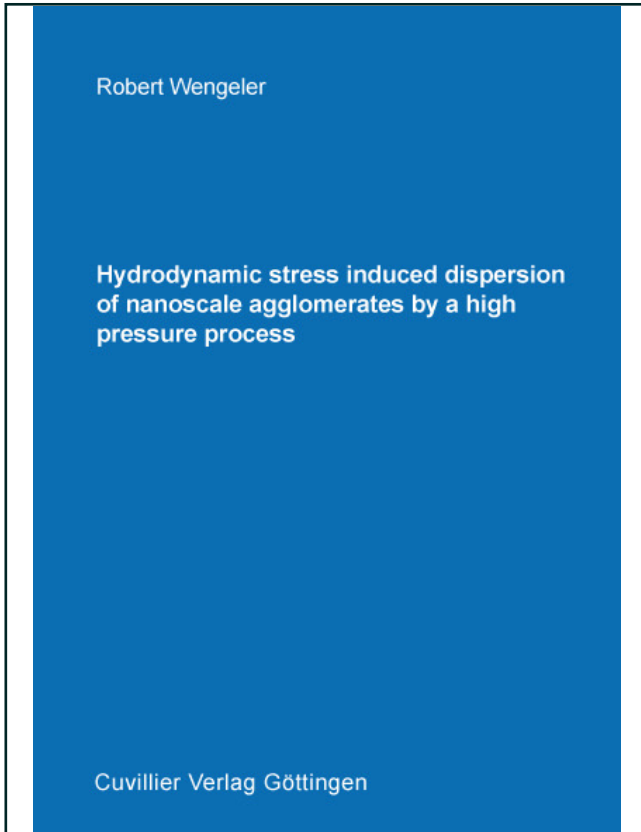




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**Hydrodynamic stress induced dispersion of  
nanoscale agglomerates by a high pressure process**



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# Chapter 1

## Introduction

Nanoscale particles have created an immense interest in industry, research and politics within the last five to ten years. They even have touched social and political debates in the context of the ‘nano’-hype of national and european research funding, nowadays resulting in further debates on their safety. New products, where nanoscale particles play a major or minor role, are introduced into the markets labelled with ‘nano’. In this area an increasing innovative action is predicted for the next years. Especially, nanoscale particles dispersed in a continuous phase are important. That is because various functional properties of materials are improved or altered by nanoscale particles. Especially processing of nanoscale particles in high turnover products like polymer composites, coatings or pharmaceutical agents is economically and technically attractive.

### 1.1 Nanomaterials - application and processing

Nanomaterials or nanostructured materials are defined as materials with internal structures of characteristic dimensions below 100 nm, which contribute to functional material properties. Nanoscale particles of this dimension play a major role as structuring, disperse phase in a continuous fluid or solid matrix. These kinds of materials are known as nanocomposites.

Nanocomposites may incorporate an increased mechanical strength, astounding abrasive and chemical resistance compared to standard composites with micron scale particles. Additionally, they may exhibit special optical properties, defined electrical or superparamagnetic characteristics (Kodas and Hampden-Smith 2000). For controlling functional properties, their structure becomes important. Nanoscale particles might be homogeneously distributed and dispersed primary particles. These would result in totally different functions than network structures or fractal agglomerates constituting the disperse phase. By providing defined structures like oriented chain-like aggregates or locally increased particle concentrations even anisotropic material properties are possible. Yet, dispersion and

structuring processes are solved for individual technical processes and still are a challenge to engineering and processing of nanoscale particles.

The process path from chemical reactants to innovative nanocomposite products leads from particle synthesis, functionalisation, dispersion and compounding, through various processing and formulation steps to product packaging and distribution. Thus the particles are passing a long value creation chain, while functionality and properties of the final product are determined already in the first three process operations. Thus, specific nanoscale properties have to be controlled throughout the individual unit operations of particle synthesis, functionalisation and dispersion and preserved in the further processes.

Also, from a process engineering viewpoint the specific nanoscale properties have to be considered. I.e. the high specific surface area and the resulting catalytic activity have to be considered for safety reasons, strong interparticle forces may lead to agglomeration but also may be used for desagglomeration and will have a significant impact on rheology and abrasiveness. Electrodynamic effects due to particle charging may be used for permeation, filtration and functionalization.

## 1.2 Problem definition

Aerosol synthesis of nanoparticles has been studied in numerous research and engineering projects on laboratory and industrial scales. At present a broad spectrum of nanoscale particles is at hand, where particle properties and synthesis processes can be readily controlled. Figure 1.1 schematically presents a typical particle synthesis route in flame technology.

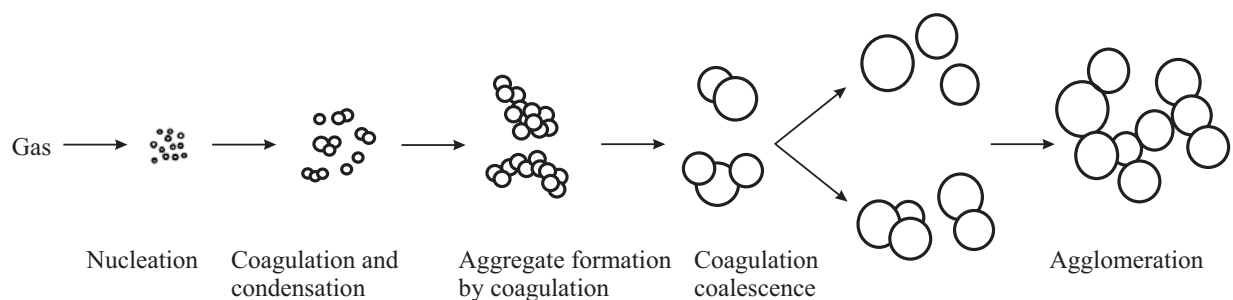


Figure 1.1: Schematic representation of particle growth and agglomeration processes in flames adapted from Kodas and Hampden-Smith (2000)

Precursor and oxidizing gases mix at high temperatures initializing the reaction, condensation and nucleation of particles. Particle sizes increase by surface reaction and coagulation due to high number densities of nuclei. Subsequently, aggregates are formed, while

coagulation and coalescence leads to larger spherical particles. Depending on process conditions non-agglomerated or strongly aggregated particles are formed. Most importantly, the temperature-residence time profile as well as the concentration of particles and chemical species, the reaction stoichiometry, have to be controlled. Each process step has undergone detailed studies on modeling, kinetics and process control. Therefore, new developments enable the tailored synthesis of structurally and chemically defined composite nanoparticles with specific flame synthesis reactors.

Yet, the production of nanocomposite materials still faces enormous challenges. Likewise to particle synthesis, the subsequent processing steps leading from individual particles to final products still need ongoing scientific investigations. Difficulties in particle processing result in slow integration of nanocomposites in consumer products. Therefore studies of manufacturing processes are needed with a focus on specific nanoscale properties and differences in processing nanoscale and conventional particles.

In the process of liquid dispersion these differences are laid clear. Pyrogenic nanoparticle dispersion is investigated in this work based on experimental studies and developing a new process understanding based on a computational fluid dynamics simulation which shall give a contribution to process development for nanomaterials. Here, special emphasis is given to the interaction of nanoparticles with each other and in multiphase liquid flow compared to macroscopic particles.

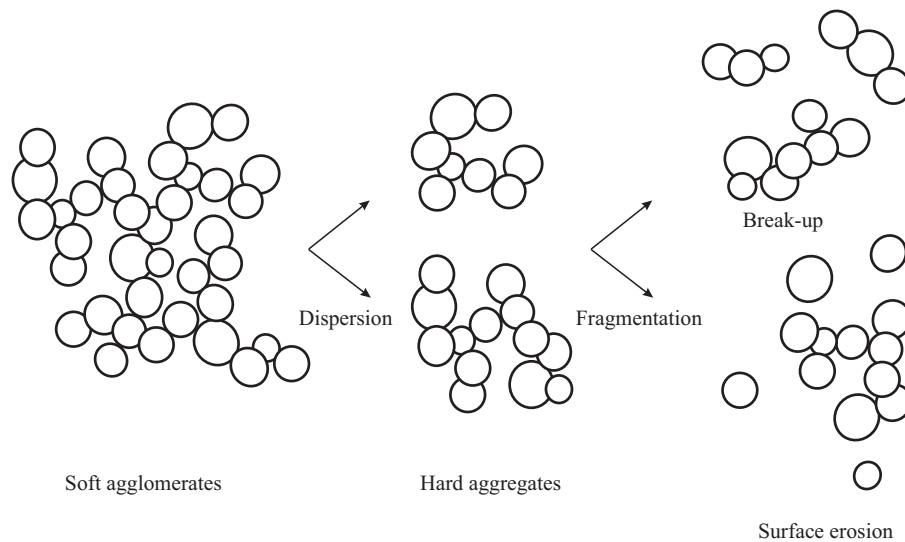


Figure 1.2: Schematic representation of the dispersion process as studied in this work distinguishing soft agglomerates and aggregates as well as break-up and erosion

Dispersion describes the agglomerate breakage and homogeneous distribution of particles in a surrounding liquid. The definition can be extended incorporating the wetting

of aerosol particles and their stabilisation. Figure 1.2 schematically shows the focus of this work. Pyrogenic nanoparticles are dispersed in liquid, where soft agglomerates desagglomeration at low mechanical energy input. Higher stresses result in a fragmentation of aggregates of pyrogenic particles, leading to a differentiation of physical and chemical bonds. Break-up and erosion mechanisms are distinguished for desagglomeration and fragmentation. Additionally, agglomerate structure is measured and studied in the dispersion process.

Computational fluid dynamics allow to quantify the stresses of the chosen, well defined high pressure dispersion system. Thus agglomerate strength and the scaling behavior of the dispersion process are analyzed and compared to other processes.

## Chapter 2

# Dispersion processes - state of the art

The state of research for dispersion process design is displayed starting with an overview on processes for dispersion, which are used for nanoparticles. Each process is introduced by describing typical machinery, its operation and process models (section 2.1). Global process models like the energy density approach and population balances, are presented and discussed in section (2.2). Physical models can include wetting, breakage and stabilisation as integral parts of a dispersion process. Since this work focuses on agglomerate breakage, wetting and stabilisation will only be discussed in brief (section 2.3), while consequently a detailed overview of breakage models is given (section 2.4). From these, open questions will be deduced in section 2.5, which are being tackled in this work.

### 2.1 Overview on dispersion processes for nanoscale agglomerates

Various processes have been realized for all kinds of different dispersion tasks. In post-synthesis processing, soft agglomerates can be dissociated by mechanical stirring with low energy agitation (Saltiel et al. 2004) or ultrasonication (Kusters et al. 1993). However, often higher stresses need to be applied in order to break even physical bonds, e.g. by stirred ball-mills (Kelsall et al. 1973), high pressure dispersion or high shear mixing (rotor-stator systems; Pohl (2005)). Only few technical realizations of the corresponding equipment can be applied to the dispersion of nanoscale or submicron sized particles, where especially high energies are required, and due to high abrasion.

Stirred ball mills are applied for comminution and dispersion of fine dispersed particles in various industries (coating, colors, mineral processing, pharmaceuticals, nutrients). A conventional stirred ball mill consists of a stirrer (orifice plates, which are mounted on a floating axle), a comminution space filled with grinding balls, and a casing with motive drive. In proximity to the orifice plate the grinding balls are accelerated by normal and

shear forces. Agglomerates are dispersed between the grinding balls due to strong shear stresses (Stehr 1982). Particles are often contaminated from the milling media during ball milling (contamination goes up to 20 – 30% mass milling media / mass nanoparticles (Breitung 2006)) and even phase transformation can be induced (Sen et al. 1999). Therefore for nanoscale dispersion and comminution autogenic processes are preferred. Fluid dynamic models of the two phase flow of nanoscale suspension and grinding balls as well as population balance models have been developed for process design.

High shear mixing is often realized by a rotor-stator system, where a high speed rotor rotates inside a stator with a narrow slit. I.e. the revolution is controlled in the range of 4,000 – 25,000  $\text{min}^{-1}$  for an Ultraturray T25 (IKA). Different multistage and inline systems for industrial applications are available (i.e. from IKA, Germany and Kinematica, Switzerland). High throughputs are possible, especially for the inline systems. In the spacing between rotor and stator energy is dissipated in form of shear and elongational stresses in turbulent flow while cavitation might add to energy dissipation by imploding bubbles.

Ultrasound sonotrodes produce sound waves, which result in cavitation and small scale turbulency. An optimal design of the process vessel concerning energy dissipation is absolutely necessary for efficient dispersion or comminution (Behrend 2002). Ultrasonication initially breaks up agglomerates, however continued ultrasonication can lead to soft reagglomeration (Aoki et al. 1987). Studies also confirm the possibility for nanoscale agglomerate dispersion (Higashitani et al. 1993; Pohl 2005). Due to low throughputs and difficult scale-up this process is predominantly used in laboratories despite a continuous process design.

In high pressure dispersion processes agglomerates desintegrate by passing a suspension through a dispersion device at high pressure drops, typically  $\Delta p > 800$  bar. Nozzles, microchannel systems, homogenization valves and others are used as dispersion device (Schultz et al. 2002). Within or in the proximity of these devices hydrodynamic stresses in the turbulent flow yield particle stressing. High pressure processes often are used for emulsification in life science and nutrition industries, especially when nanoscale droplet sizes are required. Yet, highly abrasive inorganic nanoparticle suspensions lead to short nozzle live times, thus challenging machine design. Recent developments realize pressure drops up to 3000 bar enabling new applications, especially for nanoscale agglomerates. Further, ongoing developments propose feeding the nanoscale suspension into the turbulent jet at the nozzle outlet as a ‘post-feeding-process’ (Sauter and Schuchmann 2006). Still, for solid-liquid suspensions high pressure dispersion is seldomly used, industrial applications are known for Aerosil dispersion (Lorz and Batz-Sohn 2003), where ‘Aerosil’ is the brand name for pyrogenic products by Degussa AG like silicas, titania or alumina.

## 2.2 Global process models

Global process models characterize the dispersion in a certain machine or process equipment. Two widely used models are the ‘energy density’ model for comparison in terms of energy efficiency and population balance models to characterize the dynamics of the particle size distribution within the process.

The ‘energy density’ approach considers the dispersion process as black box. It relates a mean agglomerate size  $d_{Agg}$ , as a measure for dispersion effectivity, against a specific energy input per unit volume of suspension which has been proposed as ‘energy density’ by Karbstein (1994). Figure 2.1 shows a comparison of ultrasonication, high shear mixing and high pressure homogenization based on data by Pohl (2005). His dissertation deals with granulation, wetting and re-dispersion of Aerosil 200 (Degussa) as a model substance characterizing different dispersion equipments.

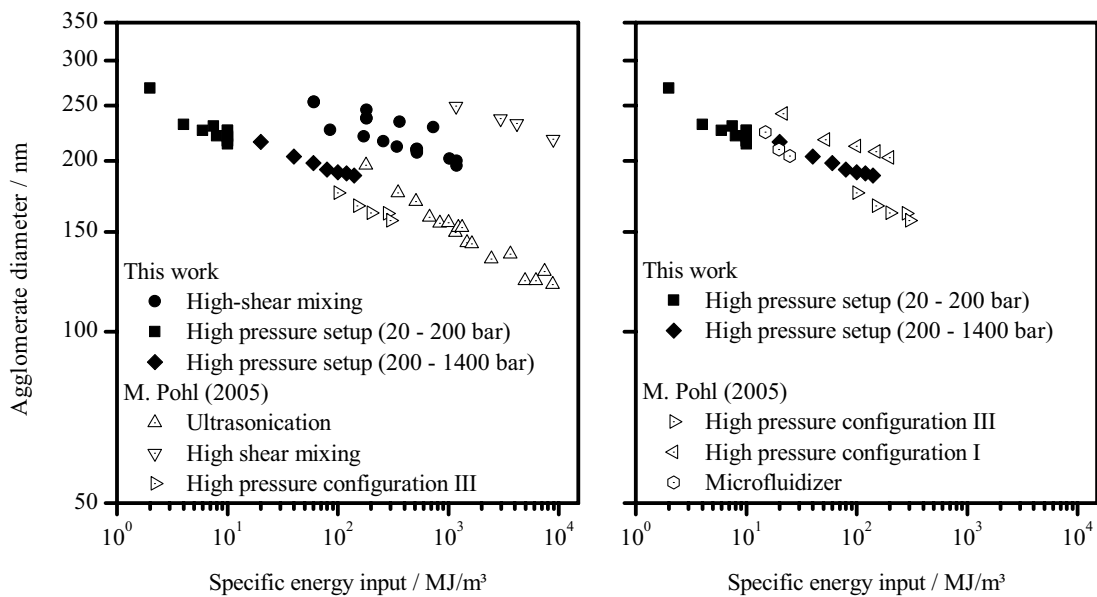


Figure 2.1: Agglomerate diameter of Aerosil 200 is plotted vs. the specific energy input. High pressure dispersion results from this work (filled symbols) and from Pohl (2005) (open symbols) are compared to different dispersion processes (left) and to different nozzle configurations (right).

The specific energy input for ultrasonication and high shear mixing was measured calorimetrically. For high pressure dispersion the pressure drop is directly equivalent to



the specific energy input

$$E_v[\text{J}/\text{m}^3] = \Delta p[\text{Pa}]. \quad (2.1)$$

Pohl (2005) measured agglomerate sizes by dynamic light scattering (DLS) using the same equipment as used in this work, at a detection angle of  $67.5^\circ$  instead of the standard angle of  $90^\circ$  used in the present study, after dispersion of Aerosil 200 and 200V at a volume concentration of  $c_v = 2.27\%$ , where only small differences between Aerosil 200 and 200V are observed. The data from this work (N4Plus, Beckman Coulter) is obtained from Aerosil 200 dispersions with  $c_v = 1\%$ . With increasing volume concentration above  $0.1\%$ , the agglomerate size decreases at a given pressure drop, yet only small changes are detected for  $c_v = 1$  and  $2.27\%$  (chapter 6.3). Pohl used different nozzles and configurations, where configuration I (figure 2.1<sub>right</sub>) represents a sapphire nozzle for jet cutting with a diameter  $d_c = 80 \mu\text{m}$ . In configuration III the same nozzle is applied, while the flow is deflected by  $90^\circ$  right after the nozzle and the pressure after the nozzle is increased by a second nozzle with larger  $d_c$  to intensify cavitation. Configuration III showed the best results of the referenced study.

Figure 2.1 shows a comparison of agglomerate diameters for the dispersion methods discussed above (left) and for different nozzle configurations (I and III) for high pressure dispersion (right). High shear mixing (Ultraturrax T25 with S25N-25F disperser) as a batch process proves to be the least energy efficient way of dispersion, since agglomerate diameters  $d_{Agg}$  at a given specific energy input are the largest; and the largest specific energy inputs are measured to obtain a defined  $d_{Agg}$ . Ultrasonication shows high specific energy inputs and leads to smallest  $d_{Agg}$  at a given  $E_v$ . High pressure dispersion leads to smallest diameters while specific energy input is limited by the maximum pressure drop ( $E_v \leq 3 \cdot 10^2 \text{ MJ}/\text{m}^3$ ). Multiple passes through the nozzle increase specific energy input, which sums up, but do not lead to further hydrodynamical stress-induced size reduction. The best high pressure configuration (III) leads to a better energy efficiency than results from this work. Figure 2.1<sub>right</sub> compares different high pressure configurations and one of the present study. Results from this study are in the same range as those of configurations I and III. Also the scaling of the  $d_{Agg}(E_v)$  is comparable.

Additionally, he measured the dispersion of Aerosil 200 in a stirred ball mill.  $d_{Agg}$  are plotted vs. the mass specific energy input  $E_m$  referring to the silica mass added to the ball mill and the power consumption of the ball mill.  $E_m$  can be converted to  $E_V = E_m \cdot c_m \cdot \rho_{Susp}$  using the particle mass concentration  $c_m$ . Resulting energies for a given  $d_{Agg}$  are a factor of  $10^4$  higher than high shear mixing. This might be due to the determination of the energy input from the total power consumption. Therefore, seemingly stirred ball mills are less energy efficient than the other techniques presented.

Concludingly, high pressure dispersion presents an energy efficient method of nanoscale

agglomerate desintegration. Dispersion results of the present study are in the range of former studies focussing on improvement of dispersion nozzle geometries.

Population balancing has been used to describe agglomeration and break-up in continuous stirred tanks (Moussa et al. 2006; Barthelmes 2000), which also can be coupled to CFD (Prat and Ducoste 2006), ultrasonication (Kusters et al. 1993, 1994) and stirred ball milling. The agglomerate size distribution is modeled as population  $n_i$  in different size classes (index  $i$ ). Breakage and agglomeration is characterized by a balance equation (Friedlander 2000):

$$\frac{\partial n_i(t)}{\partial t} = K_A - K_B \quad (2.2)$$

$K_A$  and  $K_B$  are the so-called birth rate (agglomeration) respectively death rate (breakage), which determine how agglomerates move from one class to another.  $K_A$  and  $K_B$  are related to agglomeration and breakage kernels, which model the underlying physical processes. Agglomeration is a second order kinetics process, depending on the particle concentration and interaction (Moussa et al. 2006), where the kernel has to be determined experimentally. Also, breakage kernels for ultrasonication have been determined experimentally in form of an energy density law (Kusters et al. 1994). Physical breakage kernels have been determined for collision breakage. Whereas, hydrodynamic breakage requires the coupling of fluid dynamics simulation and population balancing which has not yet been studied extensively.

These population balances have been applied to agglomeration/dispersion processes. Yet, for dispersion aggregation is negligible by particle stabilization as in this work, simplifying tremendously the population balance. Kinetic information and online measurements on the cluster mass distribution are difficult to obtain, especially for high pressure systems and nanoscale particles. Additionally, breakage kernels for turbulent breakage of nanoscale agglomerates are still unknown. The main objective of the present study is giving a physical insight into agglomerate breakage to establish breakage kernels for nanoscale agglomerates. Therefore, the physical processes for hydrodynamic agglomerate dispersion and the influence of nanoscale particle properties are investigated. Consequently the ‘energy density’ model, where the process is a black box, does not help.

## 2.3 Wetting and stabilization

Wetting and stabilization are an integral part of the dispersion process. Wetting is described as stationary process by the Young equation (2.3),

$$\cos \delta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}, \quad (2.3)$$