Chapter 1

Introduction

In many industrial processes the flow behaviour of liquids plays an important role. The macroscopic flow properties as volume flux and pressure loss are determined by the local structure of the flowing substance and production efficiency, optimization processes, security, ecological aspects or quality management might be affected extremely. Within the production of many materials suspensions are involved. The filler material affects the properties of the material that for instance may be paints and varnish, ceramics, pastes and slurries, paper, certain foodstuffs or cosmetics. Also non-industrial fields as medical science (blood circuits) and phenomena in nature like dunes formed by sedimentation are connected with the streaming of a particle-laden fluid. In the shear flow of a suspension hydrodynamic particle-particle interactions lead to stochastic particle movements and the so-called hydrodynamic diffusion takes place. A demixing might be generated if a systematic particle migration orthogonal to the flow direction is induced by gradients of the interaction frequency and of the resistance force to transverse particle movement. These phenomena were investigated experimentally and analyzed theoretically (for instance by Happel and Brenner [12]). A gradient of resistance also affects the particle drift. Such a gradient originates in the vicinity of solid boundary walls or a viscosity gradient. Near the wall the resistance coefficient regarding particle movements orthogonal to the wall is increased. An enhanced relative viscosity coming along for instance with an increased particle concentration also leads to an increased resistance coefficient. A laminar tube flow of a suspension at steady state develops a boundary layer at the wall with a low particle concentration leading to the phenomenon of pseudo wall slip resulting in a decreased pressure difference related to a constant particle flux. Due to inhomogenity the local shear rates, velocities and particle concentrations vary causing differing residence times in the tube and different degrees of mechanical strain.

The overall object of this work was the development of a phenomenological theory to describe the wall influence in a shear flow of a suspension combined with an experimental investigation. Due to time constraints the experimental analysis was confined to a chiefly qualitative character. As far as the theory is concerned an approximation of the resistance force under wall influence was set up leading to a new diffusion equation. The model was employed in order to calculate the shear rate profiles, velocity profiles and particle concentration distributions of a shear-flowing suspension including wall influence and gravity as well as the time-dependant gravity effect of a non-flowing suspension. By means of nuclear magnetic resonance (NMR) methods suspensions and solutions were analyzed experimentally to evaluate the model. This powerful technology allows the detection of spin densities of nuclei operating non-invasively. The distinction between protons and non-protons (H-NMR) makes the imaging of particle distributions and velocity profiles in suspensions possible. In this regard a special shearing device featuring an oscillating tube flow was constructed to realize a timely unlimited shearing process.

Chapter 2

Theoretical Background

2.1 Rheological Basics

2.1.1 Definitions

The main topic of the rheology (greek rheos=flow) is the constitutive behaviour of fluids. The relation between resistance and deformation is measured (rheometry), described (phenomenological rheology), expressed by mathematical modelling (theoretical rheology) and interpreted investigating the molecular processes (structure rheology).
The system response to a deformation consists of shear stresses τ_{ij} parallel to the surface areas and of normal stresses σ_{ii} perpendicular to these (cp. fig. 2.1). The representing stress tensor indicating the nomenclature is:

$$\mathbf{S} = \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{pmatrix}$$

Usually an isotropic pressure p is separated from $\mathbf{S}$

$$\mathbf{S} = -p\mathbf{E} + \mathbf{T}$$

leading to

$$\mathbf{S} = \begin{pmatrix} -p + \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & -p + \tau_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & -p + \tau_{zz} \end{pmatrix} \quad .$$

τ is called $'$extra stress tensor$'$. A flowing fluid may experience varying normal stresses. In this case the pressure is defined as:

$$\overline{p} = -\frac{(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})}{3}$$

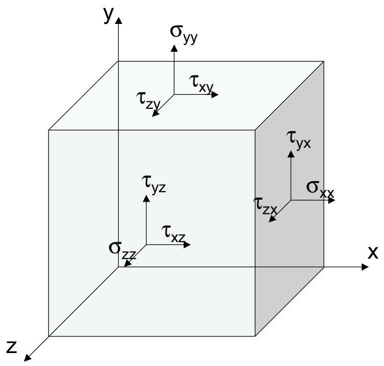

Figure 2.1: Shear stresses and normal stresses of a volume element

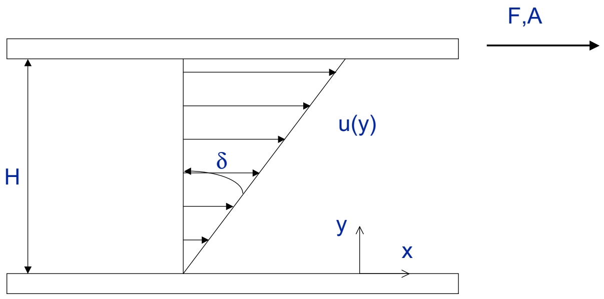

Figure 2.2: Couette Flow

Torque balance proves that $\tau_{ij} = \tau_{ji}$. The kinematics of a simple shear flow (fig. 2.2) results in the extra stress tensor

$$\mathbf{T} = \begin{pmatrix} \sigma_{xx} & \tau & 0 \\ \tau & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \quad .$$

Below the definition of the typical rheological properties is explained considering a volume element of a substance between two parallel plates at a distance of H as shown in fig. 2.2 (Couette flow). The element is sheared by moving one of the plates. To pull the plate along the fluid a force F is needed due to the occurring friction that results from molecular momentum transport caused by momentum gradients and molecular interactions. The shear stress τ is defined as the force F per area:

$$\tau = \frac{F}{A}$$

The shear strain γ is defined as the moved distance X per height unit (in the case of a Couette flow it is constant due to the linear velocity profile):

$$\gamma(y) = \frac{dX(y)}{dy} = X/H = \tan\delta$$

Here at the plates no slip is presumed. The shear angle δ is

$$\delta = \arctan\frac{X}{H}$$

The shear rate is the obtained strain per time:

$$\dot{\gamma}(y) = \frac{d\gamma}{dt} = \frac{d(u(y))}{dy} = \frac{U}{H} \tag{2.1}$$

A central rheological property is the dynamic viscosity η. Characterizing the flowability of a substance it is defined as the proportionality factor linking shear rate and shear stress:

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{2.2}$$

The dynamic viscosity strongly depends on temperature. When increasing the temperature fluids show viscosity reduction as the dominating intermolecular interactions are weakened whereas within gases a higher collision rate makes the sliding by of the shear layers more difficult leading to a rise of the viscosity. Furthermore considering suspensions the viscosity is a function of particle size and fibre length, respectively shape of particles and other properties of the system.

Shear rate dependance of viscosity Fig. 2.3 shows the viscosity dependance on the shear rate of different types of material at steady state. A special case is the newtonian fluid with a constant viscosity with respect to time as well as to shear rate. The most famous example is water. At

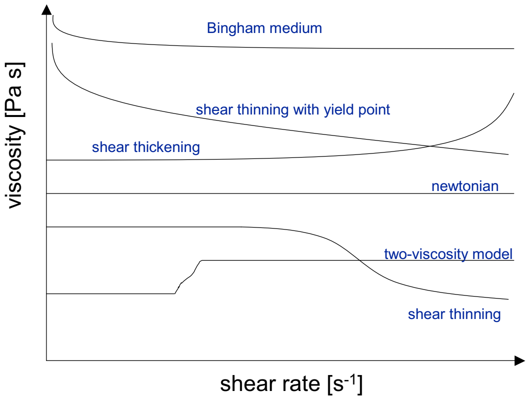

Figure 2.3: Shear rate dependance of viscosity function

higher shear rates the viscosity might decrease due to structural changes within the molecular scale of the substance. This behaviour is called shear thinning or pseudo plasticity showed by polymer solutions mostly. Shear thickening substances basically including some highly concentrated suspensions and dispersions, pastes and slurries, become more viscous at high shear rates leaving the elements of the disperse phase not enough time to sidestep each other generating transverse forces via momentum exchange. Some substances require a certain shear stress till they deform, the shear yield stress, corresponding to an infinite zero-shear viscosity. A typical example for a fluid with shear yield stress τ_F (Bingham fluid) is oil paint. Some shear thinning substances also possess a yielding point. The two-viscosity model represents substances developing two newtonian regions. A common characterization of a non-newtonian fluid is given by the Power Law (Herschel-Bulkley):

$$\eta(\dot{\gamma}) = \frac{\tau_F}{\dot{\gamma}} + k\dot{\gamma}^{n-1}$$

$\tau_F = 0$ delivers the Ostwald/de Waele law whereas $n = 1$ describes a Bingham fluid.

Time dependance of viscosity Possible time dependances of the viscosity if shearing starting from a state of rest are displayed in fig. 2.4. An increase of the viscosity is called rheopexy, a decrease of the viscosity is

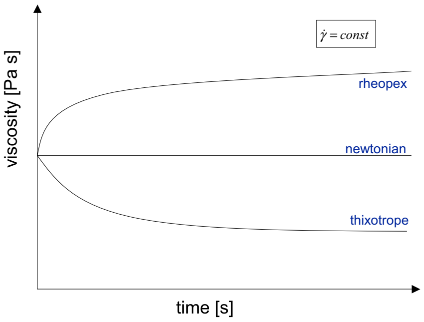

Figure 2.4: Time dependance of viscosity function

called thixotropy. Both types of behaviour occur at disperse systems originating in the structure of the disperse phase. Thixotropy also might be the consequence of changing molecular orientation or rearranging of molecular structures. The responsible mechanisms may be reversible or irreversible.
Every point of the viscosity functions in fig. 2.3 is the asymptotic value of the viscosity for $t \rightarrow \infty$ in the diagram of fig. 2.4.

A non-newtonian substance generally shows different normal stresses described by the first and the second normal stress difference:

$$\begin{aligned} N_1(\dot{\gamma}) &= \sigma_1(\dot{\gamma}) - \sigma_2(\dot{\gamma}) \\ N_2(\dot{\gamma}) &= \sigma_2(\dot{\gamma}) - \sigma_3(\dot{\gamma}) \end{aligned}$$

The first and the second normal stress coefficients are defined as:

$$\begin{aligned} \Psi_1 &= \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} \\ \Psi_2 &= \frac{N_2(\dot{\gamma})}{\dot{\gamma}^2} \end{aligned}$$

2.1.2 Disperse Systems

The viscosity function of suspensions is dependent on the viscosity of the matrix fluid as well as on the volume concentration ϕ of the disperse phase. A great amount of formulas was created to describe this relation. Our choice is the Krieger-Dougherty equation stated by Krieger and Dougherty [26] valid for suspensions with a newtonian matrix fluid of the viscosity η_0:

$$\eta(\phi) = \eta_0 \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \tag{2.3}$$

Maximum concentration ϕ_m is the theoretically maximal concentration at which the transition to bulk solid takes place implicating an infinite viscosity. Here $\phi_m = 0.68$. The relative or reduced viscosity $\eta(\phi)/\eta_0$ relates η to the viscosity of the matrix fluid.

Wall slip Most highly concentrated suspensions possess a yield stress. The system might slide along the wall as between wall and particles a thin layer of pure matrix fluid can be found. If the applied shear stress is less than the yield stress either there is no flow or flow is pure plug flow and there is no wall adhesion. Applying a shear stress higher than yield stress makes internal shear flow possible and there may be a superposition of wall slip and internal shear flow. It is possible to distinct these two by the method of Mooney. It is assumed that the volume flow is composed of the flow rate due to wall slip $\dot{V}_W$ and the flow rate due to shear $\dot{V}_S$:

$$\dot{V} = \dot{V}_W + \dot{V}_S$$

Second assumption is the dependancy of the slip velocity u_W solely on the wall shear stress:

$$u_W = f(\tau_W)$$

Then the total flow rate of a shear flow through a capillary with length L and radius R is:

$$\begin{aligned} \dot{V} &= \pi R^2 u_W + \frac{\pi R^3}{\tau_W^3} \int_0^{\tau_W} \frac{\tau^3}{\eta(\tau)} d\tau \\ \Leftrightarrow \quad \frac{\dot{V}}{\pi R^3} &= \frac{u_W}{R} + A(\tau_W) \end{aligned}$$

Measuring the volume flow using different capillaries with the same ratio L/R (for example with a twin-capillary) gives the slip velocity as the slope in the L/R,$\dot{V}/\pi R^3$-diagram.

Pseudo wall slip If the shear rates near the wall are significantly higher than farther away flow velocity increases fast within a short distance from the wall. Macroscopical observation might lead to the (wrong) impression that the system is sliding at the wall. This phenomenon is referred to as pseudo wall slip [6].

2.1.3 Rheometers

Devices for measuring rheological properties are called rheometers. There is a great variety of them, each with its own specific advantages and disadvantages. In this section only a small selection is described.
There are many types of rotational rheometers featuring an axially symmetrical design consisting of a rotating and a non-rotating component. Either the torque and with it shear stress or the angular velocity and with it the shear rate can be set obtaining in each case the other parameter being the measured quantity as a response of the system (CSS: Controlled Shear Stress, CSR: Controlled Shear Rate). Significant advantages are the realizability of different geometries, different basic tests including oscillating shear, a wide working range and the possibility of investigating the normal stresses. Within the following specific description of rotational rheometers no slip is assumed.

Parallel Plate Rheometer

The rotating element is a plate (fig. 2.5). As the local angular velocity ω of a layer of liquid is dependant on the position y and the angular velocity of

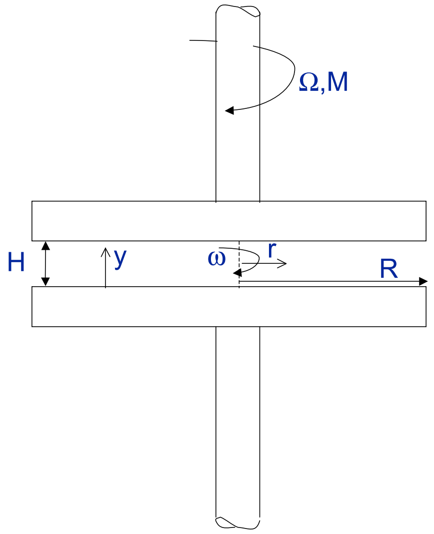

Figure 2.5: Parallel plate rheometer