**VOF-SIMULATION OF RISING AIR BUBBLES WITH MASS TRANSFER TO THE AMBIENT LIQUID**

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**ABSTRACT**

This paper presents numerical simulations of two-phase flow with high-density ratio, taking into account mass transport of a soluble component and its interfacial mass transfer. The mathematical model and the numerical method allow for different solubility of the species in the respective fluid phases, while volume changes due to mass transfer are neglected. The discontinuous changes in species concentrations at the interface are modeled by means of Henry’s law. Simulations are carried out with an extended version of the highly parallelized code **FS3D**, which employs an advanced Volume-Of-Fluid (VOF) method. Transfer and transport of oxygen is examined in case of single bubbles as well as bubble chains rising in aqueous solutions. Numerical simulations show good qualitative agreement with experimental data and render the observed mass transfer phenomena correctly.

**INTRODUCTION**

Many industrial applications based on two-fluid systems involve mass transfer operations such as extraction, gas scrubbing and waste water treatment in bioreactors. Examples in Chemical Engineering include bubble columns, loop reactors or agitated stirred reactors. For the design of efficient two-phase mass transfer reactors detailed knowledge of, say, particle sizes and shapes, slip velocities, internal circulation, swarm behavior, particle induced turbulence, particle size distributions (including coalescence and break-up) as well as the influence of surfactive species are of fundamental importance. Optimization of mass transfer units additionally requires profound understanding of the underlying mass transport and mass transfer processes. Here, numerical simulations provide a helpful tool to reduce the usually large experimental expenses for reactor design. Due to the increase in computational power, numerical simulations of two-phase flows based on continuum mechanical models with free interfaces become feasible and prove extremely useful for a better understanding of fundamental processes and phenomena.
Recently, much work has been devoted to this subject. Mass transfer of a dilute component between spherical drops and the ambient liquid has been studied in [1-3], while small surface deformations of axis-symmetric drops are allowed in [4]. The numerical simulations presented there assume that species concentrations are continuous at the phase boundary, i.e. the distribution coefficient (Henry coefficient in this context) of the dissolved species equals 1. Mass transfer due to the dissolution of a rising droplet of liquid CO₂ in the surrounding water has been investigated in [5, 6], taking into account the volume changes of the droplet. In case of dissolution of bubbles, the effect of surfactants has been studied numerically in [7, 8]. While the above mentioned contributions consider spherical or ellipsoidal drops or bubbles, theoretical studies of mass transfer across dynamically deforming interfaces require numerical methods that resolve the free phase boundary. Based on the VOF-method, mass transfer across such strongly deforming interfaces has been computed numerically in [9, 10]. The simulations presented in [9] are in 2D, either planar or axis-symmetric, with Henry coefficient equal to 1.0. The present paper is closely related to [10], where transfer of oxygen is simulated for air bubbles rising in water or aqueous solutions, taking into account the realistic jump discontinuity of the oxygen profiles at the phase boundary. Main emphasis is on single bubbles in liquids of higher viscosity to gather information about the relevant length scales involved. Furthermore, bubble chains are considered as a first step towards a better understanding of mass transfer in bubble swarms.

GOVERNING EQUATIONS

The motion of fluid particles is modeled as a two-phase flow with free phase boundary, based on continuum mechanics. We consider isothermal flows of two Newtonian fluids of constant density which are immiscible on the molecular scale. Inside the phases, balance of mass and momentum then leads to the Navier-Stokes equations, i.e.

\[ \nabla \cdot \mathbf{u} = 0 \]  
\[ \partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla p + \nabla \cdot \mathbf{S} + \rho \mathbf{g} \]  

with the viscous stress tensor

\[ S = \mu (\nabla \mathbf{u} + \nabla \mathbf{u}^T), \]

where the material parameters depend on the respective phase. Whenever distinction between the different phases is necessary, \( g \) (gas) and \( l \) (liquid) are used as phase indices. At the interface, the additional jump conditions

\[ [\rho (\mathbf{u} - \mathbf{u}_i)] \cdot \mathbf{n} = 0, \]

\[ [\rho \mathbf{u} \otimes (\mathbf{u} - \mathbf{u}_i) + p \mathbf{I} - \mathbf{S}] \cdot \mathbf{n} = \nabla_i \sigma + \sigma \kappa \mathbf{n} \]

appear, where \( \mathbf{u}_i \) is the interfacial velocity, \( \kappa = -\nabla \cdot \mathbf{n} \) is the curvature – more precisely, the sum of the local principal curvatures – of the interface and \( \nabla_i \sigma \) denotes the surface gradient.
of the surface tension. Here \( \mathbf{n} \) is the unit normal at the interface directed into the dispersed phase, say, and the notation

\[
[\Psi(x)] = \lim_{h \to 0^+} (\Psi(x + h \mathbf{n}) - \Psi(x - h \mathbf{n}))
\]

stands for the jump of a physical quantity \( \Psi \) across the interface. It is assumed that the two-fluid systems under consideration do not endure phase changes. Consequently, there are no convective fluxes across the interface and, hence, the normal component \( V = u \cdot n \) of the interfacial velocity coincides with the normal component of both the adjacent fluid velocities. Furthermore, since both fluids have non-vanishing viscosity, we suppose that there is no slip between the two phases at the phase boundary. Finally, constant surface tension is assumed. Then the interfacial jump conditions simplify to

\[
[u] = 0, \quad [p \mathbf{I} - \mathbf{S}] \cdot \mathbf{n} = \sigma \kappa \mathbf{n}.
\]

In the second equation in (7), the relation for the normal part reduces to the Young-Laplace equation, i.e.

\[
p_g - p_i = \sigma \kappa = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right),
\]

in case of stagnant fluids.

The local concentration \( c \) of a dilute chemical species is governed by the balance equation

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

where molecular fluxes are modeled by Fick’s law with constant diffusivity. This leads to the advection-diffusion equation

\[
\partial_t c + \mathbf{u} \cdot \nabla c = D \Delta c
\]

inside the phases. At the phase boundary, mass balance implies continuity of the fluxes, i.e.

\[
[-D \nabla c] \cdot \mathbf{n} = 0.
\]

Another constitutive equation is needed to determine the concentration profiles: We assume instantaneous thermodynamical equilibrium at the interface modeled by Henry’s law, i.e.

\[
c_i = c_g / H,
\]

with constant Henry coefficient \( H \). More details about continuum mechanical modeling of two-phase flows can be found in, e.g., [11] and [12].
THE NUMERICAL METHOD

Any reasonable method for the direct numerical simulation of incompressible transient two-phase flows needs to solve the Navier-Stokes equations (1), (2) together with the interfacial jump conditions (7). One basic difficulty is the fact that the material parameters of the fluid at time $t$ and position $x$ depend on which of the phases is present at $(t,x)$. The fundamental idea of the Volume-of-Fluid (VOF) method [13] employed here is to account for an additional scalar field, namely the phase indicator function, i.e. a function $f = f(t,x)$ with, say, $f = 1$ in the dispersed phase and $f = 0$ in the continuous phase. Due to the absence of phase changes, the transport of the dispersed phase is governed by the advection equation

$$\partial_t f + \nabla \cdot (u f) = 0$$

for $f$. Notice that (10) simply means that $f$ stays constant along flow trajectories.

Within this approach, discretization of the governing equations is usually done by the Finite-Volume method. Then the value of $f$ in a computational cell is given as the volume fraction of the dispersed phase in this cell. In this case the correspondences

$$
\begin{align*}
    f = 1 & \quad \text{dispersed phase} \\
    f = 0 & \quad \text{continuous phase} \\
    0 < f < 1 & \quad \text{interface}
\end{align*}
$$

hold. Hence the phase boundary is implicitly given by the values of the scalar field of $f$-values throughout the domain. Based on these values, an approximation of the interface normal can be computed. Combination of the fractional volume of the dispersed phase with the interface normal then allows for a piecewise linear interface (re-)construction, the so-called PLIC method by Rider et al. [14].

For transport of mass, we exploit the linear structure of equations (9), (10), (11) to incorporate Henry’s law into the concentration itself by considering the new scalar

$$
\tilde{c} = \begin{cases} 
    c_i & \text{inside the liquid phase} \\
    c_g / H & \text{inside the gas phase}
\end{cases}
$$

Notice that the interfacial jump of the species concentration is thereby shifted to a jump in the normal derivative. Indeed, the evolution of $\tilde{c}$ is governed by

$$
\partial_t \tilde{c} + u \cdot \nabla \tilde{c} = D \Delta \tilde{c}
$$

inside the phases and

$$
[\tilde{c}] = 0, \quad D_i \nabla \tilde{c}_i \cdot n = H D_g \nabla \tilde{c}_g \cdot n
$$

inside the phases.
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at the interface.

Computations are performed with an extended version of the three dimensional VOF-code \textit{FS3D}. The latter was developed at the ITLR Stuttgart [15] and is validated for the collision of droplets. Within \textit{FS3D}, the interface reconstruction is done by a PLIC-method which is an extension to 3D of the PLIC-algorithm mentioned above. The latter is used to advect the interface while keeping it sharp. The VOF-solver employed here is able to handle realistic density ratios of 1000 and more. Surface tension is taken into account based on a conservative approximation due to Lafaurie et al. [16]. The numerical solution of (14), (15) is based on the finite volume method. Prior to the diffusion step, the values of $\tilde{c}$ in those cells which share part of the interface are computed in such a manner that the resulting diffusive fluxes across the phase boundary will then satisfy (15). A basic validation of this approach has been performed in [17]. \textit{FS3D} is massively parallelized and the simulations presented here are run on a Siemens hpcLine with distributed memory consisting of 192 Intel Pentium-III, 850 MHz processors with 512 Mbytes working memory each. For more information on \textit{FS3D} see [18].

\textbf{MASS TRANSFER FROM RISING AIR BUBBLES}

The rate at which mass transfer between a rising air bubble and the surrounding liquid phase takes place depends on the complex interactions between the two-phase hydrodynamics, including surface deformations and convective as well as diffusive mass transport. Evidently, the mathematical model given above fails to admit exact analytical solutions of mass transport and mass transfer due to the dependence on the usually complex flow patterns. Existing analytical studies therefore rely on approximate solutions of the two-phase Navier-Stokes equations in axis-symmetric cases, like axis-symmetric Stokes flow around spherical bubbles; see [19-21] and the references given there. Even for such known velocity fields, (approximate) solutions of the species equation (9) and the interfacial jump conditions (10), (11) are only available for certain limiting cases. For this reason, numerical simulations play a large and increasing role in the investigation of mass transfer. As mentioned in the introduction, there are several numerical results concerning simulations of mass transfer, especially in simplified situations, like spherical bubbles/drops or axis-symmetric domains, which lead to two-dimensional problems [1-8]. On the other hand, experiments by Schlüter et al. [22] and Bork et al. [23] show asymmetric distributions of the dissolved component in the wake of bubbles in case of technically relevant large Reynolds numbers. A typical example is illustrated by Figure 1, showing an air bubble with strong surface deformations during its rise in water. The grey pattern which is discernible in the wake of the bubble corresponds to varying oxygen concentrations inside the water, made visible by means of laser induced fluorescence [23]. Since mass transfer processes in gas-liquid systems often involve turbulent flow fields and strongly deforming bubbles, a deeper understanding of mass transfer phenomena in such general situations is highly demanded. Consequently, theoretical investigations require three-dimensional numerical simulations of the two-phase balance equations without simplifying assumptions concerning, e.g., fluid flow or bubble shape. For computation of mass transfer and mass transport of dissolved chemical components, additional species equations have to be solved numerically.
The VOF-method, complemented by species equations, is appropriate for numerical simulation of two-phase flows with mass transfer across strongly deforming phase boundaries \[9, 10\]. This fact is illustrated by Figure 1 (right), showing the numerically computed distribution of oxygen inside the liquid phase around an 8 mm air bubble in counter-flowing water, about 0.75 seconds after the bubble was released. Inside the wake there are asymmetric regions of varying concentrations with steep gradients. During the bubbles rise, vortices are frequently shed into the wake and are advected by the flow before they vanish due to viscous dissipation. In addition to dynamical interface deformations this further contributes to turbulence, which enlarges mixing efficiency.

In principle, it is now possible to obtain, e.g., mass transfer coefficients from so-called Direct Numerical Simulations, i.e. simulations in which all physically relevant length scales are resolved by the computational grid. Unfortunately, the size of the smallest relevant length scale is often rather small and not a priori known. Concerning the hydrodynamics, a useful lower estimate is provided by the Kolmogorov length scale \(\lambda_K\), given by

\[
\lambda_K = \left(\frac{\nu^3}{\varepsilon}\right)^{1/4}.
\]  

This follows since the kinetic energy is dissipated at latest at that scale which corresponds to a local Reynolds number of 1. In (16) above, \(\nu\) denotes the kinematic viscosity of the respective phase and \(\varepsilon\) denotes the rate of energy dissipation per unit mass. For a rising bubble, the latter can be estimated as \(\varepsilon = \nu_0 g\), where \(\nu_0\) denotes the rise velocity. In case of an 8 mm air bubble rising in water, this leads to a length scale of 0.03 mm inside the liquid phase and 0.25 mm inside the gas phase. The actual grid resolution in the numerical simulation corresponding to Figure 1 is 32 cells per bubble diameter, which leads to 4 million cells with a size of 0.25 mm each. Hence inside the liquid phase, the cell size is about one order of magnitude larger than the Kolmogorov length scale. The situation becomes even worse if transfer and transport of a chemical species is taken into account: In case of rising bubbles, mass transport in a
neighborhood of the phase boundary is mainly due to diffusive fluxes in normal direction and convective transport in tangential direction. If convection dominates, extremely thin boundary layers with steep concentration gradients can build up. In such cases the smallest relevant length scales are determined by the Batchelor length scale $\lambda_B$, which is characterized by the condition that the time scales for diffusive transport of momentum and species coincide. This yields

$$\lambda_B = \lambda_K / \sqrt{Sc},$$

where $Sc$ denotes the Schmidt number, i.e.

$$Sc = \nu / D.$$ 

In case of gas-water systems with dissolution of a gaseous component in water, typical values for $Sc$ are about 600-800. Starting from a Kolmogorov length scale of 30 $\mu$m in case of larger bubbles with dynamic phase boundary, say, this leads to a Batchelor length scale of about 1 $\mu$m. From these estimates it becomes obvious that a true direct numerical simulation of mass transfer and mass transport in such gas-liquid systems is not possible yet. Therefore, in order to still gather experience about the length scales involved in such mass transfer processes, we consider air bubbles in liquids of higher viscosity.

Figure 2 shows the oxygen concentration fields around a 4 mm air bubble rising in a mixture of water and glycerol. For this system the numerical rise velocity is 0.12 m/s in reasonable agreement with the experimental value of 13.5 cm/s taken from [24]. This yields Kolmogorov length scales of about 0.7 mm inside the liquid phase and 0.24 mm within the gas phase. During its rise, the bubble takes an oblate ellipsoidal shape with aspect ratio of 0.86. The numerical simulations have been performed using two symmetry planes to enlarge the possible resolution. The actual resolution is 32 cells per bubble diameter which corresponds to a cell size of 0.125 mm. Therefore, the smallest hydrodynamically relevant length scales are resolved. In this situation, numerical simulations including mass transfer have been performed for $Sc=1$, 10, 100 and 1000.
As illustrated by Figure 2, an increase in the Schmidt number leads to a thinner concentration boundary layer at the interface. This results in steeper gradients of the concentration profiles in the direction normal to the phase boundary. Since these gradients determine the rate of mass transfer, the concentration boundary layer needs to be resolved in order to obtain results that are quantitatively correct.

While (17) gives an estimate about the magnitude of the film thickness, the true dimension of this concentration boundary layer is not a priori known. In case of mass transfer from bubbles rising in water-glycerol mixtures, information about this question can be gathered from numerical simulations: Figure 3 shows concentration profiles in the liquid phase inside the boundary layer adjacent to the interface. For Sc=1, the thickness of the concentration film (understood as the distance normal to the interface over which the concentration decreases by a factor of \( e = 2.718 \)) is about 1 mm outside of the wake. Due to the relation (17) and Sc=1, this value should coincide with \( \lambda_K \) and the latter has been estimated above as 0.7 mm. Therefore, the numerical simulation confirms this estimation. For higher Schmidt numbers the thickness decreases. With the actual resolution, the concentration boundary layer is resolved for Sc=10, in which case the concentration film has a thickness of about 0.3 mm. Sc=100
seems to be the borderline case with film thickness of approx. 0.1 mm. For Sc=1000, the boundary layer is not resolved by the computational grid. These numerical results approve the assertion that the smallest length scale relevant for mass transport is inversely proportional to square root of Sc. Moreover, equation (17) gives a good estimate of this length scale in the situation considered here.

Figure 3: Simulated oxygen profiles inside the liquid phase near the equator of the air bubble. Concentration of oxygen versus normal distance (in cm) for different Schmidt numbers.

Let us note in passing that information about the structure of the concentration profiles can be used for the development of subgrid-scale models in order to describe the flux of the dilute component across the interface with higher accuracy.

MASS TRANSFER IN BUBBLE CHAINS

Efficient mass transfer processes in gas-liquid systems require large interfacial areas. For bubble columns this means large gas hold-ups, hence bubble swarms instead of single bubbles occur. It is well known that the interaction of bubbles in a swarm has significant influence on the rise behavior of individual bubbles. Of course the same can be expected concerning mass transfer and mass transport. Investigation of mass transfer in bubble chains may serve as a first step towards a better understanding of the interactions between several bubbles concerning mass transfer.

Figure 4 shows the distribution of oxygen in the liquid phase surrounding a gas bubble rising in a bubble chain. The gas phase is composed of 90% oxygen and 10% helium. To avoid dynamic surface deformations, the bubbles rise in an aqueous CMC-solution with dynamic viscosity of 25 mPa·s. The vertical bars correspond to varying concentrations of oxygen, visualized by means of laser induced fluorescence; see [23] for more details.
Results of two-dimensional numerical solutions are shown in Figure 5. The gas phase enters through a nozzle at the bottom of the computational domain, carrying a given initial oxygen concentration. The bubbles rise in line, such that each of the subsequent bubbles rises in the oxygen wake of the preceding one. This reduces the difference in the concentrations of oxygen between locations inside the bubble and in the ambient liquid, which is the local driving force for mass transfer. Hence a smaller rate of mass transfer is observed for the successive bubbles. This also appears in numerical simulations as illustrated by Figure 6.

**CONCLUSIONS**

The VOF-method with additional species equation is appropriate to describe two-phase flows with mass transfer and mass transport. Numerical simulations of bubbles with dynamic surface deformations show good qualitative agreement with experimental data. Investigation of bubbles rising in water-glycerol mixtures confirm that the smallest relevant length scales concerning mass transfer are given by the Batchelor length scale. Finally, first simulations in 2D reproduce the experimentally observed reduction of mass transfer rates in bubbles chains compared to single bubbles.
REFERENCES


Bothe and Warnecke, VOF-Simulation of rising air bubbles


