Effect of Substrate Roughness on Wetting and Absorption

In a recent Letter, Wyatt and Klier (WK) [1] claim that surface roughness provides an explanation for (i) the extreme metastability of wetting films, and (ii) the "memory" the Cs substrates have after having been in contact with liquid He. We show here that their arguments are partly erroneous and that other explanations are more plausible.

For (i) it has been shown theoretically and experimentally that homogeneous thick films, undercooled from above to below the prewetting line have a diverging lifetime near bulk coexistence. This is a generic feature of first-order wetting transitions unrelated to any disorder in the system [2,3]. This point is stressed by the experimental observation of long-lived metastable thick films for wetting on liquid "substrates" for which disorder is absent [3]. At bulk coexistence and below the wetting temperature, a macroscopic wetting layer can coexist with nonwet surface regions; consequently, a temperature change will not limit the lifetime of a thick film. When (as in some but not all of the He/Cs experiments) part of the substrate is not covered by a thick film, the thermal nucleation barrier is less relevant; hysteresis then likely involves a pinning of the contact line.

The memory effect, (ii), is explained in [1] by the formation of "micropuddles" of liquid He in small defects of the Cs substrate, excluding capillary condensation. However, this is in conflict with their use of the Laplace pressure $p - p_0 = 2\sigma/R$ below Eq. (1). For capillary condensation, in thermodynamic equilibrium equilibration can take place through the vapor [4] and no memory effect should be expected. Because of their semicircular shape the micropuddles will not fill continuously, while, e.g., for square cavities there is no energy barrier for capillary condensation and hence no hysteresis [5]. This shows that the scenario is sensitively dependent on details of the surface topography. We believe it is more reasonable to assume the surface as a spongelike porous medium made of connected channels (a microscopic version of the disordered substrates of [6]). In a porous medium, hysteretic capillary condensation can be observed even in a complete wetting situation [5,7]. Our hypothesis is strengthened by the observation that a receding meniscus leaves a connected superfluid film [8].

WK also argue that their model explains an "extremely" asymmetric pinning of the contact line (advancing is easy, and receding is difficult). Experimental evidence for this is lacking, since the true equilibrium contact angle θ_{eq} cannot be measured on rough substrates. The relevant physical parameter is the force per unit length F acting on the triple line, $F = \sigma_{LV}(\cos\theta_{eq} - \cos\theta)$. The experimental data on contact angle hysteresis are indeed compatible with a symmetric pinning. At low temperature, the advancing angle is about 25° [9]. In some cases, a nonzero receding angle [9] has been observed. One can then assume that the contact line is close to receding when $\theta \sim 0$. Then, the pinning is symmetric if $\theta_{eq} = 18°$ which might well be the case.

WK determine the pinning energy E^* for a receding line from the energy difference ΔE between a state where a contact line covers the defect and a state where the receding line has left a puddle in the defect, which leads to $\Delta E \approx a_p \sigma_{LV}$. A proper estimate of ΔE should take into account all surfaces in the system, leading to $\Delta E \approx a_p S$, with S the spreading coefficient. ΔE is not *a priori* related to the pinning energy E^*. Following Joanny and de Gennes [10], for strong defects one has $E^* \sim a_p(\sigma_{LV} + \sigma_{SL} - \sigma_{SV}) = a_p \sigma_{LV}(1 - \cos\theta_{eq})$. With $\theta_{eq} = 18°$ and $a_p = 125$ nm^2 one obtains $E^* \sim 150$ K, roughly the value given in [11] for the pinning of an advancing line. Hence there is no reason to believe that the wetting behavior is necessarily strongly asymmetric; the behavior can simply look asymmetric because the contact angle is always small ($1 - \cos\theta < 0.1$) so that the maximum pulling force is always small compared to σ_{LV}.

This work was supported by the EC (FMRX-CT98-0171) and the DFG (SPP 1052, Grant No. BL356).

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Received 16 November 2000; revised manuscript received 4 September 2001; published 11 December 2001
DOI: 10.1103/PhysRevLett.87.279601
PACS numbers: 67.70.+n, 68.03.Cd, 68.08.Bc

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