Nanofriction of Neon Films on Superconducting Lead

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With a quartz crystal microbalance technique we have studied the nanofriction of neon monolayers deposited on a lead surface at a temperature around 7 K. Unlike heavier adsorbates, Ne is found to systematically slide at such low temperatures without any evidence of pinning. The crossing of the Pb superconducting-metal transition is not accompanied by any change in dissipation, suggesting that the electronic contribution to friction is negligible for this system.

The friction between two sliding surfaces is probably one of the oldest problems in physics [1] and certainly one of the most important from a practical point of view [2]. In principle, part of the kinetic energy of a nanoscale object moving on a metallic surface can be transferred to the internal degrees of freedom of the substrate and therefore transformed into heat through the excitation of phonons and of electronic currents at the interface [3]. However, the relative importance of these two contributions is still a matter of debate. To quantify this ratio experimentally has proven difficult because the phononic and electronic dissipation channels are both generally active. Recently, the friction of a conducting tip of an atomic force microscope sliding on a silicon sample was measured [4]. When a positive bias was applied to the sample, an increase in friction by a factor ~ 2 was observed in the p-doped regions with respect to the n-doped ones. The mechanism for this increase is not clear, but estimates of the electronic friction are far too low to explain the result.

Arguably, the most direct way to determine the importance of electronic friction is to work across the superconducting phase transition. When the substrate becomes a superconductor, the electronic mechanism is frozen out while that phononic mechanism is essentially unaffected. Krim and co-workers have studied with a quartz microbalance technique (QCM) the friction between a lead substrate and an adsorbate film of solid nitrogen a few layers thick and have found a sharp drop in friction by a factor ~ 2 when lead became superconducting [5]. The same system was studied in a different QCM experiment [6] with improved cryogenics, but complete pinning of the nitrogen film to the lead substrate was reported in the temperature range 4–14 K. Subsequent measurements with a more controlled setup confirmed that nitrogen films are quite susceptible to pinning [7]. Also, the theoretical interpretations of the original experiment by Krim *et al.* were contradictory [8]. More recently, the same group reported a drop of a factor ~ 2 in friction for nitrogen and helium films on superconducting lead [9]. However, in this experiment

(i) the film coverage was not measured but only estimated, (ii) the superconducting state of lead during the thermal scans was not directly probed, (iii) the measurements were only taken during thermal warm-up cycles after cooling down the sample cell to 4.2 K. To overcome some of these technical drawbacks, we have designed [10] a new setup for QCM measurements in ultra-high vacuum (UHV) and at a temperature as low as 4 K.

Here, we present the results of an extensive QCM study of the sliding of Ne monolayers on bare Pb across its normal-to-superconducting transition temperature T_C. The microbalance is a small quartz disk whose principal faces are optically polished and covered by two metallic films, which are used both as electrodes and as adsorption surfaces [see Fig. 1(a)]. The Pb electrodes have been grown in UHV conditions by using a magnetron source as described in [11]. The resulting Pb film morphology is quite
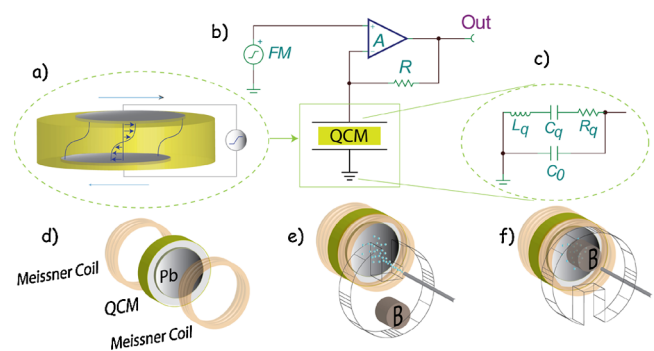

FIG. 1 (color online). QCM at resonance: arrows indicate the lateral displacements (a). Panel (b) shows the driving circuit of the QCM. In panel (c) the QCM equivalent circuit is shown, where C_q, L_q, and R_q are the motional capacitance, inductance, and resistance of the quartz plate and C_0 is the capacitance of the two electrodes. Panel (d) is a sketch of the QCM placed between two Meissner coils. Panel (e) shows gas dosing on the QCM. In panel (f) we show the application of the external magnetic field B to the QCM.

similar to that previously reported [12]: (111) terminated flat terraces with a typical size in the range between 20 nm and 100 nm. The rms roughness is 3 nm measured over an area of $2 \times 2 \ \mu m^2$.

The QCM is mounted in an UHV system [10] that comprises the main chamber housing the sample holder and a fast-entry load lock system provided with a sputtering ion gun to clean the electrodes from surface contaminants. Unlike other experiments in which the film covering the QCM is obtained by admitting a known amount of gas at high temperature and then cooling down the sample cell to the base temperature [9,13], in our setup the film is condensed directly onto the QCM, kept at the chosen low temperature, by slowly leaking high-purity gas through a nozzle facing the quartz electrode; see Fig. 1(a). The deposition rate can be varied by acting on the leak valve. Typical rates are between 20 and 90 min for the deposition of one nominal layer. No systematic difference in the QCM response is observed among measurements comprised in this ample time interval, suggesting that the data are taken under equilibrium conditions.

The QCM is placed between two Meissner coils for the detection of the superconducting transition of the Pb electrodes [see Fig. 1(d)]. The coils, of approximate diameter 5 mm and about 20 turns each, are mounted in the sample holder. One coil is driven by the reference output of a lock-in amplifier at ~ 100 kHz and the other one is connected to the lock-in input. When the Pb electrodes become superconducting, they expel the magnetic flux, causing a sharp drop in the pickup signal. The field produced by the primary coil is so small that is does not affect the transition. To avoid any possible contamination problems caused by the outgassing of the coils [7], the QCM is inserted in the sample holder at temperatures below 10 K. Close to the QCM there is also a cog wheel provided with a strong permanent magnet. By turning the wheel with the wobble stick, it is then possible to apply an external magnetic field to the lead electrodes that may destroy the superconducting phase [see Fig. 1(f)].

At resonance, the two parallel faces of the QCM oscillate in a transverse shear motion. The condensation of a film on the electrodes is signaled by a decrease of the resonance frequency $f_{\rm res}$. Any dissipation taking place at the solid-film interface is instead detected by a decrease in the corresponding resonance amplitude $V_{\rm res}$ [14,15]. The dissipation can be expressed as $\Delta(\frac{1}{Q})$, where Q is the quality factor of the QCM. In our case, Q is linearly proportional to $V_{\rm res}$ and its value at low temperature is 90 000. The QCM is driven at its fundamental mode by using a frequency-modulation (FM) technique. A commercial high-stability FM generator is connected to the noninverting channel of a wide-band amplifier; see Fig. 1(b). The amplified signal is then rectified and applied to the feedback circuit which locks the output of the FM generator to the quartz series resonance [16]. At this frequency, the voltage across the feedback resistance R is $V_{\rm res} =$

$(R/R_q)V_q$, where V_q is the voltage applied to the quartz crystal.

The graph of Fig. 2 shows representative temperature scans of the normalized pickup voltage $V_{p,\rm norm} = (V_p - V_{p,s})/(V_{p,n} - V_{p,s})$, where $V_{p,n}$ $(V_{p,s})$ is the pickup voltage measured in the normal (n) and superconducting (s) phases. Data in the absence of an external field indicate a sharp drop at a critical temperature $T_C \sim 7$ K due to the superconducting transition. Lead is known to have $T_C = 7.2$ K. The difference of 0.2 K found in our experiment simply quantifies the temperature gradient existing between the QCM electrodes and the diode thermometer housed inside the copper sample holder [10]. In correspondence to the transition, there is an increase in the resonance amplitude. This is due to the decrease ΔR in the Ohmic resistance of the Pb electrodes at T_c, which can be estimated from $\Delta R = RV_q(1/V_{\rm res,n} - 1/V_{\rm res,s})$, where $V_{\rm res,n}$ $(V_{\rm res,s})$ is the resonance amplitude measured in the normal (superconducting) phase. We find $\Delta R \sim 0.5\Omega$, to be compared with a quartz resistance $R_q \sim 24\Omega$ as deduced from the resonance quality factor determined in the normal phase. As expected, the application of an external magnetic field, achieved by simply turning the cog wheel, moves the transition to lower temperatures. The lowest (highest) observed value corresponds to the magnet touching (~ 2 mm from) the QCM holder. The transition at 6.4 K refers instead to the magnet placed at an intermediate distance, which was used for the measurements discussed below.

Figure 3 shows a typical response of the QCM across T_C. The three graphs show the evolution over time of the main system parameters: the QCM resonance frequency and amplitude, the diode thermometer reading, and the normalized pickup voltage. Initially, the lead electrodes are bare and $T = 6.99$ K. At this temperature, $V_{p,\rm norm}$ is low, suggesting that lead is in the superconducting phase. Sudden increases in the controlled temperature by 0.1 K drive the electrodes into the normal phase as shown by the high level of $V_{p,\rm norm}$. As expected, these temperature var-
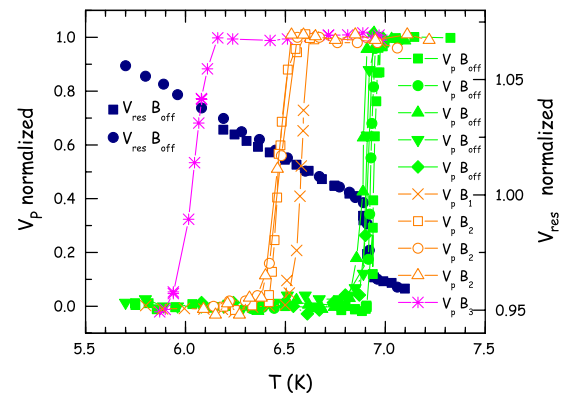

FIG. 2 (color online). Temperature response of the bare QCM. $B_{\rm off}$ means that the data are measured in the absence of an external magnetic field. $B_{1,2,3}$ refers to different distances of the permanent magnet with respect to the QCM.
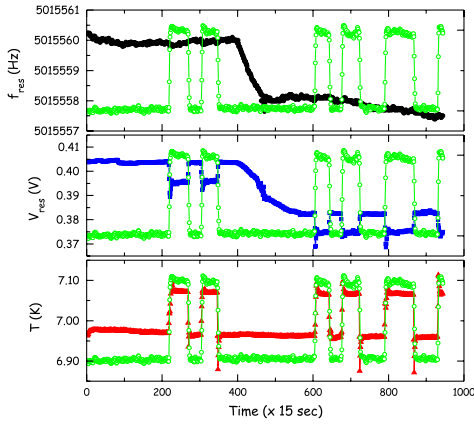
FIG. 3 (color online). Time evolution of the quartz frequency (top panel), amplitude (middle panel), and temperature (bottom panel). Open circles refer to the corresponding normalized pickup voltage, whose scales are shown on the right axes.
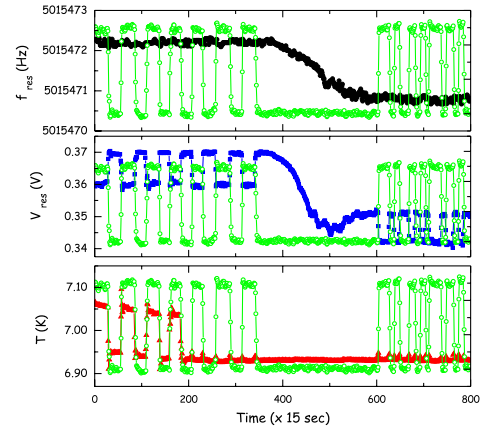

FIG. 4 (color online). Same quantities as in Fig. 3. The first four jumps in the bottom panel correspond to cyclic temperature changes, while all the others are induced by the application or removal of a magnetic field.

iations do not affect f_{res}, while V_{res} decreases in the normal phase by an amount similar to that reported in Fig. 1. At a time close to $400(\times 15)$ sec, the dosing valve is opened. This causes a linear drop in f_{res} due to the deposition of a Ne film, which is accompanied by a decrease in V_{res}. This increase in dissipation is attributed to the sliding friction of Ne over the Pb surface, and it has been thoroughly characterized in previous publications [11,12]. After a frequency shift of about 2 Hz, corresponding [11] to a film coverage of about 0.8 layers, the dosing valve is closed and the system is allowed to equilibrate. The temperature is then increased by the same amount of 0.1 K, which causes a sudden drop in V_{res}, which is practically indistinguishable from that measured with the bare electrodes. In other words, when lead becomes normal, there is no extra dissipation which can be associated with electronic friction. To be more precise, the drop in V_{res} due to the crossing of the superconducting transition is of 10 ± 1 mV, with or without a Ne film. The minimum change in dissipation which we can detect with our setup is then somewhat less than 2 mV. This implies that the upper limit to the dissipation caused by the electronic friction is $\Delta(1/Q) \lesssim 6 \times 10^{-8}$. Similar behavior has been found with different film coverages and different temperature shifts. This is at variance with the observation of a $\Delta(1/Q) \sim 4 \times 10^{-7}$ ($\sim 3 \times 10^{-6}$) reported in the case of He (N$_2$) films [9]. We point out that the data in Fig. 3 have been taken only after the QCM has undergone an extensive thermal annealing following its cool down from room temperature. The procedure consisted in thermal cycles between 7 and about 60 K, followed by Ne depositions at the chosen low temperature. Otherwise, we found an erratic response of the quartz upon Ne gas dosing (e.g. an increase in the quartz amplitude, anomalous jumps in the resonance frequency, ...) which was totally irreproducible.

Figure 4 shows the typical QCM behavior observed when the transition from the superconducting to the normal phase is instead induced magnetically. The difference in the initial frequency (-88 Hz) and amplitude (-30 mV) values with respect to the previous ones is simply due to the fact that the QCM has been warmed up to room temperature in between. This is likely due to thermal stresses and contractions in the quartz crystal and its mounting and quantifies the kind of reproducibility (± 100 Hz for f_{res}, $\pm 10\%$ for V_{res}) one gets after such ample thermal cycles. Again, the scan starts with the bare electrodes kept in the superconducting state at a constant $T = 6.96$ K. Temperature rises by 0.1 K drive the electrodes normal, and this causes a drop in V_{res}. The same result can be achieved with the application of the B field and the quartz kept at the same T. At a time close to $350(\times 10)$ sec, the sapphire leak valve is opened and a Ne film with a final coverage of ~ 0.57 ML is deposited. After the system has equilibrated, the B field is alternatively applied and removed. This causes a drop in the QCM amplitude whose size is quite similar to that observed without the Ne film. Despite the different thermodynamic path, we reach the same conclusion: the crossing of the superconducting to normal transition is not accompanied by an increase in the system dissipation attributable to the activation of the electronic friction.

This negative result implies that the increased sliding of Ne films observed on Pb plated with Kr and Xe [12] cannot be explained in terms of shielding of the electronic contribution caused by the Kr and Xe multilayers. It is also consistent with theoretical calculations of the Ohmic loss in a normal metal [17]. Adsorption of rare gases on noble metals decreases the work function of the metal. This is explained [18] as arising from the formation of a dipole layer with an effective dipole moment per atom μ. Actually, the shift in work function is directly proportional to μ [18]. The power loss associated with the lateral center-of-mass oscillations of a monolayer lattice of static dipole moments can be characterized by a decay time $\tau_d \sim \mu^{-2}$ for the energy of the film [17]. For the system parameters of a solid monolayer of Xe on Ag(111) at 77 K,

the estimated [17] decay time is $\tau_d \sim 200$ ns. This is about 100 times the slip time τ_{slip} measured in a QCM experiment [19] of Xe on Ag(111), where τ_{slip} represents the time constant of the exponential film velocity decrease due to an hypothetical sudden stop of the oscillating substrate. Very low slip times mean high interfacial viscosity and, in the case of a film locked to the substrate, $\tau_{slip} = 0$. Unfortunately, τ_d of Ne/Pb(111) cannot be calculated because this system is not so well characterized. However, the change of the work function of the (111) surface of the noble metals upon adsorption of heavy rare gases has been systematically investigated [20]. The magnitude of this shift scales with increasing polarizability of the rare gas (Ar, Kr, and Xe) and with decreasing atomic number of the noble metal (Au, Ag, and Cu). Since Ne has a polarizability 10 times smaller than Xe [18] and Pb is much heavier than Ag, it is quite reasonable to expect that the decay time of the system Ne/Pb(111) is much longer than 200 ns [21]. In the absence of a vapor [15], τ_{slip} can be easily calculated from the shifts in the resonance frequency and the amplitude of the QCM. The slip times we have measured in the normal phase of Pb are $\lesssim 5$ ns, thus at least 2 orders of magnitude smaller than the estimated τ_d. Said differently, the sliding friction of Ne on metallic Pb is dominated by the phononic contribution as found for Xe on various metals [22]. Accordingly, no change in friction is expected when Pb becomes superconducting, as we find experimentally. Since helium has a polarizability half that of neon, this argument is instead not consistent with the observation [9] of a sharp increase in dissipation of He films when the temperature is raised across the T_C of lead.

Calculations of the Ohmic contribution for the system N_2/Ag(111) at 20 K yield $\tau_d \sim 2$–20 ns, which is in the range of the slip times observed for N_2 films on metal Pb slightly above T_c [5,9]. The enhanced magnitude of the resistive loss is due to the electrostatic field arising from the quadrupolar moments of N_2 molecules forming an orientationally ordered herringbone lattice [17]. We have thus deposited N_2 monolayers on our QCM but we could not detect any change in the resonance amplitude for $T < 10$ K. The films have been deposited with rates as low as 0.5 ML/hour and then thermally annealed up to 30 K. In order to depin the film [23], we have also driven the QCM to the maximum power available with our setup, corresponding to a lateral displacement ~ 40 times larger than that employed for the investigation of the Ne films, but this was not sufficient. These results confirm our previous studies [12,24] with films of Kr, Xe, and N_2, which always show complete pinning to Pb and Au electrodes below 10 K and agree with the common observation that N_2 are highly susceptible to pinning at such low temperatures [6,7].

In summary, with a quartz microbalance we have studied the friction of Ne monolayers deposited on superconducting lead. Unlike heavier adsorbates, Ne is found to systematically slide at such low temperatures without any evi-dence of pinning. The crossing of the Pb superconducting-metal transition is not accompanied by any change in dissipation, suggesting that the electronic contribution to friction is negligible for this system probably because of the small polarizability of Ne atoms. For unambiguous evidence of the electronic mechanism, more experiments are then required, which must carefully monitor all the various parameters involved in the experiment and possibly use superconducting electrodes with higher critical temperatures to limit the complications caused by the low temperature pinning of the adsorbate.

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