Roughness of the Contact Line on a Disordered Substrate

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We present results from an experimental study on the wetting properties of superfluid helium-4 on a cesium substrate with random disorder. We have measured the roughness exponents of the contact line, and found that they are in agreement with theoretical predictions. Furthermore, we have observed a strong increase of the contact line fluctuations near the wetting transition; this temperature dependence is consistent with the theory. [S0031-9007(98)05654-3]

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It is well known that the wetting properties of ordinary solid surfaces are strongly affected by their roughness or chemical heterogeneity. In many practical situations, the contact line—where the liquid-vapor interface meets the solid substrate—is distorted by the heterogeneities; the pinning of the line causes hysteresis of the contact angle. As pointed out by De Gennes [1] and Pomeau and Vannimenus [2], the magnitude of the distortion is controlled by the balance between the pinning potential and the elastic energy of the line. In the case of the contact line, the elastic energy is nonlocal since deformations of the line are accompanied by distortions of the liquid-vapor interface [1]. Following Huse [3], Robbins and Joanny (RJ) [4] have derived scaling laws for the spatial fluctuations of the contact line in the limit of weak disorder. Although the contact angle hysteresis has been under investigation for many years [5], a direct study of the behavior of the contact line on a random substrate has not yet been performed.

In order to study the effect of the substrate disorder, we have used superfluid helium-4 on cesium. Since He was predicted not to wet Cs at low temperature [6], many experimental [7,8] and theoretical works have provided a rather good understanding of this system. For our present purpose, its main advantage is the possibility to vary the temperature up to the wetting transition and, hence, to control the contact angle θ. In this way, we are able to control the elastic energy of the contact line, which, for a given deformation, varies like $\gamma_{LV} \sin^2\theta$ [1]; here γ_{LV} is the surface tension of the liquid-vapor interface. In this Letter, we report measurements of the fluctuations of the contact line. At a given temperature, we determine the roughness exponents of the line, in agreement with predictions by RJ. Moreover, we observe a strong increase in the fluctuations near the wetting temperature, and we show that this temperature dependence is also consistent with theoretical models.

We first describe the experimental setup [9]. 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 (optical flatness $\lambda/20$, rms roughness 3 Å, diameter 30 mm) which is used as a substrate for Cs evaporation. The mirror is tilted by 4° with respect to the horizontal direction, therefore providing a well defined contact line. Its position on the mirror can be varied by adding or removing helium so that we can observe both advancing and receding menisci. The area of the mirror we use for visualization is about $10 \times 10\ \mathrm{mm}^2$. The light source as well as the imaging optics and the CCD camera are outside the cryostat, so that we can easily change the illumination and the magnification. White light is used to image the contact line; due to the large distance between the mirror and the lens, the numerical aperture is about 0.1 and the resolution about 5 μm. The effective resolution of the CCD is 768×562 pixels; when recording the fluctuations of the line, the field of view is about 10 mm and the equivalent pixel size about 15 μm. The position of the contact line is determined within 5 μm by interpolation. To measure the contact angle as well, a semireflecting plate is positioned above the mirror. Illuminating the interferometric cavity thus obtained with an expanded laser beam produces equal thickness fringes which can be mapped into the profile of the meniscus [9]. The preparation of the cesium layer is made *in situ*, using commercial getters. As reported earlier [9], the optical and wetting properties of this layer are not sensitive to the details of the evaporation process.

Before reporting our observations on a disordered substrate, it is worthwhile to go back to our earlier results [9]. We first studied an optically flat Cs layer. Even for this case, a large hysteresis is observed. For an advancing meniscus, we measure a reproducible contact angle $\theta_a^{(0)}(T) \approx 25°$ at 0.85 K. For a receding meniscus, the contact line is pinned and we usually obtain a contact angle $\theta_r = 0$. This behavior was later confirmed by Ross *et al.* [10]. This could mean that the evaporated Cs layer is heterogeneous at a length scale below optical resolution. Anyhow, this heterogeneity has a small effect on the fluctuations of the contact line. For a line 1 mm long, we have measured a rms amplitude w of the fluctuations of about 1 μm at 1.8 K and 2.5 μm at 1.9 K, very close to the wetting temperature ($T_W = 1.95$ K in our experiment). For such a substrate, the smallness of w precludes any quantitative analysis of its scaling properties. We report here observations on a disordered substrate prepared in the following manner. First, about 50 atomic layers of Cs are evaporated on the mirror. Then, some air is admitted which oxidizes this first layer at low temperature and produces defects on the surface. Finally, this surface is coated by a second Cs film 150 atomic layers thick. Of course, this process is not very well controlled and it is not possible to determine precisely the local value of the spreading power $S \equiv \gamma_{SV} - \gamma_{SL} - \gamma_{LV}$ on the whole surface. However, it is possible to obtain pertinent information on the disorder. To this aim, we Fourier transformed several images corresponding to different areas of the substrate. The power spectra of all images are similar and display a broad peak centered around 20 μm^{-1}. The disorder is, thus, rather homogeneous, and involves a characteristic length scale $d = 20$ μm. Furthermore, it should be noted that the Cs source is positioned beside the mirror so that the mean incident angle of the Cs beam is 45°. In this geometry, it is very likely that, due to the roughness, some part of the substrate is not exposed to the Cs beam. We then expect the unexposed spots to act as wettable defects. We find, indeed, that the receding contact angle is again zero in this case, as found in the previous experiment [9].

The experiment is carried out as follows. We increase the helium level in the cell at a rate such that the mean velocity of the contact line is of the order of 1 mm/min, and we record about 50 images of the line. Each image is digitized, and the profile $\eta(x)$ of the line is defined as the point of steepest gradient for each pixel column x. The whole sequence is done controlling the temperature, and is repeated for temperatures ranging from 0.8 to 1.93 K (recall that $T_W = 1.95$ K).

We first present the qualitative features of our results. Typical images of the line are displayed in Fig. 1. It is observed that the amplitude of the fluctuations increases with the temperature. This is qualitatively consistent with an elastic energy proportional to $\gamma_{LV} \sin^2\theta$ [1]. The temperature dependence arises mainly from the $\sin^2\theta$ factor which decreases by a factor 20 from 0.85 to 1.93 K.

In Fig. 2, successive positions of the line are shown for two different temperatures; the time interval is of the order of 10 s. We observe that the motion of the line is not uniform; it is composed of fast jumps as segments of the line depin from defects. This dynamics is strongly temperature dependent: depinning events involve longer parts of the line at low temperature than at high temperature. This is consistent with the fact that the line is stiffer at low temperatures. We have measured the advancing angle θ_a for a heterogeneous substrate; it is larger by a few degrees than the advancing angle $\theta_a^{(0)}$ for an optically flat substrate. Neither θ_a nor the qualitative features of the motion of the line depend on the mean velocity in our experimental range (0.5–2 mm/min), which means that the line is close to the depinning threshold. In addition to short wavelength fluctuations, $\eta(x)$ exhibits an overall curvature, especially at low temperature [Fig. 2(a)]. This is an edge effect; helium wets the sides of the mirrors which are not coated with Cs. This imposes a large slope $d\eta/dx$ at both ends of the line. Because of the stiffness of the line, the boundary

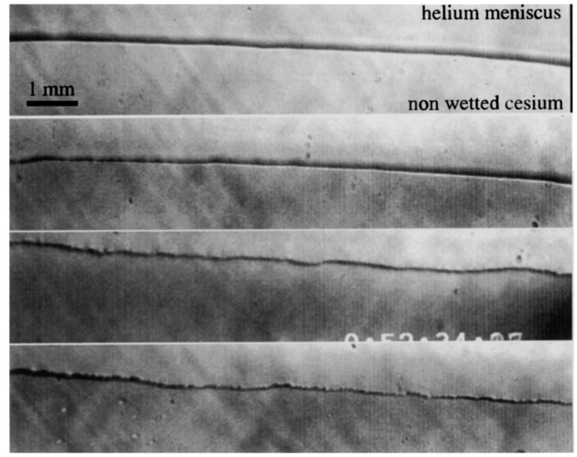

FIG. 1. Images of the contact line at different temperatures. From top to bottom 0.87, 1.72, 1.90, and 1.93 K. A few droplets can be seen ahead of the line in the last image.

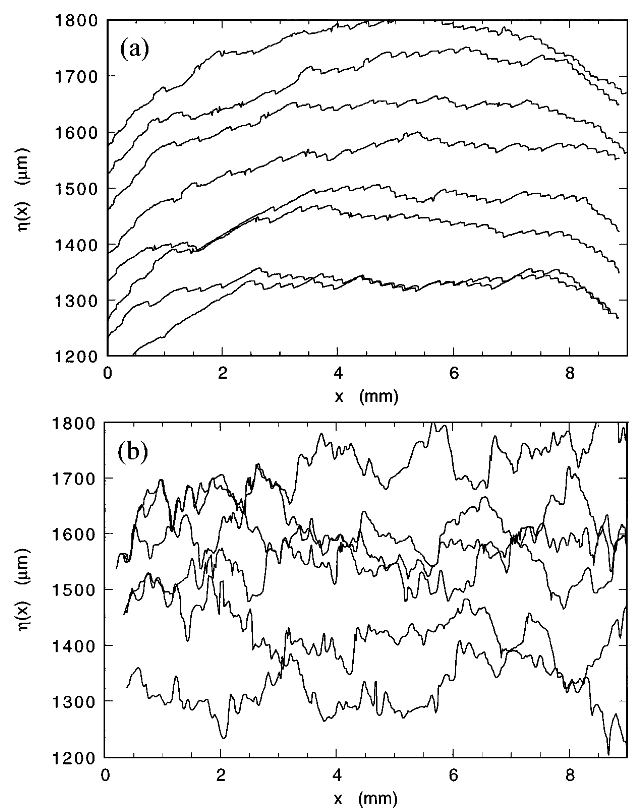

FIG. 2. Successive profiles of the contact line at 0.87 K [up (a)] and 1.93 K [down (b)]. As a function of time the line moves down; the time interval is of the order of 10 s. The small oscillations in the upper figure are due to pixel size.

conditions affect the shape of the entire line, which is not much longer than the capillary length L_C. Under our experimental conditions, $L_C = [\gamma_{LV}/(\rho g \sin\alpha)]^{1/2}$, where ρ is the liquid density, g the acceleration due to gravity, and α the tilt angle between the horizon and the substrate. This gives $L_C \approx 2$ mm, while the length of the line is about 10 mm.

In order to analyze the line fluctuations at each temperature, we computed $W(x)$ the square root of the two point correlation function:

$$W(x) = \{\langle\overline{[\eta(x + x_0) - \eta(x_0)]^2}\rangle\}^{1/2},$$

where the bar denotes an average on x_0 along the line and the brackets denote an average over all successive configurations of the line [11]. The functions $W(x)$ are plotted in Fig. 3. As $L_C \approx 2$ mm, $W(x)$ is plotted for $x < 1.5$ mm in order to neglect gravity. In order to neglect edge effects at low temperature, one has to use only the central part of the profile to compute $W(x)$; this requires also that x be smaller than a few millimeters. The smallest scale is the pixel size, i.e., 15 μm. According to RJ, the scaling of $W(x)$ depends on whether the amplitude of the fluctuations is smaller or larger than the length scale of substrate heterogeneity d. Within numerical factors, they predict $W(x) \sim A^{2/3}(d^2x)^{1/3}$ for large fluctuations $W(x) > d$ and $W(x) \sim A(dx)^{1/2}$ for small fluctuations $W(x) < d$, where A is a coefficient depending on the amplitude of the disorder. The surface disorder is characterized by the rms magnitude $\overline{h}$ of the random fluctuations of the spreading power S. The expression for A is $A \sim \overline{h}/\gamma_{LV}\sin^2\overline{\theta}$, where $\overline{\theta}$ is the contact angle for a homogeneous substrate of spreading power $\overline{S}$. The crossover between the two regimes occurs at $x \sim L_d = d/A^2$. As $d = 20$ μm, each curve $W(x)$ has been split into two parts [$W(x) < 15$ μm and $W(x) > 30$ μm] which are fitted by the expected power law dependences, respectively, $x^{1/2}$ and $x^{1/3}$. As shown in Fig. 3, the scaling of both regimes is in good agreement

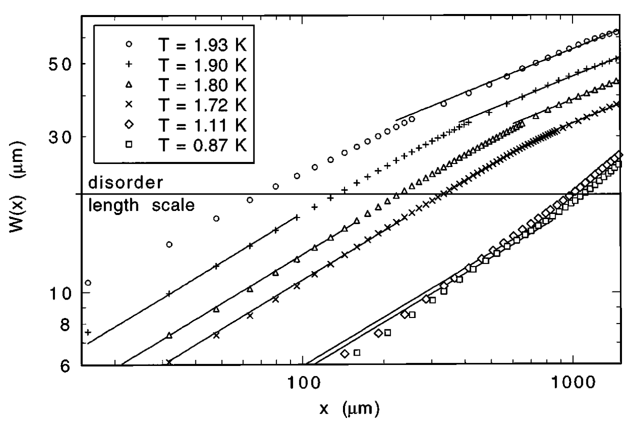

FIG. 3. Plot of $W(x)$, the square root of the correlation function at different temperatures. The scaling depends on whether $W(x)$ is smaller or larger than the length scale of the disorder.

with the expected exponents, and the crossover between occurs for $W(x) \approx d$ as predicted. The small discrepancy for the low temperature curves is probably due to edge effect. Although the dynamic range in each regime is at most one decade, the fact that all curves scales as expected provide a strong confirmation of the theoretical predictions by RJ.

A stronger test of the model can be made by analyzing the temperature dependence of the fluctuations, which arises from the temperature dependence of $A \approx \overline{h}/(\gamma_{LV}\sin^2\overline{\theta})$. $\gamma_{LV}(T)$ is well known [12]. As for $\overline{\theta}$, we assume that it is equal to the contact angle θ_0 for a perfect Cs substrate; this is consistent with the assumption of a weak disorder, i.e., $\overline{h} \ll \overline{S}$. The determination of θ_0 deserves some comments. We have measured an advancing contact angle $\theta_a^{(0)}$ on an optically flat substrate. As explained before, this substrate had certainly some microscopic wettable defects since the receding angle was zero. The experiment has been done several times, yielding very similar values, although the substrate was sometimes contaminated with dust particles acting as wettable defects. The effect of small wettable defects has been studied by other authors [13]; they have shown that the advancing angle is equal to the equilibrium angle as long as the surface fraction covered by defects is smaller than 25%. This presumably applies to our experiment, so we make the assumption that $\theta_0(T) \approx \theta_a^{(0)}(T)$ in what follows. Furthermore, we have shown that this assumption leads to a very weak temperature variation of γ_{SL} which is consistent with theoretical models [14]. Let us also note that our value for $\theta_a^{(0)}$ has been confirmed by two other groups [15,16], but Klier *et al.* found a different result [17]. Then, we have to derive an expression for $\overline{h}$. We have argued earlier that, due to the preparation of the heterogeneous substrate, some wettable defects are present. Let us make the approximation that the random component of the spreading power S is dominated by these defects and that S can take only the values $S_{\text{defect}} = 0$ or $S_0 = \gamma_{LV}(\cos\theta_0 - 1)$. It is likely to be the case since He wets anything but Cs. In this way, we expect the disorder strength $\overline{h}/\gamma_{LV}$ to be about $\sqrt{f}(1 - \cos\theta_0)$, where f is the surface fraction covered by the defects.

Using our measurements of $W(x)$ and RJ's model, we can determine the disorder strength $\overline{h}/\gamma_{LV}$ in two other independent ways: from the crossover length L_d [since $\overline{h}/\gamma_{LV} \approx (d/L_d)^{1/2}\sin^2\theta_0$] and from one of the power law prefactors corresponding to the two different regimes (we choose here the $x^{1/2}$ regime). In Fig. 4, we have plotted the values of $\overline{h}/\gamma_{LV}$ obtained from this analysis: both determinations are in good agreement. For comparison, we also plotted the quantity $(1 - \cos\theta_0)$, which is proportional to the disorder strength in our simple model for the substrate. We choose $\sqrt{f}$ so that our model agrees at low temperature with the values of $\overline{h}/\gamma_{LV}$ obtained from the experiment. This gives $f \approx 0.05$; this value should be considered as an order of magnitude

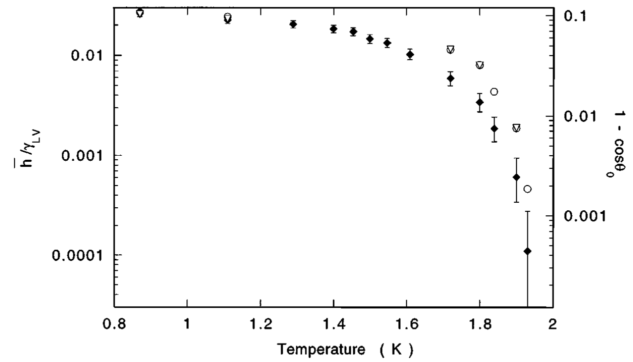

FIG. 4. Disorder strength $\overline{h}/\gamma_{LV}$ as a function of the temperature obtained from the crossover L_d (triangles) and from the prefactor of $x^{1/2}$ regime (circles). Diamonds are the values of $(1 - \cos\theta_0)$, which are proportional to the disorder strength in our simple description of the surface.

since numerical factors are missing in RJ's model. Both $(1 - \cos\theta_0)$ and $\overline{h}/\gamma_{LV}$ have the same kind of temperature dependence and decrease by roughly 2 orders of magnitude between 0.87 and 1.95 K. However, close to T_W, $\overline{h}/\gamma_{LV}$ decreases more slowly than $(1 - \cos\theta_0)$. This is easily understood from the following observation. At 1.93 K a few liquid droplets condense ahead of the line (Fig. 1); the size of these droplets is larger than d. Since they correspond to wettable parts of the substrate, this means that the wettable area of the substrate increases close to T_W, leading to a stronger disorder than inferred from the $(1 - \cos\theta_0)$ term only. Thus we believe that the predictions of Robbins and Joanny are consistent with the temperature dependence of the line fluctuations.

In our system, defects are strong, and one may wonder why the agreement is so good, since the model assumes a weakly heterogeneous substrate. Actually, the validity of the model requires that the line $\eta(x)$ is weakly distorted, which allows linearization of the Laplace equation. At the highest temperature ($T = 1.93$ K), we have $d\eta/dx < 0.5$, and the requirement is still reasonably met. Closer to T_W, the behavior of the system is quite different: the meniscus advances on the substrate through the percolation of wetted spots. Then the distortion of the line is much larger than shown in Fig. 1. One may also wonder if the equilibrium argument used by Robbins and Joanny should apply in our system, where the velocity of the line is finite. Ertas and Kardar [18] have studied theoretically the dynamics of the contact line. In the case $L > L_d$, they found the same roughness exponent for an advancing contact line at the depinning threshold. The opposite case has not been studied yet.

In conclusion, we have analyzed the roughness of the contact line at the depinning threshold, in a large temperature range. We find a quantitative agreement with the scaling laws predicted by Robbins and Joanny for a line at equilibrium that shows that the same scaling is also valid for the critical line. Although the RJ model correctly describes the roughness of the line, this model would predict a very small hysteresis for the values of the heterogeneity obtained from the scaling analysis of the line fluctuations. This is an interesting puzzle, and we think that a more accurate characterization of the substrate may be required to have a full understanding of our system.

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