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Capillary fluctuations, interface potential and the film height dependent surface tension of adsorbed liquid films

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The Capillary Wave Hamiltonian (CWH) lays at the heart of most theoretical accounts of surface phenomena, including, renormalization group analysis of wetting transitions, the study of droplet profiles, or the prediction of line tensions.

The virtue of this model is that it allows to predict the behavior of complex film morphologies solely from the properties of a flat film. Namely, the *interface potential*, $g(\ell)$, defined as the free energy of a flat film of height ℓ, and the liquid–vapor surface tension, γ_{lv}. This is achieved by defining a film profile, $\ell(x)$, that describes the film height on each point of the underlying plane. The CWH is constructed as a functional of $\ell(x)$, which assumes a free energy $g\ell(x)$, locally, but includes extra contributions due to bending of the interface via the liquid–vapor surface tension:

$$H\,[\ell\,(x)] = \int \left\{ g\left(\ell\,(x)\right) + \gamma_{lv}\sqrt{1 + \,[\nabla\,\ell\,(x)]^2} \right\} dx \qquad (1)$$

where $H[\ell]$ is the free energy of the complex film profile. Application of this result to the study of thermal capillary waves on an adsorbed flat film provides the following expectation for the spectrum of film height fluctuations:

$$\frac{k_B\,T}{A\,<\,\left|\ell_q\right|^2\,>} = g''_{cws} + \gamma_{cws}\,q^2 + O(q^4) \qquad (2)$$

where ℓ_q are the Fourier modes of the film height fluctuations, while g''_{cws} and γ_{cws}, are coefficients of the polynomial expansion in powers of the wave vector **q**. According to the classical model, the coefficient $g''_{cws} = d^2\,g(\ell)/d\ell^2$, while $\gamma_{cws} = \gamma_{lv}$.

In this paper we perform computer simulations of the capillary wave spectrum of an adsorbed film and show for the first time that [1,2]:

- The coefficient g''_{cws} precisely follows the second derivative of $g(\ell)$as obtained independently from thermodynamic integration.
- The second order coefficient, γ_{cws} is asymptotically equal to γ_{lv}, but picks–up an additional film thick dependence, which we show accurately follows $\gamma\,(\ell) = \gamma_{lv} + \xi^2 g''\,(\ell)$, where ξ is the bulk correlation length.

Our theoretical approach shows for the first time that the film height dependence $\gamma\,(\ell)$ follows from a hitherto unnoticed capillary wave broadening mechanism beyond mere interfacial displacements. Accordingly, the interfacial roughness, of order $\langle\delta\ell^2\rangle$ in the classical theory, takes an additional contribution $\langle(\nabla\ell)^2\rangle$ of order square gradient. This conclusion is shown to agree with expectations from Renormalization Group Theory.

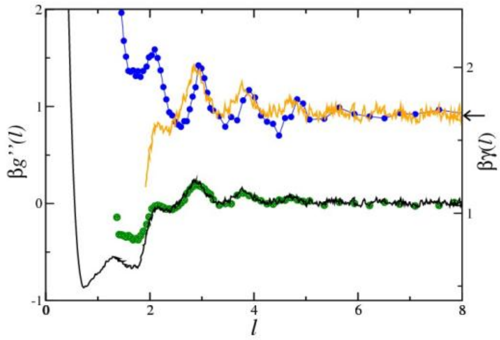

FIG. 1. Interface potentials (left axis) and surface tension (right axis) of adsorbed liquid films. Green symbols are results for $g''(\ell)$ as obtained from the CWS. Black lines are results from the interface potential as determined by thermodynamic integration. Blue symbols are results for $\gamma(\ell)$ as obtained from the CWS, while the orange lines correspond to our theoretical estimate $\gamma(\ell) = \gamma_{lv} + \xi^2 g''(\ell)$. The arrow points to the value of γ_{lv} obtained independently from the virial.

[1] L. G. MacDowell, J. Benet and N. A. Katcho, Phys. Rev. Lett. 111, 047802 (2013)

[2] L. G. MacDowell, J. Benet and N. A. Katcho, J. M. G. Palanco, Adv. Colloid Interface Sci. DOI:10.1016/j.cis.2013.11.003 (2013)