The impact of Marangoni convection on fluid dynamics and mass transfer at deformable single rising droplets – A numerical study

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Abstract

In this paper, fluid dynamics and mass transfer of single droplets rising in a quiescent ambient liquid are considered. For the first time, full three-dimensional simulations of a deformable droplet dominated by Marangoni convection induced by concentration gradients were performed. A level set based code accounting for the mutual coupling of mass and momentum transfer was developed and implemented in the open-source computational fluid dynamics (CFD) package OpenFOAM\(^®\). The liquid/liquid extraction test system toluene/acetone/water was investigated, and numerical results were compared with experimental data from literature. The code captures and reproduces the characteristic experimental results: the two-step acceleration behaviour, the temporary reduction of the drop rise velocity, and the enhancement of mass transfer depending on the initial solute concentration. The lateral break-out in the drop path at the instant of reacceleration has only been observed experimentally so far. Our simulations reproduce this phenomenon, confirming the existence of pressure gradients across the droplet. Furthermore, our results reveal that the break-out effect is governed by rear vortex detachment.

Keywords: droplet, Marangoni convection, mass transfer, CFD, level set, extraction

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Nomenclature

Latin letters

- \( a \): acceleration
- \( c \): concentration
- \( c^* \): dimensionless concentration
- \( \hat{c} \): continuous concentration
- \( D \): diffusivity
- \( \tilde{F} \): forcing term in Eq. (A.3)
- \( g \): gravitational acceleration
- \( H_s \): smoothed Heaviside-function
- \( K \): distribution coefficient in Eq. (20)
- \( n \): interface unit normal
- \( n_S \): cell face unit normal
- \( S_f \): cell face area normal
- \( t \): time
- \( v \): velocity vector
- \( V \): volume
- \( \mathbf{x} \): position vector
- \( \mathbf{x}_{ci} \): centre of cell \( i \)
- \( \mathbf{x}_s \): centre of mass of the droplet

Greek letters

- \( \alpha_F \): under-relaxation factor
- \( \delta_\epsilon \): smoothed delta function
- \( \Delta x \): grid spacing
- \( \epsilon \): smoothing parameter
- \( \epsilon_V \): tolerance for volume correction
- \( \eta \): dynamic viscosity
- \( \kappa \): curvature
- \( \rho \): density
- \( \sigma \): interfacial tension
- \( \tau \): pseudo-time
- \( \psi \): level set function
- \( \tilde{\psi} \): correction of the level set function
- \( \omega \): weighting factor
- \( \Omega \): region

Subscripts

- \( 0 \): initial condition
- \( a \): arithmetic
- \( A \): acetone
bo  break-out

c  continuous phase

cr  critical

d  dispersed phase

f  cell face

h  harmonic

i  cell index

I  interface

m  average

reacc  reacceleration

T  toluene

W  water

Superscripts

n  time step index
1. Introduction

The Marangoni convection is an interfacial tension driven phenomenon originated from gradients of temperature, composition or electric potential along the interface between two fluids. These gradients generate gradients of interfacial energy which eventually lead to a convection at the interface from regions of lower towards regions of higher interfacial tension. By momentum transfer, this convection drags the fluid layers adjacent to the interface to form spatial convection patterns, e.g. Bénard cells with closed ring vortices (Brauer, 1971). According to Sawistowski (1973), the system response can be stable (if the instability is dampened quickly by friction), unstable (the Marangoni convection patterns enhance the local gradients), or oscillating (the system generates a counter-gradient which is directed oppositely and is higher than the causative gradient).

Especially at curved interfaces, such as of droplets moving in another liquid, this convection may become quite chaotic and unpredictable. Furthermore, Marangoni convection increases the interfacial shear stress and, consequently, the drag coefficient. Therefore, the relative velocity between dispersed and continuous phase decreases, leading to a lower rise velocity and, accordingly, to a lower Reynolds number. This affects the mass transfer of a soluble component across the interface which, in turn, influences the gradients of interfacial tension at the interface. Thus, mass and momentum transfer become strongly coupled.

In this work, we focus on the solvent extraction process in liquid/liquid systems. The design of such processes is demanding and requires a detailed knowledge of mass transfer and fluid dynamics. However, these transport phenomena are governed by the complex interactions between both phases linked through interfacial phenomena, such as droplet oscillations, swarm movement behaviour, and partly/full immobilisation of the interface (e.g. by surfactants or impurities). Consequently, Bauckhage et al. (1975) remarked that interfacial phenomena are the core problem in liquid/liquid extraction design. To overcome this problem, it seems to be promising to reduce the complexity of liquid/liquid extraction processes to single droplet investigations, and to understand first and foremost the underlying mechanisms of effects induced by interfacial instabilities. In best case, the experimental investigations should go hand-in-hand with the development of a numerical model which is validated thoroughly by experimental results, revealing a more detailed look on phenomena occurring on time and length scales which are experimentally not accessible.

For the purpose of comparability and reproducibility, the European Federation of Chemical Engineering (EFCE) defined standard test systems for liquid/liquid extraction (Misek et al., 1985). One of them represents an organic/aqueous system with high interfacial tension: toluene/acetone/water (TAW). However, this system is a prime example for a system exhibiting strong interfacial instabilities. For a reliable experimental assessment of the impact of the concentration driven (or so-called solutal) Marangoni effect in liquid/liquid systems, it is necessary to exclude as much disturbance variables as possible, e.g. temperature gradients (isothermal system), contaminations or surfactants (inert materials,
pure components), chemical reactions, swarm and wall effects (single droplet in a container with large diameter compared to the droplet diameter). Droplet formation and sample taking, however, are inherent parts of the process and have to be carefully taken into account when determining the mass transfer coefficient in the drop rising/falling stage (Wegener, 2009; Wegener et al., 2009a). Jayed et al. (1989) used a dye tracer technique at hanging water droplets in toluene to show the influence of Marangoni convection on mass transfer. The higher the acetone concentration was, the more the layers adjacent to the interface were renewed by Marangoni convection induced convection. This effect has not been seen in cases without Marangoni convection and is, consequently, believed to be responsible for the measured enhancement of the mass transfer coefficient. For the mass transfer direction dispersed to continuous phase ($d \rightarrow c$) in the TAW system, Arendt and Eggers (2007) presented an optical evidence that Marangoni convection induced interfacial eruptions are stronger for higher solute concentrations. Interestingly, no eruptions were observed for the reversed mass transfer direction $c \rightarrow d$.

Both mass transfer directions were examined by Steiner et al. (1990) in the TAW system, taking care in avoiding impurities originating both from chemicals and materials. Mass transfer was more effective with toluene as dispersed phase compared to water droplets in toluene. With toluene as dispersed phase, the solute transfer direction $d \rightarrow c$ was found to be more effective than the opposite $c \rightarrow d$, which was confirmed by many authors, see, e.g., (Garthe, 2006; Henschke, 2003), but the findings of Komazawa and Ingham (1978) showed that mass transfer rates were higher for $c \rightarrow d$, and some authors found no difference at all (Schulze, 2007). An interesting result of Schulze (2007) was that no lower limit or critical concentration could be found from which on Marangoni convection becomes predominant. In all cases investigated, mass transfer was enhanced.

Steiner et al. (1990) recommended an empirical description of mass transfer using an effective diffusivity to capture the complex phenomena, a strategy which was explored by different authors, e.g. by Henschke and Pfennig (1999). Steiner et al. (1990) gave an empirical correlation for the effective diffusivity, yet no detailed explanations of the mechanisms were provided.

Wegener (2009) investigated in detail the impact of Marangoni convection on fluid dynamics and mass transfer in the TAW system, both experimentally and numerically. Water saturated toluene droplets rose in toluene saturated water, with acetone transfer across the interface, both $c \rightarrow d$ and $d \rightarrow c$. For spherical droplets, the rise velocity was found to be an excellent indicator of the strength of Marangoni convection. The higher the initial solute concentration, the lower the instantaneous velocity became, until the drag coefficient increased to that of a comparable rigid sphere (Wegener et al., 2009b). With ongoing mass transfer, the concentration gradients decreased and the Marangoni convection became weaker. At a certain time, the droplets reaccelerated to nearly the terminal velocity of a sphere with fully mobile interface, reflecting the fact that with weaker Marangoni convection the additional shear stresses decreased and the inner toroidal circulation set in. The reacceleration time grew with rising initial
concentration and decreasing droplet size. This two-step acceleration behaviour is a characteristic feature being highly reproducible, and a graphical correlation of the reacceleration time was presented (Wegener et al., 2009b). Additionally, around the moment of reacceleration, the droplets broke out from their vertical path. This phenomenon was related to the formation of the inner circulation pattern, which was initially not symmetrical. The hypothesis was that a pressure gradient occurred due to different interfacial velocities (Wegener et al., 2009b), which eventually created normal forces required to move the droplets laterally.

In terms of mass transfer, two competing mechanisms were found experimentally (Wegener et al., 2007b) as well as numerically (Wegener et al., 2009c). On the one hand, the Marangoni instabilities clearly enhanced mass transfer through a more vigorous radial mixing due to the chaotic convection pattern within the droplet. On the other hand, the increase in the drag coefficient led temporarily to a lower rise velocity and, therefore, reduced convective mass transfer. This was reflected in lower Reynolds and Péclet (Pe) numbers. Consequently, the mass transfer was more enhanced for high (strong Marangoni convection, reduced Pe) and low (weaker Marangoni convection, higher Pe) initial solute concentrations, whereas for medium concentrations (medium Marangoni convection, reduced Pe), the mass transfer enhancement was lower. In any case, the mass transfer enhancement was palpable and 2–3.5 times higher than in the system without Marangoni convection. Oscillation of droplets further increased the mass transfer; factors up to 10 were found when the mass transfer in the experiments was compared with the Kronig and Brink model (Kronig and Brink, 1950) for circulating spheres (Wegener and Paschedag, 2011). Addition of the surfactant SDS showed a decrease in the mass transfer performance compared to the pure Marangoni case, but even at high surfactant concentrations, the mass transfer was considerably more effective if compared to the Newman model (Newman, 1931) for stagnant spheres (Wegener and Paschedag, 2012). From the numerical point of view, the simulation of fluid dynamics and mass transfer of rising/falling droplets with Marangoni convection is demanding, which may explain the low number of published papers in this area so far. Anyhow, some works have been done on the topic of thermocapillary motion of bubbles (Alhendal et al., 2013; Nas and Tryggvason, 2003) or droplets (Gao et al., 2008; Wu and Hu, 2012), but without simultaneous mass transfer.

One of the first papers on mass transfer with Marangoni convection at moving droplets was published by Mao and Chen (2004). They used a 2D model of a spherical droplet in an ambient fluid phase. The flow is governed by boundary conditions and is laminar, but with no implemented back-coupling of the concentration field to the flow field. They concluded that Marangoni convection was a temporary phenomenon with a start and an end. It needed a certain time to develop and died away once the interfacial tension gradients became weaker. However, the physical properties did not correspond to a real system, and no validation with experimental results was presented. Burghoff and Kenig (2006) performed 2D simulations for the ternary TAW system and the quaternary system toluene/acetone/methyisopropylketone/water.
The droplet was assumed to be spherical, but the change in droplet radius due to mass transfer was taken into account. Moreover, densities and viscosities were concentration dependent. The Reynolds number was given explicitly, and, consequently, Marangoni convection did not influence the rise velocity. Wang et al. (2008, 2011) used the level set method in their simulations to allow for droplet deformation. Again, only 2D simulations were carried out. The results showed that the Marangoni convection increased the mass transfer coefficient and changed the deformation behaviour. Nonphysical effects in the rising velocity were reported due to the limitation of 2D simulations. Here, comparisons with own experimental data were presented, exhibiting qualitative agreement for the mass transfer coefficient as a function of time.

Numerical results of a fully three-dimensional droplet model were presented by Wegener et al. (2009c). They used the commercial software package STAR-CD by cd-adapco based on the Finite Volume Method. Velocity and concentration field were solved sequentially and were coupled via the shear stress balance containing the solute concentration dependent interfacial tension gradient (which was and can only be obtained by experimental measurements). The shape was constantly spherical, no deformation and no deviation from the vertical rise path were allowed. Both, the two-step acceleration behaviour and the mass transfer were qualitatively and in some cases also quantitatively in good agreement with measurements in the TAW system.

The Marangoni convection is inherently three-dimensional and unsteady. Hence, 2D simulations will most likely fail or show nonphysical or unrealistic behaviour (Wegener et al., 2007a). According to Engberg et al. (2014), a numerical simulation of Marangoni convection at moving droplets should fulfill at least the following requirements:

- fully three-dimensional (no symmetry planes)
- mutual coupling of velocity and concentration field via the concentration dependent interfacial tension gradient (i.e. the Reynolds number should not be constant a priori)
- allow shape deformation, oscillation and deviation from the vertical rise path
- adequate resolution of the concentration boundary layer using sufficiently small grid cells

To the best of our knowledge, no experimentally validated 3D simulations on fluid dynamics and mass transfer at deformable single rising droplets with Marangoni convection have been published so far. The aim of the present paper is to present a CFD-based model and simulation results which meet the aforementioned requirements for a physically meaningful simulation of Marangoni effects at single rising droplets. The simulation results for rise velocity, mass transfer and rise path are compared with the corresponding experimental data of Wegener et al. (2007b).
2. Mathematical model and numerical method

2.1. Moving interface

In this work, the level set method (Osher and Sethian, 1988) is used to capture the moving interface. For this purpose, we define an indicator function \( \psi \) as follows:

\[
\psi(x, t) < 0 \quad \text{in the dispersed phase} \ (x \in \Omega_d) \tag{1}
\]

\[
\psi(x, t) > 0 \quad \text{in the continuous phase} \ (x \in \Omega_c) \tag{2}
\]

Consequently, the isocontour \( \psi(x, t) = 0 \) defines the interface \( \partial \Omega = \partial \Omega_c \cap \partial \Omega_d \) implicitly. If \( \psi \) is a signed distance function, it has the following properties:

\[
|\psi(x)| = \min(|x - x_I|) \quad \text{for all} \ x_I \in \partial \Omega \tag{3}
\]

\[
|\nabla \psi| = 1 \tag{4}
\]

It has been shown that a signed distance function is a particularly beneficial choice as level set function, cf. Osher and Fedkiw (2003). An advection equation for \( \psi \) may now be used to describe the movement of the interface in a velocity field \( v \) (Osher and Fedkiw, 2003):

\[
\frac{\partial \psi}{\partial t} + v \cdot \nabla \psi = 0 \tag{5}
\]

This equation can be discretised by standard methods for partial differential equations, e.g. by the finite element method or – as in this work – by the finite volume method. Due to the advection, \( \psi \) becomes distorted and loses its properties as a signed distance function (equations (3) and (4)). The procedure to restore \( \psi \) as a signed distance function is called reinitialisation and is explained in Appendix A.

2.2. Fluid dynamics

Consisting of water, toluene and acetone, the fluids considered in this study are Newtonian, and the two-phase flow is incompressible. Therefore, the fluid dynamics can be described with the mass continuity (6) and the Navier-Stokes (7) equations:

\[
\nabla \cdot v = 0 \tag{6}
\]

\[
\frac{\partial (\rho v)}{\partial t} + \rho a + (\rho v \cdot \nabla) v
\]

\[
= \nabla \cdot (\eta (\nabla v + \nabla v^T)) - \nabla p - \rho \mathbf{g} + [\sigma \mathbf{n} + \nabla \sigma - \mathbf{n} (\mathbf{n} \cdot \nabla \sigma)] \delta_\epsilon(\psi) \tag{7}
\]

where \( \rho \) denotes the pressure and \( \mathbf{g} \) the gravitational acceleration. To simulate long rise times, the centre of the computational domain is kept approximately at the centre of mass of the droplet. The acceleration term \( a \) in the momentum equation (7) accounts for this moving reference frame and is determined with a
procedure related to a method given by Rusche (2002) as explained in Appendix B.

To express physical properties (e.g. density $\rho$ and viscosity $\eta$) in the two-phase domain, a smoothed Heaviside function is defined:

$$ H_\epsilon(\psi) = \begin{cases} 
0 & \text{if } \psi < -\frac{\epsilon}{2} \\
\frac{1}{2} + \frac{\psi}{2\epsilon} + \frac{1}{2\pi} \sin\left(\frac{\pi\psi}{\epsilon}\right) & \text{if } |\psi| \leq \epsilon \\
1 & \text{if } \psi > \epsilon
\end{cases} $$

(8)

where the parameter $\epsilon$ determines the width of the transition region from one phase to another. In terms of the grid spacing $\Delta x$, a typical value of $\epsilon = 1.5\Delta x$ was chosen for the simulations, rendering the transition region three grid cells wide.

The density is calculated with

$$ \rho = \rho_d + (\rho_c - \rho_d)H_\epsilon(\psi) $$

(9)

In the finite volume discretisation, the viscosity $\eta$ is needed on the faces of the computational cells. As pointed out by Patankar (1980), the interpolation (or averaging) of a varying viscosity has to be treated with care. Frequently, an arithmetic mean similar to the averaging of density (9) is used:

$$ \eta_a = \eta_d + (\eta_c - \eta_d)H_f(\psi) $$

(10)

where $H_f$ is the smoothed Heaviside function interpolated at the cell faces denoted with $f$. However, this average applies only when the interface is perpendicular to the cell face which corresponds to a parallel arrangement of regions with different viscosities. For a serial arrangement, a harmonic mean should be used:

$$ \eta_h = \left(\frac{H_f(\psi)}{\eta_c} + \frac{1 - H_f(\psi)}{\eta_d}\right)^{-1} $$

(11)

The relative orientation of the interface normal at the cell face $n_f$ and the cell face unit normal $n_S$ determines which mean value is appropriate. If the interface and the cell face are parallel and the normals aligned, the harmonic mean applies. In contrast, the arithmetic value is chosen for perpendicular normals. Therefore, Kothe (1998) suggested the following weighting factor:

$$ \omega = |n_f \cdot n_S| $$

(12)

Thus, the viscosity is calculated with

$$ \eta = \omega\eta_h + (1 - \omega)\eta_a $$

(13)

The last term on the r.h.s. of equation (7) represents the surface forces at the interfaces due to the interfacial tension $\sigma$. It is weighted with a smoothed delta function:

$$ \delta_\epsilon(\psi) = \begin{cases} 
0 & \text{if } |\psi| > \epsilon \\
\frac{1}{2\epsilon} + \frac{1}{2\pi} \cos\left(\frac{\pi|\psi|}{\epsilon}\right) & \text{if } |\psi| \leq \epsilon
\end{cases} $$

(14)
Consequently, the interfacial forces are transformed into volume forces according to the continuum surface force model of Brackbill et al. (1994). Acting normal to the interface, the first term in the square brackets is proportional to the curvature $\kappa$ and results in a pressure jump. The curvature is defined as the divergence of the interface unit normal $\mathbf{n}$ calculated from the level set function:

$$\mathbf{n} = \frac{\nabla \psi}{|\nabla \psi|} \quad (15)$$

$$\kappa = -\nabla \cdot \mathbf{n} \quad (16)$$

In this work, the curvature is integrated over each finite volume $V_i$ to obtain a cell averaged value:

$$\bar{\kappa} = -\frac{1}{V_i} \int_{V_i} \nabla \cdot \mathbf{n} \, dV \quad (17)$$

Applying the Gaussian theorem yields:

$$\bar{\kappa} = -\frac{1}{V_i} \int_{S_i} \mathbf{n} \cdot d\mathbf{S} \quad (18)$$

Equation (18) can be readily approximated within the finite volume framework by a sum over all faces $f$ of a cell:

$$\bar{\kappa} \approx -\frac{1}{V_i} \sum_f \mathbf{n}_f \cdot \mathbf{S}_f \quad (19)$$

In equation (19), $\mathbf{S}_f$ is a vector normal to the face $f$ with the magnitude of the face area.

The interfacial force term $\delta \sigma \kappa \mathbf{n}$ in equation (7) can lead to pressure oscillations at the interface and evoke unphysical spurious currents (Brackbill et al., 1994; Francois et al., 2006) which act similar to Marangoni convection. Consequently, it has to be ensured that these currents are limited and do not interfere with Marangoni effects. The strength of spurious currents depends on the implementation of the interfacial forces and the curvature approximation (Francois et al., 2006). In a previous work, the code was validated with numerical and experimental results for droplet rise velocities in three different liquid-liquid systems (Engberg and Kenig, 2014). Due to the good curvature approximation with the level set method, the strength of spurious currents was found to be small.

The two following terms in the square brackets of equation (7) act tangentially to the interface and may induce Marangoni convection, if the interfacial tension varies.

In the present work, the pressure-velocity coupling is achieved with a Pressure Implicit with Splitting of Operators (PISO)-algorithm (cf. Issa, 1986). In all simulations, three corrector steps were performed with the PISO-loop.

2.3. Mass transport

In this study, low concentrations of acetone were considered. Thus, the systems can be treated as diluted systems which simplifies the mathematical
description of mass transfer phenomena.

In a mass transport model, two boundary conditions at the interface have to be fulfilled: the thermodynamic equilibrium (20) which results in a concentration jump at the interface proportional to the distribution coefficient $K$ and the continuity of diffusional fluxes (21):

$$c_{Ad} = Kc_{Ac}$$  \hspace{1cm} (20)

$$D_{Ad} \nabla c_{Ad} \cdot \mathbf{n} = D_{Ac} \nabla c_{Ac} \cdot \mathbf{n}$$  \hspace{1cm} (21)

Fulfilling these boundary conditions within a front capturing framework is challenging, as there are no nodes at the interface where they could be implemented directly. In this work, a method proposed by Petera and Weatherley (2001) is used. A new concentration field which is continuous at the interface is defined:

$$\hat{c} \equiv \begin{cases} 
  c_{Ad} & \text{for } \psi \leq 0 \\
  K c_{Ac} & \text{for } \psi > 0 
\end{cases}$$  \hspace{1cm} (22)

Mass transfer simulations based on this formulation in a finite volume/volume of fluid framework were performed, among others, by Bothe et al. (2004), Onea et al. (2009) and, recently, by Francois and Carlson (2013). Wang et al. (2011) used a similar formulation in a finite difference/level set approach.

Instead of one transport equation for the dispersed phase and one for the continuous phase, coupled through the interfacial boundary conditions (equations (20) and (21)), a single transport equation is solved for the whole domain:

$$\frac{\partial \hat{c}}{\partial t} + \mathbf{v} \cdot \nabla \hat{c} - \nabla \cdot (D \hat{c}) = 0$$  \hspace{1cm} (23)

In terms of the transformed concentration, Eq. (22), the continuity of diffusional fluxes, Eq. (21), can be expressed as

$$D_{Ad} \nabla \hat{c} \cdot \mathbf{n} = D_{Ac} \frac{K}{K} \nabla \hat{c} \cdot \mathbf{n}$$  \hspace{1cm} (24)

As noted by Onea et al. (2009), the mixture diffusivity $D$ can be modified to account for the scaled continuity of diffusional fluxes, Eq. (24), and a similar formulation is used in this work.

When equation (23) is solved, the concentrations in each phase can be recalculated with equation (22). However, Onea et al. (2009) pointed out that this procedure does not obey mass conservation and the total amount of the transferred component changes in the course of a simulation. To quantify this drawback, a validation study is presented in Appendix C.

2.4. Simulation

The governing equations were implemented in the open-source CFD-toolbox OpenFOAM® and solved in a sequential manner. OpenFOAM® is written in C++ and offers a wide range of CFD codes for diverse applications. While OpenFOAM® contains several solvers for the simulation of multiphase flows,
Table 5: Physical properties at a temperature of 25 °C given by Misek et al. (1985).

<table>
<thead>
<tr>
<th>phase</th>
<th>density (kg/m³)</th>
<th>dynamic viscosity (10⁻⁴ Pa s)</th>
<th>diffusivity of acetone (10⁻⁹ m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene phase</td>
<td>862.30</td>
<td>5.520</td>
<td>2.90</td>
</tr>
<tr>
<td>aqueous phase</td>
<td>997.02</td>
<td>8.903</td>
<td>1.25</td>
</tr>
</tbody>
</table>

including various codes based on the VOF method, it does not provide a level set based solver. Moreover, the weighted essentially nonoscillatory (WENO) finite difference scheme required for the reinitialisation is not included in the official OpenFOAM® distribution. Therefore, we implemented the level set based code and the WENO scheme for this work ourselves.

Simulations of a toluene droplet with an initial diameter of \(d_0 = 2\) mm rising in water were performed. The transfer of acetone was simulated for the direction \(d \rightarrow c\) and various initial concentrations. Extensive experimental and numerical results exist for this configuration (Wegener et al., 2007b) which are compared with the simulation results of this work in Section 3.

The physical properties used for the simulations were taken from Misek et al. (1985) and are listed in Table 5. With the exception of the interfacial tension, the dependence of the physical properties on the acetone concentration was neglected and the properties of pure substances were employed. This is in line with the assumption of a dilute system. An exponential function was fitted to the experimental data of Misek et al. (1985) to express the interfacial tension in terms of the concentration of acetone in toluene \(c_{AT}\):

\[
\sigma = 0.0025 + 0.03285 \exp(-0.0145\ c_{AT})
\]  

(25)

where the units of \(c_{AT}\) and \(\sigma\) are g/L and N/m, respectively. In accordance with Wegener et al. (2009c), the distribution coefficient at 25 °C is \(K = 0.63\).

In terms of the droplet diameter, the width and depth of three-dimensional computational domain is \(8\ d_0\) and the height \(12\ d_0\). The grid used for the simulations is shown in Fig. 1. Due to the moving reference frame (cf. Section 2.2), the computational domain follows the droplet during its rise and the interface remains in the refined region. It consists of cuboid cells and is refined in the vicinity of the interface. To resolve the steep concentration gradients at the interface, the grid should be refined to the Batchelor length (Batchelor, 1959) which represents the magnitude of the smallest length scales of mass transfer and is approximately 2 \(\mu m\) in this case. The two different grids used for this investigation were refined to \(\Delta x_{128} = d_0/128 \approx 16\ \mu m\) and \(\Delta x_{240} = d_0/240 \approx 8\ \mu m\), respectively. Due to the Courant-Friedrichs-Lewy (CFL) condition, small time steps have to be chosen for the fine grid, leading to long simulation times: It takes about five weeks to simulate 1 s rise time on 24 cores. Thus, a further grid refinement is currently not feasible.

The droplets are initialised as spheres defined by the level set function. The concentration is set to a constant initial concentration \(c_{A0}\) in the droplet and is zero in the rest of the domain. These initial conditions deviate from the experi-
ments of Wegener et al. (2007b) in which droplets were formed with a capillary. As a result, mass transfer starts during the drop formation (cf. Wegener et al., 2009a) and the concentration is not homogeneous when the droplet starts to rise. Moreover, the droplet is deformed when it is released from the capillary (cf. Wegener et al., 2007b).

The boundary conditions were chosen as follows (cf. Fig. 2): Owing to the moving reference frame, the velocity at the top and the sides is equal to the frame velocity $v_F$. At the bottom, a zero gradient condition is employed for velocity. Zero gradient conditions are also appropriate for the level set function and the transformed concentration at the top, bottom and sides. To simplify the specification of boundary conditions for pressure, a modified pressure without hydrostatic contribution $p^* = p - \rho g \cdot x$ is used in the simulations (cf. Rusche, 2002). The boundary conditions for the modified pressure are a constant reference pressure at the bottom and zero gradient conditions at the top and sides. Equations (5), (6), (7) and (23) were solved in a finite volume framework. Convective terms were discretised with the Gamma scheme introduced by Jasak et al. (1999) and time was discretised with an implicit Euler scheme. The time steps were constant at 20 ms for the grid with $\Delta x_{128}$ and at 10 ms for the grid with $\Delta x_{240}$, leading to a maximum Courant number of 0.3.
Figure 2: Schematic representation of the computational domain with the boundary conditions for the simulations.

3. Results

3.1. Streamlines and concentration fields

In this section, the impact of Marangoni convection on momentum and mass transfer is demonstrated with a set of figures. Fig. 3 shows slices through the centre of the droplet parallel to the rise path for various simulations at three time steps. Streamlines are given in the left part of the figures and concentrations in the right part.

The upper row depicts results for a case with constant interfacial tension. After 0.1 s rise time, the internal circulations are already apparent. Due to the acceleration, however, the concentration field is still irregular. The internal circulations are fully developed after 0.5 s and characteristic toroidal concentration patterns can be observed. The right figure \( t = 1 \) s illustrates the long diffusion paths which lead to low mass transfer rates.

Results for a low initial acetone concentration of \( c_{A0} = 0.9 \) g/L are shown in
the middle row. The streamlines for $t = 0.1$ s indicate circulations which are disturbed by a small vortex at the rear of the droplet. The concentration field appears to be slightly more irregular than in the case without Marangoni convection. After 0.5 s rise time, Marangoni effects are already declining: The streamlines evolve into internal circulation and the isocontours of concentration become toroidal. Nevertheless, Marangoni convection has clearly enhanced internal mixing and the concentration field is less layered compared to the simulation with constant interfacial tension. Consequently, diffusion paths are shorter, resulting in higher mass transfer rates. In the next figure ($t = 1$ s), internal circulations are fully developed, but the influence of Marangoni convection can still be seen in the relatively high concentrations at the interface.

Marangoni effects are most obvious in the figures of the bottom row, with results for an initial acetone concentration of $c_{A0} = 3.7$ g/L. Highlighting the impact of a variable interfacial tension, the streamlines show no internal circulations, but several vortices of variable size. Moreover, vortices in the wake of the droplet can be observed. The influence of these vortices on the droplet trajectory will be discussed in Section 3.3. The irregular flow patterns are highly unsteady and

Figure 3: Streamlines and concentration fields of simulations without (top) and with Marangoni convection ($c_{A0} = 0.9$ g/L (middle), $c_{A0} = 3.7$ g/L (bottom)) after a rise time of 0.1 s, 0.5 s and 1 s (left to right).
lead to strong internal mixing and a relatively uniform concentration field in the whole droplet.

3.2. Transient drop rise velocity

The transient rise velocities obtained with the $\Delta x_{128}$-grid and with the $\Delta x_{240}$-grid are shown in Fig. 4 and 5, respectively. A comparison with the corresponding experimental results of Wegener et al. (2007b) demonstrates that the simulations reproduce the effect of Marangoni convection at various initial concentrations on the acceleration qualitatively well. Regarding the simulations with Marangoni convection, a better agreement with the experimental data is achieved with the finer grid ($\Delta x_{240}$). Consequently, unless noted otherwise, the following discussion concentrates on the results shown in Fig. 5.

In the simulation without Marangoni convection, the droplet accelerates quickly to its terminal rise velocity. In contrast, the acceleration with Marangoni convection is more chaotic and complex. In accordance with the experiments, an
increase of the initial concentration of acetone reduces the rise velocity until it approximately coincides with the terminal rise velocity of a rigid sphere. The droplet rises with this reduced velocity until the acetone concentration in the droplet reaches a critical concentration and the droplet reaccelerates. Regarding the instant of reacceleration, the same trend is observed in both experiment and simulation: The higher the initial acetone concentration is, the later the reacceleration begins. After the reacceleration, the droplet reaches a terminal rise velocity which is lower than the resulting terminal rise velocity without Marangoni convection. This phenomenon was also observed experimentally by Wegener et al. (2007b) and obtained numerically by Wegener et al. (2009c). The reduced terminal rise velocity obtained with the $\Delta x_{240}$-grid is about 104 mm/s and the experimental result of Wegener et al. (2007b) approximately 95 mm/s. It should be noted that the droplet has to reach the terminal rise velocity of the binary system toluene-water when the mass transfer is finished. However, in both experiments and simulations, the rise time is too short to finalise mass
transfer, and the droplets are still slowed down by Marangoni effects. Obviously, even very small mass transfer rates hinder acceleration to the terminal velocity of a droplet with freely moving interface.

The simulations without Marangoni convection agree with the experimental results for the binary system toluene-water, and a very good accordance is achieved with both grids. After a short acceleration (approximately 1 s), the droplet reaches its terminal rise velocity of 112.2 mm/s ($\Delta x_{128}$) or 113.4 mm/s ($\Delta x_{240}$). These results are consistent with the numerical results of Bäumler et al. (2011) for the same system and droplet diameter (112.6 mm/s).

In cases with Marangoni convection, the simulated droplets accelerate faster than their experimental counterparts during the first 0.3 s. This observation can be explained with different initial conditions in simulation and experiment mentioned in Section 2.4. As mass transfer starts during the drop formation in the experiments, Marangoni convection influences the acceleration of the droplet from the beginning of its rise. In the simulations, however, the initial concentration field in the droplet is homogeneous and Marangoni flow patterns have to develop during the acceleration phase. Moreover, the numerical droplet is initialised as a sphere, whereas the experimental droplet is deformed when it detaches from the capillary. This deformation also leads to a slower acceleration.

For the lowest initial concentration of $c_{A0} = 0.9 \text{ g/L}$, the numerical results differ clearly from the experimental data. While the experimental results show a long and chaotic acceleration period, the simulated droplets accelerate just slightly slower than in the case without Marangoni convection. Velocity oscillations occur only close to the terminal rise velocity. As mentioned above, the terminal rise velocity is lower than in the case without Marangoni convection.

The simulations with $c_{A0} = 1.8 \text{ g/L}$ demonstrate the influence of Marangoni convection more explicitly. Despite being shorter than in the experiments, the acceleration phase is longer than in the simulations with $c_{A0} = 0.9 \text{ g/L}$ and more irregular. In accordance with the experiments, the initial concentration is still too low to reduce the rise velocity to that of a rigid sphere. Nevertheless, both experiments and simulations show a distinct bend in the transient rise velocity at approximately 65 mm/s. In the first 1.5 s, the simulation matches the experimental data noticeably well, but the following acceleration period is again rather short.

In both the simulations and experiments, the increase in interfacial shear stress due to Marangoni convection becomes even more apparent with an initial concentration of $c_{A0} = 3.7 \text{ g/L}$: For several seconds, the rise velocity is close to the terminal rise velocity of a rigid sphere calculated with the Schiller-Naumann correlation Schiller and Naumann (1933). The simulated rise velocity and the velocity fluctuations in this period are in excellent agreement with the experimental data. In contrast, the simulated rise velocity of Wegener et al. (2009c) was higher and showed stronger fluctuations than the experimental data. Thus, our results represent a qualitative and quantitative improvement over the numerical results of Wegener et al. (2009c). The reacceleration begins after 2.9 s in the simulation, which is considerably earlier than in the experiments (6.5 s).
Furthermore, the simulated reacceleration period is, again, significantly shorter. The onset and the duration of this phase are discussed further in Section 3.4 in conjunction with the results for mass transfer.

A comparison of the numerical results for $c_{A0} = 7.5 \text{ g/L}$ leads to similar conclusions as for $c_{A0} = 3.7 \text{ g/L}$. The simulated reduced rise velocity and its fluctuations match the experimental data very well, but the onset and the duration of the reacceleration differ clearly from the experimental results. The reacceleration begins after 5.5 s, whereas the experimental onset of reacceleration is after 7.5 s.

### 3.3. Droplet trajectories

The influence of Marangoni convection on the droplet trajectories is shown in Fig. 6. In accordance with the experimental results of Wegener et al. (2007b), droplets without Marangoni convection rise in a straight path whereas deviations from the vertical path and oscillations are observed in simulations with...
Marangoni convection. The length scale of these oscillations is also consistent with the experimental data. Moreover, in both simulations and experiments, a break-out in a random direction occurs which coincides with the onset of reacceleration. Consequently, it happens the later the higher the initial concentration of acetone is.

The small-scale path oscillations occur mainly in one plane and lead, consequently, to a zigzag movement of the droplet. Fig. 7 presents a detail of the trajectory obtained with \( c_{A0} = 3.7 \text{ g/L} \) (\( \Delta x_{240} \)). The path oscillations show a quite regular period in the range of 0.4 to 0.6 s and an amplitude of approximately 0.5 mm. Similar values were also found in other simulations with Marangoni convection. A sequence of streamlines and pressure profiles in Fig. 8 obtained from the same simulation illustrates how the droplet changes its direction from \( t = 1.7 \text{ s} \) to \( t = 1.85 \text{ s} \) (compare with Fig. 7) and help to understand the mechanisms which evoke path oscillations. It should be noted that the pressure profiles are shown without the hydrostatic portion and are rescaled to reveal the pressure differences around the droplet. The leftmost picture shows the droplet moving to the left (\( t = 1.7 \text{ s} \)) with two distinct vortices in its wake. A larger area of lower pressure to the left of the droplet can be seen in the corresponding pressure profile. Consequently, a pressure gradient arises which forces the droplet to the left. In the next figure, the left vortex detaches while the right one remains attached. The pressure differences from the left to the right side of the droplet disappear. When the right vortex detaches at \( t = 1.8 \text{ s} \) (third figure), the pressure difference has reversed and changes the direction of the droplet (rightmost figure). This sequence is repeated until Marangoni
convection decreases and the final break-out occurs. Wegener et al. (2009b) suggested a possible explanation for the break-out: Marangoni convection prevents internal circulations and increases, therefore, the interfacial shear stress. When the acetone concentration decreases, variations in interfacial tension diminish and internal circulations develop. As the acetone concentration is not homogeneous, the development of internal circulations may be limited to certain parts of the droplet and still be hindered in others. Hence, inhomogeneous interfacial velocities would occur and lead to pressure gradients resulting in a lateral movement. This assumption can now be compared with the results of our CFD simulations.

Fig. 9 presents streamlines for various times including the moment of break-out of the simulation with $c_{A0} = 3.7$ g/L ($\Delta x_{240}$). In the first two pictures in the upper row (Fig. 9 (a) and (b)), the droplet rises relatively straight and the two vortices in the wake have developed. Compared to the streamlines shown in Fig. 8, the streamlines are more regular and internal circulations develop in the upper hemisphere. The detachment of the right vortex (Fig. 9 (c)) marks the beginning of the break-out. As explained above, this leads to pressure differences forcing the droplet to the left (compare with Fig. 7). The vortices in the wake of the droplet have quickly redeveloped (Fig. 9 (e) and (f)), but then the asymmetric detachment of vortices is repeated (Fig. 9 (g) and (h)). The following figures (Fig. 9 (i) to (l)) show how Marangoni convection decreases and the internal circulations develop. In the following, no vortices are formed.
in the wake any longer and the lateral movement induced by the asymmetric
detachment of the last vortices results in the macroscopic break-out.
The streamlines in Fig. 9 (g) to (k) resemble the mechanism proposed by 
Wegener et al. (2009b): Internal circulations have largely redeveloped, but small
Marangoni convection patterns remain in the lower left of the droplet. As sug-
gested by Wegener et al. (2009b), these asymmetries lead to pressure differences
resulting in a lateral movement. Furthermore, the simulation results of this in-
vestigation have shown that the droplet trajectories are governed by the vortices
in the wake of the droplet and their asymmetric detachment.
Figure 9: Streamlines for the simulation with $c_{A_0} = 3.7 \text{ g/L}$ ($\Delta x_{240}$) at the following times: 3.0 s, 3.05 s and 3.1 s ((a) to (c), first row), 3.15 s, 3.2 s and 3.25 s ((d) to (f), second row), 3.3 s, 3.35 s and 3.4 s ((g) to (h), third row), 3.5 s, 3.6 s and 3.7 s ((i) to (l), fourth row).
3.4. Mass transfer

Figs. 10 and 11 present the dimensionless mean concentration of acetone in the droplet $c^* = c_{Am}/c_{A0}$ as a function of time. Again, simulation results without Marangoni convection and with Marangoni convection for various initial concentrations as well as the corresponding experimental results of Wegener et al. (2007b) are shown. A comparison of the simulation results with and without Marangoni convection indicates that the mass transfer enhancement due to Marangoni convection is reproduced by the model. However, this enhancement is far more pronounced with the $\Delta x_{240}$-grid than with the $\Delta x_{128}$-grid. The results without Marangoni convection obtained with the $\Delta x_{240}$-grid are in good agreement with the results of Wegener et al. (2009c) and can, therefore, be considered as a reasonable reference to quantify mass transfer enhancement.

A comparison of the experimental data with the results obtained with the $\Delta x_{128}$-grid (Fig. 10) shows a distinct deviation; generally, the simulated mass transfer rates are too high. As the grid is too coarse to resolve the thin concentration boundary layer (cf. section 2.4), this outcome can be expected. Therefore, the discussions of this section will focus on the results obtained with the $\Delta x_{240}$-grid. Wegener et al. (2007b) showed that the mass transfer enhancement depended on the initial concentration of acetone: while low and high initial concentrations led to particularly high mass transfer rates, medium concentrations yielded low enhancement factors. As mentioned in the introduction, this phenomenon can be explained with the competing mechanisms of increased mixing in droplet and reduced convective mass transfer due to lower rise velocities.

This effect is also reproduced in the simulations (cf. Fig. 11). For example, the simulated mass transfer rate for an initial concentration of $c_{A0} = 0.9$ g/L is similar to the case without Marangoni convection up to a rise time of approximately 0.25 s. In this period, mass transfer is dominated by the acceleration which is similar for both cases. However, the mass transfer rate decreases after this period in the simulation without Marangoni convection and becomes almost constant when the droplet has reached its terminal rise velocity ($t \approx 1$ s). In contrast, it remains high in the simulation with $c_{A0} = 0.9$ g/L and Marangoni convection. Consequently, the mass transfer enhancement is particularly high in this case, a finding which is also reflected in the experimental results. Nevertheless, the experimental data show a reduced mass transfer rate after approximately 1 s and differ noticeably from the simulation results.

With an initial concentration of $c_{A0} = 1.8$ g/L, a slightly lower mass transfer rate than the simulation with $c_{A0} = 0.9$ g/L is obtained numerically. This may be explained with the lower rise velocity (cf. Fig. 5). The deviation from the experimental results is again obvious.

The higher initial concentrations of $c_{A0} = 3.7$ g/L and $c_{A0} = 7.5$ g/L lead to increased mass transfer rates at the beginning of the droplet rise. However, the mass transfer rates decrease after approximately 0.5 s due to the reduced rise velocity. As a result, the mass transfer enhancement is lower than for $c_{A0} = 0.9$ g/L and $c_{A0} = 1.8$ g/L. This outcome is consistent with the experimental results. While the simulation results for $c_{A0} = 3.7$ g/L differ clearly from the experimental data, a reasonable agreement is found for $c_{A0} = 7.5$ g/L.
The discussion of Fig. 5 has illustrated that transfer rates are generally higher in the simulations than in the experiments. Owing to the mutual coupling of momentum and mass transfer, this gives rise to an earlier onset and a shorter reacceleration (cf. Section 3.2). This conclusion is corroborated by the particularly early reaccelerations obtained with the $\Delta x_{128}$-grid where the mass transfer rates are even higher. Nevertheless, it is surprising that the numerical results of Wegener et al. (2009c) also point to an earlier and shorter reacceleration – despite the fact that their results for mass transfer matches the experimental data better than the present study.

Two reasons for the higher simulated mass transfer rates can be identified. First, the simple mass transport model used in this work cannot prevent convective mass fluxes across the interface. This unphysical effect occurs when a streamline crosses the interface. An analysis of the streamlines shows that this happens rarely despite the strong convective patterns evoked by Marangoni effects. Thus, we infer that convective mass fluxes play a minor role only.
Figure 11: The dimensionless mean concentration of acetone in the droplet $c^* = c_{Am}/c_{A0}$ obtained with the $\Delta x_{240}$-grid (lines) and experimental results of Wegener et al. (2007b) (symbols) for various initial concentrations as a function of time.

Second, further grid refinement would be necessary to achieve fully grid independent results. Because of the long simulation times this is, however, currently not feasible. Despite these drawbacks, we believe that the numerical results are close enough to the experimental data. Hence, the CFD simulations can be used to gain valuable insights into the complex physics of interfacial instabilities. Reacceleration and break-out mark the moment when the dominance of Marangoni convection decreases. Therefore, Wegener et al. (2007b) suggested using the concentrations in these instants as critical concentrations which can be applied to assess the influence of Marangoni effects on the fluid dynamics. They determined a range of $c_{cr} = 0.5 \text{ g/L } \pm 0.2 \text{ g/L}$ for the critical concentration in the studied system, cf. Fig 12. However, for an initial concentration of $c_{A0} = 1.8 \text{ g/L}$, Wegener et al. (2007b) found that the experimental minimum and maximum critical concentrations are distinctly higher than for any other initial concentration.

A comparison of experimental and numerical data for the critical concentrations...
presented in Fig. 12 shows that slightly higher critical values were determined in the simulations. Interestingly, the droplet with $c_{A0} = 1.8$ g/L reaccelerated at a particularly high concentration, showing a similar trend as the experimental data. Nevertheless, the break-out occurred at a lower concentration. It should be noted that no reacceleration time could be determined for $c_{A0} = 0.9$ g/L.

Figure 12: The concentrations when the droplet reaccelerates $c_{reacc}$ (▲) and when the break-out occurs $c_{bo}$ (▼) obtained with the $\Delta x_{240}$-grid as functions of the initial acetone concentration $c_{A0}$. These concentrations can be regarded as critical concentrations $c_{cr}$ for the influence of Marangoni convection on the fluid dynamics of droplets. The majority of the experimental critical concentrations of Wegener et al. (2007b), shown as average values (×) with the corresponding ranges, are within $c_{cr} = 0.5$ g/L ±0.2 g/L (dashed lines).
4. Conclusion

In this work, the influence of Marangoni convection on mass transfer and fluid dynamics of single rising droplets was studied with CFD simulations. For this purpose, we developed a CFD code which uses the level set method to capture the moving interface of the droplet and a scaling method for mass transport. The code was implemented in the open-source CFD-toolbox OpenFOAM®. Toluene droplets with a diameter of 2 mm rising in quiescent water were simulated in a fully three-dimensional domain. To quantify Marangoni effects, simulations with various initial concentrations of the transferred component acetone and with constant interfacial tension were performed. It was shown that the code captures essential characteristics of Marangoni convection, namely the mutual interaction of mass and momentum transfer, resulting in highly transient, three-dimensional velocity fields and mass transfer enhancement. The simulation results were compared with the experimental data of Wegener et al. (2007b). Regarding the transient rise velocity, a satisfactory agreement with the experimental results was achieved. The two-step acceleration, the reduced rise velocity and the terminal rise velocity of the binary system toluene/water were particularly well reproduced. In accordance with the experiments, the terminal rise velocity after reacceleration was lower than in the binary system. In contrast, the onset and the duration of the reacceleration deviated clearly from the experimental data. We believe that these discrepancies most likely stem from different initial conditions in simulation and experiment, as well as from a less satisfactory simulation of mass transfer. Compared to the experimental data, mass transfer rates are generally too high. Owing to the intense coupling of momentum and mass transfer, faster mass transfer would have to reduce the duration of Marangoni convection. It is likely that further grid refinement would improve the mass transfer results. Unfortunately, this is currently hindered by very long simulation times. In addition, the scaling model may permit unphysical convective mass transfer across the interface and, therefore, contribute to the higher mass transfer rates.

Furthermore, experimental and simulated droplet trajectories were compared. In agreement with the experiments of Wegener et al. (2007b), the droplets with constant interfacial tension rise in a straight path, whereas path oscillations are observed in simulations with Marangoni convection. We showed that these path oscillations were induced by the asymmetric detachment of vortices in the wake of the droplet. Moreover, the droplet trajectories feature a distinct break-out in a random direction which coincides with the onset of reacceleration. A similar break-out was observed experimentally by Wegener et al. (2007b). To the best of our knowledge, this effect has not been reproduced with CFD simulations before. Augmenting the theory of Wegener et al. (2009b), we have revealed that the break-out results not only from an asymmetric onset of internal circulations, but is significantly influenced by the detachment of vortices. Due to the good qualitative – and in several cases even quantitative – agreement with the experimental data, we expect that CFD simulations will help to an increasing degree to analyse complex transport phenomena at moving boundaries.
including Marangoni convection, swarm effects and the impact of surfactants. This will provide a basis for a further development of classical modelling methods, e.g. boundary layer theory for mass transfer and drag coefficients for fluid particles. Thus, we believe that CFD simulations will contribute to the design of liquid/liquid extraction processes in the near future. The droplets studied in this work remain essentially spherical. Thus, the capabilities of our CFD code to capture strong droplet deformations has not yet been exploited. Consequently, our future work will focus on Marangoni effects at oscillating droplets.
5. Acknowledgement

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Appendix A. Reinitialisation

As suggested by Sussman et al. (1994), the following partial differential equation can be solved to restore $\psi$ as a signed distance function:

$$\frac{\partial \psi}{\partial \tau} = \frac{\psi_0}{\sqrt{\psi_0^2 + \Delta x^2}} (1 - |\nabla \psi|)$$  \hspace{1cm} (A.1)

where $\tau$ is pseudo-time, $\Delta x$ grid spacing and $\psi_0$ the initial condition

$$\psi_0 = \psi(x, \tau = 0)$$  \hspace{1cm} (A.2)

During the reinitialisation, the zero level set $\psi(x, t) = 0$ is often displaced (cf. Sussman and Fatemi, 1999; Russo and Smereka, 2000) and, hence, the volume described by the level set function is changed. Fluid dynamics of droplets strongly depend on their volume which, consequently, has to be conserved exactly. To solve this problem, Hartmann et al. (2010) recently suggested adding a forcing term $\tilde{F}$ to the reinitialisation equation:

$$\frac{\partial \psi}{\partial \tau} = \frac{\psi_0}{\sqrt{\psi_0^2 + \Delta x^2}} (1 - |\nabla \psi|) + \tilde{F}$$  \hspace{1cm} (A.3)

The forcing term acts in cells adjacent to the interface and reduces the volume change during the reinitialisation; the formulation and a detailed derivation of $\tilde{F}$ can be found in Hartmann et al. (2010). In the present work, the HCR-2 scheme of Hartmann et al. (2010) was used.

Equation (A.3) is discretised in pseudo-time with a simple explicit Euler scheme in a predictor-corrector procedure. For the spatial derivatives, the third-order WENO finite difference scheme of Jiang and Peng (2000) is used. To reinitialise $\psi$, 10 pseudo-time steps with a step size of $\Delta \tau = \frac{\Delta x^2}{2}$ were performed every (physical) time step.

Despite the application of the HCR-2 scheme, volume changes still occurred in the course of a simulation. Therefore, an interface shift (cf. Gross, 2008) was implemented. After the reinitialisation, a correction $\tilde{\psi}$ is subtracted from the level set function to guarantee the following relation:

$$\frac{|V_d(\psi(x, t) - \tilde{\psi}) - V_{d, 0}|}{V_{d, 0}} \leq \epsilon_V$$  \hspace{1cm} (A.4)

where $V_d(\psi(x, t) - \tilde{\psi})$ is the droplet volume defined by the shifted level set function, $V_{d, 0} = V_d(\psi, t_0)$ is the initial droplet volume and $\epsilon_V$ is a tolerance set to $10^{-7}$ in this study. The correction $\tilde{\psi}$ is determined iteratively with a regula falsi algorithm. The shifted level set field $\psi_{\text{new}} = \psi(x, t) - \tilde{\psi}$ is then defined as the new level set function and used for the subsequent calculations. It was found that a rather small correction of $\tilde{\psi} \approx 10^{-3} \Delta x$ was required every second time step to conserve the volume. Thus, one may safely assume that the solution is not disturbed by the interface shift.
Appendix B. Moving reference frame

An approximation for the centre of mass of the droplet $x_s$ is given by the following expression:

$$x_s = \frac{\sum_i x_{ci}(1 - H_{\epsilon,i}(\psi_i))V_i}{\sum_i (1 - H_{\epsilon,i}(\psi_i))V_i}$$ (B.1)

where $x_{ci}$ are the cell centre coordinates of the finite volumes $V_i$ and $H_{\epsilon,i}(\psi_i)$ are the discrete values of the smoothed Heaviside function. The change of the moving reference frame velocity $\Delta v_F$ is calculated from the centres of mass of the current time $t^n$ and the previous time $t^{n-1}$:

$$\Delta v^n_F = \alpha_F \frac{x^n_s - x^{n-1}_s}{\Delta t}$$ (B.2)

where $\Delta t = t^n - t^{n-1}$ denotes the time step and $\alpha_F$ an under-relaxation factor set to $\alpha_F = 0.1$. Due to the under-relaxation, the coordinate system remains only approximately in the centre of mass of the droplet. However, it should be noted that it is not necessary to fix the coordinate system exactly to the centre of mass. The acceleration is obtained from

$$a^n_F = \frac{\Delta v_F}{\Delta t}$$ (B.3)

and can then be used in equation (7).
Appendix C. Mass transfer model

To assess the quality of mass transfer results obtained with the model used in this work (Eq. (23)), two test cases were considered: diffusion from a droplet at rest and mass transfer from a rising droplet. For the first test case, a toluene droplet with a diameter of 2 mm and an initial acetone concentration of 1 g/L was simulated in an axis-symmetric domain with a grid spacing of 10 µm. The continuous phase was quiescent water. The diffusivities and the distribution coefficient were the same as in Section 2.4. To limit the test case to pure diffusion, only the mass transport equation (23) was solved. An “exact” reference solution was obtained by solving the unsteady diffusion equation in a spherical coordinate system numerically with MATLAB®.

The resulting radial concentration profiles at three instants of time are shown in Fig. C.13. In comparison with the reference solution, the mass transport model, Eq. (23), leads to lower mass transfer rates from the droplet. Nevertheless, a reasonable agreement with the reference solution is achieved.

The second test case was taken from Bäumler and Bänsch (2013) and combines convective and diffusive mass transport. A toluene droplet with an initial diameter of 4 mm rising in water was simulated in an axis-symmetric domain. Densities and viscosities were set according to Table 5. Marangoni effects were not considered, and a constant interfacial tension of σ = 0.035 N/m was assumed. To facilitate the resolution of the concentration boundary layers, the diffusivities of acetone were increased by two orders of magnitude \( D_{Ad} = 2.90 \cdot 10^{-7} \text{ m}^2/\text{s}, D_{Ad} = 1.25 \cdot 10^{-7} \text{ m}^2/\text{s} \), resulting in a Batchelor length of approximately 25 µm. Simulations with three grid spacings ranging from 33.3 to 16.7 µm were performed. Bäumler and Bänsch (2013) used a very precise boundary fitted moving mesh method validated with experimental, analytical and semi-empirical results. Therefore, their data can be used as reference. The simulation results are shown in Fig. C.14. Even though our method predicts slightly lower mass transfer rates, a satisfactory agreement with the data of Bäumler and Bänsch (2013) is evident. Furthermore, our results show a good convergence with grid

![Figure C.13: Diffusion of acetone from a toluene droplet with a diameter of 2 mm in water. The solution obtained with mass transport model Eq. (23) (*) and the “exact” numerical solution (line) are shown at three instants of time.](image-url)
Figure C.14: The transient mean concentration of acetone $c^* = c_{Am}/c_{A0}$ in a toluene droplet with $d_0 = 4$ mm rising in water: Simulation results of this work in comparison with the data of Bäumler and Bänsch (2013). The diffusivities of acetone were increased by two orders of magnitude.

refinement. Consequently, our method provides reasonable predictions of mass transfer phenomena in the toluene/acetone/water system.
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