Effect of boundary ordering and long-wave fluctuations on wettability and surface melting

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A theory of the wetting of a solid substrate by a dense liquid is derived by an approach incorporating the layered short-range order and capillary fluctuations at the boundary of the wetting film. At temperatures low in comparison with the capillary energy, a quasismectic ordering of the liquid in the film causes incomplete wetting. As the temperature rises, capillary fluctuations destroy the order in the film, causing a phase transition to a state of complete wetting. This phase transition is characterized by a large-fluctuation critical behavior. A universal expression for the transition temperature provides a simple criterion for complete wetting. A description is found for the stratified growth of liquid films. This description is used to analyze data on the adsorption of helium on hydrogen. Surface melting is analyzed as a complete wetting of the surface of a crystal by the native melt. A condition for surface melting is derived. The anisotropy of the effect is studied. The relationship between surface melting and the roughening transition is analyzed.

1. INTRODUCTION

In the limit in which the pressure p of a vapor in contact with a substrate approaches the saturation point p_0, the thickness h of a liquid film adsorbed on the substrate may either remain finite or grow without bound. These two possibilities correspond to states of incomplete and complete wetting of the given substrate by the liquid. The transition between these two states–the wetting transition–has recently attracted much interest.[1,2]

In the case of complete wetting the first-order vapor-liquid transition occurs continuously (in a system with a substrate) and is accompanied by anomalies in surface properties. Correspondingly, the complete wetting of some face of a crystal by the native melt leads to barrier-free melting of the crystal from that face through the formation and unbounded thickening of the molten film on this face, when the temperature T approaches the triple-point temperature T_t. This surface-melting phenomenon has also attracted much interest.[3-6]

As the equilibrium line is approached, a wetting film can thicken either continuously or through first-order layering transitions $h_j = jd_0 \rightarrow h_{j+1} = (j+1)d_0$, where d_0 is the thickness of a monolayer. Layered growth is characteristic of crystalline films (Frank-Van der Merwe epitaxy[6]), but it has recently been observed during the adsorption of liquid films of ethylene on graphite,[7] of helium on hydrogen,[8,9] and of ethane of graphite.[10]

All of these effects can be characterized conveniently[2] by introducing a dimensional correction $V(h)$ to the free surface energy of the wetting film: $V(h) \rightarrow 0$ as $h \rightarrow \infty$. This correction serves as the potential of the interaction between the boundaries of the film. It is easy to see that incomplete wetting is equivalent to the existence of negative minima of $V(h)$ (corresponding to a bound state of the boundaries). A wetting transition occurs when such minima disappear. The increase in the thickness of the film toward the equilibrium line ($\Delta\mu \rightarrow 0$) is determined by a minimization of $V(h) + \Delta\mu n_0 h$, where n_0 is the density of the homogeneous liquid, and $\Delta\mu$ is the difference between the chemical potentials of the liquid and of the coexisting phase [$\Delta\mu = T\ln(p_0/p)$ in the case of wetting from vapor and $\Delta\mu \sim T_t - T$ in the case of surface melting, where T is in energy units]. Layering transitions occur if the thicknesses $h_j = jd_0$ correspond to minima of $V(h)$ which are separated by potential barriers.

Of particular interest in wetting phenomena are effects of fluctuations of the film boundaries,[11-15] which are described in the case of a solid substrate by the capillary Hamiltonian

$$H=\int d^2x[{}^1/_2\sigma(\nabla h)^2+V(h)], \tag{1}$$

where σ is the stiffness of the fluctuating boundary, x is the radius vector in the plane of the substrate, and the seed potential $V(h)$ is calculated for a uniform film (cf. Refs. 1, 11, 16, and 17). Fluctuations give rise to some extremely unusual properties of the wetting transition[12-14] in the Morse potential

$$V(h)=-a\exp(-h/\xi_b)+b\exp(-2h/\xi_b), \tag{2}$$

(ξ_b is the correlation length of the bulk system), which arises when the liquid-vapor system is described by a Landau functional.[11,2] Fluctuations also lead to a termination of the lines of layering transitions at critical points ($T_{Lcj}, \Delta\mu_j$) of the Ising type.[15]

In the modern theory of wetting[2] it is usually assumed that the potential (2) and the contribution of long-range van der Waals forces

$$V_{VW}(h)=A/2h^2 \tag{3}$$

exhaust the qualitative features of simple systems. It was recently shown that two qualitatively new types of potentials $V(h)$ exist in film of simple liquids: a long-range attraction of a boundary to a substrate due to hydrodynamic correlations[16] and an oscillating potential which arises in dense liquids by virtue of a well-developed stratified short-range order.[17] These correlation interactions can cause qualitative changes in the wetting picture near both the critical point and the triple point. In particular, in a situation with a hydrodynamic attraction the wetting is always incomplete in a sufficiently small neighborhood of the bulk critical point T_c (Ref. 18).

In the present paper[1)] we examine the effects of smectic short-range order of a dense liquid and of capillary fluctuations in wetting. In particular, we show that the interplay of capillary fluctuations and an oscillating potential gives rise to a new example of a large-fluctuation wetting transition. We derive simple criteria for complete wetting and for surface melting for substances with strong binding. We describe some possible layering effects during the adsorption of a liquid.

2. GENERAL FORM OF THE SURFACE POTENTIAL

It is shown in Ref. 17 that the Landau model directly describes a liquid only in the critical region, where the correlations are manifested in the existence of large-scale regions of rarefaction and compression ("bubbles" and"drops" with blurred boundaries). A description of the inhomogeneities by means of a term of the type $K(\nabla n)^2$ in the free energy density, where $n(\mathbf{r})$ is the local number density of particles, is justified when the main peak in the linear susceptibility (the structure factor) $G(k)$ of the bulk liquid occurs at a wave vector $k = 0$. In a dense liquid, the abscissa of the main peak is $k_1 \neq 0$; this situation corresponds to a stratified short-range order [and to a gradient term of the type $K|(d/dz - ik_1)n|^2$; see the Appendix]. On a plane surface this order is manifested in the circumstance that the liquid becomes ordered in the form of quasismectic layers of thickness $d_0 = 2\pi/k_1 \sim d$. A film with a thickness corresponding to a half-integer number of layers is unfavorable from the energy standpoint, while a film consisting of a whole number of layers has a specific free energy lower than that of a semi-infinite liquid. The free energy of a thin film thus oscillates around its bulk value with a period d_0, decaying over the bulk correlation length ξ_b, which is equal to the reciprocal of the half-width of the main peak in the susceptibility[17]:

$$V_1(h) = -a\cos(k_1 h)\exp(-h/\xi_b). \tag{4}$$

This component of the free energy is manifested directly in pressure oscillations in films of organic liquids between solid surfaces.[20] In the Appendix we point out a derivation, different from that of Ref. 15, of the expression for the correlation part of the potential $V(h)$. That derivation also yields a monotonic component of $V(h)$, which arises in second order in $\exp(-h/\xi_b)$ (there is a more rigorous discussion in Ref. 21):

$$V_2(h) = b\exp(-2h/\xi_b), \quad b>0. \tag{5}$$

Qualitatively, V_2 is the benefit $(b>0)$ in terms of the free energy of a smectic density wave which is excited by the substrate in the liquid. This quantity stems from suppression of the correlation near the boundary with the gas. Using $G(k_1) \approx 3$ and $\xi_b \approx 1.8d$ (Ref. 17), taking the value of the smectic order parameter at the interface with the substrate to be $\eta_{s0} \sim 1$, and using $\eta_0 \sim d^{-3}$, we find the natural estimate $b \sim Td^{-2}$ from (A4). In other words, we find a value which is on the order of the thermal energy per atomic site at the surface. On the other hand, the amplitude of V_1 in (4) and (A4) satisfies $a \sim \eta_{i0} b \sim \eta_{i0} T/d^2$, where η_{i0} is the smectic order parameter at the boundary with the gas, which is determined over length scales $\sim \xi_b$ (i.e., to the point at which long-wavelength capillary waves come into play; such waves delocalize the boundary and cause η_i to vanish[17]). It is reasonable to assume $\eta_{i0} < \eta_{s0}$ since the boundary with gas is more "porous" than a solid wall at all scales. We thus conclude $a < b$.

Far from the critical point, the constant A in (3) depends only weakly on the temperature and is less than 50 K in magnitude.[9,20] Also taking into account the mutual cancellation of the van der Waals and hydrodynamic contributions, to first order we can ignore the long-range effect in the description of strong-coupling materials, for which we have $T_t \gg 50$ K [for example, with $A = 50$ K, $T_t = 600$ K, $b = T_t d_0^{-2}$, and $\xi_b = 2d_0$ we have a derivative $V_2'(h) > V_{VW}'(h)$ for $h \lesssim 10d_0$].

The potential

$$V(h) = V_1(h) + V_2(h)$$

is shown schematically by curve 1 in Fig. 1. At a vapor pressure below the saturation level, we need to add a term $\Delta\mu n_0 h$ to $V(h)$ (the dashed line in Fig. 1). In the absence of fluctuations, the liquid vapor interface localizes at minima of $V_1(h)$ which correspond to the adsorption of an integral number of monolayers: $h_j = jd_0$. As $\Delta\mu \to 0$, the film grows by means of a first-order layering transition, but only to a finite limit h_m. To determine h_m within $\pm d_0/2$, we can replace V_1 by the envelope of its minima:

$$\tilde{V}_1 = -a\exp(-h/\xi_b), \quad a>0$$

(curve 2 in Fig. 1). Hence

$$h_m \approx \xi_b \ln(2b/a) \approx \xi_b \ln(\eta_{s0}/\eta_{i0}).$$

Formally, $\tilde{V} = \tilde{V}_1 + V_2$ is equivalent to the potential (2) with a positive definite coefficient a. Since the attraction $\tilde{V}_1$ is of longer range than the repulsion V_2 (by virtue of the inequality $\xi_b > \xi_b/2$), the wetting is incomplete. Physically, long capillary waves are suppressed at low temperatures by the potential V_1, and the film thickness grows only to the point at which the amplitude of the density wave at the gas boundary becomes comparable to η_{i0}, i.e., comparable to the value of the intrinsic order of this boundary at small scale.

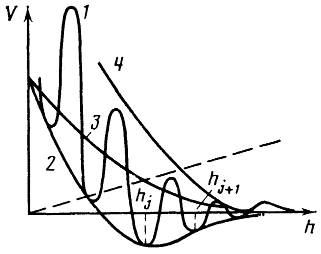

FIG. 1. Potential of the correlation interaction for (1) a film of a dense liquid on a solid substrate, (2) the envelope of its minima before renormalization, (3) the same, after renormalization, at temperatures above the wetting point and in the presence of a long-range repulsion (curve 4). The dashed line shows $\Delta\mu n_0 h$.

3. WETTING TRANSITION

As the temperature rises, the fluctuations of the boundary grow and wash out the oscillations in potential V_1. As the film becomes thicker, the confining potential weakens, so the fluctuations and this washing out become more pronounced. The fluctuations thus lead to a decrease in the decay length of V_1 through the renormalization $a \to a_R \leqslant a$, $\xi_b \to \xi_R < \xi_b$, which we will discuss below:

$$\tilde{V}_R(h) = -a_R \exp(-h/\xi_R) + b \exp(-2h/\xi_b). \tag{6}$$

A continuous wetting transition occurs (under the condition $a_R < b$) when the decay lengths of potentials V_1 and V_2 become comparable: $\xi_R = \xi_b/2$ (curve 3 in Fig. 1). Consequently, and in contrast with the wetting transition which was studied in Refs. 12 and 13 (which is caused by a decrease in the amplitude of the attractive component of the potential V), this transition involves a renormalization of the characteristic range of this component.

Let us examine the fluctuations by the standard renormalization-group procedure for two-dimensional systems[13]: With a change $\Lambda \to \exp(-l)$ in the scale $\Lambda \lesssim d^{-1}$ of the short-wave cutoff of the configuration integral, the potential is averaged over Gaussian fluctuations of the boundary:

$$V_l(h) = \int_{-\infty}^{\infty} \frac{V(h+h_1)}{[2\pi\delta^2(l)]^{1/2}} \exp\left[2l - \frac{h_1^2}{2\delta^2(l)}\right] dh_1, \tag{7}$$

where the mean square fluctuation of the boundary at wavelengths from Λ^{-1} to $\Lambda^{-1}e^l$ is $\delta^2(l) = l\delta_0^2 = lT/2\pi\sigma$. The fluctuations remain Gaussian over scales $\Lambda^{-1}\exp(l) \ll \xi_\parallel$, where the correlation length of the capillary fluctuations, $\xi_\parallel = \Lambda^{-1}\exp(l^*)$, is determined in a self-consistent way from the equation $\Lambda^2 \approx V''_{l^*}(h_m)/\sigma$. Here h_m is the minimum of V_{l^*}. The corresponding binding energy is $V_R(h_m) = V_{l^*}(h_m)\exp(-2l^*)$.

Substituting an exponential potential of the general form $V(h) = v_0\exp(-\beta h)$ into (7), we find[13]

$$V_l(h) = v_0 \exp[(2+\omega)l - \beta h], \tag{8}$$

where

$$\omega = (\beta\delta_0)^2/2 = T\beta^2/4\pi\sigma. \tag{9}$$

For V_1, the parameter β in (8) is equal to $\xi_b^{-1} \pm ik_1$. Near the triple point[17] we have $k_1\xi_b \gtrsim 10 \gg 1$, and thus

$$\operatorname{Re}\omega = T(\xi_b^{-2} - k_1^2)/4\pi\sigma \approx -\tilde{\omega}, \quad \tilde{\omega} = Tk_1^2/4\pi\sigma.$$

As we will see in the discussion below, the phenomena in which we are interested occur in the interval $1 \lesssim \tilde{\omega} < 2$. For the potential V_2 we have the parameter value $\beta = 2/\xi_b$ and $\omega = T/\pi\sigma\xi_b^2 \ll 1$. Consequently, the renormalization of V_2 is trivial: $V_{2R} \approx V_2$. The cutoff of the potentials at $h < 0$, like the interaction with the substrate, is inconsequential[13] under the condition $h_m > \delta_0^2 l^* |\beta|$. A direct substitution easily shows that this condition always holds in the discussion below. Under this condition, the power-law potentials are renormalized trivially: $V \propto h^{-2}$ (Ref. 13).

The equilibrium thickness h_m is close to a minimum of the envelope, $V'_2(h_m) \approx \tilde{V}'_{1R}(h_m)$, so the curvature of the monotonic part of potential $V''_2(h_m) \approx 2\tilde{V}''_{1R}(h_m)$ is smaller by a factor $(k_1\xi_b)^2 \sim 100$ than the curvature of the bottom of the well of the oscillatory part. Consequently, h_m is always close to one of the $h_j \approx jd_0$ (layering transitions disappear at temperatures above T_w which is the wetting point), and V_2 can be ignored in determining the correlation length: $V''_{l^*}(h_m) \approx V''_{1l^*}(h_m) \approx \sigma\Lambda^2$. For values of $\tilde{\omega}$ which are not very close to two, we can thus write

$$l^* = l_1^* \approx [h/\xi_b + \ln(\sigma\Lambda^2/k_1^2 a)]/(2-\tilde{\omega}), \tag{10}$$

$$V_{1R}(h_m) \approx -a\,(a/\sigma)^{\tilde{\omega}/(2-\tilde{\omega})} \exp[-2h/(2-\tilde{\omega})\xi_b], \tag{11}$$

i.e.,

$$\xi_R = (1 - \tilde{\omega}/2)\xi_b. \tag{12}$$

At sufficiently small values of a, the renormalized amplitude is $a_R \approx a^2/\sigma < b$, and the continuous wetting transition occurs at the point

$$T_w = 4\pi\sigma k_1^{-2} = \sigma d_0^2/\pi. \tag{13}$$

We wish to stress that, in contrast with the corresponding expression for the roughening temperature,[22] the quantity σ in (13) is not renormalized in the limit $T \to T_w$ and must be set equal to the surface tension of the macroscopic melt. This wetting transition is a limiting point of the infinite sequence of layering transitions $h_j \to h_{j+1}$. On the average, the thickness increases in accordance with

$$h \approx t^{-1}\xi_b \ln(b/a_R)/2 \propto t^{-1}, \tag{14}$$

and the correlation length is described by

$$\xi_\parallel \propto \exp[\ln(b/a_R)/2t] = \exp[\text{const}\cdot t^{-1}], \tag{15}$$

where $t \equiv (T_w - T)/T_w$. We actually have $h = h_j$ in the temperature interval in which (14) yields $|h - h_j| < d_0/2$. On layering-transition lines we have $\xi_\parallel = \infty$. In finite systems with defects, the layering transitions are smeared, and singularities may be observed in physical quantities (cf. Ref. 9 and Sec. 6 below). Near a transition the binding energy of state j is

$$V(h_j) \approx -bt\exp[-2h(t)/\xi_b] \propto t\xi_\parallel^{-2},$$

and the contact angle satisfies $\theta \propto t^{1/2}\xi_\parallel^{-1}$. The height of the barrier for the jth layering transition,

$$2b\exp[-2h(t)/\xi_b] \propto \xi_\parallel^{-2},$$

does not have a factor of t in front of the exponential function.

Within logarithmic corrections, expressions (14) and (15) are the same as those in the strong-fluctuation regime ($\omega > 2$) of a wetting transition for nonoscillating potential (2) (Refs. 12 and 13). On the other hand, the qualitative difference between the renormalized potentials in this study and in Refs. 12 and 13, combined with the existence of a universal expression for the temperature of this transition, (13), allows us to speak in terms of a new type of continuous wetting transition.

4. CRITICAL POINTS OF LAYERING TRANSITIONS

Lines of layering transitions in the T, $\Delta\mu$ plane can be found crudely from the condition

$$\Delta\mu n_0 = V_2'(h_{Lj}) + \tilde{V}_{1R}'(h_{ij}), \quad h_{Lj} \approx (j + 1/2)d_0.$$

We have

$$\Delta\mu_j^0-\Delta\mu_j(T)\propto\exp[-2T_wh_{Lj}/(2T_w-T)\xi_b], \qquad (16)$$

where $\Delta\mu_j^0\propto\exp(-2h_{Lj}/\xi_b)$.

For $T>T_w$, the potential V_2 is of longer range than the renormalized potential V_1, by virtue of the relation $\xi_R<\xi_b/2$. At sufficiently large values of h, the positive curvature $V_2''>0$ is thus dominant, and there are no free-energy barriers between h_j and h_{j+1} (Fig. 2). In this region we have

$$l^*=l_2^*\approx{}^1/_2\ln[\sigma\Lambda^2/V_2''(h)]\approx h/\xi_b+{}^1/_2\ln(\sigma\Lambda^2\xi_b^2/4b). \qquad (17)$$

Near the critical point for the layering transition (T_{Lcj}, $\Delta\mu_{Lcj}$), we cannot use the linear approximation (7), but this point is itself determined by the crossing of lines (10) and (17): $l_1^*(h_{Lj})=l_2^*(h_{Lj})$ (it is in this sense that the calculations of Ref. 15 for a crystalline film are valid). For large values of j we find $T_{Lcj}=T_w(1+\text{const}\cdot\xi_b/h_j)$. Since at $T\gtrsim T_{Lcj}$ the curvature satisfies $|V_2''|\gg|V_{1R}''|$, we have a slope $|V_2'|\gg|V_{1R}'|$, and the film thickness is determined by minimizing $V_2+\Delta\mu n_0h$:

$$h\approx{}^1/_2\xi_b\ln(T/\Delta\mu). \qquad (18)$$

The critical points thus lie on the curve

$$\Delta\mu\propto\exp[-\text{const}\cdot(T-T_w)^{-1}]. \qquad (19)$$

On the other hand, the condition for the applicability of the linear renormalization group is that l_1^* in (10) be positive. Throughout the range of applicability of our analysis, the layering-transition lines terminate at $\tilde{\omega}<2$ [the value $\tilde{\omega}=2$ corresponds to a transition to a rough state of the boundary, which fluctuates in the weak uniform potential $\propto\cos(k_1h)$; Ref. 22]. The inequality

$$T<8\pi\sigma k_1^{-2}=2\sigma d_0^2/\pi \qquad (20)$$

is therefore a qualitative condition for the observability of layering transitions.

5. LONG-RANGE EFFECTS

At sufficiently large thicknesses, the long-range repulsion V_{VW} dominates the structural contribution V_1+V_2, so we have $V>0$ and $V''>0$. In this case, (1) a barrier for wetting transitions arises (curve 4 in Fig. 1), so in the presence of a long-range effect a first-order wetting transition always occurs below the temperature T_w given by (13) (cf. Ref. 2); (2) only a finite number of layering transitions occur at any temperature. The shift of the wetting-transition temperature, $T_w\to T_w(1-t_w)$, can be estimated by equating the binding energy to the van der Waals energy:

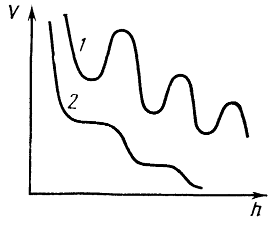

FIG. 2. The potential (1) below and (2) above the line of critical points of layering transitions.

$$bt_w\xi_{\|}^{-2}(t_w)\approx A/2h^2,$$

Hence

$$t_w\propto[\ln(T/A)+\ln\ln(T/A)+\ldots]^{-1}$$

[we have made use of condition (15) and the relations $a\sim b\sim Td^{-2}$]. The first-order wetting point transition gives us the origin of the line of first-order transitions from a thin film to a thick film at nonzero $\Delta\mu$: prewetting transitions.[2] At small values of $\Delta\mu$, the equilibrium of a thick film is determined exclusively by van der Waals forces, so its thickness $h=(A/\Delta\mu)^{-1/3}$ is large. Correspondingly, we have an energy $\sim\Delta\mu^{2/3}$, and the prewetting transition line touches the T axis: $t-t_w\propto\Delta\mu^{2/3}$. With increasing $\Delta\mu$, a thick film goes into a region in which the layering transition occurs [the ratio V_{1R}''/V_{VW}'', which determines the existence of the layering transition, contains the factor $(k_1h)^2$, which is large in comparison with the ratio $\tilde{V}_{1R}'/V_{VW}'$, which determines the prewetting effect], and the prewetting transition becomes a layering transition $h_j\to h_{j+k}$ with $k>1$. With a further increase in the temperature, k decreases, and for $t\sim[\ln(T/A)+3\ln\ln(T/A)]^{-1}$ the prewetting transition merges with one of the layering-transition lines ($k=1$).

The results of this and the preceding sections of the paper are summarized in Fig. 3. Turning on the long-range effect alters the topology of the phase diagram in Fig. 3. This perturbation may be thought of as a cut along the line of prewetting transition T_wM, followed by a counterclockwise rotation of the right edge around the point T_w. The unperturbed wetting point along with a small neighborhood of this point which contains an infinite number of layering transitions is invisible. At $T\gg A$, however, the points T_w and M are close to the unperturbed T_w ($\tilde{\omega}=1$), and the perturbation affects only a small region of the diagram.

6. LAYERING EFFECTS ON HELIUM FILMS

As we have already mentioned, the large factor $(k_1h)^2$ in the ratio V_{1R}''/V_{VW}'' makes the region in which layering effects are observed quite wide, actually not limted to high temperatures. The mobility of a classical two-dimensional electron gas above the surface of a film of superfluid ^{4}He on a hydrogen substrate undergoes oscillations as the film thickness increases, with a period $\sim d$ (Refs. 8 and 9) at $T\lesssim1$ K. With increasing temperature, these oscillations are smoothed over, and their number decreases. To describe the effect we note that V_2 is inconsequential in this temperature range (according to the data of Ref. 9, $A\approx20\text{ K}\gg T$). Equat-

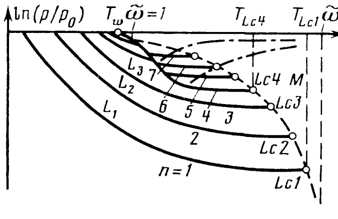

FIG. 3. Phase diagram of the adsorption of a dense liquid from a gas onto a solid substrate. L_j—Lines of layering transitions; L_{cj}—their critical points; T_w—point of wetting transition; T_wM—line of prewetting transition.

ing l_1^* from (10) to $l_{VW}^* = \ln(\sigma\Lambda^2 h^4/3A)/2$ for values of j such that h_j/ξ_b, $4\ln j \gg 1$, we find

$$T_{Lcj} = (8\pi\sigma k_1^{-2})(1 - h_j/4\xi_b \ln j). \tag{21}$$

Substituting in $\sigma = 0.35$ erg/cm^2 (Ref. 23), $k_1 \approx 2.15$ Å^{-1} (Ref. 24), and $\xi_b/d_0 = 1.6$–2.1 (Ref. 9), we find 20–30 layering transitions at $T = 0$ K, $T_{Lc9} \approx 0.5$–0.7 K, and $T_{Lc5} \approx 0.7$–0.9 K. These estimates can be compared with the observation of the maximum—ninth—oscillation in the mobility at $T \approx 0.6$ K (Ref. 9; in the experiments of Ref. 9, the film was grown by cooling a chamber initially filled with gaseous ^{4}He; the paths of the system in the T, $\Delta\mu$ plane corresponding to various amounts of the substance in the chamber are shown by the dot-dashed lines in Fig. 3). The fifth oscillation disappears at $T \approx 1$ K [since the first two layers are apparently crystalline, expression (21) holds only qualitatively at $j = 5$].

For $T > T_{Lcj}$, the parameter $l^* = l_{VW}^*$ is finite, and the second derivative of

$$V_{1R} = \exp(-l^*\tilde{\omega}) V_1 \sim h^{-2\tilde{\omega}} \exp(-h/\xi_b) \cos(k_1 h)$$

continues to oscillate. Since the square of the frequency of a capillary wave (ripplon) contains a term $\propto V''$, we would expect that electron-ripplon scattering would lead to smooth oscillations in the mobility even above T_{Lc}. Below T_{Lc}, the ripplons are unstable on a layering-transition line, and the mobility has a singularity (cf. the curves in Ref. 9). For ^{3}He the surface energy is $\sigma \approx 0.15$ erg/cm^2 (Ref. 25), so we have $\tilde{\omega} \gtrsim 3$ at $T = 1$ K, and layering effects are suppressed.[9] We wish to stress that quantum effects are unimportant for the long-wavelength ($\xi_\parallel \Lambda \gg 1$) phenomena which we are discussing here.[22]

7. SURFACE MELTING

In the case of the surface melting of a crystal of a dense substance, the van der Waals potential has an additional small factor $\sim \Delta\varepsilon \sim \Delta n \lesssim 10^{-1}$, where $\Delta\varepsilon$ and Δn are the differences between the dielectric constants and densities of the crystal and the melt. To analyze surface melting we need to incorporate fluctuations in both z_0, the position of the melt-gas interface (with a surface tension σ_0), and z_1, the atomically rough (more on this below) crystal-melt interface, with a stiffness σ_1.

Since the interplanar distance in the crystal along the normal to the surface, d_c, is generally[17] not equal to the period of the density oscillations in the melt, d_0, the phase of the layered-ordering wave excited in the melt at the interface with the crystal depends on the position of this interface with respect to the crystal lattice (Fig. 4). Therefore, the oscillatory component of the potential is no longer a function of $h = z_1 - z_0$ alone (the crystal occupies the region $z > 0$). A general expression for this component follows from symmetry considerations:

$$V_1 = -\sum_{n=-\infty}^{\infty} a_n \exp\left(-\frac{h}{\xi_b}\right) \cos\left\{2\pi\left[\frac{z_1 - z_0}{d_0} - \frac{jz_1}{d_c}\right]\right\}, \tag{22}$$

where the amplitude a_n does not exceed a or b from (4), as is easily verified in the very simple model of continuous match-

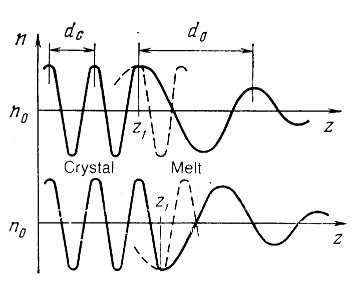

FIG. 4. Profile of the density at a crystal-melt interface for various positions of the boundary, z_1, with respect to the crystal.

ing, at the point $z = z_1$, of the density waves in the crystal $[\propto \cos(2\pi z/d_c)]$ and in the melt $[\propto \cos(2\pi z/d_0)\exp(-z/\xi_b)]$. Over length scales from Λ^{-1} to $\xi_\parallel$, the boundaries fluctuate in a manner independent of each other. Accordingly, each of the terms in (22) is transformed in accordance with (8), where we have $-l\omega \approx l\tilde{\omega}_n$, and this quantity is equal to the mean square fluctuation of the argument of the cosine determined at these scales:

$$\tilde{\omega}_n = \pi T[1/(\sigma_0 d_0)^2 + (n/d_c - 1/d_0)^2/\sigma_1]. \tag{23}$$

In ignoring V_{VW} for the complete wetting of a given face of the crystal by the melt, we must require that the potential V_2 be of longer range than V_{1R}, i.e., that the relation $\tilde{\omega}_n > 1$ hold for all n. We thus write

$$T_w = \sigma_1 d_0^2/[\sigma_1/\sigma_0 + (1 - d_0/d_c)^2]\pi, \quad d_0/2 < d_c < 3d_0/2, \tag{24}$$

$$T_w = \sigma_1 d_0^2/[\sigma_1/\sigma_0 + 1]\pi, \quad d_c < d_0/2, \tag{25}$$

and $T_t > T_w$ is the condition for surface melting. We would usually have $\sigma_1/\sigma_0 \lesssim 10^{-1}$. In crystals of simple substances, on the other hand, we would have a maximum value $d_c \approx d_0$ (Ref. 17). Consequently, T_w is much higher on close-packed faces (d_c is approximately equal to d_0) than on other faces. For example, for an fcc lead crystal we have $\sigma_0 \approx 440$ erg/cm^2 (Ref. 23), $\sigma_1 \approx 33$ erg/cm^2 (Ref. 6), $d_0 \approx d_{(111)} \approx 2.9$ Å, and $T_t \approx 600$ K. The relative positions of $T_w(d_c)$ and T_t are shown in Fig. 5. For the (111) face we have $T_w \approx 1.4T_t$, while for the (100) face we have $T_w \gtrsim 1.1T_t$, and surface melting should not occur. On the (110) face we have $T_w \approx 0.2T_t$, so surface melting does occur on

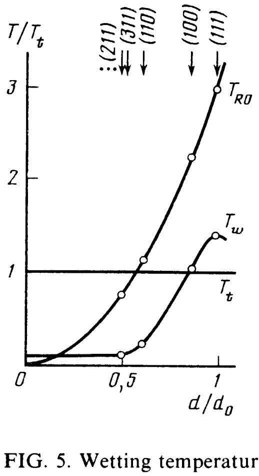

FIG. 5. Wetting temperatures for the wetting of various faces of a lead crystal by its own melt with respect to the triple point ($T_t \approx 600.5$ K). The temperatures T_{R0} from (26) are also shown.

this and on less closely packed faces.

Faces which make a small angle θ with the singular orientation warrant a special analysis. Such (vicinal) faces consist of region of singular orientation of large width $l = d_c/\theta (d_c$ characterizes a singular face), separated by monatomic steps.[6] If the singular face does not undergo surface melting, it will be characterized at $\Delta\mu = 0$ ($T = T_t$) by a finite correlation length $\xi_{\parallel}$. If $\xi_{\parallel} \ll l$, the statistical properties of the vicinal face are determined over scales shorter than those at which its nonuniformity is manifested. Consequently, surface melting does not occur in the angular internal $\Delta\theta \approx d_c/\xi_{\parallel}$ around the singular direction. As $T \to T_w$, we have $\xi_{\parallel} \to \infty$ and $\Delta\theta \to 0$.

These predictions of the theory agree with the observation of surface melting on a (110) face[3] and on less closely packed faces. They also agree with the absence of surface melting on the (111) and (100) faces and in a certain interval of orientations around these faces.[26] At $T \gg T_w$, the potential V_2 is unimportant, and the film thickness (if h is not too large) diverges logarithmically [see (18)] in accordance with Refs. 3 and 26. In this limit our model is equivalent to the model of a disorder induced by the surface.[27]

8. TRANSITION OF A MELTED FACE TO A ROUGH STATE

The temperature T_w is always higher than $2\sigma_1 d_c^2/\pi$ which is the temperature of the transition to a rough state of an isolated crystal-melt boundary.[22] We have in fact made use of this relation. When surface melting occurs, and if the temperature is sufficiently close to T_t, the surface of the crystal is replaced by two weakly coupled interfaces, the crystal-melt and melt-vapor interfaces, each of which is separately rough. Nevertheless, for any temperature $T < T_t$ there exists a finite $\xi_{\parallel}$: the correlation length of fluctuations in the film thickness. Over scales larger than $\xi_{\parallel}$ the film fluctuates as a single boundary with a tension $\sigma \approx \sigma_0 + \sigma_1$. The criterion for a transition of a macroscopic face of a crystal to a rough state below T_t is thus the inequality

$$T_t > T_{R0} = 2(\sigma_0 + \sigma_1) d_c^2/\pi. \qquad (26)$$

This condition holds for lead faces with $d \ll d_{(311)}$ (Fig. 5). On the (110) face, on the other, the transition to a rough state merges with the triple point.

9. CONCLUSION

We have thus shown that incorporating the actual correlations in a liquid which are not present in the Landau model leads to a qualitative change in the picture of wetting in the region of high densities (in particular, near the triple point). Capillary fluctuations of the boundary between the wetting film and the gas are exceedingly important here.

The quasismectic short-range order in a dense liquid gives rise to order in an adsorbed film in the form of layers parallel to the surface. Consequently, even if the liquid is strongly attracted to the substrate, the interaction V_1 of the film-gas interface with the smectic-order wave makes a wetting film of finite thickness preferred from the energy standpoint: The wetting is incomplete. In this case the smectic-order parameter η falls off monotonically toward the interface with the gas, to a value on the order of η_{i0} (curve 1 in Fig. 6). In this case, however, capillary fluctuations of the film-gas interface are suppressed. Accordingly, if the temperature T is high in comparison with the characteristic energy σd_0^2, an unbounded thickening of the film will be preferred (the smectic structure will melt in the central part of the film; see curve 2 in Fig. 6). This unbounded thickening will result in free fluctuations of the interface; i.e., in this case the wetting is complete.

The two regimes described here are separated by a second-order wetting transition, studied here for the first time, with strong divergences (14) and (15). This transition occurs at the temperature T_w given by the universal relation (13). Unfortunately, this wetting transition is like the second-order wetting transition which has been discussed previously in the Morse potential,[12] (2) (in real systems with a long-range effect, in which a first-order wetting transition occurs at $T < T_w$) in that it can occur only at an isolated point on the phase diagram of the two-component system, at which the low-range component of the potential vanishes (as a result of, for example, a cancellation of the van der Waals and hydrodynamic interactions). This second-order wetting transition can be studied, however, by the Monte Carlo method on a lattice model[28] with an antiferromagnetic interaction of the type discussed in Ref. 29.

For substances with strong binding ($T_t \gg 50$ K), the influence of the long-range effect on the qualitative characteristics of the adsorption is limted to a small neighborhood of the wetting point (Fig. 3). Accordingly, the adsorption of liquids with a triple-point temperature which satisfies condition (20) is described by the phase diagram in Fig. 3 in the region of high densities. Estimating d_0 in terms of the atomic radii, we find that for inert gases we have

$$\tilde{\omega}_t \equiv \pi T_t/\sigma(T_t) d_0^2 \approx 3$$

and layering effects are unobservable (in agreement with the data of Ref. 30). In metals, on the other hand, we have $\tilde{\omega}_t \lesssim 1$: In particular, in such low-melting metals as mercury and gallium we have $\tilde{\omega}_t \lesssim 0.3$–$0.4$, and in alkali metals we have $\tilde{\omega}_t \approx 0.9$. Melts of silicon and germanium have $\tilde{\omega}_t \approx 1.7$–$1.8$ i.e., values close to the upper limit on the observability of layering adsorption. Consequently, the theory derived above may be thought of as a general description of the wetting of solid surfaces by molten metels.[2)]

We wish to stress that the electron component of the surface potential can play a substantial role in the adsorption of metals.[31] Note also that the condition $T > T_w$ with T_w given by (13) is a necessary but generally not sufficient condition for complete wetting, since the free energy of a monolayer, for example, can be substantially lower than that which would follow from asymptotic expression (4) (cf. Ref. 32).

Nevertheless, the date available on the surface melting of lead agree with our estimates. Note that it has now become

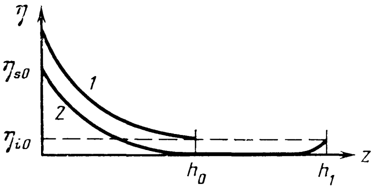

FIG. 6. Profile of the layering-order parameter in a wetting film. 1—$T < T_w$; 2—$T > T_w$,; $h_0 \sim \xi_b \ln(\eta_{s0}/\eta_{i0})$, $h_1 \gg h_0$.

possible to determine the mean square fluctuation of the surface of a crystal, $\langle z_0^2 \rangle$, by x-ray structural methods.[33] Such studies might make it possible to determine the role played by layering effects during surface melting and the interrelationship between surface melting and surface roughness. Actually, the capabilities of the theory derived here are broader than we stipulated above (as was demonstrated in the example of the analysis of the adsorption of helium). The diagram in Fig. 3 is qualitatively similar to date on the adsorption of ethylene on graphite,[7] although in the latter case ($\tilde{\omega}_t \gtrsim 3$) the layering effects during the adsorption of the melt are limited to a small neighborhood of the triple point, where two-dimensional melting effects are important. Most typically, a generalization of the analysis to molecular liquids will require incorporating electrical and liquid-crystal effects.

After this paper had been prepared for publication, a paper[10] by Nham and Hess appeared with a report of an ellipsometric study of the critical points of layering transitions during the wetting of a graphite substrate by liquid ethane. The observed phase diagram corresponds to Fig. 3 (with $T_w < T_t$); the authors assert that nine observed critical points conform well to a curve described by expression (19) (which had been published in the brief version[19] of the present paper).

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APENDIX. FREE ENERGY OF SMECTIC DENSITY WAVES IN A THIN FILM OF DENSE LIQUID

The free energy of a small density perturbation of the liquid in a film bounded by structureless surfaces is[17]

$$\Delta F\{\Delta n\} = \frac{T}{2} \int \Delta n(z_1) \Delta n(z_2) G^{-1}(\mathbf{r}_1 - \mathbf{r}_2) d^3 r_1 \, d^3 r_2. \quad \text{(A1)}$$

In a dense liquid, $G(k)$ has a well-expressed peak at point k_1, of half-width ξ_b^{-1}, where $k_1 \xi_b \approx 10 \gg 1$. The Fourier density of the perturbation is thus localized near $k = \pm k_1$; i.e., we have

$$\Delta n(z) = n_0 [\eta(z) + \eta^*(z)],$$

where $\eta(z)$ is a wave $\propto e^{ik_1 z}$ with an amplitude which varies comparatively slowly. The expansion

$$G^{-1}(k) \approx G^{-1}(k_1)[1 + \xi_b^2 (k - k_1)^2 + \dots]$$

is equivalent to a transformation of (A1) to local form (cf. Ref. 21):

$$\Delta F_b = TG^{-1}(k_1) n_0 \int_0^h \left[|\eta(z)|^2 + \xi_b^2 \left| \left(\frac{d}{dz} - ik_1 \right) \eta \right|^2 \right] dz. \quad \text{(A2)}$$

Furthermore, associated with each boundary of the film is an additional energy

$$\Delta F_j = -2Tn_0 \operatorname{Re} v_j \eta(z_j) + TG^{-1}(k_1) n_0 (\xi_b^2/\lambda_s) |\eta(z_j)|^2, \quad \text{(A3)}$$

where the index $j = s, i$ corresponds to the substrate and to the boundary with the gas ($z_s = 0$ and $z_i = h$, respectively). The complex surface fields v_j can be expressed in terms of $\eta_{j0} \exp(i\psi_j)$, which are the equilibrium amplitudes of the density waves at the isolated boundaries ($h \to \infty$). In the present analysis, these quantities, like the extrapolation length λ_s, are phenomenological constants. The first term in (A3) stems from the violation of the translational symmetry of the liquid at the given boundary.[17] It performs a phase selection among the smectic fluctuations present in the liquid in thermal equlibrium, thereby exciting a static density wave. The second term stems from the absence of an interaction of the density wave with its continuation in the region outside the film. A general solution of the variational problem for (A2) is

$$\eta = \exp(ik_1 z) \{ \eta_s \exp(-z/\xi_b) + \eta_i \exp[-(h-z)/\xi_b] \}.$$

Substituting this solution into (A2) and integrating, we find

$$\Delta F_b = TG^{-1}(k_1) n_0 \xi_b (|\eta_s|^2 + |\eta_i|^2) [1 - \exp(-2h/\xi_b)].$$

Minimizing $\Delta F_b + \Delta F_s + \Delta F_i$ with respect to η_s and η_i, we find, to within terms $\sim \exp(-2h/\xi_b)$,

$$V(h) = 2TG^{-1}(k_1) n_0 \xi_b \{ [(\xi_b - \lambda_s)/(\xi_b + \lambda_s)] (\eta_{s0}^2 + \eta_{i0}^2) \times \exp(-2h/\xi_b) - 2\eta_{s0}\eta_{i0} \cos(k_1 h + \varphi_i - \varphi_s) \exp(-h/\xi_b) \}. \quad \text{(A4)}$$

Omitting the phase of the cosine, which is of no importance here, we find (4) and (5). It is physically natural to find a situation in which correlations are weakened near a surface because the average number of neighbors of a surface atom is smaller than that of a bulk atom. This situation corresponds to $\lambda < \xi_b$ and thus $b > 0$ in (5).

1) A summary of this study has been published previously.[19]

2) At $T > 1000$ K the hydrodynamic attraction of the boundaries of the film[16] appears to be dominant, leading to incomplete wetting of semiconductors by melts.

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