Lattice Boltzmann simulation of droplet dynamics on solid surfaces

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To the memory of my dear father,
Mohammad-Ali Moradi
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Abstract

This thesis mainly focuses on computer simulation of small droplets on solid surfaces. For this purpose, different two-phase single-component Lattice Boltzmann methods are employed. However, it is not relied on the simulation results only. Rather, as far as possible, analytical estimates are provided to support the simulation results. Conversely, predictions obtained via simple scaling arguments are tested by computer simulations. The present work thus represents a combined approach where simple analytic theory and computer simulations shed light onto different aspects of the problem.

In chapter 2, a brief introduction to the both fluid dynamics and wetting phenomena related to the topic of this study is given. A short description of the lattice Boltzmann methods, used in this work, is provided in chapter 3. In chapter 4, the dynamics of droplets on flat substrates is investigated. Here, it is shown that, in the limit of Stokes flow and negligible droplet deformation, the drop’s center-of-mass velocity scales linearly with the applied force and with the second power of droplet radius as well as with the inverse of dynamic viscosity. In addition, a detailed study of dissipation loss inside droplet is performed. An important result of these investigations is that the dominant part of viscous dissipation arises from the region below the drop’s center-of-mass. Based on this observation, a simple analytic model is proposed which allows of capturing the dependence of steady state droplet velocity on the equilibrium contact angle. In chapter 5, the effect of a step wise change in the pillar density of a super-hydrophobic substrate, on the
dynamics of droplets is investigated. For the same pillar density gradient but different pillar arrangements, both motion over the gradient zone as well as complete arrest are observed. In the moving case, the droplet velocity scales approximately linearly with the texture gradient. A simple analytic model is provided reproducing the observed linear behavior. The model also predicts a linear dependence of droplet velocity on surface tension. This prediction is clearly confirmed via the computer simulations for a wide range of surface tensions. In chapter 6, it is shown that, a pressure increase inside liquid films suspending on super hydrophobic surfaces, induced by the motion of immersed solid objects, can push the films into a collapsed state. This transition is theoretically predicted for a circular disk approaching the substrate with a constant velocity. It is shown that the critical velocity, at which the transition occurs, is proportional to the third power of the distance between the disk and the substrate and is also proportional to the inverse of disk’s surface area. Using lattice Boltzmann simulations, some evidences and insights to this phenomenon are provided. In addition, the obtained analytical criterion for such a transition is examined. In chapter 7, situations in which the size of a droplet is comparable to the roughness scale of the solid substrate are considered. Possible wetting morphologies on patterned hydrophobic substrates are then explored and their dependence on the initial droplet position, droplet volume and the surface geometry is investigated. For a regular array of cubical pillars, small perturbations of a symmetric droplet state are restored by capillary forces. Larger deviations, on the other hand, may lead to completely new morphologies. These studies also suggest that the previously reported ‘reentrant transition’ upon quasi-static evaporation is not restricted to a symmetric initial state but may occur for quite non-symmetric morphologies as well. In contrast, a change in the substrate geometry may lead to a completely different behavior, fully precluding the reentrant transition.
## Contents

Acknowledgements ................................................................. v

Abstract .............................................................................. vii

1 Introduction to this thesis ..................................................... 1

2 Physical basis and fundamental equations ............................... 5
   2.1 Conservation laws in the fluid mechanics ......................... 5
   2.2 Wetting ................................................................. 9

3 The Lattice Boltzmann method .............................................. 13
   3.1 Two-phase single-component lattice Boltzmann models ....... 16
   3.2 The Swift approach .................................................. 18
   3.3 The Shan-Chen approach ........................................... 22
   3.4 The Lee-Fischer approach ......................................... 26
   3.5 Viscous stress in two-phase LB models ........................... 29
   3.6 Units ................................................................... 30

4 Dynamics of droplets on flat substrates .................................. 33
   4.1 Introduction ............................................................ 33
   4.2 Numerical model ....................................................... 36
   4.3 A simple scaling relation ........................................... 37
   4.4 Local and total viscous dissipation ................................ 43
   4.5 Similarity to the case of spherical droplets .................... 49
   4.6 Conclusion .............................................................. 49

5 Roughness-gradient–induced spontaneous motion of droplets ... 51
   5.1 Introduction ............................................................ 51
CONTENTS

5.2 Numerical model ............................................. 54
5.3 Results and discussion ....................................... 55
5.4 Conclusion ..................................................... 66

6 Cassie-Wenzel transition in Reynolds problem ............... 69
   6.1 Introduction ................................................ 70
   6.2 Theoretical solution to the problem ......................... 71
   6.3 Numerical model ............................................ 73
   6.4 Results and discussion ...................................... 75
   6.5 Conclusion .................................................. 77

7 Morphologies of small droplets on patterned hydrophobic substrates ........................................ 81
   7.1 Introduction ................................................ 82
   7.2 Numerical model ............................................ 86
   7.3 Results and Discussion ...................................... 87
   7.4 Conclusion .................................................. 97

8 Summary and outlook ........................................... 101

Bibliography ..................................................... 107

Publications related to the PhD thesis .......................... 115

Curriculum vitae .................................................. 118
List of Figures

2.1 Sketch of a liquid droplet on a perfectly flat substrate at equilibrium .................. 10

3.1 Frequently used underlying lattices in LB simulations ................................. 16

3.2 Coexistence densities versus force coefficient $g_{sc}$ for the Shan-Chen equation of state ............................................. 26

3.3 Comparison of lattice Boltzmann simulations (red dots) with Eq. (3.38) (solid line) ............................................................. 27

4.1 Sketch of the problem; droplet subject to an external gravity-like force, $g$, on a perfectly flat substrate ................................................. 34

4.2 Difference between rescaled velocity fields ..................................................... 40

4.3 $U_{cm}$ versus $g$ for different values of the effective droplet radius $R_{eff}$ as specified ................................................................. 41

4.4 $U_{cm}$ versus $R_{eff}^{2}$ for different choices of the $g$ as indicated ...................... 41

4.5 Droplet shape and corresponding momentum field inside droplet for different force densities .......................................................... 42

4.6 $U_{cm}$ versus $1/\eta$ for droplets with different degrees of deformation ............ 43

4.7 Illustration of the typical shape of a droplet and the lines along which viscous dissipation is determined ........................................... 45

4.8 Variation of the local dissipation rate $\Phi$ (panel (a)) and the relative dissipation rate $\Phi_{R}$ ................................................................. 46

4.9 Dissipation rate integrated along a horizontal line at $y$, $\Phi(y)$ ...................... 46

4.10 A similar plot as in fig. 4.9 but now for various fluid viscosity $\eta$ .................... 47

4.11 Droplet velocity versus equilibrium contact angle for two different droplet volumes as indicated ...................................................... 49

4.12 $yz$ momentum field in the plane cut at $x = Lx/2$ passing from the center of mass ................................................................. 50

5.1 The effective contact angle of droplet $\theta_{C}^{*}$, Eq. (5.1), as function of $\phi$ for different equilibrium contact angles ........................................... 52

5.2 The sketch of problem for roughness-gradient-induced spontaneous motion on a superhydrophobic surface with a step gradient of roughness ........................................ 55

5.3 Top view of two step gradient substrates ...................................................... 57
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4</td>
<td>Initial setup and final states of a spherical droplet on substrates with an</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>abrupt (step-wise) change of pillar density</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>The same set of simulations as in fig. 5.4 but for the case of cylindrical</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>droplets</td>
<td></td>
</tr>
<tr>
<td>5.6</td>
<td>The $xz$-cross section of the liquid-vapor interface</td>
<td>60</td>
</tr>
<tr>
<td>5.7</td>
<td>The $x$-component of the center-of-mass position versus time for a cylindrical</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>droplet</td>
<td></td>
</tr>
<tr>
<td>5.8</td>
<td>As the graph clearly shows the function</td>
<td>61</td>
</tr>
<tr>
<td>5.9</td>
<td>Droplet’s center-of-mass velocity versus the difference in pillar density</td>
<td>61</td>
</tr>
<tr>
<td>5.10</td>
<td>The $x$-component of the center-of-mass position versus time for a cylindrical</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>droplet</td>
<td></td>
</tr>
<tr>
<td>5.11</td>
<td>The contact area and the $x$-component of droplet’s center-of-mass position</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>versus time</td>
<td></td>
</tr>
<tr>
<td>6.1</td>
<td>Sketch of moving object in the liquid film suspended on superhydrophobic</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>stripes</td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>CW transition of a liquid film on superhydrophobic stripes</td>
<td>78</td>
</tr>
<tr>
<td>6.3</td>
<td>Velocity field of a liquid film which undergoes a CW transition</td>
<td>79</td>
</tr>
<tr>
<td>6.4</td>
<td>CW transition as a function of solid square velocity and solid square width</td>
<td>79</td>
</tr>
<tr>
<td>7.1</td>
<td>An initial state (panel (a)) which leads to a morphology shown in the</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>panel (e)</td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>Simulation for $\theta_{eq} = 100^\circ$ and $R_{eff} = 20$</td>
<td>88</td>
</tr>
<tr>
<td>7.3</td>
<td>Initial setup of the simulation, $\theta_{eq} = 100^\circ$ and $R_{eff} = 20$</td>
<td>89</td>
</tr>
<tr>
<td>7.4</td>
<td>Effect of a deviation from a perfectly symmetric initial state on the final</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>configuration</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>Initial setup of the simulation in 3D, $\theta_{eq} = 100^\circ$ and $R_{eff} = 23$</td>
<td>90</td>
</tr>
<tr>
<td>7.6</td>
<td>Time evolution of the ‘fish’ morphology upon quasi-static evaporation,</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>$R_{eff} = 23$ and $\theta_{eq} = 100^\circ$ (side view)</td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>Time evolution of the fish morphology upon quasi-static evaporation, $R_{eff} =$</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$23$ and $\theta_{eq} = 100^\circ$ (top view)</td>
<td></td>
</tr>
<tr>
<td>7.8</td>
<td>Three-phase contact line at different times for a droplet residing on the</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>top of cylindrical pillars</td>
<td></td>
</tr>
<tr>
<td>7.9</td>
<td>Observation of the reentrant transition on a regular array of cylindrical</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>pillars</td>
<td></td>
</tr>
<tr>
<td>7.10</td>
<td>A droplet falling onto a ‘lotus-like’ rough substrate, with a equilibrium</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>contact angle of $\theta_{eq} = 100^\circ$</td>
<td></td>
</tr>
</tbody>
</table>
List of Tables

7.1 LB parameters in the Swift model ........................................... 86
7.2 LB parameters in the Shan-Chen model ................................. 86
Chapter 1

Introduction to this thesis

Individual droplets can serve as ideal chemical reactors [1] or carriers of information [2]. Their behavior is also crucial in many technical processes for example, micro-fluidic labs-on-chips, ink-jet printers as well as surface preparation prior to painting or coating. In this regard, due to the various applications in micro/nano-fluidic systems [1], and its occurrence in a wide range of natural phenomena as well as its fundamental importance for surface engineering [3, 4], behavior of microdroplets on solid surfaces has recently received lots of attention both experimentally and by numerical modeling, and has become an active field of research [5]. For example, droplet spreading on chemically [6–8] and topographically patterned substrates [9–11], droplet evaporation [12], and wetting properties of superhydrophobic surfaces [4, 13] have been extensively studied in the literature.

Most of solid surfaces are naturally rough on micro-scale, and these roughnesses can dramatically change the wetting properties of surfaces [5, 14]. Accordingly, the behavior of droplets on surfaces are strongly affected by the roughnesses. The most famous evidence for the influence of roughnesses is the ‘lotus effect’ [15]. Over the last two decades, so much efforts have been devoted to produce extreme hydrophobic surfaces with the same properties as lotus leaves or insects legs aiming to find novel applications [16]. Thanks to recent achievement in nano/micro-structuring technology, it is currently possible to create desired patterns of roughnesses in a well-controlled way on
solid surfaces. This has opened new doors for performing elegant experiments on super-hydrophobic surfaces.

Although the fundamental basis of fluid flows and governing equations are theoretically well known in the continuum level, but due to the complex nature of fluids, however, the tractable analytical solutions are only available for some simplified systems. Controlled experiments, on the other hand, are, unfortunately, restricted to a limited range of parameters and obtained results are not easily reproducible. Owing to the powerful computational resources today, the computer simulations can bridge the gap between the theory and the experiments. There are different available computational fluid dynamic (CFD) methods \[17\]. Although each of these methods can successfully simulate a class of fluidic systems, but also suffers from some disadvantages; for example, the well-known molecular dynamic (MD) simulations \[18\] can, in principle, provide detailed insights and clear physical picture of the dynamics of nano-droplets on molecular scale, but, MD simulation of micro-droplets, still remains computationally demanding. Finite element method (FEM) is another example that has so far been extensively used, but it is still difficult to implement complex boundaries in this method. Fortunately, the relatively new—and still further developing—lattice Boltzmann method (LBM) has attracted the attention of many researcher as a powerful and alternative Navier-Stokes solver for simulating a wide range of fluid flows particularly those with complex boundaries and geometers \[19–25\]. The LBM can be regarded as an approximation to a mesoscopic kinetic equation, the Boltzmann equation. Because of its simple structure and, more importantly, its efficiency on parallel CPUs, it has currently become an important numerical tool for many researchers, ranging from basic science to engineering and even industrial research and development teams.

The aim of the current thesis is to gain new insights on the behavior of liquid drops deposited on solid surfaces, and to characterize this behavior with system parameters. Because of the mentioned features, the LBM is employed for the simulations in this thesis. However, this thesis is not restricted to a mere simulation study of the subject. Rather, simple scaling arguments are used in order to gain a qualitative understanding of the observed phenomena.
Introduction to this thesis

This thesis is organized as follows. In the next chapter, a brief introduction to the fluid mechanics as well as wetting is provided. The LBM is introduced in chapter 3 and the lattice Boltzmann (LB) models employed in this thesis are briefly explained. In chapter 4, the first selected problem, the steady motion of droplets on flat substrates under the action of a body force, is studied. A main finding in this problem is a characterization of drop velocity in terms of the equilibrium contact angle. The second selected problem deals with a droplet on a gradient of roughness on a super-hydrophobic surface. This issue will be addressed in chapter 5, where it is shown how the drop velocity scales with the roughness gradient and the liquid-vapor surface tension. In chapter 6, a Cassie-Wenzel transition of a suspended liquid film on a super-hydrophobic surface due to the motion of an immersed solid object is investigated. The simulation results are compared to a hydrodynamic theory showing how the velocity of the disk scales with system parameters for the Cassie-Wenzel transition. Even though in this chapter a liquid film is addressed but the obtained results are expected to remain relevant for other situations (such as a 3D drop) as well. In the last chapter, situations in which the size of droplets is comparable to the roughness scale of the solid substrate, are considered where possible wetting morphologies on patterned hydrophobic substrates and their dependence on the initial droplet position, droplet volume and the surface geometry are explored.

It should be mentioned that the chapters are provided in a relatively closed form in such a way that a reader can also study each chapter separately. In addition, it is tried to avoid reusing a symbol in different contexts. In some cases, however, in order to be consistent with the standard notation, a few symbols are reused. In order to avoid any confusion, these reuses are specifically mentioned.

In chapter 8, the thesis is summarized and the outlooks are pointed out and, finally, a publication list related to the thesis and a curriculum vitae close this thesis.
Chapter 2

Physical basis and fundamental equations

The present thesis, as it arises from its title, is based on solving the fundamental equations of fluid dynamics dealing with complex boundary conditions. These boundary conditions make the problem more interesting. For example, the interaction of fluid and solid—or liquid and its vapor—涉及 concepts such as wetting and surface tension. In the first section of this chapter, a brief overview of the basic equations of fluid mechanics is provided. In the second section, wetting and properties of superhydrophobic surfaces is discussed.

2.1 Conservation laws in the fluid mechanics

The classical fluid mechanics deals with the flow of continuum fluids [26, 27]. A fluid contains a huge number of molecules and these molecules collide with each other and propagate. According to the continuum hypothesis, the discrete structure of molecules in space is ignored and it is replaced by a continuous distribution. For the continuum hypothesis to be valid, the smallest characteristic length of considered flow must be much larger than the mean free path of the molecules. Interestingly, the continuum limit for
dense fluids is reached even for systems with a size as small as about 100 molecular radii.

Theoretical consideration of fluid flows is based on three conservation laws for the mass, momentum, and total energy of the system. These conservation laws are stated by nonlinear partial differential equations. From a theoretical point of view—and for a general case—solving these equations with appropriate boundary conditions provides all necessary information for a complete description of the considered flow on a macroscopic scale. In the following, these equations are presented.

### 2.1.1 Mass conservation

The conservation of mass is given by the ‘continuity equation’ as

\[ \partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0, \]  

(2.1)

where \( \rho \) is fluid density, and \( \mathbf{u} \) refers to the fluid velocity. It is noted that Eq. (2.1) is locally valid in the continuum level, and not beyond that. A fluid is called ‘incompressible’ if spatial and temporal variations of fluid density can be neglected. This is, e.g, the case if fluid velocity is small as compared to speed of sound, small Mach number limit (Mach number is the ratio of fluid velocity and speed of sound in the fluid, see also Eq. (2.3)). Note that in this case, even an ideal gas can be considered as an incompressible fluid. Note, however, that due to their higher sound velocity, liquids do more easily reach the incompressible limit rather than dilute gases. Note also that, in the incompressible limit, the fluid density \( \rho \) is treated as a trivial constant and thus independent of the fluid pressure \( p \). For an incompressible fluid, the continuity equation, Eq. (2.1), takes the simple form of

\[ \nabla \cdot \mathbf{u} = 0. \]  

(incompressible fluid)  

(2.2)

In a compressible fluid, infinitesimal changes in the pressure and density propagate with the speed of sound, \( c_s \), given by

\[ c_s = \sqrt{\frac{\partial p}{\partial \rho}}. \]  

(at constant entropy)  

(2.3)
2.1.2 Momentum conservation

The momentum conservation in the fluid mechanics leads to the general form of the well-known Navier-Stokes equation as

$$\partial_t (\rho u) + \nabla \cdot (\rho uu - \tau) = \rho g,$$

(2.4)

where $I$ is the identity matrix and the product $\rho g$ refers to an external force density ($g$ can be, e.g., the gravitational acceleration). The deviatoric stress tensor $\tau$, for a Newtonian fluid, is given by

$$\tau = -(p + \lambda \nabla \cdot u)I + 2\eta S,$$

(2.5)

in which $\eta$ and $\lambda$ are dynamic and bulk viscosities, respectively, and $S$ represents the strain rate tensor defined as

$$S = \frac{1}{2} (\nabla u + (\nabla u)^T).$$

(2.6)

In the above equation $(\nabla u)^T$ is the transpose of $\nabla u$. For an incompressible fluid (see Eq. (2.2)), Eq. (2.4) takes a simpler form of

$$\rho (\partial_t u + (u \cdot \nabla) u) = -\nabla p + \nabla \cdot \sigma + \rho g,$$

(2.7)

where the symbol $\sigma = 2\eta S$ is the so-called (viscous) stress tensor.

The dynamic viscosity $\eta$ is a measure of material resistance against applied stresses, and may vary strongly with temperature. Depending on the considered problem, the kinematic viscosity $\nu = \eta/\rho$ is sometimes a more relevant quantity for characterizing fluid flows. In the limit of $\eta \to 0$ the viscous term in Eq. (2.7), $\nabla \cdot \sigma$, drops out and the ‘Euler equation’ is obtained which describes the dynamics of inviscid fluids. For an incompressible fluid, one can define a ‘mean pressure’ or ‘mechanical pressure’ as $\tilde{p} = -\tau_{ii}/3$ in which the Einstein notation for the sum over repeated indices is used. However, since there is no equation of state determining the absolute value of the thermodynamic pressure in this case, only the gradient of pressure can be determined from Eq. (2.7).

In the fluid mechanics, it is more convenient to work with dimensionless equations. For this purpose, introducing a characteristic length and time
scales, $l_0$ and $t_0$ respectively, is usually sufficient. For example, the dimensionless form of the incompressible Navier-Stokes equation is given by

$$\partial_\hat{t} \hat{u} + (\hat{u} \cdot \hat{\nabla}) \hat{u} = -\hat{\nabla} \hat{p} + \frac{1}{Re} \hat{\nabla}^2 \hat{u} + \hat{g}, \tag{2.8}$$

where the dimensionless variables are defined as $\hat{t} = t/t_0$, $\hat{l} = l/l_0$, $\hat{u} = t_0 u/l_0$, $\hat{p} = t_0^2 p/(l_0^2 \rho)$, and $\hat{g} = t_0^2 g/l_0$. Similarly, the dimensionless operators $\hat{\nabla}$ and $\hat{\partial}_t$ are also written as $\hat{\nabla} = l_0 \nabla$ and $\hat{\partial}_t = t_0 \partial_{t_0}$, respectively.

The Reynolds number, Re, appeared in Eq. (2.8) is given by

$$Re = \frac{l_0^2}{t_0 \nu} \approx \frac{l_0 u_0}{\nu}, \tag{2.9}$$

where $u_0 = l_0/t_0$ is a characteristic velocity. It is easy to see that Re, in fact, is the ratio of kinetic energy and viscous energy.

Eq. (2.8) shows the similarity of the flow behavior in situations with the same Reynolds number and similar geometries (boundary conditions). The magnitude of Reynolds number determines, to a large extent, whether the flow is fully viscous, transient or turbulent. The exact numerical values of Re for these different flow regimes depends on the flow geometry. Navier-Stokes equation for steady flows with small Reynolds numbers reduces to the Stokes equation

$$\eta \nabla^2 u - \nabla p = 0, \tag{2.10}$$

which is the governing equation for many cases in micro-fluidics.

Another important dimensionless number is a the Weber number, We, given by

$$We = \frac{\rho l_0 u_0^2}{\gamma}, \tag{2.11}$$

where $\gamma$ refers to the surface tension. The We, in fact, is the ratio of inertial force and the surface forces.

### 2.1.3 Energy conservation

For non-isothermal flows, one needs to deal with energy conservation equation resulting from the first law of the thermodynamics. Since only isothermal
flows will be considered in this thesis, the energy conservation equation is presented here just for the sake of completeness. The energy conservation equation (commonly called the heat equation) is given by

\[ \rho \left( \frac{\partial E}{\partial t} + \nabla \cdot (E \mathbf{u}) \right) = -\nabla \cdot \mathbf{q} - p\nabla \cdot \mathbf{u} + \phi_{\text{vis}}, \]

which, in fact, is a balance of heat and the mechanical energy. In Eq. (2.12), \( \mathbf{q} \) is the heat flux vector (per unit area) relating to the temperature \( T \) as \( \mathbf{q} = -k \nabla T \) \((k \) is the thermal diffusivity), and \( E \) is the internal energy (per unit mass). The viscous heating term \( \phi_{\text{vis}} \) is the rate of viscous dissipation and presents a rate of gain of internal energy and the loss of mechanical energy and always has a positive value. However, it might be negligible if the flow velocity is low compared to the sound speed.

All the concepts and equations explained above can be found in standard text books on the fluid mechanics such as in references [26, 27].

### 2.2 Wetting

Wetting, in general, refers to the study of how a liquid spreads out on a solid (or liquid). This kind of spreading is extensively observed not only in daily life (e.g., rain drops on window), but also in many practical processes (e.g., ink jet printing) as well as in the nature (e.g., rise of sap in plants) [3, 28, 29].

Wetting can be considered in two types, total wetting and partial wetting, characterized by the ‘spreading parameter’, \( S \), as

\[ S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}), \]

where \( \gamma_{SV}, \gamma_{SL}, \) and \( \gamma_{LV} \) denote the surface tension of solid-vapor, solid-liquid, and liquid-vapor interface—with the dimension of energy per unit area—respectively. For the moment, consider a liquid droplet deposited on a perfectly flat and chemically homogeneous solid surface; if \( S > 0 \), the liquid completely spreads in order to lower its surface energy, and finally a film of nanoscopic thickness results. On the other hand, if \( S < 0 \), the liquid partially wets the solid and the final shape is either a spherical cap.
or a pancake (depending on the size of drop; see also below) with a specific equilibrium contact angle $\theta_{eq}$—also known as the Young contact angle—given by the Young equation [30]

$$\cos \theta_{eq} = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}. \tag{2.14}$$

A solid surface is called hydrophilic if $\theta_{eq} < 90^\circ$, and hydrophobic if $\theta_{eq} \geq 90^\circ$.

![Figure 2.1: Sketch of a liquid droplet on a perfectly flat substrate at equilibrium. A balance between the surface forces leads to the equilibrium contact angle $\theta_{eq}$.](image)

Obviously, the tendency of a liquid droplet to spread on a hydrophilic surface is higher than on a hydrophobic surface. In general, there are two forces responsible for adjusting the shape of drops, surface forces and body forces. Surface tension is responsible for the surface force, and often the gravity, $g$, acts as a body force. Equating these two forces, one can define the capillarity length $k^{-1}$ as

$$k^{-1} = \sqrt{\frac{\gamma_{LV}}{\rho g}}, \tag{2.15}$$

where $\rho$ is the fluid density [3, 31]. The distance $k^{-1}$ is generally of the order of a few mm. For drops with a radius $R \ll k^{-1}$ the surface forces are dominant and one can fully neglect the effects of gravity. In this case, the shape of droplet is a portion of a sphere (spherical cap). However, even if the condition $R < k^{-1}$ is met, one can safely neglect the effect of gravity. In the opposite limit of large droplets ($R \gg k^{-1}$) gravity dominates and the droplet takes the shape of a flat disc (pancake).
Up to now, the focus was on the perfectly flat (smooth) and chemically homogeneous substrates, but most of the solids are typically heterogeneous, and rough on the micro-scale. It has been shown that the surface roughness changes the wetting properties of the substrate. In the presence of roughnesses, the average value of the contact angle $\theta^*$, the so-called apparent contact angle, deviates from the equilibrium contact angle on a perfectly flat surface, $\theta_{eq}$. The simplest and most popular modification of the Young’s law for rough surfaces dates back to the works of Wenzel [32] and Cassie and Baxter [33], where the effect of roughness on wetting is assumed to be a mere change of the average surface areas involved in the problem. Assuming that the liquid completely penetrates into the roughness grooves (collapsed state), Wenzel obtained

$$\cos \theta_W^* = r \cos \theta_{eq},$$

(2.16)

for the apparent contact angle $\theta_W^*$. The roughness factor $r$ is the real solid area within a square of unit length. Cassie and Baxter, on the other hand, considered the case of a droplet pending on the top of roughness tips (suspended state) and obtained

$$\cos \theta_C^* = \phi \cos \theta_{eq} - (1 - \phi),$$

(2.17)

where the roughness density $\phi$ gives the fraction of the droplet’s base area, which is in contact with the solid. In this state, the ability of droplets to stick on the substrate dramatically decreases, leading to the remarkable mobility of droplets.

However, in the works of both Wenzel and Cassie-Baxter, it is assumed that the size of roughnesses are small enough compared to the size of drop. It is important to realize that both the Wenzel and the Cassie-Baxter equations do not explicitly take account of the three-phase contact line structure. This shortcoming may, however, be neglected as long as the contact area reflects the structure and energetics of the three-phase contact line [34].

The suspended state is often separated from the Wenzel state by a finite free energy barrier, which depends both on the droplet size and roughness characteristics [9, 12, 35]. This is a nice property of superhydrophobic surface
which does not allow the suspended droplets to spontaneously undergo a transition to the Wenzel state.

On a rough hydrophobic (superhydrophobic) substrate, the apparent contact angle of a droplet in the suspended state is typically higher than in the collapsed state [4, 36, 37]. Furthermore, the contact angle hysteresis significantly increases when a suspended droplet undergoes a transition to the Wenzel state [3, 5]. Indicative of stronger pinning [38] of the three-phase contact line, this feature reflects itself in a sticky behavior of liquid droplets in the collapsed state [4, 39] as compared to their high mobility in the suspended state.

It is worth introducing the Laplace pressure $\Delta P_L$, the pressure difference between two sides of a (curved) liquid-vapor interface [3]. This pressure difference, originated by $\gamma_{LV}$, is given by the Laplace formula as

$$\Delta P_L = \gamma_{LV}C_{\text{curv.}},$$

(2.18)

where $C_{\text{curv.}} = (1/R_1 + 1/R_2)$ is the curvature of the interface where $R_1$ and $R_2$ are the radii of curvature. For the special case of a flat interface both radii are infinite and therefore $\Delta P_L = 0$. In the other interesting case of a spherical interface, the both radii of curvature are identical and one obtains $\Delta P_L = 2\gamma_{LV}/R_1$. In 2D (or in the case of a cylindrical interface in 3D), however, there is only one relevant radius of curvature and the factor of 2 drops away leading to $\Delta P_L = \gamma_{LV}/R_1$. 

12
Chapter 3

The Lattice Boltzmann method

Modeling physics of fluids aiming to gain deeper insight as well as finding novel applications is at the central focus of many scientists and engineers. The lattice Boltzmann method (LBM) has recently emerged as an alternative and promising numerical method for modeling a wide range of fluid flows in both science and engineering ranging from turbulence and multi-phase flows to flow in porous media and suspensions of charged colloids [23–25, 40, 41].

Compared to other conventional methods, the LBM is particularly successful in modeling fluid flow applications dealing with complex boundaries and geometries as well as interfacial dynamics. The relatively simple and straightforward algorithm is another advantage of this method. It also benefits from its high efficiency on parallel machines.

Unlike conventional numerical models which discretize the appropriate set of partial differential equations of continuum fluid mechanics (see section 2.1), the LBM is based on a microscopic picture (collision and propagation of particles on a lattice) and discretization of the Boltzmann equation which is a (mesoscopic) kinetic equation. The LBM introduces a number of $q$ distribution functions (populations) $f_i$ ($i$ is lattice velocity index, $i = 0, 1, \ldots, q - 1$, and $q$ refers to the number of velocity directions in the LB model) for fictitious parcels of the fluid populated on lattice nodes (see fig. 3.1 for some possible lattices which guarantee the symmetry of fluid), and
then approximately solves the discrete Boltzmann equation [24, 25]. When dealing with fluid dynamical problems, the kinetic equations (e.g., the Boltzmann equation) provide a significant advantage over microscopic approaches such as Molecular Dynamics (MD) as it allows the study of larger systems and larger times as compared to MD. LBM, in fact, originates from the fact that the macroscopic dynamics of a fluid in the continuum level is the result of collective (coarse-grained) behavior of many individual particles and it hardly depends on the nature of the individual particles. Although the LBM is based on a bottom-up approach (particle picture), its major focus is on the averaged macroscopic—or a coarse-grained—behavior of fluid particles.

The discrete Boltzmann equation with Bhatnagar-Gross-Krook (BGK) collision operator [42] reads

$$\frac{\partial f^*(x, t)}{\partial t} + \nabla \cdot f^*(x, t) = \frac{1}{\tau^*} [f^*(x, t) - f_{eq}^*(x, t)], \quad (3.1)$$

where $f^*(x, t)$ is the local distribution function and the quantity $\tau^*$ is the relaxation time. Here the upper-index $^*$ is used to distinguish with the physical parameters in the Boltzmann equation and the corresponding LBM parameters given later on. The $f_{eq}^*$ refers to the equilibrium Maxwell-Boltzmann distribution function given by

$$f_{eq}^*(x, t) = \frac{\rho^*(x, t)}{(2\pi R T^*)^{3/2}} \exp(-\frac{m^*(c^* - u^*)^2}{2K_BT^*}), \quad (3.2)$$

where $m^*$ is the particle mass, $T^*$ stands for the temperature. $K_B, R,$ and $c^*$ refer to the Boltzmann constant, the universal gas constant and the microscopic velocity of fluid particles, respectively. The fluid density $\rho^*$ and the fluid velocity $u^*$ are given by

$$\rho^* = \int f^*(x, t) dc \quad \text{and} \quad (3.3)$$

$$u^* = \int f^*(x, t) c^* dc^*/\rho^*, \quad (3.4)$$

respectively.

Although it is possible to introduce the temperature in LBM via the heat equation [43, 44], Eq. (2.12), and even the thermal fluctuations [45, 46], but
the standard LBM simulates the isothermal flows. In this case, it is assumed that the temperature increase caused by viscous dissipation (heat production) is negligible and the thermal conductivity of the fluid is sufficiently high to maintain a constant temperature [47].

From here to the end of this section, all the equations are written for a fluid with an ideal gas equation of state (ideal fluid). In the following, the upper-index $^\ast$ is dropped out. The non-ideal fluids are considered in the next sections. In the LB simulations, $\Delta t$ and $\Delta x$ refer to the simulation time step and the lattice spacing, respectively. Here and in the following, $\Delta t$ and $\Delta x$ are set to $\Delta t \equiv 1$ and $\Delta x \equiv 1$ as in simulations. As already mentioned, the standard numerical scheme of the lattice Boltzmann method is based on iterations of two steps: (1) collision (relaxation) and (2) propagation (streaming). These two steps are given by

$$f_i'(x, t) = f_i(x, t) - \frac{1}{\tau} [f_i^{eq}(x, t) - f_i(x, t)] + f_i^F(x, t) \quad \text{and} \quad (3.5)$$

$$f_i(x + c_i, t + 1) = f_i'(x, t), \quad (3.6)$$

where $c_i$ refers to the LB velocity directions, $f_i$ is the LB distribution function (population) and $f_i'$ is the LB population after collision and before propagation (post-collision population). $f_i'$ is used here in order to separate the collision and propagation steps. In Eq. (3.5), the quantity $\tau$ is the so-called LB relaxation time which tunes the fluid kinematic viscosity $\nu$ via

$$\nu = (\tau - \frac{1}{2})c_s^2, \quad (3.7)$$

c_s is the so-called lattice sound speed and for all the lattices studied in this work $c_s^2 = 1/3$. In Eq. (3.5), $f_i^{eq}(x, t)$ is given by the Taylor expansion of the Maxwell-Boltzmann distribution function, Eq. (3.2), up to the second power of $\mathbf{u}$ as

$$f_i^{eq}(x, t) = \rho w_i \left(1 + \frac{\mathbf{c}_i \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{c}_i \cdot \mathbf{u})^2}{2c_s^4} - \frac{\mathbf{u} \cdot \mathbf{u}}{2c_s^2}\right), \quad (3.8)$$

and $f_i^F(x, t)$ introduces the (external) body force given by

$$f_i^F(x, t) = (1 - \frac{1}{2\tau}) \frac{(\mathbf{c}_i - \mathbf{u}) \cdot \mathbf{F}}{\rho c_s^2} f_i^{eq}, \quad (3.9)$$
in which \( F \) is the body force per unit volume (force density) \([48]\). Here, the fluid density \( \rho \) and fluid velocity \( u \) are given by

\[
\rho = \sum_i f_i \quad \text{and} \quad \rho u = \sum_i f_i c_i + \frac{F}{2},
\]

(3.10) \hspace{1cm} (3.11)

respectively, and the corresponding equation of state is \( p_t = c_s^2 \rho \) (\( p_t \) is the thermodynamic pressure). Here and in the following, the sum over \( i \) always runs from 0 to \( q - 1 \) if not otherwise stated.

Using the Chapman-Enskog analysis \([49]\), it can be shown that the Boltzmann equation with BGK collision operator recovers the nearly incompressible Navier-Stokes equations, Eqs. 2.1 and 2.4, in the limit of small Mach numbers \([22, 50]\). Interested reader can find details of the Chapman-Enskog expansion in \([47]\).

3.1 Two-phase single-component lattice Boltzmann models

A two-phase single-component LB model simulates a liquid-vapor system (non-ideal fluid) in which the liquid and the vapor coexist at equilibrium. Since throughout this thesis multi-component fluids are not considered, in
The Lattice Boltzmann method

the following, the term ‘two-phase LB models’ is simply used instead of the longer term ‘two-phase single-component LB models’. For fluids which have an analytical equation of state, similar to the van der Waals equation of state, the stability condition, \((\partial p/\partial V)_T < 0\) (\(p, V\) and \(T\) are the pressure, volume and temperature of the fluid) together with the Maxwell construction give the associated coexistence curve as function of \(T\) with a critical temperature \(T_c\) above which the liquid and vapor phases become indistinguishable from each other.

One of the possibilities to introduce non-ideal character into the lattice Boltzmann method is by introducing interaction forces between fluid particles. Each two-phase LB model obeys its own coexistence curve. In some models, however, the LB coexistence curve slightly deviates from the corresponding analytical coexistence curve. As already mentioned, although it is possible to consistently introduce the temperature into LB models, most standard LB models simulate isothermal flows at a constant temperature. Due to some numerical issues, the model may not numerically be stable for the whole range of possible temperatures, particularly at high Reynolds numbers. Therefore, finding an appropriate temperature range at which a LB code is numerically stable and thermodynamically consistent is an important issue. One further important feature of all two-phase LB models is that the interface spreads over a finite number of lattice nodes what is so-called ‘diffused interface model’. For obtaining reliable results, however, the interface width should be small compared to the smallest physical size of the problem. The density ratio is another important issue. Obviously, models with high density ratios are much closer to a realistic system.

In all these two-phase LB models, in principle, it is possible to introduce a substrate and the corresponding wetting boundary conditions. The solid phase can be, e.g, a (flat or rough) substrate, moving or fixed object, cylindrical or rectangular channel, porous media, or a combination thereof. In addition, a body force can be introduced to the two-phase LB models in a straightforward manner as in one-phase LB models (see Eqs. (3.9) and (3.5)). Moreover, implementing evaporation and condensation procedure, a well-known phenomenon for a liquid-vapor systems, is a simple task in two-phase
LB models which can be done by adding or extracting of the mass form the system in a quasi-static manner.

All two-phase LB models have an origin in the kinetic theory [51], but, in general, these models are developed based on two different approaches, free-energy based and force-based approaches. An overview of these models can be found in [52]. However, similar to any other model, each two-phase LB model has some advantages and disadvantages and is suitable for simulating a class of fluidic systems. Thus, depending on the problem that must be addressed, an appropriate model should be selected. In the following, three different two-phase LB models, employed for the simulations in this thesis, are briefly described.

### 3.2 The Swift approach

Here a short overview of a free-energy based two-phase LB model, first proposed by Swift [53, 54], is presented. After establishing the Galilean invariance [55], this model was developed further [56, 57] in order to take the wetting effect of the solid substrate into account. Since then, the approach has widely been used to study a number of problems such as stability and dynamics of droplets on topographically patterned hydrophobic substrates [57–59], effect of chemical surface patterning on droplet dynamics [59, 60] as well as chemical gradient induced separation of emulsions [61]. A detailed description of the method can be found in [56, 62].

Consider a liquid-vapor system in the presence of the solid. The equilibrium properties of this system can be obtained from the Ginzburg-Landau free-energy functional given by

\[
\Psi = \int_{V_{sys}} \left( \psi_b(\rho(x)) + \frac{\kappa}{2} (\partial_\alpha \rho(x))^2 \right) dV + \int_{S_{sub}} \psi_s dS, \tag{3.12}
\]

in which \(V_{sys}\) denotes the system volume, \(\rho(x)\) is the density of the fluid (either liquid or vapor) at point \(x\), the gradient parameter \(\kappa\) is a constant, and \(S_{sub}\) is the substrate surface area. Here and in the following, \(\alpha\), \(\beta\), and \(\gamma\)
The Lattice Boltzmann method refer to the Cartesian components \((x, y, z)\) and the Einstein convention (sum over the repeated indices) is used. In Eq. (3.12), in fact, \(\psi_b\) is the so-called bulk free energy density, and the second term in the first integral in Eq. (3.12) is the so-called interface term. One should, however, bear in mind that both \(\psi_b\) and \(\kappa(\partial_\alpha \rho(\mathbf{x}))^2/2\) contribute equally to the interface free energy. The last integral in Eq. (3.12), the \(\psi_s\) term, is the contribution of fluid-solid interface.

Considering a simple two phase model [56], \(\psi_b\) can be conveniently given in a double well form as

\[
\psi_b(\rho) = p_c(\nu_\rho + 1)^2(\nu_\rho^2 - 2\nu_\rho + 3 - 2\lambda \nu_T),
\]

in which \(\nu_\rho = (\rho - \rho_c)/\rho_c \) and \(\nu_T = (T_c - T)/T_c\) are the reduced density and reduced temperature, respectively. The critical density, pressure, and temperature are set to \(\rho_c = 7/2\), \(p_c = 1/8\), and \(T_c = 4/7\), respectively. Below \(T_c\), the model describes liquid-vapor coexistence with equilibrium liquid and vapor densities by

\[
\rho_L = \rho_c(1 + \sqrt{\lambda \nu_T}) \quad \text{and} \quad \rho_V = \rho_c(1 - \sqrt{\lambda \nu_T}),
\]

respectively. The parameter \(\lambda\) is related to the interface thickness \(D\) and the surface tension \(\gamma_{LV}\) via

\[
D = \sqrt{\kappa \rho_c^2/(4\lambda \nu_T \rho_c)} \quad \text{and} \quad \gamma_{LV} = 4/3 \sqrt{2\kappa \rho_c(\lambda \nu_T)^3/2 \rho_c}.
\]

The form of a planar interface is shown to be

\[
\rho = \rho_c(1 + \sqrt\lambda \nu_\rho \tanh[x/(\sqrt{2D})]),
\]

where \(x\) is the direction normal to the interface. It is mentioned here that due to the presence of two free parameters \(\kappa\) and \(\lambda\), the surface tension and interface width can be changed independently. Using Cahn-Hilliard approach [63], \(\psi_s\) is approximated as

\[
\psi_s = \phi_0 - \phi_1 \rho_s + \ldots,
\]

(3.19)
where \( \phi_0 \) and \( \phi_1 \) are two constants and \( \rho_s \) is the density of fluid on the solid substrate. Minimizing the free energy functional \( \Psi \), Eq. (3.12), subject to the approximation of \( \psi_s \) up to the linear term, \( \psi_s \approx \phi_0 - \phi_1 \rho_s \), one can obtain an equilibrium boundary condition for the spatial derivative of fluid density in the direction normal to the substrate, \( \partial_\perp \rho = -\phi_1 / \kappa \). In the derivative of \( \Psi \), the first term of \( \psi_s \) vanishes, and \( \phi_1 \) is related to the equilibrium contact angle, Eq. (2.14), via

\[
\phi_1 = 2\lambda_T \sqrt{2p_c \kappa \text{sign}\left( \frac{\pi}{2} - \theta_{eq} \right)} \sqrt{\cos \frac{\alpha^*}{3} - (1 - \cos \frac{\alpha^*}{3})},
\]

where \( \alpha^* = \cos^{-1}\left(\sin^2 \theta_{eq}\right) \), and the function ‘\( \text{sign} \)’ determines the sign of its argument. Considering average values for the corners, the above methodology has proved to be quite useful in the case of roughness patterns, which are made of piecewise planar surfaces as well. However, it is difficult to use this methodology for an arbitrary surface topography, since one would have to perform the awkward task of determining the surface normal vector.

This physical two-phase picture described by Eq. (3.12) is connected to the LB equation as follows. The hydrodynamics of this liquid-vapor system, as it is already known, is described by the Navier-Stokes equations, Eqs. 2.1 and 2.4. These equations in the component form read as

\[
\partial_t (\rho u_\alpha) + \partial_\beta (\rho u_\alpha u_\beta) = -\partial_\beta P_{\alpha\beta} + \nu \partial_\beta [\partial_\alpha u_\beta + \partial_\beta u_\alpha + \delta_{\beta\alpha} \partial_\gamma u_\gamma] + \rho g_\alpha \quad \text{and} \quad \partial_t \rho + \partial_\gamma (\rho u_\gamma) = 0,
\]

where \( g \) is a given acceleration such as gravitational acceleration. In this model, the phase separation occurs as a result of the choice of pressure tensor \( P_{\alpha\beta} \) obtained from the minimization of the free energy functional [55]. The pressure tensor, \( P_{\alpha\beta} \), is given by

\[
P_{\alpha\beta} = \frac{\partial \Omega^*}{\partial (\partial_\alpha \rho)} (\partial_\beta \rho) - \Omega^* \delta_{\alpha\beta},
\]

where \( \Omega^* = \psi_b(\rho) - \mu_b \rho + \kappa (\partial_\alpha \rho / 2)^2 \) and \( \mu_b = 4p_c(1 - \lambda \nu_T) / \rho_c \) is the bulk chemical potential [64]. The symbol \( \delta_{\alpha\beta} \) refers to the Kronecker delta function. For the choice of \( \psi_b \) given in Eq. (3.13), it results in

\[
P_{\alpha\beta} = p(x) \delta_{\alpha\beta} + \kappa (\partial_\alpha \rho) (\partial_\beta \rho),
\]
The Lattice Boltzmann method

where \( p(x) = p_t + \kappa \rho \nabla^2 \rho - \kappa/2(\partial_t \rho)^2 \) in which \( p_t \) is the thermodynamic pressure [28] and it is given by the equation of state of the fluid as

\[
p_t = \rho \partial_\rho \psi_b - \psi_b = p_c(\nu_\rho + 1)^2(3\nu_\rho^2 - 2\nu_\rho + 1 - 2\tau_\omega \lambda).
\]

(3.24)

In the Swift model, the lattice Boltzmann equation with BGK approximation [42] is written as

\[
f_i(x + c_i, t + 1) = f_i(x, t) - \frac{1}{\tau} (f_i(x, t) - f^{eq}_i(\rho, \mathbf{u})) + \frac{\rho w_{\sigma^*} c_i \alpha g_{\alpha}}{c_s^2}.
\]

(3.25)

In the preceding equation the index \( \sigma^* \) runs over the magnitude of the LB velocity vectors and \( w_{\sigma^*} \) depends on the underlying lattice. \( f_i \) is connected to the fluid density by \( \rho = \sum_i f_i \) and to the fluid velocity through \( \mathbf{u} = \sum_i f_i c_i \). Swift and coworkers have shown [54] that Eq. (3.25) recovers Navier-Stokes equations, Eq. (3.21) at small Mach numbers provided that the local equilibrium distribution function is chosen as

\[
f^{eq}_i = A_{\sigma^*} + B_{\sigma^*} u_\alpha c_\alpha + C_{\sigma^*} \mathbf{u} \cdot \mathbf{u} + D_{\sigma^*} u_\alpha u_\beta c_\alpha c_\beta + G_{\sigma^* \alpha \beta} c_\alpha c_\beta, \quad (i > 0)
\]

(3.26)

Putting the following constraints on the moments of \( f^{eq}_i \) (see [65, 66]),

\[
\sum_i f^{eq}_i = \rho, \quad \sum_i f^{eq}_i c_\alpha = \rho u_\alpha
\]

\[
\sum_i f^{eq}_i c_\alpha c_\beta = P_{\alpha \beta} + \rho u_\alpha u_\beta + \nu(u_\alpha \partial_\beta \rho + u_\beta \partial_\alpha \rho + u_\gamma \partial_\alpha \delta_{\alpha \beta})
\]

\[
\sum_i f^{eq}_i c_\alpha c_\beta c_\gamma = \frac{c_s^2 \rho}{3} (u_\alpha \delta_{\beta \gamma} + u_\beta \delta_{\alpha \gamma} + u_\gamma \delta_{\alpha \beta}).
\]

(3.27)

one can fully obtain the unknown coefficients \( A_{\sigma^*}, B_{\sigma^*}, C_{\sigma^*}, D_{\sigma^*}, \) and \( G_{\sigma^* \alpha \beta} \). Constraints on the zeroth and first moment of \( f^{eq}_i \) ensure that the collision term in Eq. (3.25) conserves mass and momentum. Constraint on the second moment guarantees that Eq. (3.25) correctly describes the hydrodynamics of a non-ideal fluid. The first term in this constraint bridges the free energy model and LB model, and the second term is to ensure the Galilean invariance of the LB equation in this model [55]. However, in order to determine all
the unknown coefficients, a constraint on the third moment of $f_{eq}^i$, the last
equation in Eqs. 3.27, is also needed. Now, all the coefficients in Eq. (3.26)
can be calculated as

$$A_{\sigma^*} = \frac{w_{\sigma^*}}{c_s^2} \left( \frac{p_t}{2} + \frac{\kappa}{2} (\partial_\alpha \rho)^2 - \kappa \rho \partial_\alpha \alpha \rho + \nu \partial_\alpha \rho \right)$$

$$B_{\sigma^*} = \frac{w_{\sigma^*} \rho}{c_s^2} \quad C_{\sigma^*} = -\frac{w_{\sigma^*} \rho}{2c_s^2} \quad D_{\sigma^*} = \frac{3w_{\sigma^*} \rho}{2c_s^4}$$

$$G_{1\gamma\gamma} = \frac{1}{2c_s^4} (\kappa (\partial_\gamma n)^2 + 2\nu u_\gamma \rho) \quad G_{2\gamma\gamma} = 0$$

$$G_{2\gamma\alpha} = \frac{1}{16c_s^4} (\kappa (\partial_\gamma (\rho \partial_\alpha \rho)) + \nu (u_\gamma \partial_\alpha \rho + u_\alpha \partial_\gamma \rho)) \quad (3.28)$$

Holdych and coworkers [55] have shown that Eq. (3.25) approximates the
continuity equation and at the same time the Navier-Stokes equations with
some error terms of the order of the second power of the Mach number. The
main advantage of this model over the Shan-Chen LBE method is that it
was formulated to account for equilibrium thermodynamics of non-ideal and
multi-component fluids at a fixed temperature, allowing thus to introduce
well-defined temperature and thermodynamics. The model is, therefore, con-
sistent with the ‘Maxwells equal-area reconstruction’ procedure [52].

### 3.3 The Shan-Chen approach

In order to achieve a two-phase LB model, Shan and Chen [67, 68] showed
that introducing a specific mean field cohesion force between fluid particles of
one-phase single component LB can successfully lead to phase separation. In
their seminal work, Shan and Chen describe the form of this mean field force
and give arguments how it is reflected in the thermodynamic pressure of the
system, giving rise to two coexisting liquid and vapor. Because of introducing
this mean field force between fluid particles, this approach is known as ‘force
based approach’. The form of this force acting on fluid particles is given by

$$F_{sc}(x, t) = -g_{sc} \psi_{sc}(x, t) \sum_i w_i \psi_{sc}(x + c_i, t) c_i \quad (3.29)$$

where $g_{sc}$ is the interaction strength, $\psi_{sc}(x, t)$ is the effective mass and $w_i$
has the same meaning as before used for the isotropic calculation of the force
The Lattice Boltzmann method

on the lattice. An appropriate choice of $\psi_{sc}$ that recovers the Shan-Chen equation of state [67, 68] is shown to be

$$\psi_{sc}(x, t) = 1 - e^{-\rho(x,t)}.$$ (3.30)

The full pressure tensor can be found by imposing mechanical equilibrium on a flat interface and then by expanding the force [68] as

$$P_{\alpha\beta} = \left[ c_s^2 \rho + 3g_{sc}\psi_{sc}^2 + \frac{1}{2} c_s^4 g_{sc} \psi_{sc} \Delta \psi_{sc} + \frac{c_s^4 g_{sc}}{4} |\Delta \psi_{sc}|^2 \right] \delta_{\alpha\beta} - \frac{1}{2} c_s^4 g_{sc} \partial_\alpha \psi_{sc} \partial_\beta \psi_{sc}.$$ (3.31)

The first two terms in the diagonal part of Eq. (3.31) describe the (bulk) thermodynamic pressure given by the non-ideal equation of state as

$$p_t = c_s^2 \rho + 3g_{sc}\psi_{sc}^2.$$ (3.32)

The surface tension for the flat interface between two phases is also given by

$$\gamma_{LV} = \frac{-g_{sc} c_s^4}{2} \int_{-\infty}^{+\infty} |\partial_y \psi_{sc}(\rho)|^2 dy$$ (3.33)

where the $y$ in the integral runs along the coordinate normal to the interface.

The main characteristic aspect of the Shan-Chen model, is the fact that the strength of the mean field force $g_{sc}$ fixes the values of the bulk liquid and vapor densities, surface tension and the pressure. In fig. 3.2(a) the coexistence curve of Eq. (3.32) as a function of the mean field force strength $g_{sc}$ is shown. In the original work of Shan-Chen [67, 68], the effect of the interactions are reflected on the properties of the fluid in a two step procedure. At first, the local momentum is shifted accordingly, in order to accommodate the change due to the mean field force

$$\rho u = \sum_i c_i f_i + \tau F_{sc}.$$ (3.34)

Then, in the second step, the local equilibrium distribution is evaluated with the updated velocity. This procedure, even though it incorporates the force
through a change in the momentum, produces densities for the bulk phases that not only depend on the value of the LB relaxation time \( \tau \), but also are inconsistent with the theoretical values that are obtained by the Maxwell construction of the Shan-Chen equation of state. To overcome such a difficulty, the action of the total force on every lattice node by shifting \([69]\) the local equilibrium distribution is implemented in order to accommodate the change in momentum, \( \Delta u = F_{sc}(x, t)/\rho \), that the force introduces locally in every time step. This method of incorporating the force is called exact difference method (EDM), because the change in the momentum is accommodated by the exact difference of equilibrium distributions. The rescaling of the distribution densities is done by evaluating the shift in the local equilibrium distribution along the direction \( i \) as

\[
\Delta f_i = f_i^{eq}(\rho, u + \Delta u) - f_i^{eq}(\rho, u)
\]

which can be further incorporated into the relaxation step

\[
f_i(x + c_i, t + 1) = f_i(x, t) - \frac{1}{\tau}(f_i(x, t) - f_i^{eq}(u, \rho)) + \Delta f_i.
\]

Within this method the local velocity is given by

\[
\rho u = \sum_i c_i f_i + \frac{1}{2} F_{sc}.
\]

The advantage of EDM is two-fold. Not only does it restore the \( \tau \)-independence of the densities of the vapor and the liquid phase for all values of \( \tau \); but it also reproduces the results of Maxwell construction for the same range of \( \tau \) with exceptional precision \([69, 70]\). To illustrate this aspect, simulations of a droplet of liquid surrounded by vapor with initial densities given by the Maxwell construction are performed. In fig. 3.2 (b), the values for the final vapor density for the two cases, along with the theoretical value calculated from the Maxwell construction, are plotted. From the plot, it is directly evident that the two methods coincide only for \( \tau = 1 \), where they both reproduce the correct vapor density as obtained from the Maxwell construction. For any other values of the relaxation time \( \tau \), EDM clearly captures the density value of the vapor phase correctly, while strong deviation from the expected value are observed in the Shan-Chen model.
A great advantage of the Shan-Chen model lies in the fact that arbitrary solid-boundary geometries can be introduced to the system quite easily allowing the study of liquid motion on any given solid surface. This is a highly desirable aspect for simulating fluidic systems with complex solid boundaries. A simple and at the same time powerful way to tune wetting property of the solid is to consider a solid node as fictitious immovable fluid point carrying a density \( \rho_w \), wall density, \( \left[71\right] \). Hence, regarding interactions, there is no difference between fluid and wall nodes and the surrounding liquid (vapor) creates a smooth interface which matches the fictitious wall density at the solid boundary. As a direct result, the solid-vapor and solid-liquid surface tensions can be calculated as integrals over the square of the density gradient and thus one obtains an expression for the equilibrium contact angle, Eq. (2.14), that is formed between solid and liquid (Young’s law)

\[
\cos \theta_{eq} = \frac{\int_{sv} |\partial_y \psi_{sc}(\rho)|^2 dy - \int_{sl} |\partial_y \psi_{sc}(\rho)|^2 dy}{\int_{lv} |\partial_y \psi_{sc}(\rho)|^2 dy},
\]

(3.38) where \( sl, sv \) and \( lv \) stand for the integral evaluation along the direction normal to the solid–liquid, solid–vapor and liquid–vapor interfaces, respectively \( \left[71\right] \). The two extreme cases of a liquid droplet fully wetting or dewetting on a perfectly flat surface \( \left[72\right] \), can be achieved by choosing the appropriate fictitious density for the wall boundaries, full wetting wall density, \( \rho_{wall}^w \), and full dewetting wall density, \( \rho_{wall}^d \), respectively. In this simple approach both density ratios, between liquid and vapor phases, and surface tension are fixed by the value of the interaction strength \( g_{sc} \) and therefore one has to evaluate the limiting values which lead to the extreme wetting cases, for the wall density \( \rho_w \) \( \left[71\right] \) beforehand. The calibration curve of the present LB code is shown in fig. 3.3, where measured contact angles fits to the simulated droplet shape of the three-phase contact line are compared to results obtained from the theoretical analysis of the simulated data via Eq. (3.38). The simulations are performed in 3D with a spherical droplet deposited on a flat substrate for various values of the fictitious density \( \rho_w \) of the flat substrate. A satisfactory agreement between the theoretical curve and the simulation results is observed, especially for the ranges that correspond to the hydrophobic case \( \left[73\right] \). The small deviations from the theoretical curve in the hydrophilic case can be attributed to the finite liquid–vapor interface thickness.
Figure 3.2: (a): Coexistence densities versus force coefficient $g_{sc}$ for the Shan-Chen equation of state. Solid lines denote analytic results obtained by Maxwell construction and red dots stand for lattice Boltzmann simulation results. (b): Lattice Boltzmann simulation results for the vapor density of a flat interface between vapor and liquid as a function of the relaxation time $\tau$. Two different implementations of force are compared, EDM and Shan-Chen (see the text). The dashed line denotes the value given by the Maxwell construction [71]. The size of simulation box is $L_x \times L_y = 200 \times 200$ ($D^2Q^9$), and the liquid droplet radius $R = 50$. Parameters of the simulation are $g_{sc} = -4.9$, $\rho_L = 1.818$, $\rho_V = 0.177$, the relaxation time $\tau$ is varied from 0.52 to 2.0.

3.4 The Lee-Fischer approach

The structure of The Lee-Fischer approach is somehow a combination of both the Swift and Shan-Chen approaches. It, in fact, is a free energy based approach as in the Swift model but, instead of modifying the equilibrium distribution, it introduces the interaction force between fluid particles in LB model similar to the Shan-Chen model.

As already mentioned, all two-phase LB models are diffuse interface models, and one undesirable feature of these methods is the existence of parasitic currents. These parasitic currents are small-amplitude velocity fields close to the interface. These parasitic currents are initiated by a slight imbalance between the interfacial stress term and the thermodynamic pressure-gradient term due to the truncation error. Aiming at both elimination of these undesirable parasitic currents and achieving a high density ratio, Lee and coworkers [48, 74] introduced a proper and compact isotropic discretizations for the directional and non-directional derivatives in the forcing term in order to solve
The Lattice Boltzmann method

Figure 3.3: Comparison of lattice Boltzmann simulations (red dots) with Eq. (3.38) (solid line). In the figure inlets two typical cross cuts of the droplet for the hydrophobic and hydrophilic limits, along with the density profile for the case of neutral wetting are plotted. The size of the simulation box is $120 \times 120 \times 50$. Simulation parameters are $R = 20, g_{sc} = -4.9, \rho_L = 1.818, \rho_V = 0.177, \tau = 1.0$ [73].

the discrete Boltzmann equation (DBE) for a non-ideal fluid with the BGK approximation. Similar to the Swift approach, the equilibrium properties of this model can be obtained from a free-energy-based functional consisting of a volume and a surface part. In the Swift approach, the equilibrium distribution is modified so that the pressure tensor is consistent with the pressure tensor derived from the minimization of the free energy functional. In the Lee-Fischer approach, on the other hand, an intermolecular interaction force is explicitly introduced in the discrete Boltzmann equation. The forcing term in this model is responsible for the phase separation, and is essentially the divergence of the pressure tensor, which itself results from a minimization of the free energy functional [75, 76].
Here an overview of the physical basis of this model is provided but readers are referred to the references [48, 74] for the discretization scheme and more details. The free energy functional in this model, as mentioned before, is the same as in the Swift model given by Eq. (3.12). The bulk free energy density, $\psi_b$, can be approximated [48] by

$$\psi_b(\rho) = \xi (\rho - \rho_V)^2(\rho - \rho_L)^2,$$

(3.39)

where $\xi$ is a constant and $\rho_L$ and $\rho_V$ are liquid and vapor densities. $\psi_b$ is related to the thermodynamic pressure $p_t$ by the equation of state

$$p_t = \rho \mu_0 - \psi_b,$$

(3.40)

where $\mu_0$ is the chemical potential defined as $\mu_0 = \partial \psi_b / \partial \rho$. The density profile across a planar interface at equilibrium is given [48] by

$$\rho(z) = \frac{\rho_L + \rho_V}{2} + \frac{\rho_L - \rho_V}{2} \tanh \left( \frac{2z}{D} \right),$$

(3.41)

where $z$ is the direction normal to the interface. Giving the input parameters $D$ (the interface width), $\xi$, $\rho_L$, and $\rho_V$, the gradient parameter $\kappa$ and the liquid-vapor surface tension $\gamma_{LV}$ can be computed [48] as

$$\kappa = \frac{\xi D^2 (\rho_L - \rho_V)^2}{8}$$

and

$$\gamma_{LV} = (\rho_L - \rho_V)^3 \sqrt{\frac{2 \kappa \xi}{6}},$$

(3.42) (3.43)

respectively. Minimizing the free energy functional $\Psi$, one will arrive at the equilibrium densities at the solid surface in contact with liquid and vapor phases as

$$\rho_{S,L} = \frac{(\rho_L + \rho_V)(\rho_L - \rho_V)}{2} \sqrt{1 + \Omega^*}$$

and

$$\rho_{S,V} = \frac{(\rho_L + \rho_V)(\rho_L - \rho_V)}{2} \sqrt{1 - \Omega^*},$$

(3.44) (3.45)

where $\Omega^*$ is given by

$$\Omega^* = 2 \text{sign} \left( \frac{\pi}{2} - \theta_{\text{eq}} \right) \times \left\{ \cos \left( \frac{\alpha^*}{3} \right) \left[ 1 - \cos \left( \frac{\alpha^*}{3} \right) \right]^2 \right\}^{1/2},$$

(3.46)
The Lattice Boltzmann method

where $\alpha^*$ has the same meaning as in the Swift model. This model, in a similar manner as in the Swift approach, is connected to an equilibrium boundary condition for the spatial derivative of fluid density in the direction normal to the substrate, $\partial_\bot \rho = -\phi^*/\kappa$, via $\Omega^* = 4\phi^*/(\rho_L - \rho_V)^2 \sqrt{2\kappa \xi}$. The discrete Boltzmann equation in this model is given [48] by

$$f_i(x + c_i t + 1) = f_i(x, t) - \frac{f_i - f_i^{eq}}{\tau} + \frac{(c_i - u) \cdot (F_{LF} + G)}{\rho c_s^2} f_i^{eq}, \quad (3.47)$$

where $G = \rho g$ presents a body force density with the acceleration of $g$. The equilibrium distribution function, $f_i^{eq}$, is given by Eq. (3.8).

In order to eliminate the parasitic currents, the averaged external force experienced by each particle $F_{LF}$ is written as

$$F_{LF} = \nabla \rho c_s^2 - \rho \nabla (\mu_0 - \kappa \nabla^2 \rho). \quad (3.48)$$

In the above, $F_{LF}$ models the intermolecular attraction and the effects of the exclusion volume of the molecules on the equilibrium properties of a dense gas, which is expressed in the potential form to avoid development of the parasitic currents. The advantage of this model compared to other two-phase LB models, as already mentioned, is both the elimination of parasite currents, one important step in calculation of viscous dissipation, and achieving a high density ratio which is not only more realistic but also efficiently reduces the effects arising from the flow of an abnormally dense vapor phase. One problem with this model is that some deviation in total mass due to the discretization scheme is observed. However, these deviations are not significant particularly in systems in which the velocity gradient is not very large. In this model, in order to get large equilibrium contact angles, one should consider terms with higher orders [77] in Eq. (3.19).

### 3.5 Viscous stress in two-phase LB models

In a two-phase LB model the computed viscous stress might be unreliable—particularly at the interface—if specific care is not considered. A feature of LB is the possibility of evaluating the viscous stress of the fluid through two
different routes; one can directly apply the finite-difference method on the
velocity field of the fluid and thereof calculate the viscous stress from the
macroscopic expression of the viscous stress (for a Newtonian fluid). In the
second route, which is unique in LB and computationally more efficient, one
can directly evaluate the viscous stress field via the second moment of the
distribution function as

$$
\sigma_{\alpha\beta} = - \left( 1 - \frac{1}{2} \right) \sum_i c_{i\alpha} c_{i\beta} (f_i - f_i^{eq}(\rho, \mathbf{u})) + \chi_{\alpha\beta},
$$

(3.49)
in which $\chi_{\alpha\beta}$ is a model dependent correction term [78], and can become
significant at the interface particularly if a large body force is applied. In
general, this correction term is given by

$$
\chi_{\alpha\beta} = - \frac{1}{3} \left( 1 - \frac{1}{2} \right) \sum_i c_{i\alpha} c_{i\beta} f_i^F,
$$

(3.50)
where $f_i^F$ is the forcing term in each model and accounts for both interaction
force and external body force. (see reference [78] for more details). For
example, in the Lee-Fischer model, the $f_i^F$ is the second term in the right
hand side of Eq. (3.47).

For a Poiseuille flow, a comparison between the computed viscous shear
from Eq. (3.50), the finite-difference method, and the exact analytical solu-
tion reveals that both the Lee-Fischer and the Shan-Chan approaches give ac-
curate results provided that the associated correction term is properly taken
into account [78]. The above arguments are taken into account in chapter 4
where the viscous dissipation inside a droplet is calculated using a LB code
based on the Lee-Fischer approach.

### 3.6 Units

In this thesis, all the quantities will be expressed in dimensionless LB units.
In order to express a simulation quantity with dimension $L^a T^b M^c$ in physical
units, it must be multiplied by $\Delta l^a \Delta t^b \Delta m^c$ where the scale factors for length
$\Delta l$, time $\Delta t$ and mass $\Delta m$ are fixed via comparison with a specific physical
system. However, bear in mind that an exact conversion to a specific material is not possible in the existent LB models due to the difficulties such as recovering the exact equation of state of the target material.
Chapter 4

Dynamics of droplets on flat substrates

In this chapter, dynamics of moving droplets on perfectly flat and homogeneous surfaces is addressed. Here, droplets are considered to move subject to a gravity-like body force on solid surfaces, and the dependence of steady velocity of droplets and dissipation loss inside droplets as well as droplet deformation on the system parameters are investigated both theoretically and via lattice Boltzmann simulations. Moreover, a detailed study of local dissipation loss inside droplet is performed and a simple model is suggested to relate steady velocity of moving droplets to the equilibrium contact angle.

4.1 Introduction

It is well known that liquid droplets on solid substrate move in response to an (external) potential gradient field provided that the driving force arising from this gradient field overcomes the resistance forces such as pinning. Surely, everybody has observed the falling droplets on the windowpane due to the gravitational potential on rainy days. These droplets fall at very different velocities depending on their sizes. Besides, some of smaller the droplets on the windowpane may stick on the windowpane and move only when another
It should be noted here that, interestingly, droplets may move not only in response to the gradient of external potential energy, e.g., gravitational field [79, 80] but also in situations where a gradient of surface energy exists. This chapter discusses the motion of droplet subject to the gravitational forcing, and the issue of droplet motion due to gradient of surface energy is postponed to chapter 5. Besides their frequent occurrence in nature, gravity driven droplets are important in some engineering applications, for example, condensation of vapor on a cold tube surface or coalescence of paint-droplets in the painting industry.

In contrast to resting droplets on solid surfaces (see section 2.2), the advancing contact angle is often found to be larger than the receding [72] in the case of moving droplets. This difference, known as the contact angle hysteresis, can be considered as a measure of droplet deformation and it may appear in characterizing droplet velocity [81]. Depending on the material parameters of the considered system such as dynamic viscosity \( \eta \), and \( \theta_{eq} \) as well as superhydrophobicity of the substrate, droplets show different behaviors. For example, they may perform a sliding, rolling, or tank treading motion or a combination thereof [82–84]. Associated to a very high external forcing (i.e., sufficiently large velocity), droplets are highly elongated (pearling) along the direction of the applied force and, further up, they exhibit a cuspid tail that...
emits smaller droplets and therefore change their velocities [79]. Introducing slippage at solid boundary on hydrophobic surfaces is another issue that helps to characterize droplet motion [85, 86].

Here, the focus is on the steady state motion of cylindrical droplets on flat substrates at low Reynolds numbers. The choice of cylindrical droplets is a simplification of the problem. However, the results can be generalized to spherical droplets. To underline this fact, a selected simulation for the case of spherical droplets are performed. The assumption of low Reynolds number is to ensure the absence of inertia which would give rise to additional source of dissipation, not considered in this study. Under these conditions, the fluid flow is expected not to be turbulent. Nevertheless, despite the apparent simplicity of the present problem, several issues such as dependence of center-of-mass velocity $U_{cm}$, and the dissipation loss on the material parameters and external forcing as well as the role of droplet deformation are still not fully understood [86]. The aim of this study is to address some aspects of these issues and to provide more insights to this problem. See fig. 4.1 for an illustration of the considered problem.

In the presence of a body force, a moving droplet on a solid surface reaches the steady state soon after a balance is established between the rate at which energy is imparted onto the droplet and the rate of energy dissipation. In general, there are different possible mechanisms for energy dissipation within a moving droplet: the viscous dissipation due to the velocity gradients of fluid particles, dissipation at the vicinity of the three-phase contact line which can occur itself in different ways such as due to the evaporation and condensation of three-phase contact line, and the dissipation in the precursor film which has a thickness of the order of nano-meter and may form around the droplet in contact with a solid [3, 72]. Since the numerical model that is employed here does not take account of precursor film, the focus of the present work is on the effects related to viscous dissipation only. This includes both the bulk of the droplet as well as the vicinity of the three-phase contact line.

For the case, a perfectly flat and chemically homogeneous substrate at sufficiently weak driving forces or small droplets, where the deformation of droplets can be safely neglected, the dependence of the center-of-mass ve-
locity on acceleration and droplet volume is worked out via rescaling the energy balance equation. This scaling relation in particular, it is found that the droplet velocity at the steady state is proportional to $\rho g R_{\text{eff}}^2/\eta$, where $g$ is the acceleration, e.g., gravitational acceleration, $R_{\text{eff}}$ the effective droplet radius—to be defined later on—$\rho$ the density of droplet, and $\eta$ is the dynamic viscosity of the droplet. Deviations from this simple behavior are observed in the case of strong droplet deformation which occurs for larger droplets or at high force densities. The energy dissipation is also studied by LB simulations. It is observed that the main part of dissipation takes place within a volume below the droplet’s center-of-mass. Based on this observation, a simple scaling formula is proposed which successfully captures the dependence of the droplet velocity on the equilibrium contact angle.

4.2 Numerical model

For the numeric part of this study a two-phase LB (D3Q19) code is employed. The code is based on the Lee-Fischer model which has been already introduced in section 3.4. As already mentioned, the main advantage of this model is the elimination of parasitic currents at the liquid-vapor interface allowing a reliable access to the entire velocity field inside of droplet, necessary for a calculation of the viscous dissipation inside the droplet. It should be noticed that in the presence of body force—in contrast to situations where the driving forces are capillary forces and the dynamics is slow—the finite size effect may play an important role at low density ratios. Achieving a high density ratio in this model, on the other hand, is another advantage which not only is more realistic and physically more acceptable, but also allows to significantly reduce the finite size effect related to the dissipation loss in the vapor phase. Because of both these advantages, this model is selected for the current study.

For the present simulations, a body force density (force per unit volume), $\rho g$, is applied to the liquid phase along the $z$-direction. The body force monotonously decreases to zero across the liquid-vapor interface. This accounts for the fact that the gas remains inert (static equilibrium) in the limit
Dynamics of droplets on flat substrates of zero droplet size. The LB parameters—which are all given in dimensionless LB units—are fixed as follows. The liquid and vapor densities are set to \( \rho_L = 1 \) and \( \rho_V = 0.01 \). The interface width \( D \) and the gradient parameter \( \xi \) are fixed to \( D = 5 \) and \( \xi = 0.01 \), respectively. This choice of parameters leads to \( \gamma_{LV} \approx 0.004 \) for all the simulations reported here. Depending on the case of interest, the parameters \( \theta_{eq}, R_{eff}, \tau, \) and \( g \) lie in the ranges \([35^\circ - 140^\circ], [22 - 75], [0.7 - 2.0], \) and \([10^{-7} - 10^{-5}], \) respectively. For droplets with axial symmetry (cylindrical droplets) a typical simulation box of the size \( L_x \times L_y \times L_z = 2 \times 120 \times 120 \) is used. However, for large droplets, the size of the simulation box is increased (in both the \( y \) and \( z \)-directions) ensuring that there are no finite size effects. In this case, the volume of droplet is given by \( V = S_{cyl} L_x \) where \( S_{cyl} \) is the surface of droplet’s cross-section normal to the \( x \)-direction. For the cylindrical geometry considered in this study, the droplet’s effective radius is defined as \( R_{eff} = (S_{cyl}/\pi)^{1/2} \). For spherical droplets with \( R_{eff} = (3V/4\pi)^{1/3} \) a simulation box of size \( L_x \times L_y \times L_z = 100 \times 120 \times 120 \) is used. In addition, the standard bounce-back rule is imposed at solid walls to obtain no-slip velocity conditions (zero fluid velocity at the walls) which is a well-known boundary condition and has been extensively tested and used in the literature \([87]\). For the open boundaries (in the \( x \) and \( z \)-directions), the periodic boundary condition is applied.

### 4.3 A simple scaling relation

Here, the effect of external forcing as well as the system parameters such as droplet size, characterized by \( R_{eff} \), on the steady velocity of cylindrical droplets on a flat surface is investigated. First, an analytical estimate based on scaling arguments is obtained which relates the steady velocity of droplet to the system parameters in the limit of negligible droplet deformation.

The external force does work on droplet with a rate equal to the total force applied on the droplet multiplied by the droplet’s center-of-mass velocity, \( g \rho V U_{cm} \). This, in fact, is the imparted energy to the droplet by the external body force. In the steady state, this energy is entirely transferred into dissipation. On the other hand, the total viscous dissipation \( \Phi_T \) inside
droplet is given by

$$\Phi_T = \int_V S_{ij} \sigma_{ij} dV,$$  \hfill (4.1)

where the $ij$-component of the strain rate, $S$, is given by $S_{ij} = (\partial u_i / \partial x_j + \partial u_j / \partial x_i) / 2$ and $\sigma_{ij}$ is the $ij$-component of the stress tensor, $\sigma$. The integration is over the entire volume of droplet. Due to the incompressibility of the fluid, the diagonal components of $\sigma$ do not contribute to the dissipation. One can thus restrict oneself to the case of viscous shear flow and write the stress tensor as $\sigma_{ij} = 2\eta S_{ij}$ and therefore obtain

$$g \rho V U_{cm} = \frac{1}{2\eta} \int \sigma_{ij} \sigma_{ij} dV = 2\eta \int S_{ij} S_{ij} dV. \hfill (4.2)$$

As long as the shape of the droplet is close to its equilibrium shape (in the limit of $g \to 0$), it is reasonable to take $R_{\text{eff}}$ as a characteristic length. For the flow inside droplet, the center-of-mass velocity is a characteristic velocity given by

$$U_{cm} = \frac{\int \mathbf{u}(\mathbf{r}) \rho dV}{\int \rho dV}, \hfill (4.3)$$

where $\mathbf{u}(\mathbf{r})$ is the velocity of fluid at point $\mathbf{r}$ and the integration is over the entire volume of droplet. Using $U_{cm}$ and $R_{\text{eff}}$, one can introduce dimensionless quantities such as $\hat{x}_\alpha = x_\alpha / R_{\text{eff}}$ and $\hat{u}_\alpha = u_\alpha / U_{cm}$ ($\alpha$ refers to $x$, $y$, and $z$ components). Using these rescaled quantities, the strain rate tensor can also be written as

$$S_{ij} = (U_{cm} / R_{\text{eff}})(\partial \hat{u}_i / \partial \hat{x}_j + \partial \hat{u}_j / \partial \hat{x}_i) / 2 = (U_{cm} / R_{\text{eff}})\hat{S}_{ij}. \hfill (4.4)$$

Inserting this into Eq. (4.2) yields

$$U_{cm} = \frac{g \rho R_{\text{eff}}^2}{2\eta \int \hat{S}_{ij} \hat{S}_{ij} dV} \propto \frac{g \rho R_{\text{eff}}^2}{\eta}. \hfill (4.5)$$

The proportionality relation is obtained by assuming that, in the case of an undeformed droplet subject to Stokes flow, the rescaled velocity field does not change upon a variation of the external force, droplet radius or viscosity. In the above model, the dependence of $U_{cm}$ on $R_{\text{eff}}^2$ arises from the rescaling of the strain rate tensor only and thus remains valid regardless of the
Dynamics of droplets on flat substrates

dimensionality of the space. However, when expressed in terms of droplet volume, the spatial dimension, $d$, does play a role. This is a consequence of the fact that $R_{\text{eff}} \propto V^{1/d}$. In particular, $U_{\text{cm}} \propto V$ in 2D, while $U_{\text{cm}} \propto V^{2/3}$ in 3D. In order to test the above assumption of the scale invariance, a series of lattice Boltzmann simulations are performed while varying $g$, $R_{\text{eff}}$ and $\eta$ separately, in a range where droplet shape remains unchanged. Results of this analysis are illustrated in fig. 4.2. In each case only one parameter is changed while the other parameters remain unchanged in order to see the effect of each parameter on the rescaled velocity-space field. As seen from this figure, the rescaled velocity fields are very close to each other almost in the entire droplet with deviations in the vicinity of the three-phase contact line. Noting that these deviations (being at most of the order of 10%) are limited to a small fraction of the droplet’s volume, the relative contribution of these deviations to the overall dissipation becomes quite negligible in all the cases shown. Indeed, a direct calculation of the rescaled integral appeared in Eq. (4.5) for different values of $g$, $\eta$ or $R_{\text{eff}}$ shows that the integral almost remains unchanged if the droplet deformation is negligible. Thus, the assumption of a scale invariant velocity field is a good approximation to the actual flow behavior in the studied parameter range.

The presence of a parameter range for the validity of Eq. (4.5) is evidenced in fig. 4.3, where the center-of-mass velocity $U_{\text{cm}}$ is depicted versus force density $g$ for different droplet sizes in panel (a), and $\eta U_{\text{cm}}/(g \rho R_{\text{eff}}^2)$ versus $g$ for different droplet sizes in panel (b). The quantity $\eta U_{\text{cm}}/(g \rho R_{\text{eff}}^2)$, in fact, is the twice of the rescaled integral appeared in Eq. (4.5) which is expected to be constant if the deformation can be neglected. As seen from this figure, the range of the validity of scaling relation Eq. (4.5) extends to larger $g$ as droplet size decreases. Conversely, the larger the droplet, the earlier the onset of significant deviations. A similar trend is also observed in fig. 4.4, where droplet size is varied as control parameter for three different choices of $g$. In both cases, fig. 4.3 and fig. 4.4, the deviations are accompanied by large droplet deformation.

The fig. 4.5 shows the momentum field inside the droplet. An observer moving with the droplet’s center-of-mass will confirm the presence of a well
established rotational flow. This is associated to the tendency of droplet to minimize its total dissipation loss \[83, 84\]. Interestingly, similar rolling motion are also observed in molecular dynamics simulations of polymeric liquids \[86\]. To be more precise, the motion in the upper part of droplet is dominated by a rolling flow, and the motion in the lower and close to the substrate dominated by a shear flow. In the next section, it is shown how this flow behavior reflects itself in the viscous dissipation inside droplet.

In fig. 4.5 panel (a), the body force is weak (note that the total body force is \(\rho V g\), but in fig. 4.5, the droplet volume is fixed and the force density is changed only), and the deformation is negligible; therefore, \(U_{cm}\) linearly depends on \(g\). In the middle panel, the droplet is driven by an intermediate body force, and the deformation becomes significant, so that deviations from the linear relation start to become visible (see fig. 4.3). In the panel (b), the
Dynamics of droplets on flat substrates

In the present study, the shape of droplet is determined by the competition between the surface force and the total body force. For a cylindrical droplet of the cross sectional radius $R_{\text{eff}}$ and axial length $L_x$, this leads to droplet is strongly deformed due to a sufficiently large body force and $U_{\text{cm}}$ in no longer proportional to $g$.

In the present study, the shape of droplet is determined by the competition between the surface force and the total body force. For a cylindrical droplet of the cross sectional radius $R_{\text{eff}}$ and axial length $L_x$, this leads to
Figure 4.5: Droplet shape and corresponding momentum field inside droplet for different force densities. In the left panel, the deformation is negligible and droplet is in the linear regime \((g = 10^{-7})\). The deformation becomes significant and droplet is in the transient regime in the middle panel \((g = 1.5 \times 10^{-6})\). Droplet is strongly deformed and lies in the nonlinear regime in the regime \((g = 4 \times 10^{-6})\). Other control parameters of the simulation are \(\eta = 0.16, R_{\text{eff}} = 28.2\) and \(\theta_{\text{eq}} = 90^\circ\).

\[ \gamma_{LV} L_x \leq g \rho R_{\text{eff}}^2 L_x \] as a condition for a significant deformation. By introducing the Bond number, \(Bo = \rho g R_{\text{eff}}^2 / \gamma_{LV}\), one sees that strong deformation is expected for \(Bo \geq 1\). Within prefactors of the order of unity, the same condition for droplet deformation is also obtained in the case of a spherical droplet (to see this, replace \(L_x\) by \(R_{\text{eff}}\)). As exemplified in fig. 4.5 (a), in all present studies, negligible deformation is associated with Bond numbers significantly below unity. Since the fluid viscosity \(\eta\) has no effect on the shape of droplet (see definition of the Bond number) the integral appeared in Eq. (4.5) remains unchanged upon a variation of \(\eta\). Thus, a perfect linear behavior is expected in the behavior of the center-of-mass velocity \(U_{\text{cm}}\) as a function of the viscosity. As illustrated in fig. 4.6, this expectation is nicely born out by the present computer simulations.

Here, one can also think of capillary number. The capillary number, \(\eta U_{\text{cm}} / \gamma_{LV}\), is almost orders of magnitude smaller than unity \((\sim 0.001-0.1)\) in these simu-
Dynamics of droplets on flat substrates

Figure 4.6: \( U_{\text{cm}} \) versus \( 1/\eta \) for droplets with different degrees of deformation. The labels (a)-(c) refer to deformation states shown in fig. 4.5, respectively (the velocity in the case (a) has been multiplied by a factor of 10 for better visibility). In all the cases shown, a perfect linear variation is seen in accordance with Eq. (4.5). In the left panel, simulation results for two different choice of \( R_{\text{eff}} \) and \( g \) is plotted keeping the product \( R_{\text{eff}}^2 g \) almost unchanged. In this case, the velocities of both droplets fall onto a single line which also confirms the validity of Eq. (4.5). \( \theta_{\text{eq}} \) is fixed to 90° in all cases.

4.4 Local and total viscous dissipation

This section, provides a detailed analysis of the local dissipation rate, \( \phi(r) = S_{ij} \sigma_{ij} \), inside droplet. As will be shown hereafter, the insight gained via these investigations enables one to propose a simple model capable of accounting for the dependence of the total dissipation rate, \( \Phi_T = \int \phi(r) d^3r \), on the contact angle, \( \theta_{\text{eq}} \). Equating this to the work done by the external force then yields a relation between the droplet’s center-of-mass velocity and the equilibrium contact angle.

It is noteworthy that, unlike conventional Navier-Stokes solvers, the lattice Boltzmann method does not require—although allows for—the computation of velocity gradients to obtain the local stress tensor. Rather, it offers the unique possibility of obtaining the stress tensor \textit{locally} via the non-equilibrium part of the populations. Noting that \( \phi(r) = S_{ij} \sigma_{ij} S_{ij} \sigma_{ij} / (2\eta) \), it
is thus possible within LB method to compute the local dissipation without any use of finite differences. In this regard, particular attention has been paid to a correct implementation of the stress computation (see section 3.5) as it is discussed in details in [78].

In order to figure out at which parts of droplet the energy is mainly dissipated, local dissipation rate is computed along the three lines labeled by A, B, and C in the panel (a) of fig. 4.7. The variation of $\phi(r)$ along these lines is depicted in the next panels of fig. 4.7. It is first noted that $\phi(r)$ is negligible in the gas phase, which is often the case in real experiments due to the low vapor pressure. Furthermore—as a comparison of the panels (a), (b) and (c) reveals—the strongest dissipation occurs in the vicinity of the three-phase contact line (panel (c)), which is roughly two orders of magnitude larger than the dissipation rate inside droplet (panel (b)). This behavior can be rationalized due to the fact that large velocity gradients occur near the substrate particularly in the vicinity of the three-phase contact line [88]. However, one must realize that bulk dissipation acts in a larger domain than the dissipation close to the contact line and thus may eventually dominate the overall dissipation rate if the droplet is sufficiently large.

An interesting feature, relevant for further analysis, is the fact that viscous dissipation inside droplet is mainly localized to regions below the droplet’s center-of-mass (panel (a) in fig. 4.7). This idea is further evidenced in fig. 4.8 (a), which shows the viscous dissipation integrated along a horizontal line, $\Phi(y) = \int_0^{L_z} \phi(y, z)dz$, as a function of vertical position $y$ (distance from the substrate). Indeed, as expected, viscous dissipation mainly occurs in a region specified by $y \leq Y_{cm}$ where the motion inside the droplet is dominated by shear flow (see fig. 4.5). This finding is further underlined by showing in fig. 4.8 (b) the relative contribution, $\Phi_R(y)$, to total dissipation within a region restricted between the substrate and a horizontal line at $y$, $\Phi_R(y) = \int_0^y \Phi(y')dy' / \int_0^{L_y} \Phi(y')dy'$. It is visible from fig. 4.8 (b) that 96% of total dissipation occurs in a region specified by $y \leq Y_{cm}$.

Before working out an important consequence of this observation, one must check whether the above statement remains valid upon a variation of driving force. Recalling Eqs. (4.2) and (4.5), the total dissipation rate is
Dynamics of droplets on flat substrates

Figure 4.7: (a): Illustration of the typical shape of a droplet and the lines along which viscous dissipation is determined (‘CM’ stands for the center-of-mass and $Y_{CM} \simeq 17$). The system parameters are $g = 10^{-7}$, $R_{eff} = 28.2$, $\eta = 0.16$, and $\theta_{eq} = 90^\circ$. (b-d): The variation of local viscous dissipation rate, $\phi = \sigma^2(r)/(2\eta)$, along lines A, B and C as indicated. Note that $\phi$ is almost negligible in the gas phase. It has a large value close to the substrate, but rapidly decreases far from the substrate. It is also highly enlarged in the vicinity of triple contact line.

expected to obey

$$
\Phi_T \propto g^2 \rho^2 R_{eff}^{2+d} \eta^{-1}.
$$

(4.6)

In order to verify Eq. (4.6), $\Phi(y)$ is determined for different values of $g$. Typical plots of the thus obtained results are shown in Fig. 4.9. These data clearly underline the validity of Eq. (4.6) within the studied range of parameters.
equation for a cylindrical droplet of axial length $L$ based on scaling arguments. To proceed, let us start with the energy balance.

**Figure 4.8:** Variation of the local dissipation rate $\Phi$ (panel (a)) and the relative dissipation rate $\Phi_R$ (panel (b)) as a function of $y$, corresponding to the droplet shown in Fig. 4.7. The main contribution to the total dissipation $\Phi_T$ occurs close to the substrate in a region given by $y \leq Y_{CM}$.

**Figure 4.9:** (a): Dissipation rate integrated along a horizontal line at $y$, $\Phi(y)$. (b): The same quantity as in the panel (a) but divided by $g^2$. The observed master curve supports the validity of Eq. (4.6).

In addition to supporting the validity of Eq. (4.6), the data shown in Fig. 4.9 provide further evidence for the fact that the most part of dissipation occurs in the region below the droplet’s center-of-mass. Based on this observation, a simple relation is proposed allowing to describe the dependence of droplet velocity on contact angle. The present simple analytic model is based on scaling arguments. To proceed, let us start with the energy balance equation for a cylindrical droplet of axial length $L_x$ in the steady state.
Dynamics of droplets on flat substrates

Thus, one obtains

\[ U_\text{as} = \theta \]

Neglecting droplet deformation, the droplet’s cross-section is a circular segment, but it allows to obtain a solvable analytic expression. Furthermore, the surface of the droplet below \( Y_{\text{cm}} \) is approximated as that of a rectangle of height \( Y_{\text{cm}} \) and length \( l_z \). Adopting this, the right hand side of the energy balance equation can now be estimated by

\[ (\eta/2)l_z Y_{\text{cm}} \times (U_{\text{cm}}/Y_{\text{cm}})^2 = (\eta/2)l_z U_{\text{cm}}^2 / Y_{\text{cm}}. \]

Thus, one obtains

\[ 2g \rho \pi R_{\text{eff}}^2 U_{\text{cm}} = \eta l_z U_{\text{cm}}^2 / Y_{\text{cm}}, \]
which finally yields

$$U_{cm} = 2g\rho \pi R_{\text{eff}}^2 Y_{cm}/(l_z \eta).$$

(4.11)

For the considered geometry (the cross section of droplets are a portion of circle with a contact angle of $\theta_{\text{eq}}$), the quantity $Y_{cm}/l_z$ is only a function of $\theta_{\text{eq}}$. Taking this into account, one finally arrives at

$$U_{cm} = C_{\text{fac.}} \frac{g\rho R_{\text{eff}}^2}{\eta} \left[ \frac{4 \sin^2 \theta_{\text{eq}}}{3(2\theta_{\text{eq}} - \sin 2\theta_{\text{eq}})} - \cot \theta_{\text{eq}} \right].$$

(4.12)

The validity of the model has been tested in fig. 4.11 for two different droplet radii. This simple model reproduces well the simulation results. Interestingly, the fitting prefactor, $C_{\text{fac.}}$, for both investigated droplet sizes are very close to each other (0.56 and 0.57) showing the consistency of the model. The systematic but negligible deviations at small contact angles in fig. 4.11 can be understood as follows: For droplets with small contact angles, the region above the center of mass can feel the presence of the substrate more significantly as compared to droplets of larger contact angle and, therefore, the contribution of the region below the center of mass in the total dissipation is slightly decreased (see fig. 4.8). This effect is reduced in the case of larger droplets, since the region above the center of mass is shifted further away from the substrate as droplet becomes larger. This argument thus also clarifies why the deviation at smaller contact angles in fig. 4.11 is more pronounced in the case of smaller droplet. It should be emphasized that the present approach is different from conventional approaches, where the integration is taken over the entire volume of droplet. Indeed, following the conventional route, one would obtain a different expression,

$$U_{cm} = C_{\text{fac.}} (g\rho R_{\text{eff}}^2/\eta) (1 - \cos \theta_{\text{eq}})^2/(\theta_{\text{eq}} - \sin \theta_{\text{eq}} \cos \theta_{\text{eq}}).$$

(4.13)

As shown in fig. 4.11, Eq. (4.13) is not successful in capturing the observed behavior.

It is noteworthy that an extension of Eq. (4.12) to 3D can simply be obtained by writing the energy balance equation in 3D and replacing the corresponding expression for $Y_{cm}/l_z$ by that of a spherical cap.
Dynamics of droplets on flat substrates

Figure 4.11: Droplet velocity versus equilibrium contact angle for two different droplet volumes as indicated. Full solid lines are best fit results to Eq. (4.12) while dashed lines give best fit results to Eq. (4.13) (see also the text). The force density and dynamic viscosity are fixed to $g = 10^{-7}$ and $\eta = 0.16$ respectively for both droplet sizes.

4.5 Similarity to the case of spherical droplets

Due to computational limitations, all the simulations had been so far performed for the case of cylindrical droplets. This is related to the fact that a systematic study—consisting of different series of simulations—of the obtained scaling equations using spherical droplets is computationally very expensive. But evidence both for rolling motion and the same dissipation loss behavior for the case of a driven spherical droplet can be obtained from a single simulation as shown in fig. 4.12.

4.6 Conclusion

A two-phase lattice Boltzmann method is used to study the dynamics of cylindrical droplets on a flat substrate in the Stokes limit (no inertia). Starting from the energy balance equation, a simple scaling relation, Eq. (4.5), is obtained indicating that droplet’s center-of-mass velocity scales linearly
Figure 4.12: (a): $yz$ momentum field in the plane cut at $x = Lx/2$ passing from the center of mass; a rolling motion similar to the case of cylindrical droplet is observed. (b): the relative dissipation rate $\Phi_R$ as a function of $y$ for the droplet shown in panel (a); similar to the cylindrical droplets, the main contribution to the total dissipation $\Phi_T$ occurs close to the substrate in a region given by $y \leq Y_{CM}$. The other parameters are as follows: $g = 10^{-7}$, $\eta = 0.16$, $\theta_{eq} = 90^\circ$ and $R_{eff} = (3V/4\pi)^{1/3} = 30$.

with force density and is proportional to the square of the droplet radius. At strong body forces or large droplet volumes, deviations occur which are closely associated with droplet deformation. A detailed study of the local dissipation inside droplet is also provided. A result of these investigations is that viscous dissipation mainly occurs close to the three-phase contact line and within a region below the droplet’s center-of-mass. Using the latter observation, a simple analytic expression is proposed accounting for the dependence of droplet velocity on the equilibrium contact angle. Results of LB simulations confirm the validity of this simple model.
Roughness-gradient–induced spontaneous motion of droplets

The focus of this chapter is on behavior of small droplets on rough surfaces with a gradient of roughness. More specifically, the effect of a step-wise change in the pillar density (roughness density) on the dynamics of droplets is investigated via three-dimensional lattice Boltzmann simulations. It is shown that the arrangement of pillars can play an important role on the behavior of droplets. For the same pillar density gradient but different pillar arrangements, both motion over the gradient zone as well as complete arrest are observed. In the moving case, the droplet velocity scales approximately linearly with the texture gradient. A simple model is provided reproducing the observed linear behavior. The model also predicts a linear dependence of droplet velocity on liquid-vapor surface tension. This prediction is clearly confirmed via the LB simulations for a wide range of liquid-vapor surface tensions.

5.1 Introduction

Apparently, fluid transport is a crucial issue in many practical processes involving fluids. In many cases, a convenient control of droplet transport can
become a challenging issue, for example, in chemical analytic and bioassay systems which have to rapidly respond and must be disposable and commercially inexpensive [29, 89]. In this regard, manipulation of droplet motion—which possess several benefits such as rapid mixing of fluids—is an active field of research for its promising applications in many micro-fluidic devices such as in droplet-based microfluidic laps-on-chips [90].

Various mechanisms for droplet manipulation on solid surfaces are mostly based on thermal, electrical, chemical approaches [91–95]. All these approaches give rise to a wettability gradient [96, 97], on which droplets (may) move spontaneously towards a guided route which is energetically more favorable. They thus have received significant attention in recent years for their applications in liquid directional, microfluidics fabrication [1, 98, 99], cell motility studies, micropump needles, biochips, and so on [100–106]. However, inherent problems and related difficulties, such as chemical compatibility, temperature rise, and interference of electric potential, might induce side effects and undesirable influences [89].

In this context, an alternative approach, the so-called ‘roughness-gradient approach’ may be employed to avoid at least some of these side effects. This

\[ \theta^*_{\text{C}}, \text{ Eq. (5.1)} \]

as function of \( \phi \) for different equilibrium contact angles.
approach is highly promising for finding novel applications and designing intelligent liquid in micro-devices. For example, He and Lee [107] presented a roughness-switchable device, comprising flat and roughened polydimethylsiloxane (PDMS).

In this chapter the focus is on roughness-gradient approach. More specifically, the behavior of droplets on a superhydrophobic substrate with a step gradient of roughness is addressed. While droplet behavior on homogeneous roughness has widely been investigated in the literature, only few works exist dealing with the case of inhomogeneous topography [89, 108–111]. To proceed, the main idea of this study is explained as follows. First, and throughout this chapter, it is assumed that the size of droplets considered here are smaller than the corresponding capillary length and therefore the surface forces are dominant, so that one can safely neglect the effect of gravity. As mentioned in section 2.2, droplets in the Cassie-Baxter state are highly mobile and this property can be used for an easier and faster droplet motion. The effective contact angle of droplets in the Cassie-Baxter state is given by

$$
\theta_C^* = \cos^{-1} [\phi \cos \theta_{eq} - (1 - \phi)],
$$

where $\theta_C^*$ is the effective contact angle and $\phi$ is the density roughness density, defined in the section 2.2, which is assumed to be constant. Here the question is: 'How does a droplet behave on a superhydrophobic substrate with a gradient of $\phi$?' From fig. 5.1, it is seen that $\theta_C^*$ monotonically decreases as a function of $\phi$. In the limit of $\phi \to 0$, the effective contact angle $\theta_C^*$ approaches $180^\circ$ which shows that, in this limit, the shape of droplet is a perfect sphere. The other limit, $\phi \to 1$, means that the surface is perfectly flat and the Young equation, Eq. (2.14), is recovered. As can clearly be seen from fig. 5.1, the smaller $\phi$ the larger $\theta_C^*$ and vice versa. In order to simplify the problem, a step-wise gradient of $\phi$ is considered. This is sketched in fig. 5.2 for a 2D case. As can be seen from the figure, the left side of the substrate has a smaller $\phi$ compared to the right and—according to Eq. (5.1)—appears to be more hydrophobic (larger $\theta_C^*$). In the other words the radius of the curvature at three-phase point R (receding point) is smaller than the radius of curvature at three-phase point A (advancing point). Using the equation of Laplace for the pressure, Eq. (2.18), and since the liquid-vapor surface tension is
constant, one sees that the pressure at point R must be larger than point A. This difference in the pressure imposes a driving force on the droplet, and a spontaneous droplet motion toward the right part of substrate with the larger $\phi$ is expected.

However, experimental observation of a roughness gradient induced spontaneous motion is not an easy task [110, 112]. The authors of [109, 110], for example, resort to shaking vertically the substrate in order to overcome pinning forces which lie at the heart of this difficulty.

Recently, a two-dimensional theoretical model is proposed aiming at a study of the present topic [111]. It seems that, however, computer simulations of the problem are lacking so far. The present work is aimed at filling this gap. A first direct numerical evidence for spontaneous droplet motion actuated by a gradient of pillar density is provided here. Furthermore, the influence of specific distribution/arrangement of roughness elements (pillars in the present case) on the behavior of the droplet is investigated. An important observation is that, depending on the specific arrangement of the pillars, both complete arrest and motion over the entire gradient zone can be observed for the same gradient of pillar density. This underlines the importance of the topography design for achieving highly mobile droplets. For the case of mobile droplets, a simple model for the dependence of droplet velocity on pillar density difference $\Delta \phi = \phi_{\text{Right}} - \phi_{\text{Left}}$ is provided. The model accounts for the observed linear dependence and predicts further that the velocity should scale linearly with the liquid-vapor surface tension. This prediction is also in line with the LB simulations for the studied range of parameters.

5.2 Numerical model

For the numerical part of this study, a D3Q19 LB code based on the Swift model, explained in Section 3.2, is employed. This model is a well-established two-phase LB model, particularly for two-phase system involved with wetting and capillary effects, and has been used for similar studies by other authors.
Figure 5.2: The sketch of problem for roughness-gradient–induced spontaneous motion on a superhydrophobic surface with a step gradient of roughness. The roughness (pillar) density increases from left to right giving rise to a deriving force along the same direction.

[9, 59–61, 113] The LB parameters in this model are set as follows. The LB relaxation time is set to $\tau = 0.8$ and the temperature is fixed to $T = 0.4$. For a typical choice of $\lambda = 0.1$, for example, this leads to the equilibrium liquid and vapor densities $\rho_L \approx 4.1$ and $\rho_V \approx 2.9$. Depending on the case of interest, $\kappa$ lies in the range $[0.002, 0.008]$ and the size of the simulation box is varied with values around $L_x \times L_y \times L_z = 125 \times 90 \times 90$ lattice nodes for spherical, and $L_x \times L_y \times L_z = 125 \times 25 \times 90$ for cylindrical droplets. All the LB parameters and results are given in dimensionless LB units. Periodic boundary conditions are applied in the $x$ and $y$-directions.

5.3 Results and discussion

As mentioned above, in the experimental reports which have considered the motion of a suspended droplet on surfaces with a gradient of texture, the behavior of droplets is not unique [89, 108–110]. This indicates that the roughness factor as well as the roughness density are not sufficient for a full characterization of a rough surface. Although Eq. (2.17) predicts a decrease of the effective contact angle upon an increase of roughness density and hence
a driving force along the gradient of $\phi$, the contact angle hysteresis [114] may be strong enough in order to prevent a spontaneous droplet motion [110].

The present work underlines this aspect by explicitly showing that the behavior of a droplet on substrates patterned by pillar microstructure with the same pillar density gradient, but different pillar geometries (e.g. rectangular posts with different pillar width and spacing) can be qualitatively different. While in the one case the droplet spontaneously moves due to the roughness gradient induced driving force, it may become arrested if an unfavorable geometry is chosen.

A simple way to study the effect of a gradient texture is to introduce an abrupt (stepwise) change in the roughness (pillar) density along a given spatial direction. Adopting this choice, a substrate divided into two regions is designed, each with a constant pillar density. In order to underline the crucial role of pillar arrangement on the behavior of droplet, two different cases of the same pillar density gradient as shown in fig. 5.3 are considered.

Using the two substrates shown in fig. 5.3, a series of lattice Boltzmann simulations is performed. At time $t = 0$ a spherical liquid droplet close to the top of the border line—which separates the two regions of different pillar density—is placed. It is noted that due to the initial deposition of the droplet with zero velocity and the proper choice of the height and distance of the posts and the equilibrium contact angle, the droplet remains on the top of the posts (Cassie and Baxter state) in the simulations [4]. A close look at the left panels in fig. 5.4 reveals that, both in the case of substrates A and B, the presence of a roughness gradient leads to an asymmetric spreading of droplet. However, despite this similarity of the dynamics at the early stages of spreading, the long time behavior of the droplet strongly depends on the specific arrangement of pillars. In particular, in the case of substrate A, the droplet motion is stopped on the gradient zone, while in case of substrate B it completely reaches the more favorable region of higher $\phi$. A detailed comparison of the effects of arrangements A and B on pinning forces seems quite a complicated and demanding task. The motivation in presenting this comparison is basically to underline the important role of pillar arrangement for the observation of the desired effect (roughness-gradient induced motion). From
Roughness-gradient–induced spontaneous motion of droplets

Figure 5.3: Top view of two step gradient substrates. (a): (referred to as case A), the pillar density to the left side ($x < 50$) is $\phi_{\text{Left}} = 0.187$ (square posts of length $l_a = l_b = 3$) while it is set to $\phi_{\text{Right}} = 0.321$ on the right side ($x > 50$, rectangular posts of length $l_a = 9$ and width $l_b = 3$). The spacing distance of the pillars in the $x$-direction is $d_x = 5$ and in the $y$-direction is $d_y = 3$ overall on the substrate. The height of the posts is $h_c = 6$. (c): (case B) is obtained from A by shifting the posts on each second raw horizontally by an amount of $(l_a + d_x)/2$ with $d_x = 5$, $l_a = 3$ for $x < 50$ and $l_a = 9$ for $x > 50$. All lengths are given in LB units.

In order to study the effect of droplet shape on the above phenomenon, a set of simulations using a cylindrical droplet instead of a sphere is also
Figure 5.4: Initial setup and final states of a spherical droplet on substrates with an abrupt (step-wise) change of pillar density. The cases of substrates A and B (see fig. 5.3) are compared.

performed. Due to the periodic boundary condition, simulation of cylindrical droplets is computationally less expensive. The results of these simulations, shown in fig. 5.5, are in line with the case of spherical droplets.

For further considerations, the substrate type B is used. The left panel of fig. 5.6 depicts the $xz$-cross section through the center of mass of a spherical droplet (here the radius of the spherical droplet is fixed to $R_\Omega = 40$) at different times during its motion over the step gradient zone (the pillar densities on the left and right halves of the substrate are fixed to $\phi_{\text{Left}} = 0.187$ and $\phi_{\text{Right}} = 0.375$). The corresponding footprint of the droplet (three-phase contact line) is shown in the panel (b) of fig. 5.6. The footprint of the
Figure 5.5: The same set of simulations as in fig. 5.4 but for the case of cylindrical droplets.

droplet reflects the geometry (shape and arrangement) of the posts. A trend towards increasing contact area is also observed in accordance with the lower effective contact angle in the right region (higher pillar density). A closer look at the footprints in fig. 5.6 (right panel) shows how the chess board-like arrangement of the posts allows the droplet to find the neighbor posts in the gradient direction. Next, substrate patterns of type B with various values of $\Delta \phi$ are created by keeping $\phi_{\text{Left}}$ unchanged and varying $\phi_{\text{Right}}$. Results on the dynamics of a cylindrical droplet on such texture gradient substrates are shown in fig. 5.7. A survey of the center-of-mass position versus time in fig. 5.7 reveals that the droplet motion is first linear in time until it reaches a constant value. The plateau corresponds to the case, where the droplet has completely left the region of lower pillar density. Since no driving force exists
Figure 5.6: (a): The $xz$-cross section of the liquid-vapor interface. (b): The corresponding footprint of a spherical droplet on a step gradient substrate. In the both panels, the time increases from left to right: $t = 5 \times 10^4$, $6 \times 10^5$, $1.2 \times 10^6$ and $2 \times 10^6$.

Figure 5.7: The $x$-component of the center-of-mass position versus time for a cylindrical droplet using, $\phi_{\text{Left}} = 0.187$ and $\phi_{\text{Right}} = 0.321$, 0.333, 0.35 and 0.375. The two group of curves belong to two different liquid-vapor surface tensions of $\gamma_{LV_0} = 5.4 \times 10^{-4}$ (LB units) (right; also labeled as (1) for further reference) and $4\gamma_{LV_0}$ (left).

in this state, the droplet stops and its velocity vanishes.

Using the linear part of the data shown in fig. 5.7, an average velocity for the motion of droplet’s center-of-mass upon the action of texture gradient forces is defined. Importantly, fig. 5.7 reveals the strong effect of the liquid-
**Roughness-gradient–induced spontaneous motion of droplets**

**Figure 5.8:** As the graph clearly shows, the function ‘\(\sin[x]\)’ approaches ‘\(\pi - x\)’ in the limit of \(x \to \pi\).

**Figure 5.9:** (a): Droplet’s center-of-mass velocity versus the difference in pillar density, \(\Delta \phi = \phi_{\text{Right}} - \phi_{\text{Left}}\), extracted from the linear part of the center-of-mass motion (see e.g. fig. 5.7). Results for three different liquid-vapor surface tensions are depicted. From top to bottom: \(4\gamma_{LVO}\), \(2\gamma_{LVO}\) and \(\gamma_{LVO}\), where \(\gamma_{LVO} = 5.4 \times 10^{-4}\) (LB units). In all cases, a linear variation is seen in accordance with the simple model, Eq. (5.14).

(b): A further test of Eq. (5.14), where the dependence of droplet velocity on the liquid-vapor surface tension is shown for a fixed \(\Delta \phi\).

Vapor surface tension on droplet dynamics. Both absolute values of droplet velocity for a given \(\Delta \phi\) as well as the slope of the data significantly depend upon liquid-vapor surface tension \(\gamma_{LV}\).

In order to rationalize these observations, a simple model based on scaling
arguments is provided. For the sake of simplicity, pinning effects are not considered here. Assuming $\theta_{eq} \simeq 90^\circ$ (which is the case in the simulations) and by neglecting $\phi \cos \theta_{eq}$ in the Cassie-Baxter equation, Eq. (5.1), together with the fact that $\phi^2 \ll \phi$, one can easily obtain

$$\sin \theta_C^* \propto \phi^{1/2}.$$  \hspace{1cm} (5.2)

To proceed further, the approximation $\sin \theta_C^* \simeq \pi - \theta_C^*$ is used \[110\] which is only valid when $\theta_C^*$ is close to $\pi$. This approximation has been illustrated in fig. 5.8. The assumption $\theta_C^* \simeq \pi$ is originated from the fact that the superhydrophobic surfaces result in large effective contact angles. By this, one arrives at

$$\pi - \theta_C^* \propto \phi^{1/2}.$$  \hspace{1cm} (5.3)

On the other hand, derivative of the Cassie-Baxter equation, Eq. (5.1), similarly gives

$$-d\theta_C^* \propto \frac{d\phi}{\pi - \theta_C^*}.$$  \hspace{1cm} (5.4)

Noting that the flow considered here is in the viscous regime, one can neglect inertial terms in the Navier-Stokes equation, Eq. (2.4), for incompressible fluids and write for the steady state as

$$0 = -\nabla p + \eta \Delta u,$$  \hspace{1cm} (5.5)

where $u$ is the fluid velocity, $p$ is the hydrostatic pressure and $\eta$ the dynamic viscosity. The velocity $u$ varies only over a distance of the order of the droplet radius $R$, hence

$$\Delta u \sim u/R^2.$$  \hspace{1cm} (5.6)

On the other hand,

$$\nabla p \sim -dp_{\text{Laplace}}(\theta_C^*)/R = (\gamma_{LV}/R^2)dR/R,$$  \hspace{1cm} (5.7)

assuming that the driving force originates from the Laplace pressure variation (over a length of the order of $R$) within the droplet. Here, the possibility of
droplet’s rolling in this simple model is not considered. For the case of a cylindrical droplet of unit length, the condition of constant droplet volume reads

$$\Omega = R^2[\theta^*_C - \sin(2\theta^*_C)/2].$$  \hfill (5.8)

Derivative of the receding equation constrained with the constant $\Omega$ results in

$$-2R[\theta^*_C - \sin(2\theta^*_C)/2]dR = R^2[1 - \cos(2\theta^*_C)]d\theta^*_C.$$  \hfill (5.9)

Using Eq. (5.4) and the following estimates

$$\sin(2\theta^*_C)/2 = \sin\theta^*_C \cos\theta^*_C \simeq -(\pi - \theta^*_C)$$ \quad and \quad (5.10)

$$1 - \cos(2\theta^*_C) = 2(\sin\theta^*_C)^2 \simeq 2(\pi - \theta^*_C)^2$$  \hfill (5.11)

one obtains the relation

$$dR/R \sim (\pi - \theta^*_C)d\phi \sim \sqrt{\phi}d\phi,$$  \hfill (5.12)

where $\bar{\phi}$ is defined as $(\phi_{\text{Right}} + \phi_{\text{Left}})/2$. Putting all together and after a change of notation $d\phi \equiv \Delta \phi = \phi_{\text{Right}} - \phi_{\text{Left}}$, one arrives at

$$\eta u/R^2 \sim (\gamma_{LV}/R^2)\sqrt{\phi}\Delta \phi.$$  \hfill (5.13)

Hence,

$$u \sim \frac{\gamma_{LV}}{\eta} \sqrt{\phi}\Delta \phi.$$  \hfill (5.14)

Interestingly, despite different mechanisms at work, both Eq. (5.14) and Eq. (5) in [110] predict a linear dependence of droplet velocity on $\Delta \phi$. In [110], the lateral velocity is estimated from roughness gradient induced asymmetry of dewetting of a droplet, flattened due to impact. The situation considered here is different. There is no impact and hence a related flattening is absent in the present case. Furthermore, the dynamics which is studied here is in the viscous regime whereas the high impact velocity in [110] supports the relevance of inertia. These differences show up in different predictions regarding the dependence of the droplet velocity on surface tension, fluid viscosity and density. While Eq. (5) in [110] predicts a dependence on the
square root of $\gamma_{LV}$, Eq. (5.14) suggests that, in our case, a linear dependence on $\gamma_{LV}$ should be expected.

In addition, Eq. (5.14) is therefore examined not only with regard to the relation between droplet velocity $u$ and difference in roughness density $\Delta \phi$ (panel (a) in fig. 5.9) but also it is checked how $u$ changes upon a variation of the liquid-vapor surface tension $\gamma_{LV}$ for a fixed $\Delta \phi$. Results of this latter test are depicted in the right panel of fig. 5.9, confirming the expected linear dependence of $u$ on $\gamma_{LV}$. It is noteworthy that $\gamma_{LV}$ in the right panel of fig. 5.9 varies roughly by a factor of 10 so that a square root dependence can definitely be ruled out.

It is worth emphasizing that the above discussed linear relation between droplet velocity $u$ and difference in pillar density $\Delta \phi$ is expected to hold as long as pinning forces are weaker than texture gradient induced driving force. In this case, the specific details of pillar arrangement seem to modify the prefactors entering the scaling relation, Eq. (5.14), but not the predicted linear law. fig. 5.10 is devoted to this aspect. In this figure, the dependence of $u$ on $\Delta \phi$ is compared for two slightly different ways of realizing $\Delta \phi$: In (1) $\phi_{Left} = 0.187$ while $\phi_{Left} = 0.2$ in (2). All other aspects/parameters are identical. As a consequence, since the list of investigated $\phi_{Right}$ is exactly the same, slightly higher values of $\Delta \phi$ are realized in (1) as compared to (2). If the details of pillar arrangement were unimportant, all the velocity data obtained from these two series of simulations should lie on the same line. As shown in fig. 5.10, this is obviously not the case. Rather, the linear relation between $u$ and $\Delta \phi$ seems to hold independently for each studied case.

Next it is examined how the droplet’s contact area changes with time as the droplet moves on the gradient zone. This quantity is determined by simply counting the number of grid points beneath the droplet. The time evolution of the contact area is compared to that of the center-of-mass position in fig. 7.5 (panel (a)) for a spherical droplet of radius $R_\Omega = 36$. In contrast to the center-of-mass position, which increases monotonously with time, the area beneath the droplet exhibits irregularities and oscillations.

It is presumed that these irregularities and oscillations are closely related to
Roughness-gradient–induced spontaneous motion of droplets

Figure 5.10: (a): The $x$-component of the center-of-mass position versus time for a cylindrical droplet using, $\phi_{\text{Left}} = 0.2$ and $\phi_{\text{Right}} = 0.321, 0.333, 0.35$ and 0.375 $[\gamma_{LV} = \gamma_{LV0} = 5.4 \times 10^{-4}]$. (b): Droplet’s center-of-mass velocity extracted from the linear part of the data shown in the left panel and in fig. 5.7 (labeled as (1)).

Figure 5.11: (a): The contact area and the $x$-component of droplet’s center-of-mass position versus time. (b): Footprint of the droplet on the step gradient substrate for times $t_a$, $t_b$ and $t_c$ corresponding to the extrema of the contact area as labeled in the left panel.

the dynamics of three-phase contact line. This idea is confirmed by the plot in the right panel of fig. 7.5, where droplet’s footprint is shown for times $t_a$, $t_b$ and $t_c$ corresponding to the three extrema in the contact area labeled by ‘a’, ‘b’ and ‘c’. As seen from this plot, the increase of the droplet’s base area between times $t_a$ and $t_b$ is accompanied by a significant motion of the three-phase contact line on the right side of the footprint while it remains essentially pinned to the pillars on the left side (with the exception of depinning from the
left most pillar). The state ‘b’ is, however, energetically unfavorable due to a stretched shape of the contact line. The transition from ‘b’ to ‘c’ reduces this asymmetry, thereby leading to a smaller contact area at $t_c$. It is emphasized here that such local events are not included in the Cassie-Baxter picture, Eq. (2.17).

5.4 Conclusion

A two-phase lattice Boltzmann model is used to study the dynamic behavior of suspended droplets on patterned hydrophobic substrates with a step-wise change in pillar density. It is shown that the specific arrangement of pillars may play a significant role for the dynamics of the droplet on such substrates. In particular, varying the pillar arrangement while keeping the gradient of pillar density unchanged (fig. 5.3), it is shown that both full transport over the gradient zone as well as complete arrest between the two regions of different pillar density may occur (figs. 5.4 and 5.5).

The relation between the droplet motion and the gradient of pillar density is investigated, revealing a linear dependence for the range of parameters studied (figs. 5.7 and 5.9). A simple model is provided based on the balance between the viscous dissipation and the driving force, the latter assumed as the gradient of the internal droplet (Laplace) pressure (Eq. (5.14)). The model not only reproduces the observed dependence on the pillar density gradient but also predicts a linear dependence of the steady state droplet velocity on the liquid-vapor surface tension. This prediction is in line with results of lattice Boltzmann simulations, where the liquid-vapor surface tension is varied by roughly a factor of 10 (fig. 5.9).

Moreover, comparing droplet dynamics for two slightly different ways of realizing the gradient of texture, it is shown that the gradient in pillar density does not uniquely determine the droplet velocity. Rather, the way this gradient is implemented also matters to some extent (fig. 5.10).

A detailed survey of the contact line dynamics is also provided revealing interesting pinning and depinning events leading to small amplitude oscilla-
Roughness-gradient–induced spontaneous motion of droplets

tions of the droplet’s contact area during its motion over the gradient zone (fig. 7.5).
A hydrodynamic system which contains a liquid film suspending on a super hydrophobic substrate (Cassie-Baxter state) and a moving solid object is considered. The solid object is fully immersed in the film and approaches the substrate with a constant velocity. The pressure increase inside liquid film, induced by the motion of the solid object, may cause the suspended film to undergo a Cassie-Wenzel (CW) transition. This problem is first explained theoretically and the analytical predictions are examined by lattice Boltzmann simulations. The transition begins exactly at a point beneath the center of solid object where the pressure has its maximum value. This observation is in line with the theoretical prediction. For a circular object (a disk), the height of the object at which the transition occurs is predicted to be proportional to the product of the object velocity to the power of one third and the disk radius to the power of two third. Rather good agreement is found between these predictions and simulation results obtained for square-shaped moving solid object. The deviations are probably related to the fact that the simulations do not meet all conditions and assumptions in the theory.
Chapter 6

6.1 Introduction

As already mentioned in section 2.2, droplets are found to be in the Cassie-Baxter (suspended) [33] and Wenzel (collapsed) [32] states on super-hydrophobic surfaces, and these two states are separated by a free energy barrier. Due to interesting properties of suspended droplets, such as high mobility or small contact angle hysteresis, stabilizing droplets on the Cassie-Baxter state is of high interest for many micro-fluidic applications. The free energy barrier, however, in some cases, depending on the structure of substrate and the size of droplets, may not be sufficiently large impeding a CW transition in response to environmental effects such a condensation or vibration [12, 115]. Such a transition becomes a more important issue on superhydrophobic surfaces in the limit of dilute microstructures where Cassie-Baxter state should generally be metastable [116, 117]. There are different methods such as using surfaces with noncommunicating roughness elements to prevent a CW transition [118].

The focus of this chapter is on a new problem regarding the CW transition due to the motion of a solid object in a thin liquid film on a super-hydrodynamic surface decorated with parallel stripes (see fig. 6.1 for illustration of the situation considered in the present work). Here, a liquid film is considered to simplify the problem. More specifically, additional mechanisms for dissipation related to the meniscus are neglected [119, 120]. It is also assumed that the film is initially in a Cassie-Baxter state and a CW transition may occur only to the effects related to the motion of the solid object.

The problem of a thin liquid film confined between two moving solids dates back to the pioneering work of Reynolds [121]. In this regard, for the case of a circular disk of radius $R_d$ approaching a smooth (solid) surface with a constant velocity $U_d$, the so-called Reynolds problem, applying lubrication theory and solving the creeping flow equations leads [121] to

$$F_R = \frac{3}{2} \pi \eta U_d \frac{R_d^4}{H^3},$$

provided that

$$\frac{\rho U_d H}{\eta} \ll 1,$$

where $F_R$ is the hydrodynamic resistance force imposed by the fluid on the disk, the so-called Reynolds force, and $H$ is the distance between the disk and
Cassie-Wenzel transition in Reynolds problem

the substrate. However, it has been shown that in case of a superhydrophobic surface, this resistance force is modified \[122\] as

\[
F_r = f_{eff}^* F_R = \left( \frac{b + H}{4b + H} \right) \left( \frac{3}{2} \pi \eta U_d \frac{R_d^4}{H^3} \right), \tag{6.2}
\]

where \( f_{eff}^* \) is the correction coefficient and \( b \) is the slip length defined as the distance between the solid and the point at which the flow profile extrapolates to zero. In general, the slip length \( b \) can be a function of \( H \) \[85, 123\]. For superhydrophobic surfaces, \( b > 0 \) (of the order of nano-meter to micro-meter), therefore \( f_{eff}^* < 1 \), and consequently the resistance force reduces. The force exerting on the superhydrophobic surface which may cause a CW transition is the opposite of the hydrodynamic resistance force \( F_r \).

\[\text{Figure 6.1: Sketch of the studied system used in the analytical analysis (see section 6.2). Here, } F_r \text{ is the resistant force imposed by the fluid on the moving disk; } U_d \text{ is disk velocity and } R_d \text{ is disk radius.}\]

### 6.2 Theoretical solution to the problem

Here, the system considered in the theory is sketched and briefly explained. Consider a circular hydrophilic disk of radius \( R \), which is parallel and close to a superhydrophobic substrate (see fig. 6.1). Surfaces are immersed into viscous Newtonian liquid, and the pressure at the edge of the disk is atmospheric \( (p = p_0) \). The disk moves towards the superhydrophobic substrate

\[1\text{Aleksey V. Belyaev and Olga I. Vinogradova, private communication (2011)}\]
with a constant speed $U_d$. This movement causes pressure increase in the liquid film between approaching surfaces. Maximal pressure is attained on the symmetric axis of system’s symmetry [124], and it is given by

$$p_{\text{max}} = p_0 + \frac{U_d R_d^2}{2(C_x + C_y)},$$  \hspace{1cm} (6.3)

where $p_0$ is hydrostatic pressure in liquid far from the disk and

$$C_x + C_y = \frac{H^3}{6\eta f_{eff}^*},$$  \hspace{1cm} (6.4)

where $\eta$ is the dynamic viscosity of the liquid. A pressure balance requires

$$p = p_{\text{gas}} + \frac{\gamma_{LV}}{r},$$  \hspace{1cm} (6.5)

in which $p_{\text{gas}}$ is the pressure in the trapped gas, $p$ stands for the local pressure in the film, $r$ is curvature radius of the meniscus and $\gamma_{LV}$ presents the liquid-vapor surface tension. From the above argument, a possible CW transition would begin at center of the disk. $p_{\text{gas}}$ can be determined if $U_d = 0$. A condition for the CW transition requires

$$p_{\text{gas}} = p_{\text{max}} - \frac{\gamma_{LV}}{r}.$$  \hspace{1cm} (6.6)

Assuming a flat liquid-vapor interface ($r \to \infty$), for an immobile disk, one obtains $p_{\text{gas}} \approx p_0$ and, therefore, $r$ can be estimated as

$$r \approx \frac{2\gamma_{LV}(C_x + C_y)}{U_d R_d^2 R_d^2}.$$  \hspace{1cm} (6.7)

Comparing the surface energy of the Cassie-Baxter state and the Wenzel state per unit length along the stripes, a condition for the transition can be obtained as

$$\frac{\delta}{2r} \leq \sin \left( \left| \cos \theta_{eq} \right| \frac{2e + \delta}{2r} \right),$$  \hspace{1cm} (6.8)

where $\gamma$ and $\epsilon$ are the distance and the height of the stripes (see fig. 6.1), respectively. The critical velocity for the transition, $U_{cr}$, can be obtained from an equation of the form

$$X = \sin(\lambda_X X), \quad X \leq 1.$$  \hspace{1cm} (6.9)

For $\lambda_X > 1$, nontrivial solution gives the critical velocity $U_{cr}$ as

$$U_{cr} \propto H^3 \gamma_{LV} / \delta R_d^2 \eta.$$  \hspace{1cm} (6.10)
6.3 Numerical model

In order to introduce a moving object into the LB model, a LB code should appropriately be modified. Fortunately, the problem of moving boundaries has been theoretically solved for a general case. The point is that, the momentum transferred into the fluid due to the moving boundary must correctly be introduced in LB models. In fact, the populations residing on the neighboring nodes of the boundary should appropriately be updated. For the sake of numerical simplicity, a mathematically thin solid square of zero thickness and impermeable to the fluid is considered. The solid square is immersed in the liquid and approaches the substrate with a constant velocity $U_p$ normal to the substrate. The square geometry allows for relatively simple implementation of boundary conditions. Applying the correct boundary condition is a crucial step and must be carefully done. A quadratic interpolation of bounce back rule on the solid square boundaries is imposed \[ f_i(r_j, t) = q^*(q^* + 1)\tilde{f}_i(r_j, t) + (1 - 4q^*2)\tilde{f}_i(r'_j, t) + q^*(1 - 2q^*)\tilde{f}_i(r''_j, t) - 2w_i\rho(c_i \cdot U_p)/c_s^2 \]

if $q^* < 1/2$ \hspace{1cm} (6.11)

\[ f_i(r_j, t) = (q^*/(q^* + 1))\tilde{f}_i(r_j, t) + ((2q^* - 1)/q^*)\tilde{f}_i(r'_j, t) - ((2q^* - 1)/(2q^* + 1))\tilde{f}_i(r''_j, t) - 2w_i\rho(c_i \cdot U_p)/(q^*(2q^* + 1)c_s^2) \]

if $q^* \geq 1/2$, \hspace{1cm} (6.12)

where $\tilde{i}$ stands for the velocity direction opposite to the $i$ and $q^*$ is the distance of the solid square from the nearest lattice node. $\tilde{f}_i$ denotes the post-collision distribution functions before propagation and $r_j$ is position of a lattice node. The distribution function of the first and second neighbors of a lattice node located at $r_j$ (along the direction of $i$) are given by

\[ f_i(r'_j, t) = f_i(r_j - c_i, t) \quad \text{and} \]

\[ f_i(r''_j, t) = f_i(r_j - 2c_i, t), \]

(6.13)

(6.14)
respectively. For this task, a D3Q19 Shan-Chen LB code based on the approach explained in section 3.3 is modified. The reason for the choice of the Shan-Chen approach is the simplicity in introducing the solid phase. However, since the implementation of corresponding moving boundary conditions, Eq. (6.11) and Eq. (6.12), for a circular disk is quite awkward, a square disk instead of a circular disk is implemented. If chosen sufficiently large, the shape of the disk should, however, not qualitatively change the CW transition in this problem. The implementation is such that one can control the velocity and size and the initial position of the disk. Having full periodic boundary condition in all directions, if the immersed moving disk fully fills the cross section of the simulation box, one should expect that the entire fluid moves with the velocity of the disk after a while. This test has been done as a benchmark test for a wide range of disk velocities. The obtained results are exactly according to the expectation, confirming a correct implementation of moving disk in the LB code.

Being interested on the effect of both size and velocity of the solid square on the CW transition, a specific superhydrophobic surface patterned with parallel stripes is fixed (see fig. 6.2 (a)) and correspondingly the velocity and size of the solid square are changed. In order to obtain reliable results, the velocity of the solid square must be small compared to sound speed (small Mach number). In addition, the simulation box should be large enough to reasonably reduce the finite size effects arising from the hydrodynamic interaction of the solid square with its periodic images. In order to avoid the unwanted effects of initially induced sound waves, the velocity of the solid square is gradually increased from zero to the target value. In all the results reported here, both acoustic and momentum diffusion time are at least by one order of magnitude smaller than traveling time of the solid square. These precautions allow of simulating a quasi-statistic process which is close to the situation considered in the theoretical analysis in section 6.2.

In the simulations, the interaction strength is fixed to $g_{sc} = 0.27$, giving rise to a liquid density of $\rho_L = 1.818$ and vapor density of $\rho_V = 0.134$. For this choice, one obtains full wetting for $\rho^w_{wall} = 1.75$ and the full dewetting limit for $\rho^d_{wall} = 0.25$. In addition, $\tau$ and $\rho_{wall}$ are set $\tau = 1.0$ and $\rho_{wall} = 0.65$. 
This value for $\rho_{\text{wall}}$ gives an equilibrium contact angle close to $105^\circ$ (see fig. 3.38). It should be noted that since the disk is fully immersed in the fluid, the chemical property of the disk, $\theta_{eq}$, is not important. All the LB parameters and results are given in dimensionless LB units.

6.4 Results and discussion

In fig. 6.2, a typical simulation of this phenomenon is illustrated. As seen from the figure, a CW transition due to the motion of solid square is observed. The CW transition occurs at a certain height, $H_{tr}$, for the selected values of the solid square width, $L_p$, and the solid square velocity, $U_p$. As predicted by the theory in section 6.3, the nucleation (transition) begins at a point on the substrate exactly beneath the center of the solid square (fig. 6.2 (d)). As soon as the transition begins, it propagates around the transition point, fig. 6.2 (e), and eventually extends to neighboring grooves such as in a domino, fig. 6.2 (f)-(h). The number of grooves that is fully wet depends on the system parameters.

In fig. 6.3, different cross sections of the velocity field for the case shown in fig. 6.2 (c) are plotted. The cross section of $zy$ velocity field in a plane cut at $x = Lx/2$ (across the stripes) is illustrated in fig. 6.3 (a). Similarly, fig. 6.3 (b) shows the $zx$ velocity field in the plane cut at $y = Ly/2$ (along the stripes). Both fig. 6.3 (a) and (b) show the presence of a rotational flow around the edges of the solid square. This results from the incompressibility of the fluid and the presence of the bottom substrate. The fluid which is pushed downward by the solid square must somehow move upward again in order to let density remain constant. In addition, a certain similarity is observed in the rotational flows in both directions, along and across the substrate. The reason for this symmetry is that the asymmetry in the velocity field induced close to the structured surface appears as a small perturbation and is rapidly decays away from the substrate due to the small height of the stripes compared to the height of this object. It can also be seen that a portion of fluid close to the solid square moves with almost the same velocity.
of the solid square. Furthermore, the most prominent forward flow is observed in a region around the center of the solid square. This justifies one of the basic assumptions of the theory namely that the CW transition is expected to occur at the center of the moving solid square. The $xy$ velocity field is plotted in the plane which contains the solid square, fig. 6.3 (c), and, also the same velocity field in the plane cut at $z = 10$, which touches the top of stripes, fig. 6.3 (d). From the panel (c), one can see that the velocity of fluid particles is almost zero along the direction tangential to the solid square (and close to it), particularly at the center of the solid square. An almost perfect symmetry is visible from fig. 6.3 (c). Although the pattern of flow close to the stripes, fig. 6.3 (d), is affected by the geometry of stripes because of the boundary conditions, an almost perfect symmetric flow far from the substrate is seen.

Although this phenomena can clearly be confirmed by the simulation shown in fig. 6.2 as indicated, but a larger system size and smaller ratio of $L_p/L_x$ can bring one closer to the ideal situation considered in section 6.3. For this purpose, two series of extensive simulations with a large system size ($L_x \times L_y \times L_z = 384 \times 384 \times 290$) are performed. In the present numerical scheme it is more convenient to vary $U_p$ and $L_p$ as control parameters and measure the resulting $H_{tr}$, the height at which the transition occurs. In order to compare the simulation results with Eq. (6.10), the numerical exponents $n$ and $m$ in the proportionally $H_{tr} \propto U_p^n L_p^m$ is determined. In the theory, the exponents $n$ and $m$ are analytically obtained to be $1/3$ and $2/3$, respectively. In fig. 6.4 (a) and (b), $H_{tr}$ as a function of both $U_p$ and $L_p$ are plotted. It should be remarked that different definitions of $H_{tr}$ give different consequences. Here, the simulation results are presented for two different definitions. In panels (a) and (b) the $H_{tr}$ is defined as the distance from the bottom of stripes to the position of the solid square. The simulation results are fitted to the functions $H_{tr} = C_m L_p^{2/3}$ and $H_{tr} = C_n U_p^{1/3}$ ($C_n$ and $C_m$ are two fitting prefactors) in panel (a) and panel (b), respectively. This definition is more logical since it arises from the fact that the transition begins as soon as the nucleation occurs at the bottom of groove. In addition, as the solid square moves, the flow is mainly reflected from the bottom of the substrate (note that $\delta \approx L_s$). In this case, a reasonable agreement with the theory is seen. It should be
mentioned that a perfect agreement is not expected since the simulations and the theoretical situations, however, are not exactly the same. A reason for the deviation might be the shape of the solid square. Here, a square shape is simulated while in the theory it is supposed to be a circular disk. In panels (c) and (d), on the other hand, the $H_{tr}$ is defined as the distance from the top of the stripes to the position of the solid square. This definition comes from the boundary condition where a slip length is introduced at top of stripes [124]. In this case, different exponents are obtained, i.e., $n \approx 0.5$ and $m \approx 0.8$ as a result of a best fit on the simulation results and clearly the agreement with Eq. (6.10) is not very good.

6.5 Conclusion

A two-phase lattice Boltzmann method based on the Shan-Chen approach is used to study a fluidic system consisting of a liquid film suspending on a superhydrophobic substrate and a moving solid square. The solid square is fully immersed in the film and approaches the substrate with a constant velocity normal to the substrate. The motion of the solid square gives rise to an excess pressure in the film. This causes the suspended film to undergo a CW transition. The transition begins exactly at a point beneath the center of the solid square where the pressure has its maximum value. This observation is in line with the theoretical prediction (see section 6.3). However, the height of the solid square at which the transition occurs depends on the system parameters. Analytically, it has been shown that this height is proportional to the product of the solid square velocity to the power of one third and the disk radius to the power of two third. The simulations, however, are in qualitative agreement with this theoretical prediction. Observed deviations might arise from the fact that the simulations do not meet all conditions and assumptions in the theory. In addition, the simulations confirm the formation of rotational flows induced by the motion of the solid square.
Figure 6.2: (a): The substrate considered in the simulations. The equilibrium contact angle, \( \theta_{eq} \), of the substrate is fixed to \( \simeq 105^\circ \) and the parameters \( L_s \), \( \delta \) and \( e \) are fixed to 18, 15 and 7, respectively (see fig. 6.1). (b)-(h): Time evolution of the liquid film as the solid square approaches the substrate. The liquid film undergoes a transition to the Wenzel state due to the impact of moving solid square in the panel (e). The size of simulation box and square solid square are \( L_x \times L_y \times L_z = 120 \times 120 \times 140 \) and \( L_p = 60 \), respectively. The velocity of the solid disk is \( U_p = 0.01 \).
Cassie-Wenzel transition in Reynolds problem

Figure 6.3: (a): $xz$ velocity field in the plane cut at $y = Ly/2$. (b): $yz$ velocity field in the plane cut at $x = Lx/2$. (c): $xy$ velocity field in the $xy$ plane which contains the solid square, and in the $xy$ plane cut at $z = 10$ in panel (d).

Figure 6.4: The height at which the transition occurs, $H_{tr}$, as a function of the solid square velocity, $U_p$, and the solid square width, $L_p$. In panel (a) and (b) the reference point is the bottom of stripes while in (c) and (d) it is the top of stripes (see the text).
Morphologies of small droplets on patterned hydrophobic substrates

For situations, in which the size of a droplet is comparable to the roughness scale of the solid substrate, possible wetting morphologies on patterned hydrophobic substrates are explored and their dependence on the initial droplet position, droplet volume and the surface geometry are investigated. For a regular array of cubical pillars, small perturbations of a symmetric droplet state are restored by capillary forces. Larger deviations, on the other hand, may lead to completely new morphologies. The results also suggest that the previously reported ‘reentrant transition’ upon quasi-static evaporation (a transition from the suspended state to partial penetration and then back to the suspended state) [reported in the refs. [9, 113]] is not restricted to a symmetric initial state but may occur for quite non-symmetric morphologies as well. In contrast, a change in the substrate geometry may lead to a completely different behavior, fully precluding the reentrant transition. This underlines the importance of substrate design for the use of reentrant transition as a self-cleaning mechanism.
7.1 Introduction

Wetting phenomena, as already mentioned, not only are observed in everyday life but also play an important role in many biological processes (for example, the self-cleaning property of plants) as well as technological applications (such as coating or painting) [3–5]. In the wetting phenomena often the surface forces are dominated and the structures of (solid) surface play an important role.

The equilibrium shape of small droplets is important in several micro/nano-fluidic devices such as ink-jet printing where micron-sized droplets must have a well defined shape and geometry by which one can measure the exact amount of the liquid contained, allowing the possibility of extracting and adding liquid in a convenient manner [1].

In fact, certain aspects of morphological wetting transitions of liquid drops on chemically structured surfaces (e.g. including hydrophilic and hydrophobic domains) and on topographically micro-structured surface (e.g. decorated by parallel grooves) have been already discussed in the literature [7, 8, 11, 61]. This chapter focuses on the equilibrium shapes (morphologies) of droplets and the associated transitions between these morphologies on topographically structured hydrophobic surface. However, in contrast to the typical studies on this subject, the size of droplets considered here are assumed to be of the order of surface roughness.

Study of the behavior of droplet on rough surfaces is an important field because almost all solids are rough on the micro-scale [126]. In addition, as already mentioned, there exist different techniques to create a desired topography on solid surfaces on the micro/nono-scale. It is well known that micro-structuring the surface can profoundly affect the wetting properties of solids [5, 127]. As explained in section 2.2, a droplet can usually reside on a rough surface in two different states. In the so-called collapsed or Wenzel state, the droplet penetrates into the roughness grooves and fully wets the substrate beneath it. In this state, the apparent contact angle is given by the Wenzel equation [32], Eq. (2.16). In the other state, the suspended (or Cassie-Baxter) state, the droplet resides on top of the roughness tips with-
Morphologies of small droplets on patterned hydrophobic substrates

out any contact to the bottom part of the substrate in which the apparent contact angle is given by the Cassie-Baxter equation \[ \text{[33], Eq. (2.17)} \]. These two equilibrium states correspond to local minima of the free energy, but the collapsed state is often energetically more stable and it is separated from the suspended state by a free energy barrier. These thermodynamic interpretations of the apparent contact angle are only valid as long as the contact area reflects the structure and energetics of the three phase contact line \[ \text{[34]} \]. Furthermore, the droplet should be large enough compared to the roughness scale so that the consideration of averaged quantities is sufficient.

Yet, in practice, the size of liquid droplets often changes due to the evaporation and condensation or after collision with a solid surface. Therefore, it is quite likely to find droplets whose sizes are of the order of roughness scale. Recent studies show that a change in droplet size might alter the final state of droplets deposited on structured hydrophobic surfaces \[ \text{[16, 58, 128]} \].

In the ref. \[ \text{[12]} \], Reyssat and coworkers considered the droplet size as a control parameter and observed a transition from suspended to collapsed state due to the evaporation. They explain this transition by considering the curvature of the liquid/vapor interface of air pockets beneath droplet and obtain a scaling criterion in terms of relevant characteristic lengths, i.e., droplet size, height and distance of micro pillars. Impact velocity or equivalently kinetic energy can also affect droplet’s behavior on superhydrophobic surfaces \[ \text{[119, 129]} \]. In this regard, Bartolo and coworkers suggest a threshold velocity based on a balance between dynamic and Laplace pressure \[ \text{[130]} \]. Below this threshold velocity, droplet bounces back, while it is partially pinned to the surface above this velocity. In all the mentioned references, characteristic lengths of micro-structured surface must be taken into account.

On the other hand, in the case of droplets comparable to the roughness scale, the specific geometry of the roughness also plays an important role and must therefore be taken into account explicitly. In fact, both topography and wetting of structured surface can be manipulated so that a desired morphology is obtained \[ \text{[131–133]} \]. Recently, focusing exactly on this problem, the authors of refs. \[ \text{[9, 113]} \] reported an intermediate equilibrium state (in addition to the Wenzel and Cassie-Baxter states) of a small droplet placed on
Chapter 7

a hydrophobic substrate regularly decorated with cubical pillars. Indeed, in this intermediate state, the droplet was found to neither stay on the top of the pillars nor touch the bottom of the substrate. Associated with the existence of this state is a so-called reentrant transition, where a quasi-statically evaporating droplet may switch from a stable Cassie-Baxter into the intermediate state and then go back to the Cassie-Baxter state again.

Noting that the initial droplet configurations studied in [9, 113] are of a high symmetry, here the question whether a perturbation of this initial state may lead to a different phenomenology is addressed. Indeed, large perturbations lead to a number of interesting morphologies which need not be of a high symmetry. Interestingly, the intermediate state predicted in [9] is also observed in the case of the new morphologies. The behavior of a droplet in these morphologies upon quasi-static evaporation is also discussed. Present investigations underline the robustness of the reentrant transition with respect to a change of the initial droplet position.

In the same context, the effect of surface geometry on the droplet behavior is also studied. For this purpose, a topographic structure reminiscent of the surface of a lotus leaf is created and lattice Boltzmann simulations of a quasi-statically evaporating droplet gently falling onto such a surface are performed (‘gently’ here means that kinetic energy of the droplet is smaller than surface free energies involved in the problem). In this case, the droplet continuously sinks into the area between the pillars as its size becomes progressively smaller. This can be rationalized by noting that the non-regular arrangement of ‘pillars’ allows the droplet to detach from the side walls one after another. Together with a smoother shape, this allows to avoid strong capillary forces, which would push the droplet upwards. The present simulations thus reveal the crucial role of substrate geometry for the observation of reentrant transition, if the latter is to be used as a new self-cleaning mechanism (allowing e.g. to clean the inner walls of the patterned surface, so far inaccessible to standard self-cleaning mechanisms).
Morphologies of small droplets on patterned hydrophobic substrates

Figure 7.1: An initial state (panel (a)) which leads to a morphology shown in the panel (e). The panel (a) shows 3D initial setup and panels (b) and (c) show 2D cross sections of the same setup, revealing the contact line between the liquid and the solid. Panel (f) and (g) show 2D cross section of the same final state as in (e). Here, the equilibrium contact angle and the effective droplet radius $R_{\text{eff}} = ((3/4\pi)V)^{1/3}$ ($V$ is the droplet volume) are fixed to $\theta_{\text{eq}} = 100^\circ$ and $R_{\text{eff}} = 20$, respectively.
7.2 Numerical model

Since the shape of a droplet in contact with a topographically patterned substrate can become quite complex in general, one has to resort to numerical methods in order to investigate the landscape of possible equilibrium states. For this task, two different two-phase LB models are employed. In the first part, where droplets on obstacles with rectangular shapes are simulated, a D3Q15 LB code based on the Swift approach is used (see section 3.2). In the second part, where the effect of surface geometry is addressed (obstacles are not rectangular), a D3Q15 LB code based on the Shan-Chen approach is used which allows us of introducing obstacles with arbitrary shapes (see section 3.3). The LB parameters are those which are already used. All the LB parameters and results are given in dimensionless LB units.

It is noted that all the results in the Swift model are also reproducible with the Shan-Chen model. For example, using the Shan-Chen LB code all the simulation results reported in [9] were correctly reproduced in order to ensure the consistency of the two models. It is mentioned that in all LB models, as already discussed in section 3.1, the interface spreads over a finite number of (here 3-4) lattice nodes. However, this width is an order of magnitude smaller than other relevant characteristic lengths in the systems considered here.

<table>
<thead>
<tr>
<th>$\rho_c$</th>
<th>$T_c$</th>
<th>$p_c$</th>
<th>$\rho_L$</th>
<th>$\rho_V$</th>
<th>$\lambda$</th>
<th>$\kappa$</th>
<th>$T$</th>
<th>$\gamma_{LV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>1/8</td>
<td>4/7</td>
<td>4.1</td>
<td>2.9</td>
<td>0.8</td>
<td>0.1</td>
<td>0.002</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 7.1: LB parameters in the Swift model

<table>
<thead>
<tr>
<th>$g$</th>
<th>$\rho_{\text{wall}}$</th>
<th>$\rho_L$</th>
<th>$\rho_V$</th>
<th>$\tau$</th>
<th>$\rho_{\text{wall}}^W$</th>
<th>$\rho_{\text{wall}}^d$</th>
<th>$\gamma_{LV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.27$</td>
<td>$0.6-0.67$</td>
<td>$1.81$</td>
<td>$0.13$</td>
<td>$1.0$</td>
<td>$1.75$</td>
<td>$0.25$</td>
<td>$0.156$</td>
</tr>
</tbody>
</table>

Table 7.2: LB parameters in the Shan-Chen model
The values of all LB parameters used in the simulations here are shown for the both models in the tables 7.1 and 7.2. In addition, the periodic boundary condition is applied in x and y directions.

7.3 Results and Discussion

As mentioned before, the focus here is on cases in which the size of droplet is comparable to the roughness scale. In addition, the droplet is assumed to be small enough so that gravity is negligible compared to the capillary forces. The following results are obtained using the Swift approach. We consider a hydrophobic solid surface regularly decorated with cubical pillars of width \( w_{cu} = 12 \) and spacing distance \( s_{cu} = 12 \). Since we are interested in cases in which the droplet does not touch the bottom of the substrate (thus avoiding the Wenzel state), it is ensured that the pillars are sufficiently high to fulfill this conditions.

A substrate with this arrangement of pillars has a four-fold rotational symmetry (see, for example, the substrate in fig. 7.1). In general, when a small droplet is spreading, the final equilibrium shape of the droplet reflects the symmetry of the arrangement of the pillars in contact with the droplet. For the substrate considered, this implies that one can not expect a morphology with a higher symmetry. Similarly, since it is not possible to find an array of pillars with only a three-fold symmetry, there can, consequently, also be no associated wetting morphology with this symmetry.

An initial state in which the droplet is in contact with five pillars (fig. 7.1 panels (a)-(c)) leads to a wetting morphology with a four-fold rotational symmetry (fig. 7.1 (e)-(g)). This morphology has the full symmetry of the substrate and it has already been discussed in details [9, 113], where it is shown that the equilibrium shape of the droplet can be approximately characterized by a spherical cap of radius \( R_c \) and a cylindrical part that has penetrated the substrate up to a depth \( p_d \). Both \( R_c \) and \( p_d \) depend on the volume of droplet and the equilibrium contact angle.

Besides exerting an external force, other methods that can be employed
Figure 7.2: Simulation for $\theta_{eq} = 100^\circ$ and $R_{eff} = 20$. Panels (a) and (b) show the side view of the initial shape and initial solid-liquid contact line, respectively. Panels (c) and (d) are top and side views of the resulting final state. Panel (e) shows the final shape of the droplet without the substrate for a clearer visualization.

to obtain different wetting morphologies include changing the droplet volume, initial position of the droplet or altering the chemical properties of the substrate. In the present context, the chemical properties of the substrate are
Figure 7.3: (a): Initial setup of the simulation, $\theta_{eq} = 100^\circ$ and $R_{eff} = 20$. (b): Side view of the final shape of the droplet. Panel (c) shows the final shape of droplet without the substrate for a clearer visualization.

Figure 7.4: Effect of a deviation from a perfectly symmetric initial state on the final configuration. In panel (a), a slight deviation from the initial state shown in fig. 7.1 (a,b) is corrected by restoring forces so the droplet gave back to the symmetric state shown in fig. 7.1 (a,b). A larger deviation (panel (b)), however, results in the morphology shown in fig. 7.2 (a,b).
spatially kept homogeneous and fully determined by the equilibrium contact angle.

Figure 7.5: (a): Initial setup of the simulation in 3D, $\theta_{eq} = 100^\circ$ and $R_{eff} = 23$. Panel (b) shows the number of pillars which are initially in contact with the droplet. Panels (c) and (d) show the side and top view of the final shape of the droplet. The final shape of droplet without the substrate (for a clearer visualization) is depicted in panel (e).
Figure 7.6: Time evolution of the ‘fish’ morphology upon quasi-static evaporation, $R_{eff} = 23$ and $\theta_{eq} = 100^\circ$ (side view).

It is to be emphasized here that, it is not intended to classify all possible morphologies related to a variation of droplet size, initial position and the equilibrium contact angle. Nevertheless, it is easy to understand intuitively the effect of changing these parameters separately. Increasing the size of the
droplet obviously increases the solid-liquid contact area and may result in a larger number of pillars that are in contact with the droplet. Changing the contact angle, on the other hand, leads to a change in the tendency of the droplet to penetrate into the free space between the pillars. A variation of the initial position may significantly alter the direction of spreading and hence also influence the final shape of the droplet.
Morphologies of small droplets on patterned hydrophobic substrates

Figure 7.8: (a): Three-phase contact line at different times for a droplet residing on the top of cylindrical pillars. The case A corresponds to the initial time $t = 0$ (deposition time) and B and C denote subsequent configurations. Obviously, the configuration A is unstable for the present set of parameters. Panels (b) and (c) are corresponding 3D views of the cases A and C, respectively.

First of all, it is shown that changing the number of pillars which are initially in contact with the droplet results in different morphologies. This is illustrated in the next figures. In fig. 7.2 (a), a symmetric initial configuration of a droplet of radius $R_{\text{eff}} = 20$ in contact with four pillars, having an equilibrium contact angle of $\theta_{\text{eq}} = 100^\circ$, is shown. The final state of the droplet, shown in fig. 7.2 (c), is found to be quite different from the previous case (fig. 7.1), although both states possess the full symmetry of the substrate. Yet another possible morphological transition is investigated in fig. 7.3. Here, the droplet initially is in contact with two pillars.
Figure 7.9: Observation of the reentrant transition on a regular array of cylindrical pillars upon quasi-static evaporation. Note that, in order to stabilize the initial setup ($t = 0$), the contact angle is reduced from $\theta_{eq} = 103^\circ$ to $100^\circ$ (see also fig. 7.8).

In addition, the effect of a deviation in the initial configuration of the droplet—compared to the perfectly symmetric initial state shown in fig. 7.1 (a)—is investigated. The simulations suggest that, if the initial contact point is only slightly shifted laterally or vertically, the droplet always goes over to the morphology shown in fig. 7.1 (e). If, on the other hand, the deviation in
the initial position is large, one may observe different wetting morphologies depending on the droplet size and the equilibrium contact angle. This is illustrated in fig. 7.4, where two other initial configurations, which are exactly a horizontal shift of the initial setup shown in fig. 7.1, are displayed. In this case, depending on the deviation, the droplet is found to either take the shape shown in fig. 7.1 (a,b) or fig. 7.2 (a,b).

Now a case where the droplet starts from an initial contact situation as depicted in fig. 7.5 (a,b) is considered. The radius of the droplet and the equilibrium contact angle in this case are $R_{\text{eff}} = 23$ and $\theta_{\text{eq}} = 100^\circ$, respectively. The final shape of the droplet is shown in fig. 7.5 (c). Let us call the resulting final state ‘fish morphology’ because a certain similarity with the shape of a fish is apparent. The simulation has been repeated for the same initial configuration but with different equilibrium contact angles. The simulations reveal that for $\theta_{\text{eq}} \leq 101^\circ$, the droplet goes over to the fish morphology, while for $\theta_{\text{eq}} > 101^\circ$, the droplet assumes the shape shown in fig. 7.1 (e). This behavior is consistent with the expectation that the existence of an equilibrium state with a finite penetration depth strongly depends on the equilibrium contact angle [9]. Noting that the prediction in [9] was made only for the case of a perfectly symmetric configuration, the present finding underlines its generic character and significantly extends its range of validity. It should be remarked here that, if, for example, the initial deviation or the size of droplet is not large enough, the droplet may not go over to the fish morphology but instead stay in the configuration shown in fig. 7.1(e). This transition is then found to be largely independent of the equilibrium contact angle.

In Figs. 7.6 and 7.7, the time evolution of a droplet, initially residing in the ‘fish’-like configuration, is shown during quasi-static evaporation. Evaporation is realized by subtracting, at each time step, a constant amount of mass is all the nodes on a $XY$-plane, placed sufficiently high (e.g., $z = LZ - 3$) above the droplet, thus mimicking an outflow of vapor at a constant rate. The evaporation rate is chosen such that the entire mass of droplet would be removed from the system within a time large compared to the capillary time. This is important to ensure that, at each time instant, the droplet
shape corresponds to the (local) minimum of the free energy, whence the term “quasi-static evaporation”.

As seen in Figs. 7.6 and 7.7, a transition is induced from the partially immersed state to the Cassie-Baxter-like state during quasi-static evaporation. This finding suggests that the reentrant transition described in [9] applies to droplets in a broad range of, not necessarily symmetric, wetting configurations.

Let us turn the attention to the effect of surface geometry on both droplet morphology and the reentrant transition. For this purpose, it is asked ‘what happens if the square-shaped pillar is replaced by cylindrical ones, keeping the pillar arrangement exactly the same as in fig. 7.1?’ Simulations using this new substrate are performed resorting to the Shan-Chen approach, which allows to capture substrates of arbitrary shape in a convenient way [67, 68]. As discussed in section 3.3, one has the freedom to choose the equilibrium contact angle of the droplet by changing the fictitious density of the solid boundary. In order to compare the effect of this geometry and looking for a possible reentrant transition, two simulations are performed. In the first simulation, the initial droplet’s radius, the equilibrium contact angle, the radius of cylinders and their mutual distance are fixed to $R_{\text{eff}} = 47$, $\theta_{\text{eq}} = 103^\circ$, $R_{\text{cyl}} = 13$, and $s_{\text{cyl}} = 13$, respectively.

The initial position of droplet is similar to the initial position shown in fig. 7.1 (slightly in contact with five central pillars). Figure 7.8 shows that, for the selected set of parameters, the initial symmetric morphology is unstable with respect to small perturbations and the droplet changes its morphology to the one shown in fig. 7.8(c). This can be rationalized by noting that the round shape of the cylindrical pillar’s edge significantly decreases the pinning force as compared to the sharp edges of square-shaped pillars shown in fig. 7.1. In fact, in the case of cylindrical pillars, droplet can gently depin from the round edges of pillars and find energetically more favorable morphologies in an easier way. However, it is also found that reducing the equilibrium contact angle to $\theta_{\text{eq}} = 100^\circ$ is sufficient for a stabilization of the symmetric setup. In this case, simulations upon quasi-static evaporation, fig. 7.9, reveal the presence of reentrant transition also in the case of cylindrical pillars.
In order to address the influence of geometry further, a surface pattern decorated with random obstacles of different sizes is designed which aims at imitating the surface of a lotus leaf. However one should be aware that a real lotus leaf has multiscale roughness which is not considered here [15]. For creating such a ‘lotus’-like substrate the Shan-Chen approach must be used. In this case, in order to achieve a contact angle of \( \theta_Y \sim 100^\circ \), the \( \rho_{\text{wall}} \) is chosen to be \( \rho_{\text{wall}} = 0.67 \) (see fig. 3.3). The droplet is initially situated a few lattice nodes above the obstacles. By exerting a downward body force (gravity), the droplet is accelerated downward and eventually collides with the substrate. In this way, it is tried to mimic the behavior of a rain droplet that gently falls onto a lotus leaf. Here, ‘gently’ means that the body force must be small enough compared to the capillary forces, otherwise the droplet will move to the bottom of the substrate and attain the Wenzel state. The droplet is allowed to evaporate very slowly (quasi-statically) from the beginning, which is also the case in a realistic setting. The results (fig. 7.10) show that, as the droplet collides with the obstacles, the capillary forces become dominant, hindering further penetration of the droplet into the grooves. The shape of the droplet is strongly affected by the obstacles that are in contact with the droplet. Further evaporation induces shape changes of the droplet in order to minimize its free energy. However, a reentrant transition, similar to the behavior of a droplet on a perfectly symmetric substrate, is not observed. There might be two reasons responsible for this finding. First, in the present case, the pinning forces are weaker due to the curved smooth shape of the edges of obstacles. Similarly, because of the different heights of the asperities and their asymmetric arrangement, the resulting pinning forces are also presumably not as large as in the perfectly symmetric case. Second, the droplet has more freedom to change its shape compared to a regularly patterned substrate.

7.4 Conclusion

Two different liquid-vapor lattice Boltzmann models are used to study the behavior of small droplets on substrates with both regular and arbitrary
patterns of obstacles. It is shown that, in the situations where the size of the droplet is comparable to the roughness scale, the shape of the droplet is strongly affected by the substrate geometry.

In particular, on a substrate regularly patterned with cubical posts, the different wetting morphologies that may occur depend strongly on droplet size, equilibrium contact angle and initial position of the droplet. These morphologies maintain some symmetries of the underlying substrate. Evidence is provided for the possibility of evaporation-induced transitions from a morphology with a low symmetry to another morphology possessing the maximum possible symmetry.

More importantly, the robustness of the reentrant transition on a regular array of cubical pillars [9] with regard to perturbations of the initial state is highlighted. In the case of cylindrical pillars, the pinning force at the edges of pillars significantly decreases leading to an easier change (compared to the square-shaped pillars) in the droplet morphology (fig. 7.8). Nevertheless, if the equilibrium contact angle is properly adjusted, the reentrant transition is observed (fig. 7.9). Moreover, it is demonstrated that a droplet on a substrate with a quasi-random arrangement of obstacles appears not to be subject to a reentrant transition. A qualitative understanding of this behavior may be obtained as follows. Due to a smoother shape of the obstacles on the new surface pattern as compared to sharp edges of the considered cubical posts here, pinning forces may be weaker, unable to induce the reentrant effect. Furthermore, the lack of perfect symmetry of the obstacle arrangement allows the droplet to detach from the pillars one after another as its size is continuously reduced upon evaporation. This may prevent large capillary forces which would tend to push the droplet upwards. Moreover, the free energy landscape associated with an irregular surface provides a larger number of minima and transition pathways as compared to a regular array, thereby significantly reducing the probability of a transition back to the initial state.

It is noteworthy that the newly observed reentrant transition [9, 113] opens the way for a quite new self-cleaning mechanism with the potential application to clean not only the upper part of the surface, but also the inner region (e.g. side walls) of the grooves. In this context, the results presented
above underline the importance of a careful design of the substrate pattern for the emergence of the reentrant transition. In particular, it seems that regular sharp-edged pillars are more suitable to give rise to the reentrant transition than smoothly-shaped and irregularly distributed pillars.
Figure 7.10: A droplet falling onto a ‘lotus-like’ rough substrate, with an equilibrium contact angle of $\theta_{\text{eq}} = 100^\circ$. The plots show the time evolution of the droplet shape upon quasi-static evaporation. The size of simulation box is $140 \times 140 \times 160$. 

100
Summary and outlook

This chapter is intended to give a concluding overview of the achievements of the present thesis. In addition, relevant open questions arising from these studies are pointed out.

In chapter 4, a two-phase lattice Boltzmann method based on the Lee-Fischer approach (see section 3.2) is used to study the dynamics of a cylindrical droplet on a flat substrate in the Stokes limit (no inertia effects). The droplet moves subject to a body force exerted on it in the direction parallel the substrate. Starting from the energy balance equation, a simple scaling relation, Eq. (4.5), is obtained indicating that droplet’s center-of-mass velocity scales linearly with force density and is proportional to the square of the droplet radius. At strong body forces or large droplet volumes, deviations occur which are closely associated with droplet deformation, fig. 4.3 and fig. 4.4. A detailed study of the local dissipation inside droplet was also provided, fig. 4.7. A result of these investigations is that viscous dissipation mainly occurs close to the three phase contact line and within a region below the droplet’s center-of-mass, fig. 4.8. Using the latter observation, a simple analytic expression is proposed accounting for the dependence of droplet velocity on the equilibrium contact angle Eq. (4.12). Results of computer simulations confirm the validity of this simple model, fig. 4.11.

A possible extension of the present studies would be droplet dynamics at high Reynolds numbers, where inertial effect are no longer negligible and the sim-
ple scaling obtained in the Stokes limit no longer applies. Indeed, there are some experimental studies of this interesting problem, e.g., the reference [79]. Analytical treatment of the problem being rather difficult, the LB method may provide an interesting route for a numerical study of the topic. This problem becomes more interesting when it is combined with either real solids (with a random distribution of roughnesses) or micro-structured solids (with any desired pattern of roughnesses).

In chapter 5, a two-phase lattice Boltzmann model based on the Swift approach (see section 3.2) is employed to address the dynamic behavior of suspended droplets on patterned hydrophobic substrates with a step-wise change in pillar density. The size of droplets considered are assumed to be smaller than their capillary length so that the surface forces are dominant. It is shown that the specific arrangement of pillars may play a significant role for the dynamics of the droplet on such substrates. In particular, varying the pillar arrangement while keeping the gradient of pillar density unchanged, fig. 5.3, it is also shown that both full transport over the gradient due to a significant decrease of resistant force as well as complete arrest resulting from a high resistant force between the two regions of different pillar density may occur, figs. 5.4 and 5.5. The relation between the droplet motion and the gradient of pillar density is investigated, revealing a linear dependence for the range of parameters studied, figs. 5.7 and 5.9. A simple model is provided based on the balance between the viscous dissipation and the driving force, the latter assumed as the gradient of the internal droplet (Laplace) pressure, Eq. (5.14). The model not only reproduces the observed dependence on the pillar density gradient but also predicts a linear dependence of the steady state droplet velocity on the surface tension. This prediction is in line with results of lattice Boltzmann simulations, where the surface tension is varied by roughly a factor of 10 fig. 5.9. Moreover, comparing droplet dynamics for two slightly different ways of realizing the gradient of texture, it is shown that the gradient in pillar density does not uniquely determine the droplet velocity. Rather, the way this gradient is implemented also matters to some extent, fig. 5.10. A detailed survey of the contact line dynamics is also provided revealing interesting pinning and depinning events leading to small amplitude oscillations of the droplet’s contact area during its motion over
Summary and outlook

the gradient zone, fig. 7.5.
Emphasizing on the role of geometry in this phenomenon, an interesting—and of course challenging—question is: ‘How the resistance force can qualitatively change with the geometry and size of roughnesses?’ The role of droplet size and, more importantly, the ratio of droplet size and roughness scale can be also of interest. These issues can be addressed conveniently through extensive Lattice Boltzmann simulations.

In chapter 6, a moving solid object with a shape of a square is introduced to a two-phase lattice Boltzmann method based on the Shan-Chen approach (see section 3.3). This allows of simulating a hydrodynamic system consisting of a liquid film suspending on a super hydrophobic substrate and a moving solid square. The solid square is fully immersed in the liquid and approaches the substrate with a constant velocity normal to the substrate. The motion of solid square gives rise to an excess pressure in the film. This causes the suspended film to undergo a Cassie-Wenzel transition. The transition begins exactly at a point beneath the center of the solid square where the pressure has its maximum value, fig. 6.2. This observation is in line with the theoretical prediction. However, the height of the solid square at which the transition occurs depends on the system parameters. Analytically, it is shown that this height, for a case of circular disk, is proportional to the product of the solid square velocity to the power of one third and the disk radius to the power of two third (see section 6.2). The simulations, are qualitatively in line with the predictions, fig. 6.4. The observed deviation are probably related to the fact that the simulations do not meet all conditions and assumptions in the theory. In addition, the simulations confirm the formation of rotational flows induced by the motion of the solid square, fig. 6.3. Although introducing a circular disk in the lattice Boltzmann method is awkward due to difficulties with the boundary conditions, but it is not impossible. Therefore, one next step would be overcoming these difficulties and performing more precise simulations for a more telling comparison between the theory and lattice Boltzmann simulations. Further steps would be, for example, to investigate the influence of other system parameters, such as the viscosity, or the structure of the substrate.
In chapter 7, the behavior of small droplets on substrates with both regular and arbitrary patterns of obstacles is studied. It is shown that, in the situations where the size of the droplet is comparable to the roughness scale, the shape of the droplet is strongly affected by the substrate geometry, e.g., figs. 7.4 and 7.5. In particular, on a substrate regularly patterned with cubic posts, the different wetting morphologies that may occur depend strongly on the droplet size, the equilibrium contact angle and initial position of the droplet. These morphologies maintain some symmetries of the underlying substrate. Evidence is provided for the possibility of evaporation-induced transitions from a morphology with a low symmetry to another morphology possessing the maximum possible symmetry. More importantly, the robustness of the reentrant transition [9] on a regular array of cubical pillars with regard to perturbations of the initial state are highlighted. In the case of cylindrical pillars, the pinning force at the edges of pillars significantly decreases leading to an easier change (compared to the square-shaped pillars) in the droplet morphology, fig. 7.8. Nevertheless, if the equilibrium contact angle is properly adjusted, the reentrant transition is observed, fig. 7.9. Moreover, it is demonstrated that a droplet on a substrate with a quasi-random arrangement of obstacles appears not to be subject to a reentrant transition, fig. 7.6. A qualitative understanding of this behavior may be obtained as follows. Due to a smoother shape of the obstacles on the new surface pattern as compared to sharp edges of the considered cubical posts here, pinning forces may be weaker, unable to induce the reentrant effect. Furthermore, the lack of perfect symmetry of the obstacle arrangement allows the droplet to detach from the pillars one after another as its size is continuously reduced upon evaporation. This may prevent large capillary forces which would tend to push the droplet upwards. Moreover, the free energy landscape associated with an irregular surface provides a larger number of minima and transition pathways as compared to a regular array, thereby significantly reducing the probability of a transition back to the initial state. Studies on this issue may be confined further in order to systematically illustrate the effect of the physical parameters such as the droplet size or the equilibrium contact angle as a phase diagram, or to find novel applications for a new generation of self-cleaning materials which clean not only the upper part of the surface, but
Summary and outlook

also the inner region (e.g. side walls) of the grooves. An interesting related issue, which is highly suggested for the next studies, is simulation of droplets on substrate with multi-scale roughnesses (the case in the lotus leaf) which can be done in a rather simple way in lattice Boltzmann models.
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