Model for the Extreme Wetting Hysteresis of Liquid Helium on Cesium

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Although the liquid-^{4}He–cesium system is a nearly ideal one for studying wetting phenomena, it can show extreme hysteresis which is profoundly nonideal in behavior. It is suggested that this is due to the roughness of these Cs surfaces. We show that stable micropuddles of liquid ^{4}He can form in shallow cavities on a Cs surface. It is the potential to form micropuddles, as the liquid tries to recede, which pins the contact line due to the large energy needed to create the surface of a micropuddle. This model also accounts for the memory that these surfaces have of being in contact with liquid ^{4}He.

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In many respects the Cs-liquid helium combination [1,2] represents the ideal system for studying wetting. It is established that Cs is very dry of ^{4}He at $T \ll T_w \approx 2$ K [3], the contact angle has been measured over the whole temperature range, $0 < T < T_w$ [4–6], and prewetting has been observed and shown to agree with theory [7]. However, a profound nonideality exists. Most of the surfaces formed by quench-condensing Cs vapor show extreme hysteresis; i.e., once the Cs has been in contact with bulk liquid helium at $T < T_w$, a metastable thick film ($\approx$20 nm) forms which persists essentially indefinitely. This problem has been apparent for many years and has not been resolved. We here suggest an explanation which also explains the memory these Cs surfaces have of being flooded with liquid.

A thick film of liquid helium on some Cs surfaces persists even if the thick film is contiguous with the equilibrium thin-film state along a contact line. This is a situation where there is no nucleation barrier to the thick film receding to form a macroscopic drop, which it would do in the ideal case. This clearly shows that the receding contact line is rigidly pinned. This is in contrast to the advancing contact line, which, while experiencing pinning forces, can be moved easily. We argue that this extreme asymmetry in the pinning, and hence the wetting hysteresis, is due to these quenched condensed Cs surfaces being rough which enables micropuddles of liquid helium to form under certain circumstances.

We show that these micropuddles are thermodynamically stable on rough surfaces and it is the possibility of creating these micropuddles that strongly pins the receding contact line. This is because micropuddles must be created when the contact line recedes. As it requires a high energy, compared to k_BT, to create the free surface on the micropuddle, this makes the probability of the contact line receding tend to zero. However, as the scale of roughness is lowered, the pinning energy decreases and the hysteresis becomes smaller. Indeed, very small hysteresis is observed on some other types of Cs surfaces [4].

The formation of stable micropuddles also accounts for the memory effect shown by these quenched condensed Cs surfaces; i.e., once bulk helium has flowed over part of such a surface and has apparently drained away, a subsequent addition of liquid helium flows over the same area defined by the contact line established on the first flow [8–10]. This can be readily understood if after the first application of liquid, the liquid drains and leaves micropuddles, as these help the contact line to advance when further liquid helium is added.

The quality of the materials in studying wetting is particularly important as contamination at any of the interfaces can cause large changes to the wetting behavior. In the He-Cs system the liquid helium is the more reliable component. It is very pure and interacts only with the Cs by van der Waals forces. It is superfluid over the whole range of nonwetting so it can readily flow to a thermodynamic equilibrium state. In contrast, the Cs surface must be kept chemically pure which needs great care as it is so reactive, and also it can be rough which has a profound effect on the wetting and dewetting dynamics [11].

Cs surfaces have been made in three different ways which greatly alters their properties. The first method is to freeze bulk liquid which gives a surface that is crinkled on a macroscale. This type of surface was first used to show that Cs is not wetted by helium [2,3]. It did show moderate hysteretic behavior [2] which has been explained by an inhomogeneous surface free energy [12]. The second type of Cs surface is grown on tungsten foils in equilibrium with Cs vapor. This produces the thin-film state of Cs on W which should be relatively smooth. This surface was used to measure the T-dependent decreasing and increasing contact angle and showed little hysteresis [4]. The third surface is the one most frequently used; it is formed by quench condensing Cs vapor onto a cold substrate, usually Au or Ag. Most of these surfaces show extreme hysteresis [5,6] with a few notable exceptions [13]. It is generally considered that these surfaces are rough on a microscale, with, say, a lateral correlation length of order <100 nm [11], although there are no measurements of roughness to date.

Prevost *et al.* [11] have studied the pinning of the advancing contact line on quenched condensed Cs and shown it to be a thermally activated molecular-kinetic process as proposed by Blake [14]. The force per unit length of contact line is $\sigma_{\mathrm{lv}}(\cos\Theta_0 - \cos\Theta_c)$, where σ_{lv} is the liquid-vapor interface free energy or surface tension, and Θ_c and Θ_0 are the actual and equilibrium contact angles, respectively. The pinning can be overcome by modest values of this force, and it is found that $\Theta_c - \Theta_0 \approx 1°$ [11]. In contrast, the receding contact angle on these same surfaces can be reduced to essentially zero, without any recession of the contact line. This extreme asymmetry suggests that the physical origins of the pinning in the two directions are different. Prevost *et al.* [11] suggest that the advancing contact line pinning is due to variations in local slope of the Cs surface of about 0.1 rad and estimate pinning energies of 120 K at $T = 1$ K to 60 K at $T = 1.7$ K. The characteristic area of a pinning site they estimate to be 125 nm^2.

One of the indirect indications that the quench-condensed Cs is rough, and the roughness varies from sample to sample, is the range of advancing contact angles, $\Theta_c(T)$, found on these surfaces [5,6]. For example, at 1.2 K, Θ_c varies from 15° to 30°. These are all smaller than $\Theta_c(1.2\ \mathrm{K}) \approx 41°$ found on Cs on W [4]. It is not clear if it is the pinning or the change in σ_{sl}, the solid-liquid interface free energy, due to roughness which causes the reduced contact angle. Certainly a mesoscopically rough surface, with correlation length 15 μm, shows a much reduced effective contact angle compared to the same Cs on a flat substrate, 10° and 25°, respectively [15]. However, most Cs surfaces, however prepared, have $T_w \approx 2$ K, defined as $\Theta_c(T_w) = 0$, which shows that T_w is determined by the weakest binding part of a heterogeneous surface [16].

It has been conjectured that the extreme hysteresis is due to roughness [16,17]. In order to develop some understanding of a real rough surface we start with an idealized situation; a small cavity, with a shape which is part of a sphere, in an otherwise flat surface as shown in Fig. 1(a). There are two essential attributes to this surface defect, a concavity and a rim. If this Cs surface is in an atmosphere of ^{4}He vapor at $T < T_w$, then a thin film of ^{4}He will form all over its surface including the cavity and there is no local capillary condensation [18]. The cavity does not fill with liquid as there is a substantial potential barrier between the thin-film state and the state when it is filled with bulk ^{4}He. If bulk ^{4}He is flooded over the cavity it will fill and stay filled, but the liquid will drain from the surrounding flat surface, leaving it dry with only the thermodynamic equilibrium thin film on it.

The chemical potential μ of the liquid in the cavity is given by

$$\mu = \mu_0 + mgh + (p - p_0)V\,, \tag{1}$$

where μ_0 is the chemical potential of the liquid reservoir, which is a distance h below the Cs surface, m is the ^{4}He atomic mass, V is the volume occupied by an atom in the liquid, and p_0 and p are the saturated vapor pressure and pressure of the liquid in the cavity, respectively. We see that $\mu = \mu_0$ if $p_0 - p = \rho g h$, where ρ is the liquid density.

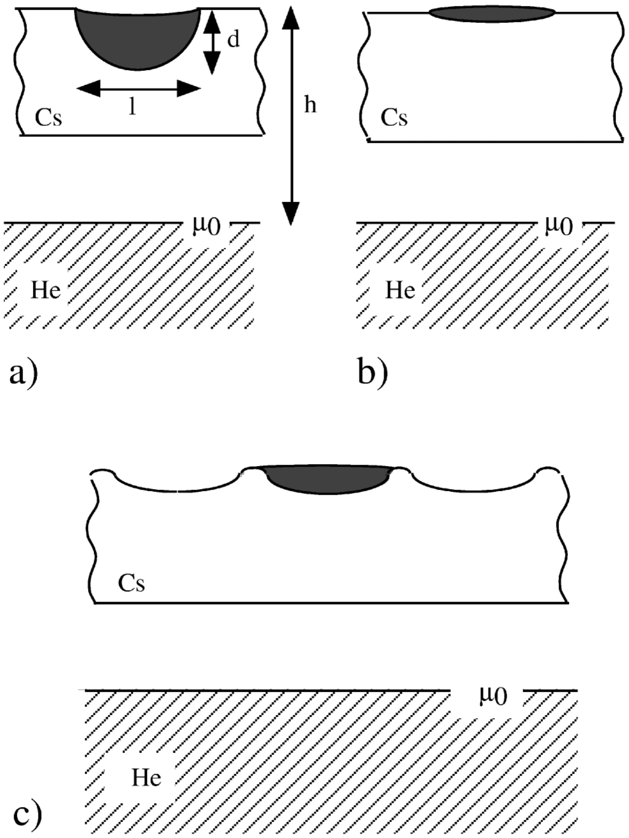

FIG. 1. The Cs surface is a height h above the bulk liquid ^{4}He; (a) shows a deep cavity of depth d and width l, filled with liquid which has a concave surface; (b) shows a shallow cavity, where van der Waals forces are important, filled with liquid with a convex surface; (c) shows a micropuddle in a concavity whose rim has a small but finite radius of curvature: the position of the contact line will be determined by the local gradient of the Cs surface and the pinning sites.

Now $p - p_0$ depends on the curvature R of the free liquid; $p - p_0 = 2\sigma_{\mathrm{lv}}/R$. So if $R = -2\sigma_{\mathrm{lv}}/\rho g h$ (the negative sign of R indicates the surface is concave), then the chemical potential of the liquid in the cavity is identical to that of the vapor and the reservoir, and the puddle is in thermodynamic equilibrium. For example, if $h = 20$ mm and $\sigma_{\mathrm{lv}} = 3.5 \times 10^{-4}\ \mathrm{J\,m^{-2}}$ then $R = -25\ \mu$m. As we expect our cavities to have a lateral length scale of <100 nm then the helium in the cavity has an almost flat surface although it is slightly concave. At the rim of the cavity, which has a very small radius of curvature, the position of the contact line on the rim adjusts so that locally the liquid makes an equilibrium contact angle with the Cs. In this way the free surface of the liquid helium can be essentially flat up to the contact line [19].

It is unlikely that the cavities will be as deep as we have considered above in which van der Waals forces can be ignored. It is more likely that the cavities will be shallow as in Fig. 1(b). the chemical potential is now given by

$$\mu = \mu_0 + mgh + (p - p_0)V - \frac{\Delta C_3}{t^3}, \qquad (2)$$

where ΔC_3 is the difference in van der Waals constants for a ^{4}He atom and Cs and with liquid ^{4}He, and t is the thickness of the liquid in the cavity at the point on the liquid side of the free surface where the pressure is p. In this case the surface of the liquid is not spherical and the radius of curvature is greatest when t is smallest. Equation (2) strictly applies to only a flat bottomed cavity; near the rim of the cavity the potential will be modified.

In a shallow cavity the surface of the liquid is convex rather than concave when it is in thermodynamic equilibrium, as shown in Fig. 1(b). We can see this by considering the center of the free surface. If the thick-film thickness at $T > T_w$ is t_0, which is given by $\rho Vgh = \Delta C_3/t_0^3$, then the radius of curvature at the center, R_c, is given by

$$R_c = -\frac{2\sigma_{\mathrm{lv}}}{\rho gh}\left(1 - \frac{t_0^3}{t_c^3}\right)^{-1}, \qquad (3)$$

where t_c is the thickness of helium at the center. We see for $t_c < t_0$ that $R_c > 0$, i.e., convex. The size of R can be estimated; for $h = 20$ mm and $t_0 = 20$ nm then $R_c = 3.5$ μm for $t_c = 10$ nm, and $R_c = 3.1$ nm for $t_c = 1$ nm. Because of the strong functional dependence of R_c on t, $R_c \sim 2\sigma_{\mathrm{lv}} t^3/\rho ght_0^3$ for $t \ll t_0$, the micropuddles are flat topped with the largest curvature near the rim of the cavity. This will essentially be the same for real rough surfaces. In Fig. 1(c) a micropuddle is shown on a surface where the rim of the concavity is shown with a continuous derivative, but with a small radius of curvature at the rim. In the absence of pinning the contact line will not in general be at the top of the rim but will be in a position where the equilibrium contact angle gives the correct free liquid shape for equilibrium. This may not always be possible because of the shape of the cavity. However, a rim with a very small radius of curvature will pin the contact line of the micropuddle as we discuss later. So on a rough surface, where the edges of the micropuddle are pinned, the curvature of the liquid surface can be such that the micropuddle is in equilibrium but the local contact angle does not have its equilibrium value.

The important conclusion is that micropuddles can form if the surface is rough enough, and be surrounded by dry Cs; i.e., the micropuddles are isolated from the bulk helium liquid but are in equilibrium with it. We shall now see how the possibility of forming these micropuddles pins the receding contact line. Consider Fig. 2(a), where the surface of the left of the contact line has never been in contact with bulk helium as the liquid has advanced from the right. So the surface to the left is dry with no micropuddles. If now the contact line moves back to point B it must leave a micropuddle between A and B, as shown in Fig. 2(b), because the pinning at A means that the contact angle will get lower and the liquid's surface will be pulled back to a point just above B before it jumps to the pinning site B. This movement of the contact line has an energy cost because a new liquid surface has been created over the puddle. the energy is simply $\sigma_{\mathrm{lv}} a_p$ where a_p is the area of the free surface of the micropuddle. This is a large energy compared to $k_B T$ for all conceivable scales of roughness.

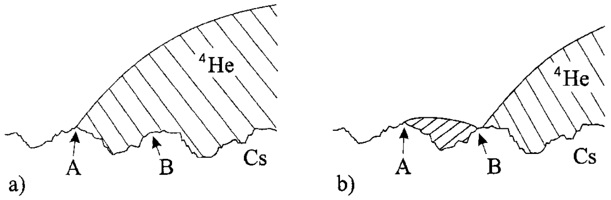

FIG. 2. (a) Shows the contact line at point A on a rough Cs surface; (b) shows the contact line after it has receded to point B and left a micropuddle between A and B.

To estimate this energy we need to know the scale of the roughness. This has not been measured for Cs but it has for the underlying Au film which is much smoother than the Cs surface [11]; the lateral scale length is $L = 50$ nm and the depth 2.5 nm. Taking $a_p \approx L^2$ then $\sigma_{\mathrm{lv}} a_p \approx 6 \times 10^4$ K. Even if $L = 5$ nm, $\sigma_{\mathrm{lv}} a_p \approx 600$ K which is nearly an order of magnitude larger than the estimated pinning energy for the advancing contact line. As the pinning energy divided by $k_B T$ occurs in the exponent in the expression for the velocity [14], then we see that the contact line is rigidly pinned.

A reasonably smooth surface might be defined as one where the pinning is the same for advancing and receding contact lines. Taking a pinning energy of 100 K [11], the length scale of the roughness is 2 nm.

The micropuddle sites are possibly the same sites that cause the pinning of the advancing contact line because around the rim of a micropuddle site there must be a ridge of Cs; e.g., points A and B in Fig. 2(b) are part of a ridge. A helium atom on top of this ridge will experience less van der Waals attraction than an atom on a plane of Cs, so this is a weaker binding area. Conversely a concavity in the Cs is a stronger binding area. So an advancing contact line will be drawn into the concavity by the stronger binding but will need energy to go over the weaker binding at the ridge. So the ridges act as pinning sites.

If we can identify the advancing contact pinning area found by Prevost *et al.* [11] as the area of the micropuddle, then we can estimate the receding contact line pinning; for 125 nm^2 the energy is 3×10^4 K, i.e., over 2 orders of magnitude larger than the pinning of the advancing contact line.

A few quench-condensed Cs surfaces do show dewetting from the metastable thick-film state [8,13] when there are contiguous dry areas already existing and [10] when there are no dry areas. In one case the receding contact angle has been measured and found to be much less than the advancing one on the same surface, again showing that the pinning is stronger for recession. The contact line receded only at $T < 0.7T_w$ which indicates that the line force $\sigma_{\mathrm{lv}}[\cos\Theta_c(T) - \cos\Theta_0(T)]$ has to have $\Theta_0(T)$ large enough to overcome the pinning.

In the case of dewetting films [8,10,13], it has been shown that the Cs surface remembers where the thick film has flowed. The formation of micropuddles by the first film explains this behavior. The next application of liquid creates a thick film with an advancing contact line which will advance because it is dragged across any micropuddles that it encounters. This is because the contact angle is initially very small when the contact line reaches the edge of the micropuddle and so the advancing force is high. Once the contact line reaches the dry surface on the far side of the micropuddle, this dragging stops and the contact line is stationary. Experiments show that the average helium thickness on the dewetted surface is ≤5 monolayers [8,10]. This thickness is consistent with micropuddles but not with a continuous film of this thickness as a film would have a lower chemical potential than μ_0 and so would be unstable against thickening.

The existence of micropuddles could be experimentally confirmed by quartz microbalance measurements or ellipsometry on surfaces that showed hysteresis or the memory effect. A systematic study would require atomic force measurements of the surface topography of various quenched condensed Cs samples coupled with micropuddle detection.

In conclusion, we have shown that micropuddles on rough surfaces can be stabilized by pressure due to the surface tension on a curved surface. Then the helium in the micropuddle has the same chemical potential as the reservoir and so it is in equilibrium. The receding contact line is pinned by the necessity to create micropuddles if it recedes. The pinning energy is proportional to the area of the free surface of the liquid in the micropuddle and so is a function of the roughness of the surface. As the roughness tends to zero so does the pinning force, and we expect only small hysteresis on smooth Cs surfaces. The formation of stable micropuddles after a surface has dewet from the thick-film state explains the long memory effect for these surfaces when they are subsequently flooded with more liquid. Furthermore, it is possible that the weak binding sites around the rim of a potential micropuddle cavity act as pinning centers for an advancing contact line, in which case the same surface topography creates advancing and receding contact line pinning centers but by different physical processes.

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[18] Some rough surfaces may well have cavities in which there is capillary condensation at low enough contact angles or high enough temperatures. We are not discussing such cavities. Rather we consider shallow cavities that do not fill by capillary condensation. The two sorts could coexist on a Cs surface. It will not be difficult to distinguish experimentally between the two.
[19] This result explains why Prevost *et al.* [15] found a flat layer of liquid helium between the mesas. These were spaced about 15 μm apart and with $h \approx 0.1$ mm, $R = 4.9$ mm, which will appear flat over a distance of 15 μm.