Wetting of Solid Surfaces by a Structured Simple Liquid: Effect of Fluctuations

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A smecticlike structure of a simple liquid adjacent to a solid surface gives rise to an attenuating oscillating potential in which the free surface of the film fluctuates. These capillary fluctuations lead to critical wetting phenomena of an earlier unknown origin. The corresponding wetting, layering, and surface melting criteria are obtained by the renormalization-group technique.

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If vapor pressure p increases close to the saturation value $p_0(T)$, a liquid film appearing on a solid surface grows in thickness either continuously, or through first-order layering transitions (LT), $h \rightarrow h+d_0$, where h and d_0 are the film and monolayer thicknesses, respectively. As $p \rightarrow p_0$, the film thickness may either unlimitedly increase ($h \rightarrow \infty$) or remain finite. The former behavior means complete wetting (the wetting angle $\theta=0$), while in the latter case the wetting is incomplete and the film may coexist with macroscopic droplets. The incomplete wetting is transformed into a complete one at a wetting transition (WT) point[1]: $T=T_w$, $p=p_0(T_w)$. At the triple point, T_t, a surface of a solid may be completely wetted by its melt; in this case surface melting (SM) occurs.[2-4]

To describe the wetting by a dense liquid (i.e., the melt) full account of its pronounced layerwise short-range order must be taken. This short-range order provides partial molecular ordering of the liquid at a solid surface. The order of the first layer is induced by the wall, the reduced order of the second layer is induced by the first one, and so on. Thus the solid wall generates in the adjacent liquid a smectic density wave: $\Delta n(z) \propto \cos(k_1 z)\exp(-z/\xi_b)$. Here z is the coordinate normal to the wall, and k_1 and ξ_b are the abscissa and inverse half-width of the main peak of the bulk liquid structure factor, respectively. No monotonic density wave is excited in a dense liquid, since $k=0$ corresponds to the *minimum* of its structure factor, i.e., to the maximum of energy.[5]

Substituting $\Delta n(z)$ into the free-energy density functional of the film having thickness h, one obtains the potential of interaction between the film-vapor and film-solid interfaces[5]:

$$V(h) = -a\cos(k_1 h)e^{-h/\xi_b} + b e^{-2h/\xi_b}. \qquad (1)$$

This is essentially an expansion of the interface potential V with respect to the density-wave amplitude $\Delta n(h)$. The first term in Eq. (1), V_1, linear in $\Delta n(h)$, arises from the density-wave cut at the interface. Its minima give preference to an integer number of smectic layers composing the film. The second term is

$$V_2(h) \propto \Delta n(h)^2 \propto \exp(-2h/\xi_b);$$

the higher harmonic $\propto \cos(2k_1 h)$ is irrelevant in the renormalization-group (RG) sense. The ordering increases the free energy of the liquid-vapor interface (free surface energies of crystals are greater than those of the corresponding melts); thus $b>0$. Since the only energy scale of the density functional is T, one has $a,b=O(T)$; T is expressed in energy units.

The smectic structure of liquid films manifests itself in oscillations of disjoining pressure (CCl_4/SiO_2),[6] in the tangential mobility of electrons suspended upon the ^{4}He film surface,[7] and in layering (ethylene/graphite).[8] It should be stressed that only near the liquid-gas critical point the main peak of the structure factor moves to $k_1=0$ (Ref. 5) and Eq. (1) transforms into the conventional nonoscillating form.[9]

Qualitatively the wetting phenomena governed by the potential (1) may be presented as follows. The equilibrium film thickness is determined by the minimum of the sum $V(h)+hn_0\Delta\mu$, where $\Delta\mu$ is the difference in bulk chemical potentials and n_0 is the liquid density. The function $V(h)$ is represented by curve 1 in Fig. 1. This form of the potential provides two main consequences: (i) The free-energy barriers separating the subsequent

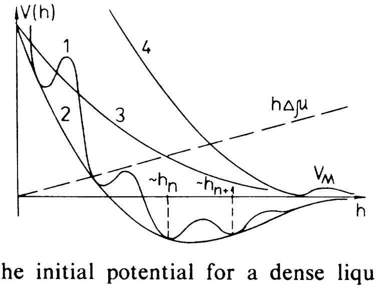

FIG. 1. The initial potential for a dense liquid film on a solid substrate (curve 1), envelope of its minima (curve 2), renormalized envelope (curve 3), and the renormalized envelope at the first-order wetting transition provided by the van der Waals forces (curve 4).

local minima $h_n = 2\pi n/k_1 = nd_0$ give rise to the LT's accompanying variation of $\Delta\mu$; (ii) for sufficiently thick films $\exp(-h/\xi_b) \gg \exp(-2h/\xi_b)$, so that the oscillating part, V_1, dominates, providing negative minima to the resulting potential (Fig. 1): $V(h_n) < 0 = V(\infty)$. Thus the wetting is incomplete.

However, at $T > 0$ the capillary fluctuations smooth the oscillations of the potential which results in a diminishing of the effective decay length of the oscillations: $\xi_b \rightarrow \xi_R < \xi_b$ in V_1 with the V_2 term being unaltered. The subscript R denotes the renormalized quantities. Above a certain temperature T_w the amplitude of V_{1R} decreases with h faster than V_{2R} since $\xi_R < \xi_b/2$. Consequently the envelope curve 2 in Fig. 1 loses its minimum and transforms into monotonic curve 3, i.e., incomplete wetting is changed to the complete type. Thus we predict that a special critical WT is provided by capillary waves propagating on the free surface of a partially ordered film. Further heating suppresses the oscillations of V_R and thus excludes LT's. Since the amplitude of the potential relief decreases with h, the critical layering temperatures are expected to decrease for larger h, i.e., for $\Delta\mu \rightarrow 0$. This behavior differs from that of solid films.[10] In the latter case, long-range order exists (i.e., $\xi_b = \infty$), so that the amplitude of $V(h)$ oscillations is constant and the layering critical temperatures increase as $\Delta\mu \rightarrow 0$.

Below we give the linear RG theory of the structure-induced wetting governed by the Hamiltonian

$$\mathcal{H} = \int d^2x \{\sigma(\nabla z)^2/2 + V(h)\}. \tag{2}$$

Here $\mathbf{x}$ is the 2D vector in the substrate plane; σ is the free surface energy of the bulk liquid. The conventional RG rescaling of the short-range cutoff, Λ, provides averaging of the potential over the capillary wavelengths between Λ^{-1} and $\Lambda^{-1}e^l$ resulting in[9]

$$V_l(h) = \int V(h)\exp[2l - (h-h')^2/2\delta^2(l)]dh'/(2\pi)^{1/2}\delta(l). \tag{3}$$

Here $\delta^2(l) = l\delta_0^2 = lT/2\pi\sigma$ is the squared displacement averaged over the interval $(\Lambda^{-1}, \Lambda^{-1}e^l)$. If $V(h) = \epsilon\exp(-\lambda h)$, Eq. (3) gives

$$V_l = \epsilon\exp[l(2+\omega) - \lambda h], \tag{4}$$

where $\omega = (\lambda\delta_0)^2/2 = T\lambda^2/4\pi\sigma$. For V_1 [Eq. (1)], $\lambda = \pm ik_1 + \xi_b^{-1}$, and for a dense liquid we have[5] $k_1\xi_b \geq 10$. Thus Eq. (4) results in

$$\mathrm{Re}\,\omega = -Tk_1^2/4\pi\sigma \equiv -\tilde{\omega}. \tag{5}$$

The longitudinal correlation length $\xi_\parallel = \Lambda^{-1}e^{l'}$, above which the capillary waves are suppressed by the field $V(h)$, may be estimated from the equation $\Lambda^{-2}\partial^2 V_{l'}/\partial^2 h^2 \equiv \Lambda^{-2}V''_{l'}(h) \approx \sigma$. If $\tilde{\omega}$ is not too close to 2, so that the linear RG theory is sufficient, the latter equation together with Eqs. (4) and (5) yields

$$(2-\tilde{\omega})l' = h/\xi_b + \ln(\sigma\Lambda^2/ak_1^2), \tag{6}$$

$$V_{1R}(h) = -a_R\exp[-h/(1-\tilde{\omega}/2)\xi_b], \tag{7}$$

where $a_R = a\exp[-\ln(\sigma/a)\tilde{\omega}/(2-\tilde{\omega})]$. For $\lambda = 2/\xi_b$, Eq. (4) yields $\omega = T/4\pi\sigma(\xi_b/2)^2 \ll 1$, and thus the renormalization does not affect V_2. In derivation of (5) and (6), we took into account that for h minimizing $V_R(h)$ we have $|V''_{2l'}/V''_{1l'}| \approx (2/k_1\xi_b)^2 \ll 1$ and l' in Eq. (6) is determined by V''_{1l} only. Evaluation of h proves that $h > \delta_0^2 l'|\lambda|$, so that the steric interface-substrate interaction may be neglected.[9]

Equation (7) means that the renormalized attenuation depth is $\xi_R = (1-\omega/2)\xi_b$. Thus, if $a_R = a^2/\sigma < b$, the absolute minimum of the curve V_R disappears at $\xi_R = \xi_b/2$, or $\tilde{\omega} = 1$, and a critical WT occurs at

$$T_w^0 = 4\pi\sigma/k_1^2 = \sigma d_0^2/\pi. \tag{8}$$

The important difference of this universal expression from the well-known one for the roughening-transition temperature is (besides the factor of 2) that in the present case the surface tension is not renormalized in the limit $T \rightarrow T_w^0$: σ in Eq. (8) is just the tension of the bulk liquid. Hence $T > T_w^0$ can serve as a useful wetting criterion.

This critical WT is a limit of an infinite sequence of LT's: $h_n \rightarrow h_{n+1} \rightarrow \ldots$. On average the film thickness and the correlation length diverge at the WT as $[t \equiv (T_w^0 - T)/T_w^0]$

$$h \propto t^{-1}; \quad \xi_\parallel \propto \exp(\mathrm{const} \times t^{-1}). \tag{9}$$

These laws coincide (up to logarithmic factors) with the ones characterizing the critical WT provided by steric repulsion in the case of nonoscillating potential[9] ($\omega = T/4\pi\sigma\xi_b^2 > 2$, regime III of Ref. 9). However, in the latter case the renormalized potential differs drastically from ours and no universal expression for the wetting temperature has been found.

Minimizing $V_R(h) + hn_0\Delta\mu$ with respect to h and using Eqs. (7), (5), and (8), one obtains the LT lines in the form $\Delta\mu_n \propto \exp[-h_n/(1-T/2T_w^0)]$ represented as $L_1, L_2, \ldots$ in Fig. 2. At the high-temperature side, each LT line ends in a critical point. In the close vicinity of this point the linear RG procedure cannot be applied. Nevertheless, the critical temperature T_{Lcn} for the $h_n \rightarrow h_{n+1}$ LT may be estimated (cf. Ref. 10) by finding the crossover of the two RG solutions: The one is valid for $T < T_{Lcn}$, where the oscillating potential dominates, and the other is valid for $T > T_{Lcn}$, where $|V''_{2R}| \gg |V''_{1R}|$, $V_{2R} \approx V_2$. The crossing occurs for such an l' that $|V''_{1l'}| \approx V''_{2l'}$ with $h \approx (h_n + h_{n+1})/2$. Making use of Eqs. (4) and (6), one gets for large h $T_{Lcn} = T_w^0(1+\text{const}\times\xi_b/h_n)$. Since for $T > T_{Lcn}$ the film thickness is determined by V_2', i.e., $h = -(\xi_b/2)\ln(\Delta\mu)$, the layering critical points form the curve $\Delta\mu \propto \exp[-\text{const}/(T-T_w)]$. For $n > 1$–2, the right-hand side of Eq. (6) is positive, and hence the LT lines end before $\tilde{\omega} = 2$. Thus the LT's occur only if

$$T < 2T_w^0 = 8\pi k_1^{-2}\sigma = 2\sigma d_0^2/\pi. \tag{10}$$

In real fluid systems the potential $V(h)$ contains a long-range part $V_{LR} = A/h^2$, provided by the van der Waals (electrodynamic)[6,7] and hydrodynamic[11] forces. The complete wetting can take place only if $A > 0$, which is usually the case for the van der Waals forces. The constant $A \leq 50$ K,[6,7] and hence, for temperatures $T \gg 50$ K, V_{LR} may be treated as a perturbation over $V_1 + V_2 = O(T)$. The long-range repulsion favors the thick film and forms a free-energy barrier V_M for wetting at low $\Delta\mu$ (curve 4, Fig. 1). Thus the critical WT is precursed by the first-order WT at T_w slightly below T_w^0. For very thick films, the second derivative V_{LR}'' dominates over the oscillations of V_1; hence the number of LT lines is finite. The resulting phase diagram is sketched in Fig. 2. Weak long-range forces disturb a small vicinity of the WT point. As $\Delta\mu$ increases, the free-energy barrier V_M moves towards the smaller h and decreases. Thus the prewetting line T_wM (Fig. 2) starts from the WT point; enters the region of LT's, thus becoming a strong LT: $h_n \rightarrow h_{n+k}$, $k > 1$; and finally merges with one of the LT lines.

Thus the range of validity of the above theory is determined by $T \gg 50$ K together with Eq. (10). For many metals $T_t/T_w^0 \leq 1$, while $T_t \sim 10^3$ and our theory is strictly applicable, at least near the triple point (see below the description of SM on lead crystals). On the other hand for noble gases one has $3T_w^0 \leq T_t \leq 100$ K and no layering effects should be expected. The critical WT of the type described above can be observed (i) in a two-component system, if the *line* of WT crosses the line $V_{LR} = 0$, where the hydrodynamic effects compensate the van der Waals ones[11]; (ii) in Monte Carlo simulations on *antiferromagnetic* lattice-spin models (cf. Tarasona and Vicente[12]).

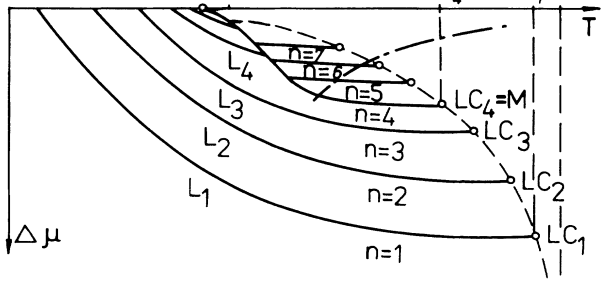

FIG. 2. Phase diagram of a fluid-solid system: L_j are the layering lines and LC_j are their critical points; T_w is the first-order wetting transition point; T_wM is the prewetting line. The dash-dotted line presents a decrease of ^{4}He vapor pressure in a closed vessel (Ref. 7) caused by temperature decrease.

For helium the ratio T/T_w^0 is not bounded from below by the triple point and the layering is observed,[7] though $V_{LR} \gg V_2$, providing complete wetting below T_w^0. As above, T_{Lcn} may be found by our taking $V_{LR,R}'' \approx V_{1R}''$, or $l_1' = l_{LR}' = \frac{1}{2}\ln(\sigma\Lambda^2 h^4/3A)$, while l_1' is determined by (6). Thus, for $h/\xi_b \gg 1$, $4\ln(n) \gg 1$, one gets

$$T_{Lcn} = (8\pi\sigma/k_1^2)\{1 - h_n/4\xi_b\ln(n)\}. \tag{11}$$

Substituting $\sigma = 0.35$ erg/cm^2, $k_1 = 2.15$ Å^{-1},[13] $\xi_b/d_0 = 1.6$–2.1 (Ref. 7) into (11), we obtain that about 20–30 LT's may exist at $T=0$ and $T_{Lc9} = 0.5$–0.7 K, $T_{Lc5} = 0.7$–0.9 K. These estimates may be compared with the ninth peak of electron mobility observed at $T = 0.6$ K [a chamber filled with gaseous ^{4}He was cooled and the ^{4}He film grew upon H_2 (Ref. 7); the phase path of the system is shown in Fig. 2 by a dash-dotted line]. The fifth peak disappears at $T = 1$ K. When $T > T_{Lcn}$ the second derivative of

$$V_{1R} = V_1\exp(-2l_{LR}') \propto h^{-2\tilde{\omega}}\exp(-h/\xi_b)\cos(k_1 h)$$

still oscillates, providing oscillations of electron-ripplon scattering amplitude. Thus as the T_{Lc} line (dashed line in Fig. 2) is crossed the oscillations of mobility are expected to change their form from singular cusps to smooth oscillations (cf. Ref. 7) rather than to disappear at once. For ^{3}He the surface tension is $\sigma = 0.15$ erg/cm^2; hence $T/T_w^0 \geq 3$ at $T = 1$ K and the layering effects are suppressed.[7]

In the SM of metals V_{LR} is extremely weak because of the small crystal-melt density difference: The law $h \propto \ln\Delta\mu$ is not changed by $h \propto \Delta\mu^{-1/3}$ up to T_t.[2] Now the crystal-melt film interface $z_1(\mathbf{x})$ fluctuates together with the free surface of the film, $z_0(\mathbf{x})$, $h = z_1 - z_0$. The potential V_1 depends not only on h, but on the interface position relative to the crystal lattice also:

$$V_1 = \sum_j a_j e^{-h/\xi_b}\cos(k_1 h - 2\pi j z_1/d), \tag{12}$$

where d is the lattice spacing normal to the interface ($d \not\equiv d_0$). Renormalizing (2), with V_1 taken from (12), by the procedure of Eqs. (3)–(7), one gets

$$\tilde{\omega} = \pi T d_0^{-2}[\sigma^{-1}d_0^{-2} + \sigma_1^{-1}(1/d_0 - j/d)^2],$$

where σ_1 is the surface tension of the *rough* (see below) macroscopic crystal-melt interface. The complete wetting occurs if, as above, the $V_{2R}(h)$ potential becomes substantial for thicknesses larger than those for V_{1R}, i.e., if $\tilde{\omega}_j > 1$ for all j values. Thus

$$T_w = \begin{cases} \pi^{-1}\sigma_1 d_0^2/(1+\sigma_1/\sigma), & \text{if } 2d < d_0, \\ \pi^{-1}\sigma_1 d_0^2/[\sigma_1/\sigma + (1-d_0/d)^2], & \\ & \text{if } d_0 < 2d < 3d_0. \end{cases}$$

$T_t < T_w$ is the criterion for SM. Usually $\sigma_l/\sigma \lesssim 0.1$. Therefore for close-packed faces, with $d \approx d_0$, T_w is substantially higher. For Pb (fcc) we have $\sigma_l = 33$,[2] $\sigma = 440$ erg/cm^2, $d_0 = d_{(111)} = 2.9$ Å, $T_t = 600$ K. Thus $T_{w(111)} \approx 1.4 T_t$, $T_{w(100)} \approx 1.1 T_t$, and no SM should be expected on these faces in accordance with recent observations.[2] A vicinal face close to (111),(100) does not melt also if the width of a terrace on such a face exceeds $\xi_\parallel(T_t)$. For the (110) face $T_w \approx 0.2 T_t$ and SM is observed.[2]

Note that T_w is always larger than $2\sigma_l d^2/\pi$, the roughening temperature of the crystal-bulk melt interface, which was used above. On the other hand, the long-wave fluctuations of thickness are suppressed by $V(h)$ for any finite h. Thus the complex crystal-melt-vapor interface exhibits a roughening transition below T_t if and only if

$$T_t > T_{Rf} = 2(\sigma + \sigma_l) d^2/\pi,$$

since in the limit $T \rightarrow T_t$, $h \rightarrow \infty$, and the renormalization of σ, σ_l due to $V(h)$ is negligible. For example, $T_{Rf} < T_t$ for the Pb(311) and higher-indexed faces. In contrast, SM occurs on the (110) face though it remains smooth up to T_t.

In summary, the dense liquid film on a solid surface has a smecticlike structure that gives rise to an attenuating periodic potential in which the free surface of the film fluctuates. At low temperatures this potential is responsible for layering transitions and incomplete wetting. As the temperature rises, capillary waves renormalize the attenuation length of the oscillating potential which results in a critical wetting transition and layering critical points. The wetting transition provides a new example of strong fluctuational critical behavior. In real systems with long-range interactions, prewetting phenomena may be observed. The theory estimates layering critical temperatures for ^{4}He/H$_2$. An extension of the analysis to a crystal surface covered with its own melt provides the SM criteria in good agreement with recent observations. An exact criterion for roughening of a melted surface is obtained also.

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