

Structure and fluctuations of adsorbed liquid films close to a first order wetting transition

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The concept of interface potential is a very convenient tool for the rationalization of wetting behavior. This potential is defined as the free energy, $g(\ell)$ of an adsorbed liquid film of height ℓ above the substrate¹ (a related quantity that is more familiar in some related communities is the concept of "disjoining pressure" which is actually obtained as the derivative of the interface potential). However, a careful analysis of this concept soon reveals important difficulties, that have their origin in the mean field approximation which is usually implied.² On the one hand, a continuous function of ℓ assumes explicitly that films of arbitrary thickness may be built, while in practice, the concave part of the thermodynamic potential should be ruled out as unstable. Secondly, due to thermal fluctuations, a film described by means of an average thickness is a poor description of its actual shape, which is actually rough as a result of capillary waves. Furthermore, the proper location of the films interface is also difficult and requires a careful analysis.³ In this communication we will attempt to find a proper order parameter that is suitable to describe the corrugated nature of the adsorbed film and allows one to properly describe its related free energy. Stemming from this analysis,⁴ one can determine the structure of the adsorbed film as seen from the liquid-vapor interface, rather than from the usual perspective that results when one places the origin at the substrate. The results are striking and reveal almost as much layering at the liquid-vapor interface than is observed at the substrate.

Within the "Surface Hamiltonian" approximation, the interface potential may be exploited in order to describe

the shape of condensates on complex or structured substrates. The total free energy is then considered as a surface integral over $g(\ell(x, y))$, with the extra cost of bending the interface weighted by the surface tension.⁵ In this paper, we will also consider the feasibility of extracting a meaningful $g(\ell)$, from the study of interfacial fluctuations of adsorbed flat films. i.e., we test whether one can calculate from simulations a continuous function, $g(\ell)$, which will simultaneously describe the wetting behavior of flat films and the deformations of such films away from planarity.

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⁵ S. A. Safran. *Statistical Thermodynamics of Surfaces, Interfaces and Membranes* (Addison-Wesley, Reading, 1994), first edition.

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