Thermally Activated Motion of the Contact Line of a Liquid ^{4}He Meniscus on a Cesium Substrate

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We have measured the contact angle of a liquid helium-4 meniscus on a cesium substrate as a function of the velocity of the three phase contact line, at various temperatures. The velocity is found to vary exponentially with the applied force. We show that the contact line advances through thermally activated jumps. Their area of about 125 nm^2 is probably related to the roughness of the cesium substrate which is evaporated at low temperature.

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The contact angle θ of a liquid meniscus on a solid substrate depends on the velocity v of the contact line (where the liquid-vapor interface meets the solid substrate). For an advancing meniscus, the contact angle θ_a is an increasing function of v. In other words, one has to apply a finite force to move the line at a finite velocity; the force per unit length F is related to the contact angle by $F = \sigma[\cos\theta_0 - \cos\theta_a(v)]$, where σ is the liquid-vapor surface tension and θ_0 is the equilibrium contact angle. Many experiments have been devoted to the measurement of v-F characteristics [1–3], and various empirical relations between v and θ have been obtained. Two opposite mechanisms have been proposed to explain experimental data. Hydrodynamic models disregard what happens at a microscopic scale at the contact line (CL), and instead describe the CL motion in terms of bulk viscous dissipation [4]. A molecular-kinetic model, first developed by Blake [5], describes the CL movement as an activated process in which the line advances through molecular jumps. Although the $v(\theta)$ functional forms are different in these two models, both fit experimental data reasonably well; thus, only the value of the physical parameters involved in the fit makes possible a discrimination between the two mechanisms [3]. For ordinary systems, it is most likely that both effects play a role in the meniscus motion and that viscous dissipation may conceal the intrinsic dynamics of the CL.

Since the discovery in 1991 that superfluid helium-4 does not wet Cesium at low temperatures [6], this system has proven to be useful for studies of some general features of the wetting transition such as the prewetting transition [7,8] or the roughness of the CL on a disordered substrate [9]. Because of its unique properties, the He-Cs system is also a good candidate to investigate the dynamics of the CL. The superfluidity of helium makes viscous dissipation negligible below 2.17 K. The temperature can be varied throughout the range below the wetting temperature ($T_W \approx 2$ K). In this temperature range, no contamination can occur and the same substrate can be used for a large number of experiments.

In this Letter, we report measurements of the dynamics of the CL for temperatures in the range 1–2 K. By studying the velocity as a function of both the applied force and the temperature, we have obtained the first direct evidence that the CL advances through thermally activated jumps. Their area is about 125 nm^2, and is probably related to the roughness of the substrate. Finally, we discuss how the CL dynamics could be modified when the pinning is weak.

We first describe the experimental setup [10]. Experiments are performed in an optical helium-4 cryostat whose temperature can be regulated within 1 mK between 0.8 and 2 K. On the bottom of the cell lies a gold mirror [11] which is used as a substrate for Cs evaporation. The cesium layer is evaporated *in situ* at low temperature ($T \approx 20$ K) using commercial getters. The thickness of the layer is of the order of 100 atomic layers. It has been shown that the properties of such Cs evaporated substrates can vary slightly from one evaporation to the next [12]. For the substrate used in this experiment, we find that the wetting temperature is $T_W = 1.85$ K. We also find that the receding contact angle is zero, as is usual for evaporated Cs substrates [10,12]. Thus all measurements are performed for an advancing CL. The mirror is tilted by an angle α of 4° with respect to the horizontal direction, therefore creating a well-defined contact line which is perfectly straight within optical resolution. A regulated flowmeter in the filling line of the cell is used to control the velocity of the CL in the range 0.1–50 μm/s.

The position $x(t)$ of the CL is determined from images taken by a CCD camera, and v is obtained by numerical differentiation. The measurement of F is more difficult, as the change in contact angle θ_a is of the order of 1°. Instead of measuring directly $\theta_a(v)$, we use the following method (Fig. 1).

A small part of the liquid-vapor interface far behind the meniscus is illuminated by a laser. Thus, we obtain interference fringes between the beam reflected at the Cs surface and the beam reflected at a partially reflecting plate which is positioned above the liquid-vapor

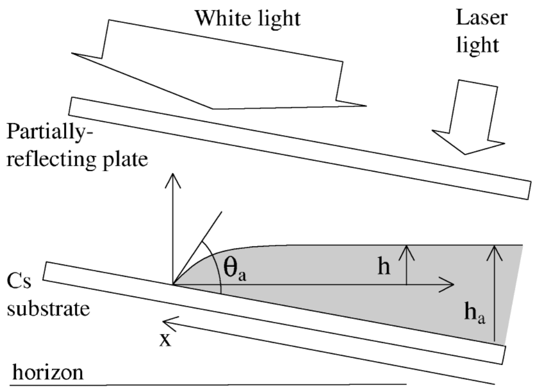

FIG. 1. Schematic view of the experimental setup. The simultaneous measurement of $h_a(t)$ and $x(t)$ allows us to determine $h(t) = h_a - x\tan\alpha$ and hence the contact angle.

interface. When the CL advances, h_a increases and so does the phase difference between the reflected beams. The resulting displacement of the fringes is measured by a photomutiplier tube (PMT). After demodulation of the PMT signal, we obtain the height of liquid $h_a(t)$ far from the meniscus. As θ_a depends on v, the liquid height h in the frame moving with the CL depends on v also. An example is given in Fig. 2: a sharp increase in the velocity leads to a shift Δh.

Assuming that the meniscus profile obeys the Laplace equation, the liquid height is given by $h/L_C = [1 - \cos(\theta_a - \alpha)]^{1/2}$, where $L_C = (\sigma/\rho g)^{1/2}$ is the capillary length ($L_C = 0.50$ mm). As $\theta_a < 25°$, one finds that $\Delta\theta_a/\Delta h = 0.164°/\mu$m. The accuracy in $\Delta\theta_a$ is of the order of 0.05°. A direct and absolute measurement of θ_a can be achieved by illuminating the cell with an expanded laser beam, and analyzing the fringe pattern [10]. Detailed measurements of θ_a have been made at $v = 1$ μm/s. We find that the contact angle decreases from 24.0° at $T = 0.85$ K to 7.1° at $T = 1.75$ K. This method cannot be used to measure precisely the velocity dependence of θ_a since the accuracy is only 0.5°. However, we have checked that both methods yield consistent values when the shift $\Delta\theta_a$ is large enough. Finally, at a given temperature, we obtain $\theta_a(v)$ with a relative uncertainty of 0.05° and a systematic uncertainty of 0.5°. It should be emphasized that we do not know the equilibrium value θ_0 of the contact angle. We have monitored the position x of the CL after stopping the flow of helium into the cell, after which h_a becomes constant. As shown in Fig. 4 below, we do not observe a steady value of x even after 1000 s. It is difficult for us to measure variations of x on a much longer time scale because of slow temperature drifts in some parts of the cryostat. As a consequence, we measure only variations ΔF of the force F.

Our measurements are summarized in Fig. 3. The velocity v is plotted as a function of F for various temperatures. Because of the fact that θ_0 is unknown, the relative position of the data points corresponding to different temperatures is arbitrary. The data are well fitted by exponentials and the slope B of the $\ln v$ vs F curves is a decreasing function of the temperature. These facts suggest that the motion of the CL is thermally activated.

In order to study the $v(F)$ dependence for values of v smaller than 0.1 μm/s, we have also analyzed the relaxation $x(t)$ of the CL when the liquid level h_a far behind the meniscus is fixed. As the line advances, the force decreases. Using once more the equation for the meniscus profile, one finds $\Delta F/\sigma = -(1 - \cos\theta_a)(\tan\alpha\Delta x/L_C)$. Since the variation of θ_a is small, the force decreases linearly with the position of the line: $\Delta F \sim -\Delta x$. Thus an exponential $v(F)$ dependence leads to a logarithmic $x(t)$ relaxation. This type of behavior is shown in Fig. 4. Moreover, we find that the values of $B(T)$ obtained from the analysis of the relaxations are in good agreement with the values obtained from the

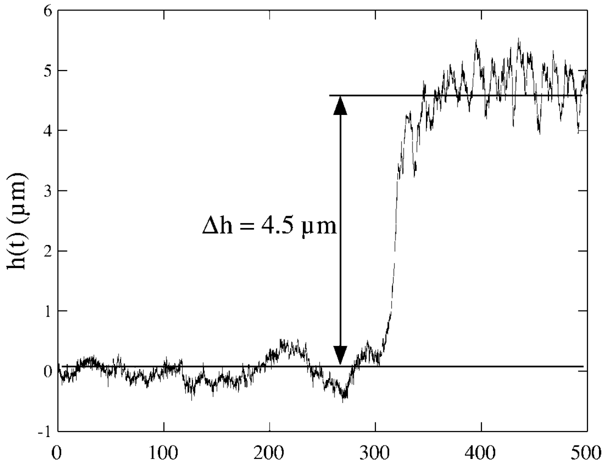

FIG. 2. Example of contact angle measurement: height $h(t)$ of the free surface as a function of time. At $t = 310$ s, the velocity is increased from 1 to 12 μm/s. It yields a shift Δh of 4.5 μm corresponding to a shift $\Delta\theta_a$ of 0.74°.

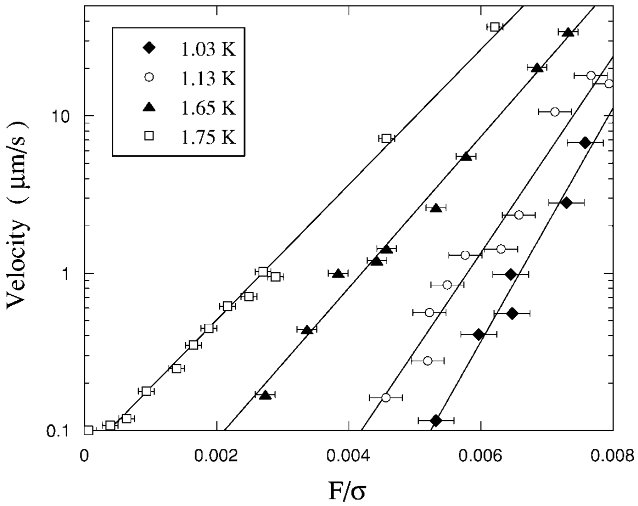

FIG. 3. Plot of the CL velocity as a function of the applied force for various temperatures. Solid lines are exponential fits to the experimental data. The relative horizontal position of the curves is arbitrary since the absolute force is unknown.

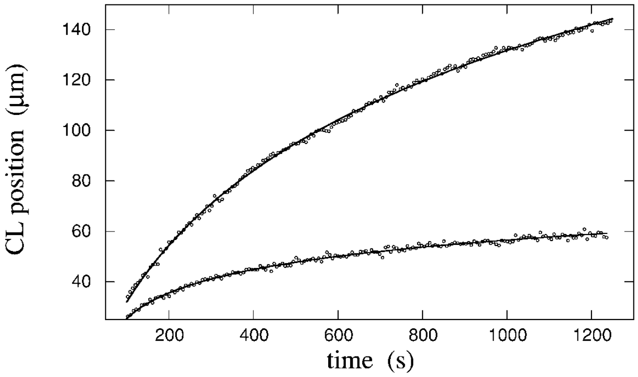

FIG. 4. Relaxation of the CL at $T = 1$ K (lower curve) and $T = 1.7$ K (upper curve). Solid lines are logarithmic fits to the data.

$v(F)$ curves. Thus we can conclude that the velocity varies exponentially with the applied force over the range 50–0.001 μm/s.

Before discussing further experimental data, it is worth verifying that the viscous dissipation is indeed negligible. The shift in contact angle due to the viscosity η of the liquid is given by [4,13]

$$\theta_a^3 = \theta_0^3 - 9\,\frac{\eta v}{\sigma}\ln\frac{L_C}{L_s}\,,$$

where L_s is the size of the inner zone in which the slipping of the liquid at the wall is assumed. One expects L_s to be of atomic size. In the usual two-fluid description of superfluid helium-4, only the so-called normal component has a nonzero viscosity, which is of the order of 15 μpoise in the range 1–1.7 K [14]. So we take this value as an upper bound for η. The effect of the viscosity is larger at small contact angle and large velocity. Taking $\theta_0 = 5°$, $v = 50$ μm/s, and $L_s = 3$ Å, one finds a shift in the contact angle of the order of 0.05°, which is small compared to the measured value (~1°). In the following, we will ignore the effect of viscous dissipation on the CL dynamics.

In order to check whether mechanical vibrations are important with respect to thermal noise, we have studied the relaxation of the CL at low temperature for various vibration levels. This was achieved using a mechanical transducer attached to the bottom of the cryostat. The most predominant resonant mode (about 10 Hz) of the helium pool was excited up to 10 times its residual amplitude. No effect was observed: therefore it seems reasonable to consider only thermal noise. Thus one expects B^{-1} to be proportional to the temperature, which is indeed the case as shown in Fig. 5.

Assuming a thermally activated process, the velocity v can be written as [5]

$$v = (s^*)^{1/2}\,\frac{kT}{h}\exp\{-U_C/kT + Fs^*/2kT\}, \qquad (1)$$

where k is the Boltzmann constant, s^* is the activation area, and U_C is the energy barrier. From the values of B, we find that the value of the activation area is $s^* =$ 125 ± 15 nm^2. This is much larger than an atomic size. In our case, we think that the size of elementary jumps of the line is fixed by the disorder of the solid surface. Indeed, the liquid-vapor interface of helium-4 is rather wide (the density changes from 90% to 10% of the bulk liquid density over a distance of 7.6 Å [15]), and one does not expect the CL to be sensitive to the atomic structure of the surface. The length scale $d = (s^*)^{1/2}$ is of the order of 10 nm; it is most probably related to the roughness of the Cs layer. As the Cs is deposited balistically at low temperature, the deposition process itself may generate a rough surface. Moreover, scanning tunneling microscopy (STM) observations of the underlying gold layer have revealed a corrugation of typical height 2.5 nm and typical length scale 50 nm [16]. Although the Cs thickness (50 nm) is much larger than the gold corrugation, it is possible that this corrugation has an impact on the final surface structure.

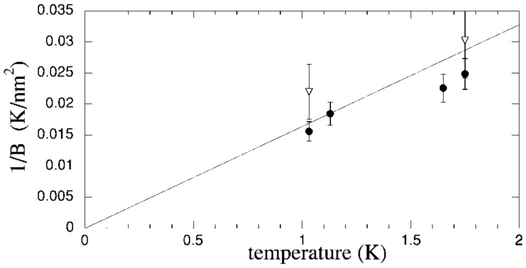

FIG. 5. Plot of the coefficient $1/B$ versus T. Values are obtained from v-F characteristics (dots) and from the relaxations of the CL (triangles).

So far, we have discussed only the value of the coefficient of F in the exponential in Eq. (1). In order to confirm our scenario for the motion of the CL, we would like to test the consistency of our data with the full expression for v. This is not possible, primarily because we do not know the equilibrium value θ_0 of the contact angle. Nevertheless, we can use Eq. (1) to compute $\theta_0(T)$ and see under what conditions reasonable values are obtained. The first term $(s^*)^{1/2}$ in the expression for v is known; the second term is a thermal frequency of the order of 10^{10} Hz. We do not know the exact value of the pinning energy U_C, which is related to the disorder of the substrate. Still, it is possible to obtain an estimate of U_C. In the case of a chemically heterogeneous substrate, the magnitude of the disorder is characterized by the rms value of the fluctuating part ΔS of the spreading power S ($S \equiv \sigma + \sigma_{SL} - \sigma_{SV}$). If s^* is the typical area of a defect, one expects the pinning energy of a defect U_C to be of order $s^*\langle\Delta S\rangle$ [17]. A rough substrate is equivalent to a chemically heterogeneous substrate in the limit where the local slope ϕ is small compared to the contact angle. One obtains [18] $U_C \sim s^*\sigma\langle\phi\rangle\sin\theta$ where θ is the true contact angle on a smooth surface. As this expression is only an estimate for U_C, we assume that $\theta \approx \theta_a(v = 1\ \mu\text{m/s})$. Using Eq. (1) and the above expression for U_C, we have computed $\theta_0(T)$ for various values of the mean slope $\langle\phi\rangle$. The simple requirement that $0 < \theta_0 < \theta_a$ leads to values of $\langle\phi\rangle$ of about 0.1 rad. This corresponds to a corrugation height of the order of 1 nm, a reasonable value. We also obtain an estimate for the pinning energy U_C, which decreases from 120 K at $T = 1$ K to 60 K at $T = 1.7$ K. This is a large value, which explains why the equilibrium value of the contact angle cannot be reached. In other words, the slow dynamics of the line may be responsible for the hysteresis that is observed in a one-hour experiment.

Our results are consistent with the hypothesis of a CL which is strongly pinned on defects of the substrate, and which advances through jumps of the same typical size as defects. Still, it is worthwhile considering some other scenarios. A local jump happening at one defect changes the CL configuration and could trigger off other jumps on neighboring sites. So a small initial jump could potentially start a much larger avalanche. Nevertheless, if the initial depinning occurs at the scale of a single defect, only the exponential prefactor in Eq. (1) would be modified by the existence of avalanches. The force and temperature dependence of the CL velocity would not be very different, as they are essentially governed by the coefficient in the exponential.

On the other hand, one expects the CL dynamics to be qualitatively different in the case of weak defects. In such a situation, a single defect does not pin the line, and pinning occurs at a length scale L_D much larger than the defect size d (which may be more rigorously defined as the correlation length of the substrate disorder). In the case of chemical disorder characterized by $\langle\Delta S\rangle$, one finds $L_D \approx d(\sigma \sin^2\theta/\langle\Delta S\rangle)^2$ [19]; physically, L_D depends on the ratio between the CL stiffness and the substrate disorder. L_D is known as the Larkin length in the context of flux lines in superconductors [20]. The CL motion can be described by a phenomenological model identical to the one originally derived in the case of superconductors [21]. As discussed in a preliminary report [22], the depinning length L^* depends on the applied force. In the limit of very small F, L^* diverges as F approaches zero. Using scaling arguments, we have found that v varies like $\exp(-F_C/F)$, where F_C is the depinning force at zero temperature. Such behavior is not observed in our experiment. In the limit $F \sim F_C$, one expects L^* to be of order L_D. This leads to a velocity varying like $\exp F$, and one recovers an expression for $v(F)$ similar to Eq. (1). However, the activation area s^* is now equal to dL_D. Since s^* is temperature independent, so is L_D. This means that the temperature dependence of the CL stiffness $[\sim \sin^2\theta(T)]$ is *exactly* canceled out by the temperature dependence of the substrate disorder. Such a coincidence seems very unlikely. Moreover, a θ^2 dependence of $\langle\Delta S\rangle$ may happen only in the case of a chemical disorder with wettable defects covering a constant fraction of the substrate area; this seems less likely than a disorder controlled by the substrate roughness. Thus, it seems to us that a strong pinning is more consistent with our experiment than a weak one.

In conclusion, we have demonstrated that, in the absence of viscous dissipation, the contact line motion is thermally activated. For a Cs evaporated film, the activation area is about 125 nm^2. This area is most probably related to the size of the defects which act as strong pinning centers for the line. A qualitatively different behavior is expected for weak defects and a small applied force.

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