The Abdus Salam
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2063-25

ICTP/FANAS Conference on trends in Nanotribology

19 - 24 October 2009

Lubrication and sliding friction levels in adsorbed films at sub-monolayer and ultra-low coverages

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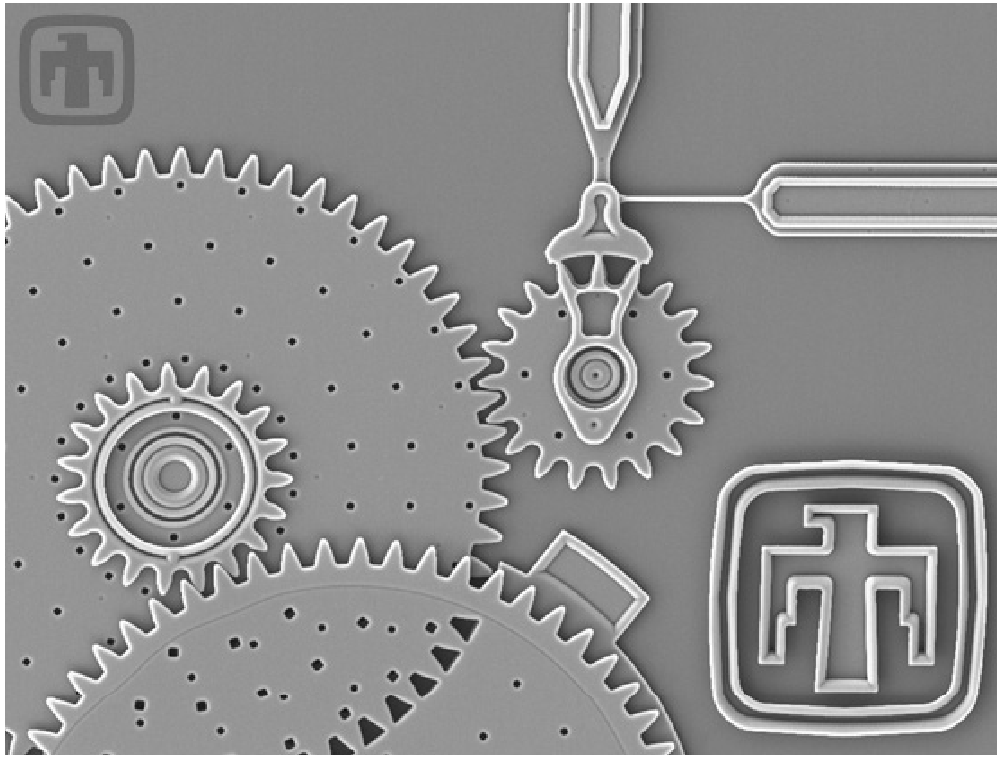
Friction of sliding adsorbed films



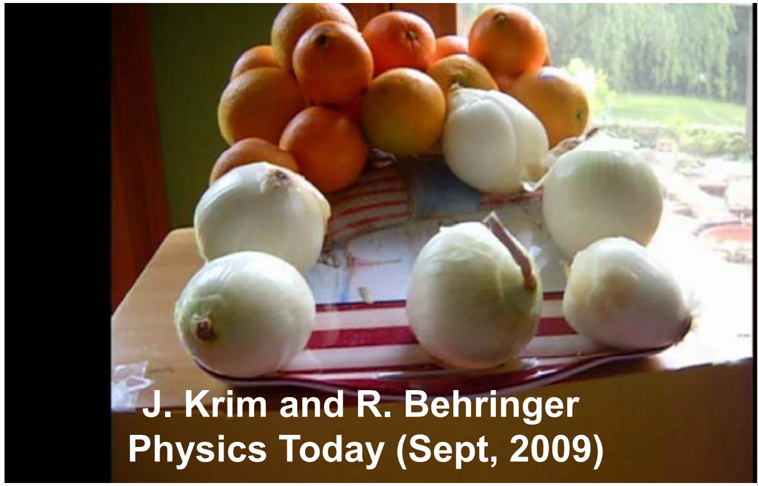
Jacqueline Krim, Department of Physics

Friction of sliding adsorbed films: topics

Thermolubricity or Cryolubricity?

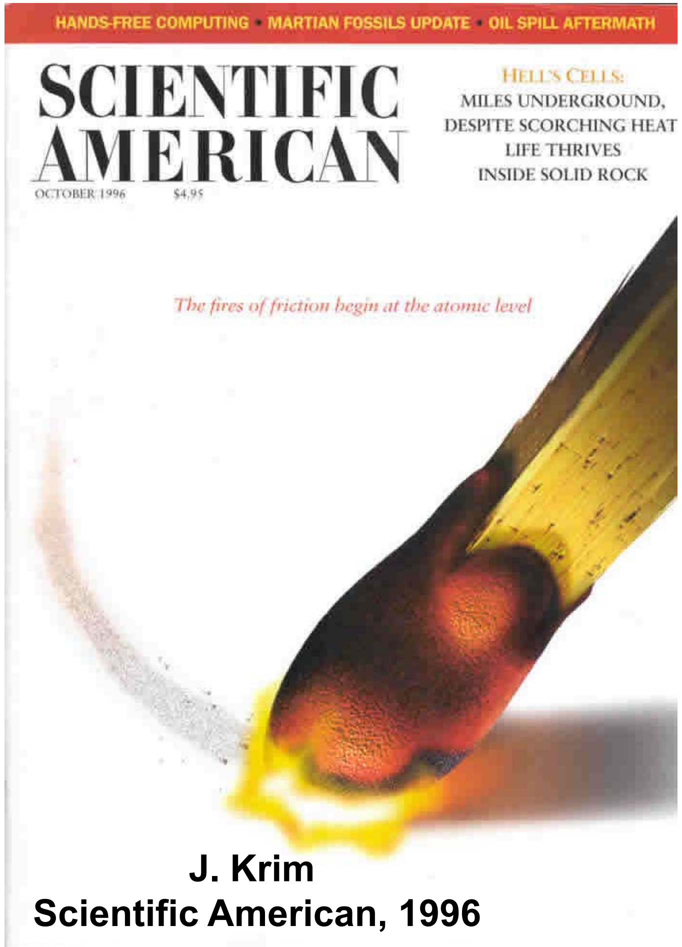
How do we include electrons in a Comprehensive treatment ?

How thin of an adsorbed layer or submonolayer can provide lubrication?



J. Krim and R. Behringer
Physics Today (Sept, 2009)

Seth Putterman,
(Nature)



J. Krim
Scientific American, 1996

Multi-functional Extreme Environment Surfaces: Nanotribology for Air and Space. MURI PI: J. Krim, NCSU

Academic Team Members	Specialty
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Judith A. Harrison,(b) Prof. of Chemistry	Computational Nanotribology
Angus I. Kingon,(h) Prof. of Materials Science & Eng	Nanomaterials Design
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Industrial Partner	Specialty
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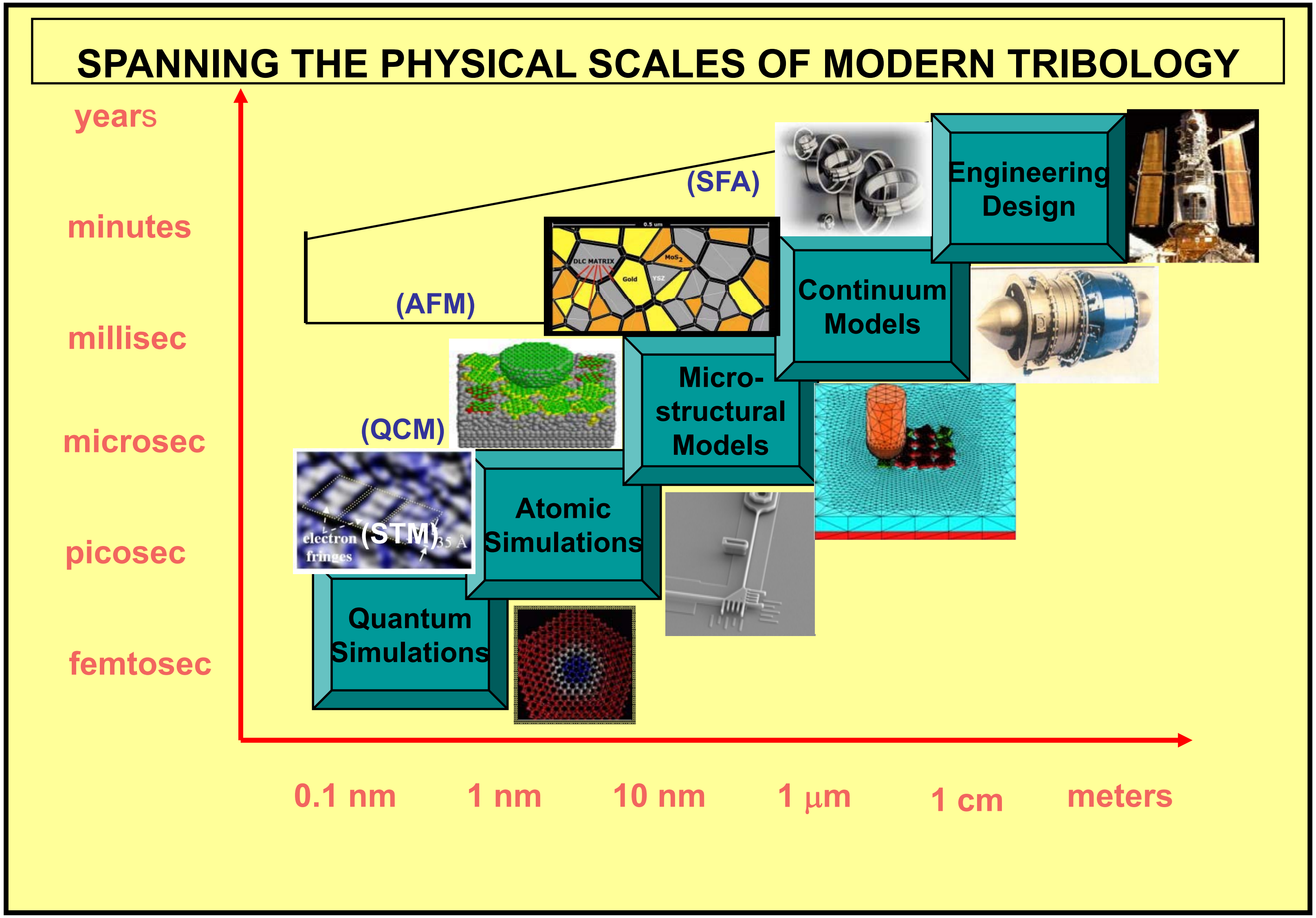
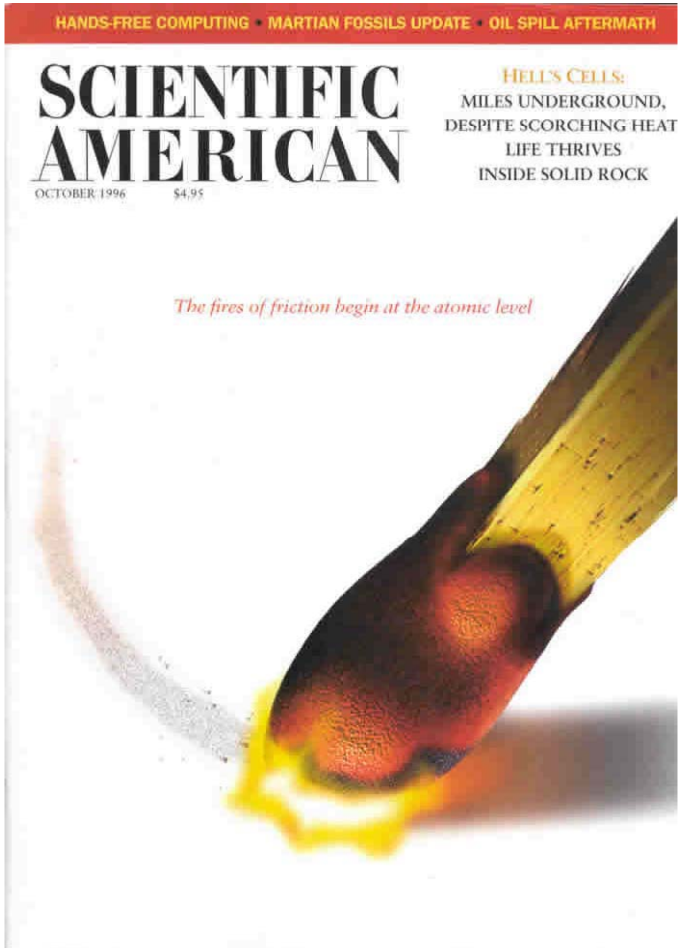
Participating Institutions: (a)North Carolina State University, (b)United States Naval Academy, (c)University of California-Irvine, (d)Sandia National Laboratories, (e)Naval Research Laboratory, (f)Wright Patterson Air Force Research Laboratory, (g) wiSpry Corp.(h)Brown University

NC STATE UNIVERSITY

Multi-functional Extreme Environment Surfaces: Nanotribology for Air and Space. MURI PI: J. Krim, NCSU



Cryolubricity or Thermolubricity?

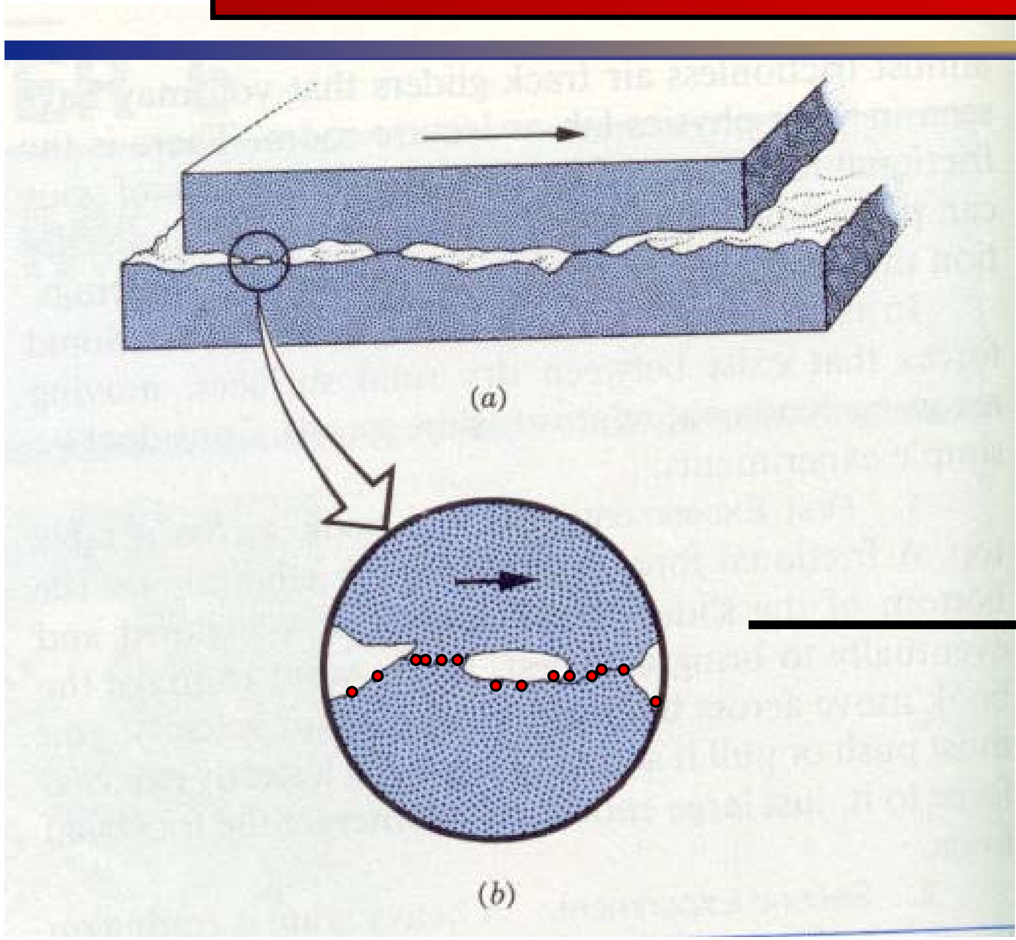


What is the temperature of a sliding Contact?

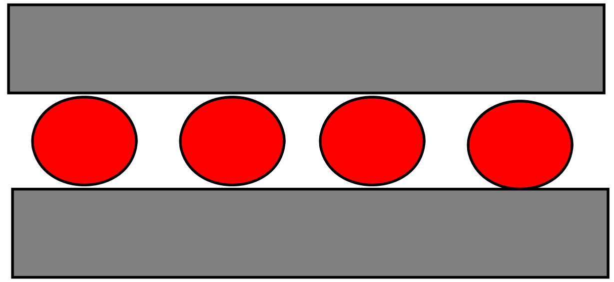
Does friction increase or decrease with Temperature?

Do adsorbed films change thermolubricity to cryolubricity?

Nanotribology



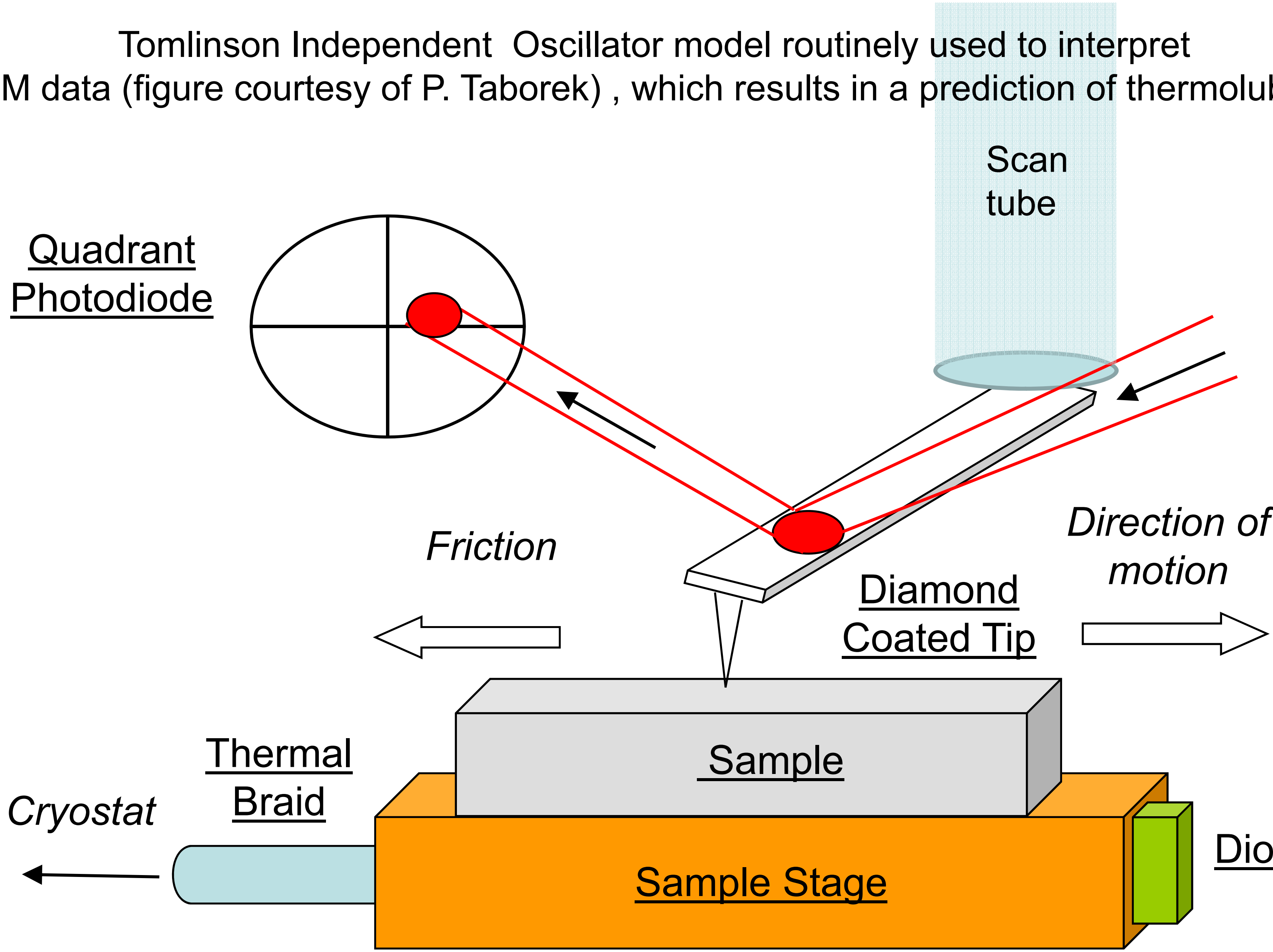
Nano: 10^{-9} meters—the scale of atoms
Tribology: The study of friction, lubrication, and wear.



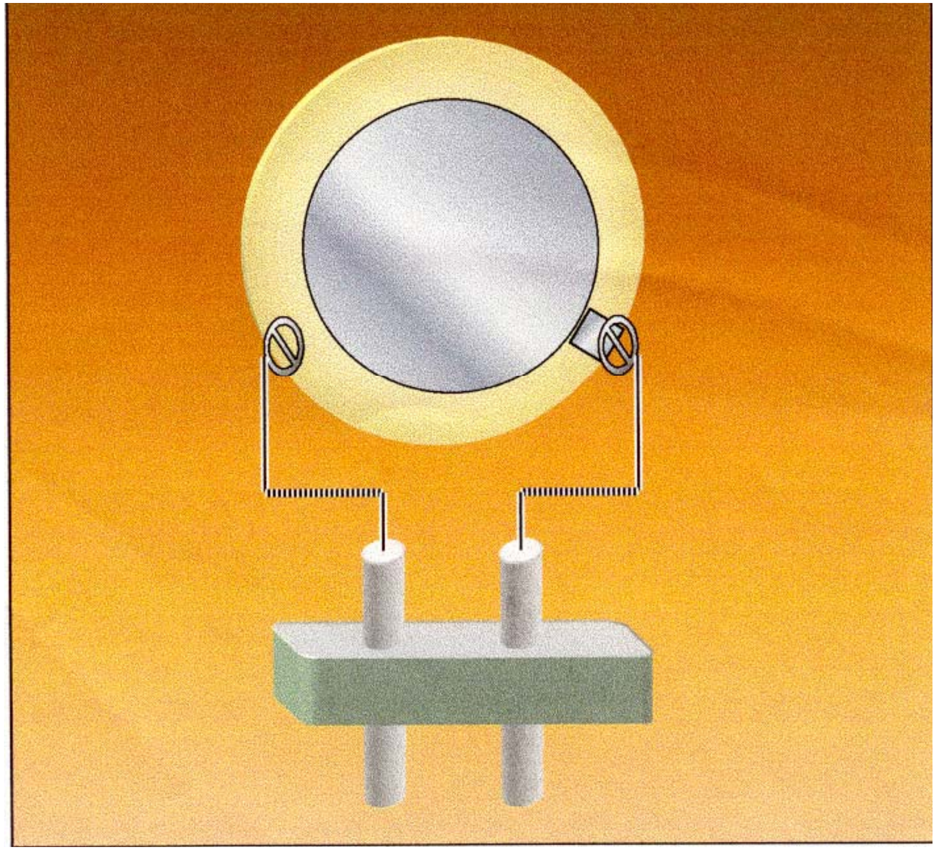
Researchers in the field of nanotribology examine micro- and nano-contacts in well-controlled geometries Often/always these contacts have thin boundary layer films on the surfaces. Knowledge of physical behaviors at this scale is thought to be key to understanding how friction works on all length scales. The film behavior in non-contacting regions covers 99^{+}% of the area, its sliding properties impact friction both inside and out of the contact.

AFM: Temperature dependence of friction

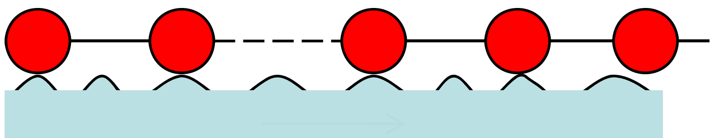
Tomlinson Independent Oscillator model routinely used to interpret AFM data (figure courtesy of P. Taborek) , which results in a prediction of thermolubricty



Quartz Crystal Microbalance (QCM)



$$F = \frac{m}{\tau} v$$



We measure frequency and amplitude change of the QCM.
Frequency shift is proportional to mass uptake:

$$\frac{\Delta f}{f^2} = \frac{-2\rho_f t_t}{\rho_q v_q}$$

Sometime Δf can be reduced if there is extreme slippage:

$$\Delta f_{film} = \frac{\Delta f_{mass}}{1+(\omega\tau)^2}$$

The amplitude is related to the quality factor:

$$\Delta\left(\frac{1}{Q}\right) \propto \Delta\left(\frac{1}{A}\right)$$

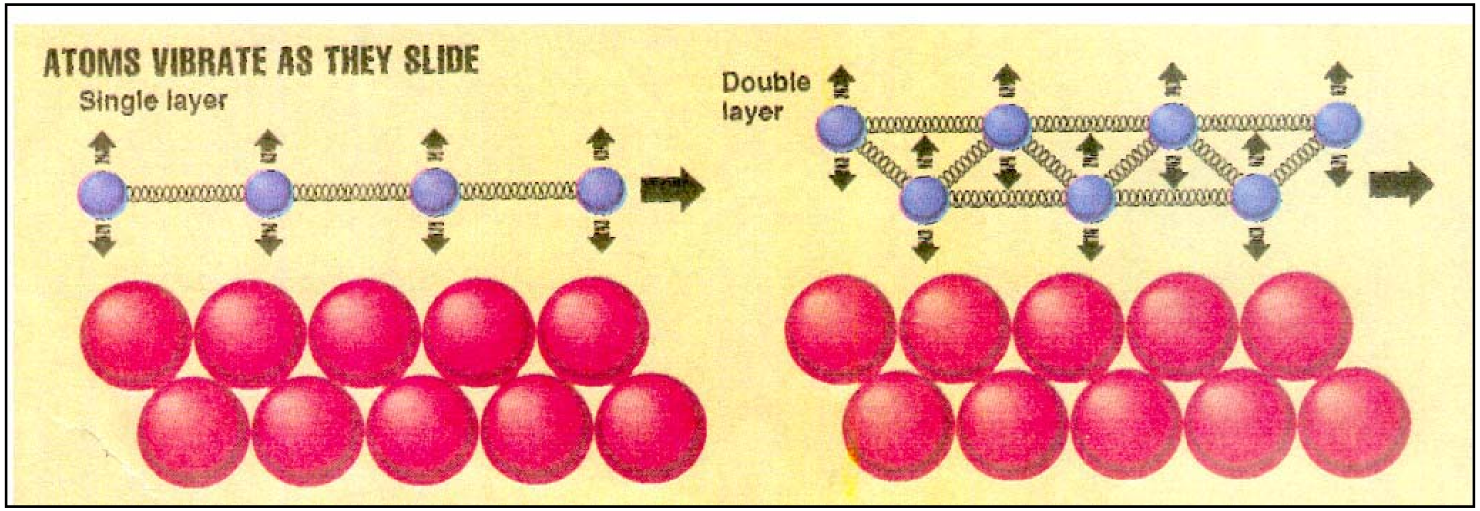
We then calculate a slip time:

$$\Delta\left(\frac{1}{Q}\right) = 4\pi\tau\Delta f$$

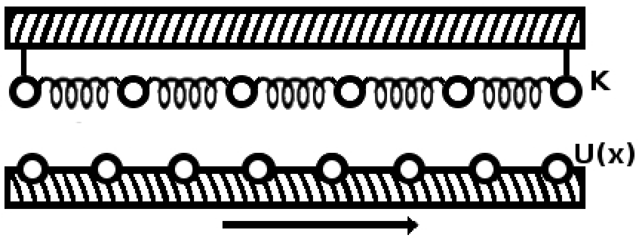
(*Krim and Widom, PRB, v. 38, n.17, 1988*)

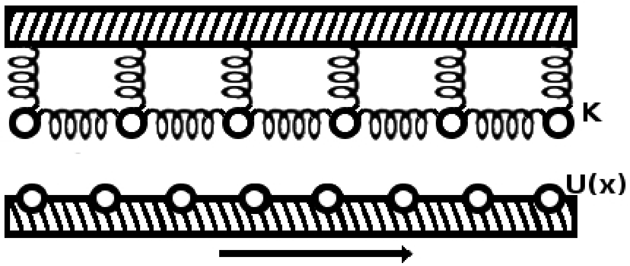
(QCM): Frenkel-Kontorova Model:

Cryolubricity

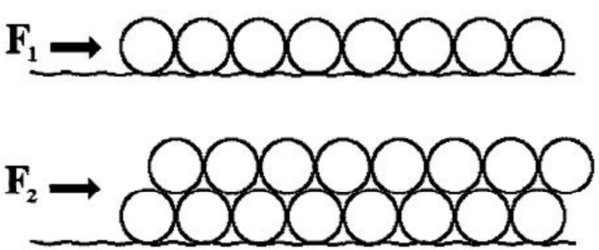


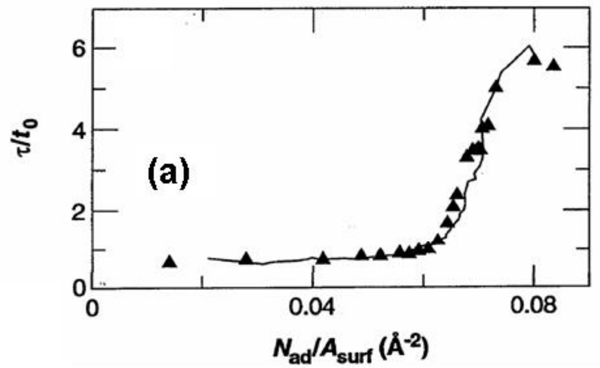
More phonons modes and higher phonon frequencies result in higher friction as temperature increases.



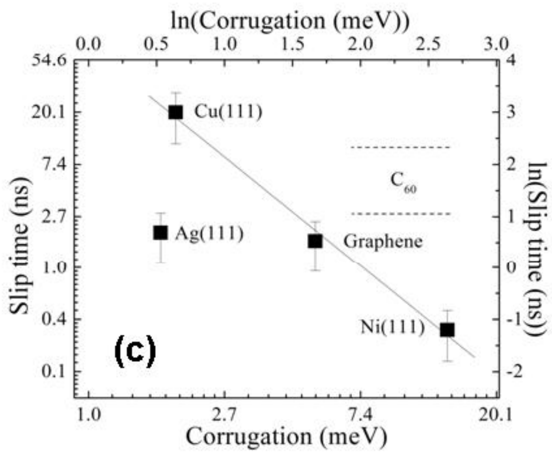


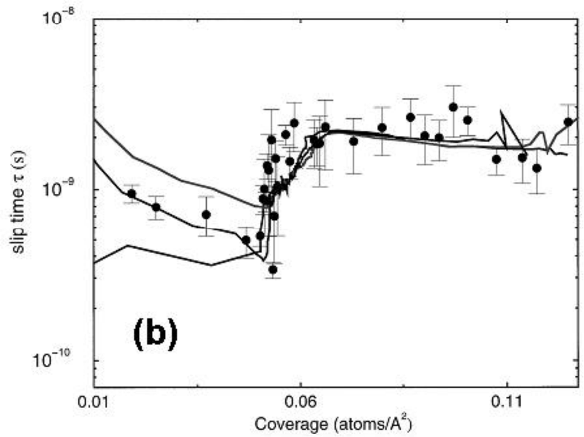
QCM confirmations of phononic friction





Solid-liquid Transition in a Kr/Au layer
Krim, PRL 1991

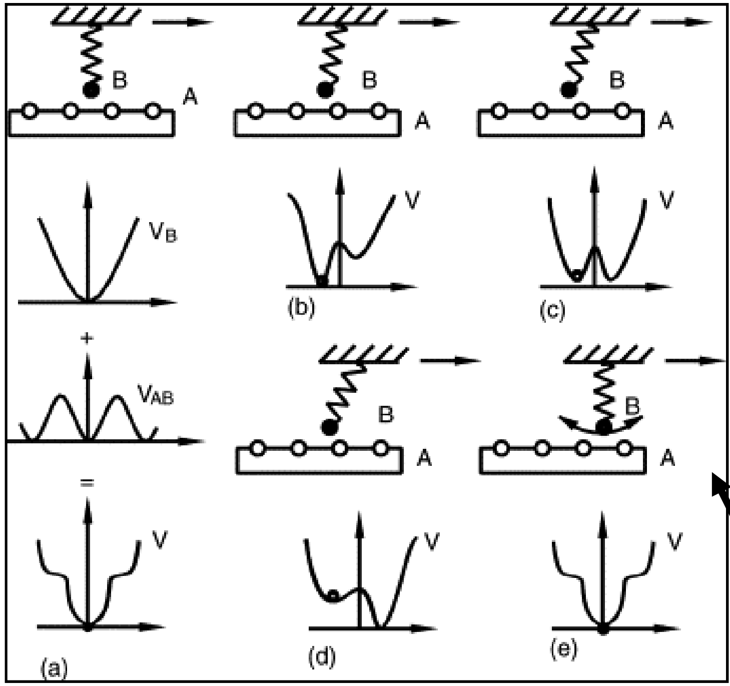


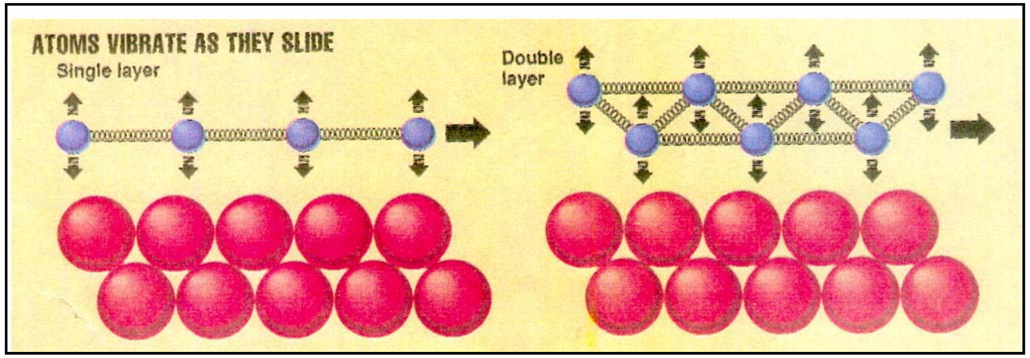


Slip time versus substrate potential corrugation
Coffey, PRL 2006

Monolayer to Bilayer in Xe/Ag
Daly, PRL 1996

Puzzle: Temperature dependence of friction.





Cryolubricity

?

Thermolubricity

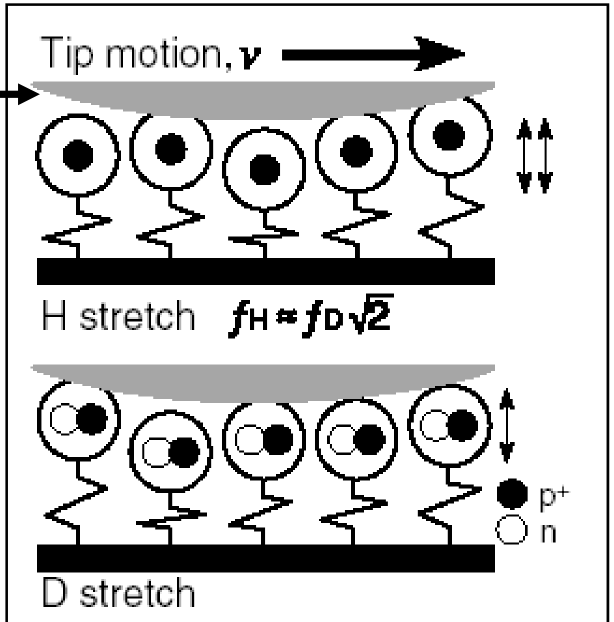
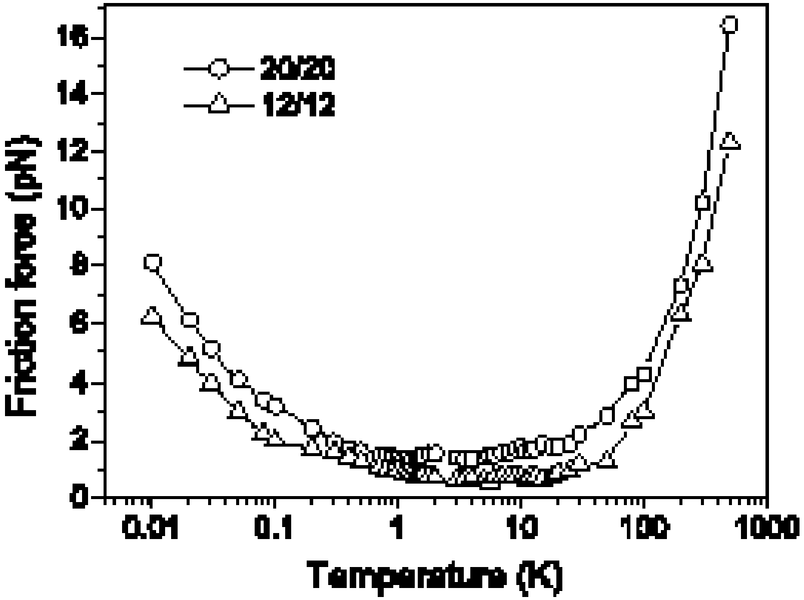


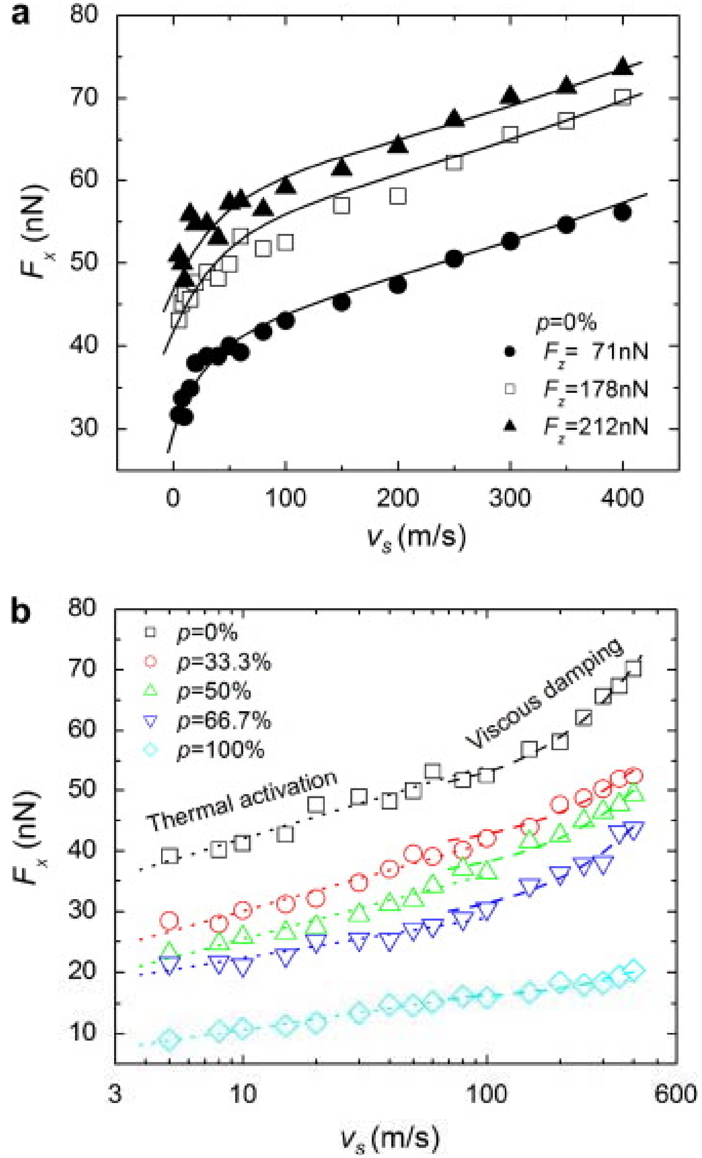
Fig. 1. A schematic of the frictional interface. Vibrating adsorbates collide with and dissipate kinetic energy from the moving tip at a rate that depends on the adsorbate's frequency and thus its mass; that is, at different rates for H than for D.

Detail of the Independent Oscillator, or Tomlinson model. When an atom moves to a position where the barrier between two minima (b-d) has disappeared (e), it is set into vibration and the energy is dissipated as a phonon. (From Xu, 2007) Note that energy dissipation occurs between steps (C) and (d) as the TIP vibrates. In an AFM, the spring attached to the tip involves the stiffness of the cantilever. Canarra et al, (Science, 2007) interpreted AFM friction as analogous to sliding adsorbed films.

Cannara et al Science 2007

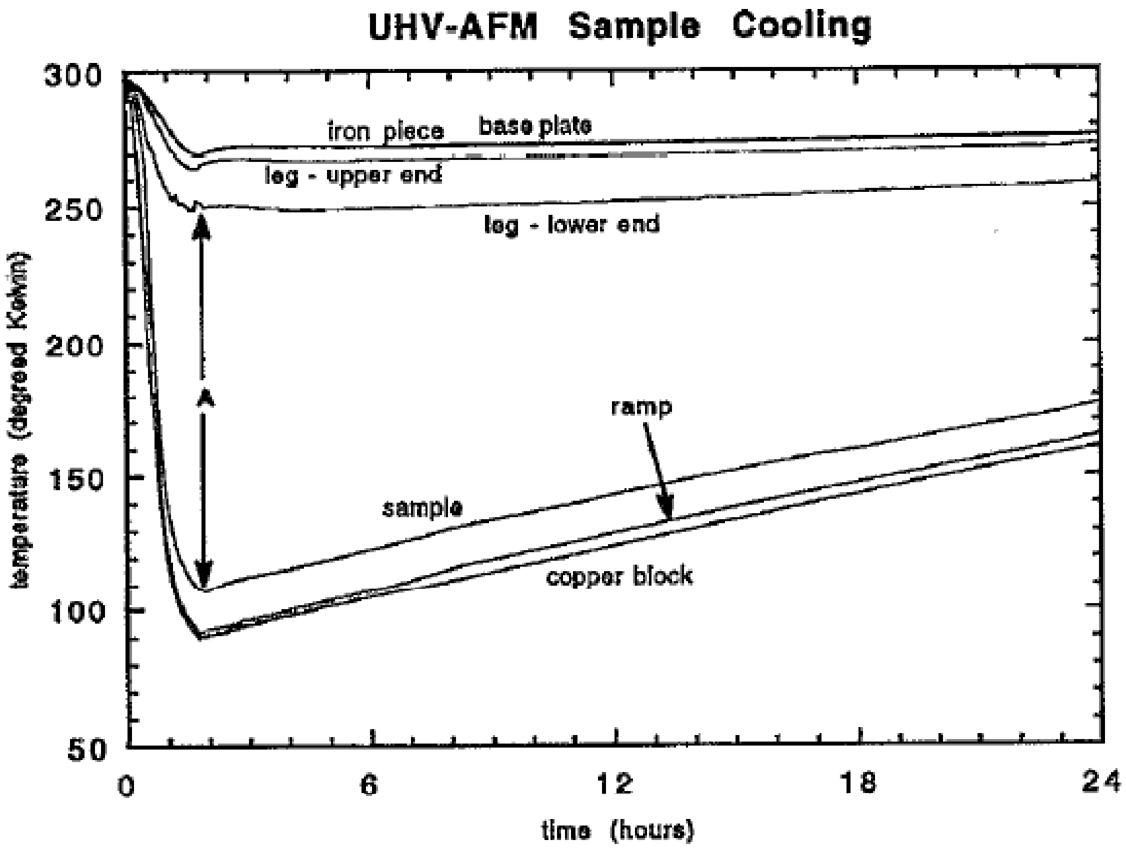
Examples of crossover from thermolubricity to cryolubricity

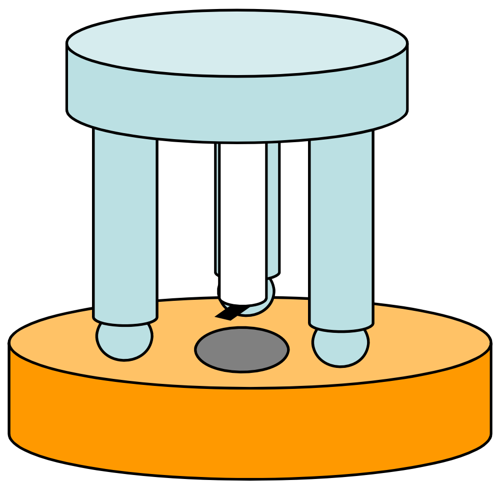




Above: The variation of the friction force between the inner and outer tubes versus the temperature for *(4, 4)/(9, 9)* DWCNTs with tube lengths of 20 layers and 12 layers of carbon atoms, respectively. The energy scale in the LJ potential is $\varepsilon = 2\varepsilon 0$. As temperature increases, the thermal jump probability saturates and the friction force becomes insensitive to temperature. (From Chen, 2009) Right: (a) Sliding velocity of the friction force Fx under various normal loads for bare Al surfaces under different normal forces. (b) semi-logarithm plots of friction force versus sliding velocity for different degrees of hydroxylation. As the sliding velocity increases, a crossover from a thermal activation to viscous damping type behavior is observed. (From Wei, 2009)

Temperature dependence of friction: Is the sample at the same temperature as the probe tip? How can we be sure?

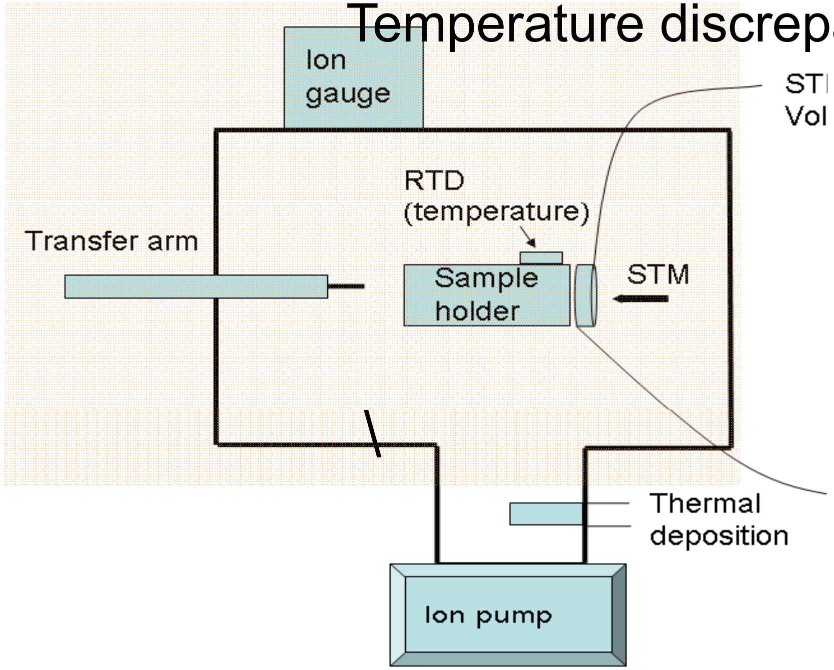


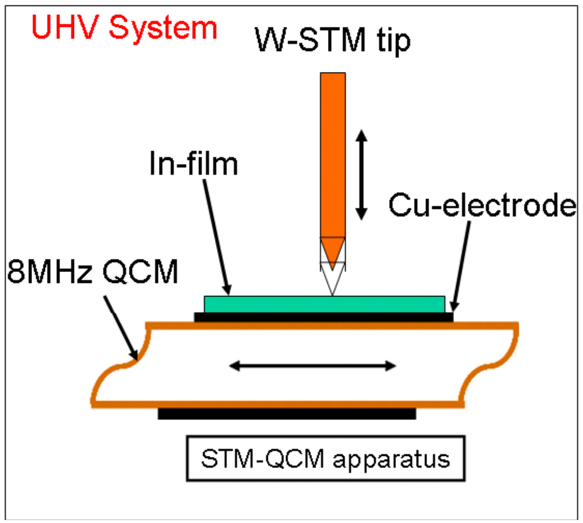


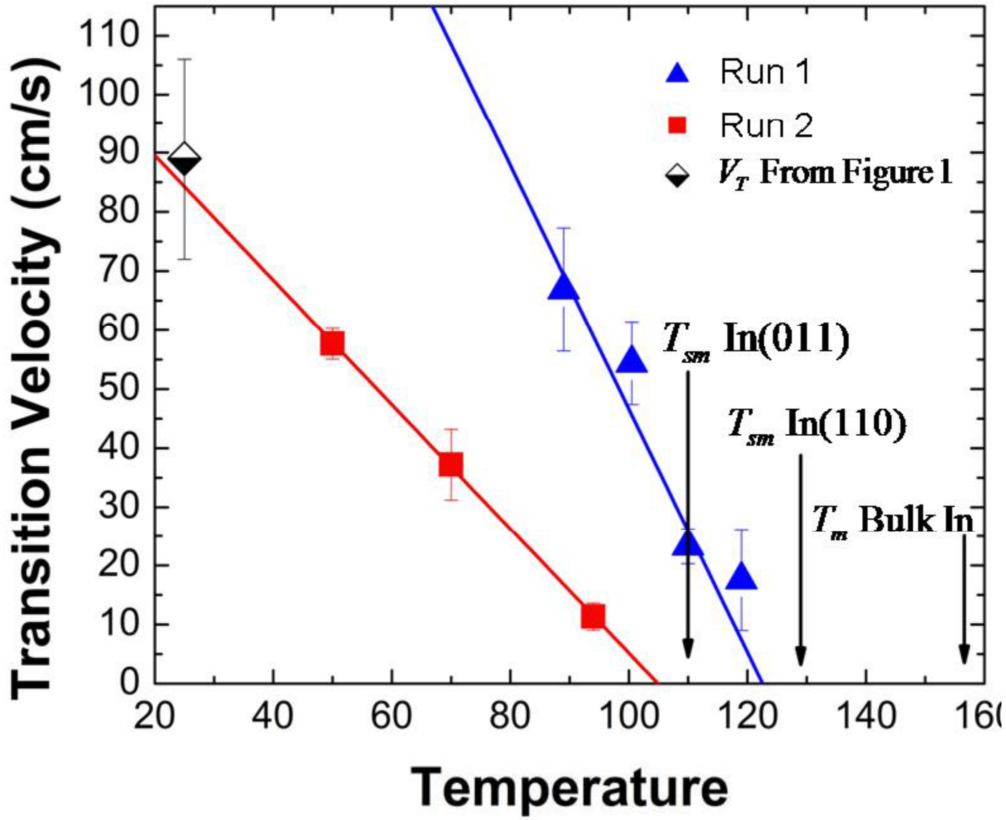
Q. Dai, R. Vollmer, R.W. Carpick, D.F. Ogletree and M. Salmeron, RSI 66, 5266(1995)

Tribo-induced melting of an asperity contact (Dawson, 2009)

Entire chamber was heated to avoid complications of Temperature discrepancies between tip and substrate







B.D. Dawson, S.M. Lee and J. Krim,
PRL, accepted. In press for late 2009/ early 2010

Puzzle: Temperature dependence of friction.

- There is much current debate on the impact, if any, of a discrepancy in the initial tip-substrate temperature for AFM measurements.

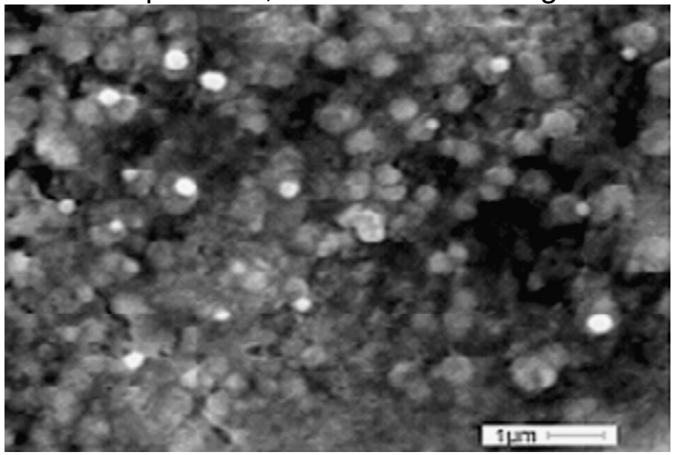
- There are reports of thermolubricity for both AFM and macroscopic scale cryotribology measurements.

- Cryolubricity has NOT been predicted by our theoretical community for macroscopic samples. But it has been reported experimentally for YBCO films.

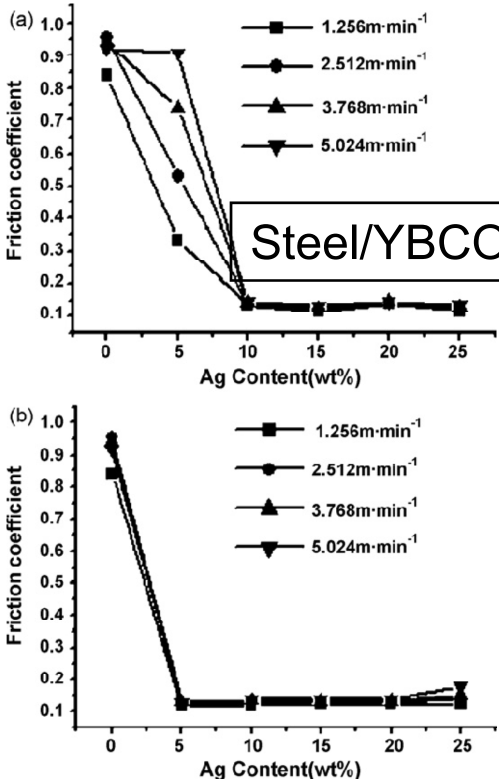
Superconductivity-dependent friction reported at the Macroscopic scale: Is this a boundary layer effect??

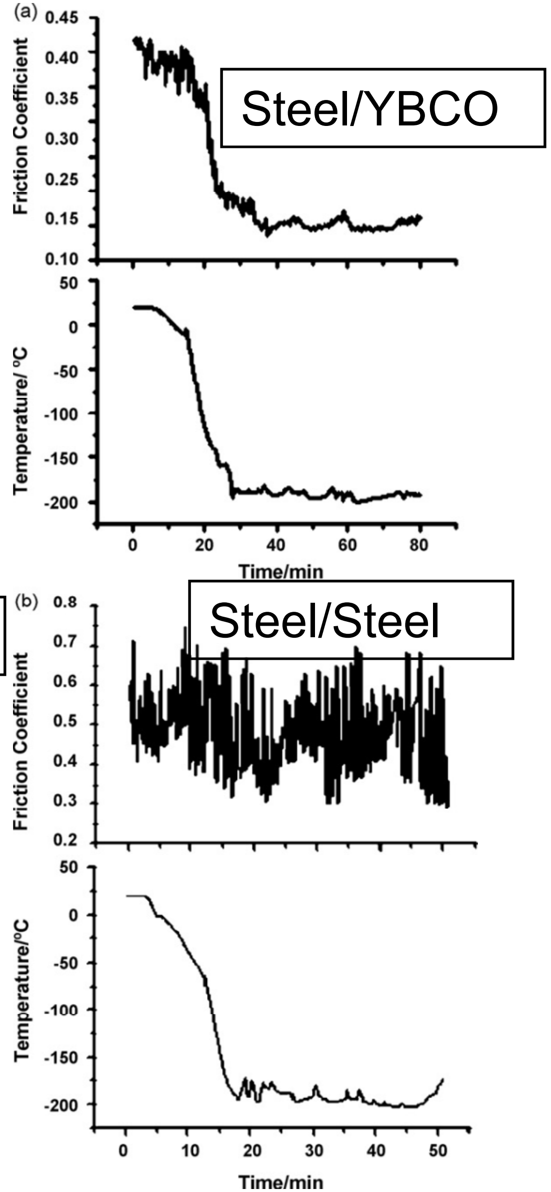
Preparation and properties of $YBa_2Cu_3O_{7-\delta}$/Ag self-lubricating composites
Qiaodang Ding, Changsheng Li, Lirong Dong, MinluWang, Yi Peng, Xuehua Yan, Wear ***265 (2008)*** *1136–1141*

- A: Friction coefficient of: (a) YBCO–steel and (b) steel–steel as function as temperature: load = 16N and sliding speed = 1.574 m/min.
- B: Friction coefficient as function of Ag content and sliding velocity at room temperature, load = 0.98N for Ag



: 75% YBCO 25% AgNO3 composite: samples were derived from both Ag and AgNO3 crystals



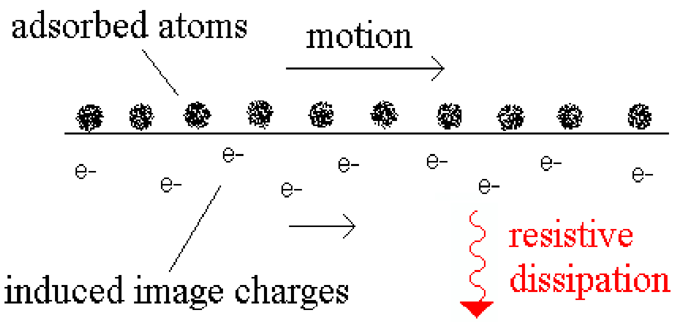


Electronic contributions to friction.

- **When an adsorbed layer slides, conduction electrons in the metal substrate are scattered into the surface, exciting electron-hole pairs*. We refer to this as a surface effect: It changes gradually at the superconducting transition.**
- **Friction could also be due (in part) to resistive dissipation in the metal substrate, a bulk effect, which changes abruptly at the superconducting transition.**

$$F_{fric} = m\eta_{el}v,$$

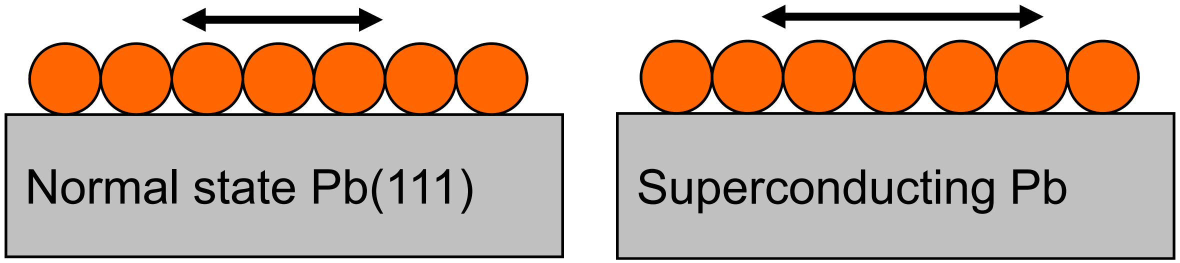
$$\eta_{el} = \frac{\rho}{\tau}$$



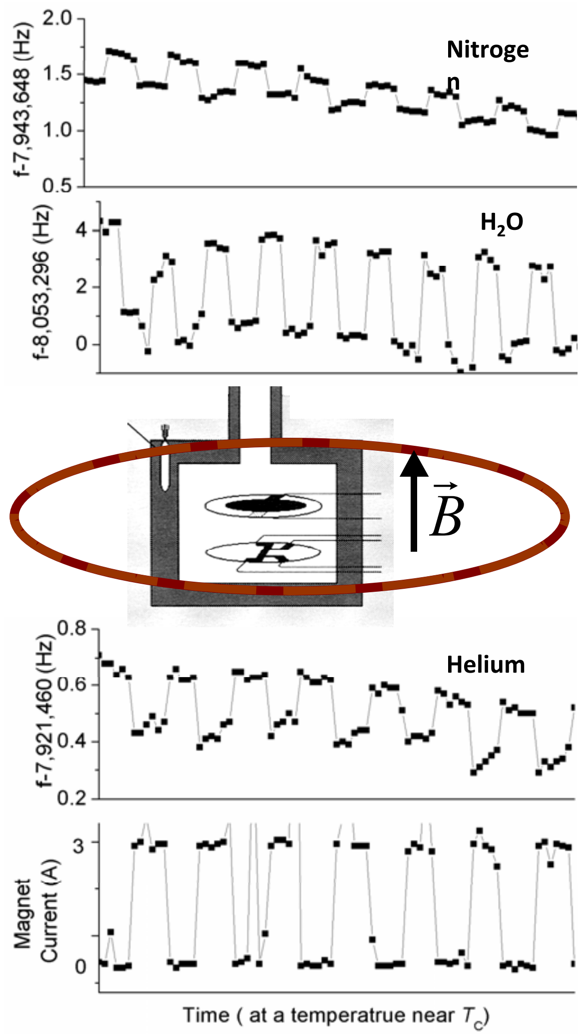
See: B.N.J. Persson, *Sliding Friction, Physical Principles and Applications*, Springer Verlag, 1998.

Electronic effects are observed in both QCM (Superconductivity-dependent Friction) and AFM

Known result: Monolayers slide with lower friction on superconductors in their superconducting state, if they do not become pinned by static friction (thermolubricity) at low temperature. Nitrogen films are very susceptible to pinning. Helium films are not. The effect is absent for Ne?

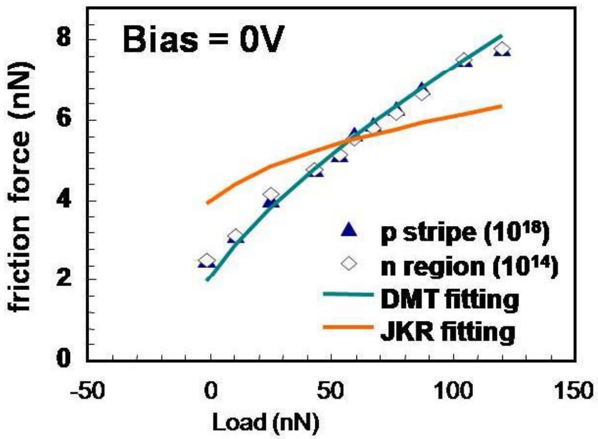


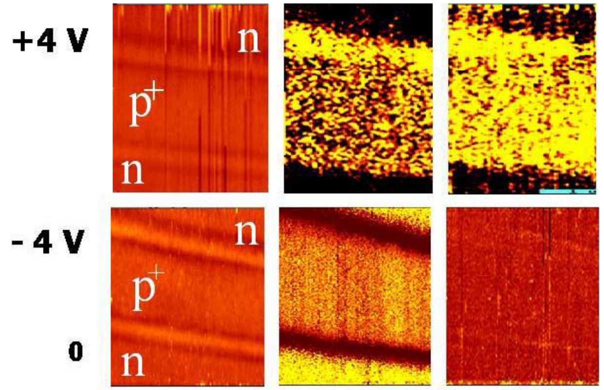
$\text{Friction}_{\text{Normal}} > \text{Friction}_{\text{Superconducting}}$

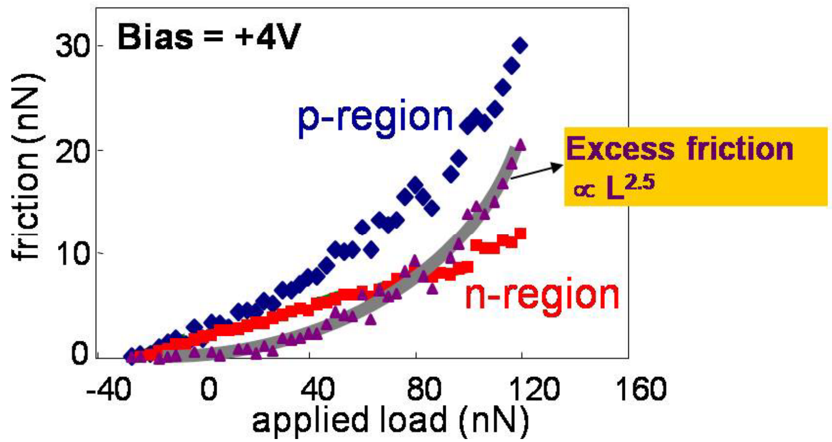


A. Dayo, Alnasrallah, and Krim, PRL (1998); M. Highland and J. Krim, PRL (2006) Superconductivity dependent friction for nitrogen, helium and water on Pb(111)

Electronic contributions to friction are commonly reported in AFM experiments, particularly by M. Salmeron & coworkers



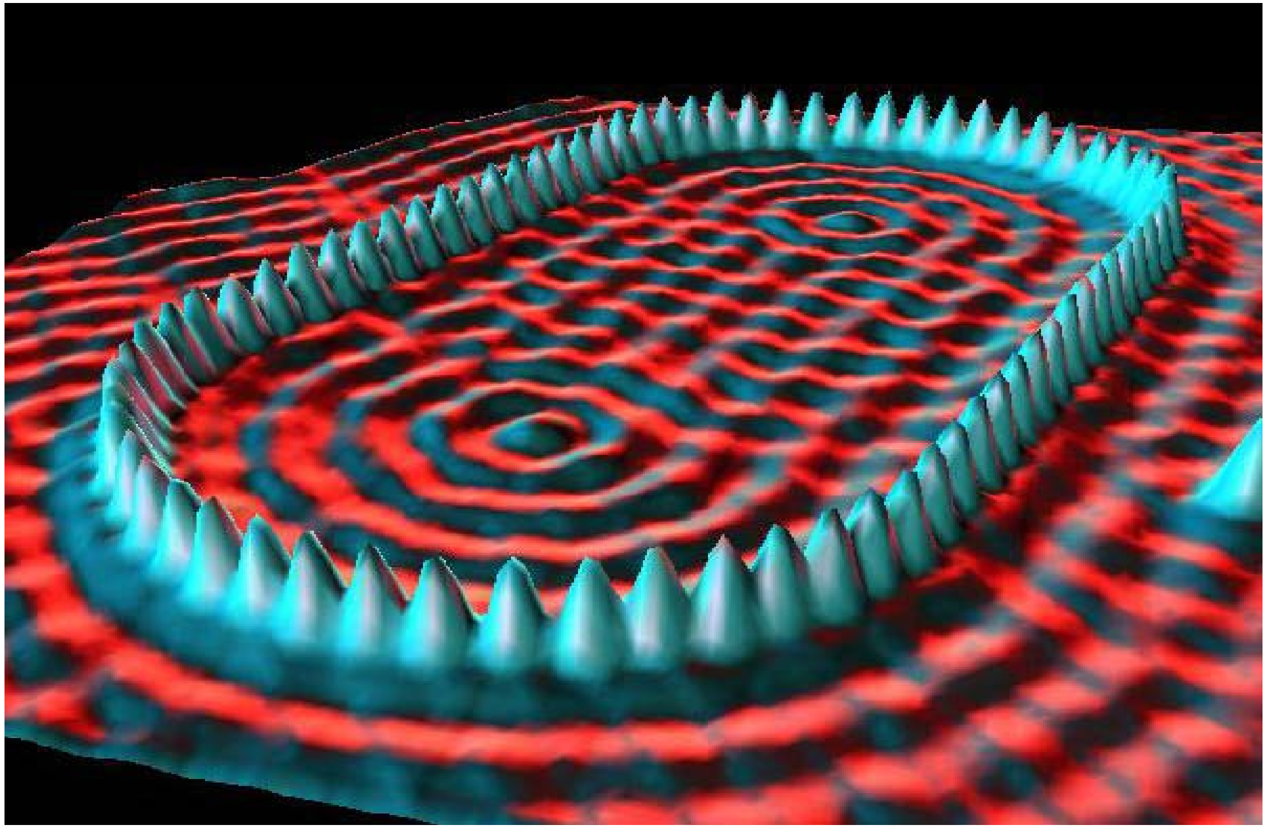




Park, JY, Qi, YB, Ogletree, DF, et al. (2007), "*Influence of Carrier Density on the Friction Properties of Silicon Pn Junctions,"* Phys. Rev. B **76 (6)**, 064108. Ogletree, DF, Park, JY, Salmeron, M, Thiel, PA (2006), "*Electronic Control of Friction in Silicon pn Junctions*," Science **313 (5784)**, pp. 186.

So what's wrong with this picture?

Electronic effects impact surface corrugation, which in turn impacts phononic friction; electonic potentials are load dependent and can even exhibit corrugation to anti-corrugation transitions.

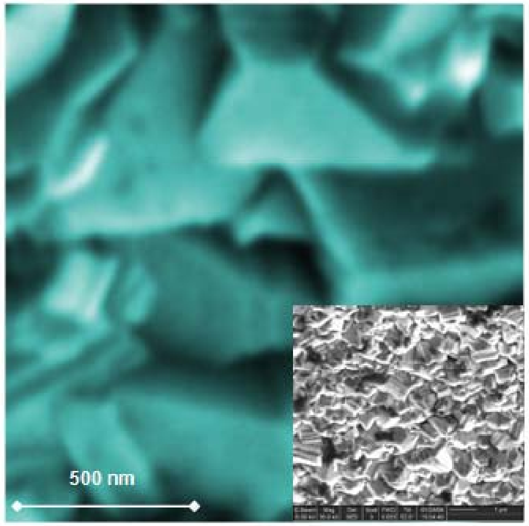


Iron on copper
Temp. = 4 K

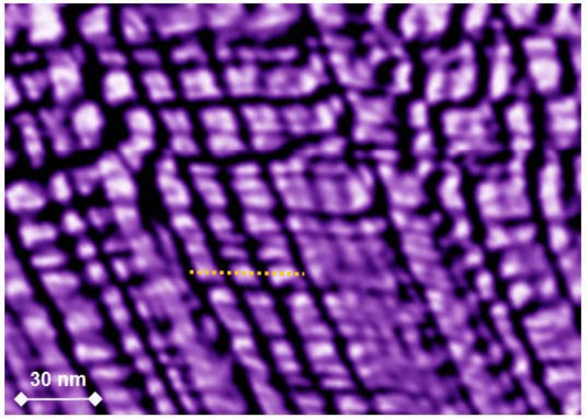
M.F. Crommie, C.P. Lutz, D.M. Eigler, E.J. Heller., *Surf. Rev. and Lett.* **2** (1)*,* 127-137 (1995)

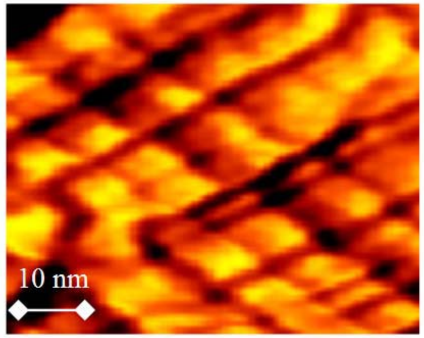
Scanning tunneling microscopy of B-doped diamond

Arrays of magic-sized nanocrystals on top of diamond grains

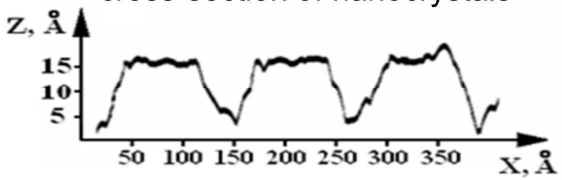


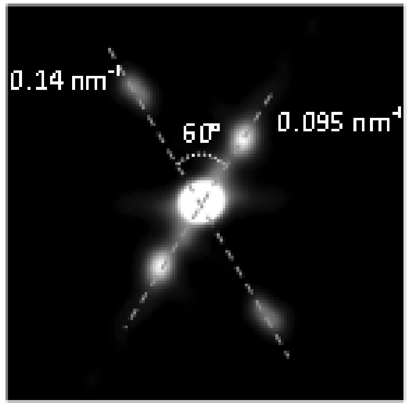
Diamond grains on large scale STM and SEM (insert) images



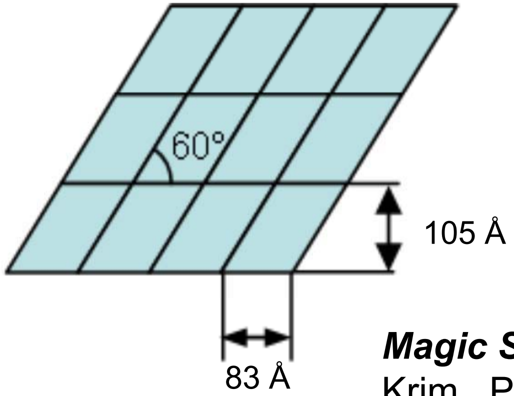


cross-section of nanocrystals





The 2D STM Fourier transform. Two 60°-rotated spatial periods whose ratio is 2/3

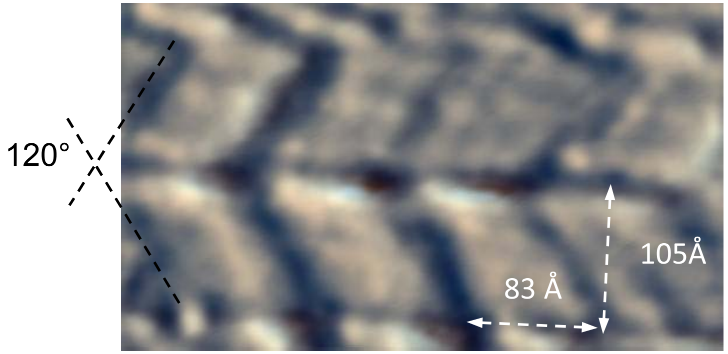


The surface of B-doped diamond is comprised of spatially ordered parallelogram-shaped nanocrystals whose height ratio is 2/3

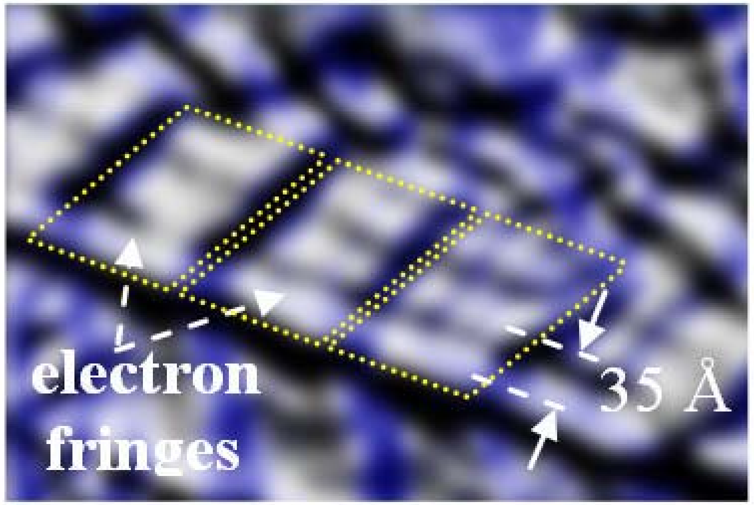
Magic Sized Diamond Nanocrystals, I. B. Altfeder, J. J. Hu, A. A. Voevodin, J. Krim, Phys. Rev. Let. **102,** 136104 (2009) ; Media coverage: Quantum Control of Diamond nanostructures, Chemical and Engineering news, April 13, 2007 vol **87**,44

Scanning tunneling microscopy of B-doped diamond

Anti-phase boundaries of nanocrystals

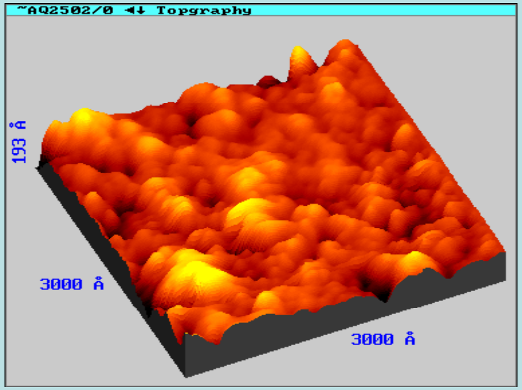


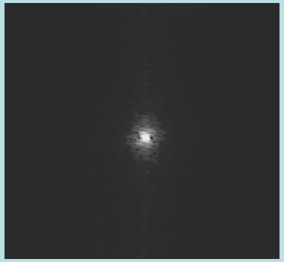
STM imaging of top surface on nanocrystals



At high boron densities diamond becomes metal (Nature **428**, 542, 2004). The 35-Å-spacing between the lateral electronic fringes is $\frac{1}{2}\lambda_F$

Comparison with undoped diamond. Real space STM image and its 2D Fourier transform do not reveal magic sizes

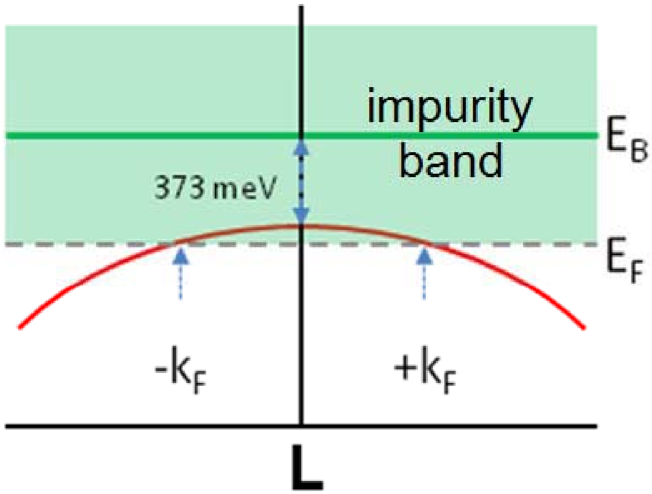


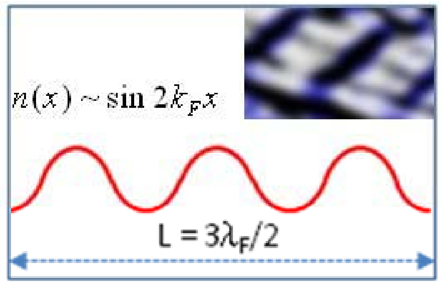


Conclusion:
Magic sizes in B-doped diamond are induced by electronic quantum size effect. Similar growth effects were previously observed for thin metal films and molecules adsorbed on metals.

I. B. Altfeder, J. J. Hu, A. A. Voevodin, J. Krim, Phys. Rev. Let. 102, 136104 (2009)

Discussion





The superstructure on surfaces of studied *B*-doped diamond samples is most likely caused by the insulator-to-metal transition at extremely high concentration of dopant (10^4 ppm).

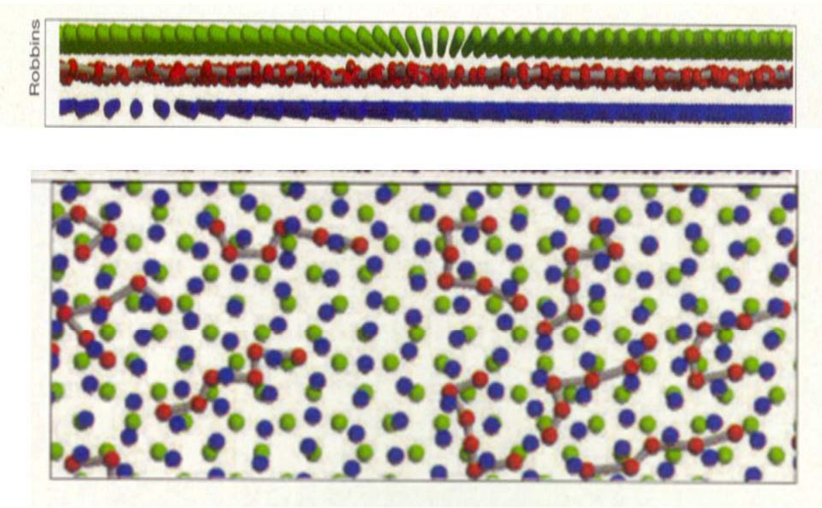
In this metallic regime, the geometries of individual nanoparticles become strongly affected by Fermi-sea-induced electronic growth mechanism with the quantum “magic” size $3\bullet_F/2$

Third topic: MEMS lubrication by thin films.

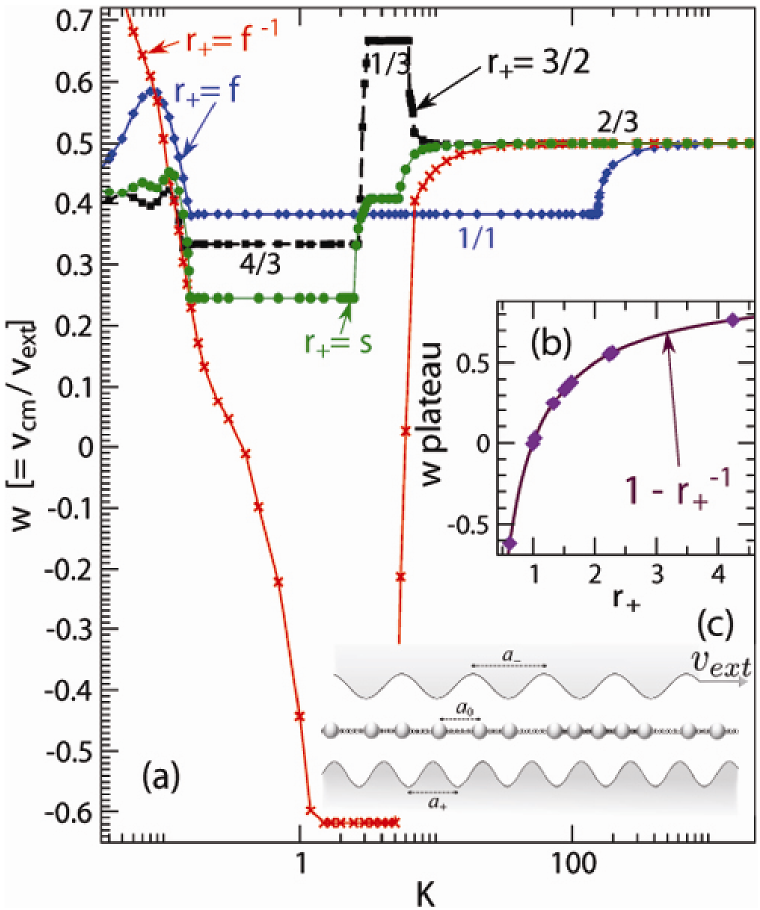
How thin of an adsorbed layer or fraction of a layer can provide lubrication?

When do adsorbed films increase friction?

Theories predict interesting behavior



Top and side view of contaminant molecules, which may lock two macroscopic surfaces together resulting in the occurrence of static friction. Courtesy of M.O. Robbins. He, Science, 1999)



Tosatti, E, Vanossi, A and coworkers(2009), "*Exactly Quantized Sliding of a Confined Solid Lubricant Under Shear*,"

Surfaces forces Apparatus studies of “full slip in “C_{60}

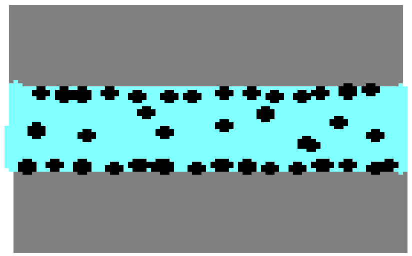
S.E. Campbell, G. Luengo, V.I. Srdanov, F. Wudl, and J.N. Israelachvili, Nature (1996)

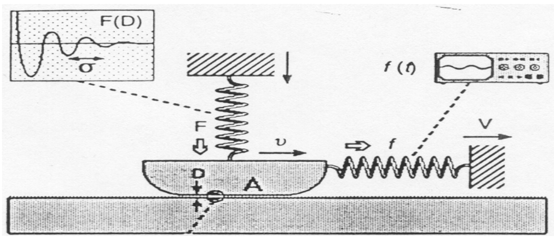
Compared toluene on mica to C_{60}/toluene solution on mica. Found that C_{60} formed 1-2 monolayers on the mica-- and these adsorbed layers “possess unusually high fluidity and are easily disrupted.”

Found that the viscous response of the fluid near the mica surface was completely different for the C_{60}/toluene solution as compared to the toluene alone. The C_{60} toluene solution exhibited full-slip boundary conditions.

Does this imply it will be a good additive to lubricants?

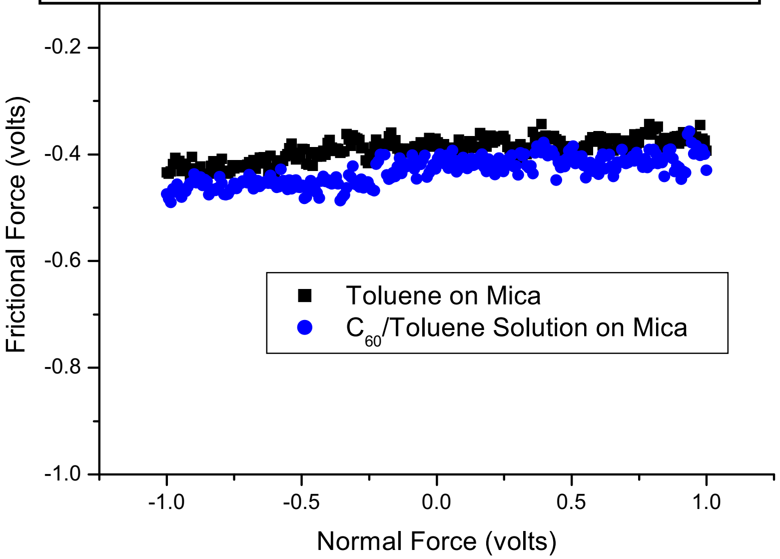

Toluene alone


C_{60}/Toluene Solution



AFM Measurements: No reduction in friction, Apparent lubricant failure, the C_{60} is “too slippery”

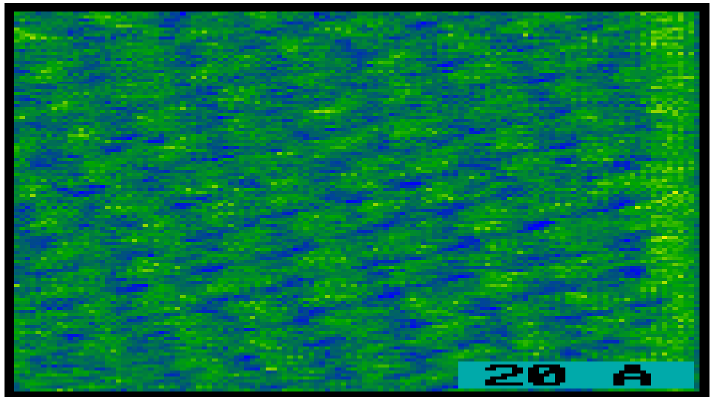
Scan speed: 500 nm/sec with silicon nitride cantilever 10% C_{60}/Toluene solution.



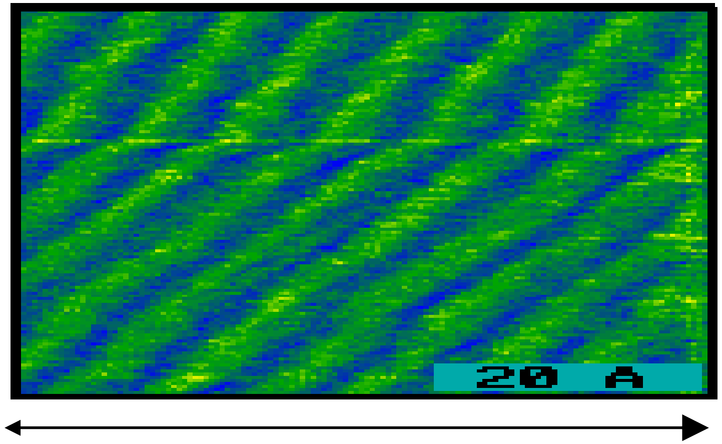
A Scanning Probe and Quartz Crystal Microbalance Study of the Impact of C_{60} on Friction at Solid-liquid Interfaces", **T.S. Coffey, M. Abdelmaksoud and J. Krim, J. Physics Cond. Matt., Special Issue, 13, 4991-4999 (2001)**

See also: C-60 Molecular Bearings and the Phenomenon of Nanomapping”, **T. Coffey, J. Krim, PRL (2006)**

Toluene on Mica

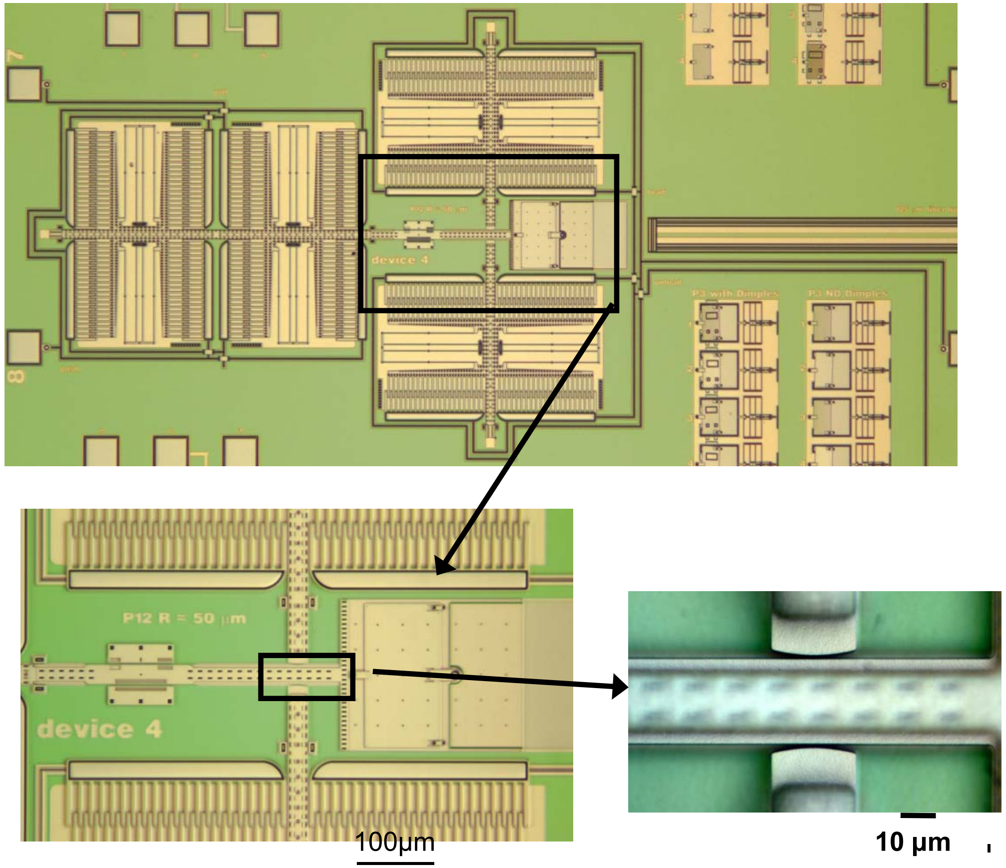


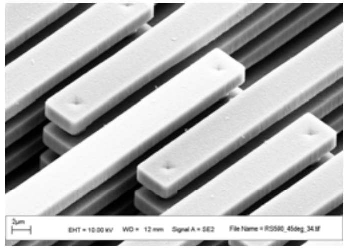
C_{60}/Toluene solution on Mica: same lattice spacing



50 angstroms

MEMS devices with rubbing contacts wear out: Can adsorbed films lubricate them?



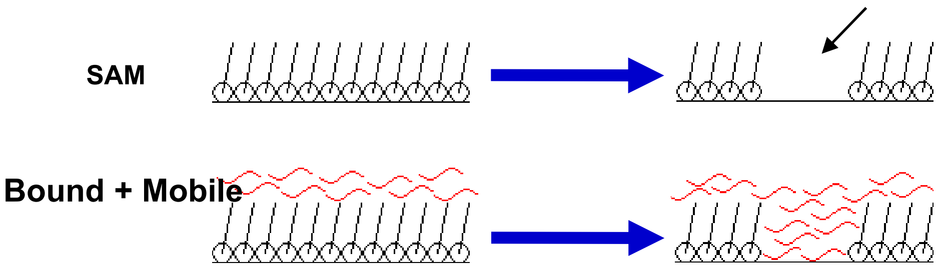


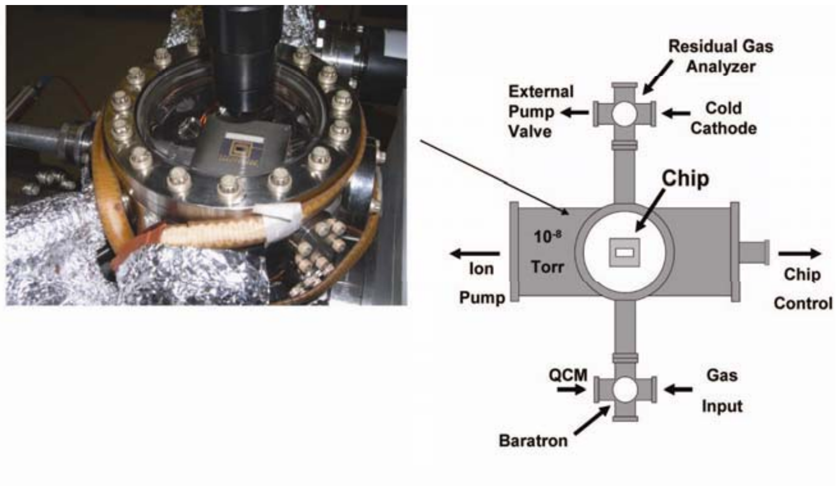
Capacitive Comb Drives

Hertzian Contact Area = 7×10^{-14} m^2

Est. Real Area of Contact 2×10^{-16} m^2

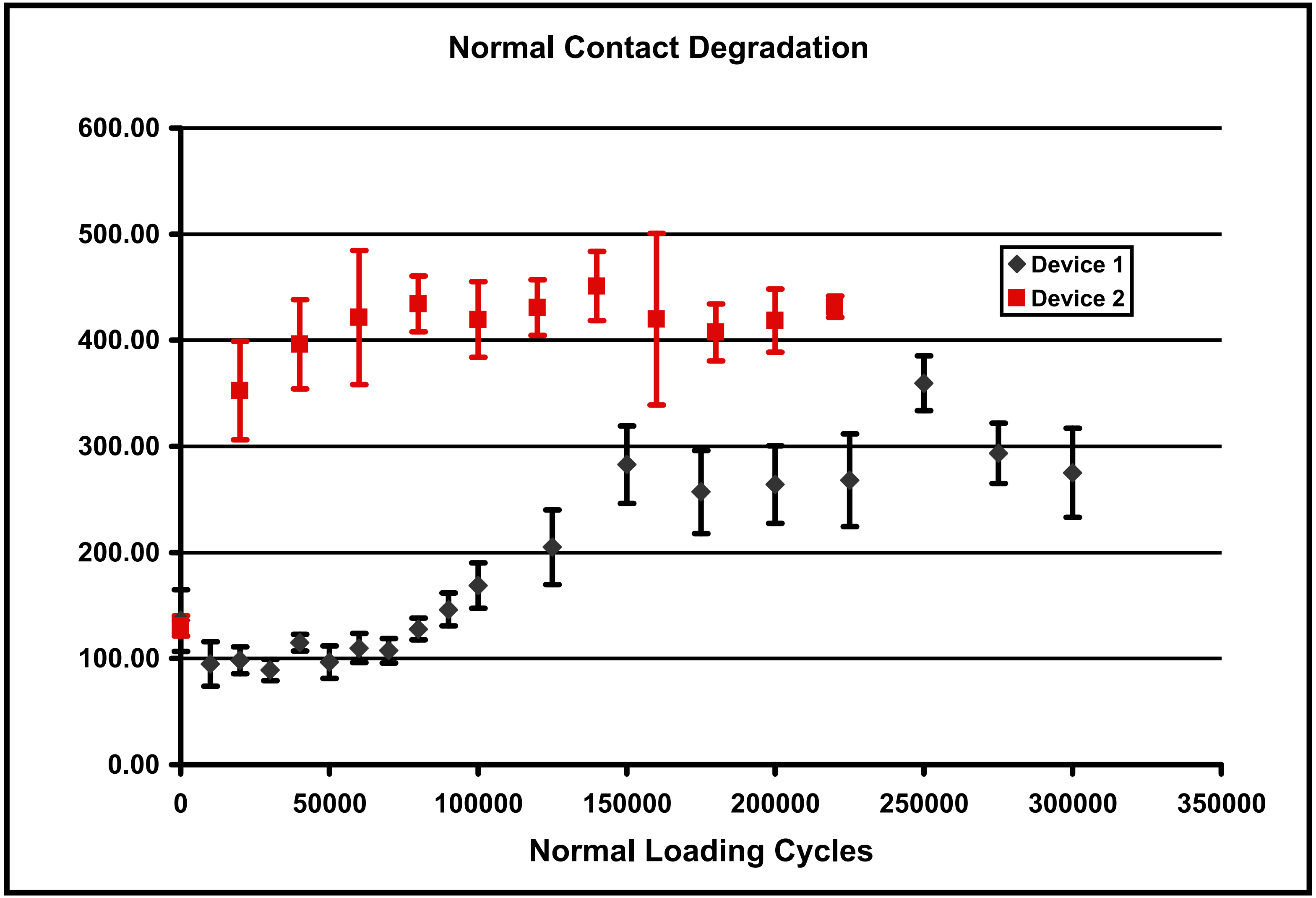
At 500nN, Contact pressure between 7MPa and 150 MPa





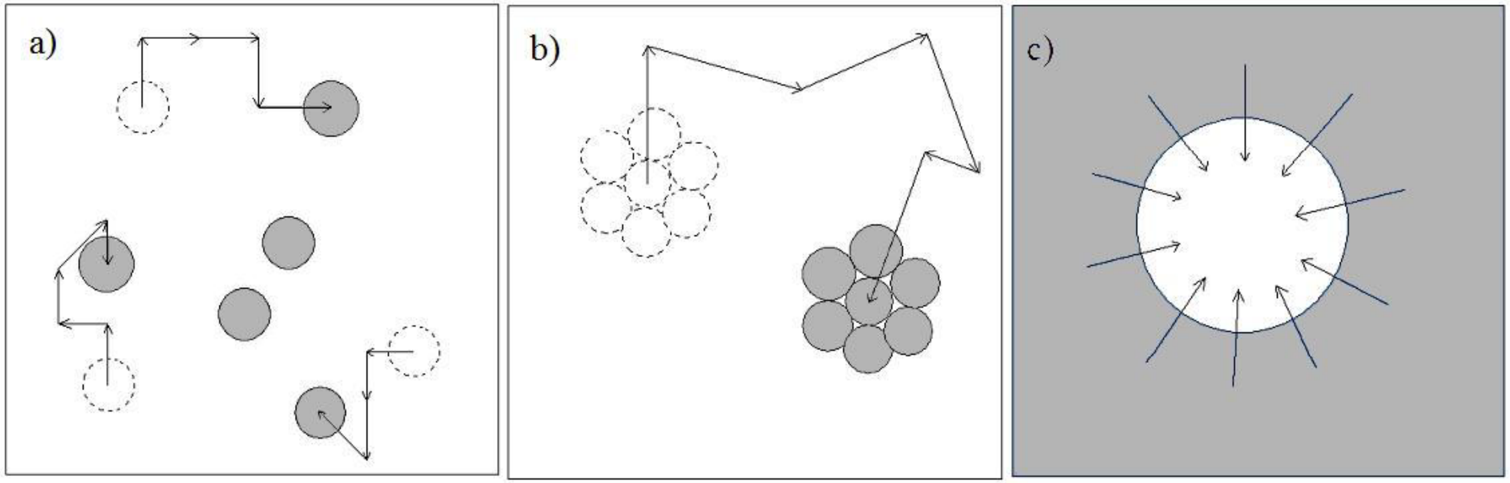
D.A. Hook, S. Timpe, M.T. Dugger, J. Krim, J. Appl. Phys., 104 (2008)

“SAMS don’t work and they never will : They rub off”*



*But there is a silver lining

Nanoscale Sliding friction and diffusion coefficients for alcohols: Note that differing lubrication mechanisms are possible



	PFTS			Si			Al		
	τ ns	D_s cm^2/s	D_i cm^2/s	τ ns	D_s cm^2/s	D_i cm^2/s	τ ns	D_s cm^2/s	D_i $cm^2/2$
Pentanol	6	1.2	$5x10^{-5}$	6	1.1	$5x10^{-5}$	0	0	0
Ethanol	4	1.1	$4x10^{-5}$	8.5	9	$1x10^{-4}$	0.5	0.1	$6x10^{-6}$
TFE	0	0	0	3.5	1.3	$2x10^{-5}$	0	0	0

Sufficient mobility exists at the nanoscale for ethanol and pentanol to diffuse both in the presence and absence of a SAMS layer

Will they lubricate differently?

Brendan P. Miller and Jacqueline Krim*

Sliding friction measurements of molecularly thin ethanol and pentanol films:How friction and spreading impact lubricity.

J. Low Temp. Phys. , Nov. 2009

Friction of sliding adsorbed films: 3 puzzles

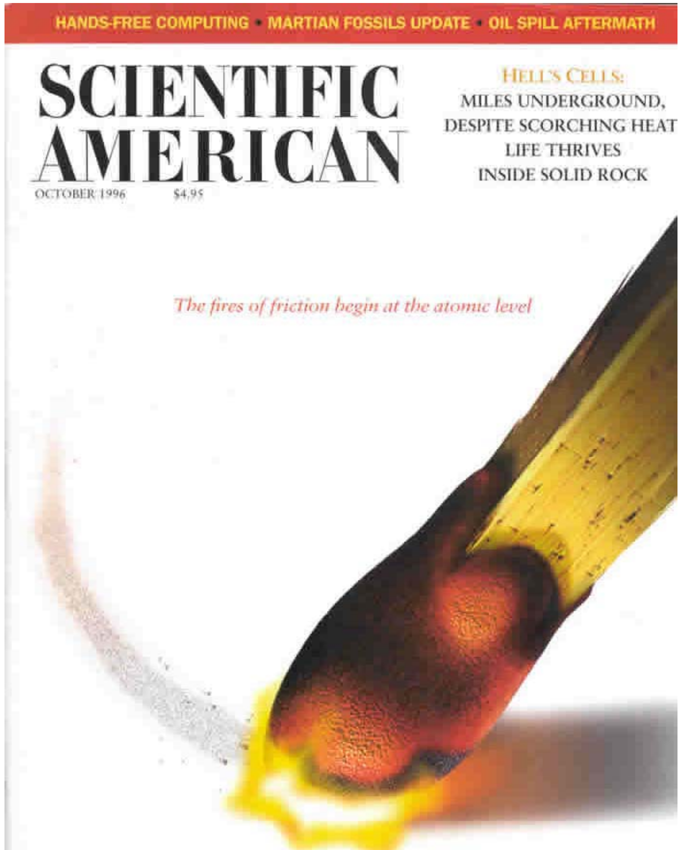
How thin of an adsorbed layer or fraction of a layer can provide lubrication? Very very thin

Thermolubricity or Cryolubricity? Both

How do we include electrons in a Comprehensive treatment ? $#@% Difficult!

J. Krim and R. Behringer
Physics Today (Sept, 2009)

Seth Putterman,
(Nature)



J. Krim
Scientific American, 1996