

## Superconductivity Dependent Friction of Water, Nitrogen, and Superheated He Films Adsorbed on Pb(111)

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We report a quartz crystal microbalance study of sliding friction levels in N<sub>2</sub>, H<sub>2</sub>O, and superheated He films adsorbed on Pb(111) substrates alternating in and out of the superconducting state. Reductions in friction upon entry into the superconducting state are greater for N<sub>2</sub> than He, consistent with a recent theory that linked electronic friction to adsorbate polarizability. Our work also reveals that repetitive cycling of an externally applied magnetic field may impact friction.

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The ability to predict sliding friction in adsorbed film systems underlies a vast range of topics in physics and nanotechnology [1], spanning the origins of static friction [2] to the design of atomic scale automobiles [3]. With the advent of new experimental techniques capable of studying the force of friction that results when a finite number of atoms are made to slide on a crystalline substrate, (nanotribology [4]) direct comparisons between experiment and theory have become increasingly realizable. One still hotly debated topic in this area is the degree to which electronic effects contribute to friction [5].

Sliding friction in adsorbed monolayers can be measured experimentally by means of the quartz crystal microbalance (QCM) technique [6]. For vibrational amplitudes above 0.4 nm [7] (vibrational amplitudes for the films studied here are close to 10 nm) the interaction is well characterized by the viscous friction law,  $F = -(m/\tau)v = -m\eta v$  where  $F$  is frictional force that resists sliding and  $m$ ,  $\eta$ ,  $\tau$ , and  $v$  are the mass, drag coefficient, slip time, and average sliding velocity of the adsorbate [6–9]. The drag coefficient  $\eta = 1/\tau$ , (also routinely defined as  $m/\tau$ ) can be written as  $\eta = \eta_{el} + \eta_{ph}$ , where  $\eta_{el}$  and  $\eta_{ph}$  represent the electronic and phononic contributions to friction [5].

Phononic friction is a wear-free energy dissipation mechanism that arises from sliding induced excitation of atomic lattice vibrations. QCM and molecular dynamics studies first documented the existence of phononic friction in the mid 1990's, more than six decades after it was first predicted [4,9]. Firm documentation for the existence of electronic contributions to friction has proven difficult, as phononic and electronic mechanisms are both generally present, with phononic mechanisms tending to dominate [1,10]. Phononic excitations diminish in magnitude at low temperatures however, providing a regime wherein electronic mechanisms are more readily discerned. Arguably, the first clear evidence supporting the existence of non-negligible electronic friction levels was reported in 1998 by Dayo *et al.* [11]. Dayo *et al.* employed a QCM to study the sliding of thin N<sub>2</sub> films adsorbed on a lead surface and observed the friction to drop by almost half when the substrate became superconducting. Given that supercon-

ducting systems exhibit a significant change in electronic properties over a narrow temperature range where changes in phononic behavior are assumed to be minimal, the changes observed at  $T_c$  were attributed to electronic mechanisms.

Dayo *et al.*'s studies drew much attention and also sparked criticism [12–17]. An effort to reproduce the result by Renner *et al.* [12] produced N<sub>2</sub> films that failed to slip at low temperature, and sliding friction measurements can only be performed on films that remain unpinning. A number of distinct theoretical treatments of superconductivity-dependent friction were also put forth that appeared to explain the observation, but not necessarily in its entirety [13–17]. While subsequent studies by our group validated Renner *et al.*'s observations insofar as confirming that nitrogen films are quite susceptible to pinning, [18] experimental comparisons with theoretical prediction have heretofore not been reported.

We focus here on the 2000 study [16] by Bruch, in which analytic calculations of the electronic friction arising from ohmic (resistive) damping of N<sub>2</sub> and Xe monolayers sliding on Pb and Ag substrates were reported to be  $\eta_{el} = 5 \times 10^6 \text{ s}^{-1}$  for Xe/Ag, and  $5 \times 10^7 \text{ s}^{-1} < \eta_{el} < 5 \times 10^8 \text{ s}^{-1}$  for N<sub>2</sub>/Pb. Differences in friction between the two systems were attributed to the presence of a quadrupole moment in the low temperature structure of solid N<sub>2</sub>. It was thus inferred that the effect would be much reduced for inert gas adsorbates such as Xe or He and increased for more polarizable and polar adsorbates, such as H<sub>2</sub>O. Unlike H<sub>2</sub>O, N<sub>2</sub> and He do not have permanent dipole moments. However, when adsorbed onto a surface at low temperatures, induced dipoles in these adsorbates are non-zero, the magnitude of which depends on the polarizability of the adsorbate.

QCM friction measurements are performed by monitoring frequency and amplitude changes that occur when films adsorb onto the surface electrodes of the oscillator. Changes in resonant frequency  $\delta f$  are proportional to the fraction of the mass of the condensed film that tracks the oscillatory motion of the substrate. Amplitude shifts are due to frictional shear forces exerted on the surface elec-

trode. They are converted to quality factor shifts  $\delta(Q^{-1})$  via a “ring-down” calibration method [6]. The experimentally observed frequency shift ( $\delta f$ ) is related to the frequency shift that would have occurred if the film were not slipping ( $\delta f_{\text{film}}$ ) according to [6]

$$\delta(Q^{-1}) = 4\pi\tau(\delta f), \quad \delta f = \frac{\delta f_{\text{film}}}{1 + (\omega\tau)^2}, \quad (1)$$

$$\frac{\delta f_{\text{film}}}{f} = -\frac{2m_f c_f}{\rho_q t_q},$$

where  $\tau$  is the slip time,  $m_f$  and  $c_f$  are the atomic mass and coverage of the adsorbed film,  $\omega$  is the angular frequency of the crystal oscillation,  $\rho_q$  ( $2.65 \text{ g/cm}^3$ ) and  $t_q$  ( $0.021 \text{ cm}$  for  $f = 8 \text{ MHz}$ ) are the density and thickness of the QCM. Therefore the values of ( $\delta f$ ) measured in the superconducting state (where friction is lower and slip times are longer) are smaller in magnitude than corresponding values in the normal state. While some of the mass of the film will always be decoupled from the oscillation, the experimentally measured frequency shift will only be substantially reduced for systems where  $\omega\tau \geq 1$  [6,19].

The microbalance crystals for these studies were overtone-polished 8 MHz AT-cut quartz that had quality factors near  $10^5$ . Thermal evaporation was employed to deposit 200 nm of 99.999% pure Pb atop the blank QCM, producing a mosaic structure with a (111) fiber texture [20]. The base pressure of the vacuum system ranged from  $5 \times 10^{-10}$  to  $1 \times 10^{-9}$  Torr and the deposition rates were on the order of 1 nm/minute. Xe isotherms performed on substrates prepared in this manner exhibit stepwise condensation features [18]. The degree of verticality of the steps present in the isotherm allows the terrace width on the surface to be estimated [21] on the order of 10 nm, typical of (111) films grown by thermal evaporation [22]. Adsorption isotherms revealed no behavior consistent with pore filling or increased surface area [23], ruling out capillary action by the adsorbates.

After preparation of the electrodes, the samples were transferred *in situ* to an adsorption cell, which was attached to an independent and portable ion pump, and then separated from the main ultrahigh vacuum chamber by means of a copper pinch-off device. This constituted a substantial improvement over the sample transfer technique employed by Dayo *et al.*, whereby samples were transferred in ambient to the experimental cell under flowing Ar gas. Within the adsorption cell, the crystal was inserted into metal socket vacuum feedthroughs that connected to external Pierce oscillator circuitry.

At sufficiently high temperatures, adsorbed films have enough thermal energy to remain sliding as they pass over pinning sites on the substrate [7].  $\text{N}_2$  layers are highly susceptible to becoming pinned at low temperature, [12,18] but superconductivity-dependent friction is readily observable whenever they are not. We have never observed pinning for He films in the temperature range 4–10 K, presumably because this temperature range is considered

“hot” for helium. We have also encountered no pinning difficulties for  $\text{H}_2\text{O}$  as an adsorbate, but we attribute this to the wetting behavior of  $\text{H}_2\text{O}$  rather than thermal effects. Water is likely to form frozen droplets on the surface that should be relatively difficult to pin. Similar effects have been reported for microspheres attached to a QCM electrode [24]. Droplet formation however renders calibration of our  $\text{H}_2\text{O}$  data meaningless, since slip time only applies to sliding layers.

Care was required in order to determine the specific conditions for gas adsorption and cell cooling rates that would allow the films to remain on the surface and not pin. For helium films, the sample cell was filled with approximately 5 torr of research grade He after being cooled to 4.2 K. As the sample warmed through the superconducting transition an estimated 1–2 monolayers remain on the surface [25]. For  $\text{N}_2$  films, approximately 100 torr of research grade gas was introduced to the cell at 85 K. As the cell cooled to 4.2 K, the  $\text{N}_2$  that initially adsorbs dewets the surface, leaving a residual  $\text{N}_2$  film on the order of  $1\frac{1}{2}$  monolayers in thickness that did not coexist with a bulk phase. For  $\text{H}_2\text{O}$  experiments, the sample cell was filled with approximately 5 torr of vapor at 300 K. Upon cooling to 4.2 K, it is likely that this system consisted of a thin water layer coexisting with bulk crystallites.

Once all samples were cooled to 4.2 K, they were allowed to warm as the frequency and amplitude of vibration (proportional to the quality factor) were monitored. To observe multiple superconducting transitions, a periodic external magnetic field of 30 G was applied to the system. Figure 1 shows a schematic of the apparatus and the frequency response of samples with adsorbed  $\text{N}_2$ , He, and  $\text{H}_2\text{O}$  in the presence of a magnetic field that repetitively served to alter or destroy the superconducting at temperatures slightly below  $T_c$ . The resonant frequencies are higher in the superconducting state (magnet current off), indicative of lower friction, and thus a more decoupled film. Data were also recorded in the absence of any magnetic field (Fig. 2). Figure 2(b), showing  $\text{N}_2$ , displays the distinctive peak in dissipation that occurs as the system slip time passes through the condition  $\omega\tau = 1$  while warming through  $T_c$  [19]. Helium films do not pass through this condition while warming through  $T_c$ . Since the critical point temperature of He is 5.19 K [26], the helium films studied here are well above their critical point temperature, and are thus referred to as superheated fluids.

Figure 3 shows frequency and dissipation of a QCM with adsorbed  $\text{N}_2$  3(a) and 3(b) and He 3(c) and 3(d) for samples warming through  $T_c$  in the presence of an intermittent magnetic field. Also shown are the values of the drag coefficient in the superconducting and normal states. Frequency shift and dissipation level differences between the superconducting and normal states are readily observable (Figs. 1–3) and straightforward to measure in a highly accurate fashion. We have thus elected to utilize these quantities for our determination of experimental slip times

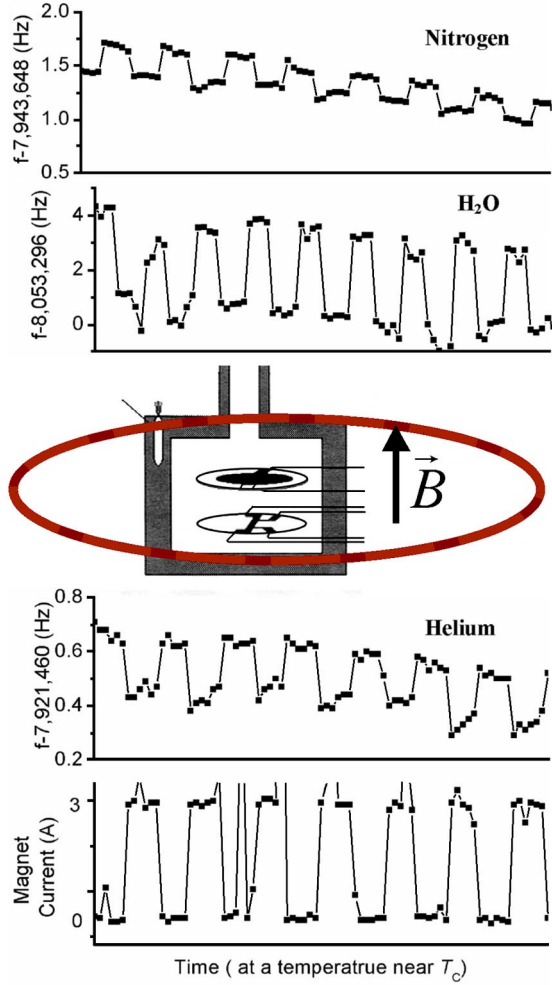


FIG. 1 (color online). Schematic of apparatus and frequency response of  $\text{H}_2\text{O}$ , He, and  $\text{N}_2$  to the presence of a magnetic field at temperatures slightly below  $T_c$ .

and drag coefficients, employing Eq. (1) to express these quantities as:

$$\begin{aligned} (\delta f)_N - (\delta f)_{SC} &= \Delta(\delta f); \\ 4\pi\tau_N(\delta f)_N - 4\pi\tau_{SC}(\delta f)_{SC} &= \Delta[\delta(1/Q)] \end{aligned} \quad (2)$$

The subscript SC denotes quantities measured in the superconducting state, while  $N$  denotes quantities measured in the normal state.

Drag coefficients were obtained numerically by employing the constraint condition that the amount of material on the surface does not change at the superconducting transition, i.e., there is no plausible mechanism for material loss or gain arising from the superconducting state of the substrate. Via Eq. (1), this condition is written numerically as  $(\delta f)_{\text{film}} = (\delta f)_{SC}[1 + (2\pi f\tau_{SC})^2] = (\delta f)_N \times [1 + (2\pi f\tau_N)^2]$ . The helium and nitrogen coverage values utilized to determine our reported drag coefficients were  $28.6 \text{ (ng/cm}^2\text{)}$  and  $41.4 \text{ (ng/cm}^2\text{)}$ , as discussed earlier. We note that slip times and drag coefficients are highly insensitive to the exact coverage assumed: Doubling these values results in a variation of  $\eta$  by only about 20%. As a

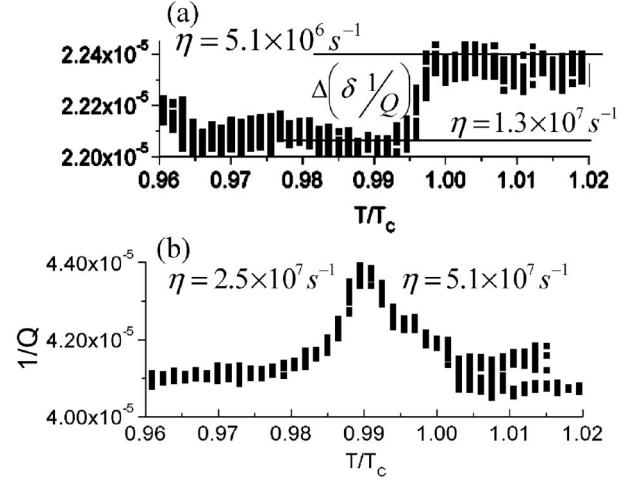


FIG. 2. Response of the QCM with adsorbed (a)  $\text{N}_2$  and (b) He layers in the absence of a cycled magnetic field.

cross-check, the present data analysis approach was also applied to the Dayo *et al.* data, where empty cell values were well established. The obtained values were in good agreement with those reported by Dayo *et al.*

Our overall results are summarized in Table I. Unexpectedly, measurements that were recorded on samples in the presence of the time changing magnetic field (em-

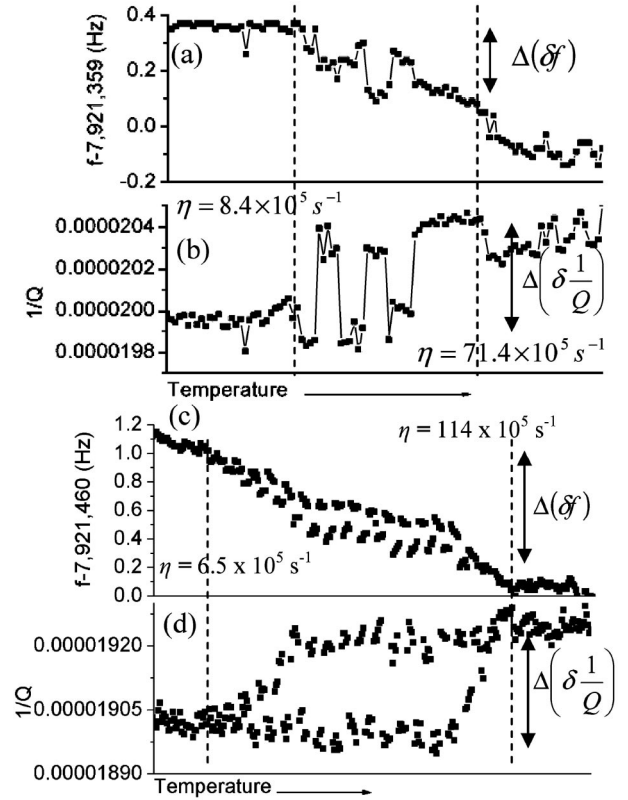


FIG. 3. Frequency and inverse quality factor response of the QCM with adsorbed (a)  $\text{N}_2$  and (b) He layers as it warms through  $T_c$  in the presence of a magnetic field that is repetitively cycled on and off.

TABLE I. The drag coefficients for sliding layers on a Pb substrate in the superconducting and normal states are shown with and without a time changing magnetic field. Also shown are the drag coefficients calculated from Bruch's theory.

	No Magnet		Cycled Magnet		Theory	
	N <sub>2</sub> /Pb (10 <sup>7</sup> s <sup>-1</sup> )	He/Pb (10 <sup>7</sup> s <sup>-1</sup> )	N <sub>2</sub> /Pb (10 <sup>7</sup> s <sup>-1</sup> )	He/Pb (10 <sup>7</sup> s <sup>-1</sup> )	N <sub>2</sub> /Pb (10 <sup>7</sup> s <sup>-1</sup> )	Xe/Ag (10 <sup>7</sup> s <sup>-1</sup> )
$\eta_{SC}$	2.5	0.51	0.084	0.065	...	...
$\eta_n$	5.1	1.3	0.714	1.14	...	...
$\eta_n - \eta_{SC}$	2.6	0.79	0.63	1.08	5-50	0.5

ployed here simply with the intention of inducing multiple transitions) consistently yielded friction levels that were reduced in magnitude from those recorded in the absence of a repetitively cycled field. The effect was observed for both N<sub>2</sub> and He sliding films, and must be mentioned for purposes of completeness in reporting. The origin of this effect remains however entirely beyond our present understanding, and far beyond the scope of our present investigation.

The present observations are consistent with a recent study reported by Coffey and Krim for Xe monolayers at 77.4 K sliding on metal substrates with varying degrees of surface corrugation [1]. In this study, it was found that phononic models of friction matched experimentally observed values so well that the electronic contribution to friction could be neglected altogether. The phononic friction levels reported in Ref. [1] are much larger than what we observe here for He sliding on Pb, presumably on account of the fact that phononic friction should be significantly reduced at 7.2 K as compared to 77.4 K. Although the fraction of electronic friction for both He and N<sub>2</sub> sliding on Pb is roughly the same (~0.40), the difference in  $\eta$  for He between superconducting and normal states,  $7.9 \times 10^6$  s<sup>-1</sup>, which is attributed to the electronic component  $\eta_{el}$ , is substantially lower than that observed for N<sub>2</sub>/Pb. The latter change,  $2.6 \times 10^7$  s<sup>-1</sup>, falls near the range of values obtained by Bruch's predictions  $5 \times 10^7$  s<sup>-1</sup> <  $\eta_{el}$  <  $5 \times 10^8$  s<sup>-1</sup> for N<sub>2</sub>/Pb.

In conclusion our results firmly support Bruch's overall observations. Further theoretical work will be needed to determine whether the existence of a quadrupole moment in an adsorbed film determines electronic friction levels in these specific systems.

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- [1] T. Coffey and J. Krim, Phys. Rev. Lett. **95**, 076101 (2005); J. Krim, Am. J. Phys. **70**, 890 (2002).  
 [2] M. H. Muser, L. Wenning, and M. O. Robbins, Phys. Rev. Lett. **86**, 1295 (2001); G. He, M. H. Muser, and M. O. Robbins, Science **284**, 1650 (1999).

- [3] M. Porto, M. Urbakh, and J. Klafter, Phys. Rev. Lett. **84**, 6058 (2000).  
 [4] J. Krim, D. Solina, and R. Chiarello, Phys. Rev. Lett. **66**, 181 (1991).  
 [5] B. N. J. Persson, *Sliding Friction: Physical Principles and Applications* (Springer-Verlag, Berlin, 2000), 2nd ed.  
 [6] J. Krim and A. Widom, Phys. Rev. B **38**, 12 184 (1988); E. T. Watts, J. Krim, and A. Widom, Phys. Rev. B **41**, 3466 (1990); M. Rodahl *et al.*, Rev. Sci. Instrum. **66**, 3924 (1995).  
 [7] L. Bruschi, A. Carlin, and G. Mistura, Phys. Rev. Lett. **88**, 046105 (2002); C. Mak and J. Krim, Phys. Rev. B **58**, 5157 (1998).  
 [8] C. M. Mate and B. Marchon, Phys. Rev. Lett. **85**, 3902 (2000).  
 [9] M. Cieplak, E. D. Smith, and M. O. Robbins, Science **265**, 1209 (1994).  
 [10] M. S. Tomassone *et al.*, Phys. Rev. Lett. **79**, 4798 (1997).  
 [11] A. Dayo, W. Alnasrallah, and J. Krim, Phys. Rev. Lett. **80**, 1690 (1998).  
 [12] R. L. Renner, J. E. Rutledge, and P. Taborek, Phys. Rev. Lett. **83**, 1261 (1999); J. Krim, Phys. Rev. Lett. **83**, 1262 (1999); R. L. Renner, P. Taborek, and J. E. Rutledge, Phys. Rev. B **63**, 233405 (2001).  
 [13] T. Novotny and B. Velicky, Phys. Rev. Lett. **83**, 4112 (1999).  
 [14] B. N. J. Persson and E. Tosatti, Surf. Sci. **411**, L855 (1998).  
 [15] J. B. Sokoloff, M. S. Tomassone, and A. Widom, Phys. Rev. Lett. **84**, 515 (2000).  
 [16] L. W. Bruch, Phys. Rev. B **61**, 16 201 (2000).  
 [17] S. Sh. Rekhviashvili, Tech. Phys. Lett. **30**, 4 (2004).  
 [18] B. L. Mason, S. M. Winder, and J. Krim, Tribol. Lett. **10**, 59 (2001).  
 [19] J. B. Sokoloff, J. Krim, and A. Widom, Phys. Rev. B **48**, 9134 (1993).  
 [20] K. L. Chopra, *Thin Film Phenomena* (McGraw-Hill, New York, 1969).  
 [21] Y. Larher, Mol. Phys. **38**, 789 (1979).  
 [22] J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. Lett. **52**, 640 (1984).  
 [23] C. L. Wang, J. Krim, and M. F. Toney, J. Vac. Sci. Technol. A **7**, 2481 (1989).  
 [24] F. N. Dultsev, V. P. Ostanin, and D. Klenerman, Langmuir **16**, 5036 (2000).  
 [25] M. Cole (private communication).  
 [26] V. V. Syhev *et al.*, *Thermodynamic Properties of Helium* (Hemisphere, Washington, 1987), Vol. 1, p. 131.