Reentrant pinning of a ^{3}He overlayer in a ^{3}He-^{4}He mixture film

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(Received 15 June 2018; revised manuscript received 22 November 2019; published 16 December 2019)

We performed quartz crystal microbalance experiments for a ^{3}He-^{4}He mixture film on an exfoliated single-crystalline graphite using a 32-kHz quartz tuning fork. The decoupled ^{3}He overlayer on the superfluid ^{4}He layer shows a reentrant pinning at a certain temperature T_{3d} under a large oscillation amplitude. The pinning state below T_{3d} is metastable. After reducing the oscillation amplitude, the ^{3}He overlayer relaxes to a stable pinning state via a depinning state. It is found that the reentrant pinning is triggered by a structure change of the underlying localized ^{4}He layer on the oscillating substrate.

DOI: 10.1103/PhysRevB.100.214508

I. INTRODUCTION

Recently, quartz crystal microbalance (QCM) experiments of ^{3}He-^{4}He mixture films were conducted, and new phenomena were reported [1,2]. Finley *et al.* measured these films on a H_2 substrate and found an additional mass decoupling different from the superfluid transition [1]. On the other hand, Oda and Hieda revealed that a ^{3}He overlayer undergoes depinning from an oscillating Au substrate above a certain amplitude [2]. They also pointed out that the superfluidity of the underlying ^{4}He layer possibly affects this pinning-depinning transition.

The pinning-depinning transition is commonly observed in various systems, e.g., physisorbed films [3–5], charge-density waves [6], vortex flow in a superconductor [7,8], and dislocations in a solid [9]. ^{3}He-^{4}He mixture films on a graphite substrate, however, have a distinctive feature. As shown in Fig. 1(a), it is known that these films show a three-layer structure at low temperature, i.e., the ^{3}He overlayer, the underlying fluid, and the localized ^{4}He layers [10,11]. Because of a strong coupling between these three subsystems, the pinning-depinning transition of the ^{3}He overlayer can be used as a probe for the underlying layers on the oscillating substrate.

As for pure ^{4}He films on a graphite substrate, 5-MHz QCM experiments revealed that the mass decoupling due to the depinning of the second atomic layer is observed until the middle of four-atom-thick films [12–14]. The ease of the depinning is caused by the incommensurability between the first and second atomic layers. This decoupling, however, vanishes when the superfluidity of the fluid layer grows to some extent. The similar mass decoupling and its vanishment are also observed for three-atom-thick films by a 32-kHz quartz tuning fork [15,16].

From comparison between these two QCM experiments, the acceleration of substrate plays an important role in the mass decoupling due to depinning [15]. In addition, its vanishment is explained by the cancellation of the mass transport due to the counterflow of the superfluid overlayer [13].

In this paper, we report the mass decoupling of four-atom-thick ^{4}He films with a small amount of ^{3}He on a graphite substrate by a 32-kHz quartz tuning fork and the reentrant pinning transition of the ^{3}He overlayer. It was found that the ^{3}He overlayer is depinned from the oscillating substrate below a certain temperature. As further decreasing the temperature, the reentrant *pinning* transition occurs to the ^{3}He overlayer. This transition reveals the structure change of the localized ^{4}He layer on the oscillating substrate.

II. EXPERIMENTS

The mass decoupling of a ^{3}He-^{4}He mixture film was measured via the QCM technique using a 32-kHz quartz tuning fork. The changes in the resonance frequency and Q value are related to the coupled mass and the energy dissipation of the film on the oscillating tuning fork. When the frictional force acting on the film is proportional to the sliding velocity v as $F \propto -v/\tau$, where τ is the slip time, the changes from no film are expressed as [17]

$$\frac{\Delta f}{f} \sim -\frac{2m}{M}\frac{1}{1+(\omega\tau)^2}, \tag{1}$$

$$\Delta\left(\frac{1}{Q}\right) \sim \frac{4m}{M}\frac{\omega\tau}{1+(\omega\tau)^2}. \tag{2}$$

Here m and M are the masses of the film and the arms of the quartz tuning fork, respectively, and ω is the angular resonance frequency. When the frictional force decreases, i.e., $\omega\tau$ increases, the film undergoes decoupling. At $\omega\tau = 1$, one-half of the adsorbed mass slides on the oscillating substrate.

In the present experiments, exfoliated single-crystalline graphite was used as the substrate. Single-crystalline graphite was obtained by dissolving a type of mineral called Franklin marble with hydrochloric acid. Exfoliation of graphite provides a large specific surface area. To exfoliate graphite via graphite oxide, pieces of the graphite were immersed in a mixture of concentrated sulfuric acid and nitric acid for 96 h. After neutralization and dehydration, the interlayer space was

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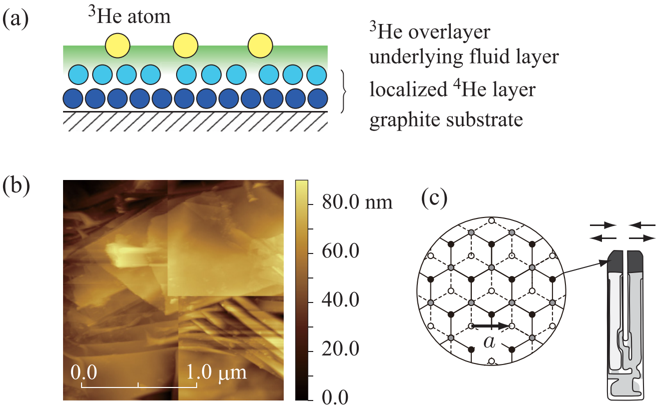

FIG. 1. (a) Schematic view of the three-layer structure of ^{3}He-^{4}He mixture films on a graphite substrate. The localized ^{4}He layer consists of two atomic layers. (b) STM image of an exfoliated single-crystalline graphite. The color scale on the right represents the height of the sample. (c) Relation between the oscillation direction of the tuning fork and the *a* axis of the graphite.

expanded via a quick heating, where a rapid decomposition rate of its functional groups creates a high-enough pressure to overcome the van der Waals interaction between graphene layers. For this purpose, the acid-treated graphite in a crucible was put in a 1050°C-preheated muffle furnace for 15 s under nitrogen atmosphere [18]. For cleaning, the graphite taken from the furnace was heat treated in a vacuum at 900°C for 4 h. A Laue photograph of the exfoliated graphite shows that the crystal orientation is still preserved in the *a*-*b* plane [19]. The typical grain size was ∼1 μm in diameter, as shown in Fig. 1(b), and the size of the atomically flat surface was found to be ∼100 nm in diameter from AFM experiments [20].

To prepare a quartz tuning fork with graphite, a 200-nm-thick silver film was deposited on a sliced piece of the exfoliated graphite. The quartz tuning fork and silver-plated graphite were pressed and heated in hydrogen atmosphere at 300°C for 1 h. The graphite was bonded on the top of both arms of the quartz tuning fork via thermal diffusion of silver. The *a* axis was adjusted to be parallel to the oscillation direction of the tuning fork [Fig. 1(c)]. After bonding, any excess graphite outside the arms was carefully removed. The *Q* value of the quartz tuning fork was better than 2×10^4 at room temperature in a vacuum. It increased with cooling and reached 1.6×10^5 at 4.2 K. To precisely control the areal density of the film, the quartz tuning fork was mounted in the sample cell with baked Grafoil disks, whose surface area (43 m^2) was predominantly larger than that of exfoliated graphite on the quartz tuning fork (0.75 cm^2). In our previous experiments [19,21], we have confirmed the equality of ^{4}He areal density between Grafoil disks and the exfoliated graphite.

The mass loading of ^{4}He was obtained from the decrease in the frequency at the monolayer completion of the ^{4}He film, at which the film sticks almost completely to the oscillating substrate, and was 0.021 Hz atoms^{-1} nm^2.

The resonance frequency was measured using a transmission circuit. In the circuit, the quartz tuning fork was placed in series with a coaxial line connecting a 50-Ω cw signal generator and a lock-in amplifier. The frequency of the signal generator was then controlled to keep the in-phase signal at zero and was locked to the resonance frequency. The quadrature signal at this frequency was the resonance amplitude. The oscillation amplitude was calibrated with the applied alternative voltage using a photograph of the oscillating tuning fork [22].

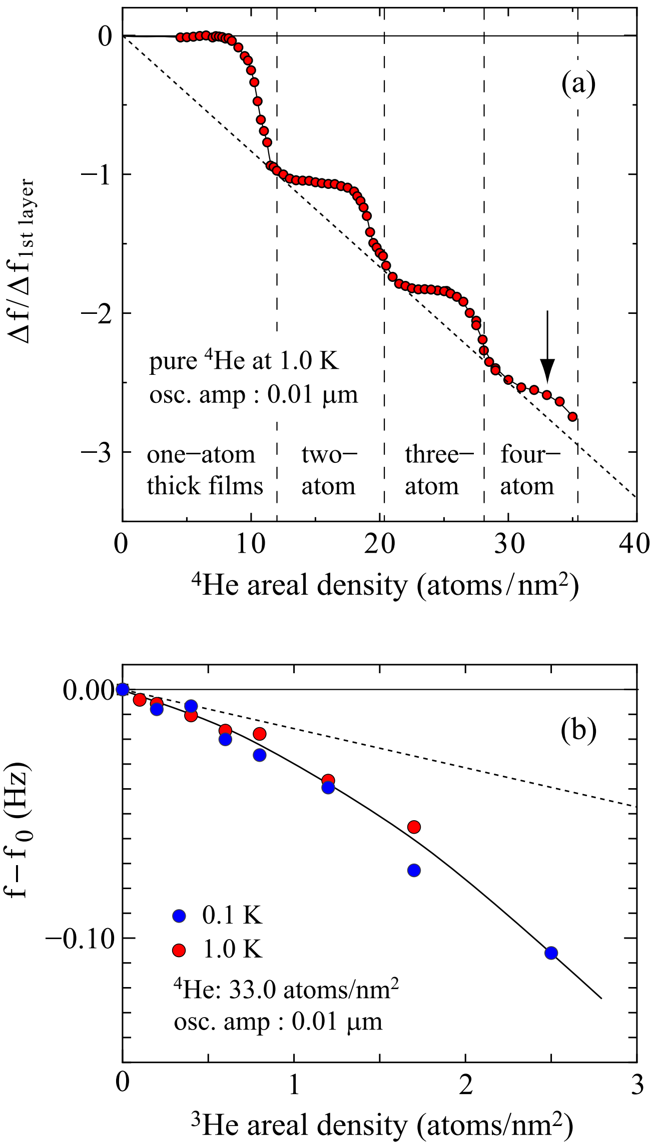

FIG. 2. (a) Decrease in the resonance frequency of pure ^{4}He films as a function of the ^{4}He areal density. The vertical axis is normalized by the mass loading of ^{4}He at the first layer completion. The vertical dashed lines represent layer completions, and the dotted line indicates the mass loading of ^{4}He. (b) Decrease in the resonance frequency from a pure ^{4}He film of 33.0 atoms/nm^2 as a function of the ^{3}He areal density. The oscillation amplitude is 0.01 μm. The dotted line indicates the mass loading of ^{3}He calculated from the areal density. The solid curve is a guide to the eye.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the decrease in the resonance frequency of pure ^{4}He films as a function of the ^{4}He areal density.

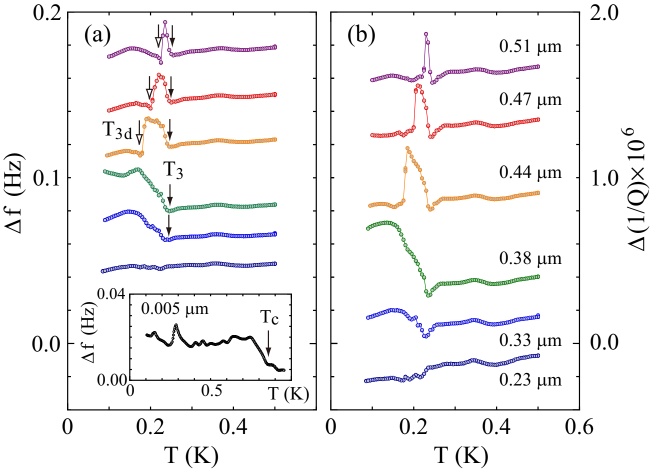

FIG. 3. Variation of (a) the resonance frequency and (b) $\Delta(1/Q)$ for a mixture film of ^{4}He with 33.0 atoms/nm^2 and ^{3}He with 1.7 atoms/nm^2. Inset: Variation in the resonance frequency for a small amplitude of 0.005 μm.

The dotted line indicates the mass loading of ^{4}He, and the vertical dashed lines represent the layer completions. It was found that a part of the ^{4}He films is decoupled between the layer completions. We also observed the mass decoupling due to superfluidity above the middle of three-atom-thick films. The decoupled fraction of the superfluid was ~0.15, which is significantly larger than that of a Grafoil substrate by torsional oscillator experiments [23].

In the present experiments, we prepared a ^{4}He film of 33.0 atoms/nm^2, which becomes superfluid at a T_c of 0.98 K. When a small amount of ^{3}He is introduced onto the ^{4}He film, the resonance frequency for *a small amplitude* of 0.01 μm decreases from that of the pure ^{4}He film, as shown in Fig. 2(b). The dotted line is the mass loading of ^{3}He, which is calculated from the ^{3}He areal density. It was found that the decrease deviates downwards from the mass loading of ^{3}He for large ^{3}He areal densities. This suggests that ^{3}He atoms drag a part of the decoupled ^{4}He and stick to the oscillating substrate together with the dragged ^{4}He [14,24]. This does not depend strongly on the temperature, i.e., ^{3}He atoms stick to the oscillating substrate at this amplitude whether or not the fluid ^{4}He overlayer is a superfluid. Conversely, ^{3}He atoms undergo decoupling at a larger amplitude, which is discussed next.

Figure 3 shows the temperature sweep data of a mixture film composed of ^{4}He with 33.0 atoms/nm^2 and ^{3}He with 1.7 atoms/nm^2 for various amplitudes. T_c was observed at 0.85 K as shown in the inset, and the fluid overlayer is a superfluid in this temperature region. These sets of data were taken during cooling. The similar behavior to the oscillation amplitude was observed from the ^{3}He overlayer with 0.4 atoms/nm^2, at least, up to 5.0 atoms/nm^2. For an amplitude of 0.23 μm, no distinct structure is observed. When the amplitude is 0.33 μm, the frequency increases gradually at a T_3 of 0.24 K, accompanied by an increase in $\Delta(1/Q)$. For an amplitude of 0.38 μm, the mass decoupling below T_3 appears more clearly. The increases in $\Delta f/f$ and $\Delta(1/Q)$ below T_3 become 7×10^{-7} and 5×10^{-7}, respectively.

We can conclude that the increase in the frequency below T_3 is caused by the mass decoupling of the ^{3}He overlayer. This conclusion is supported by an analysis of the slip time τ. τ of the ^{3}He overlayer below T_3 can be estimated from the increase in $\Delta f/f$ and $\Delta(1/Q)$ using Eqs. (1) and (2). Supposing that the ^{3}He overlayer is completely stuck above T_3, we obtain $\omega\tau \sim 0.7$ at 0.1 K for an amplitude of 0.38 μm, i.e., approximately one-third of the adsorbed mass slides at low temperature. Meanwhile, as shown in Fig. 2(b), the ^{3}He overlayer with 1.7 atoms/nm^2 causes a decrease of 0.06 Hz at 0.1 K for an amplitude of 0.01 μm. One-third of this decrease is in good agreement with the increase of 0.02 Hz in frequency below T_3 for an amplitude of 0.38 μm. Furthermore, we observed a weak hysteresis of T_3. On warming, T_3 is shifted to the high-temperature side by ~0.02 K, which also supports the mass decoupling.

The mass decoupling of the ^{3}He overlayer is also supported by the comparison with experiments of Oda and Hieda [2]. We have already reported that the acceleration determines the mass decoupling [15]. At an amplitude of 0.33 μm, the acceleration is calculated to be 1.4×10^4 m/s^2. Oda and Hieda conducted 100 MHz AT-cut QCM experiments for mixture films and revealed that the ^{3}He overlayer is depinned above an amplitude of 4.8×10^{-5} nm. The acceleration at this amplitude is 1.9×10^4 m/s^2. The two accelerations are similar, which strongly suggests that the decoupled substance is the same for both experiments.

Next we move to a larger amplitude. As seen in the figure, a new phenomenon is observed. The increase in frequency below T_3 drops abruptly at T_{3d}, accompanied by a rapid decrease in $\Delta(1/Q)$. For an amplitude of 0.44 μm, the frequency increases at a T_3 of 0.25 K and drops suddenly at a T_{3d} of 0.17 K. This behavior can be understood as the pinning of the ^{3}He overlayer when the amplitude exceeds a certain threshold. As the amplitude increases, T_{3d} shifts rapidly to the higher temperature side.

The amplitude at which ^{3}He atoms are depinned is close to the amplitude at which the second atomic layer undergoes decoupling for three-atom-thick films [25]. This suggests that a structure change of the second atomic layer causes the pinning-depinning transition of the ^{3}He overlayer, although the mass decoupling of the localized ^{4}He layer is hardly observed for four-atom-thick films because of the cancellation mechanism due to the superfluid counterflow.

To examine the nature of the reentrant pinning state below T_{3d}, we measured the relaxation in the frequency and $\Delta(1/Q)$ after switching from a large to small amplitude. The procedure for the relaxation experiments [12] was as follows. The mixture film was cooled slowly down to 0.15 K for a large amplitude and was kept at this temperature for 2 h. Next, the temperature was changed rapidly after decreasing the amplitude. The film was then kept at the new temperature. Figure 4(a) shows the variation in the resonance frequency and $\Delta(1/Q)$ for the ^{3}He overlayer with 0.9 atom/nm^2 after a reduction in amplitude from 0.69 to 0.05 μm. For an amplitude of 0.69 μm, mass decoupling occurs at a T_3 of 0.29 K while T_{3d} is 0.23 K. No mass decoupling is seen below an amplitude of 0.23 μm.

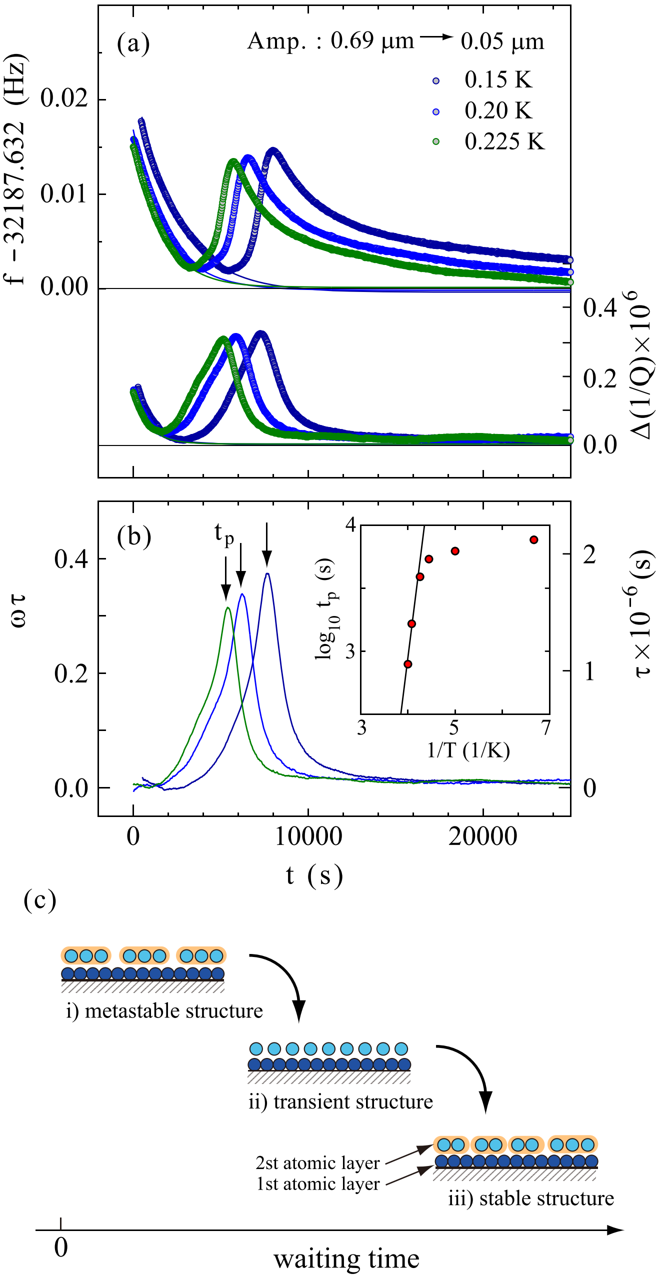

FIG. 4. (a) Relaxation of the resonance frequency and $\Delta(1/Q)$ for the ^{3}He overlayer with 0.9 atom/nm^2 after a reduction in amplitude from 0.69 μm to 0.05 μm. The solid lines are exponential curves that are fitted at the beginning. (b) $\omega\tau$ as a function of the waiting time. Inset: t_p versus $1/T$. (c) Cartoon of the time evolution of the localized ^{4}He layer.

At the beginning after the reduction in amplitude, the frequency decreases exponentially. Near the end of the exponential decrease, the frequency starts to increase accompanied by a large increase in $\Delta(1/Q)$. After additional increases, the frequency and $\Delta(1/Q)$ decrease exponentially once again. As the temperature is increased, the additional increase smears out around T_{3d} and disappears above 0.25 K. From the temperature sweep experiments for the ^{3}He overlayer with 0.9 atom/nm^2, it was found that the increases in frequency and $\Delta(1/Q)$ below T_3 are 0.015 Hz and 2×10^{-7}, respectively. The additional increases in the relaxation experiments are very close to these amounts. From the observed temperature range and the magnitude, it is concluded that the ^{3}He overlayer, which sticks at the beginning, starts to decouple after a while, and relaxes to the pinning state.

Figure 3(b) shows the slip time of the ^{3}He overlayer calculated assuming that the ^{3}He overlayer is completely stuck after a long time has elapsed. Here we used the differences in $\Delta f/f$ and $\Delta(1/Q)$ from the exponential curve at the beginning. The calculated value of $\omega\tau$ exceeds 0.3 [26]. This demonstrates that the ^{3}He overlayer slides under some *specific* conditions with small amplitude. In the inset, we plot the waiting time when $\omega\tau$ has a maximum value, t_p versus $1/T$. Above 0.23 K, t_p decreases rapidly with rising temperature and obeys Arrhenius's law with an activation energy E/k_B of 7 K. This energy is connected to the relaxation of the localized ^{4}He layer. The value is close to the previous experiments with pure ^{4}He films [12].

It is natural for ^{3}He atoms floating on the underlying fluid layer to interact with the inhomogeneous potential of the localized ^{4}He layer. In the previous experiments for pure ^{4}He films, the mass decoupling of the localized ^{4}He layer is understood as the motion of the edge dislocation between the first and second atomic layers [13]. This means that the stable structure of the localized ^{4}He layer has some inhomogeneity and that the second atomic layer undergoes a structure change on the oscillating substrate.

At the beginning of the relaxation experiments, the frequency decreases exponentially. This demonstrates that the localized ^{4}He layer is partly decoupled for an amplitude of 0.69 nm and remains a metastable structure after the reduction in amplitude, as observed for pure ^{4}He films [12].

From these considerations, we propose a following scenario for the relaxation experiments. A cartoon of the time evolution for the localized ^{4}He layer is shown in Fig. 4(c). At the beginning, the localized ^{4}He layer remains a metastable structure and the spatial inhomogeneity is high. ^{3}He atoms are pinned to this inhomogeneous potential. In the relaxation process from the metastable to the stable structures, a transient structure appears. In the transient structure the inhomogeneity is decreased, and ^{3}He atoms undergo decoupling. When the localized ^{4}He layer approaches the stable structure, the inhomogeneity is increased and ^{3}He atoms are pinned once again.

The temperature sweep experiments are also explained by the scenario. In a small amplitude, ^{3}He atoms are pinned to the inhomogeneous potential. As the amplitude increases, a structure change occurs in the localized ^{4}He layer at T_3, and ^{3}He atoms are depinned. When the temperature is decreased further, the inhomogeneity is increased. Above a certain amplitude, the localized ^{4}He layer becomes highly inhomogeneous, and ^{3}He atoms are pinned once again at T_{3d}. The plausibility of this scenario is enhanced by observations of the mass decoupling of three-atom-thick films [25]. This decoupling occurs at a nearly equal amplitude to the pinning-depinning transition in the present experiments. In addition, the decoupled mass grows rapidly as the amplitude increases, i.e., the inhomogeneity is increased in a large amplitude, which explains the amplitude dependence of T_{3d}.

Here we comment on experiments for ^{3}He-^{4}He mixture films on a H_2 substrate by Finley *et al.* [1]. The additional mass decoupling may be explained by the above-mentioned scenario. The localized ^{4}He layer (~0.60 monolayers) slides easily on the incommensurate H_2 substrate. For pure ^{4}He films, the mass decoupling is, however, hardly observed because of the cancellation mechanism due to the superfluid counterflow, while the depinning of the ^{3}He overlayer occurs for ^{3}He-^{4}He mixture films. In their experiments, ^{3}He atoms are almost completely decoupled, which results in no additional dissipation. On the other hand, Oda and Hieda observed the pinning-depinning transition of the ^{3}He overlayer with a large hysteresis [2]. We also observed a weak hysteresis both for T_3 and for T_{3d} in the present experiments. The effect of superfluidity is the subject for a future study.

IV. SUMMARY

In summary, we performed QCM experiments for a ^{3}He-^{4}He mixture film on a graphite substrate using a 32-kHz quartz tuning fork. The ^{3}He overlayer undergoes decoupling at T_3, and the decoupled one is pinned at T_{3d} on the oscillating substrate under a large amplitude. It was found that a structure change of the underlying localized ^{4}He layer triggers the pinning-depinning transition of the ^{3}He overlayer.

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[21] We prepared a quartz tuning fork with Grafoil and mounted it in the same sample cell to compare the decrease in the frequency with exfoliated graphite. In both experiments, it was found that the resonance frequency drops at the ^{4}He areal densities where the layer completions takes place on Grafoil disks in the sample cell.

[22] We took a photograph of the oscillating arm through a microscope, measuring the applied alternative voltage. Because of oscillation, its contour was blurred, whose a half width corresponds to the amplitude. The obtained amplitude from photograph was in the range of μm–10 μm and was found to be proportional to the applied alternative voltage. In the present experiments, this calibration was extrapolated to a small amplitude. The estimated accuracy was several percentages. In addition, we checked the linearity between the amplitude and the applied alternative voltage by means of a laser Doppler vibrometer using a different quartz tuning fork.

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[24] We found that pure ^{4}He films are partly decoupled from the oscillating substrate, as shown in Fig. 2(a).

[25] We found that the mass decoupling occurs above ~ 0.4 μm for three-atom-thick films of pure ^{4}He. The decoupled mass increases linearly with amplitude up to ~ 1.5 μm and reaches one third of ^{4}He monolayer for 24 atoms/nm^2.

[26] The slip time ($\omega\tau \sim 0.37$) may be underestimated because we assume that the ^{3}He overlayer is completely stuck for an amplitude of 0.05 μm. From Eqs. (1) and (2), the mass of the ^{3}He overlayer is calculated ~0.12 Hz. This value is larger than the decrease in frequency of ~0.03 Hz for the ^{3}He overlayer with 0.9 atoms/nm^2 in Fig. 2. The discrepancy is settled by assuming that the ^{3}He overlayer in the equilibrium of this amplitude is decoupled partially.