Superconductivity-Dependent Sliding Friction

A. Dayo, W. Alnasrallah, and J. Krim*

Physics Department, Northeastern University, Boston, Massachusetts 02115
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We have employed a quartz crystal microbalance technique to measure the friction associated with sliding of solid nitrogen along a lead surface, above and below the lead's superconducting transition temperature. The friction is observed to drop abruptly at the transition as the substrate enters the superconducting state. The observation signifies a new phenomenon, most likely attributable to electronic contributions to friction. While such contributions have been discussed and debated theoretically for a number of years, they have heretofore not been observed in any direct experimental fashion. [S0031-9007(98)05391-5]

Studies of the fundamental origins of friction have undergone rapid progress in recent years with the development of new experimental and computational techniques for measuring and simulating friction at atomic length and time scales [1]. The increased interest has sparked a variety of discussions and debates concerning the nature of the atomic-scale mechanisms which dominate the dissipative process by which mechanical energy is transformed into heat. While much recent attention has focused on phonon contributions to friction [2], electronic mechanisms for friction due to sliding-induced excitations of conduction electrons at metallic interfaces have also been put forward [3–6]. Such mechanisms are quite distinct from the friction associated with static charge buildup, a theoretical problem which, from Coulomb's original work on friction [7] until the present time, remains unsolved. We focus here instead on electronic contributions to friction which do not involve a buildup of excess charge near an interface, but rather the manner in which conduction electrons near a material interface respond to its sliding motion.

Direct experimental studies of electronic contributions to friction could greatly aid theoretical progress, since to date a theoretical consensus on the topic has not evolved [3–6]. A variety of intriguing applications are possible, moreover, in systems where electronic contributions are found to be significant. For example, systems characterized by substantial enough electronic friction forces would allow surface transport of adsorbed atoms or molecules via the drag forces exerted by an electrical current. While indirect and/or qualitative experimental evidence for electronic contributions to sliding friction has been suggested in a number of past studies [8], a direct and quantitative experimental measurement has never been reported.

Thus motivated, we investigated the friction associated with sliding of an arbitrary material (nitrogen) along an arbitrary superconductor (lead) above and below the metal's superconducting transition temperature. While it might be argued that phononic contributions to friction could vary somewhat from the normal to the superconducting state of the metal, the primary impact of the transition arguably remains with the superconducting material's conduction electrons and/or electron-phonon coupling effects.

We report here the results of our investigation, where we have utilized a quartz crystal microbalance (QCM) technique to record the sliding friction measurements. We observed the friction associated with nitrogen sliding over lead in its superconducting state to be approximately half that observed for its normal state. The observation signifies a new phenomenon, which is open for theoretical interpretation.

The quartz crystal microbalance technique has for decades been used for microweighing purpose, and was adapted for friction measurements in 1986–1988 by Widom and Krim [9]. A QCM consists of a single crystal of quartz which oscillates in transverse shear motion with a quality factor Q near 10^5. Adsorption onto the microbalance produces shifts in both the frequency f_0 and the quality factor Q, which are indicative of the degree to which the adsorbate is able to track the oscillatory motion of the underlying substrate. Characteristic slip times τ, and friction coefficients (i.e., shear stresses per unit velocity) η, are determined via the relations [9]:

$$\delta(Q^{-1}) = 4\pi\tau\delta f_0, \qquad \eta = \rho_2/\tau, \qquad (1)$$

where ρ_2 is the mass per unit area of the adsorbate.

For the present study, the resonant frequency was recorded directly from the output of a Pierce oscillator circuit designed to drive the QCM at its series resonant frequency. Changes in Q, which for this circuitry were proportional to changes in the electrical amplitude A of the output signal, were calibrated by comparing A to direct Q measurements taken from decay curves of the QCM oscillation signal for helium adsorption at 4.2 K [10]. (In past studies [11], the calibration was performed by monitoring the response of A to a nonadsorbing vapor with a known acoustic impedance, thus a known δQ^{-1}. This approach proved impossible for the present study, since there are no nonadsorbing vapors with which to perform such a calibration at 4.2 K.)

QCM amplitude and frequency shift data were recorded with and without nitrogen adsorbed onto the surface of

1500 Å thick lead film electrodes, above and below the superconducting transition temperature of the lead which is known to be at 7.2 K [12]. The lead electrodes were prepared by thermal evaporation of 99.9999% pure metal at 0.05–0.1 nm/s and residual gas pressure 10^{-8} torr onto 8 MHz overtone polished quartz crystals [13]. The electrodes, presumably exhibiting a (111) fiber texture [14], were briefly (10–15 minutes) exposed to air while transferring the sample [15].

Nitrogen adsorption was performed under equilibrium conditions by introducing 100–150 torr of gas into the experimental chamber at 85 K, followed by cooling the chamber to 4.2 K. A fixed amount of solid nitrogen, the equivalent of 1–2 ML, as determined by the frequency shift data, was thus present on the surface electrodes of the QCM as the friction data were recorded. Given that the quantity of adsorbed nitrogen remained nearly constant upon cooling to helium temperatures, it is likely that the adsorbed nitrogen remained in the form of a molecularly thin film as it cooled. We did not, however, seek to verify the exact morphology of the adsorbed nitrogen, as the central purpose of our study was to examine the effect of a superconducting transition on sliding friction at an arbitrary material interface.

In order to monitor transitions into and out of the superconducting state, a four-wire Pb pattern for resistivity measurements was evaporated under identical conditions onto a quartz crystal substrate and then placed in close proximity to the QCM within the experimental chamber (Fig. 1). A thermometer was located nearby, embedded into the experimental chamber wall. While the geometry did not hold all components at precisely the same temperature, it was entirely adequate for the purpose of marking transitions into and out of the superconducting

state as the experimental chamber was lowered and raised into and out of a surrounding liquid helium bath.

Initially, we performed a large number of rapid plunges of the chamber into and out of the bath in order to search for any distinguishing features in the data sets associated with the presence of adsorbed nitrogen. The resistivity sample displayed transitions into and out of the superconducting state during this initial screening process, but the presence or absence of adsorbed nitrogen had no noticeable effects. The QCM frequency shift data failed to display distinguishable characteristics associated with either the presence of adsorbed nitrogen or the superconducting transition of the electrodes. This observation was rather inconclusive, however, since the frequency data were rendered somewhat unreliable by the rapid changes in temperature and the mechanical motions associated with plunges into and out of the helium bath, which produced drifts and uncertainties in the data on the order of ± 5 Hz.

In contrast to the resistivity and QCM frequency data, the QCM amplitude data consistently exhibited distinctive features whenever adsorbed nitrogen was present. Figure 2 displays a typical data set, where inverse amplitude (A^{-1}) versus time is plotted as the chamber is plunged 4 times into (downward arrows) and raised three times out of (upward arrows) the helium bath over a period of 1000 s. The lower data set, depicted by crosses, was recorded on bare surface electrodes. No distinctive features whatsoever were ever observed in the amplitude data in the absence of adsorbed nitrogen as the QCM electrodes entered and exited the superconducting state. The upper data set in Fig. 2 was recorded with nitrogen adsorbed on the surface electrodes. Two features distinguish this data set from that recorded on bare electrodes. First, the overall dissipation level, proportional to the inverse electrical
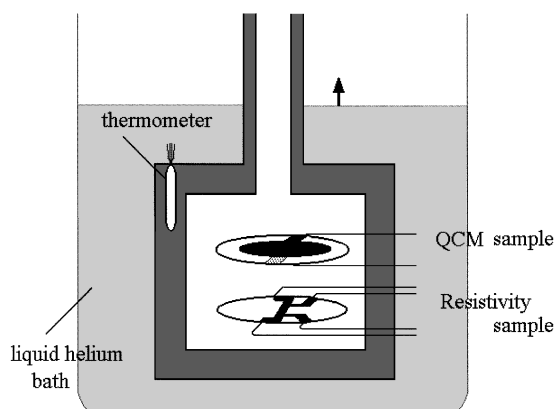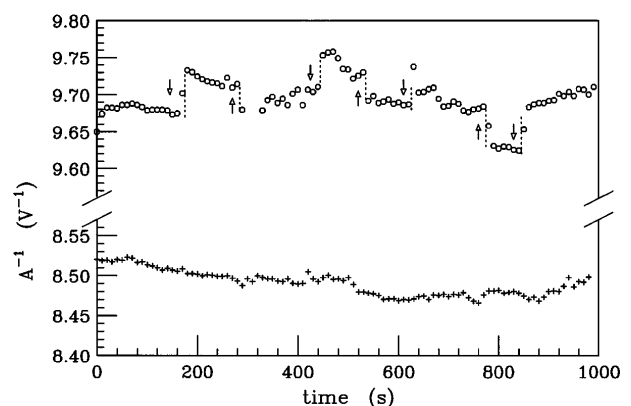

FIG. 1. Schematic of the experiment. Sliding friction measurements were carried out using a QCM, driven at its resonance frequency by a Pierce oscillator circuit (not shown). Resistance measurements using standard 4-wire technique were included to monitor the superconducting phase transitions. Data were recorded while the system was plunged in and out of a liquid helium bath, with and without adsorbed nitrogen on the Pb electrodes.

FIG. 2. Inverse QCM electrical amplitude data for bare Pb (+) and for N_2/Pb (∘) during an initial screening process to check for any characteristics associated with the superconducting transitions of the Pb electrodes. No distinctive features were observed in the absence of adsorbed nitrogen. For N_2/Pb, the overall dissipation levels due to the sliding of nitrogen on the lead surface (proportional to A^{-1}) increased, and the inverse amplitude was characterized by discontinuities when the system was plunged in (↓) and out (↑) of a liquid helium bath.

amplitude A^{-1}, is markedly increased. The additional dissipation is readily attributable to frictional energy dissipation associated with sliding of the nitrogen along the lead surface due to the oscillatory motion of the substrate. The data set is also distinguished by the presence of discontinuities as the sample enters and exits the superconducting state, indicative of differences in sliding friction levels between the normal and superconducting states.

In order to quantify these qualitative observations, high stability frequency as well as amplitude data were required. This necessitated eliminating the detrimental effects of mechanically lowering and raising the sample into and out of the liquid helium bath. We therefore first brought the sample to its superconducting state by lowering it into the liquid helium bath and allowing it to equilibrate for a long time at 4.2 K while continuously monitoring the QCM and resistivity sample data outputs. As the helium bath evaporated and the system temperature slowly rose, data were then recorded until the system's temperature was well above the superconducting transition point. The procedure was performed with and without nitrogen present on the surface and, as in the earlier screening runs, distinctive features in the QCM data occurred only in the presence of adsorbed nitrogen.

Figure 3 depicts a typical data set recorded in this manner with (circles) and without (crosses) adsorbed nitrogen present. The time axis for the two data sets is defined by assigning the resistivity sample's transition from the superconducting state to its normal state to time $t = 800$ s. The difference is transition times between the QCM and resistivity samples is attributable to slightly different warming rates between the two samples. Within experimental error, the resistivity sample's resistance displayed no sensitivity to the adsorbed nitrogen.

The QCM frequency and amplitude raw data are plotted in Figs. 3(a) and 3(b). As in the earlier screening runs, the QCM displayed no discernible features associated with the superconducting to normal phase transition of bare Pb electrodes. Indeed, we expected no striking features. The change in the QCM electrodes' electrical resistance upon entrance to the superconducting state was negligible compared to the overall system parameters and the change in the effective mass of the electrodes due to (potential) decoupling of all conduction electrons from the oscillatory motion of the QCM would have produced only a 0.15 Hz discontinuity.

When nitrogen was adsorbed on the superconducting electrode, the frequency was typically lowered by 8–12 Hz due to the additional mass loading, and the inverse electrical amplitude increased by $\delta A^{-1} = 2.8 V^{-1} \equiv \delta Q^{-1} = 1.6 \times 10^{-6}$, attributable to the energy dissipation associated with the sliding motion of the nitrogen. As the temperature increased, the transition was marked by discontinuities in both the frequency ($\delta f_0 = -5.5$ Hz) (now discernible due to increased stability of the data taking procedure) and amplitude, $\delta A^{-1} = 0.4 V^{-1} \equiv \delta Q^{-1} = 3 \times 10^{-7}$. The discontinuities in both the
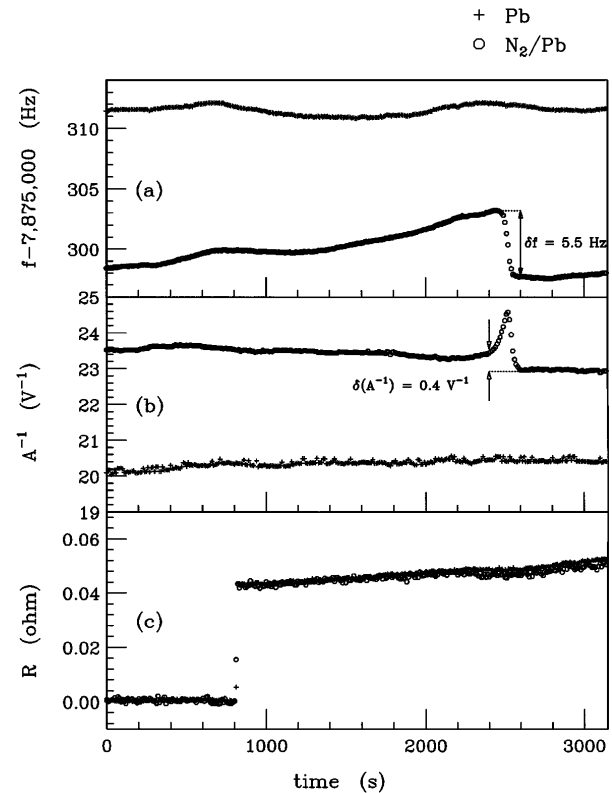

FIG. 3. Typical QCM and resistance data for bare Pb (+) and for N_2/Pb. (a),(b) As in the earlier screening runs, no distinctive features associated with the superconducting phase transitions of the substrate were observed in the absence of adsorbed nitrogen. For N_2/Pb, a frequency shift due to mass loading and an inverse amplitude shift due to the energy dissipation associated with the sliding motion of nitrogen on lead were observed. Moreover, the transition from the superconducting to normal phase of the QCM sample (at time $t = 2500$ s) was distinguished by discontinuities in both the frequency and amplitude data. The additional frequency shift indicates an increase in *effective* mass due to decreased slippage between the nitrogen layers and the Pb electrodes (the actual number of adsorbed particles remaining constant) while the additional inverse amplitude shift indicates a decrease in dissipation levels due to decreased sliding of nitrogen, attributed to the higher friction associated with the normal state. The peak in the amplitude data is associated with the system passing through the condition $\omega\tau = 1$, where dissipation is at a maximum [9]. (c) The resistance of the resistivity sample displayed no sensitivity to adsorbed nitrogen within experimental resolution. The difference in transition times between the QCM and resistivity samples is attributable to slightly different warming rates for the two samples.

amplitude and frequency at the transition were consistent with an increase in friction as the sample entered the normal state. The frequency shift was indicative of an increased effective mass due to the nitrogen tracking the motion of the oscillator more closely (the actual amount of nitrogen on the electrode could not have increased), while the decrease in energy loss associated with the normal state is consistent with less sliding of the nitrogen due to increases in the friction. The peak in the amplitude data at the transition is present on account of the fact that
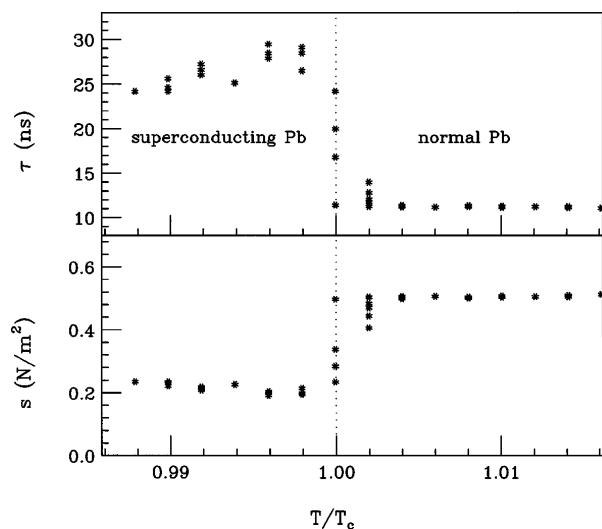
FIG. 4. Slip time τ and shear stress $s = \eta v$ (for $v = 1$ cm/s) versus T/T_c for the Fig. 3 data set. The shear stress for nitrogen sliding over the superconducting lead surface is about half that associated with sliding over lead in its normal phase.

the system happens to be passing from a regime where $\omega\tau < 1$ (with $\omega = 2\pi f_0$) to another where $\omega\tau > 1$, the dissipation being at a maximum when $\omega\tau = 1$ [9].

Quantitative analysis of the data via Eq. (1) yields the slip times and shear stresses presented in Fig. 4. (We note that a sliding speed is required to report shear stresses for QCM measurements since the apparatus operates at a time scale sufficiently short so as to be able to resolve the velocity dependence of the friction force [16].) The slip time when the lead substrate is in the superconducting phase is substantially longer than that when the substrate is in the normal state, and the shear stress, or force per unit true contact area to slide the nitrogen (plotted for a sliding speed of 1 cm/s) over the superconducting surface is half that deduced for sliding over the lead in its normal phase. The results of the analysis which yielded the Fig. 4 values can be checked for self-consistency by investigating whether the true (rather than effective) mass of the adsorbed particles, taking into account slippage $\propto \delta f_0(1 + \omega^2\tau^2)$, is constant at the transition (there is no physical argument which could justify a change in the true mass of the adsorbed nitrogen at the superconducting transition). Indeed, the self-consistency check is not only satisfied, but the total amount of nitrogen on the surface which it requires in order to be valid is the equivalent of 1.6 ML, well within experimental error of that estimated through direct observation of the frequency shift upon adsorption of the nitrogen gas.

Given that it would be essentially impossible for the self-consistency check to yield physically reasonable, not to mention equal and independently verifiable, values for the amount of nitrogen adsorbed on the surface electrodes, we are confident in attributing the higher levels of dissipation in the superconducting state to increased slippage (and thus reduced friction) between the film and the substrate.

If we associate the reduction in friction with an abrupt drop in only the conduction electron contributions when the lead enters the superconducting state, then the phonon and electronic contributions to friction in this system are approximately equal in magnitude. Substitution of this magnitude of the electronic friction into an expression derived by Persson [3] yields a value of 5 $\mu\Omega$ for the expected increase in resistance of the lead film. Our results therefore neither confirm nor contradict Persson's theory, since the prediction falls below the measurements' resolution. We note, however, that the number of superconducting electrons does not increase abruptly at the transition, so the new phenomenon we are observing may involve other effects, such as electron-phonon coupling, at the interface. It remains open for theoretical interpretation.

*Address after 6/98: Physics Department, North Carolina State University, Raleigh, NC 27695.

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