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Sliding friction of helium films in the metastable state and its relaxation

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We measured the sliding friction of ^{4}He films adsorbed on Grafoil using the quartz-crystal microbalance technique. In the low-temperature regime, this friction remains metastable after switching off the oscillation amplitude before relaxing to the value determined by the amplitude. The relaxation of this friction is qualitatively different for decreasing and increasing amplitudes. In the former case, the relaxation depends strongly on temperature and has a quasiexponential time dependence, while it has a quasilogarithmic one in the latter case. We can explain both cases of relaxation by a model of a small low-friction domain, which is created or annihilated by overcoming a potential barrier.

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Sliding friction is a fundamental problem that has been studied for many years and is certainly an important one for practical applications.[1] The development of nanoscale devices necessitates understanding of the sliding friction on a nanometer scale.[2] With the introduction of recently developed techniques, peculiar experimental observations of nanoscale friction were reported, and another field, nanotribology, has been growing rapidly.[3,4]

Regarding physisorbed films, Krim and co-workers developed the quartz-crystal microbalance (QCM) technique and measured the sliding friction of various films adsorbed on metal substrates.[5,6] Recently, Mistura and co-workers measured the sliding friction of Kr films adsorbed on Au substrates (Kr/Au).[7] When the oscillation amplitude of pulling force *slowly* increases, the friction decreases rapidly above a certain amplitude. They concluded that this behavior can be explained in terms of the melting of a commensurate solid due to pulling force.

When the pulling force changes *abruptly*, the film structure is expected to remain in a metastable state before the melting or solidification. Using the surface forces apparatus, Israelachvili and co-workers carried out stop-start experiments for ultrathin lubrication films between two shearing mica surfaces.[8] If the stopping time is longer than a certain time τ_0, a single stick-slip spike appears when sliding starts. As the stopping time becomes longer, its magnitude increases. They explained that τ_0 is a characteristic nucleation time for the solidification of film and that its process continues even after the initially rapid nucleation event is complete.

The sliding friction in the metastable state and its relaxation are related to significant information on the evolution of film structure. This is also of importance for understanding the transition between static and kinetic frictions. We measured the friction of ^{4}He films adsorbed on Grafoil (exfoliated graphite) (^{4}He/Grafoil) using the QCM technique. For ^{4}He/Grafoil at low temperatures, we found that after switching the oscillation amplitude, the friction remains metastable before relaxing to a certain value. In this paper, we report on the relaxation of the friction in metastable state and propose a microscopic model based on our experimental data.

In the QCM technique, the sliding friction of physisorbed films is obtained from the changes in the resonance frequency and Q value of the quartz crystal. When the friction is proportional to the sliding velocity $\mathcal{V}$ as $\mathcal{F}_{\text{fric}}=-(\sigma/\tau_S)\mathcal{V}$, where σ is the mass of the film per unit area, these changes are related to the slip time τ_S as

$$\frac{\Delta f}{f_{\text{res}}}=-\frac{\sigma}{M}\frac{1}{1+(\omega\tau_S)^2},\qquad \Delta\left(\frac{1}{Q}\right)=\frac{2\sigma}{M}\frac{\omega\tau_S}{1+(\omega\tau_S)^2},\tag{1}$$

where M is the areal density of the crystal and ω is the angular frequency of oscillation.[9] As the friction decreases, i.e., $\omega\tau_S$ increases, the film undergoes decoupling from the oscillating substrate and the resonance frequency increases.

In our experiments, the resonator is a 5.0 MHz AT-cut quartz crystal. The crystal was commercially available, and no special treatment was applied to the Ag electrode. At first, Grafoil was baked in a vacuum at 900 °C for 3 h, and a 300-Å-thick film of Ag was deposited onto it. The crystal and Ag-plated Grafoil were pressed together and were heated in a vacuum at 350 °C for 2 h. Then, Grafoil was bonded on both sides of the Ag electrode. After bonding, the excess amount of Grafoil was removed. To keep good thermal contact, the crystal was fixed to the metal holder with electrically conductive adhesive. After these processes, the Q value of the crystal remained better than 10^4, and the areal density of Grafoil was $7.30\ \text{g/m}^2$.[10] After being heated in 2×10^{-6} Pa at 130 °C for 5 h, the crystal was mounted in the sample cell. During transport, it was briefly (1 min or less) exposed to air. Then, the sample cell was evacuated and cooled down to 4.2 K. The experiments were carried out down to 0.35 K. Heating due to the QCM measurement was checked carefully.[11] It was found that the response of the crystal is adequately fast when the temperature of the sample cell is changed and that characteristic temperatures do not depend on the oscillation amplitude in the range of one order of magnitude.[12]

The resonance frequency and Q value were measured using a transmission circuit.[13] In the circuit, the quartz crystal was placed in series with a coaxial line connecting a 50 Ω cw signal generator and a phase-sensitive detector (PSD). The transmitted signal was multiplied in the PSD by the in-phase and quadrature references using a double-balanced mixer (DBM). The two DBM outputs through the low-pass filters were detected independently. The frequency of the signal generator was then controlled in order to keep the in-phase output zero and was locked to the resonance frequency. The quadrature output at this frequency is the resonance amplitude, and the Q value is calculated from this amplitude.

The graphite crystallites of Grafoil are oriented with their basal planes parallel to the lateral oscillation. The full width at half-maximum of the c-axis distribution is 12°, as determined by x-ray scattering. From the specific surface area of 15.4 m^2/g, and the change in the resonance frequency from bare Ag to Grafoil/Ag electrodes, the sensitivity for the mass loading of ^{4}He corresponds to 4.2 Hz/atoms nm^2. The large effective surface area and the highly oriented c axis of Grafoil make this a suitable substrate for the study of sliding friction by QCM.

To minimize the effect of desorption, Grafoil disks were put on the bottom of the sample cell. The surface area was determined through the measurement of a Kr adsorption isotherm at 77 K, and the third layer condensation of Kr films was clearly observed. In addition, the vapor correction to the resonance was also checked at room temperature. It was found that the resonance frequency and Q value change by -2.8 Hz and -1.2 ppm at 0.078 MPa of N_2. The calculated values of the viscous loading and hydrostatic effects are -1.7 Hz and $+2.3$ ppm. The vapor correction for the crystal with Grafoil is slightly different from that of the calculation[14,15] but is minimal for our experimental conditions.

The effect of tortuosity was estimated in our experiments. From the resonance frequency and Q value, the areal density σ can be calculated using Eq. (1). Around the first layer completion, it was found that the calculated and experimental values almost agree with each other and that their effect is small. Thus, most part of the film slides uniformly relative to the oscillating substrate.

Figure 1 shows the temperature dependence of the resonance frequency for various ^{4}He areal densities. It is known that ^{4}He film adsorbed on Grafoil grows up to more than five-atom-thick film in layers.[16,17] These sets of data were taken during cooling; for clarity, they are shifted vertically. Above four-atom-thick film, the resonance frequency increases above around 1.5 K due to desorption. The data shown in the figure are not corrected for the desorption.

As the ^{4}He areal density is increased above 22 atoms/nm^2, an increase in the resonance frequency is clearly observed below T_S, although it can also be seen slightly below this density. It was found that T_S does not depend on the oscillation amplitude in the range between 0.1 and 1.0 nm. (We define T_S as the intersection of the extrapolation from high temperatures and the extension of the steepest increase.) This demonstrates that decoupling of the ^{4}He film from the oscillating substrate occurs below T_S; thus, we can conclude that the sliding friction of ^{4}He films decreases below T_S.[18] In addition, it was found that T_S decreases rapidly at the second layer completion of 20 atoms/nm^2. This means that Grafoil is clean and T_S is closely related to the layer structure of the ^{4}He film. Similar behavior of the sliding friction of He films has been previously reported.[19,20] On the other hand, above 32 atoms/nm^2, decoupling due to superfluidity is observed at T_C, which is in good agreement with torsional oscillator measurements.[17] For the thinner films, there exists no signature of superfluidity in our experiments.

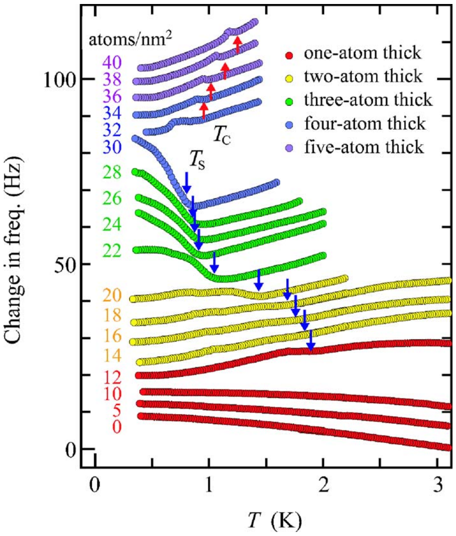

FIG. 1. (Color online) Change in the resonance frequency at an amplitude of 0.4 nm for various ^{4}He areal densities (atoms/nm^2). Different colors correspond to different film thicknesses. The arrows indicate the decoupling temperature T_S and the superfluid onset T_C. For clarity, the sets of data are shifted vertically.

Although there are many interesting features of the sliding friction of nonsuperfluid ^{4}He films such as the ^{4}He areal density dependence of T_S, we confine ourselves to a discussion of the sliding friction below T_S. We consider the three-atom-thick films in detail. Figure 2 shows the temperature dependence of the resonance frequency and the Q value for 23 atoms/nm^2 under several experimental conditions. First, we examine the oscillation amplitude dependence. The cooling processes for 0.6 and 0.2 nm oscillations are shown in Figs. 2(a) and 2(b), respectively. At both amplitudes, below T_S of about 1.0 K, the resonance frequency increases with a corresponding change in Q^{-1}. The increase in the resonance frequency at 0.6 nm is larger than that at 0.2 nm, and Q^{-1} at 0.6 nm decreases slightly. The increase means that the film decouples to a certain degree above T_S, i.e., $\omega\tau_S \geqslant 1$.

In the low-temperature regime below T_S, it was found that the sliding friction remains metastable after the amplitude has been switched. We compare two different warming processes: (1) The film is cooled at 1.0, 0.6, or 0.4 nm, and the amplitude is decreased to 0.2 nm at the lowest temperature before warming. This warming is shown in Fig. 2(c). (2) The film is cooled at 0.2 nm and is warmed while retaining this amplitude, as shown in Fig. 2(d). As seen, the resonance frequency of Fig. 2(c) decreases greatly around 0.7 K, which

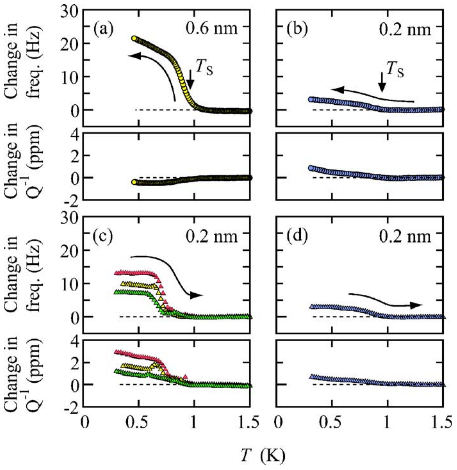

FIG. 2. (Color online) Change in the resonance frequency and the Q value for an ^{4}He areal density of 23 atoms/nm^2. The difference from the dotted line, which is the extrapolation from high temperatures, is plotted. (a) Cooling at an oscillation amplitude of 0.6 nm. (b) Cooling at 0.2 nm. (c) Warming at 0.2 nm after switching from a large amplitude at the lowest temperature. Different colors correspond to different amplitudes during cooling: red, yellow, and green are for 1.0, 0.6, and 0.4 nm, respectively. (d) Warming at 0.2 nm after cooling at the same amplitude.

means that the film after the reduction in amplitude remains in a low-friction *metastable* state at low temperatures. It should be noted that this state is determined by the amplitude before reduction. These features are common for two- and three-atom-thick films, and similar behavior was observed for ^{3}He films.

Existence of a low-friction metastable state strongly suggests that the oscillating substrate causes the rearrangement of He atoms from the stationary substrate. In an earlier work, Mistura and co-workers found a depinning transition for Kr/Au.[7] They reported that the sliding friction changes rapidly at a certain oscillation amplitude and exhibits hysteresis as a function of the amplitude, i.e., Kr films take *two* different states at a certain amplitude. In contrast, the sliding friction of ^{4}He films in the metastable state changes continuously depending on the amplitude prior to the reduction. This implies that the observed behavior is different from the transition observed for Kr/Au.

To clarify the nature of the metastable state, we measured the relaxation after decreasing and increasing amplitude. As mentioned above, the film after the reduction in amplitude remains in the low-friction metastable state. When the film was maintained at a constant temperature, the sliding friction was found to increase gradually. Figure 3(a) shows the logarithms of the change in sliding friction after the reduction in amplitude from 1.0 to 0.2 nm for 23 atoms/nm^2. The changes of the sliding friction, $|\mathcal{F}_{\text{fric}}-\mathcal{F}^0_{\text{fric}}|$, and the resonance frequency are taken from the equilibrium value of 0.2 nm at 1 K [$\mathcal{F}^0_{\text{fric}}=8.4\ \text{N m}^{-2}$ at $\mathcal{V}=1\ \text{m s}^{-1}$ (Ref. 21)], which is shown by the dotted line in Fig. 2. (Note that the friction increases in the downward direction on the vertical axis.) The friction increases slowly at first, and then almost linearly in the logarithmic plot in the latter half. Finally, it settles down abruptly to the value which is determined by the amplitude after the reduction.

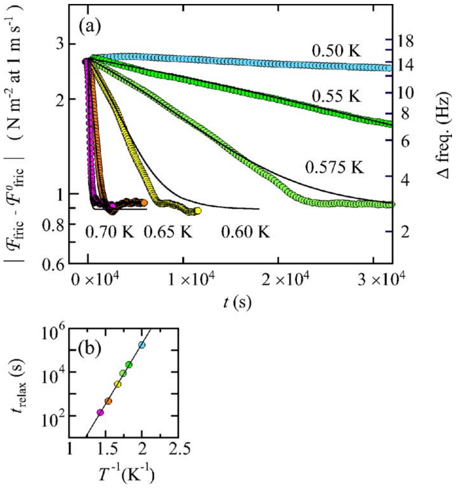

FIG. 3. (Color online) (a) Relaxation after decreasing the oscillation amplitude from 1.0 to 0.2 nm for an ^{4}He areal density of 23 atoms/nm^2. The change in sliding friction is plotted on a logarithmic scale, and the corresponding value of the resonance frequency is shown on the right. The solid lines are calculated numerically from Eq. (2) with the common parameters, $E_0/k_B=13.2$ K and $\alpha N_0/k_B=11.9$ K (see text). (b) Relaxation time t_{relax} against $1/T$.

We found that the relaxation depends strongly on temperature. The relaxation time t_{relax} can be obtained from the region where the sliding friction changes almost linearly in the logarithmic plot. Figure 3(b) shows the logarithms of the relaxation time t_{relax} against $1/T$; they lie almost on a straight line, i.e., the relaxation time obeys Arrhenius' law as $t_{\text{relax}}=t'_0\exp(E'/k_BT)$, suggesting that the relaxation is related to a thermal process. The activation energy E'/k_B is obtained to be about 13 K, and the attempt frequency $1/t'_0$ is on the order of 10^{-6} s.

It should be noted that the obtained energy is close to the activation energy of thermal defects. From the specific heat measurements, the activation energy for one-atom-thick films is in the range from 20 to 27 K.[22] Because of a weaker bonding to the substrate for three-atom-thick films, this energy is expected to decline from the value of one-atom-thick films.

In the low-temperature regime, the sliding friction decreases gradually following an increase in oscillation amplitude. Figure 4 shows this decrease after an increase in amplitude from 0.2 to 0.6 nm for 26 atoms/nm^2. The sliding friction is plotted against the logarithm of the waiting time, and the change in the friction is taken from the equilibrium value at 0.6 nm ($\mathcal{F}^0_{\text{fric}}=3.1\ \text{N m}^{-2}$ at $\mathcal{V}=1\ \text{m s}^{-1}$). The decrease in friction against the logarithm of the waiting time is almost linear in a certain region. In contrast to the relaxation after decreasing amplitude, it does not depend strongly on temperature.

A quasilogarithmic time dependence is often observed for various relaxations, e.g., the flux motion in type-II superconductor,[23] the transient creep at low temperature and stress,[24] the aging effect of the static friction,[25,26] and so on. These phenomena can be explained by requiring that the nanoscale movable units overcome a potential barrier by thermal activation. Application of an external force has the

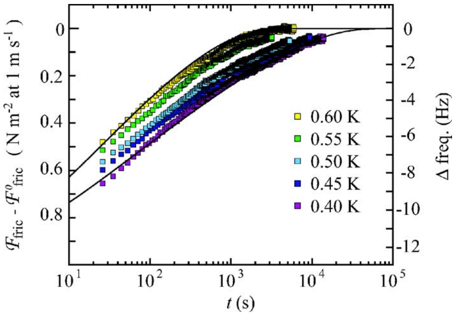

FIG. 4. (Color online) Relaxation after increasing the oscillation amplitude from 0.2 to 0.6 nm for 26 atoms/nm^2. The time scale is logarithmic. The solid lines are calculated numerically from Eq. (2) with $E_0/k_B=0.6$ K and $\alpha N_e/k_B=2.7$ K (see text).

effect of reducing this potential barrier and increasing the rate at which jumps occur.

The time dependence after both decreasing and increasing amplitudes can be explained by the following scenario. On the basis of Brownian-motion dynamics of physisorbed films, Persson clarified that a change in the sliding friction is initiated by nucleation of a small area with a different film structure when the pulling force changes abruptly.[27] The activation energy obtained from decreasing amplitude is close to the energy required to create the defect, which suggests that the rearrangement of He atoms caused by the oscillating substrate occurs in a small area. In a ^{4}He film in the low-temperature regime, we assume that on an *oscillating* substrate there always exists a small domain in which the sliding friction is small, and the decrease in the friction is proportional to the number density of the low-friction domain. The equilibrium number density N_e is determined by the oscillation amplitude, and the number density N is varied as

$$dN/dt = -(N - N_e)/t_{\rm relax}, \tag{2}$$

where $t_{\rm relax}=t_0 \exp(E/k_BT)$ is the relaxation time, which is related to the potential barrier E to create or to annihilate the domain. We also assume that the barrier is decreased by the oscillation and depends on the number density of the domain, i.e., $E=E_0+\alpha N$, where α is a constant and E_0 depends on the oscillation amplitude.

In the case of a decrease in amplitude, one can obtain $N=N_0 \exp(-t/t_{\rm relax})$ when E_0 is adequately large as $E_0 \gg \alpha N$ and $N_e=0$. Here, N_0 is the initial number density. The calculation without these approximations can be carried out numerically and is shown by the solid lines in Fig. 3(a). Regardless of temperature, E_0/k_B and $\alpha N_0/k_B$ are chosen to be the common values, 13.2 and 11.9 K. The calculation reproduces the relaxation, although it deviates slightly just before the value determined by the amplitude.

In the case of an increase in amplitude, one can obtain $N=(k_BT/\alpha)\log(1+\nu t)$ when E_0 is small because of the oscillation and $N-N_e \sim -N_e$ at the early stage. Here, $\nu = \alpha N_e/(k_BTt_0e^{E_0/k_BT})$. In the numerical calculation, the change in the resonance frequency is chosen to be 12 Hz from the measurement of the reduction in amplitude for 26 atoms/nm^2. The calculation with $E_0/k_B=0.6$ K and $\alpha N_e/k_B=2.7$ K is shown by the solid lines in Fig. 4, which agree well with the observed relaxations. It should be noted that $\alpha N_e/k_B$ is smaller than $\alpha N_0/k_B$. This is explained due to α being different because the interaction between the domains depends on the oscillation amplitude.

Thus, we conclude that this model explains the mechanism of both cases of relaxation. We are also aware that the model is based on rather limited evidence.

In summary, we have measured the sliding friction of ^{4}He films adsorbed on Grafoil. In the low-temperature regime, the sliding friction remains metastable after switching off the oscillation amplitude, and the relaxation of this friction is qualitatively different for decreasing and increasing amplitudes. We explain the relaxation by a model of a small low-friction domain. However, the configuration of He atoms in the domain is still an open question, making this a subject for future study.

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[10] The average thickness of Grafoil on each electrode is about 3.3 μm, and its effective surface area is 56 times larger than that of the bare Ag electrode.

[11] In a separate experiment, we have carried out the QCM measurement of superconducting In substrate with the same technique. The superconducting transition was detected directly by measuring a mutual induction, and no temperature gradient from the sample cell was observed within the experimental errors.

[12] The temperature at which the sliding friction T_S and T_C do not depend on the oscillation amplitude.

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