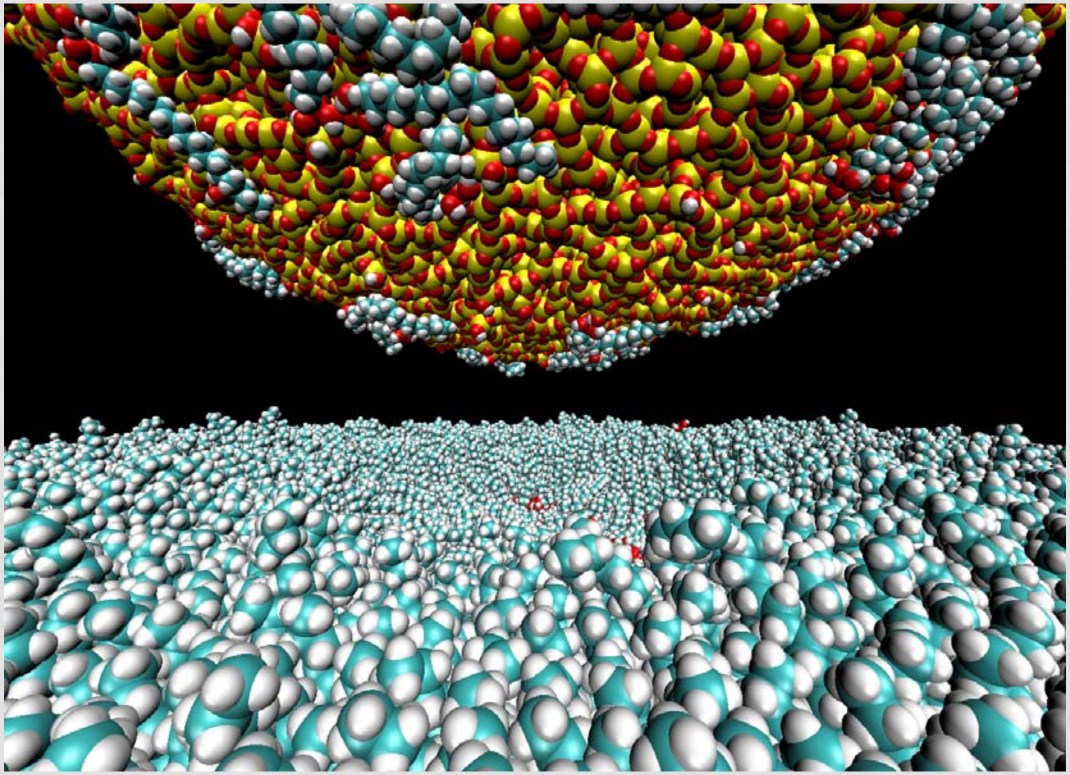
SAND2013-0875C

ATOMIC ORIGINS OF FRICTION REDUCTION IN METAL ALLOYS



Michael Chandross
Sandia National Laboratories, Albuquerque, NM

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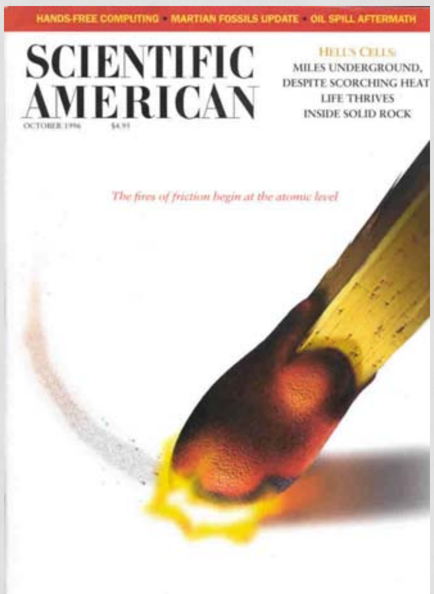
WHY TRIBOLOGY?



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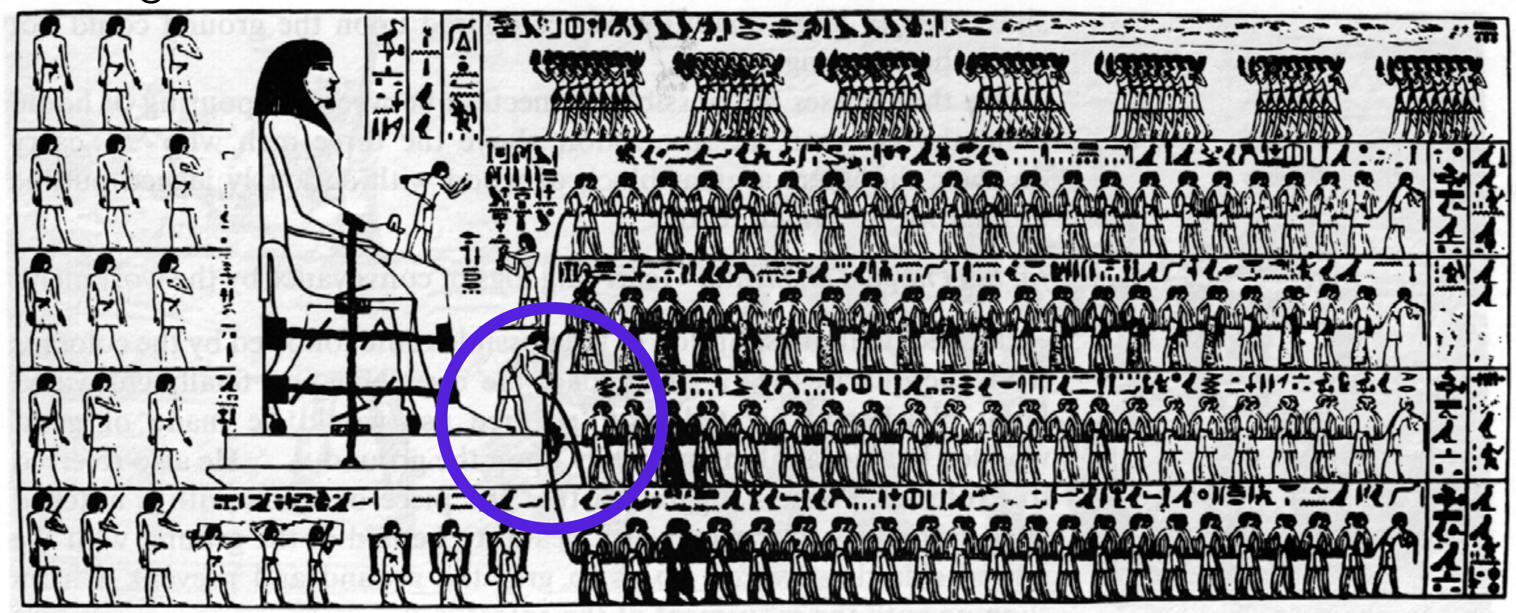
- Tribology = tribos + logy = study of friciton, lubrication and wear (1968)
    - 6% of US GDP
    - 5% of energy generated in car engine
    - Immediate impact on energy costs

ORIGINS OF TRIBOLOGY

Painting from a Grotto at El-Bersheh *ca*. 1880 BCE



Duncan Dowson, *History of Tribology*, Elsevier, 1979

<u>Macroscale: *Amontons (1699)*</u>

1) $F = \mu N$
2) $F \neq f(A_{app})$ (da Vinci)
3) $F \neq f(v)$ (Coulomb)

<u>Microscale: *Bowden and Tabor (1950)*</u>

- Relevant processes take place in and around region of contact
- Move from engineering to science

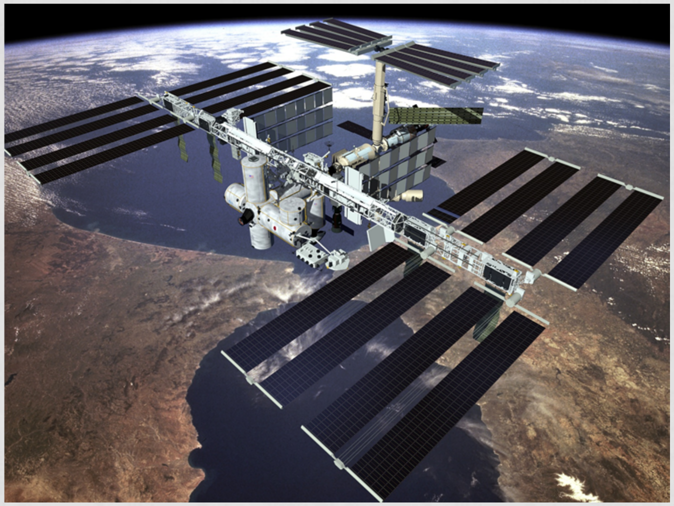
FRICTION COEFFICIENTS

Materials	Friction Coefficient
Ice on steel	0.01
PTFE (teflon) on PTFE	0.04
Rubber on Ice	0.15
Rubber on Concrete (wet)	0.3
Brick on wood	0.6
Rubber on Concrete (dry)	1.0

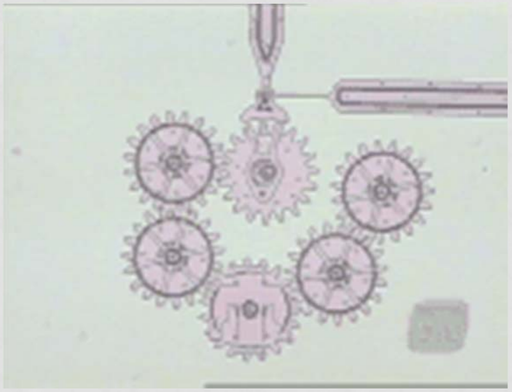
- Huge range of coefficients for different materials
- Low is not as important as predictable
- Science-based understanding of origins is important

WHY DON'T YOU JUST THROW SOME OIL IN THERE?

~50 m



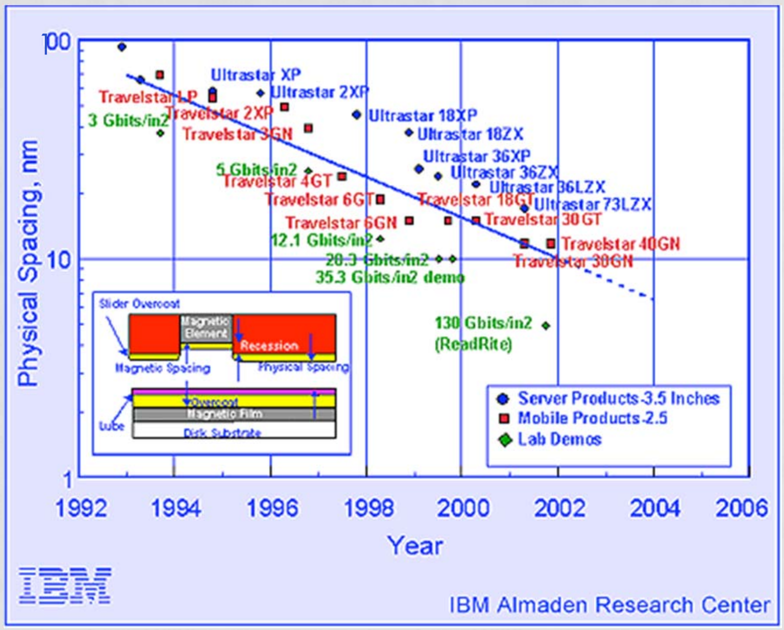
50 μm

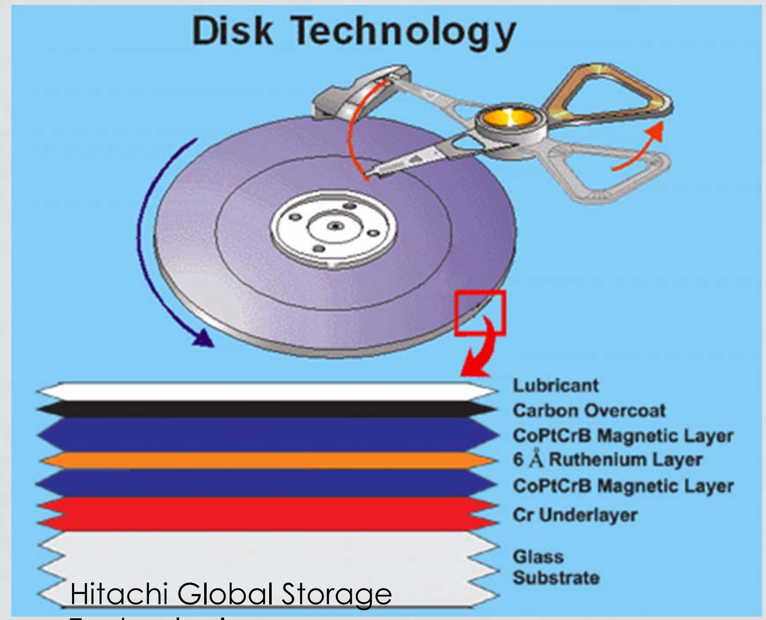


Six gear train

- Location, location, location!
- Space is a nasty place
  - UHV
  - Temperature swings from -40° C to 60° C
  - Bombardment with atomic O at ~ 1 km/s
- Tiny devices experience viscous drag

IMPORTANT APPLICATION



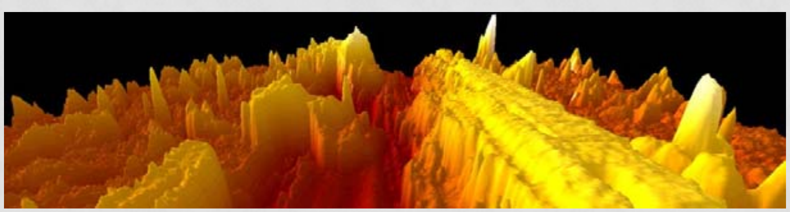


Hitachi Global Storage Technologies

- Fly heights < 10 nm, equivalent to 747
  - flying 1 cm above ground
  - Velocity of mach 800
- Contact (even in landing zone) is bad!
- Monolayer of lubricant 0.5-2 nm to protect against wear and lower surface E

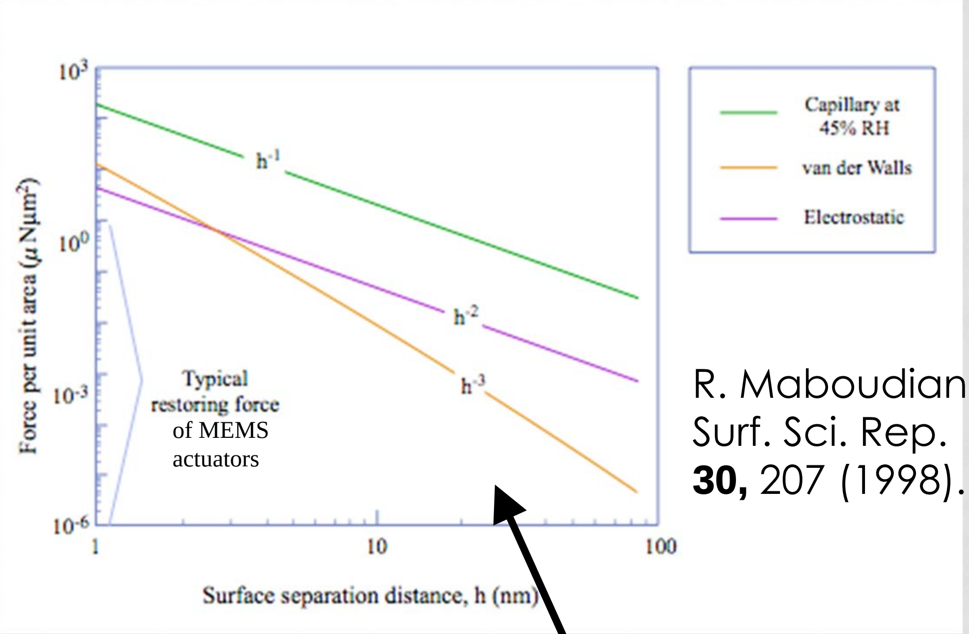
MACRO VS. NANO

vs.



- Macroscopic tribology (engineering)
  - Friction coefficient
  - Wear rate
  - Not intrinsic properties!
- Nanotribology (science)
  - Fundamental understanding
  - Requires well-defined interfaces
  - Single asperity contacts
  - Physics, chemistry, materials science, mech. engineering…

WHY IS NANOTRIBOLOGY IMPORTANT?



R. Maboudian, Surf. Sci. Rep. **30,** 207 (1998).

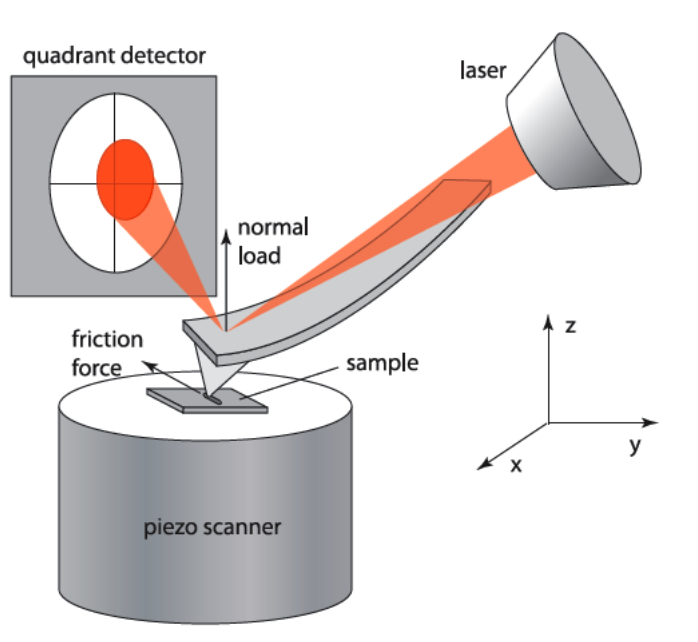
Fig. 2. Tokay gecko (*Gekko gecko*) adhering to molecularly smooth hydrophobic GaAs semiconductor. The strong adhesion between the hydrophobic surface of the gecko's toes and the hydrophobic GaAs surfaces demonstrates that the mechanism of adhesion in geckos is van der Waals force.

Autumn et al, PNAS, 2003

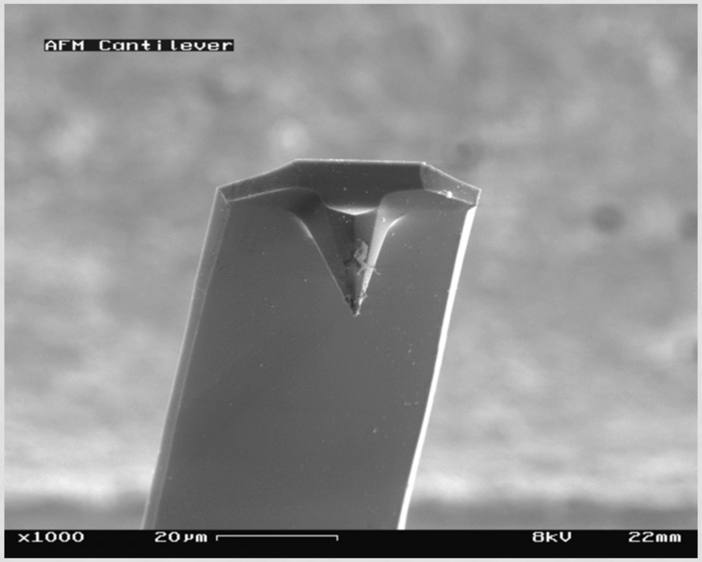
Attractive forces per 1 μm^2 for two perfectly smooth silicon surfaces as a function of separation, *h*.

See: Szlufarska, Chandross and Carpick, J. Phys. D **12**, 123001 (2008)

ATOMIC FORCE MICROSCOPY

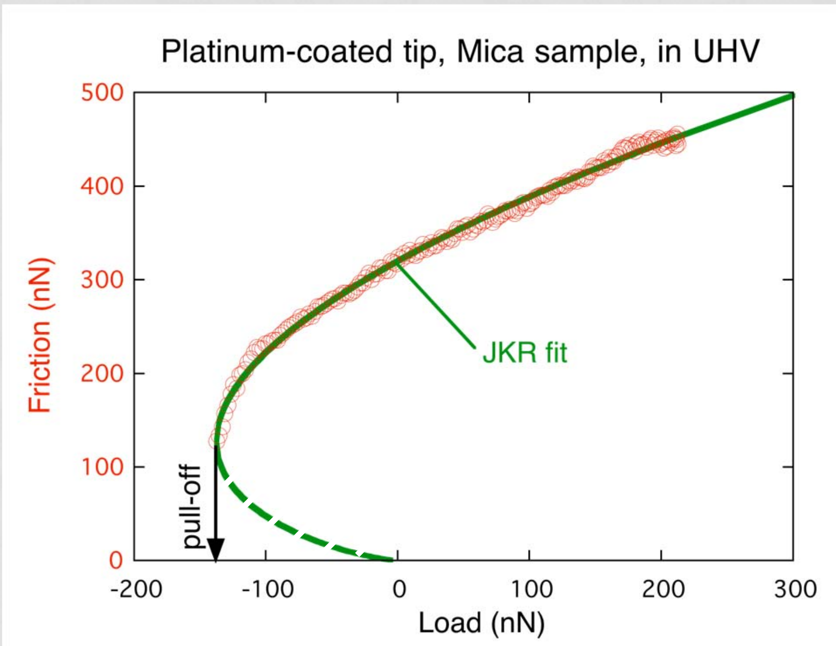


- Binnig, Quate and Gerber in 1986 (after STM)
- Sharp tip (10 – 100 nm)
- Compliant cantilever

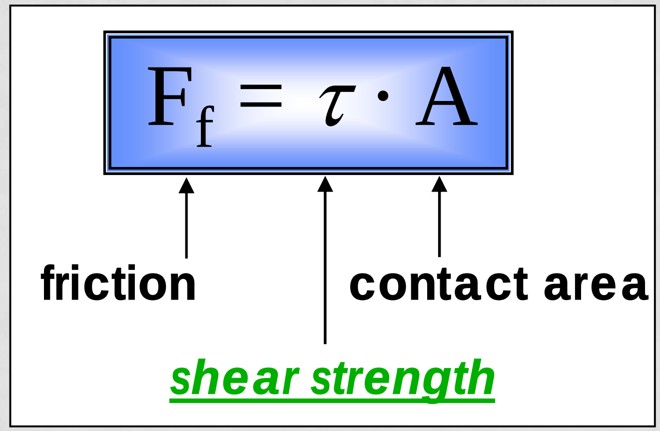


- Controllable single asperity contact
- Atomic level precision of forces and displacements
- Control of environment

SINGLE ASPERITY CONTACTS



Carpick et al., J. Vac. Sci. Technol. B, 1996
Carpick et al., Langmuir, 1996



- τ ~ Gpa (near ideal strength)
- Not Amontons-like
- F at negative loads

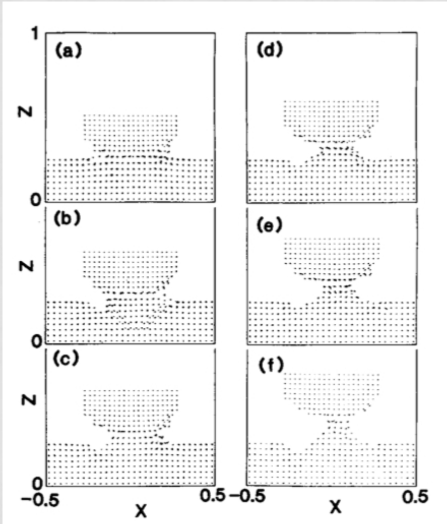
- <u>Bowden and Tabor (1950)</u>
  - A_{real} vs. A_{app}
  - $F = \tau A$
  - $\tau = \tau_o + \langle L/A$
  - $F = \tau_o A + \langle L$

Courtesy Rob Carpick, U.

INTRODUCTION: GOLD

- Gold has desirable properties
  - High conductivity 4.52 x 107 S/m
  - Doesn't corrode/oxidize
  - Can be made very thin
- Not everything is shiny…
  - High adhesion (> GPa)
  - High friction (μ = 1 – 2)

- Can we get the best of both worlds?

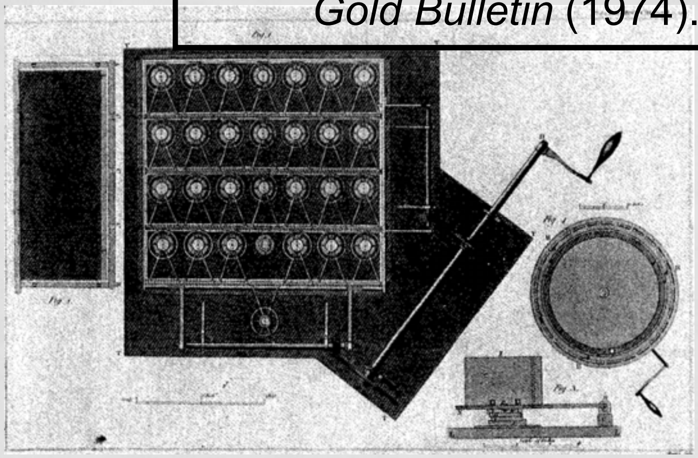


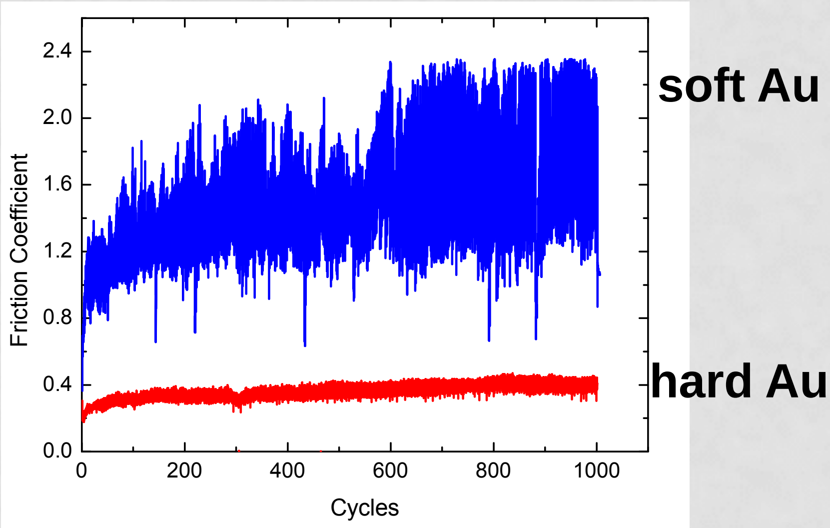
Luedtke and Landman, Comp. Mat. Sci. (1992).

ARE COMPOSITES THE ANSWER?

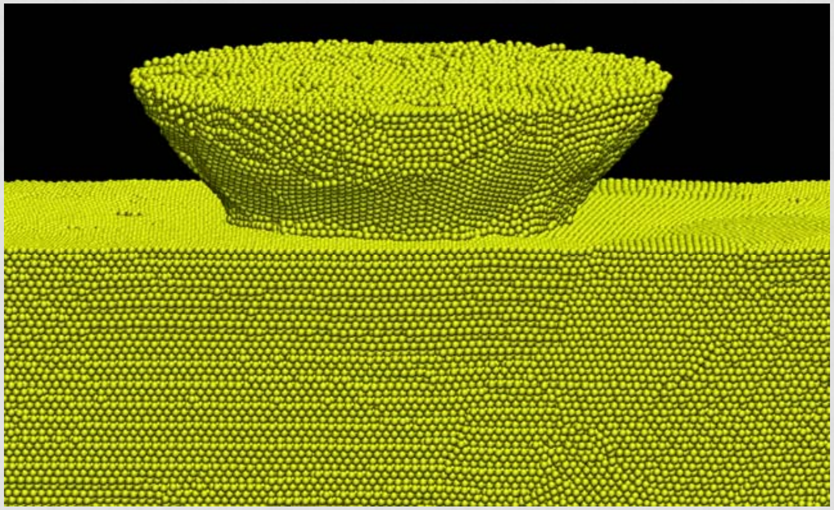
- Alloys investigated in 1798 to reduce wear in coins
  - 11 alloys (including Cu), ~ 8.3 %
  - Cavendish designed testing machine
  - None really worked
- Our goals:
  - Maintain electrical properties
  - Reduce adhesion and friction
- Questions:
  - Why do composites change μ?
  - What is the optimal composition?

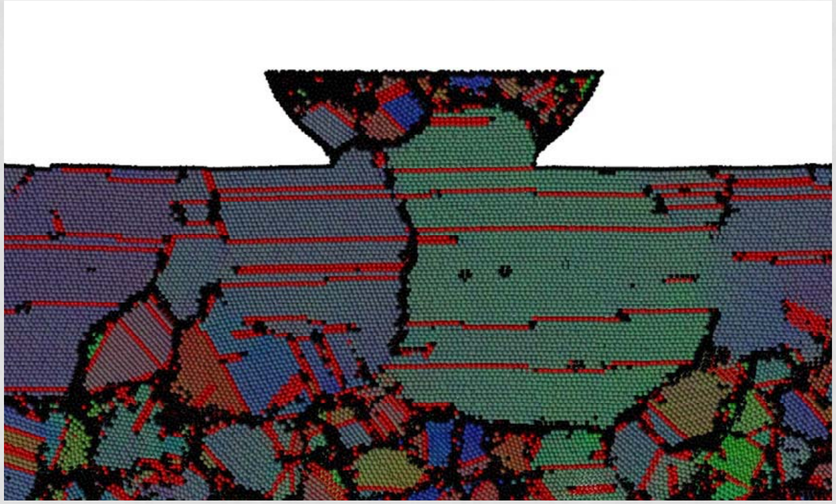
Cavendish (1798) via Chaston, *Gold Bulletin* (1974).





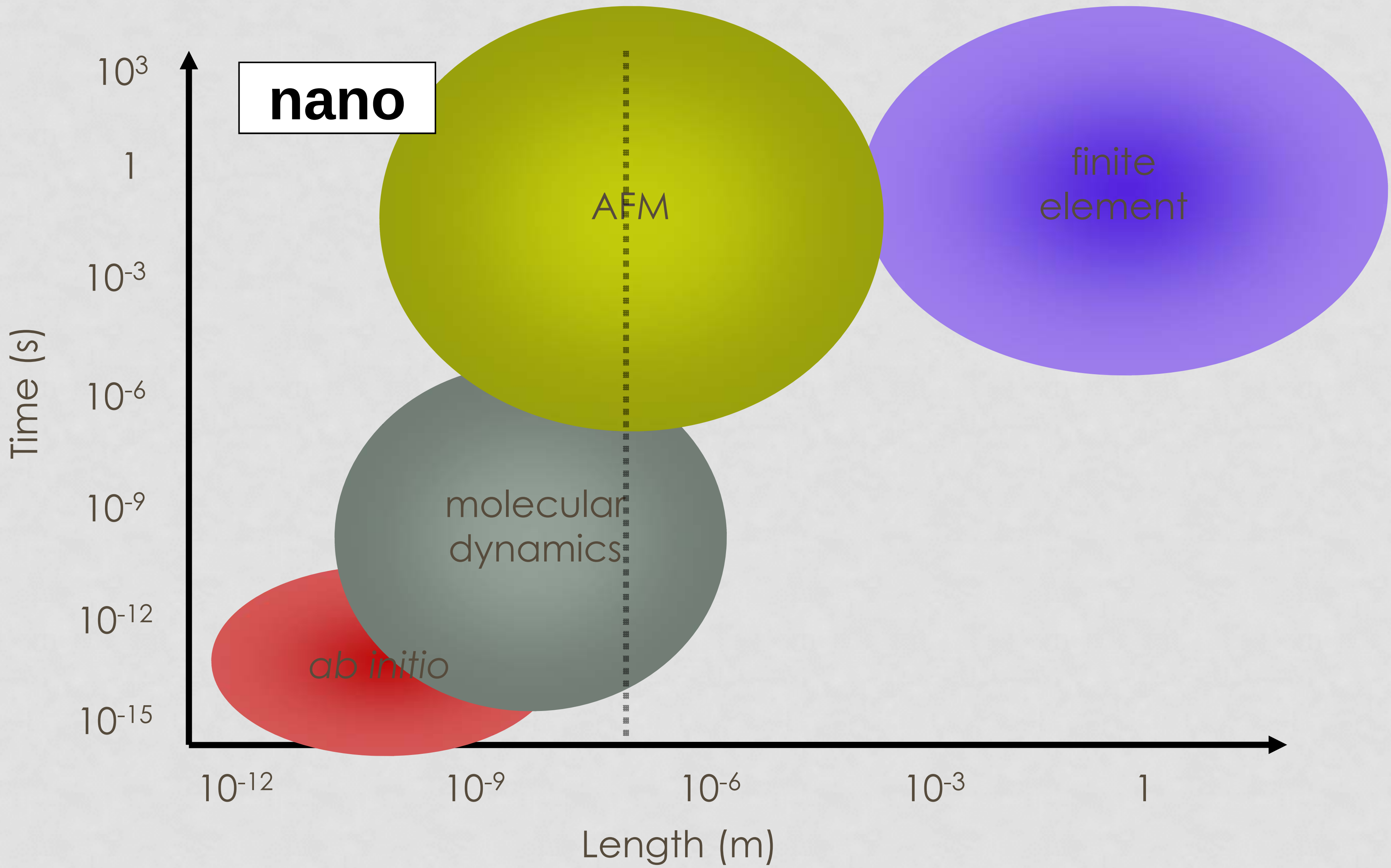
SIMULATION METHODS



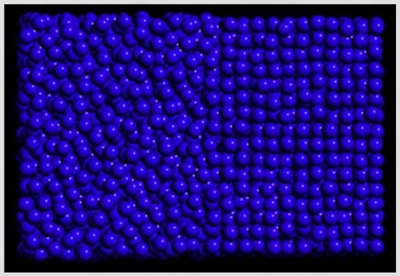


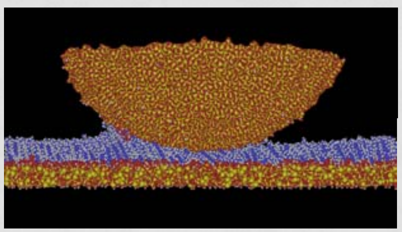
- Large scale Molecular Dynamics
  - Can track location, velocity, forces of individual atoms
  - Constraints on length and time scales
- Embedded Atom Method
  - Very accurate for mechanical properties
  - Can't easily mix without reparameterizing – switch to Ag

TIME AND LENGTH SCALES



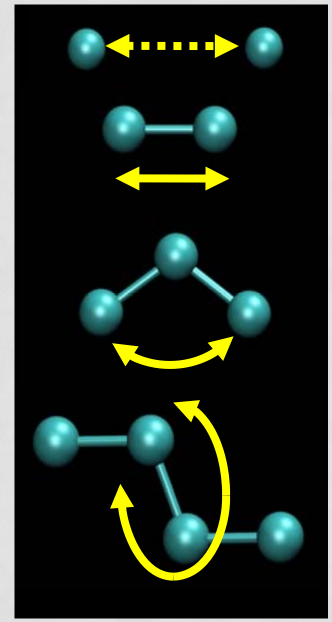
WHAT IS MOLECULAR DYNAMICS?





Initial positions and velocities

Interatomic potential

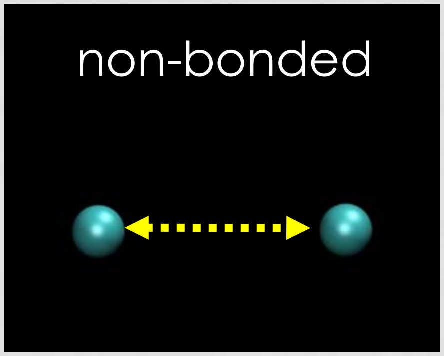


- Classical sim. technique
- Empirical interactions
- Evolve system, analyze

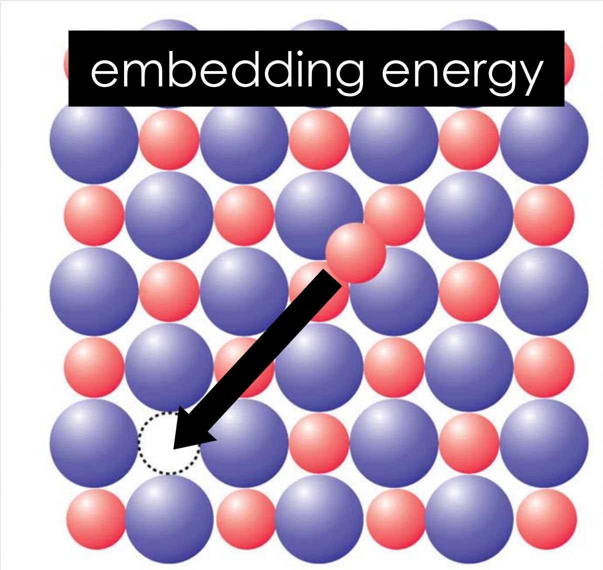
Positions and velocities at later times

Thanks to Aidan Thompson

EMBEDDED ATOM METHOD



$4\varepsilon\,[\,(\sigma/r)^{12} - (\sigma/r)^{6}\,] \quad r < r_c$



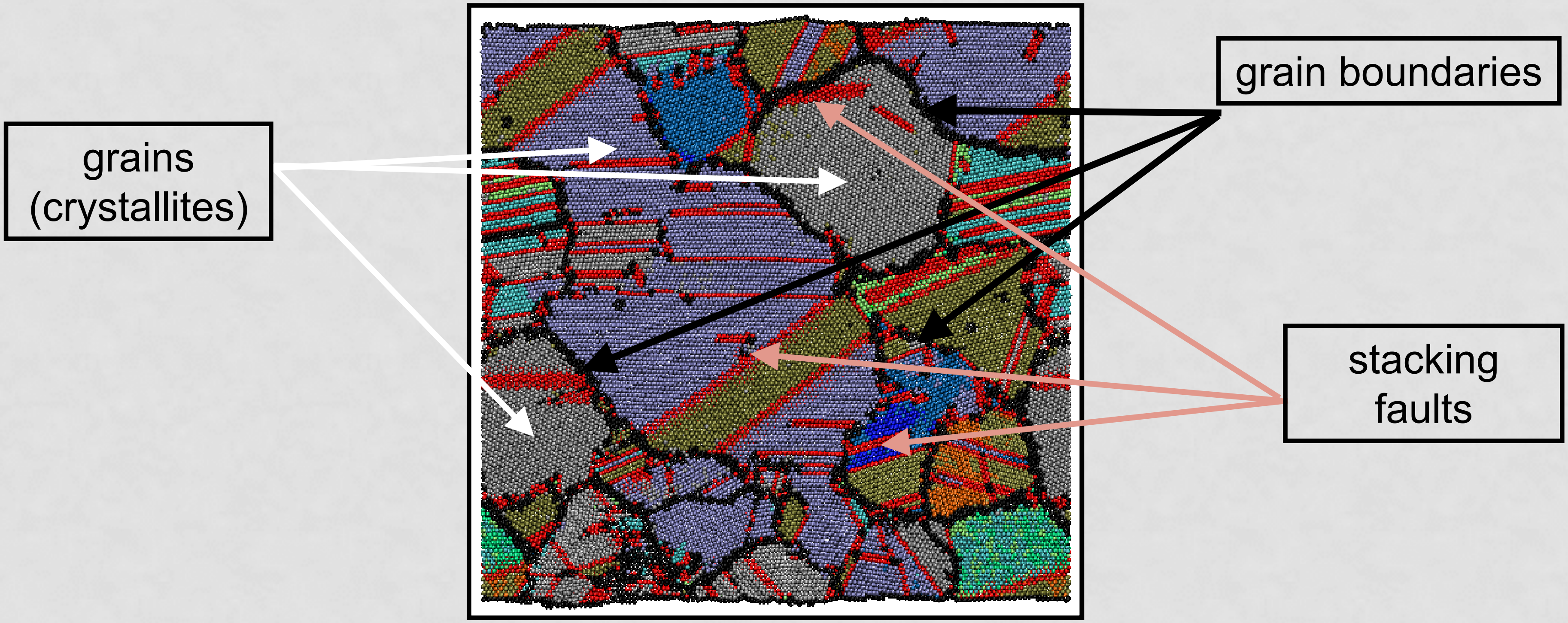
$F_{\alpha}\left(\Sigma_{i\neq j}\rho_{\beta}(r_{ij})\right)$

- Energy is sum of two terms
  - Pairwise interactions
  - Electron charge density & insertion energy
- Related to 2nd moment approximation to tight binding
- Excellent for metallic systems

MOLECULAR DYNAMICS -- SPECIFICS

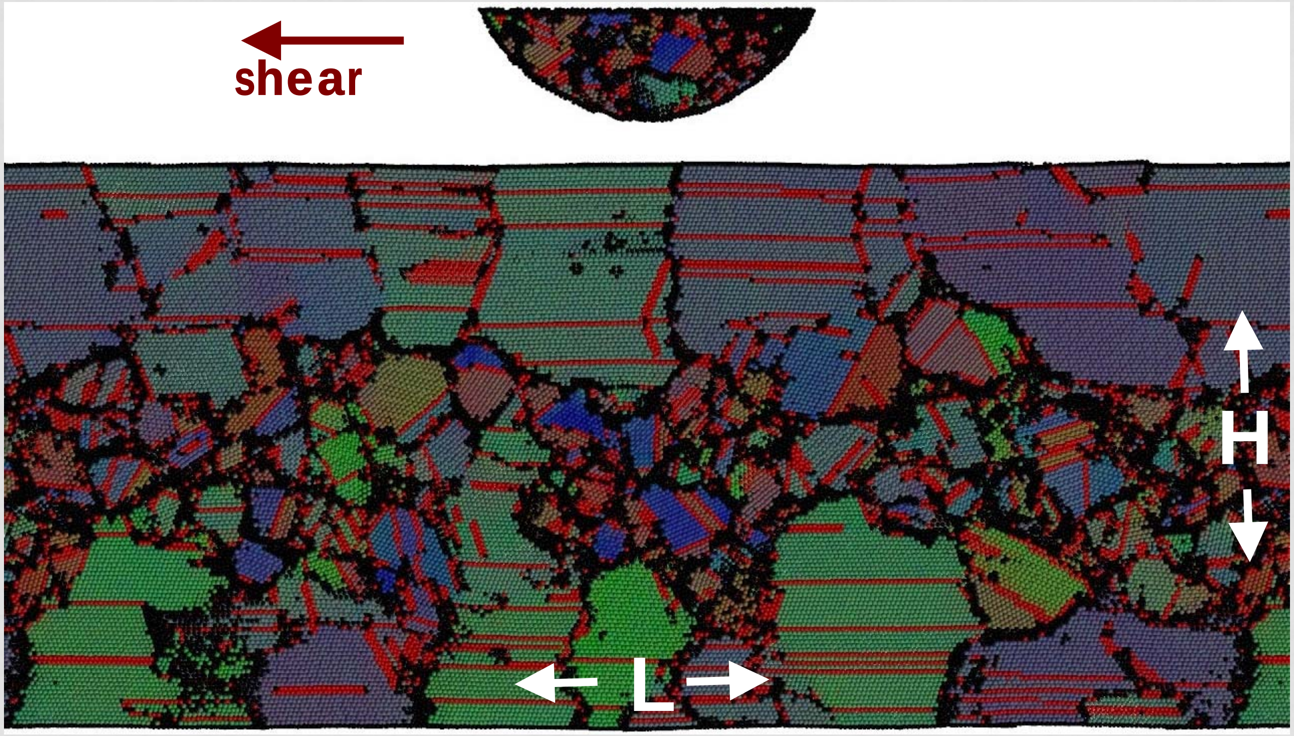
1) Choose a force field
2) Create a model system
    1) Place all the atoms
    2) Define atom types & interactions
    3) Define bonds/angles/dihedrals, etc.
    4) Decide on # of processors
3) Integrate (time step ~ 1 fs)
    1) Equilibrate (~ 1 week)
    2) Compress (~ 2 weeks)
    3) Shear (~ 4 weeks per load)
4) Analyze, make movies, etc.

GRAIN ANALYSIS



- Locally FCC atoms colored according to Euler angle
- Locally HCP atoms colored red – twins & stacking faults
- Otherwise colored black – grain boundaries

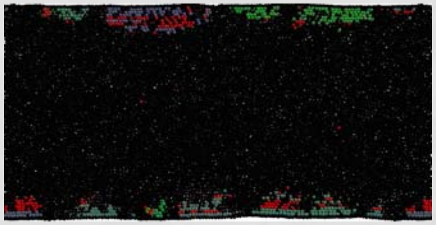
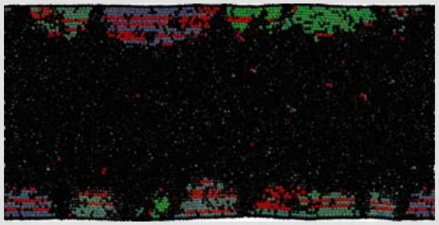
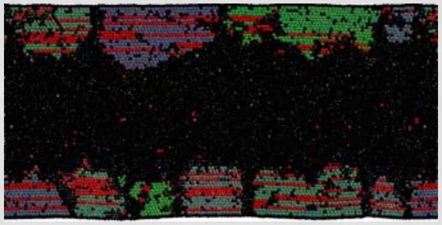
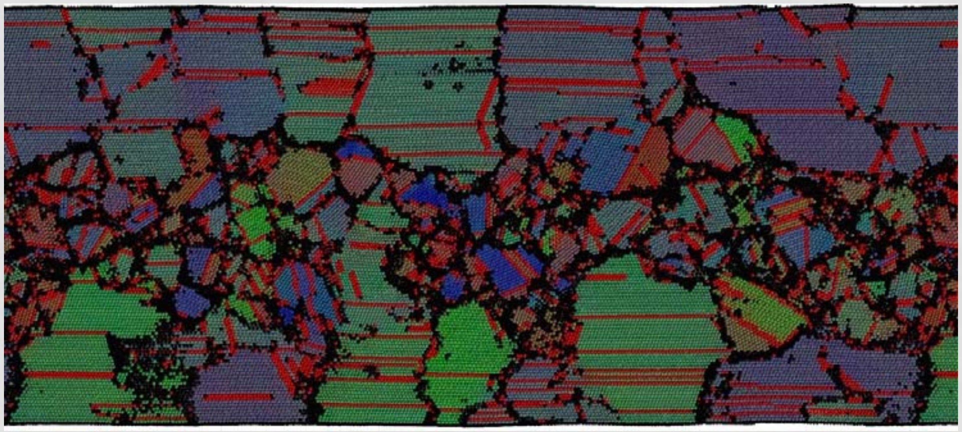
TIP-BASED FRICTION SIMULATIONS



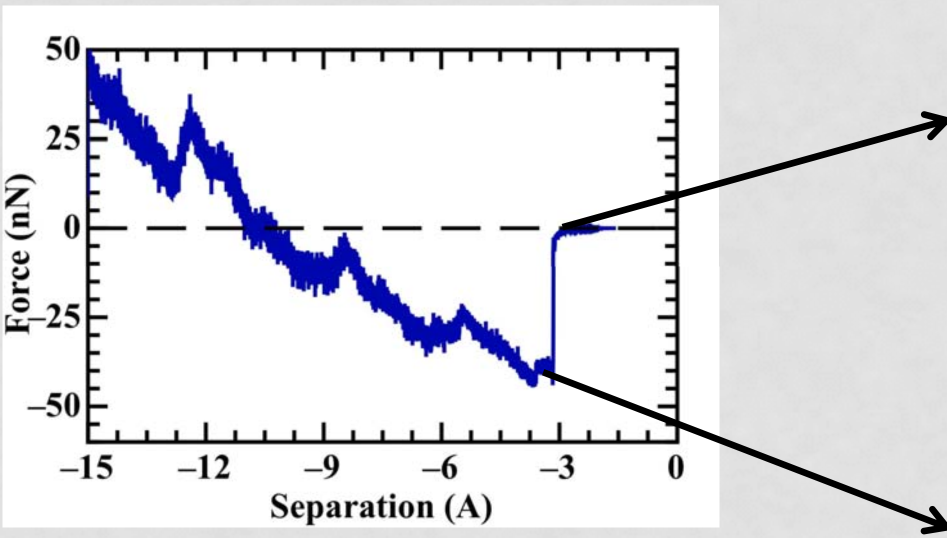
- Substrate: nanocrystalline Ag, 17 nm (W) x 34 nm (H) x 67 nm (L)
- Tip: 10 nm radius
- Shear velocity: 2 m/s (constant velocity, and separation *or* force)

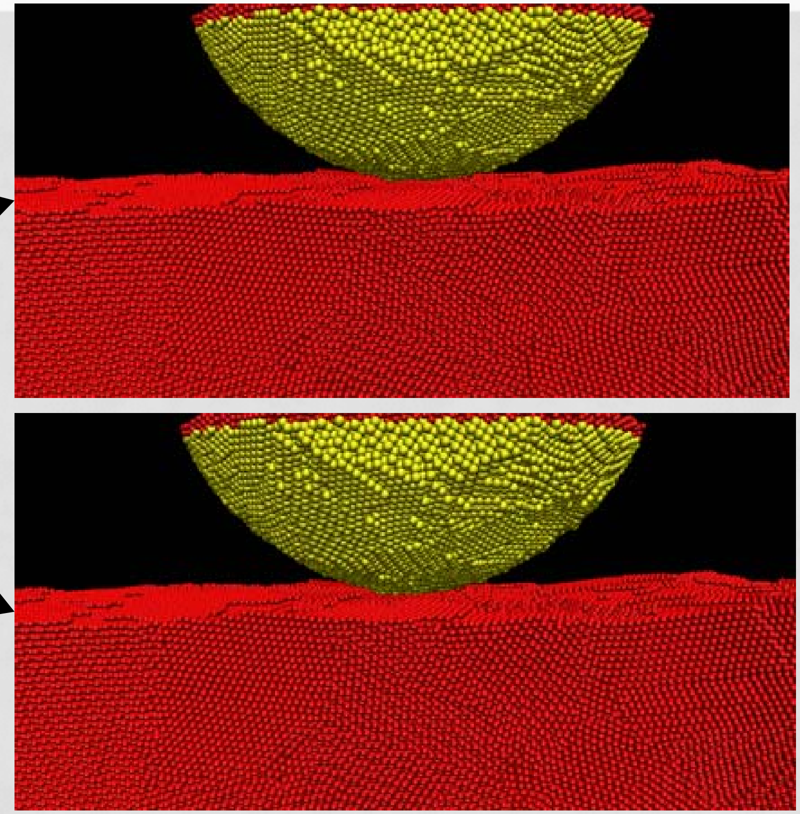
NANOCRYSTALLINE AG

- Melt & quench
  - Start with bulk FCC
  - Melt at 1800 K (20 ps)
  - Rapidly quench (100ps)
  - Grains ~ 5 nm
  - Can grow grains easily
- Metallurgy aside
  - Twins indicate that surface is aligned with {111}
  - Growth pictures indicate that {111} growth direction preferentially nucleates at surface

FORCE VS. SEPARATION

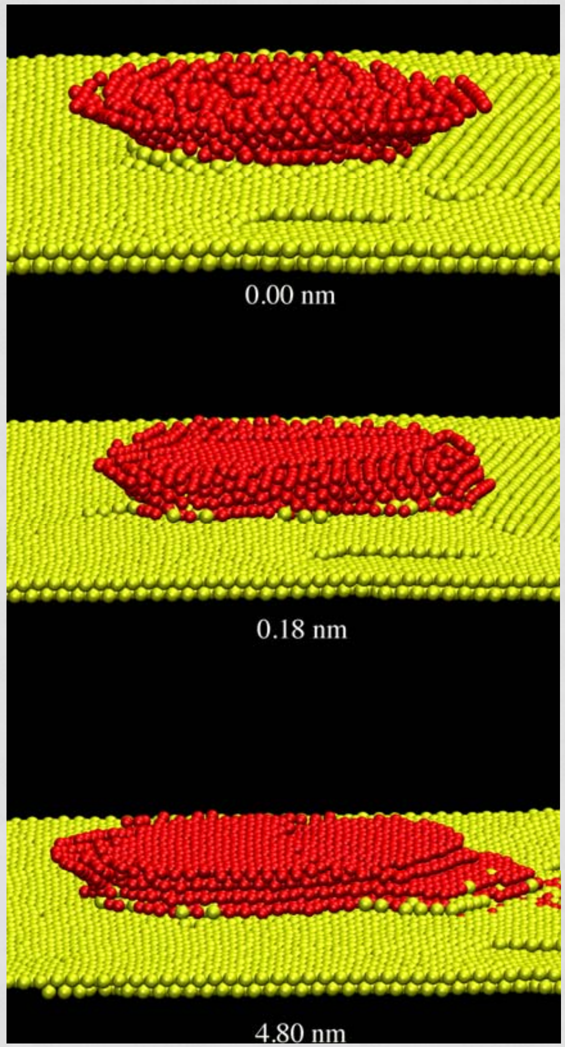


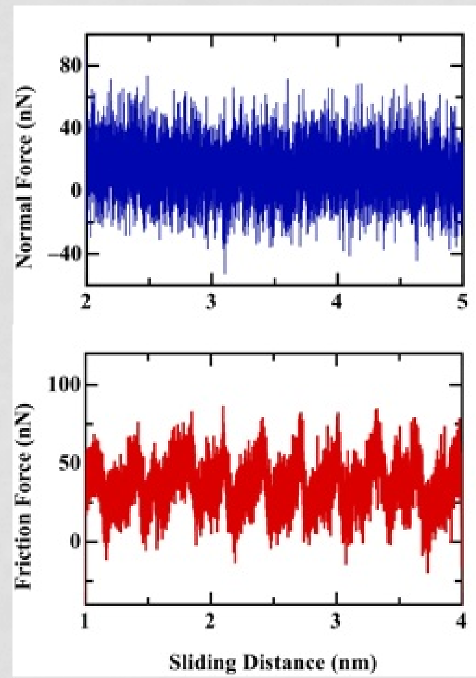


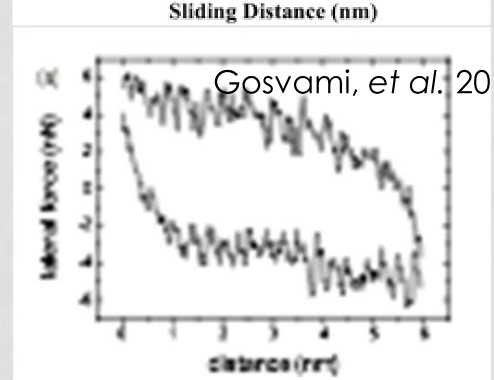
- Separation is arbitrarily defined
- Initial adhesion: ~ 40 nN / 4 Gpa
- Pressures in line with Israelachvili, *Acta Mat.* (2003).

BEHAVIOR UNDER SHEAR

- Layering of tip atoms
- Stick-slip in friction signal
- Shear induces commensurate contact
- Commensurability => high friction
- Do composites suppress this?



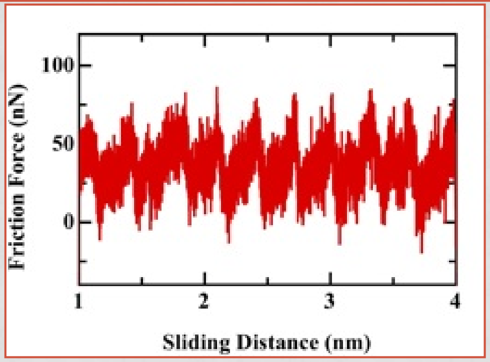


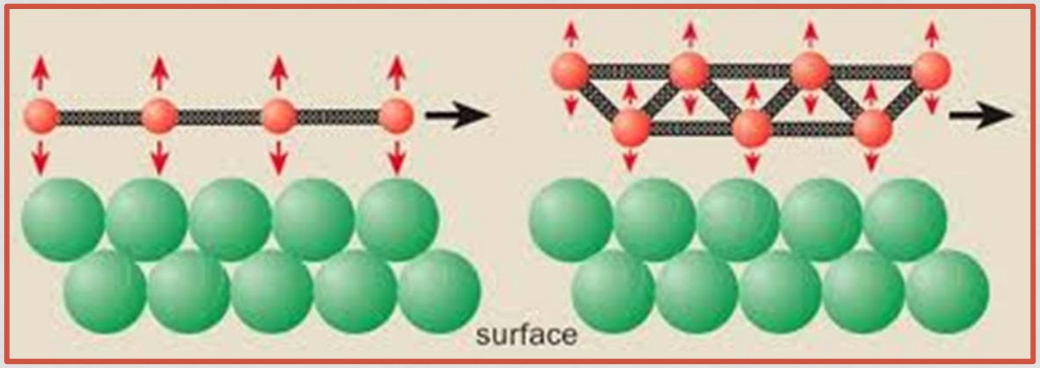


Gosvami, *et al.* 2011

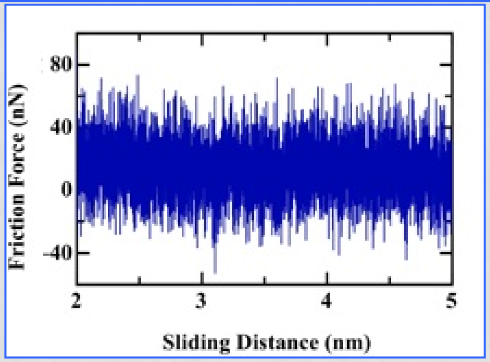
COMMENSURABILITY AND FRICTION

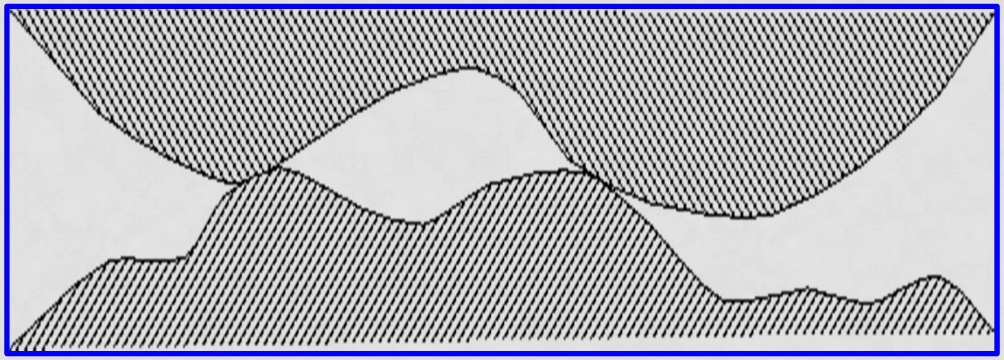
commensurate interface
(stick-slip friction)



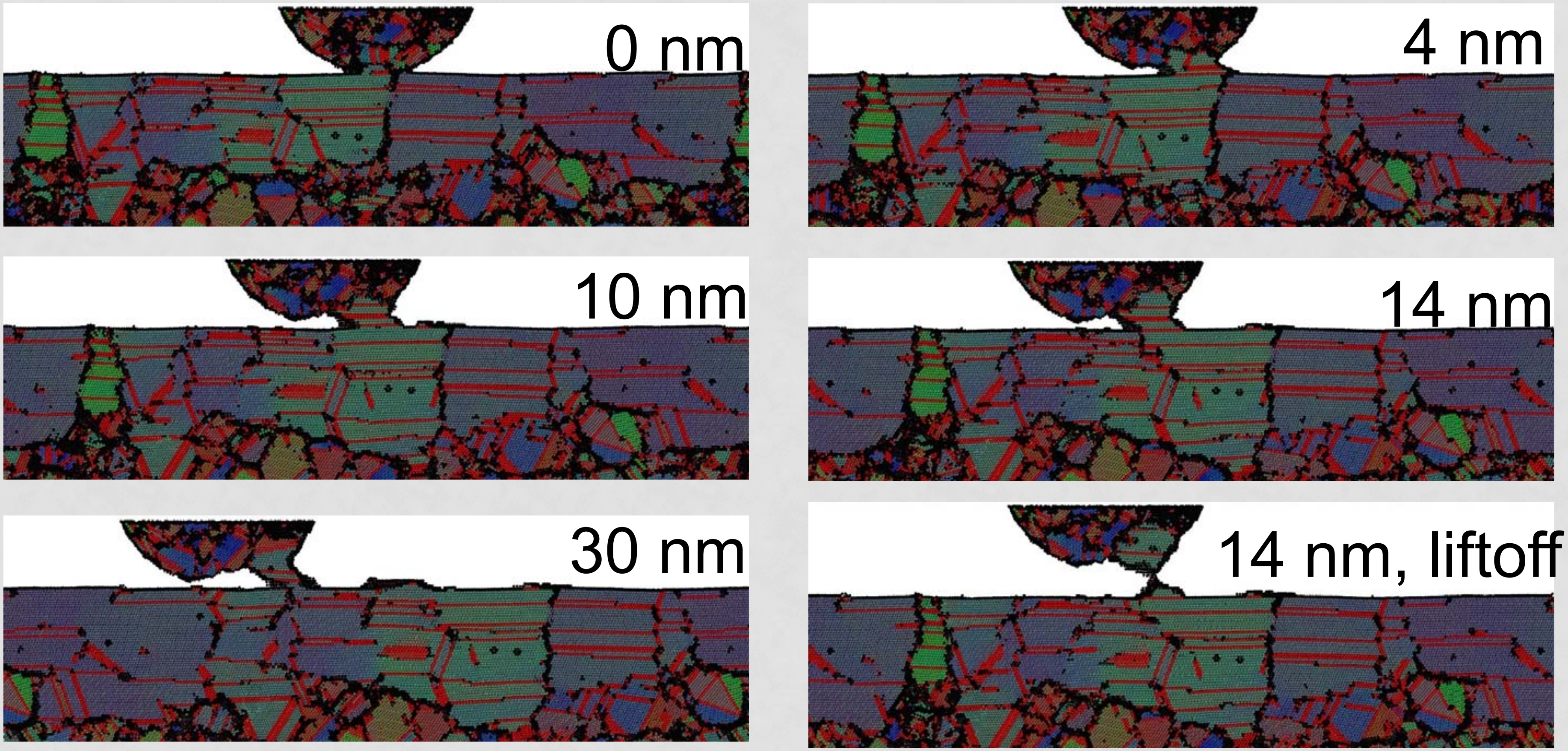


incommensurate interface
(smooth sliding)



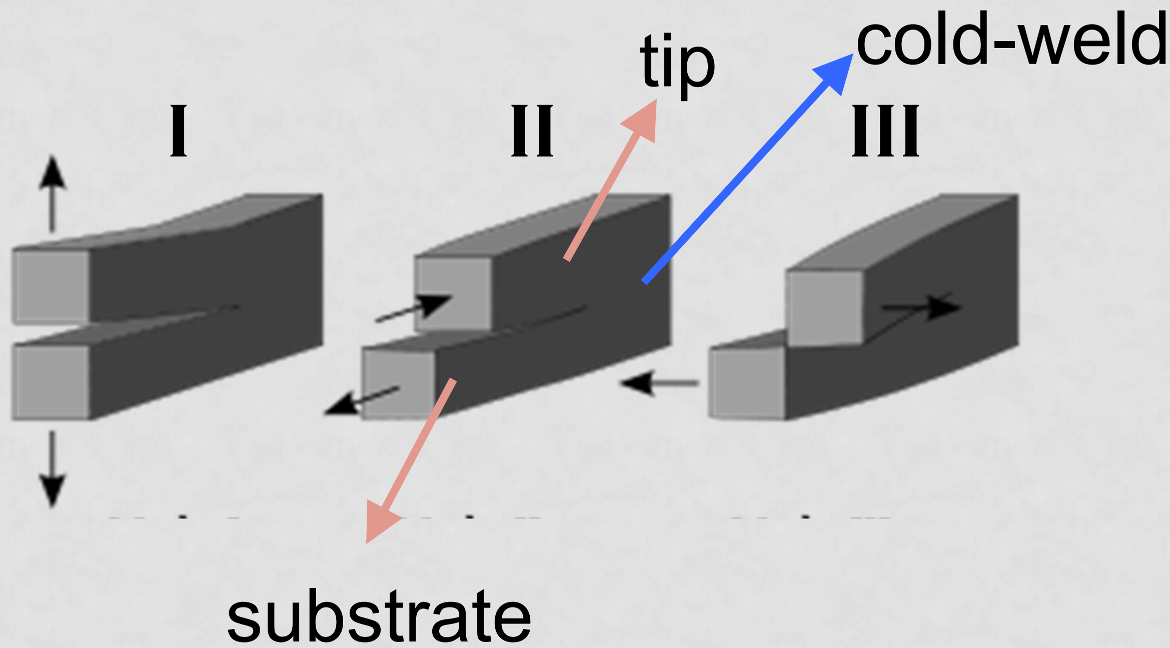


GRAIN LEVEL SNAPSHOTS



- Initially distinct grains
- After shear (adhesive load), coalescence – now a mode II crack
- Single grain forms across interface – stress induced grain growth

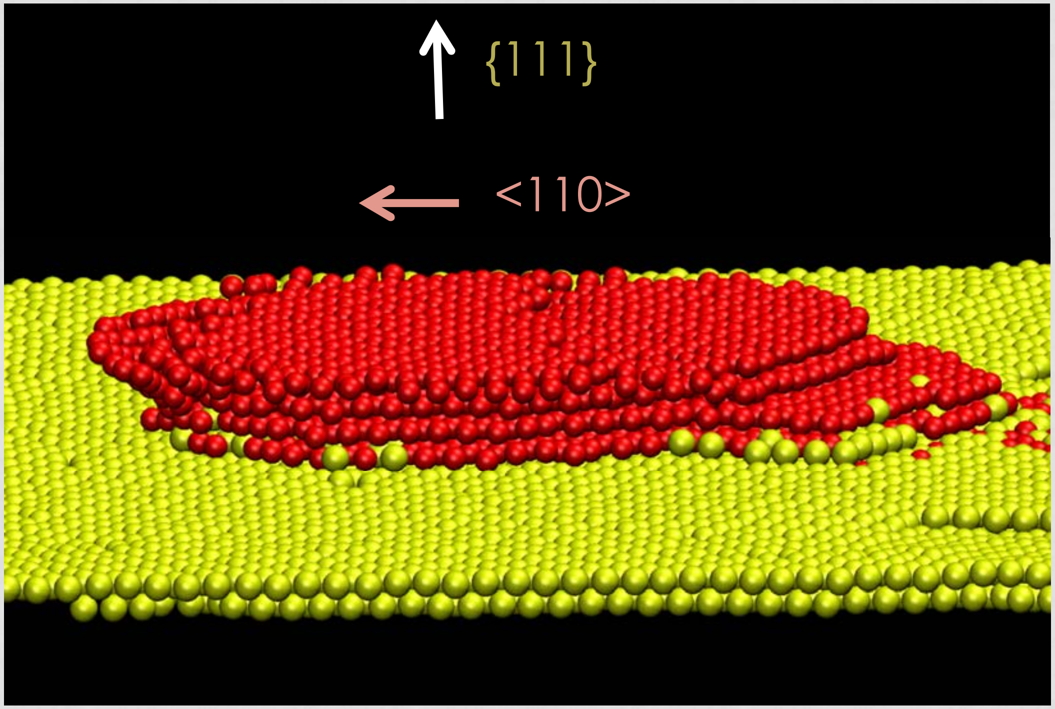
TYPES OF CRACKS



- Mode **I**: Tensile Shear
- Mode **II**: In-plane Shear
- Mode **III**: Out-of-plane Shear

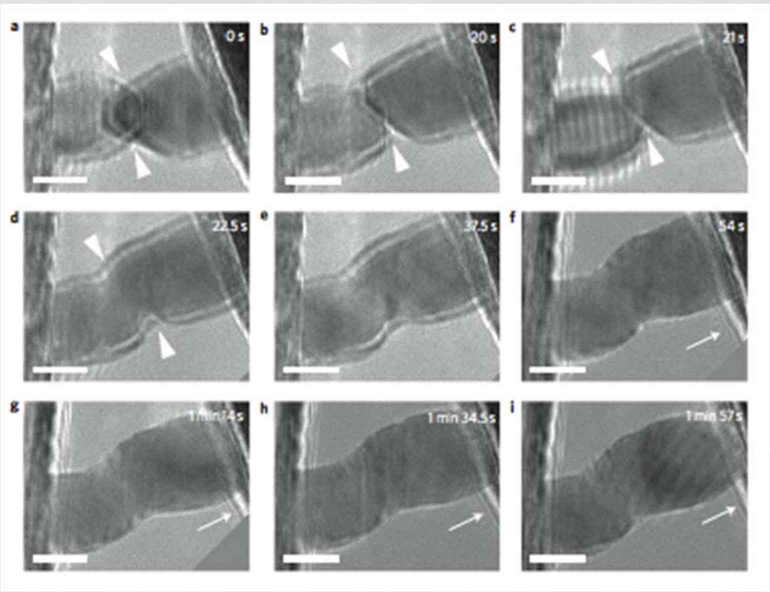
FCC SLIP SYSTEMS

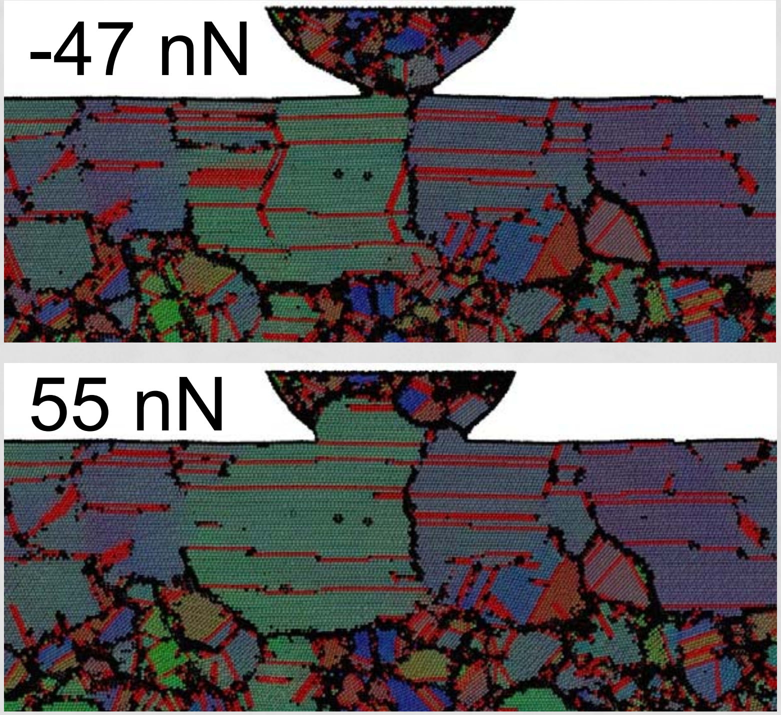
- Along {111} plane
- In <110> direction
- Ductility
- Plastic deformation
- *Not* fracture



EXPERIMENTAL VERIFICATION

Lu, *Nature Nanotech*, 2010

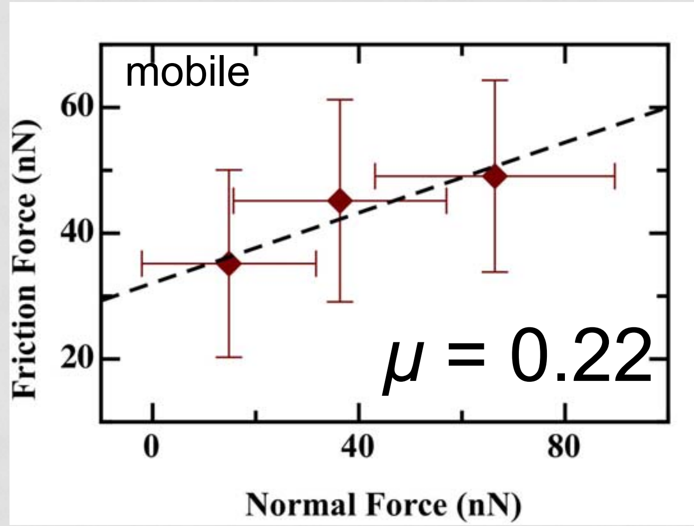


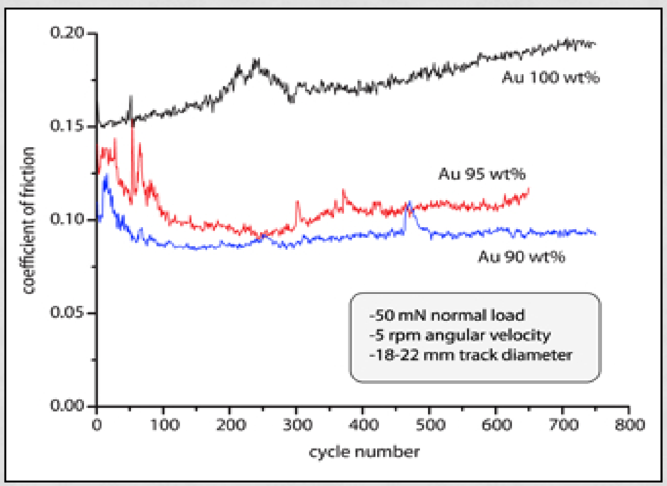


- Cold welding of single crystals with substructure evolution
- 1.5 s of contact time with little external force (exp)
- Simulations show growth with 2 ps contact under compressive load

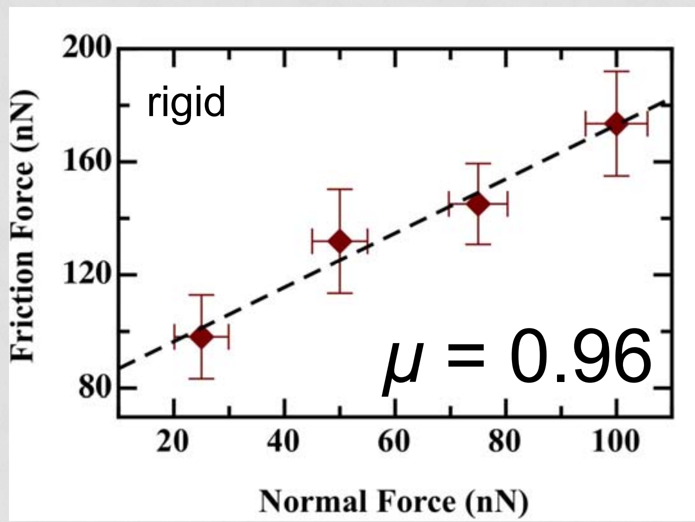
FRICTION COEFFICIENT

- Nanoscopic low load contacts:
  - μ = 0.2-0.3
  - Sawyer, et al.
  - Bennewitz, et al
- Macroscopic, high load
  - μ = 0.5-2.0
  - Hard tips, plowing
  - Compare to rigid tip simulations

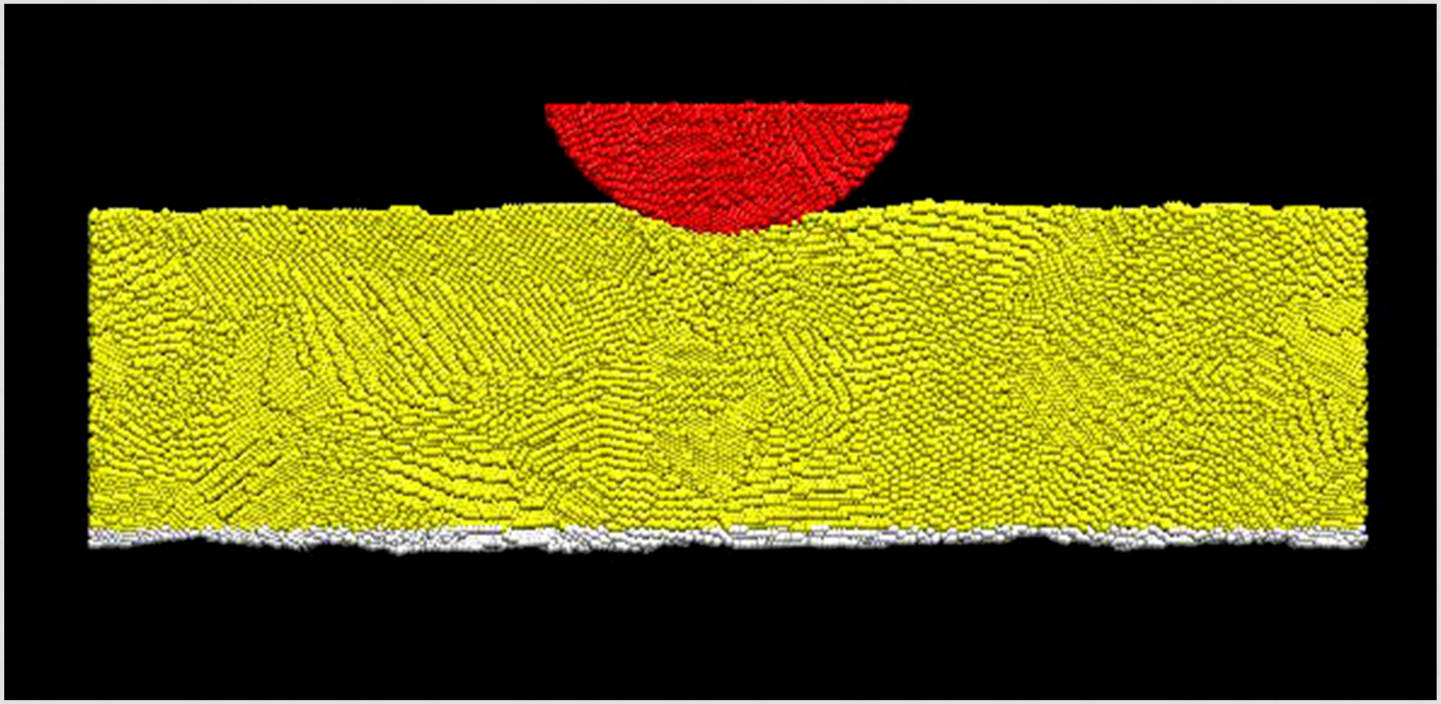




Courtesy: WG Sawyer, U. Florida



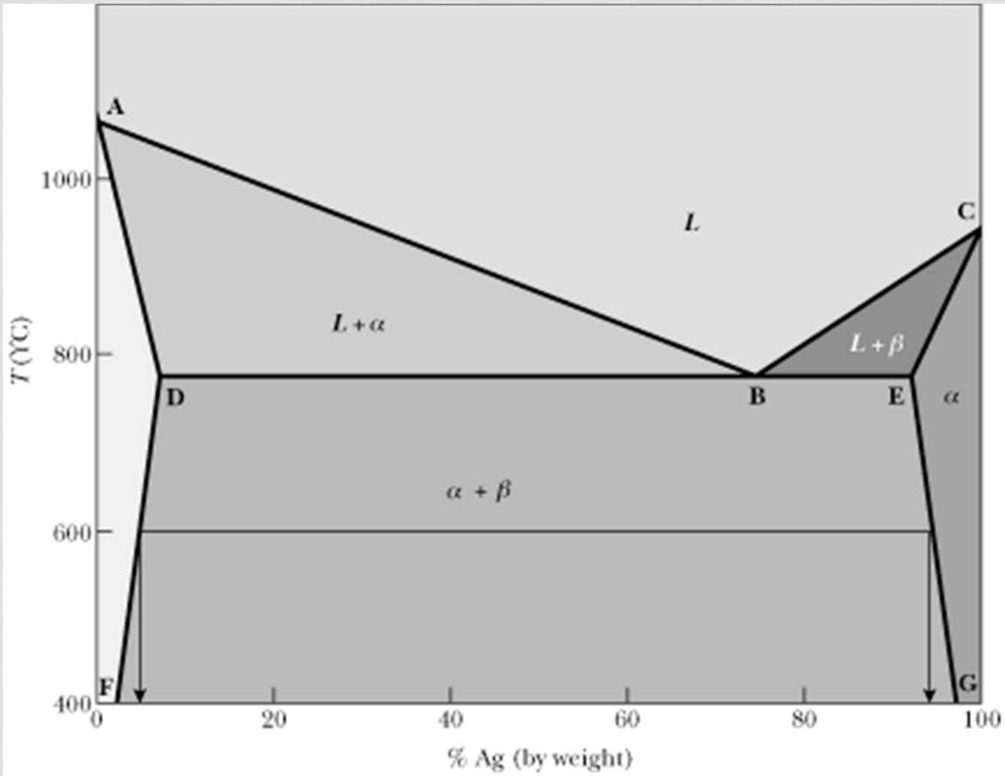
PLOWING MOVIE



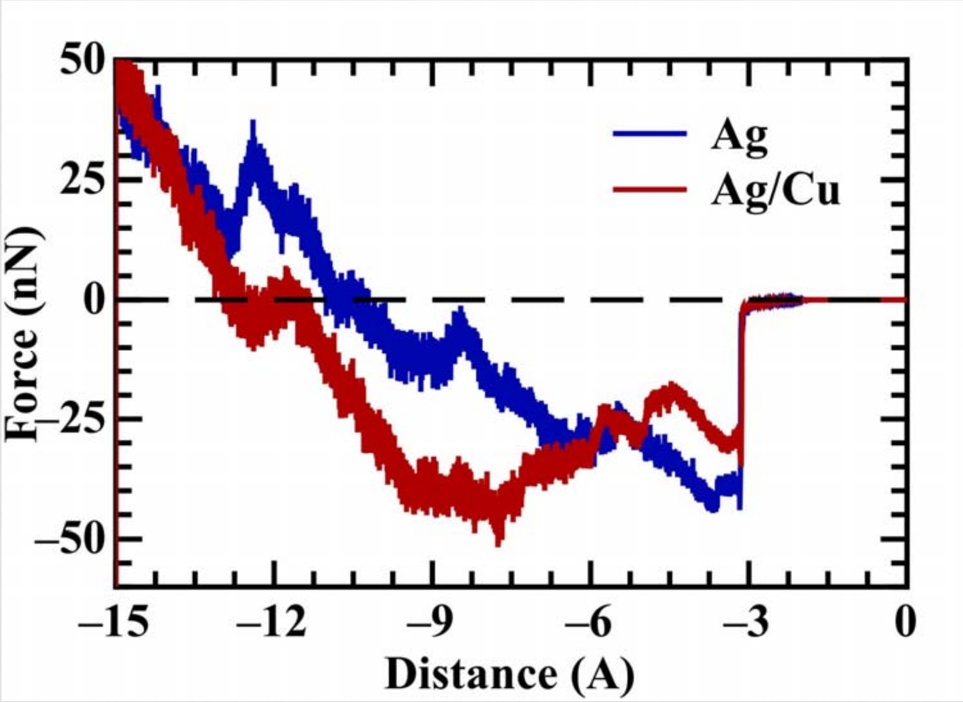
- Constant applied load of 100 nN
- Constant tip velocity of 2 m/s
- Movie shows plowing of substrate from rigid tip

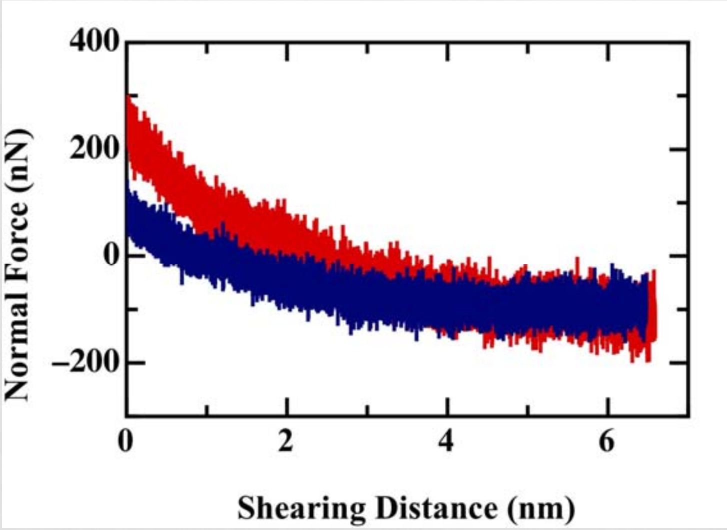
ALLOYS: AG/CU

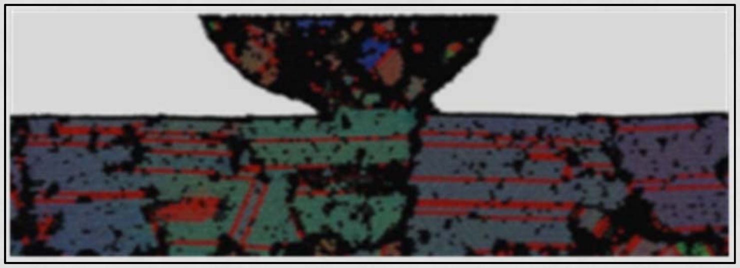
- Not many alloy potentials with Au or Ag
- Cu is not very soluble in Ag
- Sterling silver is 7.5% Cu by weight (~12% atomic)
- Our method is unorthodox, but fine on our timescales



TIP/SLAB WITH AG/CU

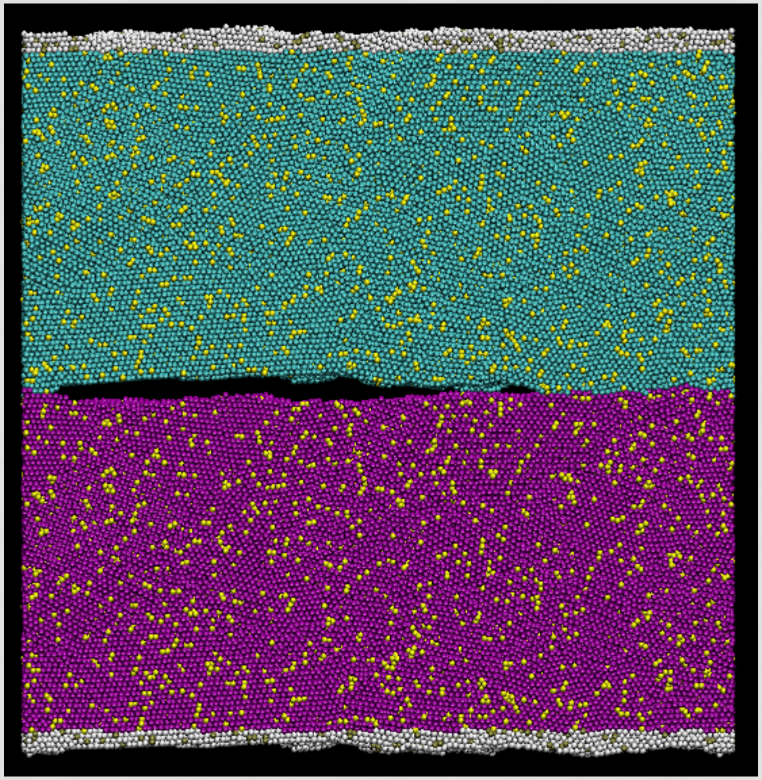


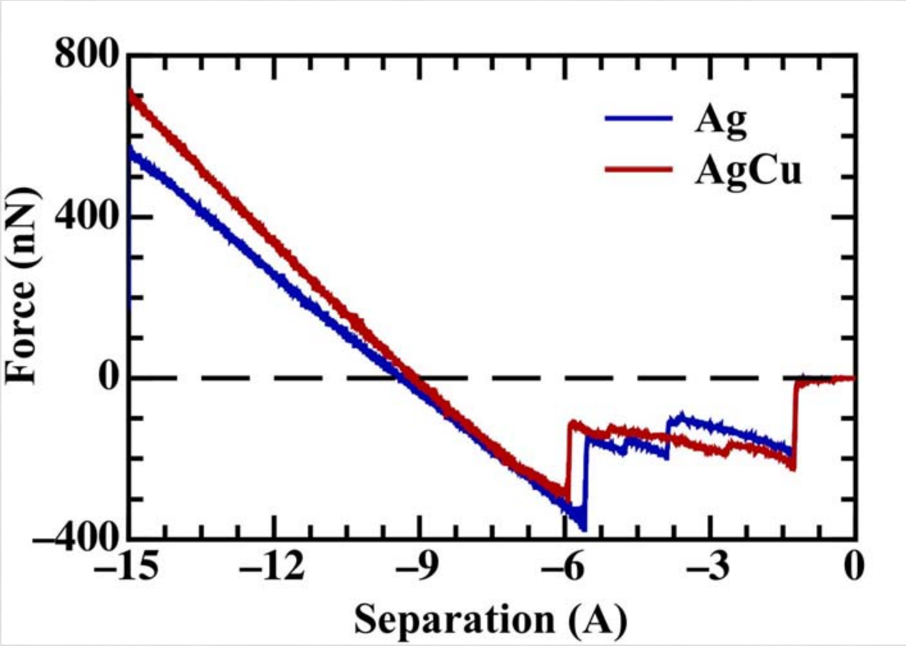




- Alloy is more adhesive (work of adhesion twice that of Ag)
- Can't measure friction with tip/slab geometry
- Alloys suppress commensurate contacts

SLAB ON SLAB GEOMETRY

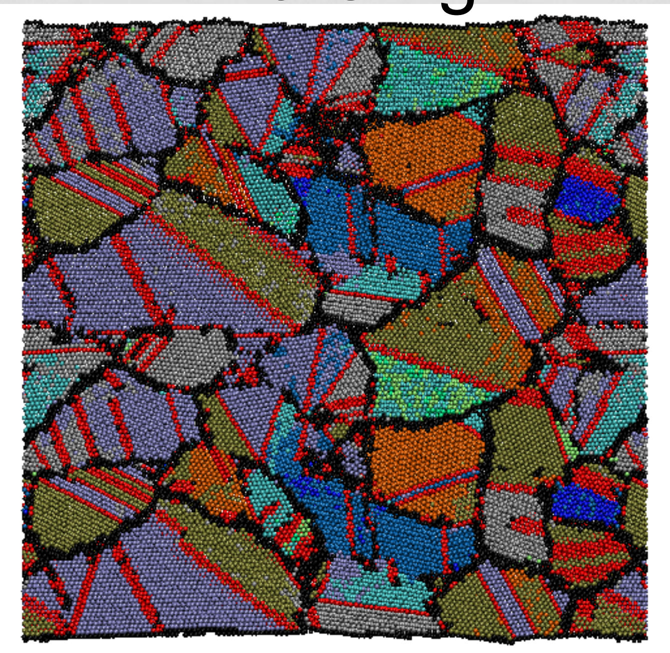




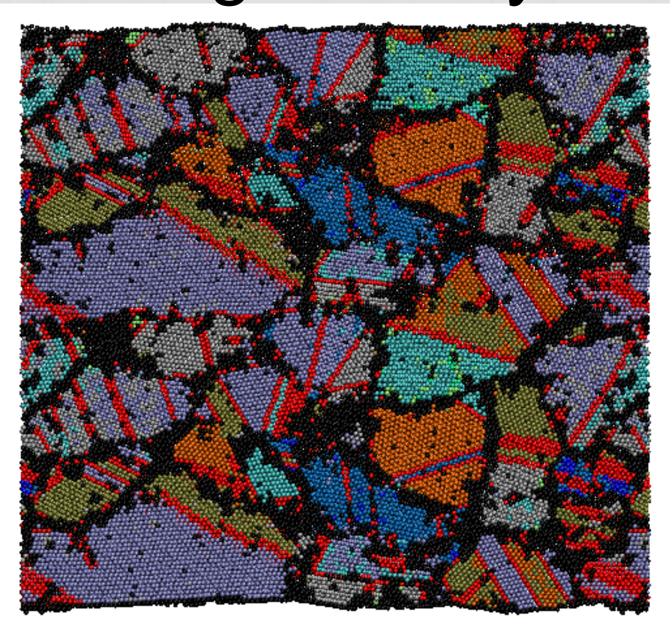
- Duplicate slab & rotate
- Bring into contact (two snap-ins from roughness)
- Adhesion is similar for Ag and Ag/Cu

SLAB ON SLAB GEOMETRY

Pure Ag

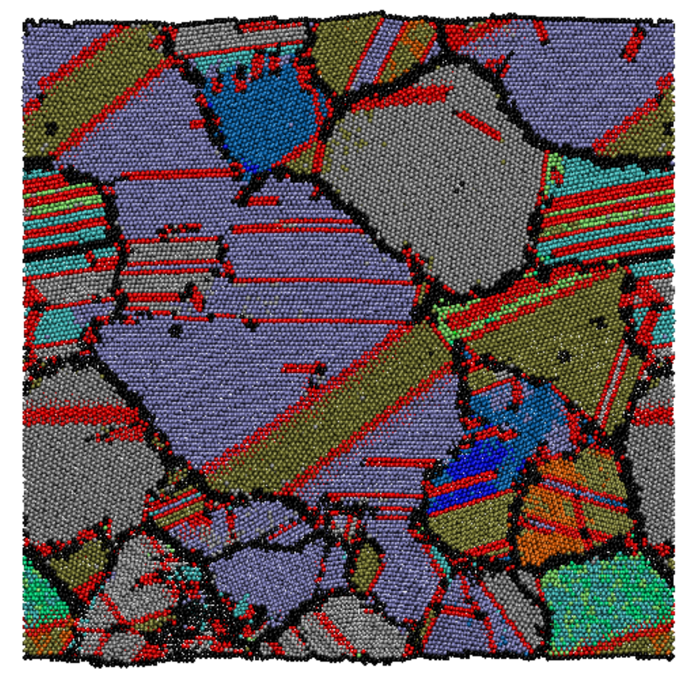


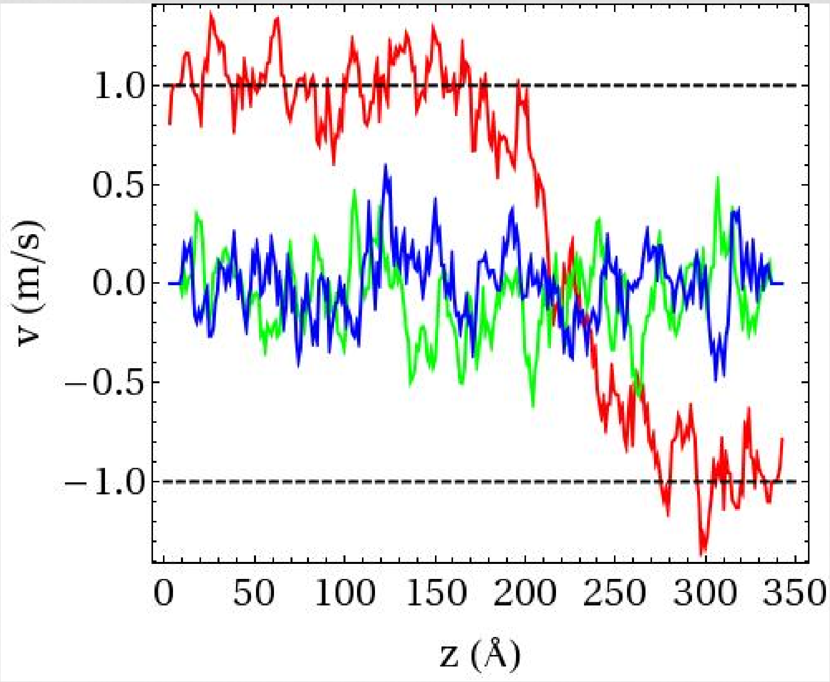
Ag/Cu alloy



- Hold in contact – some grain growth
- More disorder in alloy
- Shear using fixed atoms at top, similar to tip

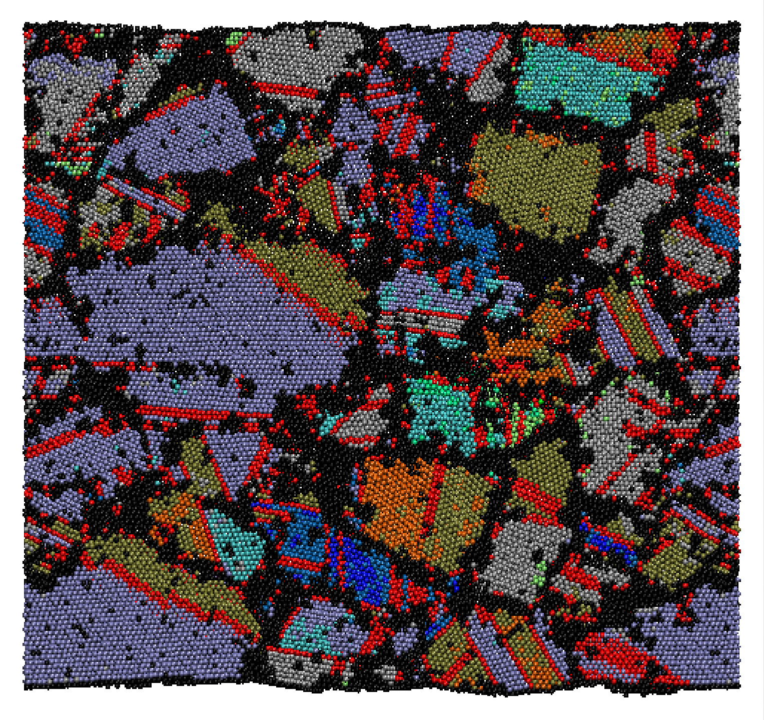
AG SLABS FAIL

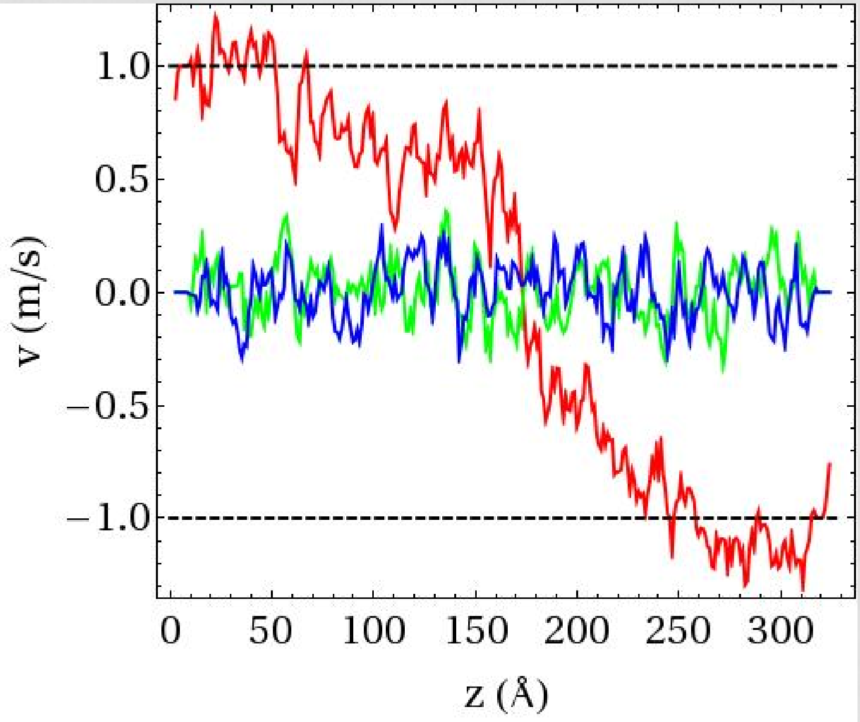




- Coalescence
- Stress induced grain growth
- Shear occurs at stacking faults, not junction -- not shearing distinct slabs

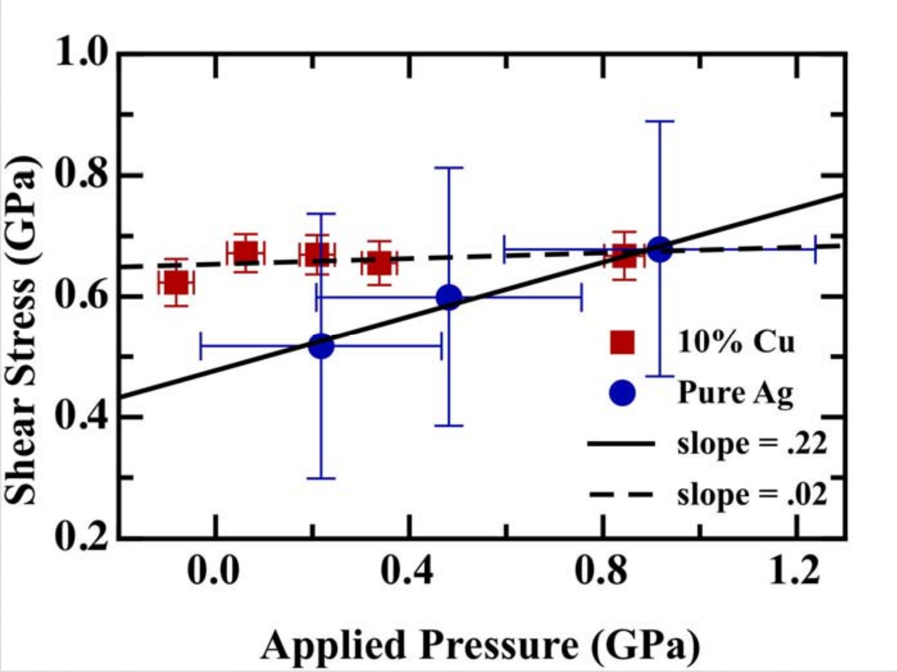
ALLOY SLABS SLIDE

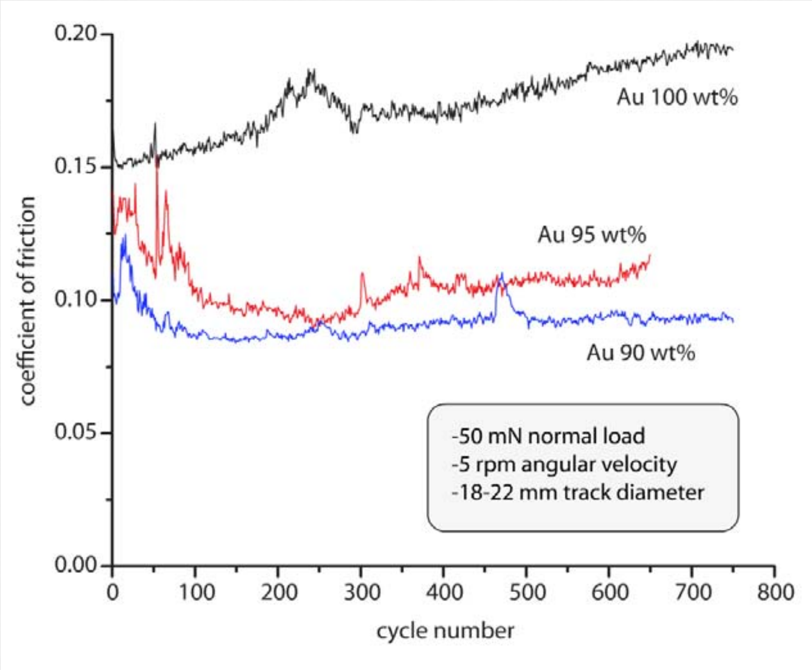




- Mechanism preventing grain coalescence allows sliding
- Shear occurs primarily at junction

COMPARISON OF FRICTION





Courtesy: WG Sawyer, U. Florida

- Alloy has lower friction
- Qualitative agreement with experiment
- No commensurate interface formed

WHAT IS THE MECHANISM IN ALLOYS?

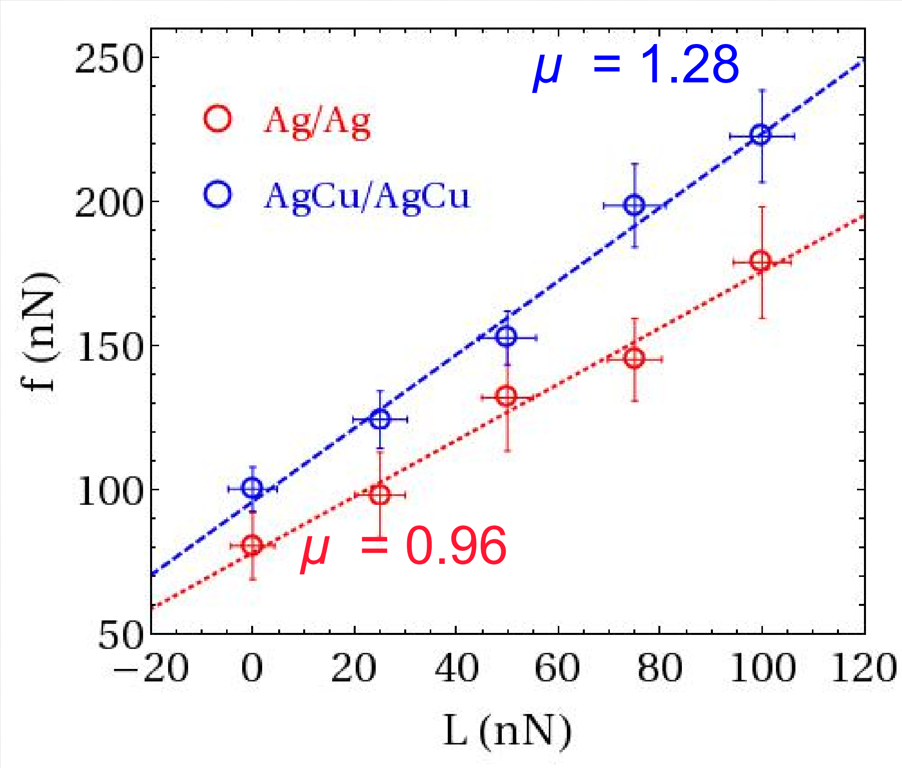
- Friction comparison slightly unsatisfying
  - Comparing tip friction to slab friction
  - $\mu_{tip} = 4 \times \mu_{slab}$ seen by us, Harrison
- Ideal comparison:
  - Same system (tip/slab or slab/slab)
  - Remove grain growth mechanism
  - Determine what reduces friction in alloys

Friction Coefficient

	sim. (Ag)	exp. (Au)
pure tip	0.22	0.2
Cu alloy slab	0.02	
Cu alloy "tip" (4x slab)	0.08	0.08

RIGID TIPS

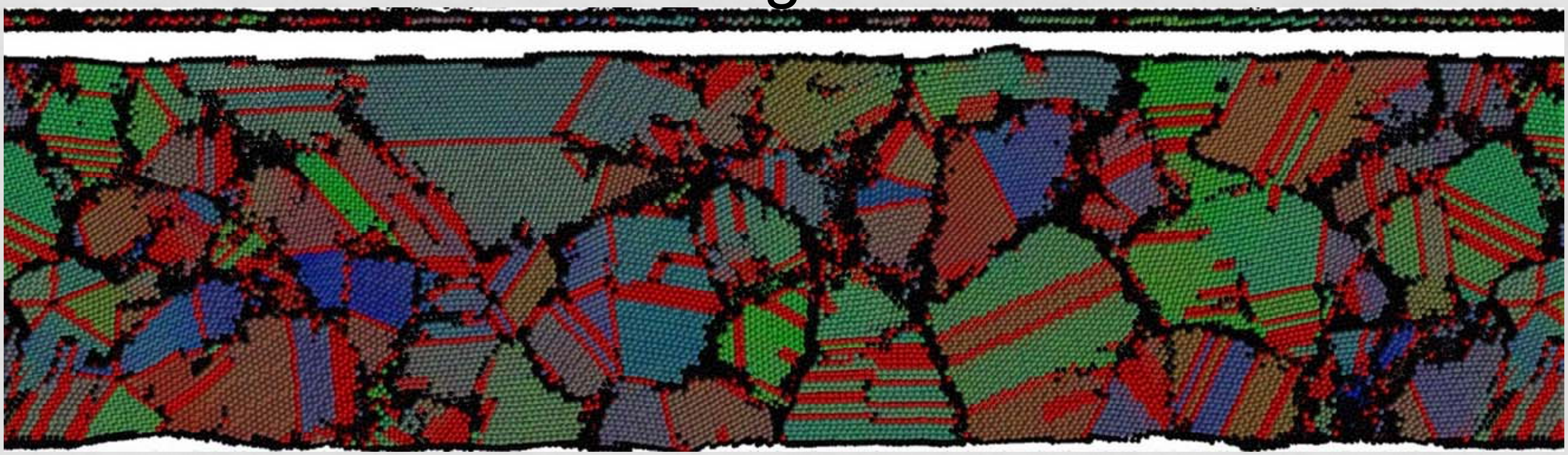
- Rigid tips => no grain growth
- *μ* slightly ***higher*** for alloy
- Shear strength essentially identical
- Materials properties have little effect
- All friction is plowing!
- Is this because of flow stress?



LOTS OF DAMAGE

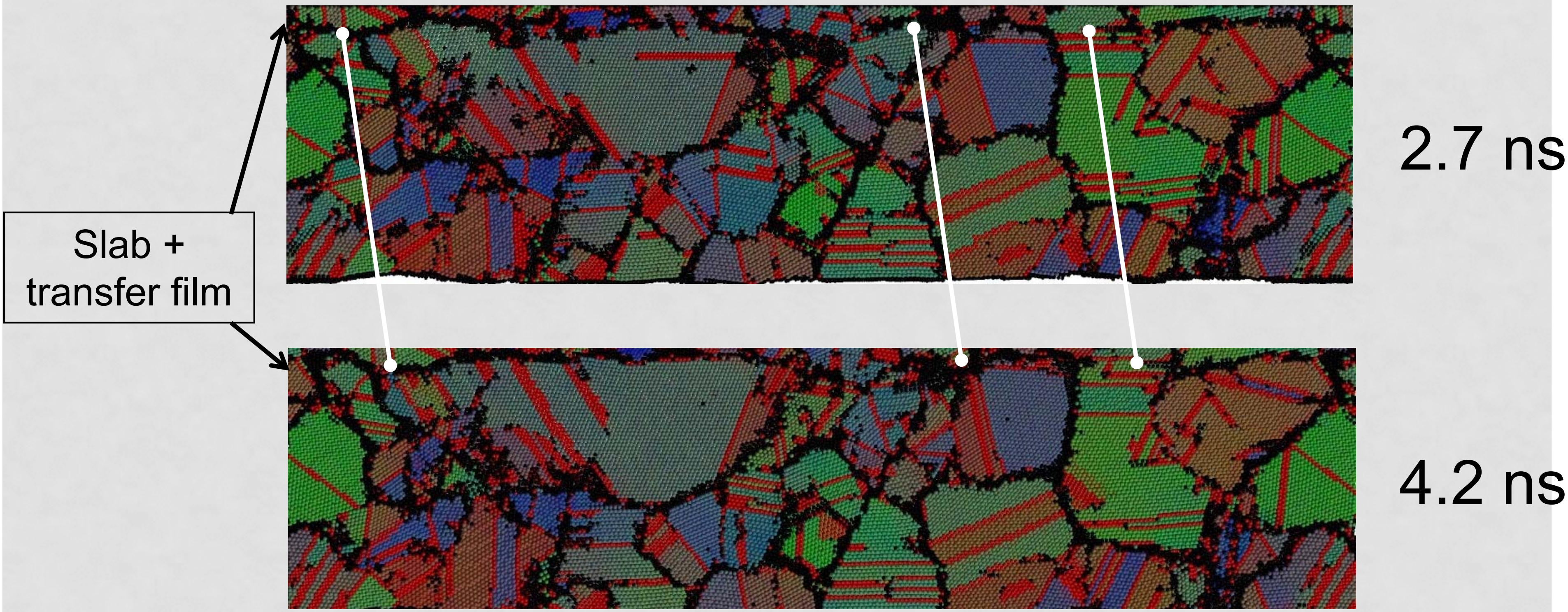
- Desires:
  - suppress grain growth *and* damage
  - simulate alloys and pure metals on same footing

RIGID SLAB ON SUBSTRATE



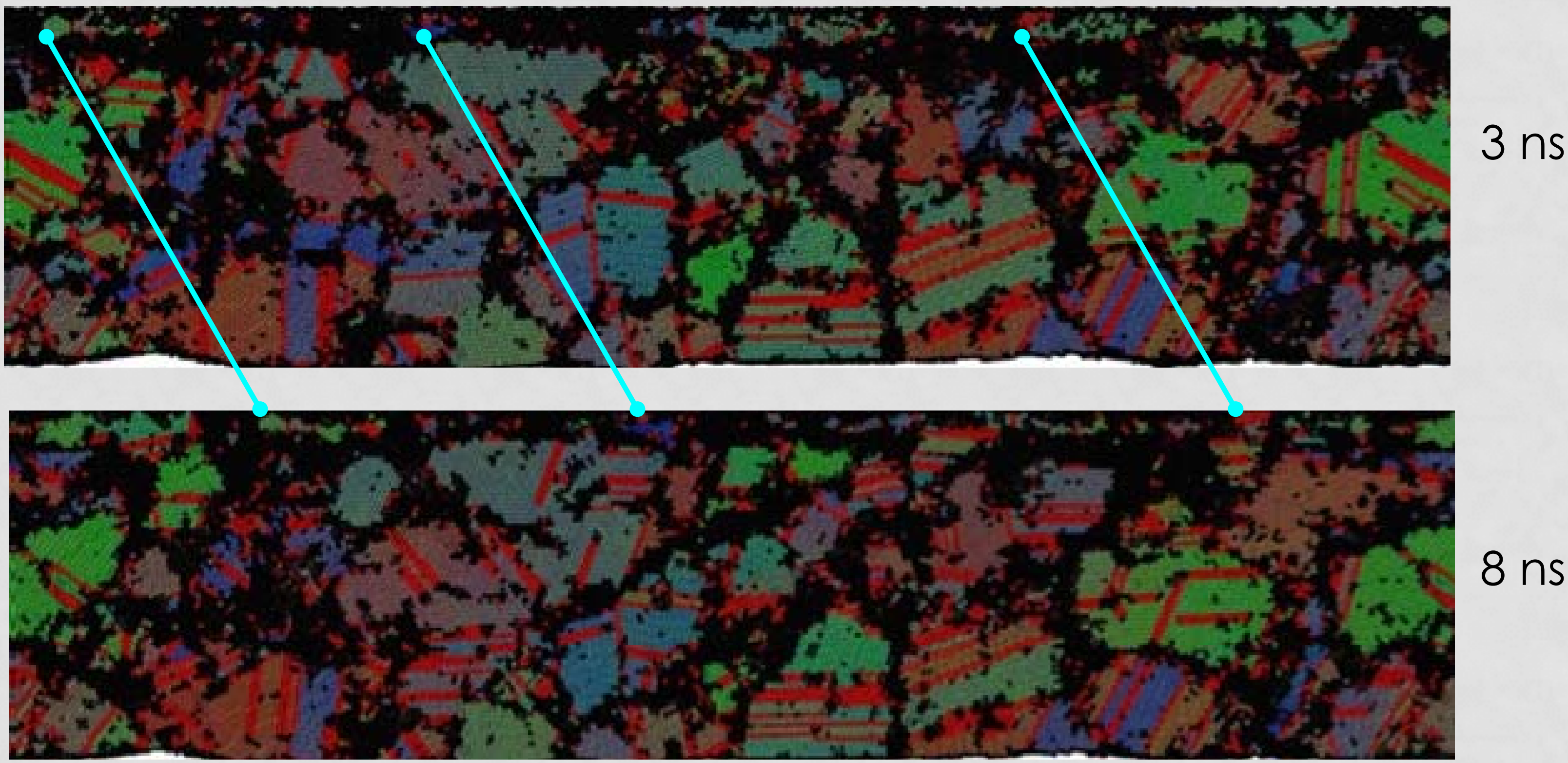
- Rigid slabs suppress grain growth
- No plowing is possible

RIGID SLAB – PURE AG



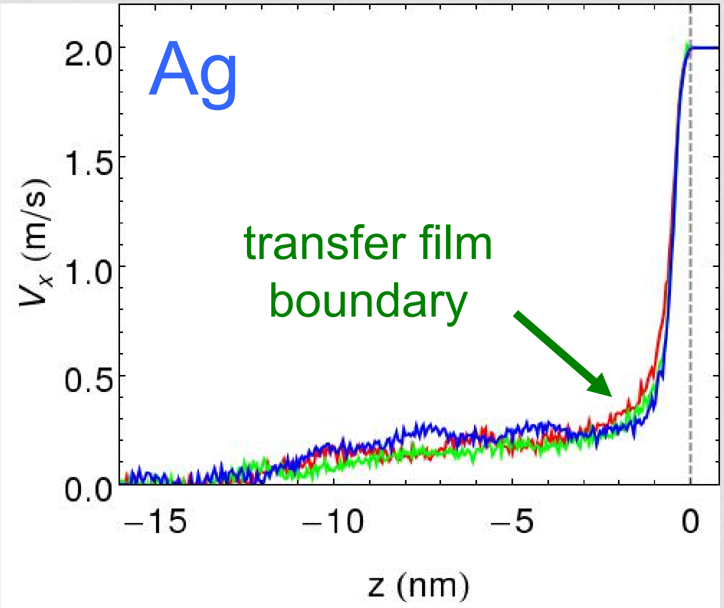
- Slight grain growth, forms transfer film
- Slides along grain boundary (of transfer film) or stacking fault depending on availability

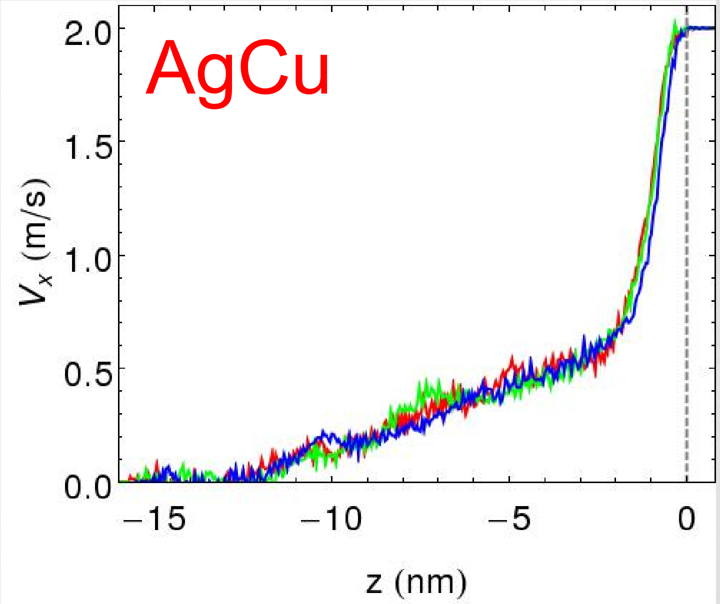
RIGID SLAB -- ALLOY



- Alloy slides at boundary, but also throughout substrate

VELOCITY PROFILES

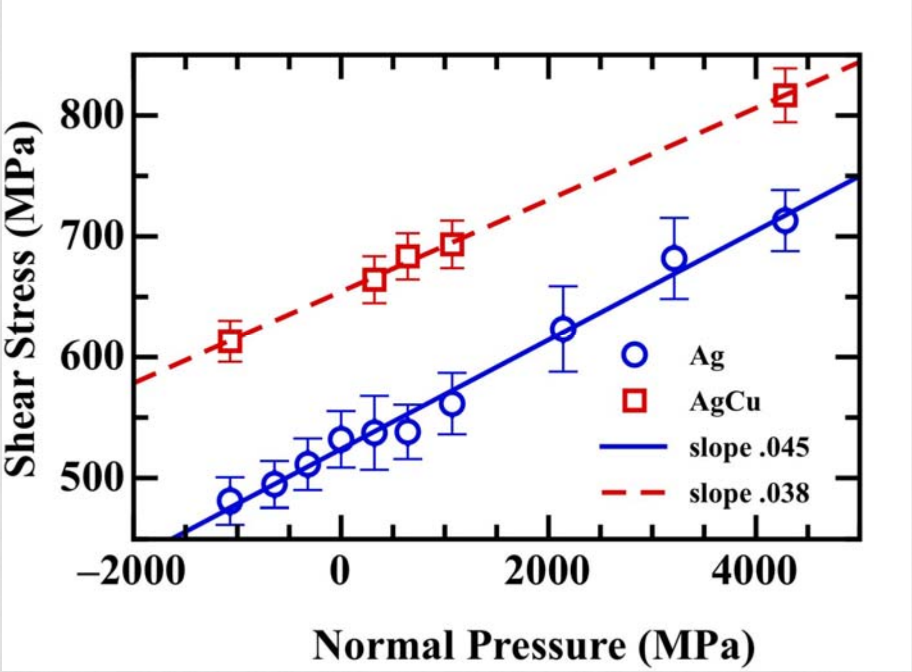




- Velocity profiles indicate liquid-like shearing
- Ag shears at transfer film
- AgCu shears at boundary, also throughout substrate
- Can extract pseudo-viscosities: Ag = 19 Pa·s, AgCu = 10 Pa·s
- Compare to Merkle and Marks, Wear (2008): Au = 2 Pa·s

RIGID SLAB FRICTION

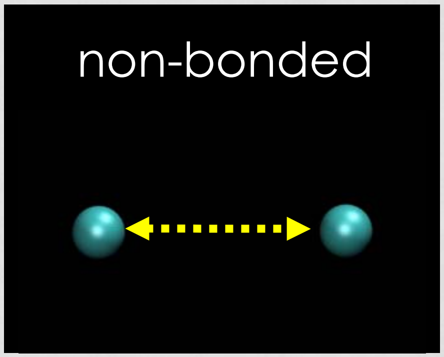
- *μ* essentially identical – grain growth suppression leads to same friction mechanism
- Alloy shear stress 23% higher (650 MPa vs 530 MPa)
- Same ratio for tips (100 nN vs 80 nN)
- This is the difference in materials properties (e.g. hardness)



CONCLUSIONS

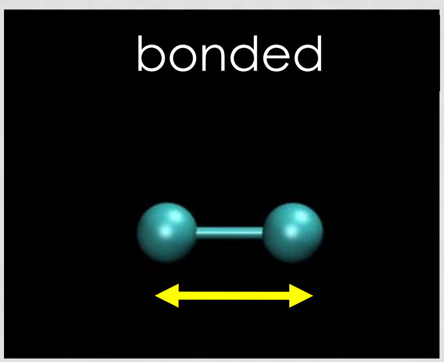
- Atomic scale mechanisms of metallic friction
- Pure metals
  - Cold welding, grain reorientation
  - Shear along slip planes -- dislocation controlled plasticity
  - Commensurate interface = high friction
- Alloys (with different lattice constants)
  - Still cold welding, but grain reorientation suppressed
  - Shear along transfer film boundary
  - Grain boundary mediated shear
  - Similar mechanism proposed in different metal (Ni) at different scales (Prasad, Battaile and Kotula, Scripta Mat. 2011)

MOLECULAR DYNAMICS -- GENERAL



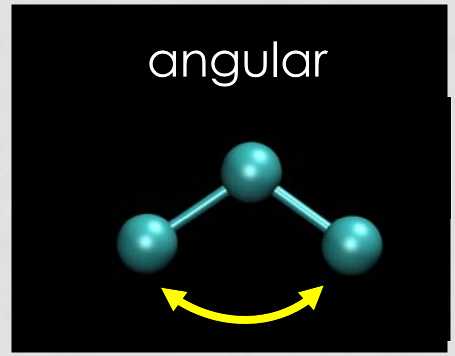
$4\varepsilon\,[\,(\sigma/r)^{12} - (\sigma/r)^{6}\,] \quad r < r_c$

$C\,q_i q_j/\varepsilon r$

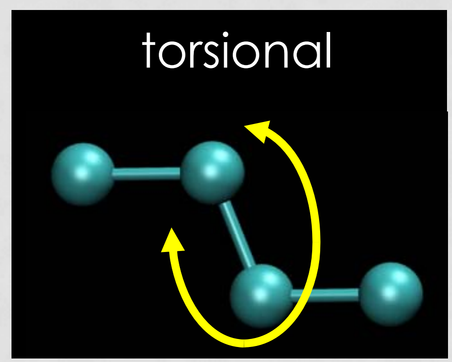


$\frac{1}{2}\,k_1\,(r - r_0)^2$

$$\int_0^t F\,dt$$

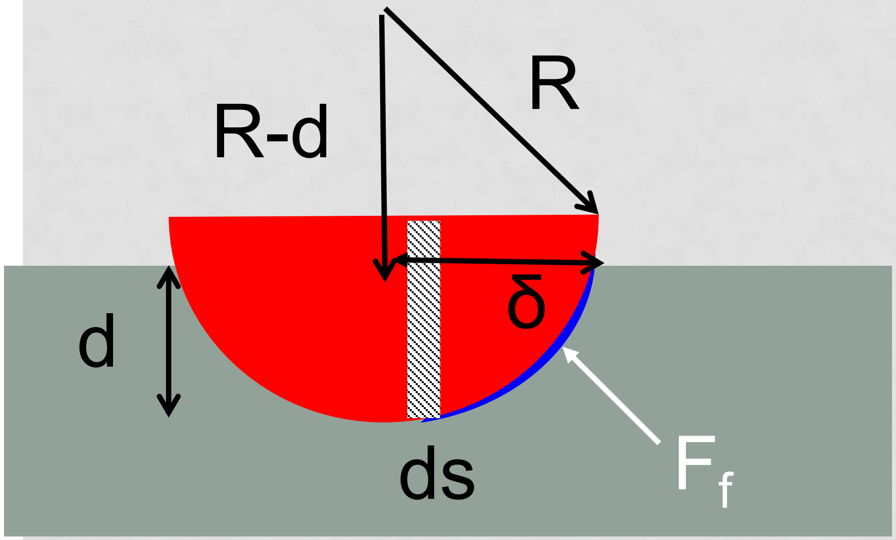


$\frac{1}{2}\,k_2\,(\theta - \theta_0)^2$



$\Sigma_n\,A_n\,\cos^{\,n-1}(\phi)$

FLOW STRESS CONTRIBUTES LITTLE



$$R \cos \theta = R - d$$

$$d \cong \delta^2 / 2R$$

$$A = \int_0^{\delta} (d - s^2 / 2R)\, ds$$

$$A = 2\,\delta^3 / 3R$$

$$F_n = \tfrac{1}{2} \pi \delta^2 H$$

$$F_f = (2\,\delta^3 / 3R)\, H$$

$$\mu = F_f / F_n \cong 0.1$$

- Flow stress contribution ~.1, independent of hardness

GRAIN GROWTH VS. TIME

- Rigid top slab
- #FCC atoms correlates to grain size
- Effects:
  - Increasing
  - decreasing system size
  - tensile stress @ fixed separation