Numerical Simulation of Coupled Wetting and Transport Phenomena in Inkjet Printing

Numerische Simulation gekoppelter Benetzungs- und Transportphänomene im Inkjet-Druckprozess

vom Fachbereich Maschinenbau der Technischen Universität Darmstadt

zur Erlangung des Grades Doktor-Ingenieur (Dr.-Ing.)

Dissertation von Thomas Antritter

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Erklärung zur Dissertation

Hiermit erkläre ich, dass ich die vorliegende Arbeit, abgesehen von den in ihr ausdrücklich genannten Hilfen, selbständig verfasst habe.

Darmstadt, den 23. November 2021

Thomas Antritter

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Abstract

Abstract

Kurzfassung

Inkjet printing is a complex process including coupled wetting, heat and species transport. The print quality depends on accurate positioning of ink droplets and correct dot sizes. Temperature differences between printhead and substrate give rise to heat transfer upon droplet impact. Furthermore, inks are complex fluids containing, among other components, surfaceactive substances. The aim of this thesis is to develop an improved understanding of the coupled transport processes and to derive recommendations for increased print quality. For that purpose, individual droplets impacting a solid substrate are studied. Furthermore, the off-centered collision of an impacting droplet with a previously applied neighboring droplet is investigated.

Droplet impact, spreading, and substrate-sided collision are studied using numerical simulation. The algebraic volume of fluid method is used to describe the two-phase flow. Special focus is put on the evaluation of interfacial forces. The contact line dynamics are described using a subgrid-scale model in combination with localized slip. The model is validated for droplet impact and substrate-sided collision using experimental data. Heat transfer between fluids and solid is taken into account. Furthermore, a novel two-field approach for the description of a soluble surfaceactive substance is introduced. Using analytical and numerical reference solutions, the method is verified regarding transport of this

Der Tintenstrahl-Druckprozess ist ein komplexes Verfahren, das gekoppelte Benetzungs-, Wärme- und Stofftransportvorgänge beinhaltet. Die Druckqualität hängt dabei von der genauen Positionierung von Tintentröpfchen und korrekten Punktgrößen ab. Temperaturunterschiede zwischen Druckkopf und Substrat führen zu Wärmeübertragung beim Tropfenaufprall. Tinten sind außerdem komplexe Fluide, welche neben anderen Komponenten auch oberflächenaktive Substanzen beinhalten. Ziel dieser Dissertation ist es, ein verbessertes Verständnis der gekoppelten Transportvorgänge zu entwickeln und Empfehlungen für verbesserte Druckqualität abzuleiten. Zu diesem Zweck wird der Aufprall einzelner Tröpfchen auf ein festes Substrat betrachtet. Des Weiteren wird die außermittige Kollision eines auftreffenden Tröpfchens mit einem zuvor applizierten Nachbartröpfchen untersucht.

Tröpfchenaufprall, -ausbreitung und substratseitige -kollision werden mittels numerischer Simulation untersucht. Die algebraische Volume-of-Fluid-Methode wird dabei zur Beschreibung der Zweiphasenströmung angewandt. Besonderes Augenmerk wird auf die Auswertung der Grenzflächenkräfte gelegt. Die Kontaktliniendynamik wird durch ein Subgridskalenmodell in Kombination mit lokalem Schlupf beschrieben. Anhand von experimentellen Daten wird das Modell für Tröpfchenaufprall und substratseitige -kollision validiert. Wärmeübertragung zwischen Fluiden und Festkörper wird mitberücksichtigt. Außerdem wird ein neuer Zwei-Feld-Ansatz zur Beschreibung einer löslichen oberflächenaktiven Substanz eingeführt. Anhand von analytischen und numerischen Referenzlösungen wird die Methode hinsichtlich des Transports surfactant with and along the interface, adsorption to the interface, and conservation of the surfactant amount.

Simulation results for the impact and spreading of individual droplets show an influence of the ink's viscosity throughout the entire process. Lower viscosity due to increased temperature produces faster spreading. It is found that within the capillary-driven regime the influence of the initial droplet temperature is small compared to the initial substrate temperature. For surfactant-laden droplets spreading over a partially wettable substrate, an additional adsorption-limited spreading regime is observed. Increasing the rate of adsorption to the liquid-gas interface results in faster spreading within this regime.

Simulations of the collision of an impacting droplet with a previously applied neighboring droplet on the substrate show an offset of the coalesced droplets towards the first droplet. This offset persists well into the capillary-driven spreading regime. It can be attributed to a flow from the second to the first droplet driven by a larger Laplace pressure jump across the interface in the region of the second droplet. Increasing the impact velocity or decreasing the droplet interval reduces this asymmetry and consequently the offset. In contrast to that, the influence of initial droplet temperatures as well as surfactant concentrations on droplet position after collision is found to be small. Nevertheless, the simulation results for the collision of surfactantladen droplets show that increasing the surfactant concentration results in further spreading on partially wetting substrates, similar to what is also observed for individual droplets.

dieses Tensids mit und entlang der Phasengrenzfläche, der Adsorption an die Phasengrenzfläche sowie der Erhaltung der Tensidmenge verifiziert.

Simulationsergebnisse zu Aufprall und Ausbreitung einzelner Tröpfchen zeigen einen Einfluss der Tintenviskosität für den gesamten Prozess. Niedrigere Viskosität aufgrund von erhöhter Temperatur führt zu schnellerer Ausbreitung. Es zeigt sich, dass innerhalb des kapillaren Benetzungsregimes der Einfluss der anfänglichen Tröpfchentemperatur gering ist verglichen mit der anfänglichen Substrattemperatur. Bei der Ausbreitung tensidhaltiger Tröpfchen über ein unvollständig benetzbares Substrat wird ein zusätzliches adsorptionslimitiertes Benetzungsregime beobachtet. Eine Erhöhung der Adsorptionsrate an die Phasengrenzfläche Flüssigkeit-Gas führt zu schnellerer Ausbreitung innerhalb dieses Regimes.

Simulationen der Kollision eines auftreffenden Tröpfchens mit einem zuvor applizierten Nachbartröpfchen auf dem Substrat zeigen einen Versatz der vereinigten Tröpfchen in Richtung des ersten Tröpfchens. Dieser Versatz bleibt weit in das kapillargetriebene Regime bestehen. Er kann auf eine Strömung vom zweiten zum ersten Tröpfchen zurückgeführt werden, die durch einen größeren Laplace-Drucksprung über die Phasengrenzfläche im Bereich des zweiten Tröpfchens getrieben wird. Eine Erhöhung der Auftreffgeschwindigkeit oder eine Verringerung des Tröpfchenintervalls verringern diese Asymmetrie und folglich den Versatz. Im Gegensatz dazu wird nur ein geringer Einfluss der anfänglichen Tröpfchentemperaturen sowie der Tensidkonzentrationen auf die Position der kollidierten Tröpfchen beobachtet. Dennoch zeigen die Simulationsergebnisse zur Kollision tensidhaltiger Tröpfchen mit größer werdender Tensidkonzentration weitere Ausbreitung auf unvollständig benetzenden Substraten, ähnlich der Beobachtungen, die für einzelne Tröpfchen gemacht werden.

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List of Symbols

Latin Symbols

Symbol	Description	Dimension ¹
A	Hamaker constant	$M \cdot L^2 \cdot T^{-2}$
а	thermal diffusivity	$L^2 \cdot T^{-1}$
b	density scaling exponent	1
С	adsorption number	1
С	concentration	$N \cdot L^{-3}$
$c_{\rm s}, c_{\ell}, c_{\rm g}$	specific heat capacity of the respective phase	$L^2 \cdot T^{-2} \cdot \Theta^{-1}$
D	diffusion coefficient	$L^2 \cdot T^{-1}$
d	diameter	L
Ε	energy	$M \cdot L^2 \cdot T^{-2}$
е	effusivity	$M \cdot T^{-5/2} \cdot \Theta^{-1}$
f	volumetric force	$M \cdot L^{-2} \cdot T^{-2}$
G	surface coverage	1
g	gravitational acceleration	$L \cdot T^{-2}$
Н	Heaviside function	1
h	characteristic length scale, film height	L
$h_{\ell \mathrm{v}}$	specific enthalpy of vaporization	$L^2 \cdot T^{-2}$
$h_{\mathrm{s}\ell}$	specific enthalpy of solidification	$L^2 \cdot T^{-2}$
j	adsorption source term	$L^{-3} \cdot T^{-1} \cdot N$
Κ	equilibrium constant	model dependent
$k_{ m ad}$	kinetic adsorption coefficient	$L \cdot T^{-1}$
$k_{ m de}$	kinetic desorption coefficient	model dependent
k	proportionality constant	1
L	error norm	of respective quantity
1	level set field	L
ℓ	length, distance	L
M	molar mass	${\sf M}\cdot{\sf N}^{-1}$
т	number of adsorption sites	1
Ν	number of evaluated points	1
n	normal vector	1
n	Freundlich exponent	1

¹ Physical dimensions following the convention of the International System of Units (SI) [27].

Latin Symbols (continued)

Symbol	Description	Dimension
p	pressure	$M \cdot L^{-1} \cdot T^{-2}$
q	error norm exponent	1
\overline{R}	ideal gas constant	$M\cdotL^2\cdotT^{-2}\cdot\Theta^{-1}\cdotN^{-1}$
R _z	max. peak to valley roughness	L
r	radius	L
S	surface area	L ²
S	surfactant related scaling prefactor	1
Т	temperature (in K)	Θ
t	temperature (in °C)	Θ
u	velocity	$L \cdot T^{-1}$
u	velocity (scalar)	$L \cdot T^{-1}$
V	volume	L ³
W	weighting factor	1
х	position (vector)	L
x	position, coordinate	L
у	coordinate	L
Z	distance to substrate, coordinate	L

Greek Symbols

Symbol	Description	Dimension
α	volume fraction	1
β	coefficient of initial concentration field	$N \cdot L^{-4}$
Г	surface excess concentration	$N \cdot L^{-2}$
Δ	difference	-
δ	(regularized) interface Dirac delta	L^{-1}
ε	ratio of microscopic and macroscopic length scales	1
ϵ	nozzle to nozzle distance	L
θ	contact angle	1
К	mean curvature	L^{-1}
Λ	wave length	L
λ	thermal conductivity	$M\cdotL\cdotT^{-3}\cdot\Theta^{-1}$
μ	dynamic viscosity	$M \cdot L^{-1} \cdot T^{-1}$
ν	kinematic viscosity	$L^2 \cdot T^{-1}$
Ξ	series coefficient	1
ξ	interface thickness parameter	L

Greek Symbols (continued)

Symbol	Description	Dimension
П	ratio of kinetic to diffusive parameters	1
ρ	density	$M \cdot L^{-3}$
Σ	interface	-
σ	surface tension, surface energy	$M \cdot T^{-2}$
ς	small value	of respective quantity
τ	time	Т
ϕ	angular coordinate	1
$\dot{\phi}$	angular velocity	T^{-1}
arphi	generic field	of respective quantity
χ	phase indicator function	1
ω	mass fraction	1

Subscripts

Symbol	Description
ad	adsorption
adv	advancing
avrg	average
b	density scaled
de	desorption
В	bulk
BKZ	Brackbill-Kothe-Zemach
Са	capillary
CFL	Courant-Friedrichs-Lewy
сс	cell center
cl	contact line
crit	critical
DAT	Deshpande-Anumolu-Trujilo
d	dynamic
dist	distance
eq	equilibrium
f	cell face
g	gas
gc	ghost cell
geom	geometric
Н	Henry
Hoff	Hoffman

Subscripts (continued)

Symbol	Description
Ι	interface
j	source term
kin	kinematic
LF	Langmuir-Freundlich
lim	limited
l	liquid
m	microscopic, mixture
max	maximum
min	minimum
mp	midpoint
r	relative, compressive, regularized
rec	receding
ref	reference
S	smoothed
S	solid, slip
vdW	van der Waals
W	wall
YGB	Young-Goldstein-Block
YL	Young-Laplace
α	volume fraction
δ	(regularized) Dirac delta-function
К	curvature
σ	surface tension
0	initial
∞	far-field
	parallel
<u> </u>	perpendicular

Superscripts

Symbol	Description
Т	transposed
*	pseudo, modified

Accents

Symbol	Description
$\overline{\overline{(\cdot)}}$	volume averaged quantity
$\overline{(\cdot)}^{i}$	quantity volume averaged in phase <i>i</i>
$\overline{\overline{(\cdot)}}_{\cdot}$	surface averaged quantity
$\frac{\overline{(\cdot)}^{i}}{(\cdot)}$	quantity surface averaged in phase <i>i</i> dimensionless variable

Dimensionless Groups

Symbol	Description	Definition
Во	Bond number	$ ho g d^2 / \sigma$
Са	capillary number	$u\mu/\sigma$
Со	Courant number	$u\Delta \tau / \Delta x$
Da	Damköhler number	$k_{\rm ad}h/D$
Fr	Froude number	u/\sqrt{gd}
Ja	Jakobs number	$c_\ell \Delta T/h_{\ell \mathrm{v}}$
Oh	Ohnesorge number	$\mu/\sqrt{ ho\sigma d}$
Pe _a	Péclet number (heat)	hu/a
Pe _D	Péclet number (species)	hu/D
Pr	Prandtl number	$\mu c/\lambda$
Re	Reynolds number	ρdu/μ
Sc	Schmidt number	$\mu/(ho D)$
St	Stokes number	$\mu_{\rm g}/(ho_\ell du)$
Ste	Stefan number	$c_{\rm s}\Delta T/h_{\rm s\ell}$
We	Weber number	$ ho du^2/\sigma$

Abbreviations

Abbreviation	Description
ALE	arbitrary Lagrangian-Eulerian
CF-VOF	color function volume of fluid
C-LS	conservative level-set
CIJ	continuous inkjet
CSF	continuum surface force
DOD	drop on demand
DSC	differential scanning calorimetry

Abbreviations (continued)

Abbreviation	Description
DS-CSF	density-scaled continuum surface force
FDM	finite difference method
FT	front tracking
FVM	finite volume method
gDS-CSF	generalized density-scaled continuum surface force
IR-VOF	interface-reconstructing volume of fluid
LFA	laser flash analysis
LS	level set
MD	molecular dynamics
PE	polyethylene
PEDOT	poly(3,4-ethylene-dioxythiophene)
PF	phase field
PIMPLE	combination of PISO and SIMPLE
PISO	pressure-implicit with splitting of operators
PP	polypropylene
PVP	poly(4-vinylphenol)
SFCD	self-filtered central differencing
SIMPLE	semi-implicit method for pressure linked equations
TVD	total variation diminishing
UV	ultraviolet
VOF	volume of fluid

CHAPTER

Introduction

The inkjet printing process is a well established method in graphical printing. Inkjet printers are probably best known as small home and office printers. Their ability to produce very low numbers of copies, down to a single copy, at affordable cost makes them an ideal choice for that purpose. However, in recent years, inkjet printing has become more and more popular for industrial purposes as well. Functional inkjet printing allows the manufacturing of electronics [42, 126], or the extension of the process to bio-medical applications [55, 111] through the use of special inks. Within the last decade, the inkjet printing process has also been increasingly used in commercial printing [85] and attracted the attention of traditional printing press manufacturers for graphical printing including label printing and printing of packaging. These applications are not only very demanding regarding resolution and print quality but also require high throughput [110]. Especially with regard to packaging and label printing, the printers have to work with a variety of substrates. Additionally, due to the complex composition of typical inks and temperature differences between printhead and substrate, heat and species transport processes occur in inkjet printing. Understanding the coupled wetting and transport processes on the scale of individual droplets¹ is of fundamental importance for the systematic development of inkjet processes as well as inks. In the remainder of this chapter, a brief introduction to the inkjet printing process, inks and substrates, the relevant length and time scales as well as current wetting related challenges is given.

1.1 The Inkjet Printing Process

Within the inkjet printing process, ink is ejected from a nozzle in the printhead. In general, inkjet printers can be categorized as either continuous inkjet (CIJ) printers or drop on demand (DOD) inkjet printers [85]. In CIJ printing, as the name suggests, a continuous jet of ink is ejected from the nozzle at the printhead. The jet then breaks up into individual droplets due to Rayleigh-Plateau instability, creating a continuous stream of individual droplets. By applying an electric charge to the droplets, unrequired

 $^{^1}$ $\,$ Within the scope of this work, the term "droplet" is used, when specifically drops with diameters on the order of 100 μm and below are meant.



Figure 1.1: Schematic representation of the piezo drop on demand inkjet printing process on a non-porous substrate.

droplets can be deflected into a collector and back into the ink reservoir by an electric field [56]. In DOD inkjet printing on the other hand, drops are only ejected from the printhead if an ink dot at the current position is required [85]. The DOD inkjet printing process can be further divided into thermal and piezo DOD inkjet by the two main approaches for droplet generation [121]. In thermal DOD inkjet printheads, a bubble nucleates and grows at a heater surface. The expanding bubble thereby pushes liquid ink out of the nozzle. Alternatively, a piezoelectric actuator can be used to push ink out of the nozzle and create a droplet [121]. After an ink jet has been ejected from the printhead nozzle and a droplet has detached, the droplet travels across a small gap of several centimeters in CIJ, or less than 1 mm for DOD, before it impacts onto the substrate [85]. Figure 1.1 shows a schematic representation of the piezo DOD inkjet process.

The impacting dorplet may encounter the substrate in different states. It may be either dry, partially pre-wetted by neighboring droplets of the same ink, or partially or completely covered by a previously applied ink. In graphical inkjet printing, the latter case occurs regularly when inks of different color are applied successively. Therefore, several scenarios of substrate-sided wetting regularly occur in inkjet printing:

- (i) Droplet impact and spreading on a dry substrate
- (ii) Off-centered collision of impacting droplets with previously applied droplets on the substrate and subsequent spreading of the coalesced droplets
- (iii) Droplet impact and spreading on a liquid film

Depending on the ink and substrate, the initial impact, collision and spreading will be accompanied or followed by additional processes. On porous substrates, the ink imbibes into the substrate, inks with volatile solvents start to evaporate, and ultraviolet (UV) or electron beam curable inks, which are also summarized as energy-curable inks [11], are polymerized and thereby fixated on the substrate. In the following section, a brief overview over typical ink compositions and print substrate types is given.

1.2 Inks and Substrates

A detailed description of common ink compositions is given by Bale [11]. Depending on the application, different ink formulations are used. They can be based on water or organic solvents as well as on waxes in the case of hot melt inkjet or acrylate monomers in the case of energy-curable inks. Additives are added to control specific properties of the ink [11]. Surfactants for example are added in order to lower the ink's surface tension and thereby improve jettability from the printhead as well as wettability on the print substrate [123]. However, they may also give rise to dynamic surface tension² effects and Marangoni flow during single droplet impact, droplet collision, and coalescence at the substrate, as will be discussed in more detail in the following chapter. Inks for graphical printing furthermore contain pigments or dye, which give the ink its color [123]. Inks for functional printing contain particles of a functional material instead [11]. Resins can be added to improve adhesion of pigments or dye to the substrate [11]. Depending on the type of ink, different mechanisms are used to deposit or fix pigments or dye on the substrate. In aqueous and solvent-based inks this is accomplished by absorption of the solvent by the substrate and/or evaporation of the solvent [11]. Hot melt inks, on the other hand, solidify with decreasing temperature and thereby fix pigments on the substrate [11]. However, as Bale [11] points out, they are largely surpassed by energy-curable inks, which similarly form a solid layer on the substrate. In these inks, the monomeric solvent is polymerized after activation e.g. through UV radiation [69]. Even though one might expect inks to show non-Newtonian behavior due to their complex composition, Bale [11] states that "the majority of common inkjet products are crudely Newtonian". Another aspect regarding viscosity, however, can not be neglected. DOD inkjet printheads require rather specific ink viscosities in order to function properly, often in the range of 8 mPas - 20 mPas [146]. Some printheads [see e.g. 37] are therefore equipped with heating units in order to lower the ink's viscosity for jetting, indicating that inks often show a substantial temperature dependence of the viscosity. Typical jetting temperatures of UV-inks were reported to be in the range of $40 \degree C - 50 \degree C$ [37].

Due to its high prevalence in graphical inkjet printing, the first print substrate that comes to mind is paper. Paper is composed of vegetal fibers that form a porous network [155]. This porosity allows inks to imbibe into the substrate. Polymeric film coatings can be used to completely close the paper pores and produce glossy surfaces [155]. But non-porous polymeric films are also often found print substrates by themselves [79]. The choice of polymer material depends on the application. Due to their low cost, polyethylene (PE) and polypropylene (PP) films are often found in packaging and labeling applications [79, 161]. Together with the ink, the film material determines the wettability of the system. Coatings on top of the polymeric film can be added to adjust the wetting properties as well as other film surface properties [79]. Since non-porous polymeric films do not absorb the ink, they are often used in combination with energy-curable inks, such as UV-inks. These inks do not require a specific ink receiving layer [69]. Label printing is, therefore, a typical application of UV-inks [69].

² The commonly used term "dynamic surface tension" is adopted throughout this work to refer to the transient behavior of the surface tension during ad- and desorption of surfactant at the liquid-gas interface.

1.3 Length and Time Scales in Inkjet Printing

This section first presents the length scales relevant to the inkjet printing process before the corresponding time scales are introduced. The relevant length and time scales span several orders of magnitude. Print widths range from centimeters up to a few meters. Before impacting the substrate, droplets have typically traveled several hundred microns to a millimeter in DOD printing or up to several centimeters in CIJ printing from nozzle to substrate [85]. Substrate thicknesses are in the range of 50 μ m to 250 μ m [e.g. 110]. Nozzle and droplet sizes on the order of 10 μ m – 100 μ m [85] are slightly below that. Due to the small droplet sizes, gravitational forces are typically small as well, whereas capillary forces become large due to the strong curvature of the interface. In terms of dimensionless groups, this will be shown in Chapter 2. Droplet spacing is on the same order as the droplet diameter. A print resolution of e.g. 1200 dpi corresponds to distances between neighboring droplet centers of 21.17 μ m. The characteristic length scale for the adsorption of surfactant to the liquid-gas interface [63]

$$h_{\rm ad} = \frac{\Gamma_{\rm eq}}{c_{\rm B,\infty}} \tag{1.1}$$

can be on the order of 100 nm. Here, Γ_{eq} is the equilibrium surface excess concentration and $c_{B,\infty}$ the bulk surfactant concentration in sufficient distance to the interface to be uninfluenced by adsorption. A detailed description of a model surfactant solution is given in Appendix G. Even smaller than h_{ad} is the size of pigments suspended within the droplets with typical sizes starting at 10 nm [85].

The characteristic time scales are in many cases directly related to the given length scales by the corresponding velocities, such as the print speed or the initial velocity of individual droplets. Industrial inkjet printers can reach print speeds up to several hundred meters per minute [83]. Even though these machines reach dimensions of several meters [110], the time between droplet deposition and drying or curing at the end of the process, therefore, remains on the order of seconds. With typical initial droplet velocities before impact on the order of several meters per second in DOD inkjet and up to 30 m s⁻¹ in CIJ [85] on the one hand, and the spacing between nozzle and substrate given above on the other hand, the droplets spend a few hundred microseconds (DOD) to a few milliseconds (CIJ) traveling from printhead to substrate. The interval between droplets jetted from the same nozzle is even smaller. For a resolution of 1200 dpi and the print speed given above, it is on the order of microseconds. The interval between neighboring droplets perpendicular to the print direction, however, may vary according to the layout of the printhead. Due to spacial limitations, the individual nozzles may not be placed in a single row but can be distributed over the printhead in multiple rows instead [38, 146]. With printhead dimensions of roughly a centimeter and assuming a print velocity of $60 \,\mathrm{m\,min^{-1}}$, droplet intervals between neighboring print columns can therefore range up to the order of ten milliseconds. Thus, intervals between neighboring droplets may vary by several orders in magnitude even if printed from the same printhead. The kinematic and capillary time scales for droplet impact and spreading,

both depend on the initial droplet diameter d_0 . Here, u_0 , μ_ℓ , and $\sigma_{\ell g}$ denote impact velocity, dynamic viscosity of the liquid and surface tension of the liquid-gas interface respectively. Within inkjet printing, they both are typically on the order of several microseconds to tens of microseconds. Due to the good wettability of typical ink-substrate systems, however, capillary spreading can continue far beyond this capillary time scale. In the case of complete wetting, it is only halted by absorption into the substrate, evaporation of the solvent, or, in the case of energy-curable inks, polymerization. The time scale for capillary spreading itself can, therefore, bridge several orders of magnitude from tens of microseconds up to several seconds. With increasing droplet size also the capillary time scale τ_{Ca} increases. On the other hand, the characteristic time scale for diffusion-limited adsorption of surfactant [63]

$$\tau_{\rm ad} = \frac{h_{\rm ad}^2}{D},\tag{1.4}$$

where D is the diffusion coefficient, is independent of the droplet size. Therefore, depending on the droplets size, capillary spreading and adsorption are not separable but interact, as is the case in the inkjet printing process [85].

1.4 Wetting Related Challenges in Inkjet Printing

Independent of the actual printing application, precise placement of droplets as well as controlled dot sizes and shapes are essential for the print quality. In functional printing, e.g. when printing an electronic circuit, unintentionally disconnected or connected droplets can leave the circuit dysfunctional. In graphical printing, inaccurate dot sizes can result in incorrect tonal values. Inhomogeneous spreading can be detrimental to sharp contours of shapes or letters. Inaccurate positioning of droplets can produce grainy images. These inaccuracies in droplet position can have their origin in a malfunction of the corresponding nozzle, e.g. due to deposit formation [186]. But also the interaction of neighboring droplets can affect their position after coalescence. Derby [51] reports that drop collision at the substrate can lead to flow reversals and therefore also receding contact lines. He furthermore states that "in the production of patterns, drops may contact and interact with other drops". This interaction between droplets is especially pronounced if penetration of the ink into the substrate is hindered [80]. For coated paper, where the coating substantially slows down the absorption of ink by the substrate, Morita et al. [122] report coalescence related print defects, so called mottling. Shifted droplet positions due to coalescence on the micrometer-scale thereby impair the macroscopic print quality. With the growing relevance of inkjet printing on non-porous substrates, e.g. for label printing [81], understanding the underlying mechanisms becomes more and more important. Heat and species transport due to heated printheads and complex ink compositions add to the complexity of the relevant processes.

In the following chapter the current state of research regarding wetting and transport processes related to inkjet printing is reviewed. The short length and time scales pose a challenge for experimental investigations, especially with respect to heat and species transport. Therefore, an additional overview of relevant numerical methods for the simulation of multiphase flows is given. This is followed by the aims and outline for the remainder of this thesis given in Chapter 3.



State of the Art

Within this chapter the fundamentals of drop impact, wetting and spreading, and drop on drop collision are summarized. Following a review regarding the physics of these phenomena, possible numerical methods for their simulation are discussed.

2.1 Drop Impact

The physics of drop impact has been widely studied over the last decades. The first part of this section focuses on the hydrodynamics of pure Newtonian liquids under isothermal conditions. In the second part of this section, the current state of research regarding heat and species transport during drop impact is summarized.

2.1.1 Fluid Dynamics of Drop Impact

The impact of liquid drops onto solid substrates can produce various outcomes, as was reviewed by Yarin [193]. Rioboo et al. [144] described six particular morphologies from their experiments: deposition, prompt splash, corona splash, receding break-up, partial rebound and complete rebound. Within the deposition scenario the droplet remains a single connected volume throughout the entire deposition process, while some oscillations may occur upon impact. For high impact velocities and especially on rough surfaces, small droplets can detach from the main drop resulting in a prompt splash. For liquids with low surface tension a corona splash can be observed as a liquid lamella detaches from the wall and decomposes into small droplets. At intermediate impact velocities, the drops initial kinetic energy can still drive the contact line diameter beyond its equilibrium value before the droplet recedes to assume its equilibrium shape. Non-wettable surfaces are prone to receding break-up at this stage. Furthermore, if the ratio of inertia to viscous dissipation is large enough, a partial or even complete rebound from the substrate may occur [193].

Governing Dimensionless Groups

Main influences on the outcome of the drop impact are inertial, viscous and surface tension forces. Therefore, as has been summarized by Josserand and Thoroddsen [97], important and commonly used dimensionless groups in the context of drop impact are the Reynolds number

$$Re = \frac{\rho_\ell d_0 u_0}{\mu_\ell},\tag{2.1}$$

relating inertial to viscous forces, and the Weber number

$$We = \frac{\rho_\ell d_0 u_0^2}{\sigma_{\ell g}},\tag{2.2}$$

relating inertial to surface tension forces. Here, ρ_{ℓ} stands for the density of the liquid phase. Alternatively, one of the above dimensionless groups can be replaced by the Ohnesorge number

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\mu_{\ell}}{\sqrt{\rho_{\ell}\sigma_{\ell g} d_0}},\tag{2.3}$$

which consists only of material properties and the initial drop diameter and is independent of the impact velocity. The influence of gravitational forces compared to inertial forces on the initial impact can be estimated by the Froude number [97]

$$Fr = \frac{u_0}{\sqrt{gd_0}},\tag{2.4}$$

where g is the gravitational acceleration. The Bond number [165]

$$Bo = \frac{\rho_\ell g d_0^2}{\sigma_{\ell g}} \tag{2.5}$$

compares gravitational forces to surface tension forces. For a droplet with $d_0 = 20 \,\mu\text{m}$, $u_0 = 5 \,\text{ms}^{-1}$, $\rho = 1000 \,\text{kg} \,\text{m}^{-3}$, and $\sigma_{\ell g} = 40 \,\text{mN} \,\text{m}^{-1}$, Froude and Bond numbers take the values Fr = 356.96 and $Bo = 9.81 \times 10^{-5}$, indicating that gravitational forces are small compared to inertial and surface tension forces for typical parameters in inkjet printing. The influence of the gas phase surrounding the drop can be expressed through the Stokes number

$$St = \frac{\mu_{\rm g}}{\rho_\ell d_0 u_0},\tag{2.6}$$

relating viscous forces in the surrounding gas phase including the gas film forming between drop and substrate to the inertia of the drop [97]. The dynamic viscosity of the gas phase is thereby denoted by μ_{g} . Depending on the surrounding gas phase, varying splashing phenomena may occur. Lowering

the ambient pressure can lead to a complete suppression of the corona splash, as was demonstrated experimentally by Xu et al. [192].

For obvious reasons regarding the print quality, splashing and rebound are undesirable phenomena in the inkjet printing process. The onset of splashing can be described by

$$\sqrt{We}\sqrt[4]{Re} > f(R), \tag{2.7}$$

where f(R) describes the surface roughness [166]. For smooth, flat surfaces, a threshold value of $f(R) \approx 50$ was identified [18]. Thus, it is sufficiently well understood how splashing can be avoided. Of the possible outcomes of drop impact, the drop deposition scenario is therefore reviewed in further detail in the following.

Impact Phenomenology in the Deposition Regime

For drop deposition without splashing, Rioboo et al. [143] presented a comprehensive classification of the subsequent regimes during single drop impact onto solid substrates based on an extensive parameter study. They studied acetone, isopropanol, ethanol, water, silicone oil and glycerine-water-mixture drops impacting on substrates with varying roughnesses and wettabilities. Drop diameters were varied between 1.2 mm and 4.9 mm. The authors focused on impact trajectories orthogonal to the substrate. According to them, the drop impact can be subdivided into a kinematic phase, a spreading phase, a relaxation phase, and finally a wetting and equilibrium phase.

For dimensionless kinematic times τ/τ_{kin} below the order of 0.1, the spreading drops take the shape of a truncated sphere. Rioboo et al. report that at this early stage, no lamella is ejected at the drop's base yet. They report that the drop diameter increases proportional to $\tau^{0.5}$ in that phase. This early spreading stage can be accompanied by a very large spreading rate. The wettability of the substrate is reported to be not influential in this phase and the authors conclude that this stage "is completely described by the impact velocity and initial diameter".

The kinematic phase is followed by the spreading phase during which the formation of a lamella, i. e. a thin film bounded by a rim at the base of the drop, can be observed. This stage is therefore also called lamella phase [176]. Rioboo et al. [143] report that substrate influences are still small in this stage. Only on hydrophobic surfaces a substrate influence was observed and even then only for dimensionless times $\tau/\tau_{\rm kin} > 2$. Furthermore, they found that larger impact velocities and drop diameters result in faster spreading while large surface tensions and viscosities slow down the drop's expansion. The authors found that the maximum diameter reached in this phase decreases with increasing viscosity, but is also reached earlier.

During the first two phases as classified by Rioboo et al. [143], the spreading rate continuously decreases until at some point the drop may begin to recede during the relaxation phase. The authors, however, reported a receding motion only for a partially wetting system with a receding contact angle between 85° and 95°. For more hydrophilic substrates with receding contact angles below 19°, no receding motion

was observed. Rough surfaces and high impact velocities favored splashing during the relaxation phase, changing the phenomenology fundamentally. Furthermore, it was reported that drops may recede past their equilibrium shape, which can then result in partial rebound from the substrate.

Rioboo et al. [143] report a wetting or equilibrium phase following the previous phases. For complete wetting systems, they observed a plateau with fairly constant drop diameter over time preceding the wetting phase. Following this plateau, the drops were observed to spread with the contact line diameter increasing proportional to $\tau^{0.1}$. This is in agreement with the theoretical and experimental findings of Tanner [169] for drop spreading in complete wetting scenarios.

Impact of Micrometer-sized Droplets

Over the last two decades, an increasing number of studies regarding the impact of droplets with diameters considerably smaller than 1 mm were reported. Kim et al. [103] e.g. studied the impact of water droplets with diameters on the order of 100 μ m onto a solid surface at impact velocities around 10 m s⁻¹ using high-speed imaging. The general impact behavior observed closely resembles that described by Rioboo et al. [143] for similar values of the dimensionless groups *Re* and *We*. Thus, the description of Rioboo et al. [143] seems applicable also to micro droplet impact.

The impact of water droplets with diameters between $36 \,\mu\text{m}$ and $84 \,\mu\text{m}$ was investigated experimentally by van Dam and Le Clerc [174]. They focused on oscillations frequencies of the droplet contour as well as air entrainment between droplet and substrate. It was found that the entrained bubble volume was largest for impact velocities of a few meters per second and decreased with increasing impact velocity. They furthermore conclude that inertial oscillations of the droplet contribute significantly to dissipation, thereby reducing the energy available for spreading.

Jung and Hutchings [98] performed droplet impact experiments with initial droplet diameters between $25 \,\mu\text{m}$ and $28 \,\mu\text{m}$ at impact velocities between $3 \,\text{m} \,\text{s}^{-1}$ and $8 \,\text{m} \,\text{s}^{-1}$. Visser et al. [176] studied the impact of droplets with a diameter on the order of $50 \,\mu\text{m}$ experimentally with a temporal resolution of 100 ns as well as numerically. Impact velocities up to $50 \,\text{m} \,\text{s}^{-1}$ were studied. They especially focused on the formation process of the lamella. In agreement with other works above, Jung and Hutchings [98] and Visser et al. [176] conclude that the spreading and deposition behavior of micrometer-sized droplets closely resembles that of larger millimeter-sized drops if initial Reynolds and Weber numbers are similar.

Derby [51] reviewed the drop impingement process with focus on the length and time scales relevant to the inkjet process. For parameters typical to the inkjet printing process, he reports that the initial kinematic phase has a duration below 1 μ s. This phase is immediately followed by impact-driven spreading. Thus, the main stages of droplet impact in inkjet printing are summed up as an impact-driven regime, followed by relaxation and/or oscillation before the droplet enters the capillary-driven regime. Spreading in this last regime is reported to be dominated by capillarity following Tanner's law [169]. For the inkjet printing process, the starting point of this phase is reported to be at about 100 μ s to 1 ms after the initial impact [51].

Air Entrainment between Drop and Solid Substrate

As the drop approaches the substrate, the thickness of the gas layer between drop and substrate decreases. For drop deposition, an initial contact between liquid and substrate has to be made at some point. However, for smooth surfaces this may not occur instantaneously. For substrates with a maximum roughnesses $R_z = 100$ nm, de Ruiter et al. [47] report bouncing and hovering of drops even on hydrophilic substrates due to the air film between drops and substrates. The drops they observed impacted the substrate with *We* of order unity. Using Multiple-Wavelength-Interferometry, they were able to resolve the evolution of the film thickness. The minimum film thickness they observed at hovering droplets was 200 nm. With the same method, de Ruiter et al. [48] observed that the entrained air film collapses once its thickness decreased below ~ 200 nm. As driving force for the rupture of the air film they suspect electrostatic interactions.

The initial contact between drop and substrate does not necessarily occur underneath the drop's center. On the contrary, several authors have reported gas entrainment at the drop's center. Hicks and Purvis [75] used numerical simulations with the Boundary-Element-Method to study the entrained air under an impacting drop. They predict a ring-shaped initial contact between drop and substrate enclosing a gas volume at the drops center. This is in line with the work of other authors [23, 174] reporting entrained air bubbles at the drop center. In their studies of water droplets impacting onto a planar glass substrate, van Dam and Le Clerc [174] observed an entrained air bubble at the substrate within the mid third of the droplet. Over a range of Weber numbers from 0.45 to 194 they report a decreasing bubble volume with increasing Weber number. Bouwhuis et al. [23] studied the entrained air volume underneath a liquid drop both experimentally and numerically. They report a maximum bubble volume depending on the initial drop velocity u_0 . For droplets with an initial radius $r_0 \approx 10 \,\mu\text{m}$, this initial velocity of $u_0 \approx 1 \,\text{m s}^{-1}$ coincides with typical values for the inkjet printing process.

2.1.2 Heat and Species Transport during Drop Impact

As can be seen from the previous section, drop impact has been subject to quite extensive research over the last decades. However, heat and species transport add to the complexity of the physical problem. After the introduction of relevant dimensionless groups within this context, research regarding heat and species transport during drop impact is summarized in the following.

Dimensionless Groups for Heat and Species Transport

When heat and species transport during drop impact are considered, additional dimensionless groups become relevant. In the context of phase-change phenomena, Jakob and Stefan numbers are of relevance. The Jakob number

$$Ja = \frac{c_{\ell} \Delta T}{h_{\ell_{\rm V}}},\tag{2.8}$$

saturation temperature and $h_{\ell v}$ is the specific enthalpy of vaporization. The analogous dimensionless

$$Ste = \frac{c_{\rm s}\Delta T}{h_{\rm s\ell}},\tag{2.9}$$

where c_s is the specific heat capacity of the solid and $h_{s\ell}$ is the specific enthalpy of solidification [10]. The Prandtl number

describes the ratio of sensible heat to latent heat of evaporation and can also be interpreted as a dimensionless superheat [12]. Therein, c_{ℓ} is the specific heat capacity of the liquid, ΔT is the difference to

$$Pr = \frac{\nu}{a} = \frac{\mu c}{\lambda} \tag{2.10}$$

describes the ratio of kinematic viscosity ν to thermal diffusivity $a = \lambda/(\rho c)$, where λ is the thermal conductivity and *c* denotes the specific heat capacity [165]. The ratio of advective to diffusive transport is expressed by the Péclet number

$$Pe_a = \frac{hu}{a},\tag{2.11}$$

where *h* denotes a characteristic length [10]. The corresponding dimensionless groups regarding species transport are the Schmidt number

$$Sc = \frac{\nu}{D} = \frac{\mu}{\rho D},\tag{2.12}$$

where D is the diffusion coefficient [165], and the Péclet number

$$Pe_D = \frac{hu}{D}.$$
(2.13)

Furthermore, in the presence of surface active substances, the Damköhler number [10]

$$Da = \frac{k_{\rm ad}h}{D},\tag{2.14}$$

describing the ratio of reaction to diffusion rates is of relevance. Therein, k_{ad} is the kinetic adsorption coefficient.

Heat Transport during Drop Impact

group for melting is the Stefan number

Spray cooling is a very effective way of heat transfer [104]. It is therefore not very surprising that numerous authors [26, 68, 71, 74] have investigated drop impact under non-isothermal conditions. In this context, however, the main focus oftentimes rather lies on how the hydrodynamics influences heat transfer than the influence of heat transfer on the drop impact and spreading processes. Some numerical studies e.g. assumed temperature independent fluid properties [e.g. 12, 74]. In these cases, the main influence of heat transfer on hydrodynamics arises from evaporation. Especially large evaporation rates were observed in the three-phase contact line region for sessile drops after the initial impact and receding

[74]. Batzdorf [12] found that especially at very small Prandtl number the evaporation rate increases considerably, which results in smaller drop diameters at a given time after drop impact. The Jakob number was found to have an indirect effect on the hydrodynamics. With increasing Jakob number the apparent contact angle increases due to increased evaporation in the three-phase contact line region and, thus, higher Jakob numbers result in smaller drop diameters. Because these effects can both be attributed to evaporation, however, they must be considered negligible for non-volatile liquids, such as typical solvents of UV-curable inks.

As was discussed in the previous chapter, inkjet inks, especially UV-curable inks, can show a considerable dependence of material properties, mainly the viscosity, on temperature. Under this aspect, studies of impacting molten wax drops are of interest. Bhola and Chandra [18] studied the solidification of molten paraffin wax drops on a planar aluminum surface. Drop diameters and initial drop temperature were reported as (3.0 ± 0.1) mm and 73 °C respectively. The highest melting point of the paraffin wax was reported as (70 ± 1) °C. The initial impact velocity was varied between 0.5 m s^{-1} and 2.7 m s^{-1} . In addition, the substrate temperature was varied between 23 °C and 73 °C. The authors observed that lower substrate temperatures resulted in smaller drop diameters but also promoted break up at higher impact velocities. They conclude that the extent of drop solidification was too small to affect the impact dynamics but increases in surface tension and viscosity were the origin of the observed change in spreading behavior on cooler substrates.

Others studied wetting dynamics and heat transfer during solder drop [9] or droplet [7, 180] deposition. Attinger et al. [7] investigated the impact dynamics of molten eutectic tin-lead solder droplets with volumes on the order of a few picoliters onto a semi-conductor wafer. Droplet diameters were varied between 50 μ m and 100 μ m, impact velocities between 1 m s⁻¹ and 2.5 m s⁻¹. Thus, length and time scales are similar to graphical inkjet applications. The initial drop temperature was 210 °C, whereas the initial substrate temperature was varied between 48 °C and 135 °C below the solders melting point of 180 °C. They found that the substrate temperature significantly influences the spreading behavior. However, in contrast to the conclusion made by Bhola and Chandra [18] for their larger molten wax drops, Attinger et al. [7] concluded that in their case this is due to solidification of the drop at the threephase contact line. A (mainly) numerical analysis of the deposition of solder droplets was presented by Waldvogel and Poulikakos [180]. Using a numerical model based on the finite element method with a Lagrangian approach, they studied picoliter-sized tin-lead solder droplets similar to the ones studied experimentally by Attinger et al. [7]. They assumed the regions of molten and solidified solder to be separated by a sharp boundary and distinct, constant material properties in each of the two regions. In their case, solidification of the solder droplets occurred on the same time scale as droplet oscillations following the initial impact. This resulted in ripples along the contour of the solidified drops. They were able to qualitatively reproduce this outcome experimentally. Whether solidification has a considerable influence on the maximum spreading diameter of molten metal drops was investigated by Aziz and Chandra [9]. They found a threshold depending on Stefan and Prandtl numbers as well as the ratio of thermal effusivities of liquid drop and solid substrate. Thus, based on their findings, the influence of solidification on the spreading behavior depends on the relation between the rate of solidification and viscous dissipation.

Species Transport during Drop Impact

In addition to the influence of temperature gradients, surface-active substances can be expected to influence the impact and spreading behavior of drops. Zhang and Basaran [199] were the first to discuss the influence of surface-active substances adsorbed to the liquid-gas interface on drop impact in detail. Water and aqueous surfactant solutions impacting onto a glass substrate were considered. They noted that time scales during drop impact are typically too short for equilibration of bulk concentrations and adsorbed surfactant. The drops studied had diameters in the millimeter range and were impacting with $0.5 \,\mathrm{m \, s^{-1}}$ to 2 m s^{-1} . The impact time scale of micrometer-sized drops at similar velocities is even smaller, thus non-equilibrium conditions can be expected within the inkjet printing process. Zhang and Basaran [199] identified "(a) dilution of surfactant due to interfacial dilatation or surface area creation, (b) convection of surfactant towards the contact line [...], and (c) replenishment or repopulation of the interface by surfactant molecules form the bulk of the drop" as the three competing mechanisms affecting the surfactant distribution along the interface. While there are some quantitative changes in the impact behavior reported, they found that the influence of impact velocity on the impact behavior of surfactant loaded drops is similar to pure liquids. However, they observed different effects of the dynamic surface tension on the maximum spreading diameter depending on the impact velocity. At low impact velocities, lower surface tensions due to added surfactant resulted in further maximum spreading, while on the other hand, at high impact velocities, smaller maximum spreading diameters compared to the surfactant-free case were observed. They attributed this to an accumulation of surfactant at the contact line, resulting in Marangoni flow towards the axis of symmetry. They observed that for a faster adsorbing surfactant, drops spread further with increasing surfactant concentration. Thus, high adsorption rates can reduce dynamic surface tension effects. For both, slower and faster adsorbing surfactants, they observed an increase of the drops final radius with an increase of the surfactant concentration. This improvement in wettability is well expected and will be briefly discussed at the beginning of the following Section 2.2.

More recently, dynamic surface tension effects have been revisited by Gatne et al. [66] and Aytouna et al. [8] for aqueous surfactant solutions. Drop diameters were on the order of a few millimeters in both studies. Gatne et al. [66] considered various surfactants and both, hydrophilic and hydrophobic substrates. They focused on comparably low Weber numbers in the range of 20 to 100. In agreement with Zhang and Basaran [199], they observed larger final spreading and reduced oscillations for the surfactant solutions compared to pure water drops. On the hydrophobic substrate, surfactants could suppress partial rebound. These surfactant dependent effects were reported to be more prominent for faster adsorbing surfactants. Aytouna et al. [8] studied the impact onto hydrophobic substrates over a wider range of Weber numbers (10 to 700) but still below the splashing threshold. Surfactants with different adsorption rates were used in the experiments. They found that especially the receding of drops is strongly effected by the adsorption kinetics in dilute solutions. This effect was observed to be more prominent at higher impact velocities, in agreement with the findings of Zhang and Basaran [199]. They attribute this to an increased surface tension due to the drops stretching.

2.2 Static and Dynamic Wetting

For the very small drops relevant to inkjet printing, inertial forces are typically small, resulting in capillary-driven spreading following the initial impact and relaxation [51]. This wetting stage is dominated by surface energies and hydrodynamic effects in the three-phase contact line region. In the following, the fundamental equilibrium characterizing the wettability of fluid-substrate pairs will be briefly introduced, before in Subsection 2.2.2 hydrodynamic effects in the three-phase contact line region will be discussed. Finally, the state of the art regarding heat and species transport in the vicinity of the contact line is reviewed.

2.2.1 Static Wetting

How well a liquid wets a solid substrate is determined by the surface energies of the interfaces solidliquid $\sigma_{s\ell}$, solid-gas σ_{sg} and liquid-gas $\sigma_{\ell g}$, the last of which is also commonly referred to as surface tension. According to Young's [197] equation

$$\sigma_{\ell g} \cos \theta_{\rm eq} = \sigma_{\rm sg} - \sigma_{\rm s\ell}, \tag{2.15}$$

sometimes also called Young-Dupré equation [45], the equilibrium contact angle θ_{eq} can also be interpreted as a balance of forces at the contact line. Figure 2.1 illustrates this balance and the equilibrium contact angle enclosed between liquid-gas and liquid-solid interfaces. For $-1 < (\sigma_{sg} - \sigma_{s\ell})/\sigma_{\ell g} < 1$, partial wetting with corresponding $180^\circ > \theta_{eq} > 0^\circ$ is expected. Depending on the fluids and substrate, also complete wetting with a contact angle $\theta_{eq} = 0^\circ$ is possible.



Figure 2.1: Surface energies at the three-phase contact line.

Heterogeneities along the solid surface, such as surface roughness or chemical structures, can hinder motion of the contact line. In that case, the apparent contact angle that needs to be exceeded to advance the contact line θ_{adv} can be larger than the contact angle corresponding to the onset of a receding motion, θ_{rec} . This results in so called contact line hysteresis [21]. For a static contact line, the momentary contact angle can then take any value between θ_{adv} and θ_{rec} .

2.2.2 Dynamic Wetting

When drops are placed onto a substrate, they are in general not in their equilibrium state given by the Young-Dupré equation. Thus, the difference in surface energies will act towards this equilibrium state. During the resulting contact line motion, the apparent macroscopic contact angle generally deviates from the static value. Many theoretical and empirical models to describe this process have been proposed. The theoretical models can be divided into two major groups [19]. Models based on molecular-kinetic theory describe contact line dynamics through the statistical dynamics of molecules in the contact line region. Within this model framework, the dynamic contact angle arises on the molecular scale. The group of hydrodynamic models, on the other hand, is based on continuum mechanics. Therein, capillary forces are balanced by viscous forces in the three-phase contact line region, resulting in viscous bending of the meniscus. Thus, the capillary number

$$Ca = \frac{\mu_{\ell} u_{\rm cl}}{\sigma_{\ell g}},\tag{2.16}$$

which relates viscous to surface tension forces, is an important dimensionless group for the description of moving contact lines. u_{cl} denotes the contact line velocity, which is typically assumed positive for wetting and negative for dewetting. A third approach, the interface formation model introduced by Shikhmurzaev [157, 158], combines hydrodynamic effects with the assumption of non-equilibrium surface tensions in the vicinity of the contact line [158] and accounts for mass transfer between the liquid-gas and the liquid-solid interfaces [19]. Finally, there is a group of contact line models based on empirical correlations directly fitted to experimental observations. The following review will focus on hydrodynamic as well as empirical models, which have previously been widely used in the engineering community [see e.g. 74, 105, 115, 178].

Singularities at the Contact Line and Possible Remedies

Moffatt [120] predicted the appearance of singularly large viscous stresses in the corner of a wedgeshaped geometry moving with a given velocity relative to the solid wall, when the classical no slip condition between liquid and solid is assumed. Huh and Scriven [84] generalized this analysis to contactline movement and found similar singularities in shear stresses, pressure and the viscous dissipation rate. They conclude that these singularities indicate failure of at least one underlying assumption. Their prime suspect is the no slip boundary condition, even though they also propose cavitation, compressibility effects or variations in material properties at the contact line as mechanisms regularizing the singularity in reality. Thus, they propose the introduction of slip and suggest the simple linear condition [125]

$$\ell_{\rm s} \frac{\partial u_{\parallel}}{\partial x_{\perp}} = u_{\parallel} - u_{\rm w,\parallel} \tag{2.17}$$

known as Navier slip model to be used in this context. Therein, ℓ_s is the corresponding slip length¹, u_{\parallel} the velocity parallel to the wall, x_{\perp} the coordinate in wall normal direction and $u_{w,\parallel}$ the wall velocity. The slip length is typically much smaller than all other relevant length scales of the flow. Rothstein [147] reviewed slip of fluids over solid surfaces. Typical slip lengths are reported to be on the order of a few nanometers to tens of nanometers. Joseph and Tabeling [96] used particle image velocimetry in order to measure flow profiles within microchannels with hydrophilic and hydrophobic surfaces. They found that the slip length was below their measurement uncertainty of ±100 nm. Exceptions seem to be rarefied gas flows, highly turbulent flows and superhydrophobic substrates, for which substantially larger slip lengths were reported [147]. As these exceptions are not relevant to the inkjet printing process, it is safe to assume that physical slip lengths are small even compared to typical ink drop diameters in the range of tens of micrometers.

The interface formation model, introduced by Shikhmurzaev [157], provides an alternative mechanism for the relaxation of the contact line singularity through the thermodynamics of the contact line region [19]. As mentioned above, the model accounts for mass transfer between the liquid-gas and solid-liquid interfaces at the wall. This is motivated by different surface properties on the interfaces and a finite relaxation time for a transition between the interfaces. Corresponding additional balance equations for the different interfaces are introduced. Aside from eliminating the stress singularity at the contact line, the model is able to reproduce experimentally observed [34, 58] rolling contact line motion [157]. The interface formation model has been criticized for the previously mentioned relaxation time being too small to be relevant for the wetting process [59]². However, a similar approach allowing for mass transfer between interfaces and bulk has recently been presented by Lukyanov and Pryer [117]. Thus, there seems to be no consensus regarding the most appropriate modeling approach for the moving contact line yet [19].

Cox-Voinov Model

A very general model for moving contact lines based on hydrodynamic theory was developed by Cox [40]. The model uses matched asymptotic expansion, where depending on the limiting process two or three regions of expansion were found to be required. Cox describes the contact line dynamics based on the ratio of the characteristic microscopic and macroscopic length scales ε , the capillary number *Ca*, and the ratio of dynamic viscosities of the two fluids. The model also accounts for cases of partial wetting with a microscopic contact angle $\theta_m > 0^\circ$, without being limited to small contact angles. Cox introduces the microscopic length scale as a molecular length scale related to slip between the fluid molecules and the solid. However, it is clarified that the actual mechanism relieving the stress singularity at the three-phase contact line is not relevant for the developed model. The leading order result for the dynamic contact angle θ_d is then given as

$$g(\theta_{\rm d}) = g(\theta_{\rm m}) + Ca \ln\left(\varepsilon^{-1}\right). \tag{2.18}$$

¹ Sometimes, as also in the work of Huh and Scriven [84], $\mu/\beta = \ell_s$ is used instead, where β is the slip coefficient.

² See [159] for the response to this criticism.

In the case of negligible influence of the second fluid [see e.g. 31]

$$g(\theta) = \int_{0}^{\theta} \frac{\vartheta - \cos\vartheta \sin\vartheta}{2\sin\vartheta} \,\mathrm{d}\vartheta.$$
(2.19)

This simplification given by Equations 2.18 and 2.19 of the more general model of Cox had previously been derived by Voinov [177]. Introducing approximations for the integrand in Equation 2.19, Voinov simplified the above equations to the well known power law for dynamic contact angle and capillary number

$$\theta_{\rm d}^3 = \theta_{\rm m}^3 + 9 \, Ca \ln\left(\varepsilon^{-1}\right) \qquad \text{for } \theta < \frac{3}{4} \, \pi \tag{2.20}$$

and

$$(\pi - \theta_{\rm d})^3 + \frac{9}{4}\pi \ln\left(\frac{1 - \cos\theta}{1 + \cos\theta}\right) = \theta_{\rm m}^3 + 9\,Ca\ln\left(\varepsilon^{-1}\right) \qquad \text{else.}$$
(2.21)

Tanner's Law

Tanner [169] studied moving contact lines in the context of spreading silicone oil drops. In order to relieve the stress singularity at the contact line, a thin layer of liquid adsorbed to the solid in front of the moving contact line was assumed. From mass and momentum balance for the contact line region and under the assumption of a Stokes flow, Tanner finds that the slope of the liquid-gas interface is described by the relation

$$\tan\theta_{\rm d} \propto \sqrt[3]{Ca},\tag{2.22}$$

which for small θ_d and complete wetting agrees with Equation 2.20. Assuming a power law³ of the form $\tan \theta_d \propto \tau^{-n}$ and volume conservation, Tanner then arrives at

$$\tan\theta_{\rm d} \propto \tau^{-0.3} \tag{2.23}$$

for the dynamic contact angle and the well known power law

$$d_{\rm cl} \propto \tau^{0.1} \tag{2.24}$$

for the temporal evolution of the contact line diameter d_{cl} of a spreading drop. The power law for the dynamic contact angle was also observed experimentally by Tanner [169] and others [33, 62, 156]. It is therefore of great practical relevance in the context of drop spreading. Equation 2.24 is also referred to as Tanner's law in the literature [e.g. 21].

³ Assuming a spherical cap as the macroscopic drop shape also results in this power law [21].
Out-of-Balance Young's Force

While the above models were derived from hydrodynamic theory, other authors developed empirical models based on measurement data. One group of empirical models for moving contact lines is based on an "out-of-balance Young's force", of which two notable correlations [105] for dynamic contact angle and capillary number take the form

$$\frac{\cos\theta_{\rm eq} - \cos\theta_{\rm d}}{\cos\theta_{\rm eq} + 1} = f(Ca).$$
(2.25)

In the model of Jiang et al. [93], the function f(Ca) is given by the relation

$$f(Ca) = \tanh\left(4.96 \, Ca^{0.702}\right) \tag{2.26}$$

and in the model of Bracke et al. [25], this function is

$$f(Ca) = 2\sqrt{Ca}.\tag{2.27}$$

It is interesting to note that the model using Equation 2.26 asymptotically approaches a contact angle of $\theta_d = 180^\circ$, while the model using Equation 2.27 reaches $\theta_d = 180^\circ$ for Ca = 1/4 [105]. Both models are based on experimental data for advancing contact lines.

Kistler Model

Another empirical model, which is based on the experimental data of Hoffman [78], was introduced by Kistler [105]. The general structure of this model,

$$\theta_{\rm d} = f_{\rm Hoff} \Big[Ca + f_{\rm Hoff}^{-1}(\theta_{\rm eq}) \Big], \tag{2.28}$$

is similar to the models derived by Voinov [177] and Cox [40] and takes partial wetting scenarios with an equilibrium contact angle $\theta_{eq} > 0^{\circ}$ into account. The difference lies in the use of the Hoffman function

$$f_{\text{Hoff}}(x) = \cos^{-1}\left\{1 - 2\tanh\left[5.16\left(\frac{x}{1 + 1.31x^{0.99}}\right)^{0.706}\right]\right\},$$
(2.29)

instead of the inverse of $g(\theta)$. The Hoffman function was motivated by the similar correlation by Jiang et al. [93] given by Equations 2.25 and 2.26 above. Kistler [105] states that the function was based on complete wetting systems with high liquid viscosity and was adjusted to improve agreement with measurement data at large capillary numbers. Hoffman's [78] experimental data covers a range of $4 \times 10^{-5} < Ca < 36$. For small capillary numbers and complete wetting, the Kistler [105] model reduces to $\theta_d = 4.54 Ca^{0.353}$ [105]. Thus, it approximates Equation 2.20 for the complete wetting case. On the other hand, the Kistler model also shows excellent agreement with the data from [78] for high capillary numbers and θ_d approaching 180°. Therefore, the Kistler model is a universal model describing the apparent dynamic contact angle as a function of viscous and surface tension forces. As such, it has already been widely used in the numerical simulation of wetting phenomena [16, 142, 145, 149, 178].

2.2.3 Heat and Species Transport during Wetting and Spreading

The influence of heat and species transport on moving contact lines and drop spreading has also previously been studied by a number of authors. A substantial amount of research regarding evaporation at the contact line has been published [e.g. 100, 137, 164, 184]. It was observed that evaporation in the three-phase contact line region leads to increased heat transfer from the substrate. Furthermore, using a hydrodynamic model of the contact line region based on lubrication theory, it was observed that the contact angle increases with increasing wall superheat, which can be attributed to hydrodynamic effects [12]. The previously discussed studies on the impact of molten wax [18] or solder drops [7, 9, 180] showed that solidification can result in slower spreading. The substrate temperature was reported to significantly influence the spreading behavior in that case [7].

Another aspect relevant to the present thesis is the influence of Marangoni stresses on the contact line region. In the context of surfactant solutions, the solutal Marangoni effect is of interest. An extension of Tanner's model [169] towards surfactant solutions was suggested for future work by de Gennes [44] in his review. Cox [41] extended his model towards insoluble surfactants in the second part of his study. Besides negligible solubility, it was furthermore assumed that the surfactant does not adsorb to the solid, diffusion along the interface can be neglected, and that the surfactant concentration is non zero but finite along the entire interface. Comparison of the macroscopic contact angles predicted by the two models by Cox for surfactant-free and surfactant-laden cases gives insight into the influence of surfactant on contact line motion. For cases with a viscosity ratio of the two fluids near zero, the presence of surfactant increases the macroscopic contact angle of the higher viscous liquid substantially for any given capillary number, ratio of macroscopic to microscopic lengths ε , and microscopic wetting angle. The results presented for a microscopic wetting angle of 40° show that $Ca \ln(\varepsilon^{-1})$ is reduced roughly by a factor of two for a given macroscopic contact angle if surfactant is added. Thus, if one assumes constant material properties and ε , the spreading rate is reduced roughly by a factor of two in the presence of surfactant. Joanny [94] came to a similar result using a much simpler approach based on a lubrication approximation of just a single region. Furthermore, the surfactant fluxes through the contact line region were considered. If the substrate is repulsive towards the surfactant, i.e. no surfactant adsorbes at the solid wall, Joanny's model predicts an increase of the dynamic contact angle compared to the contact angle predicted by Tanner [169] by a factor of $2^{1/3}$, which corresponds alternatively to a prefactor of 2 for the capillary number (see also Subsection 4.3.5). Joanny notes that the power law for spreading remains valid in this case, while only the prefactor changes.

Clay and Miksis [36] studied the spreading of drops on a dry, solid substrate using lubrication theory. Influences of temperature and insoluble surfactant on surface tension were considered. If the surfactant was not allowed to adsorb to the solid, the spreading rate of the drop was decreased. This is in agreement

with the previously discussed work [41, 94] for the moving contact line. Their model also allowed for transition of surfactant from the liquid-gas interface to the solid substrate. This adsorption was found to produce Marangoni flow towards the contact line and thereby increase the spreading rate. The opposite case of surfactant adsorbing to the liquid-gas interface from the solid substrate was found to decrease the spreading rate. Temperature and surfactant concentration gradients along the substrate resulted in drop migration. Surfactant transport along the interface in combination with contact angle hysteresis was reported to result in a pinned contact line in some cases.

Karapetsas et al. [101] focused specifically on surfactant-enhanced spreading and superspreading of drops on solid surfaces. Similar to the work by Clay and Miksis [36], their model is based on lubrication theory. However, they took solubility of the surfactant as well as the aggregation of surfactant to micella into account. Karapetsas et al. [101] report high Marangoni stresses induced by the adsorption of surfactant from the liquid-gas interface to the substrate. The thereby increased spreading rate was found to be close to experimentally observed superspreading. In a more recent study by Karapetsas et al. [102], the influence of evaporation from surfactant-laden drops on particle deposition was studied. Solutal Marangoni stresses can in this case counteract thermal Marangoni stresses. An experimental study by Marmur and Lelah [119] showed fingering instabilities during spreading and retraction of surfactant-laden drops on a previously dry glass substrate. Similar fingering instabilities at the contact line were also reported for superspreading surfactant solutions during the final stage of spreading [127].

Beyond the spreading over a dry substrate, several studies regarding the spreading of surfactant or surfactant-laden drops over a prewetted substrate have previously been presented. Marangoni flow in this case results in strong deformations of the thin film at the surfactant front [90], which can even lead to film rupture [91]. Furthermore, fingering instabilities at the drop or surfactant front have been reported for such cases [92, 182, 183].

2.3 Drop on Drop Collision

As has been discussed in Chapter 1, the collision and coalescence of drops at the solid substrate can lead to an offset in drop position. In the following two sections, studies regarding drop collision at a solid substrate will be reviewed. In Subsection 2.3.1, isothermal, surfactant-free cases will be presented, before in Subsection 2.3.2, studies regarding heat and surfactant transport will be discussed.

2.3.1 Fluid Dynamics of Drop on Drop Collision

In addition to their experiments with molten wax droplets, Schiaffino and Sonin [153] also studied the behavior of water droplets with a diameter of 50 μ m successively impacting onto a solid substrate in a straight line. Due to some overlap between the drops, two neighboring drops coalesced forming a single drop with accordingly larger volume. This coalescence apparently resulted in an offset of the position of the following drops towards the previously applied drops, as after a defined number of drops a small gap towards the following drop remained. This newly placed individual drop then was reported to become the starting point for the next group of coalesced micro-drops.

Duineveld [57] performed experimental studies of inkjet printed droplets with a volume of 160 pL impacting a solid substrate at approximately 2 m s^{-1} . On the substrate, the successively applied droplets formed lines. The liquid they used was an aqueous solution of poly(3,4-ethylene-dioxythiophene) (PE-DOT), a conducting polymer. The surface tension of the solution was reported to be similar to that of water. The viscosity was reported as 20 mPas. The droplets were printed on glass substrates with a photo-resist layer on top. Different treatments were applied to the coating, resulting in varying hydrophilicity and contact angle hysteresis between the substrates. Duineveld observed bulges along the printed line at regular intervals on substrates with receding contact angles of 0°. An additional criterion regarding flow along the line had to be fulfilled for the bulging instability to occur. If the flow rate along the line was sufficiently small, no bulging could be observed.

Recently, the formation of lines from picoliter-sized droplets has also been studied numerically using the lattice Boltzmann method [35, 198]. Zhang et al. [198] varied the overlap ratio between neighboring droplets, the droplet frequency as well as the advancing contact angle. The receding contact angle remained fixed at 5°. In agreement with the work of Soltman and Subramanian [163], they found scalloped lines for larger drop spacings. However, Zhang et al. [198] noted that the optimal droplet spacing was not independent of the droplet frequency. An optimal overlap was determined for cases where the oscillations of coalescing droplets were in phase. However, if droplet oscillations were out of phase during coalescence, scalloped lines were reported for this optimal spacing. Cheng et al. [35] found that the line quality could be improved in the out-of-phase case by decreasing the droplet spacing or increasing the wettability of the substrate by decreasing the advancing contact angle.

Similar to the impact of a drop onto a solid wall, one may expect also air entrainment between a droplet and previously applied liquid. Air entrainment between liquid-gas interfaces has previously been studied in the context of drop impact onto a liquid pool [150, 172]. Thoroddsen et al. [172] observed a critical thickness of the enclosed air film on the order of ~ 100 nm, independent of the initial drop velocity. As the critical air film thickness was reached, the air film collapsed and the drop came in contact with the liquid film. As driving force for the collapse of the enclosed film they suspect intermolecular forces. For destabilization of the air film by intermolecular forces, they conclude that rupture of the enclosed film is independent of how the critical film thickness was reached.

2.3.2 Heat and Species Transport During Drop on Drop Collision

Similar to the single drop scenario discussed in Subsection 2.1.2, several authors have also studied the influence of drop collision and coalescence at a solid substrate on heat transfer. Batzdorf et al. [13] numerically studied the horizontal coalescence of two drops impacting a superheated solid substrate simultaneously next to each other. They found that the heat flow is governed by the wetted area at high Prandtl numbers, while for Prandtl numbers of order unity, evaporation becomes more relevant. Coalescence of the two drops was found to decrease the heat flow compared to two separately impacting drops. In between the two drops, a stagnation area was observed, resulting in an upward and sideways directed flow. For larger drop spacings, collision occurred later and a thin neck was formed in between

the drops. This neck was reported to continue growing after the end of the receding phase of the two drops.

Vertical coalescence of successively impacting drops onto a superheated wall was studied experimentally by Gholijani et al. [67]. Similar to the single drop impact scenario [12, 68] they found that increasing the wall superheat resulted in smaller maximum contact line diameters due to higher evaporation rates. The maximum heat flow increased with the number of drops, which the authors attribute to the larger liquid mass on the substrate and thus the increased wetted area. Impact of the later drops on the previous drops and the already cooled substrate, however, resulted in lower maximal local heat flux. A very similar vertical coalescence scenario was also studied experimentally and numerically by Guggilla et al. [71]. Similar to Gholijani et al. [67], they found that the contact line diameter decreases with increasing wall temperature. They quantified the cooling effectiveness of later drops and found that, due to the pre-cooled substrate, it is only around 0.6 times that of the initial drop. With wall superheats above the Leidenfrost temperature, no coalescence could be observed as drops bounced to the side under these conditions.

Other authors investigated similar scenarios from a slightly different angle, focusing on wetting dynamics and deposit formation under the influence of heat transfer. Soltman and Subramanian [163] studied lines formed of droplets with a volume of 100 pL. The initial droplet velocities are reported to be in the range of 1 m s^{-1} to 2 m s^{-1} . Similar to the experiments by Duineveld [57], an aqueous PEDOT solution was used. As substrates, poly(4-vinylphenol) (PVP) coated glass slides were used. Soltman and Subramanian [163] focused their experiments on the shape and structure of the deposited line after evaporation of the solvent. Besides drop spacing and frequency, they also varied the substrate temperature in the range of 17 °C to 60 °C. For low drop spacing, beads similar to those described by Duineveld [57] were observed to form at the beginning of the line and periodically along the line. Too large drop spacings resulted in scalloped lines or even isolated drops. With sufficiently high substrate temperature or larger delay between subsequent droplets, the authors reported the droplets to evaporate individually, before the next droplet impacted the substrate. This resulted in a deposition in the shape of stacked coins. The coffee ring effect [49] was observed to be less pronounced in the case of a uniform line in comparison to circular drops. Increasing the substrate temperature was reported to increase the formation of coffee rings. In cases where thermocapillarity plays a subordinate role, this effect was very recently also predicted by numerical simulation for the evaporation of urea-water drops, whereas thermocapillarity was reported to result in increased deposit formation at the drop's center [14, 15].

Schiaffino and Sonin [153] experimentally studied the impingement of molten wax droplets from a DOD inkjet printer onto a cold Plexiglas target. The droplets were 50 μ m in diameter, corresponding to roughly 65 pL, and impacted the substrate at about 2.5 m s⁻¹. The subsequently generated droplets were jetted onto a Plexiglas substrate with equidistant offset next to each other along a line. The temperature of the substrate was varied between 20 °C and 60 °C, the initial droplet temperature was kept 14 °C above the melting point of the wax during the experiments. Upon impact, the wax droplets solidified on the substrate as their temperature decreased. The contact line was reported to solidify first, while the rest of the bead remained in a liquid state for a longer period. Lower substrate temperatures resulted in stable lines of the deposited wax with larger contact angles after solidification. On the other hand, bulging

instabilities similar to the Plateau-Rayleigh instability [139] were observed for contact angles above 90°. For smaller contact angles the contact line on both sides of the deposited line of wax was reported to be parallel.

A similar experiment was conducted more recently by Li et al. [112]. Their work was focused on the receding of contact lines after the coalescence of molten wax droplets on an aluminum drum, a phenomenon they call drawback. During the experiments, the droplet diameters were kept at a constant value of approximately $40 \,\mu$ m, which corresponds to a volume of about $34 \,\mu$ L. The impact velocity was reported to be approximately $5 \,\mathrm{m \, s^{-1}}$. Besides drop spacing and interval, they furthermore studied the influence of the substrates temperature on the coalescence outcome. They found that an increased interval between the colliding droplets increased drawback and resulted in a more round shape of the coalesced droplets. They argued that the increased interval gave the droplets more time to assume a rounder shape driven by surface tension. Also a larger overlap between neighboring droplets was observed to result in a more round shape as measured by the droplets' aspect ratio. An increased drum temperature showed similar effects, which the authors attribute to the reduced cooling rate. They developed a simple model describing drawback. Furthermore, they studied the stability and breakup of printed lines. They found that with increasing droplet spacing lines became more prone to breakup. However, their model also predicted the line to be more prone to breakup at higher drum temperatures, resulting in increased drawback, which was in agreement with their experimental observations.

Species transport during the coalescence of drops has also attracted some attention in the past. Yeh et al. [194] studied the mixing of two drops with different surface tensions after coalescence using micro particle image velocimetry and a laser microfluorescence technique. The two considered working liquids were water and an aqueous surfactant solution with a concentration below the critical micelle concentration. The drops with a volume of $0.2 \,\mu$ L were placed side by side onto a surface with wettability gradient. This gradient caused a spontaneous motion of one of the drops towards its neighbor. The authors found that the mixing of the two drops was dominated by convection, which occurred within 100 ms after coalescence. They observed that the surface tension of the stationary drop showed the largest influence on convection. For larger surface tension, stronger convection was reported. Interestingly, the influence of the surface tension of the moving drop was reported to be less pronounced. Even though the authors' focus was not on Marangoni flow, those results indicate that surface tension gradients and consequently Marangoni flow must play a minor role in the considered scenario.

Lu and Corvalan [116] studied the coalescence of viscous drops containing insoluble surfactants using direct numerical simulation. The drops were initially placed on two opposing, parallel walls with a small liquid bridge connecting them. The work was thus focused on the evolution of the drop shape after an initial liquid bridge had already formed. The authors found that surface contraction is most pronounced directly at the liquid bridge, where it results in an increasing local surfactant concentration. Marangoni flow is then induced by this uneven surfactant distribution, which hinders growth of the liquid bridge between an ethanol-water drop and reservoir were observed by Blanchette et al. [20]. Depending on the reservoir composition and drop size, they report partial or total coalescence. They partly attribute this difference to Marangoni flow at the liquid bridge.

A variety of methods for the simulation of multiphase flows has been introduced in the past. The most common continuum based approaches can be classified by their representation of the liquid-fluid interface and its evolution. Table 2.1 illustrates this classification according to the review by Wörner [189]. Beyond these methods, long wave or lubrication theory is commonly applied for the description of thin films [130] or the spreading of drops on hydrophilic substrates [36, 175, 82]. Another approach often found in drop impact simulations is the lattice Boltzmann (LB) method [e.g. 35, 198], where the flow is modeled on the meso-scale through simplified kinetic models [189]. Even more detailed simulations are based on molecular dynamics (MD), where individual molecules are resolved and interactions are modeled on the molecular scale [99]. This extremely high resolution of the simulation and corresponding computational cost limits MD simulations to very short length and time scales. In the following, the focus will be on continuum based methods.

Classification acco	ording to [189].	
	Zero Interface Thickness	Finite Interface Thickness
Lagrangian	front tracking moving mesh	
Eulerian	level set geometric volume of fluid	conservative level set algebraic volume of fluid phase field

 Table 2.1: Continuum based methods for the simulation of multiphase flows.

 Classification according to [189].

In Lagrangian type approaches, the interface is tracked either by marker points on a background mesh (front tracking, FT) or mesh vertices (moving mesh) [189]. The latter is often implemented in the form of an arbitrary Lagrangian-Eulerian (ALE) mesh. This method allows the mesh to move with the fluid (Lagrangian), to be fixed (Eulerian), or to follow any (arbitrary) relative motion in between. For the simulation of two phase flows, the interface can thereby be represented by specific cell edges (2D) or faces (3D) [77]. At the same time, the flexibility of mesh motion within the bulk phases as well as in interface tangential direction can decrease mesh distortion compared to purely Lagrangian approaches [138]. In both discussed Lagrangian methods, the interface, represented by the connection of marker points (front tracking) or mesh vertices (moving mesh), has zero thickness.

In Eulerian type methods, the transport equations are solved on a fixed background mesh. These methods have in common that the phase distribution and therefore the interface position is represented by a scalar field. Within the level-set method (LS), this field is the signed distance to the interface, which is advected with the flow [168]. Within the interface-reconstructing volume of fluid method (IR-VOF), also called geometric VOF (geom. VOF), fluxes of the two phases across cell faces are tracked using a geometric reconstruction of the interface [148]. The evolution of the interface can then be captured by the volume fraction of the two phases within a control volume. Through the signed distance within the LS method

and the geometric reconstruction within the geometric VOF method, the interface is represented with zero thickness [189].

Closely related to the geometric VOF method is the color function volume of fluid method (CF-VOF), also called algebraic VOF (alg. VOF). Instead of a geometrical advection algorithm, this method describes the evolution of the phase distribution through an advection equation for the volume fraction field. Even though specialized discretization schemes have been developed for the advection of step-like fields such as the volume fraction field (see e.g. [89]), numerical diffusion results in a slight smoothing of this step. For typical implementations, this results in an interface thickness on the order of two to three mesh widths [189]. Within the so called conservative level-set method (C-LS) [128], this smoothing is introduced intentionally through a diffusion term and counteracted by an additional convective velocity in interface normal direction. An analytical solution exists for the resulting defined profile of the volume fraction across the interface [179]. This allows the calculation of a signed distance function. Thus, the C-LS method combines aspects of algebraic VOF and LS [107]. The phase field method (PF) can be considered a diffuse interface method that is based on fluid free energy [189]. The distribution of the phases is described by the scalar phase field, the evolution of which is described by the Cahn-Hilliard equation. The diffuse interface formulation of the PF method can be motivated physically on the length scale of van der Waals type forces. However, for the simulation of macroscopic multiphase flows, the interface thickness can artificially be increased in order to lower the required numerical resolution. The interface thickness is then typically resolved with up to ten mesh widths [189].

Regarding multiphase problems on short length scales, the evaluation of surface tension forces is of particular importance. Inaccuracies in their calculation can produce artificial velocities at the interface [189]. These so called spurious or parasitic currents can arise from inconsistent discretizations of surface tension forces and pressure gradients [135], the approximate solution of the pressure equation [195], or inaccuracies in the evaluation of interface curvature [136]. They have been reported for VOF, LS, FT and LB methods [189]. Despite the fact that spurious currents have already been subject to various studies [e.g. 135, 140, 195], related aspects, such as the evaluation of interface curvature on unstructured Eulerian meshes, are still subject to current research [136, 152].

Numerical methods for the simulation of multiphase flow have in the past also been used to study heat and species transport processes and related phenomena. Table 2.2 gives an overview of numerical studies that include surfactant and/or heat transport. The table additionally marks whether topological changes, such as coalescence or impact onto a solid surface were considered and it is noted whether moving contact lines were included. Note that this indication is based on aspects that were considered in the respective references. The underlying methods may be capable of handling additional aspects that were not considered in the corresponding reference. The aim of Table 2.2 is to give an overview over the capabilities of different numerical methods, not to provide an exhaustive list. Therefore, it is not necessarily representative of all numerical studies performed over the past decades. However, it clearly shows that both, surfactant and heat transport have previously been investigated using a variety of numerical methods. All classes discussed above, i.e. Lagrangian and Eulerian methods as well as methods with finite and zero interface thickness, are represented.

		Defermented	Mathad	urfactant transport soluble/insoluble)	leat transfer	opological changes	Aoving contact line
		Kererence(S)	wiethod	S	іЦі	L	4
'n.	less	Bender et al. [15]	ALE	((1)	\checkmark		
gra	erian Lagra Zero Interface Thickn	Dieter-Kissling et al. [53], Pesci et al. [132]	ALE	√ (sol.)	/	/	
La		Esmaeeli and Tryggvason [60]	F I FT	((aal))	V	V	
		wuradogiu and iryggvason [124]	F I	√ (SOI.)		\checkmark	
		Alke and Bothe [3]	geom. VOF	√(sol.)		$(\checkmark)^a$	
		Fath and Bothe [61]	geom. VOF		\checkmark		\checkmark
		James and Lowengrub [88]	geom. VOF	$\sqrt{(ins.)}$		\checkmark	
an		Ma and Bothe [118]	geom. VOF		\checkmark		
eri		Wu and Dhir [191]	LS^{b}		\checkmark	\checkmark	\checkmark
Eul h.	h.	Berberović et al. [17]	alg. VOF		\checkmark	\checkmark	\checkmark
	E	Kunkelmann [106] and following [12, 54, 154]	alg. VOF		\checkmark	\checkmark	\checkmark
	Int	Lakshmanan and Ehrhard [107]	C-LS	$\sqrt{(\text{sol.})^c}$			
	in.	Soligo et al. [162]	PF	√(sol.)		\checkmark	
	۲ ۰	Teigen et al. [170, 171]	PF	√(sol.)		\checkmark	

Table 2.2: Overview over a selection of numerical studies based on common continuum based methodsfor the simulation of multiphase flow that include surfactant and/or heat transport. Check-
marks indicate whether the respective aspect was included in the studies.

^{*a*} Stated to be possible due to the VOF approach but not demonstrated

^b LS on a moving mesh

^{*c*} Constant bulk concentration

With regard to surfactants, Lagrangian methods benefit from the representation of the interface by mesh faces in the case of ALE [53, 132], or marker points that can be connected to a surface mesh in the case of FT approaches [124]. These approaches allow the discretization of transport equations directly on the surface mesh. Also with respect to heat transfer problems, especially those including phase change, a surface mesh can be beneficial. Batzdorf [12] for example employs a reconstruction of the interface for the evaluation of temperature gradients at the interface. The representation of the interface by a mesh, however, comes at the cost of remeshing after strong deformations of the interface or topological changes. Tryggvason et al. [173] give a detailed description of the necessary steps for their FT algorithm. The required remeshing increases code complexity and computational effort.

In Eulerian methods, topological changes occur once the distance between two interfaces becomes too small to be resolved by the numerical mesh. This so called numerical coalescence is therefore mesh dependent [189]. Since the background mesh does not follow the interface, mesh updates are not required when strong interface deformations or topological changes occur. Nevertheless, adaptive mesh refinement in the interface region can still be beneficial regarding the overall computational cost while maintaining a high resolution close to the interface [142]. The inherent ability of Eulerian methods

to capture topological changes comes with the downside of no available interface mesh. This makes modeling the transport of a species on the interface less straightforward. Methods based on geometric VOF make use of a reconstructed interface to advect the interfacial concentration of surfactant [3, 88]. Different methods regarding surfactant transport have been introduced for the PF method. Teigen et al. [170, 171] developed a model based on constant normal extension [29]. The concept of this approach is to solve a transport equation on an Eulerian background mesh for a field that takes constant values in interface normal direction within the diffuse interface region. Their model uses two separate fields for bulk and interface concentrations. This is in contrast to the model presented by Soligo et al. [162], who solve a Cahn-Hilliard like equation for the concentration in bulk and at the interface, which is represented by a single scalar field. Lakshmanan and Ehrhard [107] introduced an approach to model surfactant transport for the C-LS method. Their continuum surface transport equation describes the transport of a volumetric concentration that is localized within the interface region of finite thickness. Eulerian methods have also been widely used for the simulation of heat transfer phenomena. The simulation of evaporation requires special attention in these methods regarding the evaluation of temperature gradients and evaporative source and sink terms [12, 73, 106]. However, if evaporation can be neglected, as in [16], the modeling of heat transfer can be quite straightforward.

The discussed references indicate that, depending on the physical problem, the choice of numerical method might differ. However, even very similar scenarios have previously been studied using different methods. Thus, especially for multiphysics applications, multiple approaches may be viable.

CHAPTER 3

Aims and Outline of this Thesis

As illustrated in Chapter 1, inkjet printing is a complex multiscale process including wetting, topological changes, and heat and species transport. The print quality depends on exact dot sizes and positions. Inaccuracies in dot size and position can lead to print defects on the macroscopic scale. Impermeable, non-porous substrates are especially prone to defects related to droplet coalescence.

The aim of this thesis is to provide a better understanding of the coupled wetting and transport processes and to derive recommendations for an improved print quality. Therefore, the spreading behavior of individual as well as collided droplets is of special interest. The literature review in the previous chapter has shown that a number of aspects relevant to inkjet printing have previously been studied. However, some open questions remain, of which the following are in the focus of this thesis:

- How does heat and species transport, above all the presence of surface-active substances, influence droplet impact and spreading on the very short length and time scales relevant to inkjet printing?
- How does heat and species transport affect the collision and spreading behavior of droplets at the solid substrate on these length and time scales?

These questions are approached using two reference scenarios: The first considers the impact of individual droplets. The second scenario represents the off-centered collision of an impacting droplet with a previously applied droplet on the substrate. In order to ensure relevance of the findings for the printing industry, printer manufacturers, and ink development, all process and material parameters are closely oriented on the industrial inkjet printing process with UV-curable inks.

The short length and time scales of droplet impact, spreading and collision within the inkjet printing process limit experimental studies mostly to observations of droplet contours using high speed imaging. Temperature and concentration fields on the relevant length and time scales can not yet be resolved experimentally. Therefore, the coupled wetting and transport processes are studied using numerical simulation within the scope of this work. The review of numerical methods for the simulation of multiphase flow has shown that a multitude of approaches has been used to study different aspects related to the

present work. Thus, different numerical approaches are applicable to the physical problem considered. Within the scope of this work, the algebraic VOF method is employed using the OpenFOAM solver *inter-Foam*. The method is inherently capable of handling topological changes, such as the initial wall contact as well as the coalescence of neighboring droplets, on a fixed background mesh. Furthermore, employing *interFoam* allows the use of previous developments regarding conjugate heat transfer [12, 64, 106] and high-performance computing techniques [142]. Future works considering structured substrates may benefit from the capability of OpenFOAM to handle unstructured grids.

Other aspects relevant to this work, however, require further attention within the algebraic VOF framework. Consequently, further method development, verification and validation is necessary within the scope of this work. As discussed in Section 2.4, simulations of surface tension dominated flows are prone to spurious or parasitic currents. Moreover, even though VOF is generally capable of handling topological changes, the film rupture during droplet impact as well as the coalescence process itself are expected to be mesh dependent. Treatment of the moving contact line is still subject to ongoing research independent of the underlying numerical method. Finally, including surface-active substances into the VOF framework is not straightforward, as the method lacks a discrete representation of the liquid-fluid interface. Hence, the efforts with respect to method development, verification and validation within this work focus on the following points:

- Reduction of spurious currents
- Modeling of film rupture during droplet impact and off-centered drop collision
- Treatment of the moving contact line
- Modeling of soluble surface-active substances within the algebraic VOF framework

The remainder of this thesis is structured in the following way: In the following chapter, the mathematical description and the numerical method are presented. Special focus is put on the challenges identified above. The individual aspects of the model are then verified in Chapter 5. Furthermore, simulation results of impacting and colliding micrometer-sized acrylate droplets are compared to experimental observation for the validation of the approach. In Chapter 6, parameter studies of individual droplet impact and spreading as well as the off-centered collision of droplets at the solid substrate are presented. In addition to hydrodynamic parameters, the influence of heat and surfactant transport on the impact, spreading and collision behavior is discussed. Finally, this work is summarized in Chapter 7 and a brief outlook is given in Chapter 8.

Mathematical Description and Numerical Method

Throughout this thesis, the algebraic volume of fluid method (VOF) is employed using the OpenFOAM solver *interFoam*. In Section 4.1, the governing equations for the two phase flow will be introduced. Special focus is put on the evaluation of interface curvature. Furthermore, a generalized density scaled continuum surface force model is introduced for volume of fluid methods, and handling of the moving contact line is discussed. Due to the small droplet sizes and therefore small inertial forces, additional models for wall contact and coalescence are necessary and will be introduced in subsections 4.1.5 and 4.1.6. Following these aspects of the two phase flow, the governing equations for the transfer of heat are presented in Section 4.2. Finally, the two-field modeling approach for transport of soluble and insoluble surfactants employed throughout this work will be presented in Section 4.3, before the numerical method, including acceleration techniques and solution procedure, is presented in Section 4.4.

4.1 Hydrodynamics of the Two-Phase Flow

In this section, the balance equations for mass and momentum will be introduced. Special focus is put on the evaluation of capillary forces and treatment of the moving contact line. At the end of this section, the above-mentioned models regarding substrate contact and coalescence will be introduced.

4.1.1 Governing Equations

Within the volume of fluid method, introduced by Hirt and Nichols [76], the distribution of two fluid phases within the computational domain is described by a volume fraction field representing the fractional volume of one of the two phases within a control volume. This volume fraction field, here denoted by α , is advected according to

$$\frac{\partial \alpha}{\partial \tau} + \nabla \cdot \alpha \mathbf{u} + \nabla \cdot (\alpha (1 - \alpha) \mathbf{u}_{\mathrm{r}}) = 0, \qquad (4.1)$$

where **u** is the velocity field and τ the time. Within the algebraic VOF method, this equation is discretized using appropriate numerical schemes. While in geometrical approaches the geometric advection ensures a sharp interface, an additional artificial compressive convective term is employed in the algebraic VOF method in order to counteract numerical diffusion. $\mathbf{u}_r = k_r ||\mathbf{u} \cdot \mathbf{n}_f|| \mathbf{n}_{\kappa}$ represents the compressive velocity, where the constant $k_r = 1$ within the scope of this work and \mathbf{n}_{κ} is the interface normal vector pointing towards the phase where $\alpha = 1$. \mathbf{n}_f denotes the cell face normal vector. Together with the continuity equation for an incompressible flow,

$$\nabla \cdot \mathbf{u} = \mathbf{0},\tag{4.2}$$

the advection equation of the volume fraction field forms the mass balance for the two phases. Assuming Newtonian fluids, the momentum balance is given by

$$\frac{\partial \rho_{\rm m} \mathbf{u}}{\partial \tau} + \nabla \cdot (\rho_{\rm m} \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \left[\mu_{\rm m} \left(\nabla \mathbf{u} + (\nabla \mathbf{u})^{\mathsf{T}} \right) \right] - \nabla p + \mathbf{f}_{\rm I}, \tag{4.3}$$

where *p* is the pressure and \mathbf{f}_{I} is the sum of all force densities acting at the interface between the two phases. ρ_{m} and μ_{m} denote density and viscosity of the two phase mixture, respectively. Any material properties φ_{m} for the single field formulation throughout this work are calculated from the properties of the two phases according to $\varphi_{m} = \alpha \varphi_{1} + (1 - \alpha) \varphi_{2}$. Due to the small droplet volumes relevant to the present work, gravitational forces are neglected. The interfacial forces

$$\mathbf{f}_{\mathrm{I}} = \mathbf{f}_{\sigma} + \mathbf{f}_{\mathrm{substrate}} + \mathbf{f}_{\mathrm{coalescence}} \tag{4.4}$$

here not only contain surface tension forces \mathbf{f}_{σ} , but also additional forces $\mathbf{f}_{\text{substrate}}$ and $\mathbf{f}_{\text{coalescence}}$ accounting for liquid-solid and liquid-liquid interactions respectively. These will be described in the following subsections 4.1.5-4.1.6. The surface tension forces

$$\mathbf{f}_{\sigma} = \sigma_{\ell g} \kappa \delta_b \mathbf{n}_{\sigma} + \delta_b \nabla_{\Sigma} \sigma_{\ell g} \tag{4.5}$$

are modeled using a generalized density scaled continuum-surface-force model. They introduce the Laplace pressure jump and additionally account for Marangoni stresses. Here, $\sigma_{\ell g}$ denotes the surface tension, κ the mean curvature of the interface, δ_b the interfacial Dirac distribution and \mathbf{n}_{σ} the interface normal vector. ∇_{Σ} is the gradient along the interface. The evaluation of interfacial Dirac distribution, interface normal and curvature will be discussed in detail in the following subsections.

While Hirt and Nichols [76] originally introduced and motivated the volume fraction field as a simple marker field, Equations 4.1-4.3 can also be derived from conditional volume averaging of the sharp interface two-field formulation of the two-phase flow. In order to do so, the closure assumptions of vanishing relative velocity between the two phases and identical pressure in both phases within the averaging volume have to be made. Furthermore, small-scale (or subgrid-scale) velocity fluctuations and corresponding stresses within the averaging volume have to be assumed to be negligible [cf. 190].

4.1.2 Generalized Density-Scaled Continuum Surface Force Model

For the level-set method, Yokoi [195] introduced a density scaled modification of the classical continuum surface force model by Brackbill et al. [24]. In the following the two models are introduced, before the density scaled approach is generalized and transferred to the volume of fluid method.

Continuum Surface Force

The continuum surface force model (CSF) introduced by Brackbill et al. [24] transforms capillary forces at the liquid-gas interface into a body force in the interface region. As it does not require mesh faces to align with the fluid interface, the CSF method or similar volumetric approaches are a common choice in interface capturing methods such as volume of fluid methods as well as level set methods or hybrids of the two [136]. The surface tension forces along a section of the interface S_i within a control volume V_i are given by

$$\mathbf{f}_{\sigma,i} = \frac{1}{V_i} \iint_{S_i \cap V_i} (\sigma_{\ell g} \kappa \mathbf{n} + \nabla_{\Sigma} \sigma_{\ell g}) \,\mathrm{d}S.$$
(4.6)

Using the interface Dirac $\delta_{I}(\mathbf{x})$, the surface integral can be transformed into a volume integral. The surface tension forces are then given by

$$\mathbf{f}_{\sigma,i} = \frac{1}{V_i} \iiint_{V_i} (\sigma_{\ell g} \kappa \mathbf{n} + \nabla_{\Sigma} \sigma_{\ell g}) \,\delta_1(\mathbf{x}) \,\mathrm{d}V. \tag{4.7}$$

In differential form this results in the expression given in Equation 4.5. Within the continuum surface force model, a regularized δ at the interface is employed. A common approach in VOF methods is to calculate δ from the volume fraction field according to

$$\delta_b = \delta_1 = ||\nabla \alpha||_2. \tag{4.8}$$

Density-Scaled Continuum Surface Force

Within the context of the level set method, the regularized interface Dirac distribution δ_r as well as the smoothed Heaviside function H_r used to calculate phase distribution and material properties (similar to α in the VOF context) are calculated from the level-set field *l*, such that they satisfy the relation [195]

$$\delta_{\rm r}(l) = \frac{\mathrm{d}H_{\rm r}(l)}{\mathrm{d}l},\tag{4.9}$$

showing great similarity to the VOF approach in Equation 4.8. Note that the interface tangential component of $\nabla \alpha$ vanishes and *l* changes only in interface normal direction by definition. In both cases, the

regularized δ protrudes into both phases. Yokoi [195] noted for the level set method that this leads to larger spurious currents in the phase with lower density, because the same volumetric force applied to a lower density fluid will lead to larger accelerations compared to a fluid with higher density. In order to obtain a more symmetric acceleration, Yokoi [195] proposed the use of a density-scaled δ of the form

$$\delta_{\text{scaled}}(l) = 2H_{\text{r}}(l)\delta_{\text{r}}(l). \tag{4.10}$$

Thus, within the density-scaled continuum surface force model (DS-CSF), the scaled δ function is shifted towards the phase with H = 1, while the identity

$$\int_{-\infty}^{\infty} \delta \, \mathrm{d}l = 1 \tag{4.11}$$

of the δ distribution is maintained.

Generalization of Density Scaling

For the following it is useful to reformulate Equation 4.10 to

$$\delta_{\text{scaled}} = \frac{\mathrm{d}(H_{\mathrm{r}}(l))^2}{\mathrm{d}l},\tag{4.12}$$

making use of Equation 4.9. This also suggests the generalization¹ to

$$\delta_{\text{scaled},b} = \frac{\mathrm{d}(H_{\mathrm{r}}(l))^{b}}{\mathrm{d}l},\tag{4.13}$$

with $b \in \mathbb{R}^{>0}$, allowing different scaling intensities, from a shift in the opposite direction, i.e. towards the phase with H = 0, for 0 < b < 1 to a strong shift towards the phase with H = 1 and a rather sharp δ for $b \gg 1$. In analogy to that a generalized DS-CSF model (gDS-CSF) can also be formulated for the VOF method as

$$\delta_b = ||\nabla \alpha^b||_2 = b\alpha^{b-1} ||\nabla \alpha||_2, \tag{4.14}$$

with the case b = 2 being similar to the originally proposed density scaling by Yokoi [195] for the level set method in Equation 4.10. The Euclidean norm is represented by $|| \cdot ||_2$ therein.

Figure 4.1 shows the density scaled δ for varying *b* for the approximated α profile from Appendix B. With increasing *b*, the δ function becomes more narrow and is shifted towards the phase with $\alpha = 1$. The influence of the choice of *b* on spurious currents is investigated in Subsection 5.1.2.

¹ Thanks to Peter Hachmann for his suggestion regarding a generalization of the density scaling.



Figure 4.1: Regularized δ with different density scaling intensity according to Equation 4.14 for a typical α profile across the interface. Δx denotes the mesh size.

Interface Normal

A common approximation for the interface normal within the VOF method is

$$\mathbf{n}_{\sigma} = \frac{\nabla \alpha}{||\nabla \alpha||_2},\tag{4.15}$$

and hence

$$\delta_b \mathbf{n}_{\sigma} = b \alpha^{b-1} \, \nabla \alpha = \nabla \alpha^b \tag{4.16}$$

for the generalized density scaled CSF formulation. In this form $\delta_b \mathbf{n}_{\sigma}$ enters Equation 4.5. Once discretized, this formulation enables the evaluation of the interfacial forces contributing to the Laplace pressure jump $[[p]] = \sigma_{\ell g} \kappa$ directly at cell faces, allowing a balanced discretization of $\sigma_{\ell g} \kappa \nabla \alpha$ and ∇p , where discretization errors cancel out if $\nabla \alpha^b$ and ∇p are discretized using identical schemes. See [136] for the case with b = 1 and [195] for the density scaled case in the level-set context for a more detailed discussion of the balanced discretization. An imbalance in the discretization requires calculating the gradient of the step like α field, it is known that an interface curvature estimate based on this gradient is poor. For this reason Popinet [136] points out that the evaluation of $\delta_b \mathbf{n}_{\sigma}$ should be decoupled from the evaluation of κ . The method for the evaluation of interface curvature used throughout this work is discussed in the following section.

4.1.3 Evaluation of Interface Curvature

Rettenmaier [141] was able to show that in cases, where the exact analytical interface curvature could be used during the evaluation of surface tension forces, spurious or parasitic currents were several orders

of magnitude smaller than in cases, where they have been evaluated from the volume fraction field α . For this study, the interface curvature was evaluated (i) according to the standard *interFoam* method based on the continuum surface force model by Brackbill et al. [24], (ii) using the iso-surface reconstruction [12, 106], and (iii) with a coupled Level-Set VOF based method [2, 195]. Rettenmaier's [141] results therefore suggest that spurious currents in the algebraic volume-of-fluid method, especially for the employed extended *interFoam* solver, are to a substantial part caused by inaccuracies in curvature calculation. While some of these methods performed better than others, all of them showed increasing parasitic currents with mesh refinement. Special care has therefore been taken within this work regarding the evaluation of interface curvatures, which will be discussed in the following.

The height function method [43, 134, 167] allows second order [43] or even higher order accurate results [22], however it is typically employed on structured grids [136]. The evaluation of interface curvature within VOF on unstructured grids is subject of recent research [see e.g. 152]. For the present work the concept of calculating the interface curvature on a smoothed volume fraction field is revisited in the following and extended towards wetting scenarios. A number of different smoothing kernels have been proposed in the literature [187]. The results of Cummins et al. [43] showed that by keeping the smoothing kernel radius independent of mesh size, second order convergence can be observed. The thereby effectively increasing discretization stencil with grid refinement is obviously disadvantageous regarding the computational efficiency. Despite this limitation, interface curvatures will be calculated based on a smoothed volume fraction throughout this thesis. This smoothed field is obtained by solving the diffusion equation

$$\frac{\partial \alpha_{\rm S}}{\partial \tau^*} = D_{\rm S} \nabla^2 \alpha_{\rm S} \tag{4.17}$$

within each time step in the pseudo time τ^* . Starting with $\alpha_{S,0} = \alpha$ at $\tau^* = 0$, the above equation is solved until a specified pseudo time $\tau^* = \tau_S^*$ is reached. Together with the diffusion coefficient D_S , τ_S^* determines the thickness of the interface region in the smoothed volume fraction field α_S . The influence of $D_S \tau_S^*$ on the curvature estimate is discussed in Subsection 5.1.1. Based on the results presented therein, the values employed throughout the remainder of this thesis will be introduced. Similar to the standard *interFoam* method, the interface normal can then be calculated from

$$\mathbf{n}_{\kappa} = \frac{\nabla \alpha_{\mathrm{S}}}{||\nabla \alpha_{\mathrm{S}}||_{2} + \varsigma_{\nabla \alpha}},\tag{4.18}$$

where $\zeta_{\nabla \alpha}$ is a small² value preventing division by zero outside of the interface region. The interface curvature is calculated by

$$\kappa = -\nabla \cdot \mathbf{n}_{\kappa}.\tag{4.19}$$

As Equations 4.17-4.19 do not depend on a structured grid, this evaluation method can be directly applied to unstructured grids. At a wetted wall the interface normal depends on wettability and consequently the contact angle, which is discussed in the following.

² Throughout the present work, $\zeta_{\nabla\alpha} = 10^{-8} / \sqrt[3]{V_{avrg}}$ is used, where V_{avrg} is the average cell volume of the domain. This value is negligible compared to $||\nabla \alpha_{\rm S}||_2$ within the interface region.

Contact Angle Treatment

Even without the above introduced smoothing procedure, an adequate evaluation of the volume fraction along a partially wetted substrate is of great importance as the interface normal vectors neighboring the wall and therefore also the local interface curvature depend on the volume fraction field at the wall. Both, the standard method within *interFoam* to evaluate α at the wall as well as the method introduced by Batzdorf [12] can result in values of the volume fraction outside the physically meaningful bounds of 0 and 1. While on the one hand OpenFOAM provides a number of different limiters to ensure boundedness at the wall, Batzdorf's [12] method on the other hand relies on possibly unbounded values at the wall. In the present work, a different approach is taken, which ensures boundedness of α -values at the wall while still taking the local contact angle into account.

The algebraic volume of fluid method produces a slightly diffuse interface with a transition region approximately two to three mesh widths thick [189]. The here proposed approach makes use of this property of the advected α -field. It takes advantage of the observation that the advection of the volume fraction α based on Equation 4.1 results in a typical α -profile that, for the discretization schemes used throughout this work, can be approximated by

$$\alpha \approx 1 - \frac{1}{1 + \exp\left(2\frac{\ell - \Delta\ell}{\xi}\right)} = \frac{1}{2} \left[1 + \tanh\left(\frac{\ell - \Delta\ell}{\xi}\right) \right]. \tag{4.20}$$

Therein, ℓ is the distance from the $\alpha = 0.5$ iso-surface with $\ell < 0$ for $\alpha < 0.5$ and $\ell \ge 0$ for $\alpha \ge 0.5$. The fitting parameters were found to be $\xi \approx 0.91\Delta x$ and $\Delta \ell \approx -0.01621\Delta x$, where Δx is the local mesh width. Numerical experiments to determine this profile and corresponding parameters using the discretization schemes used throughout this work are presented in Appendix B. Inverting the above relation allows to estimate the distance to the interface based on the volume fraction field by

$$\ell_{\alpha} \approx \frac{1}{2} \xi \ln \left[\frac{\alpha_{\rm lim}}{1 - \alpha_{\rm lim}} \right] + \Delta \ell, \qquad (4.21)$$

where for numerical reasons

$$\alpha_{\rm lim} = \min(\max(\alpha, \varsigma_{\alpha}), 1 - \varsigma_{\alpha}) \tag{4.22}$$

is used.³ Using the resulting distance of wall neighboring cell centers to the interface, the distance is extrapolated to a ghost-cell layer. From geometrical considerations, assuming the radius of interface curvature to be large compared to the mesh size, it can be calculated as

$$\ell_{\rm gc} = \ell_{\rm cc} + 2 ||\mathbf{x}_{\rm cc} - \mathbf{x}_{\rm w}||_2 \cos(\theta)$$
(4.23)

on an orthogonal grid. A schematic of the contact line region is shown in Figure 4.2. Depending on the

³ Throughout this work, $\zeta_{\alpha} = 10^{-15}$ is used, which corresponds to a distance to the interface of $15.7 \Delta x$. Within the interface region, ℓ_{α} is, therefore, uninfluenced by ζ_{α} .



Figure 4.2: Schematic of the contact line region.

interface distance ℓ_{gc} , the α values in the ghost cells can then be updated using Equation 4.20. With this value, the surface normal gradient at the substrate boundary is calculated using central differencing. Similar to standard *interFoam*, the surface normal gradient at the boundary is then used to extrapolate the cell centered wall neighboring value of α to the boundary face. The extrapolation method of the α -field and its gradient to the substrate boundary introduced here, however, avoids unbounded and therefore unphysical values while it maintains boundary values consistent with the contact angle.

On a wetted wall also the smoothing kernel at the wall, or in the present case the boundary condition during the smoothing step described by Equation 4.17 above, must be chosen consistently with the contact angle. For an initially planar and sharp interface, integration of Equation 4.17 leads to an α_{s} -profile in interface normal direction as given by

$$\alpha_{\rm S}(\tau^*) = \frac{1}{2} \left(1 + \operatorname{erf}\left(\frac{\ell}{\sqrt{4D_{\rm S}\tau^*}}\right) \right). \tag{4.24}$$

In the present work, Equation 4.17 is therefore solved with a pseudo time dependent Dirichlet boundary condition according to Equation 4.24 along the substrate. The initial τ^* at the beginning of smoothing is calculated using the estimate given in Appendix B. Employing the interface distance estimate from Equation 4.21 thereby prevents decoupling of the smoothed α_s -field from α at the substrate. For values of α close to zero or one, however, the distance estimate based on Equation 4.21 becomes very sensitive to small changes in α . Therefore, outside the contact line region, a geometrical distance estimate based on the iso-surface reconstruction as described by Kunkelmann [106] and Batzdorf [12] is used. This geometrical estimate of the distance ℓ_{geom} to the interface is calculated from the distance ℓ_{cl} of a point on the wall from the iso-reconstructed contact line ($\alpha = 0.5$, see [12] for a detailed description) and the local contact angle according to

$$\ell_{\text{geom}} = \sin(\theta) \,\ell_{\text{cl}},\tag{4.25}$$

assuming a planar interface. This estimate results in $\ell_{geom} = 0$ along the substrate for $\theta = 0^{\circ}$ and $\theta = 180^{\circ}$, producing poor distance estimates for extreme contact angles. In order to combine the benefits



Figure 4.3: Depending on the local contact angle θ , the weighting of the distance evaluated from the volume fraction field is changed.

of both methods, the interface distance estimates based on the α -profile and on geometry are throughout this work blended according to

$$\ell_{\alpha_{\rm S}} = w_{\rm dist} \ell_{\alpha} + (1 - w_{\rm dist}) \ell_{\rm geom},\tag{4.26}$$

using the contact angle and α dependent weighting factor

$$w_{\text{dist}} = 4^{\sin\theta} \left(\alpha + \varsigma_{\alpha} \right)^{\sin[\max(\theta, \pi/2)]} \left(1 - \alpha + \varsigma_{\alpha} \right)^{\sin[\min(\theta, \pi/2)]}.$$
(4.27)

This ad-hoc chosen heuristical approach has the following desired properties: (i) Within the contact line region, ℓ_{α} is used, ensuring coupling of α and $\alpha_{\rm S}$ at the contact line, while at the same time (ii) for extreme contact angles close to 0° or 180° the α -profile based distance estimate ℓ_{α} is used in a larger area within the liquid or gas phase, respectively, thus avoiding constant $\alpha_{\rm S} = 0.5$ corresponding to $\ell_{\rm cl} = 0$ along the wall in these cases. Figure 4.3 shows $w_{\rm dist}$ as a function of α for different contact angles.

Once the cell centered interface normals have been calculated from the smoothed volume fraction field $\alpha_{\rm S}$ according to Equation 4.18, they are interpolated to the cell faces for curvature calculation using Gauss's theorem. Along the substrate, they are corrected according to

$$\mathbf{n}_{\kappa}^{*}|_{s} = \mathbf{n}_{w}\cos(\theta) + \frac{\mathbf{n}_{\kappa} - (\mathbf{n}_{\kappa} \cdot \mathbf{n}_{w})\mathbf{n}_{w}}{||\mathbf{n}_{\kappa} - (\mathbf{n}_{\kappa} \cdot \mathbf{n}_{w})\mathbf{n}_{w}||_{2}}\sin(\theta)$$
(4.28)

to represent the apparent contact angle θ . The unit normal vector of the solid substrate boundary oriented out of the fluid domain is here denoted by \mathbf{n}_w . To reduce possible variations of $\mathbf{n}_{\kappa}^*|_{s}$ in contact line normal direction along the substrate, $\mathbf{n}_{\kappa}^*|_{s}$ is smoothed by interpolation from cell centers to cell vertices and back to cell centers, followed by renormalization, as presented in [6]. Finally, the interface

normal vector \mathbf{n}_{κ} , including the values corrected according to the local contact angle at the wall $\mathbf{n}_{\kappa}^*|_s$, is used in Equation 4.19 to calculate the interface curvature. It should be noted that the contact angle used for the evaluation of interface curvature does not have to be constant, but can depend on other variables. Thereby, a subgrid-scale model for contact line dynamics can be employed, as is discussed in the following section.

4.1.4 Modeling the Moving Contact Line

Even for the here considered micrometer-sized droplets, resolving the flow down to the length scale of molecular slip is computationally expensive. For this reason, a dynamic contact angle model is used as a subgrid-scale model, relating the apparent macroscopic contact angle to the capillary number *Ca* and the equilibrium contact angle θ_{eq} . The model used throughout this work is based on the Kistler [105] model. As introduced in Subsection 2.2.2, the Kistler model covers the entire range of θ_d between 0° and 180° in good agreement with experimental data, which is of particular importance for the simulation of droplet impact. Here, the dynamic contact angle is calculated from

$$\theta_{\rm d} = f_{\rm Hoff} \Big[Ca^* + f_{\rm Hoff}^{-1}(\theta_{\rm eq}) \Big], \tag{4.29}$$

where $Ca^* = sCa$ is a modified capillary number, which takes the influence of surface-active substances on the subgrid-scale through the prefactor *s* into account. This approach regarding surfaceactive substances will be discussed in more detail in Subsection 4.3.5. For s = 1 and therefore $Ca^* = Ca = \mu_{\ell}u_{cl}/\sigma_{\ell g}$, this model reduces to the classical Kistler [105] model for the surfactant-free case, where u_{cl} represents the contact line velocity and μ_{ℓ} denotes the dynamic viscosity of the liquid phase. The Hoffman function is given by Equation 2.29 in Subsection 2.2.2. Different methods for the evaluation of u_{cl} have been proposed in the past [12, 114], as reviewed by Rettenmaier [141]. From comparison of simulation results for spreading drops with u_{cl} evaluated using the methods of Batzdorf [12] and Linder et al. [114] with the classical approach as described below, Rettenmaier concludes that all three models produce very similar results. Within the scope of this work, the contact line velocity is therefore calculated based on the classical approach using the projection of the velocity in cell centers adjacent to the substrate, here denoted by \mathbf{u}_{cc} , onto the substrate and normal to the contact line,

$$\mathbf{u}_{\rm cl} = (\mathbf{n}_{\rm cl} \cdot \mathbf{u}_{\rm cc}) \,\mathbf{n}_{\rm cl},\tag{4.30}$$

where

$$\mathbf{n}_{cl} = \frac{\mathbf{n}_{\kappa} - (\mathbf{n}_{\kappa} \cdot \mathbf{n}_{w}) \mathbf{n}_{w}}{||\mathbf{n}_{\kappa} - (\mathbf{n}_{\kappa} \cdot \mathbf{n}_{w}) \mathbf{n}_{w}||_{2}}.$$
(4.31)

This is a natural choice, as \mathbf{u}_{cc} is also used for the advection of the volume fraction field. However, in general, \mathbf{u}_{cc} varies across the contact line along \mathbf{n}_{cl} . Therefore, a local weighted mean contact line velocity is calculated here by weighting \mathbf{u}_{cl} with δ_2 and then applying the same smoothing procedure as

for $\mathbf{n}_{\kappa}^*|_{s}$. Similarly, δ_2 is smoothed. The local weighted mean contact line velocity \mathbf{u}_{cl}^* is then evaluated from the ratio of the two smoothed fields. At the contact line, $u_{cl} = -\mathbf{u}_{cl}^* \cdot \mathbf{n}_{cl}$ is used to evaluate *Ca*. Finally, the local *Ca* at the contact line is distributed across the contact line region. The accuracy of this contact line model is discussed in Subsection 5.1.3.

The Contact Line Singularity, Slip and Numerical Slip

In combination with a classical no-slip boundary condition at the wall, a stress singularity at the moving contact line arises [84]. Or, as Huh and Scriven [84] illustrated it: "not even Herakles could sink a solid if the physical model were entirely valid, which it is not." As discussed in Chapter 2, a common remedy for this problem is to introduce slip between fluid and solid. However, as in finite volume methods the volume fraction field at the contact line is advected based on the velocity in wall neighboring cell centers, numerical slip is always present in these methods. This allows for a motion of the contact line even if a no-slip boundary condition at the wall is used, formally. The numerical slip introduced by discretization is, however, clearly mesh dependent. In combination with a constant contact angle model, this results in a strong mesh dependence of capillary-driven flows, as was recently shown by Gründing et al. [70]. In order to compensate for the effect of a mesh dependent numerical slip, Afkhami et al. [1] introduced a mesh dependent correction to the contact line model. With this correction, mesh independent results were reported for a constant contact angle with no-slip boundary condition for the velocity field, where otherwise mesh dependent behavior was observed. On the other hand, numerical slip has been used quite successfully in combination with subgrid-scale models for the dynamic contact angle. Sikalo et al. [178] found excellent agreement between simulation results and experimental observations of impacting drops using such an approach. The spreading behavior of droplets with a volume of 6 pL using the Kistler model in combination with a no-slip boundary condition within the algebraic VOF method was investigated in [6]. Spurious currents were observed to lead to instabilities at the contact line resulting in largely overestimated contact angles. However, introducing an additional smoothing step during the evaluation of the contact line velocity, good agreement between the spreading behavior of the droplet with the Kistler model was found. Rettenmaier [141] compared various dynamic contact angle models and different methods of evaluation of the contact line velocity. However, even including the contact angle correction suggested by Afkhami et al. [1], the method was reported to yield mesh dependent results. Rettenmaier [141] therefore suggested incorporation of the Navier slip model in the framework as a possible remedy.

While the use of a dynamic contact angle model seems to produce accurate results even with a standard no-slip boundary condition in some cases, in other cases with similar setup a considerable mesh dependence was observed. It is therefore unclear, whether numerical slip is sufficient when using a subgrid-scale model for the contact angle. For this reason, a localized slip model is introduced here, which provides free slip at the contact line and no-slip for the bulk phases. The model is based on the *partialSlip* boundary condition of OpenFOAM. The *partialSlip* boundary condition consists of the no penetration condition,

$$\mathbf{u} \cdot \mathbf{n}_{\mathrm{W}} = \mathbf{u}_{\mathrm{W}} \cdot \mathbf{n}_{\mathrm{W}},\tag{4.32}$$

for the wall normal component, where \mathbf{u}_{w} is the wall velocity, while for the wall parallel component \mathbf{u}_{\parallel} a blending factor is used to blend between a Dirichlet boundary condition with $\mathbf{u} = \mathbf{u}_{w}$ and a Neumann boundary corresponding to free slip. This corresponds to an OpenFOAM *mixed* boundary [cf. 108, 129] for the wall tangential component, where the boundary face values of a field are calculated from

$$\varphi_{\rm w} = w \,\varphi_{\rm ref} + (1 - w) [\varphi_{\rm cc} + \ell_{\rm ccw} (\mathbf{n}_{\rm w} \cdot \nabla \varphi)_{\rm ref}]. \tag{4.33}$$

Therein, ℓ_{ccw} denotes the distance from the wall neighboring cell center to the wall. Thus, depending on the weighting factor w, the boundary face values are determined by the reference value φ_{ref} , corresponding to a Dirichlet condition (w = 1), or the reference gradient $(\mathbf{n}_w \cdot \nabla \varphi)_{ref}$, corresponding to a Neumann condition (w = 0). With $\mathbf{u}_{\parallel,ref} = \mathbf{u}_{\parallel,w}$, the Dirichlet contribution corresponds to the classical no-slip condition, whereas $((\nabla \mathbf{u}_{\parallel})[\mathbf{n}_w])_{ref} = \mathbf{0}$ for the reference gradient in wall normal direction corresponds to a free-slip condition. The weighting factor $0 \le w \le 1$ allows blending between no-slip and free-slip at the wall. Within the scope of this work,

$$w = w_{u} = 1 - 4\alpha_{s}(1 - \alpha_{s}) \tag{4.34}$$

is used, which results in free-slip at the contact line, no-slip elsewhere, and a smooth transition in between. In that way, the contact line singularity and related (numerical) issues are mitigated, while the standard no-slip condition can be used away from the contact line. The instantaneous, apparent contact angle then depends on the subgrid-scale model presented above. The influence of free-slip vs. no-slip on droplet spreading dynamics in conjunction with a dynamic contact angle will be evaluated in Subsection 5.1.3.

4.1.5 Modeling Substrate Contact

The very small drop volumes relevant to the present thesis are accompanied by low inertial and gravitational forces. At the same time, surface tension forces play a major role. As discussed in Subsection 2.3.1, droplet bouncing has been observed experimentally in certain cases. In other cases, the entrained gas film between droplet and substrate was observed to rupture, presumably due to intermolecular forces. In reference experiments shown later on in Subsection 5.2.1, no bouncing was observed for inkjet typical impact parameters. Previous work [4] preceding the present thesis, however, showed a substantially delayed rupture of the entrained gas film. Intermolecular forces over an entrained film between substrate and liquid had been neglected therein. Within the present work, an attractive force between liquid and solid, motivated by intermolecular interactions, is introduced to ensure rupture of an entrained film. The pressure due to van der Waals interaction arising between two half spaces with parallel, planar surface is [86]

$$p_{\rm vdW} = -\frac{A}{6\pi h^3},\tag{4.35}$$

where *A* is the Hamaker constant and *h* the distance between the two planes. Even though this is an integral measure over both half spaces, the contribution of molecules outside the interface region is small, as the van der Waals potential is proportional to r^{-6} . Here, *r* is the center to center distance of two atoms or small molecules. Similar to the surface tension forces, this effect is therefore introduced as the volumetric force

$$\mathbf{f}_{\text{substrate}} = \begin{cases} \frac{A_{\text{sl}}}{6\pi(z+z_{\text{min}})^3} \,\delta_b \mathbf{n}_{\text{w}} \, \left[\max(-\mathbf{n}_{\text{w}} \cdot \mathbf{n}_{\kappa}, 0) \right]^8 & \text{for } z \le z_{\text{crit}}, \\ 0 & \text{else} \end{cases}$$
(4.36)

acting at the liquid-gas interface. For a planar substrate, the distance to the substrate *z* is easily evaluated. Addition of z_{\min} avoids singular stresses for z = 0 and is chosen on the order of tens of nanometers.⁴ The wall contact model is limited to the vicinity of the wall, where $z \le z_{crit}$.⁵ The introduced force always acts along the wall normal \mathbf{n}_w towards the substrate. The ad-hoc chosen weighting $[\max(\mathbf{n}_w \cdot \mathbf{n}_\kappa, 0)]^8$ ensures that $\mathbf{f}_{substrate}$ acts only on interfaces entraining gas between liquid and solid with the force being largest for parallel boundaries of the entrained gas film. This weighting therefore ensures that $\mathbf{f}_{substrate}$ acts only in the very early stage of droplet impact. Even though van der Waals forces are expected to show no substantial influence for film thicknesses above a few hundred nanometers, this model provides a mechanism to ensure wall contact also on meshes, where these length scales can not be resolved. In these cases the interactions must be shifted to larger length scales by artificially increasing *A*. The influence of the choice of *A* on the film rupture will be discussed in Subsection 5.1.4.

4.1.6 Modeling Coalescence

In analogy to the model for substrate contact, also the coalescence between two liquid-gas interfaces is modeled. The volumetric force acting at the interfaces liquid-gas is determined according to

$$\mathbf{f}_{\text{coalescence}} = \begin{cases} -\frac{A_{\ell\ell}}{6\pi(h+h_{\min})^3} \,\delta_b \mathbf{n}_{\sigma} & \text{for } h \le h_{\text{crit}} \,\wedge\,\kappa \ge \kappa_{\min} \,\wedge\,||\mathbf{x} - \mathbf{x}_{\min}||_2 < h/2 + d_h, \\ 0 & \text{else,} \end{cases}$$
(4.37)

where *h* is the thickness of the film they enclose. h_{\min} limits the coalescence force for small film thicknesses and h_{crit} restricts the coalescence model to interfaces actually bounding a thin film.⁶ Furthermore, $\mathbf{f}_{\text{coalescence}}$ acts in interface normal direction \mathbf{n}_{σ} . In order to determine the film thickness, first a distance field ℓ to the interface is required. This distance field is calculated from the smoothed volume fraction field α_{s} obtained from the solution of Equation 4.17. Inverting the expected analytical solution given in Equation 4.24 results in

$$\ell = \sqrt{4D_{\rm S}(\tau^* - \tau_0^*)} \,\mathrm{erf}^{-1}(2\alpha_{\rm S} - 1) \tag{4.38}$$

 $z_{\rm crit} = 1 \,\mu{\rm m}$ is used throughout this work.

⁴ Throughout this work, $z_{\min} = 25$ nm is used. The resulting decrease in attractive force is compensated by the chosen $A_{s\ell}$.

⁶ Throughout this work, $h_{\min} = 25 \text{ nm}$ and $h_{crit} = 1 \mu \text{m}$ are used in analogy to the substrate contact model.

for the distance field, where the inverse error function is approximated according to [188]. The conservative Level-Set method [128, 179] similarly makes use of Equation 4.38 for the reinitialization of the distance field. Here, the offset in pseudo time τ_0^* accounts for the finite interface thickness in the α -field and is estimated using the approximation for the transition of α across the interface given in Equation B.3. After the distance field has been calculated, local minima in the distance field are identified. Cells with $||\nabla \ell||_2$ below a certain threshold⁷ are marked as midpoints between two interfaces. The film thickness at these marked cells can then be approximated by $h \approx 2\ell$. At this point, a filter regarding the interface geometry is applied: Midpoints enclosed by concave interfaces, as determined by $\kappa < \kappa_{\min}$, are identified and excluded from further evaluation.⁸ This ensures that the coalescence model is not applied for underresolved entrained bubbles. Starting from the remaining midpoints, the information of the local film thickness is then passed in both directions back to the bounding interfaces of the film. For that purpose the algorithm proposed by Kunkelmann [106] to distribute information to neighboring cells, which was originally developed to distribute interface normals, is employed. Starting from cells already containing the information, in this case the local film thickness h, this algorithm simply copies the information into neighboring cells sharing a face with the donor cell. If a receiving cell has multiple donor cells, the values are averaged. In the present case, this process is repeated until the information has been distributed over both interfaces bounding the film. Similarly, the original position of the identified film midpoint \mathbf{x}_{mp} is passed back to the interfaces. Based on the distance $||\mathbf{x} - \mathbf{x}_{mp}||_2$ of the interface cell to the identified midpoint, a final filter is applied.⁹ This final filter is necessary to limit application of the coalescence model at the edge of an entrained gas film. Similar to the substrate contact model, this coalescence model provides a mechanism to ensure experimentally observed coalescence in the simulation of droplet collision at small We. The influence of the choice of $A_{\ell\ell}$ is investigated in Subsection 5.1.5.

4.2 Heat Transport

Within the present work, the focus is on non-volatile liquids. Therefore the energy balance does not include source terms due to phase change. Furthermore, it can be assumed that viscous dissipation effects are negligible. The basis for this assumption is discussed in Appendix A. Using Fourier's law, the energy balance in the fluid domain can then be described by the equation

$$\frac{\partial (\rho c)_{\mathrm{m}} T}{\partial \tau} + \nabla \cdot ((\rho c)_{\mathrm{m}} T \mathbf{u}) = \nabla \cdot (\lambda_{\mathrm{m}} \nabla T), \qquad (4.39)$$

where $(\rho c)_m$ is the volume averaged volume specific heat capacity of the liquid and gas phase within a control volume and λ_m similarly the averaged thermal conductivity. If a control volume is completely

⁷ Cells with $||\nabla \ell||_2 < 0.4$ are marked as midpoints throughout this work.

⁸ Midpoints with $\kappa < \kappa_{\min} = -2 \times 10^5 \, \text{m}^{-1}$ are excluded from further evaluation.

⁹ Throughout this work $d_h = 0.75 \,\mu\text{m}$ is used.

filled by one of the phases, these averaged material properties reduce to the values of respective phase. Due to the absence of convection this reduces to

$$\frac{\partial \rho_{s} c_{s} T}{\partial \tau} = \nabla \cdot (\lambda_{s} \nabla T), \qquad (4.40)$$

within the solid, with ρ_s , c_s and λ_s being the density, specific heat capacity, and thermal conductivity of the solid, respectively. The temperature fields within the two domains are coupled iteratively similar to the method of Batzdorf [12].¹⁰ During this coupling, a Neumann boundary condition is employed for the solid domain, and a Dirichlet condition for the fluid domain. It is beneficial regarding stability of the coupling if the Neumann condition is employed for the domain with greater thermal conductivity [185]. In the majority of impact scenarios considered in this work, this criterion is met by applying boundary conditions as described above. In order to improve stability also for the remaining cases, temperatures at the coupled boundary are underrelaxed between subsequent iterations. The coupling is considered converged once the maximum change of temperature between subsequent iterations has fallen below a certain threshold value.¹¹ By ending the iterative process after solving for the temperature in the solid domain, where the Neumann boundary condition and therefore the heat flux is prescribed, conservation of energy across the solid-fluid interface is ensured.

4.3 Species Transport

In this section the transport model for a soluble surfactant employed throughout this thesis is presented. It is based on a two-field formulation, treating bulk and interface concentrations as two coupled fields. In the following, the governing equations of the two-field approach will be presented, followed by a detailed description of the evaluation of the area specific concentration in the interface region in Subsection 4.3.2. In Subsection 4.3.3 the coupling between bulk and interface concentrations will be introduced.

4.3.1 Two-Field Approach for Bulk and Interface Concentrations

Classical surface equations of state relate the local surface tension to the area specific surface excess concentration of the surfactant. It is thus beneficial to track this species excess at the interface separately from the bulk concentration. On the other hand, in the case of soluble surfactants the transport processes within the bulk can influence the adsorption of surfactant to the liquid-gas interface. Therefore, a two-field approach, which allows to distinguish between the two concentrations, is employed here.

¹⁰ The temperature equation could alternatively be discretized into a single linear equation system for fluid and solid domain, which made the iterative coupling unnecessary. Such a functionality is e.g. provided by the block coupled matrix implementation in the foam-extend project. However, at the time this thesis is written, this functionality is not available for the OpenFOAM Foundation release used throughout this work.

¹¹ Similar to [12], a threshold value of 10^{-4} K is used.

Bulk Concentration

The bulk concentration is tracked using a convection-diffusion equation. It is a simplification of the continuum-species-transport model derived by Deising et al. [50] to the case of solubility of the species in only one of the two phases, namely the phase with $\alpha = 1$. Deising et al. [50] showed that conditional volume averaging introduces an additional term at the interface arising from diffusive fluxes, compared to a single phase convection-diffusion equation. It is shown as the second term on the right-hand side of Equation 4.41. The volume averaging procedure results in a single transport equation for the bulk concentration valid in the entire fluid domain. This allows conservative transport of the species on the Eulerian background mesh within a finite volume framework. The transport equation, simplified to solubility in only the liquid phase and extended by a sink or source term to account for ad- or desorption at the interface as well as a compressive convective term similar to the one for the advection of the step-like α -field is then given by

$$\frac{\partial c_{\rm B}}{\partial \tau} + \nabla \cdot (c_{\rm B} \mathbf{u}) + \nabla \cdot (c_{\rm B} (1-\alpha) \mathbf{u}_{\rm r}) = \nabla \cdot (D_1 \nabla c_{\rm B}) - \nabla \cdot \left(\frac{c_{\rm B}}{\alpha + \varsigma_{\alpha}} D_1 \nabla \alpha\right) - j_{\rm B}.$$
(4.41)

Here, $c_{\rm B}$ denotes the bulk concentration averaged over both phases. Within the liquid phase it takes the value of the bulk concentration averaged over the liquid phase and is zero in the gas phase. At the interface, $c_{\rm B}$ shows a transition region similar to α . The local average bulk concentration in the liquid phase is evaluated from

$$\overline{c_1}^1 = \frac{c_{\rm B}}{\alpha + \varsigma_{\alpha}}.\tag{4.42}$$

Here, again, the small value ζ_{α} is added in the above two equations to avoid division by zero.¹² The same compressive velocity \mathbf{u}_{r} as for the advection of α is introduced. The bulk diffusion coefficient of the species within the liquid phase is denoted by D_{1} , and j_{B} represents source terms accounting for adand desorption to and from the liquid-gas interface. The evaluation procedure for j_{B} will be discussed in Subsection 4.3.3 below.

Boundary Condition for $c_{\rm B}$ on a Wetted Wall

From Equation 4.41 one can see that a simple Neumann boundary condition for $c_{\rm B}$ with vanishing normal gradient does only guarantee vanishing fluxes into a wall if the wall normal gradient of the volume fraction field also vanishes at the wall. This, however, is only the case for walls completely immersed into the liquid, or wetted walls with a constant contact angle of 90°. A Neumann boundary condition, therefore, cannot be the correct choice for the volume averaged bulk concentration $c_{\rm B}$ at an impermeable wall. For that reason, in analogy to the conditional volume averaging procedure used to derive

¹² Note that ς_{α} is negligibly small compared to α within the liquid phase and the interface region, while $c_{\rm B}$ is zero within the gas phase. The influence of ς_{α} on results is, thus, also negligible.

Equation 4.41, conditional area averaging is here applied to the boundary. Starting with the Neumann boundary condition for the sharp interface concentrations

$$\mathbf{n}_{\mathrm{w}} \cdot \nabla c_i = 0, \qquad i = 1, 2, \tag{4.43}$$

the two boundary conditions are conditioned with the indicator function χ_1 , integrated over an averaging area S_w of the wall boundary and summed up, resulting in

$$\frac{1}{|S_{w}|} \int_{S_{w}} \chi_{1} \mathbf{n}_{w} \cdot \nabla c_{1} + (1 - \chi_{1}) \mathbf{n}_{w} \cdot \nabla c_{2} \, \mathrm{d}S = 0.$$

$$(4.44)$$

Therein c_1 is the concentration in phase one and c_2 is the concentration in phase two. χ_1 is defined such that it takes the value 1 within phase 1 and 0 elsewhere. For solubility of the species only in the first phase, the second term within the integral becomes zero. Taking advantage of the identity of the indicator function

$$\frac{1}{|S_{w}|} \int_{S_{w}} \chi_{1} dS = \frac{|S_{w,1}|}{|S_{w}|}, \qquad (4.45)$$

where $S_{w,1}$ is the area within the averaging area covered by phase 1, the averaged boundary condition can be rewritten as

$$\mathbf{n}_{w} \cdot \left(\underbrace{\frac{1}{|S_{w}|} \int\limits_{S_{w}} \chi_{1} dS}_{=\overline{\chi_{1}}} \cdot \underbrace{\frac{1}{|S_{w,1}|} \int\limits_{S_{w,1}} \nabla c_{1} dS}_{=\overline{\nabla c_{1}}^{1}} \right) = 0.$$
(4.46)

Here, in analogy to the notation utilized in [50] for volume averaging, the overbar notation was introduced to denote averaging over the entire averaging area by $\overline{(\cdot)}$, or the respective phase *i* within the averaging area by $\overline{\overline{(\cdot)}}^i$. Assuming $\overline{\overline{\nabla(\cdot)}}^i = \overline{\nabla(\overline{(\cdot)})}^i$ in analogy to Deising et al. [50], thereby disregarding commutation errors, this expression can be further simplified to

$$\mathbf{n}_{\mathrm{W}} \cdot (\overline{\overline{\chi_1}} \,\nabla \overline{\overline{c_1}}^1) = 0. \tag{4.47}$$

Through partial integration one can then obtain

$$\mathbf{n}_{\mathrm{w}} \cdot \left[\nabla(\overline{\overline{\chi_1}} \ \overline{\overline{c_1}}^1) - \overline{\overline{c_1}}^1 \ \nabla\overline{\overline{\chi_1}}\right] = 0, \tag{4.48}$$

which can be further simplified to

$$\mathbf{n}_{\mathrm{w}} \cdot \left[\nabla \underbrace{(\overline{\chi_{1} c_{1}})}_{=c_{\mathrm{B}}} - \underbrace{\overline{c_{1}}}_{=\frac{c_{\mathrm{B}}}{\alpha} \approx \frac{c_{\mathrm{B}}}{\alpha + c_{\alpha}}} \nabla \underbrace{\overline{\chi_{1}}}_{=\alpha}\right] = 0.$$
(4.49)

Thereby, assuming equivalence of volume averaging at the boundary and area averaging over the boundary, the averaged quantities $c_{\rm B}$ and α can be identified. Thus, one obtains that the wall normal components of the two diffusive fluxes in Equation 4.41 must cancel out at a wetted wall according to

$$\mathbf{n}_{\mathrm{w}} \cdot \nabla c_{\mathrm{B}} = \frac{c_{\mathrm{B}}}{\alpha + \varsigma_{\alpha}} \, \mathbf{n}_{\mathrm{w}} \cdot \nabla \alpha. \tag{4.50}$$

This is also expected intuitively from Equation 4.41 for an impermeable wetted wall. Note that this boundary condition reduces to $\mathbf{n}_{w} \cdot \nabla c_{B} = 0$ away from the three-phase contact line and introduces a second term only at the contact line, where $\mathbf{n}_{w} \cdot \nabla \alpha \neq 0$.

Interface Concentration

Lakshmanan and Ehrhard [107] introduced a method for soluble¹³ surfactants based on the conservative level-set method. In analogy to the CSF model for surface tension, they transfer the area specific surface excess concentration Γ into a volumetric concentration $c_{\rm I} = \delta_r \Gamma$ by multiplying with the regularized interface Dirac distribution. For this volumetric concentration located at the interface, they then solve a transport equation which accounts for convection, diffusion and adsorption. In a second step, they solve a "compression transport equation" in order to counteract numerical diffusion during advection of the delta-like concentration. They also included a diffusive term in this compression transport equation to ensure smoothness. This compression-diffusion equation is solved in pseudo time.

Similar to the work of Lakshmanan and Ehrhard [107], a transport equation for a volumetric surface excess concentration at the interface is solved in the present work. In analogy to the advection of the volume fraction field, however, the compressive flux is here directly included into the transport equation. Furthermore, in analogy to Lakshmanan and Ehrhard [107], a diffusive term is added to ensure sufficient smoothness. The transport equation for the volumetric surface excess concentration then reads

$$\frac{\partial c_{\mathrm{I}}}{\partial \tau} + \nabla \cdot (c_{\mathrm{I}} \mathbf{u}) + \nabla \cdot (c_{\mathrm{I}} w(\alpha) \mathbf{u}_{\mathrm{r}}) = \nabla \cdot (D_{\mathrm{I}} \nabla_{\Sigma} c_{\mathrm{I}}) + \nabla \cdot (D_{\mathrm{I},\mathrm{S}} \nabla c_{\mathrm{I}}) + j_{\mathrm{I}}, \qquad (4.51)$$

where the same compressive velocity \mathbf{u}_{r} as for α and c_{B} is utilized. Lakshmanan and Ehrhard employed a compressive flux proportional to

$$w_1(\alpha) = 1 - 2\alpha. \tag{4.52}$$

¹³ The bulk concentration was assumed to be constant in their work.



Figure 4.4: Weighting function for the compressive flux towards the interface.

Within the scope of this work,

$$w(\alpha) = w_2(\alpha) = \operatorname{sgn}(\frac{1}{2} - \alpha)(1 - 4\alpha(1 - \alpha))$$
 (4.53)

is used, which applies compression more smoothly around the interface. Figure 4.4 shows the two weighting functions in comparison for a smooth α -field according to Equation 4.20. $D_{\rm I}$ is the diffusion coefficient for diffusion along the interface. These diffusive fluxes are assumed to be negligible compared to convective species transport along the interface for the parameter studies presented in Chapter 6. Results presented in sections 6.1.4 and 6.2.4 show that Marangoni flow leads to a quick homogenization of the surface excess concentration and thus justify this assumption. Nevertheless, diffusion along the interface can be considered using the above approach, as is demonstrated in Subsection 5.1.6.1. The second diffusive term ensures sufficient smoothness, where $D_{I,S} = ||\mathbf{u}_r||_2 D_{I,S,0}$ and $D_{I,S,0} = 0.4 \Delta x$ was found to yield good results, as will be shown in Subsection 5.1.6. Ad- and desorption is accounted for through the source term j_1 . The evaluation of source terms will be discussed in detail in Subsection 4.3.3. In order to be able to introduce source terms using standard kinetic models, as well as for the evaluation of surface tension using the corresponding surface equations of state, first the area specific excess concentration needs to be calculated from the volumetric concentration located at the interface. This is discussed in the following section. It should be noted that, due to the formulation in terms of a volumetric concentration, a species conservative discretization of Equation 4.51 using the FVM on the Eulerian background mesh is straightforward.

4.3.2 Evaluation of Surface Excess Concentration

Even though the initial volumetric surface excess concentration could be determined simply from $c_{\rm I} = \delta \Gamma$, the evaluation of the area specific surface excess concentration is not as straightforward. While the δ -like $c_{\rm I}$ is transported directly by solution of the transport equation 4.51 given in the previous section,

the regularized interface Dirac representing the interface, $\delta_1 = ||\nabla \alpha||_2$, is a result of the advection of the step-like α -field. Discretization errors introducing numerical diffusion and dispersion in general act differently on these two fields. At the same time, the ratio c_1/δ_1 is very sensitive to slight inconsistencies between the two fields. In order to compensate for such inconsistencies in alignment and width of the two peaks, a compression-diffusion equation is solved for both fields in pseudo-time τ^* . For the volumetric surface excess concentration this equation reads

$$\frac{\partial c_{\mathrm{I},\mathrm{S}}}{\partial \tau^*} + \nabla \cdot (c_{\mathrm{I},\mathrm{S}} w(\alpha) \mathbf{u}_{c,\delta}) = \nabla \cdot (\mathbf{n}_{\kappa} \otimes \mathbf{n}_{\kappa} D_{c,\delta} \nabla c_{\mathrm{I},\mathrm{S}}).$$
(4.54)

The interface δ -function is treated similarly according to

$$\frac{\partial \delta_{\mathrm{I},\mathrm{S}}}{\partial \tau^*} + \nabla \cdot (\delta_{\mathrm{I},\mathrm{S}} w(\alpha) \mathbf{u}_{c,\delta}) = \nabla \cdot (\mathbf{n}_{\kappa} \otimes \mathbf{n}_{\kappa} D_{c,\delta} \nabla \delta_{\mathrm{I},\mathrm{S}}).$$
(4.55)

In both equations $\mathbf{u}_{c,\delta} = 1 \,\mathrm{m \, s^{-1} \, n_{\kappa}}$ denotes a compressive velocity resulting in alignment of $c_{\mathrm{I},\mathrm{S}}$ and $\delta_{\mathrm{I},\mathrm{S}}$ with the interface. The compressive flux is weighted using $w(\alpha) = w_1(\alpha)$ as given by Equation 4.52 in the previous section. Together with the anisotropic diffusive term acting in interface normal direction this results in a defined width of the smoothed peaks in interface normal direction. Throughout this work the diffusion coefficient $D_{c,\delta}$ is chosen such that $Pe = \frac{||\mathbf{u}_{c,\delta}||_2 \Delta x}{D_{c,\delta}} = 1$. Starting from c_{I} and $\delta_{\mathrm{I},\mathrm{S}}$ are solved in pseudo time until $\tau_{\mathrm{S,max}}^*$ within each time step. Throughout this work $\frac{||\mathbf{u}_{c,\delta}||_2 \tau_{\mathrm{S,max}}^*}{\Delta x} = 4$ was found to yield reasonable results, as will be shown in Subsection 5.1.6, while keeping the computational effort low.¹⁴ The above partial differential equations of Γ are discretized in time using the implicit Euler scheme and a minimum of four steps in pseudo time are enforced, resulting in a Courant number of approximately 1. After this realignment, the excess species per interfacial area is calculated from

$$\Gamma = \frac{c_{\mathrm{I},\mathrm{S}}}{\delta_{\mathrm{I},\mathrm{S}} + \varsigma_{\nabla\alpha}}.\tag{4.56}$$

Due to the diffusive term in the realignment equations, $c_{I,S}$ and $\delta_{I,S}$ have a width of a few cells in interface normal direction. Therefore, the information about the area specific surface excess concentration Γ is available in the entire interface region. It allows the evaluation of surface tension, which for surfactant solutions is typically described as a function of Γ . But also for the evaluation of non-linear adsorption kinetics Γ is required, as will be discussed in the following section.

4.3.3 Coupling of Bulk and Interface Concentrations

Throughout this work, bulk and interfacial surfactant concentrations are coupled through a model describing the adsorption kinetics. Therein the adsorption rate depends on the subsurface bulk concentra-

¹⁴ In cases with graded mesh, the maximum mesh size at the interface was used for the evaluation of the smoothing parameters.

tion and the current surface excess concentration. Source terms are first evaluated for the volumetric surface excess concentration based on the concentration fields from the previous time step or iteration. Based on these source terms $j_{\rm I}$ located at the interface, the source terms $j_{\rm B}$ for the concentration in the bulk are evaluated. Using these source terms, the two transport equations for $c_{\rm B}$ and $c_{\rm I}$ are solved. This solution procedure is repeated within each time step until the maximum relative change of $j_{\rm I}$ and $j_{\rm B}$ has fallen below a certain threshold.¹⁵ In the following paragraphs, the evaluation procedure for sorption source terms is presented.

Source terms j_{I} for the surface excess concentration

Within the scope of this work, adsorption and desorption are described by Langmuir-Freundlich kinetics [30], i.e.

$$\frac{\partial \Gamma}{\partial \tau} = k_{\rm ad} c_{1,\rm I} \left(1 - \frac{\Gamma}{\Gamma_{\rm max}} \right)^{1/n} - k_{\rm de} \left(\frac{\Gamma}{\Gamma_{\rm max}} \right)^{1/n}, \tag{4.57}$$

which were found to describe a surfactant solution similar to UV-curable inks for inkjet printing with excellent agreement to experimental observations. The model fit and comparison to experimental data for this model surfactant solution is shown in Appendix G. In Equation 4.57, the maximum surface excess concentration is denoted by Γ_{max} , while k_{ad} and k_{de} are the adsorption and desorption rate coefficients. The subsurface bulk concentration at the liquid-gas interface is denoted by $c_{1,I}$. The exponent *n* describes cooperativity of surfactant molecules during adsorption [72], where 1/n can also be interpreted as the number of adsorption sites occupied by a single surfactant molecule [30]. For n = 1, this model reduces to the more widely used Langmuir-Hinshelwood kinetics [see e.g. 32]. For an equilibrium between between surface excess and bulk concentrations, i.e. $\partial \Gamma/\partial \tau = 0$, the kinetic model reduces to the Langmuir-Freundlich isotherm, also known as Sips isotherm [160]

$$\frac{\Gamma}{\Gamma_{\rm max}} = \frac{(K_{\rm LF}c)^n}{1 + (K_{\rm LF}c)^n},\tag{4.58}$$

with the adsorption equilibrium constant $K_{\rm LF} = k_{\rm ad}/k_{\rm de}$.

In order to be able to treat sorption source terms semi-implicitly within each iteration, Equation 4.57 is linearized to

$$\frac{\partial \Gamma}{\partial \tau}\Big|_{\Gamma_{0}} \approx k_{ad}c_{1,I} \left(1 - \frac{\Gamma_{0}}{\Gamma_{max}}\right)^{1/n} - k_{de} \left(\frac{\Gamma_{0}}{\Gamma_{max}}\right)^{1/n} - \left[k_{ad}c_{1,I} \left(1 - \frac{\Gamma_{0}}{\Gamma_{max}}\right)^{\frac{1-n}{n}} + k_{de} \left(\frac{\Gamma_{0}}{\Gamma_{max}}\right)^{\frac{1-n}{n}}\right] \frac{\Gamma - \Gamma_{0}}{n\Gamma_{max}}$$
(4.59)

¹⁵ Throughout this work a threshold value of 1×10^{-3} is used.

using Taylor series expansion around $\Gamma = \Gamma_0$. After rearranging to

$$\frac{\partial \Gamma}{\partial \tau}\Big|_{\Gamma_{0}} \approx \underbrace{k_{ad}c_{1,I}\left(1 - \frac{\Gamma_{0}}{\Gamma_{max}}\right)^{\frac{1-n}{n}}\left[\left(1 - \frac{\Gamma_{0}}{\Gamma_{max}}\right) + \frac{\Gamma_{0}}{n\Gamma_{max}}\right] + k_{de}\frac{1-n}{n}\left(\frac{\Gamma_{0}}{\Gamma_{max}}\right)^{1/n}}{A}}_{A} - \underbrace{\frac{1}{n\Gamma_{max}}\left[k_{ad}c_{1,I}\left(1 - \frac{\Gamma_{0}}{\Gamma_{max}}\right)^{\frac{1-n}{n}} + k_{de}\left(\frac{\Gamma_{0}}{\Gamma_{max}}\right)^{\frac{1-n}{n}}\right]}_{B}}_{B} \Gamma, \qquad (4.60)$$

the adsorption terms are transferred to volumetric source terms,

$$j_{\rm I} = A\delta_{\rm I} + Bc_{\rm I},\tag{4.61}$$

by multiplication with $\delta_I = ||\nabla \alpha||_2$. For n = 1, the expression reduces to the volume averaged Langmuir-Hinshelwood kinetics

$$j_{\rm I} = k_{\rm ad} c_{1,\rm I} \left(\delta_{\rm I} - \frac{c_{\rm I}}{\Gamma_{\rm max}} \right) - k_{\rm de} c_{\rm I}, \tag{4.62}$$

as it was previously presented in [5], similar to the work of Lakshmanan and Ehrhard [107].

The evaluation of Equation 4.61 requires the subsurface bulk concentration $c_{1,1}$ to be available throughout the entire interface region and in its vicinity. Directly at the interface, Equation 4.42 provides a good estimate. Within the gas-phase, however, where both $c_{\rm B}$ and α approach zero, this estimate becomes sensitive to small inaccuracies. For this reason the liquid bulk concentration $\overline{c_1}^1$ weighted by the density scaled δ -function δ_2 ,

$$c_{1,\delta_2} = \overline{c_1}^1 \delta_2 = \frac{c_{\rm B}}{\alpha + \varsigma_\alpha} \delta_2, \tag{4.63}$$

is distributed over the interface region. For that purpose

$$\frac{\partial c_{1,\delta_2,S}}{\partial \tau^*} = D_{1,I} \nabla^2 c_{1,\delta_2,S}$$
(4.64)

and

$$\frac{\partial \delta_{2,S}}{\partial \tau^*} = D_{1,I} \nabla^2 \delta_{2,S} \tag{4.65}$$

are integrated in pseudo time until τ_{\max}^* , starting from c_{1,δ_2} and δ_2 . The diffusion coefficient $D_{1,I}$ together with τ_{\max}^* determine the smoothing intensity and thereby, how far the information is distributed over the

interface region. Within the scope of this work, $\frac{D_{1,I}\tau_{max}^*}{\Delta x^2} = 4$ is used.¹⁶ Finally, the bulk concentration within the interface region is evaluated from

$$c_{1,\mathrm{I}} = \frac{c_{1,\delta_2,S}}{\delta_{2,\mathrm{S}} + \varsigma_{\nabla\alpha}}.\tag{4.66}$$

It should be noted that the employed isotropic diffusion introduces smoothing in interface tangential direction. Together with $D_{1,I} \tau^*_{max}$, this smoothing, however, decreases with increasing mesh resolution.

Source terms $j_{\rm B}$ for the bulk concentration field

Applying source terms for the bulk concentration field directly within the narrow interface region can lead to numerical instabilities. A similar effect was described by Hardt and Wondra [73] and following works [12, 106] for mass sink and source terms due to evaporation within the VOF method. For their scenario, Hardt and Wondra [73] therefore proposed to calculate a smeared source term field based on the solution of an inhomogeneous Helmholtz equation. Source and sink terms on both sides of the interface are then rescaled to ensure global mass conservation.

A similar approach is taken here for the distribution of sink and source terms due to adsorption and desorption at the liquid-gas interface. However, instead of smearing the interfacial source terms into both bulk phases followed by rescaling, the source terms are here distributed only towards the liquid phase, where in general $c_B \neq 0$. For this purpose, the advection-diffusion equation

$$\frac{\partial j_{\rm B}}{\partial \tau^*} + \nabla \cdot (j_{\rm B}(1-\alpha)\mathbf{u}_{\rm r}) = \nabla \cdot (D_{j,\rm B}\nabla j_{\rm B}) - \nabla \cdot \left(\frac{j_{\rm B}}{\alpha+\varsigma_{\alpha}}D_{j,\rm B}\nabla\alpha\right)$$
(4.67)

is solved in pseudo time, starting from $j_{B,0} = j_I$. Similar to the diffusive fluxes in Equation 4.41, diffusion of source terms acts only within the liquid phase. Furthermore, similar to Equation 4.41 the compressive velocity \mathbf{u}_r acts within the gas phase and the interface region towards the liquid phase. Similar to the previously introduced smoothing steps, j_B is advanced up to a given pseudo time τ^*_{max} , where the parameters are chosen such that $\frac{D_{j,B}\tau^*_{\text{max}}}{\Delta x^2} = 4$. Within the FVM, Equation 4.67 is solved in a conservative manner, thereby species conservation is maintained. Figure 4.5 shows the so distributed bulk source terms j_B in comparison with the interface source terms j_I for a sessile droplet. Compared to the δ -like distribution of j_I around the interface, j_B is smoothed and shifted into the liquid phase.

¹⁶ In cases with graded mesh the maximum mesh size at the interface was used for the evaluation of the smoothing parameters.



Figure 4.5: Distribution of adsorption source terms j_{I} and j_{B} for the interface and bulk concentration fields on a hemispherical droplet, as indicated by the α -field.



The surface tension of a surfactant solution, where the surfactant consists of a single species, is related to bulk and surface excess concentrations through the Gibbs adsorption equation [32],

$$\Gamma = -\frac{1}{\overline{R}T} \left(\frac{\partial \sigma_{\ell g}}{\partial \ln c} \right)_{T,p}.$$
(4.68)

By inserting Equation 4.58 for Γ and integrating over $\ln c$, one obtains

$$\sigma_{\ell g,0} - \sigma_{\ell g} = \overline{R} T \Gamma_{\max} n^{-1} \ln \left(1 + (K_{\rm LF} c)^n \right) \tag{4.69}$$

for the equilibrium surface tension as a function of the bulk concentration. Therein, the surface tension of the pure solvent is denoted by $\sigma_{\ell g,0}$. This can be reformulated as the surface equation of state in terms of surface excess concentration

$$\sigma_{\ell g,0} - \sigma_{\ell g} = -\overline{R}T\Gamma_{\max}n^{-1}\ln\left(1 - \frac{\Gamma}{\Gamma_{\max}}\right)$$
(4.70)

by inserting Equation 4.58. It should be noted that despite the employed equilibrium assumption, Equation 4.70 is found to yield good results also in transient cases, as is demonstrated in Appendix G. For n = 1, the above two equations reduce to the widely used Szyszkowski and Frumkin equations [32] respectively, the corresponding surface tension equations of state for the Langmuir isotherm. Equation 4.70 allows the evaluation of the local surface tension directly from Γ . Since Γ evaluated from Equation 4.56 is available in the entire interface region, also $\sigma_{\ell g}$ is available in the same region. This is a prerequisite for the application of the CSF approach described in Subsection 4.1.2.
4.3.5 Surfactants at the Moving Contact Line

The Kistler [105] model introduced above to describe the contact line motion does not take surfaceactive substances within the liquid into account. It was originally developed empirically based on the experimental data by Hoffman [78] for advancing contact lines of silicon oils with varying viscosities. For complete wetting and small dynamic contact angles, it approximates the relation

$$\theta_{\rm d,0} = k \sqrt[3]{Ca},\tag{4.71}$$

derived from lubrication theory by Tanner [169] for a steadily moving contact line [105]. Therein k is a proportionality constant. Joanny [94] developed a model based on lubrication theory to account for insoluble surfactants at a moving contact line. It is assumed that the solid surface is repulsive to the surfactant molecules, meaning that the surfactant adsorbs preferentially to the liquid-gas interface instead. Depending on the affinity of the surfactant to the solid substrate, varying surfactant fluxes through the contact line region are considered, resulting in different velocity profiles and therefore varying viscous friction in the contact line region. For a surfactant that does not adsorb to the solid, as is also assumed throughout this work, Joanny finds as a result of that

$$\theta_{\rm d} = \theta_{\rm d,0} \sqrt[3]{2}, \tag{4.72}$$

where $\theta_{d,0}$ corresponds to the contact angle predicted by Tanner [169]. Thus, the presence of the surfactant increases the predicted contact angle by a constant prefactor of $\sqrt[3]{2}$. By substituting Equation 4.71 into Equation 4.72, one obtains

$$\theta_{\rm d} = k \sqrt[3]{2\,Ca}.\tag{4.73}$$

Thus, for a given contact angle, the capillary number must be exactly half of the capillary number in the surfactant-free case. To account for this effect, while maintaining boundedness of the dynamic contact angle between 0° and 180°, a capillary number $Ca^* = 2Ca$ modified in the sense of Joanny is used as argument of the Kistler model within the scope of this work. This results in slowing of the contact line due to immobilization of the liquid-gas interface and therefore increased friction within the three-phase contact line region similar to the model prediction by Joanny. The modification of the Kistler model proposed here has shown good agreement with experimental observations, as will be discussed in Subsection 5.2.1. Note also that the much more elaborate model introduced by Cox [41] based on matched asymptotic solutions for micro, meso and macroscopic flow shows, for given slip length and macroscopic length scale, qualitatively and quantitatively comparable slowing of the contact line compared to the surfactant-free case. The model predicts this similar behavior if the viscosity ratio of the two fluids is either large, or small, as is typically the case for liquid surrounded by a gas phase.

In addition to a change in the flow profile due to Marangoni stresses, surfactants also influence the equilibrium contact angle. Besides the capillary number, this is the second argument of the Kistler

model, Equation 4.29. To account for the change of the equilibrium contact angle, this contact angle is evaluated from the Young-Dupré Equation 2.15 with the momentary, local surface tension $\sigma_{\ell g}$ at the three-phase contact line. A similar approach regarding the equilibrium contact angle has been employed by Karapetsas et al. [101]. Within the scope of this work, the required difference $\sigma_{s\ell} - \sigma_{sg}$ is determined from the contact angle in the absence of surfactant. For $\sigma_{\ell g} < \sigma_{sg} - \sigma_{s\ell}$, an equilibrium contact angle of $\theta_{eq} = 0^{\circ}$ is used in the contact line model.

4.4 Numerical Method

The model is implemented in the open source CFD library OpenFOAM. OpenFOAM employs the Finite-Volume-Method. Basic principles of the FVM can be found in [151]. The implementation used throughout this work is based on *interFoam*, the algebraic VOF solver of OpenFOAM. A detailed description and evaluation thereof was given by Deshpande et al. [52]. The employed discretization schemes are listed in Appendix C. In the remainder of this section, the employed acceleration techniques will be briefly introduced, before in Subsection 4.4.2 the solution procedure including heat and species transport will be presented.

4.4.1 Acceleration Techniques

Measures taken within the scope of this work to reduce the required computational effort can be divided into two categories: Adaptive time stepping maximizes individual time step sizes during the simulation while ensuring stability and the required temporal resolution. Adaptive mesh refinement allows reducing the total number of grid cells compared to a static mesh by automatically increasing the mesh resolution locally, where required. These methods and respective criteria for adaption are briefly discussed in the following.

4.4.1.1 Adaptive Time Stepping

The computational cost of a simulation directly depends on the number of time steps. It is therefore beneficial to choose the time step size as large as possible while ensuring sufficient accuracy and above all stability of the simulation. Several criteria for the time step size have been proposed to ensure the stability of the numerical simulation. The Courant-Friedrichs-Lewy condition [39],

$$\Delta \tau < \Delta \tau_{\rm CFL} = \frac{\Delta x}{u},\tag{4.74}$$

for explicit discretization of advection in time, is probably the most widely known. Here, $\Delta \tau$ denotes the time step size and Δx the mesh width. Brackbill et al. [24] introduced another criterion based

on the propagation of capillary waves. According to this criterion, capillary waves with a wavelength corresponding to the mesh width can be resolved if

$$\Delta \tau < \Delta \tau_{\rm BKZ} = \sqrt{\frac{(\rho_{\ell} + \rho_{\rm g})\Delta x^3}{4\pi\,\sigma_{\ell g}}}.$$
(4.75)

This criterion becomes increasingly restrictive with decreasing mesh sizes, as the maximum time step $\Delta \tau_{\rm BKZ,max} \propto \Delta x^{3/2}$. Galusinski and Vigneaux [65] argued that the criterion of Brackbill et al. [24] does not take viscosity into account and proposed another stability criterion, which was evaluated for the *interFoam* solver by Deshpande et al. [52]. Based on 80 simulations, the latter proposed the criterion

$$\Delta \tau \le \Delta \tau_{\text{DAT}} = \max\left(10 \frac{\mu \Delta x}{\sigma_{\ell g}}, 0.1 \sqrt{\frac{\rho \Delta x^3}{\sigma_{\ell g}}}\right). \tag{4.76}$$

Especially on fine meshes, this can pose a substantially weaker restriction on the time step size as compared to Equation 4.75. Even though this criterion ensures stability, a previous study [4] had shown that it does not accurately resolve capillary waves during the impact-driven stage of droplet impact. Therefore, throughout this work, the time step is adjusted according to Equation 4.74 and Equation 4.75 during the impact-driven stage, while during later stages the time step size is chosen according to

$$\Delta \tau < \Delta \tau_{\text{spreading}} = \min(\Delta \tau_{\text{DAT}}, 100 \Delta \tau_{\text{BKZ}}, \Delta \tau_{\text{CFL}}).$$
(4.77)

The additional limitation by $\Delta \tau \leq 100 \Delta \tau_{BKZ}$ therein was chosen somewhat arbitrarily, but was found to produce convergence of the coupling between contact line dynamics and macroscopic flow within the PIMPLE loop, which is described towards the end of Subsection 4.4.2.

4.4.1.2 Adaptive Mesh Refinement and Load Balancing

Local mesh refinement allows for higher spatial resolution specifically in regions where this is required, while a coarser grid can be used, where a correspondingly lower resolution is acceptable. By discretizing the domain accordingly, the total number of cells and thereby the computational cost can be reduced. This is especially relevant for 3D cases. Within the scope of this work, a high spatial resolution is required especially within the liquid and in the interface region.¹⁷ Because the interface position varies with time, a static local refinement is not optimal. For the 3D cases presented in this work, the mesh is therefore adaptively refined once within the liquid region ($\alpha > 0.5$) by splitting each hexahedral cell inside this region into eight child cells. Within the interface region a second refinement level is added, thus each

¹⁷ The interface region is determined based on $\nabla \alpha$, where all cells with $(1/N) \sum_{f}^{N} |\mathbf{n}_{f} \cdot \nabla \alpha| > 10^{-2} \,\mathrm{m}^{-1}$ as well as their three neighboring cell layers in both directions are included in the interface region. Here, *N* denotes the number of faces of the specific cell. \mathbf{n}_{f} is the cell face normal vector.

child cell is again split into eight children. Throughout this work, the method and implementation presented by Rettenmaier et al. [142] is used for adaptive mesh refinement and load balancing.

4.4.2 Solution Procedure

How the different aspects of the model presented within this chapter are tied together is shown in Figure 4.6. The solution algorithm follows a segregated approach, where the different transport equations are solved in a consecutive manner within each time step. The overall algorithm is a modification of the solution procedures presented by Batzdorf [12], Rettenmaier [141] and Franz [64], which themselves are based on the *interFoam* solver of OpenFOAM.

After the initialization of mesh and fields, the above introduced criteria for adaptive time stepping are used to advance the time step. Throughout this work, adaptive mesh refinement and load balancing are employed only in three-dimensional cases. Afterwards, the advection equation for the volume fraction field α is solved. Unphysical values of α below 0 or above 1 are clipped to 0 and 1, respectively.¹⁸ Similar to the work by Batzdorf [12], entrapped gas at the substrate is removed during the initial impact. Here however, this removal is more strictly limited to underresolved gas in cells with $0.5 < \alpha < 1$ at the solid-liquid interface and outside the region of the liquid-gas interface. Based on the advected α field, the interface is updated. First, the contact angle field at the wetted wall is updated. Afterwards, the smoothed volume fraction field is calculated, taking the adapted contact angle into account. This smoothed field is then used to calculate interface normals and interface curvature. Finally, the forces modeling substrate contact and coalescence are calculated. The evaluation of the thickness of the entrained film required to calculate the coalescence force introduces substantial computational cost. For this reason, the distance between two interfaces is updated only every 10th time step throughout this work. Due to the small Courant numbers on the order of 0.02 enforced by the time step criterion in Equation 4.75, however, changes in interface position between subsequent time steps are correspondingly small. Furthermore, for the droplet simulations presented in this work, the evaluation of $f_{substrate}$ and $\mathbf{f}_{\text{coalescence}}$ can be skipped entirely during the later capillary spreading regime. Based on the new α -field, the averaged material properties are updated.

Following the interface update, the coupled transport equations for surfactant concentrations are solved. First, the source terms accounting for adsorption and desorption to the liquid-gas interface are calculated based on the previous concentration fields. For that purpose, the bulk concentration at the interface is evaluated according to Equations 4.63–4.66. Afterwards, the source terms $j_{\rm I}$ can be calculated directly from Equation 4.61. The bulk source terms are then calculated from Equation 4.67, before the transport equation 4.41 is solved. Bulk and interfacial surfactant concentrations are iteratively coupled by updating the source terms and solving the transport equations until the relative change in source terms falls below a certain threshold value.¹⁹ Once the coupling has converged, the surface excess concentration Γ

¹⁸ For the reference case presented in Subsection 6.2.4, this results in a liquid volume of 2.093×10^{-20} m³ and a vapor volume of 2.477×10^{-20} m³ being removed from the computational domain over the course of the simulated time frame, whereas the total liquid volume within the domain is 6×10^{-15} m³.

¹⁹ Throughout this work, a threshold value of 10^{-3} is used.



Figure 4.6: Solution procedure.

is updated.²⁰ Furthermore, unphysical negative bulk concentrations are set to zero and the bulk concentration field is rescaled to ensure global species conservation.²¹ The local surface tension is evaluated from Γ . After the update of the concentration fields, the energy balance is solved iteratively in fluid domain (Equation 4.39) and solid domain (Equation 4.40).

Finally, the coupled equations for pressure and velocity are solved. OpenFOAM employs the PISO algorithm [87] for instationary problems. The PISO algorithm is embedded into an outer loop similar to the SIMPLE algorithm [28] for steady flow problems. This outer loop, the so called PIMPLE loop, allows underrelaxation within each time step and can improve convergence behavior. Since the dynamic contact angle and the pressure-velocity coupling are interdependent through surface tension forces, another interface update is included in the PIMPLE loop throughout this work. By using this approach, contact line instabilities similar to those reported in [6] could be avoided. This coupling allowed larger time steps in the spreading phase according to Equation 4.76. Time is incremented until the end of the simulation has been reached and the simulation terminates.

²⁰ In some cases the coupling diverged in individual time steps, typically while topological changes occurred. In these cases the sorption source terms were set to zero for the concerning time steps.

²¹ For the reference case presented in Subsection 6.2.4, 7.846×10^{-19} mol were redistributed over the course of the simulated time frame, whereas the total surfactant amount within the computational domain is 1.489×10^{-15} mol.

CHAPTER 5

Verification and Validation

After the introduction of the governing equations and the numerical procedure in the previous section, verification and validation cases for the presented method and model are presented in this chapter. This chapter follows the structure of the previous chapter: First, the proposed method for the evaluation of capillary forces is verified. This is further divided into the evaluation of interface curvature, the density-scaled CSF approach and the model for the moving contact line. The sensitivity of the results towards parameters of the wall contact and coalescence models is evaluated. Following this, the two-field approach for surfactant transport is verified. The verification cases consider transport with the interface as well as the adsorption process and Marangoni flow. Finally, the model is applied to droplet impact and collision and compared to experimental results

5.1 Verification

Within this section the verification cases mentioned above are presented. Results of the numerical method are compared to exact analytical solutions. Thereby, the ability of the numerical method and its implementation to reproduce the expected behavior is demonstrated.

5.1.1 Curvature Calculation

Due to the dominance of surface tension over inertial and gravitational forces for the micrometer-sized droplets considered throughout this work, the droplets are expected to quickly assume the shape of a spherical cap upon impact. Therefore, the method to evaluate interface curvature is first verified for the case of sessile droplets with a spherical cap shape and varying contact angles. In a second step, the evaluation of a non-constant interface curvature is considered using a cosine-shaped interface as reference.

Sessile Drop

The method presented in Subsection 4.1.3 is applied to a droplet with a volume of 6 pL with a constant smoothing parameter $D_S \tau_S^* = 5 \times 10^{-14} \text{ m}^2$. In all cases, the droplet is initialized as a spherical cap with an α -profile in interface normal direction according to the one found in Appendix B. Contact angles of 90°, 45°, 22.5° and 11.25° with the substrate are considered. For the case with 90° contact angle, the boundary condition for the smoothed field $\mathbf{n} \cdot \nabla \alpha_S = 0$ is employed along the substrate. For the remaining cases, the boundary values during smoothing are corrected according to the method given in Subsection 4.1.3. An axisymmetric setup takes advantage of the rotational symmetry of the problem. Figure 5.1 shows a schematic of the computational domain and initial condition. The mesh resolution is varied between $5.544 \times 10^{-2} r_0$ and $3.465 \times 10^{-3} r_0$, where $r_0 = 11.273 \,\mu\text{m}$ is the radius of a spherical 6 pL droplet. The results are compared to curvatures obtained from the standard curvature method based on $\nabla \cdot (\nabla \alpha / (||\nabla \alpha||_2 + \varsigma_{\nabla \alpha}))$ as well as the iso-surface-based method by Kunkelmann [106] and Batzdorf [12] with the corresponding treatment of the substrate boundary. The results are evaluated regarding their L_1 , L_2 and L_{∞} error norms, where

$$L_q = \left(\sum_{i=1}^N \frac{(|\kappa_i - \kappa_{\text{exact}}|)^q}{N}\right)^{\frac{1}{q}} \quad \text{for } q = 1, 2, \tag{5.1}$$

and

$$L_{\infty} = \max_{i=1,\dots,N} |\kappa_i - \kappa_{\text{exact}}|$$
(5.2)

Therein, κ_i represents the curvature interpolated to a point of a reconstructed $\alpha = 0.5$ iso-surface, κ_{exact} is the exact interface curvature, and *N* is the total number of evaluated points.



Figure 5.1: Volume fraction field for a hemispherical droplet on a mesh with 64×256 cells corresponding to a mesh size of $\Delta x = 1.386 \times 10^{-2} r_0$.

The results are shown in Figures 5.2 and 5.3. For the hemispherical droplet, the standard method and the iso-surface method show relative errors in interface curvature on the order of several percent in the L_1 norm and up to the order of 100% for the maximum error. The iso-surface-based method shows a noticeable improvement compared to the standard approach throughout all mesh resolutions, which is

in agreement with the findings of Kunkelmann [106]. However, both methods show increasing errors with decreasing mesh size. This is a further indication that the non-converging behavior of these two methods regarding spurious currents observed by Rettenmaier [141] is likely caused by errors in interface curvature. On the other hand, evaluation of interface curvatures on the smoothed volume fraction field $\alpha_{\rm S}$ shows decreasing errors with mesh refinement throughout all error norms. The method shows roughly second order convergence. Such behavior of curvature estimation based on a smoothed volume fraction field has also previously been reported by Cummins et al. [43] for smoothing kernels, where the kernel radius is independent of the mesh size. On the finest grid considered here, curvature errors are two orders of magnitude lower for the smoothed approach compared to the other methods. In the cases with contact angles below 90°, the curvature errors increase throughout all considered methods compared to the 90°-case. The iso-surface shows again an improvement compared to the standard approach. For the droplet with a 45° contact angle, evaluation of curvature from $\alpha_{\rm S}$ shows further improvement on finer meshes with respect to the L_1 -norm. However, the maximum error (L_{∞}) , which is located near the solid wall, increases for the finest meshes. Looking at the L_{∞} -norm, the approach using $\alpha_{\rm S}$ and the iso-surface produce comparable results on finer meshes for a contact angle of 45°. For even smaller contact angles, however, the approach based on the smoothed volume fraction field shows again substantially smaller errors in all considered error norms compared to the remaining methods.

Cosine Interface

As shown above, calculation of the interface curvature on a smoothed volume fraction field can result in more accurate values. However, in the above presented case, the exact curvature was constant along the entire interface. An additional test case with a cosine shaped interface according to

$$y = r_{\min} \cos\left(\frac{2\pi x}{\Lambda}\right),\tag{5.3}$$

where $r_{\min} = \Lambda / (2\pi)$, was therefore considered. Figure 5.4 shows the two-dimensional computational domain and the volume fraction field for a mesh size of $\Delta x = \Lambda / 64$. Again, the α -profile in interface normal direction is set according to the profile found in Appendix B. The parameter determining the smoothing intensity $D_{\rm S} \tau_{\rm S}^*$ is varied between $2^{-12} r_{\rm min}^2$ and $r_{\rm min}^2$.

Figure 5.5 shows the L_2 and L_{∞} error versus mesh size. A case without any smoothing, i.e. the standard gradient-based approach, is shown for comparison. In the unsmoothed case $(D_S \tau_S^* / r_{\min}^2 = 0)$, the errors can again be observed to increase with mesh refinement. For the larger of the considered smoothing parameters $(D_S \tau_S^* / r_{\min}^2 \ge 2^{-6})$, no mesh dependence can be observed. The errors remain fairly constant for all considered resolutions. However, the errors decrease with reduced smoothing. For even smaller smoothing parameters, the errors show a dependence on the mesh resolution. On coarser meshes, the errors follow the unsmoothed case, whereas with increasing mesh resolution, the errors start to decrease. In the case of $D_S \tau_S^* / r_{\min}^2 = 2^{-8}$, the errors again approach a constant level on the order of approximately 1%. For the two smallest considered smoothing parameters, the errors show a substantial mesh dependence even for the smallest considered Δx .



Figure 5.2: Curvature errors for a hemispherical, sessile droplet (left) and a sessile droplet with a contact angle of 45° (right) for different methods of curvature calculation.



Figure 5.3: Curvature errors for a sessile droplet with a contact angle of 22.5° (left) and with a contact angle of 11.25° (right) for different methods of curvature calculation.



Figure 5.4: Domain, boundary and volume fraction field for a cosine shaped interface on a mesh with 64×256 cells, i. e. a mesh size of $\Delta x = \Lambda / 64$.



Figure 5.5: Curvature errors for a cosine shaped interface for different smoothing parameters.

The independence of mesh resolution for the larger smoothing parameters suggests that the gradients on the smoothed interface are sufficiently resolved even on the coarser grids, while a quite substantial error in interface curvatures is introduced through the smoothing procedure itself. Due to the smoothing, curvatures are underestimated on wavy interfaces. This error, however, decreases with decreasing $D_S \tau_S^*$ and thereby decreasing smoothing. Reduced smoothing thereby requires a higher mesh resolution in order to resolve the gradients in the smoothed volume fraction field. A smoothing parameter of $D_S \tau_S^* / R_{min}^2 = 2^{-8}$ here proves to be sufficient to decrease the relative curvature error down to the order of 1%. For two phase flow simulations, the minimum curvature radius R_{min}^2 is typically unknown a priori. For the droplet impact and collision cases considered within the scope of this work, the largest curvatures are expected during the initial impact phase, whereas in the later capillary spreading phase curvature is expected to decrease monotonically. Accuracy of the hydrodynamic model including curvature dependent surface tension forces is evaluated in sections 5.2.1 and 5.2.2 by comparison with experimental results.

5.1.2 Generalized Density-Scaled Continuum Surface Force Model

In order to evaluate the ability of the generalized density-scaled continuum surface force model (gDS-CSF) to reduce spurious currents, a sessile hemispherical droplet with a volume of 6 pL is simulated over a period of 1 ms. The density and viscosity of the drop are $\rho_{\ell} = 1000 \text{ kg m}^{-3}$ and $\mu_{\ell} = 20 \text{ mPa s}$. Density and viscosity of the surrounding phase are assumed to be $\rho_{g} = 1 \text{ kg m}^{-3}$ and $\mu_{g} = 20 \text{ µPa s}$, resulting in density and viscosity ratios of 1 : 1000. The surface tension of the system is assumed to be 40 mN m^{-1} . The gradient of the volume fraction field in wall normal direction is set to $\mathbf{n}_{w} \cdot \nabla \alpha = 0$ at the wall corresponding to a contact angle of 90°. Gravitational forces are neglected. The droplet and its surrounding phase are initially at rest. The simulation is performed on the mesh from the discretization study for the smoothed curvature model (see previous section) with a mesh size $\Delta x = 2.772 \times 10^{-2} r_0 = 312.5 \text{ nm}$. The time step size is adjusted according to the criterion by Deshpande et al. [52], Equation 4.76. A constant smoothing parameter of $D_s \tau_8^* = 5 \times 10^{-14} \text{ m}^2$ is employed here. Assuming the optimal choice based on the previous section to be $D_S \tau_8^* / R_{\min}^2 = 2^{-8}$, the maximum curvature still accurately captured after smoothing is $\kappa_{\max} = 2.8 \times 10^5 \text{ m}^{-1}$, or about twice (1.98 times) the curvature of the hemispherical droplet. Therefore, this choice of $D_S \tau_8^*$ results in moderate smoothing of the main curvature while still allowing to capture capillary waves of shorter wavelength reasonably well.

Figure 5.6 shows the maximum velocities 1 ms after the beginning of the simulation. Since the droplet is initialized in its hemispherical equilibrium state, any velocity within the computational domain must to be considered artificial. The intensity of the density scaling is varied through the parameter b, ranging from no density scaling for b = 1 to quite substantial over weighting of capillary forces in the higher density phase for b = 4. Furthermore, the density-scaled δ was calculated on the unsmoothed as well as the smoothed volume fraction fields α and α_s . Without density-scaling, spurious velocities exceed 1 mm s⁻¹. In the case of δ being calculated on the smoothed volume fraction field, spurious velocities become especially large, since without density scaling the capillary forces are applied in an even larger region in the phase with lower density and viscosity. Increasing b to 2 shows the lowest spurious currents in both cases. Spurious velocities can be reduced below 1 mm s⁻¹, with δ from α_s showing slightly favorable



Figure 5.6: Influence of density scaling on the maximum spurious velocity for a hemispherical droplet.

results. Increasing *b* beyond 2 shows increasing spurious velocities in both cases. These findings confirm the original formulation of the DS-CSF model, as b = 2 reproduces the weighting proposed by Yokoi [195]. As was pointed out by Yokoi, this weighting leads to fairly constant symmetric accelerations in both phases, minimizing spurious velocities. Consequently an even stronger weighting within the higher density phase shows no benefit. Furthermore, it should be noted that calculation of δ on α_s leads to a constant offset of the applied capillary forces towards the higher density phase independent of the mesh resolution. As the curvature calculated from $\nabla \cdot \mathbf{n}$ in general varies in interface normal direction, this introduces a systematic error in the Laplace pressure jump depending on $D_S \tau_s^*$. On the other hand, if δ is calculated on α , the regularized δ becomes more sharp and moves closer to the interface center with increasing mesh resolution. Thus, the offset to the expected interface position decreases with mesh refinement in this case. In order to avoid a systematic offset towards the higher density phase independent of the mesh resolution, while still reducing the magnitude of spurious currents below 1 mm s⁻¹,

$$\delta_2 = 2 \alpha ||\nabla \alpha||_2 \tag{5.4}$$

will be used to apply forces at the interface throughout this thesis.

5.1.3 Contact Line Model

In the present work, contact line motion is described by a subgrid-scale dynamic contact angle model correlating the capillary number *Ca* and the macroscopic contact angle (see Subsection 4.1.4). Because the volume fraction field is advected with velocities interpolated from cell centers to cell face centers, contact line motion is possible even if a no-slip boundary is prescribed at the substrate wall. This slip introduced through the discretization is also called numerical slip [70]. As the distance from wall boundary faces to wall neighboring face centers is dependent on the mesh resolution, the amount of numerical slip decreases with mesh resolution. While, for a constant contact angle, relying solely on numerical



Figure 5.7: Dynamic contact angle dependence on capillary number compared to the Kistler model (left) and droplet diameter over time (right) for different boundaries for the velocity field at the wall on a mesh with 128x256 cells.

slip results in severely mesh-dependent results [70], it is unclear whether modeling slip is necessary if a dynamic contact angle model is employed.

In order to evaluate the influence of slip in combination with a subgrid-scale model for contact line dynamics on contact line motion, a droplet with a volume of 6 pL is considered similar to the previously discussed verification cases. The test case discussed here is based on the spreading droplet scenario presented in [6]. The droplet is initialized in hemispherical shape and is initially at rest. The material properties are the same as in the previous subsection. The equilibrium contact angle is here assumed to be $\pi/16$ or 11.25°. Therefore, starting from the initial hemispherical shape, the droplets spread outwards during the simulated period of 1 ms. The Kistler [105] model is used to model the dependence of the contact angle on contact line motion.

Figure 5.7 shows the dynamic contact angle over the capillary number for the spreading droplets in comparison with the Kistler-Model. The results were obtained on a mesh with 128×256 cells. The values shown were evaluated from the volume fraction field by evaluating the slope of the $\alpha = 0.5$ iso-surface at the contact line in order to determine the contact angle, and the change in contact line position between previous and following write intervals for the contact line velocity. As the contact angle calculated in the subgrid model for contact line motion is not directly imposed on the volume fraction field, but introduced through Equation 4.28 by correction of interface normals at the wall, the droplet contour can deviate from the imposed contact angle. Nevertheless, both, the local-slip model as well as the no-slip model show good agreement with the expected behavior. The no-slip approach shows a slight offset towards larger contact angles for a given capillary number, or in other words, an offset towards smaller capillary numbers for a given contact angle. This can also be observed in the spreading behavior as shown by the contact line radius over time presented in Figure 5.7. The case with the no-slip condition shows slightly slower spreading compared to the case with local slip at the contact line. In order to determine the influence of mesh resolution in this context, additional simulations on coarser grids were performed. Figure 5.8 shows the L_2 and L_{∞} errors of contact angles over mesh size. On the



Figure 5.8: Contact angle errors during droplet spreading compared to the Kistler dynamic contact angle model.

coarser grids, the two boundary conditions show very similar errors. With mesh refinement, however, the local-slip model leads to noticeably smaller errors. For the finest grid, the maximum error during the entire evaluated spreading period is 1.17° for the local-slip model, whereas for the no-slip model it is 2.66° .

Even though differences between the local-slip and the no-slip model become more noticeable on finer grids, the overall change in spreading behavior as depicted in Figure 5.7 is small. These findings indicate that relying on numerical slip can produce reasonable results if a subgrid-scale model for the contact line dynamics is employed. This is in line with previous works that have successfully taken this approach as demonstrated by verification with the subgrid-scale model [6] or validation with experiments [178]. Above all, it should be noted that the mesh dependence in the present case using the Kistler model as subgrid-scale model is substantially smaller compared to the constant contact angle scenario presented in [70]. Nevertheless, since the local-slip model showed slightly favorable results here, it is used throughout the remainder of this thesis.

5.1.4 Substrate Contact

In order to investigate the influence of the wall contact model introduced in Subsection 4.1.5 on simulation results, the impact of a droplet onto a planar substrate was studied. The droplet with a volume of 6 pL impacts the substrate at an initial velocity of 5 ms^{-1} . At the beginning of the simulation, it is in

 Table 5.1: Material properties for the sensitivity study of the substrate contact model to Hamaker constant and mesh size.

	ρ / kg m $^{-3}$	μ / mPas	$\sigma_{\ell \rm g}$ / mN m $^{-1}$	$ heta_{ m eq}$ / °
liquid	1000	20	40	11 25
gas	1	0.02	-10	11.25



Figure 5.9: Computational domain, initial and boundary conditions for the single droplet impact scenario.

spherical shape and placed at a distance of half a droplet radius r_0 above the substrate. The material properties for this case are given in Table 5.1. Figure 5.9 shows a schematic of the domain and initial condition. Therein, $p_{\rm YL} = 2\sigma_{\ell g}/r_0$ represents the Laplace pressure. The influence of the Hamaker constant $A_{s\ell}$ used to model attractive interaction between liquid and solid was studied for different mesh sizes, where in all cases the mesh size decreases gradually towards the substrate. The minimal and maximal mesh sizes differ by a factor of 1.6.

The results of this sensitivity study are presented in Figure 5.10. Figure 5.10a shows the time passed after the beginning of the simulation before the droplet first makes contact with the substrate. For this evaluation, contact is defined as an intersection of the $\alpha = 0.5$ iso-line with the substrate. With increasing $A_{s\ell}$, the contact time decreases. Depending on $A_{s\ell}$, different trends regarding the mesh resolution can be observed. For $A_{s\ell} \ge 1 \times 10^{-13}$ J, the contact time decreases monotonously with mesh refinement. For the largest considered value of $A_{s\ell}$, it reaches a fairly constant contact time slightly above 1 µs for the three finest meshes. The cases with $A_{s\ell} \le 1 \times 10^{-14}$ J show an increasing trend of the contact time with mesh refinement.¹ Corresponding to the later substrate contact for smaller values of $A_{s\ell}$, the droplet has already spread further over the entrained gas film in the corresponding cases. This results in larger initial contact radius corresponding to the position of film rupture is shown in Figure 5.10b. However, comparison with the initial contact radius for $A_{s\ell} = 1 \times 10^{-13}$ J indicates an additional delay for $A_{s\ell} \le 1 \times 10^{-14}$ J, as contact is made at a similar position, but at a later instant. Figure 5.10c shows the contact line radius 10 µs after the start of the simulation. For 1×10^{-14} J $\leq A_{s\ell} \le 1 \times 10^{-12}$ J this radius shows only a small dependence on the mesh resolution. For smaller values of $A_{s\ell}$, a decreasing trend with increasing mesh

¹ Preliminary studies with the standard *interFoam* method for curvature calculation and the corresponding contact angle treatment had shown in some cases no contact with the substrate even after 10 µs, which originally motivated development of the contact model.



(c) Contact line radii after 10 µs

Figure 5.10: Sensitivity of the initial substrate contact towards the Hamaker constant $A_{s\ell}$ for varying mesh resolutions.

resolution can be observed, which is in line with the later substrate contact. The largest considered value of $A_{s\ell} = 1 \times 10^{-11}$ J on the other hand results in an increased contact line radius at the given time.

With regard to three-dimensional droplet collision, which is going to be investigated in Section 6.2, it is due to the required resources for such 3D simulations essential that droplet impact is captured reasonably well also with intermediate mesh resolution. This requires that, similar to reference experiments to be shown in Subsection 5.2.1, delayed contact or even bouncing on the entrained gas film should not occur even on such meshes. At the same time, the value of the Hamaker constant should be chosen as close as possible to realistic physical values, which are typically on the order of 10^{-20} J to 10^{-19} J [46]. $A_{s\ell} = 1 \times 10^{-13}$ J presents itself as a reasonable compromise, ensuring early contact between the drop and the solid substrate in agreement with experimental observations, as will be shown towards the end of this chapter.

5.1.5 Coalescence

The coalescence model is evaluated similarly to the model for substrate contact. Based on the offcentered droplet collision at the solid substrate, the sensitivity of the coalescence process towards the respective Hamaker constant is studied. The test case is based on the reference case for the parametric study presented in Section 6.2. Two droplets with a volume of 6 pL are considered. The material properties are given in Table 5.2 and are based on an acrylate monomer and air. The Kistler model in conjunction with the Joanny-type correction for surface-active substances is employed to describe the contact line dynamics. For the substrate contact model, $A_{\ell\ell} = 1 \times 10^{-13}$ J was chosen. At the beginning of the simulation, the first droplet has already impacted the substrate and has spread to a radius of 31.15 µm. The initial conditions for the first droplet and its surroundings were mapped from the 2D reference impact simulation presented in Subsection 6.1.2. The second droplet impacts the first droplet and the substrate at 5 m s⁻¹. The offset between the two droplets is $\epsilon = 21.17 \,\mu$ m. The simulation takes advantage of the one symmetry plane of the problem. Figure 5.11 shows a schematic representation of the computational domain and the initial conditions. In order to reduce the computational cost of the simulation, adaptive mesh refinement was used. The basic mesh therefore consists of only 60 × 24 × 26 cells. Grading towards the substrate was employed. Cells containing liquid were refined at least once.

Table 5.2: Material properties for the sensitivity study of the coalescence model regarding the Hamaker
constant $A_{\ell\ell}$.

	$ ho$ / kg m $^{-3}$	μ / mPas	$\sigma_{\ell \rm g}$ / mN m $^{-1}$	$ heta_{ m eq}$ / °	
liquid	1105	9	40.70	11.95	
gas	1.189	0.018	40.79	11.23	







Figure 5.12: Sensitivity of coalescence time towards the Hamaker constant $A_{\ell\ell}$



Figure 5.13: Sensitivity of the spreading behavior towards the Hamaker constant $A_{\ell\ell}$ (left) and schematic representation of the collided droplets (right)

An additional refinement layer was added to the interface region. This results in mesh sizes along the contact line of 253.7 nm. The largest mesh sizes of $1.879 \mu \text{m}$ are located within the gas phase and outside of the interface region.

The results of these droplet collision simulations are presented in Figures 5.12 and 5.13 for varying Hamaker constants $A_{\ell\ell}$. Figure 5.12 shows the coalescence time over $A_{\ell\ell}$. Therein, $\tau = 0$ corresponds to the moment of impact of the second droplet on the substrate under the assumption of it being a rigid sphere moving with constant velocity u_0 . Coalescence is here determined based on the $\alpha = 0.5$ iso-surface. Increasing $A_{\ell\ell}$ from 1×10^{-16} J to 1×10^{-14} J were observed to shift the coalescence time by approximately 1 µs. The influence of this on the contact line position, however, is negligible. Figure 5.13 shows the extension of the two droplets in longitudinal direction. Even though the instant of initial coalescence workers slightly, the considered cases show virtually identical spreading behavior. While the coalescence model ensures initial contact between the droplets, the results regarding contact line motion have to be considered insensitive to the choice of $A_{\ell\ell}$. In the remainder of this work a value of $A_{\ell\ell} = 1 \times 10^{-15}$ J will be used.

5.1.6 Surfactant Model

The model for transport of a soluble surface-active substance within the two-phase flow and coupling of the surfactant concentrations to the momentum balance through Marangoni-stresses introduced in Chapter 4 does not depend on an explicit representation of the interface by the mesh geometry. While similar methods have previously been developed in the context of the conservative level-set method [107] and the phase field method [171], this is a novel approach in the context of algebraic volume of fluid methods. As such, special care has to be taken regarding the verification of the model. For that reason, the individual aspects of the surfactant model will be verified individually in the following. First, transport of a passive scalar with the interface is evaluated in Subsection 5.1.6.1. Second, the coupling of bulk and interfacial concentrations through the adsorption model will be investigated in Subsection 5.1.6.2. Third, the coupling of local surfactant concentrations to the momentum balance through Marangoni-stresses will be considered in Subsection 5.1.6.3. The model for surfactant transport within the liquid bulk is a special case of the model presented in [50], which has already been thoroughly verified therein. Therefore, in Subsection 5.1.6.4 only the global conservation of surfactant will be evaluated in order to ensure the conservative property of both, adsorption model and the newly introduced boundary condition for the volume averaged bulk concentration field on a wetted wall.

5.1.6.1 Transport with the Interface

The verification cases for surfactant transport with the interface in interface normal and interface tangential direction are presented in the following paragraphs.

Advection in Interface Normal Direction

In order to verify the model for the advection of species with the interface, an expanding drop is considered. This case therefore also includes stretching of the interface. A similar test case was presented by James and Lowengrub [88]. The spherical drop is initialized with a radius of $r_0 = 1$ m and center r = z = 0. The constant, point-symmetric and divergence-free velocity field,

$$\mathbf{u} = \frac{r \, \mathbf{e}_r + z \, \mathbf{e}_z}{(r^2 + z^2)^{\frac{3}{2}}} \, \dot{V}_0, \qquad r, z > 0, \tag{5.5}$$

is set in an axisymmetric reference frame, where r and z are the coordinates in radial and axial direction respectively, and $\dot{V}_0 = 1 \text{ m}^3 \text{ s}^{-1}$. An initial species concentration

$$\Gamma(\phi, \tau = 0) = \frac{\cos(\phi) + 1}{2} \Gamma_0$$
(5.6)

is prescribed, with $\Gamma_0 = 1 \text{ mol m}^{-2}$. ϕ denotes the angle enclosed between a point on the drops surface and the axis of symmetry in direction \mathbf{e}_z . For the given velocity field and initial conditions, the drop's radius evolves according to

$$r(\tau) = \sqrt[3]{3\dot{V}_0}(\tau + \tau_0), \tag{5.7}$$

where $\tau_0 = \frac{1}{3}s$. The species concentration then evolves with increasing radius according to

$$\Gamma(\phi, r(\tau)) = \frac{\cos(\phi) + 1}{2} \Gamma_0 \frac{r_0^2}{r(\tau)^2}.$$
(5.8)

The computational mesh makes use of the axial symmetry of the problem. Instead of defining a point source at the droplet's center, a small volume is excluded from the computational domain and an inlet with inlet velocities according to the velocity field given above is set. Three layers of local mesh refinement are added surrounding this inlet in order to accurately capture the fluxes at the inlet.

Figure 5.14a shows the evolution of the interfacial species concentration with time as a function of the angular coordinate ϕ for a mesh resolution of $\Delta x = 0.025 r_0$. The expected behavior of a decreasing maximum species concentration as the drop expands is captured in excellent quantitative agreement with the analytical solution, represented by the dashed lines. At the same time, the initial cosine-shaped concentration profile in angular direction is maintained. This also finds expression in the error of the model prediction compared to the analytical solution shown in Figure 5.14b. With increasing mesh resolution, the error decreases below 1% in all error norms. Total variation diminishing (TVD) discretization schemes, as employed here for the advection of excess surfactant, are known to reduce to first order accuracy in the vicinity of extrema [89]. The observed convergence rate agrees well with this expectation.



Figure 5.14: Verification results for species advection with the interface in interface normal direction. The graph on the left shows the results (solid lines) for a mesh resolution of $\Delta x = 0.025r_0$ with the analytical reference (dashed lines) in comparison. The influence of mesh resolution on the error norms are shown on the right for $\tau = 2.5$ s.

Advection and Diffusion in Interface Tangential Direction

For the verification of species transport in interface tangential direction, again a two-dimensional test case is considered. This time, the circular cross-section of a cylindrical rod with radius r = 1 m is considered. A constant, axisymmetric velocity field,

$$\mathbf{u} = (x \, \mathbf{e}_z - z \, \mathbf{e}_x) \, \dot{\phi},\tag{5.9}$$

with angular velocity $\dot{\phi} = 2\pi s^{-1}$ is prescribed. The initial concentration at the liquid gas interface is similarly to the previous test case set to

$$\Gamma(\phi, \tau = 0) = \frac{\cos(\phi) + 1}{2} \Gamma_0.$$
(5.10)

In interface tangential direction, also diffusive species transport might occur, therefore diffusion along the interface is taken into account in the following. The local concentration then evolves according to

$$\Gamma(\phi,\tau) = \frac{e^{-D_{\mathrm{I}}\tau}\cos(\phi - \dot{\phi}\tau) + 1}{2}\Gamma_0.$$
(5.11)

Two cases, one without diffusion ($D_{\rm I} = 0$) and one with diffusion in interface tangential direction ($D_{\rm I} = 0.1 \,{\rm m}^2 \,{\rm s}^{-1}$ and thereby $Pe_D = 125.66$) were considered. Figure 5.15a shows the species concentration as a function of the angular coordinate after one full rotation around the cylindrical rod for two different values of the diffusion coefficient. The profile expected from the analytical solution and represented by



Figure 5.15: Verification results for species advection along the interface in interface tangential direction. The graph on the left shows the results (solid lines) for a mesh resolution of $\Delta x = 0.0125r_0$ with the analytical reference (dashed lines) in comparison. The influence of mesh resolution on the error norms are shown on the right. Both diagrams represent the results after one full rotation around the axis of symmetry.

the dotted line is captured by the numerical model with good quantitative agreement. For the case with slight diffusion in tangential direction, the amplitude of the concentration profile has slightly decreased, as is expected from the analytical solution. The largest deviations of the model prediction from the analytical solution can be observed around the maximum concentration, where the numerical solution shows small superimposed oscillations with very short wavelength. Such so-called 'waviness' [109] is known to appear with explicit temporal discretization of convective terms using central differences [89]. Jasak et al. [89] compared various advection schemes for the advection of \sin^2 and semi-ellipse profiles. Even though these profiles are similar to the $c_{\rm IF}$ profile advected here, the results presented in [89] show no oscillations for self-filtered central differencing (SFCD) and van Leer schemes. Advection in interface tangential direction therefore seems to pose a special challenge regarding the discretization schemes. However, the overall errors observed here are still in an acceptable range of at most a few percent on reasonable mesh resolutions, as can be seen from Figure 5.15b. The case with diffusion in interface tangential direction shows slightly smaller errors in all error norms. The difference, however, is small.

Overall, the presented model for species transport with the interface shows good quantitative agreement with the analytical solutions for both, interface normal and interface tangential advection. Furthermore, diffusion along the interface can be captured with reasonable accuracy. The presented model thus proves capable of describing the convective and diffusive transport of a species with and along the interface. Note that this is accomplished without relying on a direct representation of the interface by mesh faces, allowing topological changes such as drop impact, collision or breakup without a mesh update.

5.1.6.2 Adsorption

Similar to the work presented in [5], the one-dimensional problem of adsorption from the bulk to a planar liquid-gas interface is considered as verification case. Langmuir-Hinshelwood kinetics are assumed, presenting the special case of n = 1 of the Langmuir-Freundlich kinetics, since for this case numerical and analytical reference solutions are available. The interface is assumed to be initially free of surfactant ($\Gamma_0 = 0$). The two limiting cases for the mixed kinetic model of (i) diffusion-controlled adsorption and (ii) Langmuir-Hinshelwood kinetics are used as reference. In the diffusion-controlled limit, the temporal evolution of excess surfactant at the interface can be described by the Ward-Tordai [181] equation,

$$\Gamma(\tau) = 2\sqrt{\frac{D}{\pi}} \left(c_{\infty}\sqrt{\tau} - \int_{0}^{\sqrt{\tau}} c|_{x=0}(\hat{\tau}) \mathrm{d}\sqrt{\tau - \hat{\tau}} \right),$$
(5.12)

together with the Langmuir isotherm, where $c|_{x=0}$ represents the subsurface bulk concentration and c_{∞} is the bulk concentration away from the interface. In order to obtain a reference solution for the numerical model presented in this work, the above equation was integrated numerically using the C++

code provided by Li et al. [113]. In the case of the adsorption kinetics being the rate determining step, the sorption process can be described by the Langmuir-Hinshelwood kinetic model,

$$\frac{\partial \Gamma}{\partial \tau} = k_{\rm ad} c |_{x=0} - \left(\frac{k_{\rm ad} c |_{x=0} + k_{\rm de}}{\Gamma_{\rm max}}\right) \Gamma, \tag{5.13}$$

with a constant subsurface concentration of $c|_{x=0} = c_{\infty}$. The solution of this ordinary differential equation,

$$\Gamma(\tau) = \frac{\Gamma_{\max} k_{ad} c_{\infty}}{k_{ad} c_{\infty} + k_{de}} \left\{ 1 - \exp\left[-\left(\frac{k_{ad} c_{\infty} + k_{de}}{\Gamma_{\max}}\right) \tau \right] \right\},$$
(5.14)

then represents the temporal evolution of excess surfactant at the interface.

The model was verified for the adsorption of heptanol to the liquid-gas interface of a heptanolwater solution, which is expected to show mixed-kinetic behavior. The diffusion coefficient of heptanol in water is $D = 5.3 \times 10^{-10} \,\mathrm{m}^2 \,\mathrm{s}^{-1}$, the kinetic coefficients are $k_{\rm ad} = 6 \times 10^{-4} \,\mathrm{m} \,\mathrm{s}^{-1}$ and $k_{\rm de} = 6.6 \times 10^{-3} \,\mathrm{mol} \,\mathrm{m}^{-2} \,\mathrm{s}^{-1}$, and the maximum surface excess concentration $\Gamma_{\rm max} = 6 \times 10^{-5} \,\mathrm{mol} \,\mathrm{m}^{-2}$ [95]. A bulk concentration of $c_{\infty} = 0.941 \,\mathrm{mol} \,\mathrm{m}^{-3}$ was assumed. For the heptanol-water solution, this results in a ratio of kinetic to diffusive parameters $\Pi = Da C G^{-1} = \frac{\Gamma_{\rm max} k_{\rm ad}^2}{k_{\rm de} D} = 6.17$, where $C = c_{\infty} \,k_{\rm ad}/k_{\rm de}$ and $G = \Gamma_{\rm eq}/\Gamma_{\rm max}$ are adsorption number and equilibrium surface coverage [63], respectively. Additionally, one diffusion and one adsorption limited case were considered by increasing the kinetic adsorption rate coefficients such that $\Pi = 1 \times 10^3$ and increasing the diffusion coefficient such that $\Pi = 1 \times 10^{-2}$ respectively.

The numerical results for the mixed-kinetics model were obtained on a one-dimensional mesh with a resolution of $\Delta x = 1.875 \times 10^{-7}$ m. Local mesh refinement down to a mesh size of $\Delta x = 2.930 \times 10^{-9}$ m was used to resolve the concentration gradients at the interface in the early stages of the diffusion-limited case ($\Pi = 1 \times 10^3$). The domain size is $15 h_{ad}$, with $h_{ad} = \Gamma_{eq}/c_{\infty}$ being the characteristic length scale of the diffusion-controlled adsorption process [63]. Therein, Γ_{eq} denotes the equilibrium surface excess concentration for $\tau \to \infty$ and the given bulk concentration. The interface position is, just as for the two- and three-dimensional cases shown in the following chapter, implicitly given by the volume fraction of the liquid phase α . It is placed at $10 h_{ad}$ from the boundary, therefore leaving 2/3 of the domain for the diffusion process to the interface. The two reference solutions consider only diffusive transport and adsorption kinetics, respectively, without convective transport within the bulk phase. The fluids are therefore assumed to be at rest. The solution of the advection equation for the volume fraction field, as well as the momentum balance, were omitted accordingly.

The results for the three cases are shown in Figure 5.16 in comparison with the reference solutions introduced above. As expected, the heptanol-water solution shows mixed kinetic behavior with a transition from the adsorption-limited regime to the diffusion-limited regime after approximately 1 ms for the bulk concentration considered here. Outside the transition region, excellent agreement with the corresponding reference solutions can be observed. Similarly, for $\Pi = 1 \times 10^3$ and $\Pi = 1 \times 10^{-2}$, excellent agreement between the solutions from the mixed kinetic model and the corresponding reference



Figure 5.16: Verification of the mixed kinetics model with numerical (dashed) and analytical (dotted) reference solutions. A similar figure has appeared previously in [5].

solutions is found over the entire considered time frame from $1 \mu s$ to 10 s. Thus, the presented sorption model is proven suitable for the simulation of adsorption processes to a fluid interface given by the volume fraction field. Supplementary 2D verification cases supporting the results shown here are presented in Appendix D.

5.1.6.3 Marangoni-Effect

To verify the implementation of Marangoni stresses, the numerical model was applied to a viscous drop with a fixed surfactant distribution along the interface. This test case has previously been used for the verification of solutal Marangoni stresses in the sharp [124] as well as the diffuse [171] interface context. The drop is initialized as a sphere with radius r_0 on an axisymmetric grid. It is kept in its initial shape, meaning the transport equations for the volume fraction field and the surfactant concentration are not solved. A linear surface tension model,

$$\sigma = \sigma_0 \left(1 - \frac{\Gamma}{\Gamma_{\text{max}}} \right), \tag{5.15}$$

was employed for this test case. The interfacial surfactant concentration c_{I} was initialized such that the surface tension decreases linearly in direction of the axis of symmetry according to

$$\sigma(z) = \sigma_0 \left(1 - \frac{2z + 15r_0}{30r_0} \right), \tag{5.16}$$

where z denotes the coordinate in axial direction and z = 0 represents the position of the drops center. The same dimensional material properties as in [171] were chosen for the drop and the surrounding fluid, i.e. $\rho_1 = \rho_2 = 0.2 \text{ kg m}^{-3}$, $\mu_1 = \mu_2 = 0.1 \text{ Pa s}$ and $\sigma_0 = 1.0 \text{ N m}^{-1}$. Equation 5.16 results in a



Figure 5.17: Error of bubble velocity compared to the analytical solution from Young et al. [196].

surface tension gradient $\partial \sigma / \partial z = \sigma_0 / 15 r_0$ identical to the one imposed by Teigen et al. [171]. The drop radius is set to $r_0 = 0.5$ m in agreement with [171]. With these properties, the expected terminal velocity of the drop is then [cf. 171, 196]

$$u_{\rm YGB} = \frac{2\sigma_0}{15(6\mu_1 + 9\mu_2)} = \frac{2}{225} \frac{\sigma_0}{\mu_1} = \frac{4}{45} \,\mathrm{m\,s^{-1}} = 0.0\overline{8} \,\mathrm{m\,s^{-1}}.$$
 (5.17)

With a Reynolds number of $Re = 8/45 = 0.1\overline{7}$, the above parameters thus result in a droplet motion within the creeping flow regime, where Equation 5.17 is valid. The computational domain used for the simulation of the drop motion has a length of $16r_0$ in axial direction and a width of $8r_0$ in radial direction. A mesh study was performed to investigate the influence of mesh resolution on the accuracy of the surface tension induced flow. The coarsest considered computational grid has a mesh width of $\Delta x = 0.8 r_0$ on the coarsest level and is refined in two layers towards the droplet. Thus, the mesh size at the droplet varies between $0.2r_0$ on the coarsest considered resolution and $1.25 \times 10^{-2} r_0$ on the finest. At the boundaries, p = 0 for outwards and $p = -0.5 \rho ||\mathbf{u}||_2^2$ for inwards directed flow, while for the velocity in boundary normal direction $\mathbf{n} \cdot \nabla \mathbf{u} = 0$ and the tangential component of the velocity $\mathbf{u}_{\parallel} = 0$. Surface tension forces are applied according to Equation 4.7, where $\delta_2 = 2 \alpha ||\nabla \alpha||_2$ was used, introducing slight density scaling. With the fixed volume fraction field and concentration fields, the pressure velocity coupling is solved until a steady state is reached.² The local surface tension is thereby calculated from Equations 4.56 and 5.15, thus the evaluation method of Γ from $c_{\rm I}$ and α is included in this verification case.

Figure 5.17a shows the velocity field within the drop in a spatially fixed reference frame as well as the local surface tension along the interface for the case with highest grid resolution. Due to the lower surface tension at the top of the drop, which results in a smaller Laplace pressure jump across the interface, a net flow from the drop's bottom to its top can be observed. Along the interface, however, the

² The maximal change in \overline{u}_z/u_{YGB} over the last write interval of 100 s within each simulation is 4.20×10^{-4} .

surface tension gradient induces Marangoni flow in the opposite direction, slowing the drop's movement through the surrounding fluid. In order to compare the numerical results with the reference solution from Young et al. [196], the mean drop velocity in axial direction can be calculated from

$$\overline{u}_z = \frac{\sum_{i=1}^N u_{i,z} \alpha_i V_i}{\sum_{i=1}^N \alpha_i V_i},$$
(5.18)

where $u_{i,z}$ and α_i denote the axial velocity and volume fraction within the computational cell *i* respectively. V_i stands for the volume of cell *i*. Figure 5.17b shows the relative error in the terminal mean drop velocity for varying mesh sizes. The graph clearly shows a decreasing error with mesh refinement. The observed convergence rate is approximately of first order. The agreement with the reference solution and the decreasing error with meh refinement show that the employed model is capable of capturing surface tension forces including Marangoni stresses accurately.

5.1.6.4 Global Surfactant Conservation

Finally, the global conservation of surfactant for the introduced method is studied within this section. For this purpose, a surfactant-laden droplet with a volume of 6 pL impacting a solid substrate is considered. The initial bulk concentration is 0.248 mol m^{-3} . The excess concentration at the liquid-gas interface was assumed to be initially zero. Thus, the total amount of surfactant within the droplet is 1.489×10^{-15} mol. The two fields are coupled through Langmuir-Freundlich kinetics using the method-ology introduced in Subsection 4.3.3. This setup corresponds to the reference case for the impact and spreading of surfactant-laden droplets, which will be discussed in more detail in Section 6.1. Therein also further details regarding the material and process parameters as well as the simulation setup are given. The considered time frame up to 3 ms includes the initial impact as well as the following relax-





ation and spreading phases of the droplet. During these phases, the contact angle changes between a maximum of 175° upon impact and a minimum of 33° at the end of the considered time frame. Thus, the boundary condition for the volume averaged bulk concentration field introduced in Subsection 4.3.1 is here verified for the non-trivial case of a contact angle that is (in general) deviating from 90°. Furthermore, as surfactant adsorbes to the interface in the considered case, the coupling of bulk and interface concentrations can be evaluated regarding species conservation as well.

Figure 5.18 shows the surfactant distribution between bulk and interface. Starting with initially no surfactant adsorbed to the interface, the amount of surfactant at the interface increases notably on the time scale of 100 μ s to milliseconds. At the same time, the amount of surfactant within the bulk decreases by the same amount, such that the total amount of surfactant remains practically constant. The deviation in the total surfactant amount at the end of the simulation compared to the beginning is 4.512×10^{-19} mol or 0.030 % of the initial amount. Thus, the developed model is able to conserve the total surfactant with good accuracy.

5.2 Validation with Experiments

The above presented verification cases showed that the presented method is able to correctly reproduce the expected model behavior. Comparison of the fitted Langmuir-Freundlich adsorption model with experimental data is shown in Appendix G. In order to validate the model for the impact and collision of micrometer-sized droplets, additional simulations were performed. For that purpose, droplets impacting and colliding on a glass slide were studied. The simulation results are compared to experimental observations of individual droplet impact (Subsection 5.2.1) and colliding droplets (Subsection 5.2.2).

5.2.1 Impact and Spreading

For the validation of the numerical model with respect to the hydrodynamics of micrometer-sized droplet impact, the simulation results were compared to observations from a reference experiment³. In this reference experiment, acrylate monomer droplets with a volume of (7.3 ± 0.2) pL were jetted from an inkjet printhead onto a planar glass slide. The droplets impacted in substrate normal direction and in the direction of gravitational acceleration. The impact and subsequent spreading of the droplets was observed from the side, parallel to the substrate, using high speed imaging. The frame rate of the camera was $216000 \, \text{s}^{-1}$. The droplet velocity had previously been determined from recordings of droplets in flight, slightly above the substrate. The mean droplet velocity before impact was thereby determined to $u_0 = (2.0 \pm 0.1) \, \text{m s}^{-1}$. The density of the jetted monomer is $\rho_{\ell} = 1105 \, \text{kg m}^{-3}$, its dynamic viscosity $\mu_{\ell} = 9 \, \text{mPas}$ and its surface tension at the interface liquid-air is $\sigma_{\ell g} = 40.79 \, \text{mN} \, \text{m}^{-1}$. In terms of dimensionless groups, this corresponds to Re = 5.91, We = 2.61, and Oh = 0.27. The first and third row in Figure 5.19 show the droplet contour in side view over the course of approximately 200 µs. The upper half of the contour shows the droplet, the lower half its reflection on the glass slide. The instant of initial contact between substrate and droplet $\tau = 0$ was estimated from the observed distance between

³ Many thanks to Sebastian Wilhelm and Heidelberger Druckmaschinen AG for providing the experimental data.



Figure 5.19: Side view of impacting 7.3 pL droplets from the reference experiment (first and third row) and the numerical simulation (second and fourth row) in comparison. Images from the experiment provided by Heidelberger Druckmaschinen AG.

the droplet and its reflection in the first frame and the known impact velocity. Shortly after the impact ($\tau = 1.48 \,\mu$ s), the droplet shape closely resembles a truncated sphere, as is expected for the initial kinematic phase. At $\tau = 6.11 \,\mu$ s, the droplet flattens slightly before relaxing to an almost hemispherical shape at $\tau = 20.00 \,\mu$ s. In the following, the droplet slowly spreads further while maintaining the shape of a spherical cap.

The second and fourth row in Figure 5.19 show the droplet contour from the numerical simulation at corresponding time steps in comparison. For the simulation, the droplet was initialized in spherical shape with volume, velocity and material properties according to the experiment. The assumed properties of the surrounding gas $\rho_g = 1.189 \text{ kg m}^{-3}$ and $\mu_g = 18 \,\mu\text{Pas}$ correspond to air at 20 °C [165]. The equilibrium contact angle $\theta_{eq} = 53.39^\circ$ of the acrylate monomer on the glass slide was calculated from



Figure 5.20: Droplet radii from experiments and numerical simulation in comparison. Experimental data provided by Heidelberger Druckmaschinen AG.

the droplet volume and the equilibrium radius observed in the experiment. In order to describe the contact line dynamics, the Kistler contact line model with the correction of the capillary number in the sense of Joanny [94] was used for the results shown in Figure 5.19. Taking advantage of the axial symmetry of the problem, a two-dimensional simulation was performed. The setup is similar to the one shown in Figure 5.9. The domain was discretized with 192 × 204 cells with decreasing mesh sizes towards the substrate in axial direction. The mesh sizes therefore vary between 157.5 nm and 250.7 nm. The droplet contours from the numerical simulation show the same qualitative behavior as described above for the experimental observation. The droplet assumes the shape of a truncated sphere in the early, kinematic stage of the impact process, followed by a flattening due to inertial forces and the subsequent relaxation to an almost hemispherical shape. Afterwards, the droplet continues to spread, while maintaining the shape of a spherical cap in agreement with the experiment. The droplet contours thus show excellent qualitative agreement between numerical simulation and experimental observations throughout the presented time frame.

The simulation also quantitatively shows excellent agreement with experimental observations. Figure 5.20 shows the droplet radius from experimental observations in comparison with numerical results. Results for the standard Kistler model are shown in addition to the results obtained in conjunction with the scaled capillary number in the sense of Joanny [94]. The experimental data shown is the result of ten individual droplets impacting onto the glass slide. The results show excellent reproducibility of the experiment. A slight variation in the position of the droplet within the last frame before contact to the substrate was accounted for by determining $\tau = 0$ individually for each repetition of the experiment. The experimental radii were then obtained from the fit of a circular shape to the droplet and the intersection of said shape with the substrate plane. Therefore, they represent the contact line radius. The circular shape is an excellent approximation of the droplet contour during later spreading, however, during the initial impact the droplets briefly deviate from this shape over the course of a few micro seconds, as can be seen from Figure 5.19c. During this short period, the experimental radii evaluated from the circular

fit quickly increases to a temporal maximum over the course of several micro seconds before slightly decreasing as the drop relaxes. Afterwards, the contact line radius increases again until it reaches its equilibrium radius. The contact line radii from the numerical simulation show initially a rapid increase. In the double logarithmic plot, a turning point can be observed after approximately 20 µs. However, no receding of the contact line occurs in the simulation. Because the evaluation method employed on the experimental data is expected to slightly overpredict the contact line radius while the droplet flattens due to inertia, also the maximum droplet radii from the numerical simulation are plotted. These show a temporal maximum in agreement with the experimental data. Thus, the discrepancy between the contact line radius from the numerical simulation and the experiment can likely be attributed to the deviation of the droplet profile from the assumed circular shape during this instant. Interestingly, the contact line model plays a subordinate role in the very early spreading stage. However, in the later capillary spreading regime, the Joanny-type correction results in the expected reduction of the spreading rate. As could be expected, the same equilibrium radius is reached independently of the dynamic contact angle model. Comparison between the two numerical simulations and the experiment show better agreement if the Joanny-type correction is employed. Since the correction accounts for surface-active substances at the contact line, these results suggest that surface-active impurities are present in the acrylate monomer. Even though the exact origins of the discrepancy remains unclear, the Joanny-type correction will be used throughout this work even for cases with no added surfactant, due to its better agreement with the spreading behavior of the acrylate monomer.

5.2.2 Collision

In addition to the validation case presented in the previous section, the off-centered collision of two droplets at the solid substrate was considered for the validation of the numerical model⁴. Again, acrylate monomer droplets with a volume of 7.3 pL impacting a glass slide at a velocity of 2 m s^{-1} were considered. Two droplets were successively applied to the substrate. The delay before the second drop was sufficiently long for the first droplet to reach its equilibrium radius. After the deposition of the first droplet, the substrate was moved $\epsilon = 21.17 \,\mu\text{m}$ to the side before the second drop was jetted from the same nozzle. This offset between the droplet positions corresponds to a print resolution of 1200 dpi. Figure 5.21 shows a schematic representation of the droplet positions as viewed from the top. The extension of the collided droplets in longitudinal direction, as measured from the corresponding nozzle position, is here denoted by r_1 for the first droplet and r_2 for the second droplet. It was evaluated from a polynomial fit to the drop contour as viewed from the side. This assumption for the droplets' profile approximates the actual shape very well at later times. However, similar to the case of a single droplet, it introduces some uncertainties for the very early stages during collision.

For the numerical simulation, the first droplet was initialized as a spherical cap sitting on the substrate and is initially at rest. The second droplet was initialized as a sphere, similar to the single droplet case presented in Subsection 5.2.1. The offset between the axes of symmetry of the two droplets corresponds to the one in the experiment. The same material properties as for the single droplet case were used. Only

⁴ Thanks to Heidelberger Druckmaschinen AG for conducting the experiment and providing the experimental data for this reference case.



Figure 5.21: Droplet radii in longitudinal direction from experiments and numerical simulation in comparison (left) and schematic representation of the collided drops (right). Experimental data provided by Heidelberger Druckmaschinen AG.

the contact angle $\theta_{eq} = 33.91^{\circ}$ was adjusted for the apparently more wettable glass slide in the collision experiment. It was evaluated from the radius of the first droplet before collision and the known volume of the droplet under the assumption of a spherical cap shape. The Kistler model in conjunction with the Joanny-type correction for surface-active substances was used to describe the contact line dynamics. Domain and mesh are chosen identical to the case presented in Subsection 5.1.5 with mesh sizes between 253.7 nm along the contact line and 1.879 µm within the gas phase outside the interface region.

Figure 5.21 shows the experimental data in comparison with the numerical results. For the simulation results, the maximum radii are shown in addition to the contact line position. Upon impact of the second drop, a large peak in r_2 can be observed from the experimental data. This peak then rapidly decreases. Over the course of the next micro seconds, r_2 increases only slightly. r_1 shows no sudden change after the impact of the second droplet. However, in the following the now coalesced droplets spread also in the direction of the first droplet. After approximately 1 ms, the elongation of the coalesced droplets maintains a fairly constant level. Similar to the experiment, r_1 from the simulation shows no sudden change after the impact of the second droplet. The following increase in r_1 as well as the final plateau show excellent agreement between numerical simulation and experimental data. The peak in the maximum elongation in direction r_2 from the numerical simulation is substantially smaller compared to the experimentally obtained values. This might be attributed to an overestimation of r_2 in the polynomial fit to the droplet profile in the experiment. In the following spreading phase, experiment and simulation show very good agreement. After 1 ms, the second droplet begins to recede in longitudinal direction as it spreads further in transversal direction to assume the ideal equilibrium shape of a spherical cap with the equilibrium contact angle given above. Such a receding motion was not observed in the experiment. This can likely be attributed to contact angle hysteresis and therefore pinning of the contact line on the glass slide in the experiment. The numerical model does not account for this effect. This limitation of the numerical model must be kept in mind for the interpretation of the results shown in the following section. However, since the wettability of print substrates typically is very good, receding contact lines were only observed in a small number of the considered cases. This restriction of the model was thus deemed acceptable for the present work.

CHAPTER **6**

Results and Discussion

This chapter presents the simulation results on droplet impact and substrate-sided droplet collision. First, the results on the impact and spreading behavior of individual droplets will be presented in Section 6.1. The results on colliding droplets are presented in Section 6.2. For both scenarios, the influence of hydrodynamic parameters, heat, and surfactant transport on the impact and spreading behavior is discussed. Within each section, one reference case will be presented from which individual parameters will be varied in the following.

6.1 Single Droplet Impact and Spreading

This section presents the impact and spreading behavior of individual, micrometer-sized droplets. First, isothermal and surfactant-free cases are presented. Following this, the influence of temperaturedependent viscosity on the impact behavior of droplets in non-isothermal scenarios is discussed. Finally, the influence of surfactants on droplet impact and spreading is discussed.

6.1.1 General Simulation Setup

The simulations presented in the following all share a setup similar to the one given in Subsection 5.2.1, rescaled for the slightly smaller droplet volume of 6 pL considered throughout the remainder of this work. All parameters and material properties are motivated by inkjet printing with UV-curable inks. Unless noted otherwise, the droplet's initial velocity is $u_0 = 5 \text{ m s}^{-1}$ and the material properties are those given in Table 6.1, corresponding to an acrylate monomer similar to those used as main component of UV-curable inks and air as the surrounding gas phase. These dimensional parameters correspond to $Re_{ref} = 13.84$, $We_{ref} = 15.27$, and $Oh_{ref} = 0.28$. Motivated by typically good wettability of print substrates, an equilibrium contact angle of 11.25° is assumed unless noted otherwise. Thermal conductivity and heat capacity were determined for this acrylate monomer using differential scanning calorimetry (DSC)

and laser flash analysis (LFA). The measurement results are shown in more detail in Appendix F. For isothermal cases, a constant dynamic viscosity of 9 mPas is set, whereas for the non-isothermal cases a temperature dependence of the viscosity according to the Andrade equation [133] is assumed. Thus, throughout this chapter, the liquid viscosity is set according to

$$\mu_{\ell} = \begin{cases} 9 \,\text{mPas} & \text{for isothermal cases} \\ \mu_{\text{ref}} \exp \frac{T_{\text{ref}}}{T} & \text{for non-isothermal cases.} \end{cases}$$
(6.1)

With $\mu_{ref} = 2.587 \times 10^{-5}$ Pas and $T_{ref} = 1949.61$ K, this produces a viscosity of 9 mPas at a temperature of 60 °C and a viscosity of 20 mPas at 20 °C in non-isothermal scenarios. Typical UV-curable inks show similar viscosities at room temperature, while print heads are heated in order to lower the viscosity into a jettable range. Depending on the print head, the window of jettable viscosities varies [see e.g. 38, 146]. Nevertheless, the assumed model produces viscosities well within the printable range presented by Hutchings et al. [85] for the given temperatures.

For cases including surfactant, diffusion and adsorption related parameters are closely associated to the ones determined in Appendix F for the model surfactant solution. This surfactant solution consists of the previously mentioned acrylate monomer and a radically cross-linkable surfactant, a combination typical for UV-curable inks. The characteristic length scale for the adsorption process $h_{ad} = \Gamma_{eq}/c_{\infty}$, however, is increased by a factor of 20. This deviation from the real system is necessary in order to be able to resolve concentration gradients near the interface with reasonable mesh resolution. The sensitivity of the results towards h_{ad} is discussed in Subsection 6.1.4. Table 6.2 shows the rescaled model parameters of the surfactant solution. For a one-dimensional adsorption process, these parameters in combination

	$ ho$ / kg m $^{-3}$	μ / mPas	$\sigma_{\ell \rm g}$ / mN m $^{-1}$	$ heta_{ m eq}$ / °	$c_{(p)} / \mathrm{J kg^{-1} K}$	λ / W m ⁻¹ K
solid ^a	910	-	_		1710	0.22
liquid ^b	1105	Eqn. 6.1 ^c	40.70	11.25^{d}	1832	0.597
gas ^e	1.189	0.018	40.79		1006.4	$2.587 imes 10^{-2}$

Table 6.1: Material properties of the bulk media.

^{*a*} Corresponding to PP at 20 °C [165]. Specific heat capacity interpolated from values for 0 °C and 50 °C.

^{*b*} Corresponding to the acrylate monomer

^c The viscosity of isothermal cases corresponds to the acrylate monomer. The temperature dependence in non-isothermal cases was motivated by UV-curable inks.

^d Experimental observations have shown very good wettability, which makes reliable measurements of the contact angle difficult. Here, a contact angle of $\theta_{eq} = 11.25^\circ = \pi/16$ was assumed.

^{*e*} Corresponding to air at 20 °C and 1 bar [165].

K	Г	n	מ	k .	k.	σ.
	1 max		D	^ad		0 lg,0
$m^3 mol^{-1}$	$molm^{-2}$	1	$\mathrm{m}^2\mathrm{s}^{-1}$	$\mathrm{ms^{-1}}$	$\mathrm{mol}\mathrm{m}^{-2}\mathrm{s}^{-1}$	$\rm mNm^{-1}$
3.359×10^{-38}	1.478×10^{-4}	6.559×10^{-2}	4.76×10^{-10}	1.752×10^{-3}	5.217×10^{34}	40.79

 Table 6.2: Rescaled parameters of the adsorption model.


Figure 6.1: Computational domain, initial and boundary conditions for the single droplet impact scenario.

with the corresponding initial concentrations result in identical transient behavior of the surface tension compared to the reference surfactant solution. Unless otherwise noted, a reference bulk concentration of 0.248 mol m⁻³ is considered, which corresponds to a mass fraction of 2% in the model ink.

Figure 6.1 shows a schematic representation of the computational domain, initial and boundary conditions. Subdomains for both, the fluid and solid region are shown. However, the solid region is only relevant to non-isothermal cases. It is taken advantage of the rotational symmetry of the problem and both subdomains are discretized with 192×204 cells. This discretization corresponds to the one used for the validation case in Subsection 5.2.1. Also similar to the validation case, mesh grading towards the substrate is used within the fluid domain in order to increase mesh resolution at the wall. The ratio between largest and smallest mesh width is again 1.6, with a minimum mesh size of 147.5 nm at the solid-fluid interface. Identical grading is also used within the solid domain towards the fluid in order to increase resolution at the coupled boundary. Just as for the validation case, the time step size is adjusted according to the criterion by Brackbill et al. [24] presented in Equation 4.75 for the initial impact. Starting at 50 µs after the beginning of the simulations, larger time step sizes are allowed according to the criterion presented in Equation 4.77. Furthermore, the height of the fluid domain is reduced to $2r_0$ at that time in order to lower the computational cost of the simulation. The influence of the domain size on the simulation results is presented in Appendix E for a non-isothermal case.

6.1.2 Influence of Hydrodynamic Parameters

Starting from an isothermal, surfactant-free reference case, several hydrodynamic parameters are varied. After discussion of the impact and spreading behavior of this reference case, results for varied Weber and Ohnesorge numbers as well as equilibrium contact angles are presented.

Results of the Reference Case

Figure 6.2 shows the contact line radius over time for the reference scenario of an acrylate droplet impacting the substrate as described above. The observed behavior is in excellent qualitative agreement with the behavior described by Derby [51] for the impact of micrometer-sized droplets within inkjet printing. Upon impact, the droplet spreads in the impact-driven regime with $r \propto \tau^{0.5}$. After a few micro-seconds, the droplet enters the relaxation phase from which it transitions to the capillary-driven regime. Even though Tanner's [169] law was derived for the complete wetting case, the here considered partially wetting system shows good agreement with the corresponding power law $r \propto \tau^{0.1}$ within this regime. A slight deviation can be observed after around 2 ms. This deviation can be attributed to air that was entrapped upon impact of the droplet. With the entrained air forming a central bubble within the droplet, the thickness of the liquid film above this bubble decreases as the droplet spreads, which leads to film rupture. Air entrainment under micrometer-sized droplets has previously also been observed experimentally [23, 174]. Nevertheless, due to the low resolution of the entrained gas film as well as the increased Hamaker constant for the wall contact model, the bubble volume found in the simulation



Figure 6.2: Contact line radius of the reference case of the following parameter study and spreading regimes according to Derby [51].

is subject to uncertainty. Furthermore, on a slightly heterogeneous substrate, the bubble position and volume may vary or the entrained gas film might even disperse into multiple bubbles. Thus, the observed influence of the entrained air on the late spreading behavior is subject to further uncertainty. After 10 ms the droplet is still spreading and has not yet reached its equilibrium contact line radius of $33.81 \,\mu m$ expected for a spherical cap shaped droplet of the given volume and with the given contact angle.

Weber Number

In the following, the influence of the Weber number on microdroplet impact and spreading is discussed. Starting from the previous reference case with $We_{ref} = 15.27$, the Weber number is varied by adjusting the initial velocity between 1.25 m s^{-1} and 10 m s^{-1} . Thus, typical jetting velocities within the inkjet printing process on the order of several meters per second are covered by these values. The influence of these changes on the impact and spreading behavior is depicted in Figure 6.3. Normalized with the kinematic time scale $\tau_{kin} = d_0/u_0$, one can observe spreading according to $r \propto \tau^{0.5}$ within the impact-driven regime throughout all cases. The contact line radius at the transition to the relaxation regime increases with increasing *We*. Thus, the transition towards the relaxation regime occurs at a larger τ_{kin} with increasing *We*. Scaling the results with the capillary time scale $\tau_{Ca} = d_0 \mu_\ell / \sigma_{\ell g}$ shows that towards the end of the simulated time frame of 10 ms, all cases coincide and follow Tanner's law. It is notable that even for the relatively large initial velocity of 10 m s^{-1} corresponding to $We = 4 We_{ref}$, there is virtually no influence of the initial velocity on further spreading for $\tau > 100 \tau_{Ca}$ or, in terms of dimensional values, $\tau > 500 \,\mu$ s. For the printing process, this implies that diameters of individual dots can be assumed to be independent of the impact velocity, whereas the spreading of overlapping dots may be affected by the droplets initial velocity. This aspect will be further addressed in Section 6.2.



Figure 6.3: Contact line radius for varying Weber number at constant Ohnesorge number scaled with the kinematic time scale τ_{kin} (left) and the capillary time scale τ_{Ca} (right).

Ohnesorge Number

Another influencing factor studied is the Ohnesorge number adjusted by means of the liquid viscosity. The Weber number is thus kept constant. Starting from the reference case discussed above corresponding to an Ohnesorge number $Oh_{ref} = 0.28$, the viscosity is varied between 4.5 mPas and 22.5 mPas. The results are again evaluated using kinematic and capillary time scales. Figure 6.4 presents the evolution of the contact line radius over time. Scaled with au_{kin} , the results show again spreading according to $r \propto au^{0.5}$ within the impact-driven regime. With increasing viscosity, the radius at the end of the impactdriven regime decreases, which is in line with the findings of Rioboo et al. [143]. However, the transition to the relaxation regime occurs simultaneously for all considered cases. It is interesting to note that the simulation predicts slightly later rupture of the entrained air film under the droplet with increasing viscosity and, therefore, later initial substrate contact. In the later capillary-driven regime, the spreading rate shows a substantial dependence on Oh. Scaling the spreading process with τ_{Ca} compensates this effect and comparison with Tanner's law again shows good agreement. Slight deviations in this stage can be attributed to the escape of entrained air. However, for identical scaling throughout all cases, as is the case by scaling with τ_{kin} , the varied viscosity shows a substantial influence especially in the later spreading stage. Thus, the liquid viscosity has to be considered an important influencing factor for the spreading of individual droplets. Since the viscosity is temperature-dependent in typical inks, heat transfer may influence the overall spreading behavior. This will be addressed in Subsection 6.1.3.



Figure 6.4: Contact line radius for varying Ohnesorge number at constant Weber number scaled with the kinematic time scale τ_{kin} (left) and the capillary time scale τ_{Ca} (right).

Equilibrium Contact Angle

Finally, the influence of the equilibrium contact angle on the impact and spreading behavior of individual droplets is investigated. Starting from the reference scenario with $\theta_{eq,0} = 11.25^{\circ}$, the contact angle is varied between 0° and 45°. Figure 6.5 shows the contact line radius over time for varying wettability. Because both time scales τ_{kin} and τ_{Ca} are independent of the contact angle, the results are presented only for one scaling. For the values of θ_{eq} considered here, no influence of the substrates wettability



Figure 6.5: Contact line radius for varying contact angle at constant Weber and Ohnesorge numbers scaled with the kinematic time scale τ_{kin} . The black dashed lines represent the equilibrium radii corresponding to the respective contact angles.

on the impact-driven regime can be observed. Also the relaxation regime is unaffected by θ_{eq} for the given parameters. This is in line with the findings of Rioboo et al. [143], who have found an influence of wettability on the first spreading phases only under very hydrophobic conditions. Only as the droplets approach their equilibrium state, as indicated by the black dashed lines, the influence of the equilibrium contact angles becomes notable, slowing spreading during the capillary-driven regime. For the larger considered contact angles $\theta_{eq} \ge 22.5^{\circ}$, the droplets reach their equilibrium state within the simulated time frame of 10 ms. However, only a minor influence of θ_{eq} on the spreading behavior within the considered time frame can be observed for $\theta_{eq} \le 11.25^{\circ}$. Once more, the escape of entrained air results in slight deviations between the different cases. Just as the droplet with $\theta_{eq} = 2 \theta_{e,0}$ reaches its equilibrium radius, the entrapped bubble escapes the droplet, resulting in the small oscillation observable in the contact line radius.

6.1.3 Temperature Dependence

As observed above, the liquid's viscosity has an influence on droplet impact and spreading throughout the entire spreading process. In combination with a substantial dependence of ink viscosity on temperature, this suggests that temperature differences between print head and substrate and the resulting heat transfer upon droplet impact can influence the spreading behavior. The thermal Marangoni effect is here assumed to be negligible compared to temperature dependent viscous effects and the solutal Marangoni effect considered in Subsection 6.1.4. Unless otherwise noted, thermal conductivity and specific heat capacity of the gas, liquid and solid are set as listed in Table 6.1, corresponding to air, acrylate monomer, and polypropylene, respectively. The surrounding air is assumed to be initially at substrate temperature. Throughout this section, the influence of initial droplet and substrate temperatures as well as the substrate's thermal conductivity on the spreading process are investigated. First, however, the spreading behavior and the evolution of the temperature field are discussed in more detail for a selected reference case.

Results of the Reference Case

As non-isothermal reference case, the impact of a droplet with a homogeneous temperature of 60 °C onto a substrate at 20 °C is chosen. Figure 6.6 shows the droplet contour and the temperature within droplet and solid substrate 48.9 μ s after impact. An entrapped bubble can be seen in the droplet center at the substrate. The assumed rotational symmetry enforces the ring-like shape of the second bubble surrounding the central bubble. Upon impact, the droplet's base is abruptly cooled down, while the substrates temperature increases locally. The initial contact line temperature upon contact shows good agreement with the value expected based on effusivities,

$$T_{\rm c} = \frac{e_{\ell} T_{\ell,0} + e_{\rm s} T_{\rm s,0}}{e_{\ell} + e_{\rm s}} = 319.26 \,\rm K, \tag{6.2}$$

where $e_i = \sqrt{\lambda_i \rho_i c_i}$ is the thermal effusivity of phase *i* [165]. T_c is shown in Figure 6.7 as a dashed line in comparison with the temperature evaluated at the contact line over time. As the droplet spreads outwards over still cool substrate, the contact line temperature decreases further. While this decrease is quite smooth for later times, some spikes in contact line temperature can be observed during the first 3 µs of the impact process. This coincides with the rupture and collapse of the air film between droplet and substrate. However, as the entrained air film is not fully resolved, it is unclear whether this behavior is physical. On the time scale of several milliseconds, the contact line temperature, the viscosity at the contact line increases, as is depicted on the right-hand side of Figure 6.7. The resulting spreading behavior is shown in Figure 6.8 as contact line radius over time. It shows very good qualitative agreement with the different spreading regimes identified by Derby [51] for the inkjet printing process. It is interesting to note that even though the viscosity at the droplet foot and the contact line changes substantially, the evolution of the contact line radius is still in good agreement with $r \propto \tau^{0.5}$ expected for



Figure 6.6: Temperature field within a droplet with 60 °C initial temperature 48.9 μ s after impact onto a PP substrate at 20 °C initial temperature.



Figure 6.7: Contact line temperature and dynamic viscosity of the bulk liquid evaluated at the contact line for the reference case.



Figure 6.8: Contact line radius of the non-isothermal reference case for the following parameter study.

isothermal cases in the kinematic regime and Tanner's law in the capillary-driven regime. Only towards the end of the considered time frame of 10 ms, slight deviations can be observed. These, however, must again be attributed to the escape of entrained air in the droplets center and are, therefore, not related to the viscosity at the contact line.

Initial Temperatures

In the following, the influence of initial droplet and substrate temperatures on the spreading behavior is discussed. The initial droplet temperature is varied between 20 °C and 60 °C and their impact was simulated for substrate temperatures of 20 °C and 60 °C. The results of these simulations are presented in Figure 6.9. The results are scaled with τ_{Ca} , where the liquid viscosity at substrate temperature is inserted. All considered cases show qualitatively very similar behavior in agreement with the previously discussed cases. With increasing initial droplet temperature, the contact line radius at the end of the



Figure 6.9: Contact line radius for varying initial droplet temperature at initial ambient and substrate temperatures of 20 °C (left) and 60 °C (right) scaled with the capillary time scale τ_{Ca} .



Figure 6.10: Contact line radius for varying initial droplet temperature at initial ambient and substrate temperatures of 20 °C (solid lines) and 60 °C (dashed lines) scaled with the kinematic time scale τ_{kin} (left) and the capillary time scale τ_{Ca} (right).

impact-driven regime increases. Within the later capillary-driven regime, however, the different cases collapse onto a single line. This can be explained by the contact line temperature approaching the corresponding ambient temperature, which is identical for all three cases within each graph. Again, overall good agreement with Tanner's law can be observed within the capillary-driven regime. Direct comparison of the cases for different substrate temperatures, as depicted in Figure 6.10, gives additional insights into the impact and spreading behavior. Scaling with the capillary time scale leads to very similar spreading behavior in the later capillary-driven regime independent of the initial droplet or substrate temperatures. Thus, similar to the cases with varying *Oh* discussed above, τ_{Ca} accurately accounts for the influence of different viscosities on capillary-driven spreading. Scaling with τ_{kin} reveals that the influence of the initial substrate temperature on the impact-driven regime is negligible compared to the initial droplet temperature. This is remarkable, as the droplet foot abruptly changes temperature upon impact depending on the substrate temperature, as already discussed above. Consequently, the

observed spreading behavior indicates that the droplet foot and with it also the contact line region play a subordinate role in this very early spreading stage. The bulk temperature, which remains largely constant on the very short time scale of several microseconds upon impact, determines the contact line radius at the end of the impact-driven regime. Thus, the difference in spreading behavior must be attributed to differing viscous dissipation within the liquid bulk rather than in the contact line region.

Thermal Conductivity of the Substrate

Finally, the thermal conductivity of the substrate is varied, starting from the reference case with material properties corresponding to PP. Thereby, the thermal effusivity and diffusivity are modified. The minimum and maximum values of thermal conductivity considered are $0.0198 \text{ W m}^{-1} \text{ K}^{-1}$ and $22 \text{ W m}^{-1} \text{ K}^{-1}$. Similar to the reference case, a 60 °C droplet impacts a 20 °C substrate. The evolution of the local temperature at the three-phase contact line over time is depicted in Figure 6.11 on the left hand side for varied thermal conductivity of the solid substrate. As the substrate effusivity is directly linked to its thermal conductivity, the initial contact temperature between liquid and solid is directly affected by varying the conductivity. Therefore, with increasing λ_s , the initial contact temperature decreases. Also during the following spreading, the temperature at the three-phase contact line decreases more rapidly for larger thermal conductivities of the substrate. This results in quite substantial contact line temperature differences between the considered cases during the impact-driven, relaxation, and early capillary-driven regimes. As noted above, spreading in the initial impact-driven regime is dominated by bulk effects. It is therefore not surprising that the substrate's thermal conductivity shows little to no influence on the spreading behavior in this stage, as can be seen in the plot on the right-hand side of Figure 6.11. However, within the relaxation regime differences start to show. With increasing thermal conductivity and the resulting larger heat transfer from droplet to substrate, the droplets' spreading rate decreases. For the two largest considered values of λ_s , the contact line temperature approaches the substrate temperature rather quickly, resulting in similar spreading behavior from then on. However, for the lower thermal conductivities, differences in the spreading behavior remain noticeable during the entire simulated time frame.



Figure 6.11: Contact line temperature (left) and diameter (right) for varying thermal conductivities and, therefore, varying thermal effusivities and diffusivities of the substrate.

6.1.4 Interaction between Wetting and Surfactant Transport

Within this section, the influence of surfactants on the impact and spreading behavior of individual droplets is discussed. Unless otherwise noted, material properties are identical to the ones introduced in Subsection 6.1.1. The model parameters related to surfactant transport are given in Table 6.2. The initial bulk concentration of $c_{0,\text{ref}} = 0.248 \text{ mol m}^{-3}$ chosen as reference for the following parameter study corresponds to a mass fraction of 2% in the reference system, which is on the same order as the concentrations presented for UV-curable inkjet inks by Bale [11]. The Damköhler number with h_{ad} based on this initial concentration is Da = 6.95. The concentration is initialized homogeneously within the liquid bulk. For the reference case, it is furthermore assumed that the surface excess concentration initially is zero. Regarding the inkjet printing process, this implies the assumption that fresh interface is generated at the print head nozzle with a sufficiently high rate, such that no surfactant can accumulate at the interface. For the selected reference surfactant solution with adsorption taking place largely on the time scale starting at 100 μ s and ranging up to 10 ms, this assumption is valid for a permanently active nozzle with correspondingly high droplet frequencies. The time between droplet generation and impact on the substrate is on the scale of hundreds of microseconds. Adsorption during this time is small and for the reference case assumed to be negligible. Unless otherwise noted, a partial wetting scenario with an equilibrium contact angle of $\theta_{eq} = 50.67^{\circ}$ in the absence of surfactant is considered, which results in an equilibrium contact angle of $\theta_{eq,surf} = 11.25^{\circ}$ for the here considered surfactant solution and reference concentration. In the following, the general impact and spreading behavior of micrometer-sized droplets containing surfactant is introduced for the reference scenario. After that, the sensitivity of the results towards the increased characteristic length scale for adsorption h_{ad} is discussed. In the remainder of this section, the influence of the initial surfactant distribution and wettability of the substrate are investigated. Finally, the influence of initial bulk concentration and rate coefficients on the impact and spreading behavior is studied.

Results of the Reference Case

The simulation results for the surfactant-laden reference case are shown in Figure 6.12. Once again, good agreement of the contact line radius over time with the general behavior summarized by Derby [51] can be observed. Impact-driven, relaxation and capillary-driven driven regimes can be identified. The surface excess concentration Γ at the contact line increases with time as the droplet spreads and surfactant adsorbs to the interface. It is interesting to note that the deviation from the power-law-like behavior around 10 µs coincides with the relaxation regime. Within this regime, there is a brief period in which the interfacial area decreases (see e.g. Figure 5.19), which increases the overall excess surfactant at the interface in addition to the ongoing adsorption process. Local convective transport towards the contact line further adds to this increase. Due to the overall still very low values of Γ , however, these effects are barely noticeable in the local surface tension at the contact line. More substantial changes in surface tension start to occur 100 µs after droplet impact and become even more pronounced on the time scale of milliseconds. This is in agreement with the predictions of the 1D model for the adsorption of surfactant presented in Appendix G. The graph in the bottom right of Figure 6.12 shows the equilibrium



Figure 6.12: Contact line radius, surface excess concentration and surface tension evaluated at the contact line, and contact angle of the reference case of the following parameter study.

contact angle as evaluated from the Young-Dupré equation Equation 2.15 and the dynamic contact angle as predicted by the dynamic contact angle model for the impacting and spreading droplet. Corresponding to the high contact line velocity during impact, the dynamic contact angle θ_d initially is close to 180° and then decreases rapidly through the relaxation regime. After a slight undershoot it then continues to decrease in the capillary-driven regime. Finally, the dynamic contact angle follows the equilibrium contact angle θ_{eq} . Changes of the equilibrium contact angle during the first 100 µs are small. This can be explained by the initially fairly constant surface tension and the lower sensitivity of the contact angle towards surface tension changes for larger contact angles. For later times, θ_{eq} decreases noticeably. Despite this decrease, the lowering of the equilibrium contact angle by adsorption of surfactant becomes the rate determining step for further spreading. This change in the rate determining mechanism can be identified as the beginning of an adsorption-driven wetting regime, which can be observed for surfactant solutions on partially wettable substrates in addition to the stages also observable for single component liquids. Figure 6.13 shows $\overline{c_1}^1$, Γ and $\sigma_{\ell g}$ for selected time steps. Throughout the presented time frame, surface excess concentration and corresponding surface tension are homogeneous across the entire interface.



Figure 6.13: Concentration fields and local surface tension for a spreading droplet upon impact.

This homogeneity despite the different subsurface bulk concentrations indicates that Marangoni stresses quickly equilibrate any surface tension gradients. As the surfactant adsorbs to the liquid-gas interface, it can be seen that the subsurface bulk gets depleted of surfactant. This effect is especially pronounced near the three-phase contact line. However, it should be noted that the modifications to the material properties in comparison to the real reference system lead to an overestimation of this effect. The sensitivity of the spreading process towards the characteristic adsorption length is therefore investigated in the following.

Sensitivity to the Characteristic Length of the Adsorption Process

The characteristic length scale for the adsorption process $h_{ad} = \Gamma_{eq}/c_{\infty}$ describes the ratio of equilibrium surface excess and bulk concentrations. From surfactant conservation, it can be interpreted as the thickness of the bulk layer at the interface, from which the entire surfactant is required to equilibrate concentrations at a planar interface. This length scale is varied by adjusting the initial $\overline{c_1}^1$. The equilibrium surface excess concentration, surface tension as well as the diffusive and kinetic time scales are kept constant by scaling diffusion and adsorption rate coefficients accordingly. Thus, the main difference



Figure 6.14: Influence of the characteristic adsorption length scale on the spreading behavior of a surfactant laden droplet.

between the here considered cases is that the proportion of surfactant at the interface after equilibration compared to the total amount available within the droplet increases with increasing h_{ad} . Hence, the surfactant within the droplet is depleted more easily by adsorption to the interface with increasing h_{ad} . Figure 6.14 shows a case with increased h_{ad} in comparison with the reference case discussed above. It can be seen that during impact-driven, relaxation and the capillary-driven regimes, h_{ad} shows no noticeable influence on the contact line radius as well as the contact angle. During these spreading regimes, the graphs for both considered values of h_{ad} coincide. However, in the adsorption limited final spreading regime, the increased $h_{\rm ad}$ leads to slightly slower spreading. As the droplet bulk gets depleted of surfactant, the adsorption rate decreases, which results in slightly larger $\sigma_{\ell g}$ and θ_{eq} for a given time after impact. Because the adsorption of surfactant is the rate determining step for further spreading in the adsorption limited regime, this leads to the observed decrease in the spreading rate. Similar depletion effects have been reported in [5]. For the therein considered heptanol-water based model solution, depletion of surfactant due to the increasing interfacial area of the droplet even resulted in a substantial increase in surface tension as the droplet spread. However, for the here considered surfactant solution, influences on the actual spreading behavior are small. Furthermore, as discussed above, $h_{ad,0}$ is already increased compared to the real surfactant solution. Thus, despite the small droplet size, surfactant depletion can be expected to play only a minor role for the surfactant solution considered here.

Initial Surfactant Distribution

As discussed at the beginning of this section, the initial surfactant distribution between bulk and interface likely depends on the interval between subsequent droplets ejected from an individual nozzle. Furthermore, depending on the initial droplet velocity and the distance between nozzle and substrate, adsorption of surfactant to the liquid-gas interface between droplet generation and impact may become relevant. Therefore, the influence of the initial surface excess concentration on the impact and spreading behavior is studied. It is assumed that the total amount of surfactant within each droplet remains constant. Thus, on the partially wetting system, all cases are expected to approach the same equilibrium state. In addition to the partially wetting system, a perfect wetting scenario was considered here. Figure 6.15 shows contact line radius, local surface tension at the contact line, and contact angles in comparison for the two cases.

First, the partial wetting scenario shown in Figure 6.15a is considered. Within the initial impact-driven stage, the droplets with larger Γ_0 spread slightly further. With increasing Γ_0 , the initial surface tension decreases and the initial Weber number increases accordingly. Similar behavior has been observed for varied *We* discussed in Subsection 6.1.2 above. However, the following relaxation regime already shows a qualitatively different behavior. While lower *We* resulted in faster capillary spreading in the kinematic scaling, here the cases with larger Γ_0 and thereby larger initial *We* spread faster. This can be attributed to the additional dependence of θ_{eq} on Γ . As noted above, adsorption is negligible for times below 100 µs upon impact. Thus, the initial difference in surface excess concentration is largely preserved until the beginning of the capillary spreading phase. This leads to the observed increased spreading rate in the capillary-driven regime and a later entry into the purely adsorption limited regime for cases with larger Γ_0 . It is interesting to note that upon impact, the local surface tension drops substantially below the



Figure 6.15: Influence of the initial surfactant distribution on the spreading behavior of a surfactant laden droplet on partially and perfectly wettable substrates.

initial value, as surfactant accumulates at the rapidly outwards moving contact line. As the spreading rate decreases, Marangoni flow redistributes the surfactant and the local surface tension increases again. In all cases, the surface tension tends towards the expected equilibrium value of 26.36 mN m^{-1} based on the total surfactant amount towards the end of the simulation.

The perfect wetting scenario shows qualitatively as well as quantitatively excellent agreement with the partial wetting cases during the impact-driven and relaxation regime. Similar to the surfactant-free cases with varied equilibrium contact angles discussed in Subsection 6.1.2, there is little influence of the substrate on spreading shortly after impact. Additionally, it can be seen here that the influence of the initial surfactant distribution on the first two spreading regimes upon impact is independent of the substrate. Good agreement between the two substrates can be observed for the surface tension at the contact line. However, with the transition to capillary spreading, differences to the partial wetting cases arise in the contact line radius and the dynamic contact angle. Opposed to the partial wetting case, an increased initial surface excess concentration results in slower capillary spreading in the perfect wetting scenario. This can be traced back to the predictions of the contact line model. In the perfect wetting case, a constant $\theta_{eq} = 0^{\circ}$ independent of the surface excess concentration is predicted. The influence of surfactant on the equilibrium state, therefore, vanishes in this scenario. What remains is the increased capillary number for lower surface tensions. With increased capillary number, the contact line model predicts larger θ_d for a given contact line velocity. Thus, the droplets with larger surface excess concentration are observed to spread slower. This is a competing effect to the lowering of θ_{eq} by the decrease in surface tension in the partial wetting scenario. In the perfect wetting case, the Ca based effect becomes the dominant factor, whereas in the partial wetting case the increased wettability with increasing surface excess surfactant governs the process. As long as the system remains perfectly wetting, the model, therefore, suggests that an increase in surface tension can result in slightly faster droplet spreading.

Initial Surfactant Concentration, Adsorption and Diffusion Rate Coefficients

Through the initial bulk concentration, the total surfactant amount per droplet was varied. Similar to the surfactant reference case above, it was once more assumed that there is no excess surfactant at the interface before droplet impact and the previously considered partially wettable substrate is assumed. All remaining parameters correspond to the reference case as well. The results are shown in Figure 6.16a. In agreement with the observations from the measurements presented in Appendix G, the adsorption rate decreases with decreasing bulk concentration. As introduced in Chapter 1, for diffusion-limited adsorption, the characteristic time scale for adsorption to a planar interface from a sufficiently large bulk is $\tau_{ad} = h_{ad}^2/D$ [63]. The lower adsorption rate for lower bulk concentrations, therefore, manifests itself in larger surface tensions with decreasing $c_{B,0}$ for any given time after impact. There is no observable influence of these different adsorption rates on the initial spreading behavior, as can be seen from the contact line radius. However, within the adsorption limited regime, decreasing $c_{B,0}$ results in quite substantial reductions of the spreading rate. For $\tau \gtrsim 100 \tau_{kin}$, further reduction of θ_d is limited by θ_{eq} in all three cases considered here. However, following the different adsorption rates, θ_{eq} decreases slower with decreasing bulk concentration, which results in the observed differences in spreading behavior.



Figure 6.16: Influence of the initial surfactant concentration and adsorption time scale on the spreading behavior of a surfactant laden droplet.

Varying the adsorption rate directly through adsorption and diffusion rate coefficients instead of the bulk concentrations produces very similar results, as can be seen from the comparison of Figure 6.16a with Figure 6.16b. For these simulations, the characteristic time scale for adsorption τ_{ad} is increased by reducing the diffusion coefficient D_1 accordingly. The adsorption kinetic parameters k_{ad} and k_{de} are scaled proportional to D_1 . With increasing τ_{ad} , slower spreading in the adsorption limited regime can be observed. The contact line radii for the by up to a factor of 16 increased values of τ_{ad} compared to the reference case show furthermore excellent quantitative agreement with the cases with by down to a factor of 1/4 varied initial bulk concentration. For a sufficiently large droplet, where depletion of surfactant is negligible, this behavior is expected, as $\tau_{ad} \propto D_1^{-1}$ but $\tau_{ad} \propto c_{\infty}^{-2}$. Correspondingly, good agreement can also be found for the contact angles. Only slight differences compared to Figure 6.16a can be observed in contact line surface tension, especially during the earlier spreading regimes, which can likely be attributed to different scaling of the adsorption kinetic time scale between the two scenarios.

6.2 Droplet Collision at the Solid Substrate

This section presents the off-centered collision of an impacting droplet with a previously applied droplet on the substrate. Furthermore, the spreading behavior of the collided droplets is discussed. Isothermal and surfactant-free cases are presented at the beginning of this section. These are followed by a discussion of the influence of temperature-dependent viscosity on the collision and spreading behavior in non-isothermal scenarios. At the end of this section, the influence of surfactants on droplet collision and subsequent spreading will be discussed.

6.2.1 General Simulation Setup

The setup of the simulations presented in this section is similar to the one shown in Subsection 5.2.2, with a slightly smaller droplet volume of 6 pL considered here. The material parameters correspond to those of the respective cases of single droplet impact in the previous section. The center to center distance between impact positions of the two droplets is kept at a fixed value of $\epsilon = 21.17 \,\mu\text{m}$. This corresponds to a print resolution of 1200 dpi. Unless otherwise noted, a droplet interval of 10 ms is assumed for surfactant-free cases. The increasing sensitivity of θ_{eq} towards changes in $\sigma_{\ell g}$ with increasing droplet radius makes the surfactant-laden system more prone to instabilities at later times. Therefore, a droplet interval of 2 ms is chosen for the surfactant-laden droplets. Throughout all cases, the initial conditions for the first droplet and its surroundings are results obtained from the 2D simulations presented in Section 6.1 mapped onto the 3D mesh. The second droplet is initialized as a sphere with homogeneous initial velocity, pressure, temperature, and concentrations. Within each considered case, the initial conditions of the second droplet correspond to those of the first droplet prior to its impact.

The mesh for the fluid domain is identical to the one introduced in Subsection 5.1.5. In the solid domain relevant for non-isothermal cases, the mesh mirrors its counterpart on the fluid side. A schematic of the computational domain is shown in Figure 6.17. It is taken advantage of the one remaining plane of symmetry. In order to further decrease computational cost, adaptive mesh refinement was used,



Figure 6.17: Computational domain, initial and boundary conditions for the droplet collision scenario.

adding one level of refinement within the liquid phase and a second level at the liquid-gas interface. This results in mesh sizes varying from 253.7 nm at the contact line to 1.879 μ m within the gas phase outside of the interface region. During the impact of the second droplet, the time step size is adjusted according to the criterion by Brackbill et al. [24] presented in Equation 4.75. For $\tau > 50 \,\mu$ s, larger time step sizes according to Equation 4.77 are used. In order to further decrease the computational cost of the simulations, the height of the fluid domain is at the same time decreased to 2 r_0 for surfactant-free cases¹.

¹ Some cases with reduced fluid domain size and including surfactant transport showed instabilities in the vicinity of the top boundary.

6.2.2 Influence of Hydrodynamic Parameters

The structure of this section follows Subsection 6.1.2 for the impact of an individual droplet. First, results for a reference setup are discussed and compared to the single drop scenario. Following this, the influence of Weber and Ohnesorge numbers as well as the equilibrium contact angle on collision and subsequent spreading are presented. In addition to the parameters varied for the individual droplets, the influence of the interval between neighboring droplets on their collision and spreading behavior is studied here as well.

Results of the Reference Case

Figure 6.18 shows the extension of the colliding droplets along the substrate in longitudinal direction. r_1 denotes the distance from the outermost point of the contact line along the plane of symmetry on the side of the first droplet to its center of impact. r_2 is the corresponding value for the second droplet. See the inset in Figure 6.18 for a schematic representation of r_1 and r_2 . At the beginning of the simulation, both values correspond to the first droplet 10 ms after impact. With a contact line radius of 31.15 µm, it extends 9.98 µm beyond the impact center of the second droplet. Similar to the individual droplet impacting onto a planar substrate, the second droplet's base flattens as it approaches the first droplet and the substrate. A thin gas film is entrained between the droplets, which quickly ruptures and leaves a small amount of air encapsulated within the droplets. After ~ 1 µs, the second droplet spreads beyond the contact line of the first droplet, which leads to a rapid increase of the combined droplets' elongation. In the following period the elongation remains fairly constant, as the droplets relax and spread in transversal direction. During this entire period, the contact line at the remote side of the first droplet remains largely unaffected by the second droplet's impact, as can be seen from the evolution of r_1 .



Figure 6.18: Spreading behavior of two colliding droplets for the isothermal, surfactant-free reference case upon impact of the second droplet (left) and the initial impact and spreading behavior following their individual kinematic contact time with the substrate, τ_0 (right).

Furthermore, the larger interface curvature at the second droplet results in a locally increased Laplace pressure, which drives the flow towards the first droplet. This is illustrated in Figure 6.23b below. After $\sim 1 \text{ ms}$, the droplets approach a circular shape and continue to spread in all directions. At this moment, the droplets' center is still shifted noticeably towards the first droplet. 10 ms upon impact of the second droplet, this offset still persists. This shift of the collided droplets agrees qualitatively with the findings of Schiaffino and Sonin [153] for water droplets placed in a line onto the substrate. The graph on the right of Figure 6.18 shows the spreading behavior of the second droplet in comparison with the initial spreading behavior of the first droplet, i.e. a droplet without the influence of a neighboring droplet within the first 10 ms upon impact. Compared to the uninfluenced droplet, the second droplet spreads slightly further within the impact-driven stage. However, in the absence of a neighboring droplet, capillary spreading continues already tens of microseconds later. The second droplet, on the other hand, is held back by the internal flow towards the first droplet as well as the spreading in transversal direction and returns to the spreading rate observed for the individual droplet only after several milliseconds.

Weber Number

Starting from the reference scenario, simulations with varied Weber number were performed by adjusting the initial velocity accordingly. The results of these simulations are shown in Figure 6.19. The contact line radius of the first droplet 10 ms after its impact is largely determined by the capillary spreading regime and, therefore, shows little dependence on *We*. As a result of that, the state of the first droplet before impact of the second droplet is quite similar in all cases considered here. Scaled with τ_{kin} , the cases with $We \ge 1$ all show similar spreading behavior within the impact-driven regime, as is also observed above for individual droplets. For smaller *We*, however, spreading in the impact-driven regime is noticeably delayed. Furthermore, for $We = 1/4 We_{ref}$, the second droplet collides with the first before contacting the substrate, entraining gas between the two droplets and pushing the edge of the first droplet outwards.





This outwards motion of the edge of the first droplet results in the initial increase of r_1 in that case. The second droplet continues to expand over the first droplet, entraining additional gas at the edge of the underlying droplet, until the gas film between second droplet and substrate ruptures. This results in the observed sudden increase of r_1 in this case. Similar to the individual droplet cases, larger contact line radii at the end of the impact-driven stage can be observed for larger We. However, even for the largest considered We, the remote side of the first droplet remains unaffected during these early stages upon impact of the second droplet, as can be seen from r_1 . Since the influence of the first droplet substantially slows spreading in longitudinal direction at the beginning of the capillary-driven regime, differences in r_2 depending on We persist substantially longer than similar differences in contact line radii of individual droplets. Scaling the results with τ_{Ca} reveals similar behavior of r_1 for all cases. Furthermore, the spreading behavior shown by r_2 coincides for $We \leq 1/4 We_{ref}$ towards the end of the considered time frame. However, for larger We, differences in r_2 remain up to the end of the simulation 10 ms after impact of the second droplet. Thus, the interaction between neighboring droplets prolongs the influence of We on spreading compared to individually impacting and spreading droplets. Furthermore, within the considered time frame, the offset of the collided droplets towards the first droplet decreases with increasing We.

Ohnesorge Number

In the case of varied viscosity and thereby varied Oh, the contact line radius of individual droplets 10 ms after impact differed between the considered cases. Larger Oh produce smaller radii at the corresponding τ_{kin} . Therefore, the initial conditions just before the impact of the second droplet differ noticeably depending on Oh. Figure 6.20 shows the spreading behavior of two colliding droplets and their subsequent spreading for varied Ohnesorge numbers. Depending on Oh, different behavior in the impact-driven regime can be observed. While for $Oh \leq Oh_{ref}$ a smooth increase of r_2 with similar spreading rate across



Figure 6.20: Influence of the Ohnesorge number on the spreading behavior of two colliding droplets.

these cases can be observed, cases with larger Ohnesorge numbers show a sudden jump in r_2 . Thus, the cases with smaller *Oh* show qualitative agreement with the impact behavior of individual droplets, whereas the cases with larger *Oh* differ. In the latter cases, the second droplet spreads beyond the contact line of the first droplet, while entraining a gas film between the two droplets as well as between second droplet and substrate. Once this film ruptures, the outermost contact line position jumps from the contact line of the first droplet to the contact line of the second droplet. Throughout all cases, however, the contact line radius of the second droplet at the end of the impact-driven regime decreases with increasing *Oh*, which is similar to the observations made for individual droplets. In line with the previously presented results, r_1 remains fairly constant throughout the impact-driven and relaxation regimes. In the capillary-driven regime, the graphs for r_1 coincide if the corresponding scaling with τ_{Ca} is applied. This is in agreement with the behavior observed for individual droplets. However, r_2 shows a slightly different behavior. With increasing *Oh*, more rapid spreading can be observed in the capillary-driven regime, when scaling the results with τ_{Ca} . For larger *Oh*, this produces a slightly smaller offset of the collided droplets towards the first droplet.

Equilibrium Contact Angle

Similar to the scenarios considered for individual droplets, the influence of the substrate's wettability on wetting and spreading is studied here for colliding droplets. 0,Especially for the larger considered equilibrium contact angles, where the first droplet reaches its equilibrium within the considered droplet interval of 10 ms, the initial conditions just before the impact of the second droplet substantially depend on θ_{eq} . Figure 6.21 shows the subsequent collision and spreading behavior for varied θ_{eq} . The influence of the first droplet on r_2 seems to be small in the impact-driven regime, as most curves coincide for this early stage. Similar behavior has been observed for the impact of individual droplets. The only exception here presents the perfectly wettable substrate ($\theta_{eq} = 0$), where rupture of the entrained gas film and,





thereby, contact of the second droplet with the substrate is delayed. Larger θ_{eq} result in slightly smaller r_2 at the end of the impact-driven regime. Once more, the remote end of the first droplet remains unaffected during this initial regime, as indicated by the constant value of r_1 . On the perfectly wettable substrate, qualitatively similar behavior compared to the reference case can be observed. Spreading in longitudinal direction is slowed by the liquid volume shifting towards the first droplet, while the droplets spread in transversal direction. Once the collided droplets' contact line has assumed a fairly circular shape by spreading in transversal direction, spreading in longitudinal direction continues with similar rate in all directions. In the course of this, the perfectly wetting system shows slightly faster spreading compared to the reference case with $\theta_{eq} = 11.25^{\circ}$. In contrast to this, larger θ_{eq} result in a different spreading behavior. Even though these droplets continue spreading in longitudinal direction at first as well, this process is reversed towards the end of the considered time frame. As the droplets spread in transverse direction towards their expected equilibrium shape of a spherical cap with corresponding equilibrium contact angle, receding in longitudinal direction starts as soon as the local contact angle falls below the respective θ_{eq} . It should be noted that contact angle hysteresis is not considered here, therefore, the receding motion is likely overestimated compared to a technical surface with surface roughness or other heterogeneities. This is in line with the discrepancy between the ideally smooth substrate in the simulation and a real substrate observed in Subsection 5.2.2. Without contact angle hysteresis, the decrease of r_2 results in a shifted position of the coalesced droplets towards the first droplet. Contact line pinning due to contact angle hysteresis in combination with overall moderate wettability of the substrate could possibly reduce this offset by reducing the receding motion observed for r_2 .

Droplet Interval

In addition to the parameters varied for individual droplets, the interval between subsequent, neighboring droplets is also studied. Similar to the previously discussed simulations, the initial condition of the first droplets just before impact of the second droplet is taken from the results for individual droplets. The droplet interval is varied between a maximum of $\Delta \tau_0 = 10$ ms, corresponding to the interval of the reference case for colliding droplets discussed above, and a minimum of $\Delta \tau_0/10 = 1$ ms. Even for the shortest considered interval, the first droplet has therefore already entered the capillary-driven regime before the impact of the second droplet. The results of these simulations are shown in Figure 6.22 represented by the contact line positions r_1 and r_2 along the plane of symmetry. With a shorter interval, the first droplet has had less time to spread before the second droplet impacts. Correspondingly, the contact line radius of the first droplet is smaller just before collision in these cases. This results in a smaller overlap between the two droplets before collision for shorter intervals. Despite this difference, the initial spreading of the second droplet, as indicated by r_2 , is unaffected by the droplet interval. Throughout the impact-driven and relaxation stages, the graphs of r_2 coincide for all considered values of $\Delta \tau$. Similarly, during these first two stages of the second droplet's impact, the remote end of the first droplet shows no noticeable influence of the second droplet's impact. In the capillary-driven regime, however, differences in the spreading behavior depending on the droplet interval arise. With decreasing $\Delta \tau$, the spreading rate on the side of the second droplet increases. This results in larger values of r_2 for smaller values of the droplet interval at the end of the considered time frame. This is in contrast to the larger con-



Figure 6.22: Coalesced drops with different droplet interval.



Figure 6.23: Pressure and velocity fields 18.87 μ s after impact of the second droplet for droplet intervals of $\Delta \tau = 1 \text{ ms}$ and $\Delta \tau = 10 \text{ ms}$. Pressures exceeding 5 kPa are marked in white.

tact line radius of the first droplet before the impact of the second droplet with larger droplet intervals, and the corresponding larger extension along the plane of symmetry. As the droplets spread within the capillary-driven regime, the differences in r_1 depending on $\Delta \tau$ decrease. Nevertheless, even at the end of the simulated time frame of 10 ms, shorter droplet intervals correspond to smaller values of r_1 . Thus, together with the larger values of r_2 in these cases, shorter droplet intervals result in smaller offsets of the collided droplets towards the first droplet. This outcome is not surprising, as one would expect a perfectly symmetrical result and, therefore, no offset at all for the simultaneous impact of two droplets. Nevertheless, two mechanisms can be identified that lead to the observed behavior. Those are related to the smaller overlap between droplets as well as the larger interface curvature on the first droplet for shorter droplet intervals. For the coalesced droplets to be shifted towards the first droplet, a flow towards the first droplet is necessary. A decreased overlap, as is the result of shorter droplet intervals, also leads to a smaller cross sectional area available for this flow. Furthermore, since with larger droplet intervals the first droplet will have had more time to spread before the impact of its neighbor, its curvature will typically be lower. Thus, the Laplace pressure within this droplet is smaller and the pressure gradient between the two droplets is larger in these cases. As a result, short droplet intervals are beneficial to exact positioning of droplets. Figure 6.23 shows the pressure and velocity fields along the plane of symmetry for droplet intervals of $\Delta \tau = 1 \text{ ms}$ and $\Delta \tau = 10 \text{ ms}$ in comparison.

6.2.3 Temperature Dependence

As has been shown in Subsection 6.1.3, initial temperatures in combination with temperature-dependent material properties can influence the spreading behavior of droplets. While this previous section focused on individual droplets, the coupling of heat transfer and droplet spreading is studied here for the collision and coalescence of two droplets at the solid substrate. First, the evolution of the temperature field in droplets and substrate is discussed for a reference scenario. This reference setup is then used as starting point for the variation of droplet and substrate temperatures.

Results of the Reference Case

The reference case considered here corresponds to the one used to study the temperature dependence of individual droplet impact in Subsection 6.1.3. Droplet spacing and domain size are chosen as described in Subsection 6.2.1. A droplet interval of $\Delta \tau = 10 \,\mathrm{ms}$ is assumed. Figure 6.24 shows the temperature field in the collided droplets and the substrate underneath upon impact and collision. During the droplet interval of 10 ms, the first droplet has approached the ambient and substrate temperature of 20 °C. Upon impact, the volume of the second droplet, which impacts the substrate at 60 °C, can be clearly identified in the temperature field. The small transition range indicates that convective transport within the droplets plays only a minor role. The simulation results show entrapped air between the two droplets. Once more, it should be noted that the exact location and amount of entrapped air cannot be predicted accurately by the presented method. Nevertheless, air entrainment has also been observed experimentally for micro droplet impact on solid substrates [23] and for droplets impacting a liquid surface [172], as discussed earlier. Thus, air entrainment is plausible in the present case. Upon impact, heat is transferred from the second droplet to the first droplet and to the substrate. This results in a local increase of the substrate surface temperature. The increase is most pronounced, where the second droplet makes direct contact with the solid substrate. The substrate surface temperature in this region shows good agreement with the value expected according to Equation 6.2 based on the initial temperatures and effusivities of liquid and solid phases. The initial increase in substrate surface temperature is less pronounced, where the second droplet impacts the first droplet. With increasing time, the second droplet shifts slightly towards the first, as has been observed also for the isothermal cases. The entrained air contracts and forms several smaller bubbles underneath the second droplet with one larger bubble underneath its center. As the droplets continue to spread over the cool substrate, the base temperature in the region of the second droplet decreases. This decrease is especially pronounced at the three-phase contact line and noticeable already tens of microseconds after impact. On the other hand, the temperature at the top of the second droplet remains fairly constant close to the initial droplet temperature within this time frame. With time, further heat is transferred to the substrate and the surrounding gas





Figure 6.24: Temperature of liquid and solid phases after off-centered collision of two droplets on a solid substrate. Figures on the left show the cut through droplet and substrate along the plane of symmetry. The top view on the right shows temperatures along the liquid-gas interface and on the substrate surface. White + symbols in the top view indicate the nozzle position for the two droplets.

phase such that the maximum temperature within the computational domain decreases to 298.07 K after 1 ms and 294.13 K after 10 ms of spreading. In the following, the influence of initial temperatures on the collision and spreading behavior will be discussed.

Initial Temperatures

Figure 6.25 shows the influence of the initial droplet temperature on the spreading behavior of two colliding droplets for different ambient and substrate temperatures (60 °C and 20 °C). The initial conditions for the first droplet including the temperature field are mapped onto the 3D mesh from the corresponding results presented in Subsection 6.1.3. Furthermore, the same temperature dependence of the viscosity as for individual droplets is also assumed in the collision scenario. At 20 °C ambient and substrate temperature, a slight outwards motion of the contact line in direction of the second droplet (r_2) can be observed, before the air film between second droplet and substrate ruptures and r_2 increases rapidly. The moment of rupture depends notably on the initial droplet temperature. At lower temperatures and, therefore, higher viscosity of the droplet, the film ruptures later. Furthermore, the spreading rate in the impact-driven regime is smaller and the extent of the collided droplets in direction of the second droplets, as indicated by r_2 , is smaller towards the end of this first regime. Similar behavior is also observed for varied liquid viscosity and therefore varied Oh in the isothermal scenarios above. In addition, similar to the observations made for isothermal cases, an extended period of reduced spreading in longitudinal direction can be observed for all considered droplet temperatures, while the droplets spread mostly in transversal direction. During the first stages upon impact, i.e. the impact-driven, relaxation, and the early capillary-driven spreading, r_1 remains fairly constant. In the later capillary-driven regime, spreading in longitudinal direction continues, as indicated by the increase in both r_1 and r_2 . Within this regime, the values of r_1 at a given time after impact of the second droplet are independent of the initial droplet temperature. This can be explained by the contact line temperature at this point being similar to the ambient and substrate temperature, independent of the initial temperature of the first droplet.





Small differences in r_2 persist in this late spreading stage, with lower initial temperatures resulting in smaller values of r_2 . Thus, the increased mobility of the second drop with higher initial temperature due to the corresponding lower viscosity results in a slightly smaller offset of the collided droplets towards the first droplet. However, compared to other previously discussed factors, such as the Weber number or the droplet interval, the temperature influence has to be considered small. Varying the initial droplet temperature at an increased ambient and substrate temperature of 60 °C, as depicted in the graph on the right-hand side of Figure 6.25, results in the same qualitative behavior. The overall lower viscosity at this increased ambient temperature leads to faster spreading, as indicated by the slightly larger values of r_1 and r_2 for any given time in these cases.

6.2.4 Surfactant Influence on Droplet Collision and Spreading

Finally, the influence of surfactant on the collision and subsequent spreading of two droplets on the solid substrate is studied in this section. The interaction of collision and surfactant transport is discussed in detail for a reference scenario. Following that, the influence of initial surfactant concentration and distribution is analyzed, for which perfect and partial wetting scenarios are considered.

Results of the Reference Case

The reference case considered here corresponds to the one studied for the surfactant dependence of individual droplet impact in Subsection 6.1.4. Droplet size, droplet spacing, and domain size are chosen as described in Subsection 6.2.1. A droplet interval of $\Delta \tau = 2 \,\mathrm{ms}$ is assumed. Within the chosen reference case, the liquid-gas interface is assumed to be initially free of excess surfactant. As discussed above, for the surfactant solution considered here, this is a valid assumption for high droplet frequencies and correspondingly short droplet intervals from the same nozzle. During the droplet interval of 2 ms, surfactant within the first droplet has had time to adsorb to the liquid-gas interface. Even though this interval is too short for a complete equilibration of concentrations, the adsorbed surfactant results in a fairly homogeneous surface tension of 31 mN m⁻¹, which is substantially below the surface tension of the acrylate monomer. The initial conditions for the first droplet were mapped from the results obtained for individual droplet impact. Thus, shortly after impact, the different surface excess concentrations on the two droplets results in a considerable difference in surface tensions. Figure 6.26 shows the surface excess concentrations along the liquid-gas interface of the collided droplets together with the velocity field. The difference in surface excess concentrations along the interface is clearly visible and shows a steep gradient between the two droplets. It is interesting to note that the maximum surface excess concentration can be found at an entrapped air bubble. During the contraction of the entrained gas film to a spherical bubble, its interfacial area decreases. Even though initially only half of the films bounding interface was covered in surfactant, this results in the observed high surface coverage on the entrapped bubble. Shortly after impact, the velocity field within the second droplet is directed towards the first droplet and upwards, while the second droplet relaxes. Already 18.87 µs after the second droplet's impact, Marangoni flow driven by the surface tension gradients along the interface becomes noticeable. Along the liquid-gas interface, this flow is directed from the first to the second droplet and causes a



Figure 6.26: Surface excess concentration and velocity after off-centered collision of two surfactant-laden droplets. Figures on the left show the velocity field along the plane of symmetry. The top view on the right shows velocities along the liquid-gas interface. White + symbols in the top view indicate the nozzle position for the two droplets.

redistribution of surfactant along the interface. Surface tension gradients decrease accordingly. Since it takes hundreds of microseconds to several milliseconds for the here considered surfactant to diffuse to and adsorb at the interface, these changes in surface excess concentration must be largely attributed to convective transport along the interface. However, despite the Marangoni flow towards the second droplet, a bulk flow towards the first droplet can be observed. Driven by the larger interface curvature and, therefore, larger Laplace pressure of the second droplet, this bulk flow has already been observed and discussed above for the surfactant-free cases. In the surfactant-laden case presented here, the surface tension gradient between the droplets adds to this effect and increases the pressure gradient between the droplets further. The surface tension gradients caused by different surface ages, therefore, lead to competing effects upon collision of the two droplets. These act in addition to the competing effects of surfactant at the three-phase contact line discussed in Subsection 6.1.4 for the impact of individual surfactant-laden droplets. In order to evaluate how these competing effects influence the spreading behavior and position of the collided droplets, cases with varying surfactant distributions and initial concentrations will be discussed in the following.

Initial Surfactant Distribution

Just as for the impact of a single droplet, different initial surfactant distributions between bulk and interface are considered here for colliding droplets. The total amount of surfactant per droplet is kept constant between cases. The case with initial surface excess concentration $\Gamma_0 = 0$ corresponds to the reference case discussed in the previous paragraph. For all presented cases, the initial conditions for the first droplet correspond to the results obtained for the impact of individual droplets. The second droplet is initialized identical to the first droplet, with a droplet spacing fixed to $\epsilon = 21.17 \,\mu\text{m}$. The droplet interval is kept at 2 ms. Figure 6.27 shows the spreading behavior on the previously considered partially wettable substrate ($\theta_{eq} = 50.67^{\circ}$ for $\sigma_{\ell g} = \sigma_{\ell g,0}$) and on a perfectly wettable substrate ($\theta_{eq} =$ 0°) in comparison for different initial surfactant distributions. First, the partially wettable substrate is considered. Before the impact of the second droplet, the different expansions of the first droplet depending on Γ_0 can be observed. As discussed above, differences in Γ persist into the millisecond time scale, which results in differing contact angles. Nevertheless, the influence of Γ_0 on the impact-driven spreading for the second droplet has to be considered small, as can be seen by the evolution of r_2 over time. Only towards the end of the impact-driven regime, small differences arise. A higher surface excess concentration results in smaller surface tensions and, thus, facilitates slightly further spreading. A similar effect, even though much more pronounced, has been observed and discussed above for varied Weber numbers. Once more, the opposite end of the coalesced droplets shows no sign of the collision at first, as indicated by the mostly constant values of r_1 . Over the period $\tau_{kin} \leq \tau \leq 10 \tau_{kin}$, little to no spreading in longitudinal direction can be observed. Only towards the end of the considered time frame, r_1 and r_2 continue to increase noticeably. Thereby, larger values of Γ_0 show faster spreading. This indicates that also for colliding droplets, the adsorption of surfactant and the related lowering of the microscopic contact angle plays an important role in further spreading. Compared to these partial wetting cases, the perfect wetting scenario shows a slightly different behavior. First of all, the surface tension has no influence on the equilibrium contact angle in this case. Thus, with increasing surface tension, the subgrid-scale model for contact line motion predicts higher contact line velocities for a given contact



Figure 6.27: Influence of the initial surfactant distribution on the spreading behavior of two colliding droplets on partially and perfectly wettable substrates.

angle. For the single droplet, this results in slightly faster spreading for lower values of Γ_0 , as discussed above in Subsection 6.1.4. As a result, the initial value of r_2 before collision and, thus, the overlap between the two droplets is larger in these cases. Upon impact of the second droplet, r_2 increases rapidly. While the spreading rate in this impact-driven regime shows no substantial dependence on the initial surfactant distribution, higher surface excess concentrations lead to slightly larger values of r_2 at the end of the impact-driven regime. This behavior is similar to the partial wetting scenario. However, in the following capillary-driven regime, small differences arise once more. Similar to the behavior observed for individual droplets, lower surface excess concentrations result in slightly faster spreading in direction of the second droplet. The opposite end of the droplet, indicated by r_1 , however, shows a different behavior. Even though lower values of Γ_0 have lead to larger initial values of r_1 , droplets with larger initial surface excess concentrations catch up in the capillary-driven regime. This may be attributed to the reduced Marangoni flow in these cases. Low initial surface excess concentrations, therefore, seem to be beneficial for reducing the offset towards the first droplet on a perfectly wettable substrate. However, an offset persists even for $\Gamma_0 = 0$ and the overall influence has to be considered small.

Initial Surfactant Concentration

Finally, the influence of the initial surfactant concentration on the spreading behavior of two colliding droplets is studied. Starting from the reference setup for droplet collision under the influence of soluble surfactant ($c_0 = c_{0,\text{ref}}$, $\Gamma_0 = 0$), the surfactant concentration is halved in two steps. The previously considered partially wettable substrate is considered here. The results are shown in Figure 6.28. With increasing bulk concentration, the contact line radius of the first droplet before the impact of its neighbor increases slightly. Nevertheless, the spreading of the second droplet in longitudinal direction, as indicated by r_2 , shows no influence of the initial bulk concentration during the impact-driven and relaxation regimes. During its impact, the contact line position on the remote end of the collided droplets



Figure 6.28: Influence of the initial bulk surfactant concentration on the spreading behavior of two colliding droplets.

 r_1 remains constant. Also in the following, the droplets' elongation remains constant, while they spread in transversal direction to assume a spherical cap shape. On the time scale of tens of au_{kin} , the contact line proceeds to move in longitudinal direction and differences depending on the initial bulk concentration start to show. While for the largest considered bulk concentration the contact line moves further outwards, a receding motion can be observed for the lower concentrations. As has been discussed in Subsection 6.1.4, the rate of adsorption increases with the bulk concentration. Therefore, the adsorbed amount of surfactant within this adsorption-driven regime, and through Young-Dupré with it the contact angle, depend on the initial bulk concentration. For this reason, the different initial bulk concentrations result in a spreading behavior after collision similar to the behavior observed for varied equilibrium contact angles discussed in Subsection 6.2.2. Similar to these cases with larger contact angles, it should be noted also for the present case that the onset of the receding motion on a technical rough surfaces is expected to occur at lower receding contact angles due to contact angle hysteresis, an aspect that is not included in the employed model. Regarding the position of the collided droplets along their longitudinal direction, no clear influence of the bulk concentration can be observed. However, regarding the coverage of the partially wettable substrate with ink, larger surfactant concentrations prove beneficial also for the colliding droplets. These findings conclude the results of droplet collision simulations within this thesis. In the following section, implications of the results presented in sections 6.1 and 6.2 for the printing process are discussed.

6.3 Implications for the Printing Process

Several implications for the inkjet printing process can be derived from the previously presented results. For individual droplets, the Weber number shows no substantial influence on the spreading behavior for the later capillary-driven regime with $\tau > 100 \tau_{Ca}$, or in terms of dimensional values $\tau > 500 \,\mu$ s. Within the capillary-driven regime, lower *Oh* promote faster spreading.

Considering heat transfer phenomena in combination with temperature-dependent viscosity, the droplet diameter at the end of the impact-driven regime is found to be mostly dependent on the initial droplet temperature, whereas the later capillary-driven spreading is governed by the viscosity and, therefore, the temperature at the three-phase contact line. This is further found to depend on the substrate and ambient temperature as well as, for a considerable time within the earlier capillary-driven regime, on the thermal conductivity of the substrate. By decreasing heat transfer towards the substrate either through an increase of the substrates temperature or a decrease of its thermal conductivity, the capillary spreading rate on the time scale of milliseconds can be increased.

The equilibrium contact angle determines the final droplet radius, however, it has little influence on the initial spreading. Through the Young-Dupré equation, the surfactant distribution influences this equilibrium contact angle and, thus, spreading on a partially wettable substrate. For the here considered surfactant solution, the influence of the initial surfactant distribution persists well into the capillary-driven regime. Furthermore, it is observed that adsorption to the liquid-gas interface can become the rate determining step for further spreading. Thus, larger initial surface excess concentrations as well as increased adsorption rates can produce larger droplet diameters within this adsorption limited spreading regime. Aside from the diffusion and adsorption rate coefficients, the bulk surfactant concentration provides means to adjust the adsorption rate of surfactant.

Regarding substrate-sided, off-centered collision of droplets, the droplet position upon impact needs to be considered. Throughout all considered cases, an offset of the coalesced droplets towards the first applied droplet is observed. While the influence of *We* can be considered negligible for individual droplets, increasing the Weber number proves to be beneficial in reducing the droplet offset. Furthermore, it is found that the droplet interval can play a major role in reducing the offset after collision. The Ohnesorge number, on the other hand, shows negligible influence on the droplet position, while, similar to the cases of individual droplets, decreasing *Oh* produces overall larger droplets. Increasing the substrate temperature shows similar effects due to the temperature-dependent viscosity. Even though temperature differences between print head and substrate produce viscosity gradients between neighboring droplets, the influence of the initial droplet temperature is found to be small regarding both, droplet position and dot size.

On substrates with intermediate wettability, a receding motion in longitudinal direction could be observed, while the droplets spread in transversal direction. A similar effect could also be observed at lower surfactant concentrations and partially wettable substrates. Hindering this receding motion by introducing contact angle hysteresis, e.g. through a rough surface, could help reducing droplet offset. Surface tension gradients upon coalescence introduced competing effects of increased bulk flow on the one hand and Marangoni flow on the other.

CHAPTER 7

Summary and Conclusions

Inkjet printing is a complex process including wetting as well as heat and species transport. The macroscopic print quality depends on accurate dot sizes and positions. Therefore, a good fundamental understanding of the underlying wetting and transport processes is vital for the further development of inks as well as the printing process itself. The process bridges multiple length scales between the contact line region and droplet dimensions. Moreover, relevant time scales span from microseconds during the initial impact-driven stage to tens of milliseconds for capillary spreading. Heat and species transport phenomena occur on similar time and length scales as impact, collision, and spreading. Thus, these processes are not separable, but their interaction has to be taken into account. Despite the wide range of length and time scales, their absolute values still have to be considered small.

Numerical simulation allows a detailed analysis of these coupled transport processes on the relevant short length and time scales. Within this work, the algebraic volume of fluid method implemented in OpenFOAM was employed to model the multiphase flow. The contact line dynamics was described using an empirical subgrid-scale model in combination with localized slip. Furthermore, special attention has been put on the evaluation of interfacial forces. A generalized density-scaled CSF model was formulated for the volume of fluid method. Heat transfer between fluid domain and solid substrate was taken into account. Moreover, the model was extended by a novel two-field approach for soluble surfactants. In order to ensure relevance of the results to the printing community, all process parameters and material properties were motivated by typical inks and substrates. This includes the parameters for the adsorption of surfactant to the interface liquid-gas. The Langmuir-Freundlich adsorption model proved to be suitable to describe the transient surface tension behavior of a surfactant solution, as it might be found in UV-curable inks.

Introducing density scaling to the evaluation of surface tension forces was found to reduce spurious currents in simulations with a large density ratio. The influence of slip in the contact line region on spreading was found to be small. Nevertheless, with increasing grid resolution, errors in contact line dynamics are larger for a no-slip boundary condition prescribed at the entire wall compared to localized slip at the contact line. The newly developed two field approach for a soluble surfactant shows satisfying agreement with analytical and numerical reference solutions regarding transport with the interface, adsorption to the interface as well as overall conservation of surfactant. Regarding hydrodynamics, the model shows excellent agreement with experimental observations of individually impacting picoliter-sized droplets as well as the initial collision behavior with a neighboring droplet at the substrate. Discrepancies between experiment and simulation were found for the collided droplets approaching their equilibrium state, where the simulation showed a receding contact line, which was not observed in the experiment.

Simulation results of single droplet impact show that the impact velocity and with it the Weber number has no substantial influence on droplet diameters within the capillary spreading regime, despite appreciably larger diameters at the end of the impact-driven regime with increasing *We*. More relevant to capillary spreading is the viscosity of the liquid. In combination with the temperature dependence of ink viscosity, this provides means to control the spreading rate in the capillary regime. For an acrylate droplet impacting onto a polypropylene substrate, the influence of the initial droplet temperature on capillary spreading, however, is small compared to the influence of substrate temperature. Reducing heat transfer to the substrate increases the influence of the initial droplet temperature. Results for surfactant-laden droplets impacting a partially wettable substrate show an additional, adsorption limited spreading regime. In this regime, the spreading rate depends on the adsorption of surfactant to the interface liquid-gas. Thus, spreading depends on adsorption and/or diffusion rate coefficients of the surfactant solution in this regime. These parameters depend on the type of surfactant and solvent, and can therefore typically not be adjusted independently in a real ink. However, the surfactant concentration, which can easily be adjusted, shows a very similar influence on the adsorption rate and consequently the spreading behavior.

All simulation results for off-centered droplet collision at the substrate conducted within the scope of this work show an offset towards the first droplet. This offset persists well into the capillary spreading regime and onto the millisecond time scale. Upon collision, a bulk flow from the second to the first droplet driven by larger interface curvature on the second droplet can be observed. Further initial spreading due to larger initial velocities reduces this effect. Similarly, reducing droplet intervals also reduces the asymmetry and therefore the offset. Conversely, the influence of heat transfer on the droplet position after collision was found to be small. During the collision of droplets with different initial surfactant distribution, competing bulk and Marangoni flows can be observed. Thus, the results show no strong trend depending on initial surfactant distribution. Similar to this, the initial bulk concentration shows no substantial influence on the position of the collided droplets. However, on the considered partially wettable substrate, larger bulk concentrations show overall further spreading, which is in agreement with the observations made for individual droplets.

In conclusion, the developed model has proven suitable for the simulation of droplet impact, spreading, and collision on the micrometer length scale. It allows a detailed analysis of coupled wetting processes on the one hand, and heat and species transport processes on the other hand. Using this model, influencing factors and related mechanisms regarding impact, spreading, and collision behavior could be identified. Thus, this work provides both means for further studies as well as concrete measures to engineer the impact, collision, and spreading behavior of picoliter-sized droplets.
CHAPTER **8**

Outlook

The method developed within the scope of this work can be used to study additional parameter combinations for droplet impact, spreading, and collision. However, the findings of this work also motivate additional model developments. Some of the simulation results for colliding and coalescing droplets presented in this thesis show receding contact lines. This is in contrast to the experimental observations shown. In the presence of both advancing and receding contact line motion, contact angle hysteresis becomes relevant. Future work on colliding and coalescing droplets should therefore take this effect into account. As contact angle hysteresis hinders receding motion of the contact line, it might directly affect the final dot shapes upon collision and the overall position of the collided dots. Both of these aspects are directly related to print quality.

With respect to surface-active substances, the model can be extended towards adsorption and desorption processes at the solid-liquid interface. Including these aspects in the model allows studying them on length and time scales relevant to inkjet printing. Due to the small droplet volume, additional adsorption to the substrate could lead to depletion of surfactant within the droplet. Adsorption and desorption at the substrate could furthermore give rise to Marangoni flow in the three-phase contact line region.

Within the scope of this work, the collision of partially overlapping droplets at the solid substrate was studied. However, within the inkjet printing process, droplets can also impact onto a closed film of a previously applied ink, e.g. of a different color. The ink layers may exhibit different material properties. Beyond that, different surface ages may result in surfactant concentration gradients upon impact. The model developed within the scope of this work could provide insight into these phenomena with parameter combinations and material properties relevant to inkjet printing. Further development of the model should take different bulk material properties between subsequently applied inks into account.

Instead of a closed film, ink may also be applied as a pattern. Printing of a second layer on top of such an ink pattern further increases the complexity of the process. Simulating the interaction between such a pattern of liquid ink and an impacting droplet is the logical next step to the simulations of substrate-sided collision of two droplets conducted within the scope of this work. However, when using UV-curable inks,

the underlying ink pattern may also be partially or completely polymerized. The OpenFOAM code employed throughout this work is implemented for unstructured grids. Furthermore, all model extensions introduced within the scope of this work were made with applicability to more complex geometries in mind. Thus, by adjusting the geometry of the computational domain, the developed model may also be used to study wetting on substrates structured by a previously applied, polymerized ink pattern.

In combination with experimental investigations, numerical simulation can help to identify the relevant influencing factors on the above aspects. Through parameter studies, a better understanding of the underlying mechanisms and processes can be gained. This understanding is vital for streamlined development of the printing process as well as inks and substrates. It will not only contribute to improved print quality but also help reducing development times for new printing machines and consumables. However, also other technologies, such as e.g. microfluidic applications, may benefit from an improved understanding of the underlying phenomena.

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APPENDIX

Estimation of Dissipation during Droplet Impact and Spreading

During droplet impact and spreading, the system's initial kinetic energy and its potential regarding surface energy is dissipated. With respect to the energy balance in Section 4.2, this raises the question, whether dissipation can have an effect on the droplets temperature.

According to the first law of thermodynamics for a closed, adiabatic, and work free system containing droplet, substrate, and surrounding gas phase

$$E_1 - E_0 = 0. (A.1)$$

Therein, assuming negligible potential energy due to gravity,

$$E_0 = \frac{1}{2} \rho_\ell V u_0^2 + S_{\ell g,0} \sigma_{\ell g} + S_{sg,0} \sigma_{sg} + U_0$$
(A.2)

is the energy of the system before droplet impact, and

$$E_1 = S_{\ell g,1} \sigma_{\ell g} + S_{sg,1} \sigma_{sg} + S_{s\ell,1} \sigma_{s\ell} + U_1$$
(A.3)

is the energy within the system after reaching the equilibrium diameter. *S* denotes the respective surface areas as indicated by the indices, *V* the droplet volume, and *U* the inner energy of the system. Using the Young-Dupré equation 2.15 and the geometrical relation $S_{sg,0} = S_{sg,1} + S_{s\ell,1}$ the change of the inner energy can be expressed by

$$U_{1} - U_{0} = \underbrace{\frac{1}{2}\rho_{\ell}Vu_{0}^{2}}_{=E_{\text{kin},0}} + \underbrace{(S_{\ell g,0} - S_{\ell g,1} + S_{s\ell,1}\cos\theta_{\text{eq}})\sigma_{\ell g}}_{E_{\text{I},1} - E_{\text{I},0}}.$$
(A.4)

In the following, it is assumed that the entire dissipated energy contributes only to an increase of the inner energy of the droplet itself without any contribution to the surrounding gas or solid substrate. This is the case with the largest expected influence of dissipation on the droplets mean temperature. With

$$U_1 - U_0 = \rho_\ell c_\ell V \Delta T_{01}, \tag{A.5}$$

the change in the mean temperature can be evaluated. For a droplet with a volume of 6 pL impacting at 5 m s⁻¹ and spreading to an equilibrium contact angle of 11.25°, which corresponds to the reference case in Section 6.1, and furthermore assuming the respective material properties of the reference case, this results in an increase of the mean droplet temperature by $\Delta T_{01} = 0.012$ K. In order to produce a local temperature increase of 1 K, the change in inner energy, and thus dissipation, would have to be limited to a volume of 0.071 pL. This corresponds to just 1.2% of the droplet volume. Hence, even if dissipation were limited to only a small region, e.g. at the contact line, the temperature increase would be small and can be expected to be quickly dispersed to the solid, the surrounding gas, and the remaining droplet volume. Nevertheless, it is interesting to note that for the here considered case, the change in surface energy $E_{I,0} - E_{I,1} = 6.09 \times 10^{-11}$ J is on the same order of magnitude as the initial kinetic energy $E_{kin,0} = 8.29 \times 10^{-11}$ J. This highlights once more the importance of capillarity for droplet impact and spreading processes on the micrometer scale.

APPENDIX B

Determining the Volume Fraction Profile

In order to calculate the interface normals in boundary cells, α must be extrapolated towards the boundary faces (see Subsection 4.1.3). In the present work, this is done by taking advantage of the fact, that the transition from phase 1 to phase 2 typically occurs over approximately three mesh widths for the algebraic VOF method implemented in *interFoam*. The exact shape of the profile in this transition region is here further investigated for discretization of the convective terms in the α -advection Equation 4.1 with the SFCD-scheme used throughout this work. Note that Equation 4.1 is, aside from the lack of a diffusive term, identical to the conservative level set initialization (see e.g. [179] as reference for the C-LS approach). However, for odd-order spatial derivatives in the leading term of the truncation error, the discretization introduces numerical diffusion [89]. For that reason, the expected profile for the C-LS-field after reinitialization,

$$\alpha_{\text{approx.}}(\ell) = \frac{1}{2} \left(1 + \tanh\left(\frac{\ell - \Delta\ell}{\xi}\right) \right), \tag{B.1}$$

is here also assumed for the α -profile resulting from Equation 4.1, where ℓ is the signed distance to the interface and ξ as well as $\Delta \ell$ are fitting parameters.

To determine the fitting parameters, the advection of the α field was studied on a one dimensional case with a domain length of $1000\Delta x$, where $\Delta x = 1 \text{ m}$ is the mesh width. Both, advancing and receding interfaces were studied, i.e. the interface was advected towards phase 2 or phase 1, respectively. The initial condition for the advancing case is $\alpha = 1$ for $0 \le x < 2\Delta x$ and $\alpha = 0$ for $2\Delta x \le x \le 1000\Delta x$ and vice versa in the receding case. The velocity $u = 1 \text{ m s}^{-1}$ is kept constant along the entire domain. In order to study the discretization influence, the Courant number *Co* is varied between 10^{-2} and 1.25×10^{-3} . In all cases, the interface is first advected for an initialization period of 899 s with the corresponding time step in order to reach a steady state. Following the initialization, the α -field is evaluated while the interface is advected one cell further. While the α -profile, due to its sharp transition, is poorly resolved in each single timestep, the low Courant numbers allow a much higher resolution by comparing the α -field in subsequent time steps and accounting for the interface motion with the known velocity. Figure B.1a



sional interface.

(a) Volume fraction profile for an advancing one dimen- (b) Volume fraction profile for a receding one dimensional interface.

Figure B.1: Volume fraction profile in interface normal direction after advection in advancing and receding direction in comparison with different approximations.

and Figure B.1b show the observed profile for Co = 0.01 releative to the expected interface position based on initial condtion and velocity. The least-squares fit was calculated for the varying Co numbers and advacing and receding cases in a band of $\pm 50\Delta x$ around the interface.

The results are shown in Table B.1 and Table B.2 for the two cases. Furthermore, the discretization independent values of the fitting parameters were estimated using the Richardson extrapolation based on the three finest resolutions. The relative errors depending on Co and compared to that estimation are displayed in Figure B.2a and Figure B.2b. As could be expected due to the employed temporal discretization scheme, first order convergence can be observed. For the considered Courant numbers, the relative errors are small, with a maximum of a few percent. To verify that the offset $\Delta \ell$ is not due to accumulating errors during advection, the integral value of α over the entire domain was evaluated at the end of the simulation. It was found to be $902\Delta x^3$ for the advancing case ($98\Delta x^3$ for the receding case) independent of the Courant number, the exact values expected for the given velocity, initial condition, and simulated time.

Furthermore, the profiles are identical between the advancing and receding case up to the fourth significant digit of the estimated discretization independent values. Therefore, the α -profile as a function of distance to the interface can be approximated by

$$\alpha_{\text{approx.}}(\ell) = \frac{1}{2} \left(1 + \tanh\left(\frac{\ell + 0.016 \, 21\Delta x}{0.9095\Delta x}\right) \right).$$
(B.2)

Со	$\xi / \Delta x$	$\Delta \ell \ / \ \Delta x$
0.01	0.9048839166	-0.0166353172
0.005	0.907 193 039 6	-0.0164263648
0.0025	0.9083458712	-0.0163206275
0.00125	0.908 921 588 6	-0.0162671605
Richardson Extrapolation	0.909 495 912 3	-0.0162124695
(Order)	1.0017492464	0.9837648055

Table B.1: ξ and $\Delta \ell$ for varying *Co* number in the advancing case

Table B.2: ξ and $\Delta \ell$ for varying *Co* number in the receding case

Со	$\xi / \Delta x$	$\Delta \ell$ / Δx
0.01	0.9048833806	-0.0166350043
0.005	0.9071919175	-0.0164264466
0.0025	0.9083457640	-0.0163209163
0.00125	0.9089214316	-0.0162676152
Richardson Extrapolation	0.9094945989	-0.0162132202
(Order)	1.0031432987	0.9854195266



Figure B.2: Error in the fitting parameters compared to the estimated discretization independent solution for a moving one dimensional interface.

The approximation as well as the expected discretization independent fits for advancing and receding interface are shown in Figure B.1a and Figure B.1b in comparison to the simulation results. Excellent agreement between both fits and the actual interface profile obtained from the simulation were found. Furthermore, the profile is also well approximated by

$$\alpha_{\rm erf} = \frac{1}{2} \left(1 + \operatorname{erf}\left(\frac{\ell}{\sqrt{4 \cdot 0.2986\Delta x^2}}\right) \right). \tag{B.3}$$

This provides a good estimate of the initial condition for the substrate wall boundary during smoothing introduced in Subsection 4.1.3. See Figure B.1 above for a comparison of the different approximations.



Discretization Schemes

Operator	Term	Scheme
$\partial \varphi / \partial \tau^{(*)}$	default	Euler
$\overline{ abla arphi}$	default	Gauss linear
$\nabla \cdot \varphi$	$\mathbf{u}\alpha$ $\mathbf{u}_{r}(1-\alpha)\alpha$ $\rho_{m}\mathbf{u}\otimes\mathbf{u}$ $\rho c_{m}\mathbf{u} \otimes\mathbf{u}$ $\rho c_{m}\mathbf{u}T$ $\mathbf{u}c_{B}$ $\mathbf{u}_{r}(1-\alpha)c_{B}$ $\frac{D_{1}\nabla\alpha}{\alpha+\varsigma_{\alpha}}c_{B}$ $\mathbf{u}c_{I}$ $\mathbf{u}_{r}w_{2}(\alpha)c_{I}$ $\mathbf{u}_{c,\delta}w_{1}(\alpha)c_{I,S}$ $\mathbf{u}_{c,\delta}w_{1}(\alpha)\delta_{LS}$	Gauss SFCD Gauss SFCD Gauss SFCD Gauss limitedLinear 1 Gauss SFCD Gauss SFCD Gauss linear Gauss vanLeer Gauss vanLeer Gauss SFCD Gauss SFCD
interpolation	$ \frac{\mathbf{u}_{r}(1-\alpha)j_{B}}{\frac{D_{j,B}\nabla\alpha}{\alpha+\varsigma_{\alpha}}j_{B}} $ default	Gauss SFCD Gauss linear
$\overline{\nabla \cdot \nabla}$	dofault	linear limited 0.2
$\frac{\mathbf{v}\cdot\mathbf{v}\varphi}{\mathbf{r}\cdot\mathbf{\nabla}\varphi}$		
$\mathbf{n}_f \cdot \mathbf{v} \varphi$	default	limited 0.3

 Table C.1: Discretization schemes used throughout this thesis. All schemes are listed as named in Open-FOAM (see e.g. [129]).

Appendix

Adsorption to a Curved Interface

In addition to the 1D verification cases presented in Subsection 5.1.6.2 corresponding to adsorption to a planar interface, here the adsorption to a curved interface is considered. First, adsorption to the interface of a spherical bubble within a heptanol-water solution is considered. Furthermore, the adsorption of surfactant dissolved in a drop to the drop's liquid-gas interface is of particular relevance for the present thesis. Pesci [131] studied such a case for a mixed-kinetics process as well as a purely diffusion-limited process. In the following, the numerical method presented and employed within this thesis is verified for theses three cases.

Adsorption to the Interface of a Spherical Bubble

Similar to the case presented in Subsection 5.1.6.2, the interface is assumed to be initially free of excess surfactant ($\Gamma_0 = 0$). Identical material properties for the heptanol-water solution as in Subsection 5.1.6.2 are considered. A bubble radius of $5 h_{ad}$ is assumed. The curved interface results in a slight change of the reference solution for the diffusion-controlled limit compared to the case with a planar interface. Once more, the C++ code provided by Li et al. [113] is used to obtain the reference solution for the diffusion controlled limit. On the other hand, under the assumption of a constant subsurface concentration, the reference solution for the adsorption-kinetics limited process, Equation 5.14, remains unchanged compared to the 1D case. The numerical results for the mixed-kinetics model were obtained on a 2D axisymmetric mesh with a resolution of $\Delta x = 1.875 \times 10^{-7}$ m similar to the 1D case. A domain size of $15h_{ad} \times 15h_{ad}$ is used. Figure D.1 shows the surface excess concentration from this simulation in comparison with the two reference solutions. The observed adsorption behavior is very similar to the 1D case for a planar interface. The heptanol-water solution shows mixed-kinetic behavior. The adsorption process is initially limited by adsorption kinetics. The numerical solution coincides with the corresponding analytical reference solution for small surface ages. After approximately 1 ms, a transition to the diffusion-limited regime can be observed. For later times ($\tau > 100 \,\mathrm{ms}$), again excellent agreement between the solution obtained with the presented numerical method and the corresponding reference solution can be observed.



Figure D.1: Verification results for mixed-kinetic adsorption to the curved interface of a bubble. The graph shows numerical results (solid line) in comparison with the corresponding analytical (dotted line) and numerical (dashed line) reference solutions. A similar figure has appeared previously in [5] for adsorption to a planar interface.

Adsorption to the Interface of a Spherical Drop: Mixed Kinetics

In the following, the numerical method presented in this thesis will be verified for adsorption to a curved interface from the bulk of a drop. First, the mixed-kinetics case is studied. The case and corresponding analytical solution have been introduced by Pesci [131], following previous similar studies by Muradoglu and Tryggvason [124]. Diffusive transport within the bulk of a spherical drop with radius $r_0 = 1$ m is considered. Adsorption to the liquid-gas interface is described by the kinetic model

$$\frac{\partial \Gamma}{\partial \tau} = k_{\rm ad,H} c|_{r=r_0}.$$
 (D.1)

The concentration within the liquid bulk is assumed to initially take the constant value $c(\tau=0, r) = c_0 = 1 \text{ mol m}^{-3}$, whereas the initial surface excess concentration is $\Gamma(\tau=0) = \Gamma_0 = 0$. Bulk diffusion and adsorption rate coefficients are $D = 1 \text{ m}^2 \text{ s}^{-1}$ and $k_{\text{ad},\text{H}} = 1 \text{ m s}^{-1}$, respectively. The analytical solution to this problem for the bulk concentration is given by [131]

$$\hat{c}(\hat{r},\hat{\tau}) = \sum_{k=1}^{\infty} \Xi_k \frac{\sin(\Lambda_k \hat{r})}{\hat{r}} e^{-\Lambda_k^2 \hat{\tau}},\tag{D.2}$$

where $\hat{c} = c/c_0$, $\hat{r} = r/r_0$ and $\hat{\tau} = \tau D/r_0^2$. The eigenvalues Λ_k result from the boundary conditions for the bulk diffusion equation and are given by

$$\Lambda_k \cot \Lambda_k = 1 - \frac{k_{\rm ad,H} r_0}{D}.$$
 (D.3)

The coefficients Ξ_k can be evaluated from the initial condition for the bulk concentration field according to

$$\Xi_k = \frac{\int_0^1 \hat{r} \sin(\Lambda_k \hat{r}) d\hat{r}}{\int_0^1 \sin^2(\Lambda_k \hat{r}) d\hat{r}}.$$
 (D.4)

The analytical solution for the surface excess concentration is [131]

$$\hat{\Gamma} = \frac{r_0^2 c_0 k_{\rm ad,H}}{\Gamma_{\rm eq} D} \sum_{k=1}^{\infty} \frac{\Xi_k}{\Lambda_k^2} \left(1 - e^{-\Lambda_k^2 \hat{t}} \right), \tag{D.5}$$

where $\hat{\Gamma} = \Gamma/\Gamma_{eq}$ and Γ_{eq} is the equilibrium surface excess concentration for $\tau \to \infty$. Figure D.2 shows this analytical solution in comparison with numerical results. For the analytical solution, the first 10⁴ terms of the series were evaluated. The numerical solution was obtained on a 2D axisymmetric mesh with 300×300 cells and a domain size of $1.5 r_0 \times 1.5 r_0$. Excellent agreement between analytical and numerical results can be observed for the evolution of the bulk concentration. The surface excess concentration shows a slight overestimation of the adsorption rate in the numerical solution. Nevertheless, good overall agreement of the numerical solution with the analytical reference is found.



Figure D.2: Verification results for mixed-kinetic adsorption to the curved interface of a drop. The graph shows numerical results (solid lines) in comparison with the corresponding analytical solution (dashed lines).

Adsorption to the Interface of a Spherical Drop: Diffusion-Limited

Similar to the previous case, adsorption of surfactant to the interface of a spherical drop with radius $r_0 = 1 \text{ m}$ from its bulk is considered here. This case has also previously been introduced by Pesci [131]. For the diffusion-limited process, it is assumed that bulk and surface excess concentrations are in equilibrium at the interface according to the Henry isotherm [32]

$$\Gamma = K_{\rm H} c|_{r=r_0},\tag{D.6}$$

where $K_{\rm H} = 1 \,\mathrm{m}$ is the equilibrium constant. Similar to the previous case, the interface is assumed to be initially free of excess surfactant, thus $\Gamma(\tau=0) = \Gamma_0 = 0$. However, a non-constant initial bulk concentration $c(\tau=0,r) = c_0 - \beta r$ is set, where $\beta = 0.8 \,\mathrm{mol}\,\mathrm{m}^{-4}$. Similar to the mixed-kinetics case, $c_0 = 1 \,\mathrm{mol}\,\mathrm{m}^{-3}$ and $D = 1 \,\mathrm{m}^2 \,\mathrm{s}^{-1}$. Using the dimensionless variables $\hat{c} = (c - c_\infty)/(c_0 - c_\infty)$, $\hat{r} = r/r_0$ and $\hat{\tau} = \tau D/r_0^2$, where c_∞ is the equilibrium concentration, the solution to this problem is given by Equation D.2 [131]. The eigenvalues are given by [131]

$$\Lambda_k \cot \Lambda_k = 1 + \frac{K_{\rm H}}{r_0} \Lambda_k^2. \tag{D.7}$$

The coefficients Ξ_k were here computed from the initial condition for the bulk concentration using a least squares fit, while evaluating the first 10⁴ terms of the series. The evolution of the surface excess concentration can be described by [131]

$$\hat{\Gamma} = \frac{r_0(c_0 - c_\infty)}{\Gamma_{eq}D} \sum_{k=1}^{\infty} \Xi_k \frac{\sin\Lambda_k - \Lambda_k \cos\Lambda_k}{\Lambda_k^2} \left(1 - e^{-\Lambda_k^2 \hat{t}}\right).$$
(D.8)

For the numerical simulation using the method introduce in Chapter 4, linear adsorption kinetics according to

$$\frac{\partial \Gamma}{\partial \tau} = k_{\rm ad,H} c|_{r=r_0} - k_{\rm de,H} \Gamma, \tag{D.9}$$

with adsorption and desorption rate coefficients $k_{ad,H} = 100 \text{ m s}^{-1}$ and $k_{de,H} = 100 \text{ s}^{-1}$ were assumed. These kinetic parameters produce rapid equilibration of surface excess and subsurface bulk concentrations, while $K_H = k_{ad,H}/k_{de,H} = 1 \text{ m}$. Similar to the setup presented in the previous paragraph, a 2D axisymmetric mesh with 300 × 300 cells and a domain size of $1.5 r_0 \times 1.5 r_0$ is used. Figure D.3 shows the numerical results in comparison with the above reference solution. The results for the bulk concentration field show excellent agreement with the reference solution. Also the numerical results for the surface excess concentration coincide with the corresponding reference solution. Thus, overall excellent agreement between numerical and reference solutions can be observed in this verification case for diffusion-limited adsorption to the interface of a spherical drop.



Figure D.3: Verification results for diffusion-limited adsorption to the curved interface of a drop. The graph shows numerical results (solid lines) in comparison with the corresponding reference solution (dashed lines).

Appendix

Sensitivity Towards the Domain Size

In order to study the influence of the domain size on the observed droplet impact and spreading behavior, a simulation with increased domain size is considered. The domain size is expected to be most critical in non-isothermal cases due to heat transfer to substrate and gas phase. Thus, the non-isothermal reference case for the impact of an individual droplet, as presented in Subsection 6.1.3, is studied. Compared to the reference case, domain dimensions are doubled, such that for the initial impact, both fluid and solid domains have a size of $8 r_0 \times 8 r_0$, where r_0 is the initial droplet radius before impact. Similar to the cases presented in Section 6.1, the height of the fluid domain is halved for $\tau > 50 \,\mu$ s. Within the central part of the enlarged domain, which corresponds to the original, smaller mesh used for the parameter study, the mesh widths of the original grid are kept. Outside this region, the mesh widths are increased by a factor of 2. Droplet impact is, thus, simulated on a grid with 67392 cells for the fluid domain and another 67392 for the solid domain. For $\tau > 50 \,\mu$ s the number of cells in the fluid domain is reduced to 35136.





Figure E.1 shows the simulation results for the increased domain size in comparison with the results discussed in Subsection 6.1.3. The initial impact behavior shows no influence of the domain size. Only towards the end of the impact-driven regime, the dorplet on the larger domain reaches a slightly larger contact line radius. For the following capillary-driven regime, the plots once more coincide. In the simulation results obtained using the original domain, slight variations in the spreading rate related to the escape of entrained air can be observed. The results obtained using the larger domain do not show this behavior. Since air entrainment is linked to the initial impact, this difference in the capillary-driven regime is likely related to the earlier difference between the two cases towards the end of impact-driven regime. Nevertheless, doubling the domain size shows only a small influence on the overall spreading behavior. The domain size chosen for the parameter study can therefore be considered sufficiently large to accurately capture the impact and spreading behavior.
Appendix

Thermal Properties of the Model Ink

Within the scope of this work, the thermal properties of an acrylate monomer, as might be used in UV-inks, was determined for the simulations presented in Chapter 6. The specific heat capacity was measured by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 821e. These DSC measurements were conducted with a sample of 20.17 mg between 10 °C and 75 °C. The specific heat capacity of the acrylate monomer was evaluated from the measurement data in the relevant temperature range between 20 °C and 60 °C. The mean value is $c_p = 1832.43 \,\text{J kg}^{-1} \,\text{K}^{-1}$ with a standard deviation of 79.11 J kg⁻¹ K⁻¹. The thermal diffusivity was evaluated by laser flash analysis (LFA) using a Netzsch LFA 477 Nanoflash. LFA measurements for 20 °C, 40 °C, and 60 °C were performed. The results are presented in Figure E1. A mean value of $a = 0.295 \,\text{mm}^2 \,\text{s}^{-1}$ with standard deviation $2.154 \times 10^{-3} \,\text{mm}^2 \,\text{s}^{-1}$ is observed. The measurement data shows no temperature dependence of *a*. From *a* together with c_p and a density of $\rho_{\ell} = 1105 \,\text{kg} \,\text{m}^{-3}$, the thermal conductivity of the acrylate monomer $\lambda = 0.579 \,\text{W} \,\text{m}^{-1} \,\text{K}^{-1}$ follows. The values are summarized in Table E1.



Table F.1:	Thermal properties	of the
	acrylate monomer	

c_{ℓ}	/	${ m Jkg^{-1}K^{-1}}$	1832.430
а	/	$\mathrm{mm}^{2}\mathrm{s}^{-1}$	0.295
λ	/	$\mathrm{W}\mathrm{m}^{-1}\mathrm{K}^{-1}$	0.597

Figure F.1: Thermal diffusivity of the acrylate monomer from laser flash measurements.

Characterization of the Model Surfactant Solution

Within the scope of this thesis, a model surfactant solution is considered as starting point for parameter variations. The components of this model solution, i.e. the surfactant itself and the solvent, were chosen similar to those used for UV-curable inkjet inks. However, in order to be able to conduct isothermal experiments at room temperature as reference for the numerical simulation, the fluid properties, especially the viscosity of the solvent, was required to be within a jettable range under such ambient condition. Current printheads for high-performance graphical printing have a viscosity window ranging from 2 - 10 mPa s to 8 - 20 mPa s depending on the printhead [146]. Therefore, an acrylate monomer with a viscosity¹ of 9.0 mPa s was selected. The surfactant considered is a polymeric, radically crosslinkable acrylate. Dynamic surface tension data, i.e. the surface tension as a function of surface age for similar surfactant solutions, can also be found in [11].

Maximum Bubble Pressure Measurements

A common way to determine the dynamic surface tension of a surfactant solution is by maximum bubble pressure tensiometry [32]. During this experimental procedure, one end of a capillary is submerged into the surfactant solution. Then, the maximum pressure required to produce a bubble from said capillary is measured. The minimum bubble radius and, therefore, according to the Young-Laplace equation the maximum pressure, corresponds to a hemispherical bubble at the tip of the capillary. The surface tension can therefore be calculated from the Young-Laplace equation, using the maximum pressure and the known radius of the capillary. By varying the bubble frequency, the surface tension can be measured for different surface ages.

In order to characterize the dynamic surface tension behaviour of the model surfactant solution, measurements using a Krüss BP100 bubble pressure tensiometer at several surfactant mass fractions ranging from 0.01% to 10% were performed. For comparison, the acrylate monomer without added surfactant was also considered. In order to eliminate the risk of contamination of the lower concentrations with

¹ Thanks to Heidelberger Druckmaschinen AG for providing the viscosity data.



Figure G.1: Dynamic surface tension data from maximum bubble pressure tensiometry for the model surfactant solution.

additional surfactant, the experiments were conducted in order of increasing surfactant mass fraction. The diameter of the capillary was determined to 0.361 mm by a calibration measurement with purified water. Figure G.1 shows the measured data. Each data point shown represents the average over ten consecutive bubbles for the given surface age and concentration. In addition, three repetitions of the entire measurement cycle are presented for mass fractions $\leq 1\%$, showing excellent reproducibility of the measurement. The shortest time scales that could be resolved were surface ages of approximately 5 ms. Throughout all mass fractions, the dynamic surface tension was measured for surface ages of at least up to 2.5 s with additional measurements at larger surface ages for mass fractions $\omega \geq 0.01\%$.

The measurement data show a substantial dependence of the transient behavior on the surfactant mass fraction. While for a mass fraction of 0.01% the surface tension deviates notably from the $\omega = 0$ case only for surface ages greater than 1 s, the surface tension for the $\omega = 10\%$ case has reached a surface tension of 25.52 mN m⁻¹ already after 5 ms. Interestingly, even the in comparison very small mass fraction of 0.01% is sufficient to reduce the surface tension below 30 mN m^{-1} . The surfactant can therefore be considered very efficient in decreasing the solvents surface tension. With a decrease of the surface tension down to roughly half the surface tension of the solvent, the surfactant can also be considered reasonably effective. In fact, the model surfactant solution shows quite similar behaviour compared to the UV-curable inks with silicone surfactants presented in [11]. The surface tension of these inks shows a decrease from 35 mN m^{-1} to approximately 22 mN m^{-1} for surfactant mass fractions ranging between 0.15% and 0.5%. For these systems, the decrease in surface tension starts on a time scale of 1 ms and surface tension continues to decrease up to a time scale of several seconds to one minute.

For the surfactant solution studied here, a surface tension peak of up to 46 mN m^{-1} can be observed for $\omega \leq 1\%$ and surface ages below 10 ms. Since this peak can be observed even in the case without added surfactant, this behaviour can not be attributed to the surfactant, but must be of different origin. This could be either surface-active impurities in the acrylate monomer or measurement artifacts on these very short time scales. The cause for this short term behaviour remains unclear. In the following, focus will

instead lie on determining a suitable model to describe the sorption process at the liquid gas interface of the added surfactant.

Adsorption Model

It is assumed that in thermodynamic equilibrium the surface excess concentration Γ and the bulk concentration *c* are related according to the Langmuir-Freundlich isotherm, also known as Sips isotherm [160]

$$\frac{\Gamma}{\Gamma_{\rm max}} = \frac{(K_{\rm LF}c)^n}{1 + (K_{\rm LF}c)^n},\tag{G.1}$$

where Γ_{max} is the maximum surface excess concentration, K_{LF} is the adsorption equilibrium constant and n describes cooperativity during adsorption [72]. The adsorption isotherm was introduced by Sips [160] to account for saturation of the surface with adsorbent. For n = 1 the above equation simplifies to the well known and most commonly used non-linear isotherm, the Langmuir isotherm [32]. Langmuir's equation assumes the surfactant surface molecules not to interact with each other. In that respect the Langmuir-Freundlich isotherm presents an empirical modification, where 0 < n < 1 can be interpreted as negative cooperativity and n > 1 as positive cooperativity [72]. Through Gibb's adsorption equation

$$\Gamma = -\frac{1}{\overline{R}T} \left(\frac{\partial \sigma_{\ell g}}{\partial \ln c} \right)_{T,p}$$
(G.2)

bulk and surface excess concentrations are related to the surface tension. Inserting Equation G.1 for Γ and integrating over $\ln c$ results in

$$\sigma_{\ell g,0} - \sigma_{\ell g} = \overline{R} T \Gamma_{\text{max}} n^{-1} \ln \left(1 + (K_{\text{LF}} c)^n \right), \tag{G.3}$$

expressing the equilibrium surface tension as a function of the bulk concentration. $\sigma_{\ell g,0}$ denotes the surface tension of the pure solvent. With Equation G.1, this can be reformulated as the surface equation of state

$$\sigma_{\ell g,0} - \sigma_{\ell g} = -\overline{R}T\Gamma_{\max}n^{-1}\ln\left(1 - \frac{\Gamma}{\Gamma_{\max}}\right).$$
(G.4)

Note that for n = 1 the above two equations reduce to the Szyszkowski and Frumkin equations [32] respectively, the corresponding surface tension equations of state for the Langmuir isotherm.

Transport of surfactant to the interface is described by

$$\frac{\partial c}{\partial \tau} = D\nabla^2 c, \tag{G.5}$$

where *D* is the diffusion coefficient of surfactant within the bulk liquid. Surface excess concentration and bulk subsurface concentration at the liquid-gas interface Σ are connected through the boundary condition

$$\frac{\partial \Gamma}{\partial \tau} = \mathbf{n} \cdot D \nabla c \quad \text{on } \Sigma, \tag{G.6}$$

where **n** denotes the interface normal vector pointing towards the liquid phase. Closure of the model requires one additional condition at the liquid gas interface. This could be equilibrium between surface excess and bulk subsurface concentrations according to Equation G.1, assuming diffusion-limited behavior. However, here an additional kinetic model,

$$\frac{\partial \Gamma}{\partial \tau} = k_{\rm ad} c \left(1 - \frac{\Gamma}{\Gamma_{\rm max}} \right)^{1/n} - k_{\rm de} \left(\frac{\Gamma}{\Gamma_{\rm max}} \right)^{1/n}, \tag{G.7}$$

for the adsorption of surfactant molecules at the liquid-gas interface is considered. Therein, k_{ad} and k_{de} stand for adsorption and desorption rate coefficients respectively. From comparison of Equation G.7 for the stationary case with Equation G.1, it can be seen that the presented kinetic model is consistent with the Langmuir-Freundlich isotherm if $K_{LF} = k_{ad}/k_{de}$. Chan et al. [30] motivated the above kinetic model as a generalization of Langmuir adsorption kinetics, where molecules occupy m = 1/n = 1 or m = 1/n = 2 adsorption sites. This introduces an alternative, physical interpretation of the cooperativity parameter n: For 0 < n < 1 a single surfactant molecule occupies more than one adsorption site. Note that even though a kinetic model for the adsorption process is introduced, this may not necessarily be the rate determining step. However, the introduction of the kinetic model allows, depending on the parameters, modeling of diffusion-limited, adsorption-limited, as well as a combination of the two, so called mixed-kinetic behavior.

Model Fit

In order to determine the required parameters for the adsorption process of the model surfactant at the liquid-gas interface, Equation G.5 was discretized using the finite difference method, assuming a point symmetric bubble. Boundary conditions at the liquid-gas interface were set according to Equations G.6 and G.7. A 1D-FDM code was developed in *MATLAB* to solve the above equations. Additionally, a gradient descent algorithm was implemented in order to fit the model parameters to the measurement data, minimizing the root mean square deviation of the model prediction from measurement data for surface ages > 0.1 s for a selected mass fraction and taking into account the equilibrium surface tension at a specified additional concentration according to

$$\min_{\Gamma_{\text{max},K_{\text{LF}},n,D}} \sqrt{\left(\sigma_{\text{fit,eq}} - \sigma_{\text{m,eq}}\right)^2 + \sum_{i=1}^N \frac{\left(\sigma_{\text{fit},i} - \sigma_{\text{m},i}\right)^2}{N}}.$$
(G.8)

With the density of the acrylate monomer $\rho_{\ell} = 1105 \text{ kg m}^{-3}$ and a molar mass of the surfactant *M*, the molar concentrations corresponding to the mass fractions given above was first estimated according to $c \approx \omega \rho_{\ell}/M$. The surface tension of the acrylate monomer $\sigma_0 = 40.79 \text{ mN m}^{-1}$ was evaluated from the dynamic surface tension data for surface ages > 1 s. Similarly, the equilibrium surface tension for $\omega = 10\%$ was evaluated to $\sigma_{m,eq} = 21.14 \text{ mN m}^{-1}$. The model parameters Γ_{max} , K_{LF} , *n* and *D* were then fitted to the transient measurement data σ_m for $\omega = 0.1\%$ and the equilibrium value $\sigma_{m,eq}$ for $\omega = 10\%$. For this model fit, the adsorption rate coefficient k_{ad} was set sufficiently large, such that adsorption would be limited by diffusion towards the interface. Optimization was stopped once the optimization step size, i.e. the relative change of the fitting parameters between subsequent iterations, fell below 10^{-6} . This resulted in a value of $2.63 \times 10^{-4} \text{ N m}^{-1}$ of the objective function.

Figure G.2a shows the measurement data in comparison with the fitted model. The model shows very good agreement with measurement data for the fitted mass fraction of $\omega = 0.1\%$ as well as the equilibrium surface tension for $\omega = 10\%$. Furthermore, the model shows good agreement with the measured transient behaviour for all mass fractions $\omega \le 1\%$. The equilibrium surface tension for intermediate mass fractions appears to be slightly overpredicted by the model fit. Furthermore, in the diffusion-limited scenario shown by the dashed lines, the model predicts a more rapid equilibrium surface tension predicted by the model fit as a function of the bulk surfactant mass fraction. As could also be seen from the transient measurement data, very small amounts of surfactant are sufficient to substantially lower the equilibrium surface tension compared to the solvents surface tension of $\sigma_0 = 40.79 \,\mathrm{mN}\,\mathrm{m}^{-1}$.



Figure G.2: Model fit in comparison with measurement data and predicted equilibrium surface tension. Dashed lines in (a) represent the diffusion-limited model fit, solid lines represent mixed kinetic behavior.

Scaling the measurement data with the characteristic time scale for diffusion limited adsorption τ_{ad} reveals excellent agreement between the measurement data for low to intermediate surfactant mass fractions, as can be seen from Figure G.3a. This supports the assumption of a diffusion-limited process for these concentrations. However, the larger concentrations show a noticeable deviation from the remaining curves with slower adsorption in the scaled respresentation. This suggests an additional lim-

itation in the adsorption process for larger concentrations on short time scales. Therefore, in a second step, the adsorption rate coefficient k_{ad} was determined such that deviations from a diffusion-limited case were below a threshold of 1×10^{-4} N m⁻¹ for the fitted mass fraction $\omega = 0.1$ %. Thus a diffusionlimited adsorption process is ensured at this intermediate mass fraction. The so found value of k_{ad} also represents an estimate for the lower limit of the adsorption rate coefficient. Results from the 1D model with $k_{ad} = 2 \times 10^{-3} \text{ m s}^{-1}$ were used as approximation of the ideal diffusion-limited process. Figure G.3b shows the deviation from this reference case for surface ages 0.1 s to 10 s in the L_2 norm as a function of k_{ad} . It can be seen that the deviation increases exponentially with decreasing k_{ad} . For the lowest adsorption rate coefficients the surface tension remains almost constant during the considered time frame. Therefore, the deviation approaches a constant level for the lowest values of k_{ad} . With increasing adsorption rate coefficient, the deviation from the diffusion-controlled limit decreases continuously. For $k_{\rm ad} \gtrsim 4.53 \times 10^{-5} \,\mathrm{m \, s^{-1}}$, the deviation falls below the threshold of $1 \times 10^{-4} \,\mathrm{N \, m^{-1}}$. The corresponding model prediction for $k_{\rm ad} = 4.53 \times 10^{-5} \,\mathrm{m \, s^{-1}}$ is shown in Figure G.2a in comparison with the measurement data and the results from the diffusion-limited model. By including the effects of the adsorption kinetic model, the agreement between model prediction and measurement data could be slightly improved for the case of $\omega = 1\%$, while leaving the cases with smaller mass fractions virtually unchanged. However, for mass fractions \geq 5%, the equilibration rate is still overestimated in the way that the measured data shows a smoother approach to the equilibrium surface tension than is predicted by the model. An aspect of the surfactant that is not covered by the presented model (and is outside the scope of this work) is that, as a polymer, it may not have a single defined molecule structure but show a distribution in molar mass. This could present an explanation for the observed smoother transition towards the equilibrium surface tension. However, even with the assumption of a defined molecular mass, the model, even though fitted only for two mass fractions, predicts the behavior of the model surfactant solution surprisingly well over a very wide range of bulk concentrations. Thus, the Langmuir-Freundlich isotherm in conjunction with the corresponding kinetic model proved to be a suitable model for the considered surfactant solution.

Additional externally provided data of the diffusion coefficient of the considered surfactant gave further insight into the behavior of the surfactant solution. Assuming a constant hydrodynamic radius of the surfactant molecule for the solvent considered here, a diffusion coefficient $D \approx 1.19 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ could be calculated from Stokes-Einstein equation. With that, the model parameters can be rescaled such that the diffusive time scale is left unchanged and the molar mass of the surfactant can be determined to $M = 4.45 \text{ kg mol}^{-1}$. The resulting, final model parameters are shown in Table G.1.

$K_{\rm LF}$	/	${ m m}^3{ m mol}^{-1}$	$1.6794619649 imes 10^{-39}$
$\Gamma_{\rm max}$	/	$\mathrm{m}^2\mathrm{mol}^{-1}$	$1.4781783401 imes10^{-4}$
п			$6.5587137759 imes10^{-2}$
D	/	$\mathrm{m}^2\mathrm{s}^{-1}$	1.19 $\times 10^{-12}$
$k_{ m ad}$	/	${ m ms^{-1}}$	$\gtrsim 8.7617953335 imes 10^{-5}$
$k_{ m de}$	/	$\mathrm{mol}\mathrm{m}^{-2}\mathrm{s}^{-1}$	$\gtrsim 5.2170251644 imes 10^{34}$
$\sigma_{\ell \mathrm{g},0}$	/	${ m N}{ m m}^{-1}$	$4.0789333333\times10^{-2}$

Table G.1: Parameters of the surfactant model



(a) Measurement data scaled according to [63] for diffusion-limited adsorption

(b) Deviation from a reference case with $k_{\rm ad} = 2 \times 10^{-3} \, {\rm m \, s^{-1}}$ for $\omega = 0.1\%$ as a function of adsorption rate.

Figure G.3: Measurement data scaled based on the time scale for diffusion-limited adsorption according to Ferri and Stebe [63] (a) and deviation from the diffusion-limited case as a function of the adsorption rate coefficient k_{ad} for a mass fraction of 0.1% based on the 1D model (b).

Publications

Peer Reviewed Articles

D. Gründing, M. Smuda, **T. Antritter**, M. Fricke, D. Rettenmaier, F. Kummer, P. Stephan, H. Marschall, D. Bothe. A comparative study of transient capillary rise using direct numerical simulations. *Applied Mathematical Modelling*, 86:142-165, 2020.

T. Antritter, M. Mayer, P. Hachmann, M. Wörner. Suppressing artificial equilibrium states caused by spurious currents in droplet spreading simulations with dynamic contact angle model. *Progress in Computational Fluid Dynamics*, 20(2):59-70, 2020.

T. Antritter, P. Hachmann, T. Gambaryan-Roisman, B. Buck, P. Stephan. Spreading of Micrometer-Sized Droplets under the Influence of Insoluble and Soluble Surfactants: A Numerical Study. *Colloids and Interfaces*, 3(3):56, 2019.

Conference Contributions (Not Reviewed or Abstracts Only)

T. Antritter, P. Hachmann, T. Gambaryan-Roisman, B. Buck, P. Stephan. Coupled Wetting and Transport Processes in Micro Droplet Impact and Collision of Droplets. *Micro Flow and Interfacial Phenomena*, virtual conference, June 7-9, 2021.

T. Antritter, P. Hachmann, T. Gambaryan-Roisman, P. Stephan. Numerische Untersuchung gekoppelter Benetzungs- und Transportprozesse bei Tropfenaufprall und -kollision im Inkjet-Druckprozess. *Jahrestreffen ProcessNet-Fachgruppe Wärme- und Stoffübertragung*, virtual conference, February 24-26, 2021.

T. Antritter, T. Gambaryan-Roisman, P. Stephan. Spreading of pre-heated, surfactant-laden droplets on a cool substrate. *Wetting Dynamics*, Bonn, Germany, September 28-30, 2020.

T. Antritter, T. Gambaryan-Roisman, P. Stephan. Numerical Investigation of the Influence of Sorption Processes on Spreading of Surfactant-Laden Droplets. *Fundamental Fluid Dynamics Challenges in Inkjet Printing*, Leiden, Netherlands, July 22-26, 2019.

T. Antritter, T. Gambaryan-Roisman, P. Stephan. Numerische Untersuchung des Einflusses von Sorptionsprozessen auf das Benetzungsverhalten tensidhaltiger Tropfen. *Jahrestreffen ProcessNet-Fachgruppe Computational Fluid Dynamics*, Frankfurt, Germany, March 18-20, 2019.