Complete Wetting on Rough Surfaces: Statics.

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Abstract. – We study the profile of a thin liquid film completely wetting a rough solid surface. The long-wavelength undulations of the liquid interface follow those of the solid surface, while short-wavelength undulations are strongly damped. There is Lorentzian damping of wavelengths smaller than the healing length ξ determined by a balance between surface tension and disjoining pressure. Undulations with wavelength smaller than the mean film thickness e are exponentially damped. We study in detail the case where the binary interactions between molecules may be described by an inverse power law potential such as the Van der Waals potential. These results are relevant for recent ellipsometry and grazing incidence X-ray scattering experiments.

Introduction. – Wetting of solid surfaces by liquids has many practical applications and consequently has been an important area of both applied and basic research for many years. However, many of the more complicated «real» wetting processes are, at best, only partially understood. The main reason for this is the great sensitivity of any interfacial phenomenon such as wetting to roughness[1] and inhomogeneity of the solid surface, and to contaminations of the liquid.

The aim of the present letter is to consider, theoretically, the effect of surface roughness on thin liquid films. We concentrate here on the static properties, namely the shape of a liquid-vapor interface and its correlation with the roughness of the underlying solid surface.

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[1] Throughout this paper, we will refer to *any* solid whose surface is not microscopically smooth as being rough, to be distinguished from the same term used for surfaces undergoing a roughening transition.

Our predictions can be compared with two recent experiments. In the first, roughness of a solid glass substrate was correlated with the fluctuations of a thin water film (thickness of the order of 100 Å) using grazing incidence synchrotron X-ray diffraction [1]. In the second, drops of silicon oil (PDMS) spreading on etched glass, fused silica and mica were studied by ellipsometry [2].

In the case of *partial wetting*, i.e. when the contact angle θ_e is finite, surface roughness (as well as chemical inhomogeneities or contaminations) has been shown to cause *contact angle hysteresis*: the advancing and receding contact angles are unequal [3-5]. It is useful in this situation to think of the roughness as a random surface field which pins the solid/liquid/vapor contact line and thus causes hysteresis in the contact angle.

In the case of *complete wetting* (zero contact angle) a thin liquid layer completely covers the solid surface. As shown below, surface roughness leads to roughening of the liquid/vapor interface. We identify three examples of wetting films that can be treated in a similar fashion: i) a thin liquid film in equilibrium with its undersaturated vapor; ii) a liquid film on a horizontal plate located at height h above a liquid reservoir; iii) a nonvolatile liquid whose total volume is conserved [6]. In the last two cases the vapor phase could be instead a second liquid.

We address here the structure of such wetting films on a rough solid surface [7-9] as shown in fig. 1. The solid surface is specified by its height $\zeta_S(\rho)$ above each two-dimensional vector ρ in a reference plane. The stable liquid-vapor interface $\zeta_L(\rho)$ (called the liquid surface below) is determined by minimizing the free energy F. We take the bare solid-vapor interface as the reference state and express ΔF as

$$\Delta F = \int \mathrm{d}^2 x \left\{ (\gamma_{SL} - \gamma_{SV}) \sqrt{1 + |\nabla \zeta_S|^2} + \gamma \sqrt{1 + |\nabla \zeta_L|^2} + P(\zeta_L) + \Delta \mu (\zeta_L - \zeta_S) \right\}, \tag{1}$$
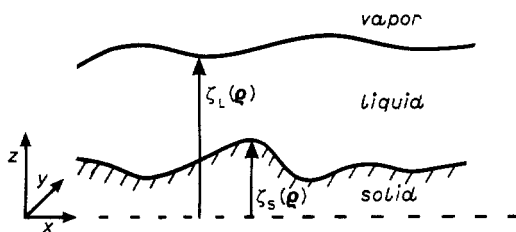

Fig. 1. – A liquid film between a vapor and a rough solid surface. The solid/liquid and liquid/vapor interfaces are at heights $\zeta_S(\rho)$ and $\zeta_L(\rho)$ above the $(z = 0, x, y)$ reference plane, respectively.

where the gradients are with respect to the vector x in the reference plane. The first two terms represent the change in interfacial energy with γ_{SV}, γ_{SL} and γ the solid-vapor, solid-liquid and liquid-vapor surface tensions, respectively. These interfacial energies describe interfaces separating semi-infinite regions of each phase. The third term, $P(\zeta_L)$, represents the interaction per unit area between liquid and solid surfaces, and vanishes as $|\zeta_L - \zeta_S| \to \infty$. The final term is the chemical potential difference between liquid and vapor phases integrated over the volume of the film.

To find an expression for $P(\zeta_L)$, we assume pair interactions between molecules, $U_{ij}(r)$, where i and j are any of the relevant phases: vapor (V), liquid (L) or solid (S). The contributions to P come from interactions between solid and vapor regions:

$$P(\zeta_L(x)) = \int_{\zeta_L(x)}^{\infty} \mathrm{d}z \int \mathrm{d}^2 \rho \int_{-\infty}^{\zeta_S(x+\rho)} \mathrm{d}z' \, w(\rho, z' - z), \tag{2}$$

where $w(r) = n_L^2 U_{LL}(r) - n_L n_S U_{LS}(r) - n_V n_L U_{LV}(r) + n_V n_S U_{VS}(r)$, and the n_i are number densities for each phase. The last term in w is the solid-vapor interaction. The first three include a finite-size correction to the liquid energy, and corrections to the interfacial energies. The last two terms are negligible for a low density vapor, but are important if the phase is a second liquid. For films with thickness $\zeta_L - \zeta_S$ larger than molecular sizes, the complicated short-range structure in U_{ij} only contributes to the surface tensions in eq. (1). P is determined by the long-range tails of the U_{ij}. Note that eq. (2) is a local function of the liquid profile, but a nonlocal function of the rough solid surface.

The form of the chemical potential difference in (1) is different for cases i)-iii). For case i), $\Delta\mu = -T \log(p/p_{sat})$, where p is the vapor pressure and p_{sat} the saturated pressure. For case ii), $\Delta\mu = \Delta\rho \, gh$ reflects the hydrostatic pressure where $\Delta\rho$ is the density difference between liquid and vapor and g the gravitational acceleration. Finally, for case iii), $\Delta\mu$ is the Lagrange multiplier associated with conservation of the total liquid volume.

Minimizing the free-energy functional (1) and (2), using the Euler-Lagrange equation, leads to an integro-differential equation for $\zeta_L(x)$:

$$\gamma \nabla \cdot \{\nabla\zeta_L(x)[1 + |\nabla\zeta_L(x)|^2]^{-1/2}\} = -\Pi_d(\zeta_L(x)) + \Delta\mu \,, \tag{3}$$

where Π_d is the disjoining pressure:

$$\Pi_d(\zeta_L(x)) = -\delta P(\zeta_L(x))/\delta\zeta_L(x) = \int d^2\rho \int_{[\zeta_L(x)-\zeta_S(x+\rho)]}^{\infty} dz \, w(\rho, z) \,. \tag{4}$$

Both P and Π_d are positive for wetting films.

For inverse power potentials the integral over z in eq. (4) is simplified. As an example we consider a nonretarded Van der Waals interaction between molecules [2], $U_{ij} = -\alpha_{ij} r^{-6}$. For simple fluids the strengths, α_{ij}, of the interactions between phases are proportional to the relative polarizabilities. Defining the Hamaker constants $A_{ij} = \pi^2 n_i n_j \alpha_{ij}$ and integrating over z, we find

$$P(\zeta_L) = (3A/8\pi^2) \int d^2\rho \, \rho^{-4} \{1 - \zeta_{SL} tg^{-1}(1/\zeta_{SL})^{-(1/3)}(1 + \zeta_{SL}^2)^{-1}\} \,, \tag{5}$$

$$\Pi_d(\zeta_L) = (3A/8\pi^2) \int d^2\rho \, \rho^{-5} \{tg^{-1}(1/\zeta_{SL}) - \zeta_{SL}(1 + \zeta_{SL}^2)^{-2}[5/3 + \zeta_{SL}^2]\} \,. \tag{6}$$

Here $A = A_{LS} + A_{LV} - A_{LL} - A_{SV}$, $\rho = |\rho|$, and for convenience a dimensionless variable $\zeta_{SL}(x, \rho) = [\zeta_L(x) - \zeta_S(x+\rho)]/\rho$ is introduced. As a check, it is easy to verify that $\Pi_d(e) = A/6\pi e^3$ when both interfaces are planar and parallel: $\zeta_L(x) - \zeta_S(x+\rho) = e$.

We note that so far no assumption has been introduced except the implicit assumption of no overhangs (ζ_S and ζ_L single-valued functions of x). Thus, in principle, solving eq. (3) exactly will give the liquid profile $\zeta_L(x)$. However, since eq. (3) cannot in general be solved analytically, we proceed by linearizing it here. A numerical solution of eq. (3) will be presented elsewhere [11].

Linear response approximation. – We choose the reference plane so that the average height of the solid surface vanishes, $\langle\zeta_S\rangle = 0$, and define the average film thickness $e \equiv \langle\zeta_L\rangle$.

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[2] We use here the classical theory of Van der Waals forces, summing binary interactions between particles [10]. A more complete treatment would require use of Lifshitz theory as has been done in ref. [7].

Equations (3) and (4) are then linearized in ζ_S and $(\zeta_L - e)$ assuming $|\nabla \zeta_L(x)| \ll 1$. This results in an equation for the mean thickness, $\Pi_d(e) = \Delta \mu$, and ~~an equation for the~~ fluctuations

$$\xi^2 \nabla^2 \zeta_L(x) = [\zeta_L(x) - e] - \int d^2\rho \, K(x - \rho) \zeta_S(\rho) , \qquad (7)$$

where the surface-tension-dependent *healing length* ξ is defined as

$$\xi^2 = \gamma / \int d^2\rho \, w(\rho, e) , \qquad (8)$$

and the kernel $K(\rho)$ is

$$K(\rho) = w(\rho, e) / \int d^2\rho \, w(\rho, e) . \qquad (9)$$

For the special case of a long-range inverse power law interaction, $w(r) = A\pi^{-2} r^{-2n-2}$ ($n \geqslant 1$):

$$\xi = (n\pi\gamma/A)^{1/2} e^n , \qquad K(\rho) = (n/\pi) e^{2n} (\rho^2 + e^2)^{-n-1} . \qquad (10)$$

The nonretarded Van der Waals interaction corresponds to $n = 2$, $\xi = e^2 \sqrt{2\pi\gamma/A}$.

The shape of the liquid interface $\zeta_L(x)$ is obtained by Fourier transforming eq. (7):

$$\tilde{\zeta}_L(q) = \tilde{\zeta}_S(q) \tilde{K}(q)/(1 + q^2 \xi^2) , \qquad (11)$$

where the two-dimensional Fourier transform of $f(x)$ is $\tilde{f}(q) = \int d^2x f(x) \exp[-iq \cdot x]$ and $\tilde{K}(q)$, $\tilde{\zeta}_S(q)$ and $\tilde{\zeta}_L(q)$ are the Fourier transforms of $K(\rho)$, $\zeta_S(\rho)$ and $[\zeta_L(\rho) - e]$, respectively.

Equation (11) is the central result of this paper. It relates the liquid profile to the solid one. Experimentally, in grazing incident X-ray diffraction [1], the scattered intensities from the solid and liquid surfaces $I_S(q)$ and $I_L(q)$ are proportional to the mean squared height fluctuations, $\langle \tilde{\zeta}_S^2(q) \rangle$ and $\langle \tilde{\zeta}_L^2(q) \rangle$, respectively. The ratio of these intensities is thus

$$I_L(q)/I_S(q) \propto (1 + q^2 \xi^2)^{-2} \tilde{K}^2(q) . \qquad (12)$$

For inverse power law interactions, $\tilde{K}(q)$ can be calculated exactly:

$$\tilde{K}(q) = (2/\Gamma(n)) (qe/2)^n K_n(qe) , \qquad (13)$$

where K_n is the modified Bessel function of the second kind of order n, and Γ is the gamma-function.

Discussion. – Our linear response approximation is a generalization of the so-called Deryagin approximation [10] for interactions between smooth spheres. In our context the latter approximation amounts to replacing $\zeta_S(x + \rho)$ by $\zeta_S(x)$ in eqs. (2) and (4). The equation for $\zeta_L(x)$ then depends only on ζ_S at the same x [3]. In eq. (7), $K(x)$ becomes a delta-function,

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[3] Wetting of rough surfaces was studied within the Deryagin approximation by P. G. de Gennes, Collège de France Lectures, 1984-85, unpublished.

implying $\bar{K}(q) = 1$. The intensity ratio, eq. (12), is reduced to a Lorentzian square function of the momentum transfer q. This functional form for correlations is also obtained in mean-field theories for other random systems [12].

Our more general treatment takes into account nonlocal contributions to the disjoining pressure. We distinguish between two limiting physical regions: i) long-wavelength fluctuations of the solid surface, $qe \ll 1$ and $q\xi \ll 1$, are followed by the liquid interface, $\tilde{\zeta}_L(q) \sim \tilde{\zeta}_S(q)$; ii) short-wavelength fluctuations are damped by the liquid/vapor surface tension for $q\xi \gg 1$, and by averaging of the contribution to the local disjoining pressure for $qe \gg 1$. The Deryagin approximation excludes the latter effect.

For inverse power potentials the nonlocal form of Π_d leads to exponential damping of short wavelength fluctuations, $qe \gg 1$. For Van der Waals interactions this also implies $q\xi \gg 1$ since $\xi > e$. One finds

$$\tilde{\zeta}_L(q)/\tilde{\zeta}_S(q) \sim (qe)^{3/2}(q\xi)^{-2} \exp[-qe]. \tag{14}$$

The X-ray intensity ratio is $I_L/I_S \sim (qe)^{-1}(e/\xi)^4 \exp[-2qe]$.

In general, undulations of the solid surface will be followed more closely as the film thickness decreases (e and ξ become smaller), and the liquid interface will become smoother as the thickness increases. Numerical solutions [11] show that this trend continues even when the linear approximation is no longer valid (*i.e.* when the r.m.s. roughness is of order e). Results of recent experiments on thin water [1] and PDMS [2] films clearly show this behavior over the range of e studied. Quantitative comparison with our results should be possible for PDMS which is a good Van der Waals fluid. However, thermal fluctuations of the liquid interface which contribute an additional roughness (3 Å for water) must be included in a detailed comparison.

Our predictions can be extended to two types of experimental situations where roughness is superimposed on films whose average thickness varies slowly with position. The advantage here is that (at least in principle) a whole range of thicknesses can be analyzed in a single experiment and compared with theory.

The first example is complete wetting of a vertical solid plate. Above a macroscopic meniscus of height $h_0 = \sqrt{2\gamma/\Delta\rho g}$, there is a static Rollin film whose thickness, $e(h)$, is due to a balance between the disjoining pressure $\Pi_d(e)$ and the drop in hydrostatic pressure $\Delta\rho gh$. For Van der Waals interactions [13]: $e(h) = (A/6\pi \Delta\rho gh)^{1/3}$. Using eq. (10) we define a local healing length: $\xi(h) = (A/2\pi)^{1/6} \gamma^{1/2}(3 \Delta\rho gh)^{-2/3}$. If the solid has a small roughness with a typical wavelength λ, the surface of the liquid film is smooth if $\lambda \ll \xi(h)$ and follows the solid roughness for $\lambda \gg \xi(h)$ (because $e < \xi$). This introduces a characteristic height $h_c \sim (A\gamma^3)^{1/4}/(\Delta\rho g\lambda^{3/2})$ above which the film surface starts to be rough. This height is in general much larger than the capillary length.

The second example is complete wetting on a horizontal solid surface where the macroscopic drop is preceded by a microscopic precursor film. The profile of this precursor film is obtained by equilibrating the viscous forces and the long-range Van der Waals forces [14]. In the early stages of spreading, the profile decays as $e(x) \simeq A/6\pi\eta ux$, x being the distance from the macroscopic edge of the drop, η the viscosity, and u the advancing velocity. On a rough surface, comparing $\xi(x)$ with the typical wavelength λ of the roughness leads to a minimum thickness below which the liquid profile becomes rough: $e_c = (a\lambda)^{1/2}$, where $a = \sqrt{A/2\pi\gamma}$ is a microscopic length. Thus, we predict a «wiggly» tip of the precursor film interface [4].

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[4] Viscous terms may modify this result at large u.

In conclusion, in this paper we present a theoretical calculation of the interplay between a rough solid surface and induced roughness in the liquid interface above it. We suggest a few experimental situations where such roughness may be of importance. Techniques such as X-ray diffraction [1] and ellipsometry [2] can be used to check the predictions presented here. Other interesting situations such as wetting on self-affine or fractal [15] surfaces as well as capillary rise in rough capillaries and other geometries will be addressed elsewhere. In addition, natural continuations of the study presented here will be to look at the influence of roughness on dynamics of complete wetting [11] and the role of roughness in rupture of thin liquid films.

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