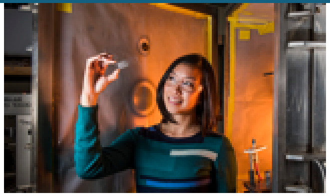
SAND2022-4600C

Tribochemisty of Molybdenum Disulfide



PRESENTED BY

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NNSA National Nuclear Security Administration

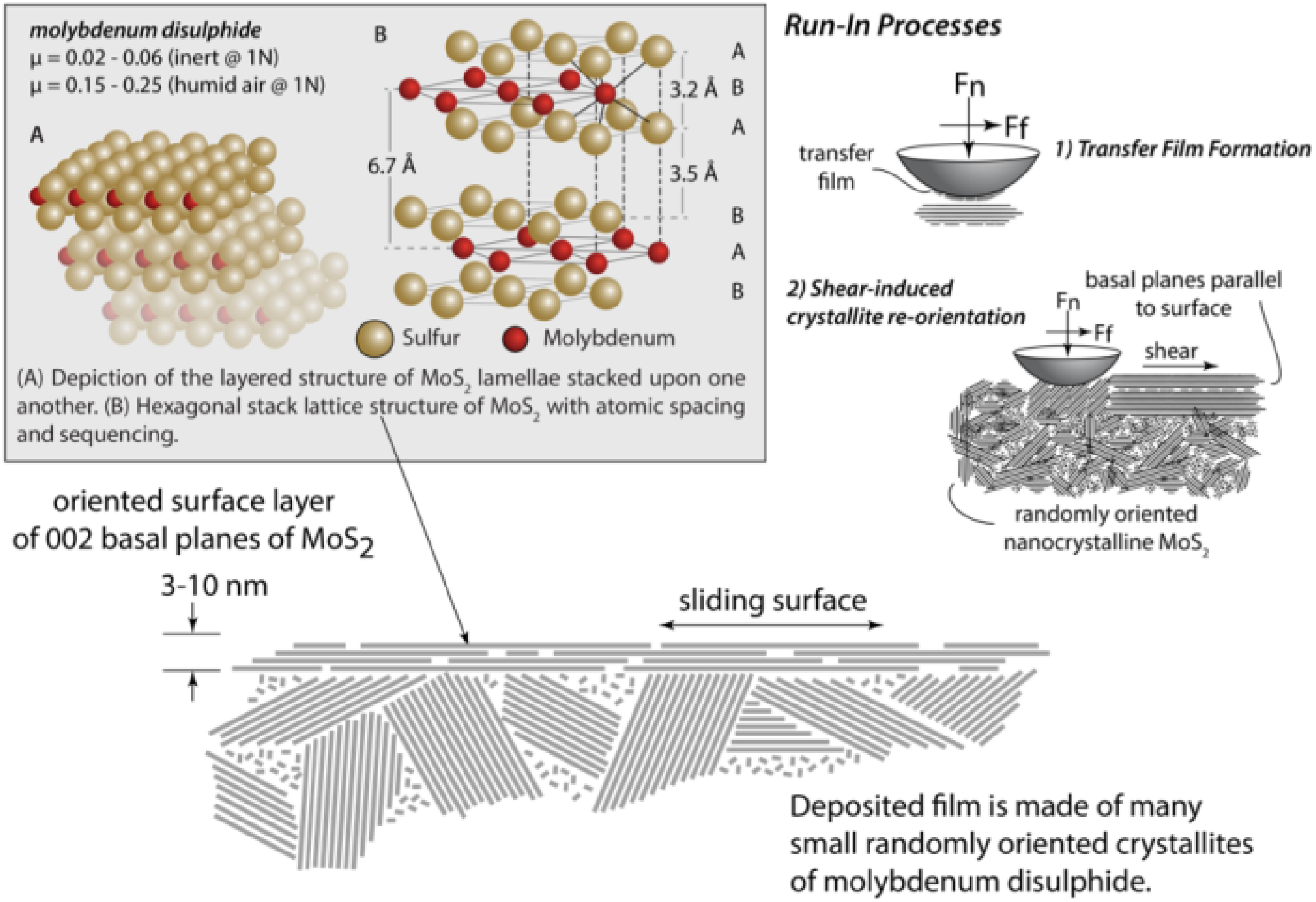
U.S. DEPARTMENT OF ENERGY

LEHIGH UNIVERSITY SURFACE INTERFACES AND MATERIALS TRIBOLOGY LABORATORY

MoS_2 is a Versatile Lubricant

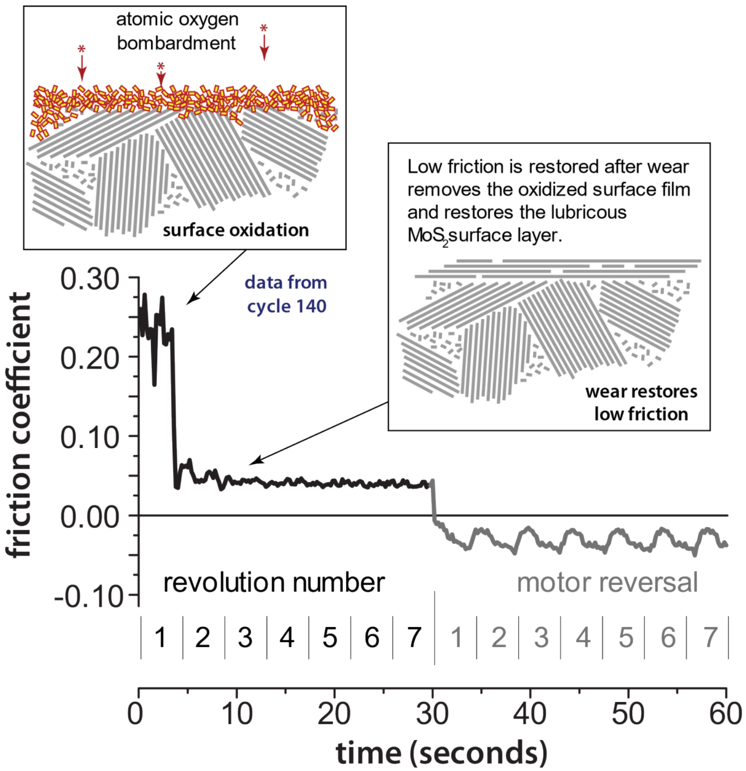
- Dry lubricant
  - Superlubric ($\mu < 0.01$) in dry environments
  - Coaster brakes, CV joints, ski wax, bullets…
  - Satellites, aircraft engines
  - Self-lubricating composites with polymers
- Other uses:
  - Catalysis (desulfurization, electrolysis of water)
  - Memristor/memcapacitors
  - Flexible circuits

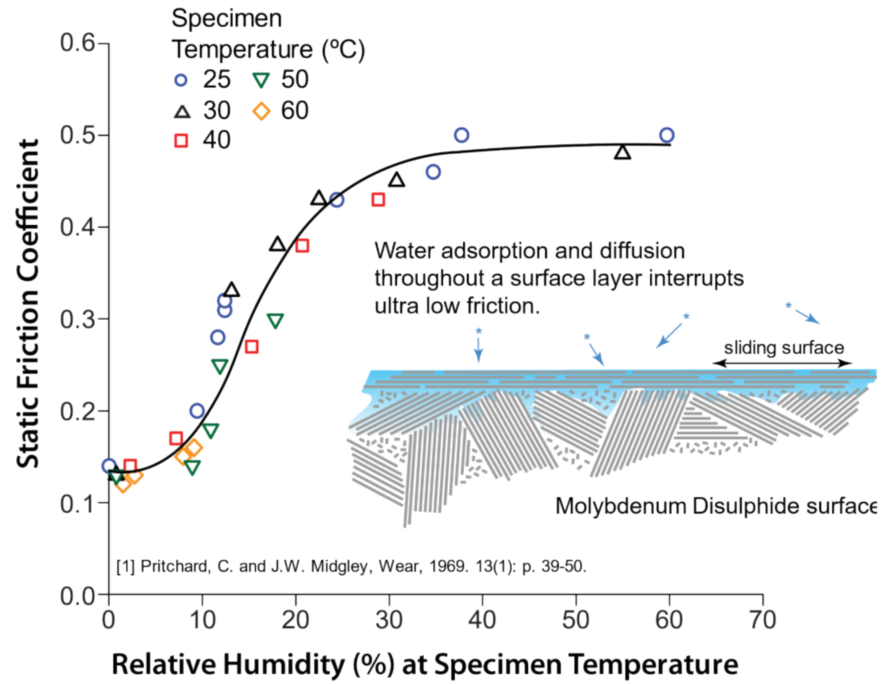
How Does it Work?



- Hexagonal structure, form thin, weakly bound lamella
- Issues: run-in and oxidation

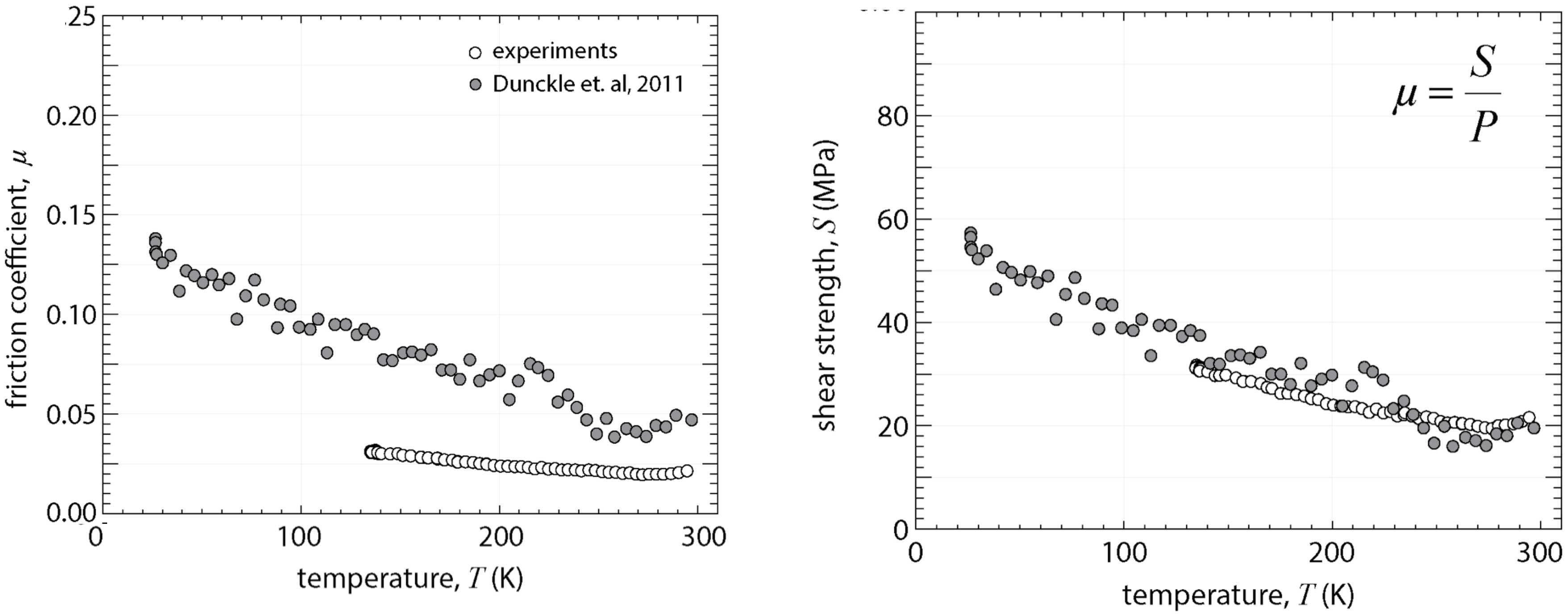
Environment (oxygen and water) affect friction





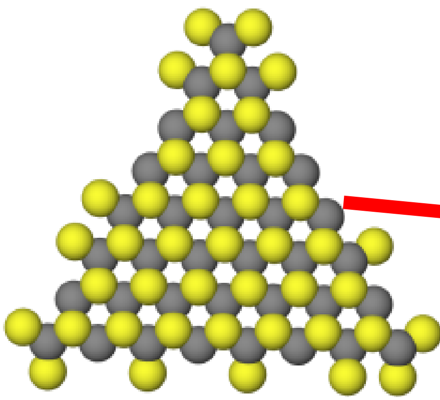
- Oxidation
  - space (AO - fast)
  - air at high temps (O_2 – fast)
  - Air at room temp (H_2O – slow)
- Water enhances static and kinetic friction
  - From environment
  - From inside the film

Start with pure MoS_2 -- Temperature Dependence

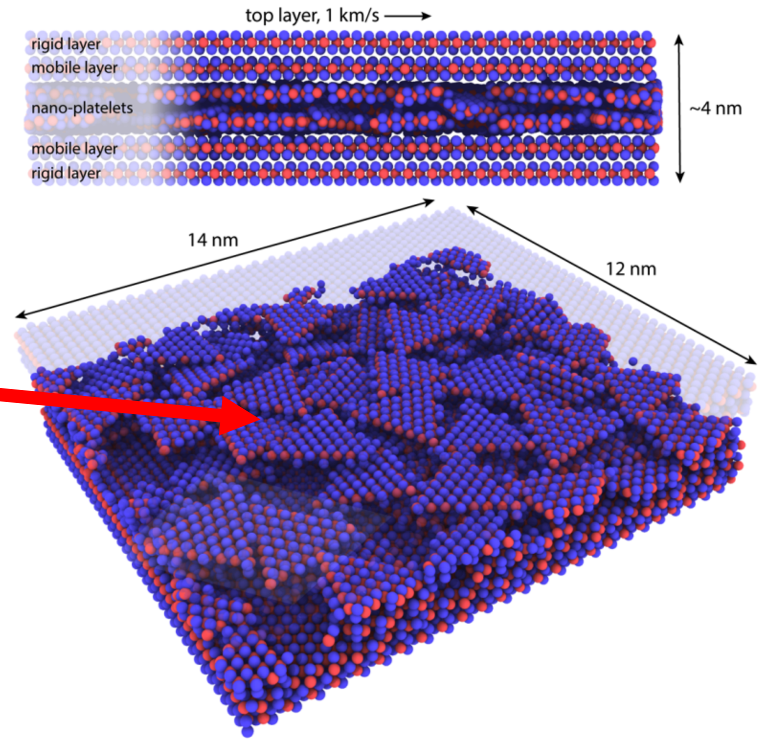


- non-Arrhenius behavior
- Singer (1990) showed contact is purely elastic
  - $\mu = S_0/P + \alpha$
  - S ~ 25 MPa at 300K
  - Implies sheets sliding on sheets
- Use simulations to understand the shape

Molecular Dynamics Simulations

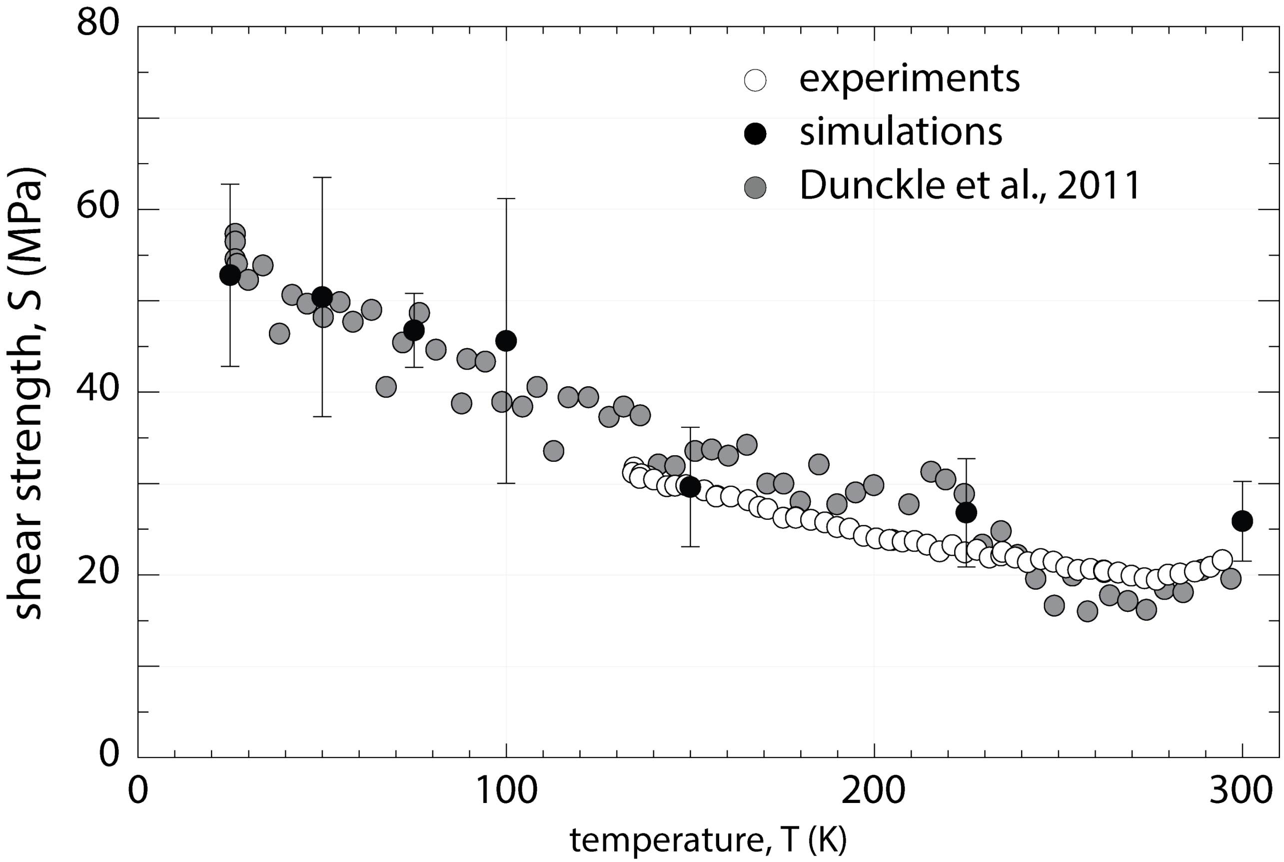


stoichiometric nanoplatelet



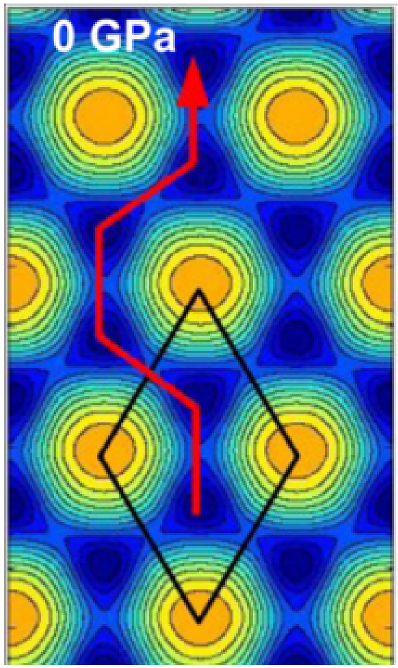
- Sandwich 64 nanoplatelets
  - Mobile lamella on top & bottom
  - Fixed lamella (rigid layer) to control load and speed
- ReaxFF: Vasenkov, et al., J. Appl. Phys. 2012
  - Slow technique with (reasonably) accurate chemistry
  - Lots of simulations => small & fast.

Fundamental Behavior: Shear Strength

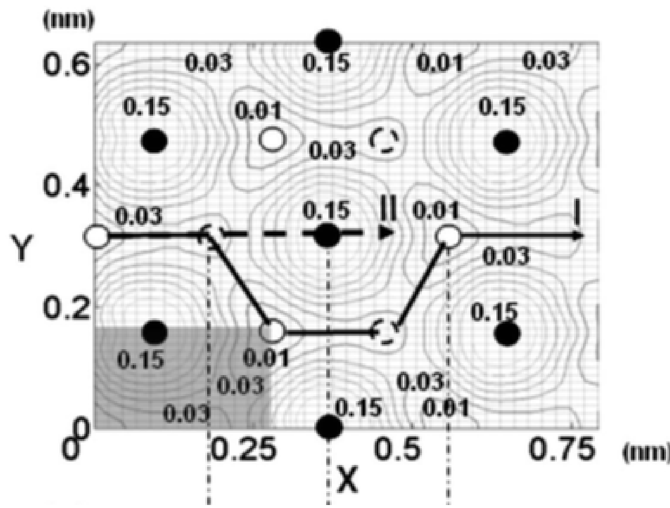


- All shear strengths collapse!
- What causes this shape?

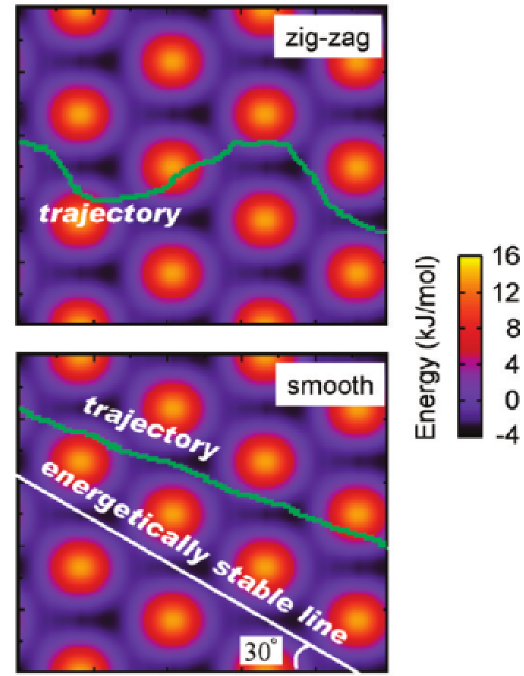
Elastic contact => Energy Barriers: Previous work



Levita et al.,
J. Phys. Chem. C 2014



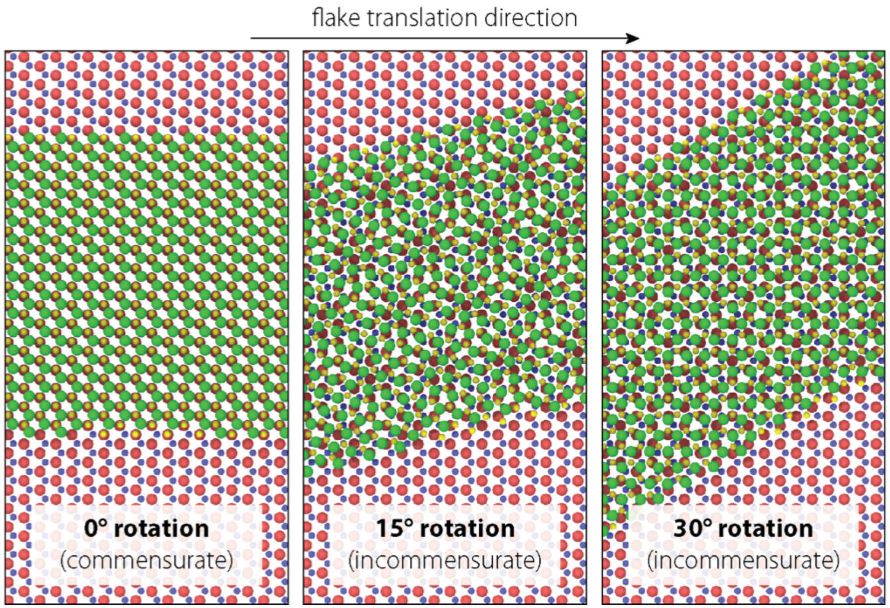
Liang et al.,
Phys. Rev. B 2008

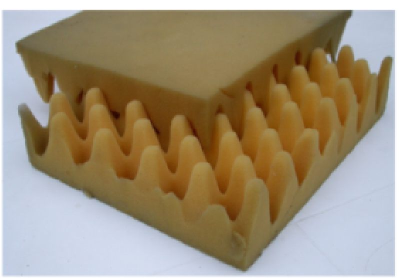


Onodera et al.,
J. Phys. Chem. B 2010

Previous work has calculated energetic barriers to sliding, but only for commensurate contacts

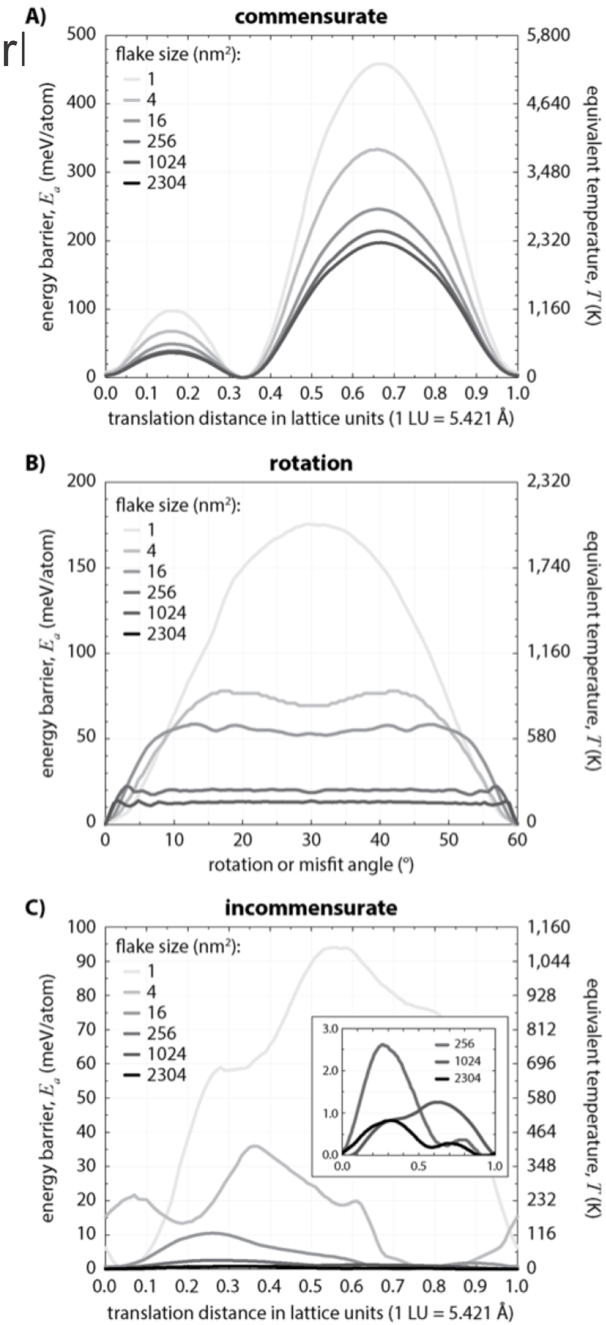
Elastic contact => Energy Barriers: Our worl





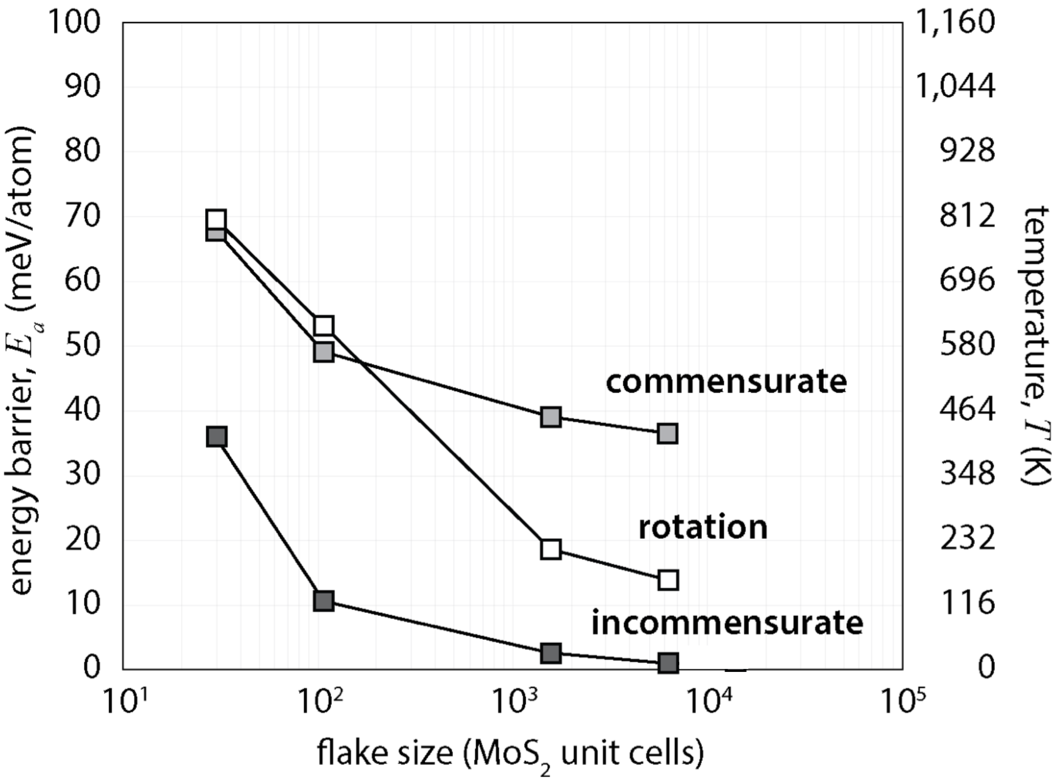
commensurate
egg shell

incommensurate
egg shell



Nudged elastic band calculations for barriers

Barriers converge with increasing flake size; make a toy model



Probability & Failure to cross barrier:

$$p_n \propto \exp\left(\frac{-E_n}{kT}\right)$$

$$f_n = 1 - p_n$$

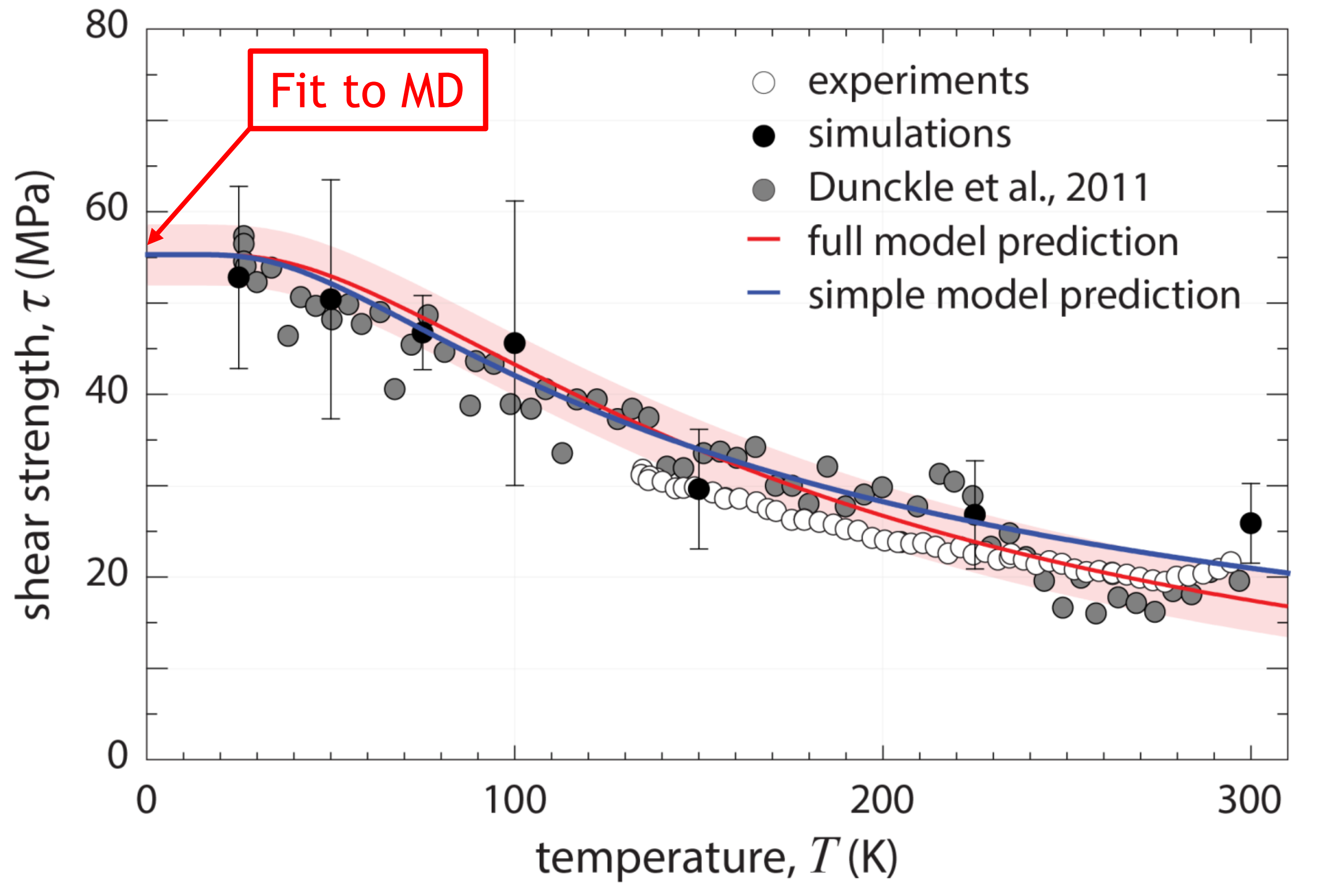
Total sliding probability & friction:

$$p_{slide} = p_r p_i + f_r p_c$$

$$f_{slide} = 1 - p_{slide} = 1 - \left(p_r p_i + f_r p_c\right)$$

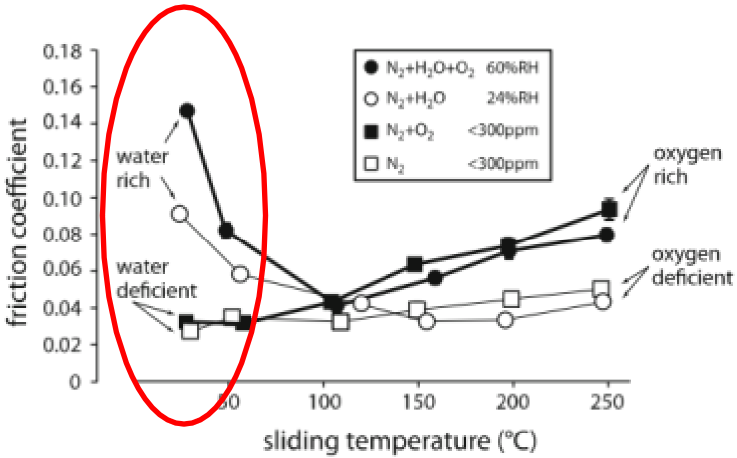
Results of toy model

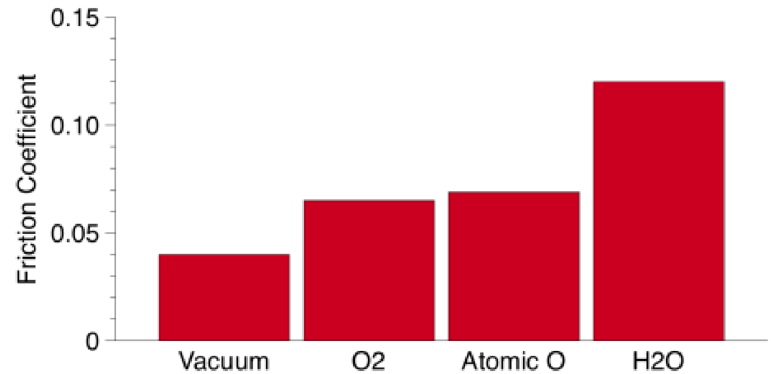
$$f_{slide} = C_0 \left[1 - \exp\left(-\frac{E_r}{kT} \right) \right]$$



Curry, et al., *ACS Applied Nano Materials* (2018)

Friction in Environments

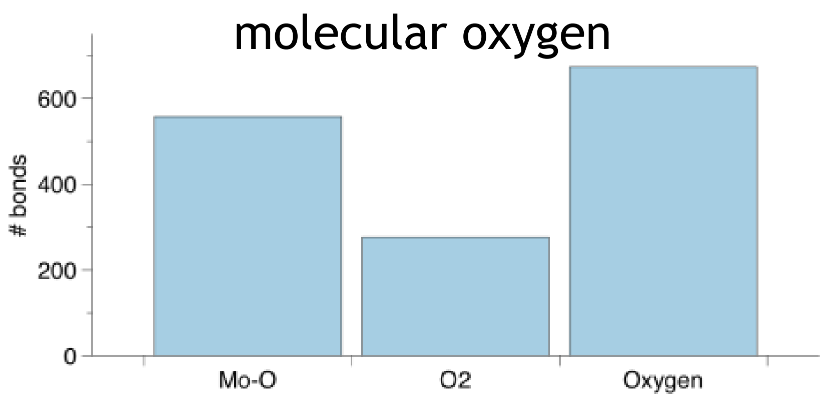


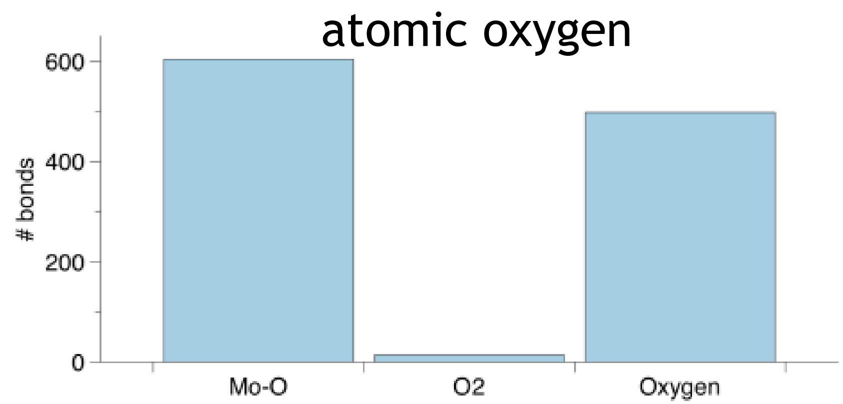


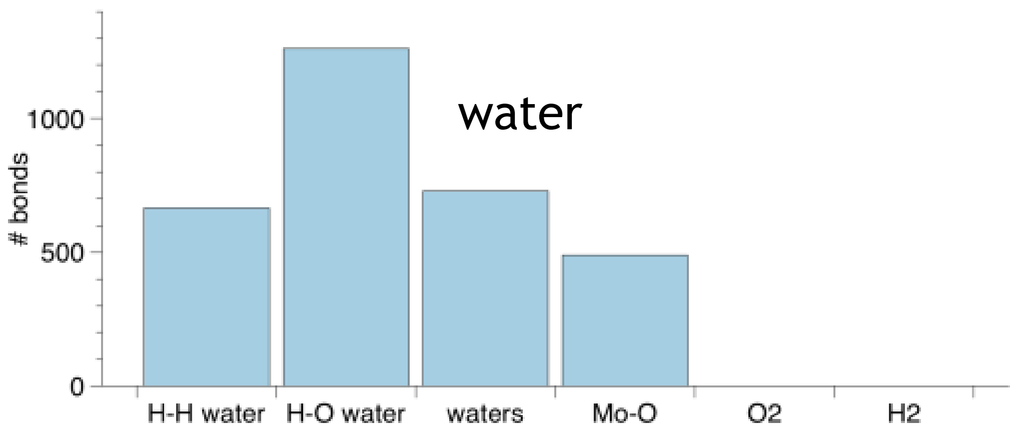
Khare and Burris, Tribo. Lett. 2013

•Changes with added oxygen or water match experimental results quite well (for MD…)

Is there chemistry?

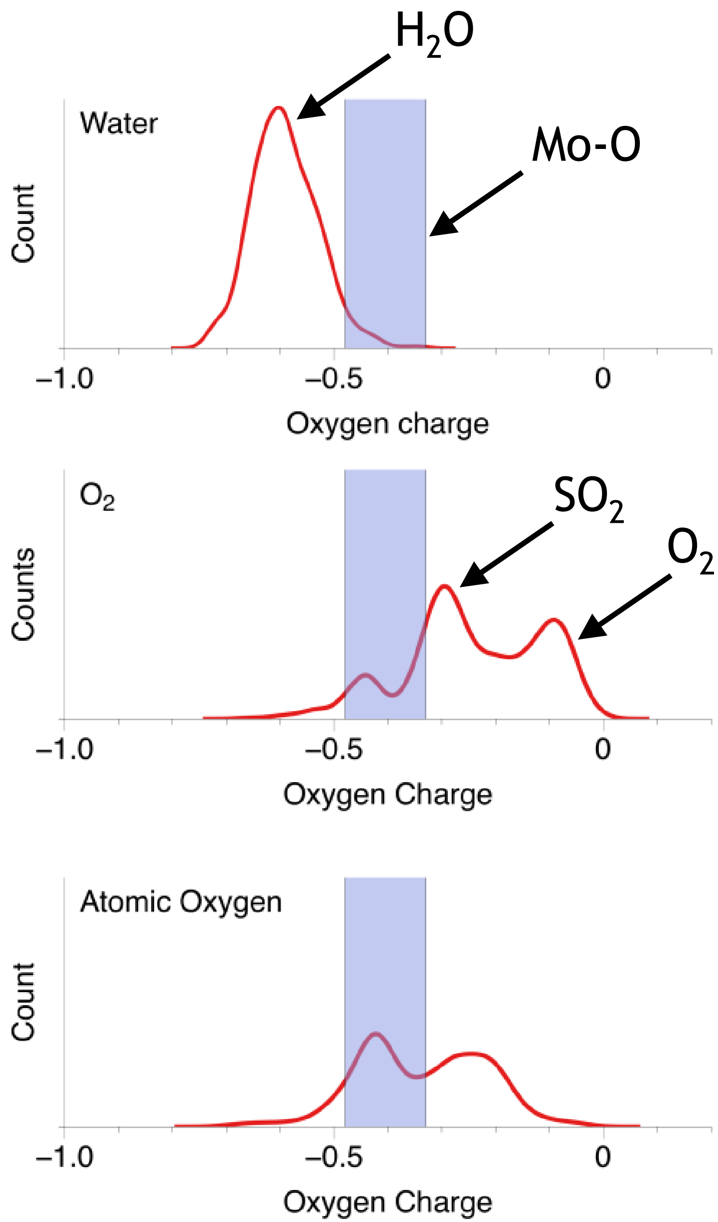


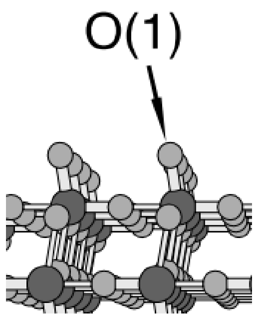




- Water does not dissociate (no O2 or H2 formed)
- Molecular O shows little dissociation (mostly in O2)
- Atomic oxygen forms little O2
- *Not much…*

Charge on Oxygens confirms chemistry

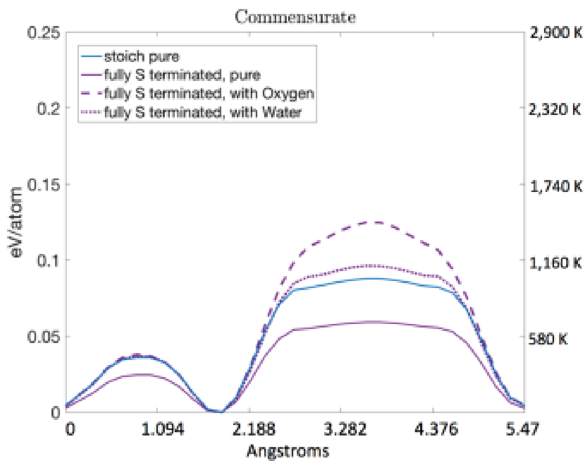


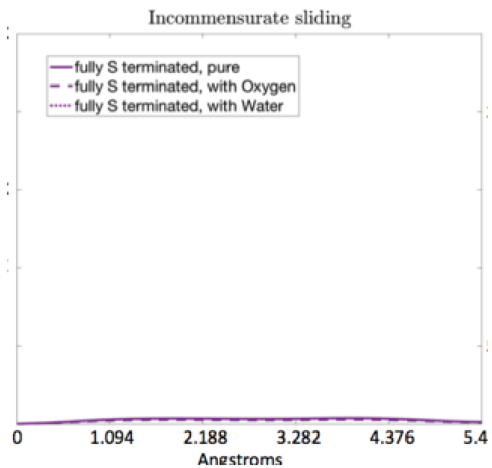


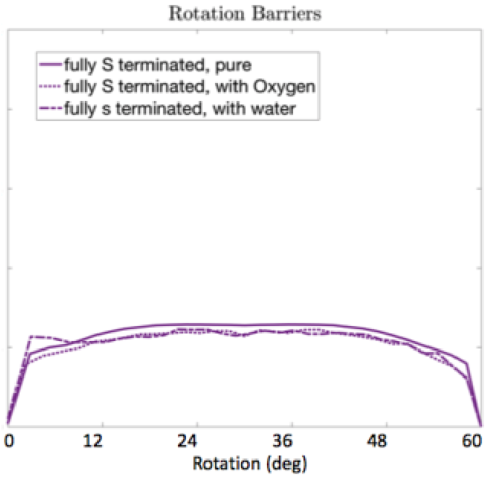
Tokarz-Sobieraj et al.
Surf. Sci. 2001

- Oxygen bonded to Mo has partial charge from -0.48 (Tokarz-Sobieraj et al. Surf. Sci. 2001) to -0.33 (Yin et al., J. Mol. Model 2001).
- Oxygen in water has partial charge from -0.6 to -0.8(Astrand, et al., J. Phys. Chem. A 1998).
- Water shows only physisorption
- Atomic oxygen shows chemisorption
- Molecular oxygen shows slight amount of chemisorption

What happens to the energy barriers?





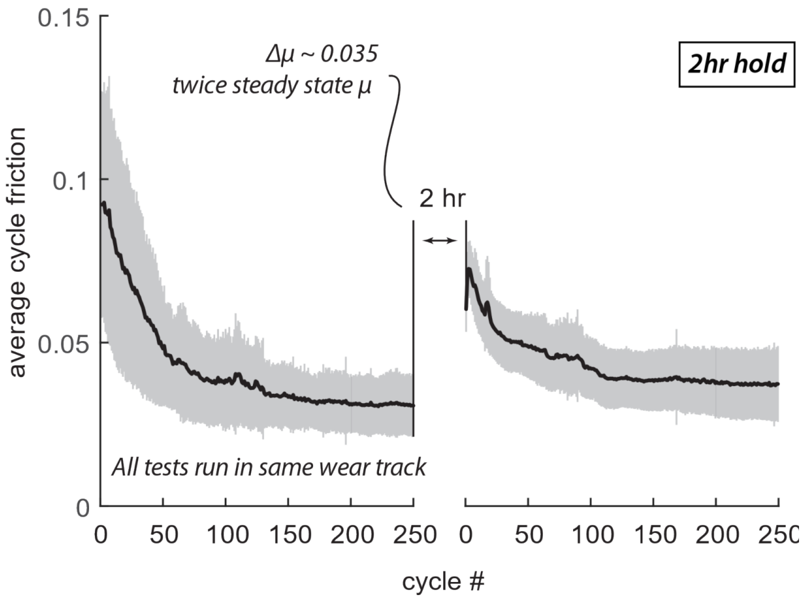


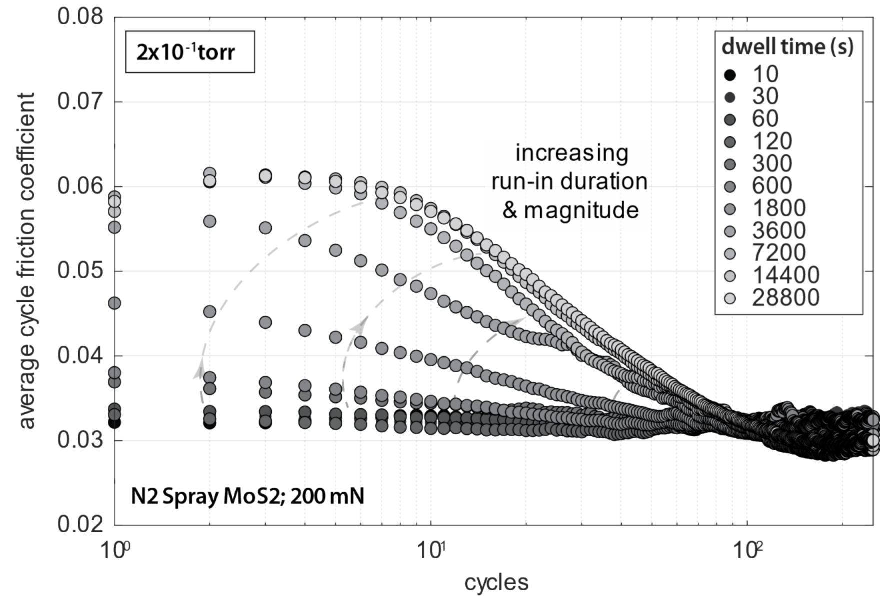
Not much…

So why does the friction go up?

Run-in and re-run-in

- Recipe for success: run film in to steady state… and watch friction increase upon return

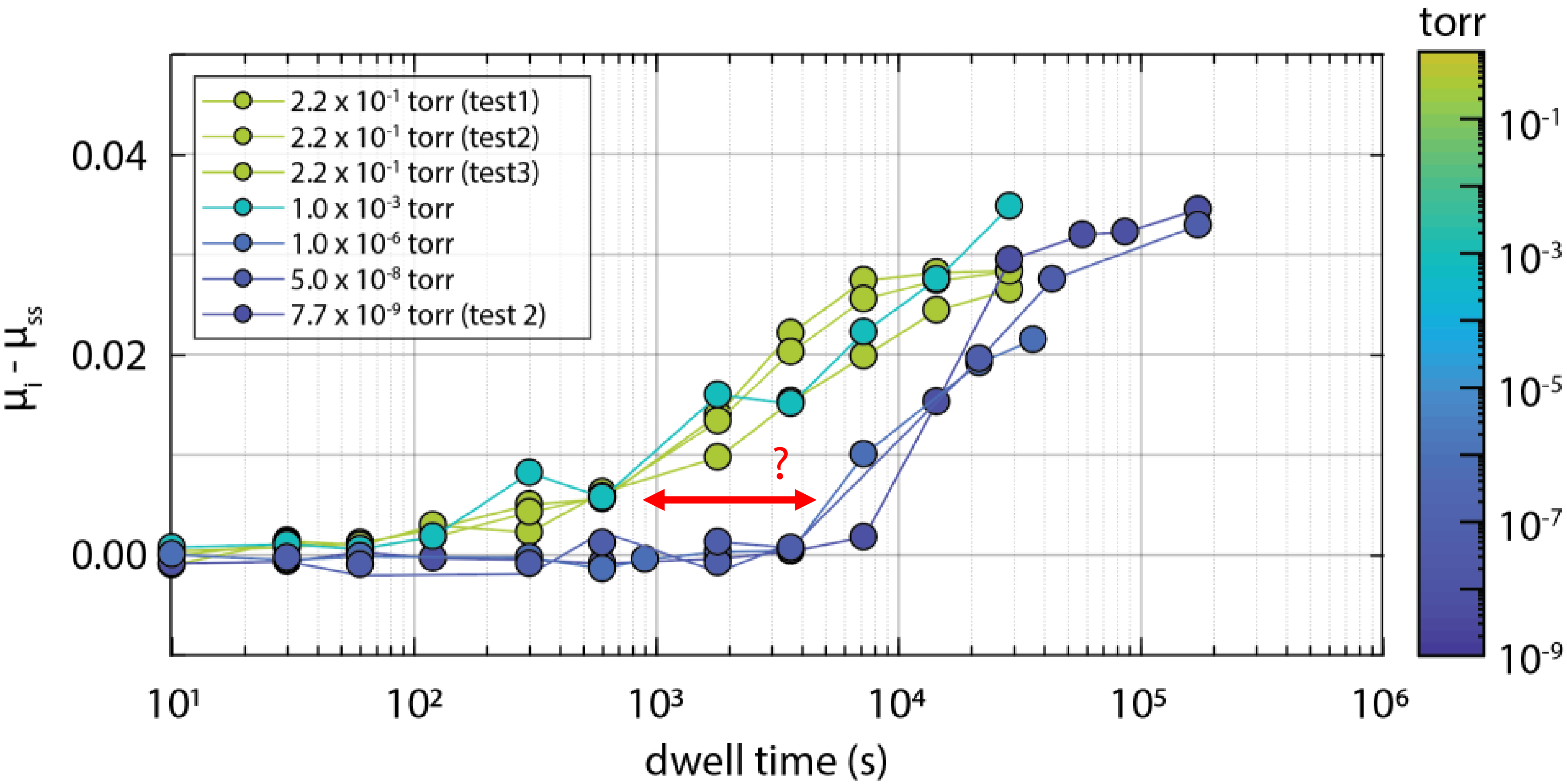




- Increase in initial friction increases with time in between; run-in duration also affected

- Also seen in vacuum

Pressure Matters too!

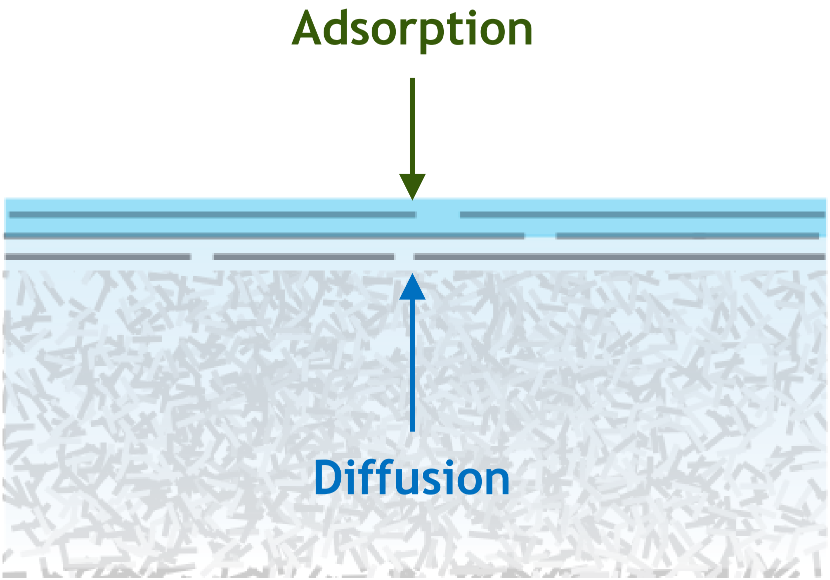


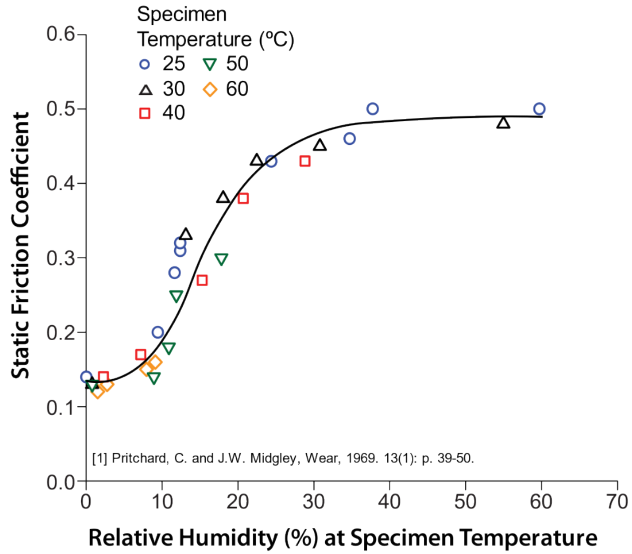
- difference between previous steady state and returning initial friction
- Stop time from $2x10^{-1}$ to $7x10^{-9}$ torr
- Low and high pressures are different

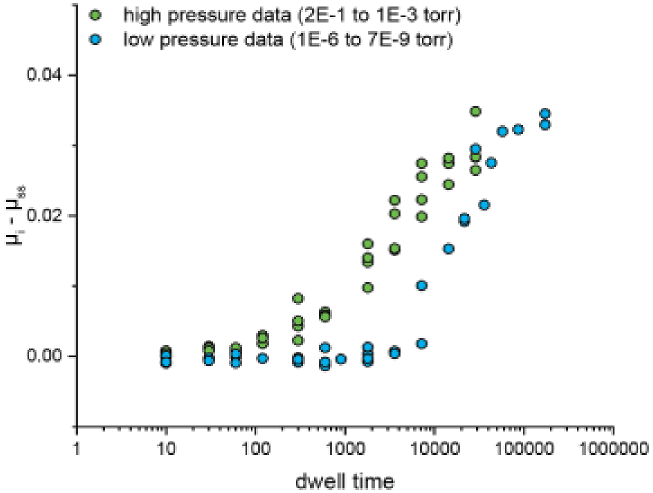
Environmental factors change shear strength

- Simple theory: adsorption and diffusion

- Not a new idea:
  - Johnston & Moore 1964
  - Pritchard & Midgeley, 1969
  - Colbert, Ph.D. thesis 2012





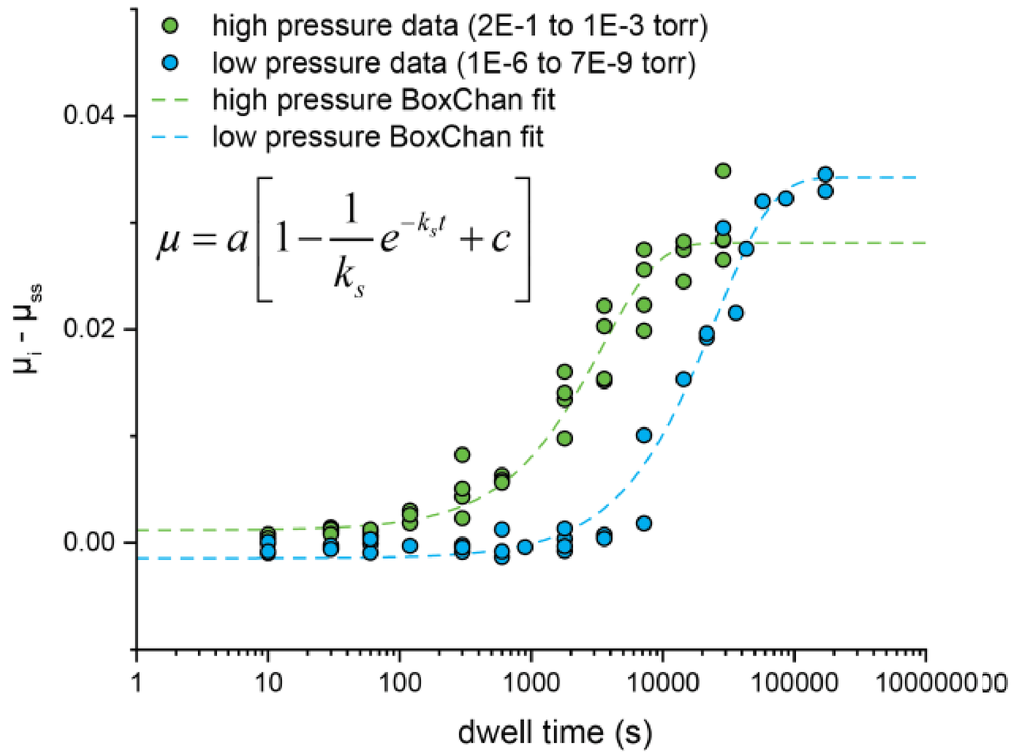


Simple Coverage Model

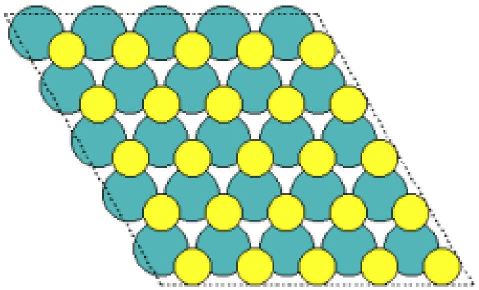
- simple fractional coverage model
- coverage θ depends on available sites
- two variables:
  - k = rate of arrival
  - s = sticking coefficient
  - $k = k_1 + k_2$, $s = s_1 + s_2$

$$\frac{d\theta}{dt} = k \cdot s(1-\theta)$$

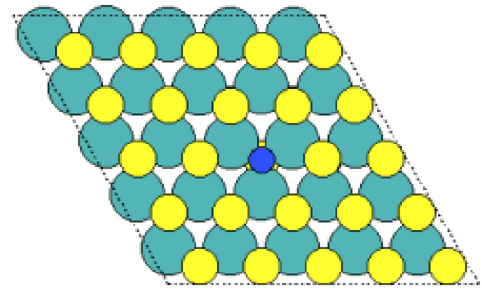
$$\theta = 1 - \frac{1}{k \cdot s} e^{-k \cdot s \cdot t}$$



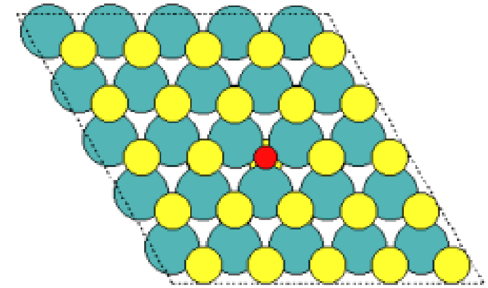
Propensity for adsorption/infiltration



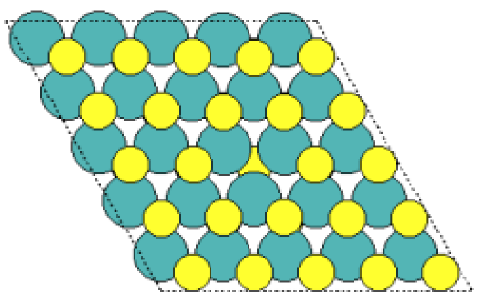
Defect free



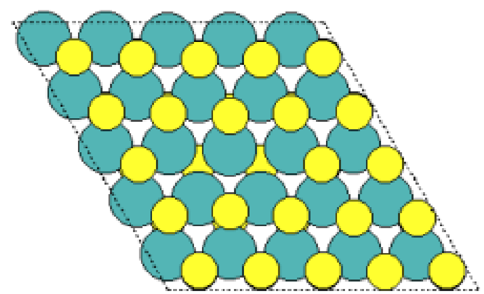
N dopant



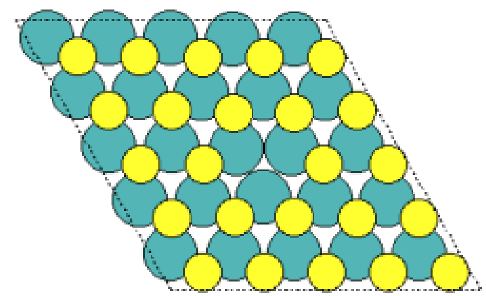
O dopant



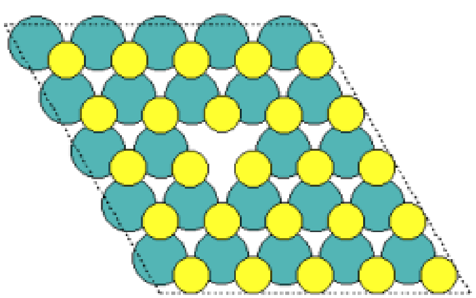
1 S vacancy



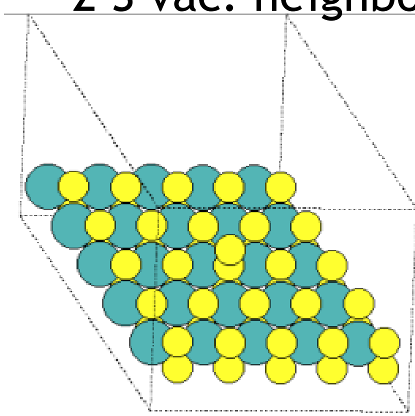
2 S vac: neighbors



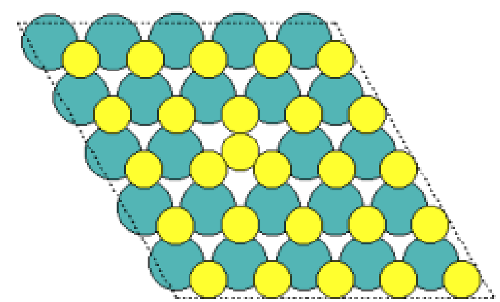
2 S vac: stacked



Mo vacancy



S adatom



S sub Mo

Adsorption Energies

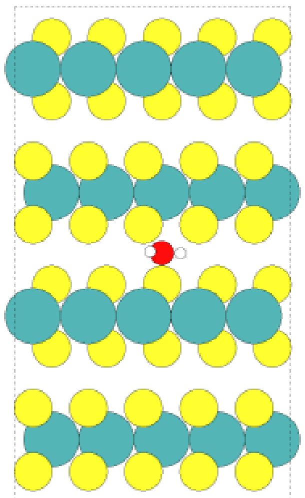
Water on defect free MoS2 ~ -12 kJ/mol

Sulfur vacancies ~ -22 to -24 kJ/mol

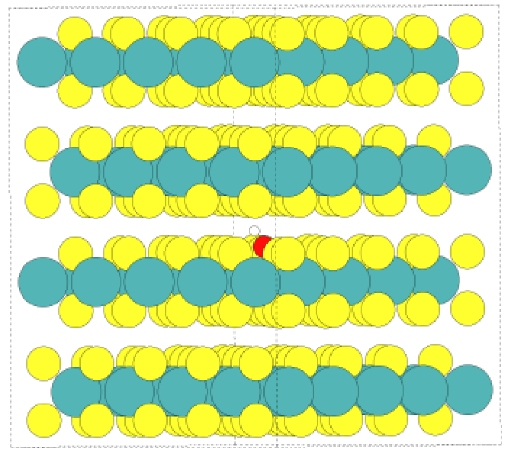
N or O dopants ~ -31 kJ/mol

Defect	BE kJ/mol	BE eV/H2O
intrinsic	-12.1	-0.13
1Svac	-23.8	-0.25
2Svac-neigh	-22.4	-0.23
2Svac-stack	-22.9	-0.24
Movac	-21.4	-0.22
Ndopant	-31.8	-0.33
Odopant	-31.1	-0.32
S-adatom	-25.8	-0.27
SsubMo	-90.7	-0.94

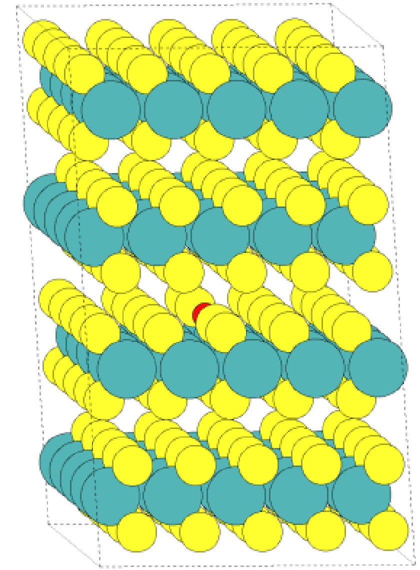
What About *Between* Sheets?



pure



sulfur vacancy



oxygen doped

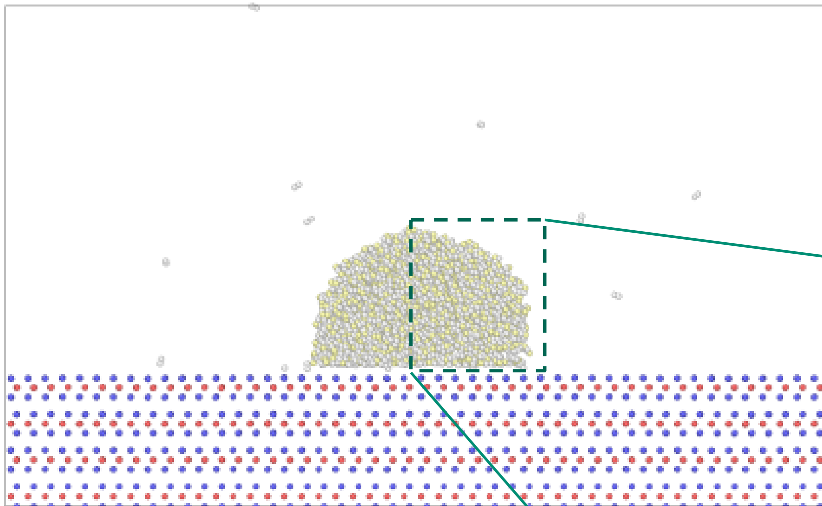
	Intrinsic	1Svac-A	1Svac-B	1Svac-C	1Svac-D	Odop-A	Odop-B	Odop-C	Odop-D
dry	0.0	-0.1	-0.2	-0.2	-0.2	-0.1	-0.2	-0.2	-0.2
pos1	1.4	0.1	-0.1	0.0	0.0	0.9	0.4	0.8	0.5
pos2	1.3	0.1	0.0	0.0	0.0	0.9	0.5	0.8	0.5
pos3	1.3	0.1	-0.1	0.0	0.1	0.9	0.5	0.8	0.5
pos4	1.3	0.1	-0.1	0.0	0.1	0.9	0.5	0.8	0.5
pos5	1.3	0.1	-0.1	0.0	0.1	0.9	0.4	0.8	0.5
pos6	1.3	0.1	-0.1	0.0	-0.1	1.1	0.5	0.9	0.8
pos7	1.3	0.1	-0.1	0.0	-0.1	0.9	0.4	0.8	0.8
pos8	1.3	0.1	-0.1	0.0	0.1	0.9	0.4	0.8	0.5
Avg	**1.3**	**0.1**	**-0.1**	**0.0**	**0.0**	**0.9**	**0.5**	**0.8**	**0.6**

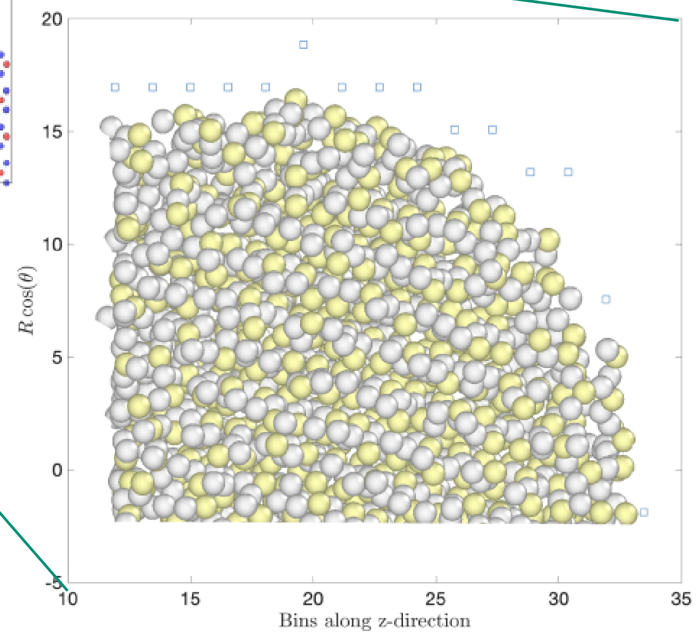
%change from defect-free

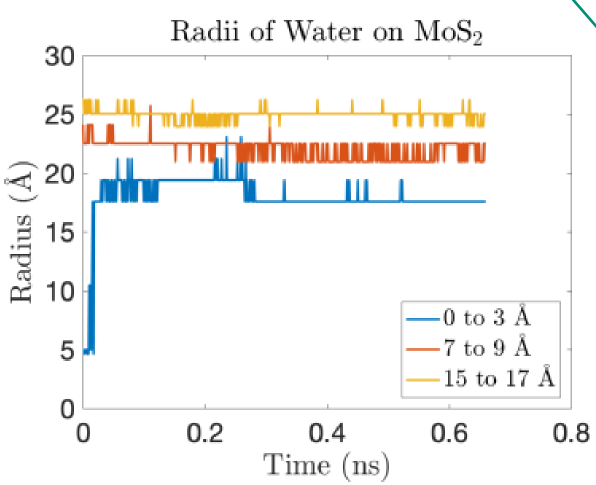
meV/Mo	Intrinsic	1Svac-A	1Svac-B	1Svac-C	1Svac-D	Odop-A	Odop-B	Odop-C	Odop-D
Total energy change	23.0	-0.1	-0.2	0.2	-1.9	13.9	4.6	13.9	7.2
BE of water	13.4	-2.7	-3.1	-2.4	-5.2	7.6	1.6	7.6	3.6
Energy from volume change	9.6	2.6	2.7	2.6	2.6	6.1	3.0	6.2	3.6

Wetting indicates infiltration is unlikely

Similar with defects (sulfur vacancies or oxygen substitution)





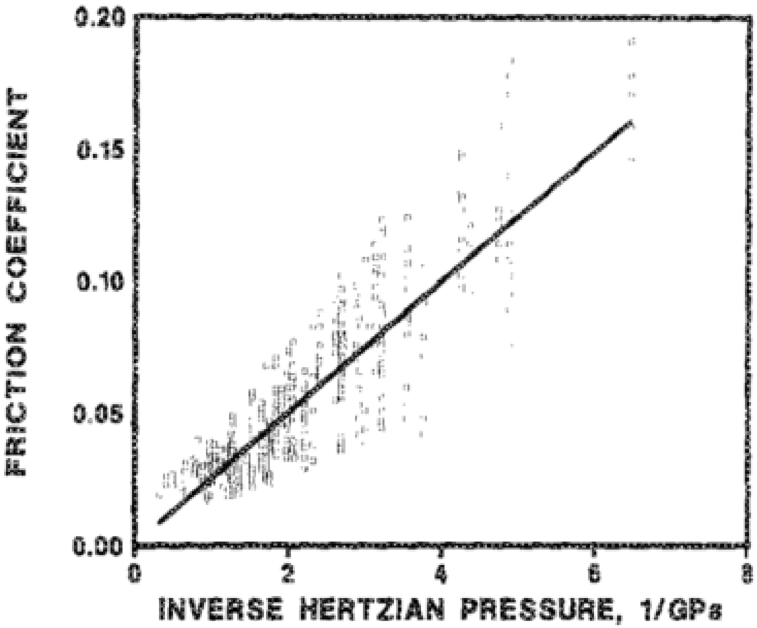


Summary

- MoS2 shows purely elastic contact
- Shear is predominantly due to inter-lamellar interactions
- Simple model predicts temperature dependence
- No chemistry with water, little with molecular O, lots with atomic O
- Environment hinders formation of large sheets
- Run-in and re-run-in strongly affected by water
  - Adsorption from vapor (at high and low pressures)
  - Diffusion from bulk (low pressure only)
  - Baking out helps!

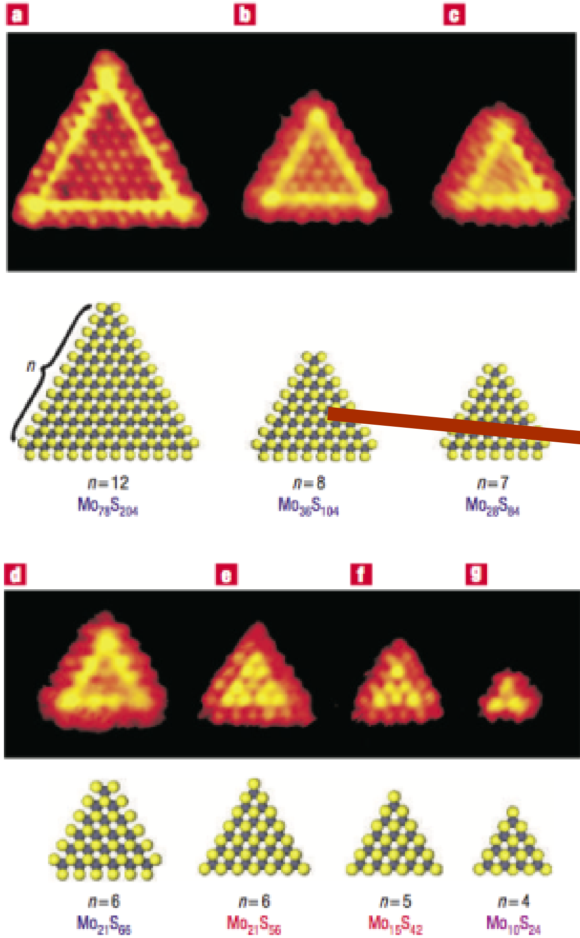
Non-Amontonian Behavior

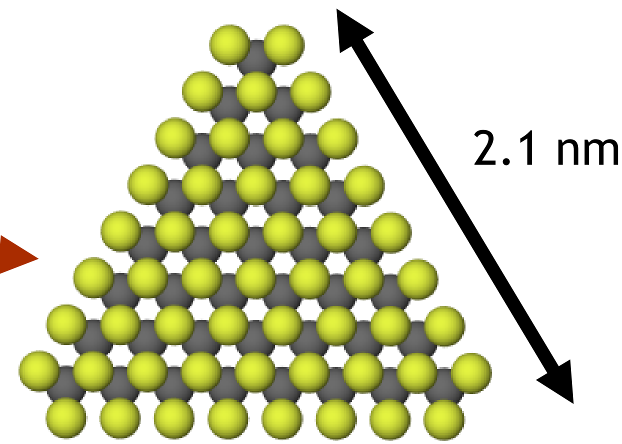
Singer, et al., Appl. Phys. Lett. 1990



- Singer's explanation:
  - $\mu = S/P$
  - Expand $S = S_0 + \alpha P$
  - $\mu = S_0/P + \alpha$
  - $\mu = S_0 \pi \, (3R/4E)^{2/3} L^{-1/3} + \alpha$
  - $S_0 = 25 \ MPa$
- Contact is purely elastic => sheets sliding over sheets

Molecular Dynamics Simulations



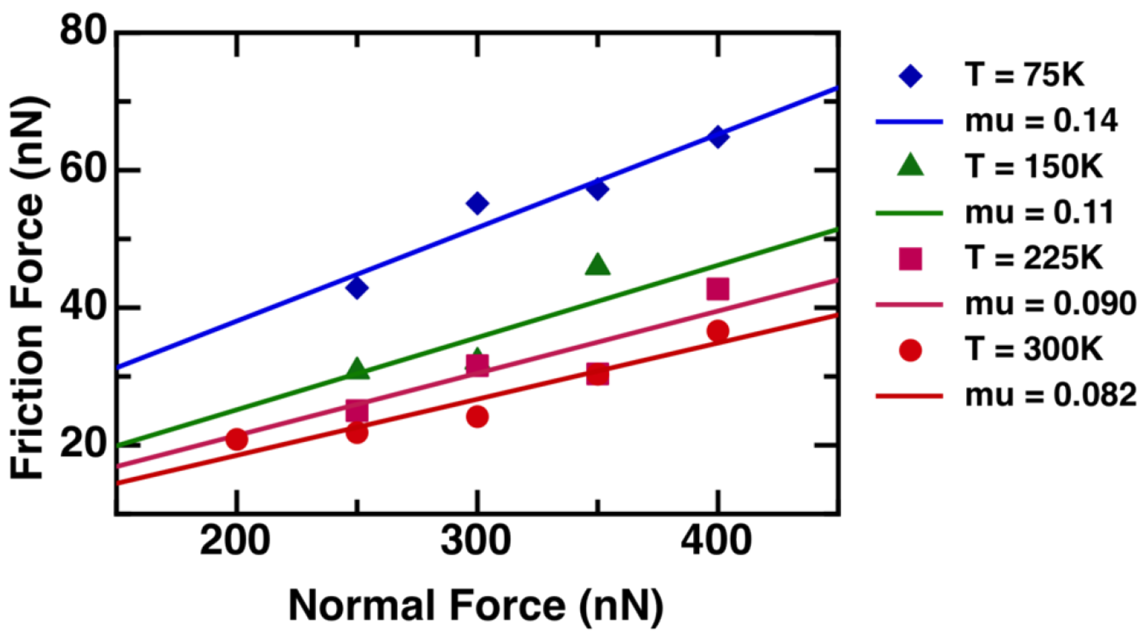


$Mo_{36}S_{104}$

Lauritsen et al., Nature Nanotech. 2007

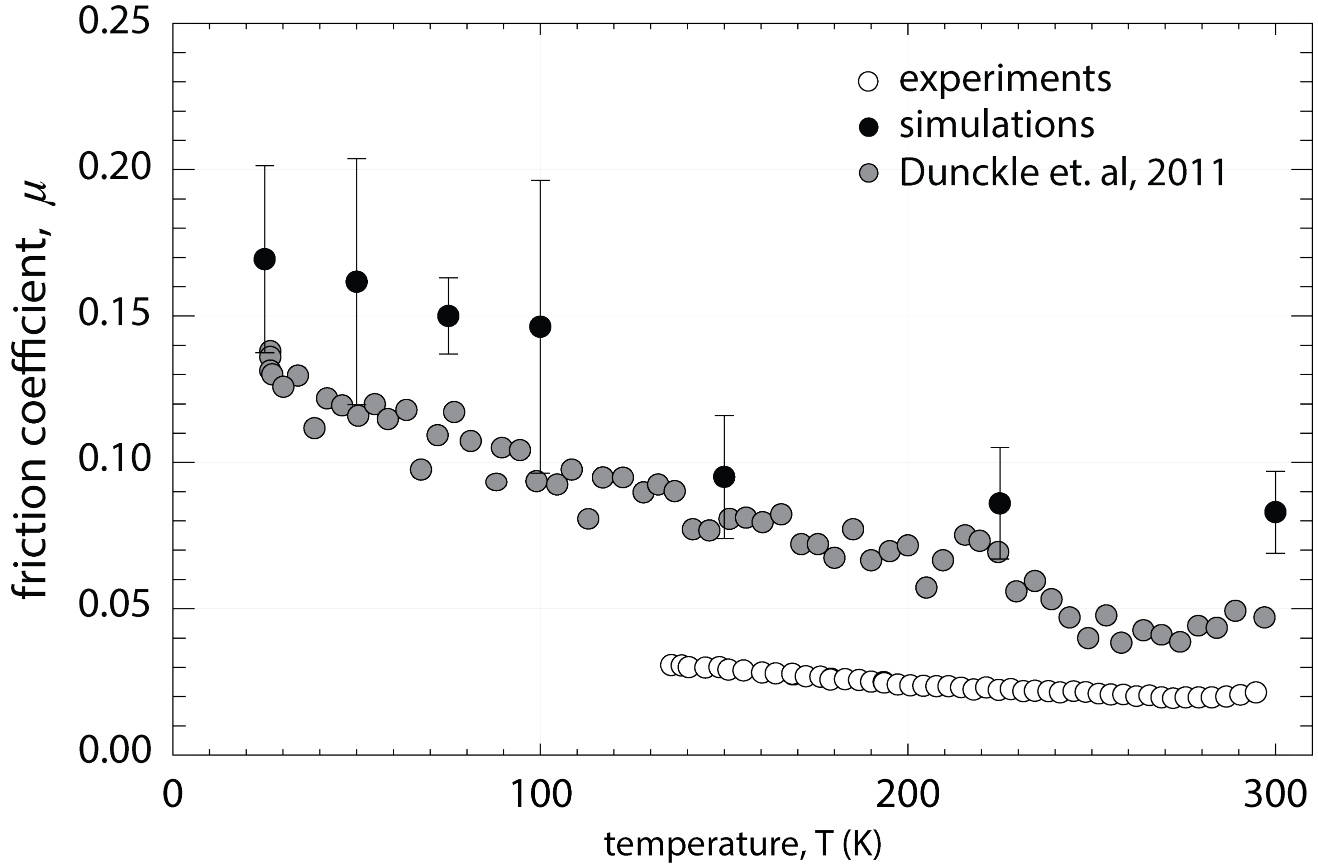
- Start with nanoplatelets
- Defect free platelets are non-stoichiometric

Molecular Dynamics Simulations



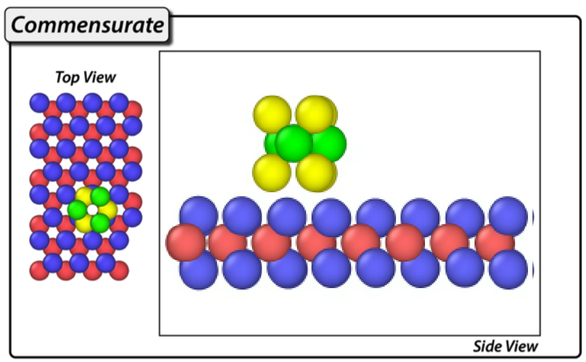
- Six loads at each temperature
- $\mu = dF_f/dF_n$ gives friction coefficient
- Contact conditions => $A \propto F_N$, can use to calculate shear stress

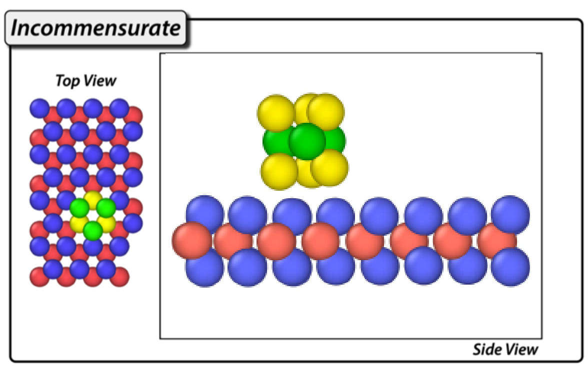
Friction vs. Temperature

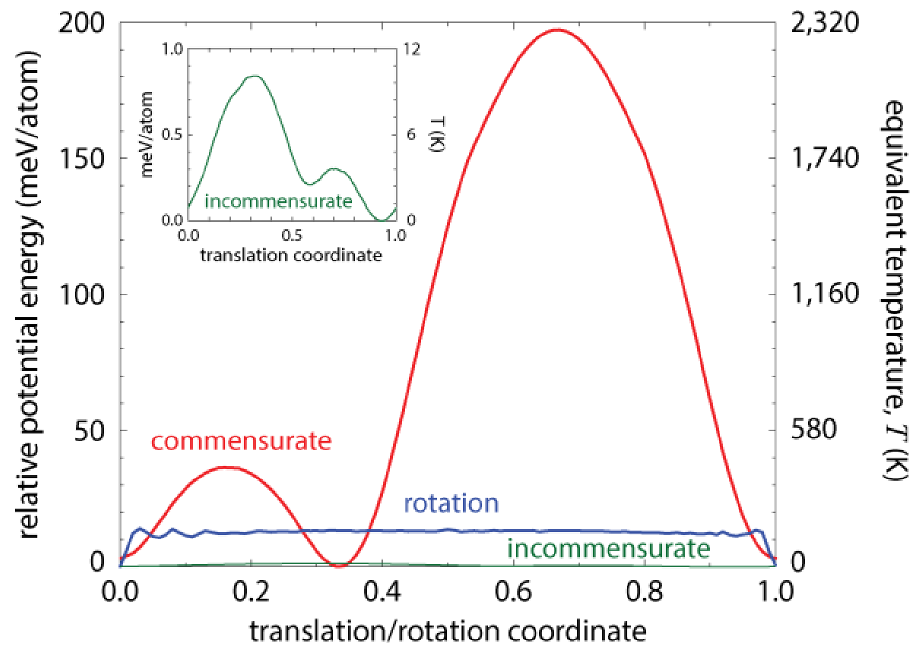


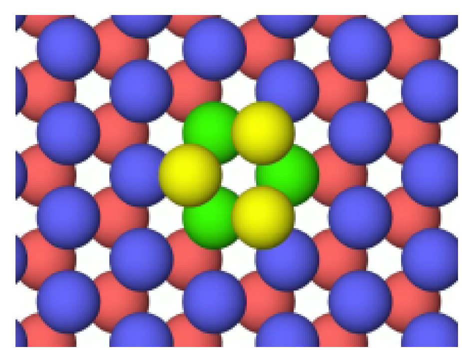
- MD has more defects, expect higher mu
- Functional form is the same

Commensurate vs. Incommensurate Sliding





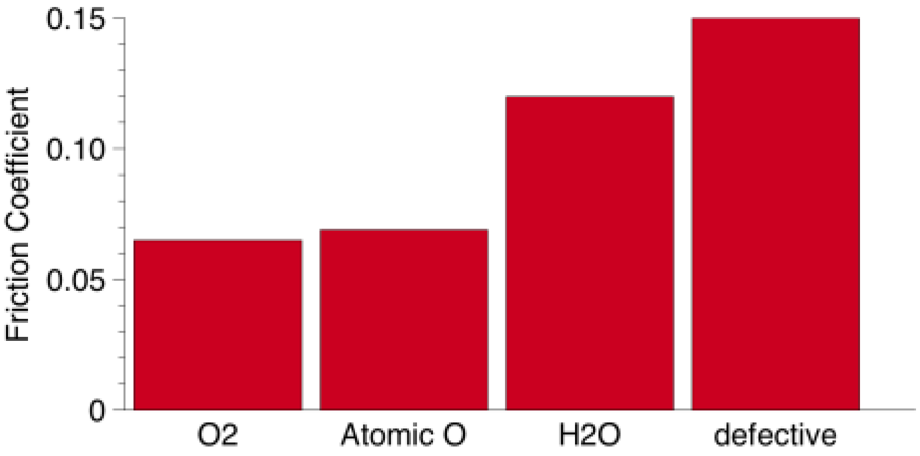


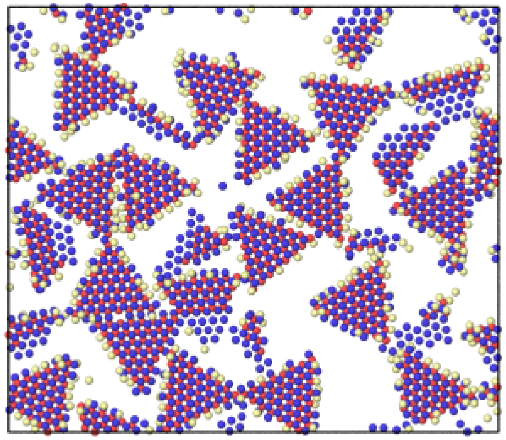


rotation

- Commensurate barrier ~= 300 K
- Incommensurate barrier ~= 10K
- Rotation barrier ~= 150K

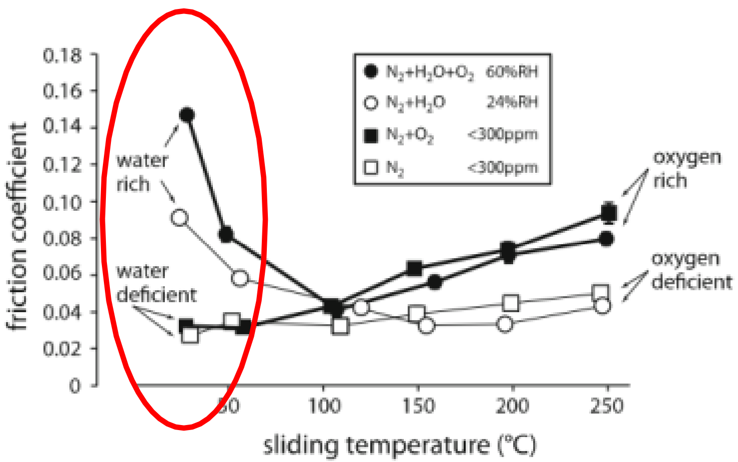
What happens with oxygen and water?



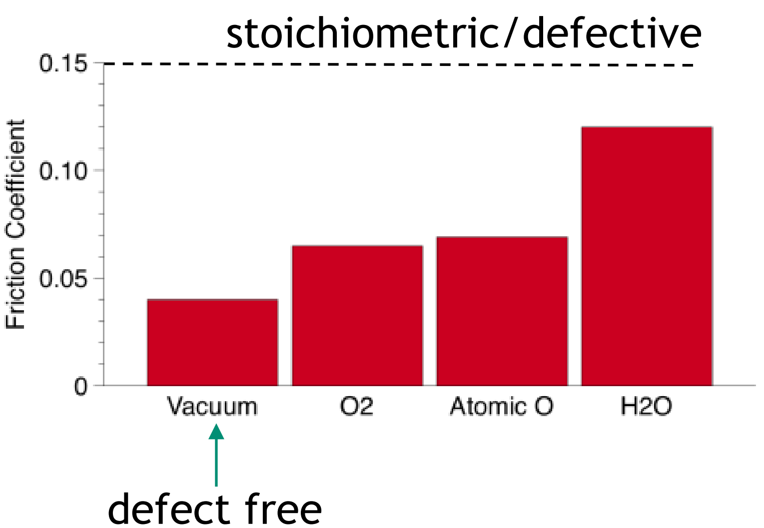


- Friction goes down?
- This is unfair…
  - Water and oxygen passivate defect sites
  - Need to do this in the pure system, too
  - Look at non-stoichiometric (i.e. defect-free) nanoplatelets

Friction in Environments

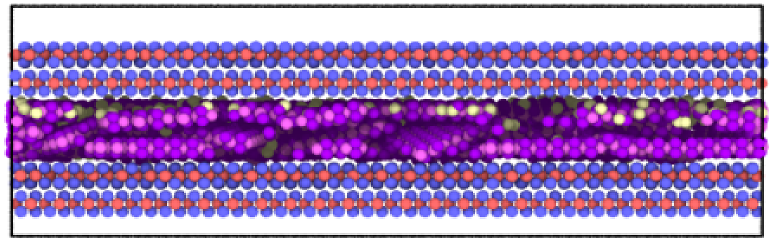


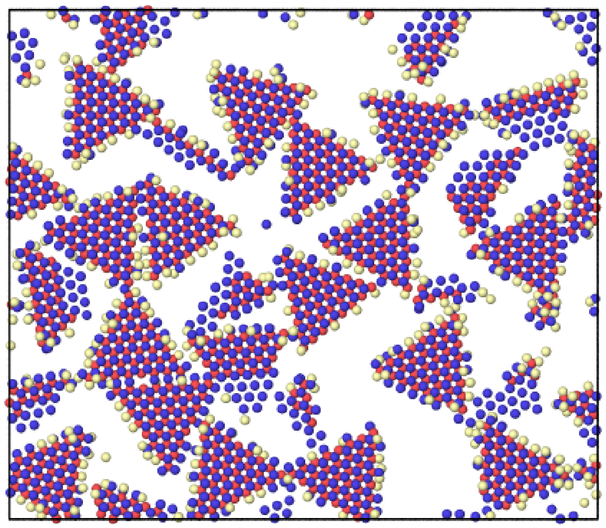
Khare and Burris, Tribo. Lett. 2013



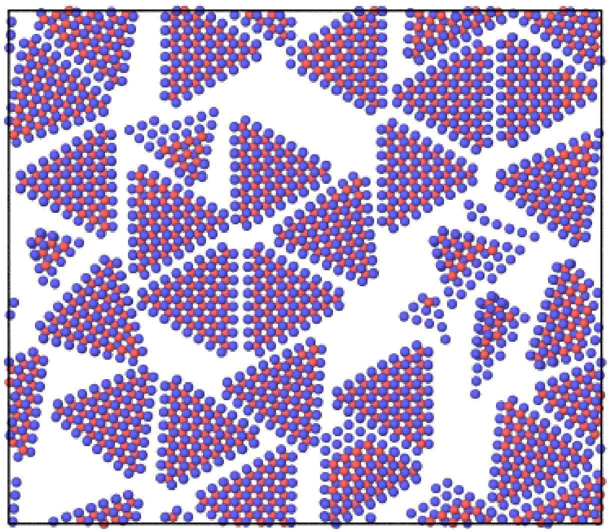
•Changes with added oxygen or water match experimental results

Effects of Oxygen on Inter-platelet bonding





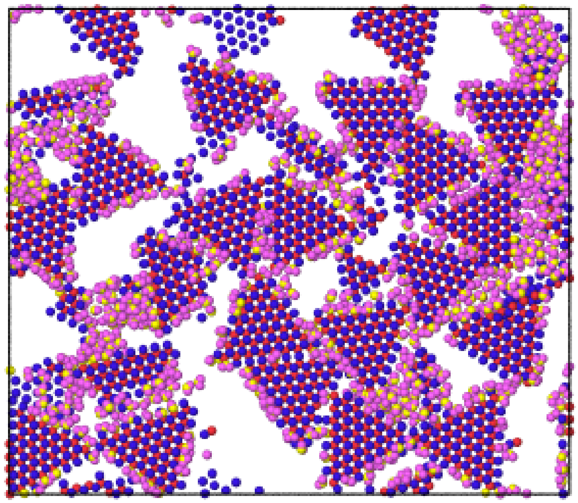
oxygen passivated



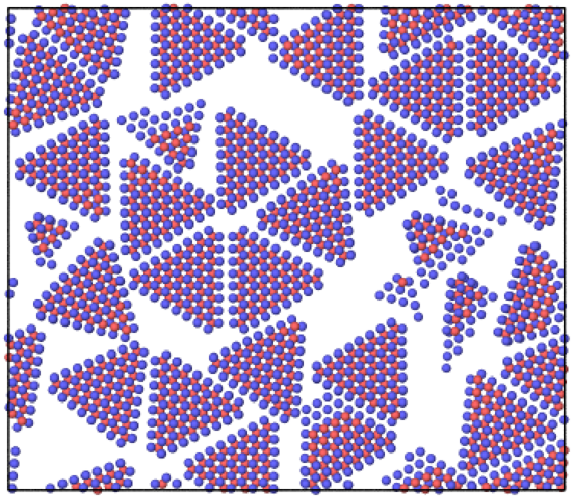
defect free

- Oxygen bonds to defect sites & prevents formation of larger sheets
- Molecular oxygen looks very similar

Effects of water on Inter-platelet bonding



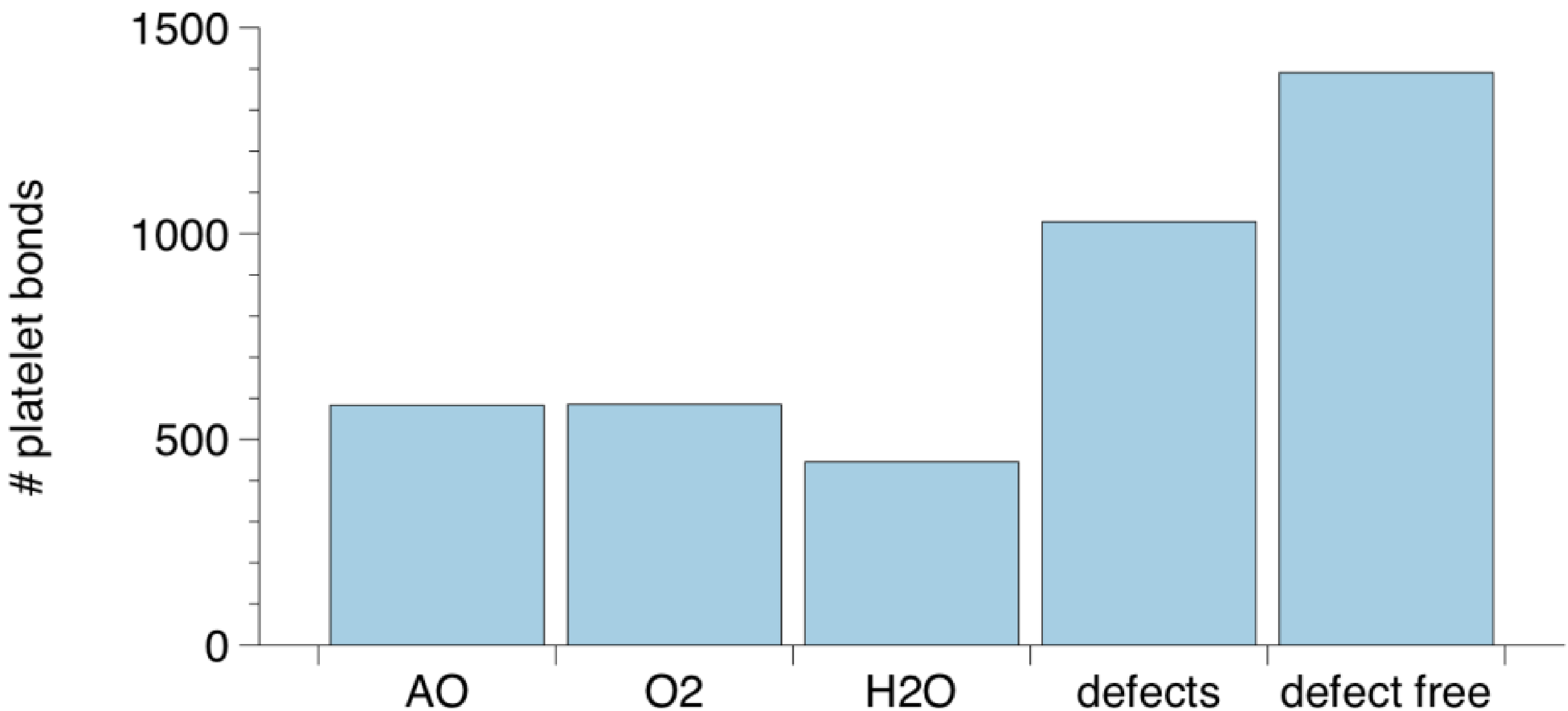
water passivated



defect free

- Water also bonds to defect sites & prevents formation of larger sheets
- Water aggregates with itself more than oxygen does

Counts of inter-platelet bonds confirm

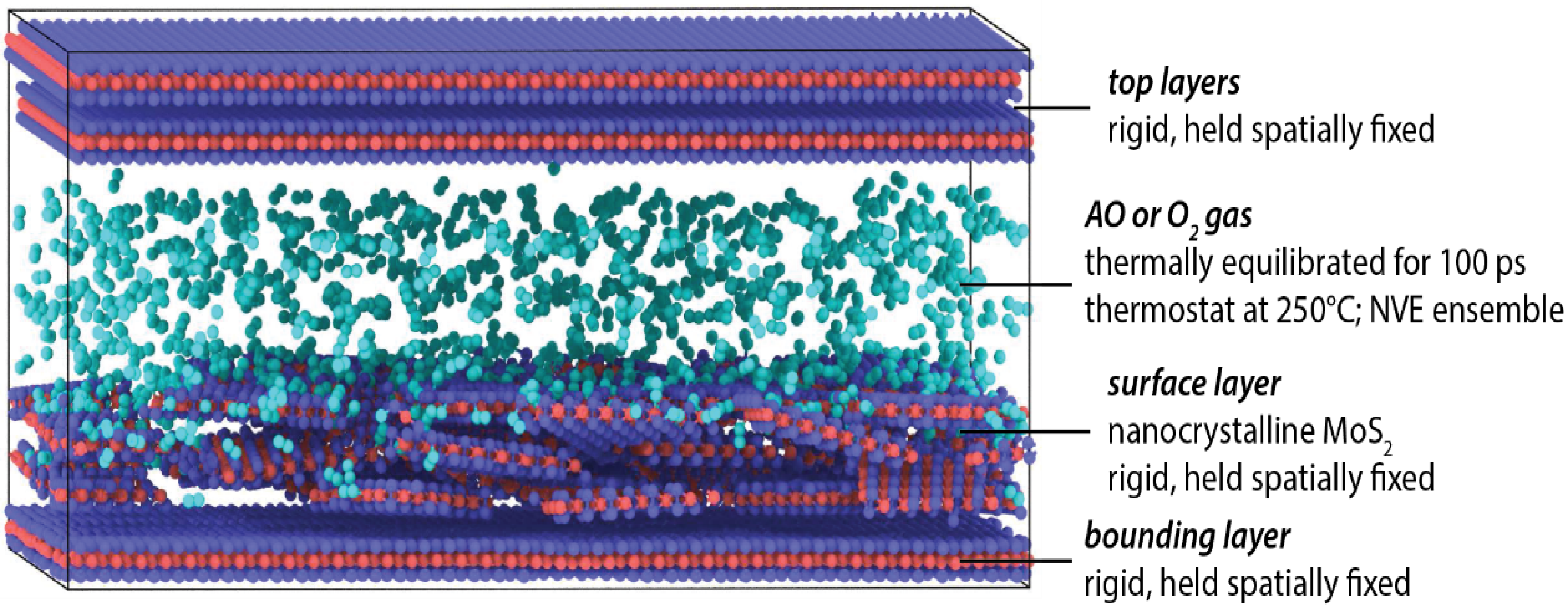


Environmental species interrupt formation of larger flakes

Summary

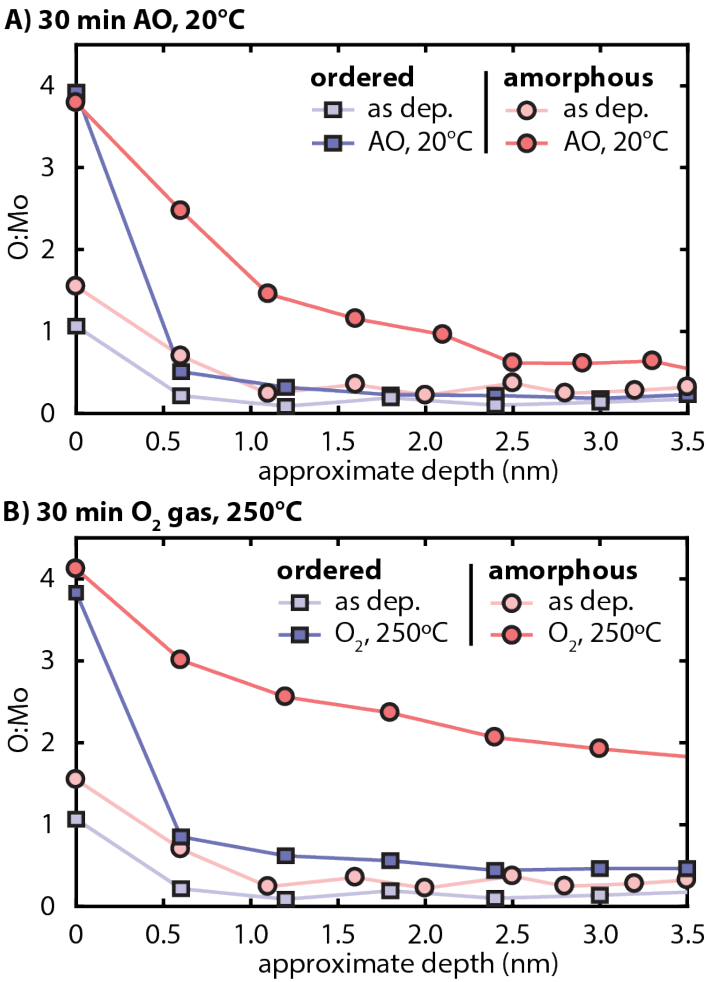
- MoS2 shows purely elastic contact
- Shear is predominantly due to inter-lamellar interactions
- MD calculates correct shear strengths as a function of temperature
- Developed simple model based on probabilities:
  - Energy barriers determine the shear strength
  - Rotate, and slide incommensurately
  - Fail to rotate and slide commensurately
- Incommensurate sliding is the most important – can neglect commensurate
- Simple model predicts temperature dependence

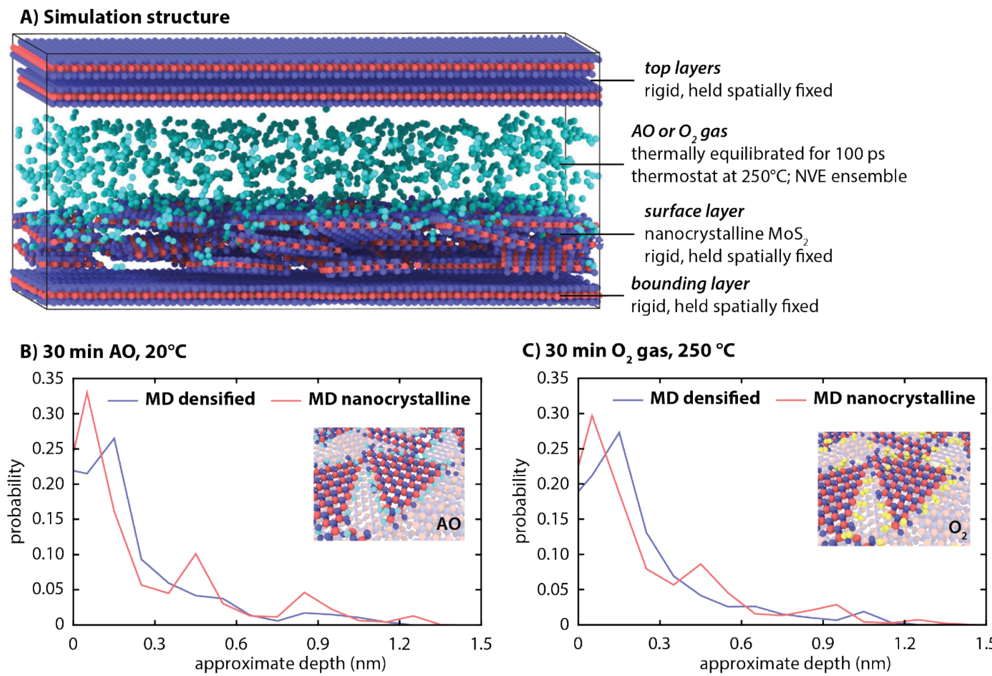
What about chemistry?



- Take systems that have “run-in” (i.e. reached steady-state shearing)
- Remove top layers
- Apply O2, AO or H_2O at 100 atm
- Replace top layers

LEIS experiments





Curry, et al, ACS Appl. Mater. Interfaces, 2017

MD accurately represents oxygen depth profiles as seen in LEIS experiments