

# THREE-DIMENSIONAL SIMULATIONS OF MASS TRANSFER AT SINGLE DROPLETS

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## ABSTRACT

Mass transfer between a drop and its surrounding can cause differences in the surface tension which, in turn, leads to Marangoni convection. An exact prediction of the concentration range relevant for this effect and of its influence on the mass transfer rate and the relative velocity between the drop and the continuous phase is not yet possible, neither experimentally nor by simulation. The reason is the chaotic and inherently three-dimensional character of the phenomenon and the strong coupling between momentum and mass transfer.

This paper reports three-dimensional simulations of a whole drop (without symmetry assumptions). They were carried out using the commercial CFD code Star-CD. Relative velocities and mean concentrations in the drop were transiently simulated and compared with experimental results. For the concentrations a very good agreement was found for different initial concentrations. The velocities coincide qualitatively well and in some aspects also quantitatively. The main reason for differences is the process of drop formation and release in the experiments, which is not described in the simulations.

## NOMENCLATURE

$c$	concentration	$g/l$
$\bar{c}$	averaged concentration in the drop	$g/l$
$c^*$	dimensionless concentration	
$D$	diffusion coefficient	$m^2/s$
$dt$	time step	$s$
$Fo$	Fourier number	
$n$	face normal	
$p$	pressure	$Pa$
$R$	Radius of the drop	$m$
$t$	time	$s$
$\mathbf{t}$	tangential vector	
$\mathbf{v}$	velocity	$m/s$
$\mu$	viscosity	$Pa \cdot s$
$\rho$	density	$kg/m^3$

$\sigma$	interfacial tension	$Pa \cdot s/m$
$\boldsymbol{\tau}$	stress tensor	$N/m^2$
$\nabla_s$	Nabla operator along interface	

## Subscripts

0	initial
1	dispersed phase
2	continuous phase
A	acetone
$i$	interface
$n$	normal
$t$	tangential

## INTRODUCTION

The Marangoni effect caused by concentration gradients during mass transfer over an interface has been known for a couple of decades. The usual understanding of the process was not sufficient to describe the mass transfer enhancement in certain concentration ranges. Changes in the drop rise velocity or the linear rise path are also known but observed rarely, since they are suppressed in the case that surfactants are present in the system. Nevertheless, a quantitative description of the phenomenon is still missing, even if the number of different investigations is not small. Sternling and Scriven (1959) and others (e.g. Hennenberg et al., 1979, Hennenberg et al., 1980, Nakache et al., 1983, Slavtchev and Mendes, 2004) tried to derive the concentrations for the onset of Marangoni convection theoretically. But some groups found that their predictions does not hold for the toluene/acetone/water system (e.g. Mendes-Tatsis et al., 2002).

Mass transfer at a plain interface has been investigated e.g. by Molenkamp (1998) under low gravity conditions. He found Marangoni convection for the desorption of acetone from water into air and was able to describe his measurements by CFD simulations.

The effect of Marangoni convection on mass transfer was experimentally observed by a couple of groups (Henschke and Pfennig, 1999, Schulze et al., 2003). Recently it was even possible to formulate a quantita-

tive measure for the end of Marangoni convection in the system water / acetone / toluene based on the drop velocity and the concentration (Wegener et al., 2006). The simulation of the phenomenon is more difficult, because the chaotic convection structures need to be described. Henschke and Pfennig (1999) modeled the increase in the mass transfer by an additional dispersion coefficient. It does not depend on the actual concentration in the drop and needs to be determined experimentally. Therefore, it is not a promising approach for the simulation. Other groups like Mao and Chen (2004) and Yang and Mao (2005) used a complex modeling approach including interface deformation based on the volume of fluid (VOF) or level set methods. Their promising results have not yet been validated experimentally.

Our own results have shown, that two-dimensional (axisymmetric) simulations of a drop with a fixed shape but variable relative velocity to the continuous phase can describe the mass transfer in a system without Marangoni convection quantitatively (Paschedag et al., 2005a) and in a system with Marangoni convection qualitatively correct Paschedag et al., 2005b). Quantitative agreement could not be gained for a system with Marangoni convection, because the structure of Marangoni convection is chaotic and thus inherently asymmetric. Therefore, three-dimensional simulations are necessary.

## NUMERICAL SETUP

We investigate the transient mass transfer of acetone from a toluene drop to the surrounding water phase. Drops of 2 mm diameter have been studied for different initial solute concentration (up to 30 g/l acetone). The size has been chosen such that it is large enough to be reproducible in experiments but small enough for deformations to be insignificant. For the system considered the Schmidt number is about 220 in the drop and 715 in the continuous phase.

The simulations are carried out with the commercial CFD-code Star-CD extended by user subroutines (USR). Star-CD uses the finite volume method at unstructured grids. Time is discretized by the second-order Cranck-Nicholson-scheme while for space discretization the MARS-scheme is used, a version of QUICK with a limiter. For our simulations the VOF method for handling two-phase systems was not applied even though it is a feature of Star-CD. Instead, a fixed shape of the drop was assumed. This is a realistic approach for the drop size investigated and allows an accurate location of the interface at defined grid faces. There the jump condition is implemented.

The geometry modeled includes the drop and a cylinder with a diameter of five times the one of the drop (see Fig. 1). This size is sufficient to avoid effects of the domain boundaries on the flow field and the mass transfer in the surrounding of the drop. The whole domain is discretized in about 135,000 cells for the results presented here. Grid refinement is planned to judge the discretization error.

In the drop as well as in the domain of the continuous phase Navier-Stokes-equation and mass balance are solved separately:

$$\begin{aligned}\nabla \cdot \mathbf{v} &= 0 \\ \rho \frac{\partial \mathbf{v}}{\partial t} &= -\rho \mathbf{v} \cdot \nabla \mathbf{v} + \mu \nabla^2 \mathbf{v} - \nabla p \\ \frac{\partial c}{\partial t} &= -\mathbf{v} \cdot \nabla c + \nabla(D \nabla c)\end{aligned}\quad (1)$$

The coupling between the phases works by USR's for the domain boundary containing the jump conditions:

tangential stress:

$$\boldsymbol{\tau}_{nt,1} = \boldsymbol{\tau}_{nt,2} + \mathbf{t} \cdot \nabla_S \sigma \quad (2)$$

mass flux:

$$D_1 \left. \frac{\partial c_1}{\partial n} \right|_i = D_2 \left. \frac{\partial c_2}{\partial n} \right|_i \quad (3)$$

The normal stress needs not to be considered due to the fixed shape and incompressibility of the drop. The interfacial tension  $\sigma$  is a function of the acetone concentration. It was fitted to the experimental data from Misek et al. (1985).

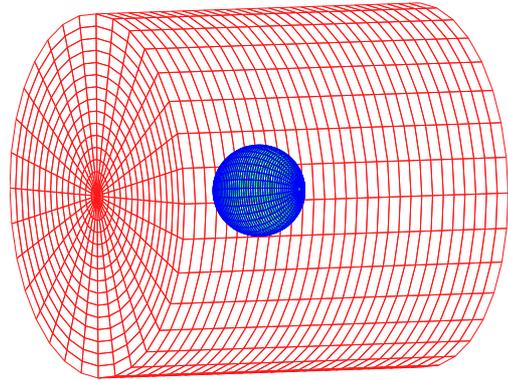


Figure 1: Grid of the simulated domain consisting of the drop and a cylindrical surrounding

In addition, the no-slip condition and thermodynamic equilibrium of the concentrations are assumed.

The dependency of the surface tension  $\sigma$  on the concentration, which is required to compute the surface gradient of  $\sigma$ , has been determined experimentally. For the system toluene/acetone/water a higher order polynomial expression for the whole relevant concentration range was found.

Marangoni convection does not only influence the mass transfer but also the drop rise velocity. Therefore, the actual drop rise velocity is determined by a force balance at the interface. In the system we use, the drop is fixed in the middle of the domain and the relative velocity of the phases is given by the inlet velocity of the continuous phase in the axial direction. Therefore, we can consider changes in the drop rise velocity by no deviation of the particle path from the vertical direction.

Eq.(2) and (3) are discretized and implemented as boundary conditions for each phase at the interface. Since the computation of the boundary values needs to be based on the values of the previous time step this is a first order fully explicit procedure which requires small time steps for accuracy as well as for stability. The formal maximum time step size can be derived from the Courant-criterion which leads to particularly small values because the cells near the interface are very thin. On the other hand, very small time steps lead to unstable fluctuations in the computation of the relative velocity (see RESULTS). Therefore a moderately larger time step is used which is still much smaller than the one required for the time discretization of the balance equations using the Crank-Nicholson-scheme.

Extension from former two-dimensional simulations to the actual three-dimensional model of the full 360°-domain requires the parallelization of the code. In general, this is foreseen in Star-CD but the handling of the user-subroutines, namely the computation of the drop rise velocity from the forces at the interface, demands user-defined domain decomposition and adaptation of the USR. Concerning the number of cells, the simulations have a medium size, the major reason for the high numerical effort is the relatively small time step required. Therefore, the parallelization of the code is efficient only for a small number of processors. The use of 9 processors instead of a single one reduces the wallclock time required for a simulation of 1 s from 105 hours down to an acceptable 19 hours.

## VALIDATION EXPERIMENTS

Experiments have been carried out to study the physical behavior of the drop and to validate simulations.

The results from the quantitative analysis of the measurements and the resulting interpretation for the interaction of Marangoni convection with the drop rise velocity and deviations from the vertical particle path have been documented by Wegener et al. (2006). A detailed description of the experimental setup can be found there as well.

The experimental setup is shown in Fig. 2. The central part is a glass column filled with the continuous phase. At the bottom the drop is formed at a capillary by a Hamilton pump. For the collection of the drops a funnel is used that can be installed at different heights. This is used to control the contact time between drop and continuous phase. The average solute concentration remaining in the drop after the contact is analyzed by gas chromatography. The transient drop rise velocity is determined using a high speed camera.

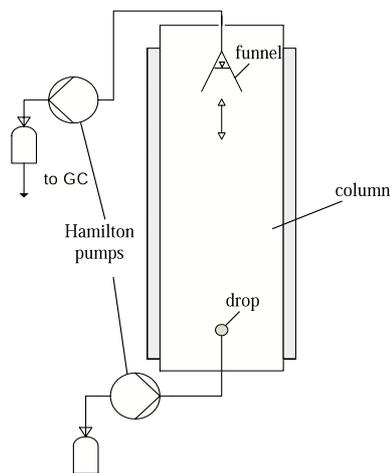


Figure 2: Experimental setup

## RESULTS

Simulations have been carried out for the mass transfer of acetone from a toluene drop to the surrounding water. Two initial acetone concentrations have been compared: 1.8 g/l and 30 g/l. For both initial concentrations the effect of Marangoni convection has been proven experimentally. Fig. 3 shows the comparison between simulation and experiments for the average concentration on the drop.

Very good agreement between simulations and experiments was found. This concerns the relative mass transfer rate of both concentrations as well as the good coincidence between the simulated curves and the measurement points. Especially for the 1.8 g/l case the simulation meets the slope of the experimental curve perfectly. This is a significant measure for

the correct implementation of the variable interfacial tension and the resulting Marangoni convection, since the slope of the curve is related to the mass transfer rate which depends strongly on the convective flow structure.

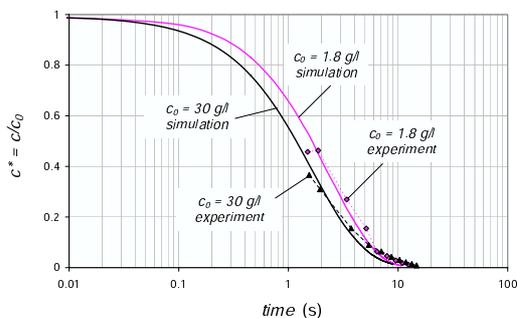


Figure 3: Mean solute concentration as a function of time. Comparison between experiments and simulations

A more theoretical classification of the results is shown in Fig. 4. The two numerical results from Fig. 3 are compared with simulations based on the same physical parameters but in one case with the assumption of a constant interfacial tension (right curve) and in the other case for an infinitely high diffusion coefficient in the drop (left curve). Dimensionless presentation has been chosen to allow comparison of the different concentrations.

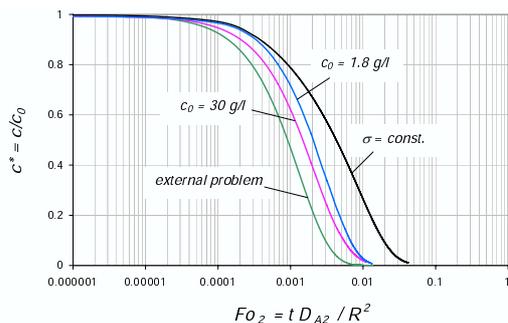


Figure 4: Classification of the simulated mean concentrations in the drop by comparison with limiting cases

The first simulation corresponds to an equivalent system without Marangoni convection. As discussed in the introduction, Marangoni convection leads to an improved mass transfer to the interface and therefore to an acceleration of the mass transfer between the

phases. This acceleration is visible for both initial concentrations and it is more pronounced for 30 g/l. The second curve shows the so-called external problem which is historically used to divide the mass transfer resistance in the drop from the one in the surrounding (Brauer, 1979). The external problem assumes perfect mixing in the drop and is therefore the limiting case for the mass transfer enhancement which can be reached by additional transport mechanisms inside the drop like Marangoni convection. It can be seen from Fig. 4 that the mass transfer in the two real cases is slower than in the external problem and that the real case curves are well between the limiting cases.

Fig. 5 shows the dimensionless concentration distribution in the drop in a cut in flow direction. In the first plot the interfacial tension is constant, in the other ones it is variable and the initial concentration varies. All figures correspond to a mean dimensionless concentration on the drop of 0.3 but it is obvious that the structures are significantly different depending on the initial concentration. The toroidal structure is more and more transformed into a chaotic structure the higher the initial concentration is and the higher therefore the gradients in interfacial tension are. This effect in the concentration field originates from an analogous change in the flow field.

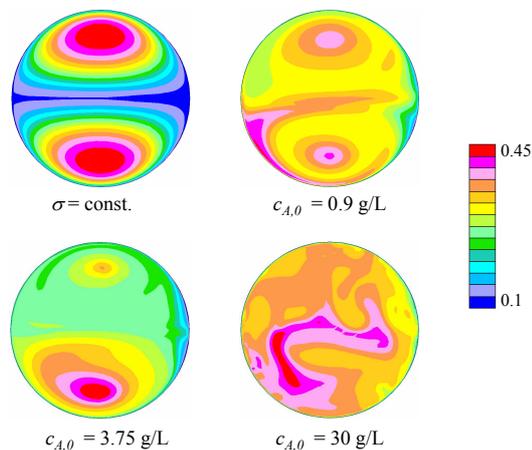


Figure 5: Dimensionless concentration distribution in the drop in a cut in flow direction at  $c^* = 0.3$  for different initial concentrations.

A second measured value which is influenced by Marangoni convection is the drop rise velocity (see Fig. 6). The differences in interfacial tension lead to different local velocities of the interface. Con-

sequently, the drag coefficient of the drop with Marangoni convection has about the same size as the one of a rigid sphere and the drop rise velocity is therefore reduced. For the 2 mm toluene drop in water the rise velocity of the equivalent rigid sphere is about 60 mm/s (gray line, corresponds to  $Re \approx 140$ ) while the one of the drop with freely moving interface ( $\sigma = \text{const}$ ) is about 100 mm/s (brown line, corresponds to  $Re \approx 230$ ). The crosses show the experimental result: Firstly, the drop accelerates to the velocity of the rigid sphere. Marangoni convection hinders a further acceleration. With time, the concentration in the drop is reduced and the differences in interfacial tension are no more relevant, Marangoni convection vanishes and the drop accelerates nearly to the velocity of the drop with freely moving interface.

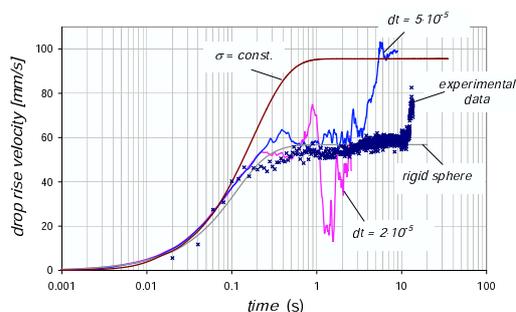


Figure 6: Drop rise velocity: limiting cases of the rigid sphere and the system with constant interfacial tension, experimental values and results of simulations with different time steps

The best impression is given by the video added. It shows the concentration of acetone in both phases for a  $90^\circ$  segment of the sphere. The view is perpendicular to the axis, so that both cutting planes are visible. The color scale is adapted to the temporary concentration maximum to keep the behavior visible. At the beginning, the structure is chaotic and fast fluctuations in space and time can be seen. With time they slow down and become more rough and at a certain point the toroidal structure characteristic for the undisturbed flow is visible. At the beginning this structure is not fully symmetric but it stabilizes more and more at both cutting planes. Together with the stabilization of the toroidal concentration structure the drop accelerates as shown in the blue curve in Fig. 6.

There were some stability problems in the simulation concerning this intermediate plateau effect, which are

best visible in the magenta curve but remain partly also in the blue one. Inaccuracies in the computation of the forces at the interface by adding them over all interfacial cells cause fluctuations in the computed rise velocity. For time steps smaller  $5 \cdot 10^{-5}$  s the instabilities rise to strong fluctuations which exceed physically meaningful values. For time steps of  $5 \cdot 10^{-5}$  s there are still fluctuations, but they remain within a reasonable range. At a simulated time of about 8 s the drop accelerates again in the simulation and stabilizes at the velocity of the drop with constant interfacial tension.

While the two velocity levels are well predicted and coincide also with the theoretical ones, the time of the second acceleration is not. There are two possible reasons for that. On one hand there are inaccuracies in the simulation. As the instabilities show, some problems remained in the simulation of the drop rise velocity which are not completely solved yet. The second reason can be found in the experiments. The mass transfer and the formation of internal flow structures starts with the formation of the drop and not with its separation from the capillary. These effects can not be considered in the simulations. Therefore, the initial state of the drop is slightly different in the experiments from the one in the simulations. This can cause differences in the results.

## CONCLUSION

Three-dimensional simulations of the mass transfer of acetone from a toluene drop to the aqueous surrounding have been carried out. In the concentration range considered, the mass transfer causes Marangoni convection related to the concentration dependence of the interfacial tension. This enhances the mass transfer compared to the case with constant interfacial tension but not as much as an instantaneous ideal mixing in the drop would do. The simulations show very good agreement with the measured transient mean concentration in the drop. This is a significant improvement to the two-dimensional simulations done before and shows, that the influence of the interfacial convection pattern can be reflected by the simulations if its chaotic structure is resolved well enough.

Both limiting cases have been simulated and it is shown that the results for the real cases lie between them.

A second aspect considered is the drop rise velocity which is also influenced by Marangoni convection. As long as the chaotic flow structures exist, the drop reaches only the velocity of a rigid sphere with the same properties. After reduction of the concentration

and the formation of a toroidal flow structure it accelerates again to a higher rise velocity. This two-step acceleration was found experimentally as well as numerically and in both cases the stable velocities correspond to the theoretical values. A difference was found for the onset of the second acceleration which may be caused by effects from the formation phase of the drop which is not described numerically.

Based on the results presented, a parameter study will be carried out which can be the basis for the formulation of a rule in which cases Marangoni convection can be expected and in which cases not. First clues were gained from experimental investigations, but simulations have less restrictions to the choice of parameters and allow therefore a more flexible detection of critical values.

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