Chapter 1

Introduction

In today's process industry the efficient supply of oxygen as an oxidant is a central part for various kinds of applications. To utilize oxygen for a process the gas has to be dissolved in the liquid reaction medium. This is mostly done by aeration of the medium where the oxygen is provided by mass transfer across gas-liquid interfaces in multiphase contact apparatuses. The optimization of these complex two-phase reactor systems is still of high interest in terms of saving resources as well as enhancing yields. This study is motivated by the fields of biocatalytic and chemical process engineering. The low solubility of oxygen in liquids under ambient conditions is often limiting the effectiveness of the reaction. For fast chemical reactions in multiphase flows, the mass transfer limitation is usually the bottleneck for a process optimization and becomes crucial with regard to process design and scale up. This results in a high demand for efficient aeration techniques in process industry.

Concerning enzymatic oxidations, not only optimizing the mass transfer is of interest. Most enzymes are sensitive to shear forces which can lead to enzyme denaturation and therefore to a reduced productivity. Commonly used aeration techniques generate macroscopic bubbles with diameters in the order of several millimeters. Here, critical aspects in terms of occuring shear stresses are the bubble formation, the relative velocity between rising bubbles and the liquid phase as well as bubble break-up and coalescence. Also, excessive foaming resulting in a reduced enzyme activity has to be prevented. Therefore, bubble dynamics characterized by the bubble size distribution as well as rising velocities are crucial parameters with a direct influence on the performance of the reactor and therefore a central point for research.

Within this study, a novel aeration technique using fine bubbles is analyzed. The aeration with microscopic bubbles smaller than 100 μm, which can dissolve into the liquid very quickly, is a promising alternative to conventional aeration. Due to their small size and the acting surface tension, fine bubbles appear nearly spherical, resulting in the highest volume

specific interfacial surface areas and therefore high mass transfer rates. Furthermore, fine bubbles are characterized by their low rising velocities of just a few millimeters per second due to the small acting buoyancy forces. This leads to smaller induced shear forces at the bubble interface as well as long residence times in the system. The number of bubbles reaching the surface of the liquid phase is reduced compared to macroscopic bubble aeration which benefits the efficiency of the mass transfer and reduces the foaming at the same time.

The potential of using fine bubble aeration in process engineering is investigated experimentally in this work. The results are presented from smallest to largest bubble sizes and with rising level of complexity. The smallest observed bubbles at nanometer scale (ultrafine bubbles) offer the highest volume specific interfaces. In the last ten years, research on ultrafine bubbles has been increased especially in Asia. This relatively young field of research is controversially discussed due to conflicts between reported stabilities of ultrafine bubbles and conventional thermodynamic approaches. A first proof of existence of ultrafine bubbles is adressed in one part of this work as well as an evaluation of their utilization possibility for process engineering.

For determining the efficiency of different fine bubble aeration techniques, different reactor concepts are investigated at laboratory scale with a focus on hydrodynamic and mass transfer characteristics. Therefore, three frequently used reactor systems are considered:

- bubble column reactor

- jet reactor

- stirred tank reactor

For a better understanding of mass transfer effects at microscopic scale, the dissolution process of single fine bubbles is analyzed by means of laser induced fluorescence.

Chapter 2

State of the art and basic knowledge

Within this chapter, the fundamentals on fine bubbles with a maximum diameter of $d_B = 100\,\mu m$ and their applicability for process industry are given. The focus is on clarifying the terminology of fine and ultrafine bubbles as well as characterizing their behavior with regard to hydrodynamics and mass transfer. Therefore, the relevant basics of bubbly flows are described in general and the differences between macrosopic bubbles and fine bubbles are pointed out. In consideration of process applications, the basic knowledge on aerated stirred tank reactors is explained within this context.

2.1 Definition and fundamentals of fine bubbles

The smallest existing bubbles with diameters of several micrometers and smaller are characterized by physical and thermodynamic properties differing from those of macroscopic bubbles. This chapter clarifies the terminology of fine bubbles and points out different possible applications of fine bubble technology. The fundamentals of ultrafine bubbles are discussed in detail due to a lack of a unified accepted theory about their thermodynamic stability.

2.1.1 Classification of fine bubbles

In order to achieve a uniform definition all over the world for the different bubble size ranges, the technical committee 281 "Fine bubble technology" (ISO/TC 281) has been established in 2013 by the International Organization for Standardization (ISO). The ISO/TC 281 has classified fine bubbles with regard to their size and characteristics within the standard ISO 20480. This work follows the recommendation of ISO 20480, where a **fine bubble** is defined as a gas-filled cavity with a diameter smaller than $100\,\mu m$. Fine bubbles are further divided

into **microbubbles** with diameters larger than 1 μm and **ultrafine bubbles (UFB)** with diameters smaller than 1 μm (compare figure 2.1). In literature, often the term nanobubble is used instead of ultrafine bubble. Due to ISO/TS 80004-1, specifying a nano-object being smaller than 100 nm, the term nanobubble can indicate missinterpretations and is not used within this work. Microbubbles and ultrafine bubbles differ not only in size but also in their physical properties and application possibilities. Therefore, the fundamentals on microbubbles (see section 2.2.3) and ultrafine bubbles (see section 2.1.3) are considered separately. Due to greater similarities in the characteristics of microbbbles and conventional bubbly flows, both scales (microscopic and macroscopic bubbles) are discussed together in chapter 2.2.
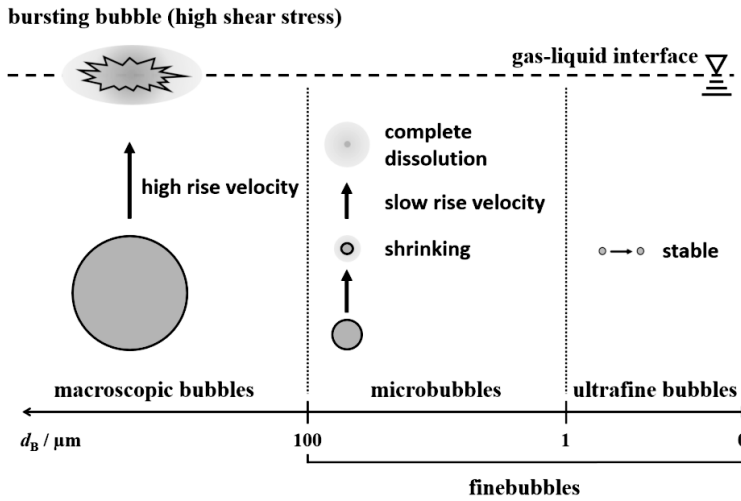

Fig. 2.1 Characteristics and classification of fine bubbles according to ISO 20480 and a comparison with macroscopic bubbles based on [Tho20]

2.1.2 Fields of application for fine bubbles

In the last decades, there has been a strong increase in world wide research on bubbles at diameters of several micrometers and smaller. The fields of application studying these fine bubbles are numerous. In the 1980s and 1990s the potential of fine bubbles as ultrasound contrast agent for medical diagnostics was found [Mil81, DJ91, Sch95, Shi97, Cal98] and later on, microscale bubbles are used for more efficient water treatment by flotation and ozonation [Chu07, Chu08, Bur97, DR94]. Due to their characteristics, fine bubbles have

found further applications in recent years. Today, fine bubbles are also used for drag reduction in liquid flows [Ush12, Ush13], cleaning applications [Wu08, Ush11], to improve the fuel efficiency of gasoline engines [Oh13, Nak13] and in aggriculture as well as food industry [Ebi13, Liu13b] or the biochemical process industry [Mah15, Dem12, Doi05, Dru15, Li18, Pet14, Qi02, Yin13, Zim09]. This diversity is reflected in a worldwide increase of research with regard to fine bubbles over the last 40 years. This is quantified by the still growing annual number of scientific papers published on the subject of fine bubbles as shown in figure 2.2.

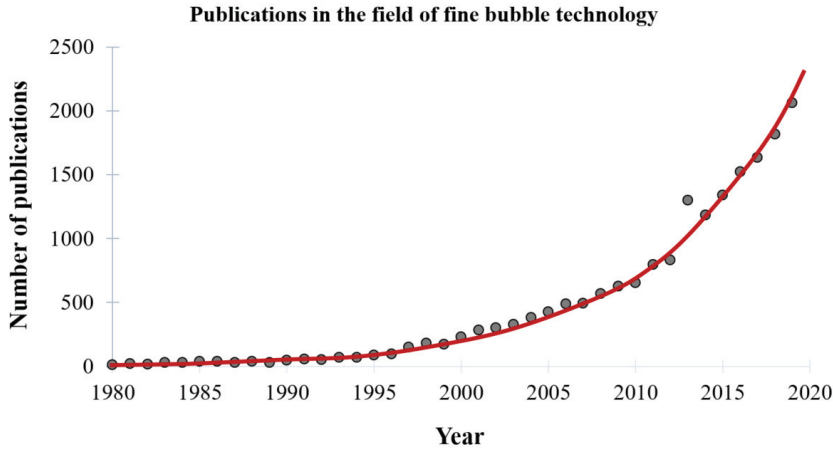**Publications in the field of fine bubble technology**

Fig. 2.2 Annual number of papers published on the subject of fine bubbles for the last 40 years

Starting early with the research on fine bubbles, Japan has now a leading role in this field. In Japan, many research groups are working on fine bubbles by focusing not only on fundamental studies, but also on industrial applications. In 2013, the Fine Bubble Industries Association (FBIA), and in 2015, the Union of Fine Bubble Scientists and Engineers (FBU) have been established in Japan to foster the scientific exchange and the collaboration with industrial partners. Initiated by this, more and more reasearch projects on fine bubbles have started outside of Japan during the last years.

2.1.3   Characteristics and physical models describing ultrafine bubbles

The existence of UFB and their application for processes is a controversely discussed topic in todays scientific community [Alh16, Bal12]. The disagreement about the stability of gas

bubbles in the nanometer scale is based on the occurance of mass transfer from the gaseous phase inside the bubble into the liquid phase due to a present concentration gradient. Epstein and Plesset [Eps50] as well as Ljunggren and Eriksson [Lju97] have shown, by solving the differential equation governing the shrinkage of a small spherical gas bubble in a liquid phase, that there is no thermodynamic stability of such small bubbles. An UFB inside a liquid describes a metastable system. Any small disturbance is sufficient to disrupt the system, leading to either a shrinking or a growing of the bubble. Even in saturated liquid, a bubble with a diameter of $d_B = 1000$ nm would dissolve in approximately 0.02 seconds [Alh16]. The decisive factor which has to be considered is the surface tension σ which results in an increase of pressure inside the bubble. The total pressure inside a bubble

$$p_B = p_{atm} + p_{hyd} + p_{YL} \tag{2.1}$$

is composed of the atmospheric pressure p_{atm}, the hydrostatic pressure due to the liquid p_{hyd} and the Laplace pressure p_{YL}. According to the Young-Laplace equation, the Laplace pressure

$$p_{YL} = \frac{4\sigma}{d_B} \tag{2.2}$$

results due to the acting surface tension and increases with a decrease of the bubble diameter. For example, the Laplace pressure of an oxygen bubble in water gets more than ten times the atmospheric pressure at a diameter of $d_B = 70$ nm. Epstein and Plesset [Eps50] have pointed out the influence of the surface tension by showing that only a neglection of the surface tension from the calculation leads to a stable UFB in saturated liquid. For UFB, a distinction must be made between surface UFB, sticking to mostly hydrophobic surfaces, and bulk UFB. As the usable measurements techniques and possible explanation approaches differ for these two kinds, they are considered seperately.

Surface ultrafine bubbles

In contradiction to the theoretical work negating an existence of stable UFB, Parker et al. [Par94a] have found first evidence that nanoscale bubbles are stable for several hours at hydrophobic surfaces. Force measurements between two hydrophobic surfaces moving slowly towards each other in water have shown an increased attraction which cannot be explained by the acting van der Waals force. Additionally, the attraction force is not homogeneously distributed over the surfaces. Steps and discontinuities in the force have been measured along the surface, which is attributed to the presence of nanosclae bubbles at the

surface [Att13, Par94a]. By using atomic force microscopy (AFM), a first direct experimental evidence of surface UFB has been found by Lou et al. [Lou00] and Ishida et al. [Ish00] in 2000. The AFM enables a visualization of the gas-liquid-solid three-phase contact line and therefore information about bubble size and contact angle [vL11]. With the use of infrared spectroscopy, Zhang et al. [Zha07] have succeded to identify the substance inside the bubble as well as proving its gaseous state. Besides proving the existence of surface UFB, Zhang et al. [Zha07] could determine the pressure inside the UFB beig in the same magnitude as the atmospheric pressure. There are multiple theories which try to explain the existence of surface UFB by solving the contradiction between the calculations and the measurements. The theories are devided into two groups: one refering to **geometric effects** and the other refering to **thermodynamic effects**.

Geometric effects

A central part of most theories is the correct modeling of the surface tension of an UFB. Zhang et al. [Zha06b] and Attard et al. [Att13] have used the dependency of the contact angle on the surface tension to show that the literature values are not applicable for surface UFB. The contact angles measured by using the AFM data deliver up to 100% larger values compared to the macroscopic advancing contact angle [Zha06b, Zha06a]. This is pointing out a much lower value of the actual surface tension. The geometric effects influencing the surface tension consider the disturbance of the bubble shape and the influence of the curvature [Tol49, Kay86, Fra00]. Since the literature values and most measurement techniques for surface tensions assume a planar interface, there is a source of error. To quantify the change in surface tension due to geometric curvature, Attard et al. [Att13] have used molecular simulations which have shown that this effect is only significant for bubbles smaller than 1 nm. Therefore, **geometric effects** are negligible for the stability of UFB.

Thermodynamic effects

A **thermodynamic effect** is the influence of supersaturation of the liquid on the surface tension [Moo03, Moo04]. As reported by Epstein and Plesset [Eps50], a supersaturated liquid is required for longterm stability of a bubble. Using analytics (virial method) as well as Monte Carlo simulations, He et al. [He05] have pointed out the influence of supersaturation on the surface tension. The surface tension is reduced by a factor of up to five depending on the degree of supersaturation [He05]. Thus, a supersaturation of the liquid has two positive effects on the stability of UFB by reducing the concentration gradient as well as the pressure

inside a bubble due to a lower surface tension. As it is hard to achieve an absolute clean liquid, there are also theories which rely on contaminations that adhere to the interface lowering the surface tension [Duc09]. A layer of contamination around the bubble would additionally act as a barrier for diffusion. Another approach relying on thermodynamic effects is the dynamic equilibrium model stated by Brenner and Lohse [Bre08]. For surface UFB, independent of gas type and temperature, the Knudsen number Kn is always larger than one [Sed11, Sed12]. In that case, the fluid dynamics based on a continuum mechanics approach can no longer be used to model the problem. Statistical methods must be used instead. Applying these to a surface UFB, indicate a upward movement of the gas molecules inside the bubble inducing a circulation of the gas-rich liquid close to the surface [Sed11, Sed12]. Benefitted by the flow field, Brenner and Lohse [Bre08] explain the stability of the UFB due to a balance in the incoming and outgoing gas flux of the UFB. This "dynamic equilibrium" ensures that surface UFB are reaching a stable size. The achievement of the dynamic equilibrium is benefitted by the fact that the mass transfer from the bubble into the liquid does not get accelerated by an increasing Laplace pressure. As reported by Lohse and Zhang [Loh15], the curvature of a surface nanobubble reduces during the shrinking process due to the pinning of the contact line, leading to a reduced Laplace pressure.

Bulk ultrafine bubbles

Bulk UFB, being completely surrounded by the liquid phase, differ from surface UFB not only by their ideal spherical shape and the absence of a third solid phase. In contrast to surface UFB, for a bulk UFB the Knudsen number of the gaseous phase is no longer larger than one [Sed12]. Hence, the fluid dynamics and therefore models suitable for surface UFB are not transferable. Though, a stability due to a reduced surface tension caused by either supersaturation of the liquid phase or contaminaton of the interface could be also valid for bulk UFB. One of the biggest challenges in research on bulk UFB is the existing lack of suitable measurement techniques. Regarding the surface tension, there is so far no possibility of a measurement neither directly nor indirectly (as done by using the contact angle dependency for surface UFB). A first approach has been done by Ohgaki et al. [Ohg10] using attenuated total reflection infrared spectroscopy to characterize the hydrogen bonds at the gas-liquid interface of nitrogen UFB in water. Some research on bulk UFB focuses on how the presence of UFB influences liquid properties, which requires highly accurate measurement systems. One approach is the measurement of the liquid density, reducing with rising number density of UFB [Ohg10]. Using nuclear magnetic resonance (NMR) spectroscopy, the paramagnetic effect of water is analyzed. Samples of water including

UFB show an increase in the spin-lattice relaxation time T_1 compared to UFB free samples [Ush10, Liu13b]. The higher T_1 values are attributed to the presence of a gaseous compound changing the physiochemical properties of the sample. A central part of UFB research is finding a suitable measurement technique for their detection and a clear evidence of their gaseous state. Commonly used are laser-based measurement techniques relying on the effect of dynamic light scattering (DLS) [Cho05, Ohg10, Ush10, Wan19]. One of these techniques is the Nanoparticle Tracking Analysis (NTA), delivering information about particle size distributions as well as concentrations (compare chapter 4.1). A disadvantage of these systems is that they cannot distinguish between solid and gaseous phases since both diffract the light similar at the nanoscopic scale. Therefore, further methods are additionally used to classify the physical state of the particles. By instantaneously freezing a droplet containing UFB (using for example liquid nitrogen), freeze-fractured replica are created. Analysis of these replica, using transmission electron microscopy (TEM), identify UFB by their smooth surface in contrast to solid nanoparticles [Ohg10, Uch11]. The freeze-fractured replica also give information about number density distribution and concentration of UFB inside the sample.

Using molecular dynamics (MD) simulations, Weijs et al. [Wei12] have shown that bulk UFB are stable in pure liquid under special conditions. A cluster of UFB stabilizes itself when the bubbles are at a distance smaller than five times their diameter. This shielding effect is produced by the saturation of the liquid in between of the UFB [Wei12]. To have the bubbles stable for long time, bubble collision has to be avoided. One possibility is the addition of salt which slows down the coalescence of UFB at low concentrations [Jin07]. Another possible explanation is the existence of electrostatic repulsion forces between the bubbles to maintain the distance. This explanatory approach is in good accordance to many other theories explaining the stability of bulk UFB due to an electrokinetic potential at the gas-liquid interface. Measurements of the zeta potential are used to quantify the electrical charge of the UFB [Kim00, Cho05]. An accumulation of negatively charged ions at the interface would create a negative pressure. The "coulomb repulsion force" is acting opposite to the surface tension and compensates its effect on the mass transfer [Bun09, Duv12]. Furthermore, Duval et al. [Duv12] make the electric interaction between charged UFB and ions being in solution accountable for the reported long lifetime of UFB up to several days [Ush10, Ebi13, Wei13, Wan19]. One possible explanation for the electrical charge of an UFB is the adsorption of hydroxyl ions at the interface [Kel96, Ush10, Wan19]. In contaminated liquid, Yasui et al. [Yas16] have shown that the dynamic equilibrium model of Brenner and Lohse [Bre08] is also applicable for bulk UFB which are covered with hydrophobic material.

If more than 50% of the bubble surface is covered, the gas enrichment at the hydrophobic material leads to a balance of the incoming and outgoing gas flux.

Especially with regard to bulk UFB many different theories exist, relying on different physical effects. Some models are just applicable under special conditions and as well an interaction of different effects are responsible for the stability of UFB in aqueous solutions. Table 2.1 gives an overview of today's theories explaining an UFB stability and their respective restrictions. The fact of still having no measurement technique for a direct detection of UFB and a missing worldwide accepted theory proving their stability is leading to the existing controversy in the scientific community on that topic.

Table 2.1 Overview of published theories explaining the stability of UFB

physical effect	application	restriction	reference
influence of curvature on σ	surface UFB and bulk UFB	negligible for $d_B > 1\,\text{nm}$	[Tol49], [Kay86], [Fra00], [Att13]
influence of supersaturation on σ	surface UFB and bulk UFB	maximum reduction of σ up to $1/5$	[Moo03], [Moo04], [He05]
contamination of interface	surface UFB and bulk UFB	no quantification	[Duc09], [Yas16]
dynamic equilibrium of gas in- and outflux	surface UFB	$Kn > 1$	[Bre08], [Sed11], [Sed12]
diffusive shielding	bulk UFB	theoretical model	[Wei12]
electrically charged surface	bulk UFB	theoretical model	[Kel96], [Ush10], [Duv12], [Wan19]