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A modified phase-field method for the investigation of wetting transitions of droplets on patterned surfaces

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ABSTRACT

A variant of the phase-field method, suitably modified to enable equilibrium (static) computations, is proposed for the calculations of the equilibrium wetting states of a droplet on patterned surfaces. Complemented by a parameter continuation method and stability analysis, the method is capable of mapping the solution space of the wetting states and computing the energy barriers of the wetting transitions. The wetting behavior of a droplet on a patterned surface, e.g. an array of pillars, is generally affected by the orientation, surface density (distance), size, and the shape of the pillars. The focus is on the effect of the shape (fine features) of the pillar, isolated from the effect of the pillar array; a simple system of a droplet lying on a single pillar is considered. The wetting on technologically feasible shapes of pillars is studied and the pillars are evaluated individually as single units with respect to the energy barrier of the transition from the Cassie–Baxter (CB) state to the Wenzel (W) state. The study brings out the intricate solution space of the wetting states on a single pin-shaped or rippled pillar. For example, 15 in total stable (impregnating) and unstable equilibrium states are calculated for the rippled pillar at a contact angle of 60°, which makes the calculation of the energy barrier more complex as it increases the number of potential transition paths. The evaluation verifies that the energy barrier of the CB to W transition is quite higher for pillars with re-entrant geometric features, in contrast to pillars with sharp protruding edges. Pin-shaped and inverted conical frustum pillars demonstrate the greater energy barrier of CB to W transition. The inherent flexibility of the phase-field method (handling of droplet breakup and coalescence) in combination with the mapping of the solution space, can facilitate the design of surface patterns with desired wetting behavior.

1. Introduction

The practice of patterning innately hydrophobic surfaces, converting them to superhydrophobic, or even superoleophobic, is greatly established [1,2] with a breadth of applications including self-cleaning surfaces [3], microfluidic valves [4,5], etc. A patterned surface exhibits superhydrophobic behavior when a droplet sits on top of the protrusions, wetting a small area of the surface known as the Cassie–Baxter (CB) state, which encompasses large apparent contact angles and low contact angle hysteresis. The CB equilibrium state is often metastable, as an adequately large perturbation can possibly

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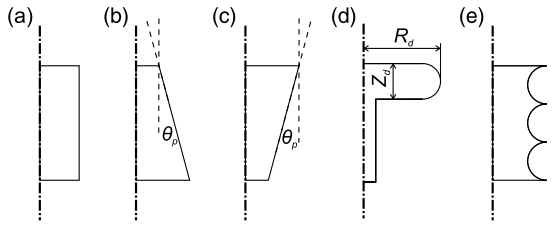

Fig. 1. Axisymmetric pillars of equal volume and height: (a) cylindrical, (b) conical frustum $\theta_p = 15°$, (c) inverted conical frustum $\theta_p = -15°$, (d) pin-shaped, and (e) rippled.

lead the system to the Wenzel (W) state, where the droplet collapses, wetting also the lateral walls of the protrusions. The strong droplet pinning and high contact angle hysteresis are undesirable attributes of the W state for applications that require robust hydrophobic behavior and therefore, a possible transition from CB to W (CB–W) should be inhibited. A useful metric for the resistance of a surface to wetting transitions is the energy barrier [6–8], defined as the energy required for the transition between two metastable states. A high CB–W energy barrier (corresponds to CB–W transition) suggests a robust superhydrophobic patterned surface.

The CB and W states are represented as energy minima on the free energy landscape of the system and the transition path between these states is bound to cross an energy saddle, which represents an unstable equilibrium state. The energy difference between the saddle and the CB or W state yields the energy barrier of the CB–W or W–CB transition, respectively. Often, however, even simple droplet–pillar systems display an abundance of equilibrium states that can either be stable or unstable. The determination of possible transition paths becomes then increasingly difficult and somewhat obscure, but we can claim that the value of the energy barrier lies in the interval bounded by the barrier computed with the highest and lowest energy saddle. This applies also in the case where the transition path involves intermediate stable states between CB and W, with the droplet partially wetting the structure (impregnating states), where the system traverses pairs of basins (minima) and saddles that correspond to intermediate impregnating states.

The computation of equilibrium states and energy barriers can be accomplished through several approaches based on fundamentally different methods such as molecular dynamics (MD) [7,9,10] or lattice Boltzmann (LB) [11–13]. More commonly used approaches, utilize the Young–Laplace (YL) equation [14,15], but cannot handle droplet breakup or coalescence and additionally, the usual formulation of YL yields impossible solutions when applied to systems with re-entrant geometries. Another class of methods, such as the level-set [16,17] and phase-field method [18–21], utilize implicit functions to represent separate phases and have been successfully implemented into capillary problems. Both methods have an inherent capability to simulate droplet breakup and coalescence, as well as interactions with complex solid geometries. Many formulations of the phase-field method (e.g. Cahn–Hilliard) have an advantage over other level-set methods by enforcing naturally the conservation of mass, but were originally formulated as a system of PDEs for transient computations. For the purposes of this work, the transient states are irrelevant and therefore, we propose a variant of the phase-field method, suitably modified to enable equilibrium computations. The proposed variant of the phase-field method allows the direct calculation of the energy of a state, thus enabling the smooth calculation of the energy difference between the states. The method can be coupled with a parameter continuation method to map the solution space of droplet-pillars systems, extracting the required equilibrium states for the calculation of energy barriers. The stability of each state is determined by solving an eigenvalue problem.

The modified phase-field method can be successfully applied to any system of droplet on an arbitrarily patterned surface that displays superhydrophobic behavior, but we confine this study to structured surfaces. Many prevalent designs that promote superhydrophobic behavior are arrayed surfaces with protruding micro-features such as cylindrical, rectangular and conical frustum pillars [22–24] or miscellaneous pillars with re-entrant profiles [25,26]. The coarse geometric characteristics, such as the density of the array or the size of the pillars have a significant impact on the wetting behavior of the surface, but equally so, do the fine features and details of the pillar shape. In attempt to focus on the effect of the fine features, each type of pillar is studied individually as a single unit, in order to isolate it from the effect of the array of pillars. The focus of the study is on technologically feasible axisymmetric micro-pillars (Fig. 1). The proposed methodology, including the variant of the phase-field method, the stability analysis and the continuation method is applied to study the effect of the fine features of the pillar on the energy barrier of the CB–W transition.

This work is organized as follows: In Section 2 the proposed phase-field method is presented, along with the stability analysis approach and Section 3 contains the results for single pillar–droplet systems with an extensive analysis of the energy barriers. The concluding remarks are presented in Section 4.

2. Phase-field method for equilibrium computations

Consider a pillar–droplet system, where three immiscible phases are in contact: solid (pillar), liquid (droplet) and gas (air). Each phase is represented by a scalar dimensionless variable, denoted φ, which assumes the value 1, wherever the phase exists and -1 otherwise. The necessity of diffuse interfaces for this class of methods leads to some overlapping between phases, i.e. the interfaces have thickness. Theoretically, φ tends asymptotically to either 1 or -1, which translates