Electronic Sliding Friction of Atoms Physisorbed at Superconductor Surface

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The electronic component of sliding friction of physisorbed atoms oscillating above a flat metal surface is calculated using the frequency dependent image potential theory of Tomassone and Widom extended to a two-fluid model superconductor. Our results suggest a theoretical picture for the recent experiments of Krim *et al.*, who observed that the sliding friction of adsorbates on vibrating metal surfaces undergoes a sharp drop in its temperature dependence at the transition to the superconducting state. We propose a tentative qualitative interpretation which allows us to clarify some questions concerning these experiments as posed by Persson and Tosatti.

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In the present rapid development of the experimental as well as theoretical investigations of sliding friction at the atomic scale, one of the fundamental questions concerns the microscopic mechanisms responsible for the sliding force and their relative importance. For adsorbate atoms moving along a flat metal surface, a reasonable theoretical picture has been proposed [1], assuming two basic contributions to the frictional dissipation, namely phonon emission and *e-h* pair excitation in the bulk of the substrate. This distinction between both mechanisms is not readily observable, however, as most experiments measure only the global friction force.

Recently, J. Krim with collaborators have applied the quartz crystal microbalance method of measuring microscopic sliding friction [2] to the case of a physisorbed nitrogen adlayer sliding over a lead substrate at low temperatures [3]. As the temperature is lowered below the superconducting transition temperature of lead, the friction drops suddenly to about half of its value above the transition point. The authors have suggested that this jump may be attributed to the sudden switch-off of the electronic contribution to the friction force, while the remainder is interpreted as a phonon contribution that is roughly temperature independent. Thus, by cooling the metal substrate down below its superconducting temperature, the electronic and phonon contributions to sliding friction could be directly assessed.

This straightforward connection between the experimental results of [3] and the fundamental mechanisms of friction has been contested. Persson and Tosatti [4] argue that the abrupt change of the friction force contradicts the qualitative picture, according to which the substrate electrons contribute to friction through their surface scattering due to the motion of the adatoms relative to the substrate. Only the condensate electrons are excluded from scattering below the superconducting transition, and their concentration grows from zero gradually, not abruptly. The authors do not propose any clear-cut mechanism accounting for the experimental findings of [3], but several comments they make agree with our point of view and may serve to suggest a framework for our treatment of the problem. More recently, Popov [5] starts from a similar observation for the surface drag current, but he notes that charge neutrality requires also a bulk charge backflow. For the case of substrate formed by a thin nearly perfect slab, when the hydrodynamic description is valid, he suggests that an abrupt change in dissipation due to this backflow at the superconducting transition may be responsible for the drop in friction.

In our approach, we are guided by several considerations. First, it is required that the explanation of the friction drop be an extension of the existing picture of the electronic friction in the normal state [6–8]. Thus, the *e-h* excitations of the substrate induced by the adsorbate sliding are generated by a short-range unretarded longitudinal Coulomb field fluctuating thanks to the adatom motions.

Second, it is accepted that the actual substrate is a real, “dirty” film of lead which is not thin compared to the electron transport mean free path and the screening radius, but, at the same time, it is thin with respect to the superconducting coherence length. A simple two-fluid picture of the electrons is then appropriate [9].

Third, it is to be expected that the substrate is covered by an unspecified nonmetallic (“oxide”) layer contributing perhaps to the nonelectronic part of friction, but acting, at the same time, as a spacer between the substrate proper and the mobile adsorbate layer.

A schematic model permitting study of the electronic friction force above and below the superconducting transition and respecting the three conditions is then a physisorbed atom oscillating parallel to the surface at a distance which is sufficient to permit using the image charge approximation for the interaction potential. Such a situation has been studied by Tomassone and Widom

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[8], and we may follow their approach. The only major change that has to be done is to employ an appropriate local dielectric function corresponding to the superconducting state of the metal below the transition temperature. To this end, the dielectric function is expressed in terms of the complex conductance in the two-fluid model [9,10]. The normal phase conductance is chosen in the Drude form, a simple Gorter-Casimir expression [10] is used for the two-fluid model.

Let us assume that the half space $z < 0$ is filled by the (superconducting or normal) substrate and the adsorbed atom is above it at a height h. A central role in the model is played by the retarded Green's function of the scalar electromagnetic potential in the Coulomb gauge. This Green's function is, for $z, z' > 0$, given by [8]

$$G_R(\boldsymbol{r}, \boldsymbol{r}', \omega) = \frac{1}{R} - \lim_{\epsilon \to 0^+} \left[\frac{\varepsilon(\omega + i\epsilon) - 1}{\varepsilon(\omega + i\epsilon) + 1} \right] \frac{1}{R_{\text{image}}}, \tag{1}$$

where

$$R = |\boldsymbol{r} - \boldsymbol{r}'| = \sqrt{(x - x')^2 + (y - y')^2 + (z - z')^2}, \tag{2}$$

and

$$\begin{aligned} R_{\text{image}} &= |\boldsymbol{r} - \boldsymbol{r}'_{\text{image}}| \\ &= \sqrt{(x - x')^2 + (y - y')^2 + (z + z')^2}. \end{aligned} \tag{3}$$

The first term is the vacuum term, while the other is the image term caused by the presence of the interface. Further, the following relation connects the dielectric function with the conductivity of the substrate

$$\lim_{\epsilon \to 0^+} \varepsilon(\omega + i\epsilon) = 1 + \frac{i\sigma(\omega)}{\omega \varepsilon_0}. \tag{4}$$

This is a generalization of the expression used by Tomassone and Widom, which consists in taking conductivity of the substrate as frequency dependent, as is essential in the present case.

It may be asked to what extent this image-charge picture employing local dielectric function is appropriate for the superconductor. The figure of merit here is the product $k\xi_0$, where k is a characteristic momentum and ξ_0 is the zero-temperature coherence length. For the case of adsorbate kept apart by a spacer layer and for a dirty sample, this product may be sufficiently small to justify qualitatively the image potential description.

Now, we rederive in a simple manner the formula for sliding friction of an adatom oscillating above the surface. The adatom will be represented by a rigid distribution of classical charges. It is then sufficient to find the force on a unit point charge driven along a given trajectory $\boldsymbol{r}_d(t)$:

$$\begin{aligned} \boldsymbol{F}(t) &\equiv \boldsymbol{E}[\boldsymbol{r}_d(t), t] \\ &= -\int_{-\infty}^{t} dt' \, \nabla_{\boldsymbol{r}} G_R[\boldsymbol{r}_d(t), \boldsymbol{r}_d(t'), t - t']. \end{aligned} \tag{5}$$

At any instant t, the force is a causal functional of the whole trajectory $\boldsymbol{r}_d(t')$, $t > t'$. Let us expand $G_R(\boldsymbol{r}, \boldsymbol{r} + \{\boldsymbol{r}' - \boldsymbol{r}\}, t - t')$ in a Taylor series around $\boldsymbol{r} = \boldsymbol{r}_d(t)$ with respect to the deviation $\boldsymbol{r}' - \boldsymbol{r} = \boldsymbol{r}_d(t') - \boldsymbol{r}_d(t)$. The zeroth order term yields the image-charge induced attractive force that binds the adatom to the surface. We are particularly interested in the first order term, because it contains all linear dependence on the pulling velocity $\boldsymbol{v}'_d = \frac{d}{dt'}[\boldsymbol{r}_d(t') - \boldsymbol{r}_d(t)]$. Thus, it is relevant to the linear sliding friction coefficient. For this linear part of the force we get

$$\begin{aligned} F_i(t) = &\int_{-\infty}^{t} dt' \, \nabla_i \nabla'_j G_R[\boldsymbol{r} = \boldsymbol{r}_d(t), \boldsymbol{r}' = \boldsymbol{r}_d(t), t - t'] \\ &\times [r_d^j(t) - r_d^j(t')]. \end{aligned} \tag{6}$$

As the vacuum term does not contribute to friction, evaluation of the derivatives of the Green's function at coinciding points causes no problem. We will use the following notation:

$$\mathcal{G}_{ij}[\boldsymbol{r}_d(t), \omega] = \nabla_i \nabla'_j G_R[\boldsymbol{r} = \boldsymbol{r}_d(t), \boldsymbol{r}' = \boldsymbol{r}_d(t), \omega]. \tag{7}$$

In the case of a lateral motion of the adsorbate, which interests us most, this function does not depend on t, since it depends only on the height above the surface h, which remains constant. So, we can write using the Fourier transform

$$\begin{aligned} F_i(t) = &\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} [\mathcal{G}_{ij}(h, \omega \to 0) - \mathcal{G}_{ij}(h, \omega)] \\ &\times r_d^j(\omega). \end{aligned} \tag{8}$$

If we assume the oscillatory driven motion of the adsorbate parallel to the surface, i.e., $\boldsymbol{r}_d(t) = \boldsymbol{r}_0 \sin\omega_d t$, $\boldsymbol{v}_d(t) = \boldsymbol{v}_0 \cos\omega_d t = \omega_d \boldsymbol{r}_0 \cos\omega_d t$, where $\boldsymbol{r}_0$, $\boldsymbol{v}_0$ are parallel to the surface, we obtain the result

$$\begin{aligned} F_i(t) = &[\mathcal{G}_{ij}(h, \omega \to 0) - \operatorname{Re}\mathcal{G}_{ij}(h, \omega_d)] r_d^j(t) \\ &+ \frac{1}{\omega_d} \operatorname{Im}\mathcal{G}_{ij}(h, \omega_d) v_d^j(t). \end{aligned} \tag{9}$$

The first term represents a reactive force caused by the interaction of the adsorbate with the substrate (renormalization of the lateral motion eigenfrequency), and the second term is the desired expression for the sliding friction force linear in the velocity.

Tomassone and Widom calculated the friction force for a linear translation of the adatom with a constant velocity. This is a limit of our result when $\omega_d \to 0$ and $\boldsymbol{v}_0 = \omega_d \boldsymbol{r}_0 =$ constant. Within this limit, we reproduce exactly the results of Tomassone and Widom [8] in the cases when the adsorbate is represented by a point ion and a permanent dipole. The result for the dipole differs from the above one for an ion only in the geometrical factor given by the various derivatives of the Green's function due to the different electric nature of this kind of adsorbate. The case of true van der Waals coupling of the adsorbate, i.e., when the attraction is caused by the quantum fluctuations of the dipole moment of the adsorbate, is more subtle and will be analyzed in detail in future work. The adsorbates in the first monolayer exhibit nonzero net dipole moment as pointed out by Tomassone and Widom, and thus our result for classical dipole may describe well even the case of a realistic quantum adsorbate-substrate bond.

To summarize this formal part, for an adsorbate consisting of any distribution of classical charges, and oscillating with frequency ω_d parallel to the surface, the microscopic friction coefficient Γ, defined by $\boldsymbol{F}_{\text{friction}} = -\Gamma \boldsymbol{v}$, is proportional to

$$\Gamma(\omega_d) \propto \frac{1}{\omega_d} \operatorname{Im} \frac{\varepsilon(\omega_d + i0^+) - 1}{\varepsilon(\omega_d + i0^+) + 1} . \tag{10}$$

This factor contains full information about the effect of the metal substrate.

Now, we proceed to analyze the effect of the superconducting transition on this factor, and, thus, on the friction force. First, we evaluate the conductivity of the substrate in the simple two-fluid model of the superconductor. In this model, the conductivity consists of two additive terms, the first one due to the superfluid component, and the other one due to the normal fluid component

$$\sigma(\omega) = \sigma_S(\omega) + \sigma_N(\omega) . \tag{11}$$

Denoting by x the ratio of the density of normal electrons to the total electron density,

$$x = \frac{n_N}{n} , \tag{12}$$

we may use (11) both above ($x = 1$), and below ($x < 1$) the phase transition. We also use notations m^* for the effective mass of the electrons and ω_{pl} for the electron plasma frequency in the substrate, $\omega_{pl}^2 = \frac{ne^2}{\varepsilon_0 m^*}$.

The superfluid component experiences no friction force due to disorder and its long-wave limit behaves like

$$\sigma_S(\omega) = \frac{i n_S e^2}{m^* \omega} = i(1 - x)\varepsilon_0 \frac{\omega_{pl}^2}{\omega} . \tag{13}$$

The normal fluid is assumed to satisfy the Drude formula for the ac conductivity, with the proper electron density $x\,n$, both below and above T_c:

$$\sigma_N(\omega) = \frac{n_N e^2 \tau}{m^*} \frac{1}{1 - i\omega\tau} \doteq \frac{n_N e^2 \tau}{m^*} = x \varepsilon_0 \omega_{pl}^2 \tau . \tag{14}$$

The relaxation time in the Drude formula is limited by phonon and disorder related scattering and may then be bracketed between 10^{-14} s and 10^{-11} s (corresponding to pure lead at 300 and 7 K). Since the experimental setup is a quartz crystal microbalance arrangement with the driving frequency being roughly $\omega_d \approx 10^7\ \text{s}^{-1}$, we use the dc limit of the normal conductivity, $\omega = 0$, neglecting thus its frequency dependence.

Introducing the conductivity (11) into (4) and (10), we obtain an explicit result for the linear friction coefficient

$$\begin{aligned} \Gamma(x, \omega_d) &\propto \frac{2}{\omega_{pl}^2 \tau} \frac{x}{x^2 + [\frac{1 - x - 2(\omega_d/\omega_{pl})^2}{\omega_d \tau}]^2} \\ &\doteq \frac{2}{\omega_{pl}^2 \tau} \frac{x}{x^2 + (\frac{1-x}{\omega_d \tau})^2} . \end{aligned} \tag{15}$$

The small term $\omega_d^2/\omega_{pl}^2 \approx (10^7\ \text{s}^{-1}/10^{15}\ \text{s}^{-1})^2$ has been neglected, as it does not change the results.

Temperature enters this expression in two different ways. First, the relaxation time τ and the plasma frequency ω_{pl} are slightly temperature dependent, yielding a moderate temperature dependence of the friction coefficient in the normal state. Around the transition point, these parameters have a smooth temperature dependence and in the close vicinity of T_c they are approximately constant.

Second, and more importantly, temperature enters the above result (15) through the variation of x, the fractional normal fluid density, with temperature. To obtain this temperature dependence around the transition point, we may employ the Ginsburg-Landau description. The lead film in the actual experiment [3] was about 1500 Å thick. Thus, it is bracketed by the Pippard and the GL coherence lengths:

$$\xi_0 \approx 830\ \text{Å} < \text{film thickness} \ll \xi(T) \sim \xi_0 \left(\frac{T_c}{T_c - T} \right) , \tag{16}$$

for $0 < T_c - T \ll T_c$. Under these conditions, the GL theory leads to a simple result [11], namely that the superfluid density is constant across the width of the film and has the same temperature dependence as in the bulk. For definiteness, we assume this temperature dependence to be of the simple yet qualitatively correct Gorter-Casimir form [10] $n_S(T)/n = 1 - x(T) = 1 - (T/T_c)^4$. We introduce this relation into (15), and obtain the final dimensionless relation for the friction coefficient at T close below the transition point

$$\frac{\Gamma(T, \omega_d)}{\Gamma_0} \doteq \frac{1}{1 + [\frac{4(1 - T/T_c)}{\omega_d \tau}]^2} = \frac{1}{1 + (\frac{t}{\Delta t})^2} , \tag{17}$$

with $t = (T_c - T)/T_c$ and the half-width of the jump

$$\Delta t = \frac{\omega_d \tau}{4} . \tag{18}$$

By Γ_0 we have denoted the approximately constant value of the friction in the normal state just above the critical temperature. The half-width of the jump depends on the value of τ. For a "typical" $\tau \approx 10^{-12}$ s, it is of the order of 10^{-5}. This represents a smooth, but very steep step. This is fully consistent with the experimental results of Krim and collaborators [3].

Another, indirect, method for determining the electronic component of friction, proposed by Persson [6], is based on an approximate Galilean transformation of the electron fluid to the reference frame in which the adsorbate is stationary. This is achieved by applying an electric field to the substrate covered by the adsorbate. The electron fluid then moves collectively with some drift velocity with respect to the stationary adsorbate while the ion cores stay at rest. The Ohmic dissipation caused by the adsorbates in one reference frame must be equal to the electronic friction energy dissipation rate in the other. Sokoloff [7] showed by a model calculation that up to a directional factor the two points of view are equivalent and, therefore, the Persson's approach yields results correct at least in order of magnitude for the electronic sliding friction above metals in normal state.

As argued by Persson and Tosatti [4] this method fails for a superconducting substrate. They claim that the sudden drop of the substrate resistivity does not explain the drop in the friction since the concentration of the normal fluid that is responsible for the dissipation decreases continuously below the critical temperature. In light of the above calculations we see, however, that they omit the fact that the superconducting and normal parts of the electron fluid do not contribute to the friction additively and that the scattering of the normal electrons from the adsorbate is therefore screened out by the superconducting component.

To put it in other words, in our picture, the Krim phenomenon is given by a current-current response rather than by a charge density effect visualized by Persson and Tosatti. The screening by the superfluid phase in this picture amounts to a properly renormalized current vertex. This renormalization is absent in the description assumed in [4]; the two pictures differ only in this point.

The work of Popov [5] apparently concerns a physical situation entirely different from ours: Electron scattering on imperfections is but weak, and the electron fluid is assumed to be in a hydrodynamic regime. A steady (zero frequency) drag gives rise to a surface drag flow and to a bulk backflow. The dissipative properties of the *backflow* change abruptly at the superconducting transition. No doubt our model with a dominating disorder scattering is close to the actual situation in [3]. There are, however, many deeper features common to both approaches: accent on the current-current correlation, and the jump in the friction force originating from a current component *other than the dissipative drag current.* In [5], it is the backflow, in our case the idle component of the total current. It may be speculated that both models are limiting cases of a unified picture.

To conclude, we have presented a model that yields the temperature dependence of the electronic friction coefficient above a superconductor surface in agreement with a recent experiment by Krim. The sudden drop in friction is caused by the presence of the superconducting fluid which even in a tiny concentration screens out the disturbance by the adsorbate, and thus the electronic part of the friction vanishes abruptly as originally proposed by Krim. Our results differ from those of Persson and Tosatti due to the fact that the contributions to the friction force from the normal and superfluid electrons are not additive, which was an implicit assumption in their paper. Although our model is rather simplified, namely, we considered the adsorbate as a classical charge distribution rather than a quantum fluctuating dipole, we believe that it captures the main physical features of the system under study correctly. Generalization to a more realistic picture in which both the adsorbate and substrate will be treated fully quantum mechanically is being developed.

Note added.—Just prior to submission of our paper, we noticed that a very similar one by J. B. Sokoloff, M. S. Tomassone, and A. Widom appeared at the Los Alamos e-print archive.

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