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Anisotropic Wetting of Hydrophobic and Hydrophilic Surfaces - Modelling by Lattice Boltzmann Method

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Abstract

Anisotropic wetting on unidirectionally textured surfaces was investigated by Lattice Boltzmann Method. Previously published experimental data were used to validate the numerical model. New analysis were carried out by changing static contact angle of grooved surfaces from hydrophilic to hydrophobic ($\theta_s = 50 - 150°$). Presented results suggests that anisotropic wetting on unidirectionally textured surfaces is governed by spreading along the grooves by capillary action and mainly is dominant in Wenzel state on hydrophilic surfaces. Transition to Cassie-Baxter state on hydrophobic surfaces ($\theta_s > 90°$) significantly reduces the effect of anisotropic wetting. Structured texture and/or chemical heterogeneity can be potentially used to manipulate droplets in case of hydrophobic surfaces.

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1. Introduction

Surface wettability is an important property of engineering surfaces characterized by a static contact angle between liquid and solid surface at the triple-phase contact line. Surfaces with static contact angle $\theta_s < 90°$ are considered to be hydrophilic and generally have good wettability properties. Surfaces with contact angle $\theta_s = 90 - 150°$ are hydrophobic and surfaces with $\theta_s > 150°$ and sliding angle less than 10° are considered to be super-hydrophobic and are often used for liquid repelling applications [1].

When the surface morphology is uniform in different directions, such surface is considered to be isotropic and usually the wettability of such surface is also isotropic. Therefore, apparent contact angle measured from different directions will be very similar. In engineering applications perfect isotropy is impossible to achieve. However, on anisotropic surfaces where properties of surface will change in different directions [2,3], the wettability of surface is often anisotropic. Apparent contact angle is usually smaller in direction perpendicular to surface anisotropy ($\theta_\perp$) and larger in parallel direction ($\theta_{||}$) as presented by Ma et al. in [4].

Wettability in general can be affected by physical roughness and chemical heterogeneity therefore it is important to stress that both factors are important and physicochemical properties should be considered especially in analysis of anisotropic wetting.

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Nature has created several example of anisotropic wetting like butterfly wings, shark skin or water striders legs [1]. Nature inspired biomimetic surfaces have attracted in recent years significant attention thanks to new microfabrication techniques like femto-second lasers machining [5], direct writing or interface lithography as reviewed by Cheng et al. [6]. Fundamental and applied research profit from the ability to fabricate well defined structured surfaces to investigate liquid-solid interface dynamics and interactions. Potential applications of controlled adhesion, friction and wettability [7] include: micropumps, biochips, microfluidic devices, droplets manipulation, drag reduction coatings etc...

In this paper we focus on the influence of static contact angle on anisotropic wetting on unidirectionally textured (grooved) surfaces. Hydrophilic and hydrophobic surfaces are investigated numerically by lattice Boltzmann method.

2. Numerical simulations by lattice Boltzmann method

Influence of static contact angle (θ_s) was investigated numerically by lattice Boltzmann method. "This mesoscopic approach has the benefit that liquid free surfaces do not require special tracking or reconstruction at each time step; they arise naturally as part of the liquid-gas phase separation model, which in this case is the popular Shan-Chen multiphase model. In addition, there is no need to specify the dynamic contact angle as a geometrical constraint at the contact line. Instead, the surface energy of the solid is effectively specified through a parameter related to the static contact angle via Young's equation. These features make the method well suited to the simulation of flows involving both large and topological changes in free-surface shape..." [8].

"Rather than solving the Navier-Stokes equations by conventional direct discretisation of the partial differential equations, the LB approach is based on a velocity space discretisation of the Boltzmann equation in which molecular velocities are represented by a set of (typically in 3D) 19 microscopic velocities, $\vec{e}_a$ ($a = 0, \ldots, 18$). The $\vec{e}_a$ are given by the zero vector and the vectors connecting each node to its 18 nearest neighbours in a cubic lattice structure, and each has associated with it a probability distribution function, f_a. The macroscopic fluid density, ρ, and velocity, $\vec{u}$, at each lattice node are found from moments of the distribution functions:

$$\rho = \sum_{a=0}^{18} f_a \text{ and } \rho\vec{u} = \sum_{a=0}^{18} f_a \vec{e}_a. \tag{1}$$

The dynamics of the flow emerge as the values of f_a across the whole lattice evolve following a two-step process at each time step: (i) relaxation towards a local Maxwellian equilibrium distribution, capturing the effect of molecular collisions, and (ii) 'streaming', in which the value of each f_a moves along its associated vector to the neighbouring node. Using a single relaxation time, τ, which is related to the fluid kinematic viscosity, the process can be written as

$$f_a(\vec{x} + \vec{e}_a, t + \Delta t) = f_a(\vec{x}, t) - \frac{[f_a(\vec{x}, t) - f_a^{eq}(\vec{x}, t)]}{\tau} \tag{2}$$

where the local Maxwellian equilibrium distribution is given by:

$$f_a^{eq}(\vec{x}, t) = w_a \rho \left[1 + 3\frac{\vec{e}_a \cdot \vec{u}}{c^2} + \frac{9}{2}\frac{(\vec{e}_a \cdot \vec{u})^2}{c^4} - \frac{3}{2}\frac{\vec{u}^2}{c^2} \right] \tag{3}$$

for $a = 0, \ldots, 18$. Here w_a are weights associated with each vector $\vec{e}_a$, $\vec{x}$ is the position within the lattice, t the time, Δt the time step, and c the lattice speed. Using a multiple scale analysis, it can be shown that the Navier-Stokes equations can be obtained from the lattice Boltzmann equation [9].

... In this work the Shan-Chen [10] model is used since it was found to give the closest qualitative agreement with the free-surface shapes seen in the experiments. This efficient model introduces an interaction potential between neighboring lattice nodes, which can be expressed as:

$$\vec{F}(\vec{x}, t) = -G\psi(\vec{x}, t) \sum_{a=0}^{18} w_a \psi(\vec{x} + \vec{e}_a, t)\vec{e}_a \tag{4}$$

where $\vec{F}$ is fluid-fluid interaction force, G is an interaction strength parameter (negative for particle attraction), and ψ is a potential function that depends on density: $\psi(\rho) = \rho_0 [1 - \exp(-\rho/\rho_0)]$

where $\rho_0 = 1$. This model produces a non-ideal equation of state supporting the coexistence of a heavy phase of density ρ_h and a light phase of density ρ_l" [11].

Two relaxation times, $\tau_h = 1.0$ and $\tau_l = 0.54$, for the heavy and light phases respectively, are used to capture the different viscosities of the phases, and a linear interpolation based on local density value is used to calculate the relaxation time locally at every lattice node. Setting the lattice spacing at $dx = 1.25 \times 10^{-5} m$ and time step as $dt = 2.6 \times 10^{-7} s$ produce the conditions for water simulation with surface tension calibrated by free oscillations of

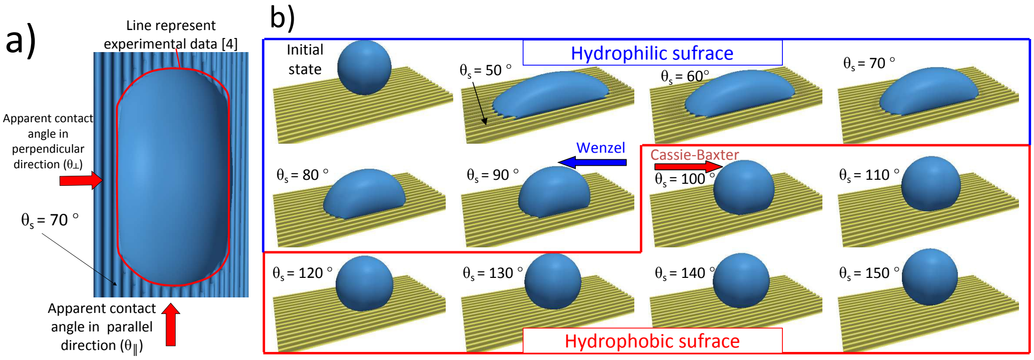

Fig. 1. (a) Validation of lattice Boltzmann method, where red contour corresponds to experimental data ; (b) Anisotropic wetting ($\theta_s = 50 - 90°$) in Wenzel state for hydrophilic surfaces and quasi-isotropic wetting ($\theta_s = 100 - 150°$) in Cassie-Baxter state.

droplet corresponding to $\sigma = 71.5 mN/m$. Interaction strength parameter was set to $G = -6$ resulting in densities $\rho_h = 2.65$ and $\rho_l = 0.0734$ expressed in lattice units for heavy and light fluid phases respectively. Droplet radius was set to $400 \mu m$. Different approaches can be used for partial wetting modelling [12]. In this paper wetting property of solid surface was modelled using local adhesion force acting on lattice nodes located in bulk fluid with neighbouring solid nodes. This force can be expressed as:

$$\vec{F}_{adh}(\vec{x}, t) = -G_{adh}\psi(\vec{x}, t) \sum_{a=0}^{18} w_a \vec{e}_a \tag{5}$$

where G_{adh} is the strength parameter which is proportional to static contact angle (θ_s). For the fluid parameters used in this paper the following linear approximation was used: $G_{adh} = 0.0289 \times \theta_s - 5.0864$.

Numerical model was calibrated using experimental published data [4]. Good agreement was found between the experimental data and our lattice Boltzmann simulation (Fig. 1a). Validated model was subsequently used to investigate influence of static contact angle defined locally on textured surface with grooves of $75 \mu m$ x $75 \mu m$ x $75 \mu m$. Both hydrophilic and hydrophobic surfaces were considered and transition between Cassie-Baxter and Wenzel state were analysed.

3. Results - Static contact angle in anisotropic wetting

Anisotropic wetting was observed for hydrophilic surfaces were droplets penetrate the surface texture. In this study we consider unidirectional morphology with physical texture prepared in form of grooves on surface. When water penetrate the grooves, this state is called Wenzel state and due to small size of grooves, water will easily spread along the channels which are considerably smaller than capillary size for water which is around $2 mm$. Driven by capillary action water can easily spread. On engineering surfaces roughness in direction parallel to grooves is very small, usually in range of few microns therefore, contact line is not pinned. In direction perpendicular to morphological surface texture, liquid have to overcome grooves of $75 \mu m$ and will be pinned at the edge of top part of texture, before it will fill the next groove. Classical example of pinning can be considered for surface with static contact angle $\theta_s = 90°$. When contact line arrive to the edge of the top surface of texture it will be pinned until the fluid will go over the edge and will be able to advance down on vertical wall of groove. This mechanism can significantly limit the spreading in direction perpendicular to surface anisotropy. Therefore the grooves form physical barrier for liquid to spread. This phenomenon combined with capillarity effect along the grooves will result in droplet contact line deformation and anisotropic wetting.

Presented in Fig. 1a simulations of droplet deposition on grooved surface indicates the transition between Wenzel and Cassie-Baxter state and significant influence of anisotropic wetting on hydrophilic surfaces ($\theta_s < 90°$). When surface is hydrophobic and droplet resides on top of surface texture, influence of anisotropic morphology is barely noticeable (Fig. 2a Cassie-Baxter region). Transition between Cassie-Baxter and Wenzel state can be clearly estimated to take place around $\theta_s = 90 - 100°$. On hydrophobic and hydrophilic grooved surface spreading in direction perpendicular to texture is rather similar (Fig. 1b contact length in perpendicular direction), whereas spreading along the grooves stimulate anisotropic wetting (Fig. 1b contact length in parallel direction).

In case of hydrophobic and superhydrophobic surfaces further analysis is needed. Structured texture and/or chemical heterogeneity can be potentially used to manipulate droplets in case of hydrophobic surfaces [1].

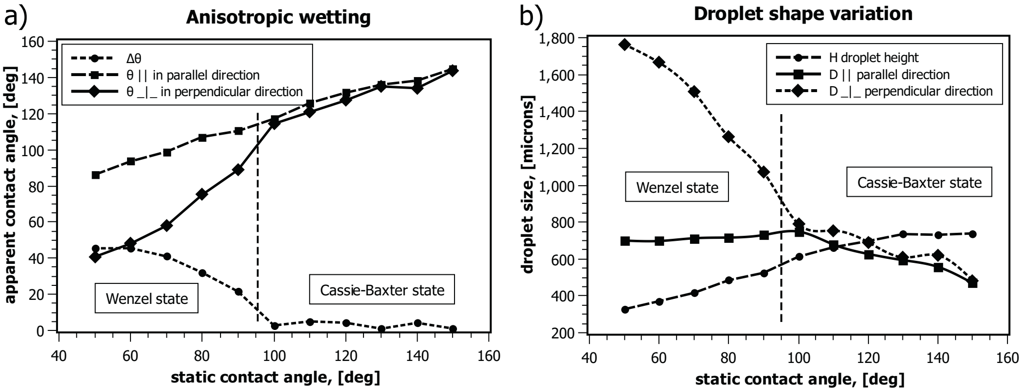

Fig. 2. (a) Influence of θ_s of textured surface on anisotropic wetting: $\theta_{\|}$, $\theta_{\perp}$, $\Delta\theta = \theta_{\|} - \theta_{\perp}$, where $\theta = 2\arctan(2H/D)$; (b) Droplet shape variations as a function of θ_s: H-droplet height, $D_{\|}$-solid-liquid contact size in parallel direction, $D_{\perp}$-solid-liquid contact size in perpendicular direction.

4. Conclusions

Influence of static contact angle (θ_s) on anisotropic wetting on unidirectionally textured surface was investigated numerically by lattice Boltzmann method. Static contact angle ($\theta_s = 50 - 150°$) was defined locally at the textured solid wall and the droplets were deposited directly above the textured surface and left to reach equilibrium state. Apparent contact angle in direction parallel ($\theta_{\|}$) and perpendicular ($\theta_{\perp}$) to surface anisotropy was measured. Analysing presented results the following conclusions can be formulated:

- Anisotropic wetting on unidirectionally textured (grooved) surfaces is mainly observed in Wenzel state on hydrophilic surface, when liquid spreads along the grooves by capillary effect,
- On unidirectionally textured surface transition between Cassie-Baxter and Wenzel state take place at $\theta_s \approx 90°$ when it is favourable for liquid phase to penetrate vertical side of grooves,
- In Cassie-Baxter state on textured hydrophobic surface an effect of anisotropic wetting is significantly reduced,
- Due to surface anisotropy apparent contact angle should be measured not only from one side but from different directions including top view.

Further work in the area of surface anisotropy and morphology influence on solid-liquid interface is currently investigated by authors and will be published shortly.

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