Chapter 1

Introduction

In many multiphase contact apparatuses in chemical engineering, bio-chemical and pharmaceutical industry, new insights into mass transfer processes across fluidic interfaces are essential for process optimization and reliable process control. The need for high quality drugs in pharmaceutical industry or for sustainable production of specialty and bulk chemicals provides the driving force for more detailed investigations. Multiphase contact apparatuses are used to transfer gaseous reactants from a highly dispersed gas phase across the gas-liquid interface into a liquid solvent. The gas transfer should be immediately and ideal everywhere, since the dissolved gas is going to be consumed by a chemical or biochemical reaction and side reactions or a malnutrition of cells are often minimized by avoiding high gradients of concentration. This means, that the mass transfer performance from the dispersed gaseous into the continuous liquid phase can be the bottle neck for a certain process and therefore be dominant for a whole production and its process efficiency. In general, mass transfer across interfaces can be influenced by global and local boundary conditions. For example, the physical properties of the fluids or global boundary conditions e.g. temperature and pressure can effect the potential of mass transfer, which means the saturation of a fluid by a certain specie, which directly affects the potential mass difference, which can occur at the interface. Also, local boundary conditions can be affected e.g. by fluid dynamic conditions as, for example, kinetic energy of the fluid elements or dissipation and mixing. The transferred mass at the interface into the continuous phase needs to be transferred away from the interface and mixed into the bulk, where it can consumed by a preferred chemical reaction. This already shows, that there are several ways to influence the mass transfer performance by controlling the boundary and local conditions in gas-liquid contact apparatuses.

The coupling of fluid dynamics, mass transfer and chemical reaction have been investigated for decades, but due to its interlinked complexity usually simplified or isolated

approaches regarding one or two transfer processes are taken into account only. For example, mass transfer processes across gas-liquid interfaces have been investigated to understand the coupling of hydrodynamics and mass transport processes and to describe and correlate them for certain geometries of gas-liquid flow apparatuses and usually small ranges of process parameters. An important parameter for instance is the bubble rise velocity v_B that affects the fluid dynamic conditions for the dissolution process in bubbly flows. Therefore, for example, free rising bubbles in pure and contaminated systems [Cli78] [Alv05] have been investigated to understand the influence of bubble size and fluid properties such as viscosity and surface tension. Interaction with geometrical reactor parameters has also a strong influence on the flow structure around bubbles, their shapes and behavior [Kri99] [Bro65]. Elongated bubbles in channels are called Taylor bubbles [Tay61] and can be found in multiphase reactors of various scales such as monolith reactors, pipe reactors many more. For a hydrodynamic description of Taylor bubble flows, it is required to distinguish two flow conditions; the rising Taylor bubble which induces a flow field around the bubble by the buoyancy force, and the pressure-driven flow where bubbles are transported through a channel by the flowing liquid. Taylor bubbles are rising by buoyancy as long as the pipe or channel diameter D is larger than the critical inner diameter D_{crit} calculated by the critical Eötvös number Eo_{Dcrit}. The Eötvös number

$$Eo_D = \frac{(\rho_l - \rho_g) \cdot g \cdot D_h^2}{\sigma} \quad (1.1)$$

is defined as the ratio of the buoyancy force to the interfacial tension, where σ is the interfacial tension, ρ_l and ρ_g are the densities of the liquid and gaseous phases, g is the magnitude of the gravitational acceleration and D_h is the hydraulic diameter of a channel. D_{crit} is about 5.4 mm in a pure air-water system, but D_{crit} is of course strongly depending on the systems surface tension. Transport processes at sequential gas-liquid Taylor flows in small channels ($D_h < D_{crit.}$) are often used in "Lab-On-a-Chip" micro fluidic devices or other simple continuous small scale applications, where pressure differences are needed to provide these flow structures, but those are off-topic in this work. For buoyancy driven flows in channels $D_h > D_{crit.}$, it is known that the rising velocity v_B of Taylor bubbles is independent of the bubble volume. The independence of v_B on the bubble volume enables the suspension of Taylor bubbles at a fixed elevation in vertical channels by an equivalent counter current flow. Filla [Fil81] has shown the applicability of bubble fixation by a counter current flow and measured the liquid side mass transfer of single CO_2 Taylor bubbles by a photographic technique in a vertical tapered channel. Esteves and de Carvalho [Sen93] conducted experiments on the mass transfer from very long single Taylor bubbles, of which the ratio of bubble length to D_h is larger than 10, in large channels of $D_h = 32$ mm. Hosoda et

al. [Hos14a] carried out experiments on the mass transfer from single CO_2 bubbles in vertical pipes of 12.5 - 25mm. They have developed a following Sherwood number correlation for Taylor bubbles rising in vertical pipes according to

$$Sh = \frac{k_L \cdot d_{eq}}{D_L} = (0.49\lambda^2 - 0.69\lambda + 2.1)\, Pe^{1/2} \tag{1.2}$$

where k_L is the mass transfer coefficient, D_L the diffusion coefficient and λ the diameter ratio, which is the ratio of the sphere volume equivalent bubble diameter d_{eq} to D_h. Here the Peclet number Pe is defined by

$$Pe = \frac{v_B \cdot d_{eq}}{D_L}. \tag{1.3}$$

Eq. 1.2 is valid for $\lambda = 0.6$ and applicable to the prediction of long-term dissolution processes of single CO_2 Taylor bubbles in water ($D = 12.5 - 25$ mm).
Though several studies on the mass transfer from Taylor bubbles in channels were carried out as discussed above, our knowledge on mass transfer from single buoyancy-driven Taylor bubbles in smaller channel diameters and on effects of channel cross-sections on the mass transfer are still rudimentary, especially for $D_{crit.} < D_h < 12.5$ mm. Additionally, Taylor bubbles in these channels sizes combine some main advantages compared to free rising bubbles, like the volume independent rise velocity and the suppressed shape dynamics even for comparable large bubbles. Therefore, these Taylor bubbles with low Eo number are the ideal multiphase system to investigate global and local transport processes at rising or fluid dynamically fixed bubbles. This enables even close-ups of the interface during a untypical long time period for bubbly flows.

During past decades, empirical correlations on the characterization of global transport processes and their general interaction in reactive bubbly flows and enabled to design effective industrial processes. Nowadays, the fast development of Computational Fluid Dynamics increased the pressure on the experimental research to provide even local data of transport processes and chemical reactions for validation and to understand the complex interaction of timescales of transport, mixing and reaction for an optimized production with high yield and selectivity. The combination of global and local measuring techniques in the complexity reduced multiphase system of Taylor bubbles enables new insights into fluid dynamics and mass transfer process as well as the overall mass balance of the transferred specie. The transfer from aqueous systems to industrial relevant solvent systems is the key use-case for new, fast and safe methods for reactive process design. The validation of global and local data from CFD and experimental investigations at Taylor bubbles will enable new insights into the interlinked transfer processes of reactive systems and will lead to reliable process control for "transparent" chemical plants in times of industry 4.0.

Chapter 2

State of the art and basic knowledge

2.1 Gas-liquid flows in channels

In chemical engineering contact apparatuses like bubble columns or pipe reactors (e.g. heat exchangers) are used, for the dispersion of one phase into another, to create a large interfacial area between those phases, enabling a high specie transfer and good mixing conditions. Here flow maps help to choose the ideal flow condition to design a reactor for a given reaction. Usually, the chemical reaction is expected in the liquid phase, where two or more reactants are brought into contact, which were either transported from gas to liquid phase or have been pre-dissolved. Thereby, the mass transfer from the gas into the liquid phase is often a critical point in terms of efficiency but a controllable process by adapting flow rates, interfacial area and mixing [Hew69, Kra17].

If a gaseous phase is dispersed into a liquid, bubbles are generated due to the interfacial tension between the two phases. Here the liquid is defined as continuous phase and the gaseous phase is the dispersed phase. The multiphase regimes can be adapted by the variation of the volume flow rates of both phases, where in gas-liquid flows usually the gas hold up ε_g is used, which is the ratio of the gas volume V_g to the total volume V_{total} of the system. The occurring regimes are characterized by visual differences and flow phenomena. The flow regimes depend also strongly on the reactor geometry and its solid walls, e.g. vertical channels, solid internals, stirrers or heat exchangers, which define the absolute boundaries of the fluid dynamics system. Typical flow regimes of gas-liquid systems in vertical channels can be seen in Fig. 2.1, which are described as bubbly, film/annular, plug or slug flow. The actual visual display of the regimes can vary, depending on fluid viscosity and interfacial effects, which become actually more dominant, with smaller reactor geometry. To enable local investigations in multiphase sytems, a reduction of the complexity is needed to reduce stochastic phenomena, to establish quasi steady conditions and to ensure a high experimental
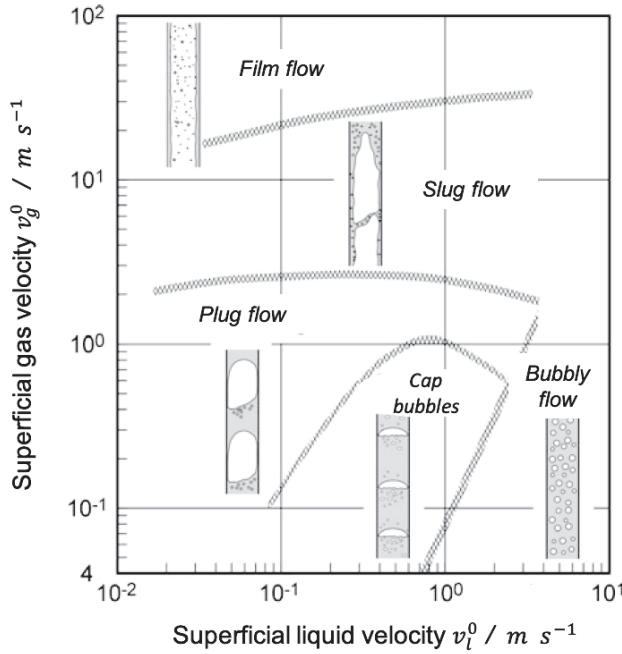
Fig. 2.1 Multiphase flow regimes in vertical pipes in terms of superficial gas velocity v_g^0 vs. superficial liquid velocity v_l^0 after Kraume [Kra17].

reproducibility. These are required conditions to enlarge the possibility of fundamental research to identify general interactions and dependencies of local transport phenomena. In the following chapter, the fundamental processes of fluid dynamics and mass transfer are described on simplified single bubble models, before the influence of channel walls on the transport processes is introduced. Afterwards, the main scientific findings of historical and recent investigations on rising bubbles in vertical channels will be introduced, before the lack of knowledge in this research field leads to the scientific goals of this work.

2.2 Transport processes in bubbly blows

2.2.1 Fluid dynamics at free rising bubbles

Industrial multiphase applications usually require a high gas hold up ε_g, which is the ratio between the gas volume V_g and the total reactor volume $V_{tot.}$ and a strong mixing to ensure a high specific interfacial area a enabling a high mass transfer from gas to liquid phase. The high phase interaction and fluid mixing leads to a high number of homogeneous distributed small bubbles in those reactors and therefore establish homogenous conditions for reactant transfer and following reactions. But those bubbles cannot be approximated as a single free rising bubbles. Bubbles in swarms or plumes influence massively their movement, shape dynamics and wake structures and therefore the mixing inside the liquid bulk phase. These combined effects are influencing the local temporal mass transfer performance, the selectivity of chemical reactions and therefore the overall process efficiency. The empirical correlations for a process design are usually depending on the simplified rise regime of single bubbles, because those are much easier to reproduce and to investigate with e.g. optical techniques than bubble swarms with their stochastic behavior. The investigation of local phenomena of transport processes in complex interlinked stochastic multiphase systems would require an enormous experimental or numerical effort. To ensure the accessibility of local mass transfer processes or even chemical reactions, usually strongly simplified multiphase systems are chosen. In this way the experimental reproducibility is enhanced, which aids to verify observed phenomena and derive the cause and impact of the interrelation of transfer processes. Therefore, fundamental research in multiphase flows is usually done with single bubble experiments to understand the impact of parameter variations on specific processes, before the findings are transferred to more complex gas-liquid flows with a higher grade of interaction and stochastic behavior.

The movement or rising of gaseous particles or bubbles in multiphase gas-liquid systems has been investigated since decades, by many scientists describing the fundamentals for various systems and conditions e.g. Brauer [Bra71] and Clift [Cli78]. This work focuses on water based systems with different gaseous phases under standard conditions (T, p, etc.) and excludes special phenomena of viscous effects, like non-newtonian fluids. In the following, the main fundamental findings are summarized and introduced for additional details the reader is refered to basic literature from e.g. Clift et al. or Brauer.

In general, particle movement in multiphase systems is described as the movement of a relatively small separated phase volume, which is dispersed into another continuous phase, where the particle can be solid (excluded here) or fluid (either gas or liquid) and the continuous phase is fluid (either gas or liquid). Depending on the density ρ_i of both phases, the particle

can sink or rise in the continuous phase. This is described with the buoyancy force

$$F_{B,i} = g \cdot \Delta\rho_i \cdot V_i \tag{2.1}$$

where, i is the phase indicator, ρ is the density and V is the volume of the phase. If a particle is dispersed inside a fluid and has a lower density than the continuous fluid it displaces, the force balance will be negative and therefore pointing against the gravitational acceleration g, which leads the particle to rise. If the density of both phases is the similar or identical, the particle is neutrally buoyant and follows the motion of the continuous phase. The movement of a spherical particle that has a relative velocity to the surrounding liquid velocity, e.g. a small bubble, is often parameterized using the dimensionless Reynolds number

$$Re = v_P \cdot d_B / \nu \tag{2.2}$$

which is determined as the ratio of inertial to viscous forces. Here, v_p is relative velocity of the bubble with a diameter d_B and ν is the viscosity of the continuous phase. In the following, the moving dispersed fluid particle, indicated by the subscript P is generally a gaseous bubble, indicated with the subscript B, and the continuous phase is an aqueous solution.

The movement of a bubble can be described by the force balance of the buoyancy force Eq. 2.1, here for a spherical bubble,

$$F_B = g \Delta\rho \, d_B^3 \, \frac{\pi}{6} \tag{2.3}$$

and the counter acting drag force,

$$F_D = C_D \, d_B^2 \, \frac{\pi}{4} \frac{\rho_l \, v_B^2}{2} \tag{2.4}$$

which is mainly effected by the fluid properties like density ρ_l, the bubble diameter d_B, the drag coefficient C_D and the relative bubble velocity $v_{B,rel}$. With the force balance between Eq. 2.3 and Eq. 2.4 the rise velocity of a bubble can be calculated as

$$v_B = \sqrt{\frac{4}{3} \frac{d_B \, g \, \Delta\rho_i}{C_D \, \rho_l}}. \tag{2.5}$$

In stagnant liquid v_l, the absolute rising velocity $v_{B,abs}$ of a bubble is equal to the relative velocity $v_{B,rel}$. For flowing liquids $v_l \neq 0$ the relative motion has to be taken into account according to

$$v_{B,rel} = v_{B,abs} - v_l. \tag{2.6}$$

The influence of the physical properties of the gaseous phase on the bubble movement, such as density ρ_g and viscosity η_g, can usually be neglected compared to the properties of the fluid such as density ρ_l, surface tension σ and dynamic viscosity η_l. The drag of any particle depends on friction between the dispersed particle and the continuous phase. For low Reynolds numbers the friction dominates and fluid particles have the same drag coefficient than rigid particles according to Stokes law, where

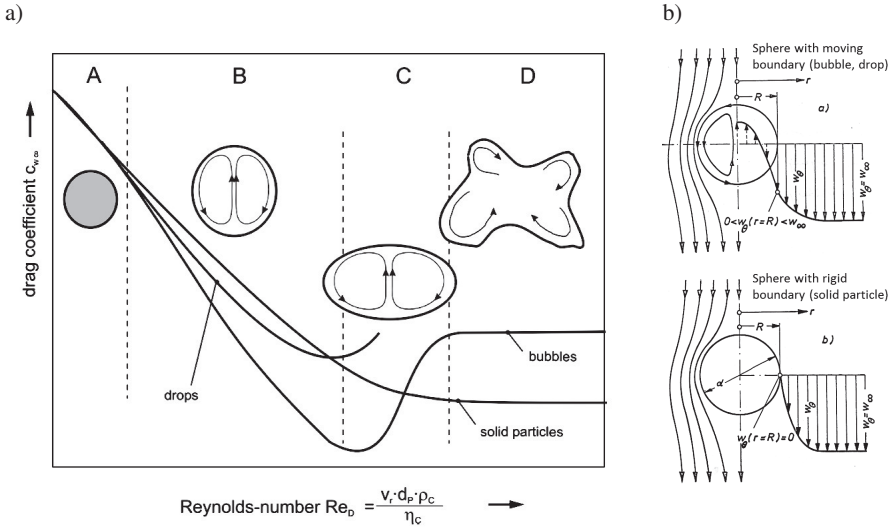$$C_D = \frac{24}{Re}; \ Re \leq 0.1 \tag{2.7}$$

a)

b)

Fig. 2.2 Interface mobility and fluid properties affecting the drag coefficient of particles. a) Drag-coefficient of solid (no-slip), fluid and gaseous particles [VDI15] ; after Peebles [Pee53]; b) Theoretical comparison of the interface mobility of fluid and solid particles and their effect on the local velocity field [Bra71].

gas, liquid and solid particles have the same C_D (compare regime A in Fig. 2.2 a)). In regime B, fluid particles start to develop internal circulation flows, induced by friction between the phases at the interface, which changes the boundary condition from no-slip to slip at the interface in Fig. 2.2 b). Therefore, the higher liquid velocity at the interface leads to a reduced friction and to a lower C_D than for solid particles. The overall C_D for particles in regime B is given as

$$C_{D,tot} = \frac{8}{Re}\left(\frac{2+3\kappa}{1+\kappa}\right) \tag{2.8}$$

the dynamic viscosity of dispersed (η_d) and continuous phase(η_c), where its ratio is named κ

$$\kappa = \frac{\eta_d}{\eta_c}. \tag{2.9}$$

With increasing Re number of fluid particles, those are first being deformed to ellipsoidal and further to irregular shapes, which influences the particle cross-sectional area in flow direction and leads to dynamic changes in Drag-coefficients compared to solid particles with constant cross-sectional areas [Pee53], as shown in Fig. 2.2 a). According to Fig. 2.2) regime B, it is obvious that C_D of spherical droplets lay in between solid particles ($\eta_p \to \infty \Rightarrow \kappa \to \infty \Rightarrow C_{D,p} = \frac{8}{Re} \cdot 3 = \frac{24}{Re}$) and bubbles ($\eta_b \to 0 \Rightarrow \kappa \to 0 \Rightarrow C_{D,p} = \frac{8}{Re} \cdot 2 = \frac{16}{Re}$). The ability of a fluid particle to deform from a sphere into an ellipsoid or irregular shape is affected by the fluid properties and the interfacial tension of the fluids. Usually, there are three dimensionless numbers in fluid mechanics to describe the movement and shape of dispersed fluid particles; the earlier defined Reynolds number, the Eötvös number 1.1 and the Morton number. The ratio of viscous forces and surface tension σ defines in the Morton number

$$Mo = \frac{g\,\eta_c^4\,\Delta\rho}{\rho_c^2\,\sigma^3} = \frac{We^2}{Re^3 \cdot Fr}, \tag{2.10}$$

which depends only on fluid properties. The Morton number can also be expressed by the ratio of other dimensionless number like the Weber number We

$$We = \frac{\rho_c\,v_B^2\,d_B}{\sigma}, \tag{2.11}$$

and the Froude number

$$Fr = \frac{v}{\sqrt{g\,d_B}}. \tag{2.12}$$

But not only the fluid properties itself can affect the behavior of dispersed bubbles and drops, also impurities or process additives with surface active parts can reduce the surface tension or the interfacial mobility, which leads to different rise velocities for bubbles in pure and contaminated water. This effect is shown in Fig. 2.3 and can additionally change the transition of the rise regime B to C and C to D for free rising bubbles (compare Fig. 2.2). The reason for this effect of contamination are introduced in the following chapter.