

SUPPLEMENTARY MATERIAL OF THE ARTICLE

Capillary Contact Angle in a Completely Wet Groove

A.O. Parry,¹ A. Malijevský,² and C. Rascón³

¹*Department of Mathematics, Imperial College London, London SW7 2BZ, UK*

²*Department of Physical Chemistry, Institute of Chemical Technology Prague,*

16628 Praha 6 Czech Republic; ICPF, Academy of Sciences, 16502 Prague 6, Czech Republic

³*GISC, Departamento de Matemáticas, Universidad Carlos III de Madrid, 28911 Leganés, Madrid, Spain*

I. DFT: EXTERNAL POTENTIAL AND NUMERICAL METHODS

For a groove of depth D and width L , the integral of the wall-fluids interactions(s) over the volume of the walls can be performed analytically, and determined as:

$$V(x, z) = V_1(z) + V_2(x, z; D) + V_2(L - x, z; D) \quad (1)$$

where the subscripts 1 and 2 refer to the contributions from the side and bottom walls, respectively. These have strengths characterised by the two parameters

$$\alpha_i = -\frac{1}{3}\pi\epsilon_i^w \rho_w \sigma^6. \quad (2)$$

Here,

$$V_1(z) = \frac{2\alpha_1}{z^3}, \quad (3)$$

while

$$V_2(x, z; D) = \alpha_2(\psi(x, z) + \psi(x, D - z)), \quad (4)$$

with

$$\psi(x, z) = \frac{2z^4 + x^2z^2 + 2x^4}{2x^3z^3\sqrt{x^2 + z^2}} - \frac{1}{z^3}. \quad (5)$$

Using the external potential $V(x, z)$, we numerically solve the Euler-Lagrange equation for the equilibrium profile $\rho(x, z)$ on a two-dimensional Cartesian grid with a spacing 0.05σ using a Picard iteration scheme. We chose a groove with depth $D = 50\sigma$, which is deep enough to observe the meniscus unbinding and, hence, the order of the capillary condensation. To model the boundary with the bulk reservoir at the top of the groove, we use the simple boundary condition $\rho(x, D) = \rho_b \exp[-V(x, D)/k_B T]$, where ρ_b is the bulk vapour density.

II. PHASE BOUNDARY τ_w OF THE MENISCUS TRANSITION

The effective Hamiltonian (6) is equivalent to the standard capillary-wave model of 2D wetting with a potential that belongs to an Intermediate fluctuation regime, between the two fluctuation dominated Strong- and Weak-regimes. This is because the ℓ^{-2} leading order term in the potential is marginal, since it decays with the same exponent as the entropic repulsion. This type of transition was studied extensively in the 1980s, first by Chui and Ma [27], and Kroll and Lipowsky [28] and later, and more thoroughly, by Lipowsky and Nieuwenhuizen [26], who allowed for the presence of a short-ranged attraction/repulsion in addition to a purely hard wall repulsion for $\ell < 0$. Using standard transfer matrix methods, the latter authors showed that the Intermediate fluctuation regime shows three sub classes of phase transitions depending on the nature of the short-ranged contribution. In our case, this corresponds to the ℓ^{-3} term and, because this is repulsive and large (since it is a factor of L bigger than the attraction), it can be reliably modelled as a short-ranged hard wall. This maps the model directly onto the analysis of Chui and Ma or, equivalently, to sub-regime C of Lipowsky and Nuiwenhuizen. Thus, for example, our equation (6) can be read off directly from the location of the vertical phase boundary of sub regime C in Fig. 1 of Lipowsky and Nieuwenhuizen [26].