

# Phase Transitions in Soft Condensed Matter

Edited by

**Tormod Riste**

Institute for Energy Technology  
Kjeller, Norway

and

**David Sherrington**

Imperial College of Science, Technology, and Medicine  
London, United Kingdom

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## WETTING OF ROUGH SOLID SURFACES BY LIQUIDS

David Andelman\*, Jean-Francois Joanny<sup>⊙</sup> and Mark O. Robbins<sup>#</sup>

(\*)School of Physics and Astronomy, Tel Aviv University, Tel Aviv 69978, Israel. (⊙)Ecole Normale Supérieure de Lyon, 46, Allée d'Italie, 69364 Lyon cedex 07, France. (#)Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218, U.S.A.

### INTRODUCTION

Recently, newly introduced experimental techniques have advanced our understanding of the phenomena of wetting and spreading of solid surfaces by thin liquid films ranging in thickness between few dozen Angstroms to a fraction of a micron. Among others these include ellipsometry<sup>(1)-(3)</sup> and grazing incidence X-ray diffraction using a synchrotron source<sup>(4)(5)</sup>. From a theoretical point of view, simple models for profiles of thin liquid films and their relation to the shape of the solid substrate have been proposed for smooth solid surfaces<sup>(6)</sup>, wetting on fibers<sup>(7)</sup>, wetting of porous media and fractals<sup>(8)</sup>. In this short contribution we focus only on the static behavior of thin liquid films that completely wet a rough solid surface<sup>(9)-(11)</sup>. Our predictions can be tested using the experiments mentioned above<sup>(1)-(5)</sup>.

When a liquid completely wets a solid surface, its *contact angle*  $\theta_c$  is zero and the liquid completely covers the solid with a thin layer. The thickness of the liquid layer depends on several factors: i) the undersaturation vapor pressure for volatile liquids; ii) the height of the horizontal solid surface above a reservoir of liquid; iii) the conserved volume of the liquid layer in the case of nonvolatile liquids such as silicone oils (PDMS)<sup>(12)</sup>.

We consider here the structure of such a thin liquid film which completely wets a *rough* solid surface. By rough we mean any surface that is not atomically smooth and that can be described by its height  $\zeta_S(\vec{\rho})$  above a two-dimensional reference plane defined by the vector  $\vec{\rho}$ . The free energy associated with such a thin film depends on the local height of the liquid-vapor interface taken with respect to the same reference plane  $\zeta_L(\vec{\rho})$  and can be expressed as

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

The first two terms represent the change in interfacial energy with respect to the bare solid surface.  $\gamma_{SL}$ ,  $\gamma_{SV}$  and  $\gamma$  are the solid-liquid, solid-vapor and the liquid-vapor surface tensions, respectively. The third term,  $P(\zeta_L)$ , comes from the long-range

interactions such as Van der Waals in nonpolar liquids. The last term is the chemical potential difference between the liquid and the vapor integrated over the volume of the film.

Using the variational principle, an Euler-Lagrange equation can be derived for the liquid-vapor profile  $\zeta_L(\vec{x})$

$$\gamma \vec{\nabla} \cdot \left\{ \frac{\vec{\nabla} \zeta_L(\vec{x})}{\sqrt{1 + |\vec{\nabla} \zeta_L(\vec{x})|^2}} \right\} = -\Pi_d(\zeta_L(\vec{x})) + \Delta\mu \quad (2)$$

where the disjoining pressure,  $\Pi_d = -\delta P/\delta \zeta_L$ , is positive for attractive long-range forces. For non-retarded Van der Waals interactions between any two molecules  $U_{ij} \sim r_{ij}^{-6}$ , the disjoining pressure is calculated to be

$$\Pi_d(\zeta_L) = \frac{3A}{8\pi^2} \int d^2\vec{\rho} \frac{1}{\rho^5} \left\{ \text{tg}^{-1} \left( \frac{1}{\zeta_{SL}} \right) - \frac{\zeta_{SL}(5 + 3\zeta_{SL}^2)}{3(1 + \zeta_{SL}^2)^2} \right\} \quad (3)$$

where  $\zeta_{SL}(\vec{x}, \vec{\rho}) = (\zeta_L(\vec{x}) - \zeta_S(\vec{x} + \vec{\rho})) / |\vec{\rho}|$  and  $A$  is the Hamaker constant.

Equations (2) and (3) completely specify the liquid-vapor profile  $\zeta_L$  as a function of the random solid surface  $\zeta_S$ . In the case of a flat surface  $\zeta_S(\vec{x}) = \text{const}$ , it is easy to verify that  $\Pi_d(e) = A/6\pi e^3$ , where  $e$  is the film thickness. We proceed by presenting the linearized version of (2) and (3). Numerical studies of (2) and (3) for one-dimensional corrugation will be presented elsewhere<sup>(13)</sup>.

### LINEAR RESPONSE APPROXIMATION

For weakly fluctuating solid surfaces, (3) can be linearized in  $\zeta_S$  and  $\zeta_L - e$ . In addition, keeping only the leading order in  $\vec{\nabla} \zeta_L$  in (2) and choosing  $\langle \zeta_S \rangle = 0$ , we get an equation for the average profile  $\langle \zeta_L \rangle = e$ ,  $\Pi_d(e) = \Delta\mu$ , and a linear equation for the fluctuation of  $\zeta_L$

$$\xi^2 \nabla^2 \zeta_L(\vec{x}) = (\zeta_L(\vec{x}) - e) - \int d^2\vec{\rho} K(\vec{x} - \vec{\rho}) \zeta_S(\vec{\rho}) \quad (4)$$

where the characteristic length in (4)

$$\xi = \sqrt{\frac{Ae^4}{2\pi\gamma}} \quad (5)$$

is called the *healing length* and the kernel in (4) is

$$K(\rho) = \frac{2e^4}{\pi(\rho^2 + e^2)^3} \quad (6)$$

Equation (4) can be solved separately for each Fourier component yielding

$$\tilde{\zeta}_L(q) = \tilde{\zeta}_S(q) \frac{\tilde{K}(q)}{1 + q^2 \xi^2} \quad (7)$$

where  $\tilde{\zeta}_L$ ,  $\tilde{\zeta}_S$  and  $\tilde{K}(q)$  are the Fourier transforms of  $\zeta_L$ ,  $\zeta_S$  and  $K(\rho)$ , respectively.

## DISCUSSION

The competition between surface tension and disjoining pressure determines to what extent a thin liquid film follows the undulations of a rough solid substrate and is seen in (7). Long-wavelength fluctuations of the solid surface,  $qe \ll 1$  and  $q\xi \ll 1$  are followed by the liquid film,  $\zeta_L(q) \simeq \zeta_S(q)$  while the short-ones,  $q\xi > qe \gg 1$  are strongly damped.

$$\zeta_L(q) \simeq (qe)^{3/2}(q\xi)^{-2} \exp(-qe) \zeta_S(q) \quad (8)$$

Our linear response theory (7) is a generalization of the so-called Deryagin approximation<sup>(14)</sup> which amounts to calculating only the local contribution to the disjoining pressure. In our approach this is achieved by replacing the true kernel  $K(\rho)$  by a Dirac delta function  $K(\vec{\rho}) = \delta(\vec{\rho})$  in (4) or  $\tilde{K}(q) = 1$  in (7). The main discrepancy between the improved result (7) and the local approximation occurs in the short-wavelength limit,  $qe \gg 1$ . While we get an exponential damping with a characteristic length being the film thickness,  $\zeta_L(q)/\zeta_S(q) \simeq (q\xi)^{-2}$  for the Deryagin approximation for any  $q\xi \gg 1$ . Note that  $\xi = e^2/a$ ,  $a$  being a molecular length, is always bigger than  $e$ .

A quantitative comparison of our results with experiments should be possible for Van der Waals (non-polar) liquids such as PDMS (silicone oil) spreaded on various preprepared rough surfaces like etched glass, fused silica and mica<sup>(1)</sup>. In a grazing incidence X-ray diffraction experiment<sup>(4)(5)</sup>, the ratio of intensities scattered from the liquid and solid surfaces  $I_L(q)/I_S(q)$  is proportional to the ratio of the  $q$ -component of the mean-squared height fluctuations of the two surfaces,  $\langle \zeta_L^2(q) \rangle / \langle \zeta_S^2(q) \rangle$

$$I_L(q)/I_S(q) \simeq \frac{\tilde{K}^2(q)}{(1 + q^2\xi^2)^2} \quad (9)$$

In the limit  $qe \gg 1$ , (9) reduces to  $I_L(q)/I_S(q) \simeq (e^3/q\xi^4) \exp(-2qe)$ .

We conclude with several remarks on related results and possible extensions of the model presented here. The formalism for non-retarded Van der Waals interactions has been extended to any inverse power law interaction  $U_{ij} \sim r_{ij}^{-n}$  and generalized expression for the healing length  $\xi$  and the kernel  $K(\rho)$  have been found<sup>(9)</sup>. Numerical studies of (2)–(3) for simple corrugated surfaces like surfaces with square-well grooves<sup>(13)</sup> confirm qualitatively the damping found within the linear response theory even in the limit where the r.m.s. fluctuation of the roughness is of the same order of magnitude as the film thickness. Complete wetting of chemically heterogeneous surfaces can be modeled by a position dependent Hamaker constant  $A(\vec{\rho}, z)$ <sup>(15)</sup>. Within a linear response theory, a direct analogy exists between roughness and chemical heterogeneities<sup>(13)</sup>.

Height-height correlations in position space,  $\langle \zeta_L(0)\zeta_L(\vec{\rho}) \rangle$  can be obtained by an inverse Fourier transform of  $\langle \zeta_L^2(q) \rangle$ . The height-height correlation of the liquid interface depends on the correlations of the solid surface. We have treated three types of surfaces: (a) solid surfaces with short-range correlations characterized by a Gaussian-like decay  $\langle \zeta_S(0)\zeta_S(\vec{\rho}) \rangle \sim \exp(-\rho^2/\sigma^2)$ ; (b) solid surfaces with algebraically decaying correlations,  $\langle \zeta_S(0)\zeta_S(\vec{\rho}) \rangle \sim |\vec{\rho}|^{-\alpha}$ ,  $\alpha > 0$ ; and (c) Self-affine solid surfaces where  $\langle \zeta_S(0)\zeta_S(\vec{\rho}) \rangle \sim |\vec{\rho}|^\alpha$ ,  $0 < \alpha < 2$ . In all three cases, the correlations of the liquid film depend both on the solid surface structure and on the healing length. In the latter case, for example, the liquid interface is composed of smooth sections up to length scales of order  $\xi$ . For length scales bigger than  $\xi$ , the liquid film has a self-affine behavior which follows the solid.

For a closer comparison with experiments, thermal fluctuations have to be included in the model as an additional source of roughness of the liquid interface<sup>(16)</sup>. Even in the limit where we predict a smooth and flat liquid interface, e.g. when  $\xi$  is big, thermal fluctuations will always cause a r.m.s. roughness of the order of a few Angstroms. They have been found to be about  $3\text{\AA}$  for thick water films<sup>(17)</sup>.

Finally, we mention two interesting experiments where roughness is superimposed on films whose average thickness varies smoothly with position. The first example is complete wetting of a vertical solid plate. Above a macroscopic meniscus, there is a static Rollin film. For Van der Waals interactions<sup>(6)(18)</sup>, the film thickness,  $e(h) \sim h^{-1/3}$ , and we can define a local healing length using (5),  $\xi(h) \simeq (A\gamma^3 h^{-4})^{1/6}$ . For solid surfaces with small roughness with typical wavelength  $\lambda$ , there will be a crossover from a relatively smooth liquid film for  $\lambda \ll \xi(h)$  to a "wiggly" film for  $\lambda \gg \xi(h)$ . Thus, there is a characteristic height  $h_c \sim (A\gamma^3)^{1/4} \lambda^{-3/2}$  above which the film starts to follow the rough solid.

For a horizontal geometry, a similar prediction holds for the precursor film preceding the macroscopic drop. Since the thickness of the precursor film is found<sup>(6)</sup> to vary as  $e(x) \sim x^{-1}$ ,  $x$  being the distance from the macroscopic edge of the drop, wiggles are expected to be found at the tip of the precursor film where the thickness is smaller than  $e_c \simeq \sqrt{a\lambda}$ ,  $a$  being a microscopic length  $a \simeq \sqrt{A/2\pi\gamma}$ .

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