observed during run-in
- Return sliding does not appear to follow typical arrhenius behavior, more so (1-exp) functional form

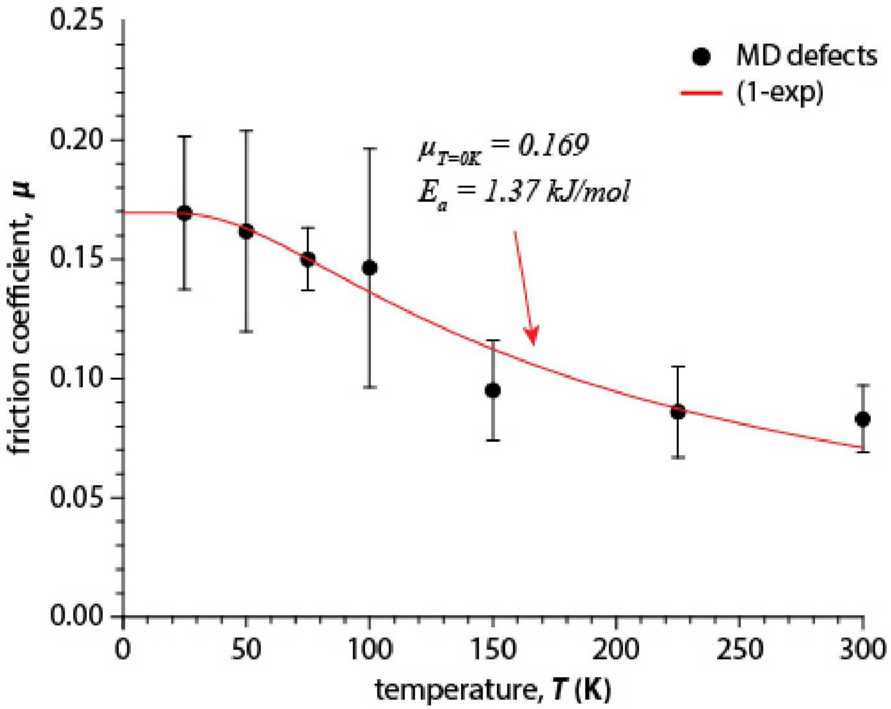


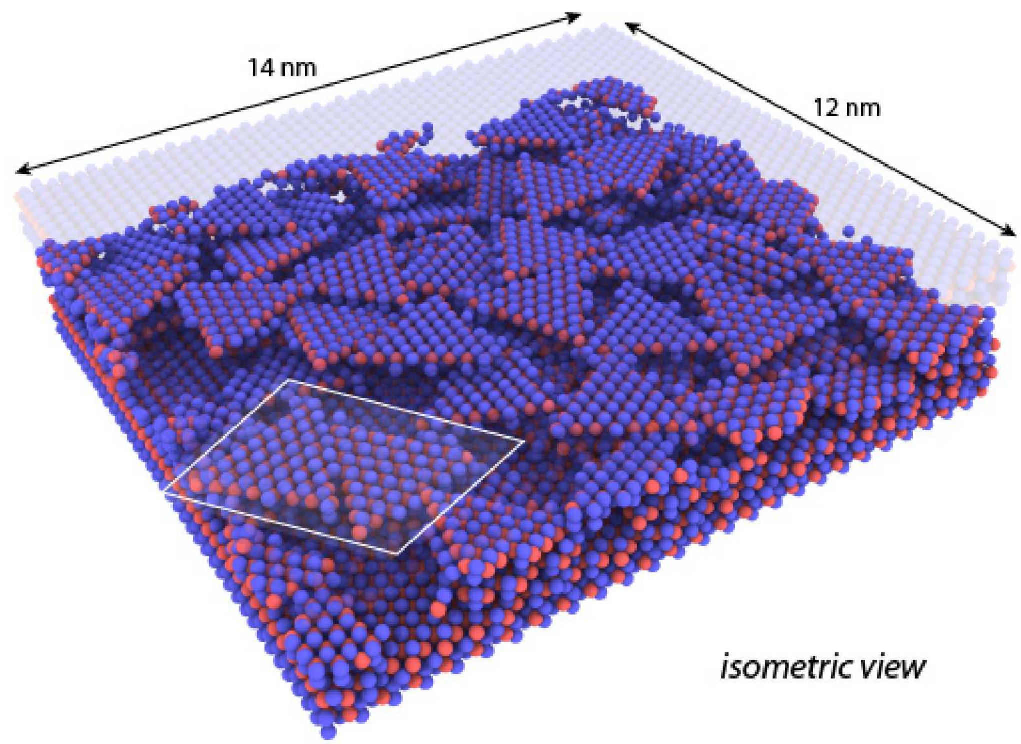


Molecular Dynamics Study of MoS_2 Temperature Dependence



side view





isometric view

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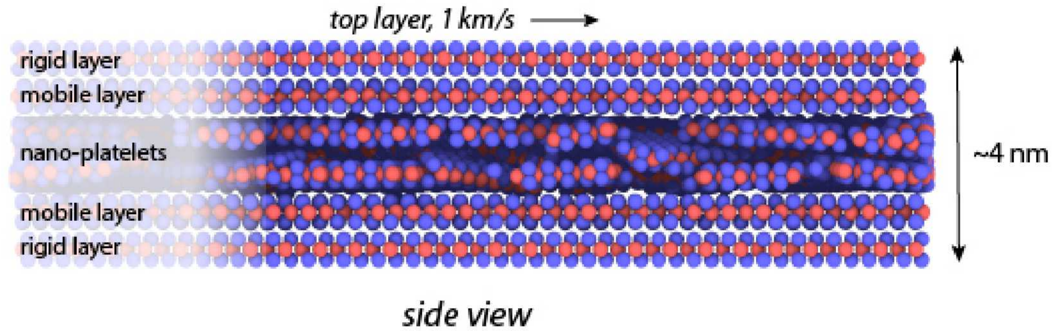

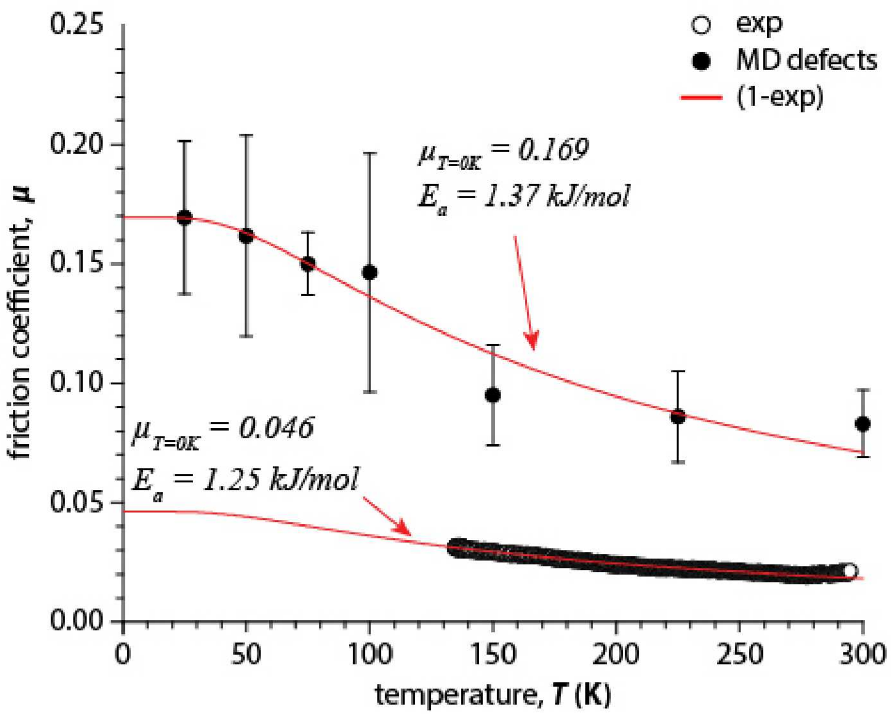

Analysis

- MD simulations show higher levels of friction, yet result in similar activation energy to experiments

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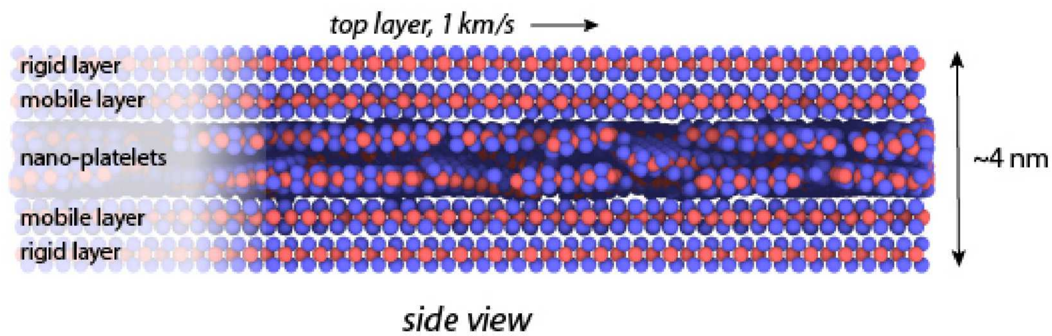

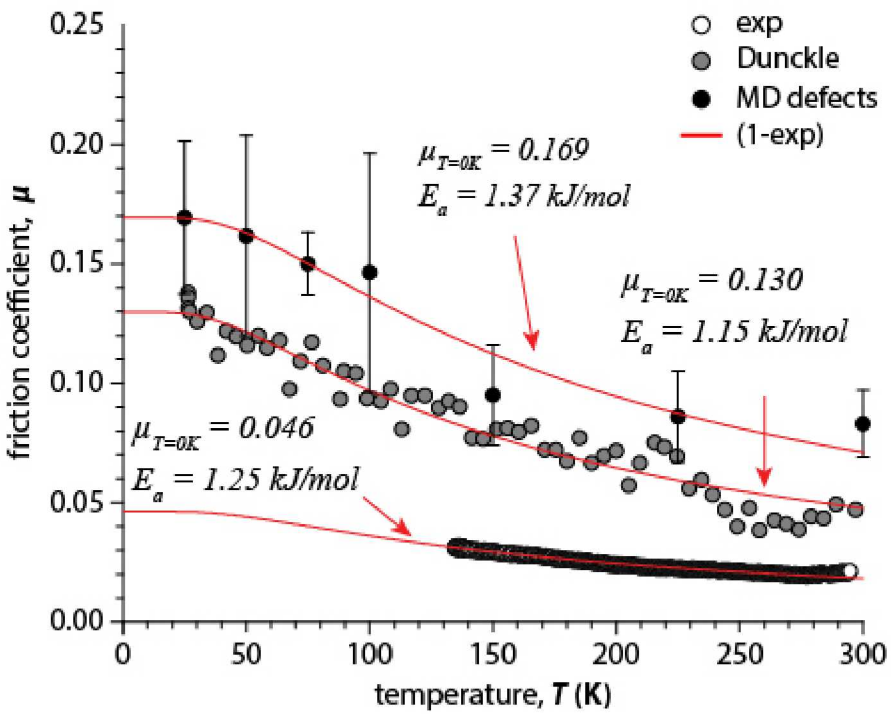

Analysis

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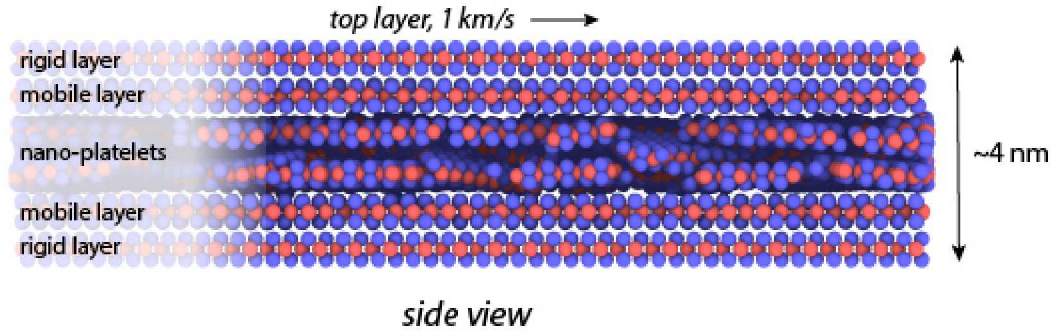
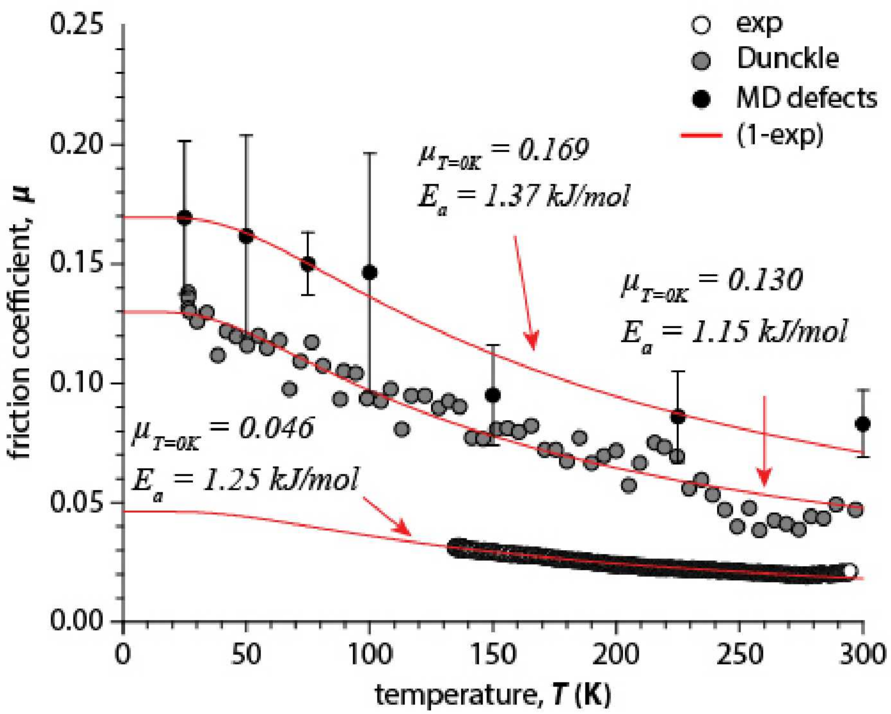
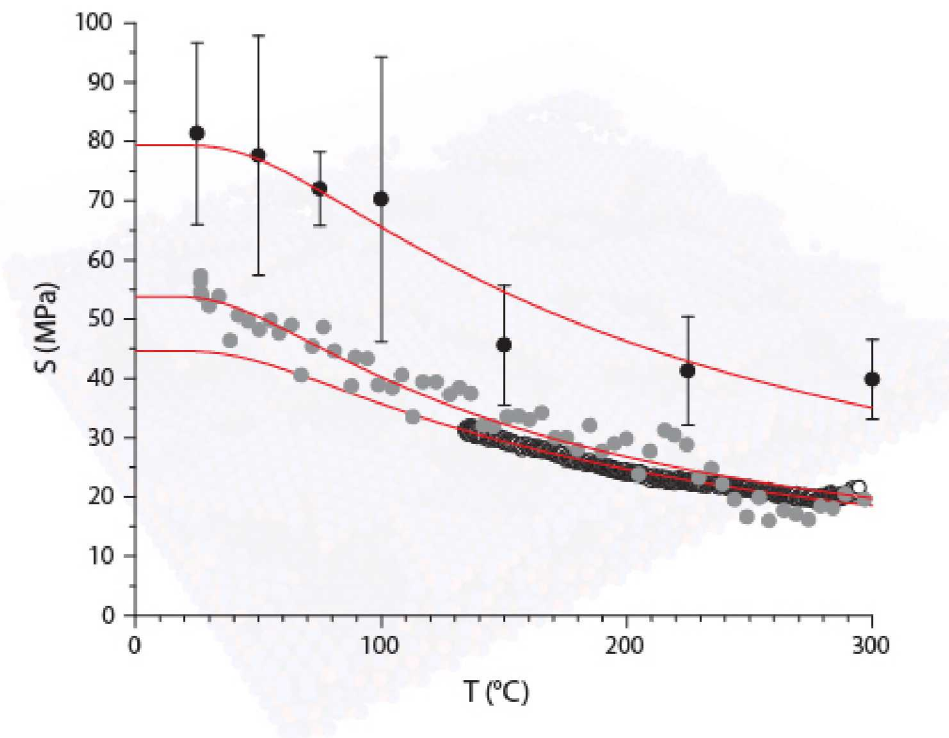
- Results from Dunckle et al show similar trends, extending to lower temperatures
- Discrepancies in levels of friction

Molecular Dynamics Study of MoS_2 Temperature Dependence

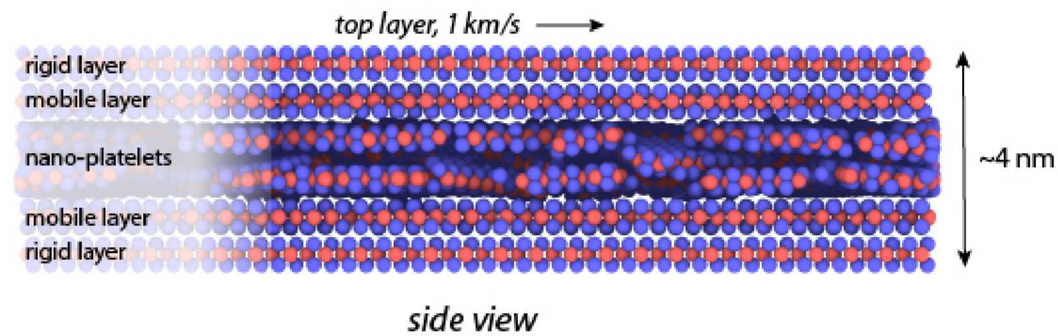




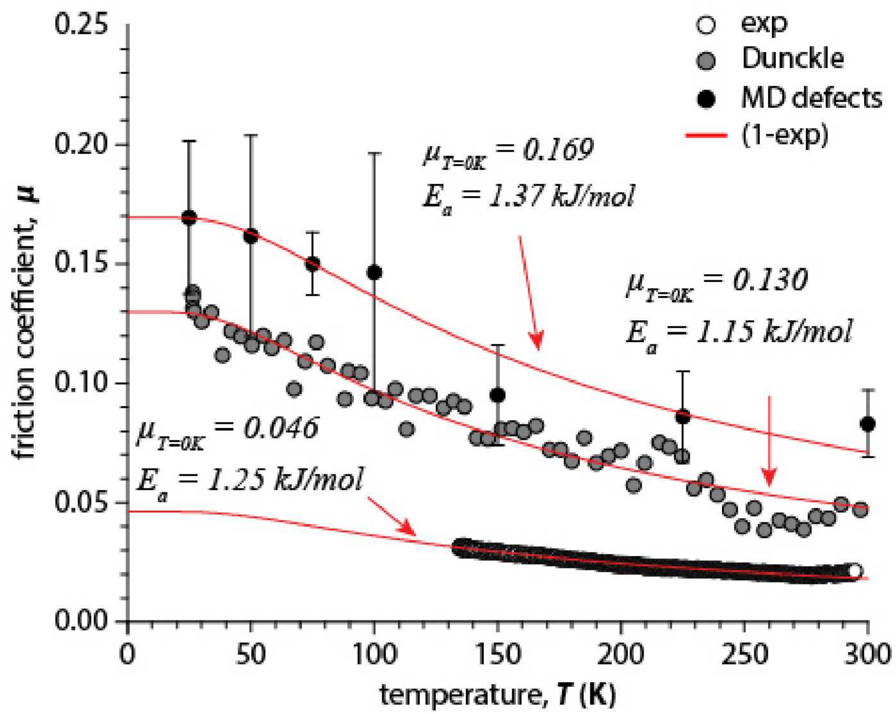


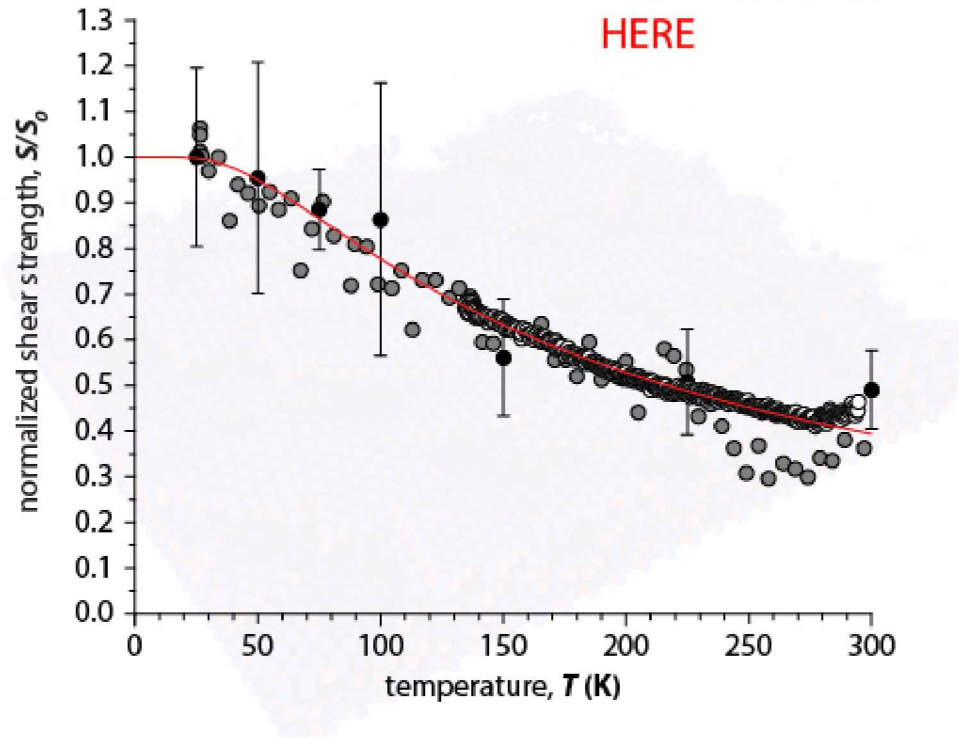
- *Data collapses when plotting normalized shear strength*

Molecular Dynamics Study of MoS_2 Temperature Dependence



SHEAR STRENGTH EQUATIONS GO HERE





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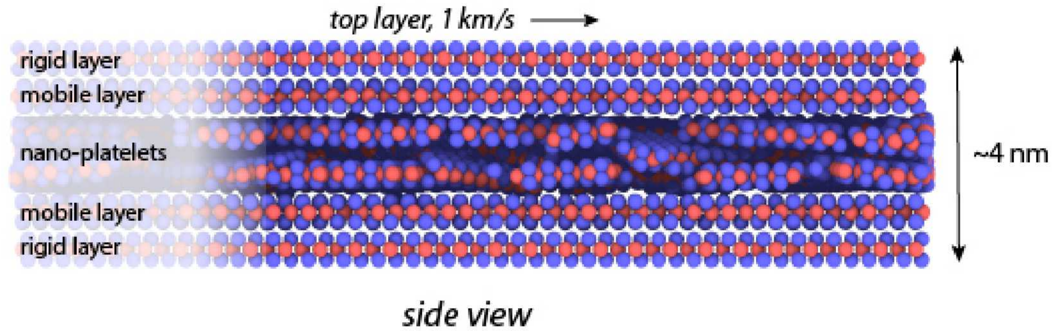
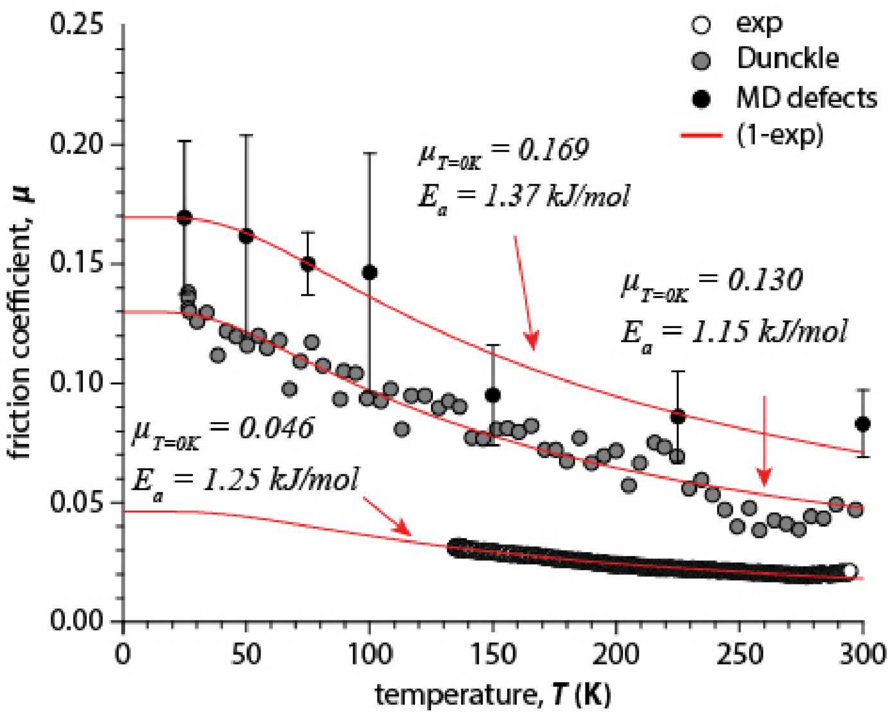
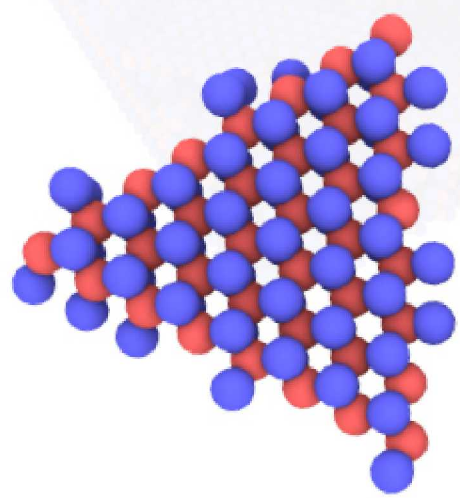




Mind the Gap

- Noticeable difference between simulations and experiments is defect density

- Simulations had many defects in order to maintain stoichiometry:



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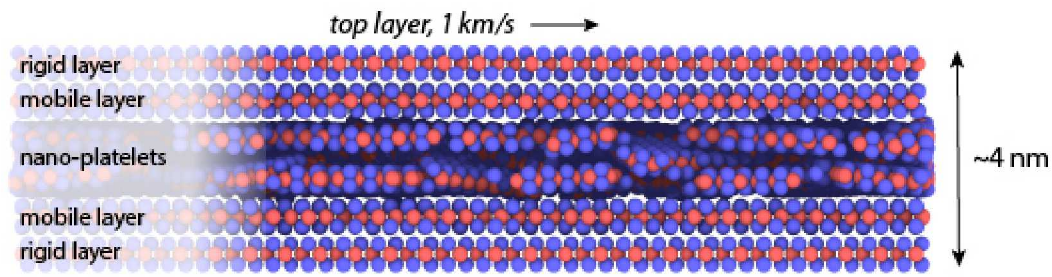

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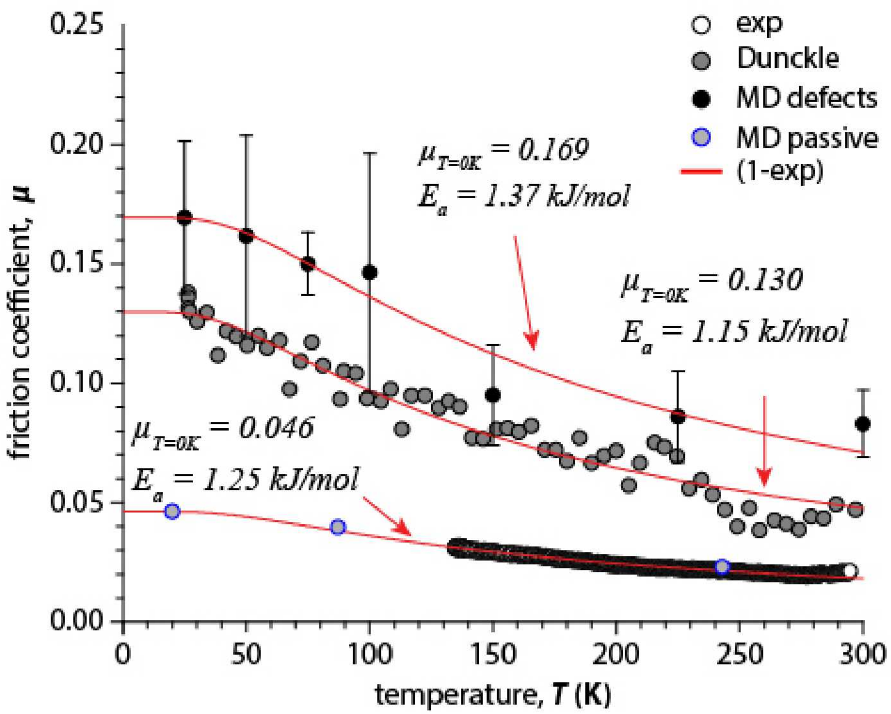

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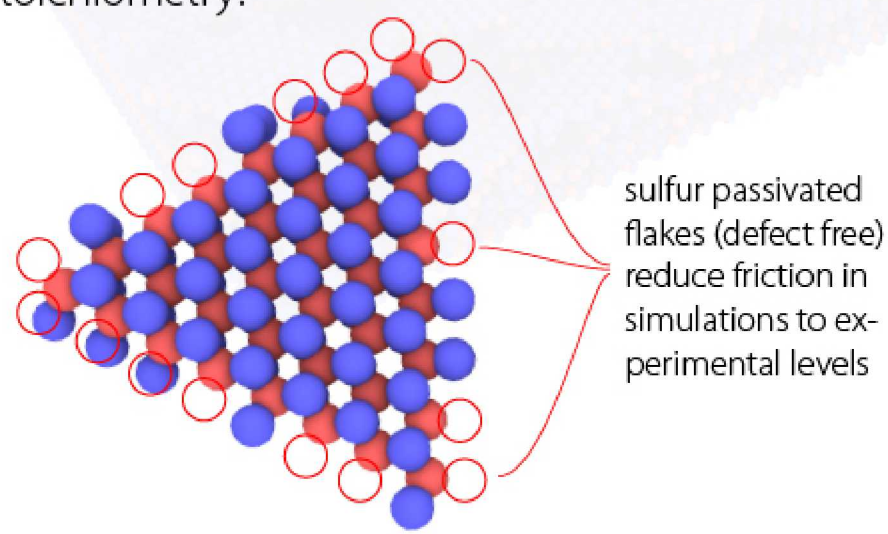
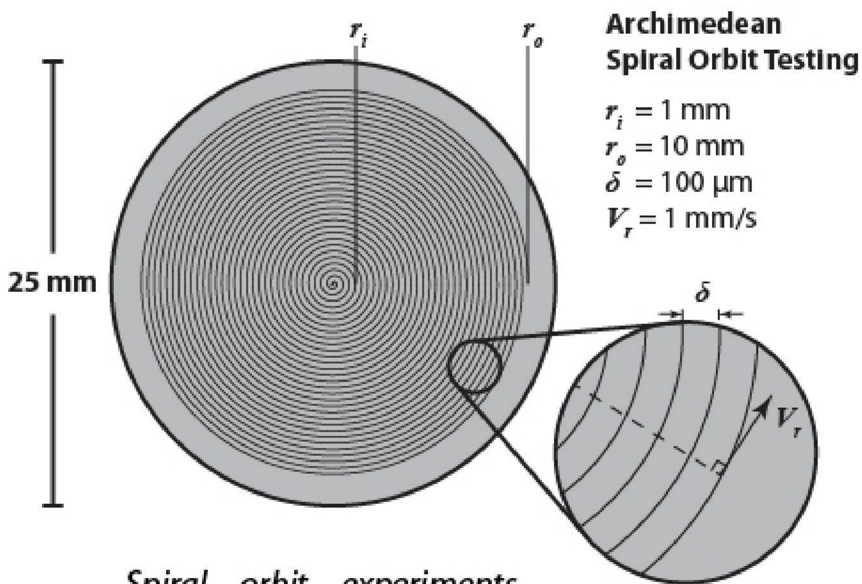
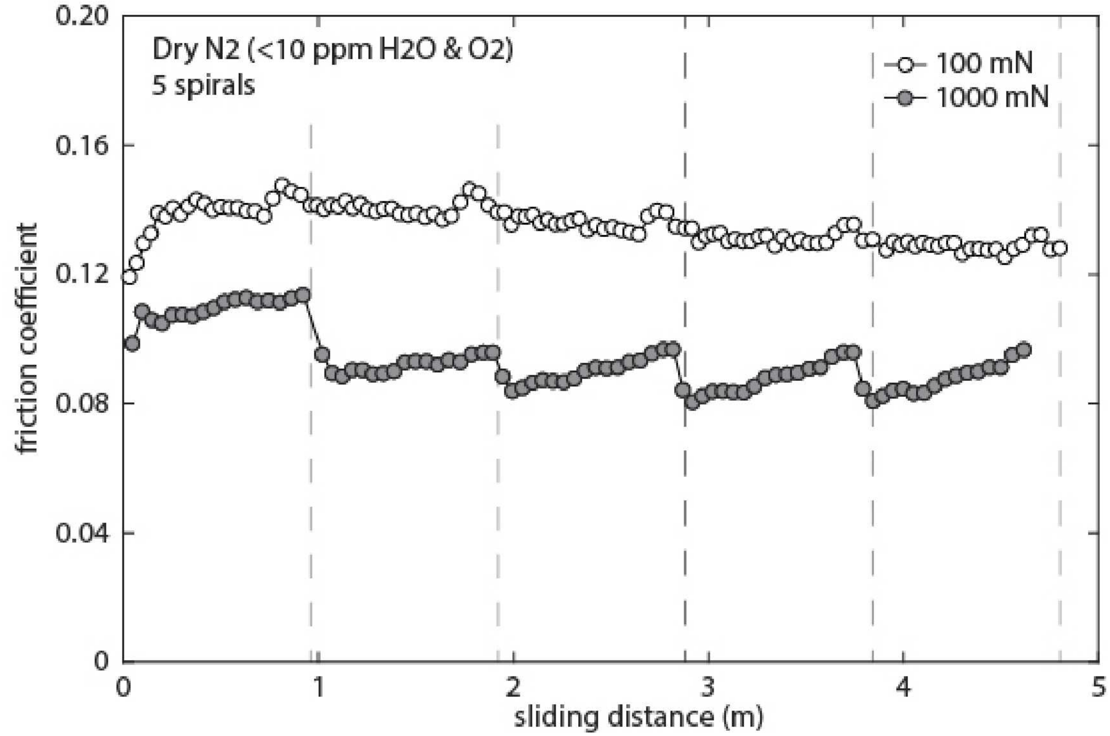


Spiral Orbit MoS2: Endless Run-In and Role of Defects



Spiral orbit experiments enable continuous sliding on unburnished MoS2

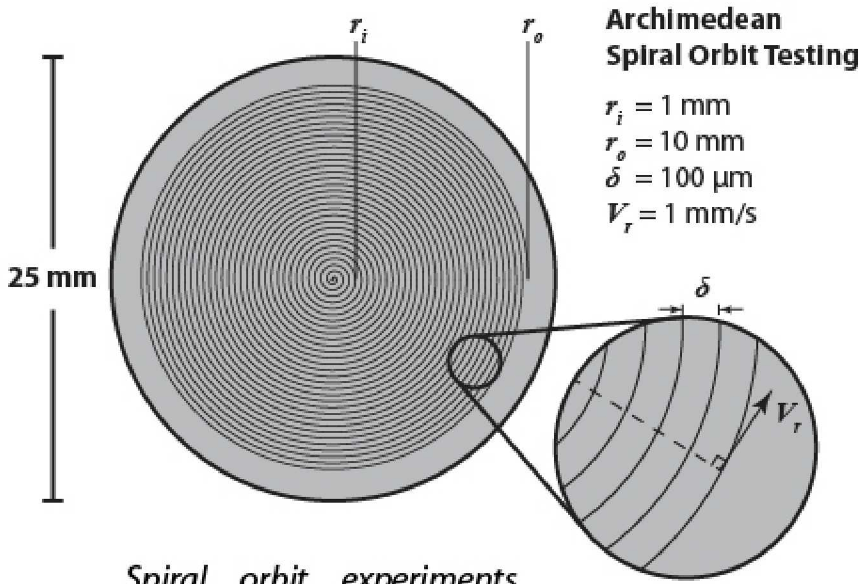


Analysis

- Friction remains high over meters of unidirectional sliding, useful method in testing role of defects

- Sheds light on role of TF formation in reducing friction.

Spiral Orbit MoS2: Endless Run-In and Role of Defects



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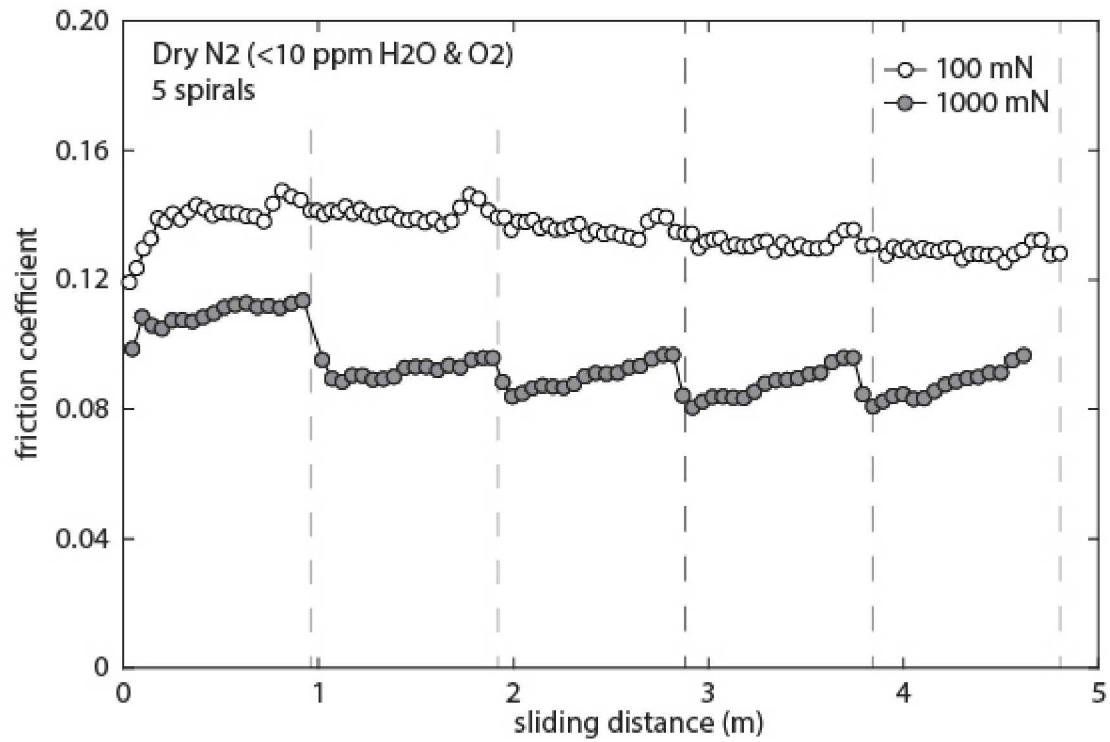


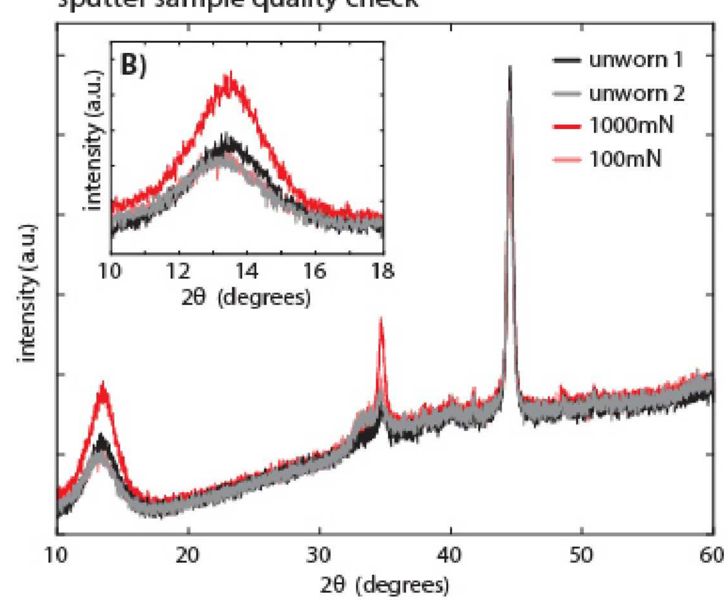
Analysis

• Friction remains high over meters of unidirectional sliding, useful method in testing role of defects

• Sheds light on role of TF formation in reducing friction.

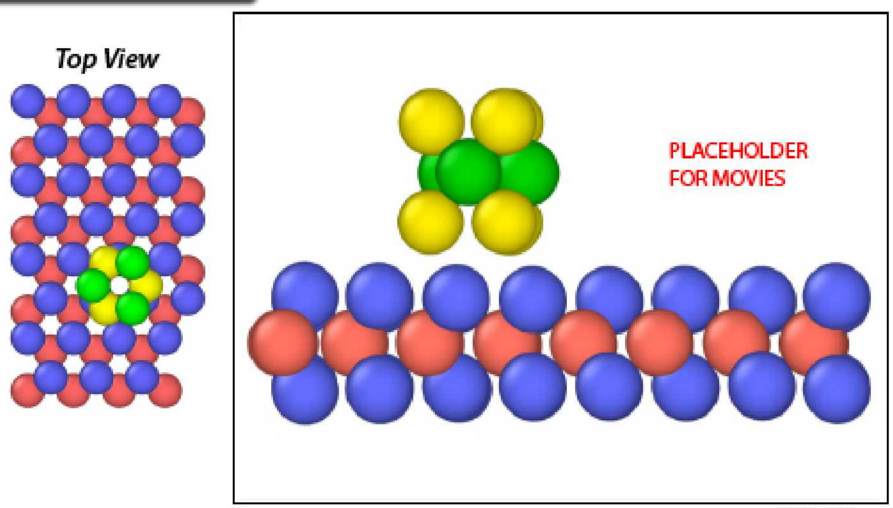
• Load dependence noticed at 100/1000 mN test cases. Increased loads run-in faster, exhibit higher degree of re-orientation sooner, as confirmed by XRD

sputter sample quality check

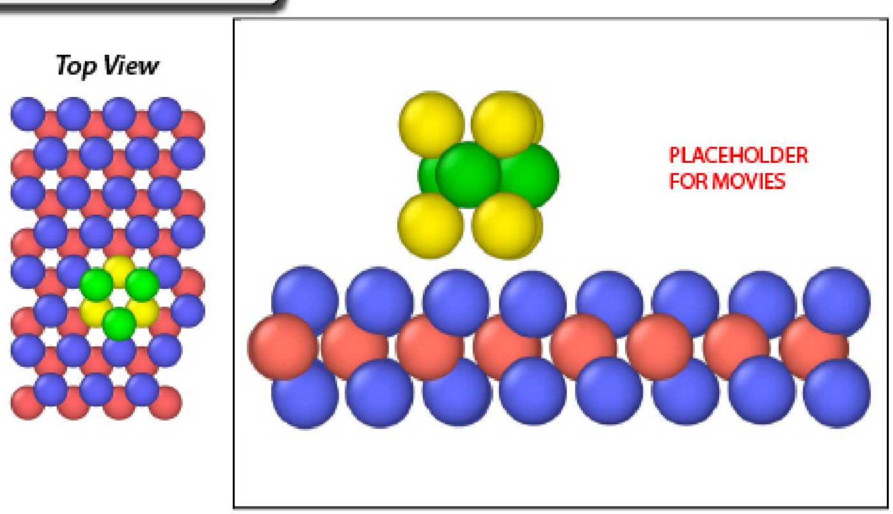


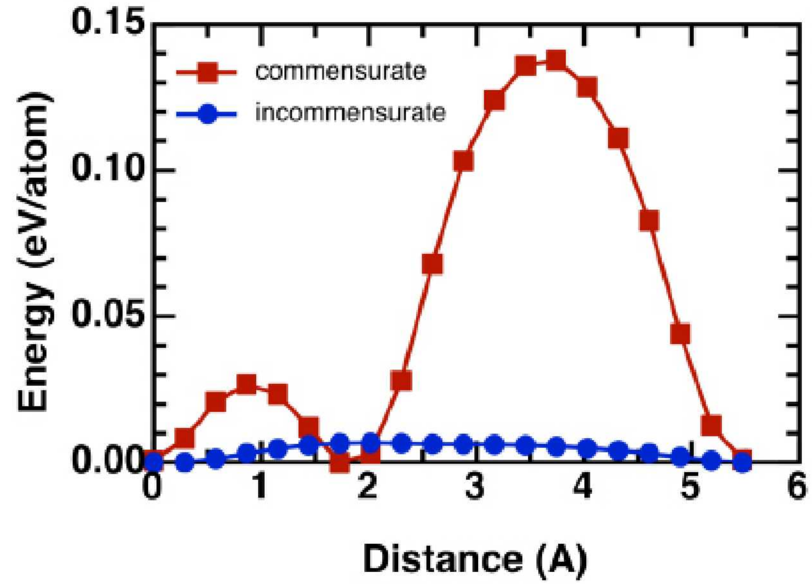
Are Effects of Commensurate Contact Observed in MoS_2?

Commensurate



Incommensurate





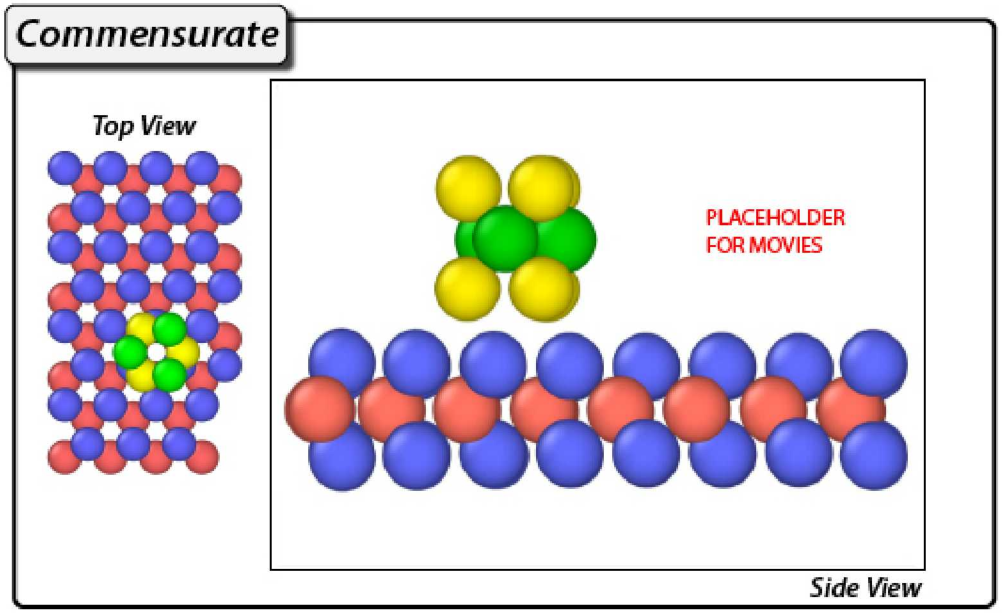
excellent agreement with DFT in T. Liang et. al, Phys. Rev. B77 (2008) 104105-1

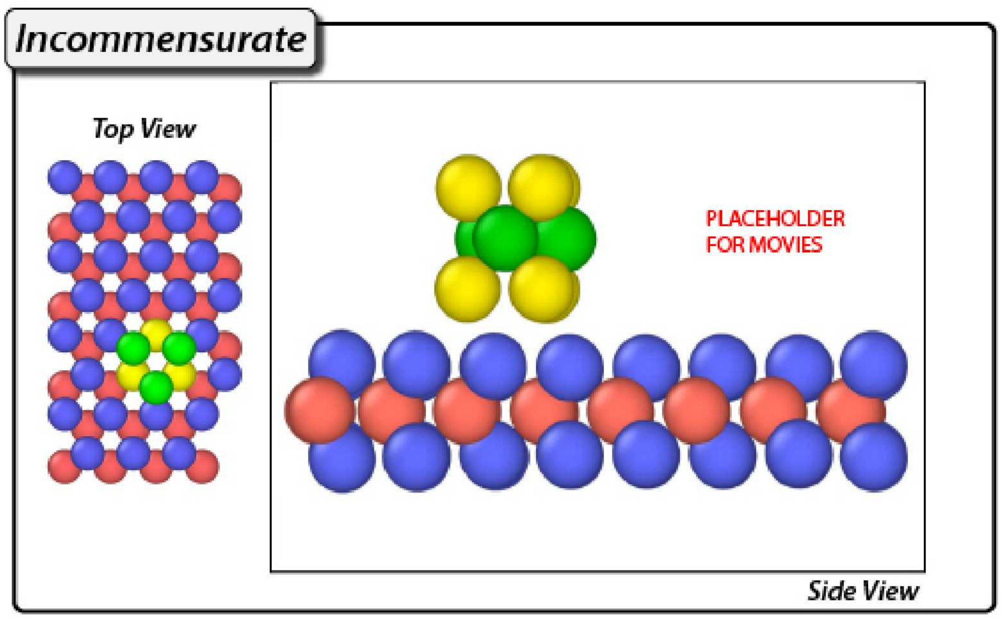
- Lattice rotation (commensurability) plays an important role in the interfacial shear strength of materials, leading to superlubric conditions
- Molecular dynamics with nudged elastic band

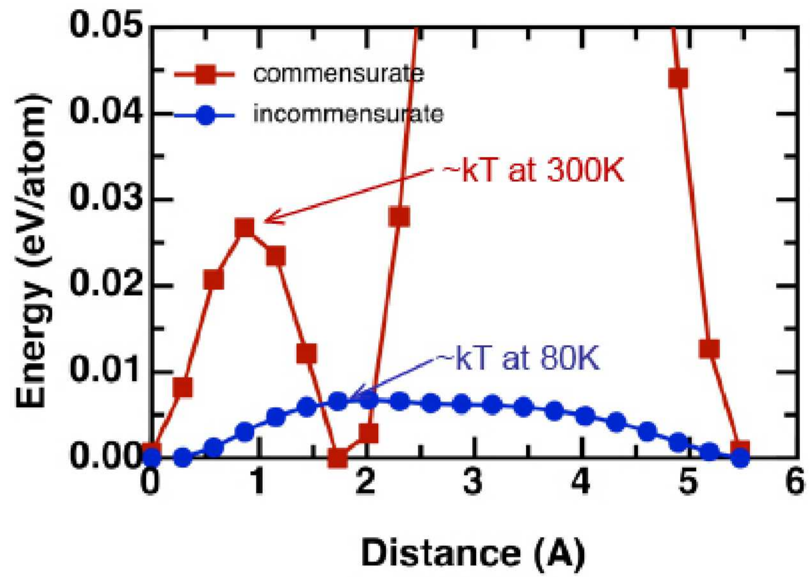
commensurate egg shell

incommensurate egg shell

Are Effects of Commensurate Contact Observed in MoS_2?







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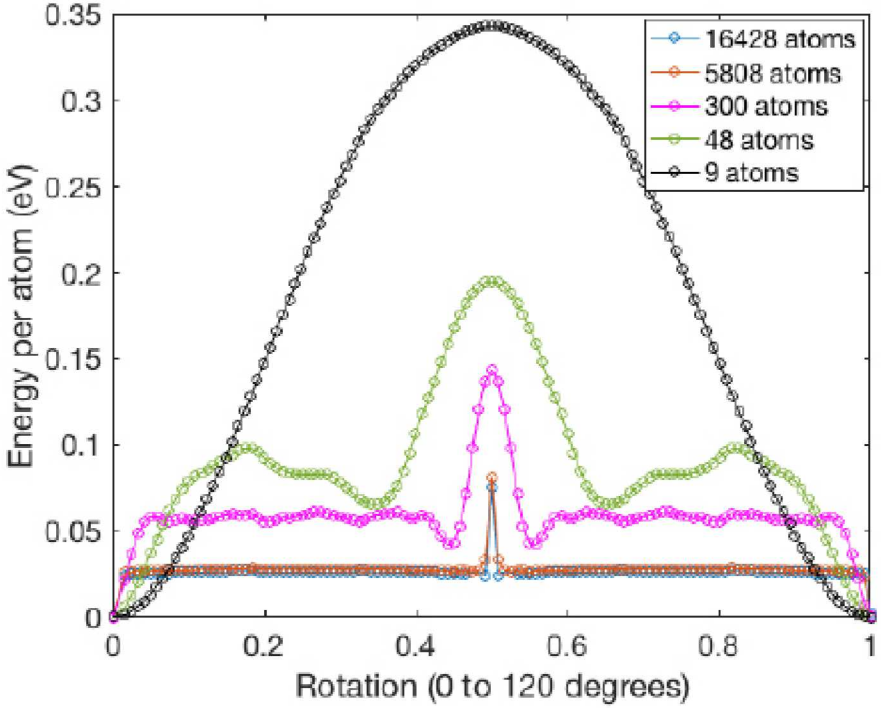
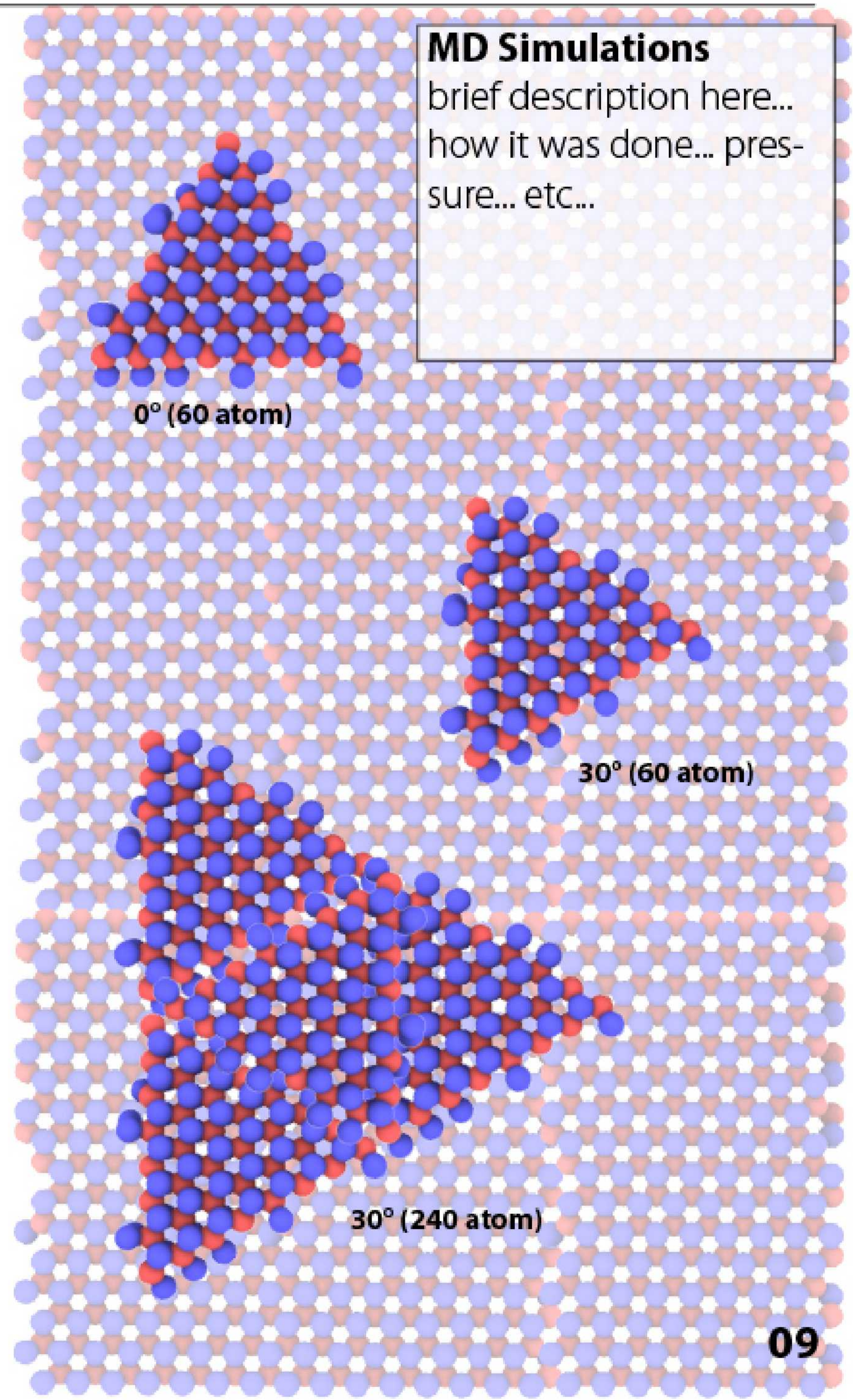
- Lattice rotation (commensurability) plays an important role in the interfacial shear strength of materials, leading to superlubric conditions
- Molecular dynamics with nudged elastic band
- Commensurate barrier ~10x incommensurate
- Activation energy from exp/sim = 1.3 kJ/mol, NEB = 0.66 kJ/mol

commensurate egg shell

incommensurate egg shell

Flake Rotation Energy Barriers



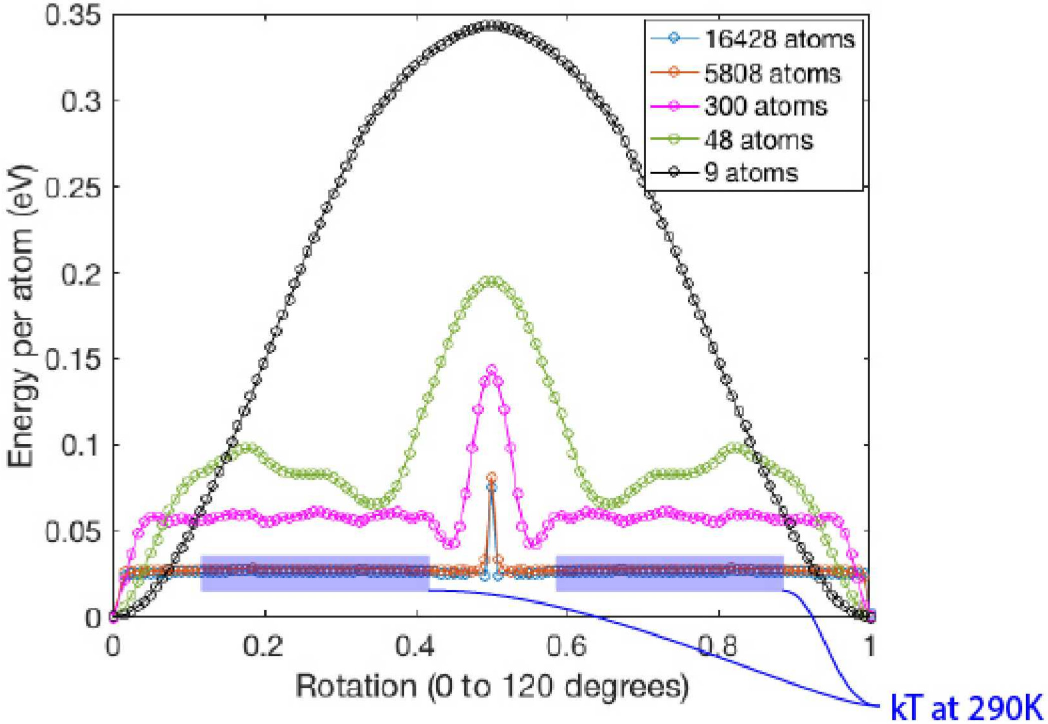


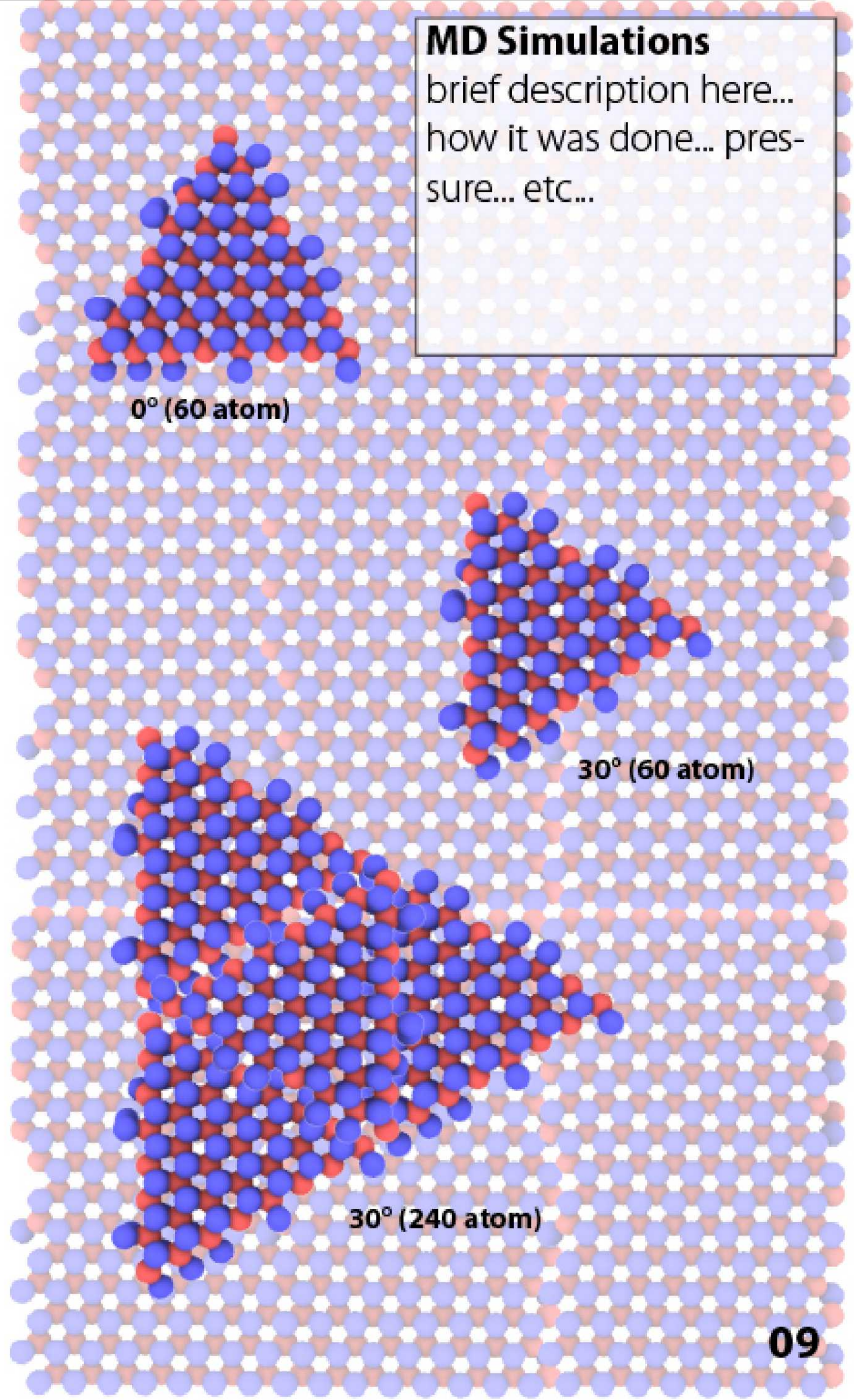
Analysis

- Symmetry about 60°; only takes a few degrees to become incommensurate

- Local maxima occurs at 60° regardless of symmetry

Flake Rotation Energy Barriers





Analysis

- Symmetry about 60°; only takes a few degrees to become incommensurate
- Local maxima occurs at 60° regardless of symmetry
- Energy barrier to rotation converges at larger flake sizes ~ **kT at 290K**

Sandia National Laboratories

Thermokinetics Model of Friction

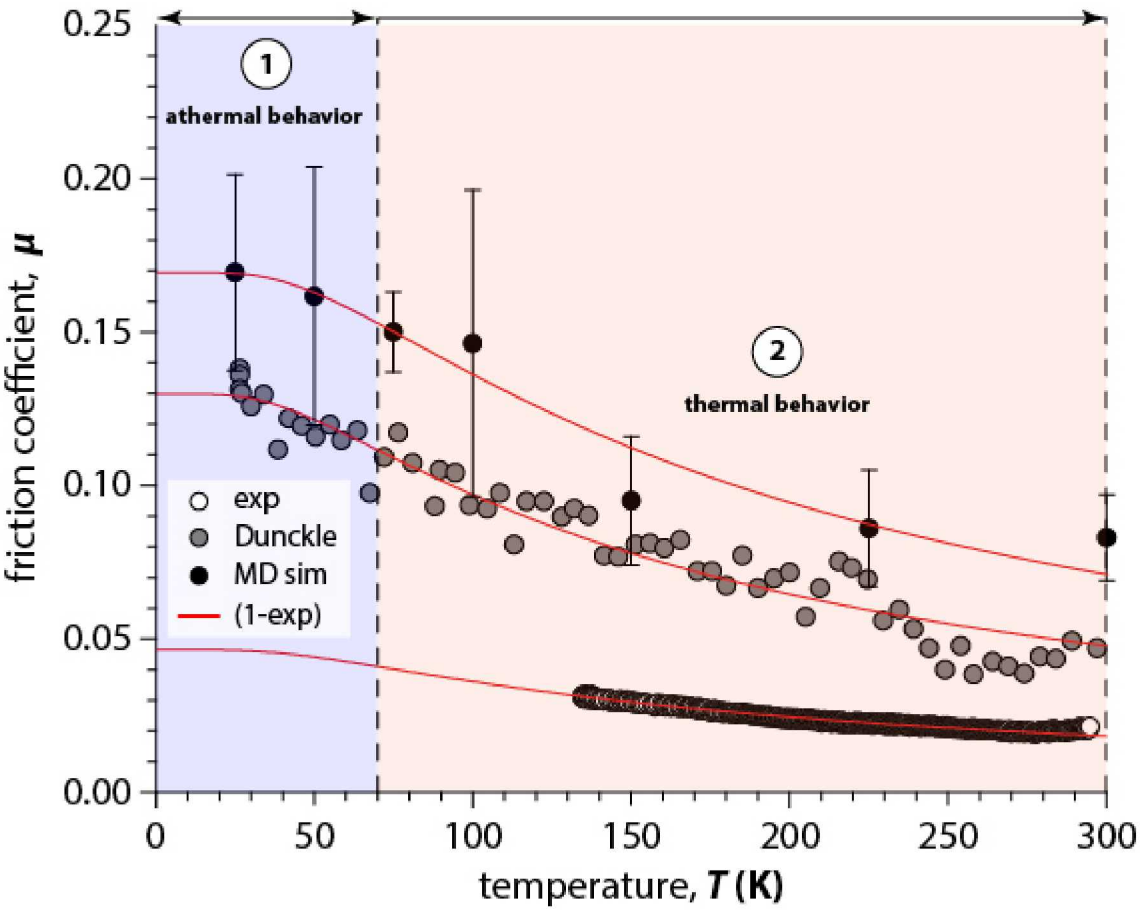
commensurability

defect density

$$\mu \propto S_{film} = S_0 \cdot f(\Phi, \rho_{def}) \cdot \left[1 - \exp\left(-\frac{E_a}{RT}\right)\right]$$

fundamental shear strength of defect-free MoS2

temperature dependence



temperature dependent regimes

1) not enough thermal energy to translate & rotate, stress driven

2) energy barriers to incommensurate translation are overcome and thermal energy drives flake mobility reducing friction

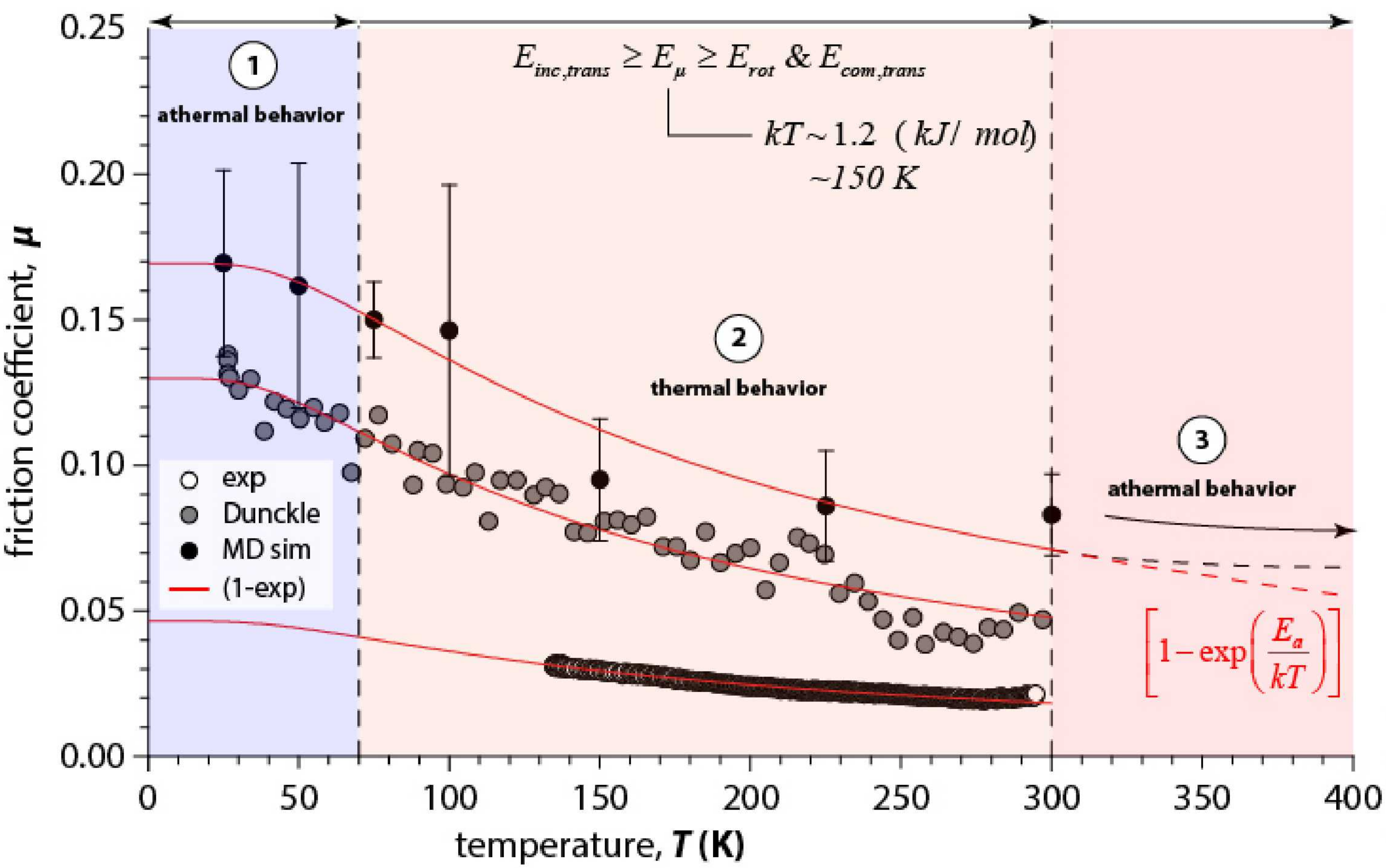
$$E_{inc,trans} \approx 0.006 \ (eV / atom)$$
$$kT @ 70K$$

Thermokinetics Model of Friction

commensurability — defect density

$$\mu \propto S_{film} = S_0 \cdot f(\Phi, \rho_{def}) \cdot \left[1 - \exp\left(-\frac{E_a}{RT}\right)\right]$$

fundamental shear strength of defect-free MoS2 — temperature dependence



temperature dependent regimes

1) not enough thermal energy to translate & rotate, stress driven

2) energy barriers to incommensurate translation are overcome and thermal energy drives flake mobility reducing friction

$$E_{inc,trans} \approx 0.006 \ (eV/atom)$$
$$kT @ 70K$$

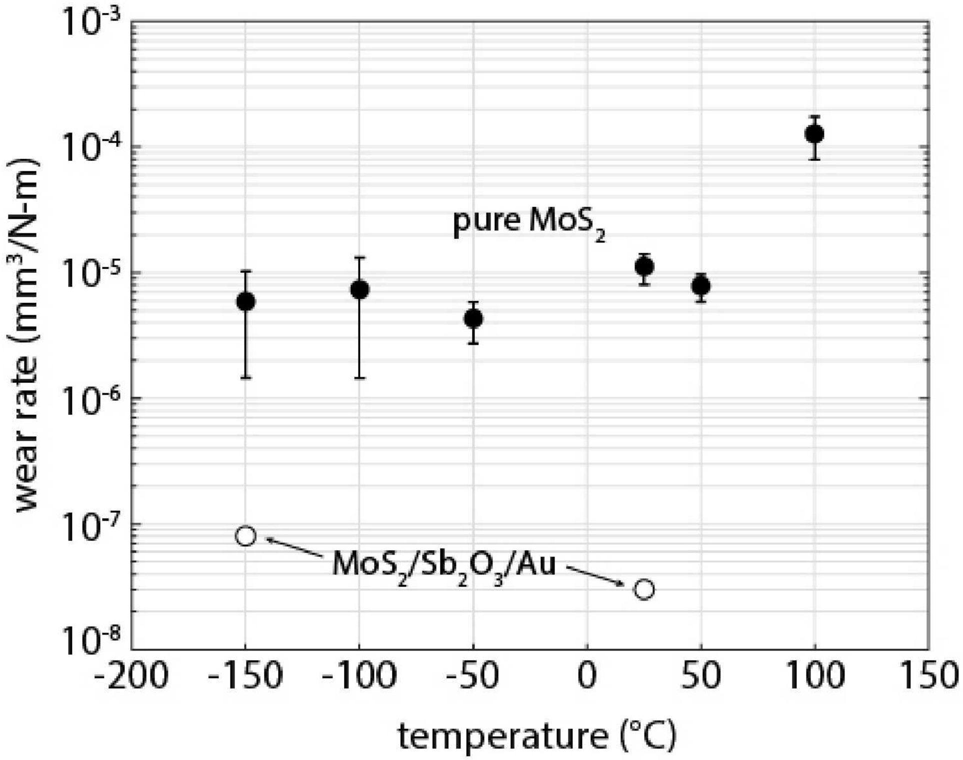
3) Overcome energy barrier to commensurate sliding, excess thermal energy enhances flake mobility and leads to unstable interfaces

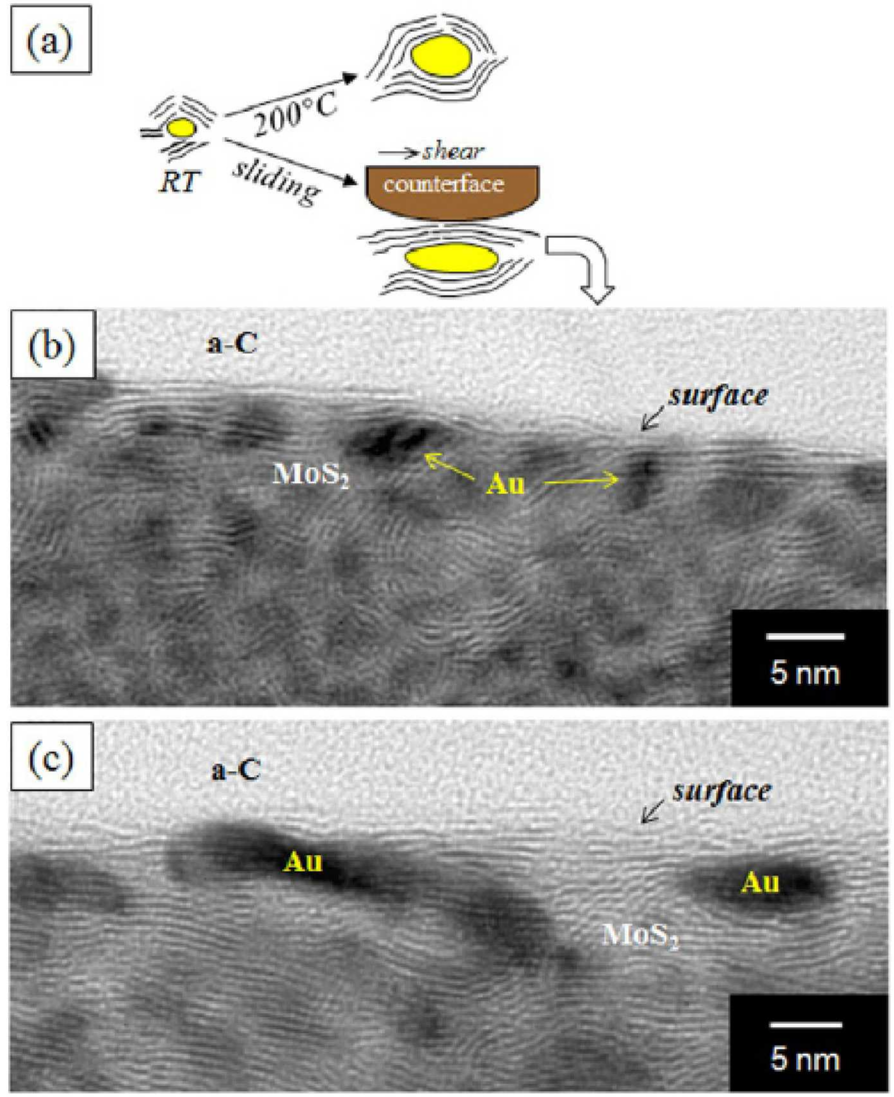
$$E_{rot} \approx 0.025 \ (eV/atom)$$
$$kT @ 290K$$

$$E_{com,trans} \approx 0.027 \ (eV/atom)$$
$$kT @ 313K$$

- return to athermal behavior
- deviation from (1-exp) model fits
- instability allows for flakes to be easily pushed out of contact, amplifying wear

Do Composites Help Pin MoS_2 Lamellae?





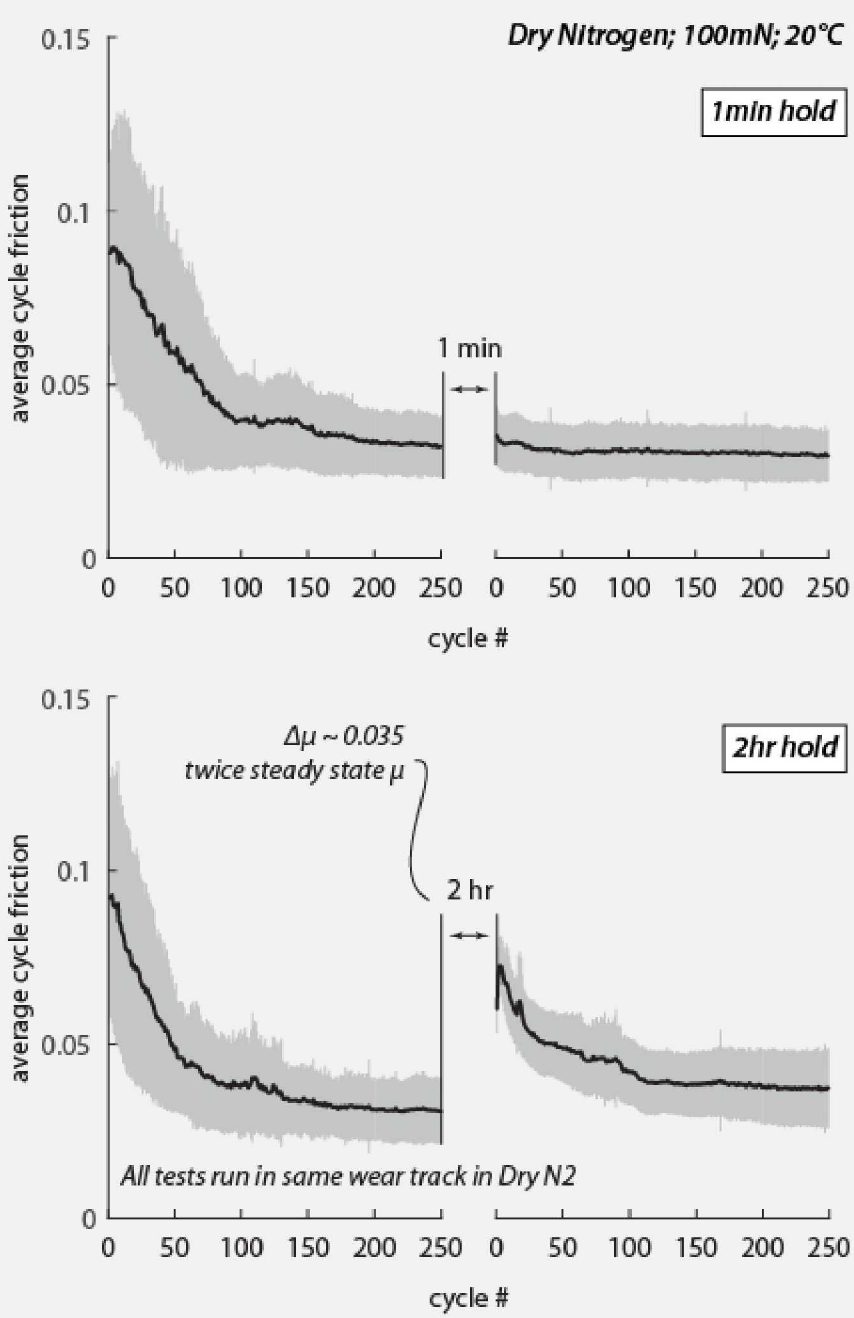
ref: Scharf et al. ACS Applied Materials&Interfaces 2013

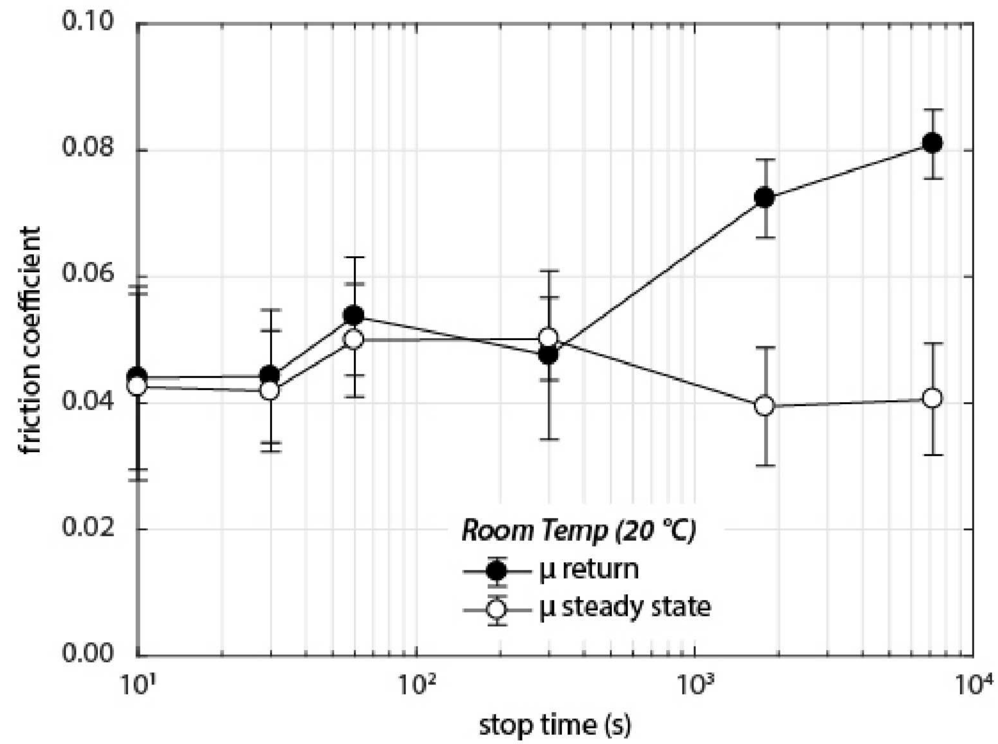
Wear occurs at higher temperatures for pure MoS_2 but not composites

Colbert has shown for MoS_2 composites that cold temps produce small, flaky wear debris & high temps produce a range of debris sizes.

May be a bi-product of crystallite mobility

Stop-Time Studies: The Link Between Run-In & Commensurability?





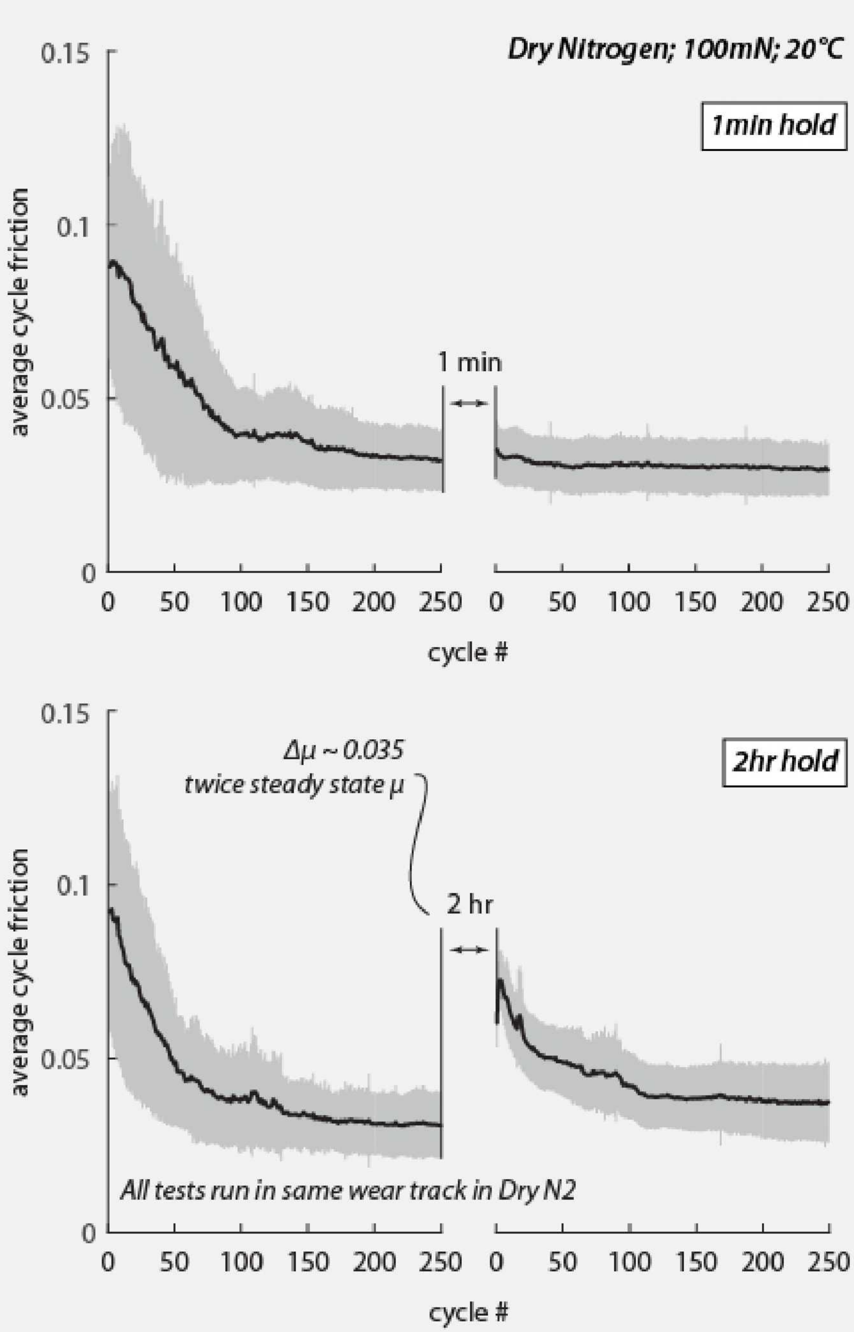
Stop times:	10s; 30s; 1min; 5min; 30min; 2hr
Environment:	Dry Nitrogen
Test Type:	Reciporacting Pin on Flat
Load:	100mN
Sample:	N_2 Sprayed MoS_2

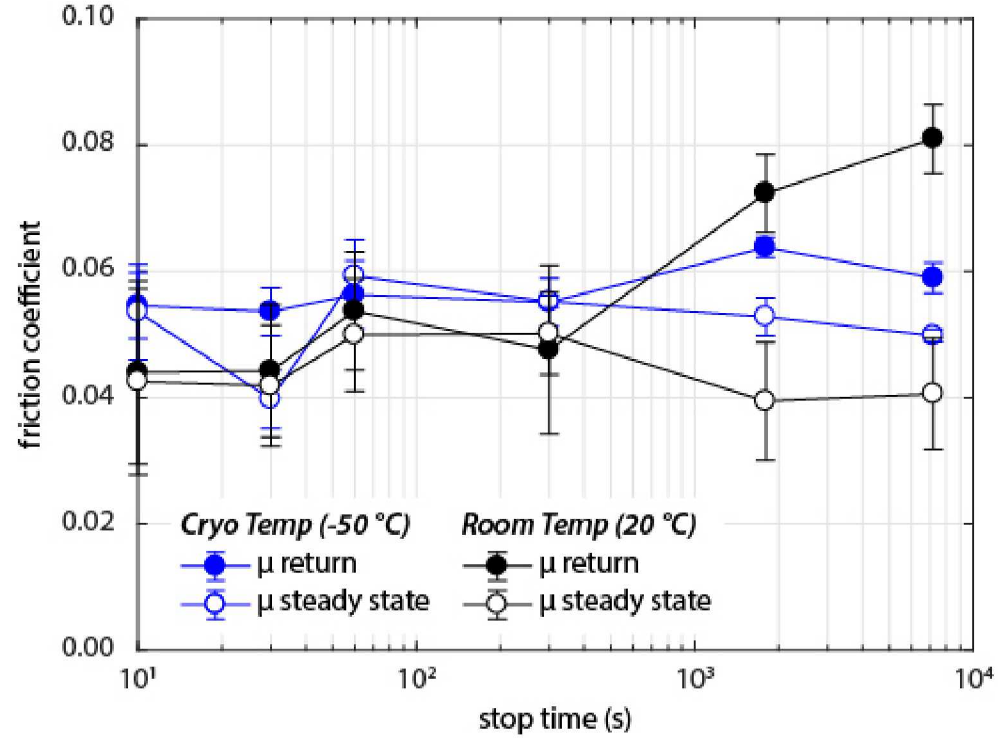
Analysis

(1) longer wait times show higher μ return.

(2) barring effects of trace amounts of water - increased run-in friction may be structural in nature

Stop-Time Studies: The Link Between Run-In & Commensurability?





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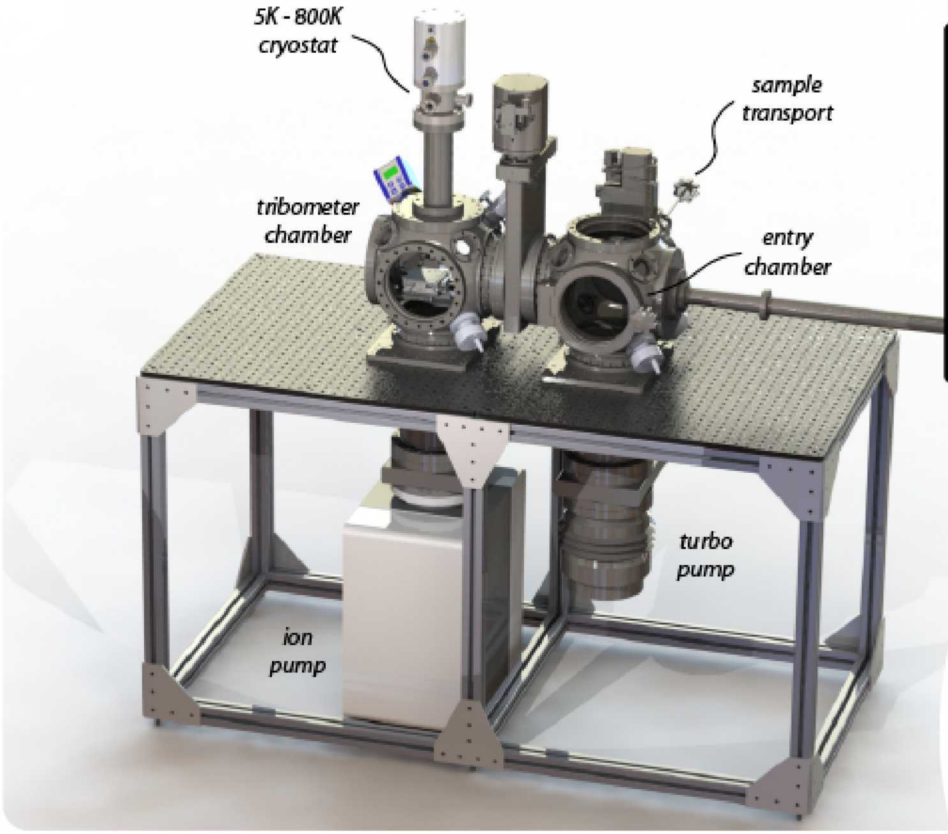
Analysis

(1) longer wait times show higher μ return.

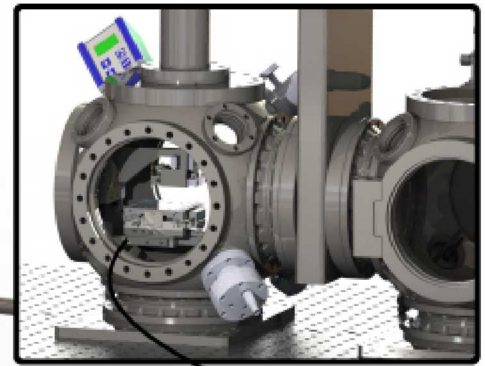
(2) barring effects of trace amounts of water - increased run-in friction may be structural in nature

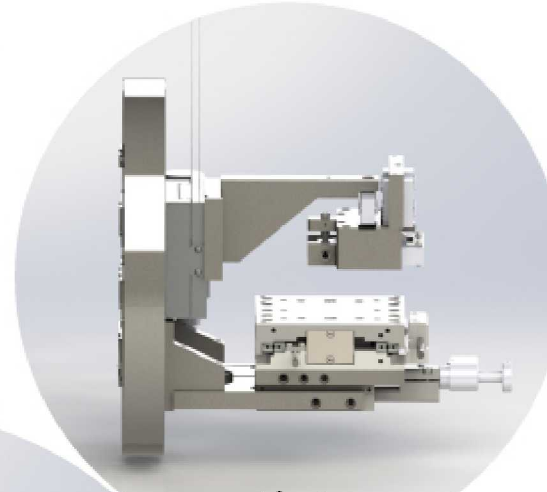
(3) lower temps give higher steady state μ and closer to μ return at higher wait times, possibly by thermally limiting flake rotation

UHV Fast-Entry; Extreme Temperature Tribometer

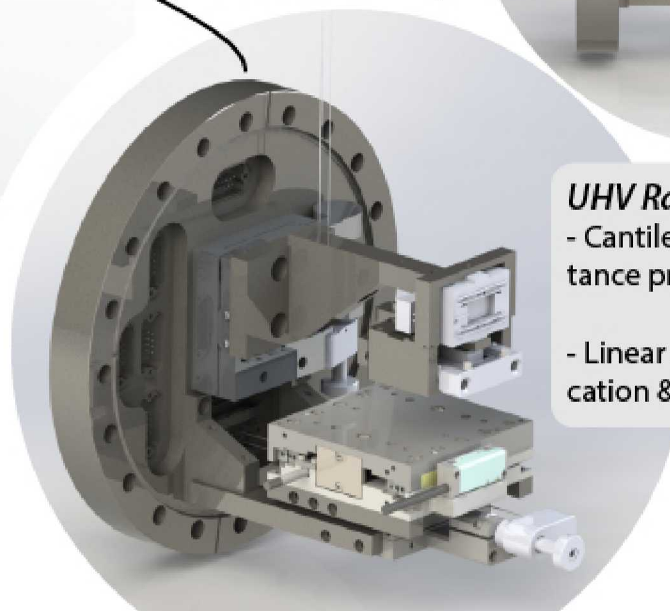


tribometer chamber





side view



iso view

UHV Rated Tribometer
- Cantilever flexure and capacitance probe based load metering

- Linear servo drive stage reciprocation & full XY sample positioning

UHV System
- 5K - 800K temperature range cryostat
- Fast Entry Chamber with inert purging chamber
- Transportable sample rod to carry samples under vacuum for short periods of time
- UV Bakeout Lamps
- Modular design to allow for additional equipment in the future

Studies Enabled
- Lower temperature ramps to confirm temperature dependence & compare to MD
- Clean environments with very near negligible level of contaminants (and water)

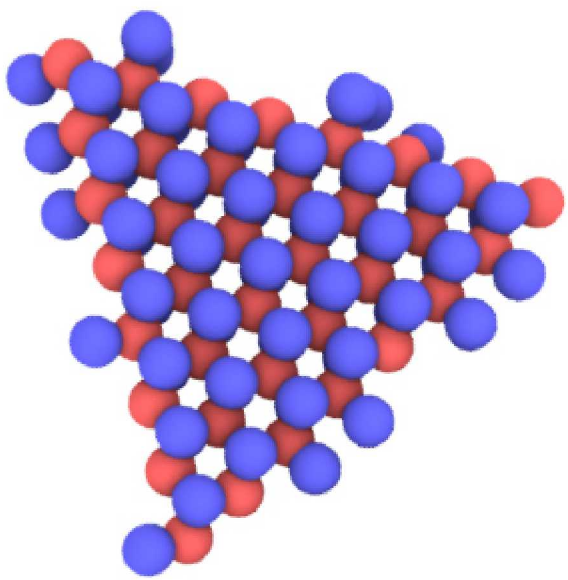
Concluding Remarks

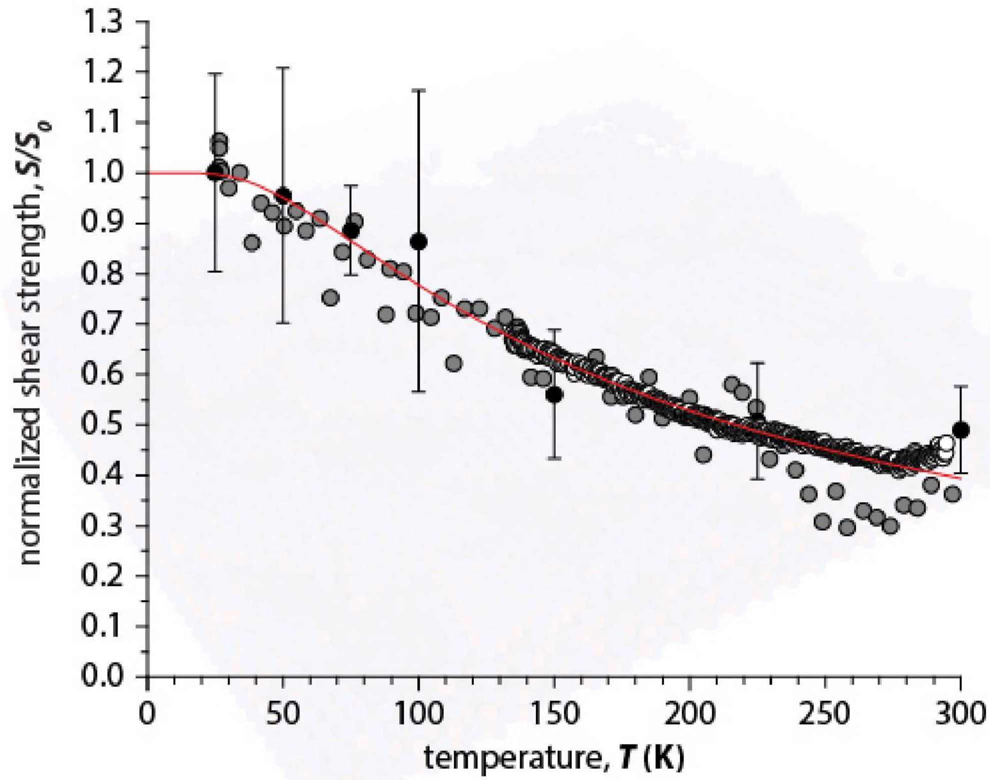
- MoS_2 exhibits a thermal to athermal transition in friction and wear at room temperature

- Experiments and MD suggest there is a functional form to this temperature dependence

- Differences in energy barriers for commensurate vs incommensurate may be part of the explanation for gap between temperature resolved experiemnts & MD results

- "Stop Time" studies provide experimental evidence that crystal relaxation may be occuring over time and increasing friction due to commensurate contact



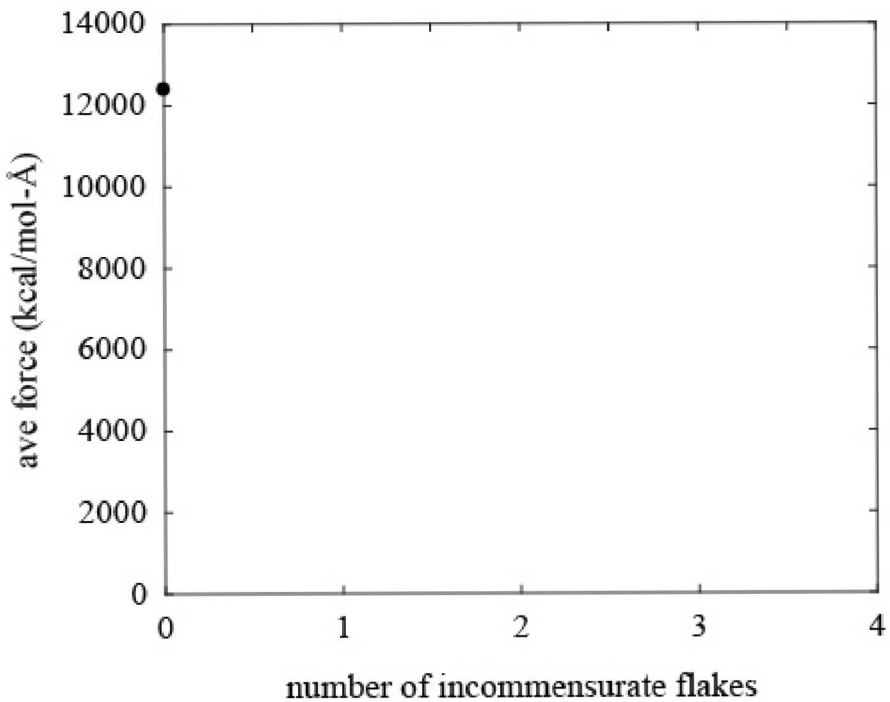


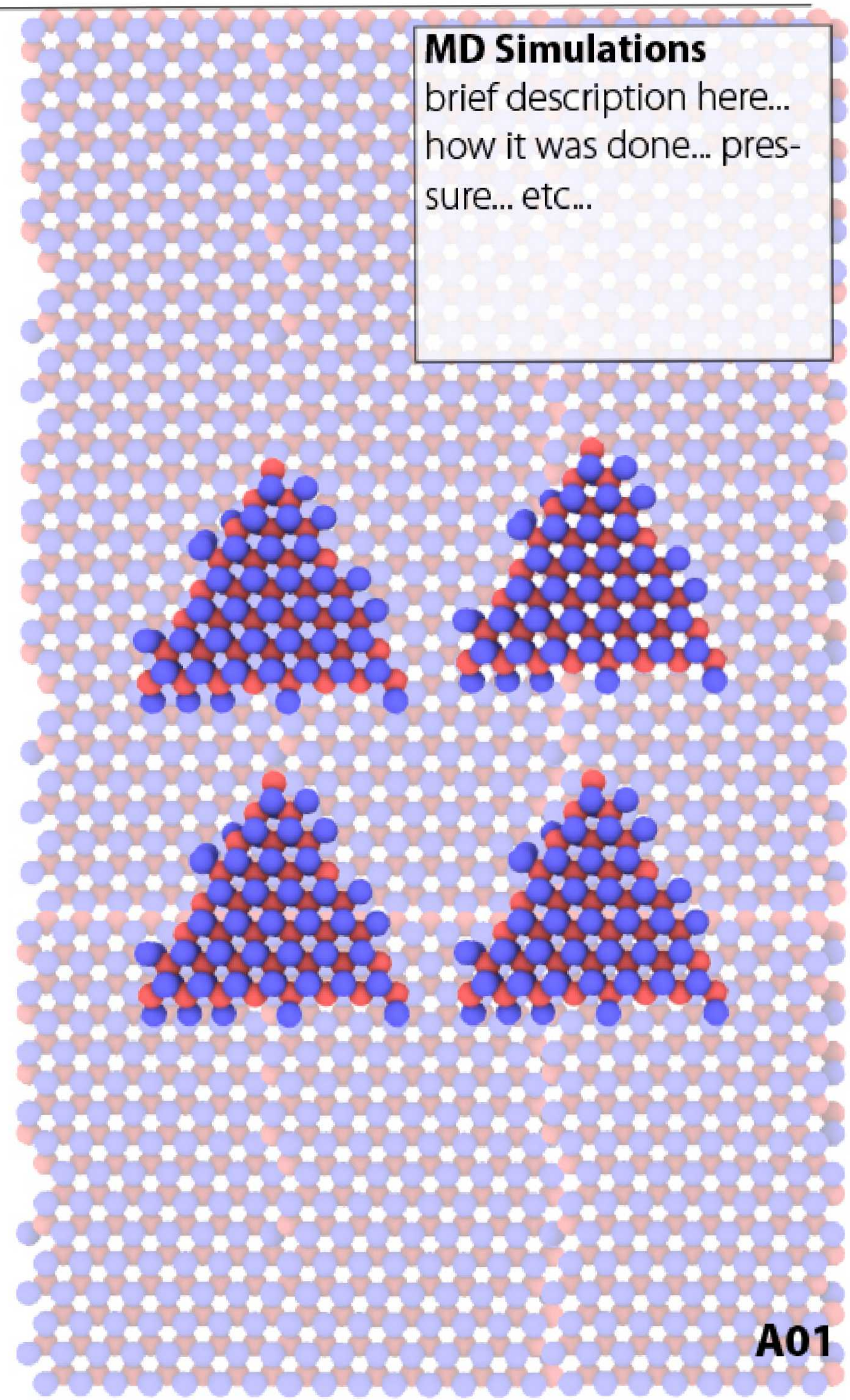
Thank you

Questions?

Appendix

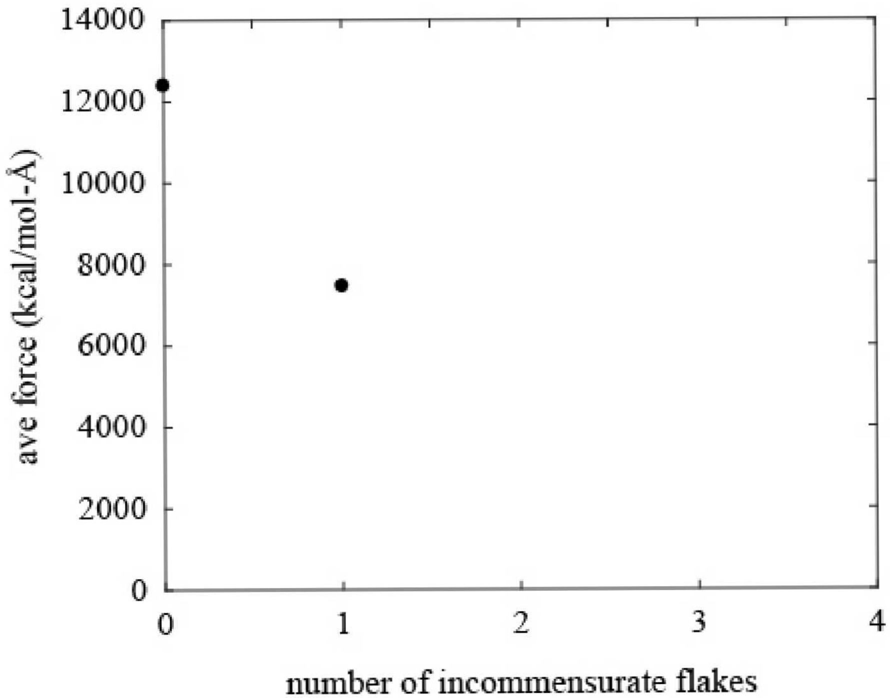
Commensurability Rule of Mixtures

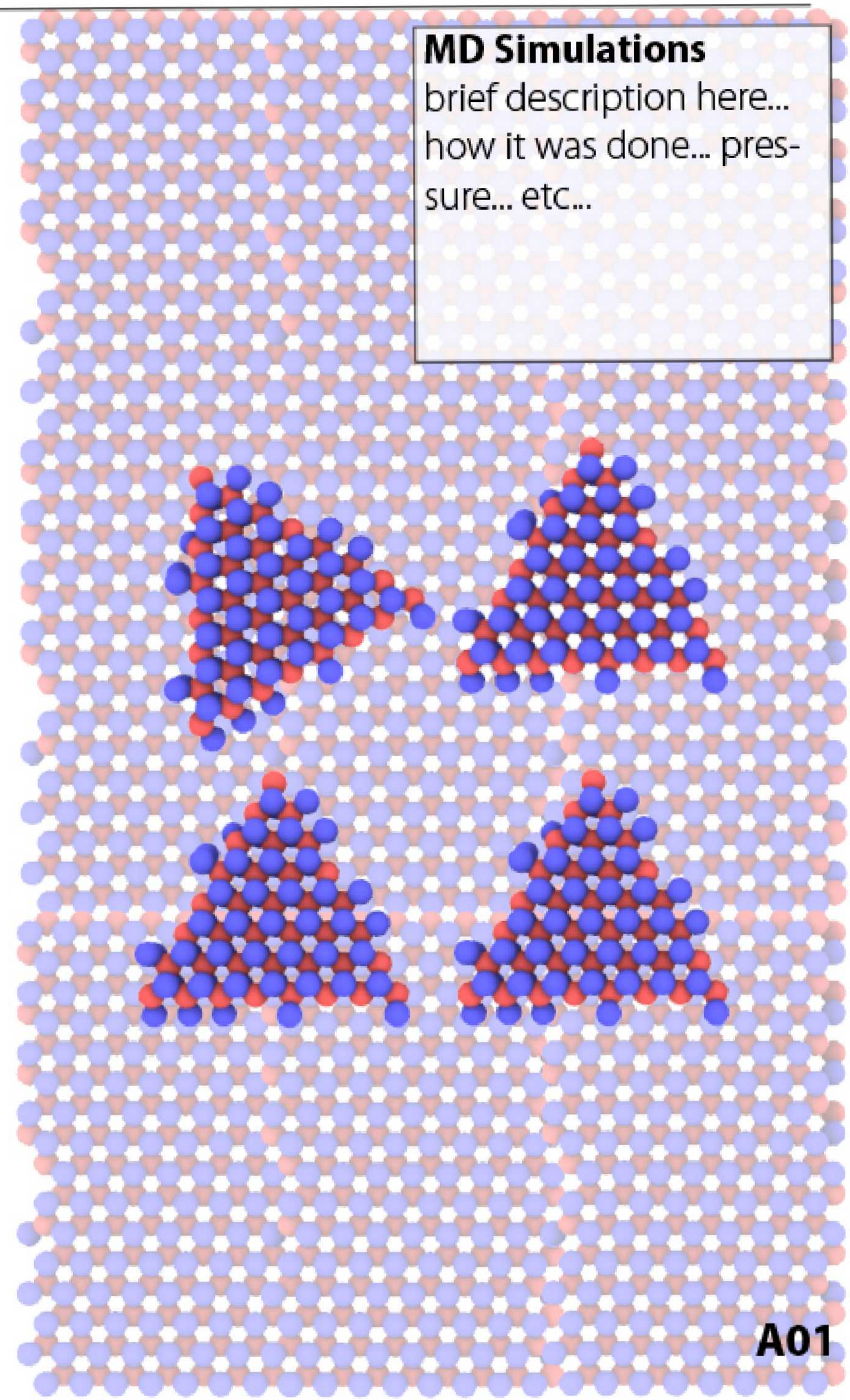




Analysis

Commensurability Rule of Mixtures

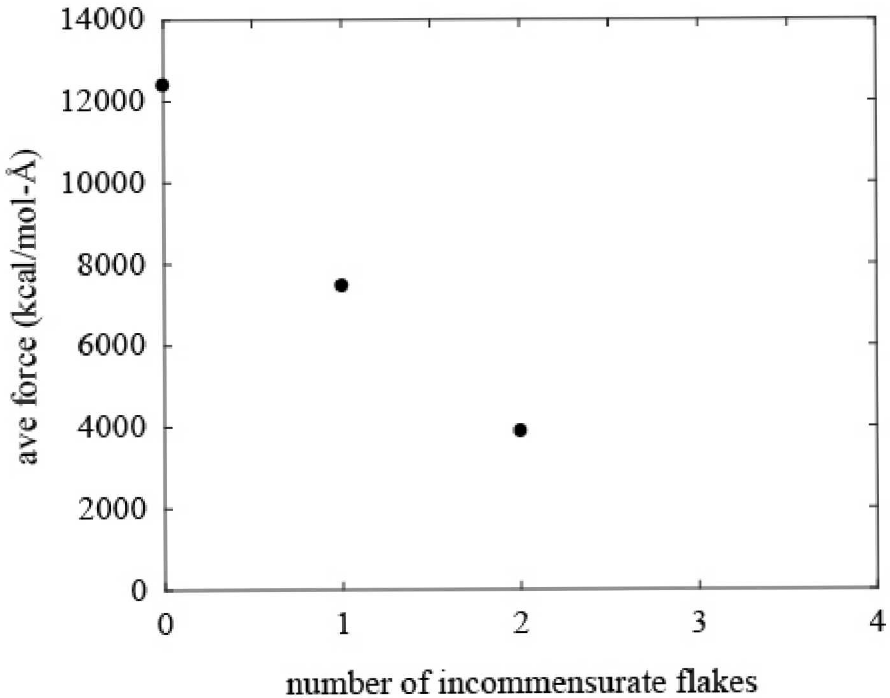


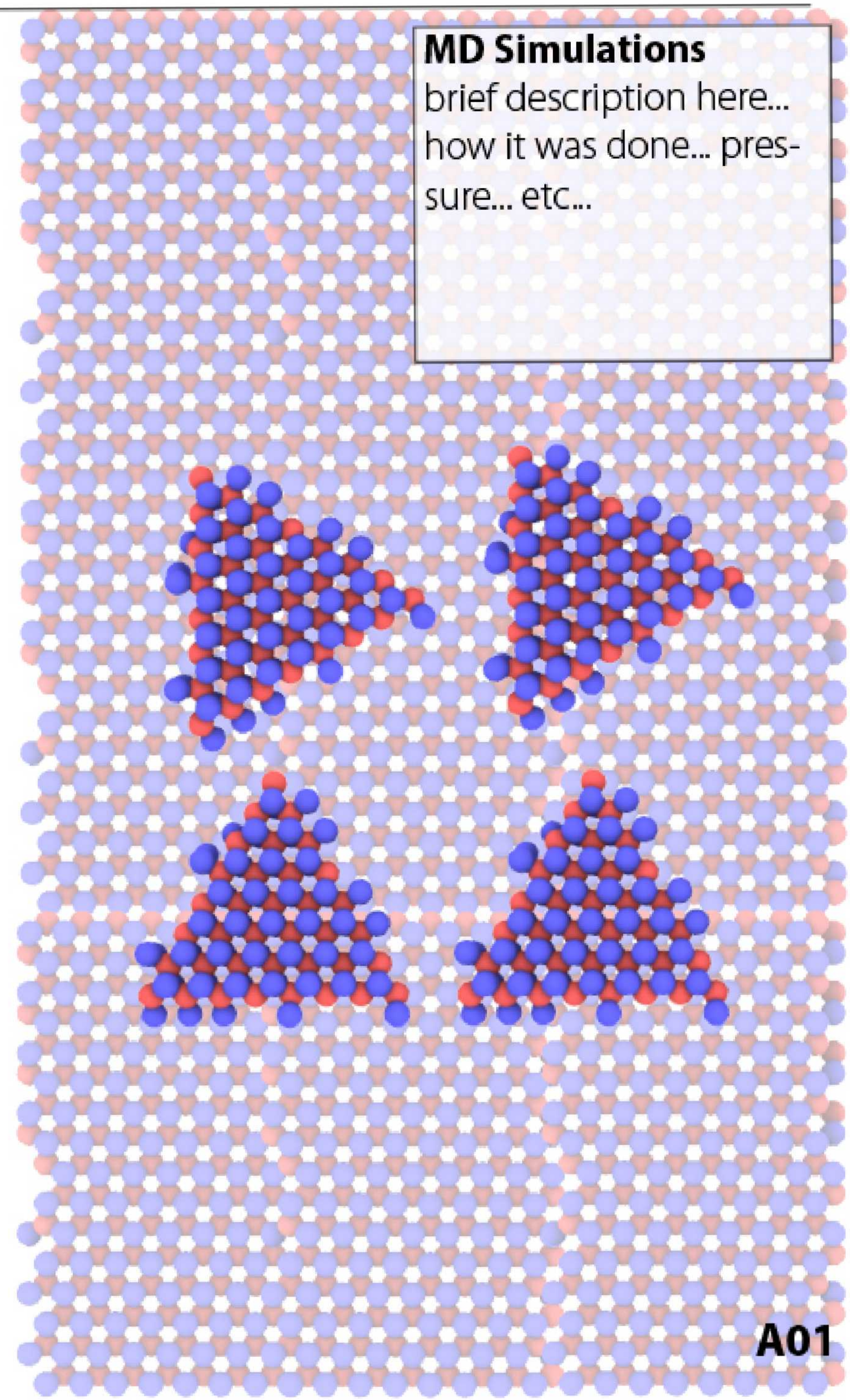


Analysis

- Additional incommensurate flakes reduce friction force

Commensurability Rule of Mixtures





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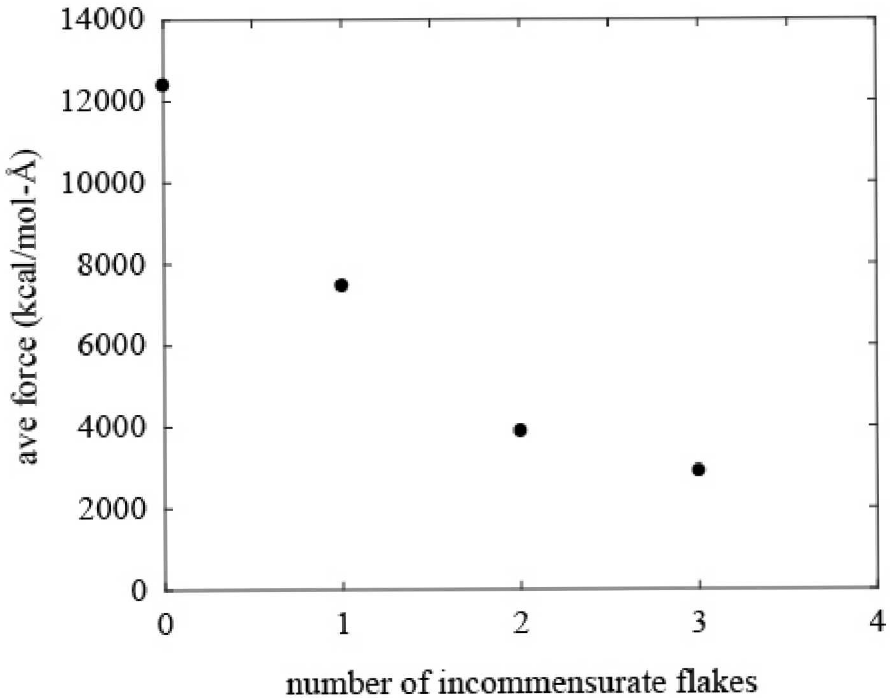

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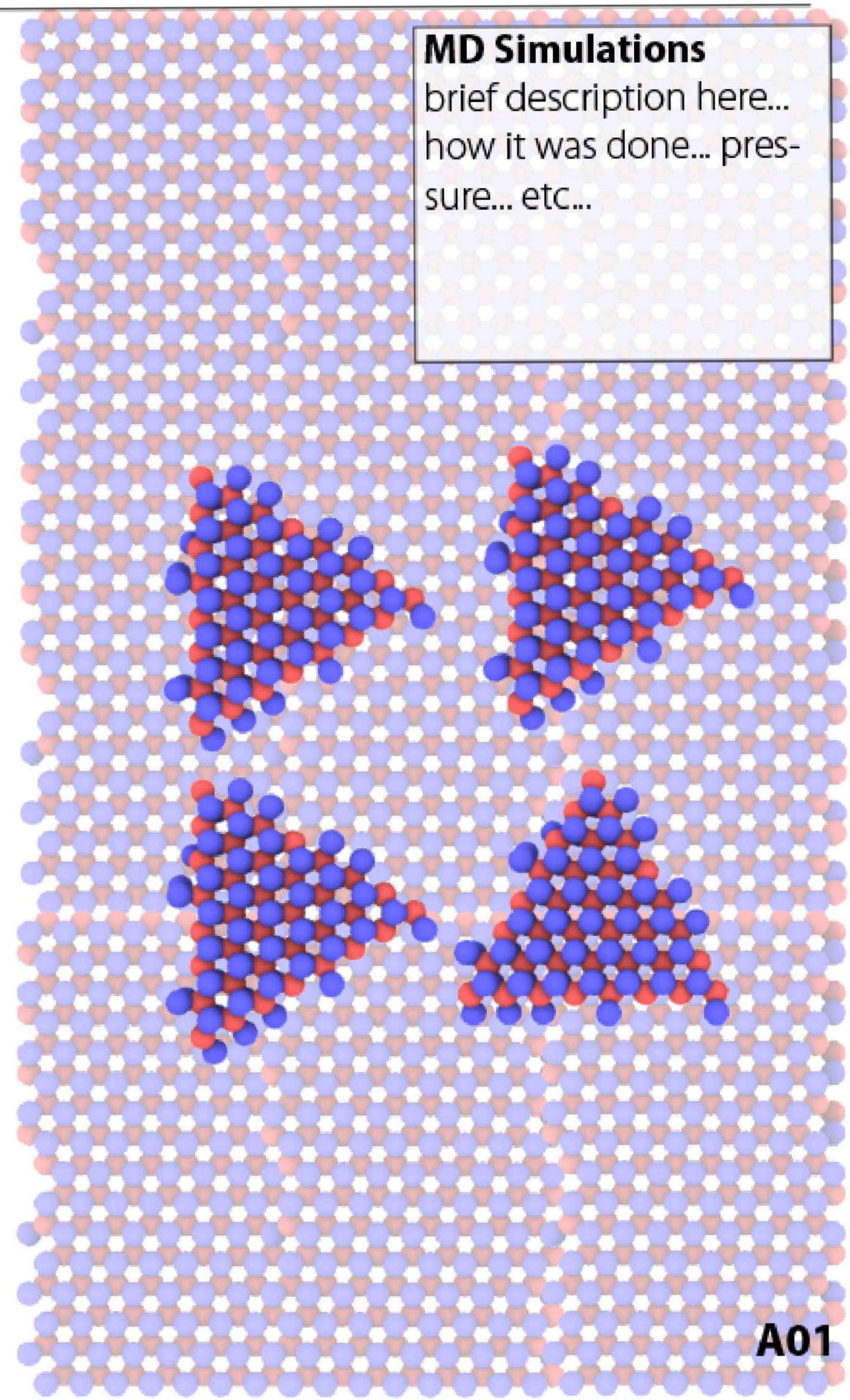

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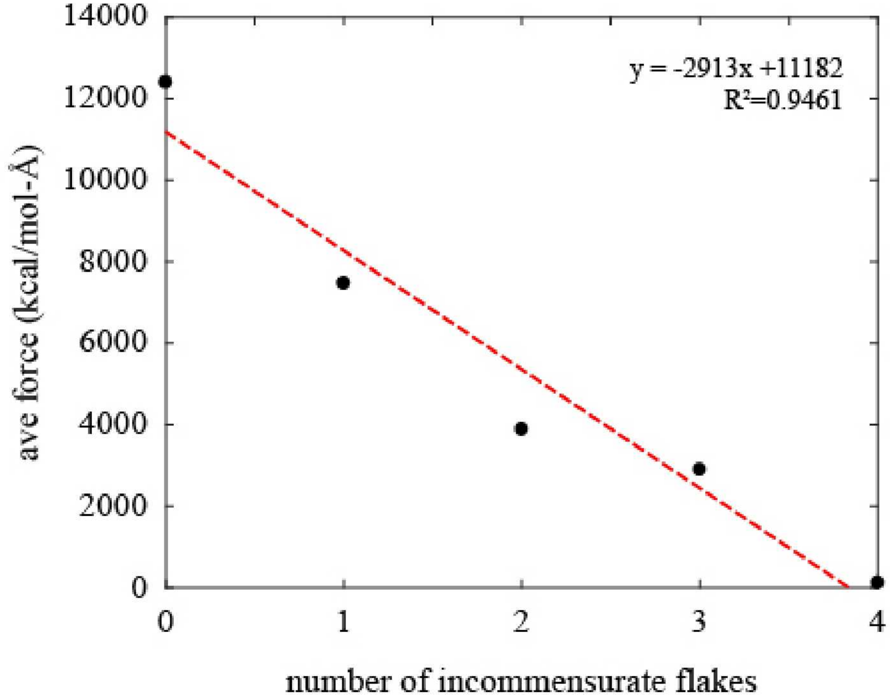
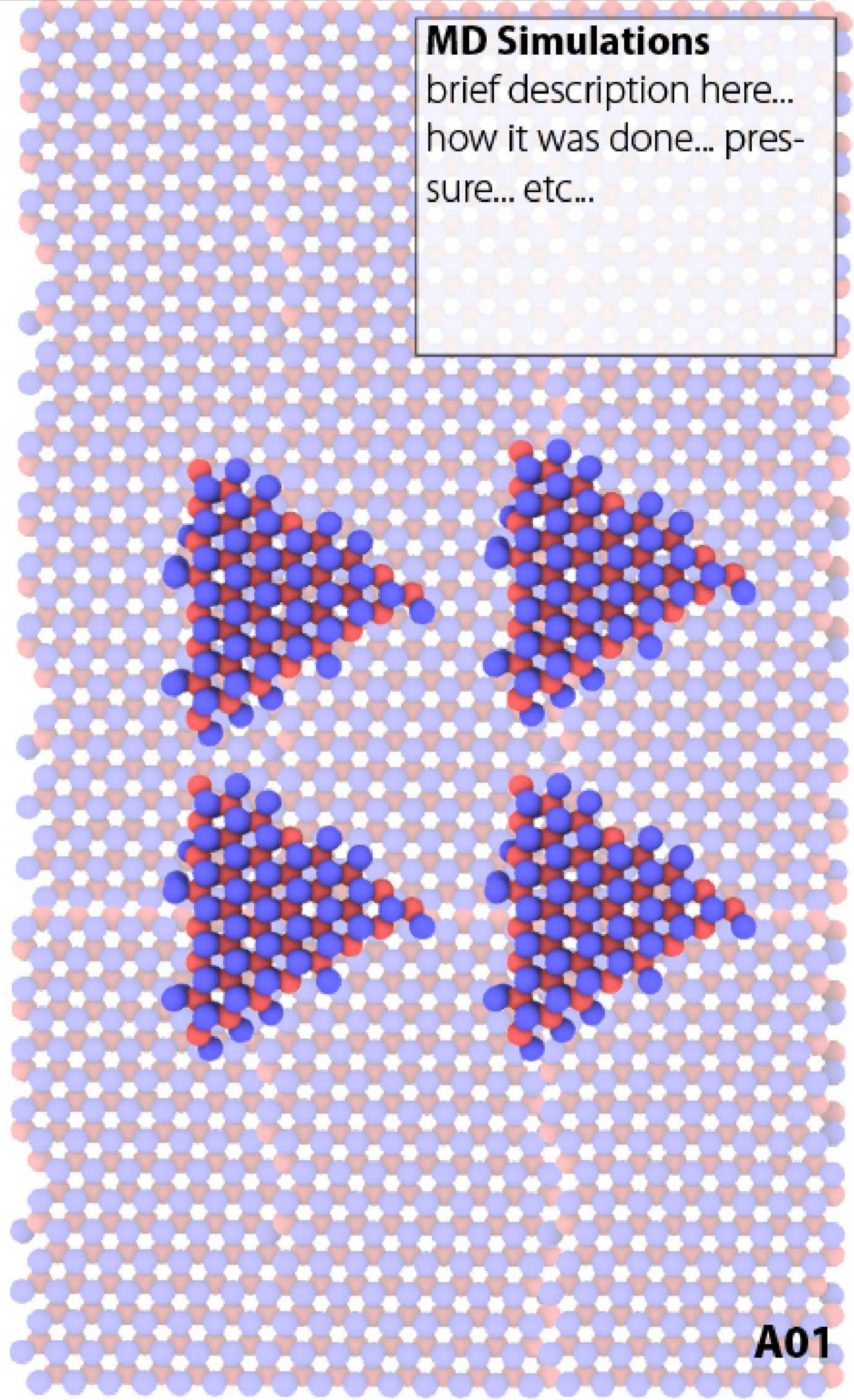


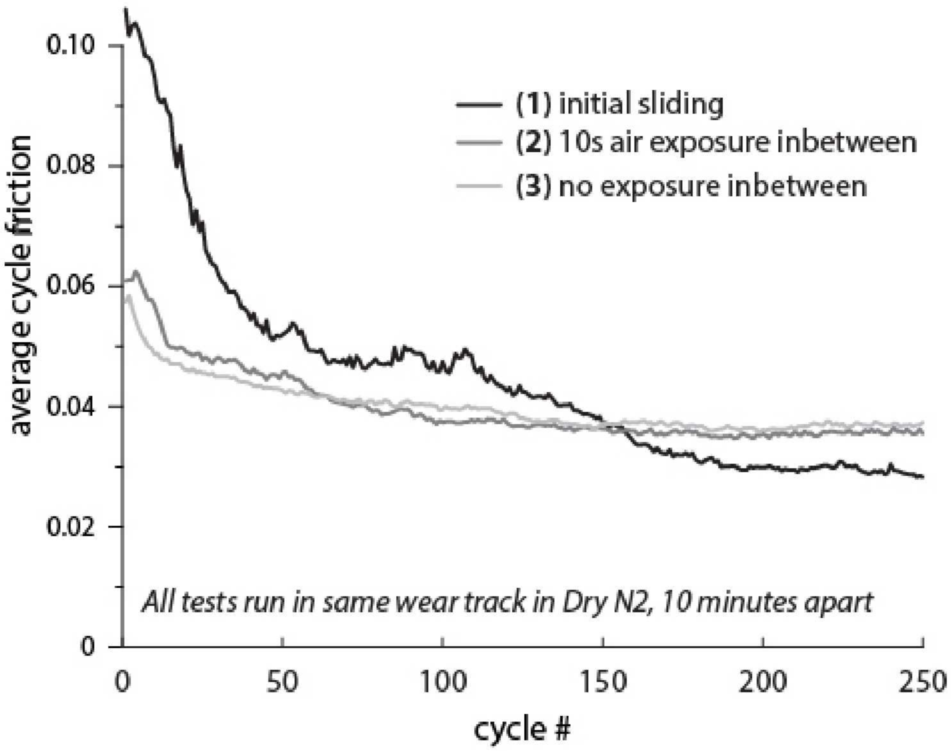
Analysis

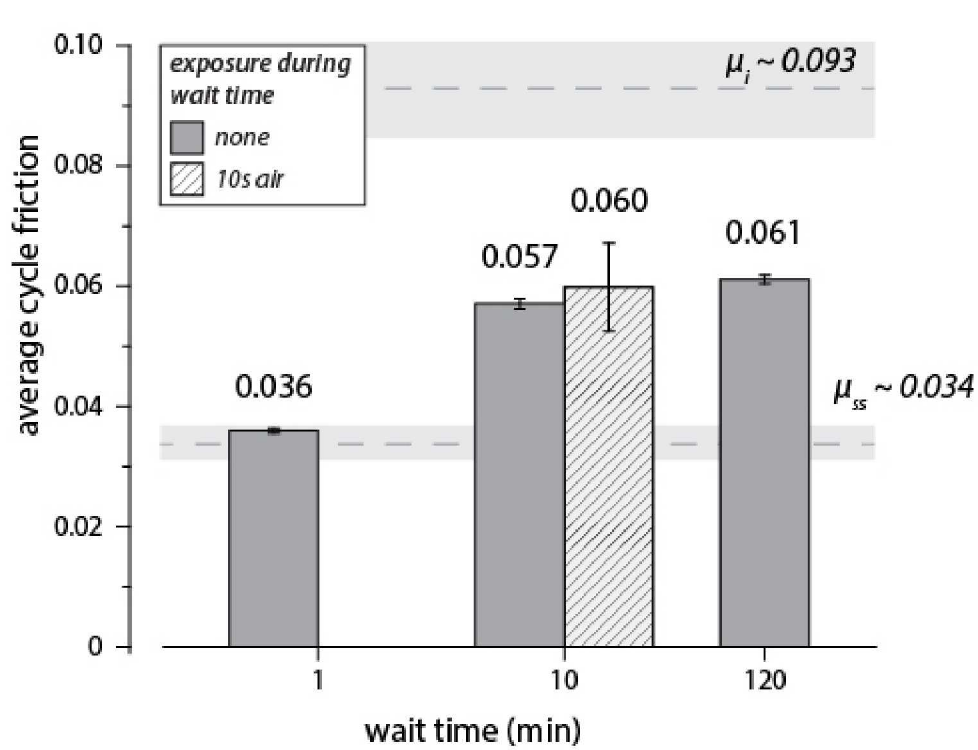
- Additional incommensurate flakes reduce friction force

- Appears to follow a linear rule of mixtures, can be used to refine model



Commensurability or Water?





Method

(1) Initial sliding in dry N_2
- In the 10 min wait between tests, exposed tribometer to lab air via glovebox antechamber

(2) Resumed sliding in dry N_2 (after poisoning)
- Waited 10 min in dry N_2

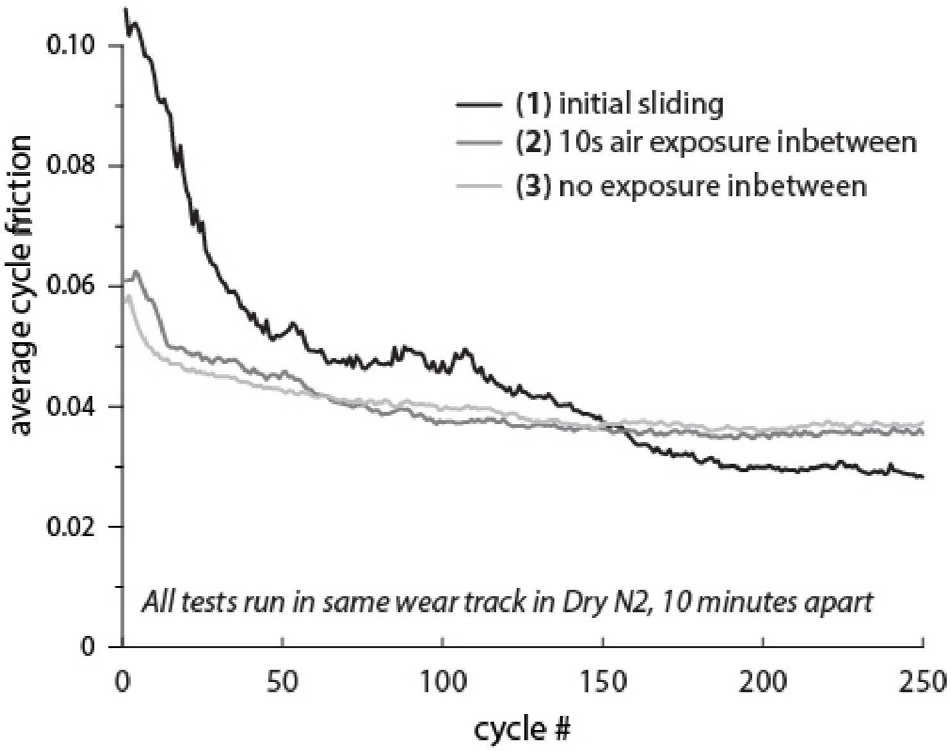
(3) Resumed sliding in dry N_2 (no poisoning)

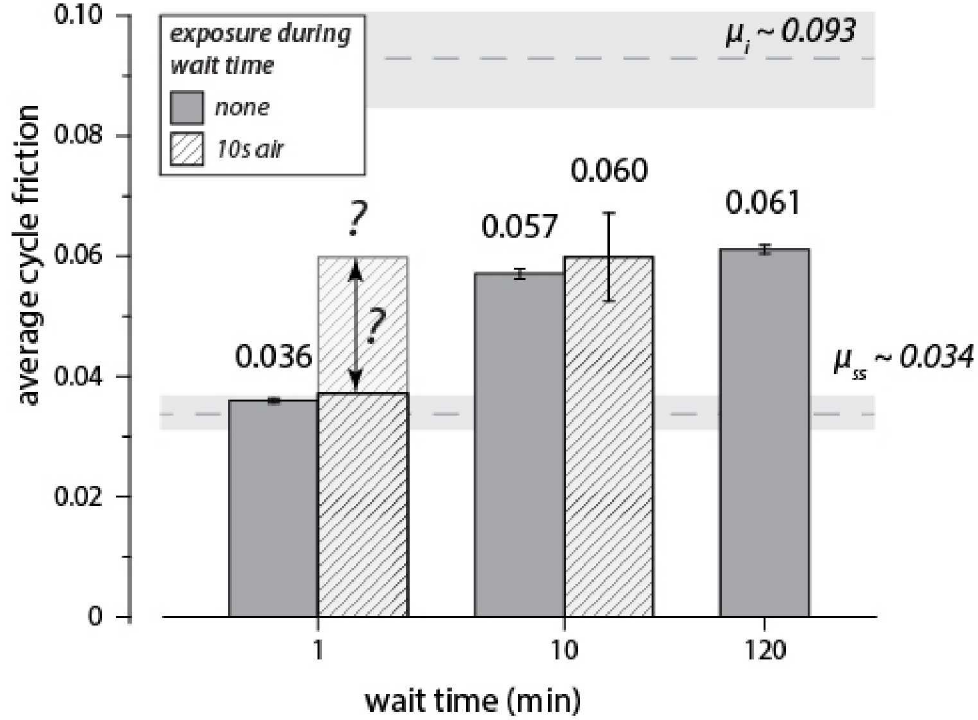
Discussion

(1) What causes "re-run-in" - flake re-orientation or water?

(2) Poisoning surface in between showed no increase over samples sitting in dry N_2

Commensurability or Water?





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Discussion

(1) What causes "re-run-in" - flake re-orientation or water?

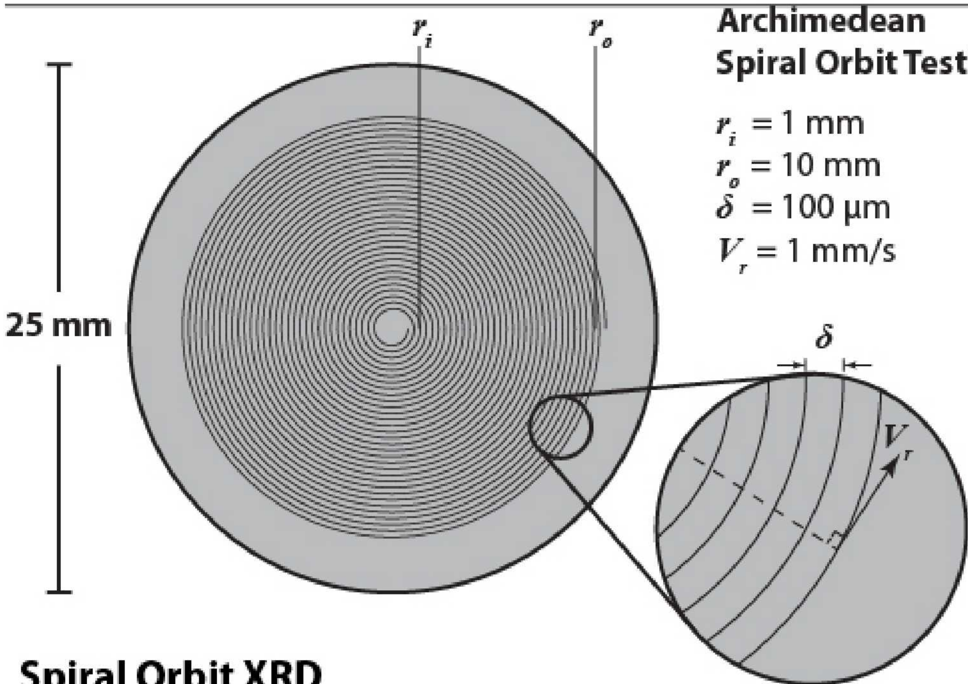
(2) Poisoning surface in between showed no increase over samples sitting in dry N_2

(3) Restricted by antechamber pump down times

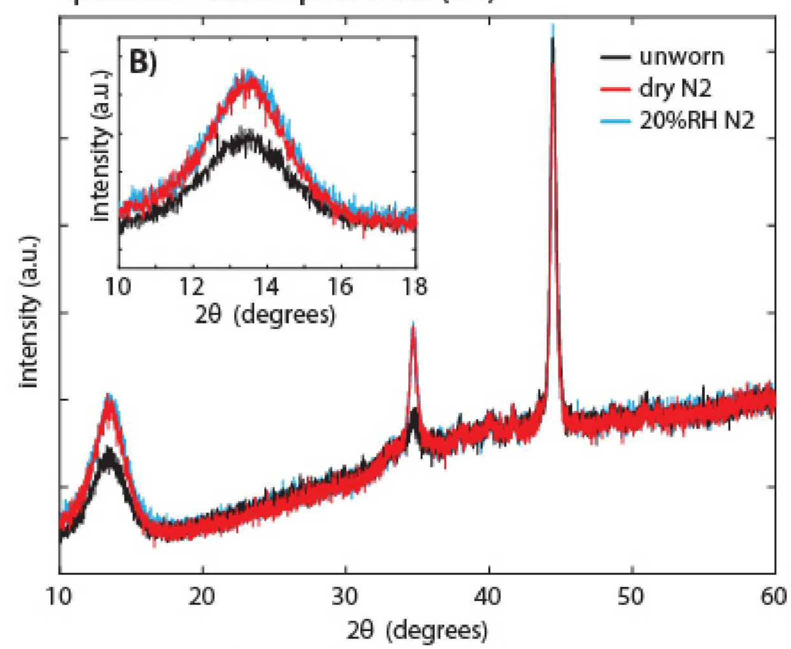
Assessing Running Film Formation: Spiral Orbit & XRD

Archimedean Spiral Orbit Testing

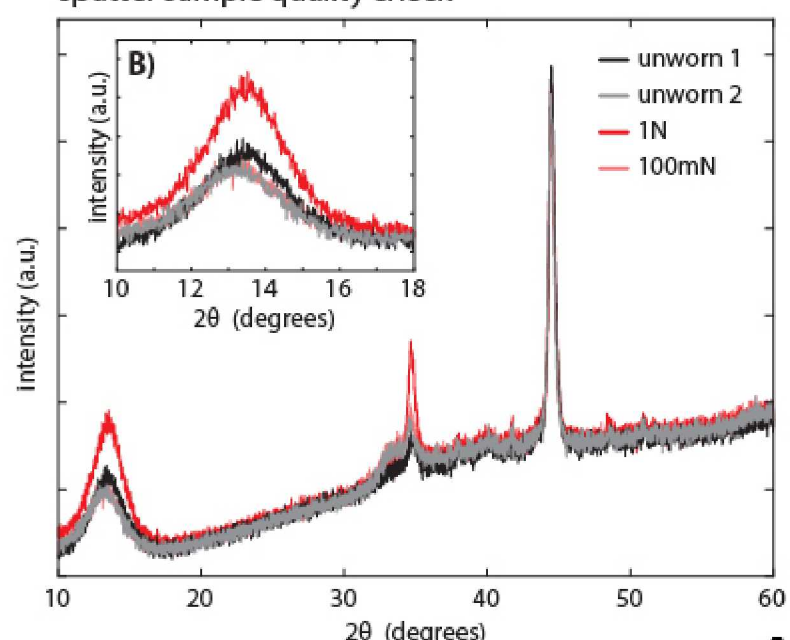
r_i = 1 mm
r_o = 10 mm
δ = 100 µm
V_r = 1 mm/s



sputtered MoS2 spiral orbit (1N)



sputter sample quality check



Spiral Orbit XRD

- to enable XRD measurements, large worn spirals were made

XRD Parameters

- scanned on Panalytical Empyrean XRD; Cu Kα radiation
- Pixcel 3D detector; scanning line (1D) mode
- Bragg-Brentano HD incident beam optic

Analysis

- testing in 20 %RH N2 at 1N showed no differences from dry N2
- orientation is not harmed, cannot comment on RF formation

- sample to sample unworn are similar (black and grey lines)
- high load caused increase in (002) peak and (100) peak
- indicative of more basal ordering at higher loads than 100 mN