Tribo-Induced Melting Transition at a Sliding Asperity Contact

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(Received 22 June 2009; published 12 November 2009)

Observation of a tribo-induced transition from solid to liquidlike behavior is reported for a scanning tunneling microscope tip in sliding contact with an indium electrode of a quartz crystal microbalance (QCM). In particular, at a sufficiently high asperity sliding speed (about 1 m/s) and/or sample temperature, a change in the contact mechanics is observed that is consistent with melting in terms of both the QCM response and an energy analysis. The results confirm that the surface, rather than bulk, melting point temperature is the more relevant quantity for tribological considerations.

DOI: 10.1103/PhysRevLett.103.205502 PACS numbers: 68.35.Af, 61.46.—w, 62.20.Qp, 68.18.Jk

The physics of temperature rise in a sliding asperity contact is a topic of wide-ranging impact, spanning micro-electro-mechanical systems (MEMS) [1] to frictional behavior at geological faults [2,3]. The topic has been widely debated for decades, beginning with a mathematical treatment by Blok in 1937 for evaluating temperature rise at rubbing interfaces [4], and continuing to the present day [5,6]. There remains, however, a lack of experimental corroboration, particularly for single asperity contacts. This is due to both the inherent difficulty of characterizing a buried interface [7] and the fact that the physics of surface melting [8], confinement [9], and scaling effects [10] must be taken into consideration.

We report here an in situ observation of a tribo-induced transition from solid to liquidlike behavior for a STM tip in high sliding speed contact with an indium electrode of a QCM, constituting the first such observation for a single asperity nanoscale contact. Previous experimental investigations employed ex situ observations or temperature sensors with contact resolution limited to a few microns [11–13]. Prior studies of STM tip interactions with metals have reported that surface melting—and the related effect of surface diffusion—could impact tribological behavior [14–16]. These measurements were however carried out under no shear or very slow lateral speeds, i.e., conditions at which the temperature rise due to friction is predicted to be very small. The present studies confirm these conclusions at realistic sliding speeds (0.01 to 2 m/s), and therefore constitute a significant advance in terms of both the sliding speeds and length scales (nm) at which the studies were performed.

Transverse-shear mode quartz crystals (8 MHz “AT-cut”) were employed for the measurements reported here. The QCM electrodes consisted of ~10 nm thick titanium layers with 50 nm thick copper films deposited atop them. The copper film rms surface roughness was ~3.3 nm at a length scale of 500 nm, consistent with previous results [17]. The sample was mounted within a small vacuum system onto a STM (McAllister 525DT) holder that was modified to enable QCM oscillation, and the chamber was evacuated to 4 × 10⁻⁹ Torr or lower. A 50 nm thick indium film (99.99% purity; rms roughness 4.6 nm over 500 nm lateral width) was deposited in situ onto the top electrode by thermal evaporation. Imaging was performed in constant-current mode at a bias voltage of 200–500 mV and tunneling current of 0.5–1.0 nA. Sliding contact data were recorded by operating the microscope in a current versus height spectroscopy mode, with typical z-motion range of 2–3 nm for the results presented here. Electrochemically etched tungsten tips were employed for both imaging and sliding contact. Temperature was measured to within 1°C with a thermometer located approximately 1 cm from the QCM. The entire chamber temperature was raised uniformly, avoiding interface temperature ambiguities associated with setups where the sample, but not the tip, temperature is varied. Changes in the piezoelectric calibration of the QCM and STM from heating were less than 0.001 and 10%, respectively, falling below experimental resolution for the data reported here.

The QCM’s amplitude of oscillation was measured directly using the STM as described by Borovsky et al. [18] and calibrated with the electronic amplitude measured by an oscilloscope. We were thus able to accurately discern the vibration amplitude even when the tip was in sliding contact with the surface. SEM images of the tungsten tips show a nominal radius of ~0.75 μm, with STM images showing a contact radius of ~200 nm (inset of Fig. 4). Then, assuming Young’s modulus values of 11 and 411 GPa, and Poisson ratios of 0.5 and 0.28 for indium and tungsten [19,20], respectively, the calculated average Hertzian contact pressure is ~1.6 GPa, comparable to the 3.3 GPa contact pressure previously reported for a tungsten tip in contact with a silver electrode [21].

Figure 1 shows typical results for QCM frequency change (Δf) versus velocity, each measurement being performed at 5 different locations close to the electrode center to a depth of 3 nm using the same tip. For the Fig. 1 data set, the originally positive frequency shifts display a reversible transition to negative shifts above ~90 cm/s. We define the “transition velocity”, vₜ, as the average of...
the fastest positive frequency shift velocity with the slowest negative shift velocity. The inset of Fig. 1 shows typical changes in amplitude. The transition velocity is expected to depend on contact area, tip sharpness, film thickness, surface contamination (or lubrication), and temperature. However, a velocity dependent melting transition should always extrapolate to the melting temperature at $v_t = 0$, irrespective of the tip-sample combination. We therefore performed the measurements with tips of varying contact radii, and, as expected for melting, the transition velocities for all data sets dropped with increasing temperature and extrapolated in all cases to $114 \pm 9^\circ C$.

The observed transition is reversible and thus cannot be associated with irreversible tip blunting or chemical reaction phenomena. To demonstrate this, Fig. 2 displays typical frequency shift data for a tip (not the same as that employed in Fig. 1) that is in contact with the electrode as the velocity is increased and decreased. The first part of Fig. 2 shows an indentation in which the substrate speed was initially below the transition velocity, eliciting an initial positive $\Delta f$ from the crystal. The speed was then increased and $\Delta f$ became negative until the tip was retracted from the surface. Reverse behavior is observed when the procedure is performed in the reverse order.

Figure 3 presents representative data sets for the dependence of the transition velocity on system temperature. The difference in transition velocities between the runs can again be attributed to different tip morphologies [21], confirmed by the difference in the magnitude of $\Delta f$ between the runs. Run 1 had a $\Delta f$ approximately 5 times larger than run 2, corresponding to a contact radius $\sim \sqrt{5}$ larger [21]. By varying the tip morphology, the temperature runs confirm that the transition is consistent with melting since these, and all other data sets, converge at higher temperatures and extrapolate in all cases to $114 \pm 9^\circ C$. This implies that a liquid is present with no frictional energy supplied at this temperature. These values agree well with the reported values for surface melting of indium [In(110) and In(011) reported as $129^\circ C$ and $110^\circ C$, respectively [8]]; thus, we conclude that the onset of the observed liquidlike response of the QCM is due to surface melting of the substrate from tribological energy dissipation. We attribute the frequency shift sign reversal to the onset of a finite surface melted layer present on the QCM. This type of transition would be reversible, and would reduce the stiffness of an originally solid contact, thus...
giving rise to a negative frequency shift rather than the anticipated positive frequency shift [21,22].

We observed the velocity dependent frequency shifts presented in Figs. 1–3 repeatedly and for a variety of tips. Although we expect various local factors to influence the exact velocity at which the transition occurs, we find that (i) the transition is always observed as the temperature of the system is raised towards the surface melting point temperature of indium, (ii) is always observed to be below the melting point temperature of indium (156.6 °C), and (iii) is completely reversible. We now discuss this, and other potential mechanisms for the experimentally observed behaviors, and conclude that melting is the most likely, if not the only, viable explanation of the observed transition.

(i) The tip goes from sticking to sliding.—Borovsky et al. [23] have recently shown that under normal operating conditions, full slip is readily attainable for an indenter probe in contact with an oscillating QCM. In their results, a positive frequency shift was always reported, whether they had full slip or stuck conditions, and in all cases they found a nonzero bandwidth shift indicating some form of tribological energy dissipation. We assert that even if the tip goes from being stuck to sliding, there is some frictional dissipation mechanism still involved during the stuck portion, and the difference in the sign of the frequency shift is not accounted for by a transition of this type.

(ii) The tip becomes blunter and/or there are irreversible effects occurring with increased amplitude (chemical, plastic deformation, etc.).—According to theoretical models for a probe-QCM setup, positive frequency shifts are expected as long as the area of contact is smaller than the acoustic wavelength of the probe-substrate system [21,24]. From STM images the radius of the worn region is ~200 nm (inset of Fig. 4), while for both indium and tungsten the wavelength of 8 MHz acoustic waves is on the order of hundreds of microns [20], with the “real” area of contact expected to be much less [21]. Thus, there is at least 3 orders of magnitude difference between the contact radius and the acoustic wavelengths, and the models should hold for our experimental system. Also, the repeatable nature of the experiment rules out the possibility that tip blunting is the sole reason for the velocity dependent sign of $\Delta f$.

(iii) The transition is related to enhanced diffusion rather than melting.—Upon tip retraction the tip in some cases remains vertically stuck at light pull-off forces—in which case the tip is unstuck by using the coarse retract controls of the STM. This can be attributed to formation of a “neck”, such as that reported in [14,16], due to enhanced diffusion effects. The sign of $\Delta f$ does not depend, however, on whether the tip becomes stuck upon retraction or not, and the velocities reported here are at least 6 orders of magnitude larger than previously reported metal tip-substrate experiments [14–16]. Also, our applied contact pressure, nominally 1.6 GPa, creates a confined geometry that fundamentally differs from the “necking” results of [14,16], illustrated by a recent AFM study demonstrating solidlike behavior for confined water at room temperature [9]. Another consideration is the “windshield wiper effect” documented by Abdelmaksoud et al. [25], whereby mobile adlayers with liquidlike diffusivities were brushed aside by the STM tip, leaving the QCM contact bare. These considerations strongly suggest that a critical thickness of liquid needs to be present for the observed transition to occur.

(iv) The heat generated via friction melts the indium.—Generally speaking, when a finite liquid [26], viscoelastic [27], or solid contact [21] is made with a QCM, either a negative or positive frequency shift is observed, with the magnitude of the frequency shift proportional to the area of contact. In these cases, the sign of the frequency shift has remained positive for solid contacts and negative for viscoelastic or liquid contacts. Additionally, reports of initially negative frequency shifts becoming positive over time for cells deposited on a QCM have been attributed to the stiffening of the adsorbed cells [28]. The velocity dependent frequency shift reversal we observe is consistent with these observations; i.e., a transition from a solid (stiff) contact to a liquid contact occurs due to frictional energy dissipation. These frequency responses can be interpreted by attributing positive frequency shifts to an added stiffness in the resonator from the elastic restoring forces of the contact, with negative frequency shifts attributed to a liquid contact damping the resonator. To the authors’ knowledge, the observation of a velocity dependent frequency shift reversal has not been previously reported.

To estimate whether the heat generated at an interface is sufficient to melt the substrate, we look at the steady state solution to the heat equation for a heat source of heat flux $q$ contacting a semi-infinite body over an area of radius $a$, with the result [29]:

\[ T(x,t) = \frac{q}{4\pi \kappa} \ln \left( \frac{a^2}{x^2} \right) \]

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where $\kappa$ is the thermal diffusivity of the substrate, $\ln$ is the natural logarithm, and $T(x,t)$ is the temperature at a distance $x$ from the source at time $t$. The logarithmic term indicates that the temperature decays exponentially with distance from the source, and the magnitude of the temperature rise is proportional to the heat flux $q$. Therefore, for a heat source of heat flux $q$, the temperature rise at a distance $x$ from the source is given by:

\[ T(x) = \frac{q}{4\pi \kappa} \ln \left( \frac{a^2}{x^2} \right) \]
\[ \Delta T = \frac{qa}{k}, \]  

(1)

where \( k = 81.6 \, \text{W/(m} \cdot \text{K)} \) is the thermal conductivity of indium.

To calculate the heat flux supplied to the interface, we approximate the energy dissipation when the tip comes into contact with the QCM. We calculate the kinetic energy of the quartz/electrode system using the measured oscillation amplitude with a previously measured QCM amplitude distribution [30]. The dominant term of the kinetic energy (by 3 orders of magnitude) comes from the quartz crystal itself, taking the form:

\[ \text{KE}_{\text{quartz}} = \frac{2\pi R^2 d p [A \omega \cos(\omega t)]^2 (1 - e^{-2b})}{16b}, \]

(2)

with \( R \) the electrode radius, \( d \) the thickness of the crystal, (half of a wavelength when operated in the fundamental mode), \( p \) the density of quartz, \( \omega \) the angular frequency, \( A_0 \) the maximum amplitude of oscillation at the center of the electrode, \( t \) time, and \( b \) a constant of the amplitude distribution which we assume to be 3 [30]. Using the changes in amplitude from Fig. 1, we can find the change in energy per cycle, which when multiplied by the frequency yields the power dissipated. Figure 4 shows the results of these calculations along with the calculated maximum temperature rise assuming that half of the dissipated power went into the indium as heat flux (with the other half going into the tungsten tip) at a contact radius of 200 nm. The results show that ample energy dissipation is present to melt the indium.

We have reported here our observation of a velocity dependent transition from solid to liquidlike behavior for an STM tip in sliding contact with an indium electrode of a QCM, the first such observation for a sliding asperity contact. The velocity dependent nature of the frequency shift implies a change in the mechanisms of frictional dissipation; e.g., the contact region changes from solid to liquid. An analysis of the change in kinetic energy of the QCM when the tip comes into contact with the substrate shows that ample energy is dissipated to melt the indium, with temperature studies indicating that the onset of this transition is close to indium’s surface melting temperature. The results suggest that the surface, rather than bulk, melting point temperature is the more relevant quantity for tribological considerations.

This work has been supported by the Extreme Friction MURI program, AFOSR No. FA9550-04-1-0381, and by NSF DMR0320743 and DMR0805204. D. B. Brenner and D. Irving are gratefully acknowledged for many useful discussions.