Pseudo-contact angle due to superfluid vortices in $^4\text{He}$

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We have investigated spreading of superfluid $^4\text{He}$ on top of polished MgF$_2$ and evaporated SiO$_2$ substrates. Our results show strongly varying contact angles of 0 - 15 mrad on the evaporated layers. According to our theoretical calculations, these contact angles can be explained by a spatially varying distribution of vortex lines, the unpinning velocity of which is inversely proportional to the liquid depth.

Wetting phenomena in superfluid $^4\text{He}$ have been under intense investigation during the past few years. After the theoretical prediction by Cheng et al. [1], it was found out by Nacher and Dupont-Roc [2] that, indeed, the alkaline metal Cs is not wetted by superfluid $^4\text{He}$. Recently, Klier et al. [3] measured $\theta = 48^\circ$ for the contact angle on top of an evaporated Cs film using capillary rise methods. Subsequent optical experiments [4,5] gave slightly smaller values $\theta = 25 - 32^\circ$, and they also revealed strong hysteresis between advancing and receding liquid fronts. This hysteresis cannot be fully explained in terms of external disorder, although roughness of the advancing contact line has been found to agree with classical scaling laws [6].

Similarly, hysteretic variation of small contact angles was observed in optical experiments where spreading on top of a commercial antireflection coating was investigated [7]. In this Letter we report a detailed investigation on this kind of contact lines and present results, both theoretical and experimental, which show that a high density of pinned superfluid vortices leads to apparent contact angles of a few degrees in the surface profile. In our experiments at 1 K, such contact angles were visible on top of evaporated SiO$_2$ layers but not on a smooth, bulk MgF$_2$ substrate. The difference follows from the larger amount of pinning sites for superfluid vortices on the evaporated films than on a polished surface. Our results suggest strongly that intrinsic disorder, i.e. pinned vortices cannot be neglected when considering the contact line dynamics of $^4\text{He}$-II, e.g. on evaporated Cs films.

Vortices are always present in thin $^4\text{He}$ superfluid films; even in bulk liquid it is difficult to reach a vortex-free state [8]. This is attributed to the fact that vortex core radius $a_0$ is about 1 Å [9] in $^4\text{He}$-II and, hence, pinning sites of atomic size $b$ can trap vortices strongly. Due to the atomic size, a large number of pinning sites can be found on the surface, easily up to densities on the order of $10^{16}$ m$^{-2}$.

Unpinning of vortices in a thickening film is caused by the interaction between neighboring vortices. A vortex will adjust itself to the flow field caused by an adjacent vortex line by bending [10]. Once its radius of curvature is smaller than the liquid layer thickness $h$, the vortex becomes unbound. Using a hemispherical pinning site of radius $b$, Schwarz calculated the unpinning velocity $v_0$ numerically [10]. His results can be summarized by

$$v_0 = \left(\kappa_4 / 4\pi h\right) \ln(b/a_0),$$

(1)

where $\kappa_4 = 2\pi h/m_4$. Since the pinning potential is deep, $\sim 100$ K for a typical atomic site of $b = 1$ nm, thermally activated unpinning at 1 K is effective only in the vicinity of $v_0$ [1] and the geometric law of Eq. (1) is a good approximation in our region of interest. If we assume that unpinning is caused by a single nearby vortex inducing a velocity $v = (\kappa_4/2\pi r)$, then we obtain $2h$ for the minimum intervortex distance within logarithmic accuracy. Hence, the maximum areal density $n_0$ of vortices in a spatially varying film can be estimated by the relation [12]

$$n_0(R) = \frac{1}{4h^2(R)},$$

(2)

where $R$ denotes the position in the plane of the substrate.

The free energy of a superfluid film with a vortex density can be written as

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\[ E_s = \int_V n_p U(\mathbf{r})dV + \int_S \sigma dS, \]

where \( n_p \) is the particle density and \( \sigma \) is the surface energy per unit area. The potential \( U(\mathbf{r}) \) denotes the energy per atom of mass \( m_4 \):

\[ U(\mathbf{r}) = m_4 g z - \frac{\gamma(z)}{\pi} + \frac{1}{4\pi n_p} \kappa^2 n_v(\bar{R}) \ln(l/a_0), \]

where \( \gamma(z) \) is a function governing the strength of the van der Waals interaction (vdW), which decreases towards higher \( z \) due to the retardation effects that are known to be important for distances larger than about 5 nm \[13\]. The last term denotes the kinetic energy due to vortices with superfluid density \( \rho_s \). The distance \( l \) is the upper cut-off for the vortex flow field that can also be expressed as \( \simeq 1/2\sqrt{n_v(\bar{R})} \). We set the logarithmic term equal to one in our calculation, which means that we underestimate the influence of vortices a bit. We also neglect the retardation effects. The vdW term in Eq. (3) is approximated by the interaction energy between two flat surfaces, \( A/12\pi h^2 \) per unit area, where \( A \) is the conventional Hamaker constant.

The minimization of Eq. (4) depends crucially on the behavior of vortex density with increasing film thickness. When \( n_v(\bar{R}) \) is below the critical unpinning limit given by Eq. (2), the kinetic energy of vortices \( E_v^{\text{vort}}(h) \propto h \). On the other hand, when vortices start to become unpinned and their density follows the maximum value of \( 1/4h^2 \), then \( E_v^{\text{vort}}(h) \propto 1/h \) and, in fact, the gradual elimination of vortices by unpinning favors thickening of the film. This behavior leads to two stable minima in \( E_s(h) \) as is illustrated in Fig. 1 without surface tension.

The lower local minimum at film thickness \( h_1 \) is given by the competition between vdW forces and the elastic tension of vortices, which leads to the relation

\[ h_1 = \left[ \frac{2A}{3\rho_s \kappa^2 \ln(l/a_0)n_v} \right]^{1/3}. \]

By setting \( n_v \) to its upper limit \( n_0 = 1/4h_1^2 \), Eq. (5) can be used to solve for the minimum thickness \( h_1 = h_i \) below which no vortex-thinned film can exist. When \( h < h_i \), the van der Waals force wins over the vortex tension caused by any vortex density below the limit of Eq. (5). In other words, the vdW attraction will always limit the vortex density below the value of \( n_0^{\text{crit}} = 1/4h_i^2 \). Using \( \ln(l/a_0) = 1 \), \( \rho_s = 140 \text{ kg/m}^3 \), and \( A = -5.9 \cdot 10^{-21}\text{ J} \) measured for \( \text{CaF}_2 \), we obtain \( h_i = 12 \text{ nm} \) and \( n_0^{\text{crit}} = 1.9 \cdot 10^{15} \text{ m}^{-2} \).

At a larger thickness, another minimum is obtained when the decrease of energy due to elimination of vortices is balanced by an increase in the gravitational energy, which yields the value

\[ h_2 = \left[ \frac{\kappa^2 \rho_s \ln(l/a_0)}{16\pi g \rho} \right]^{1/3}, \]

when \( n_0 > 3 \cdot 10^{10} \text{ m}^{-2} \). Here we assume that there is a fluid reservoir at the level of the substrate. Note that the above value is much larger than the thickness of a regular vdW film because the vortex energy dies away as \( 1/h \). A transition between thin (Eq. 5) and thick (Eq. 6) films leads to an abrupt kink in the slope, reminiscent of a contact angle in the surface profile. Since the substrate is completely wet, we call this edge a pseudo-contact angle in order to make a clear distinction with a true three phase contact line.

In our numerical calculations the one-dimensional surface profile \( h(x) \) was taken to be defined in \( N \) equidistant points \( x_1, ..., x_N \) along the substrate. Then the minimum of the discretized free energy \( E(h_1, ..., h_N) \), where \( h_i = h(x_i) \), was determined numerically with standard methods under the requirement that the total volume of the fluid remains constant. For the surface tension we used the zero-temperature value of \( \sigma = 375 \mu\text{J/m}^2 \). [14]

Fig. 2 illustrates the behavior of different energy terms when a cross-over from a thin to a thick film takes place. On the thin film side the vortex density is taken to be \( n_{v0} = 10^{13} \text{ m}^{-2} \), which corresponds to a unpinning thickness of 160 nm. For films thicker than that, \( n_v(\bar{R}) \) follows its maximum value \( n_0 \) given by Eq. (5). First, when the film thickness increases from 70 nm, the flow energy grows quickly \((\propto h)\), followed by a strong increase in the surface energy and by a rapid decrease in the vdW energy. The kinetic energy reaches its maximum at the thickness when vortices start to become unpinned. Above the unpinning threshold, the surface energy gradually relaxes to zero, while the vortex energy is reduced to a value balanced by the gravitational potential of the fluid. The inset displays the corresponding surface profile. An angle of 31 mrad is visible as the film breaks off from the substrate. For the pseudo-contact angle, we take the maximum slope of the surface with respect to the substrate.
The calculated pseudo-contact angle $\theta_p$ as a function of the vortex density $n_{v0}$ is displayed in Fig. 3. Results at small $n_{v0}$ calculated on a substrate inclined by 3.5 mrad from the horizon show that the pseudo-contact angle goes smoothly to the value of the substrate inclination, i.e., there is no observable contact angle at small vortex densities $n_{v0} \sim 10^{10}$ m$^{-2}$. The calculations on horizontal substrate, on the other hand, indicate a discontinuous vanishing of $\theta_p$ at $n_{v0} = 3 \cdot 10^{10}$ m$^{-2}$.

Our experiments were performed on a dilution refrigerator equipped with a two-beam interferometer; for details we refer to Ref. 14. The investigated substrates were inclined by $\sim 5$ mrad from the horizon. We made experiments on three different substrates: 1) Bulk MgF$_2$, 2) AR-coating of Hebbar-type, and 3) AR-coating of V-type. In our measurements at 1 K and below, bulk MgF$_2$ was always covered by a smooth $^4$He-II film whereas substrates 2 and 3 were not; we limit our observations to low temperatures because, in this range, the regulation of liquid level worked well and stable fluid fronts could be obtained.

Wetting behavior on top of the polished MgF$_2$ substrate is illustrated in the upper part of Fig. 4. It displays a smooth surface profile, deduced from the interferogram shown in the inset. The shape of the surface can be accounted for by the regular van der Waals film formula as can be seen from the fit to the data. This kind of a film is well in accordance with the measurements by Sabisky and Anderson using CaF$_2$ and SrF$_2$ substrates. The lower part of Fig. 4 illustrates the behavior of $^4$He-II on top of evaporated Hebbar-coating. A distinct pseudo-contact angle of 6 mrad is observed in the profile. Similar surface shapes were also seen on top of the V-coating.

Strong hysteresis between advancing and receding front was observed on the V-coating as well as on the Hebbar-coating. The contact angle was found to be zero for receding liquid whereas the advancing front displayed pseudo-contact angles in the range of 0 - 15 mrad. Moreover, when shaking the cryostat, the liquid left behind tracks which were preferred by the next advancing front. All these features are nicely explained by a variation in the density of trapped vorticity in thin superfluid films.

According to Fig. 3, the experimentally measured pseudo-contact angles of 1 - 15 mrad correspond to $n_{v0} = 10^{10} - 5 \cdot 10^{11}$ m$^{-2}$. These densities are clearly larger than the values measured by Ellis and Li who got values on the order of $10^9$ m$^{-2}$ in their third sound measurements. However, all our densities are much smaller than the physical maximum value $1.9 \cdot 10^{15}$ m$^{-2}$ limited by the vdW attraction (see Eq. 9).

It has been suggested by Williams and Wyatt that surface charge might play a role in helium spreading on top of an AR-coating. Because of the polarizability of helium atoms, the energy density in the areas exposed to an electric field $E_0$ decreases by $\Delta E_{\text{eq}} = \frac{1}{2} \chi \epsilon_0 E_0^2$ where $\chi$ is the dielectric susceptibility. If strong enough electric fields with sharp spatial gradients were formed, the surface profile could display distinct borders with pseudo-contact angles. However, the irregular behavior observed in our experiments is against the model of Williams and Wyatt: if frozen charge is important then a rather reproducible pattern should be seen when the liquid front is taken back and forth over the substrate.

Our substrates were checked for uniformity using an atomic force microscope (AFM). The roughness was found to be 0.4, 1.0, and 1.0 nm rms for samples 1 - 3, respectively. In addition, morphology of the roughness was found to be different: for sample 1, the roughness was mostly caused by long, continuous scratches, while samples 2 and 3 showed irregular, granular-like patterns. Hence uniform, “granular” roughness on mesoscopic scale appears to favor vortex pinning as expected. Moreover, we used the AFM to deposit surface charge and to follow directly its decay. We found that the lifetime of charge on our substrates was on the order of ten minutes, which was far too short to leave any appreciable amount of charge behind after the mounting and cool-down procedures lasting for several hours.

Recently, Herminghaus considered the effect of Bernoulli pressure on contact lines. His calculation basically applies to the spreading situation where vortex nucleation limits the superflow and thereby governs the spreading dynamics. He obtained contact angles on the order of 5 degrees. However, in order to get stable liquid fronts with a finite contact angle in this way, a continuous heat flux should be present in our experiments, which is not the case. Moreover, the pattern of the heat flux should be a rather complicated, time-dependent function of the position on the substrate.

On the basis of the present experiments and calculations, we believe that the elastic energy of pinned vortices influences spreading of helium on top Cs, causing extra hysteresis in the indigenous contact angle and pinning of the contact line. In the case of Cs, even an order of magnitude larger density of vortices is possible, since the evaporation of metal is done at low temperatures in order to avoid oxidation. Plenty of pinning sites were observed in recent flow experiments where solid air or solid hydrogen had been evaporated at low temperatures.

To conclude, quantized vortices play a role in the spreading of superfluid when there are plenty of pinning sites for vortices. The elastic tension of vortex lines leads to thin film sections that look like non-wetted regions even though they are covered by $^4$He-II. Our calculations on pseudo-contact lines at the borders of these thin film regions are in good agreement with experimental results obtained on evaporated antireflection coatings. Owing to unpinning of vortices in thick fluid layers, strong hysteresis with respect to advancing and receding liquid front is produced. This
finding corroborates with our results, as well as recent experiments on Cs films. Hence, the dynamics and pinning of a superfluid contact line can be strongly influenced by vortices on atomically rough substrates.

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FIG. 1. Energy per unit area vs. the thickness $h$ of the superfluid layer. Total energy neglecting surface tension is drawn by the solid line. The substrate level is taken as zero for the gravitational energy, the vdW energy is zero at $z = \infty$, and the vortex contribution is calculated for the density $n_{v0} = 10^{13}$ m$^{-2}$. For other parameter values, see text. The two minima $h_1$ and $h_2$ given by Eqs. 3 and 4, respectively, exist only when $3 \cdot 10^{10}$ m$^{-2} < n_{v0} < 1.9 \cdot 10^{15}$ m$^{-2}$.

FIG. 2. Energy densities and the surface profile (inset) calculated at $n_{v0} = 10^{13}$ m$^{-2}$ across the thin-to-thick film transition region. The solid curve is surface tension, dash-dotted is vortex energy and the dashed curve is the van der Waals interaction energy. The maximum slope yields the pseudo-contact angle $31$ mrad.

FIG. 3. Pseudo-contact angle $\theta_p$ vs. vortex density $n_{v0}$ calculated for substrate inclination of 0 (○) and 3.5 mrad (●).

FIG. 4. Interferograms and the corresponding surface profiles measured on bulk MgF2 substrate (upper frame) and on Hebbar-coating (lower frame); the dashed lines denote the substrates inclined from the horizon. The profiles have been calculated along the white lines marked in the interferograms. The surface on top of MgF2 fits the standard vdW film formula illustrated by the solid curve. On the Hebbar-coating a pseudo-contact angle $\theta_p = 6$ mrad is visible.
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