

Friction and pinning of nitrogen films on lead substrates near the superconducting transition

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We have used a quartz crystal microbalance to study the dynamical properties of thin films of solid nitrogen adsorbed on a lead substrate in the temperature range $4\text{ K} < T < 14\text{ K}$. Simple mechanical models relate the frequency shift and the Q of the microbalance to the friction at the N_2/Pb interface. By varying either the magnetic field or the temperature, the Pb substrate could be prepared in the superconducting or normal state. Our experiments indicate that superconductivity has no effect on the behavior of the microbalance. Furthermore, experiments in which the N_2 layer thickness was varied by *in situ* evaporation showed that solid nitrogen films are rigidly pinned on our low-temperature substrate for velocities below approximately 0.6 m/sec.

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The microscopic interactions that give rise to macroscopic frictional forces between solid bodies in contact are not completely understood. In principle the interaction is mediated by the electrons or the phonons in each medium, but the relative importance of these two mechanisms has not been clearly established.¹⁻⁴ Recently, Dayo, Alnasrallah, and Krim⁵ (DAK) have developed a novel experimental technique that utilizes the superconducting phase transition to help identify the contributions of electrons and phonons to frictional forces. When a superconductor is driven from the normal to the superconducting state the electron density of states is drastically altered by the formation of a gap in the energy spectrum, but the phonon modes are essentially unaffected. Comparison of the frictional forces at a metal/insulator interface on either side of the superconductor/normal transition can therefore help to determine the role of electronic coupling in friction at low temperature. DAK used a quartz microbalance technique to study friction between a lead substrate and an adsorbed film of solid nitrogen a few monolayers thick. Their results implied that the frictional forces at the Pb/N_2 interface drop abruptly by approximately a factor of 2 as the lead becomes superconducting. In a previous Comment we have reported results of similar experiments that show no dependence of the friction on the superconducting transition and in fact show that in our samples the nitrogen is completely pinned to the substrate.⁶ The purpose of this paper is to document the experimental data that lead to those results.

We used 8 and 5 MHz overtone AT-cut quartz crystal microbalances (QCM's) to study the mechanical properties of a nitrogen adsorbate on a lead substrate. The QCM behaves electrically as an RLC circuit⁷ with a resonant frequency of $1/2\pi\sqrt{LC}$ and Q of $\frac{1}{2}\sqrt{L/C}$. Each of these electrical parameters are determined by measuring the response of the QCM at a number of discrete frequencies near the resonance using a HP4396A network analyzer and fitting the measurements to an equivalent circuit model similar to that described in Ref. 7. Changes in the resonant frequency and Q can be related to changes in the mechanical properties of an adsorbed layer, as described in Ref. 8.

The quartz crystals, which had mirrorlike gold electrodes, were used as received from the manufacturer.⁹ A 1500 Å thick lead film was thermally evaporated onto the gold elec-

trodes on each side of the QCM in a conventional laboratory bell jar with a residual gas pressure of 1.5×10^{-6} torr. The sample was then transferred through air and loaded into the experimental cell, which was immediately pumped down to 10^{-6} torr. The cell was flushed several times with 99.9995% purity N_2 and then pressurized to 5500 torr. The apparatus was then cooled to 4.2 K over a 36 hour period.

The experiment cell was an oxygen-free (OFHC) copper can suspended within a vacuum space with a weak thermal link to the cryogenic bath. This provided an isothermal environment with good temperature control; a similar apparatus was previously used for high-precision thermodynamic measurements.¹⁰ The cell contained a germanium resistance thermometer, a heater, and a QCM secured to a common copper block. The cell was also equipped with a cold valve on the nitrogen fill line. Closing this valve after loading the cell at room temperature eliminated the possibility of subsequent thermal-gradient-induced mass transport. Mutual inductance coils on opposite sides of the microbalance, shown in Fig. 1, were used to probe the superconducting state of the lead. A magnet coil in the external bath could be used to produce a magnetic field perpendicular to the Pb films, which could drive the superconducting films normal even at temperatures below T_c .

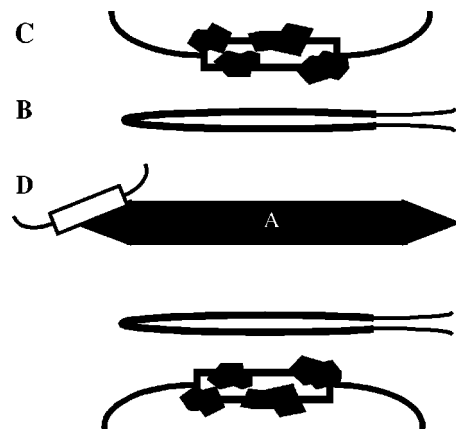


FIG. 1. The QCM (A) was placed between mutual inductance coils (B), used to sense the superconducting state of the Pb substrate. Charcoal covered resistors (C) were used to evaporate N_2 *in situ*. A heater (D) epoxied onto the beveled edge of the QCM was used to locally heat the QCM to remove the N_2 film.

For some experiments it was important to add and remove nitrogen from the QCM in a controlled way. To accomplish this, some of the QCM's had a small resistor epoxied to the beveled edge. This typically reduced the Q by approximately a factor of 5. Fractions of a watt of power dissipated in this resistor in vacuum at low temperature would locally increase the temperature of the QCM by hundreds of kelvins, which would desorb most of the adsorbed nitrogen. The local temperature could be monitored quite accurately, since the resonant frequency has a temperature coefficient of approximately 25 Hz/K over a wide temperature range. Nitrogen could be added to the QCM using a thermal evaporation technique. 1/8 watt resistors with 40 mesh charcoal particles epoxied to their surfaces were placed inside each mutual inductance coil. During the cool-down, the charcoal became saturated with N_2 . At low temperatures, a few milliwatts of power were sufficient to desorb N_2 at a rate corresponding to several monolayers per minute onto the QCM.

Our first set of experiments utilized equilibrium solid N_2 films that form spontaneously as the apparatus is cooled. It is well known that solid films do not wet solid substrates,^{11,12} and previous investigations have shown that the equilibrium thickness of molecular solids on QCM surfaces is a few layers.^{10,12} We investigated the frictional properties of such equilibrium films by repeatedly ramping the cell temperature up and down in the vicinity of 7.2 K, which is the bulk T_c for lead. Although the superconducting transition in the lead films is clearly evident from the mutual inductance signal in Fig. 2(b), we observed no change in the frequency shift within our resolution of 0.1 Hz resolution, as shown in Fig. 2(c). In contrast, DAK reported a 5 Hz jump in frequency in a similar experiment.

We considered several possible explanations of our failure to detect any change in the properties of the oscillator above and below the superconducting transition of the substrate film. Some of the possibilities include (1) relative motion and friction between the adsorbed nitrogen and the substrate could have a finite value, but the friction is independent of superconductivity, or (2) the nitrogen adsorbate could be so strongly bound to the substrate that there is no relative motion and therefore no friction throughout the temperature range of interest, and no effect due to superconductivity, or (3) due to inevitable thermal gradients during cool-down, the nitrogen could be preferentially deposited on the cold walls of the cell, in which case the nitrogen coverage on the QCM would be below its equilibrium value. The extremely low adsorbate coverage might again lead to no friction and no observable effects of superconductivity.

To distinguish among these possibilities it is important to establish the properties of the bare oscillator, and to study the dependence of the frequency shift and Q as a function of adsorbate coverage at a constant temperature. Since friction must vanish in the limit of zero coverage, this type of measurement provides a direct quantitative method of measuring the friction without relying on possible effects due to changes in the substrate. The reference state that approximated zero coverage was produced by applying power to the heater on the QCM and raising the temperature to 160 K for approximately 30 s, which desorbed all but the most tightly

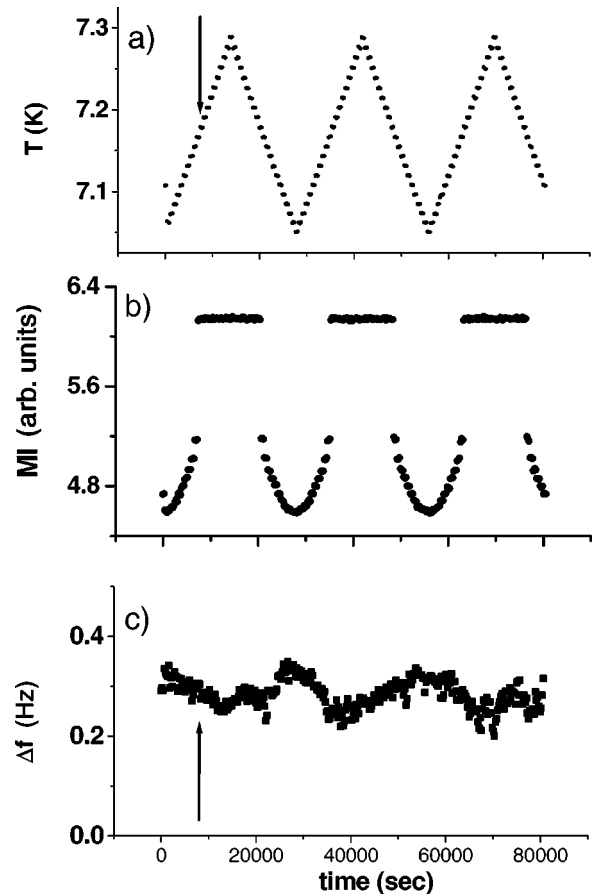


FIG. 2. Temperature of the cell as a function of time. The arrow marks the position of the superconducting transition as detected by the mutual inductance coils. (b) Mutual inductance (MI) signal as a function of time. The discontinuities mark the superconducting transition. The flat regions are in the normal state. (c) Frequency shift of the QCM as a function of time during the temperature ramps. The arrow marks the first excursion across the normal phase/superphase boundary. Df varies by less than 0.1 Hz and there are no features associated with the transition.

bound molecules on the surface. After the oscillator cooled back to 4.2 K, a frequency shift corresponding to the removal of 2.5 atomic layers of nitrogen was detected, consistent with our expectations for the equilibrium film thickness.

The charcoal evaporation sources were subsequently used to deposit 9.5 atomic layers of N_2 on each side of the QCM. The changes in the frequency and R (proportional to $1/Q$) of the oscillator during one of the nitrogen evaporations are shown in Fig. 3. The frequency drops monotonically and reaches a lower constant level after the evaporation, indicating additional mass on the QCM. The dissipation increases by about 1% during the evaporation, but returns to its initial value after the evaporation heaters are turned off. The small increase in dissipation was a transient thermal effect that was observed during each evaporation. Figure 4 shows that the addition of 9.5 layers of N_2 to a nominally bare substrate from which the equilibrium N_2 film had been removed had no detectable effect on the dissipation and thus no detectable friction.

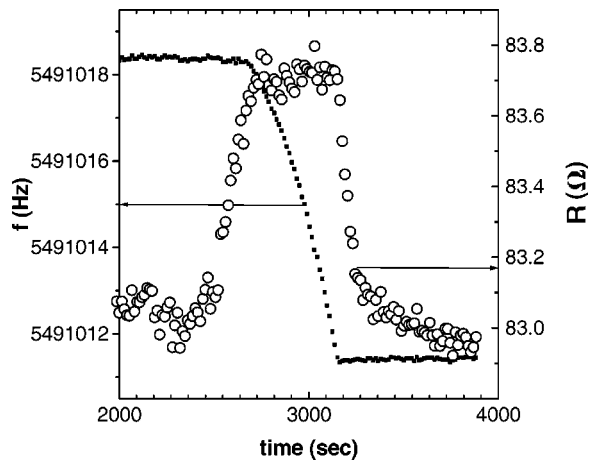


FIG. 3. *In situ* evaporation of nitrogen onto a bare lead substrate at 4.2 K. The figure shows the frequency (filled points) and the resistance R (open points) of the QCM. During the evaporation, the frequency drops by about 7 Hz, which corresponds to approximately 9.5 layers of N_2 . The dissipation as measured by R rises slightly during the evaporation, but returns to its initial value when the deposition is complete. The dissipation due to the added N_2 layers is thus below our detection threshold.

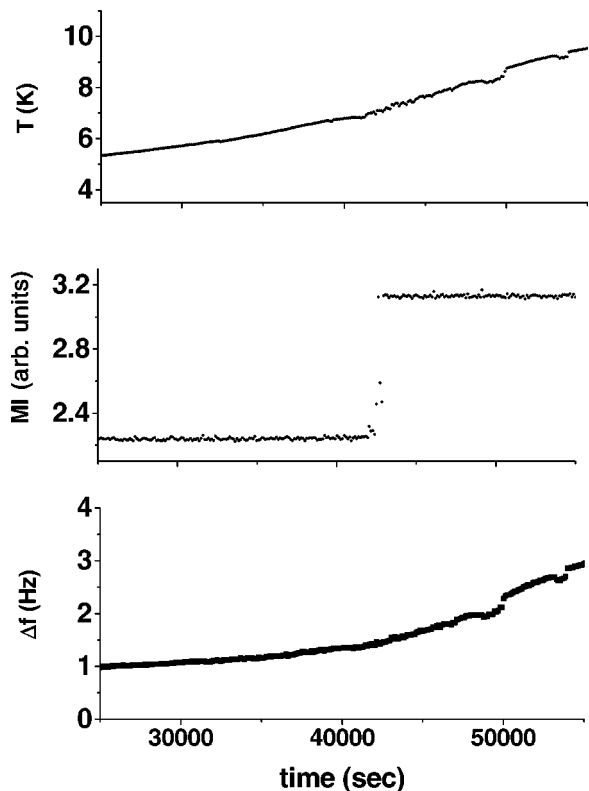


FIG. 4. Effects of superconductivity on the QCM signal for a N_2 film 9.5 layers thick evaporated *in situ*. The temperature is varied from 5.2 to 10 K. No features in the frequency are observed at the transition, which occurred at a time of approximately 41 000 s. The gradual 2 Hz change in Δf through this range is due to the temperature dependence of the oscillator and is observed even without a Pb film on the QCM.

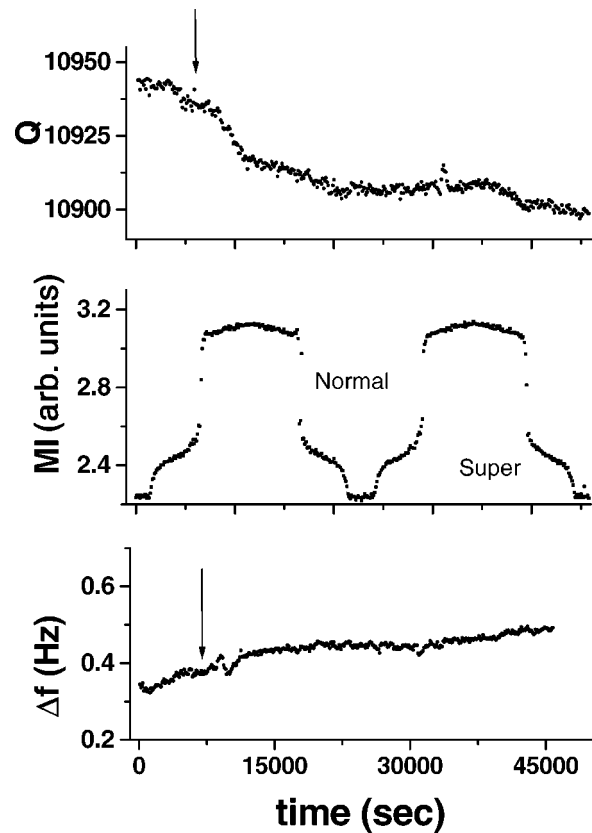


FIG. 5. Effects of crossing the superconducting transition at $T = 7.0$ K using an external applied magnetic field. A sawtooth wave form is applied to the external magnet coil, which drives the Pb film from the superconducting state, corresponding to the mutual inductance signal $MI = 2.2$, to the normal state, corresponding to $MI = 3$. There are no features in either Q or Δf associated with the transition.

The data of Fig. 3 were taken at 4.2 K, so the substrate was superconducting. To check for possible effects of superconductivity on friction for thicker, nonequilibrium films, the temperature was ramped through the transition as shown in Fig. 4. As for the equilibrium thickness films, no shift in the frequency was observed to within our resolution of 0.1 Hz. We also checked for possible superconducting effects by crossing the supernormal boundary at fixed temperature by sweeping the magnetic field, as shown in Fig. 5. In contrast to the zero field case, a magnetically induced superconducting phase transition is first order, resulting in a discontinuous change in the electron density of states. The mutual inductance signal shows that the substrate made several transitions from super to normal, but the transition had no noticeable effect on the frequency shift or Q . This experiment was repeated using a variety of substrates, QCM's, and different adsorbate thicknesses, but no effects attributable to a difference in the friction properties between the superconducting and normal substrate were observed.

Our experimental data show that all of the nitrogen films we investigated were rigidly pinned to the substrate. Since there is no relative motion between substrate and adsorbate, there is no friction, and our experiment therefore provides no information about the possible effects of superconductivity

on electronic friction mechanisms. The rigid coupling between substrate and adsorbate we observe is in fact expected on general theoretical grounds. Persson and Volokitin^{13,14} have argued that in the limit of small driving amplitudes and low temperatures, an arbitrarily small amount of surface disorder will pin an adsorbed film. For sufficiently large-amplitude motions, however, the surface accelerations and forces can presumably become large enough to overcome the pinning potential and to cause relative motion of the adsorbate. In an attempt to depin our nitrogen films, we increased the power used to drive the QCM from our usual operating value of -50 dBm to -10 dBm, which corresponds to a variation of the drive voltage from 7×10^{-2} V to 7×10^{-4} V. We estimate the amplitude of oscillation A from the formula $A \cong dVQ$, where d is the appropriate piezoelectric coefficient^{15,16} and V is the drive voltage. Increasing the power by four orders of magnitude corresponds to an increase in the amplitude of oscillation by two orders of magnitude from approximately 1.6×10^{-9} m to 1.6×10^{-7} m. The maximum velocity of the substrate is ωA , which ranged from 0.0028 to 0.56 m/s for our QCM's. Even at the highest drive powers investigated, we observed no change in the frequency or Q associated with the superconducting transition. Apparently in our samples, even substrate accelerations $\omega^2 A > 10^6$ g are insufficient to depin the adsorbate.

In summary, we have used the quartz microbalance technique to search for sliding friction between adsorbed solid nitrogen films and lead substrates. We have driven the lead substrates through the superconducting transition by changing the temperature at zero applied magnetic field and by sweeping the magnetic field at fixed temperature. We located

the superconducting transition by monitoring the magnetic susceptibility of the lead on the microbalance. We have studied adsorbed nitrogen films grown in equilibrium at high temperatures and then cooled to a few degrees and nonequilibrium films evaporated onto the lead film at low temperature. In all cases we have directly verified that nitrogen was present on the substrate and was not removed by some spurious means such as temperature gradients before the superconducting transition was reached. In no case did the microbalance signal change at the superconducting transition. Indeed in all cases the microbalance dissipation was completely independent of the presence of the adsorbed nitrogen, indicating that the nitrogen film was pinned to the substrate. This result stands in contrast to the sharp signals in both the dissipation and resonant frequency observed by DAK at a temperature that they inferred to be the lead transition temperature. We speculate that the contrasting results are due to subtle differences in the lead films. The lead substrate preparation technique we used was nominally identical to the one used by DAK as described in their paper. This technique necessarily exposes the lead surface to oxidation and contamination due to its exposure to air in the laboratory. Differences in humidity or the chemical composition of other contaminants in the laboratory environment might result in different densities or strengths of pinning centers. If this is the case, further insight into the electronic contribution to sliding friction from the superconductivity technique must await the study of contamination free surfaces made and maintained in UHV.

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