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Wetting behavior of liquid ^{4}He on rough Cs films: Pinning, memory effect, and micropuddles

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The liquid ^{4}He-cesium system is a nearly ideal one for studying wetting phenomena. However, it can show nonideal behavior such as an extreme wetting hysteresis and a memory of being in contact with liquid ^{4}He. We believe that this is caused by the roughness of the Cs surface. We review the wetting characteristics of Cs surfaces produced by various methods, and we qualitatively classify Cs surfaces according to the strength of pinning of the contact line. New data are presented on quench-condensed Cs surfaces that show that the pinning can be weak and the contact line can move freely to dewet this Cs. We discuss how micropuddles can form on strong-pinning surfaces, and we discuss how this leads to the memory effect and changes the effective pinning. These phenomena should be generally relevant to the wetting behavior of rough surfaces.

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I. INTRODUCTION

In many cases of wetting or nonwetting of liquids on solids, the liquid is not ideal and the surface of the solid is not perfect. The liquid is usually not pure, and impurities can migrate to the interface where they can have a dominant effect. The whole industry of surfactants relies on this, where a very small amount of surfactant, in relation to the total weight of the system, can completely alter the character of the system. Common examples of this are detergents and emulsifiers. Solid substrates are also difficult to clean, but clean surfaces can be obtained by cleaving or carefully preparing in ultrahigh vacuum. However, when these surfaces are exposed to air, they can adsorb water and other molecules from the atmosphere and they might also chemically react with them. If the surfaces have been washed in water or solvent, then they readily pick up the impurities in these fluids. For example, it is very difficult to remove traces of detergent, below one monolayer, from glass by repeated rinsing in water.

Besides chemical impurities, solid surfaces usually have some degree of roughness, and this is often not characterized. Roughness can have, and usually does have, a profound effect on the wetting behavior. Most simply it increases the surface area of the interface and so modifies Young's equation: i.e., $\cos\Theta = f(\sigma_{\mathrm{sv}} - \sigma_{\mathrm{sl}})/\sigma_{\mathrm{lv}}$. Here f is the ratio of the area of the rough interface to the area of the ideal smooth interface and σ is the interface free energy where s, l, and v denote solid, liquid, and vapor. Roughness may also cause capillary condensation in holes and grooves of suitable geometry which will change the local shape of the free liquid surface and the mobility of the contact line. Roughness can also pin the contact line directly so that the wetting dynamics is completely changed.

It was hoped that the system of liquid ^{4}He on alkali-metal surfaces[1,2] would overcome many of these problems. Liquid ^{4}He is exceptionally clean. The only impurity is ^{3}He, and this can be reduced to better than 1 part in 10^{12}.[3] Also it is superfluid at $T < T_\lambda = 2.17$ K, so that thermodynamic equilibrium is more likely to be attained. Although alkali metals are extremely reactive, which makes the preparation of clean surfaces a significant problem, it seems possible to prepare and maintain chemically clean surfaces. Hence the ^{4}He-Cs system approaches an ideal system for studying wetting and many important characteristics have been established. The wetting temperature T_w is reasonably reproducible at 2.0 K (see, e.g., Refs. 4–7), which is well below the critical temperature of ^{4}He, where Cahn has shown wetting must occur,[8] and as there is no triple-point for ^{4}He, there is no question of triple-point wetting.[9] The contact angle has been measured from $T \ll T_w$ up to $T = T_w$.[5] The prewetting line has been seen for the first time.[10] The thermodynamic thin-film state[11] which occurs in the nonwet regime (see Fig. 1) has been shown to be very thin when $T \ll T_w$ and $\Delta\mu \approx 0$, with a statistical thickness which is orders of magnitude less than one monolayer (ML).[12]

Despite these successes, different methods of preparing the Cs have shown different values of the contact angle $\Theta(T)$ (Refs. 5 and 13–17) (see Fig. 2). Furthermore, many Cs surfaces show hysteretic wetting, with the receding contact angle, in many cases, found to be zero. This shows that the

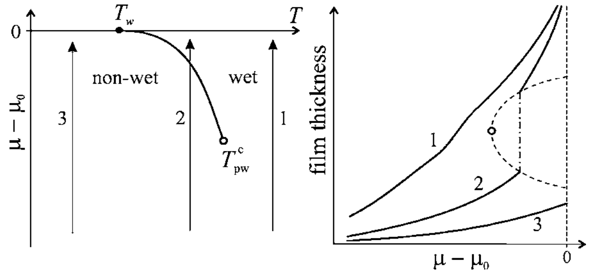

FIG. 1. Left: Shown are different paths (adsorption isotherms) in the plane chemical potential ($\Delta\mu = \mu - \mu_0$) vs temperature T. In the nonwet regime the equilibrium film is the thin-film state. Path 1 corresponds to a standard adsorption isotherm in the wetted regime, path 2 crosses the prewetting line, and path 3 corresponds to an adsorption isotherm completely in the nonwetting regime. Right: The film thickness as function of $\Delta\mu$ is shown for the three paths. In the case of path 3, and path 2 up to the pre-wetting line, the film thickness is very thin, but finite—i.e., the so-called thin-film state.

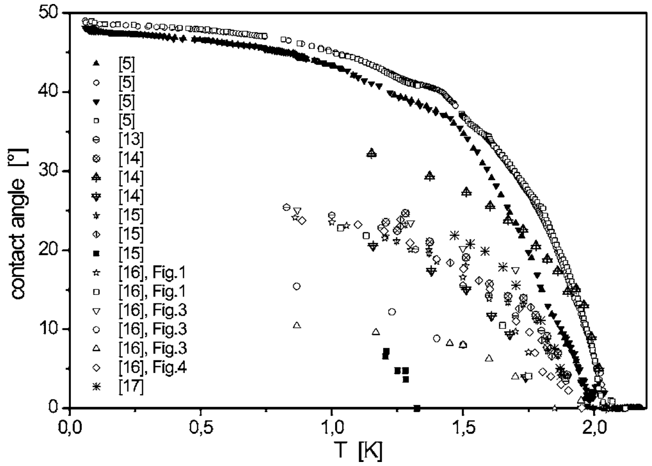

FIG. 2. Different values of measured contact angles. Open symbols show advancing, solid symbols receding contact angles. Data in Ref. 5, Fig. 3, are on Cs grown on tungsten, showing advancing and receding Θ. Data in Refs. 13–17 are on quench-condensed Cs (qcCs). Reference 13, Fig. 4, standard qcCs; Ref. 14, Fig. 3, standard qcCs, surfaces 1, 2, and 3; Ref. 15, Fig. 2, two standard qcCs, showing advancing and receding Θ; Ref. 16, Fig. 1, standard qcCs, at velocities of 0.01 and 1 mm/s of moving contact line; Ref. 16, Fig. 3, one standard qcCs and two structured, rough qcCs (S1 and S1B); Ref. 16, Fig. 4, structured, moderately rough qcCs (S2). Stars show averaged values from Ref. 17.

receding contact line is strongly pinned. The advancing contact line, however, can move, and it has been shown that the motion takes place by thermal activation across pinning sites.[7,16,18,19] The dynamics of helium wetting Cs has been reviewed.[20]

This variety in $\Theta(T)$ is ascribed to various degrees of roughness of the Cs surface.[21] Although there has been no actual measurement of the roughness of surfaces used in wetting studies, it is widely accepted that quench-condensing Cs vapor onto a cold substrate gives a rough surface. Recently there have been measurements of the topography of the surface of thick Cs films, by *in situ* surface tunneling microscopy at 4.2 K, which show that the surface is rough.[22] When quench-condensed Cs films are annealed, the contact line pinning is reduced and the receding contact angle Θ_r becomes finite for $T < 1.3$ K.[15] It is thought that the surfaces on bulk Cs (Refs. 12 and 23) and on Cs films grown on tungsten at elevated temperatures $300 < T < 500$ K (Ref. 5) are smoother than the quench-condensed ones, as the contact angle on these surfaces have a very small temperature hysteresis.

Despite this variation in the Cs surfaces, the wetting temperature of the ^{4}He-Cs system shows little variation with the different sample preparation methods. This is probably due to two factors. The first is that just below T_w, the pinning becomes very weak and goes to zero at T_w, and so the equilibrium state is more readily attained near $\lesssim T_w$. The second is that some measurement techniques are sensitive to the weakest binding areas of the Cs and so these Cs films will show the same T_w if they have some areas of pure Cs. The measured value of T_w is often only determined with T increasing, due to the need to remove the metastable helium film which persists on cooling through T_w. There are a few exceptions to this where the Cs spontaneously dries and T_w is similar on warming and cooling.[5,24]

The strong pinning on rough Cs surfaces which causes the extreme hysteresis of the movement of the contact line can also cause a dramatic memory effect. This manifests itself when such a Cs surface is partially flooded with liquid helium and is then fully drained, so that there is apparently no helium film left on it. When it is flooded again the liquid readily flows out to the original boundary between the dry and covered region and needs to be forced to go beyond this boundary. Hence the Cs surface has a memory of where it was originally flooded.[25] A similar effect is seen with sliding helium drops on inclined Cs surfaces.[6,15] Where a drop has once slid, another drop slides more easily along the same path.[15] This memory effect has been explained by the ability of micropuddles of liquid ^{4}He to exist on Cs in thermodynamic equilibrium and so can persist indefinitely.[26]

In this paper we review the various pinning results and present new data on quench-condensed Cs films. We define a qualitative scale of pinning which enables us to categorize most of the measured characteristics of the partial wetting of Cs by liquid helium. We discuss examples of the memory effect and explain how micropuddles can account for this behavior. We shall emphasize that the micropuddles are not formed by capillary condensation which seems not to be universally appreciated at present.

II. QUALITATIVE SCALE OF PINNING

Different Cs surfaces pin helium drops and films with a wide range of pinning forces on the contact line. These pinning forces are seldom measured directly but are inferred from qualitative observation such as hysteresis of the contact angle and whether the contact line moves or not when a force is applied. As the force per unit length is typically $\sigma_{\mathrm{lv}}(\cos\Theta_0 - \cos\Theta)$, where Θ_0 and Θ are the equilibrium and instantaneous values of the contact angle, it has a maximum value of $2\sigma_{\mathrm{lv}}(T)$. Thus, seeing if the contact line moves under the maximum force that can be applied is a meaningful, if qualitative, observation. The spectrum of the reported behaviors can be grouped into broad categories: i.e., strong, medium, and weak pinning. This has the advantage of classifying ^{4}He-Cs systems into groups with similar properties. This classification can be refined in the future as more controlled Cs surfaces are prepared and as their properties are measured with higher resolution.

A. Strong pinning

Strong pinning means that the contact line cannot be made to recede, although it can be made to advance. Strong pinning of the contact line is exhibited by the majority of quench-condensed Cs samples. As this preparation method is the most popular one, most published results have been obtained with such surfaces. We first consider the contact line around a macroscopic drop of liquid helium on a horizontal Cs surface[6,14,15] [see Fig. 3(a)]. If liquid is added to the drop, then the gravitational force on the drop increases which

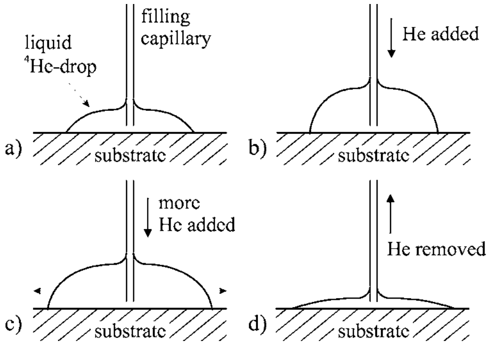

FIG. 3. Schematic sketch of advancing and receding contact angle, with extreme contact angle hysteresis: (a) ideal equilibrium, (b) helium is added to the drop which causes the advancing contact angle to increase, (c) when more helium is added the contact line advances when a sufficiently large advancing angle is reached, and (d) helium is removed and so the contact angle decreases. However, the contact line does not move.

changes its shape [see Fig. 3(b)]. The contact angle is increased above its equilibrium value which in turn increases the force on the contact line. The contact line advances when the instantaneous contact angle is sufficiently large so that the force on the contact line can overcome the pinning force [see Fig. 3(c)]. A similar behavior can be seen when the contact line is forced to move up a plane surface, inclined at a small angle (4°) to the horizontal.[7,13] In this case the contact angle is increased by increasing the volume of liquid in the reservoir. If liquid is removed from the drop or reservoir, the receding contact angle is found to decrease to zero. There is then a maximum receding force on the contact line, but the contact line remains in the same position and does not recede on the time scale of the observations [see Fig. 3(d)].

If liquid helium films are used instead of bulk helium, then there are different possibilities depending on the strength of the pinning and whether or not the helium film is in contact with a wetted boundary. These are shown in Fig. 4. In Fig. 4(a) we see that if there is no pinning, a helium film not in contact with a wetted boundary just contracts a droplet which then evaporates. In Fig. 4(b), the film drains to the wetted area when there is no pinning. In Figs. 4(c) and 4(d) there are a few strong pinning sites on an otherwise weak pinning Cs surface. The contact line recedes rapidly between the strong pinning sites, producing a scalloped edge. The contact line recedes more slowly than in Fig. 4(a) as the contact line has to jump out of the strong pinning sites. Figure 4(d) is similar to Fig. 4(b) except for the scalloped contact line and slower movement. In Figs. 4(e) and 4(f) the strong pinning holds the contact line stationary, and if the film evaporates, many stable micropuddles can be left on the Cs.

A stationary contact line due to strong pinning is observed on a particularly disordered substrate.[17,27] The pinned contact line holds a saturated film on the Cs. We note that the helium films on the Cs and the wetted substrate will be in equilibrium. The helium film on the Cs will have an equilibrium thickness which is a little thinner than the helium film on the wetted boundary, because of the weaker binding of helium to the Cs than to the bounding material.[28]

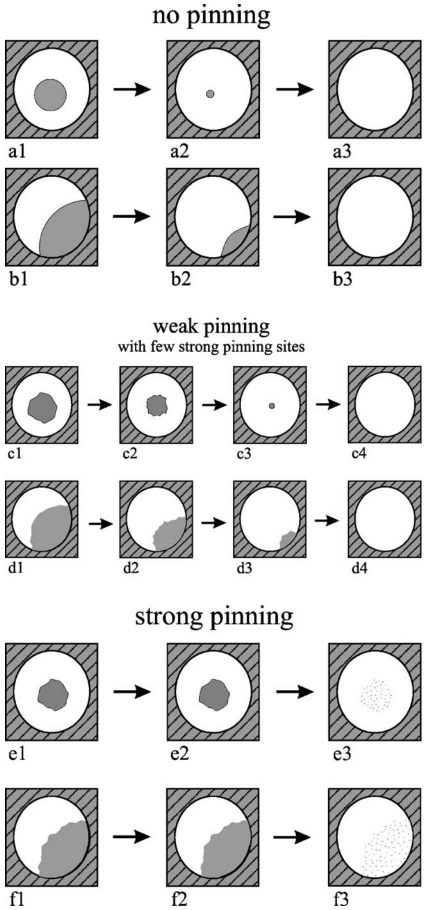

FIG. 4. Schematic sketch of the behavior of a helium film on Cs with no pinning, weak pinning, and strong pinning. a1, c1, and e1 show the initial helium film not touching the wetted boundary (shown as hatched gray area) and b1, d1, and f1 the initial helium film which touches the wetted boundary. Between a1 and a2 the contact line (CL) recedes as there is no pinning and the helium forms a drop, and by a3 the drop has evaporated. Between b1 and b2 the CL recedes as the film drains to the wetted boundary without any pinning, and this process is complete by b3. Between c1 and c2 the film starts to contract but the CL is pinned at a few strong sites. This creates a scalloped CL. The CL recedes in jumps until a drop is formed in c3 which has evaporated by c4. Between d1 and d2 the film starts to contract by draining to the wetted boundary. A scalloped CL is formed which recedes in jumps as the film drains in d3, and by d4 the draining is complete. For strong pinning there is no change between e1 and e2 and between f1 and f2; i.e., the contact lines are fixed. The film goes by evaporation leaving micropudlles in the area covered by the initial helium films in e3 and f3.

Another possibility is that the helium film completely covers the Cs. Then a dry hole must be nucleated before the contact line can recede. So if a hole is not nucleated, then nothing can be said of the pinning.

When Cs surfaces do not spontaneously dry at $T \ll T_w$, it is more likely to be due to strong pinning than the inability to nucleate a hole. This notion is supported by experiment; a hole can be created by evaporating the helium film using, for example, a laser beam,[29] so creating a partially covered Cs surface. The hole is usually seen to remain a constant size, showing that the contact line is strongly pinned and that lack of nucleation is not the reason for the stable film.

If a Cs surface is cooled through T_w, in a vapor of helium, the helium film that is present in equilibrium at $T>T_w$ sometimes remains on the Cs, as a metastable film, at $0<T<T_w$. This happens, for example, in quartz microbalance experiments.[4,10] To study the wetting at $T<T_w$, this thick helium film has to be removed by heating the Cs. The Cs surface is then covered with the thermodynamically stable thin-film state of helium, perhaps as thick as one or two monolayers at $T\lesssim T_w$,[4] but going rapidly to very low coverage as T is lowered. This inability to spontaneously dry as the temperature is slowly lowered through T_w is more likely to be due to a nucleation barrier rather than pinning, as the pinning is zero at T_w. It is likely that rough surfaces can increase the helium film thickness on them,[30] and this would increase the nucleation barrier and make spontaneous drying less probable.

These strong pinning surfaces show the memory effect described earlier. It is found from sliding drops[6,15] that once the surface has been in contact with liquid helium, the contact line can advance with much less force than is required on a bare Cs surface. This memory effect is attributed to stable micropuddles[26] and will be discussed later.

B. Medium pinning

The main feature of medium pinning is that the receding contact angle is not zero, as it is for strong pinning; nevertheless, it is much smaller than the advancing contact angle. These surfaces do not show the memory effect with helium drops.[15] With medium pinning, the contact line of a helium film recedes slowly and in jumps, in some temperature range.[31]

A small nonzero contact angle has been exhibited by a few quench-condensed Cs films, which are presumably smoother than those showing strong pinning. These Cs films were condensed onto a substrate at 4 K and then annealed at near 80 K for 40 min.[15] The measurement of the advancing contact angle on a horizontal Cs surface shows a temperature dependence similar to that when there is strong pinning,[6] but when liquid is removed from the drop at the lowest temperature 1.2 K, the contact angle drops considerably, but remains nonzero, and the contact line recedes. One such sample showed a receding contact angle $\Theta_r(T)$, which decreases as the temperature is raised, and went to zero at 1.3 K. This means that for $1.3<T<T_w=1.9$ K the hysteresis was extreme, as is seen with strong pinning.[15]

Measurements of drops sliding on these Cs surfaces, when they are inclined, do not show a memory effect when $\Theta_r>0$ (Ref. 15); i.e., drops subsequent to the very first drop have to reach the same size in order to slide. This indicates that, when the receding contact angle is greater than zero, no helium is left on the Cs after the drop has slid down; i.e., no micropuddles are formed.

C. Weak pinning

The prominent feature of weak pinning is that the receding contact angle is nearly equal to the advancing contact angle at all temperatures; i.e., there is only a small hysteresis in the temperature dependence of the contact angle. As the hysteresis must vanish when the pinning is zero, this means that these surfaces have weak pinning. Also the Cs spontaneously dries as T is reduced through T_w and so there does not appear to be a noticeable barrier to nucleating dry spots in the saturated helium film at $T=T_w$.

The only Cs surfaces that have been shown to have all these characteristics are Cs films grown on tungsten.[5,24] These are prepared at temperatures above room temperature. The Cs film is grown in near equilibrium conditions, so it is likely to be the smoothest surface yet prepared. Spontaneous drying is seen on bulk Cs surfaces which are also prepared above room temperature.[12,23] These include the first surfaces to show that Cs is not wetted by liquid ^{4}He.[23]

In this paper we report on quench-condensed Cs films that show spontaneous drying. This indicates that the pinning is weak on these surfaces. For thick helium films [≈ 1 μm (Ref. 32)] on such weak pinning surfaces, the contact line is seen to recede after the initial flooding of the Cs surface. There are sometimes a small number of strong pinning sites, so that the receding contact line jumps from site to site and the contact line has a scalloped shape, as the line is concave between these sites (see Ref. 31 and Figs. 5–8).

III. PINNING EXAMPLES

A. Strong pinning examples

Strong pinning has been seen in the majority of quench-condensed Cs films. These films are made by evaporating Cs from a getter dispenser (SAES getter source) or from pure Cs in a glass ampoule and letting the vaporized Cs condense onto a cold substrate.[14] The substrates are, in some cases, held just above helium temperature—i.e., $4.2<T<10$ K—and sometimes at liquid nitrogen temperatures ≈ 77 K. It is considered beneficial to have a warm temperature as then the atoms lose their energy more slowly and so the Cs atoms have a longer period of mobility on the substrate. This means that the atoms can reach a packing which is closer to the equilibrium bulk solid Cs. If the atoms lose their energy rapidly, the atoms stay where they land, and then the quench-condensed film is likely to be amorphous and also rough.

Sometimes the Cs films are annealed to higher temperatures than the one at which they were formed[14] in an attempt to obtain Cs films closer to equilibrium. However, the problem with raising the temperature is that the "vacuum" in the experimental cell becomes poorer. At temperatures around 4.2 K the vacuum is good, as the vapor pressure of the harmful molecules—e.g., O_2 and H_2O—is negligible. If the temperature is raised, the vapor pressure rises rapidly from outgassing surfaces and so there is a substantial risk that the Cs surface will be contaminated. The effects of annealing are not found to be large but these Cs surfaces can show medium pinning,[15] which is discussed in the next section.

The Irvine group[6,14,15] has reported many measurements of advancing contact angles over the temperature range 1.2–2.0 K (see Fig. 2). Their samples show a range of $\Theta_a(T)$; e.g., $\Theta_a(T=1.2\text{ K})$ has a range 20°–32°. It is possible that some of this variation is due to different pinning strengths.

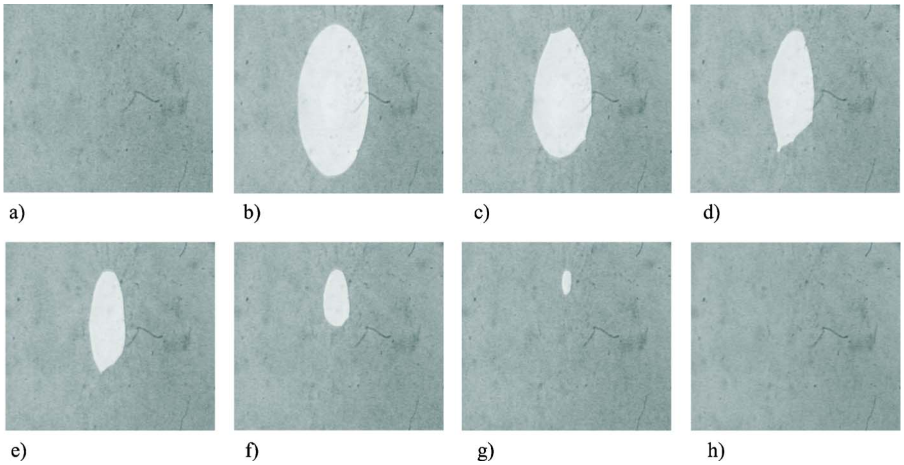

FIG. 5. (Color online) A time sequence of images showing a receding contact line of a helium film (light tone), ≈ 1 μm thick, on a weak pinning surface at $T \approx 1.6$ K with $T_w \approx 1.85$ K. The images are produced by surface plasmon microscopy. (a) Dry Cs surface, (b) image after film has spread to its maximum size, pictures (c)–(g) show the shrinking of the helium film, and (h) the helium film has completely disappeared, hence the Cs surface is left dry, as in (a). The lifetime of the film is ≈ 1.4 s. Each image is about 4 mm wide.

As the approach to equilibrium is logarithmic in time,[18] variations in contact angle are seen over periods of 20 min. Stronger pinning leads to larger $\Theta_a(T)$ in order to overcome the pinning. It also leads to longer times to approach equilibrium, so the measured values of $\Theta_a(T)$, after a fixed time interval from the imposed change in conditions, are further from the equilibrium value.

All the quench-condensed Cs samples measured by the Paris groups[7,13,16,17] show receding contact angles of zero. The advancing contact angles show a similar range of values to those found by the Irvine group. The Paris group[18] has made detailed studies of the relaxation of the contact angle with time and has shown that the advance of the contact line is a thermally activated depinning process. The fact that the contact line is not seen to recede is due to the limited force that can be applied, $\sigma_{\mathrm{lv}}(1-\cos\Theta_0)$, as $\cos\Theta_r = 1$. However, it is possible that the pinning strength can be different for a receding contact line than for an advancing one,[33] so then it is impossible to gauge the pinning force for a receding contact line from the pinning of the advancing line.

When these Cs surfaces are partially flooded with a thick helium film, the receding contact line is seen to be pinned.[31,34] The film thickness has been measured as a function of time, after the flooding, and it is found that after ≈ 5 s the film is too thin to be detected (<5 ML). It is assumed that the film disappears by evaporation[31] because the contact line appears stationary throughout the period that the film is getting thinner.

As the movement of the contact line is due to thermally activated jumps from the pinning sites,[18] a stressed contact line is not stationary, but it can creep so slowly that it apparently does not move in the observation time. So the longer the time that the contact line appears stationary, for a given stress, the stronger the pinning force must be.

B. Medium pinning examples

There are at least two reported examples of quench-condensed Cs surfaces which show a nonzero value of the

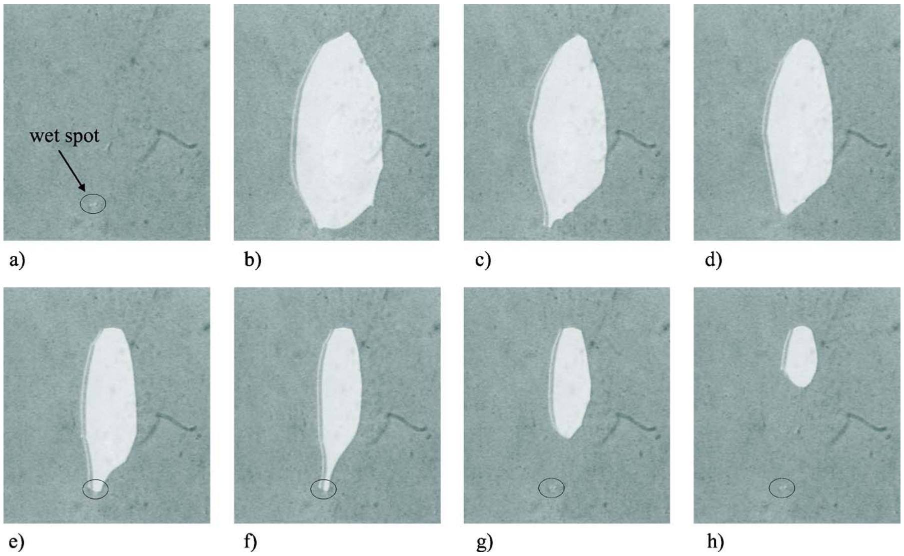

FIG. 6. (Color online) The effect of a few strong pinning sites on the contact line of a receding helium film (light tone) on a slightly different area of the same surface as in Fig. 5, at $T \approx 1.6$ K. (a) Dry Cs surface with wet spot on it, (b) 0.22 s after deposition of a helium droplet, (c) $t=0.30$ s, (d) $t=0.44$ s, (e) $t=0.58$ s, (f) $t=0.62$ s, (g) $t=0.80$ s, and (h) $t=0.96$ s. Note the scalloped edges caused by the few strong pinning sites and how the wet spot strongly pins the contact line [see image (f)]. The ghost line on the left of the image is an artifact. Each image is about 4 mm wide.

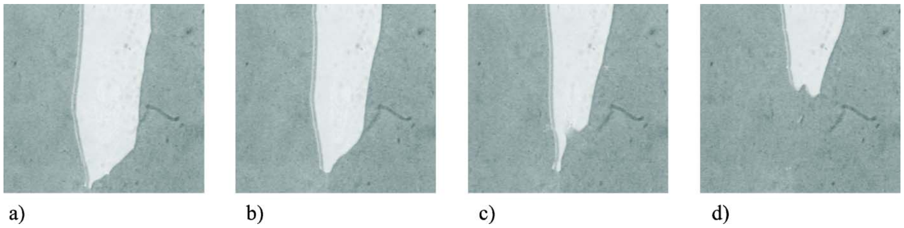

FIG. 7. (Color online) Detailed behavior of a receding contact line around a strong pinning site, on a weak pinning surface at $T \approx 1.6$ K and $T_w \approx 1.85$ K, after about 0.5 s from the drop. The time sequence of the surface plasmon images is shown at (a) $t=0$, (b) $t=0.10$ s, (c) $t=0.18$ s, and (d) $t=0.26$ s. Each image is about 4 mm wide.

receding contact angle.[15] When the volume of a liquid helium drop is decreased, by withdrawing the liquid through a capillary tube at the lowest measured temperature, 1.2 K, the contact angle decreases from its value of 25°, when the contact line is advancing, to 7° when the contact line is receding. As the equilibrium contact angle is not known on this surface, the force on the contact line, for advancing and receding, cannot be calculated. The receding contact angle rapidly drops as the temperature is raised and becomes zero at 1.3 K. Presumably the receding contact line is strongly pinned at $T > 1.3$ K. The change in pinning of the receding contact line, as the temperature increases through $T=1.3$ K, can be understood if the pinning force is equal to F_{max} at $T=1.3$ K, so that for $T < 1.3$ K, F_{max} is greater than the pinning force, and for $T > 1.3$ K, F_{max} is less than the pinning force. This means that the pinning force does not decrease as fast as $F_{max}(T)$ with temperature at 1.3 K. The maximum force per unit length of contact line, $F_{max}(T)$, on the receding contact line is $\sigma_{\mathrm{lv}}(1-\cos\Theta_0)$. The change in this force between 1.2 and 1.3 K is 4.6×10^{-6} N m^{-1} which is small compared to $F_{max}(1.3\text{ K})=8.0\times10^{-5}$ N m^{-1}, using data from Refs. 24 and 36. The temperature dependence of the pinning force will depend on the physical mechanism of the pinning site, but it is expected to go continuously to zero at T_w,[18] as does $F_{max}(T)$. However, the movement of the contact line in a prewetting transition, just off liquid-vapor coexistence, has been shown to be very temperature dependent for $T \geqslant T_w$.[19]

When nonequilibrium contact angles cannot be measured, as for thick liquid helium films on Cs, then the pinning is inferred from the movement of the contact line. The mobility of the contact line can be very temperature dependent. On one Cs film[31] with an exceptionally low wetting temperature, $T_w=1.68$ K, if the surface is flooded at $T < 1.55$ K, the average helium film thickness decreases to <5 ML in a few seconds, without the contact line moving. Also in this temperature range, a memory of the contact line remained. At $1.55 < T < 1.65$ K the same Cs spontaneously dries with the contact line receding with large scale jumps towards the wetted boundary.[31] In this case, the pinning force must decrease faster with temperature than $F_{max}(T)$ at this temperature, to account for this behavior. This is opposite to the behavior of the drops described above.

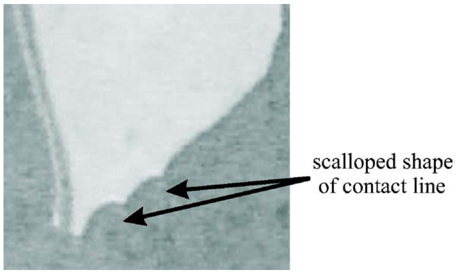

FIG. 8. (Color online) The scalloped shape of the contact line of a helium film. The image is a magnification of Fig. 6(c). The frame is about 1 mm wide.

This difference can be resolved if with medium pinning the maximum force that can be applied to the contact line is about the same as the pinning force on the contact line. Then for some Cs surfaces the pinning force is larger and for others it is smaller than F_{max}, in different temperature ranges. The temperature dependence of the pinning is sensitive to the details of the roughness.

C. Weak pinning examples

The first experiment that showed Cs was not wetted by liquid helium used a bulk Cs sample, solidified from molten Cs in a glass tube.[23] The Cs was in the shape of a toroid with the outer surface melted onto the glass at just above room temperature. Helium gas was introduced into the glass tube which was then sealed. This helium formed a saturated film at $T=2.17$ K.[35] The absence of a helium film on the Cs was detected by the thermal conductivity of the section of the glass tube containing the Cs. When the superfluid helium film flowed freely up the walls of the tube, the tube acted as a highly conducting heat pipe. However, when there was no helium film on the Cs, the thermal conductivity was much smaller. The Cs, apparently, spontaneously dried as T decreased through $T_w=1.95$ K,[35] which shows that the pinning on bulk Cs is very weak.

Bulk Cs was used in the experiment that showed that Cs is very dry at $T \ll T_w$ when abutted by a wetted boundary with a saturated film on it.[12] The Cs ring stopped a helium film flowing up a post. This was monitored by a pulsed heater which would evaporate any helium that crossed the Cs. The experiment was cooled down in a saturated vapor pressure of helium, so there was a saturated film on the post above the Cs ring. This film on the post had to be removed before the sensitive detection could begin, which was done by larger heater pulses, the so-called cleaning pulses. If there had been a saturated film on the Cs, then it would be impossible to remove the helium film from the top of the post, as it would have been replenished by the film flow. This film flow was shown in a separate experiment which had no Cs ring. So again we see that the surface of bulk Cs spontaneously dries.

The first contact angle measurements were done with Cs films grown on W plates at temperatures above the melting point of Cs (≈ 28 °C).[24] Ultrahigh-vacuum techniques, including baking at 200 °C, were used to clean the W plates and the inside of the stainless steel cell before the Cs was introduced. Cs has a wetting transition on W at 160 °C, so below this temperature the Cs should be in a thermodynamic thin-film state on the W. Measurements showed that there were about 20 ML of Cs on the W plates.[24] This Cs film was prepared slowly by cooling from 200 °C over several days to ensure that it was in an essentially equilibrium state.

Helium was only introduced into the cell after it had been cooled to 4.2 K. As this is above T_w, a saturated film would have formed on the Cs. The contact angle was determined by measuring the upward force on the bulk helium due to the surface tension force, $\sigma_{lv}\cos\Theta$ per unit length of plate.[5] On cooling, the upward force was seen to change at ≈ 1.95 K due to the receding contact angle increasing from zero. After cooling to 60 mK, the system was warmed and the advancing contact angle was seen to go to zero at 2.05 K.[5,24] The higher transition temperature must be identified with T_w—i.e., $T_w = 2.05$ K. This behavior shows that Cs spontaneously dries just below T_w on cooling. Such spontaneous drying is not seen with medium or strong pinning Cs surfaces. This Cs surface showed very little contact angle hysteresis, with the receding contact angle only a little lower than the advancing angle over the entire temperature range. The measurements were done by slowly changing the temperature over several days, so that the time for contact line movements was orders of magnitude longer than in any other contact angle measurement. This means that equilibrium values were more nearly attained. This is demonstrably the most ideal Cs surface, from a wetting perspective, that has been created.

Quench-condensed Cs surfaces can also show weak pinning. We now describe unpublished results that show that the contact line of a thick helium film can readily recede. The Cs surface is horizontal and forms part of a surface plasmon optical system, which enables the helium film to be visualized (see, e.g., Refs. 29, 31, and 34. The Cs was evaporated from a SAES getter and quench-condensed onto an Ag film at liquid helium temperatures. This Ag film was thermally evaporated onto a polished glass prism at room temperature and had a thickness of 53 nm. A temperature sensor, mounted to the side of the glass prism, showed that it increased in temperature from 4.2 K to about 80 K by the end of the Cs evaporation process. The evaporation rate was about 0.3 ML per minute, and the final Cs film thickness is about 10 nm. The film thickness is estimated from the shift of the surface plasmon resonance, which was monitored during the evaporation process. The preparation technique is nominally the same as described in Ref. 31).

A drop of helium is allowed to fall onto the Cs surface, and it spreads out to form an elliptical patch a few millimeters in size. From this area and the drop size we estimate the film thickness to be ≈ 1 μm. The patch does not reach the wetted boundaries of the Cs. After spreading out, the liquid helium in the film evaporates and the contact line recedes. From the evaporation rate we estimate that the helium film is approximately 3 μK above the ambient temperature 1.6 K. A video sequence of the subsequent shape of the patch shows that the contact line recedes readily except for a few strong pinning centers that momentarily hold the contact line while the rest of the contact line recedes (see Figs. 5–7). This leads to a scalloped shape to the patch, with a concave line between adjacent pinning centers, clearly shown in Fig. 8. The patch takes about 1.4 s to recede completely. Repetitions of this sequence, every few minutes, show that the time-dependent shape of the contact line is reproduced each time. However, this is due to nearly exact repetitions of the dynamics of the film spreading and then receding, and has nothing to do with the memory effect, as we would not expect any micropuddles on such a weak pinning surface. So, apart from the small number of stronger pinning sites which determines the shape of the contact line, this Cs surface shows weak pinning.

D. Discussion of pinning sites

The nature of pinning sites on Cs surfaces has not been identified because of the difficulty in studying them. Any deviation of the Cs from a pure smooth surface is going to cause some pinning. We now consider some possibilities. A rough but pure Cs surface has continuous undulations on a range of length scales which leads to a range of pinning strengths. Hills and craters on the surface cause pinning because they change the shape of the helium surface. This changes the area and total surface energy needed to accommodate the local change in the angle at the contact line. This surface energy varies with position of the contact line, and so there is a corresponding variation of the force on the contact line.

If the Cs surface is not uniformly pure, then areas of less purity will be stronger binding regions for the helium. In the extreme, these could be wetted areas which would strongly pin the contact line. If an area had strong binding but was still not wetted, then the local contact angle would be lower. This, then, has a similar effect on the helium shape as hills and craters. It lowers the potential energy at the stronger binding sites and so pins the contact line.

Finally, there can be particles of foreign material on the Cs—for example, dust—as many substrates are not prepared in a clean room. Dust will certainly be wetted by helium and so causes a very strong pinning center. When Cs is evaporated, it may only partially cover the dust particle, so that where there are Cs shadows, a wetted region will be left. We believe that dust is probably the cause of the low density of stronger pinning sites seen on the weakest-pinning, quench-condensed Cs surfaces (see, for example, Figs. 5–8.

The bulk Cs samples only suffer from large scale roughness because chemical impurities such as Cs_2O dissolve in the bulk molten Cs.[37] Dust is also unlikely, as the samples are prepared under vacuum. The Cs on W plate probably has, at most, the underlying roughness of the W, as chemical impurities are eliminated by vacuum distillation and the UHV technique prevents contamination by dust particles.

IV. MEMORY EFFECTS

A Cs surface which has been covered with helium, but is then apparently free of helium, can show a memory of being

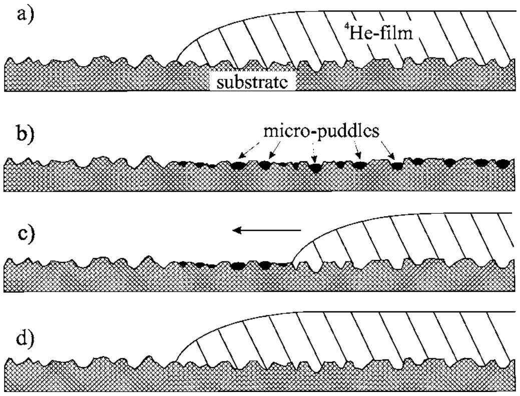

FIG. 9. Schematical sketch of the memory effect: (a) liquid covers part of the surface, (b) liquid drains or evaporates away, leaving micropuddles, (c) liquid is pulled across the micropuddles, and (d) the contact line stops when it reaches the end of the region of micropuddles.

covered with liquid helium. This surface must be different from the initially helium-free surface. A helium-free Cs surface can be obtained by either cooling the Cs to $T < T_w$ in a vacuum or by transiently heating a surface that has had helium on it, but still below T_w, so that all the helium evaporates from the surface. The memory effect can be seen by partially covering this surface with liquid helium and letting the helium disappear by, for example, running off or by slow evaporation. Liquid helium is then added again to the Cs. The added liquid helium flows much more readily over the area of Cs that had previously been in contact with the liquid helium. It has been suggested that the memory is caused by micropuddles of liquid helium, which are left behind after the first contact with helium (see Fig. 9) and that these micropuddles are in thermodynamic equilibrium and so are long lived.[26] The formation of the micropuddles affects the dynamics of slipping of bulk helium drops and the presence of micropuddles affects the dynamics of reflooding.

The memory effect with slipping drops was seen by Ross and co-workers.[6,15] The Cs surface was inclined at 10° to the horizontal, and drops of helium fell onto it from a capillary, which was clearly above the droplet that formed on the Cs. This droplet grew as it collected more drops from the capillary. The shape of the droplet was directly imaged optically. The stationary droplet was in equilibrium with the difference in advancing and receding contact angles, balancing the effect of gravity. When the droplet was sufficiently large, gravity could not be compensated by the contact angles and the drop slid down the incline.

Two different behaviors were observed. The Cs surfaces were all prepared by quenched condensation and most showed the memory effect. That is, the very first droplet on Cs behaved differently to subsequent ones; the first drop was much larger when it slipped. The first contact with liquid helium is changing the Cs surface so that the subsequent drops are more weakly pinned, and we believe that this is due to micropuddles left behind by the first droplet when it slides. The energy cost of creating the micropuddles is borne by the first drop and this increases its pinning. The later drops all behaved similarly, so the micropuddles are not changed by the subsequent contact with liquid helium.

A second type of behavior was shown by only two Cs surfaces:[15] subsequent drops slid at the same size as the very first drop—i.e., no memory effect. These Cs surfaces are further distinguished by their contact angle hysteresis. They both had a nonzero receding contact angle, over a range of temperature, in contrast to those Cs surfaces exhibiting the memory effect, which have a receding contact angle of zero. This suggests that, if the pinning of the receding contact line is weaker, then not only is the receding contact angle not zero, but also micropuddles are not formed. In other words, the formation of micropuddles requires strong pinning.

The memory effect is also seen with helium films on Cs.[31,34] It is found that if a Cs surface is partially flooded, so that there is a well-defined contact line observed by surface plasmons, then a subsequent flooding goes out to the previous contact line. The reflooding must not be more vigorous than the first one because if there is more momentum in a subsequent drop of liquid helium, then this can push the contact line further out. If a new contact line is formed, it becomes the new boundary for subsequent floodings. This is an important point as it distinguishes the memory effect from merely exact repetitions of the procedure. The irregular shape of the contact line also indicates that the surface has an easier area for flooding, rather than the unlikely possibility that each drop of helium falling on the Cs has exactly the same dynamics to take the helium film out to the identical boundary each time.

The helium film disappears in less than 4.5 s, presumably by evaporation,[31] without the contact line moving. The fixed position of the contact line during this time indicates that it is strongly pinned. After ≈4.5 s the surface plasmon intensity is exactly the same on the area of the Cs that has not been flooded as on the area that has.[31] The resolution of this optical technique, in imaging mode, is ≈5 ML of liquid helium, so we conclude that the helium has an average thickness, over the whole surface, which is less than this.

V. MICROPUDDLES

Micropuddles are envisaged to fill shallow craters in the Cs surface.[26] Such shallow craters can only be filled by flooding and cannot be filled by condensation from the vapor. Such capillary condensation only occurs in small-angle wedges.[38] So these shallow craters are free of liquid helium even if there is an appreciable helium vapor pressure. This is an important point which is not always appreciated. They are only filled if the surface is flooded. After such a flooding, some helium evaporates or condenses until the helium in the micropuddle is in equilibrium with the reservoir of helium in the cell. The chemical potential of the helium in the micropuddle is determined by van der Waals attraction to the Cs and its pressure. The pressure must be higher than in the reservoir to compensate for the strong van der Waals attraction in a shallow micropuddle. The pressure in the liquid, at the free surface, is determined by the curvature of the surface. This will be a function of the position, across the micropuddle, depending on the depth of the liquid helium and hence the van der Waals attraction. The contact line at the

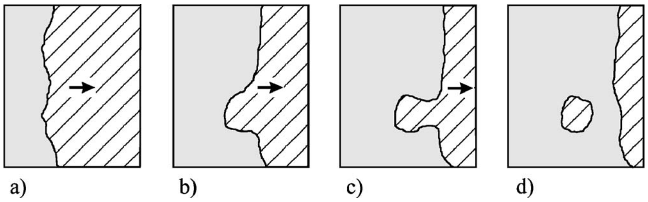

FIG. 10. Schematical of receding contact line [from (a) to (d)] and formation of micropuddle [at (d)]. The gray background shows a nonwetting surface (e.g., Cs) and the hatched part a receding liquid (e.g., ^{4}He). See text for more details.

edge of the micropuddles must be strongly pinned to stop the contact line receding. The contact angle, if it can be defined on such a small scale, must be much lower than the equilibrium value.

Once the shape of the free surface of the micropuddle is such that the chemical potential of the liquid in it is the same as the reservoir, the micropuddle can exist indefinitely. This explains the persistence of memory. However, if the temperature of the micropuddles is raised above that of the reservoir, then the helium can be evaporated away, due to the differential effect of temperature on the chemical potential of the liquid and vapor. In this way the Cs surface can be made completely free of helium.

We envisage the formation of a micropuddle as follows. When the first droplet slides down an inclined Cs surface or the contact line of a helium recedes, micropuddles can be left behind, as shown schematically in Fig. 10. When the receding contact line reaches the edge of a crater, it encounters stronger pinning due to the geometry of the edge [Fig. 10(b)], so the contact line is held at the crater but recedes at each side [Figs. 10(b) and 10(c)]. As this proceeds, the contact line necks off, as is shown in Fig. 10(d), and the micropuddle is left and the contact line recedes to the next crater. After the micropuddle is left in this dynamic process, it adjusts its volume and shape by evaporation or condensation, to reach equilibrium with the reservoir.

We now consider a contact line advancing over a surface with micropuddles. When the contact line reaches a micropuddle, it has a force on it which tends to pull it across the micropuddle. So an area dotted with micropuddles has less pinning to an advancing contact line than when the same surface is bare. This explains why films of helium flood out to the previous contact line and no further, unless there is an extra driving force.

A contact line receding over a surface with micropuddles is equivalent to a contact line receding over the same surface for the first time. The dynamics of the receding contact line are independent of previous contact with liquid helium.

For a droplet sliding down an inclined plane, the second and subsequent droplets slide easier. This is because the first droplet creates micropuddles, and this reduces the effective pinning on the advancing contact line of subsequent drops. The force on the receding contact line is unchanged. This fact that the force on the advancing contact line is lower for the second drop immediately indicates that the maximum advancing contact angle will be lower in the presence of micropuddles compared to the same surface without them.

VI. CONCLUSIONS

In this paper we have tried to systematize many of the studies of the partial wetting of liquid ^{4}He on Cs. We have suggested that the large variation in the values of the contact angle and the extreme hysteresis seen in the pinning of the contact line stem from the roughness of the Cs surface, which is caused by the different methods and their details of preparing the Cs sample for the wetting studies. We have suggested that the results can be categorized into three broad groups depending on the pinning of the receding contact line.

The strong pinning group consists of Cs surfaces which show no receding of the contact line during the time of the experimental observation. The medium pinning group contains those Cs surfaces which show a receding contact line over some temperature range, but with a large hysteresis in the contact angle. These surfaces have a much larger advancing angle than the receding angle. The third group has very little pinning, and so the receding contact line moves easily, as does the advancing contact line. Also the contact angle hysteresis is very small when there is weak pinning. It is only in this weak pinning group that Cs surfaces, covered in liquid helium above T_w, show spontaneous drying as the temperature is lowered through T_w.

The surfaces that show that the strongest pinning are made by quench-condensed evaporated Cs onto a cold substrate. This technique can produce very rough Cs.[22] However, the few Cs surfaces in the medium pinning group are also quench condensed, so it would appear that it is possible to create smoother surfaces by this technique. It has been found that annealing these surfaces can reduce the strength of the pinning, as annealing, presumably, makes the Cs smoother. The weakest pinning surfaces are those formed on bulk Cs and Cs films grown on tungsten at elevated temperatures, although we have shown an example of a quench-condensed Cs film with weak pinning near T_w.

From a consideration of the temperature dependence of the mobility of the receding contact line, on medium pinning surfaces, we conclude that the pinning force on the receding contact line is about equal to the maximum force that can be applied to the receding contact line. As these are both temperature dependent, it appears that for some samples the pinning force just exceeds the maximum force that can be applied, as the temperature increases towards T_w, and for others the opposite occurs.

Cs surfaces that show strong pinning of the receding contact line, with a corresponding receding contact angle of zero, have a memory of being in contact with liquid helium. The strong pinning allows micropuddles of helium to remain on the surface after the liquid helium has apparently disappeared. The micropuddles must be strongly pinned around their perimeter, so that the curvature of the surface can adjust. This allows the pressure inside the micropuddle to have a value which makes the chemical potential equal to that of the helium reservoir. The pressure must be high enough to counteract the van der Waals attraction in the shallow micropuddle. As the micropuddles can reach thermodynamic equilibrium, they are long lived.

We suggest a mechanism for micropuddles being left behind when a bulk helium droplet slips down an inclined plane and when a helium film evaporates away. Once part of a Cs surface is dotted with micropuddles, if the surface is reflooded, then the advancing contact line is pulled out to the boundary where the micropuddles end. Similarly once a slipping drop has left an area covered with micropuddles, another drop does not have to expend energy creating new micropuddles, so the next drop starts sliding down with less force applied to the drop.

We have presented new data that show helium films receding on quench-condensed Cs surfaces. In a narrow temperature range $T \lesssim T_w$, the pinning of the receding contact line is generally weak except for a few strong pinning points, which are probably dust particles. This causes the receding contact line to move in relatively large jumps as it depins from each strong site in turn. This behavior occurs a few tenths of a kelvin below T_w, and at lower temperatures the receding contact line is strongly pinned.

We conclude that the general behavior of the wetting of liquid ^{4}He on Cs can be qualitatively understood in terms of the strength of the pinning of the receding contact angle, together with the fact that there is a maximum force that can be applied to the contact line because the value of the contact angle must lie between 0 and π.

ACKNOWLEDGMENTS

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[28] If the helium film is initially thicker (thinner) than the equilibrium thickness d (given by $m_4 gh = \Delta C_3 / d^3$, where h is the height of the film above the bulk liquid surface and ΔC_3 is the difference in the van der Waals constants of the substrate and the liquid helium, for a helium atom), then the film will evaporate (condense) and reach the equilibrium thickness, typically ≈20 nm.

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