SUPPLEMENTARY MATERIAL

"*Abrupt onset of the capillary-wave spectrum at wall-fluid interfaces*"

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Here we present a detailed account of the theoretical calculations that lead to the paper's results.

Our study is based on a simple square-gradient density functional model of fluid adsorption in systems with short-ranged forces near a wall situated in the $z = 0$ plane. We adopt a magnetic notation with local order-parameter $m(\mathbf{r})$, for which the free-energy functional is written

$$F[m] \;=\; \int d\mathbf{r}\, \left\{ \frac{1}{2}\,(\nabla m)^2 + \phi(m) \right\} + \int d\mathbf{x}\;\phi_1(m_1) \tag{1}$$

where $\phi(m)$ is a double-well bulk potential and $\phi_1(m) = c\,m^2/2 - h_1 m$ is the surface interaction, which couples to the magnetisation at the wall m_1 via a surface enhancement c and a surface field h_1. For simplicity, we assume an Ising symmetry denoting the bulk spontaneous magnetization m_0 and $\kappa = 1/\xi_b$ the inverse of the bulk correlation length. We begin by supposing that the bulk magnetic field is $h = 0^-$ so that the bulk magnetization at subcritical temperatures takes the value $-m_0$. Minimizing $F[m]$, assuming translational invariance along the wall, yields the Euler-Lagrange equation

$$m''(z) \;=\; \phi'(m) \tag{2}$$

which has a first integral that determines the equilibrium magnetization profile $m(z)$:

$$m'(z) \;=\; \pm\sqrt{2\left(\phi(m) - \phi(m_0)\right)} \tag{3}$$

together with the boundary condition $m'(0) = c\,m_1 - h_1$. The $\pm$ signs apply for the cases $m_1 < -m_0$ and $m_1 > -m_0$ respectively, to which we shall return shortly. The elegant graphical solution (or Cahn construction [1]) based on the well-known analogy with the mechanical conservation of energy [2], determines both the equilibrium profiles and the Nakanishi-Fisher global surface phase diagrams [3].

Here, we focus on the properties of the correlation function $G(\mathbf{r},\mathbf{r}') = \langle m(\mathbf{r})m(\mathbf{r}')\rangle - m(z)m(z')$ which we study via its transverse Fourier transform $G(z,z';q)$, where $\mathbf{q}$ is a 2D wavevector parallel to the wall with modulus q. This correlation function satisfies the inhomogeneous Ornstein-Zernike equation [2, 4] which, for our square-gradient model, reduces to

$$(\mathcal{L} + q^2)\,G(z,z';q) \;=\; \delta(z-z') \tag{4}$$

where

$$\mathcal{L} \;=\; -\partial_z^2 + \phi''\big(m(z)\big) \tag{5}$$

together with the boundary condition $\partial_z G(z,z';q)|_{z=0} = c\,G(0,z')$, and we have set $k_BT = 1$. This is similar to the equation for the propagator in simple quantum mechanics and has an analogous spectral expansion

$$G(z,z';q) \;=\; \sum_n \frac{\psi_n^*(z)\,\psi_n(z')}{E_n + q^2} \tag{6}$$

with normalised wavefunctions satisfying the Shrödinger-like equation

$$\mathcal{L}\,\psi_n(z) = E_n\,\psi_n(z) \tag{7}$$

together with boundary conditions $\psi_n'(0) = c\,\psi_n(0)$ and $\psi_n(\infty) = 0$. In general, the sum (6) contains both bound states, for which $E_n < \kappa^2$, and a continuum of scattering states with higher energies $E_n \geq \kappa^2$.

For the "m^4" potential

$$\phi(m) \;=\; -\frac{t}{2}\,m^2 + \frac{u}{4}\,m^4 \tag{8}$$

where $t = T_c - T$ and $u > 0$, the profiles following from (3) are given explicitly by the simple hyperbolic functions

$$m(z) \;=\; \begin{cases} m_0 \tanh \dfrac{\kappa(\ell - z)}{2} & \text{for} \quad m_1 > -m_0 \\[2ex] -m_0 \coth \dfrac{\kappa(z + z_0)}{2} & \text{for} \quad m_1 < -m_0 \end{cases} \tag{9}$$

where $\kappa = \sqrt{2t}$ and $m_0 = \sqrt{t/u}$. Defining the parameter $\tau = m_1/m_0$, or equivalently $\tau = \tanh \frac{\kappa\ell}{2}$ for $1 > \tau > -1$ and $\tau = -\coth \frac{\kappa z_0}{2}$ for $\tau < -1$ allows us to link the familiar Cahn construction with the eigenvalue spectrum over the whole range of allowed equilibrium, metastable and unstable thin film profiles, and is related to c and h_1 via the simple quadratic relation

$$\tau^2 \;-\; 2\,\frac{c}{\kappa}\,\tau \;+\; 2\,\frac{h_1}{m_0\,\kappa} \;-1 \;=\; 0 \tag{10}$$

determining the corresponding values of ℓ and z_0.

The bound state eigenfunctions are given explicitly by

$$\psi_n(z) \propto e^{-\sqrt{k^2 - E_n}\,z}\, f\left(\frac{m(z)}{m_0}\right) \tag{11}$$

where $f(x) = x^2 - 2\sqrt{1 - E_n\,\xi_b^2}\;x + 1 - \frac{4}{3}E_n\,\xi_b^2$, with corresponding eigenvalues satisfying

$$\frac{\sqrt{k^2 - E_n} - \kappa\,\tau}{\sqrt{k^2 - E_n} + c} = \frac{f(\tau)}{1 - \tau^2} \tag{12}$$

which shows a 2D/3D crossover (a non-thermodynamic singularity) when the ground-state eigenvalue reaches the value $E_0 = \kappa^2$, yielding the following equation for the location of the crossover τ_*:

$$\kappa\,\tau_*(\tau_*^2 - 1) \;=\; c\left(\tau_*^2 - \frac{1}{3}\right) \tag{13}$$

Note that, for the "m^4" potential (8), the lines of critical and first-order wetting occur along

$$\frac{1}{2}\left(\tilde{c}^{\,2} + 1 + 2\tilde{h}_1\right)^{3/2} - \;\frac{1}{2}\left(\tilde{c}^{\,2} + 1 - 2\tilde{h}_1\right)^{3/2} - \;3\,\tilde{c}\,\tilde{h}_1 \;=\; 1 \tag{14}$$

where $\tilde{c} = c/\kappa$ and $\tilde{h}_1 = h_1/\kappa\,m_0$. For $c > 0$, a special solution of this is $c\,m_0 = h_1$, corresponding to the line of critical wetting. Therefore, the intersection of the lines of dimensional reduction and first-order wetting occurs when

$$\tau_w = \tau_* \tag{15}$$

which determines the value of $c_\dagger$. Using (10), (13) and (14) yields the numerical result

$$c_\dagger \approx -0.3375\,\kappa \tag{16}$$

Finally, we note that the Cahn construction determines that, for $c < 0$, the adsorption of the microscopic wetting layer is zero when $h_1 = -c\,m_0$, which from (14) occurs for the point on the line of first-order wetting transitions at which

$$c = (1 - 2^{1/3})\,\kappa \tag{17}$$

Together with the result for $c_\dagger$, this determines that the temperatures $T_{\rm DR}$ and $T_{\Gamma=0}$, which define regimes (i), (ii) and (iii) along the line of first-order wetting for $c < 0$, satisfy

$$\frac{T_c - T_{\rm DR}}{T_c - T_{\Gamma=0}} \;\approx\; 0.5931 \tag{18}$$

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