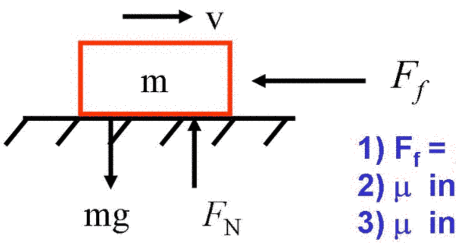
QCM Studies of Adsorbed Monolayers

J. Krim, T.Coffey and M. Highland

Supported by AFOSR and NSF



Classical Laws of Friction:

1) $F_f = \mu F_N$
2) μ independent of apparent contact area
3) μ independent of sliding speed

$$F_f = \mu F_N$$

$$\mu_s \geq \mu_k$$

For solid-fluid interfaces, "viscous friction" applies, where,

$$F = (m/\tau)\, v$$

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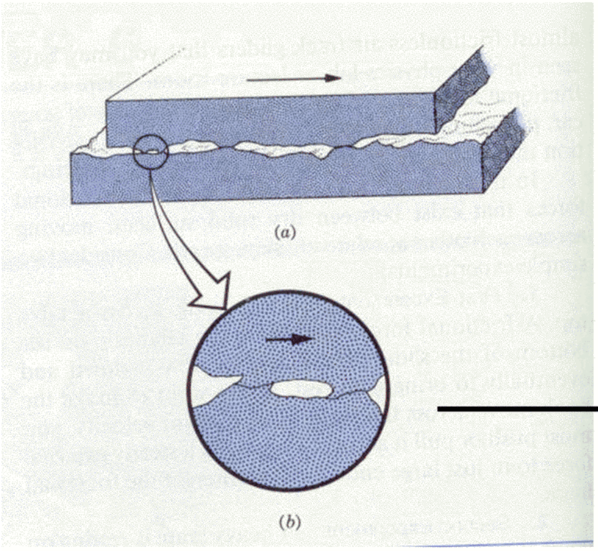
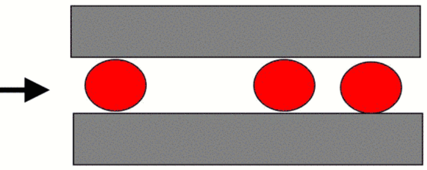




Nanotribology

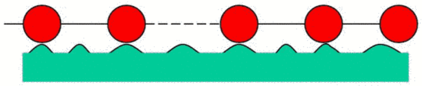
Nano: 10^{-9} meters--molecular scale
Molecular time scales: 10^{-12} s
Tribology: The study of friction, lubrication, and wear.

Researchers in the field of nanotribology examine micro- and nano-contacts in well-controlled geometries Often these contacts have mobile adsorbates on the surfaces. Knowledge of physical behaviors at this scale is thought to be key to understanding how friction works on all length scales.

Focus today is on adsorbed layers sliding along well characterized substrates in open geometries, examining the impact of substrate corrugation and substrate superconductivity.

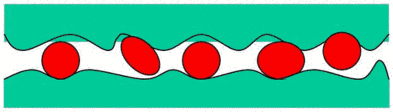
$$\mathbf{F = (m/\tau)\, v}$$

(a)



(b)

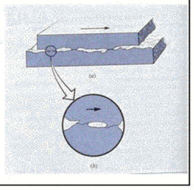
$$\mu_s \geq \mu_k$$

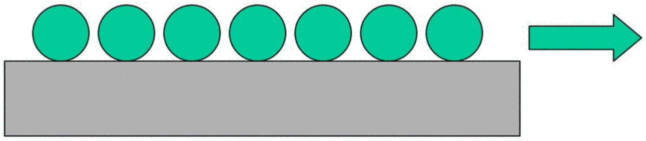


(a) On an open surface, both solid and liquid films slides are characterized by a viscous friction law. (QCM, ``blowoff experiments)

(b) In a confined geometry(SFA, AFM?), static friction and stick-slip phenomena are ever-present and overall friction levels are substantially higher for comparable sliding speeds. This may arise from a mobile particles' pinning of counterface materials?

"realistic contact" combines both (a) and (b)





We investigate the sliding friction of thin adsorbate layers adsorbed on clean metal surfaces.

Small, two-dimensional tribological system → easy comparison with theory.

Easily modeled system:

- inert adsorbate
- rigid substrate

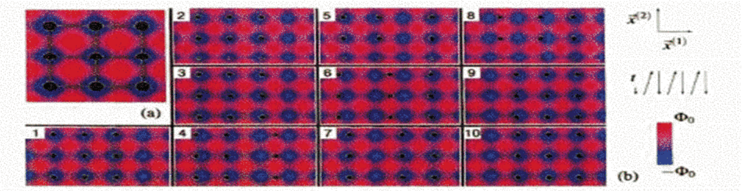
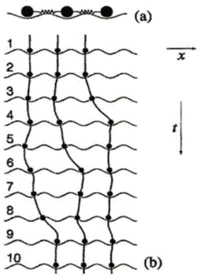


FIG. 2 (color). (a) Sketch of the 2D atomic scale "car" built by six chains arranged in an array of 3 × 3 particles. The surface potential $\Phi(\vec{x})$ is shown using the color code at the right. (b) Motion of the 2D atomic scale car sketched in (a); the black disks indicate the particles' position in relation to the surface potential in the ten numbered snapshots in time intervals of $(5b/2\pi)\sqrt{m/\Phi_0}$. The time $(25b/x)\sqrt{m/\Phi_0}$ of a full oscillation of the respective $a_{i,j-k}(t)$ and hence of a single step of length b to the right is shown. The parameters are identical to those in Fig. 1.



Atomic Scale Engines: Cars and Wheels

M. Porto et al.,
PRL **84,** 1608 (2000)

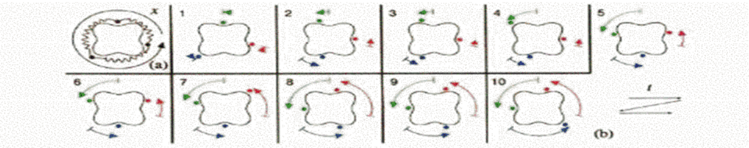


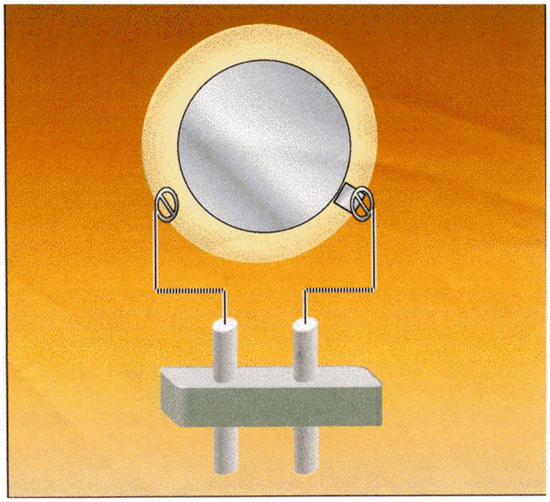
FIG. 3 (color). (a) Sketch of the atomic scale "wheel," showing the angular surface potential $\Phi(x)$ and the ring of $N = 3$ particles on a circle of circumference of length $\ell = 4b$. (b) Motion of the atomic scale wheel. The colored disks indicate the particles' position in relation to the angular surface potential in the ten numbered snapshots in time intervals of $(5b/2\pi)\sqrt{m/\Phi_0}$, where the arrows indicate the displacement relative to the first snapshot. The time $(25b/\pi)\sqrt{m/\Phi_0}$ of a full oscillation of $a_{i,j-k}(t)$ and hence of a rotational step of length b counterclockwise is shown (for the fourfold symmetry of the example this is equivalent to an angle $\pi/2$). Except $g = 1/3$ and $c = 3/10$, the parameters are identical to those in Figs. 1 and 2.

Measuring friction with a quartz crystal microbalance (QCM)

- Thin crystal disk oscillates in a shear mode
- Adsorbed material lowers the resonant frequency
- If the shear stress is below about 10^3 N/m^2, it will "slip" enough to be detected by the QCM:
- The slip time is deduced from Q and f:

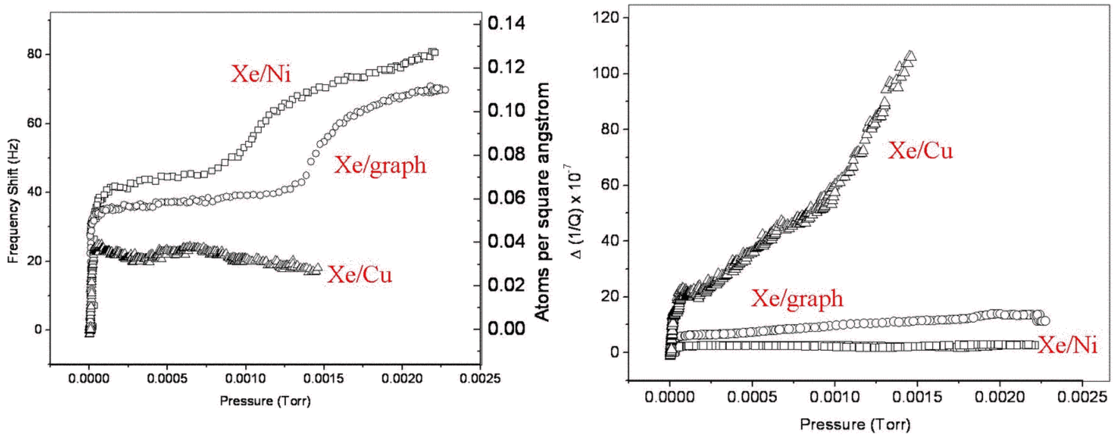
$$\delta(Q^{-1}) \propto \delta(A^{-1})$$

$$\delta(Q^{-1}) = 4\pi\tau\delta f$$

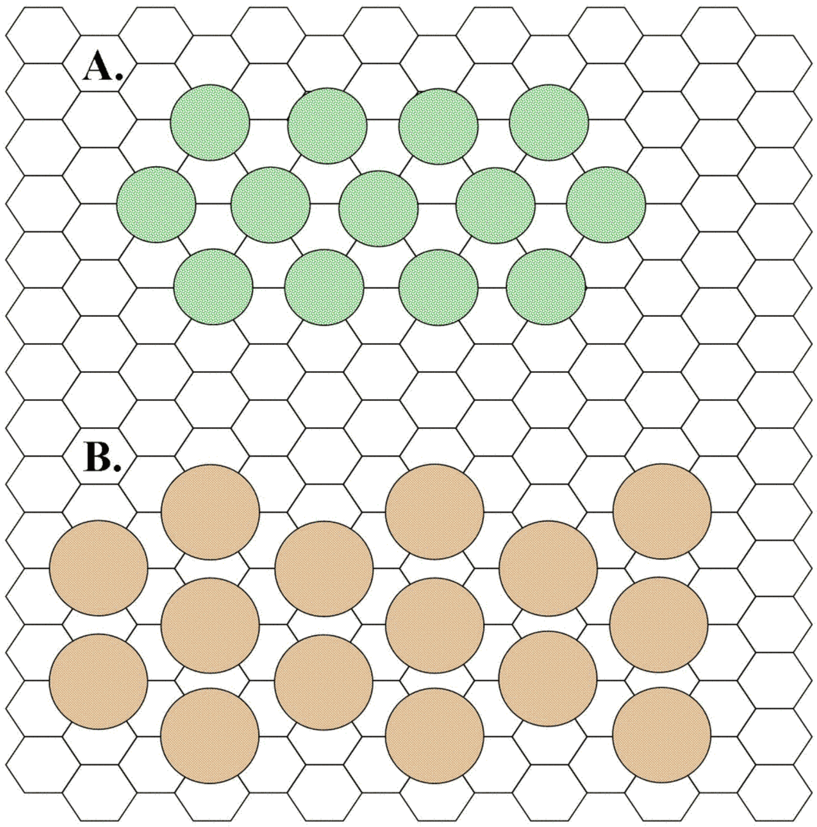


(*Krim and Widom, PRB, v. 38, n.17, 1988*)

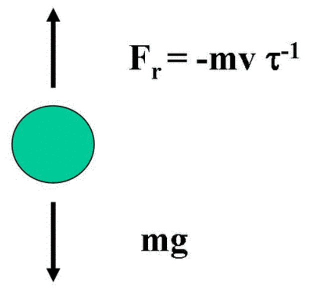
QCM Data--Xenon Isotherms



The high slippage (low friction) of Xe/Cu(111) data causes a reduced frequency shift.



Terminal Velocity: $v_t = g\tau$

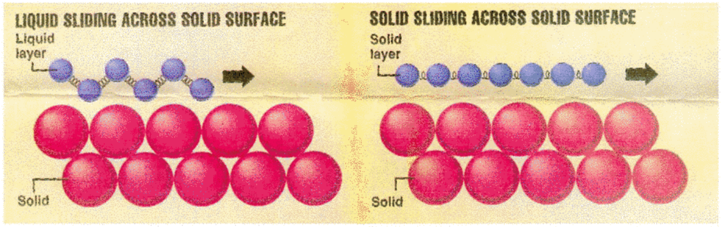


For air, $\tau \sim 100$ s $v_t \sim 1000$ m/s

For Kr/Ag, $\tau \sim 2$ ns $v_t \sim 2$ nm/s

(a) Krypton on gold

Slippery when dry

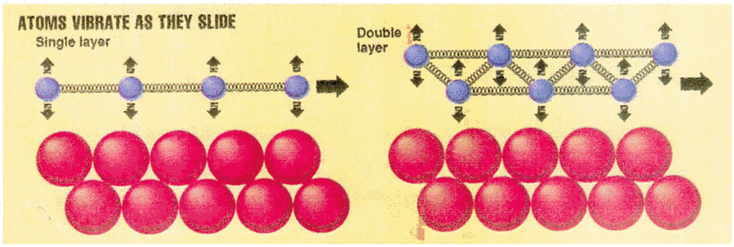


Figures from *Dallas Morning News*, Aug. 14 1995

J. Krim, D.H. Solina, and R. Chiarello, *Phys. Rev. Lett.* **66**, 181 (1991)

Friction due to sound waves (phonons) produced by sliding

(b) Xenon on silver



C. Daly and J. Krim, *Phys. Rev. Lett.* **76**, 803 (1996)

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

No static friction!

Phononic Friction

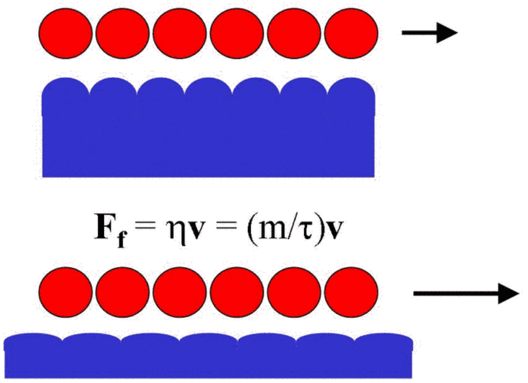
Phononic friction may be related to the variation of the adsorbate/substrate interaction potential. This is the atomic scale surface corrugation that the adsorbate "sees". For constant substrate lattice spacing, Cieplak et al.[1] observed that the sliptime, τ varied with corrugation strength, C, as:

$$\tau \sim C^{-2}$$

Friction is also related to the damping, $\eta_{=}$, that comes from substrate phonon modes and/or electronic friction.[2], giving rise to :[3]

$$\eta = \eta_{=} + a\,C^2$$

Here, a is a constant dependent on temperature, coverage, etc.



$$\mathbf{F_f} = \eta \mathbf{v} = (m/\tau)\mathbf{v}$$

1. Cieplak, Smith, and Robbins, Science 265, 1209 (1994).
2. Persson and Nitzan, Surf. Sci. 367, 261.
3. T. Coffey and J. Krim, August 15, 2005 PRL

QCM Measurements of Xe/Ag(111)

Published originally in Daly and Krim, PRL 76, (1996) 805.

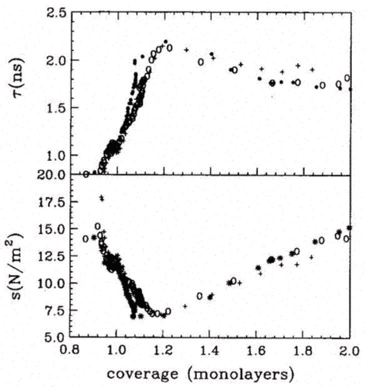


FIG. 4. Slip time τ and shear stress $s = \eta v$ (for v = 1 cm/s) versus coverage for three different Ag(111) surfaces. The shear stress for the two-atom-thick bilayer 15.1 ± 0.5 N/m^2 is approximately 25% greater than that associated with the one-atom-thick monolayer, 11.9 ± 0.4 N/m^2.

*2.2 ns slip time for compressed monolayer
*27% greater shear stress for the bilayer than the monolayer

Modeling Efforts

1. Persson and Nitzan, Surface Science 367

They assumed that the contribution from the corrugation, C, was negligible, and attributed the friction to the damping, $\eta_{=}$. They believed the damping came from electronic friction.

$$\eta = \eta_{=} + \cancelto{0}{a\,C^2}$$

2. Tomassone et al., PRL 79 (24) 4798.

They assumed that the contribution from the damping, $\eta_{=}$, was negligible, and attributed all friction to the corrugation, C.

$$\eta = \cancelto{0}{\eta_{=}} + a\,C^2$$

New Xenon Experiments using QCM

Since there is a lack of knowledge about the Xe/Ag(111) system, these issues have been difficult to resolve. Parameters such as the corrugation of the xenon-silver interaction potential have not been measured. We developed a QCM experiment based on systems in which the corrugation is known **and the substrate lattice spacing is "constant".**

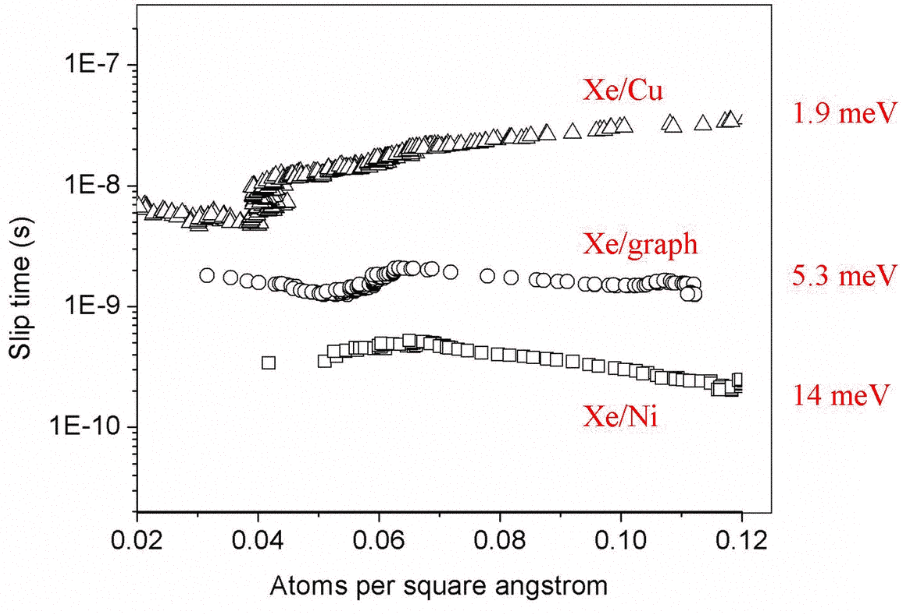
System	Surface Corrugation (meV)	Substrate Spacing (nm)	Xenon Spacing (nm)
Ag(111)	0.69 – 2.7[1]	0.236	0.439 – 0.452
Cu(111)	1.9[2]	0.255	0.4414
Ni(111)	14[3]	0.249	0.441
Graphene/Ni(111)	5.3[4]	0.249	0.441

Xe/Cu(111) is commensurate at 77 K.

Note: All table values are for 77 K.

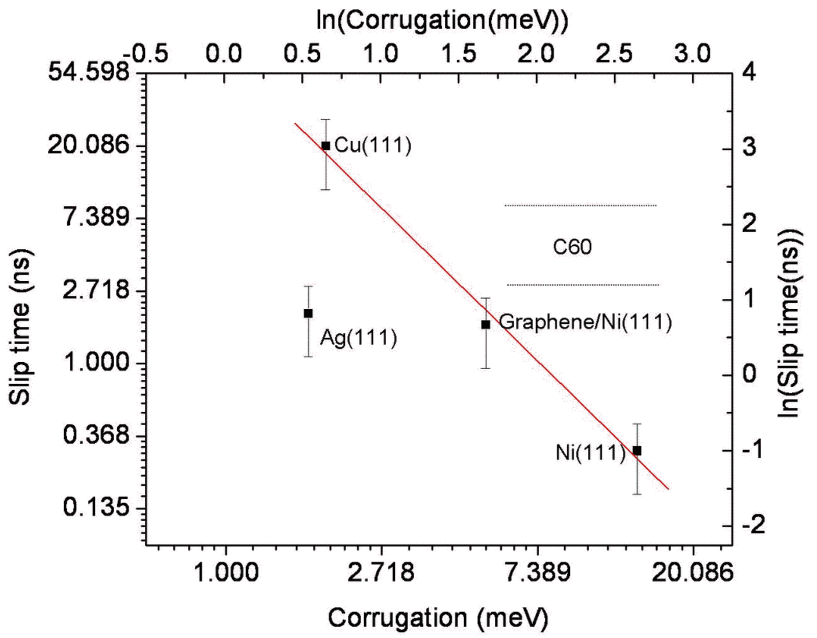
1. Estimated value from email conversation with L. Bruch
2. Braun et al., PRL 80, p. 125 (1998). HAS measurement.
3. Nabighian and Zhu, Chemical Physics Letters 316, p. 177, (2000). Diffusion rate measurement.
4. Kariotis et al., J. Phys. C 19 p. 5717 (1987). Study of xenon on graphite. For QCM measurements, we must use graphene, not graphite, grown on Ni(111). Here, the graphene spacing matches the Ni(111).

QCM Data--Xenon Slip Times



$\tau \sim U_o^{-2}$

QCM Data--Xenon Slip Time Analysis



The line is the fit to the Xe/Cu(111), Xe/Ni(111), and Xe/graphene/Ni(111) data. It has a slope of –2.1 and an intercept of 4.25 (on the natural log scale).

Conclusions for phononic friction

System	Slip Time (ns)	Surface Corrugation (meV)	Substrate Spacing (nm)	Xenon Spacing (nm)
Cu(111)	20	1.9	0.255	0.4414
Ag(111)	2.2	0.69 – 2.7	0.236	0.439 – 0.452
Graphene/Ni(111)	1.7	5.3	0.249	0.441
Ni(111)	0.3	14	0.249	0.441

The xenon monolayer slip times for Cu(111), Ni(111), and Graphene/Ni(111) are very well fit by the equation:

$$\eta = \cancel{\eta_{=}} + a\,C^{2}$$

Small electronic component

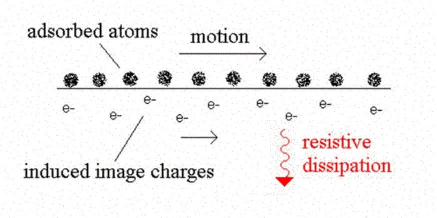
As expected, both the corrugation and substrate lattice spacing impact the friction, however we expected the systems close to a commensurate state to exhibit high friction, and they did not. For example, the slip time for the compressed xenon monolayer on C_{60}: 5.5 ns once it started sliding.

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.

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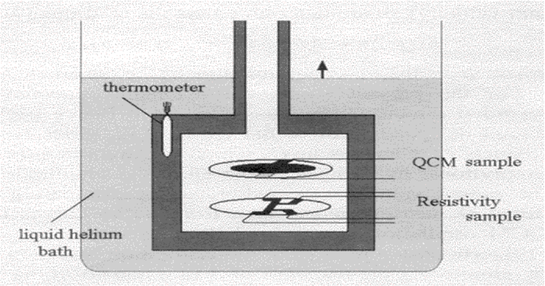
Probing the electronic component of friction

- A thin film of adsorbed atoms is formed on a Pb substrate.
- The system is cooled to just below the superconducting transition temperature.
- δf and $\delta(V^{-1})$ are monitored as the system warms through the transition.



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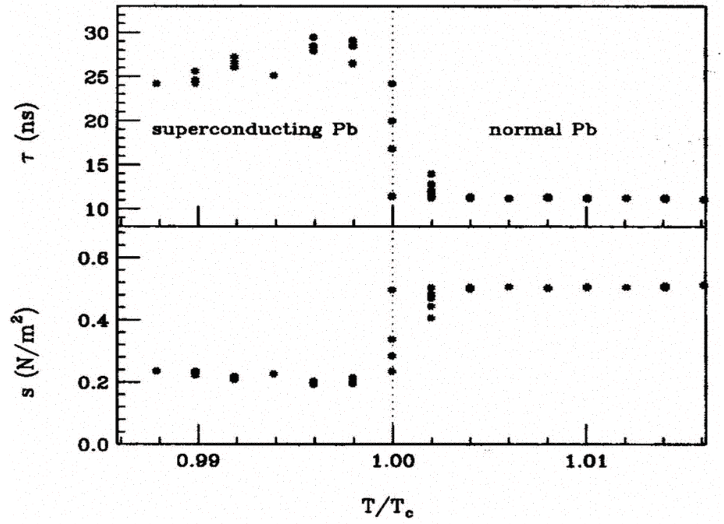
Prior results for nitrogen on lead



- Total Friction abruptly drops by ~half below the superconducting transition (*Dayo, Alnasrallah, and Krim*,(DAK) *PRL, v.80, n.8, 1998*).

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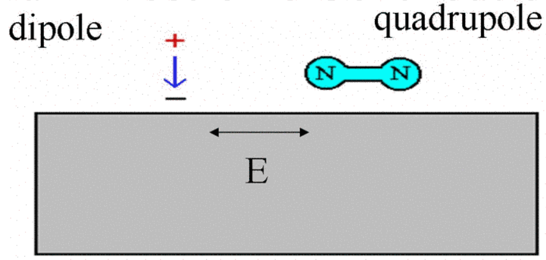
Bulk Electronic Contributions



- This is a small effect (*B. N. J. Persson and E. Tosatti, Surf. Sci. 411, 855 1998*)
- Friction from normal and superconducting electrons not additive (*T. Novotný and Velický , Phys. Rev. Let. 83(20), 4112-14, 1999*).
- Quadrupole moments can result in large dissipation, assuming a N_2 herringbone lattice (*L. W. Bruch, Phys. Rev. B, 16, 201, 2000*). **This effect will be much smaller for rare gases and larger for CO**
- If the adsorbed layer donates charge to the metal, then bulk electronic contributions can be significant (*J. B. Sokoloff, M. S. Tomassone, & A. Widom, Phys. Rev. Let. 84(3), 515-17, 2000*).

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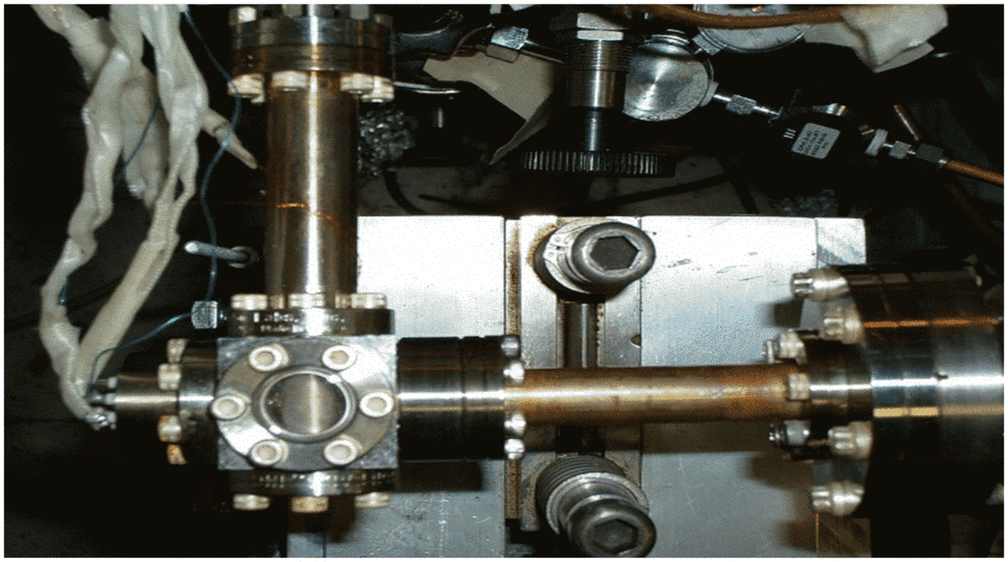
- Improvements to the 1998 Dayo apparatus.

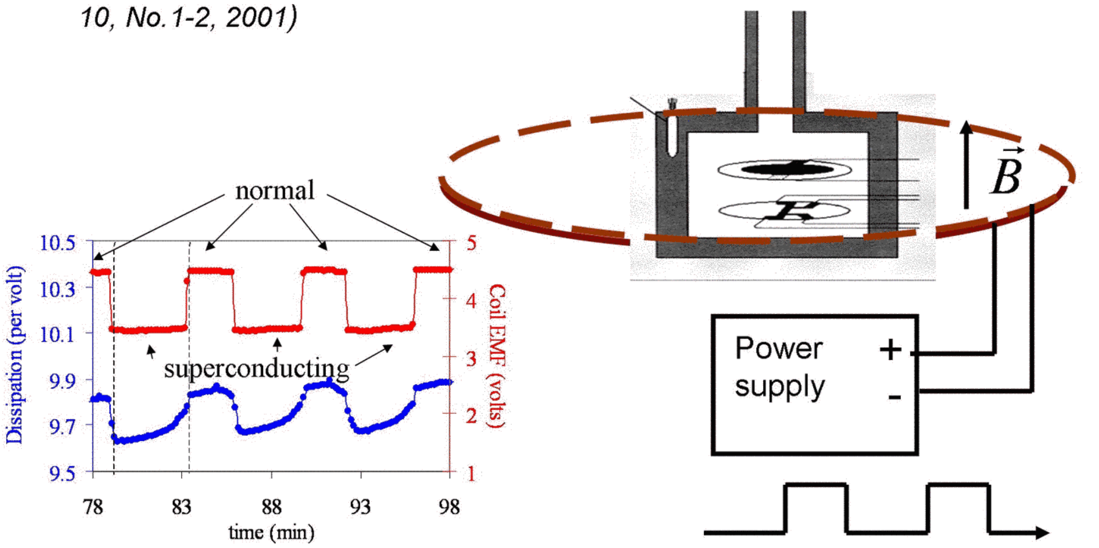
Copper Pinch-off Tube



Magnet Breakdown

Mason observed abrupt changes in friction by

- Thermal Cycling
- Applying a Magnetic Field below T_C (*B.L.Mason, Tribology Letters, 10, No.1-2, 2001*)



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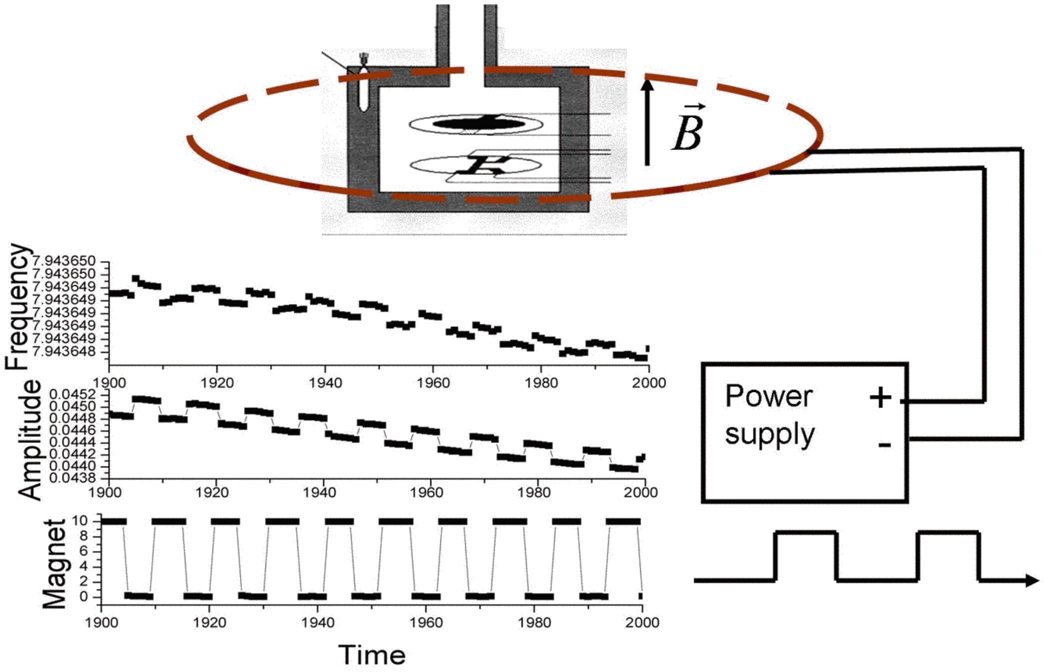
Magnet Breakdown



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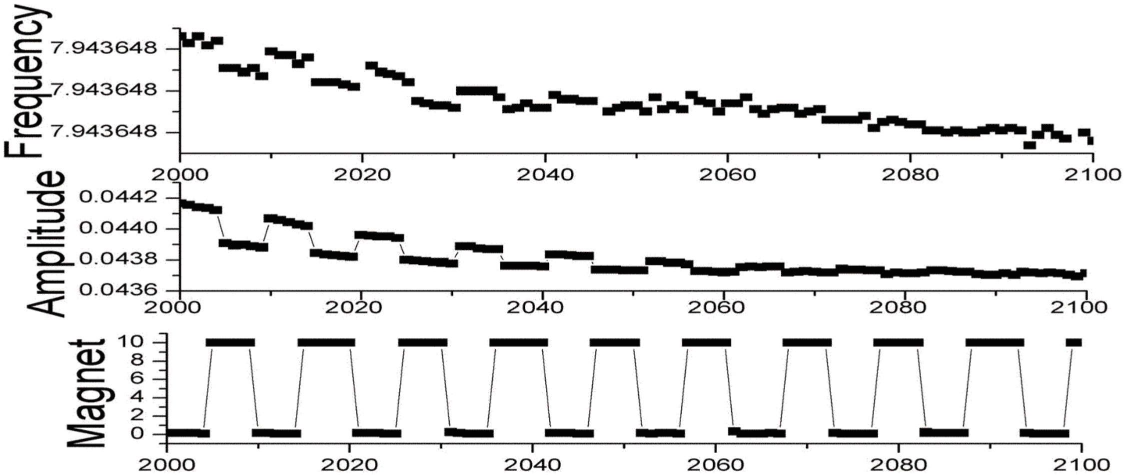
The effect fades away as magnet continues to switch



Data by M. Highland : to be published

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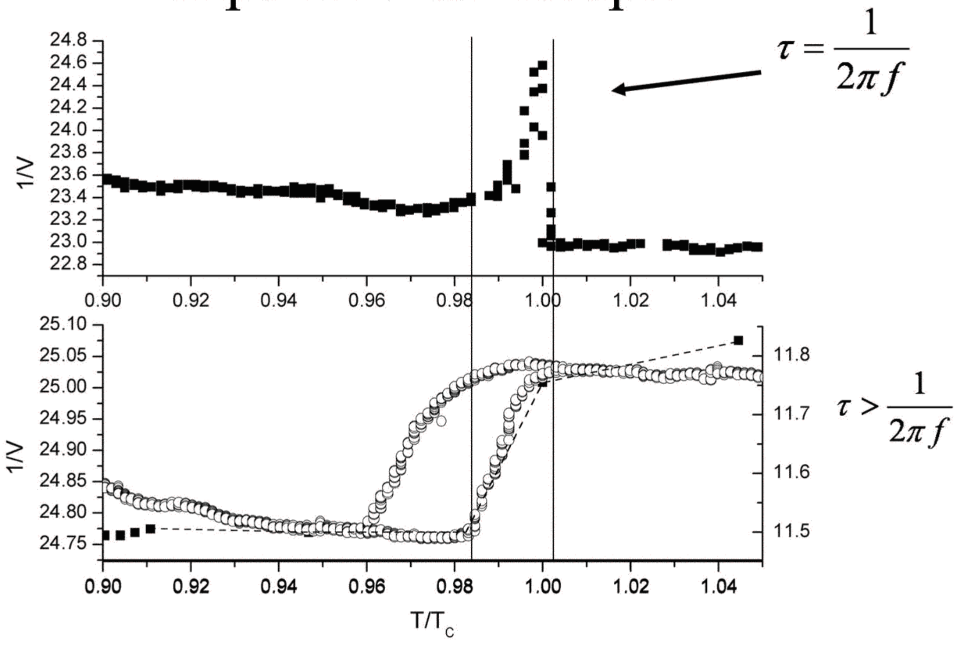
Transition as recorded in different experimental setups.



$\tau = \frac{1}{2\pi f}$

$\tau > \frac{1}{2\pi f}$

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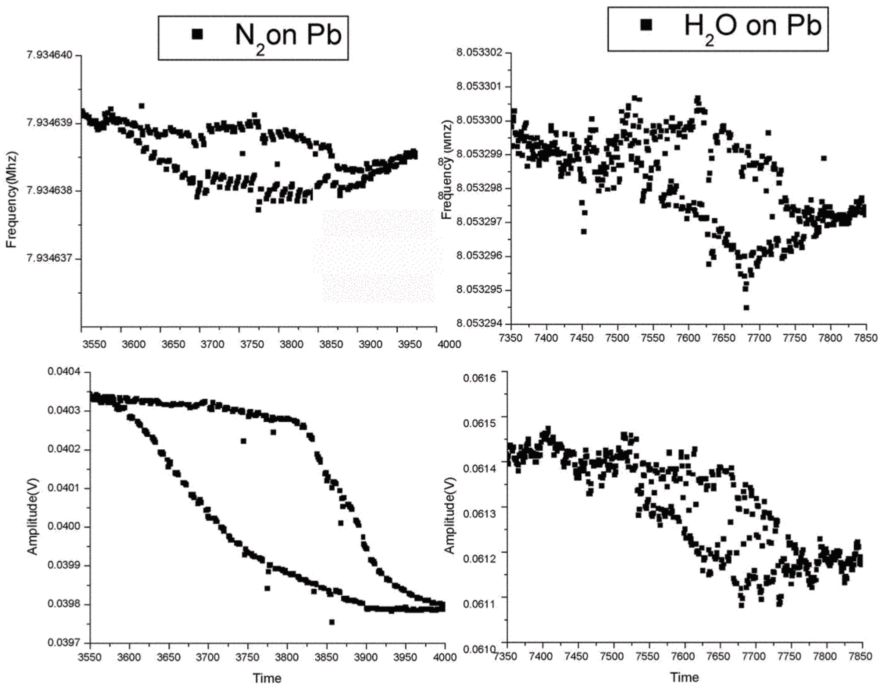
We see the effect for both N_2 and H_2O



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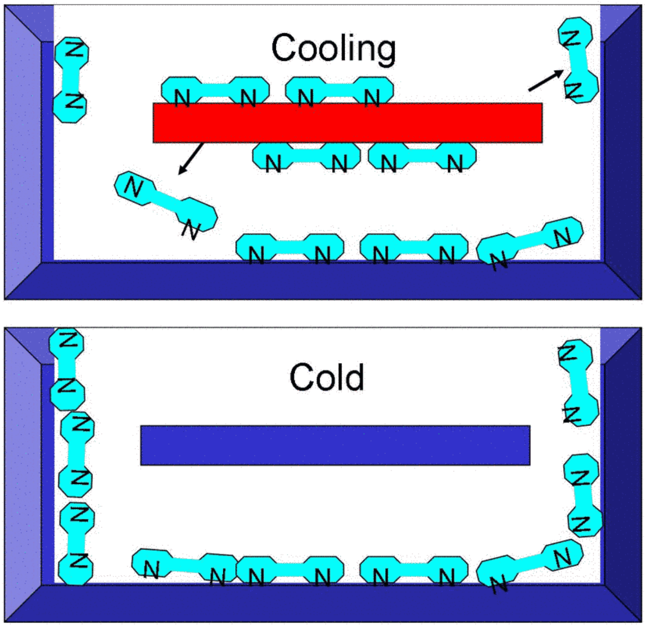
- But where is the effect for inert gases??
- Studies of Ar, Xe and Ne have been inconclusive. The effect has never been observed for these adsorbates, but….
- A variety of experimental difficulties are associated with confirmation of a null result.
- These include both desorption of the adsorbate, as well as sticking.

Thermal Characteristics



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Pb Film Micro-Patterning

- •Recent experiments have shown anti-dots have a strong effect on superconducting characteristics
- •Similar effects may be exhibited thermally evaporated films

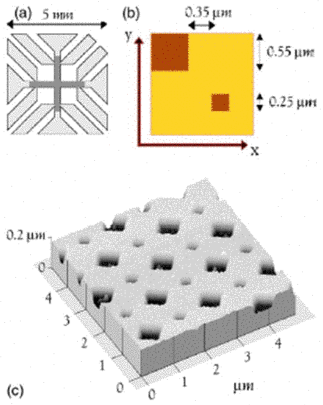

FIG. 1. (Color online) Layout of the Pb film with a composite array of square antidots of two different sizes. (a) Geometry of the sample showing the patterned area in dark gray. (b) Schematic presentation of a unit cell of the antidot array. (c) Atomic force micrograph of a 5×5 μm^2 area of the composite antidot array. The lattice period d is 1.5 μm; the antidot sizes are $a_1 = 0.55$ μm and $a_2 = 0.25$ μm.

Silhanek, A..V., et. al. Phys. Rev. B 72, 14507, 2005

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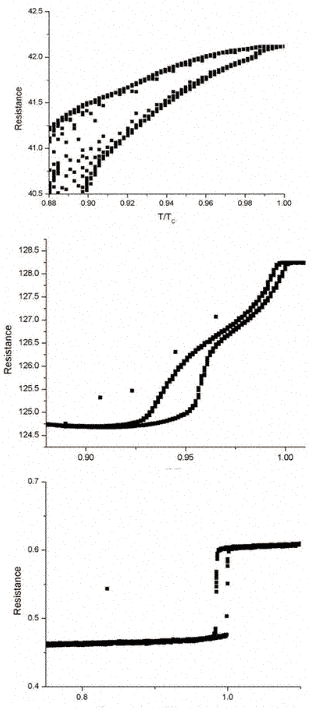
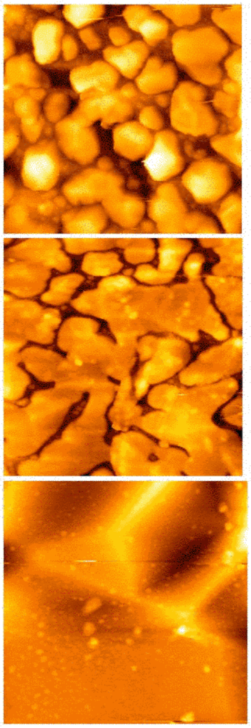
Surface Morphology

- Surface Morphology has a strong effect on the resistance transition. *M. Highland and J. Krim, to be published.*

- Both thickness and residual gas pressure effect the film growth mode





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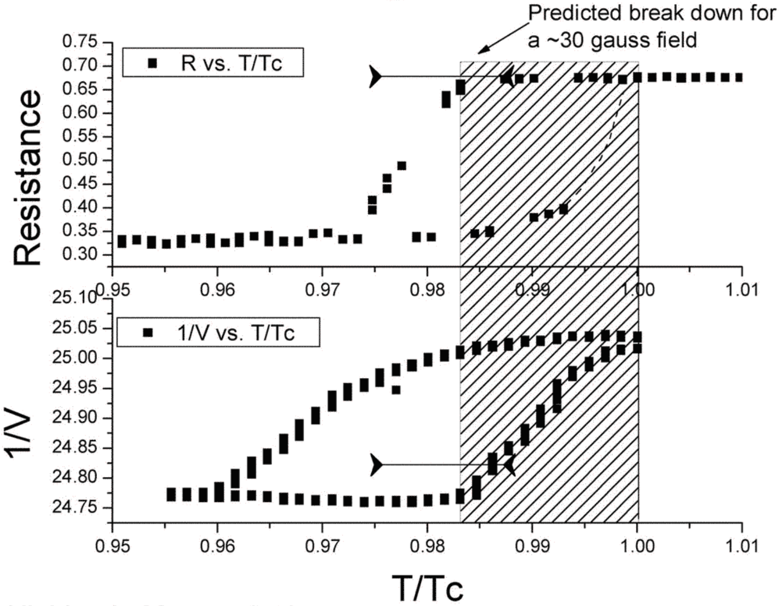
Transition as compared with resistor



Data by M. Highland : Manuscript in preparation

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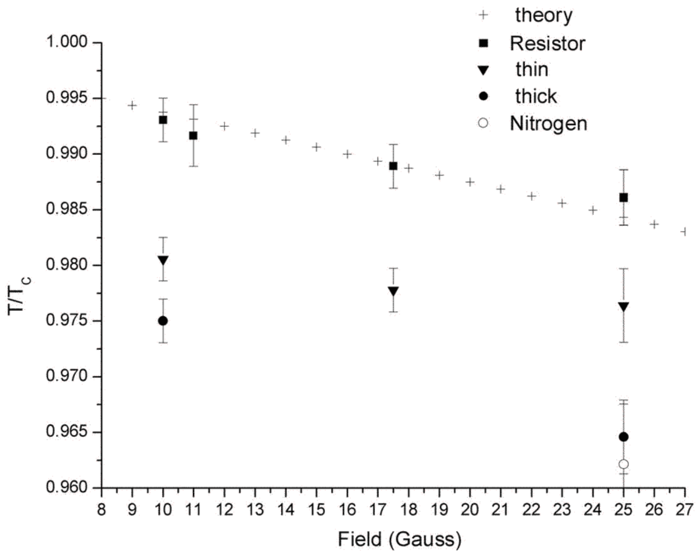
The width of the temperature region is similar for both N_2 and H_2O: He will be studied next.

- Dependence on field strength was observed using water
- Variation of film thickness was originally to isolate surface and bulk effects



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Conclusions

- Superconductivity dependent friction occurs for both N_2 and H_2O sliding on Pb.
- Electronic friction effects may be far smaller in rare gas adsorbates than polar molecules.
- Pb substrate morphology can influence the superconducting transition temperature, allowing us to study transitions at 4K
- Future studies of Helium adsorbates should allow to document a null effect for rare gases, if present.

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