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Dimple-assisted dewetting in rotating superfluid films

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A superfluid wetting film on a solid substrate responds to rotation above a threshold velocity by formation of vortices which connect the free film surface with the substrate. The vortices cause localized deformations (''dimples'') at the film surface. It is proposed that surface dimples can support the heterogeneous nucleation of critical holes upon undercooling of the wetting film into a nonwet state, leading to a reduction of the lifetime of the metastable wetting layer. [S0163-1829(98)52622-7]

It was recently observed in experiment that ^{4}He undergoes first-order wetting and prewetting transitions on the weak binding substrates Cs and Rb.[1] An even richer wetting behavior is displayed by ^{3}He-^{4}He mixtures on Cs.[2–5] The hysteresis associated with the first-order wetting transitions was found to be unusually asymmetric: while an overheated thin film decays rapidly by nucleation of critical droplets, an undercooled thick film remains on the substrate in a long-lived metastable state.[6] This feature, which is also present in interfacial dewetting transitions in binary liquid mixtures,[7] was recently explained on the basis of the topology of the wetting phase diagram.[8] As indicated in Fig. 1 by a double-headed arrow, an overheating experiment leads away from the prewetting line $h_p(T)$ for $T>T_w$, while the path of undercooling runs parallel to the bulk coexistence line for $T<T_w$. In either direction the path crosses $h_p(T)$ so that, in general, the decay of the initial state will occur by homogeneous nucleation of critical nuclei, i.e., critical droplets on the nonwet wall or critical holes in the thick wetting layer. Both the size and the excess free energy E_c of the critical nuclei are infinite at the prewetting line $h_p(T)$, and at the bulk coexistence line $h \equiv \mu - \mu_c = 0$ for $T<T_w$.[8–10] The latter has been interpreted as a line of first-order surface transitions between a microscopic liquid layer on the wall for $h \to -0$, and an infinitely thick liquid layer on the wall for $h \to +0$, while at $h=0$ wet and nonwet regions can coexist at the surface.[8] The finite distance of the endpoint of the overheating path from the solid line in Fig. 1 leads to a finite value of E_c^{drop}, while E_c^{hole} is practically infinite for the endpoint of the undercooling path. Since the nucleation rate behaves as $I \sim \exp(-E_c/kT)$, thermal fluctuations are not sufficient in this situation to bring about the decay of the metastable thick film.

In order to facilitate hole formation, energy can be transferred to the system from some external source, e.g., by heating[4] or by laser irradiation.[12] The purpose of the present paper is to point out that when the helium film is *superfluid*, its *rotation* can be used to assist hole formation. As Feynman pointed out,[13] a vortex deforms the fluid-fluid interface locally into a *surface dimple*, i.e., a macroscopic depression of the interface in the vicinity of the vortex. The presence of the dimple affects the nucleation kinetics: the initial state from which a critical hole forms upon undercooling is now different from that of a flat film, since the interface has assumed an inhomogeneous profile of lower free energy. A change of the excess free energy of a critical hole, and hence of the lifetime of an undercooled wetting layer, can therefore be expected.

In order to determine the properties of the surface dimple and to compare them with those of critical holes, the idealized situation of a single, rotationally symmetric dimple will be discussed in the following. It is realized experimentally, e.g., when a stationary vortex exists at the center of a rotating cylindrical beaker. We let f be the local height of a superfluid wetting film covering a weak-binding alkali metal substrate, and introduce a reference frame with the zero level located at the equilibrium film thickness F. The deviation from the flat film surface is then given by $\zeta \equiv f - F$. The vortex velocity field is purely azimuthal, i.e., $v = v_\theta(r)$. The shape of the rotationally symmetric surface deformation $\zeta(r)$ of the free surface can be determined from the interface Hamiltonian[14]

$$\mathcal{H}[\zeta] = 2\pi \int_0^\infty dr\, r [(\gamma/2)(\nabla\zeta)^2 + \phi(\zeta) - \mathcal{R}(r)\zeta]. \quad (1)$$

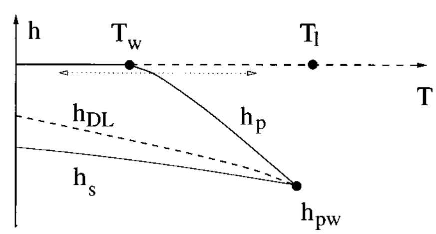

FIG. 1. Schematic phase diagram of a superfluid system with a wetting transition, shown in the parameters chemical potential deviation from bulk coexistence, $h \equiv \mu - \mu_c$, and temperature T. Indicated are the wetting transition point $h=0, T=T_w$, the prewetting critical point $h_{pw} = h(T_{pw})$, and the λ-transition point T_l at bulk coexistence. The prewetting line $h_p(T)$ is drawn solid, as well as its continuation for $T<T_w$ (see text). For $T(h_p)<T<T_l, h \leqslant 0$, a thick superfluid film can be stable on the wall [the region of surface superfluidity for $h<0$ is not shown, since its location depends on surface preparation (see Ref. 11)]. A typical path of overheating and undercooling across the prewetting line is indicated as a double-headed arrow. The thin solid line $h_s(T)$ is the lower spinodal curve. The meaning of the line $h_{DL}(T)$, intervening between $h_p(T)$ and $h_s(T)$, is discussed in the text.

The first contribution in Eq. (1) is the interfacial free energy of the fluid-fluid interface with surface tension γ, within a squared-gradient approximation to the surface.[14] The second term is the interface potential $\phi(\zeta)\equiv\phi(f)-\phi(F)$, with $\phi(f)=A/f^2-hf+V_{sr}(f)$. It contains a long-range van der Waals contribution whose strength is measured by the Hamaker constant A.[15] Further, $h\equiv\mu-\mu_c$ is the chemical potential deviation from coexistence, and finally $V_{sr}(f)$ is a short-range contribution, describing the properties of the thin film state. Since we are concerned here with the induction of a breakdown of the thick film, we do not pursue further the question as to what is the surface free energy of the thin film in the rotating system.

The last term in Eq. (1) is the kinetic surface free energy due to the vortex. Assuming a vortex core in solid-body rotation, one has $v_\theta\sim r$ for $r<\xi$ and $v_\theta\sim 1/r$ for $r>\xi$. Thus one finds

$$\mathcal{R}(r)=\begin{cases}-R_0/r^2, & r>\xi\\ -(R_0/\xi)^2[2-(r/\xi)^2], & r<\xi,\end{cases} \tag{2}$$

where $R_0=\varrho_s\kappa^2/8\pi^2$, with ϱ_s as the mass density of the superfluid and κ as the circulation quantum.[16]

The profile of the surface dimple follows from the variational equation $\delta\mathcal{H}[\zeta]/\delta\zeta(r)=0$,

$$\frac{d^2\zeta(r)}{dr^2}+\frac{1}{r}\frac{d\zeta}{dr}=\gamma^{-1}\left(\frac{\partial\phi(\zeta)}{\partial\zeta}-\mathcal{R}(r)\right), \tag{3}$$

together with the boundary conditions $\zeta'(0)=0$, $\zeta(\infty)=0$. The latter condition, for the sake of simplicity, neglects all sidewall effects of the experimental cell.[17]

For $T>T_w$, the thick film is thermodynamically stable, so that $\phi(\zeta)$ has a global minimum at $\zeta=0$. The interface potential can then be approximated by the parabolic potential $\phi(\zeta)=[\phi''(F)/2]\zeta^2$ with $\phi''(F)=6AF^{-4}$, so that Eq. (3) becomes linear in ζ. Outside the core Eq. (3) assumes a dimensionless form in the scaled variables $\tilde{\zeta}\equiv(\gamma/R_0)\zeta$ and $\tilde{r}\equiv r/a$ with the capillary length $a\equiv(\gamma/[\phi''(F)])^{1/2}$, i.e., the vertical scale of the dimple is determined by the ratio of kinetic and surface tension contributions, while the radial scale is controlled by the ratio of surface tension and interface potential. Due to its linearity, the dimple Eq. (3) can be solved in closed form by Green's-function techniques.[14] The depth of the dimple and its radius at half-depth behave according to

$$F_d\equiv|\zeta(0)|\approx\frac{R_0}{2\gamma}[\ln(2a/\xi)]^2, \tag{4}$$

$$R_d\equiv|r(\zeta=\zeta(0)/2)|\approx\xi\exp[(\gamma F_d/R_0)^{1/2}],$$

while for the dimple free energy one has from Eq. (1)

$$E_d\equiv-\mathcal{H}[\zeta]=(R_0^2/\gamma)I_0, \tag{5}$$

where I_0 is of the order $\mathcal{O}[\ln(a/\xi)]$ (including a constant contribution from the core). Note that $\mathcal{H}[\zeta]$ is *negative*, expressing the fact that the rotating thick film lowers its free energy by forming the dimple. Equation (4) shows that $R_d\gg F_d$, so that the shape of the dimple is qualitatively similar to that of a critical hole close to the prewetting line $h\leqslant h_p(T), T>T_w$ (called the "predewetting regime" in Ref. 18).

As Eqs. (4) and (5) show, F_d and E_d are increased by a decrease in the surface tension γ. This behavior becomes even more pronounced in the limit $\gamma\to 0$. If, in a crude approximation, one were to neglect the surface term completely, one obtains for the depth of the dimple and its radius

$$F_d\approx\frac{2R_0}{\gamma}\frac{a^2}{\xi^2}\sim F^4,\quad R_d\approx\xi. \tag{6}$$

This result is confirmed (up to a numerical factor) by the solution of Eq. (3), when the complete surface expression $[1+(\nabla\zeta)^2]^{1/2}$ is taken into account.[19] For $\gamma\to 0$, the dimple acquires a craterlike shape and comes to resemble qualitatively closer to a critical hole at $h\to -0, T<T_w$ (Ref. 8; the "partial dewetting" regime of Ref. 18). Its excess free-energy scales as $E_d\sim F^4$, which compares with the result $E_c^{hole}\sim F_c^2$ for critical holes in the nonrotating system, where F_c is the depth of the critical hole.[8,18] From these considerations we conclude that E_d is usually finite, but diverges (formally) in the limit $\gamma\to 0$.

For $T<T_w$, the thick film is metastable. Hence the global minimum of $\phi(\zeta)$ at $\zeta=0$ is turned into a local one and the parabolic approximation to the interface potential does not suffice anymore. Equation (3) then has *two* solutions which fulfill the conditions $\zeta'(0)=0$, $\zeta(\infty)=0$. They differ, however, in their initial conditions and in their free energies: the dimple solution remains as a minimum of $\mathcal{H}$, while the critical hole is a saddle point of $\mathcal{H}$ with a depth $F_c>F_d$. These two physically different solutions can only exist as long as the thick film minimum of ϕ is sufficiently pronounced. At the spinodal line h_s (see Fig. 1) the minimum and maximum of ϕ degenerate,[20] where the maximum of ϕ characterizes the free-energy barrier. The free energies of the dimple and of the critical hole approach each other for $h\to h_s$. When $E_d=E_c^{hole}$, both dimple and hole cease to exist, and the thick film state has to decay. This happens *before* $\phi(\zeta)$ has lost its extrema. Technical details of this mechanism will be presented elsewhere.[21]

The condition $E_d(h,T)=E_c^{hole}(h,T)$ defines a *dimple line* $h_{DL}(T)$ in the lower nucleation region, indicated schematically as a dashed line in Fig. 1. For $h>h_{DL}(T)$, the nucleation barrier is reduced so that thermal nucleation is facilitated by the presence of the dimple, while for $h_{sp}<h<h_{DL}(T)$ a nucleation barrier for the decay of the thick film is already surmounted due to the presence of the dimple.

In order to illustrate the relevance of these findings for the experiment, we now apply the above results to the helium-alkali systems. Only the limiting case $T=0$ is treated here. This amounts to neglect the temperature dependence of the system parameters, as well as additional finite temperature mechanisms briefly mentioned in the conclusions. Table I contains the system parameters for liquid ^{4}He and a phase-separated ^{3}He-^{4}He bulk mixture. Table II lists the results that follow from an application of the formulas of the previous paragraphs. Note that for the helium systems it is customary to write the Hamaker constant $A=\varrho_0\Delta C_3/2$, where ΔC_3 is the excess of the van der Waals coefficient of the

TABLE I. System parameters.

	γ (K Å^{-2})	ϱ_0 (Å^{-3})	R_0/γ (Å)
free ^{4}He-surface	0.27	0.022	0.49
^{3}He-^{4}He interface with ^{4}He-vortex	0.02	0.010	6.80

TABLE II. Numerical estimates of F_d and R_d.

	$\varrho_0 \Delta C_3(K)$	F (Å)	a (Å)	F_d (Å)	R_d (Å)
^{4}He-Cs	13.86	100	805	13	187
^{4}He-Rb	10.34	100	932	14	206
^{3}He-^{4}He-Cs	6.3	100	1.19×10^6	$\approx 10^{12}$	≈ 1

substrate interactions over that in the fluid, and ϱ_0 is the number density of the wetting liquid.[1]

a. ^4He-Cs/^4He-Rb. As shown in Table II, the magnitude of F_d for pure ^{4}He is fairly small for both Rb and Cs, while the radius of the dimple is already considerable: $R_d \approx 2F$. This illustrates its similarity to a critical hole near the prewetting line. The depth F_d changes by a factor of 3 in going from film thicknesses of about 100 Å to 800 Å. Of the two substrates Rb is preferable to Cs to test dimple-assisted dewetting in experiment, especially if it is correct that ^{4}He wets Rb down to $T=0$ at coexistence, i.e., when the prewetting line is detached from the bulk coexistence line.[22,23] The prewetting phenomena of ^{4}He on Rb occur at very low temperatures so that the thick film state is superfluid. Also, a metastable superfluid film has probably been observed in experiment.[23]

b. ^3He-^4He-Cs. As shown in Table I, the ^{3}He-^{4}He interface has a lower surface tension than the ^{4}He-vapor interface. Assuming that in the phase-separated mixture a vortex is present only in ^{4}He, the calculated depth of the dimple at the ^{3}He-^{4}He interface is enormous, since it exceeds the film thickness by several orders of magnitude. This indicates that the undercooled system in the presence of a dimple would be unstable.

In conclusion, it has been proposed that the vortex dimple in a rotating superfluid film can be used as a tool in a dewetting experiment to facilitate the nucleation of critical holes. In general, the dimple leads to a reduction of the free-energy barrier for nucleation, whereby the magnitude of the effect strongly depends on the surface tension of the film. Since a reduction in surface tension changes the dimple shape from a rather flat, wide dimple with resemblance to a critical hole near $h_p(T)$ to a craterlike dimple similar to a critical hole at $h=-0$, $T<T_w$, dimple-assisted dewetting could possibly be useful in studies of the lifetime of undercooled wetting films and for tests of the scaling behavior of critical holes.[18] Undercooling of a rotating film can also serve as an indirect means to study dimples, which have proved difficult to observe by optical techniques alone.[14,17] This applies especially to the region close to the dimple line h_{DL} in Fig. 1, where both the dimple and the critical hole cease to exist.

The present work relies on a number of approximations which affect the proposed scenario in both quantitative and qualitative aspects. E.g., for $T>0$ normal liquid is present, changing the thermodynamic state of the wetting layer. Several additional mechanisms have been ignored, e.g., thermal vortex nucleation processes[16] as well as substrate effects, which exert pinning forces on the vortex. Effects of substrate disorder are known to be relevant for the helium-alkali system.[24,25] Further, a realistic discussion of the properties of dimples in He-mixtures would require a detailed study of the phase diagrams of ^{3}He-^{4}He films on alkali substrates, as recently calculated by Pettersen and Saam.[26] The reduction of the surface tension leads to reentrant wetting.[2] Also, the possibility of ^{3}He bound states at the Cs-He interface arises.[27,5] In reentrant wetting, the topology of the phase diagram in Fig. 1 changes, whereby the nonwet region below the prewetting line separates into a nonwet region at intermediate temperatures, and a newly appearing wet region at lower temperatures. For the parameters of Table I, γ is so low that the ^{4}He film always wets the substrate at $T=0$, and there is no metastable film. Evidently, the values of Table II represent extremes, as is already clear from the (unphysical) result for the dimple depth.

Finally, dimple-assisted dewetting is enhanced by several mechanisms which increase the dimple size (and hence its free energy), as the presence of normal liquid,[19] or gravity.[14] Another interesting possibility for a direct modification of the size of the dimples is by placing charges at the free surface.[28,29]

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