

Adsorption in a phase field model for wetting

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Surface wetting can be described by using phase field models [1]. In these models, often either the contact angle or the surface tensions between the solid and the fluid are prescribed directly on the wall in order to represent the solid-fluid interaction. However, the interaction of the wall and the fluid are not strictly local. The influence of the wall, which can be described by wall potentials [2], reaches out into the fluid, which is the reason for the formation of adsorbate layers. The investigation shows how such a wall potential can be included into a phase field model of wetting. It is found that by considering this energy contribution, the model is able to capture the adsorbate layer.

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1 Model

In this work, a phase field model is used to describe surface wetting. It is based on [1] where the free energy F is defined as a function of the continuous order parameter φ (with $\varphi = 0$ in the gas phase and $\varphi = 1$ in the liquid phase). The order parameter can be seen as a normalized density, expressed as

$$\varphi = \frac{\rho - \rho''}{\rho' - \rho''}, \tag{1}$$

where ρ' is the density of the liquid phase and ρ'' is the density of the gas phase.

In contrast to other phase field models for wetting, a wall potential term is added to the free energy, replacing the surface energy contribution in [1]. While the surface energy acts only at the wall, the wall potential accounts for an energy contribution also in its proximity. It is used to describe the wall-fluid interaction resulting from the force that the wall executes onto the fluid and leading to adsorbate layering in the fluid. Different wall potentials [2] have been developed to describe the interaction which consists of an attractive and a repulsive part. In this work, a simple model potential u_{wall} is used:

$$u_{\text{wall}}(z) = \frac{1}{z^2} - \frac{\alpha}{z}, \tag{2}$$

where z is the distance from the wall and α is a parameter that can be adapted to investigate different wall-fluid pairings.

The free energy functional used in this work is

$$F = \underbrace{\int_{\Omega} \left[12 \frac{\gamma_{lv}}{l^e} f(\varphi) + \frac{3}{4} \gamma_{lv} l^e |\nabla \varphi|^2 \right] dV}_{I_1} + \underbrace{\lambda \int_{\Omega} [\varphi - \varphi_0] dV}_{I_2} + \underbrace{\int_{\Omega} \varphi u_{\text{wall}}(z) dV}_{I_3} \tag{3}$$

and consists of three parts I_1, I_2 , and I_3 . I_1 includes the double well potential

$$f(\varphi) = \varphi^2(1 - \varphi)^2 \tag{4}$$

and a gradient dependent term. Here, the surface tension is given by γ_{lv} , and l^e is the interface width. The second integral I_2 in Eq. (3) couples the phase field to the mass conservation equation via a global constraint as in [1], using λ as the Lagrange multiplier and φ_0 as the φ -field of the initialization. The last term I_3 in Eq. (3) accounts for the contribution of the wall potential u_{wall} to the free energy.

The static equilibrium condition

$$\delta_{\varphi} F = 0 \tag{5}$$

is approached with an Allen-Cahn evolution equation

$$\frac{\partial \varphi}{\partial t} = -M \frac{\delta_{\varphi} F}{\delta \varphi}. \tag{6}$$

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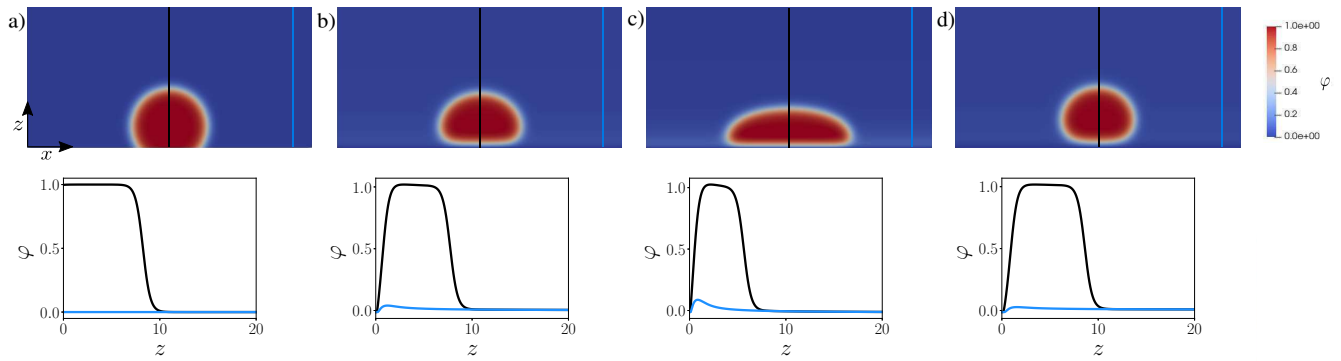


Fig. 1: Droplet sitting on a wall. a) Initialization. b) static equilibrium for $\alpha = 2.828$, c) $\alpha = 5$, d) $\alpha = 2$. Top: Contour plots, bottom: Order parameter φ along the black and the blue line shown in (a).

2 Numerical examples

A droplet is initialized sitting on a wall surrounded by a gas phase. Its static equilibrium is calculated for different wall-fluid pairings described by different values for the parameter α in Eq. (2). The simulation is carried out in a 2D domain. At the wall, the density equals 0, which with Eq. (1) leads to

$$\varphi(z=0) = \varphi(\rho=0) = \frac{-\rho''}{\rho' - \rho''} \quad (7)$$

as a Dirichlet boundary condition. On the other boundaries of the integration domain, the Neumann condition

$$\nabla\varphi \cdot \vec{n} = 0 \quad (8)$$

is imposed.

Equation (6) is solved using implicit backward Euler time integration until the solution field (φ, λ) at time step $n+1$ fulfills the condition

$$\max(|(\varphi_{n+1}, \lambda_{n+1})^T - (\varphi_n, \lambda_n)|) < \text{tol} \quad \text{with} \quad \text{tol} = 10^{-5}. \quad (9)$$

As a final step, Eq. (5) is then solved directly. A “box constraint” is applied to the solution field of the order parameter to assure non-negativity of the density in the entire computation domain.

Figure 1 shows a) the initialization and b)-d) the calculated equilibrium states for three different values for α . Below the contour plots, a plot of φ along a line cutting through the droplet (black) and through the gas domain (blue) is shown. It can be seen that the resulting contact angle is influenced by the wall-fluid pairing. For all three cases, φ increases rapidly from a value of zero density at the wall where repulsive forces are present. An adsorbate layer is formed in the gas phase that can be observed as a peak in φ at a small distance from the wall where attractive forces reign. Inside the droplet, φ raises to a slightly over-saturated liquid phase. Particularly visible in c), a peak of φ is also present inside the droplet. Including wall potentials into more elaborate phase field models as the one presented in [3] could therefore enable these models to capture an adsorption layer and its effect on the contact angles.

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