Surface Wetting with Droplets: A Phase Field Approach

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In order to be able to predict the static solution of three dimensional wetting scenarios, a free energy functional that is dependent on a continuous order parameter is formulated. This free energy functional can be linked to molecular dynamics (MD) simulations by input parameters. Static equilibrium configurations can be computed by minimizing the overall free energy using an evolution equation of Allen-Cahn type. Details of the presented model are followed by illustrative examples that demonstrate the pertinency of the approach.

1 Phase Field Model

Wettability of structured surfaces, which can be investigated using molecular dynamics (MD) simulations with force fields [1], plays an important role in a variety of production processes. The high numerical costs for the MD simulations motivate the development of the presented phase field model which is linked to MD simulations by input parameters and allows for a treatment of larger scales. A continuous order parameter $\varphi(\boldsymbol{x}, t) \in [0, 1]$ indicates the spatial distribution of the two phases liquid and gas with $\varphi = 0$ where there is gas and $\varphi = 1$ where there is liquid. The free energy F of the domain Ω is dependent on φ and defined as

$$F = \int_\Omega \left[12 \frac{\gamma_{GL}}{\kappa} f(\varphi) + \frac{3}{4} \gamma_{GL} \kappa |\nabla \varphi|^2 \right] \mathrm{d}V + \lambda \left(\int_\Omega h(\varphi) \mathrm{d}V - V_0 \right) + \int_{\partial \Omega_s} [h(\varphi) \gamma_{SL} + (1 - h(\varphi)) \gamma_{SG}] \, \mathrm{d}S. \quad (1)$$

Equilibrium droplet shapes and wetting conditions are computed by an Allen-Cahn evolution equation,

$$\dot{\varphi} = -M \frac{\delta F}{\delta \varphi}, \quad (2)$$

which by itself does not conserve the liquid volume. In the vicinity of the solution $\delta F = 0$ is solved directly. The first contribution to F (eq. (1)) consists of the separating double well potential $f(\varphi) = \varphi^2 (1 - \varphi)^2$ as well as the gradient of the order parameter φ. The separation and gradient terms are weighted in such a way that the width of the transition zone between gas and liquid in the solution state can be defined by κ. The surface tension between liquid and gas is given by γ_{GL}. To ensure a liquid volume conservation a global Lagrange multiplier λ is introduced (second contribution to (1)). As this liquid volume constraint does not need to conserve the liquid volume in each finite element but within the entire domain, λ represents only one (global) additional degree of freedom for the entire discretized system. The third contribution to the free energy (eq. (1)) allows to define specific contact angles Θ without a geometric formulation but by including the surface tension between a potentially structured solid surface and the liquid γ_{SL} as well as between the solid and the gas phase γ_{SG} into the free energy of the system [2]. The parts of the boundary where Ω is bounded by a solid surface are denoted by $\partial \Omega_s$. Note, that only the difference $\gamma_{SG} - \gamma_{SL}$ influences the weak form of the free energy F, but not the individual values of γ_{SG} and γ_{SL}. The analytic contact angle Θ^a can be computed by Young's equation

$$\cos(\Theta^a) = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{GL}}. \quad (3)$$

In the volume constraint as well as the energy contribution of the solid surface, the regularized interpolation function $h(\varphi) = \varphi^3(6\varphi^2 - 15\varphi + 10)$ is used [3]. The model is discretized using three-dimensional finite elements. Analogously to the two-dimensional case reported in [4], the volume energy contributions are discretized by 8-node-elements and the solid surface energy contributions by 4-node-elements.

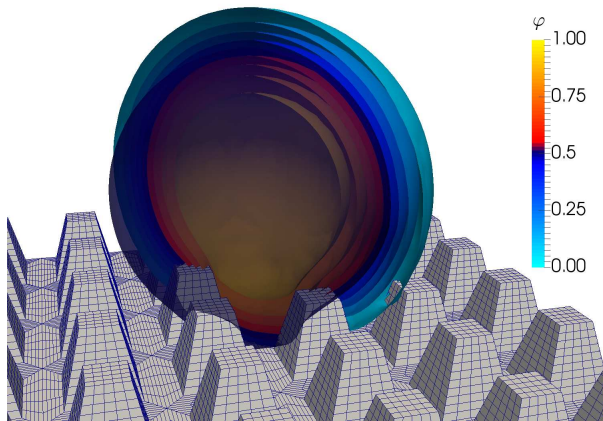* Corresponding author: e-mail fdiewald@rhrk.uni-kl.de, phone +49 (0) 631 205 3099, fax +49 (0) 631 205 2128

Fig. 1: Droplet on hydrophobic structured surface, input parameters are reported in Table 1(a).

Table 1: Dimensionless input parameters (and analytic contact angle) for (a) droplet on structured surface and (b) droplet on cylindrical pedestal.

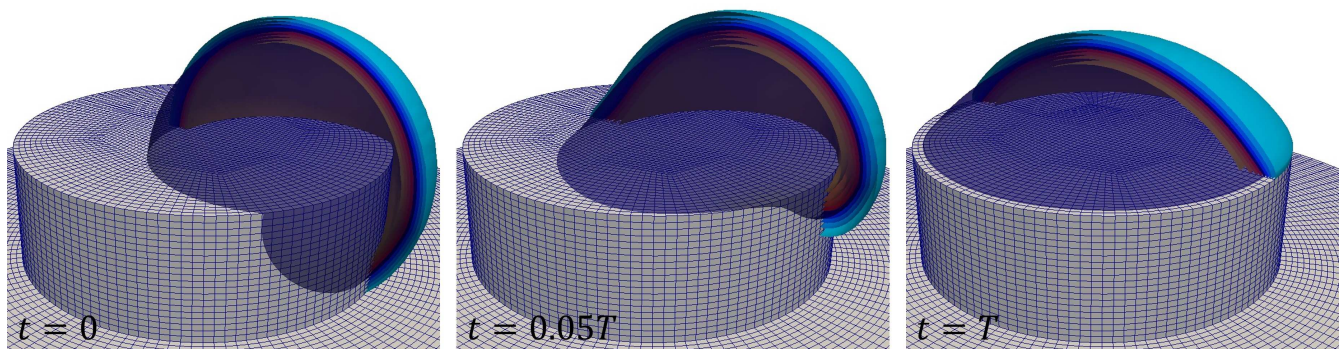| parameter	value (a)	value (b)
γ_{GL}	1.000	0.403
$\gamma_{SG} - \gamma_{SL}$	-0.866	0.285
κ	2	3
M	500	500
Δt	0.005	0.005
Θ^a	150°	45°

Fig. 2: Droplet on cylindrical pedestal for different solution states, input parameters are reported in Table 1(b).

2   Numerical Examples

This section demonstrates the ability of the presented model to compute the static solution of three-dimensional droplets on structured surfaces. The first scenario considers a droplet on a hydrophobic structured surface and can be seen in Fig. 1. The input parameters as well as the analytic contact angle are reported in Table 1(a). The lower width and the height of each frustum are κ and the smallest distance between each frustum is 0.5κ. The plot in Fig. 1 shows various isosurfaces of the phase field variable φ. It is clear to see how the structured surface influences the shape of the droplet, perturbing it from its circular shape. Interestingly, the $\varphi = 0.5$ isosurface is not in contact with the bottom of the structured surface which indicates partial dewetting. The second scenario under consideration is a droplet on a cylindrical pedestal. The input parameters as well as the analytic contact angle can be found in Table 1(b). The diameter of the pedestal is approx. 13.3κ and the height of the pedestal is approx. 4.2κ. The three plots in Fig. 2 show various isosurfaces of the phase field variable φ at different computation times t. The full runtime of the computation is given by T, therefore the first plot shows the initialization state and the last plot the final static solution. Even though the computation was initialized with a droplet sitting at the side of the pedestal, the droplet is moving towards the top of the pedestal as the computation evolves. In the final static solution, the droplet is located symmetrically at the middle of the pedestal (epitaxial Cassie state). This shows that the configuration in which the droplet is sitting on top of the pedestal is energetically more favourable than the one with the droplet sitting on the side of the pedestal. Future work will include the incorporation of a free energy density function corresponding to a thermodynamic equation of state.

References

[1] S. Becker, H.M. Urbassek, M. Horsch, and H. Hasse, *Langmuir* **30**, 13606-13614 (2014).
[2] M. Ben Said, M. Selzer, B. Nestler, D. Braun, C. Greiner, and H. Garcke, *Langmuir* **30**, 4033-4039 (2014).
[3] N. Moelans, B. Blanpain, and P. Wollants, *Calphad* **32**, 268-294 (2008).
[4] F. Diewald, C. Kuhn, R. Blauwhoff, M. Heier, S. Becker, S. Werth, M. Horsch, H. Hasse, and R. Müller, *PAMM* **16**, 519-520 (2016).