Doctoral Thesis

Flow and extrudability of highly unsaturated wet powders

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Flow and Extrudability of Highly Unsaturated Wet Powders

A dissertation submitted to the
Swiss Federal Institute of Technology Zurich
for the degree of
Doctor of Sciences

presented by
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## Notation

### Latin Letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>$a$</td>
<td>$m$</td>
<td>distance between two particles</td>
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<tr>
<td>$a'$</td>
<td></td>
<td>fitting parameter</td>
</tr>
<tr>
<td>$A$</td>
<td>$m^2$</td>
<td>cross sectional area</td>
</tr>
<tr>
<td>$A_{LL}$</td>
<td>$J$</td>
<td>Hamaker constant for a liquid in vacuum</td>
</tr>
<tr>
<td>$A_{PLP}$</td>
<td>$J$</td>
<td>effective Hamaker constant for the interaction between two particles in a liquid</td>
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<td>$A_{PP}$</td>
<td>$J$</td>
<td>Hamaker constant for two particles in vacuum</td>
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<td>$b$</td>
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<td>$B$</td>
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<td>$c$</td>
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<td>$C$</td>
<td>$Pa$</td>
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<tr>
<td>$Ca$</td>
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<td>$d$</td>
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<td>$s^{-1}$</td>
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<td>$m$</td>
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<td>$C$</td>
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<td>$f$</td>
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<td>function of Poisson’s ratio and Young’s modulus</td>
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<td>force</td>
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<td>normal force in the plane of maximum shear force</td>
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<td>$m$</td>
<td>height</td>
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<td>van der Waals adhesive force at zero normal force</td>
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<td>–</td>
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<td>$I$</td>
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<td>number of particles in the discrete size interval $i$</td>
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<td>$Pa$</td>
<td>(pre-) compaction pressure</td>
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<td>particle size frequency</td>
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<td>$-$</td>
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<td>$m$</td>
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<td>2$^\text{nd}$ radius of curvature of a liquid bridge</td>
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<td>1$^\text{st}$ dimensionless radius of curvature of a liquid bridge</td>
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<td>2$^\text{nd}$ dimensionless radius of curvature of a liquid bridge</td>
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<td>radius of outer cylinder</td>
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<td>$s$</td>
<td>time</td>
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<td>$Pa$</td>
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<td>$Pa$</td>
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<td>$m$</td>
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<td>$v$</td>
<td>$m \cdot s^{-1}$</td>
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<td>$m \cdot s^{-1}$</td>
<td>velocity vector</td>
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<td>$v_l$</td>
<td>$m \cdot s^{-1}$</td>
<td>relative velocity between liquid and solid</td>
</tr>
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<td>Meaning</td>
</tr>
<tr>
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<td>----------</td>
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<tr>
<td>$v_{ram}$</td>
<td>$m \cdot s^{-1}$</td>
<td>ram velocity</td>
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<td>$m^3$</td>
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<td>$V_{Bridge}$</td>
<td>$m^3$</td>
<td>volume of a liquid bridge</td>
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<td>state of stress in $yz$-plane</td>
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<tr>
<td>$V_l$</td>
<td>$m^3$</td>
<td>liquid volume</td>
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<tr>
<td>$V_P$</td>
<td>$m^3$</td>
<td>particle volume</td>
</tr>
<tr>
<td>$V_s$</td>
<td>$m^3$</td>
<td>solid volume</td>
</tr>
<tr>
<td>$V_{total}$</td>
<td>$m^3$</td>
<td>total volume</td>
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<td>state of stress at the wall</td>
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<td>coordinate</td>
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<td>$x$</td>
<td>$m$</td>
<td>particle diameter</td>
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<td>$x^*$</td>
<td>$m$</td>
<td>harmonic mean diameter</td>
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<td>number weighted median diameter</td>
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<td>$x_{50,3}$</td>
<td>$m$</td>
<td>volume weighted median diameter</td>
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<td>$m$</td>
<td>particle diameter at which $Q_3$ is 90%</td>
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<td>$x_i$</td>
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<td>particle diameter at the upper limit of the size interval $i$</td>
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<td>$\bar{x}_i$</td>
<td>$m$</td>
<td>mean particle diameter in the size interval $i$</td>
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<td>height of the fictitious cone outside of the barrel</td>
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<td>$x_{cone}$</td>
<td>$m$</td>
<td>total height of the cone</td>
</tr>
<tr>
<td>$x_{cyl}$</td>
<td>$m$</td>
<td>height of the cylindrical part of the barrel</td>
</tr>
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<td>$x_{ram}$</td>
<td>$m$</td>
<td>distance between ram and origin</td>
</tr>
<tr>
<td>$y$</td>
<td>$m$</td>
<td>coordinate in horizontal direction</td>
</tr>
<tr>
<td>$Y$</td>
<td>$N \cdot m^{-2}$</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>$z_i$</td>
<td>–</td>
<td>ionic valence</td>
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**Greek Letters**

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<td>angle</td>
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<td>half filling angle of the liquid bridge</td>
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<td>$\dot{\gamma}$</td>
<td>$s^{-1}$</td>
<td>shear rate</td>
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<td>$\hat{\gamma}$</td>
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<td>deformation amplitude</td>
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<td>$\gamma_{SG}$</td>
<td>$N \cdot m^{-1}$</td>
<td>solid-gas interfacial tension</td>
</tr>
<tr>
<td>$\gamma_{SL}$</td>
<td>$N \cdot m^{-1}$</td>
<td>solid-liquid interfacial tension</td>
</tr>
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<td>$rad$</td>
<td>contact angle</td>
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<td>distance of the apex from the origin</td>
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<td>height of the die inlet region</td>
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<td>$\eta_M$</td>
<td>$Pa \cdot s$</td>
<td>dynamic viscosity of the matrix phase</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$rad$</td>
<td>cone angle</td>
</tr>
<tr>
<td>$\theta_F$</td>
<td>$rad$</td>
<td>critical cone angle</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>$K$</td>
<td>temperature</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>$-$</td>
<td>power law parameter</td>
</tr>
<tr>
<td>$\kappa_{vdW}$</td>
<td>$-$</td>
<td>coefficient describing van der Waals force between two particles</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$-$</td>
<td>lateral stress ratio</td>
</tr>
<tr>
<td>$\lambda_E$</td>
<td>$-$</td>
<td>ratio of horizontal and vertical stress at the wall</td>
</tr>
<tr>
<td>$\lambda_{iE}$</td>
<td>$-$</td>
<td>ratio of horizontal and vertical stress near the wall</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$-$</td>
<td>friction coefficient</td>
</tr>
<tr>
<td>$\mu_E$</td>
<td>$-$</td>
<td>friction coefficient at the wall</td>
</tr>
</tbody>
</table>

continued on next page
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{iE}$</td>
<td>—</td>
<td>friction coefficient near the wall</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$kg \cdot m^{-3}$</td>
<td>angle of friction</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$kg \cdot m^{-3}$</td>
<td>density</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>$kg \cdot m^{-3}$</td>
<td>bulk density</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>$kg \cdot m^{-3}$</td>
<td>liquid density</td>
</tr>
<tr>
<td>$\rho_P$</td>
<td>$kg \cdot m^{-3}$</td>
<td>particle density</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>$kg \cdot m^{-3}$</td>
<td>solid density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$Pa$</td>
<td>normal stress</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>$Pa$</td>
<td>empirical parameter denoting the yield stress in the die entry region at zero velocity</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>$Pa$</td>
<td>consolidation stress, 1st principal stress</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>$Pa$</td>
<td>2nd principal stress</td>
</tr>
<tr>
<td>$\sigma_c$</td>
<td>$Pa$</td>
<td>unconfined yield strength</td>
</tr>
<tr>
<td>$\sigma_C$</td>
<td>$Pa$</td>
<td>compressive stress acting in a plane</td>
</tr>
<tr>
<td>$\sigma_h$</td>
<td>$Pa$</td>
<td>horizontal stress</td>
</tr>
<tr>
<td>$\sigma_{hi0}$</td>
<td>$Pa$</td>
<td>horizontal stress at the barrel wall 11.5 mm above the die</td>
</tr>
<tr>
<td>$\sigma_{hi}$</td>
<td>$Pa$</td>
<td>horizontal stress near the wall</td>
</tr>
<tr>
<td>$\sigma_{LG}$</td>
<td>$N \cdot m^{-1}$</td>
<td>surface tension</td>
</tr>
<tr>
<td>$\sigma_M$</td>
<td>$Pa$</td>
<td>center of Mohr stress circle</td>
</tr>
<tr>
<td>$\sigma_{pre}$</td>
<td>$Pa$</td>
<td>preshear normal stress</td>
</tr>
<tr>
<td>$\sigma_R$</td>
<td>$Pa$</td>
<td>radius of Mohr stress circle</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>$Pa$</td>
<td>solids (effective) stress</td>
</tr>
<tr>
<td>$\sigma_v$</td>
<td>$Pa$</td>
<td>vertical stress</td>
</tr>
<tr>
<td>$\sigma_{v0}$</td>
<td>$Pa$</td>
<td>load on the top of the bulk solid in a silo</td>
</tr>
<tr>
<td>$\sigma_{vi}$</td>
<td>$Pa$</td>
<td>vertical stress near the wall</td>
</tr>
<tr>
<td>$\sigma_W$</td>
<td>$Pa$</td>
<td>wall normal stress</td>
</tr>
<tr>
<td>$\sigma_z$</td>
<td>$Pa$</td>
<td>uniaxial tensile strength</td>
</tr>
<tr>
<td>$\sigma_{LB}$</td>
<td>$Pa$</td>
<td>uniaxial tensile strength in the pendular state</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$Pa$</td>
<td>shear stress</td>
</tr>
<tr>
<td>$\hat{\tau}$</td>
<td>$Pa$</td>
<td>shear stress amplitude</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>$Pa$</td>
<td>wall shear stress in die land at zero velocity</td>
</tr>
<tr>
<td>$\tau_{pre}$</td>
<td>$Pa$</td>
<td>preshear shear stress</td>
</tr>
</tbody>
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continued on next page
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_W )</td>
<td>Pa</td>
<td>wall shear stress</td>
</tr>
<tr>
<td>( \phi )</td>
<td>rad</td>
<td>angle which a plane encloses with the 1st principal stress plane</td>
</tr>
<tr>
<td>( \phi_e )</td>
<td>rad</td>
<td>effective angle of friction</td>
</tr>
<tr>
<td>( \phi_{lin} )</td>
<td>rad</td>
<td>angle of the linearized yield locus</td>
</tr>
<tr>
<td>( \phi_m )</td>
<td>–</td>
<td>solid mass fraction</td>
</tr>
<tr>
<td>( \phi_{Nutr.} )</td>
<td>–</td>
<td>mass fraction of Nutriose powder in the Nutriose solution</td>
</tr>
<tr>
<td>( \phi_{sf} )</td>
<td>rad</td>
<td>angle of friction at steady-state in a shear plane</td>
</tr>
<tr>
<td>( \phi_{st} )</td>
<td>rad</td>
<td>angle between steady-state yield locus and ( \sigma )-axis</td>
</tr>
<tr>
<td>( \phi_v^* )</td>
<td>–</td>
<td>solid volume fraction at saturation</td>
</tr>
<tr>
<td>( \phi_{air} )</td>
<td>–</td>
<td>air volume fraction</td>
</tr>
<tr>
<td>( \phi_{v,r} )</td>
<td>–</td>
<td>residual liquid volume fraction in the capillary pressure curve</td>
</tr>
<tr>
<td>( \phi_{v,sat} )</td>
<td>–</td>
<td>liquid volume fraction at complete saturation</td>
</tr>
<tr>
<td>( \phi_x )</td>
<td>rad</td>
<td>angle of wall friction</td>
</tr>
<tr>
<td>( \chi )</td>
<td>Pa(^{-1})</td>
<td>compressibility</td>
</tr>
<tr>
<td>( \psi )</td>
<td>V</td>
<td>electric potential</td>
</tr>
<tr>
<td>( \psi_s )</td>
<td>V</td>
<td>Stern potential</td>
</tr>
<tr>
<td>( \omega )</td>
<td>s(^{-1})</td>
<td>angular velocity</td>
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**Indices**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^* )</td>
<td>value at the fictitious cone wall before extrusion</td>
</tr>
<tr>
<td>( 0 )</td>
<td>before extrusion</td>
</tr>
<tr>
<td>( 1 )</td>
<td>particle with diameter ( x_1 )</td>
</tr>
<tr>
<td>( 1 )</td>
<td>1st principal stress</td>
</tr>
<tr>
<td>( 2 )</td>
<td>particle with diameter ( x_2 )</td>
</tr>
<tr>
<td>( 2 )</td>
<td>2nd principal stress</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>denotes the plane inclined by an angle ( \alpha ) with the first principal stress plane</td>
</tr>
<tr>
<td>( \text{air} )</td>
<td>gas phase in the bulk solid</td>
</tr>
<tr>
<td>( b )</td>
<td>bulk</td>
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<table>
<thead>
<tr>
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<th>Meaning</th>
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</thead>
<tbody>
<tr>
<td>die</td>
<td>die</td>
</tr>
<tr>
<td>$E$</td>
<td>emptying state</td>
</tr>
<tr>
<td>$f$</td>
<td>filter</td>
</tr>
<tr>
<td>$h$</td>
<td>in horizontal direction</td>
</tr>
<tr>
<td>$i$</td>
<td>index number</td>
</tr>
<tr>
<td>$i_n$</td>
<td>near the cone wall</td>
</tr>
<tr>
<td>$j$</td>
<td>time step</td>
</tr>
<tr>
<td>$k$</td>
<td>index number</td>
</tr>
<tr>
<td>$l$</td>
<td>liquid</td>
</tr>
<tr>
<td>$max$</td>
<td>maximum value</td>
</tr>
<tr>
<td>$meas.$</td>
<td>measured</td>
</tr>
<tr>
<td>$min$</td>
<td>minimum value</td>
</tr>
<tr>
<td>$M$</td>
<td>center of Mohr stress circle</td>
</tr>
<tr>
<td>$Nutriose$</td>
<td>binder Nutriose</td>
</tr>
<tr>
<td>$pre$</td>
<td>preshear or pre-compaction</td>
</tr>
<tr>
<td>$P$</td>
<td>particle</td>
</tr>
<tr>
<td>$r$</td>
<td>index defining the type of particle size distribution</td>
</tr>
<tr>
<td>$ram$</td>
<td>ram</td>
</tr>
<tr>
<td>$s$</td>
<td>solid</td>
</tr>
<tr>
<td>$s + f$</td>
<td>solid and filter</td>
</tr>
<tr>
<td>$sh$</td>
<td>shear to failure</td>
</tr>
<tr>
<td>$simul$</td>
<td>simulated</td>
</tr>
<tr>
<td>$total$</td>
<td>the entire bulk/all slices</td>
</tr>
<tr>
<td>$v$</td>
<td>in vertical direction</td>
</tr>
<tr>
<td>$vdW$</td>
<td>van der Waals</td>
</tr>
<tr>
<td>$W$</td>
<td>at the wall</td>
</tr>
<tr>
<td>$x$</td>
<td>coordinate in vertical direction</td>
</tr>
<tr>
<td>$y$</td>
<td>coordinate in horizontal direction</td>
</tr>
</tbody>
</table>
Abstract

Partially saturated (wet) powders consist of a bulk solid whose cavities are to a certain extent filled with a liquid binder. The presence of air significantly affects the flow behavior of such systems due to interparticle frictional forces at particle contact points. The role of the binder is ambiguous as it increases normal forces between particles by capillary low pressures and surface tension forces at the contact line between liquid and solid but on the other hand reduces the coefficient of internal friction by acting as a lubricant on the particle surface. In addition to interparticle friction, interlocking effects impede the extrusion of wet powders and, in extreme cases, result in blocking. A combination of shear and normal forces can transform a wet powder into a state of increased saturation in which shear forces are reduced by a more effective wetting of the particles and their arrangement in shear layers.

Several authors worked on extrusion of pastes or highly saturated wet powders and mostly used the empirical approach from Benbow and Bridgwater (1993) to describe the flow in the die entry region and the die land. The wet powders considered in this thesis exhibit solid/liquid volume ratios between one and eight. A substantial air volume fraction causes a flow behavior which can not be described with approaches commonly used in paste extrusion. Shear forces in the die are small compared to shear forces in the die entry region. When the material is deformed to pass from the barrel into the die, elongational flow in the core is associated with shear flow in a conically shaped, outer region. Microstructural transformations in this region, which is referred to as „transition shear zone“, have a major impact on the extrusion pressures.

In this thesis, the relationship between the microstructure and the flowability/extrudability of wet powders is discussed. The influence of particle size/size distribution, particle shape, distribution and amount of binder, mechanical prehistory and phase separation phenomena (liquid phase migration) are elucidated.

A model for the determination of stress fields during ram extrusion in the barrel is presented. The development of the vertical stress, the wall normal and the wall shear stress are calculated as a function of the distance between die and ram.

Shear cell measurements of wet glass beads powders are analyzed and yield loci are modeled. On the basis of these data, the powders are classified into systems which are in the pendular, funicular and capillary state. The transition from the funicular into the capillary state at a saturation of about 80% is of special interest as it is associated with a distinct improvement of the flowability and the extrudability. An increase in packing density of wet powders at higher normal stresses increases interparticle contact areas and normal stresses. On the other hand the saturation is increased resulting in reduced coefficients of internal frictional.
These two mechanisms compete with each other so that both an increase and a decrease of shear stresses may occur.
Zusammenfassung


Scherzellenmessungen von feuchten Glaskugelpulvern werden analysiert und modelliert. Auf dieser Grundlage werden die Pulver in den Brückenzustand, den Übergangszustand und den
1 Introduction

Extrusion is a widely used technology in polymer, food, pharmaceutical, ceramic, cosmetic and chemical industries. The fields of application range from reactive processing including polymerization and grafting reactions to compounding, blending, devolatilization, extrusion cooking and - in particular - shaping (White, 1991).

In food industry breakup of cell walls from starch particles, size reduction and gelatinization of starch particles as well as texturizing of proteins are important application fields of extruders. An extract of typical applications is listed in table 1.1.

Table 1.1: Extrusion in the food and agrochemical industry after Van Zuilichem and Stolp (1987).

<table>
<thead>
<tr>
<th>Human Food</th>
<th>Agro-Chemicals</th>
<th>Animal Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch based</td>
<td>Protein rich</td>
<td>Cattle-, pig- and fishfeeds</td>
</tr>
<tr>
<td>Pasta</td>
<td>Sausages</td>
<td>Fertilizers</td>
</tr>
<tr>
<td>Bakery products</td>
<td>Scrap meat/fish</td>
<td>Vegetables/soups</td>
</tr>
<tr>
<td>Confectionaries</td>
<td>Milk proteins</td>
<td>Cellulosic material</td>
</tr>
<tr>
<td>Cereal snacks</td>
<td>Germ extrusion</td>
<td>Sucrose base chemicals</td>
</tr>
<tr>
<td>Breakfast cereals</td>
<td>Soft cheese</td>
<td>Spices</td>
</tr>
<tr>
<td>Instant cooked foods</td>
<td>Oilseed meals</td>
<td>Maltodextrins</td>
</tr>
<tr>
<td>Potato products</td>
<td>Health foods</td>
<td>Cocoa waste material</td>
</tr>
</tbody>
</table>

Following Van Zuilichem and Stolp (1987) extruders mostly offer a reasonable economic solution due to their high temperature and short time processing. For example many conversions can be carried out at lower water contents than in conventional processes. This means in practice lower drying costs for gelatinized starch matrices or for texturized proteins shorter residence times.

Many foods processed in extruders are transformed from a wet powder into a pasty state or a viscoelastic liquid (biopolymer) along the extruder channel by the effect of high temperature, high pressure and intense shearing action (Weert et al., 2001). Typical examples are breakfast cereals and cereal snacks on the basis of rice, corn, wheat, soy or potato flours blended with other ingredients (such as sugars, spices, nutrients, fats, proteins). Typically the moisture content varies between 8% and 36%.

In the pharmaceutical industry different powdered lactose, microcrystalline cellulose and silicified microcrystalline cellulose are used as excipients in tablets due to their ability to adsorb large quantities of water (Harrison et al., 1984) associated with an improved compactibility (Aljaberi et al., 2009). They are blended with active ingredients and small amounts of water (35%-65%) forming wet powder systems which are processed in extruders where cylinders of uniform size and shape are formed. Subsequently, the extrudates are
tabletted or filled into capsules (Vervaet et al., 1995), sometimes with a spheronization and a coating process as intermediate steps.

In wet powders solid particles are bound by a liquid which can be existing not only in form of discrete liquid bridges but also as a continuous phase enclosing limited numbers of particles forming saturated clusters. Air inclusions between the particles constitute the third phase and essentially affect the flow properties of wet powders as opposed to saturated systems (suspensions and pastes). Coulomb frictional forces at particle contact points as well as adhesive forces due to the surface tension of the liquid require high shear stresses to make wet powders flow. However, the role of the binder liquid is ambivalent as it increases the cohesion but on the other hand reduces the coefficient of internal friction between the particles by acting as a lubricant on the particle surface.

In practice particles are often partially or entirely dissolvable. Depending on moisture, temperature, pressure and contact time they can deform or sinter. These effects significantly influence the flow behavior but were not further considered in this thesis.

Wet powder flow is impeded by particle interlocking effects which become a major issue when the material is forced through a cross-section reduction. The extrusion of wet powders using any type of die is, in extreme cases, hindered by blocking of the material in the die inlet region.

Previous work at our laboratory (Arancio, 2006) showed that the combination of shear and elongational flow in the die entry region of an extruder barrel can cause a microstructural transformation of wet powders (Figure 1.1). In the outer regions of highest acting shear stresses an arrangement of the particles in shear layers and a compression of air cells lead to significantly reduced shear stresses during flow. The reduction of entrapped air cells ideally results in a local saturation of the system making it a 2-phase-suspension (2S) where viscous friction instead of solid friction dominates the flow behavior. The core material remains in a wet powder state but by the outer region acting as a slip layer extrusion pressures are reduced.

Following Bransby (1984) there are many other areas of difficulty in wet powder handling such as the discharge from hoppers, the emptying of drums and cans, flow on vibratory conveyors, cake discharge from filters, wall deposits in dryers etc. Extrusion of wet powders with minimized binder content is associated with reduced potential drying costs. An understanding of the mechanisms of wet powder flow including the impact of process and material parameters on the flowability and stress states is required for the design of product specific processes without the risk of blocking.

In order to avoid misunderstanding of the terminology when reading this thesis, the following expressions are defined at this point:

Wet solids are all types of bulk particulate materials, which have significant liquid content (Bransby, 1984). These include pastes, cakes, slurries, wet powders etc.
Pastes are liquid-saturated, dense assemblies of particles. Some authors distinguish them from concentrated suspensions (chapter 2.1.3).

Wet powders are partially saturated bulk solids in which particles bound by liquid bridges and saturated particle clusters coexist in any proportions. The particle network is close to the maximum random packing density. Foamed suspensions, in which no stress transmission between particles (also known as effective stress) is possible due to an excess of liquid, are not considered as wet powders.
2 Background

2.1 Paste flow

Continuum mechanical approaches allow for the mathematical description of material deformation. Rheology is commonly applied to pure liquids, melts, emulsions and dispersions. Approaches used for bulk solids strongly differ from rheological considerations although the transition from a highly concentrated suspension to a wet powder or vice versa is smooth. Fundamental rheological aspects are described below. Subsequently, the state of knowledge in paste flow with the focus on extrusion will be discussed (chapter 2.1.3). In chapter 2.2 an excerpt of plasticity theory is presented by means of which the mechanics of bulk solids is described.

2.1.1 Rheological fundamentals

In rheology it is generally assumed that a material is incompressible. The overall pressure cannot influence material behavior (Madosko, 1994). A constitutive equation describes the relation between deformation and stress. Each deformation must be in compliance with the principles of conservation of mass and conservation of momentum. Considering a control volume $V$ in a flowing system, mass can be carried into and out of this volume. The rate of change of mass in this volume equals the net flux of mass across its surface. This yields the continuity equation:

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{v}$$

(2.1)

$\rho$ is the density of the material and $\mathbf{v}$ is the velocity vector. The rate of momentum change within $V$ is defined by the convection through the surface, by contact forces acting on the surface and by body forces acting on the volume. It follows the equation of motion:

$$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \mathbf{T} + \rho \mathbf{g}$$

(2.2)

$\mathbf{g}$ is the body force vector and $\mathbf{T}$ is the stress tensor

$$\mathbf{T} = -p \mathbf{I} + \mathbf{T_E}$$

(2.3)
whereas I is the identity matrix. $T_E$ is referred to as viscous stress tensor. It contains all the stresses which are caused by the deformation of a material. Constitutive equations are usually written in terms of it. Eq. 2.1 and Eq. 2.2 are universal, i.e. they apply both to liquids and solids. However, for solids there is no flow, so that the left side of Eq. 2.2 simply becomes $\rho a$ where a represents the acceleration of the body.

In case of a Newtonian fluid, the viscous stress tensor is proportional to the deformation tensor $\mathbf{D}$:

$$T_E = 2\eta \mathbf{D}$$  \hspace{1cm} (2.4)

$2\mathbf{D}$ is equal to $\nabla \mathbf{v} + (\nabla \mathbf{v})^T$ and in Cartesian coordinates this means:

$$2\mathbf{D} = \begin{bmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{bmatrix} = \begin{bmatrix} 2\frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} & \frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \\ \frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} & 2\frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \\ \frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} & \frac{\partial v_z}{\partial y} + \frac{\partial v_y}{\partial z} & 2\frac{\partial v_z}{\partial z} \end{bmatrix}$$

For a given temperature the dynamic viscosity $\eta$ is constant. From the constitutive equation 2.4 it follows the Newtonian law

$$\tau_{xy} = \eta \frac{dv_x}{dy} = \eta \dot{\gamma}$$  \hspace{1cm} (2.5)

whereas $\dot{\gamma}$ is referred to as shear rate. The only normal stress in steady shear of a Newtonian liquid is the hydrostatic pressure. Low molecular weight liquids show Newtonian flow behavior while high polymers exhibit a Newtonian plateau at small deformation rates. An upper Newtonian plateau at high shear rates is observed for many suspensions and polymer solutions.

The most widely used form of constitutive equation for non-Newtonian fluids is derived through the power law model:

$$\tau_{ij} = \kappa |II_{2D}|^{(n-1)/2}(2D_{ij})$$  \hspace{1cm} (2.6)

$II_{2D}$ is the second invariant of $2\mathbf{D}$:

$$II_{2D} = \frac{1}{2} [tr(2\mathbf{D})^2 - tr((2\mathbf{D})^2)]$$  \hspace{1cm} (2.7)

$$tr2\mathbf{D} = 2(D_{11} + D_{22} + D_{33})$$  \hspace{1cm} (2.8)

$\kappa$ and $n$ are temperature dependent. Most non-Newtonian materials show shear-thinning ($n<1$) but shear-thickening ($n>1$) is often observed for concentrated suspensions. Many polymers and dispersions show viscosity functions $\eta(\dot{\gamma})$ which can be approximated by the
2.1 Paste flow

power law model. Plastic materials show a yield stress below which little or no deformation occurs. A phenomenon typical for polymeric materials is viscoelasticity. When a viscoelastic material is instantaneously subjected to a step increase in strain, the stress relaxes exponentially. In contrast, a purely viscous liquid would instantly relax to zero stress while an elastic solid would show no relaxation at all. For small shear strains the stress relaxation, expressed in terms of the relaxation modulus

\[ G(t) = \frac{\tau(t)}{\gamma} \]  \hspace{1cm} (2.9)

is independent of the strain \( \gamma \). In this case the material behavior is called linear viscoelastic. In other words linear viscoelasticity of a particular material defines a region of stress in which the strain varies linearly with stress (Macosko, 1994). If a material is subjected to a sinusoidal shear deformation

\[ \gamma(t) = \dot{\gamma} \cdot \sin(\omega t) \]  \hspace{1cm} (2.10)

with the amplitude \( \dot{\gamma} \) and the angular frequency \( \omega \), the shear stress at linear viscoelastic material behavior is:

\[ \tau = \dot{\tau} \cdot \sin(\omega t + \delta_\tau) = \dot{\gamma} \left[ G'(\omega) \cdot \sin(\omega t) + G''(\omega) \cdot \cos(\omega t) \right] \]  \hspace{1cm} (2.11)

The phase shift

\[ \delta_\tau(\omega) = \arctan \left( \frac{G''(\omega)}{G'(\omega)} \right) \]  \hspace{1cm} (2.12)

describes to what extent viscous and elastic deformation contribute to the shear stress. The viscous contribution is expressed in terms of the loss modulus \( G'' \), the elastic deformation in terms of the storage modulus \( G' \). The absolute value of the complex modulus

\[ G^*(\omega) = G'(\omega) + iG''(\omega) \]  \hspace{1cm} (2.13)

is linked with the complex viscosity \( \eta^* \) as follows:

\[ |\eta^*(\omega)| = \frac{|G^*(\omega)|}{\omega} \]  \hspace{1cm} (2.14)
2.1 Paste flow

2.1.2 Suspensions

In a suspension discrete particles are randomly distributed in a continuous liquid. The particles alter the flow field in terms of hydrodynamic disturbances. Small particles (<1 µm) generally have a more pronounced effect on suspension viscosity due to colloidal forces between the particles. Suspension rheology involves manifold phenomena such as shear thinning, shear thickening, yield behavior and time effects like thixotropy and rheopexy. The viscosity of dilute suspensions of Newtonian incompressible matrix liquids and rigid, spherical particles which are much smaller than the scale of motion can be calculated with the simple Einstein equation under the condition of no wall slip and negligible inertia effects:

\[ \eta = \eta_M \cdot (1 + 2.5\phi_v) \]  \hspace{1cm} (2.15)

where \( \eta_M \) ist the viscosity of the matrix liquid and \( \phi_v \) is the volume fraction of particles. Eq 2.15 is valid for the limiting case \( \phi \to 0 \). In suspensions with non-spherical particles orientation effects can have an impact on the viscosity. The extent of orientation is determined by the balance of hydrodynamic forces and Brownian motion. The orientation of nonspherical particles influences the velocity field around it and is often accompanied by shear thinning and elastic effects. At high matrix viscosities and high shear rates as well as in suspensions with large particles, the impact of particle orientation on the viscosity is more pronounced.

At particle volume fractions larger than 1% particle-particle interaction increasingly disturbs the flow resulting in higher viscosities. In the case of small particles rotary Brownian motion and translational diffusivity cause interparticle forces that lead to elasticity and shear thinning (Russel and Gast, 1986). Elastic effects are also observed in colloidal systems where interparticle forces result from an electric potential. Van der Waals forces are based on induced dipoles in the molecules of neighboring particles and lead to attraction. The magnitude of the van der Waals attraction depends on the effective Hamaker constant \( A_{PLP} \) which is a function of the Hamaker constant \( A_{PP} \) of the particle (in vacuum) and the Hamaker constant \( A_{LL} \) of the surrounding medium:

\[ A_{PLP} = \left( \sqrt{A_{PP}} - \sqrt{A_{LL}} \right)^2 \]  \hspace{1cm} (2.16)

The resulting attractive force between two equally sized spheres is a function of the particle distance:

\[ F_{vdW} \sim \frac{x}{a^2} A_{PLP} \]  \hspace{1cm} (2.17)

where \( x \) denotes the particle diameter and \( a \) is the distance between the particle surfaces. Electrostatic forces arise from a narrow double layer (Stern layer) of ions around an electrically charged particle. Counterions outside this layer form a diffuse double layer (Guy-Chapman layer) whose concentration gradually decreases towards the bulk concentration.
The thickness of the electrostatic double layer is a measure of the electrostatic repulsion between two particles and is expressed in terms of the Debye length

\[ l_D = \left( \frac{\epsilon_r \epsilon_0 k_B \Theta}{e^2 N_A \sum (c_i z_i^2)} \right)^{1/2} \]  

(2.18)

in which \( \epsilon_r \) is the relative dielectric constant of the suspension, \( \epsilon_0 \) the absolute dielectric constant, \( k_B \) the Boltzmann constant, \( \Theta \) the absolute temperature, \( e \) the charge of an electron, \( N_A \) the Avogadro constant, \( c_i \) the ion concentration of type \( i \) and \( z_i \) the corresponding ionic valence. The Debye length is the distance from the particle surface at which the potential has decreased to

\[ \psi = \frac{1}{\text{exp}(1)} \cdot \psi_s \]  

(2.19)

where \( \psi_s \) denotes the (Stern-) potential at the border of the Stern layer. According to Macosko (1994) an electrostatic repulsion becomes noticeable when particles approach close enough for the double layers to overlap.

From a great distance suspended particles appear electrically neutral because their charge is compensated in the diffuse double layer. However, when a particle moves, the diffuse double layer is partially sheared off. As a consequence a potential difference between the particle and the surrounding liquid appears which is referred to as zeta potential \( \zeta \). It is a measure of the electric surface potential of the particle and can be determined by applying an electric field in which the particle moves with a velocity \( v \):

\[ \zeta = 4\pi \frac{v \cdot \eta}{E \epsilon_r \epsilon_0} \]  

(2.20)

\( E \) is the electric field strength, \( \eta \) the viscosity of the matrix liquid.

The total potential is the sum of the attraction and repulsion potentials. As a result the total potential has a minimum close to the surface where two adjacent particles are in a very stable position and a less pronounced minimum at a larger distance where particles are weakly kept in position. To reach the primary minimum, a potential barrier has to be surmounted. In electrostatically stabilized suspensions, i.e. if electrostatic repulsion dominates over van der Waals attraction, a primary electroviscous effect appears. The viscosity is increased by the distortion of the charge cloud around the particles. The second electroviscous effect denotes the energy dissipation by electrostatic repulsion keeping particles apart from each other resulting in a viscosity increase. The effect of electrostatic forces is larger at low shear rates. Therefore shear thinning and yield stresses may appear (Krieger and Eguiluz, 1976).

Other interparticle forces in suspensions include polymeric forces by polymers adsorbed to particle surfaces (steric repulsion or flocculation (Napper, 1983)) and external fields like gravity. Another effect increasing the suspension viscosity is the immobilization of liquid molecules by their adsorption at the particle surface (Weipert et al., 1993).
In the absence of any potentials, nondilute suspensions of monodisperse, hard spheres be-
have Newtonian at low and high shear rates and a shear thinning is observed for medium
rates. At high shear rates shear thickening might become an issue due to complex structural
changes. When the particles are large (>1 µm), the shear thinning region is shifted to low
shear rates. Inertia effects play a major role and the reversibility in structural changes is
small due to the lack of Brownian motion.
When the particle packing density comes close to its maximum (74% for monodisperse
systems), the viscosity of a suspension of hard spheres approaches infinity (Weipert et al.,
1993). At particle volume fractions >20% the particle size distribution becomes important
due to a larger maximum packing density in polydisperse compared to monodisperse sys-
tems. This leads to a decrease in viscosity.
At particle volume fractions ≥ 40% shear thickening at high shear rates may occur. Dila-
tion of densely packed particles can be caused by shear, because the particles need more
space to flow than they do at rest.

2.1.3 Pastes

Benbow and Bridgwater (1993) paraphrase pastes as a mixture of solid and liquid, the
relative amounts being such that the resulting material can be moulded readily. The bulk
density is close to the maximum random packing density. Typical liquid volume fractions
are between 35%-50%. As a consequence, no particle can move over a distance of about one
particle diameter without perturbing the position or the shape of its neighbors. Products
made of pastes are foods, tiles, porcelain, thermocouple tubes, catalyst pellets, fertilizers,
cosmetics, pencil leads etc. Microcrystalline cellulose pastes in combination with water are
often subject of scientific investigations as they play a major role as excipients in pharma-
ceutical industry.
Many authors (Basterfield et al., 2005; Martin et al., 2006; Mascia et al., 2006; Rough et al.,
2002) do not differentiate between highly concentrated suspensions and pastes. In contrast,
Van Damme et al. (2002) distinguish pastes from suspensions by arguing that jamming
occurs in pastes only. Additionally, a disagreement exists with respect to saturation. While
Van Damme et al. (2002) and Basterfield et al. (2005) define pastes as liquid-saturated
assemblies of particles, Benbow and Bridgwater (1993), Martin et al. (2006), Mascia et al.
(2006) and Rough et al. (2000, 2002) reported on an initial compaction stage during ram
extrusion of pastes as a result of air inclusions which, in the true sense, made these systems
wet powders, presumably in the capillary state (see chapter 2.3.3 for details!).

Physico-chemical interactions between the particles can have an impact on flow properties
of pastes (Van Damme et al., 2002). Franks and Lange (1999) carried out unconstrained
uniaxial compression tests of saturated and preconsolidated alumina powder compacts.
They observed a brittle material failure at high preconsolidation which they explained with
the particles being in the primary minimum of the interaction potential. In contrast they
stated plastic flow at smaller consolidation pressures and assumed that the majority of
the particle separation distances was such that the particles were in a weaker secondary
minimum. They observed a dependency of flow stresses on pH values but DLVO theory
2.1 Paste flow

Pastes flow was not applicable to predict this behavior due to small separation distances and high salt concentrations. Colloidal pastes exhibit a reversibility of structural changes due to Brownian motion. Pastes of large particles are not able to relax to their original structure after subject to stresses causing defects.

Pastes generally show yield behavior, i.e. they do not deform at stresses below a plasticity threshold. After Mascia et al. (2006) yield stress behavior and wall slip make standard rheological testing of pastes difficult. During flow, slip planes form while the relative position of particles within each plane remains unchanged (Basterfield et al., 2005; Benbow and Bridgwater, 1993; Gröger et al., 2003; Van Damme et al., 2002). This is of particular interest in die entries and die lands during extrusion (Benbow and Bridgwater, 1993). Following Basterfield et al. (2005) stagnant zones in a rectangular die entry are bounded by slip planes which form an approximately conical exit geometry. In jamming situations, as they occur in the die entry region during extrusion, interparticle tribological effects influence paste flow. The interparticle friction is modulated by the interstitial fluid which can act as a lubricant but also enables physico-chemical surface modifications (Van Damme et al., 2002). Following Rough et al. (2002) the deformation of the solids matrix in a paste is hindered by frictional effects within the paste material and at the barrel wall. Several authors (Basterfield et al., 2005; Benbow and Bridgwater, 1993) tried to analyze the flow mechanisms in the die inlet region as this is the problematic area where blocking can occur (Fekete et al., 2004).

Paste flow is accompanied by dilatancy as the particles expand in the direction perpendicular to the shear plane. After Van Damme et al. (2002) interparticle Coulomb friction, that is a tangential force which is proportional to the normal force, appears in pastes whereas the liquid modifies the coefficient of friction. The lubricating power of the liquid in a paste, which is responsible for a reduction of interparticle friction, increases with increasing liquid viscosity (Van Damme et al., 2002). Additionally, higher liquid viscosities generate higher extrusion pressures but on the other hand produce extrudates with a high shape retention (Benbow and Bridgwater, 1993). Paste flow is very sensitive to the amount of liquid. Extra liquid fills the pores between the particles and hence changes the film thickness. Shear stresses at given shear rates increase with increasing solid concentrations. Beyond a critical solid content spaces between the wetted particles are created and the material is then a wet powder that is ultimately too hard to extrude (Benbow and Bridgwater, 1993). If there is an excess of liquid in the paste, the material cannot any more retain its shape which is why the range of liquid contents usable for extrusion is rather narrow. Particle size/size distribution and shape influence paste flow. Broader particle size distributions and small particles require smaller amounts of liquid to fill interstices.

**Paste extrusion**

For the design of extrusion processes of pastes, ram extruders are frequently used. They are composed of a barrel in which a sample is fed. A ram forces the material through the die into the die land. The movement of the ram can be speed controlled or pressure controlled. Advantages of ram extruders are the accurate control of the flow rate and high applicable
2.1 Paste flow

pressures. Furthermore they permit the product of highest quality but the throughput is restricted (Benbow and Bridgwater, 1993).

In the works of Benbow and Bridgwater (1993), Martin et al. (2006), Mascia et al. (2006) and Rough et al. (2000, 2002) extrusion pressures (the vertical pressures exerted on the ram) are shown as a function of time all of them featuring the qualitatively same behavior (Figure 2.1): the extrusion pressure initially increases by the compaction of the paste in the barrel. The system is in an unsaturated (wet powder) state due to enclosed air cells. Subsequently, the pressure increases due to the deformation of the paste at the die entry and the frictional shearing in the die land (Rough et al., 2000). After surmounting a yield stress (commencement of extrusion) the pressure can either decline or increase. A decreasing amount of material in the barrel leads to a decreasing extent of wall friction and thus to lower extrusion pressures. However, if the liquid in the barrel migrates towards the die, a re-increase in the pressure may be observed (chapter 2.1.3). When the ram reaches the static zone in the die entry region, the pressure starts to re-increase.

![Figure 2.1: Extrusion pressure against ram displacement for the extrusion of a microcrystalline cellulose paste (water content 55%). * indicates commencement of extrusion. Rough et al. (2002).]

In paste extrusion there is an important relation between extrusion pressure and extrudate velocity. Benbow and Bridgwater (1993) established the following empirical equation relating the extrusion pressure to barrel and die geometry and throughput:

\[ p = p_1 + p_2 = 2(\sigma_0 + \alpha v^b)ln(D_0/d_{die}) + 4(\tau_0 + \beta v^c)(l_{die}/d_{die}) \]  

(2.21)

The first term describes an uniaxial extension of a paste with an uniaxial yield stress \( \sigma_0 + \alpha v^b \).
2.1 Paste flow

from a barrel into a die. The stresses on planes perpendicular to the direction of strain are assumed to be zero. $D_0$ is the barrel diameter, $d_{\text{die}}$ the die diameter, $l_{\text{die}}$ the die length. $\sigma_0$ denotes the (uniaxial) yield stress at zero velocity and $\alpha$ is a measure of the velocity effect on the yield stress. $b$ takes non-linear behavior into account. The second term describes the pressure drop in the die land. Shearing only takes place in a thin layer near the wall where viscous effects are important. $\tau_0$ is the wall shear stress extrapolated to zero velocity and $\beta$ accounts for the dependency of the wall shear stress on the velocity. $c$ describes non-linearity. In these considerations the assumption is made that the wall shear stress is independent of the local pressure. Benbow and Bridgwater (1993) mention that partially saturated solids (wet powders) may satisfy the assumptions made, if there is sufficient liquid at the wall to achieve lubrication. The parameters $\sigma_0$, $\alpha$, $b$, $\tau_0$, $\beta$ and $c$ are determined from a series of measurements with varying ram velocities and die lands of different lengths. An additional term representing the effects of wall friction in the barrel can be included (Rough et al., 2002).

As an alternative to the approach proposed by Benbow and Bridgwater, Adams et al. (1997) proposed an elasto-viscoplastic model to approximate the rheological behavior of pastes. This involved the assumptions that there is no plastic flow if a yield criterion is not satisfied and also that the elastic and viscoplastic strain rates are additive. The elastic component of the strain rate tensor was obtained from the constitutive equation for a linear elastic solid. The viscoplastic components followed from a Herschel-Bulkley relationship. Basterfield et al. (2005) developed a model for the orifice extrusion of a Herschel-Bulkley material using a spherical coordinate system taking into account both shear and extensional flow in the die entry region. In contrast to the model of Benbow and Bridgwater, only physically meaningful parameters were used.

**Liquid phase migration in paste extrusion**

Liquid phase migration in paste extrusion, in the following referred to as LPM, is an intensively discussed phenomenon. LPM, variously known as phase redistribution, dewatering or drainage, occurs since the solid and the liquid phase move at significantly different rates under the application of a pressure gradient. As a result, the extrudate is initially very wet while relatively dry and stiff regions develop near the ram during extrusion. A steady rise in extrusion pressure as the ram moves downwards suggests the occurrence of LPM (Benbow and Bridgwater, 1993) as yield and/or shear stresses increase by a decreasing water content. The extent of LPM is larger at slow extrusion velocities since extrusion pressures are smaller producing a paste with a higher porosity, and hence a higher permeability. Furthermore the liquid has more time to flow through the particle skeleton. LPM is usually detrimental as it leads to poor and inconsistent extrudate quality and in extreme cases to extruder jamming (Benbow and Bridgwater, 1993). On the other hand it creates liquid layers next to the boundaries in the die entry region which lubricate the paste flow and cause apparent slip which can dramatically reduce extrusion pressures (Martin et al., 2006).

LPM is reduced by using fine powders or powders with broad particle size distributions. Rough et al. (2000) assessed the extrusion velocity above which no LPM occurs. This
threshold value depends on the ratio of characteristic timescales for extrusion and for the material to dewater (Wroth and Houlsby, 1984). Thus LPM can be avoided by selecting appropriate processing speeds, increasing liquid viscosity or developing formulations with a low permeability.

Wroth and Houlsby (1984) derived a criterion that can predict the drainage state of a process. According to this a system is undrained if

$$\left(\frac{x^2}{H}\right)\left(\frac{\sigma_s}{\chi \phi_v}\right)\left(\frac{t}{\eta}\right) < 300$$

(2.22)

where $x$ is the particle diameter, $H$ the maximum distance the liquid can cover, $\sigma_s$ the solids stress during paste flow, $\phi_v$ the volume fraction of the solid, $\chi$ the compressibility of the particle skeleton, $t$ the process time and $\eta$ is the viscosity of the liquid. The inequality 2.22 gives the minimum rate at which a paste extrusion process can be conducted without significant LPM. The criterion is limited by the accuracy of the estimated coefficient of permeability (Martin et al., 2006).

Not only pressure gradients in the barrel are considered as being responsible for LPM. Mascia et al. (2006) argue that high solids volume fraction systems have to increase in volume in order to undergo extensional shear as occurs in the die entry region of the extruder (dilatancy). This involves a local suction effect in the pore pressure, additionally giving rise to stiffer static zones. There is another approach to explain phase migration by Leighton and Acrivos (1987), after which shear induced particle migration occurs, due to net forces from the variation of particle collision frequency with shear rate. This approach appears to be appropriate when the particles are not continuously in contact with each other, for example in lower solids fraction pastes (Martin et al., 2006).

When a paste undergoes compaction and extrusion, it is subjected to a total stress, which is the sum of the stresses imposed upon the solid and the liquid phases. The liquid stress is also referred to as pore pressure. Rough et al. (2002) used an approach based on Darcy’s law to predict liquid phase permeation rates:

$$v_l = \frac{B \Delta p_l}{\rho g \Delta z}$$

(2.23)

$\Delta p_l$ is the pore pressure gradient, $v_l$ the superficial velocity of the water, $B$ the coefficient of permeability which is a function of porosity and liquid saturation. Rough et al. (2002) showed that the Carman-Kozeny model overpredicted permeabilities by up to three orders of magnitude (Rough et al., 2002) and used instead the following equation proposed by Brooks and Corey (1966):

$$B = \left(\frac{\phi_v - \phi_{v,r}}{\phi_{v,sat} - \phi_{v,r}}\right)^c \cdot \exp\left(\frac{\epsilon - 1}{0.0185}\right)$$

(2.24)

where $\phi_{v,sat}$ is the liquid volume fraction at saturation, $\phi_{v,r}$ is the residual liquid content in the capillary pressure curve and $c$ is a constant. Rough et al. modeled the liquid phase
motion in the barrel with a slice element method, calculating the amount of liquid in each slice element at incremental time steps while neglecting the impact of the ram velocity. The density across the face of the compact was assumed to increase linearly from the die to the top of the material in the barrel. A compaction curve was used to describe the relationship between the density and the total stress $\rho(\sigma_v)$. With this function the total vertical stress could be determined as a function of $z$. The pore pressure at $z = 0$ was zero because of the open die. Thus the total stress at the bottom was equal to the solids stress at the bottom. The difference between the total stress in a slice and the solid stress was the pore pressure. With a simple Janssen-Walker analysis the solid stress at the top was determined (Nedderman, 1982):

$$\sigma_s(z_{max}) = \sigma_s(z = 0) \cdot e^{4\phi_x \lambda \Delta z / D_0} \quad (2.25)$$

where $\phi_x$ is the wall friction coefficient of the paste which was assumed to exponentially depend on the liquid mass fraction. $\lambda$ denotes the Rankine stress ratio at a presumed effective angle of friction of $30^\circ$. In chapter 2.2.5 the inadmissibility of this assumption will be discussed.

### 2.2 Powder flow

Flow properties of bulk solids can not be described with the rheological relations applying to solids and liquids. In contrast to liquids, bulk solids can transfer shear forces in a static state and normal forces acting on different cutting planes of an infinitesimal volume element differ as long as the bulk solid is not in a fluidized state. The vertical stress within a bulk solid in an upright container does not linearly increase from the top to the bottom but increases disproportionately due to shear forces acting on the container walls.

#### 2.2.1 Stresses in bulk solids

A volume element of a bulk solid which is large compared with the size of the particles is shown in Figure 2.2. The planar state of stress is considered.

The normal stresses $\sigma_x$ and $\sigma_y$ and the shear stresses $\tau_{xy}$ and $\tau_{yx}$ are exerted on the element. In bulk solids mechanics compressive stresses are positive, tensile stresses negative. The first index of the shear stresses denotes the direction of a straight line which is normal to the considered surface. The second index is the direction in which the shear stress acts on the plane. By definition the direction of a shear stress is obtained by rotating the vector normal to the shear plane clockwise by $90^\circ$. It follows from a balance of momentums that the shear stresses exerted on two planes which are perpendicular to one another have the same absolute value but different algebraic signs.
2.2 Powder flow

An equilibrium of forces on a volume element of a bulk solid with triangular cross-sectional area is shown in Figure 2.3. No shear stresses are assumed to be exerted on the horizontal and vertical cutting planes. Stresses in a cutting plane inclined by an arbitrary angle $\alpha$ with the horizontal ($x$-) plane follow from balances of forces in horizontal and vertical direction:

$$\sigma_\alpha = \frac{\sigma_v + \sigma_h}{2} + \frac{\sigma_v - \sigma_h}{2} \cos(2\alpha)$$  \hspace{1cm} (2.26)$$

$$\tau_\alpha = \frac{\sigma_v - \sigma_h}{2} \sin(2\alpha)$$  \hspace{1cm} (2.27)$$

Eq. 2.26 and Eq. 2.27 characterize pairs of values $(\sigma_\alpha, \tau_\alpha)$ on a circle with the center

$$\sigma_M = \frac{\sigma_v + \sigma_h}{2}$$  \hspace{1cm} (2.28)$$

and the radius

$$\sigma_R = \frac{\sigma_v - \sigma_h}{2}$$  \hspace{1cm} (2.29)$$

and straight lines connecting these pairs of values with the center of the circle are inclined by an angle of $-2\alpha$ to the $\sigma$-axis (Figure 2.3). Thus the stresses in all cutting planes at arbitrary inclination angles $\alpha$ can be determined by means of this circle which is referred to as Mohr stress circle. The stresses in two planes lying perpendicular to one another are opposed in the Mohr stress circle. There are always two planes perpendicular to one another
2.2 Powder flow

on which no shear stresses are acting. These planes are called principal stress planes and the larger of the two normal stresses on these planes is the major principal stress, $\sigma_1$, the smaller one is the minor principal stress, $\sigma_2$. In Figure 2.3 the vertical and the horizontal cutting planes are principal stress planes. In the Mohr stress circle the principal stresses are defined by the points of intersection with the $\sigma-$axis.

The state of stress of a bulk solid volume element is exactly defined if the Mohr stress circles in three principal stress planes perpendicular to each other are known. Altogether there are three principal stresses whereas in bulk solids mechanics the mean principal stress is referred to as $\sigma_3$. For many applications in bulk solids technology it is sufficient to consider only one plane, i.e. the two-dimensional state of stress. Generally, the plane is considered in which the smallest minor and the largest major principal stresses are acting since this is the plane with the largest shear stresses (Schulze, 2008).

2.2.2 Yield loci

States of stress causing plastic deformation (flow) depend on the mechanical history of a bulk solid. Strongly consolidated powders require larger normal and/or shear stresses to initiate flow. For each consolidation state there is a characteristic line (yield limit) in the $\tau - \sigma-$diagram representing all states of stress giving rise to yielding. Mohr stress circles located below this yield limit only lead to an elastic deformation of the bulk solid. Mohr

Figure 2.3: Equilibrium of forces for a tri-angular bulk solid specimen (left), corresponding Mohr stress circle representing all stress states (right) in the considered plane. Taken from Schulze (2008).
stress circles touching the yield limit lead to flow and stress circles partially lying above the yield limit are physically not possible.

A characterization of a bulk solid with respect to its flow behavior is mostly realized by the measurement of (individual) yield loci with shear testers: in a first step, a bulk solid specimen between two horizontal platens is loaded vertically by a normal stress $\sigma_{\text{pre}}$. Then the top platen is moved with a constant velocity to shear the specimen. This shear deformation requires a shear stress which increases until a steady-state is reached where both the shear stress and the bulk density remain constant. After this preconsolidation step the bulk solid specimen is loaded with a normal stress $\sigma_{\text{sh}} < \sigma_{\text{pre}}$. Again the specimen is sheared. The shear stress increases linearly with time (elastic deformation) until reaching a critical value $\tau_{\text{pre}}$ at which the material fails associated with a drop of the shear stress.

The bulk density $\rho_b$ and the shear stress $\tau_{\text{pre}}$ attained at steady-state flow are characteristic for the applied normal stress at preshear, $\sigma_{\text{pre}}$. Pairs of values $(\sigma_{\text{sh}}, \tau_{\text{sh}})$ are called shear points.

As the preshear stress $\sigma_{\text{pre}}$ is larger than the shear stress $\sigma_{\text{sh}}$, the bulk solid specimen after preconsolidation is called overconsolidated with respect to $\sigma_{\text{sh}}$. This means that steady shear at $\sigma_{\text{sh}}$ would lead to a lower bulk density and a lower shear stress than shear at $\sigma_{\text{pre}}$. When the shear stress $\tau_{\text{sh}}$ is reached, the material dilates and consequently the shear stress decreases. All shear points $(\sigma_{\text{sh}}, \tau_{\text{sh}})$ are points of the individual yield locus of the consolidated specimen in the $\sigma - \tau$--diagram. In order to determine a complete yield locus, several tests must be performed where the specimen is first consolidated at identical preshear stresses $\sigma_{\text{pre}}$ and subsequently sheared to failure at different normal stresses $\sigma_{\text{sh}} < \sigma_{\text{pre}}$. The yield locus is the curve through all measured shear points. It ends at that point where it is tangent to the the so-called end Mohr circle which defines the state of stress in the preconsolidation step or in other words the state of stress at (isochoric) steady-state flow. The end Mohr circle cannot be determined before the yield locus has been measured as the preshear point $(\sigma_{\text{pre}}, \tau_{\text{pre}})$ is the only known point. The major principal stress of the end Mohr circle is called consolidation stress $\sigma_1$. Characteristic physical parameters such as friction angles and the unconfined yield strength are generally denoted as a function of $\sigma_1$.

The location and the shape of a yield locus depend on the preshear/preconsolidation stress. Yield loci for larger preshear stresses (higher bulk densities) are always located above yield loci of lower preshear stresses (lower bulk densities). Figure 2.4 illustrates a yield locus in the $\tau - \sigma$--diagram and the following associated flow parameters:

- $\sigma_c$ is the unconfined yield strength, i.e. the compressive strength of the bulk solid at uniaxial compressive load in the absence of side walls.
- $\sigma_z$ is the uniaxial tensile strength resulting from the Mohr stress circle which intersects the origin and touches the extrapolated yield locus. See Figure 2.5 for details! In case of a linearized yield locus with the slope $m$ and the $\tau$-axis intersection point $C$, it follows from geometrical considerations:

$$
\sigma_z = \frac{2C}{m} \left[ \frac{\sin(\arctan(m))}{1 + \sin(\arctan(m))} \right]
$$

(2.30)
2.2 Powder flow

In contrast, the isostatic tensile strength corresponds to the intersection of the yield locus with the $\sigma -$axis. $C$ denotes the cohesion which is the intersection point of the yield locus with the $\tau -$axis. $\phi_e$ is the effective angle of (internal) friction which is the slope of the effective yield locus. The effective yield locus is a straight line through the origin touching the end Mohr circle and has to be distinguished from the steady-state yield locus which is a tangent at all end Mohr stress circles representing steady-state flow at different stress levels. $\phi_{sf}$ denotes the angle of internal friction at steady-state flow and can be determined graphically by drawing a line through the origin and the preshear point. $\phi_{sf}$ characterizes the internal friction at steady-state flow in the cutting plane parallel to the shearing velocity.

2.2.3 Molerus’ model for dry cohesive powders

At particle sizes below 100 $\mu$m adhesive forces have a major impact on the flow behavior. This is due to the large number of particle contact points. In dry bulk solids van der Waals and electrostatic forces lead to cohesiveness. The influence of adhesive forces on the flow behavior increases with decreasing particle size (Schulze, 2008).

Molerus described the flow behavior of dry cohesive bulk solids by taking van der Waals adhesive forces into account for the calculation of steady-state and individual yield loci (Molerus, 1978). The simple Coulomb law after which the shear stress $\tau$ and the normal stress $\sigma$ in the shear plane are interrelated by
2.2 Powder flow

\[ \tau = C + \mu \sigma, \quad (2.31) \]

does not take into account that van der Waals adhesive forces between particles strongly depend on the particle distance and hence on the acting normal force. The value of the coefficient of friction \( \mu \) would vary at different normal stresses when using Coulomb’s law for the approximation of a yield locus of a compressible, cohesive bulk solid. It would decrease with increasing normal stress \( \sigma \) as the contribution of the van der Waals adhesive forces to the interparticle friction decreases. Kendall (1986) discussed the inadequacy of Coulomb’s friction law for the description of wall yield loci.

According to Molerus van der Waals adhesive forces at particle contacts depend on the normal force as follows:

\[ F_{vdW} = H_0 + \kappa_{vdW} F_N \quad (2.32) \]

\( H_0 \) and \( \kappa_{vdW} \) are material specific constants. In analogy with Eq. 2.26 the normal force resulting from an external stress, which acts in a plane inclined by an angle \( \phi \) against the first principal stress plane, is:

\[ F_N(\phi) = F_M + F_R \cos(2\phi) \quad (2.33) \]

\( F_M \) is the center, \( F_R \) the radius of a circle describing the forces actually acting on the considered bulk element. From a physical point of view this circle corresponds to the Mohr
stress circle but instead of stresses forces are considered. At particle contacts the total compressive force $F_C$ acting on an arbitrary cutting plane is the sum of the external force $F_N$ (Eq. 2.33) and the van der Waals adhesive force $F_{vdW}$ (Eq. 2.32):

\[ F_C(\phi) = F_M + F_R \cos(2\phi) + H_0 + \kappa_{vdW} (F_M + F_R \cos(2\phi)) \]  

(2.34)

During steady-state flow the shear force transmitted at an interparticle contact in the shear plane is proportional to $F_C(\phi)$ whereas the proportionality factor is the coefficient of friction $\mu = \tan(\rho)$. $\rho$ is the angle of internal friction of the powder. In all other planes the shear force $T$ is smaller than $\tan(\rho) \cdot F_C(\phi)$:

\[ T(\phi) = F_R \sin(2\phi) \leq \tan(\rho) \cdot F_C(\phi) = \tan(\rho) \cdot [H_0 + (1 + \kappa_{vdW})(F_M + F_R \cos(2\phi))] \]  

(2.35)

On the basis of these relations, Molerus (1978) derived a function $\sigma_R = f(\sigma_M)$ which, for a monodisperse bulk solid with the specific parameters $H_0$, $\kappa_{vdW}$ and $\rho$, defines an array of Mohr stress circles describing the state of stress at steady-state flow:

\[ \sigma_R = \sin(\phi_{st}) \left( \sigma_M + \frac{\tan(\rho)}{\tan(\phi_{st})} H_0 \right) \]  

(2.36)

with

\[ \tan(\phi_{st}) = (1 + \kappa_{vdW}) \tan(\rho) \]  

(2.37)

and

\[ \sigma_0 = \frac{(1 - \epsilon)k(\epsilon)}{\pi x^2} H_0 \]  

(2.38)

$\epsilon$ is the porosity, $k$ the coordination number and $x$ the particle diameter. $\phi_{st}$ is the slope angle of the steady-state yield locus resulting from $\kappa_{vdW}$ and $\rho$. The steady-state yield locus which is an envelope of the Mohr stress circles defined by Eq. 2.36 is a straight line which includes an angle $\phi_{st}$ with the $\sigma-$axis (Molerus, 1978).

An approach which is analog to Molerus’ model will be presented in chapter 4.4.4 for wet bulk solids in the pendular state (chapter 2.3.3).
2.2 Powder flow

2.2.4 Wall yield loci

The friction between a bulk solid and a solid surface (wall) is described by the angle of wall friction

\[ \phi_w(\sigma_W) = \arctan \left( \frac{\tau_W}{\sigma_W} \right) \]  

(2.39)

where \( \tau_W \) denotes the shear stress, \( \sigma_W \) the normal stress exerted by the bulk solid on the wall (and vice versa). The wall yield locus, describing the kinematic wall friction and defined by the pairs of values \((\sigma_W, \tau_W)\), is often a straight line through the origin. In this case \( \phi_w \) is constant. If the wall yield locus is not a straight line and if it does not pass through the origin, \( \phi_w \) must be determined as a function of \( \sigma_W \). Wall yield loci are measured by moving a bulk solid specimen over a wall material sample with a constant velocity. The bulk solid specimen is subjected to a vertical normal stress, \( \sigma_W \). When shear is initiated, the wall shear stress increases and finally reaches a steady value, \( \tau_W \). In this way, shear stresses are determined for incrementally varied wall normal stresses. Fekete et al. (2007) measured wall yield loci of wet limestone powders on stainless steel plates. When liquid was added to the powder, liquid bridges formed between the particles and the wall. These adhesive forces resulted in an increased wall shear stress. The shear stress dropped rapidly when an excess of liquid in the plane of contact between the particles and the surface made capillary forces disappear and the liquid act as a lubricant.

2.2.5 Stress fields in silos

The knowledge of the stresses in silos is fundamental for silo design to guarantee flow of the bulk solid without arching, to evaluate the mechanical load of silo walls, feeders and inserts and to prevent particle damage by high stresses.

Qualitative distributions of the wall normal stresses and mean vertical stresses and the directions of the major principal stress are illustrated in Figure 2.6. After filling, the wall normal stress increases in the vertical part from the top to the bottom, asymptotically tending towards a maximum. There is a discontinuity in the wall normal stress at the transition into the hopper. In the hopper, the wall normal stress can increase or decrease (Weipert et al., 1993). The state of stress in the bulk solid in the filling state is referred to as active state of stress. Vertical stresses are larger than horizontal stresses and in the silo axis the vertical stress is the major principal stress.

When the silo is emptied, the so-called passive state of stress develops. By the bulk solid flowing downwards through the converging hopper, it is compressed horizontally whereas the vertical stress is reduced. The major principal stresses in the cone axis are now oriented in horizontal direction. In the cylindrical part of the silo the active state of stress remains unchanged. The stress peak at the transition from the active to the passive state of stress is called „switch“.
Figure 2.6: Qualitative distributions of the wall normal stress, $\sigma_W$, and the vertical stress, $\sigma_v$, plotted against the vertical coordinate of a silo. The lines within the silos show the directions of the major principal stress. a) active state of stress in the filling state, b) passive state of stress in the emptying state in the lower part of the hopper, c) passive state of stress in the entire hopper d) passive state of stress in a funnel flow silo (Schulze, 2008).
The stress states in the vertical part of a silo can be calculated with the slice element method after Janssen (1895): an equilibrium of forces for a slice-shaped volume element of infinitesimal thickness $dz$ and cross-sectional area $A$ yields:

$$\sigma_v = \frac{g \rho_b A}{\lambda \tan(\phi_x) U} \left( 1 - \exp \left( -\frac{\lambda \tan(\phi_x) U z}{A} \right) \right) + \sigma_{v0} \exp \left( -\frac{\lambda \tan(\phi_x) U z}{A} \right) \quad (2.40)$$

$\sigma_v$ is the vertical stress which is assumed to be constant across the cross-sectional area, $\sigma_{v0}$ is an external vertical load acting on the top of the bulk solid, $g$ is the acceleration due to gravity, $U$ is the perimeter of the slice, $z$ is the vertical coordinate pointing top down and $\lambda$ is the lateral stress ratio

$$\lambda = \frac{\sigma_h}{\sigma_v} \quad (2.41)$$

whereas $\sigma_h$ is the horizontal stress. There are many approaches to estimate $\lambda$. Rankine’s coefficient is the ratio of the minor to the major principal stress in the active plastic state of stress which is the state at steady-state flow:

$$\lambda = \frac{\sigma_2}{\sigma_1} = \frac{1 - \sin(\phi_e)}{1 + \sin(\phi_e)} \quad (2.42)$$

Eq. 2.42 implies that the horizontal and the vertical stresses are principal stresses, which is only the case in the axis of the vertical silo part. Additionally, the assumption of the active plastic state of stress is only justified if the bulk solid in the vertical part has the possibility to sufficiently dilate in horizontal direction. This is usually impossible due to the stiffness of the silo walls (Schulze, 2008).

The material in the vertical part is subjected to uniaxial compression which is why a minor principal stress develops which is, for a given major principal stress, larger than at steady-state flow. The Mohr stress circle at uniaxial compaction (called active elastic state of stress) is located below the Mohr stress circle representing steady-state flow (Figure 2.7). As a consequence, the lateral stress ratio is larger than that predicted with Eq. 2.42.

After Schulze (2008), a method to determine the lateral stress ratio at uniaxial compression with sufficient reliability is a test in a modified oedometer in accordance with a ISO-guideline (TC98/SC3/WG5, 1990). This standard describes the vertical compression of a bulk solid sample in a cylindrical mould while measuring the resulting horizontal stress.


In chapter 4.7, a model will be presented for the calculation of the stress distributions in a wet powder being extruded from a cylindrical barrel into a die. Motzkus’ model was used as a basis for the determination of the stresses in the die entry region. It will be discussed in the following section.
2.2 Powder flow

Motzkus’ model

Motzkus (1974) developed an approximation method for the calculation of stresses in hopper cones in the filling and emptying state. He assumed an active-plastic stress state near the cone wall in the emptying states. In the following, the essential outcomes are summarized. A detailed derivation of the formulae can be found in Motzkus (1974). The assumed states of stress near the wall and at the wall are shown in Figure 2.8.

The horizontal stress and the vertical stress ($\sigma_{hi}$ and $\sigma_{vi}$) near the wall are not principal stresses. $\sigma_{vi}$ is larger than $\sigma_{hi}$. In the emptying state, the Mohr stress circle near the wall touches the effective yield locus. Thus the location of $\sigma_{hi}$ and $\sigma_{vi}$ on the Mohr stress circle is defined. This approximation made by Motzkus is based on experimental data of the stresses in the emptying state of a silo.

It follows from the condition that the vertical stress $\sigma_v$ is constant over the cross section that the shear stresses $\tau_{xy}$ and $\tau_{xyi}$ are identical. Sliding of the material along the wall accounts for the fulfillment of Eq. 2.39. With these conditions the stress circle describing the state of stress at the wall is defined.

Sliding fracture at the cone wall is only possible up to a cone angle $\theta_F$ where the stress circle at the wall is identical to the stress circle in the vicinity of the wall. In case of larger cone angles $\theta > \theta_F$ there are no more solutions fulfilling all boundary conditions (Schulze, 2008). Motzkus assumes that in this case the wall yield criterion (Eq. 2.39) is not fulfilled and that the material moves along the wall by material failure instead of sliding fracture.

The critical cone angle $\theta_F$ separating sliding fracture from material failure follows from geometrical considerations at the stress circles:

Figure 2.7: Active-plastic and active elastic state of stress (Schulze, 1991).
2.2 Powder flow

Figure 2.8: Top: definition of the stresses acting in the vicinity of the wall and at the wall. Below: state of stress in the cone in the emptying state after Motzkus (1974). W denotes the wall, Hor (Hor_i) the plane with the normal stress \( \sigma_h = \sigma_y \) and Ver (Ver_i) the plane with the normal stress \( \sigma_v = \sigma_x \). The index i denotes a volume element near the wall.
2.2 Powder flow

\[ \theta_F = 45^\circ - \frac{1}{2} \cdot \left( \phi_x - \phi_e + \arcsin \left( \frac{\sin(\phi_x)}{\sin(\phi_e)} \right) \right) \]  

(2.43)

The following relations can be derived from Figure 2.8 under the assumption that the vertical stress \( \sigma_v \) is constant over the cross section:

\[ \mu_iE = \frac{\tau_{xyi}}{\sigma_{hi}} = \tan(\phi_e) \]  

(2.44)

\[ \lambda_iE = \frac{\sigma_{hi}}{\sigma_{vi}} = \frac{1 - \sin^2(\phi_e)}{1 + \sin^2(\phi_e)} \]  

(2.45)

\[ \lambda_E = \frac{\sigma_h}{\sigma_v} = \frac{(1 - \tan(\theta) \cdot \tan(\phi_x)) - \mu_iE \lambda_iE \cdot \tan(\theta)(1 + \tan^2(\phi_x) - (\tan^{-1}(\theta) - \tan(\phi_x))^2)}{1 + \tan^{-1}(\theta) \cdot \tan(\phi_x)} \]  

(2.46)

\[ \mu_E = \frac{\tau_{xy}}{\sigma_h} = \mu_i \lambda_iE \lambda_E \]  

(2.47)

In case of sliding fracture (\( \theta \leq \theta_F \)), the factor

\[ K = \frac{\sigma_W}{\sigma_v} \]  

(2.48)

is calculated as follows:

\[ K = \frac{\lambda_E + 1}{2} + \frac{\lambda_E - 1}{2} \cos(2\theta) + \mu_E \lambda_E \cdot \sin(2\theta) \]  

(2.49)

If material failure occurs (\( \theta > \theta_F \)), \( K \) is:

\[ K = \frac{\lambda_iE + 1}{2} + \frac{\lambda_iE - 1}{2} \cos(2\theta) + \mu_i \lambda_iE \cdot \sin(2\theta) \]  

(2.50)

The equations 2.49 and 2.50 are used to determine the factor \( K \) which in combination with an equilibrium of forces for an infinitesimal volume element in the hopper can be used to calculate the development of the vertical stress (chapter 4.7).
2.3 Wet powders

In wet powders, solid particles adhere to each other by liquid bridges or saturated particle clusters bound by a capillary low pressure. Wet powders are unsaturated systems. As a consequence of the air inclusions, wet powders are highly cohesive. In saturated systems, capillary forces and surface tension forces occur only at the interface to the surrounding atmosphere.

2.3.1 Liquid bridges between two spherical particles

A liquid bridge between two spherical particles produces an adhesive force which arises from a pressure deficiency in the bulk of the liquid and from an attraction between liquid and solid which is caused by the action of the surface tension of the liquid at the three-phase contact line. The resulting force can be zero or even repulsive for certain bridge geometries associated with imperfect wetting (Lian et al., 1993).

The force of a liquid bridge depends on the separation distance between the particles, the surface tension of the liquid, the geometry and the volume of the bridge and on the contact angle between the liquid and the solid surface. There is rupture beyond a critical separation distance. The capillary pressure in a liquid bridge is calculated from the Laplace-Young equation,

\[
\Delta p = \frac{\sigma_{LG}}{\tau} = \sigma_{LG} \left[ \frac{1}{r_1} + \frac{1}{r_2} \right] = \sigma_{LG} \left[ \frac{1}{r(1 + r^2)^{1/2}} - \frac{j}{(1 + r^2)^{3/2}} \right]
\]  

relating the mean curvature \(1/\tau\) of the liquid to the pressure deficiency \(\Delta p\). \(r(z)\) is the meridional bridge profile as a function of the coordinate \(z\) on the axis of the liquid bridge, \(r_1\) and \(r_2\) are local principal radii of normal curvature in orthogonal directions at points along the meridional bridge profile. The dot notation refers to differentiation with respect to \(z\) in agreement with Figure 2.9.

Except for some special cases, the Laplace-Young equation cannot be solved analytically. The total force of a liquid bridge between two particles is the sum of the axial component of the surface tension acting on the three-phase contact line and the Laplace hydrostatic pressure in the interior of the bridge:

\[
F = \pi \sigma_{LG} x \sin(\beta) \sin(\beta + \delta) - \frac{\pi}{4} x^2 \Delta p \cdot \sin^2(\beta)
\]

\(\sigma_{LG}\) is the surface tension of the liquid, \(\beta\) the half filling angle and \(\delta\) the contact angle. The pressure deficiency across the air-liquid interface, \(\Delta p\), is defined by Eq. 2.51. The force component arising from the surface tension at the three-phase contact line is always attractive, while the Laplace pressure component is proportional to the curvature of the bridge surface and can be repulsive or attractive (Willett et al., 2000).
2.3 Wet powders

Figure 2.9: Toroidal approximation of a liquid bridge between two spherical, equally sized particles.

surface curvature with respect to the interior of the bridge, the Laplace pressure is negative (in the notation defined by Eq. 2.51) and the resulting force component attractive.

The toroidal approximation for the solution of Eq. 2.51 proposed by Fisher (1926) treats the meridional profile of the liquid-air interface as an arc of a circle leading to a simple solution (Figure 2.9). With this approximation good results are obtained in the case of small separation distances and bridge volumes (Mehrotra and Sastry, 1980; Orr et al., 1975). However, in the toroidal approximation the surface curvature is not constant along the meridional profile of the bridge (Willett et al., 2000). This is inconsistent with the Laplace-Young equation (Lian et al., 1993). Depending on if the mean curvature of the liquid bridge at the neck or at the three phase contact line is employed, different results are obtained.

In the so-called gorge method (Hotta et al., 1974) the capillary pressure deficiency is calculated by considering the area at the neck and the surface tension force is obtained by taking the tangent at the neck as the orientation of the force:

\[
F_{LB} = 2\pi r_2 \sigma_{LG} - \pi r_2^2 \Delta p
\]

A simple approach to spheres of unequal size was proposed by Derjaguin (Israelachvili, 1992): the harmonic mean diameter \(x^*\), defined by

\[
\frac{1}{x^*} = \frac{1}{2} \left( \frac{1}{x_1} + \frac{1}{x_2} \right)
\]
substitutes the particle diameter $x$ in the applied expression for the adhesive force of the liquid bridge. $x_1$ and $x_2$ are the diameters of the two spheres.

In the framework of this thesis, an approximation proposed by Heady and Cahn (1970) was used. The force is calculated by assuming the dimensionless radii $r^*_1$ and $r^*_2$ to be arcs of a circle (toroidal approximation, curvature at the neck):

$$r^*_2 = \frac{r_2}{x} = \frac{\sin(\beta)}{2} + \frac{r_1}{x} \left[ \sin(\beta + \delta) - 1 \right] \quad (2.55)$$

$$r^*_1 = \frac{|r_1|}{x} = \frac{(1 - \cos(\beta)) + a/x}{2 \cdot \cos(\beta + \delta)} \quad (2.56)$$

Thus the liquid bridge adhesive force is:

$$F_H = \sigma_l x \pi \sin(\beta) \left[ \sin(\beta + \delta) + \frac{\sin(\beta)}{4} \left( \frac{1}{r^*_1} - \frac{1}{r^*_2} \right) \right] \quad (2.57)$$

$a$ is the distance between two particles. $\beta$ can be calculated implicitly from the following equation:

$$x_w = \frac{m_l}{m_s} = \frac{1 - \phi_m}{\phi_m} = 6k \left( \frac{V_{Bridge}}{2\pi x^3} \right) \rho_l / \rho_s \quad (2.58)$$

$k = \pi/\epsilon$ is the mean coordination number of a particle. According to Pietsch and Rumpf (1967) the normalized volume of the liquid bridge is:

$$\frac{V_{Bridge}}{2\pi x^3} = \left[ r^*_1^2 + (r^*_1 + r^*_2)^2 \right] r^*_1 \cos(\beta + \delta) - \frac{r^*_1^3 \cos^3(\beta + \delta)}{3} - r^*_2^2 (r^*_1 + r^*_2)^2 \cdot \left[ \cos(\beta + \delta) \sin(\beta + \delta) \left( \frac{\pi}{2} - \beta - \delta \right) \right] - \frac{1}{24} (2 + \cos(\beta))(1 - \cos(\beta))^2 \quad (2.59)$$

### 2.3.2 Static contact angles of wet powders

If a liquid droplet spreads on a rigid solid surface, the angle at which the liquid-vapor interface meets the solid-liquid interface is called contact angle $\delta$. The contact angle is determined by the three interfacial tensions $\gamma_{SG}$, $\gamma_{SL}$ and $\sigma_{LG}$ which depend on the chemical properties of the three phases, the pressure and the temperature. An equilibrium of forces at the three-phase contact line yields the Young-equation:

$$\cos(\delta) = \frac{\gamma_{SG} - \gamma_{SL}}{\sigma_{LG}} \quad (2.60)$$
A surface is wetted by adhesion, immersion or spreading (Kossen and Heertjes, 1964). A necessary condition for wetting is that the work $W$ is larger than zero (Harkins and Dahlstrom, 1930):

$$W_{\text{adhesion}} = \sigma_{LG} \cdot (1 + \cos(\delta))$$  \hspace{1cm} (2.61)

$$W_{\text{immersion}} = \sigma_{LG} \cdot \cos(\delta)$$  \hspace{1cm} (2.62)

$$W_{\text{spreading}} = \sigma_{LG} \cdot (\cos(\delta) - 1)$$  \hspace{1cm} (2.63)

It follows that the contact angle $\delta$ is a useful measure of the wettability. The measurement of contact angles of powders is difficult. Bartell and Osterhof (1927) and Bartell and Benner (1942) compressed a powder in a cylinder at one end of which liquid could penetrate the powder. A differential pressure at the other end of the cylinder was increased until penetration stopped. With the average pore radius $r_{\text{pore}}$ it followed:

$$\Delta p = \frac{2\sigma_{LG} \cdot \cos(\delta)}{r_{\text{pore}}}$$  \hspace{1cm} (2.64)

In another liquid penetration method proposed by Washburn (1921), which was similarly also applied by Teipel and Mikonsaari (2004), the mass of penetrating liquid $m_l$ is measured as a function of time $t$ yielding

$$m_l^2 = \text{const} \cdot \rho_l^2 \cdot \sigma_{LG} \cdot \cos(\delta) \cdot \frac{\eta}{2} \cdot t$$  \hspace{1cm} (2.65)

whereas the constant depends on the powder packing density which is calculated from Eq. 2.65 when a liquid with a contact angle $\delta=0^\circ$ is used. Kossen and Heertjes (1964) developed a sessile drop method to determine the contact angle for granular material. The powder was pressed into a liquid saturated cake and the height of a large drop of the liquid was measured and used for the calculation of the contact angle between the solid and the liquid. The following relations arised from their considerations:

the Young-equation for the state of equilibrium of the liquid on a porous solid differs from a system with a compact solid surface. In the case of saturation, the surface porosity $\epsilon_s$ is the area fraction of wet surface. It follows:

$$\langle \gamma_{SG} \rangle_{\text{porous}} = \epsilon_s \sigma_{LG} + (1 - \epsilon_s)\gamma_{SG}$$  \hspace{1cm} (2.66)

$$\langle \gamma_{SL} \rangle_{\text{porous}} = (1 - \epsilon_s)\gamma_{SL}$$  \hspace{1cm} (2.67)
2.3 Wet powders

Consequently, the Young-equation for a porous mass can be written as

\[ \frac{\gamma_{SG} - \sigma_{SL}}{\sigma_{LG}} (1 - \epsilon_s) = -\epsilon_s + \cos(\delta^*) \]  

(2.68)

where \( \delta^* \) is the apparent contact angle. Comparing Eq. 2.60 with 2.68 yields:

\[ \cos(\delta)(1 - \epsilon_s) = -\epsilon_s + \cos(\delta^*) \]  

(2.69)

With Eq. 2.69 the contact angle between the solid and the liquid can be calculated from the apparent (measured) contact angle of the liquid on the saturated powder surface.

Apart from the chemical composition, the surface roughness of the solid has an impact on contact angles. Macroscopically observed contact angles of rough surfaces are different from microscopic contact angles which are described by the Young-equation 2.60 (Marmur, 1992). After Palzer et al. (2001), the macroscopic contact angle, which is measured against the tangent to the macroscopic solid surface, depends on the local inclination of the solid surface at the three-phase contact line. In the case of partially wetting liquids (\( \delta < 90^\circ \)), measured contact angles are often smaller on rough surfaces than on smooth surfaces. This might be explained by a penetration of the liquid into the surface roughness due to capillary forces. The resulting contact angle is the so-called receding angle (Palzer et al., 2001) which is the velocity dependent dynamic contact angle during dehumidification processes. When humidifying a solid, the larger advancing angle is observed.

2.3.3 Wet powder classification

A bulk solid containing a liquid can be classified into three characteristic states (Figure 2.10).

In the pendular state discrete liquid bridges bind the particles. In the funicular state a larger amount of liquid is present partially filling the cavities while in some areas there are still liquid bridges. In the capillary state no more liquid bridges are present, but all particles are enclosed in saturated clusters.

In the capillary state the capillary pressure determines the tensile strength of wet powder compacts. The contribution of the surface tension drops to zero (Iveson et al., 2002). Oversaturation leads to the droplet state where the tensile strength becomes zero. Provided that the liquid is uniformly distributed in the bulk solid, the tensile strength is calculated as follows (Schubert, 1973):

\[ \sigma_z = S p_k \]  

(2.70)

The saturation \( S \) is the volume fraction of the cavities which is filled with liquid:
2.3 Wet powders

Figure 2.10: Schematic illustration of the three characteristic wet powder states. a) pendular state, b) funicular state, c) capillary state.

\[
S = \frac{V_l}{V_{total} - V_s} = \frac{1 - \phi_m}{\frac{\rho_l}{\rho_s} - \phi_m \frac{\rho_l}{\rho_s}} = \frac{\rho_s}{\rho_l} \frac{1 - \phi_m}{1 - \epsilon} \tag{2.71}
\]

\(V_l\) denotes the liquid volume, \(V_{total}\) is the total volume, \(V_s\) the solid volume, \(\phi_m\) the mass fraction of the solid, \(\rho_l\) the liquid density, \(\rho_s\) the particle density and \(\rho_b\) is the bulk density of the wet powder. Given the solid and the liquid mass, \(m_s\) and \(m_l\), of the wet powder, the following relations apply:

\[
\rho_s = \frac{m_s}{V_s} \tag{2.72}
\]

\[
\rho_l = \frac{m_l}{V_l} \tag{2.73}
\]

\[
\phi_m = \frac{m_s}{m_s + m_l} \tag{2.74}
\]

\[
\rho_b = \frac{m_s + m_l}{V_{total}} \tag{2.75}
\]

\[
\epsilon = 1 - \frac{\frac{V_s}{V_{total}}}{1 - \frac{m_s/\rho_s}{V_{total}}} = 1 - \phi_m \frac{\rho_b}{\rho_s} \tag{2.76}
\]
2.3 Wet powders

The capillary pressure \( p_k \) in Eq. 2.70 is obtained from a capillary pressure curve illustrating \( p_k \) as a function of \( S \) for both the humidification and dehumidification process. More details about capillary pressure curves can be found in Schubert (1982).

In the pendular state the tensile strength of an agglomerate can be calculated from the adhesive force of the liquid bridge between two particles by means of the widely accepted Rumpf equation:

\[
\sigma_z = (1 - \epsilon) \frac{k F_H}{\pi x^2} \tag{2.77}
\]

in which \( F_H \) is the adhesive force and \( k \) is the coordination number. Rumpf’s equation is based on the assumption of a monodisperse and regular random packing and on interparticle bindings which are statistically distributed over the particle surfaces and in the space.

After Smith et al. (1929), the value of the coordination number can be approximated by

\[
k \approx \frac{\pi}{\epsilon} \tag{2.78}
\]

It was shown that for polydisperse systems the Sauter-diameter \( x_{1,2} \), which is a measure of the volume specific surface of the particles, can be used as a representative particle size with respect to the agglomerate strength (Iveson et al., 2002; Pietsch, 1965; Rumpf and Turba, 1964). A definition of the Sauter-diameter will be given in chapter 3.3.

The pendular state passes into the funicular state at a saturation \( S_p \) which depends on geometry, while the capillary state starts at a saturation \( S_c \) between 80% and 90%. In case of monodisperse random packing \( S_p \) is 34% (Flemmer, 1991). In real systems it is between 25% and 50% (Pierrat and Caram, 1997). After Schubert (1973), the tensile strength in the funicular state is between two limiting cases:

1. The binding mechanisms of the pendular state and the capillary state are superposed. At \( S = S_p \) the tensile strength is \( \sigma^{LB}_{z} \) which is calculated with Eq. 2.77 whereas the adhesive force is the liquid bridge force. If \( S = S_c \), Eq. 2.70 is used for the determination of \( \sigma_z \). At a saturation \( S_p < S < S_c \), each component is weighted according to the prorated distance from \( S \):

\[
\sigma_z = \sigma^{LB}_{z} \frac{S_c - S}{S_c - S_p} + p_k S_c \frac{S - S_p}{S_c - S_p} \tag{2.79}
\]

2. Each of the binding mechanisms acts exclusively, i.e.

\[
\sigma_z = \sigma^{LB}_{z} \frac{S_c - S}{S_c - S_p} \tag{2.80}
\]

or
\[
\sigma_z = p_k S_c \frac{S - S_p}{S_c - S_p}
\]  

(2.81)

Schubert (1973) measured the tensile strength of wet powder agglomerates for variously saturated limestone particles with a Sauter-diameter of 71 µm. The porosity was kept constant at 41.5%. The experimental results as well as the theoretically obtained tensile strengths are shown in Figure 2.11.

Figure 2.11: Tensile strength \( \sigma_z \) of a limestone powder vs. saturation, capillary pressure curve \( p_k(S) \) in the case of dehumidification (Schubert, 1973).

The course of the tensile strength in the pendular state is determined by the strength of the liquid bridge as all other parameters in Rumpf’s equation (2.77) remain unchanged. Except for a sharp increase at small saturations < 10%, the tensile strength is nearly constant.

In the funicular state the tensile strength increases in spite of a decreasing capillary pressure. The fraction of the pores contributing to the strength of the agglomerate increases due to the increasing saturation.

In the capillary state a maximum tensile strength is reached at that point where the capillary pressure is equal to the capillary entry pressure (Schubert, 1973):

\[
p_k = const \cdot \frac{1 - \epsilon \sigma_{LG}}{\epsilon x}
\]  

(2.82)

The constant typically has values between 6 and 8. At higher saturations, an overwetting of the agglomerates results in a rapid drop of the tensile strength by a capillary pressure drop reaching a value of zero at complete saturation.
Gröger et al. (2003) used a Cohesive Discrete Element Method (CDEM) to investigate tensile strengths and shear strengths of fine granular materials in the pendular state. A good general agreement with Rumpf’s equation was found and divergences explained by the existence of stretched liquid bridges.

For the determination of the regime boundaries, Bier et al. (1979) measured the electrical power consumption of a planetary mixer while slowly adding a liquid binder into the powder. From the shape of the curve characteristic phases were established allowing to avoid overwetting, which would make the system unworkable, and undersaturation associated with unstable agglomerates.

Malamataris and Kiortsis (1997) conducted similar experiments with lactose and sulfadiazine powders and different liquids (water, isopropanol, water/isopropanol and liquid paraffin) which were mixed in a three blade impeller in a cylindrical vessel. They identified the range of funicular agglomeration from the measurement of the torque. Furthermore they made compression tests of wet powders in the funicular state and found that all liquids, independently of their wetting behavior, acted as lubricants between the particles resulting in a reduced resistance against compression.

Other authors used shear cells (Pilpel, 1971), split bed shear testers (Shah et al., 2000) or split plate tensile testers (Khan and Pilpel, 1986) to identify the stages of agglomeration formation during wet powder granulation.

Podczeck and Wood (2003) measured the density of dried wet powder agglomerates made from Lactose monohydrate and an aqueous HPMC solution with a Helium pycnometer and determined Young’s modulus with a dynamic mechanical analyzer. They identified a sudden increase in the density and Young’s modulus at a liquid mass fraction of 6% and interpreted this behavior as the transition from the pendular into the funicular state. At a mass fraction between 13% and 15% the density started to fluctuate with increasing liquid content whereas Young’s modulus reached a maximum before dropping down. This was explained with a transition into the capillary state. Similarly, they stated an increasing bulk density between 5% and 14%, measured with a shear cell, interpreting this as the result of increasing capillary forces in the funicular state in contrast to increasing disjoining forces in the capillary state above 14%.

### 2.3.4 Wet powder compressive strength

Following Iveson et al. (2002), the resistance to shear deformation of wet powders arises from tribological interactions between touching particles and particle interlocking. Interlocking depends on particle size and shape. Lubricating films lower interparticle friction on a particle and macroscopic level (Cain et al., 2000). Internal friction in a granular body is not strongly strain-rate dependent (Iveson et al., 2002). Buoyancy forces can be neglected for particles smaller than 1 mm in diameter (Princen, 1968).

Small particles (Rumpf and Turba, 1964), broad particle size distributions (Kristensen et al., 1985a; Linkson et al., 1973) and low porosities increase the strength of wet granules (Kristensen et al., 1985b; Newitt and Conway-Jones, 1958). The effect on the interparticle friction is dominant in the case of fine and broadly sized powders. The addition of liquid results in a decrease of the granule strength (Iveson et al., 2002).
2.3 Wet powders

Corresponding to Eq. 2.52, the granule strength increases with increasing surface tension as both the surface tension force at the three-phase contact line and the capillary pressure are proportional to the surface tension. When a wet powder is compressed, the internal friction between layers of moving particles must be surmounted in addition to the tensile strength of the bonds in the fracture plane (Iveson and Page, 2001). The effect of the liquid on interparticle friction and on liquid bridge forces is conflicting. Wet powders made from non-spherical particles can trap liquid in crevices on the particle surface and much of the binder is not accessible for inter-particle bonding. Furthermore an irregular particle shape leads to a higher coordination number, more interlocking and higher friction coefficients (Iveson and Page, 2005). At low strain rates frictional forces are the controlling factor in determining the (unconfined) compressive strength of wet powders (Iveson et al., 2002; Simons and Pepin, 2003). At low deformation speeds, expressed in terms of the dimensionless capillary number,

\[
Ca = \frac{\dot{\epsilon} \eta x}{\sigma_{LG}} \quad (2.83)
\]

(\(\dot{\epsilon}\)=bulk strain rate) the dimensionless flow stress,

\[
Str = \frac{\sigma_{c}x}{\sigma_{LG}} \quad (2.84)
\]

is independent of the strain rate (\(Ca < 10^{-4}\)) and capillary forces and interparticle friction are the predominant parameters in controlling the compressive strength of wet powders (Simons and Pepin, 2003). At higher capillary numbers viscous forces become dominant and the compressive strength increases with increasing strain rate. This behavior was confirmed by Iveson and Page (2005) in numerous measurements of the compressive strength of wet powder systems with particles of different size and shape. As the capillary number increased, the failure mode changed from brittle cracking to ductile plastic flow coinciding with the transition from strain-rate independent flow to strain-rate dependent flow. This change in failure mode is the opposite of that observed for fully saturated systems, i.e. pastes (Iveson and Page, 2004)\(^1\). Following this theory there is a single failure plane at low \(Ca\)-numbers with the rest of the bulk material remaining relatively undeformed. At high capillary numbers, when viscous forces exceed strain-rate insensitive capillary and friction forces, failure occurs over an extended zone where each layer only experiences a small portion of the bulk strain. This inhibits the formation of cracks and results in plastic flow (Iveson and Page, 2004).

\(^1\)Concentrated pastes and suspensions usually exhibit shear dilatancy. This results in a reduction of the pore pressure. At high strain rates, liquid is unable to flow in fast enough to fill the dilated regions and cavitation occurs. This results in a transition from ductile to brittle behavior (Franks et al., 2000; Smith, 1997). In partially saturated systems the pore pressure remains essentially constant because air can flow freely into and out of the assembly (Iveson and Page, 2004).
3 Materials and Methods

Wet powders were prepared by mixing hard and insoluble bulk solids with a Newtonian binder in different proportions. In this chapter, the components of these wet powders are presented. We also discuss the characterization techniques which were applied to investigate the particle size distributions, the particle and liquid mass densities, the liquid rheology, the liquid surface tensions and the contact angles between liquid and solid. Two methods are presented to prepare wet powders for the measurement of compaction curves, for the batch-wise ram extrusion and for shear cell measurements. The setup and the execution of the three last-named testing methods are explained in detail. Finally, we describe µ-computed tomography which was used to analyze the microstructure of wet powder extrudates.

3.1 Solid particles

Sepasil® The silica flours Sepasil® B 5/63 and Sepasil® B 20/100 (Sihelco AG, Birsfelden, Switzerland) consist of the same raw material but different sieve fractions. They are hydrophilic and contain more than 99% quartz.

Spheriglass® 3000 The glass microspheres Spheriglass® 3000 (Potters Industries Inc., Valley Forge, PA, USA) are manufactured from a hydrophilic soda-lime (A) glass. According to the manufacturer they are hard, smooth and shaped spherically allowing for a close packing and high filling degrees.

Sikron® B 800 The hydrophilic silica flour Sikron® B 800 (Sihelco AG, Birsfelden, Switzerland) is a very fine and cohesive powder and has a quartz mass fraction of 99%.

The dry powders were analyzed with respect to their particle size distribution and their particle density. Pictures taken with an inverse light microscope (DM IRB, Leica Microsystems, Wetzlar, Germany) give information about the particle shape (chapter 4.1).

3.2 Liquid binder

Nutriose® is the name given to a range of soluble fibers promoted by Roquette (Lestrem, France). It is a food dextrin and available as an agglomerated powder. We used as binder Nutriose® FM 06, a dextrin derived from maize. The weight average molecular weight is reported to be 5000 g/mole. Its chemical structure is depicted in Figure 3.1.
Aqueous solutions of Nutriose® FM 06 show Newtonian flow behavior. The viscosity can easily be adjusted through the Nutriose® concentration. Nutriose® FM 06 shows no retrogradation. Tests demonstrated that the viscosity of a 63% w/w solution in a closed beaker did not change over three months. Viscosity functions and densities of three Nutriose® FM 06 solutions with concentrations of 60, 63 and 70% are presented in chapter 4.2.

In the following, Nutriose® FM 06 will be referred to as Nutriose. The solid powders will be abbreviated as Sepasil B 5/63, Sepasil B 20/100, Spheriglass and Sikron.

### 3.3 Laser diffraction

Particle size distributions of the solid powders were measured with the laser diffraction particle size analyzer LS 13 320 (Beckman Coulter, Krefeld, Germany). Its technology is based on the theories of Mie scattering, Fraunhofer diffraction and Polarization Intensity Differential Scattering (PIDS) providing a measurable particle size range from 0.4 µm to 2000 µm. When light illuminates a material with a dielectric constant, different from that of the surrounding medium, light is scattered depending on the wavelength of the light and on optical properties of the material. Scattering phenomena comprise diffraction, reflection, refraction and absorption. The extent of scattering depends on the ratio of the complex refractive index of the material and its surrounding medium. If a particle scattering light is much smaller than the wavelength of the light, the electric field traversing the particle is uniform throughout the particle. Particles falling within this range have a radius in the order of magnitude of 20 nm to 30 nm. If the particle is assumed to be transparent, Rayleigh’s theory of light scattering applies. Light is scattered by the polarization of a single dipole, if the refractive index of the particle differs from the refractive index of the surrounding medium. As the intensity of the scattered light increases as the sixth power of the particle radius, its intensity is dominated by larger particles. Furthermore, the intensity of the
scattered light is inversely proportional to the fourth power of the wavelength of incident light.

Mie’s theory is applied when the particle radius is in the order of magnitude of the wavelength of the light. The electrons in these particles no longer sense the same magnitude and direction of the electric field. In Mie’s theory many intensity maxima and minima of the light scattered by spherical particles appear as a function of the scattering angle whereas the numbers and positions of these maxima and minima depend on the refractive-index difference and the particle size. Additionally, interferences are taken into account. When the particle size is much larger than the wavelength of the incident light and in the case of highly absorptive particles, edge effects dominate the scattering patterns. Bending of light at the boundaries of particles cause interference effects. If the particles are additionally highly absorptive (absorption coefficient > 0.5) and the refractive-index ratio is larger than 1.2, scattering effects can be described as Fraunhofer diffraction, a simplified form of Mie’s theory.

The LS 13 320 is equipped with 126 detectors measuring the light intensity at varying scattering angles. A 780 nm laser is used as light source. Additionally, PIDS lamps with wavelengths of 450, 600 and 900 nm are installed. The PIDS technology included in the LS 13 320 coulter analyzes the difference in scattered intensity between horizontally and vertically polarized light signals as a function of angle for these three different wavelengths of light and is used to achieve a higher accuracy for submicron particles which offer limited information in diffraction patterns.

In the framework of this thesis the determination of the particle size distribution by the control software (Version 5.04.28, Beckman Coulter Inc., Miami FL, USA) followed from Mie’s theory in the case of Spheriglass glass beads (refractive index 1.51, absorption coefficient 0). Fraunhofer diffraction was the theory applied to the silica powders. A universal liquid module was used with demineralised water (refractive index 1.332) as the continuous phase. The pump velocity was adjusted to 60 %, the measurement time to 90 s. The solid particles were suspended in a beaker with demineralised water and filled with a pipette into the liquid module until a laser obscuration between 9 % - 12 % and a PIDS obscuration of about 60 % was reached. Each measurement was carried out in triplicate. Volume weighted particle size frequencies

\[ q_{3,lg}(x_i) = \frac{1}{\sum_{k=1}^{\infty} m_k \Delta x_i \, lg(exp(1))} \]

were calculated and plotted versus the particle diameter on log-log axes. \( m_i \) is the mass of all particles in the size range from \( x_i - \Delta x_i/2 \) to \( x_i + \Delta x_i/2 \). The cumulative particle size distribution

\[ Q_3(x_i) = \frac{\sum_{j=1}^{i} m_j}{\sum_{k=1}^{\infty} m_k} \]

was calculated to determine the volume weighted median diameter \( x_{50,3} \).
and the characteristic diameters $x_{10,3}$ and $x_{90,3}$:

$$Q_3(x_{10,3}) = 0.1$$  \hspace{1cm} (3.4) \\
$$Q_3(x_{90,3}) = 0.9$$  \hspace{1cm} (3.5)

Additionally, the surface weighted mean diameter, called Sauter diameter, was determined:

$$x_{1,2} = \sum_{i=1}^{\infty} (x_i q_2(x_i) \Delta x_i)$$  \hspace{1cm} (3.6)

$q_2(x_i)$ is the surface weighted particle size density distribution:

$$q_2(x_i) = \frac{x_i^2 n_i}{\sum_{k=1}^{\infty} x_k^2 n_k \Delta x_k}$$  \hspace{1cm} (3.7)

$n_i$ is the number of particles with a diameter in the size range from $x_i - \Delta x_i/2$ to $x_i + \Delta x_i/2$.

### 3.4 Gas pycnometry

According to manufacturer’s data all solid powders are free from inner porosities so that their particle density and their solid density are identical. The determination of the particle density was carried out with an AccuPyc 1330 helium pycnometer (Micromeritics Instrument Corp., Norcross, USA). The device works by measuring the amount of displaced gas. The pressures observed upon filling a sample chamber and then discharging it into a second empty chamber allow computation of the sample solid phase volume. Gas molecules rapidly fill the tiniest pores of the sample. Only the true solid phase of the sample displaces the gas (Doyle, 2006). A standard sample cup was filled with the dry sample powder by at least two-thirds. The cup with the sample was weighed and inserted into the cell chamber of the AccuPyc 1330 which was then closed with a cap. Prior to measurement the pressure of the helium tank was adjusted to about 1.9 bar. The measurement was then started and carried out three times. The manufacturer states an accuracy of measurement of 0.03 % of reading plus 0.03 % of nominal full-scale sample chamber volume.
3.5 Liquid densimetry

The density of Nutriose solutions was measured with a DMA 38 density meter (Anton Paar GmbH, Graz, Austria). The measurement method is based on the fact that the natural mechanical frequency of oscillation of a U-shaped tube filled with a sample is a function of the sample density. A harmonic oscillation of the tube is electromechanically driven and the period of oscillation as an output parameter is used to determine the density of the sample.

The tube was filled slowly and continuously with the sample by means of a plastic syringe until the visible part of the tube was full and no more air bubbles were visible. The temperature was regulated by Peltier elements and set at 20°C. The accuracy of measurement is declared by the manufacturer as being 0.001 g/cm³.

3.6 Rheometry

Viscosity functions of the Nutriose solutions were measured with the Modular Compact Rheometer MCR 300 (Physica Messtechnik GmbH, Stuttgart, Germany). A CC27 coaxial cylinder geometry with rotating inner and static outer cylinder (Searle principle) was used. The outer radius of the shear gap was \( R_a = 14.46 \text{ mm} \), the inner radius \( R_i = 13.33 \text{ mm} \). The length of the inner cylinder was \( L = 40 \text{ mm} \). In case of a Newtonian fluid, the shear rate in the gap is:

\[
\dot{\gamma}(r) = \frac{1}{r^2} \frac{2R_i^2 R_a^2}{R_a^2 - R_i^2} \omega
\] (3.8)

By measuring the torque \( M \), exerted by the sheared liquid on the rotating inner cylinder, the wall shear stress at the radius \( R_i \) can be calculated:

\[
\tau(R_i) = \frac{M}{2\pi R_i^2 L}
\] (3.9)

Hence the dynamic viscosity at the wall of the inner cylinder is equal to the ratio of the shear stress and the shear rate at the radius \( R_i \):

\[
\eta(R_i) = \frac{\tau(R_i)}{\dot{\gamma}(R_i)}
\] (3.10)

A Peltier element integrated in the MCR 300 regulated the temperature of the non-rotating outer cylinder which was adjusted to 20°C. The outer cylinder was filled with 18 ml of liquid before inserting the inner cylinder. The measurement was started when the target temperature was reached. Viscosity functions were determined at fixed shear rates in the range 0.1 s\(^{-1}\) to 100 s\(^{-1}\).
3.7 Surface tension measurements

A pendant-drop tensiometer built at the Laboratory of Food Process Engineering, ETH Zurich, was used to measure surface tensions of the Nutriose solutions. The method, described in detail by Gunde et al. (1992, 2001) is based on the determination of the profile of a drop pendant at the end of a vertical capillary of radius \( r \) held by the surface tension \( \sigma_{LG} \). The shape of a drop pendant in a cuvette is described by the Laplace equation (Eq. 2.51) defining the pressure difference \( \Delta p \) at any point of the interface between the drop and the surrounding medium.

Drops formed at the tip of a vertical stainless steel capillary with a radius of 0.6 mm were analyzed with respect to their profile by acquiring images with a CCD camera (Sony DFW-500, Tokyo, Japan). The drop profile was used for a numerical fitting of the Laplace equation for a pendant drop providing information about the surface tension and the drop volume. The numerical fitting was realized by a software algorithm implemented in Matlab 7.7.0 (The MathWorks, Inc., Natick, USA). The temperature of the syringe (Hamilton series 1000, Bonaduz, Switzerland) feeding the capillary was adjusted to 20 °C by means of a circulating water bath. The number of pictures taken of the pendant drop was set at 1 min⁻¹. Thus the development of the surface tension over the time could be recorded. An exponential decay was observed in the case of all liquids investigated which was due to impurities diffusing towards the drop surface. The measurement was stopped when the steady-state value could be assessed by the decay of the surface tension being less than 1 mN/m per 100 min. The cuvette in which the drop was hanging was filled with Nutriose solution up to 2 mm below the drop to saturate the surrounding atmosphere and to prevent shrinkage. Each sample was analyzed in duplicate or triplicate.

3.8 Wet powder preparation

Two different procedures were carried out to prepare wet powder masses for batchwise ram extrusion. In the first method described here the wet powder was produced by transforming the liquid into a powdery state in a spray chilling process before it was blended with the solid powder:

1. In a first step the Nutriose solution (\( \phi_{Nutr.}=63 \% \) w/w) was solidified by spray chilling: the liquid solution consisting of demineralised water and Nutriose was stored in a 3l double wall vessel connected to a rotary vane pump (SRU/S-0005-V08, Catag Ag, Basel, Switzerland). The wall temperature of the vessel and of the pipe connecting the pump with the spray nozzle was adjusted to 90 °C by means of a circulating water bath to realize a low viscosity (0.05 Pas) of the liquid in the nozzle. This improved the atomization by producing smaller droplet sizes and increasing the extent of filament disruption. A two-component nozzle (1/4 VMAU, Spraying Systems Co., Wheaton II, USA) was used and the air pressure set at 2 bar by means of a pressure-reducing valve. The air was heated at 65 °C to extend the solidification time of the liquid in the spray tower, causing more disrupted liquid filaments. The liquid pressure exerted
3.8 Wet powder preparation

by the rotary vane pump was 6 bar. The spray tower built at the Laboratory of Food Process Engineering, ETH Zurich, had a height of 1.7 m and a diameter of 1 m. Liquid nitrogen was sprayed into the tower in a vertically and horizontally central position by two nozzles orientated upwards and downwards. The liquid nitrogen was stored in a pressure tank (Apollo 100, Messer Griesheim GmbH, Germany) and its flow was controlled manually by means of a pressure valve in such a manner that a temperature of \(-90^\circ\text{C}\) was maintained at 30 cm above the conical outlet of the spray tower. The solidified and powdery Nutriose solution was stored in a cooling chamber at \(-24^\circ\text{C}\).

2. The spray chilled Nutriose powder was sieved to get rid of large particles, clumps and filaments (Vibratory Sieve Shaver, Fritsch, Idar Oberstein, Germany). All particles >150 µm were discarded.

3. The solidified binder particles were mixed with the silica or glass particles at \(-24^\circ\text{C}\) in a free fall mixer with a vessel volume of 0.5 l. The rotational axis of the mixer enclosed an angle of 45° with the symmetry axis of the cylindrical vessel. The rotational speed was set at 60 rpm, the mixing time at 60 min.

4. After mixing, the material was uniaxially compacted in a material testing apparatus (Zwick Z010, Zwick GmbH & Co. KG, Ulm, Germany), equipped with a 10 kN load cell, at 20 °C (control software testXpert V.10.11). The aim of this step was to realize a well-defined mechanical prehistory of the wet powder prior to extrusion. 4 x 10 g of wet powder mass were filled into a barrel made from brass with a diameter of 20 mm and a length of 210 mm. The bottom was closed by a temporary cover. Each of the portions was compacted by a ram with a piston speed of 0.5 mm/s. Compaction pressures of 16, 32, 64, 127, 190 or 255 bar were applied. The proportioning of the wet powder guaranteed sufficiently homogeneous wet powder compacts (chapter 3.9).

The second wet powder preparation method consisted of the following process steps:

1. The solid powder was mixed with the spray dried Nutriose powder in the free fall mixer mentioned above. The rotational speed was 60 rpm, the mixing time 60 min. Representative sampling and measurements of local solid concentrations showed that the mixing efficiency was higher than 98 %.

2. The powder mixture was given into a Duplex kneader (Laboratory kneader MKD 0.6-H60, IKA®-Werke GmbH & Co. KG, Staufen, Germany) where demineralised water was added in drops at a rotational speed of the kneader of 50 rpm. Afterwards the material was kneaded for one hour at 50 rpm while the temperature of the kneader wall was kept at 20 °C by means of a circulating water bath.

3. The wet powder mass was pressed through a sieve with a mesh size of 4 mm to make it a granular material.

4. The granules were compacted in the material testing machine like the wet powder mass prepared with the method described before.

The mixing efficiencies of both wet powder preparation methods were verifiably high and no inhomogeneities were visible. Nevertheless wet powder masses prepared with these two methods significantly differed in their microstructure. The kneading step in the second
method led to a more effective wetting of the particle surfaces resulting in a reduced coefficient of internal friction. The impact on the compressibility and on extrusion pressures of wet powders will be elucidated in chapter 4.5 and chapter 4.6.

3.9 Compaction curves

Compaction curves illustrate the saturation, the bulk density or the porosity of a bulk solid which is uniaxially compacted in a barrel. Wall friction causes an exponentially decreasing vertical pressure in the barrel. As a consequence, the powder at the bottom is subject to a smaller pressure than the powder below the ram resulting in an inhomogeneous microstructure. This effect can be minimized by ensuring a small aspect ratio \( H/D_0 \) of the height of a powder compact and its diameter.

During compaction the powder mass is plastically deformed. If the walls of the barrel complied to such an extent that the flow was isochoric, the state of stress could be described by means of an end Mohr stress circle of an individual yield locus. However, as the walls are more or less stiff, the state of stress during compaction is not active-plastic but active-elastic and the horizontal stress ratio is larger than at steady state flow (chapter 2.2.5).

Compaction curves were measured with the Zwick Z010 material testing apparatus equipped with a 10 kN load cell. A barrel was put into a double wall fitting which was tempered at 20\(^\circ\)C by a circulating water bath. The bottom of the barrel was closed by a temporary cover. The ram with a diameter of 20 mm and a length of 230 mm was mounted on the traverse of the material testing apparatus. 10 g of wet powder were filled into the barrel and compacted by the ram with a ram velocity of 0.01 mm/s until a compaction pressure of 255 bar was reached. During compaction the actual height of the ram and the force applied by the ram were recorded by the software testXpert V.10.11.

The aspect ratio \( H/D_0 \) was smaller than unity at any compaction pressure and hence such that a decrease of the acting vertical stress by wall friction could be neglected. This was verified by measuring compaction curves at different filling heights.

The recorded distance between the die and the temporary cover had to be corrected because of an elastic deformation of some components of the material testing apparatus. This resulted in a measured height of the compacted powder less than its true value. To quantify this elastic deformation, a measurement with the identical setup was carried out without any powder in the barrel. The elongation of the total setup is shown in Figure 3.2 as a function of the vertical force applied by the ram.

The compliance of the setup can be approximated by a straight line through the origin with a slope of \(-8.005 \times 10^{-5}\) mm/N. Thus the correct height of the cylindrical powder compact in the barrel is:

\[
H = H_{\text{meas.}} + F \cdot 8.005 \times 10^{-5} \text{mm/N} \tag{3.11}
\]
3.10 Static contact angle measurements

Contact angles between binders and solids were needed to evaluate the wetting of the particles during wet powder preparation and to assess liquid bridge forces as they influence wet powder cohesion and internal friction.

To determine contact angles, saturated wet powder tablets were pressed in the Zwick Z010 material testing apparatus with the same setup as used for the measurement of compaction curves (chapter 3.9). Wet powder masses were prepared by mixing the solid powder with the spray dried Nutriose powder and kneading the mixture with demineralised water in the Duplex kneader (chapter 3.8). The solid mass fraction was chosen in such a manner that the saturation was unity at the applied piston pressure of 200 bar according to compaction curves. In this way, 5 g of wet powder were compacted and the formed tablets were manually pressed out of the barrel with the piston after removing the temporary cover at the bottom of the barrel. The tablets were put on the stage of a goniometer (ramé-hart Model 100, ramé-hart instrument Co. Netcong, NJ, USA) which could be aligned in such a manner that the surface of the tablet was even. A small droplet of liquid sample was put on the aligned tablet surface with a microsyringe and the angle between the droplet and the tablet surface at the left and the right edge of the profile was determined with an integrated cathetometer. This procedure was repeated three times resulting in the determination of six angles per
3.11 Ram extrusion

Wet powders were extruded through cylindrical dies in batch quantities. The extrusion trials were partly carried out in the Zwick Z010 material testing apparatus and partly in a high pressure capillary rheometer (Rheograph 2002, Göttfert, Buchen/Odenwald, Germany). The Zwick Z010 allowed the simultaneous measurement of the vertical stress applied by a ram and the wall normal stress in the barrel 11.5 mm before the die by means of a 350 bar pressure transducer (MPS 01210-0000-3,5CB, Dynisco, USA) which was attached to a connection flange between the barrel and the die (diameter 20 mm). The applied vertical stress was recorded by the control software of the material testing apparatus, whereas the wall normal stress was registered by a Labview 8.5 (National Instruments, Austin, USA) measuring software. The number of measuring points per time was adjusted to 2 s⁻¹. A technical drawing of the setup is shown in Figure 3.3.

![Technical drawing of the setup for the ram extrusion with the material testing apparatus.](image)

Barrels containing 40 g of pre-compacted wet powder were hold in a coaxial position with the flange and tempered at 20°C by a double wall fitting. Their bottom end was now open after the temporary cover had been removed. The outer diameter of the dies was 30 mm,
the inner diameter was 12 mm, 14 mm or 18 mm. They had lengths of 10 mm, 15 mm or 20 mm. When one of the two shorter dies was used, steel shims were laid below the die so that there was no free space between the die and the flange. This guaranteed a leakproof hub of the die in the centering of the flange.

Extrusion trials were carried out in the high pressure capillary rheometer to measure the wall normal stress in the barrel at different distances from the die giving an insight into the effect of the pressure reducing wall friction. The rheometer consisted of a double wall fitting for the barrels (T=20 °C), again containing 40 g of pre-compacted powder, to which a flange was attached with an inner diameter of 20 mm and four mountings for pressure transducers (Figure 3.4). As sharp-edged silica particles would have damaged the membranes of the pressure transducers, the mountings for the transducers were built so that the transducer membranes were not flush with the wall of the flange but fixed in a position where they measured the pressure transferred by a highly viscous silicone gum (BW 400, Wacker Chemie AG, München, Germany) which was filled into a small cylindrical hole (diameter 2 mm, length 5 mm) in the wall of the flange prior to extrusion, see Figure 3.4. The dies were mounted in the centering at the bottom end with another flange.

Extrusion trials were carried out with constant ram velocities in the range between 0.05 mm/s and 1 mm/s. A Lab View 8.5 (National Instruments, Austin, USA) program recorded the wall normal stresses transduced by the four pressure sensors as a function of time (two measuring points per second). The extrusion was stopped when the ram was about 1 cm before the die. The time at stoppage and the exact position of the ram were noted down in order to reconstruct afterwards the measured stresses as a function of the distance between the die and the ram. Extrusion trials were generally carried out in duplicate.
3.12 Liquid phase migration

The distribution of the binder in wet powder extrudates was determined gravimetrically. For this purpose, the extrudate was detached from the die, whereas the separation plane between the material in the barrel (or the die) and the extrudate lied anywhere between the two ends of the die. The length of the extrudate was measured with a caliper. The extrudate was dissected with a cutter in eight segments of the same length. Each of the segments was immediately weighed and put into a 50 ml polypropylene beaker. The segments were suspended in about 10 ml of demineralised water and carefully stirred to dilute the Nutriose solution and to desagglomerate particle aggregates. The strongly diluted and low-viscosity Nutriose solution was filtered out by a funnel filter and a cellulose filter paper with a particle retention of 2.5 µm and a diameter of 90 mm (No.42, Whatman International Ltd, United Kingdom). The dry weight of the filter paper had been determined prior to the filtration in a HR73 halogen moisture analyzer (Mettler-Toledo (Schweiz) GmbH, Greifensee, Switzerland) at a temperature of 120 °C. A low pressure during filtration was realized by a water-jet vacuum pump. After filtration, the remaining humidity on the particles was evaporated in the moisture analyzer at 120 °C until the weight of the powder on the filter paper did not change by more than 1 mg within two minutes. Thus the binder liquid mass fraction in a segment yielded:

\[ \phi_{m,l} = 1 - \frac{m_{s+f} - m_f}{m_{total}} \]  

(3.12)

whereas \( m_{s+f} \) is the mass of the dried powder and the filter paper, \( m_f \) is the dry mass of the filter paper and \( m_{total} \) is the total mass of the segment after extrusion. The accuracy of measurement of this method with respect to \( \phi_{m,l} \) was about 0.5 %. Preliminary tests showed that very fine particles flowing through the filter paper at the beginning of filtration did not influence the result. The measured binder mass fractions were plotted over the distance from the extrudate front and approximated by a polynomial fit curve of 2nd degree. This is illustrated by an example in Figure 3.5.

3.13 µ-computed tomography

The microstructure of wet powder extrudates was investigated with a µ-tomographic imaging system (µCT 40, Scanco Medical AG, Brüttisellen, Switzerland). The measurements were carried out by b-cube AG (Zurich, Switzerland). The µCT 40 scanner is equipped with a 5 µm focal spot X-ray tube as a source. A two-dimensional CCD, coupled to a thin scintillator as a detector permits acquisition of 210 tomographic images in parallel. The long axis of the investigated samples was oriented along the rotation axis of the scanner. The X-ray tube was operated at 50 kVp and 160 µA with an integration time set at 300 ms and all projection frames were recorded 3 times and then averaged. Scans were performed at an isotropic, nominal resolution of 8 µm.
Extrudates of Sepasil B 5/63 particles bound by a 63% Nutriose solution were segmented with a cutter. Segments at 10, 40 and 70 mm distant from the extrudate front, each of which had a length of 10 mm, were analyzed with respect to their radial air cell distribution. As the drying of the samples could not be controlled, the samples were dried at ambient conditions within a period of two days before their analysis. The scan height was restricted to 3.2 mm for all samples, which resulted in a measurement time of two hours per sample. The solid particles and the dried Nutriose were separated from the air inclusions by a global thresholding procedure, with a threshold value adjusted to 20% of the maximum grayscale value. An outer mask which identified the envelope of the sample was generated automatically. This mask defined the total volume of interest for each sample. Furthermore, from this total mask, 9 overlapping hollow cylindrical masks (the width of the hollow cylinder was always 20% of the overall sample dimension) were calculated, with the smallest cylinder starting at the center and the largest hollow cylinder covering the outside of the sample, to analyze the radial distribution of air inclusions within the sample. Within all masks the volume fraction of the air volume related to the total mask volume was calculated.

### 3.14 Shear cell measurements

A ring shear tester (RST-XS, Dr. Dietmar Schulze Schüttgutmesstechnik, Wolfenbüttel, Germany) was used to measure yield loci and wall yield loci of wet powders. The preparation of wet powder masses consisted of the mixing of the spray dried Nutriose
powder with the solid powder followed by the kneading of the blend with demineralised water in the Duplex kneader as described in chapter 3.8. The material was subsequently pressed through a sieve with a mesh size of 0.25 mm by means of a spatula to get a powder consisting of fine particle agglomerates. In this way, it was avoided to generate large air inclusions when filling the material into the shear cell. The size of the mesh did not influence the measurement results because the microstructure determining the course of the yield loci was exactly defined in the preconsolidation step making void the preceding mechanical treatment of the powder.

The sieved powder was filled into an aluminum shear cell (type XS-Mr) with a cross section of 24 cm$^2$ and a specimen volume of 30 cm$^3$ (Figure 3.6). In combination with this shear cell the ring shear tester was able to exert normal stress loads between 0.22 kPa and 23 kPa.

![Figure 3.6: Shear cell and lid, type XS-Mr (Dr. Dietmar Schulze Schüttgutmesstechnik, Wolfenbüttel, Germany).](image)

At the bottom of the shear cell a ring was attached with vanes protruding into the powder to prevent wall slip when the sample was sheared. The lid of the shear cell was also equipped with entrainers preventing wall slip.

The shear cell was filled beyond its upper edge and the excess material was carefully scraped off with a spatula so that the powder surface was flush with the upper edge. The filled shear cell was weighed and placed on the ring shear tester. After placing the lid on the powder, the loading rod was inserted into the crossbeam of the lid and the tie rods were hung into the crossbeam and the shear force pick-ups connected to the load cells. The assembled shear tester is depicted in Figure 3.7.

By means of the loading rod, the normal force in the preconsolidation step and during shear to failure was adjusted. The bottom ring was rotated at a circumferential speed of about 1 mm/min while the lid was prevented from rotation by the two tie rods. The shear force in the shear plane exerted by the powder on the lid was recorded by two load cells to which
3.14 Shear cell measurements

Figure 3.7: Ring shear tester RST-XS with assembled shear cell XS-Mr (Dr. Dietmar Schulze Schüttgutmesstechnik, Wolfenbüttel, Germany). 1. shear cell, 2. drive head, 3. lid with attached crossbeam, 4. loading rod, 5. tie rod, 6. shear force pick-up and load cell, 7. centering device.

For the measurement of an individual yield locus, the preshear stress $\sigma_{\text{pre}}$ and three to five normal stresses $\sigma_{\text{sh}} < \sigma_{\text{pre}}$ were defined. The system was presheared until the shear stress $\tau_{\text{pre}}$ was constant. Then the powder was sheared with the smallest of the defined normal stresses until the powder failed which could be recognized by the maximum in the course of the shear stress $\tau_{\text{sh}}$. Subsequently, the powder was preconsolidated again and sheared to failure under the next higher normal load. This was repeated for all selected normal stresses. To verify that the powder flow properties had not changed during the measurement, the determination of the shear stress under the smallest normal load was repeated at the end of the measurement. Each of the matching data pairs $(\sigma_{\text{sh}}, \tau_{\text{sh}})$ was one point of the individual yield locus specific for the applied consolidation stress. Shear points of incipient flow located to the left of the point at which the yield locus touches the Mohr stress circle defining the unconfined yield strength were admitted. In opposition to the majority of dry bulk solids, the wet powders considered here were able to transfer high tensile stresses with the result that Mohr stress circles clearly extending into the region of negative (tensile) normal stresses were tangent to the yield locus.

A typical course of the shear stress and the bulk density over time is illustrated in Figure 3.8. Yield loci were measured for preshear stresses of 2, 5, 10 and 20 kPa. All yield loci were determined in duplicate or triplicate and exhibited an excellent reproducibility.

For the determination of wall yield loci, a wall friction cell, type WM (Dr. Dietmar Schulze Schüttgutmesstechnik, Wolfenbüttel, Germany), was used. Its geometry is illustrated in
3.14 Shear cell measurements

Figure 3.8: Shear stress and bulk density of a wet powder as a function of time during the measurement of an individual yield locus.

Figure 3.9.

A wall material sample of lathed, disc-shaped brass was inserted into the cell so that its surface was about 4 mm below the upper edge of the cell. Two facing entrainer bars attached to the cell reached into notches of the brass disc to ensure that it rotated (Figure 3.10).

Again the powder was filled into the cell in such a manner that the powder was flush with the upper edge. The lid was equipped with pyramidal milled-out portions to prevent slip along the lid wall. When the wall friction cell was rotated, a relative motion between the rotating brass disc and the bulk solid provided a shear force was exerted on the lid. As the friction between the powder and the wall sample was smaller than the internal friction of the bulk solid, it was ensured that the bulk solid slid along the sample wall without forming an inner shear zone (Schulze, 1997). As in the case of the shear cell XS-Mr, the lid was connected with the load cells by two tie rods and the normal force was adjusted by a loading rod connected with the crossbeam of the lid. After a normal load was set, the wall friction cell was rotated with a circumferential speed in the order of magnitude of 1 mm/min until the measured shear stress was constant. Wall shear stresses $\tau_W$ for seven normal loads (0.3, 1, 2, 5, 10, 15 and 20 kPa) $\sigma_W$ were determined, each of the data pairs $(\sigma_W, \tau_W)$ being a point of the wall yield locus. Like individual yield loci, wall yield loci were measured in duplicate or triplicate and showed an excellent reproducibility.
3.14 Shear cell measurements

Figure 3.9: Geometry of the wall friction cell, type WM (Dr. Dietmar Schulze Schüttgutmessotechnik, Wolfenbüttel, Germany).

Figure 3.10: Wall friction cell with spacer discs and wall material sample (Dr. Dietmar Schulze Schüttgutmessotechnik, Wolfenbüttel, Germany).
4 Results

The results of this thesis are arranged as follows: first the powder solids and the liquid binders are characterized with respect to the physical properties that are relevant for the description of wet powder flow. A subsequent analysis of wet powder shear flow in a ring shear cell is presented together with a semi-empirical model by means of which individual yield loci of a glass beads powder in the pendular state are calculated. In the following, compaction curves are shown for the demonstration of the impact of particle and liquid properties on the compressibility of wet powders. Finally, relationships between the microstructure and stress fields during wet powder ram extrusion are highlighted and completed by a continuum mechanical model by means of which the states of stress in an extruder barrel can be calculated.

4.1 Characteristics of the powder solids

Figure 4.1 depicts the particle size distributions of Sepasil B 5/63, Sepasil B 20/100, Spheriglass 3000 and Sikron B 800 which were determined by laser diffraction.

![Figure 4.1: Particle size distributions of the bulk solids.](image-url)
4.1 Characteristics of the powder solids

Sepasil B 5/63 contains a larger mass fraction of particles < 10µm than Sepasil B 20/100 but a smaller mass fraction of particles > 100µm (Table 4.1). It exhibits a broader particle size distribution than Sepasil B 20/100 related to its median diameter $x_{50,3}$.

Table 4.1: Characteristic parameters of the particle size distributions.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{50,3}$</td>
<td>µm</td>
<td>23.7</td>
<td>59.5</td>
<td>11.2</td>
</tr>
<tr>
<td>$Q_3(10\mu m)$</td>
<td>%</td>
<td>17.1</td>
<td>5.0</td>
<td>35.7</td>
</tr>
<tr>
<td>$1 - Q_3(100\mu m)$</td>
<td>%</td>
<td>1.6</td>
<td>12.2</td>
<td>0.7</td>
</tr>
<tr>
<td>$(x_{90,3} - x_{10,3})/x_{50,3}$</td>
<td>-</td>
<td>2.1</td>
<td>1.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Spheriglass glass beads are smaller in size than Sepasil 5/63 silica particles but exhibit a comparable distribution width. Finally Sikron B 800 silica particles have a bimodal size distribution and are very fine-grained. There are no particles larger than 10µm.

The particle shapes of the four powders are illustrated in the light micrographs in Figure 4.2. Sepasil B 5/63 and Sepasil B 20/100 particles are sharp-edged, aspherical and of varying shape. Spheriglass glass beads are spherical without any edges. Sikron particles tend to agglomerate due to their small particle size which results in an important impact of van der Waals adhesive forces. The primary particles show a more homogeneous shape than Sepasil silica particles.

Figure 4.2: Light micrographs of the bulk solids. a) Sepasil B 5/63, b) Sepasil B 20/100, c) Spheriglass 3000, d) Sikron B 800.

According to manufacturer’s data all particles are free from inner porosities. Furthermore, they are hard and brittle. Spheriglass glass beads exhibit a Young’s modulus of 68.9 kN/mm$^2$. Quartz crystal typically has a Young’s modulus of 76.5 kN/mm$^2$ (Almaz Optics, 2009). However, in contrast to the round shape of the glass beads, the sharp edges of Sepasil B 5/63 and Sepasil B 20/100 particles can cause high stress peaks which may lead to particle breakage. For the same reason attrition can occur, when the silica particles move relative to each other under high pressure.
4.2 Characteristics of the liquid binders

The pycnometrically obtained particle densities are listed in Table 4.2.

Table 4.2: Particle densities.

<table>
<thead>
<tr>
<th>Particle density $\rho_P$ g/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sepasil B 5/63 2.649 ± 0.001</td>
</tr>
<tr>
<td>Sepasil B 20/100 2.649 ± 0.001</td>
</tr>
<tr>
<td>Spheriglass 3000 2.460 ± 0.001</td>
</tr>
<tr>
<td>Sikron B 800 2.670 ± 0.001</td>
</tr>
</tbody>
</table>

4.2 Characteristics of the liquid binders

The viscosity functions of the Nutriose solutions used in this work, which were determined by rheometry, are shown in Figure 4.3.

![Figure 4.3: Viscosity functions of Nutriose solutions at different Nutriose mass fractions (T=20°C).](image)

The solutions show Newtonian flow behavior. In Table 4.3 the dynamic viscosities are summarized as a function of the Nutriose mass fraction.

The surface tensions obtained from measurements with the pendant-drop tensiometer and the liquid densities are listed in Table 4.4.
4.3 Contact angle

Table 4.3: Dynamic viscosities (T=20°C).

<table>
<thead>
<tr>
<th>Nutriose conc. $\phi_{nutr.}$</th>
<th>Dynamic viscosity $\eta$ (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 $\pm$ 0.01</td>
<td>0.70</td>
</tr>
<tr>
<td>63 $\pm$ 0.01</td>
<td>1.42</td>
</tr>
<tr>
<td>70 $\pm$ 0.02</td>
<td>11.25</td>
</tr>
</tbody>
</table>

Table 4.4: Surface tensions and liquid densities (T=20°C).

<table>
<thead>
<tr>
<th>Nutriose conc. $\phi_{nutr.}$</th>
<th>Surface tension $\sigma_{LG}$ (mN/m)</th>
<th>Density $\rho_l$ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 $\pm$ 63 $\pm$ 70</td>
<td>73 $\pm$ 68 $\pm$ 75</td>
<td>1.280 $\pm$ 1.300 $\pm$ 1.338</td>
</tr>
</tbody>
</table>

As mentioned in chapter 3.7 surface active impurities caused an exponential decay of the surface tension over the time. The steady-state value was assessed when the decay was less than 1 mN/m per 100 min. The amount of impurities is not controllable so that this procedure might have caused the differences between the surface tensions shown in Table 4.4. There is no obvious impact of the Nutriose concentration on the surface tension, which is close to that of pure water (72 mN/m).

The density of the liquid increases with increasing Nutriose concentration.

4.3 Contact angle

The contact angles between Nutriose solutions and Spheriglass particles were determined as described in Chapter 3.10 with the static drop method. The true contact angles were calculated from the apparent contact angle by means of Eq. 2.69. A summary of the obtained data is given in Table 4.5.

Table 4.5: Contact angles between Nutriose solutions and Spheriglass (T=20°C).

<table>
<thead>
<tr>
<th>Nutriose conc. $\phi_{nutr.}$</th>
<th>Contact angle $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 $\pm$ 63 $\pm$ 70</td>
<td>57.5° $\pm$ 3.1°</td>
</tr>
<tr>
<td>63 $\pm$ 68 $\pm$ 75</td>
<td>77.9° $\pm$ 6.8°</td>
</tr>
<tr>
<td>70 $\pm$</td>
<td>77.6° $\pm$ 3.6°</td>
</tr>
</tbody>
</table>

The Spheriglass glass beads are wetted by the Nutriose solutions, based on the contact
angles of $\delta < 90^\circ$. An increase of the Nutriose concentration from 60% to 63% results in an increase of the contact angle while there is no clear difference between Nutriose solutions with a concentration of 63% and 70%. The roughness of the saturated powder tablets on which the liquid droplets were placed to measure the apparent contact angle is supposed to have had an impact on the results which could not be assessed. A saddle formation on air filled pores as described by Palzer et al. (2001) is another possible measurement error. However, the utilization of the measured values for the modeling of wet powder flow (chapter 4.4.4) revealed that they are suitable for the calculation of interparticle adhesive forces.

4.4 Mechanics of bulk solids

4.4.1 Yield loci of dry powders

Yield loci of the solids in the dry state were determined in order to get an impression of both the adhesive forces between the particles and of the internal friction during flow. The effective angle of friction $\phi_e$ was considered an adequate measure of these frictional forces. It was measured for three different consolidation stresses. The results are shown in Figure 4.4.

![Figure 4.4: Effective angle of friction of the powder solids as a function of the consolidation stress.](image)

The effective angle of friction decreases with increasing consolidation stress. At small consolidation stresses van der Waals adhesive forces are relatively large compared to the external...
normal load. With increasing consolidation they become less important as they do not increase to the same extent as the external load. Consequently the ratio of the shear stress to the superimposed normal stress decreases with increasing consolidation. This behavior is most pronounced in case of Sikron whose very fine particles cause high van der Waals forces making the powder the most cohesive of the samples considered here. Both Sepasil powders show a weak relationship between the consolidation stress and the effective angle of friction. Due to the larger particles, the impact of van der Waals forces is significantly smaller. However, the effective angle of friction is by far greater than it is in case of Spheriglass glass beads. The explanation for that is given by the sharp-edged and inhomogeneous particle shape of the silica particles in contrast to the spherical glass beads.

An extrapolation of the measured yield loci to a normal stress of 0 Pa allows for an approximation of the cohesion of the powders. This is illustrated in Figure 4.5.

![Figure 4.5: Cohesion of the powder solids as a function of the consolidation stress.](image)

Again the strong adhesive forces between the Sikron silica particles are noticeable in terms of a high cohesion. Spheriglass glass beads exhibit a minor cohesion. Nevertheless it is higher than the cohesion of both Sepasil silica particles due to the smaller particle size and the more regular particle shape/smooth particle surface resulting in higher van der Waals forces. Sepasil B 20/100 is less cohesive than Sepasil B 5/63, presumably as a consequence of the larger particles and the more narrow particle size distribution. In these considerations differences between the Hamaker constants were not taken into account. According to Dahneke (1972) the Hamaker constant for the interaction of two bodies (in air) of crystalline quartz is between $7.65 \times 10^{-20}$ J and $10.7 \times 10^{-20}$ J. Glass beads have a Hamaker constant of $6.5 \times 10^{-20}$ J (Dong et al., 2003). The van der Waals adhesive force between two bodies (of equal size) is proportional to the Hamaker constant,
4.4 Mechanics of bulk solids

proportional to the particle diameter and inversely proportional to the squared distance (Fayed and Otten, 1997). As the Hamaker constants of the silica particles and the glass beads are close to each other, the differences in their van der Waals adhesive forces are essentially determined by the particle size, shape and roughness. In Appendix A.1 it is demonstrated that in case of Spheriglass glass beads a flattening of two adjacent particles leads to a maximum increase of the van der Waals adhesive force by about 5%.

4.4.2 Yield loci of partially saturated powders

Wet powders show a pronounced anisotropy of the stresses acting in the bulk when they are subjected to compression and/or shear. Furthermore shear stresses are normal force dependent. This is why wet powder flow is described by mechanical approaches developed for bulk solids.

In this chapter the influence of preconsolidation, binder fraction and binder viscosity on interparticle adhesive and frictional forces is discussed. These considerations are made for wet powders consisting of liquid-bound Spheriglass glass beads. This system was chosen because its well defined particle shape and smooth surface allow for a theoretical description of liquid bridge bonding forces on the basis of which the flow behavior can be modeled. See chapter 4.4.4 for details!

Yield loci of liquid-bound Spheriglass glass beads at various preshear stresses are depicted in Figure 4.6.

![Figure 4.6: Measured shear points (full symbols), preshear points (empty symbols) and linearized yield loci of Spheriglass glass beads bound by a 63 % Nutriose solution ($\phi_m=82\%$).]
The full symbols are measured shear points, the empty symbols the corresponding preshear points. In all cases the resulting yield loci could be fitted by straight lines with high accuracy. The preshear points are not points of the yield loci but lie slightly below them. This is a commonly observed phenomenon: when shearing action stops, a weak consolidation occurs, with the effect that shear to failure accounts for a higher shear stress than needed for steady-state flow even if the normal stress is unchanged. The location of the yield loci in Figure 4.6 is consistent. Higher preshear stresses lead to higher shear stresses causing failure of the system. The slope is nearly identical for all yield loci. This is in agreement with observations of Pierrat et al. (1998) who measured yield loci of several wet powders and observed that the addition of liquid displaced the yield locus by a constant factor, which was equal to the isostatic tensile strength, while the linearized angle of internal friction $\phi_{\text{lin}}$ did not vary when the moisture content was changed. A linearized angle of internal friction which is independent of the liquid content was also detected by Richefeu et al. (2006) for sand/water and glass beads/water systems.

An extrapolation towards a normal stress $\sigma$ of 0 Pa yields the cohesion $C$ which corresponds to the intersection with the $\tau$-axis. Except for a solid mass fraction of 78% an increased preshear stress results in an increased cohesion due to a denser packing of the system which is accompanied by stronger liquid bridges and higher frictional forces between the particles. Yield loci were measured at varying binder mass fractions and for preshear stresses of 5 kPa, 10 kPa and 20 kPa. The resulting values of the cohesion are summarized in Figure 4.7. Additionally, the saturation after preconsolidation is shown.

![Figure 4.7: Cohesion (quadratic symbols) and saturation (round symbols) of Spheriglass glass beads bound by a 63% Nutriose solution at varying binder mass fractions and preshear stresses of 5 kPa, 10 kPa and 20 kPa.](image)

The dotted line in Figure 4.7 displays an assumed development of the cohesion at a preshear
stress of 20 kPa. It could not be experimentally verified because the load limit of the ring shear cell was exceeded when trying to measure the corresponding yield loci.

In the dry state the cohesion of the powder is clearly smaller than in any of the considered wet states. For a given preshear stress the cohesion is to some extent constant in the saturation range \(35\% \leq S < 10\%\) \((94\% > \phi_m \geq 82\%)\). When the saturation lies between 35\% and 80\% an increase in the cohesion is observed independently of the preshear stress. In case of the preshear stress of 20 kPa a saturation of 80\% is reached at a liquid mass fraction of 22\% \((\phi_m=78\%)\). When the system was presheared with 10 kPa and 5 kPa respectively, the saturation in the steady-state was slightly lower \((72.9\% \text{ and } 76.9\%)\). The cohesion increases for the two lower preshear stresses if the liquid fraction is increased from 20\% \((\phi_m=80\%)\) to 22\% \((\phi_m=78\%)\). However, it drops in case of the preshear stress of 20 kPa corresponding to a saturation of 80\%.

In analogy to the dependency of the tensile strength on the saturation described by Schubert, these results can be interpreted as follows: both the tensile strength and the cohesion are essentially influenced by adhesive forces and interparticle friction and they describe stress states where no external compressive force is present. In case of a linear yield locus, the tensile strength and the cohesion are proportional to each other (Eq. 2.30).

As discussed in chapter 2.3.3 and shown in Figure 2.11 the tensile strength of a wet powder system with a given porosity is not a function of the saturation as long as the system is in the pendular state (the domain of low saturation values \(S < 10\%\) is not considered). In the range \(82\% \leq \phi_m \leq 94\%\) in Figure 4.7 the porosity of the wet powder is nearly constant at constant preshear stress. The minimum and maximum porosities in this range are listed in Table 4.6.

Table 4.6: Minimum and maximum porosity of the presheared Spheriglass powder bound by a 63\% Nutriose solution in the domain \(82\% \leq \phi_m \leq 94\%\).

<table>
<thead>
<tr>
<th>preshear stress (\sigma_{pre}) (kPa)</th>
<th>Minimum poros. (\epsilon_{min})</th>
<th>Maximum poros. (\epsilon_{max})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>63.2%</td>
<td>65.4%</td>
</tr>
<tr>
<td>10</td>
<td>58.7%</td>
<td>62.4%</td>
</tr>
<tr>
<td>20</td>
<td>54.6%</td>
<td>56.4%</td>
</tr>
</tbody>
</table>

Additionally, the slope of the yield loci in this domain is rather constant with a maximum standard deviation of 6.1\%, see Figure 4.8. Thus the tensile strength and the cohesion are approximately proportional to one another.

As a consequence of these considerations, the invariance of the cohesion in the domain \(35\% \leq S < 10\%\) (Figure 4.7) indicates, that the tensile strength in this domain is invariant. In agreement with Schubert (1973) the wet powder system is in the pendular state up to \(S_p = 35\%\). It subsequently passes into the funicular state and finally reaches a state of overwetting at \(S_c = 80\%\), corresponding to the capillary state.
4.4 Mechanics of bulk solids

Figure 4.8: Slope of the linearized yield loci of Spheriglass glass beads bound by a 63% Nutriose solution for binder mass fractions between 82% and 94% and preshear stresses of 5 kPa, 10 kPa and 20 kPa.

The impact of the binder viscosity on the yield loci was investigated by varying the Nutriose concentration (60%, 63% and 70%). The dynamic viscosities of these solutions are 0.7 Pas, 1.4 Pas and 11.3 Pas respectively (chapter 4.2). Again preshear stresses of 5 kPa, 10 kPa and 20 kPa were used. The resulting yield loci are shown in Figure 4.9.

Within the accuracy of measurement, the yield loci do not depend on the binder viscosity. This supports Iveson’s finding (chapter 2.3.4) that the binder viscosity does not affect the flow behavior of wet powders at low deformation rates.

4.4.3 Wall yield loci

The barrel used for the measurement of compaction curves and for ram extrusion was made of lathed brass (chapter 3.14). A plate of this material fitting into the ring shear cell was fabricated and applied for the determination of wall yield loci.

Wall yield loci were measured for various solid fractions (Figure 4.10). At solid mass fractions $\geq 82\%$ the wall yield loci are more or less straight lines going through the origin. As a consequence, the angle of wall friction, defined as the ratio of wall shear stress and normal stress (Eq. 2.39), is constant and does not depend on the normal stress. In these cases solid friction is the force dominating sliding of the material along the wall. The wet powders with 82%, 84% and 100% solids exhibit wall frictional angles of 18.4°, 18.6° and
4.4 Mechanics of bulk solids

Figure 4.9: Measured shear points (full symbols), preshear points (empty symbols) and linearized yield loci of Spheriglass glass beads bound by Nutriose solutions with different dynamic viscosities ($\phi_m = 82\%$).

Figure 4.10: Wall yield loci of wet Spheriglass glass powders on a brass plate at varying solid mass fractions ($\phi_{Nutr.} = 63\%$).
A further addition of liquid to a solid mass fraction of 80% leads to an ongoing increase of the wall shear stress. However, the friction angle now decreases with increasing normal stress. The impact of the normal force on the wall shear stress is nearly lost - except for small normal stresses < 2000 Pa - if the liquid content is 22% ($\phi_m=78\%$). Moreover the wall shear stress is clearly lower than at higher solid fractions. Another illustration of these results is given in Figure 4.11. Now the wall shear stress is shown over the solid mass fraction at varying normal stresses.

Starting with the dry powder the addition of liquid results in an increasing wall shear stress coming along with liquid bridges forming in the plane of contact between the particles and the plate. At moderate normal stresses $\leq 10038$ Pa this trend continues until a liquid content of 20% ($\phi_m=80\%$) is reached. At normal stresses of 15 038 Pa and 20 039 Pa a decrease and reincrease of the wall shear stress is observed when the liquid content is increased from 14% to 20%. This might be the result of the competition between an increasing number of liquid bridges and reduced capillary pressures in regions where partially saturated clusters are present, because at higher normal stresses the air volume fraction is more reduced by the compaction and release of air.

In all cases the wall shear stress drops when the liquid mass fraction is further increased to 22% ($\phi_m=78\%$). Additionally, the normal force dependency of the wall shear stress is significantly reduced. In the contact plane between the plate and the particles the system seems to be close to the suspension state. The voids between the particles are to a major degree filled with liquid and the effect of the air has become less important. These results are in good agreement with the observations of Fekete et al. (2007) mentioned in chapter 2.2.4.
The viscosity has no influence on wall yield loci of wet glass beads powders with 82\% solids (Figure 4.12). This is again in agreement with Iveson’s theory of negligible viscous forces in case of small deformation speeds (chapter 2.3.4).

Figure 4.12: Wall yield loci of Spheriglass glass beads bound by Nutriose solutions with different dynamic viscosities ($\phi_m=82\%$).

### 4.4.4 Model for the determination of wet powder yield loci

After Iveson et al. (2002) the tensile force of a liquid bridge acts to pull particles together and this normal force at particle contacts influences interparticle friction. Based on this relation a semi-empirical physical model was developed which allows for the prediction of individual yield loci of wet powders in the pendular state. It reflects the acting forces determining the stress states of these systems at incipient flow and during steady-state flow.

The fundamental considerations presented here are an adaptation of Molerus’ model for dry cohesive powders (chapter 2.2.3) to wet powder systems. The following assumptions are made:

- van der Waals forces can be neglected in wet powders as they are smaller than liquid bridge forces by roughly one order of magnitude (Seville et al., 2000). As well electrostatic forces are not considered since they are usually negligible in liquid-bound systems (Iveson et al., 2002).
- viscous liquid friction needn’t be considered at small deformation speeds like those in ring shear cells (chapter 4.4.2).
• Rumpf’s equation can be applied. The system is simplified as a bulk solid of monodisperse, spherical particles with a representative particle diameter \( x_{1,2} \). The tensile strength is uniquely the result of normal forces between the particles while the impact of friction is neglected.

• it follows from the last assumption that all liquid bridges have the same shape and strength. The force of a liquid bridge is given by Eq. 2.55 to Eq. 2.59.

• flattening of the particles can be neglected.

Based on these assumptions, tensile strengths of wet glass powders with 80\%, 82\% and 84\% solids were calculated as a function of porosity. They are illustrated in Figure 4.13 and compared with experimental data resulting from an extrapolation of measured yield loci as described by Pierrat and Caram (1997). Pietsch and Rumpf (1967) showed that the force of a liquid bridge between two equal spheres is nearly independent of the particle separation distance \( a \) at filling angles \( \beta \geq 10^\circ \) and separation distance/particle diameter ratios \( a/x \leq 0.001 \). The experimental data needed for the calculation of the tensile strengths are listed in Table 4.7.

Table 4.7: Material parameters of Spheriglass glass beads bound by a 63 % Nutriose solution

<table>
<thead>
<tr>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_{1,2} )</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>( \sigma_t )</td>
<td>( mN/m )</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>( g/cm^3 )</td>
</tr>
<tr>
<td>( \rho_l )</td>
<td>( g/cm^3 )</td>
</tr>
<tr>
<td>( \delta )</td>
<td>( deg )</td>
</tr>
<tr>
<td>( a/x_{1,2} )</td>
<td>( - )</td>
</tr>
</tbody>
</table>

In the region 60\% < \( \epsilon < 70\% \) the tensile strengths calculated with Eq. 2.57 and 2.77 are close to the experimentally obtained values. However, at lower porosities the experimental and the calculated data do not agree. The main reasons might be:

1. the tensile strengths might be overestimated, if the applied linear extrapolation is inaccurate. The yield loci could exhibit a curvature towards lower shear stresses in the region of negative normal stresses. This is well-known in case of dry powders (Schulze, 2008). Gröger et al. (2003) demonstrated in CDEM simulations that in the range of small tensile loads the yield locus of fine granular materials in the pendular state appeared to be the straight extension of the graph for positive loads. However, depending on the packing structure, the yield locus bended sharply until it met the point of the isostatic tensile strength as the tensile load increased further. In contrast other authors considered a linear extrapolation as an appropriate method (Fekete et al., 2007).

2. low porosities (\( \epsilon < 60\% \)) are caused by high consolidation stresses. High consolidation stresses result in a high packing density of the bulk. As a consequence, frictional
forces between the particles have an increasing impact on the tensile strength of the wet powder which are not taken into account in Rumpf’s model.

Other possible sources of errors are the assumption of monodispersity and a wrong value of the contact angle (chapter 4.3). The difficulty in measuring the tensile strength of granular materials was reported by several authors (Gröger et al., 2003; Schweiger and Zimmermann, 1999). Schubert and Wibowo (1970) showed that even for one type of tensile tester, the tensile strength varies with the height of the sample. The calculated values in Figure 4.13 are nearly independent of the solid mass fraction. This is in accordance with Schubert’s statement that the tensile strength at a given porosity is not a function of the saturation if the system is in the pendular state (chapter 2.3.3).

**Approach for the calculation of yield loci**

The equilibrium of forces of a two-dimensional bulk solid volume element provides Eq. 2.26 and Eq. 2.27 which describe the normal and shear stresses acting on this element as a function of the angle which the considered plane encloses with the first principal stress plane. With the center of the Mohr stress circle

\[
\sigma_M = \frac{\sigma_1 + \sigma_2}{2}
\]  

(4.1)
and the radius

\[ \sigma_R = \frac{\sigma_1 - \sigma_2}{2} \]  

(4.2)

Eq. 2.26 can be transformed to:

\[ \sigma(\phi) = \sigma_M + \sigma_R \cdot \cos(2\phi) \]  

(4.3)

In analogy the shear stress is:

\[ \tau(\phi) = \sigma_R \cdot \sin(2\phi) \]  

(4.4)

As Molerus postulated, the shear force in the shear plane during steady-state flow is proportional to the compressive stress \( \sigma_C(\phi) \) whereas the proportionality factor is the friction coefficient \( \tan(\rho) \). In all other planes the shear force is smaller than \( \tan(\rho) \cdot \sigma_C(\phi) \):

\[ \tau(\phi) \leq \tan(\rho) \cdot \sigma_C(\phi) \]  

(4.5)

In contrast to van der Waals forces, liquid bridge forces between the particles are assumed not to solely depend on the normal stress acting on the \( \phi \)-plane like expressed by Eq. 2.32. Instead they are a function of the packing density or porosity of the particles at a given liquid fraction. In turn the porosity depends on the consolidation stress \( \sigma_1 = \sigma_M + \sigma_R \).

Thus the compressive stress acting on the \( \phi \)-plane is equal to the sum of the external normal stress and the tensile strength resulting from the liquid bridge forces:

\[ \sigma_C(\phi) = \sigma(\phi) + \sigma_z(\sigma_1) \]  

(4.6)

Eq. 4.4 yields with Eq. 4.3, Eq. 4.5 and Eq. 4.6:

\[ \sigma_R \cdot \sin(2\phi) \leq \tan(\rho) \cdot [\sigma_M + \sigma_R \cdot \cos(2\phi) + \sigma_z(\sigma_1)] \]  

(4.7)

It follows from a transformation:

\[ \sigma_R(\sin(2\phi) - \tan(\rho) \cdot \cos(2\phi)) \leq \tan(\rho) \cdot [\sigma_M + \sigma_z(\sigma_1)] \]  

(4.8)

The left side of Eq. 4.8 has its maximum at:

\[ \phi = \frac{\pi}{4} + \frac{\rho}{2} \]  

(4.9)

Insertion of Eq. 4.9 into Eq. 4.8 leads to:
\[ \sigma_R = \sin(\rho)(\sigma_M + \sigma_z(\sigma_M + \sigma_R)) \] (4.10)

Eq. 4.10 is an implicit equation for the calculation of \( \sigma_R \) as a function of \( \sigma_M \) in case of steady-state flow. The adhesive force \( \sigma_z \) follows from Eq. 2.57 and Eq. 2.77. The porosity needed to solve Eq. 2.77 is a function of the consolidation stress \( \sigma_1 \). However, the consolidation stress is only accessible by measuring a complete yield locus because the end Mohr circle is defined as a circle which is tangent to the yield locus. Without the knowledge of the yield locus only one point of the end Mohr circle - the preshear point - is known. This problem is solved as follows: the porosity of the wet powder at isochoric (steady-state) flow can be easily measured as a function of the preshear stress by means of a ring shear cell. Compared to the duration of a yield locus measurement with at least three shear points, this measurement is not very time-consuming. In case of wet Spheriglass powders a good approximation for the porosity is given by the following fit function:

\[ \frac{\epsilon}{P_{ab}} = \frac{a'}{\sigma_{pre}^b} \] (4.11)

\( a' \) and \( b \) are fitting parameters. In case of wet glass powders with \( \phi_m=80 \%, 82 \% \) and \( 84 \% \) (\( \phi_{Nutr.}=63 \%) \) the variance of this function lies between \( 0.2\%-1.2\% \).

As a simplification it is assumed that the angle between the shear plane and the first principal stress plane is \(-45^\circ\). A consideration of the Mohr stress circle reveals that the preshear point in this case corresponds to \( \sigma_{pre} = \sigma_M \) and \( \tau_{pre} = \sigma_R \). Thus the function \( \epsilon = f(\sigma_M) \) is known and can be used for the calculation of \( \sigma_R = f(\sigma_M) \).

The error caused by the assumption of a \(-45^\circ\)-angle between the shear and the first principal stress plane was analysed:

\[ \frac{\Delta \epsilon}{\epsilon} = \frac{d\epsilon}{d\sigma_{pre}} \frac{\Delta \sigma_{pre}}{\epsilon} \] (4.12)

\( \Delta \sigma_{pre} \) is the difference between the true preshear stress and the preshear stress following from the simplification:

\[ \Delta \sigma_{pre} = \sigma_{pre} - \sigma_M \] (4.13)

The relative error of the porosity as a function of the preshear stress for different wet Spheriglass powders is illustrated in Figure 4.14.

At low preshear stresses \( \leq 5 \text{kPa} \) the relative error is up to 7.4\%. At 10 kPa and 20 kPa the error lies below 3\% in all cases and can be considered as sufficiently small. A preshear stress approaching the central value \( \sigma_M \) of the end Mohr circle with increasing preconsolidation stress is a commonly observed phenomenon and explains the reduced relative error at higher preshear stresses.
4.4 Mechanics of bulk solids

The angle of friction $\rho$ in Eq. 4.10 can be obtained from the measurement of one individual yield locus by conversion of Eq. 4.10 and use of Eq. 2.57 and Eq. 2.77. For a given system it is independent of the consolidation stress (which is a verification of the validity of the model) and can be used for the calculation of any other yield locus. Table 4.8 summarizes the values of $\rho$ for the wet glass beads powders. Expected values and standard deviations are listed. They follow from three measured yield loci. With increasing solid mass fraction the friction coefficient increases because of a reduced amount of liquid acting as a lubricant.

<table>
<thead>
<tr>
<th>Solid mass fract. $\phi_m$</th>
<th>Angle of friction $\rho$</th>
<th>Standard dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>deg</td>
<td>deg</td>
</tr>
<tr>
<td>80</td>
<td>35.7</td>
<td>0.7</td>
</tr>
<tr>
<td>82</td>
<td>38.4</td>
<td>1.0</td>
</tr>
<tr>
<td>84</td>
<td>40.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The calculation of the points of incipient flow simply follows from:

$$\sigma_R^{sh} = \sin(\rho)(\sigma_M^{sh} + \sigma_z^{pre}(\sigma_1^{pre}))$$  \hspace{1cm} (4.14)

Eq. 4.14 is used to calculate the radius $\sigma_R^{sh}$ of a Mohr stress circle with the center $\sigma_M^{sh}$. 

Figure 4.14: Relative error of the porosity following from the assumption of a $-45^\circ$-angle between the shear and the first principal stress plane. Wet Spheriglass powders of varying compositions.
touching the individual yield locus. This is based on the assumption that the tensile strength \( \sigma_z(\sigma^{\text{pre}}) \) of the system preconsolidated with the consolidation stress \( \sigma^{\text{pre}}_1 \) does not change after the preshear step. An elastic recovery after the removal of the external normal stress is excluded.

### Model results

The model presented above can be used to calculate the state of stress of wet powders in the pendular state during steady-state flow and to determine shear points describing the state of stress at incipient flow. It is a semi-empirical model. Two material functions are needed:

1. the porosity as a function of the preshear stress \( \epsilon = f(\sigma^{\text{pre}}) \).
2. the angle of friction \( \rho = f(\phi_m, \phi_{\text{Nutr.}}) \) obtained from the measurement of one yield locus.

In the first step the end Mohr circle defined by its center \( \sigma_M \) and its radius \( \sigma_R \) is calculated as a function of \( \sigma_M \) with Eq. 4.10. Then the shear points \( \sigma^h \) are determined with Eq. 4.14 for various normal stresses \( \sigma^h_M < \sigma_M \). An envelope at these stress circles is the individual yield locus for the specified preshear stress \( \sigma^{\text{pre}} = \sigma_M \). In Appendix A.2 it is demonstrated that a line which is tangent to the stress circles defined by Eq. 4.14 is a straight line with the slope \( \tan(\rho) \) and the axis intercept \( \tan(\rho) \cdot \sigma_z \). This means that the angle of friction \( \rho \) is simply the slope angle of the linearized yield locus \( \phi_{\text{lin}} \) defined by Schulze (Schulze, 2008)\(^1\).

Measured and calculated end Mohr circles are shown in Figure 4.15. In the upper figure (\( \phi_m = 80\% \)) the two larger modeled stress circles were partially removed in order to make the measured circles visible. In case of the lowest preshear stress of 2 kPa all three systems (\( \phi_m = 80\%, 82\% \) and \( 84\% \)) exhibit a discrepancy in the order of magnitude of 30\% (with respect to \( \sigma_r \)) between the modeled and the experimental data. On the other hand there is an excellent agreement at higher preshear stresses. Here the relative error is in the order of magnitude of 1\%. This is in opposition to the non-negligible deviations of the calculated and experimentally obtained tensile strengths shown in Figure 4.13. This might be a hint that the extrapolated yield loci are too high, whereas Rumpf’s model predicts the tensile strengths with higher accuracy.

In Figure 4.16 modeled yield loci (dotted line) and measured shear points are shown for the case of a solid mass fraction of \( \phi_m = 82\% \) at four different preshear stresses (\( \sigma_M = 3.3 \text{ kPa}, 8 \text{ kPa}, 11.7 \text{ kPa} \) and \( 25.2 \text{ kPa} \)). Again there is a noteworthy discrepancy between the model and the experiment at the lowest preshear stress but a good agreement at higher preshear stresses. All wet glass beads powders whose yield loci were determined with the model

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\(^1\)The slope angle \( \phi_{\text{lin}} \) of the linearized yield locus and consequently \( \rho \) as well are not friction angles in the true sense as a friction angle is usually calculated from the arc tangent of the ratio of shear stress to normal stress (Schulze, 2008).
4.4 Mechanics of bulk solids

Figure 4.15: Measured (black) and calculated (grey) Mohr stress circles at steady-state flow of Spheriglass glass beads bound by a 63 % Nutriose solution.
Figure 4.16: Measured shear points and modeled yield loci (dotted line) of Spheriglass glass beads bound by a 63% Nutriose solution ($\phi_m = 82\%$). Various preshear stresses.
presented here ($\phi_m=80\%$, 82\% and 84\%, $\phi_{Nutr.}=60\%$, 63\% and 70\%) showed a similarly good agreement between the modeled and the experimental data (Appendix A.3).

### 4.5 Compaction curves

Compaction curves showing the saturation of an uniaxially compacted powder over the stress vertically applied by a ram are an adequate measure of interparticle frictional forces and interlocking effects under high normal loads. They feature an excellent reproducibility. Ohnishi and Watano (2006) carried out uniaxial compression tests of lactose monohydrate mixed with various additives and water and stated a good correlation of the compression energy with the strength of granules produced with an extrusion granulator. Excessive compression energies were reflected in extruder overloads. The compression test was shown to be able to estimate extrusion loads and appropriate water contents.

At external normal stresses of up to 250 bar, adhesive forces become negligible. Nevertheless capillary forces can have an impact on the stress transfer within the powder because they affect the distribution of the liquid in the bulk.

In Figure 4.17 compaction curves of wet Sepasil B 5/63, Sepasil B 20/100, Spheriglass and Sikron powders are illustrated.

![Compaction curves](image)

Figure 4.17: Compaction curves of Sepasil B 5/63, Sepasil B 20/100, Spheriglass and Sikron powders bound by a 63\% Nutroise solution.

Those systems which are not labeled with „kneaded“ were prepared by mixing the spray chilled binder with the solid powder at $-24^\circ C$ as described in chapter 3.8. The two systems labeled with „kneaded“ were premixed in the laboratory kneader according to the second
4.5 Compaction curves

procedure explained in chapter 3.8. As the particle densities of the four powders are different, the solid mass fraction is not an appropriate measure of the liquid content. In Table 4.9 the volume fractions

\[ \phi_v^* = \frac{V_s}{V_s + V_l} = \frac{\phi_m}{\phi_m + (1 - \phi_m) \rho_s / \rho_l} \]  

(4.15)

of the wet powders are summarized. It is important to mention that the volume fraction \( \phi_v^* \) refers to the saturated state of the wet powder where no more air is present.

Table 4.9: Volume fractions of the wet powders.

<table>
<thead>
<tr>
<th></th>
<th>( \phi_m )</th>
<th>( \phi_v^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sepasil B 5/63</td>
<td>70</td>
<td>53.4</td>
</tr>
<tr>
<td>Sepasil B 5/63</td>
<td>75</td>
<td>59.6</td>
</tr>
<tr>
<td>Sepasil B 20/100</td>
<td>75</td>
<td>59.6</td>
</tr>
<tr>
<td>Sikron</td>
<td>75</td>
<td>59.4</td>
</tr>
<tr>
<td>Spheriglass</td>
<td>80</td>
<td>67.9</td>
</tr>
</tbody>
</table>

Compaction curves generally approach a value of one with increasing compaction pressure. However, many systems never reach complete saturation if entrapped air cells are protected by powerful particle hulls. This phenomenon is more pronounced for irregularly shaped particles where interlocking effects play a major role. In Figure 4.17 the glass beads powder exhibits a higher saturation than both non kneaded Sepasil powders with a solid mass fraction of \(75\%\) at any compaction pressure. The round particle shape and smooth particle surface allows for a denser packing despite a significantly lower liquid content. The particles can more easily slide along each other while the more bumpy particle shape of the Sepasil particles favors the formation of stable particle clusters with entrapped air cells.

A pre-kneading of a wet powder clearly increases its compressibility, as demonstrated by the two compaction curves of the kneaded and non kneaded Sepasil B 5/63 powder with \( \phi_m=75\% \). The saturation of the kneaded system lies above that of the non kneaded system over the whole pressure range. The kneading causes a more uniform wetting of the particles coming along with reduced interparticle friction by the liquid acting as a lubricant.

The compaction curve of Sepasil B 20/100 with \( \phi_m=75\% \) as opposed to Sepasil B 5/63 reveals the impact of the particle size distribution width on the compacting behavior. Both powders consist of the same raw material but Sepasil B 5/63 features a broader particle size distribution. As a consequence of this, a denser packing is favored by small particles sliding into the voids between the bigger ones.

If the solid mass fraction is reduced from \(75\\%\) to \(70\%\), the improved lubrication of the particles leads to reduced interparticle friction and lower stresses required for powder compaction. This will be considered in further detail in the next section.

The compaction curve of Sikron shows a comparatively low increase of the saturation in
the range of small compaction pressures but finally reaches the highest saturation of all wet powders considered in Figure 4.17. This can be explained by the quite regular particle shape and the small particle size, which prevents the system from entrapping large air inclusions.

Figure 4.18: Porosity of dry and wet Sepasil B 5/63, Sepasil B 20/100, Spheriglass and Sikron powders at uniaxial compaction.

Figure 4.18 depicts the porosity of some selected wet powders as well as the porosity of the corresponding solid powders in the dry state as a function of the compaction pressure. Although the binder reduces frictional forces between the particles, the wet powders do not necessarily exhibit a higher packing density than the dry powders at a given compaction pressure. The liquid itself has a certain volume which prevents the particles from approaching each other. A reduction of the porosity is only possible by release or compression of air. Figure 4.18 shows that the packing density of Sepasil B 20/100 and Sepasil B 5/63 (unkneaded) is lower in the dry state than with a binder fraction of 25%. By contrast, the more uniform distribution of the binder resulting from pre-kneading the powders reduces the interparticle friction to such an extent that a denser packing of the powders can be reached than in the dry state. Examples of this are Sepasil B 5/63 as well as Sikron.

The impact of the liquid content on compaction curves of wet Sikron powders is shown in Figure 4.19. At solid mass fractions of 72% ($\phi^s_m=55.6\%$) and 73% ($\phi^s_m=56.8\%$) the system is completely saturated at 10 bar. An increase in the solid mass fraction by only one percent to $\phi^s_m=74\%$ ($\phi^s_m=58.1\%$) totally changes the course of the compaction curve. Until about 150 bar the system is in the wet powder state before passing into a pasty state. A further decrease of the liquid fraction shifts the curve further downwards which means that higher pressures are necessary to compress and release the air remaining in the system. All wet
powders considered here have been pre-kneaded before compaction. A determination of the particle size distribution after compaction showed that no particle comminution occurred (Appendix A.4).

Analogous measurements for Sepasil B 5/63 illustrate the impact of its more irregular particle shape and the larger particle size, see Figure 4.20. Again there is a shift downwards of the compaction curves if the solid mass fraction is increased. However, a compaction pressure of 230 bar is already required at $\phi_m=72\%$ ($\phi^*_v=55.8\%$) to make the system a paste. The sharp-edged, irregularly shaped particles seem to form strong clusters in which a substantial volume fraction of air is entrapped.

The influence of the binder viscosity was investigated for Spheriglass glass beads. Figure 4.21 illustrates the compaction curves for Nutriose concentrations of 60\%, 63\% and 70\% ($\eta=0.7$ Pas, 1.4 Pas and 11.3 Pas). The curves are nearly identical which once more confirms that the binder viscosity has no impact on shear stresses during wet powder flow at small deformation rates. The same behavior was observed for Sepasil B 5/63.

In summary, it can be stated that compaction curves reflect in a clear manner the impact of particle size/size distribution, particle shape and particle lubrication by a liquid on the compressibility of wet powders.

The bulk density of a compacted powder significantly differs from the bulk density of a powder compacted in a ring shear cell. In the latter case, a superimposed shear creates a microstructure in which the particles are more densely packed and oriented in shear layers. Additionally, a steady-state is reached during the preconsolidation in the shear cell with a
4.5 Compaction curves

Figure 4.20: Compaction curves of Sepasil B 5/63 bound by a 63% Nutriose solution at varying solid mass fractions.

Figure 4.21: Compaction curves of Spheriglass bound by Nutriose solutions of different viscosities ($\phi_m=82\%$).
horizontal stress ratio being lower than that for the case of uniaxial compaction (Schulze, 2008).

4.6 Wet powder ram extrusion

The ram extrusion in a high pressure capillary rheometer or in a universal material testing machine allows for a systematic investigation of wall normal stresses in the barrel before the die as well as microstructural changes in a wet powder as a result of shear and compression in the die inlet region. The universal material testing machine can additionally be used to measure the vertical stress applied by the ram. The focus of this thesis is on the procedures in the die inlet region where blocking as a result of interparticle friction and interlocking is an important issue. In view of this, there are a couple of advantages of the batchwise ram extrusion over a continuous screw extrusion:

- exact control of the volumetric flow rate by a specified ram velocity. By contrast, variations in the filling degree of the extruder screws may involve flow rate fluctuations in the output of a screw extruder, making an analysis more difficult.
- exactly defined mechanical history of the wet powder being extruded by well defined preceding process steps (mixing, kneading and pre-compaction, see chapter 3.8).
- the focus is on the procedures in the die and the die inlet region. Questions such as the filling degree of the screws, the composition of the screws and its impact on the mixing efficiency, limitations by the maximum torque accepted by the screws, etc. are no longer important.
- small amounts of wet powder required for a measurement.

4.6.1 Wall normal stress in the barrel

Highly unsaturated systems, i.e. wet powders in the pendular or the funicular state, require higher extrusion pressures than pastes. Additionally, there is a qualitative difference in the pressure development as opposed to pastes or highly saturated wet powders. When the extrusion of a highly unsaturated wet powder is initiated, the extrusion and the wall pressure\(^2\) usually exhibit a characteristic course over the time as shown in Figure 4.22. Before the wet powder enters the die, a minor pressure increase is observed which is the result of an elastic compression. This pressure is much lower than the pressure generated during the preceding compaction step. When the material starts to enter the die, an acceleration of the material in the core in axial direction causes a relative motion of the powder particles in a thin layer in the outer regions of the inlet zone. Increasing particle interlocking and interparticle friction in these regions lead to an ongoing increase in the pressure. A small amount of powder is caught in a static dead zone where no flow occurs. In the core, the wet powder flows as a plug while shearing action in the outer, approximately

\(^2\)In the following the vertical stress exerted by the ram will be referred to as extrusion pressure and the wall normal stress in the barrel as wall pressure.
4.6 Wet powder ram extrusion

Conically shaped regions, leads to an arrangement of the particles in shear layers. In addition to this, air cells are compressed, partially solved in the liquid and presumably squeezed into the inner, non-sheared regions of the wet powder. Consequently, a highly saturated phase forms with strongly reduced interparticle frictional forces and - supported by the layering of the particles - reduced shear forces in the direction of flow compared to the randomly packed and less saturated material in the core. In the ideal case the microstructural modifications in the shear layers result in a phase transition from a 3-phase wet powder (3P) into a 2-phase suspension (2S). With advancing time this transition shear zone propagates upwards and comprises more material in the vicinity of the barrel axis.

At that point where a transition shear zone has developed, the wall pressure starts to decrease again and finally reaches a steady value provided that no liquid phase migration occurs. The transition shear zone reduces the flow resistance for the following material entering the die. The peak pressure is referred to as critical pressure $p^*_c$. It is a process and material characteristic pressure and can be considered as a measure of the mechanical interactions between the particles and the microstructural transformations during extrusion.

A visualization of the shearing action in the barrel can be realized by alternately compacting material with different colors in the barrel before the extrusion step. In Figure 4.22 this is shown for a wet Sikron powder which was longitudinally cut at two different points of time during the extrusion. The first sample was taken shortly after the material started to enter the die. The picture demonstrates that shearing in the barrel is nearly negligible as the flow profile exhibits only a marginal curvature. Furthermore the dead zone in the rectangular die inlet region is visible. The arrows are estimated velocity vectors to illustrate the differences in the flow velocity in the core and in the outer regions. Another sample was taken during steady-state flow where the ram has nearly reached the die. The shear zone at this point is significantly more developed and has propagated, as mentioned above.

The wall pressure in Figure 4.22 depicts a typical course of a wet powder extrusion being initiated. However, the pressures generated during the extrusion are the result of numerous interactions between the particles and are to a certain extent left to chance. There is sometimes a second pressure peak after the critical pressure has been surmounted. Moreover critical pressures - even if characteristic for material/process combinations - are subject to a certain degree of fluctuation. This is why high standard deviations of the critical pressures of up to 20% have to be accepted.

In the subsequent sections it will be discussed how the critical pressure depends on process and material parameters. Microstructural aspects are captured by $\mu$CT measurements and investigations of the liquid phase distribution in the extrudate. These findings provide a basis to postulate mechanisms explaining the relationships between extrusion pressures and microstructural processes.
4.6 Wet powder ram extrusion

Figure 4.22: Typical course of the wall pressure over time measured 10 mm above the die. Longitudinal cut of extruded wet Sikron powder shortly after the start and in steady-state ($\phi_m = 75\%$).

4.6.2 Influence of die geometry

A longitudinal cut of the extrudates of wet Sikron and Sepasil B 5/63 powders - alternately pre-compacted in red and in gray color - demonstrates the impact of shear in the die inlet region. The cuts are shown in Figure 4.23.

In the outer region of the extrudates the material has been sheared to a great extent while the inner region was hardly sheared and almost flowed as a plug. This inner region extends over about 75% of the extrudate diameter. The traced profiles in Figure 4.23 demonstrate that the shearing action is not a function of the die length. As a consequence, shear in the die can be neglected. This is supported by measurements of the critical pressure at die lengths of 10 mm and 15 mm as shown in Figure 4.24.

The critical pressure of wet Sepasil B 5/63 powder is illustrated for ram velocities of 0.05 mm/s, 0.2 mm/s and 1 mm/s. It was measured at 10 mm, 20 mm, 30 mm and 50 mm distance from the die. Wall friction in the barrel leads to a decreasing critical pressure towards the die. Within the commonly observed fluctuations, the critical pressure does not depend on the die length.

Consequently shear forces in the die and in the barrel have minimal impact in comparison to shear forces within the die inlet region. After the material has developed a stable transition shear zone, it slides through the die without experiencing noteworthy wall shear stresses.
Sikron B800 Sepasil B5/63

die length $l_{\text{die}}=15 \text{ mm}$

die length $l_{\text{die}}=10 \text{ mm}$

Figure 4.23: Longitudinal cut of Sikron and Sepasil B 5/63 extrudates bound by a 63% Nutriose solution extruded through two dies of different lengths ($\phi_m=75\%$, $d_{\text{die}}=12 \text{ mm}$, $v_{\text{ram}}=0.2 \text{ mm/s}$, $p_c=32 \text{ bar}$). Before extrusion 10 x 4 g of alternately gray and red colored material was compacted in the barrel.

This behavior is common to all wet powder systems considered in the framework of this thesis.

In Figure 4.25 a longitudinal cut of wet Sepasil B 5/63 in the barrel, in the die and after the die is depicted. The contrast of the picture was changed for reasons of clearness. The broadness of the non-sheared material in the extrudate decreases from the extrudate front towards the barrel. In the die entry region an ongoing buildup of the transition shear zone is identifiable.

The impact of the die diameter on the critical pressure of wet Sepasil B 5/63 powder is illustrated in Figure 4.26.

The critical pressure is plotted over the reciprocal value of the die diameter which was 12 mm, 14 mm or 18 mm. The influence of wet powder pre-kneading is also illustrated. The critical pressure is generally higher at smaller die diameters because of a larger contraction of the material in the die inlet as well as an increased acceleration of the inner regions and increased radial stresses, both enforcing interparticle friction and interlocking. The critical pressure increases disproportionately to the reciprocal die diameter. The impact of wet powder pre-kneading is remarkable. The uniform wetting of the particles with liquid realized in the precedent kneading step reduces the critical pressure by up to two thirds. The influence of the ram velocity on critical pressures will be discussed in chapter 4.6.5.
4.6 Wet powder ram extrusion

Figure 4.24: Critical pressures of Sepasil B 5/63 bound by a 63\% Nutriose solution at varying distances from the die, varying ram velocities and two different die lengths ($\phi_m=75\%$, $d_{\text{die}}=12\text{ mm}$, $p_c=32\text{ bar}$).

Figure 4.25: Longitudinal cut of Sepasil B 5/63 bound by a 63\% Nutriose solution in the barrel, in the die and after the die ($\phi_m=75\%$, $d_{\text{die}}=12\text{ mm}$, $l_{\text{die}}=15\text{ mm}$, $p_c=32\text{ bar}$).
4.6 Wet powder ram extrusion

Figure 4.26: Critical pressure of Sepasil B 5/63 bound by a 63% Nutriose solution as a function of the die diameter and the ram velocity ($\phi_m=75\%$, $l_{die}=15\,$mm, $p_c=32\,$bar). Kneaded and non-kneaded samples.

4.6.3 Influence of pre-compaction

The pre-compaction of wet powders ensures a well defined mechanical history before the extrusion. It improves the reproducibility of the extrusion trials by defining the state of stress in the bulk which would otherwise be more or less random. The pre-compaction pressure has an essential influence on the development of the extrusion pressure and on the critical pressure.

Figure 4.27 shows the critical pressure of a wet glass beads powder measured at a distance of 10 mm from the die as a function of the pre-compaction pressure. In spite of the large standard deviation a clear trend is observed: at a pre-compaction pressure of $p_c=32\,$bar, the critical pressure is the highest. Another less pronounced peak is observed at $p_c=128\,$bar. The compaction curve of this material shows that the saturation at $p_c=32\,$bar is about 78%.

Similar results were found for other systems and other die diameters (Figure 4.28). In the case of Sepasil B 5/63 ($d_{die}=12\,$mm) and Spheriglass ($d_{die}=12\,$mm and $d_{die}=14\,$mm) the highest critical pressure is observed when the saturation obtained during pre-compaction was 78% and 80% respectively. Sepasil B 20/100 exhibits a continuously increasing critical pressure ($d_{die}=18\,$mm) or a strong increase of the critical pressure from $p_c=190\,$bar to $p_c=255\,$bar ($d_{die}=14\,$mm). The compaction curve of Sepasil B 20/100 reaches its maximum value of $S=75\%$ at $p_c=255\,$bar.

From these results it can be concluded that a saturation of about 80% is a critical value.
4.6 Wet powder ram extrusion

Figure 4.27: Critical pressures of Spheriglass bound by a 63\% Nutriose solution as a function of the pre-compaction pressure at varying ram velocities ($\phi_m=82\%$, $d_{die}=12$ mm, $l_{die}=20$ mm). Beneath: Compaction curve.
Figure 4.28: Critical pressures of Sepasil B 5/63, Sepasil B 20/100 and Spheriglass bound by a 63% Nutriose solution as a function of the pre-compaction pressure at varying die diameters ($d_{die}=10\text{mm}$, $v_{ram}=0.5\text{mm/s}$). All systems were non-kneaded. Beneath: Compaction curves.
above which the voids between the powder particles are filled with liquid to such an extent that an effective wetting of the particles reduces interparticle frictional forces and critical pressures. This mechanism competes with an increased strength of the pressagglomerates formed in the pre-compaction step and resulting from a denser packing of the particles. This is why the critical pressure sometimes shows a slightly increasing tendency with increasing pre-compaction pressures even if the saturation is higher than 80%.

The observation of reduced flow resistances at \( S > 80 \% \) is in agreement with the observations for the tensile strength made by Schubert and for the cohesion of wet powders discussed in chapter 2.3.3.

The influence of the Nutriose concentration and the dynamic viscosity of the binder on critical extrusion pressures seems to be marginal. As only three concentrations of the Nutriose solutions were tested, no systematic analyses are available. The observed tendencies are shortly discussed in Appendix A.5 for a wet Spheriglass powder.

### 4.6.4 Concept for state diagrams

On the basis of the results presented in chapter 4.4.2 and chapter 4.5 a concept for state diagrams of wet powders was developed. Figure 4.29 shows compaction curves of Sepasil B 5/63 at varying solid mass fractions. For \( \phi_m = 75 \% \) the compaction curves of an unknheed and a kneaded system are depicted. Kneading is associated with a mechanical energy input \( E_m \) which changes the compaction behavior (chapter 4.5).

When measuring the compaction curves shown here, the energy input was not recorded. This is why no numerical values of it are given in Figure 4.29. They could be determined by measuring the torque \( M \) of the kneader shaft versus the time \( t \):

\[
E_m = \int_0^t M\omega dt'
\]  

\( \omega \) is the angular velocity of the shaft. The determination of compaction curves after different kneading times or rotational speeds allows to define the saturation \( S \) of a given system as a function of \( E_m \) and \( p_c \). If the critical saturation values \( S_p \) and \( S_c \) are known as defined in chapter 2.3.3, a classification of any uniaxially compacted system into the pendular, the funicular and the capillary state can be carried out. With this knowledge the risk of blocking during extrusion can be assessed by taking into account the impact of the saturation on critical pressures as described in chapter 4.6.3.

### 4.6.5 Liquid phase migration

In paste extrusion a decreasing pore pressure inside the material in the barrel presses the liquid from the region below the ram towards the die. The extent of liquid phase migration depends on the pore pressure gradient, the binder viscosity and the permeability (chapter 2.1.3). In wet powders, a continuous pore pressure gradient along the entire sample in the barrel can not be built up, because there is no contiguous liquid phase. Nevertheless, liquid
4.6 Wet powder ram extrusion

Figure 4.29: Concept for a state diagram of wet powders: compaction curves at varying solid mass fractions and different mechanical pretreatments. Sepasil B 5/63 as an example. The curves fix plains (here shown for \( \phi_m = 75\% \)) which illustrate the state of the systems defined by the saturation \( S_p \) (transition from the pendular into the funicular state) and \( S_c \) (transition into the capillary state).

can be squeezed out of the pores by local excess pressures due to a compression of the particle skeleton. In other words, larger compaction pressures result in a higher packing density of the particles and hence to liquid phase migration. Wall friction in the barrel causes a gradient of the vertical stress as a consequence of which the liquid flows towards the die.

The functional relationship between the permeability of a wet powder and the porosity, the saturation, the particle size distribution, the particle shape, and liquid properties is very complex and so far the models describing the relationship (chapter 2.1.3) are not reliable. In the following, the term „pressure“ or „wall pressure“ denotes the wall normal stress. Higher wall normal stresses in the barrel involve higher vertical normal stresses in the barrel which lead to liquid phase migration. The stress fields in the barrel will be discussed in detail in chapter 4.7. Liquid phase migration results in a higher liquid phase fraction in the extrudate front than in the parts leaving the die at the end.

When dies with large diameters are used (here: 18 mm), liquid phase migration is negligible as the stress gradient is comparatively small. Apart from the die diameter, the extrusion speed and the pre-compaction pressure are process parameters which have an impact on liquid phase migration.

A strong relationship between the wall pressures in the barrel and the extent of liquid phase migration was observed when extruding wet Sepasil B 5/63 powder. The liquid phase distribution in the extrudates of extruded Sepasil B 5/63 powders bound by a 63%
Nutriose solution is shown in Figure 4.30.

![Graph showing axial liquid phase distribution in the extrudate at varying ram velocities.](image)

**Figure 4.30:** Axial liquid phase distribution in the extrudate at varying ram velocities (Sepasil B 5/63, $\phi_m=75\%$, $\phi_{Nutr.}=63\%$, $d_{die}=12$ mm, $l_{die}=15$ mm, $p_c=32$ bar).

The bulk value of the binder mass fraction was $\phi_{m,l}=25\%$. At $v_{ram}=0.05$ mm/s the extrudate exhibits a liquid content in the extrudate front of more than 28% while the part leaving the die in the end has a liquid content of about 22%. Between the extrudate front and its end the liquid mass fraction falls monotonously. Increasing the ram velocity to 0.2 mm/s provides a qualitatively similar liquid phase distribution but the range is smaller (from 27% to 24.5%) because the liquid has less time to flow and the permeability is lower due to higher extrusion pressures. If the velocity is further increased to 1 mm/s, the curve exhibits a modified characteristic. The front of the extrudate contains the overall liquid mass fraction of 25%. This value reaches approx. 26.3% at a distance of 70 mm from the front before falling again to 23% at the end\(^3\). Differences in the local liquid content in the extrudates were visually noticeable. An increase of the liquid mass fraction made the extrudate surface look smooth and shiny. Extrudates were softer and more ductile. In contrast, the dry parts of the extrudates exhibited cracks in the surface and brittleness.

The development of the wall pressure corresponding to the liquid phase distributions in Figure 4.30 at distances of 10 mm, 20 mm, 30 mm and 50 mm from the die are illustrated in Figure 4.31.

The x-axis shows the ram position fixed at 0 mm at the die inlet. Each of the four curves falls down to a pressure of 0 bar when the ram reaches the position of the pressure sensor. The curves exhibit an increase until the individual critical pressure is reached, then fall.

\(^3\)The length of the extrudates was not always the same because the sample sometimes broke at the outlet of the die, sometimes at the die inlet. Some material always remained in the barrel before the die. As a consequence of this, the mass balance of the liquid is not fulfilled in the curves depicted in Figure 4.30.
Figure 4.31: Wall pressures as a function of the distance between the die and the ram measured at distances of 10 mm, 20 mm, 30 mm and 50 mm from the die (Sepasil B 5/63, $\phi_m=75\%$, $\phi_{Nutr.}=63\%$, $d_{die}=12$ mm, $l_{die}=15$ mm, $p_c=32$ bar).
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again and finally reach a steady value or increase again. By measuring the pressure at different distances from the die, the impact of wall friction becomes obvious. First, the pressure closest to the ram (50 mm distance from the die) starts rising, followed by the pressures at 30 mm, 20 mm and 10 mm. The pressure decreases towards the die due to the wall friction of the wet powder. In case of \( v_{\text{ram}} = 0.05 \text{ mm/s} \) and \( v_{\text{ram}} = 0.2 \text{ mm/s} \) a steady-state is reached where the pressure over the ram position nearly remains constant. The value of the first peak clearly increases with increasing extrusion velocity because the particles in the die inlet zone have less time to align themselves and to move relative to each other into the die resulting in stronger interlocking and larger frictional forces. When the pressure gradient has built up, the effect of liquid phase migration becomes visible. At the lowest extrusion velocity the liquid has sufficient time to flow towards the die, initiated by the pressure gradient. Consequently, the binder mass fraction in the die inlet region exceeds the total value, the particles are lubricated to a larger extent resulting in lower frictional forces and the development of a transition shear zone along which the subsequent material can slide. The consequence of a drier powder flowing into the die at the end of extrusion does not seem to have a major effect on the pressures. As soon as a stable slip zone has formed, the critical point of extrusion has been surmounted.

Increasing the ram velocity generally results in higher wall pressures because the particles have less time to move relative to each other, so that frictional forces and interlocking effects become stronger (Figure 4.32). Additionally, a larger extent of liquid phase migration at slow extrusion speed supports the formation of a transition shear zone and results in reduced critical pressures.

Another parameter influencing liquid phase migration and the extrudability of a wet powder is the pre-compaction pressure. Extrudates pre-compacted with 32 bar and 255 bar are compared in Figure 4.33 and Figure 4.34.

The increased packing density of the particles at \( p_{\text{c}} = 255 \text{ bar} \) results in a lower permeability of the powder. This leads to a reduced flow velocity of the liquid relative to the particles. Moreover, the extent of liquid phase migration increases with increasing compressibility of a wet powder. In a highly compressible system, compaction squeezes liquid out of the pores. Thus a strongly pre-compacted powder displays minimal liquid phase migration. The absence of additional liquid required to lubricate the particles in the die inlet zone causes the pressure closest to the die (10 mm) to continuously grow until the system blocks. This observation does not conflict with the impact of the pre-compaction pressure on the critical pressure illustrated in Figure 4.28. The critical pressure is the value of the first appearing peak and is not associated with the following trend of the pressure curve. Figure 4.35 shows the liquid distribution in wet Spheriglass extrudates at varying extrusion speeds. The process parameters were the same as with the Sepasil B 5/63 powder shown in Figure 4.30. In case of the glass beads nearly no LPM can be detected. This can be
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Figure 4.32: Critical pressures at varying ram velocities of pre-kneaded Sepasil B 5/63 ($\phi_m=75\%$, $\phi_{Nutr.}=63\%$, $l_{die}=15\text{ mm}$, $p_c=32\text{ bar}$).

Figure 4.33: Axial liquid phase distribution in the extrudate at pre-compaction pressures of 32 bar and 255 bar (Sepasil B 5/63, $\phi_m=75\%$, $\phi_{Nutr.}=63\%$, $d_{die}=12\text{ mm}$, $l_{die}=15\text{ mm}$, $v_{ram}=0.2\text{ mm/s}$).
Figure 4.34: Wall pressures as a function of the distance between the die and the ram at pre-compaction pressures of 32 bar and 255 bar (Sepasil B 5/63, $\phi_m=75\%$, $\phi_{Natr.}=63\%$, $d_{die}=12$ mm, $l_{die}=15$ mm, $v_{ram}=0.2$ mm/s) and a die with a 45° conical inlet (same, $p_c=32$ bar).
attributed to the lower compressibility of the glass beads system in comparison to the wet silica powder (Figure 4.36). Due to the round shape of the glass beads and their smooth surface the particles are already densely packed at low compaction pressures.

Figure 4.35: Axial liquid phase distribution in the extrudate at varying ram velocities (Spheriglass, $\phi_m=82\%$, $\phi_{Nutr.}=63\%$, $d_{die}=12\ mm$, $l_{die}=15\ mm$, $v_{ram}=0.2\ mm/s$).

The effect of an insufficiently developed transition shear zone is also observed if the rectangular die is replaced by a die with a 45° inlet. As the wet powder slides along the wall of the 45° inlet and not along a well developed slide zone, the pressure above the die shows a strong re-increase (Figure 4.34). In this case the system did not block but the increasing tendency of the pressure demonstrates that the system was close to a jamming situation. The differences between the 45° and a 90° die inlet are shown in the flow patterns in Figure 4.37.

The profile on the right exhibits an inlet region where several differently stained thin layers are superimposed forming the shear zone. The 45° die (left) does not show several layers adjacent to the wall demonstrating that there is slip along the wall which apparently causes higher shear forces than the transition shear zone.

### Radial liquid phase distribution

Numerous wet Sepasil B 5/63 extrudates were analyzed to determine the extent of radial liquid phase migration. To do this, individual segments of the extrudates were divided into an inner part (diameter 9 mm) and an outer part and liquid mass fractions determined as described in chapter 3.12. Within the accuracy of measurement no differences in the liquid content in the outer and the inner regions of the extrudates were detected.
Figure 4.36: Porosity of Spheriglass ($\phi_m=82\%$) and Sepasil B 5/63 ($\phi_m=75\%$) bound by a 63\% w/w Nutriose solution, compressibility at 50 bar.

Figure 4.37: Flow pattern in the die inlet zone for a 90° (left) and a 45° die inlet (Sepasil B 5/63, $\phi_m=75\%$, $\phi_{Nutr.}=63\%$, $d_{die}=12\text{ mm}$, $l_{die}=15\text{ mm}$, $v_{ram}=0.2\text{ mm/s}$, $p_c=32\text{ bar}$).
4.6.6 Microstructure of extrudates

Air inclusions within dried extrudates were detected and quantified with a µCT scanner (chapter 3.13). With this method volume fractions of air anywhere in the bulk can be determined. The accuracy of measurement depends on several factors:

- choice of threshold separating air and solid. The extent to which the x-rays are absorbed depends on the physical density of the screened material. In the wet powder systems considered, solid particles, dried Nutriose, and air inclusions were coexisting and they differed in their absorbing properties. To extract the air inclusions, a binary picture was generated separating the air from any other material. This required the determination of a threshold value defining the degree of x-ray absorption below which the material was considered as air. Depending on the choice of this value (here 20% of the maximum grayscale value), different results were obtained.

- limited scanner resolution. The resolution of the scanner is limited to 8 µm. The number of air inclusions smaller than 8 µm is expected to be non negligible. Nevertheless their contribution to the air volume fraction might be small. An air inclusion of 10 µm for instance makes a thousandfold contribution to the air volume compared to a 1 µm air cell.

- sample preparation artifacts. The drying of the extrudates caused a transformation of the Nutriose into the glassy state. This was associated with a shrinking of the binder volume and hence increased the air volume.

As a consequence of these restrictions the absolute values of the air volume fractions ascertained by means of µCT are to be viewed critically. To receive an impression of the exactness of this method, air volume fractions of a wet Sepasil B 5/63 powder detected with the µCT scanner were compared to the fractions resulting from weight, volume and composition of the material:

\[
\phi_{air} = \frac{V_{air}}{V_s + V_l + V_{air}} = 1 - \frac{m_s \rho_s + m_l \rho_l}{V_{total}} = \epsilon \cdot (1 - S)
\]  

The powder was compacted in a cylindrical barrel with a diameter of 20 mm and a vertical stress of 128 bar. Three samples were analysed. The results are summarized in Table 4.10. The true air volume fraction of the dried compacts is underestimated by up to 31.8%. A further increase in the threshold, which would theoretically increase the obtained air volume fraction, would deteriorate the linear correlation between true and measured values and is therefore not admissible. The main reason for the discrepancy between these data might be the limited resolution of the µCT scanner. Consequently, the µCT measurements have to be considered as being of qualitative nature. Figure 4.38 shows a 2D picture of the cross-sectional area of a Sepasil B 5/63 extrudate.
Table 4.10: Air volume fraction of wet powder pressagglomerates analysed both with µCT and gravimetrically ($\phi_m=75\%$, $p_c=32$ bar).

<table>
<thead>
<tr>
<th>Sample</th>
<th>µCT</th>
<th>gravimetry, dried</th>
<th>gravimetry, wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.3</td>
<td>20.9</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>13.7</td>
<td>17.5</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>14.1</td>
<td>19.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Figure 4.38: 2D µCT picture of a dried extrudate (Sepasil B 5/63, $\phi_m=75\%$, $d_{die}=12$ mm, $l_{die}=15$ mm, $v_{ram}=0.2$ mm/s, $p_c=32$ bar).
The white pixels are the detected air inclusions while solid particles and binder are integrated in the black areas. The analysis of extrudate slices of a thickness of 0.5 mm reveals that the air volume fraction increases from approximately 11% in the outer zones to about 30% in the centre, independent of the location of the measurement in the extrudate (Figure 4.39).

With the knowledge of the liquid phase distribution (Figure 4.31), the saturation of the wet powder as a function of the radius can be determined (Figure 4.39). The saturation is approximately 48% in the centre and reaches 78% in the outer regions. Like the air volume fraction, the radial course of the saturation is independent of the axial location of measurement. Additionally, no influence of the ram velocity on the radial air cell distribution is found. This is demonstrated in Appendix A.6.

The µCT measurements clearly reveal the effect of compression and shear in the die inlet region on the microstructure within the extrudates. The outer regions are more densely packed and highly saturated and hence can act as shear zone with reduced frictional forces between the particles.

As discussed above, the true values of the air volume fraction might be higher. By contrast, the air volume fraction after extrusion was by far lower. By assuming that the air volume fraction of the wet extrudates is approximately 38% of the value measured for the dry extrudates (according to Table 4.10), it follows a saturation in the center of 76% and in the outer ring of 91%.

Figure 4.39: Air volume fraction and saturation of a dried extrudate at distances of 1 cm, 4 cm and 7 cm from the extrudate front. µCT measurement (Sepasil B 5/63, \( \phi_m = 75 \), \( d_{die} = 12 \text{ mm} \), \( l_{die} = 15 \text{ mm} \), \( v_{ram} = 0.2 \text{ mm/s} \), \( p_c = 32 \text{ bar} \)).
The impact of the pre-compaction pressure on the air volume fraction of dry extrudates can be seen in Figure 4.40. There is a slight tendency that the air volume fraction increases with increasing pre-compaction pressure although the total porosity decreases with increasing pressure (Figure 4.18). This can be explained by stronger particle aggregates generated by higher pre-compaction pressures. Stronger aggregates exhibit higher yield values. Thus a densification by shear during extrusion requires higher shear forces in case of a stronger pre-compaction. However, the differences in the air volume fractions are moderate. Two µCT pictures of extrudates pre-compacted with 16 bar and 255 bar are shown in Figure 4.41.

Figure 4.40: Mean air volume fraction in dried extrudates at varying pre-compaction pressures (Sepasil B 5/63, \(\phi_m=75\%\), \(d_{\text{die}}=12\,\text{mm}\), \(l_{\text{die}}=15\,\text{mm}\), \(v_{\text{ram}}=0.2\,\text{mm/s}\)).

### 4.7 Modeling of wet powder ram extrusion

The batchwise ram extrusion of a wet powder in the Zwick Z010 allows for simultaneously measuring the vertical stress applied by a ram and the horizontal wall stress at any location of the cylindrical barrel containing the material which is pressed through the die. The impact of material and process parameters on critical stresses was quantitatively investigated in chapter 4.6.

To better understand wet powder flow during ram extrusion the knowledge of the stress fields in the barrel is required. By assessing the influence of wall friction, interparticle friction and die geometry on these stress fields product specific processes can be designed. Based on bulk solid mechanical approaches by Janssen (1895), Schulze (1991) and Motzkus (1974), a semi-empirical model was developed to calculate vertical stresses, wall normal stresses and wall shear stresses in the barrel above the die during wet powder extrusion.
Material parameters needed for the model are the effective angle of internal friction as a function of the bulk density, the angle of internal friction at steady-state flow in the shear plane, the angle of wall friction, the compressibility of the bulk and the lateral stress ratio at uniaxial compaction. The calculation of the stress fields requires the input of the vertical stress applied by the ram as a function of the distance between the ram and the die.

### 4.7.1 Description of the model

The relationships described in the following are based mainly on the approaches which Motzkus (1974) and Schulze (1991) developed for the design of hoppers (chapter 2.2.5). Their models allow for the approximation of the stress fields in dry bulk solids in the filling and in the emptying state. However, they did not describe the development of the stresses over the time but considered the state of equilibrium at a given filling height of the hopper. To adapt these models to the batchwise wet powder extrusion, the following assumptions are made:

- Gravitational forces can be neglected.
- The stress state is two-dimensional. It is assumed that the largest and the smallest of the three principal stresses decide whether the powder compact fails and flows, independent of the intermediate principal stress (Walker, 1966). The stresses on the infinitesimal volume elements are the compressive stresses $\sigma_x$ and $\sigma_y$ and the shear stresses $\tau_{xy}$ and $\tau_{yx}$. The definition of the signs is shown in Figure 2.2.
- The vertical stress is uniformly distributed over the cross section. This is a simplification commonly used for the design of hoppers and was amongst others shown by Walters (1972) to be justified.
• The transition shear zone in the die inlet region (which grows with time) can be considered as an axially symmetric conical wall. The apparent angle of wall friction is equal to the internal angle of friction at steady-state flow in the shear plane, \( \phi_{sf} \), which follows from the individual yield loci of the wet powder. The material above the die entry region is referred to as the cylindrical part.

• The stresses in the cone can be determined following Motzkus’ slice element method (Motzkus, 1974). The adequacy of this approach was concluded from a good agreement of experimental and modeled data.

The balances of forces are set up for the virtually non-sheared regions in the extruder barrel, i.e. the cylindrical part and the inner region of the conical part. Hence the static dead zone and the transition shear zone are not included into the balances. Homogeneously structured slice elements are considered moving vertically towards the die. The influence of the procedures in the transition shear zone on the modeled stress fields expresses itself in its impact on the vertical stress applied by the ram. This stress is an input parameter in the model emanating from which the stresses in the barrel are calculated stepwise top down.

**Approach for the calculation of the stresses in the cylindrical part**

A slice element method is used to calculate the stresses in the cylindrical part of the barrel. With the assumptions mentioned above the equilibrium of forces yields (Figure 4.42):

\[
\tau_w \pi D_0 dx = Ad \sigma_v
\]  
(4.18)

After introducing the angle of wall friction

\[
tan(\phi_x) = \frac{\tau_W}{\sigma_W}
\]  
(4.19)

and the lateral stress ratio

\[
\lambda = \frac{\sigma_W}{\sigma_v}
\]  
(4.20)

an ordinary differential equation for the vertical stress is obtained:

\[
\frac{d\sigma_v}{dx} = \frac{4}{D_0} tan(\phi_x) \lambda \sigma_v
\]  
(4.21)

Integrating Equation 4.21 from a height \( x_{i-1} \) to a height \( x_i \) yields:

\[
\sigma_{v,i-1} = \sigma_{v,i} \cdot exp \left( \frac{4}{D_0} \cdot tan(\phi_x) \cdot \lambda(x_{i-1} - x_i) \right)
\]  
(4.22)
4.7 Modeling of wet powder ram extrusion

Figure 4.42: Slice element in the cylindrical part of the barrel.

The angle of wall friction $\phi_x$ as a function of the normal stress was determined by means of a ring shear cell (chapter 4.4.3). There are many approaches for $\lambda$ (chapter 2.2.5), which depends on bulk solid properties, wall friction, stiffness of the barrel wall, and the vertical stress amongst others (Schulze, 2008). The vertical and the horizontal stress in the cylindrical part are principal stresses only in the barrel axis. In the model described here $\lambda$ was determined experimentally by uniaxial compaction of the wet powders in a barrel identical to that used for ram extrusion (active elastic state of stress, chapter 2.2.5). The wall normal stress and the vertical stress exerted by the ram were simultaneously measured, while the amount of compacted powder was small in order to neglect wall friction effects (chapter 3.9).

**Approach for the calculation of the stresses in the conical part**

Figure 4.43 shows the forces acting on a slice element in the conical part (die inlet region).

The equilibrium of forces on a slice of infinitesimal thickness is:

$$\sigma_v A + \tau_w \cos(\theta) \cdot \frac{dx}{\cos(\theta)} 2\pi r(x) + \sigma_w \sin\theta \cdot \frac{dx}{\cos(\theta)} 2\pi r(x) = \sigma_v A + d(\sigma_v A) \quad (4.23)$$

The cross sectional area is:
4.7 Modeling of wet powder ram extrusion

![Diagram of slice element in the conical part of the barrel.](image)

Figure 4.43: Slice element in the conical part of the barrel.

\[ A = \pi \cdot \tan^2(\theta)x^2 \]  

(4.24)

With the apparent angle of wall friction

\[ \tan(\phi_{sf}) = \frac{\tau_W}{\sigma_W} \]  

(4.25)

and the definition of the factor \( K \) (2.48) it follows:

\[ \frac{d\sigma_v}{dx} - 2 \sigma_v \left[ K \left( 1 + \frac{\tan(\phi_{sf})}{\tan(\theta)} \right) - 1 \right] = 0 \]  

(4.26)

An integration of Eq. 4.26 from a height \( x_{i-1} \) to a height \( x_i \) yields:

\[ \sigma_{v,i-1} = \sigma_{v,i} \left( \frac{x_{i-1}}{x_i} \right)^{2[K(1+\frac{\tan(\phi_{sf})}{\tan(\theta)})-1]} \]  

(4.27)

The determination of the factor \( K \) results from Motzkus’ model (chapter 2.2.5) and is calculated with Eq. 2.49 if \( \theta \leq \theta_F \) (according to Eq. 2.43) or with Eq. 2.50 if \( \theta > \theta_F \). Inserting \( K \) into Eq. 4.27 yields the vertical stress in the conical part of the barrel as a function of the height \( x \). After a conversion, Eq. 4.27 can also be written in the following form:

\[ \sigma_{v,i-1} = \sigma_{v,i} \left( \frac{x_{i-1}}{x_i} \right)^m \]  

(4.28)
4.7 Modeling of wet powder ram extrusion

with

\[ m = \begin{cases} 
\frac{2\mu E \lambda_E}{\tan(\theta)} & \text{if } \theta < 45^\circ \end{cases} - \frac{1}{2} \left[ \phi_s f - \phi_v (\sigma_v) + \arcsin \left( \frac{\sin(\phi_s f)}{\sin(\phi_v (\sigma_v))} \right) \right] \]

\[ \frac{2\mu w \lambda_E}{\tan(\theta)} & \text{otherwise} \]

The wall normal stress \( \sigma_W \) follows from Eq. 2.48, the wall shear stress from Eq. 4.25.

4.7.2 Calculation of the stresses as a function of time

During ram extrusion the powder is displaced downwards by a ram with a constant ram velocity. With the model described here, the vertical stresses and the wall (shear and normal) stresses are calculated as a function of time and the ram-to-die distance respectively. The load superimposed by the ram was taken from experimental data. The stress fields were calculated using Matlab through the following procedure. A copy of the code is attached in Appendix A.7.

1. Specification of the geometry at the beginning of the extrusion according to Figure 4.44: the barrel diameter \( D_0 \), the distance between the ram and the origin \( x_{\text{ram},0} \), the height of the conical die inlet region \( \Delta x_{\text{inlet}}(x_{\text{ram},0}) \), and the die diameter \( d_{\text{die}}(x_{\text{ram},0}) \) are defined. The cone angle is:

![Figure 4.44: Geometry at the beginning of the extrusion.](image)
4.7 Modeling of wet powder ram extrusion

\[ \theta = \arctan \left( \frac{0.5 \cdot (D_0 - d_{\text{die}})}{\Delta x_{\text{inlet}}} \right) \]  
(4.29)

The upper end of the cone is located at:

\[ x_{\text{cone}}(x_{\text{ram}, 0}) = \frac{D_0}{2} \tan(\theta). \]  
(4.30)

Consequently the height of the apex of the cone at the beginning of the extrusion is:

\[ x_{\text{apex}} = x_{\text{cone}}(x_{\text{ram}, 0}) - \Delta x_{\text{inlet}}(x_{\text{ram}, 0}). \]  
(4.31)

2. Specification of the number of slice elements \( n_0 \). The total volume of the powder in the barrel can be calculated as follows:

\[ V_{\text{total}, 0} = \frac{\pi}{4} D_0^2 x_{\text{cyl}}(x_{\text{ram}, 0}) + \frac{1}{3} \pi \left( \frac{D_0}{2} \right)^2 x_{\text{cone}}(x_{\text{ram}, 0}) - \frac{1}{3} \pi \left( \frac{d_{\text{die}}(x_{\text{ram}, 0})}{2} \right)^2 x_{\text{apex}} \]  
(4.32)

The volume of one slice element at the beginning is:

\[ V_{i, 0} = \frac{V_{\text{total}, 0}}{n_0} \]  
(4.33)

3. Before extrusion, the wet powder is pre-compacted in the material testing machine with a vertical stress \( \sigma_{v, \text{pre}} \) in several small quantities. By neglecting an elastic re-extension after pre-compaction, the mass of each slice element before extrusion is:

\[ m_{i, 0} = \rho_b(\sigma_{v, \text{pre}}) \cdot V_{i, 0} \]  
(4.34)

4. Calculation of the lower bounds \( x_{i, 0} \) and heights \( h_{i, 0} \) of the \( n_0 \) slice elements. The lower bound of the first element is \( x_{1, 0} = x_{\text{apex}} \). In the conical part of the barrel the height \( h_{i, 0} \) of an element \( i \) is determined in such a manner that the function

\[ V_{i, 0} = \frac{1}{3} \pi \cdot \tan^2 \theta \cdot (3x_{i, 0}^2 h_{i, 0} + 3h_{i, 0}^2 x_{i, 0} + h_{i, 0}^3) \]  
(4.35)

is fulfilled. In the cylindrical part the height is:

\[ h_{i, 0} = \frac{V_{i, 0}}{\frac{\pi}{4} D_0^2} \]  
(4.36)

The bounds and the height of the slices are calculated from the bottom to the top. There is one slice whose lower bound is in the conical part \( (x_{i, 0} < x_{\text{cone}}(x_{\text{ram}, 0})) \) and its upper bound in the cylindrical part. Here the height \( h_{i, 0} \) is calculated by combining Eq. 4.35 and Eq. 4.36 in such a manner that the volume of this slice is equal to \( V_{i, 0} \):
4.7 Modeling of wet powder ram extrusion

\[ V_{i,0} = \frac{1}{3} \pi \cdot \tan^2(\theta) \cdot (3x_{i,0}^2(x_{\text{cone}}(x_{\text{ram},0}) - x_{i,0}) + 3(x_{\text{cone}}(x_{\text{ram},0}) - x_{i,0})^2x_{i,0} + (x_{\text{cone}}(x_{\text{ram},0}) - x_{i,0})^3) + \frac{\pi}{4} D_0^2(x_{i,0} + h_{i,0} - x_{\text{cone}}(x_{\text{ram},0})) \] (4.37)

The lower bound of each slice element can be calculated from:

\[ x_{i+1,0} = x_{i,0} + h_{i,0} \] (4.38)

5. Calculation of the stresses immediately after pre-compaction. \( \sigma_{v,i,0} \) is at any height equal to \( \sigma_{v,\text{pre}} \). The wall normal stress in the cylindrical part is:

\[ \sigma_{W,i,0} = \lambda(\sigma_{v,i,0}) \cdot \sigma_{v,i,0} \] (4.39)

As it is assumed that the pre-compaction is performed slice by slice, wall friction can be neglected before extrusion starts (\( \tau_{W,i,0}=0 \)). This results in \( \sigma_{v,i,0} \) and \( \sigma_{W,i,0} \) being principal stresses. Although there is no conical part in the barrel at this moment (static zone develops during extrusion), the stresses acting at the wall of the fictitious cone can be calculated. Simple considerations on a Mohr stress circle with \( \sigma_1 = \sigma_{v,i,0} \) and \( \sigma_2 = \sigma_{W,i,0} \) lead to:

\[ K_{i,0} = \sin^2(\theta) + \lambda \cos^2(\theta) \] (4.40)

\[ \sigma_{W,i,0}^* = K_{i,0} \sigma_{v,i,0} \] (4.41)

\[ \tau_{W,i,0}^* = \sigma_{v,i,0} - \frac{\lambda(\sigma_{v,i,0}) - 1}{2} \sin 2\theta \] (4.42)

6. Calculation of the stresses during flow. The actual height of the ram at time step \( j \) corresponds to the upper bound of the last slice element:

\[ x_{\text{ram},j} = x_{n_0-(j-1)} + h_{n_0-(j-1)} \] (4.43)

The height \( x_{i,j} \) always refers to the same basing point (see Figure 4.44). The vertical stress acting from above on the last slice \( \sigma_{v,n_0-(j-1),j} \) is the stress measured in the material testing machine when the ram is located at a distance \( x_{\text{ram},j} \) from the die. The vertical stresses in the cylindrical part \( (x_{i,j} \geq x_{\text{cone}}(x_{\text{ram},j})) \) are calculated as follows:

\[ \sigma_{v,i,j} = \sigma_{v,i+1,j} \cdot \exp \left( \frac{4}{D_0} \tan(\phi_x) \cdot \lambda(\sigma_{v,i+1,j})(x_{i,j} - x_{i+1,j}) \right) \] (4.44)
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The wall normal and shear stress are:

\[ \sigma_{W,i,j} = \lambda(\sigma_{v,i,j}) \cdot \sigma_{v,i,j} \]  
(4.45)

\[ \tau_{W,i,j} = \tan(\phi_x) \cdot \sigma_{W,i,j} \]  
(4.46)

In the conical part \((x_{i,j} < x_{cone}(x_{ram,j}))\) the vertical stress follows from:

\[ \sigma_{v,i,j} = \sigma_{v,i+1,j} \left( \frac{x_{i,j}}{x_{i+1,j}} \right)^{m_{i,j}} \]  
(4.47)

with

\[ m_{i,j} = \begin{cases} 
\frac{2\mu_{E,i,j} \lambda_{E,i,j}}{\tan(\theta)} & \text{if } \theta < \theta_F = 45^\circ - \frac{1}{2} \left[ \phi_{sf} - \phi_e(\sigma_{v,i+1,j}) \right] + \arcsin\left( \frac{\sin(\phi_{sf})}{\sin(\phi_e(\sigma_{v,i+1,j}))} \right) \\
\frac{2\mu_{E,i,j} \lambda_{E,i,j}}{\tan(\theta)} & \text{otherwise}
\end{cases} \]

and

\[ \mu_{E,i,j} = \tan(\phi_e(\sigma_{v,i+1,j})), \]  
(4.48)

\[ \lambda_{E,i,j} = \frac{1 - \sin^2(\phi_e(\sigma_{v,i+1,j}))}{1 + \sin^2(\phi_e(\sigma_{v,i+1,j}))}, \]  
(4.49)

\[ \lambda_{E,i,j} = \frac{1 - \tan(\theta) \cdot \tan(\phi_{sf}) - \mu_{E,i,j} \lambda_{E,i,j} \cdot \tan(\theta) \cdot (1 + \tan^2(\phi_{sf}))}{1 + \tan^{-1}(\theta) \cdot \tan(\phi_{sf})} 
+ \mu_{E,i,j} \lambda_{E,i,j} \cdot \tan(\theta) \cdot (\tan^{-1}(\theta) - \tan(\phi_{sf}))^2 \]  
(4.50)

\[ \mu_{E,i,j} = \mu_{E,i,j} \frac{\lambda_{E,i,j}}{\lambda_{E,i,j}}. \]  
(4.51)

The wall normal stress can be calculated with:

\[ \sigma_{W,i,j} = K_{i,j} \sigma_{v,i,j}, \]  
(4.52)

\[ K_{i,j} = \begin{cases} 
\frac{\lambda_{E,i,j} + 1}{2} + \frac{\lambda_{E,i,j} - 1}{2} \cos(2\theta) & \mu_{E,i,j} \lambda_{E,i,j} \cdot \sin(2\theta) & \text{if } \theta < \theta_F \\
\frac{\lambda_{E,i,j} + 1}{2} + \frac{\lambda_{E,i,j} - 1}{2} \cos(2\theta) & \mu_{E,i,j} \lambda_{E,i,j} \cdot \sin(2\theta) & \text{otherwise}
\end{cases} \]

Finally, the shear stress at the cone wall follows from:
4.7 Modeling of wet powder ram extrusion

\[ \tau_{W,i,j} = \tan(\phi_{sf}) \cdot \sigma_{W,i,j} \] (4.53)

The stresses are calculated at each discrete time step. At the end of one time step the number of slice elements is reduced by one. All elements are shifted downwards so that the element \( i \) at time step \( j \) corresponds to element \( i - 1 \) at time step \( j + 1 \). From time step \( j \) to time step \( j + 1 \) the elements are displaced by the volume of the first element at time step \( j \) which is assumed to leave the barrel. Therefore the lower bounds and heights of all slice elements have to be recalculated while it is supposed that the bulk density after the displacement is equal to the bulk density at the preceding time step (the true bulk density at \( j + 1 \) is calculated after the calculation of the stresses).

As the transition shear zone in the die inlet region expands with time, a function \( x_{cone}(x_{ram,j}) \) has to be defined on the basis of experimental data. Figure 4.45 shows the longitudinal cut of a glass beads/Nutriose powder (\( \phi_m = 82\% \)) in the die inlet region. The contrast of the pictures was adjusted for reasons of clearness. Prior to extrusion, 10 slices of wet powder mass (4 g each) were uniaxially compacted in the barrel. The color of the slices was alternately gray and red. This way flow profiles and the extent of the transition shear zone were visualized. In picture a) the powder has just entered the die. The static zone is limited to a small region of a height of 5 mm above the die. At a later stage of the extrusion (picture b), the shear zone extends to a distance of about 10 mm from the die. Additionally, the profile shows that the outer region of the mass flowing into the die with a significantly lower velocity than the material in the core has expanded. In picture c this shear zone has further propagated upwards and again an increased thickness at the entrance into the die can be observed. If this shear zone of the powder is assumed to have a flow velocity which is negligibly small compared to the flow velocity in the core, the die inlet region can be considered a cone moving upwards with a constant cone angle \( \theta \). This is accompanied by an apparent reduction of the die diameter. In the program described here a function \( x_{cone}(x_{ram}) \) was defined on the basis of these experimental data. The geometrical relations are illustrated in Figure 4.46.

Figure 4.45: Longitudinal cut of a glass beads/Nutriose® powder in the die inlet region at different time steps.

The die diameter at time step \( j \) is:
4.7 Modeling of wet powder ram extrusion

\[ d_{\text{die}}(x_{\text{ram},j}) = D_0 - 2 \frac{D_0 - d_{\text{die}}(x_{\text{ram},0})}{2} \frac{x_{\text{cone}}(x_{\text{ram},j}) - x_{\text{apex}}}{\Delta x_{\text{inlet}}(x_{\text{ram},0})} \] (4.54)

This shift of the cone leads to a dissection of the slice elements below \( x_{\text{cone}}(x_{\text{ram},j}) \). The new volume of the slice elements in the cone is calculated as follows:

\[ V_{i,j} = \frac{1}{3} \pi (x_{i+1,j} - x_{i,j})(R^2 + Rr + r^2) \] (4.55)

with

\[ R = \frac{(d_{\text{die}}(x_{\text{ram},j}))}{2} + \tan(\theta) \cdot (x_{i+1,j} - x_{\text{apex}}) \] (4.56)

and

\[ r = \frac{(d_{\text{die}}(x_{\text{ram},j}))}{2} + \tan(\theta) \cdot (x_{i,j} - x_{\text{apex}}). \] (4.57)

The actual mass of the element is:

\[ m_{i,j} = \rho b_{i+1,j-1} V_{i,j} \] (4.58)

This modification of the mass of the slice elements is taken into account in the calculation of the lower bounds and heights in the following time step. It has to be taken into account that the calculation of the height of a slice element in the cone by solving
4.7 Modeling of wet powder ram extrusion

Eq. 4.35 accounts for the replacement of \( x_{i,j} \) by \( (x_{i,j} - \Delta x_{\text{apex}}(x_{\text{ram}})) \). Equally, \( x_{i,j} \) and \( x_{i+1,j} \) have to be corrected for the calculation of \( \sigma_{v,i,j} \) by means of Eq. 4.47.

The calculated wall normal stresses at distances of 10 mm, 11.5 mm and 13 mm are calculated at each time step and averaged to be compared with the measured pressure. The exact position of the pressure sensor is 11.5 mm. However, the sensor membrane has a diameter of approximately 3 mm which is why the modeled values are averaged. As long as the wall normal stress of interest is in the cylindrical part of the barrel, it can be calculated with Eq. 4.45. In the conical part the horizontal normal stress at the barrel wall is assumed to be identical to the horizontal normal stress at the cone wall. The horizontal normal stress follows from a consideration of the Mohr stress circle at the cone wall:

\[
\sigma_h(i,j) = \begin{cases} 
\lambda E_{i,j} \sigma_v(i,j) & \text{if } \theta < \theta_F \\
\lambda_t E_{i,j} \sigma_v(i,j) & \text{if } \theta \geq \theta_F
\end{cases}
\]

**4.7.3 Experimental data**

The following material properties were implemented in the program:

1. Bulk density \( \rho_b \) as a function of the vertical stress \( \sigma_v \) at uniaxial compaction. This function was obtained from the measurement of a compaction curve.
2. Effective angle of friction \( \phi_e \) as a function of the bulk density \( \rho_b \) resulting from shear cell measurements.
3. The lateral stress ratio \( \lambda \) at uniaxial compaction as a function of \( \sigma_v \).
4. The angle of wall friction \( \phi_x \) as a function of the wall normal stress \( \sigma_W \) obtained from shear cell measurements.

The material function \( \rho_b = f(\sigma_v) \) was derived from the experimental data shown in Figure 4.47. 10 g of wet powder were compacted in the material testing machine with a ram velocity of 0.01 mm/s.

A good approximation of the compaction curves was obtained by using fit functions of the following form:

\[
\frac{\rho_b}{g/cm^3} = a' + b \cdot \sigma_v + c \cdot (1 - \exp(-\sigma_v/d))
\]  \hspace{1cm} (4.59)

\( a' \), \( b \), \( c \) and \( d \) are fitting parameters. The lateral stress ratio \( \lambda \) at uniaxial compaction is depicted in Figure 4.48 for a wet Spheriglass powder with \( \phi_m=82\% \), as an example. The amount of wet powder in the barrel was 20 g, the ram velocity 0.2 mm/s. The four measured curves illustrated in Figure 4.48 demonstrate the commonly observed variations in the function \( \lambda(\sigma_v) \).

The functions approximating \( \lambda \) are of the same form as those used for the approximation of the bulk density.
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Figure 4.47: Compaction curves of Spheriglass bound by a 63% w/w Nutriose solution and fit function implemented in Matlab.

Figure 4.48: Lateral stress ratio of Spheriglass glass beads bound by a 63% w/w Nutriose solution (φ_m=82%) at uniaxial compaction and fit function implemented in the Matlab code.
In the framework of this thesis, the calculation of the stress fields during ram extrusion was performed for wet Spheriglass beads bound by a 63% Nutriose solution and solid mass fractions of $\phi_m = 82\%$, 84\% and 86\%. The three wet powders feature angles of wall friction on milled brass which are independent of the normal stress (chapter 4.4.3) within the measurement range of the ring shear cell (Table 4.11).

Table 4.11: Angles of wall friction of Spheriglass glass beads bound by a 63% Nutriose solution on a milled brass plate.

<table>
<thead>
<tr>
<th>solid mass frac. $\phi_m$</th>
<th>Angle of wall friction $\phi_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>°</td>
</tr>
<tr>
<td>82</td>
<td>$18.4 \pm 0.7$</td>
</tr>
<tr>
<td>84</td>
<td>$18.6 \pm 0.2$</td>
</tr>
<tr>
<td>86</td>
<td>$19.8 \pm 0.1$</td>
</tr>
</tbody>
</table>

With the ring shear cell used the effective angle of internal friction $\phi_e$ could be determined for bulk densities of up to $1.39\text{ g/cm}^3$. For simplification it was assumed that $\phi_e$ is uniquely a function of the bulk density. Due to the limited measuring range of the ring shear cell, an extrapolation towards higher bulk densities was necessary (Figure 4.49). $\phi_e$ was assumed to have a constant value of $21.79^\circ$ at bulk densities $\geq 1.9\text{ g/cm}^3$ ($\phi_m = 82\%$). Thus this measurement is a rough estimation of the real data.

Figure 4.49: Effective angle of internal friction of Spheriglass glass beads bound by a 63\% w/w Nutriose solution ($\phi_m = 82\%$).
The function describing the height of the transition shear zone $\Delta x_{inlet}(x_{ram} - x_{apex,0})$ as a function of the distance between die and ram is shown in Figure 4.50.

Figure 4.50: Height of the conical part of the barrel as a function of the distance between the die and the ram

### 4.7.4 Calculated stress fields

Experimentally obtained and calculated stresses of wet Spheriglass powder with a solid mass fraction of 82% are illustrated in Figure 4.51. In the diagram on the left the vertical stress as well as the measured and the calculated wall normal stresses at a distance of 11.5 mm from the die are plotted against the distance between the die and the ram. A good agreement between the experimental and modeled wall normal stress is found.

Modeled vertical stresses and stresses at the wall as a function of the x coordinate at different time steps are shown in the diagram on the right. The vertical stress decreases exponentially in the cylindrical part of the barrel and decreases to 0 Pa in the die inlet region. There is a buckling at the passage from the cylindrical part into the cone.

The wall normal stress $\sigma_W$ slightly decreases in the cylindrical part and exhibits a peak stress at the passage into the die inlet region where it equally drops to zero. The shear stress $\tau_W$ at the wall which is linked with $\sigma_W$ by $\phi_x$ and $\phi_{sf}$ respectively, shows the same tendency as $\sigma_W$.

The observation of the stresses dropping to 0 Pa at the die inlet is in agreement with experimental observations (chapter 4.6.2) since stresses in die are negligibly small as shown in chapter 4.6.2.

The results for two Spheriglass systems with solid mass fractions of 84% and 86% are shown in Figure 4.52 and Figure 4.53. The course of the stresses is qualitatively the same as discussed above. In case of $\phi_m=84\%$ again a good agreement between calculated and measured wall normal stresses is found, while there is a non negligible discrepancy in the
4.7 Modeling of wet powder ram extrusion

**Figure 4.51:** $\phi_m=82\%$. Left: Vertical stress applied by the ram and measured and calculated wall normal stress at a distance of 11.5 mm from the die versus the distance between the die and the ram. Right: Vertical stress, wall normal stress and wall shear stress as a function of the distance from the die at different times (Spheriglass, $\phi_{Natr.}=63\%$, $d_{die}=12\mm$, $l_{die}=20\mm$, $v_{ram}=0.2\mm/s$, $p_c=32\bar$).

Wall normal stress at $\phi_m=86\%$. However, in view of the complexity of the stress states, the result is considered as being satisfying.
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Figure 4.52: $\phi_m=84\%$. Left: Vertical stress applied by the ram and measured and calculated wall normal stress at a distance of 11.5 mm from the die versus the distance between the die and the ram. Right: Vertical stress, wall normal stress and wall shear stress as a function of the distance from the die at different times (Spheriglass, $\phi_{Nutr.}=63\%$, $d_{die}=12$ mm, $l_{die}=20$ mm, $v_{ram}=0.2$ mm/s, $p_c=32$ bar).

Figure 4.53: $\phi_m=86\%$. Left: Vertical stress applied by the ram and measured and calculated wall normal stress at a distance of 11.5 mm from the die versus the distance between the die and the ram. Right: Vertical stress, wall normal stress and wall shear stress as a function of the distance from the die at different times (Spheriglass, $\phi_{Nutr.}=63\%$, $d_{die}=12$ mm, $l_{die}=20$ mm, $v_{ram}=0.2$ mm/s, $p_c=32$ bar).
5 Conclusions

Flow properties of highly unsaturated wet powders were investigated. The presence of air inclusions makes these systems very cohesive by capillary and surface tension forces. Additionally, particle contact points generate strong interparticle frictional forces and increase the risk of jamming during extrusion. The packing structure of the solid phase and the distribution of the liquid phase have a major impact on extrusion pressures.

Yield loci of three silica powders and one glass beads powder were determined to assess the impact of particle shape, particle size and particle size distribution on their flow behavior. It was demonstrated that Sikron B 800 silica powder shows a pronounced cohesivity due to a small particle size associated with large van der Waals adhesive forces. Sepasil B 5/63 and Sepasil B 20/100 silica powders exhibit sharp-edged particles resulting in high interparticle frictional forces while Spheriglass 3000 glass beads feature the smallest angles of internal friction. The more narrow particle size distribution of Sepasil B 20/100 in comparison to Sepasil B 5/63 leads to a lower packing density and reduced cohesion.

The powders were blended with Newtonian Nutriose solutions to form a wet powder. In a first principal part, wet Spheriglass powders were investigated with a ring shear cell. All measured yield loci are approximately linear in the measurable range of positive normal stresses. The cohesion at different preshear stresses and various solid mass fractions allows for the determination of the pendular, the funicular and the capillary state as a function of the saturation. The funicular state of Spheriglass glass beads bound by a 63 % Nutriose solution reaches from a saturation of about 35 % to 80 % which is in agreement with Schubert (1973).

In a viscosity range between 0.7 Pas and 11.3 Pas both yield loci and wall yield loci are independent of the binder viscosity. This is in agreement with the phenomenon, observed by several authors, that at low strain rates viscous liquid friction does not contribute to the shear stress.

The wall shear stress of the glass beads on a plate made from brass increased by increasing capillary forces, when binder was added. However, when exceeding a critical value of 20 % w/w binder, a drop of the wall shear stress occured and there was nearly no more impact of the normal stress. This demonstrated, that a lubricating film had developed in the shear plane between the glass beads and the plate and that solid friction had been significantly reduced in favor of viscous liquid friction.

A linear extrapolation of the yield loci towards negative normal stresses in order to determine the uniaxial tensile trength seems to lead to an overestimation although decribed in literature. This is concluded from the discrepancy between tensile strengths obtained from
a linear extrapolation and tensile strengths calculated with the established Rumpf-equation (Rumpf, 1970) and is supported by literature data.

A semi-empirical model was developed on the basis of which individual and steady-state yield loci of wet powders in the pendular state can be calculated for any preshear stress. It is based on the assumption that discrete liquid bridges between the particles are responsible for compressive forces in the wet powder in addition to external loads. As input parameters the Sauter diameter of the solid powder, the surface tension of the liquid, the contact angle between solid and liquid, the particle and the liquid density and the angle of internal friction are needed. The mean separation distance was assumed to be negligible in accordance with Pietsch and Rumpf (1967). At preshear stresses larger than 2 kPa the agreement between modeled and experimentally obtained yield loci was excellent for all wet Spheriglass systems investigated.

In a second principal part, the ram extrusion of wet powders at minimal binder fractions was investigated. This situation significantly differs from the flow in the shear cell, because normal and shear stresses are much larger and elongational flow in the die entry region in combination with strong shear forces in the outer regions make the flow very complex. When wet powders are extruded, they are close to a jamming situation in the die inlet region. While the material in the center of the barrel above the die is axially accelerated, a conically shaped shear zone develops in the outer regions. The combination of shear and pressure in this region causes the formation of highly saturated and densely packed shear layers with reduced shear stresses. Ideally, the system is transformed into a suspension state. This process is referred to as 3P2S transition. Once a critical pressure has been overcome at the beginning of extrusion, a steady-state is reached, provided that no liquid phase migration occurs.

Compaction curves showing the saturation or the bulk density of a wet powder over an uniaxial vertical pressure, are an appropriate measure of the impact of interparticle friction on wet powder flowability. It was shown that compaction curves reflect the flow resistance of wet powders during ram extrusion. Factors favoring both the compaction and the extrusion of wet powders are smooth particle surfaces, regular particle shapes, broad particle size distributions, a uniform distribution of the binder and high binder fractions. Shear helps to cover the particles with liquid resulting in reduced interparticle friction.

Shear forces in the barrel and the die were negligible compared to shear forces in the die inlet region. The structural transformations in the die inlet region are decisive for extrusion pressures and determine if blocking occurs. Critical pressures are independent of the die length while a reduction of the die diameter leads to an increase in required extrusion pressures.

An essential impact of pre-compaction pressures on critical extrusion pressures was observed. When the saturation of the wet powder was higher than 80% after pre-compaction, reduced interparticle friction, due to a more effective wetting, caused a decrease of critical pressures. This phenomenon competes with an increased strength of the wet powders by higher packing densities.
Liquid phase migration is a known phenomenon in paste extrusion. A gradient in the pore pressure causes a flow of the liquid phase relative to the particles towards the die. In wet powders, there is no contiguous liquid phase. As a consequence, no pore pressure gradient can build up over the whole sample length in the barrel. However, local pressure gradients by a denser packing of the particles squeezes the liquid out of the pores. Air cells are compressed, pressed into other pores or released. In (saturated) pastes a pore pressure gradient and liquid phase migration can also occur, if the particle skeleton exhibits a low compressibility as described by Darcy’s law (Rough et al., 2002). In case of wet powders, a compression of the particles is required to initiate liquid phase migration. Liquid phase migration was pronounced for Sepasil silica particles while it was not observed for Spheriglass glass beads. The extent of liquid phase migration is larger at low extrusion velocities where the binder has sufficient time to flow relative to the particles towards the die. This helps in reducing critical pressures by the lubricating properties of the binder. On the other hand, the extrudate is inhomogeneous in its binder fraction if liquid phase migration occurs and drier material can cause a re-increase of the extrusion pressure. Higher extrusion pressures result in a more pronounced squeezing effect, but reduce the permeability of the particle network. This is why high pre-compaction pressures decrease the extent of liquid phase migration.

µCT measurements allow for the detection of air inclusions in the extrudate. Mainly due to a limited resolution of 8 µm there was an underestimation of about 20%-30% with respect to the air volume fraction. Nevertheless radial distributions of air in the extrudate could be demonstrated. The measured air volume fraction in the extrudate core was approximately three times higher than in the outer region due to higher shear stresses in the outer region.

A model was developed based on an approach from bulk solids mechanics which calculates the stress fields during ram extrusion in an extruder barrel. The barrel was assumed to have a conical shape in the die inlet region, so that balances of forces could be set up for the material in the center, approximately flowing as a plug into the die. The structural changes in the shear zone were reflected by the vertical stress applied by the ram which is an input parameter of the model. To calculate the stress states in the conical part, a model was used which Motzkus (1974) had developed for powder flow in hoppers. As input parameters for the model developed in the framework of this thesis, the lateral stress ratio at uniaxial compaction, the compressibility, the effective angle of internal friction, the angle of internal friction at steady-state flow in the shear plane and the angle of wall friction were implemented in the model.

The vertical stress, the wall normal stress and the wall shear stress decrease exponentially in the cylindrical part above the die inlet region. The vertical stress exhibits a buckling at the transition into the conical part, while the wall normal stress and the wall shear stress feature a peak. In the conical part all stresses drop until reaching a value of zero at the die inlet. This is in agreement with experimental observations and is one of two aspects demonstrating the correctness of the model. The second one is the wall normal stress measured above the die. The calculated and experimentally obtained data are in good agreement.

To extend the findings obtained in the framework of this thesis, a reliable method to mea-
sure the uniaxial tensile strength of wet powder compacts would allow for a comparison with extrapolated and modeled data. From a scientific point of view, the modeling of the yield loci should be complemented by a modified Rumpf-equation taking polydispersity into account.

Contact angles could be determined with higher accuracy with the method described by Washburn (1921) using water instead of Nutriose solutions. As the solutions have nearly the same surface tension as water, the assumption of similar contact angles seems to be justified.

DEM modeling might help to visualize and better understand the structural transformations in the die inlet region. Additionally, µCT measurements with higher resolution would give further insights into the microstructure of the extrudates.

A systematic investigation of the impact of the binder viscosity on extrusion pressures could demonstrate if the observation of negligible viscosities in the case of yield loci also applies to extrusion pressures.

The determination of yield loci at high normal stresses would be useful to evaluate frictional forces in the (2S) suspension state under high pressures and to determine the effective and the steady-state angle of internal friction at the stresses occurring during extrusion.


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A.1 Determination of a tangent to two circles.  

A.2 Measured (black) and calculated (grey) Mohr stress circles at steady-state flow of Spheriglass glass beads bound by a 60 % and a 70 % Nutriose solution ($\phi_m=82\%$).  

A.3 Measured shear points and modeled yield loci (dotted line) of Spheriglass glass beads bound by a 63 % Nutriose solution for solid mass fractions of 80 % and 84 %.  

A.4 Volume weighted particle size frequency of Sikron B 800 before treatment, after kneading in the Duplex kneader ($\phi_m=75\%$, $\phi_{Nutr.}=63\%$), and after uniaxial compaction.  

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A Appendix

A.1 Impact of flattening on the van der Waals adhesive force between two particles

The van der Waals attraction between two particles results from an attractive component, obtained by integrating the molecular attractions over the volumes of the neighboring bodies, and a repulsive component, obtained from an expression from the continuum theory of elasticity. Flattening augments both the attractive and repulsive components of the interaction between particles. This effect is greater in case of large particles and soft materials (Dahneke, 1972). Dahneke derived the following equation for the maximum van der Waals adhesive force between two adjacent particles:

\[ F_{\text{max}} = \frac{Ar}{12a^2} \left( 1 + \frac{A^2f^2}{108a^7r} \right) \]  
(A.1)

\( A \) is the Hamaker constant between the two adjacent species, \( r = x/2 \) represents the radius, \( a \) is the separation when attractive and repulsive forces on the sphere tips just compensate each other, \( f = 2(1-\nu^2)/Y \) is a mechanical property depending on Poisson’s ratio \( \nu \) and Young’s modulus \( Y \). The first term in Eq. A.1 is the adhesive force between two unflattened spheres, the second term is the increase in adhesive force due to flattening of the spheres (Dahneke, 1972). With the parameters \( x = 5.1 \mu m \), \( A = 6.5 \times 10^{-20} \text{ J} \), \( \nu = 0.21 \), \( Y = 6.89 \times 10^4 \text{ N/mm}^2 \) and \( a = 4 \times 10^{-10} \text{ m} \) (in agreement with Dahneke) it follows: \( F_{\text{max}} = 9.04 \times 10^{-8} \text{ N} \). If only the first term of Eq. A.1 is taken into account, the result is: \( F = 8.63 \times 10^{-8} \text{ N} \). Thus flattening leads to an increase of the van der Waals adhesive force by 4.7\%. 

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A.2 Tangent to two circles

The determination of the slope $m_{tang}$ and the axis intercept $\tau_0$ of a straight line which is tangent to two circles I and II can be realized as follows:

1. determination of the root $A(\sigma_A, 0)$ of a straight line connecting any two points of the circles whose connecting lines with the centers of the circles are parallel to each other (Figure A.1). A linear equation through these points yields:

$$\sigma_A = \sigma_M^I - \sigma_R^I \frac{\sigma_{II}^I - \sigma_M^I}{\sigma_R^I - \sigma_R^I}$$  \hspace{1cm} (A.2)

2. calculation of the slope and the axis intercept of a line which goes through point A and is tangent to any of the two circles (here: circle I): Thales’ circle has the diameter $\sigma_M^I - \sigma_A$. Its center is located at $(\sigma_M^I + \sigma_A)/2$. The intercept of Thales’ circle with circle I is point $B(\sigma_B, \tau_B)$ whose connecting line with point A is the tangent to the circles I and II. The equation of Thales’ circle is:

$$\left(\frac{\sigma_M^I - \sigma_A}{2}\right)^2 = \left(\sigma - \left(\frac{\sigma_M^I + \sigma_A}{2}\right)\right)^2 + \tau^2$$  \hspace{1cm} (A.3)

The equation of circle I is:

$$\sigma_R^I = (\sigma - \sigma_M^I)^2 + \tau^2$$  \hspace{1cm} (A.4)

A transformation and equalization of Eq. A.3 and Eq. A.4 yields:

$$\sigma_B = \sigma_M^I - \frac{\sigma_R^I}{\sigma_M^I - \sigma_A}$$  \hspace{1cm} (A.5)
A.2 Tangent to two circles

\[ \tau_B = (\sigma_R^2 - (\sigma_B - \sigma_M^2)^2)^{\frac{1}{2}} \]  \hspace{1cm} (A.6)

Thus the slope and the axis intercept of the tangent to the circles I and II are:

\[ m_{\text{tang.}} = \frac{\tau_B}{\sigma_B - \sigma_A} \]  \hspace{1cm} (A.7)

\[ \tau_0 = \frac{\tau_B \cdot \sigma_A}{\sigma_A - \sigma_B} \]  \hspace{1cm} (A.8)

A.2.1 Tangent to an array of circles with a linear relationship between the center and the radius of the circles

An array of circles is defined by the following relationship between the center of the circle and its radius:

\[ \sigma_R(\sigma_M) = \sin(\rho)\sigma_M + \sin(\rho)\sigma_z \]  \hspace{1cm} (A.9)

\( \sin(\rho) \) and \( \sigma_z \) are constants. A tangent to any two of these circles can be shown with Eq. A.2, Eq. A.5, Eq. A.6, Eq. A.7 and Eq. A.8 to have the slope

\[ m_{\text{tang.}} = \tan(\rho) \]  \hspace{1cm} (A.10)

and the axis intercept

\[ \tau_0 = \tan(\rho)\sigma_z \]  \hspace{1cm} (A.11)

As a consequence, the tangent to the whole array of circles is a straight line with the slope \( m_{\text{tang.}} \) and the axis intercept \( \tau_0 \).
In chapter 4.4.4 measured and modeled yield loci are compared. The following figures constitute a completion of these results and demonstrate that the model presented allows for a calculation of the yield loci of the wet glass beads powders in the pendular state.

Figure A.2: Measured (black) and calculated (grey) Mohr stress circles at steady-state flow of Spheriglass glass beads bound by a 60% and a 70% Nutriose solution ($\phi_m = 82\%$).
Figure A.3: Measured shear points and modeled yield loci (dotted line) of Spheriglass glass beads bound by a 63% Nutriose solution for solid mass fractions of 80% and 84%.
A.4 Particle size distribution of Sikron B 800 after uniaxial compaction

The particle size frequency $q_{3,lg}$ of Sikron B 800 after wet powder preparation in the Duplex kneader and after uniaxial compaction with a pressure of 255 bar was measured (Figure A.4). Within the accuracy of measurement no particle comminution was observed.

Figure A.4: Volume weighted particle size frequency of Sikron B 800 before treatment, after kneading in the Duplex kneader ($\phi_m=75\%$, $\phi_{Nutr.}=63\%$), and after uniaxial compaction.
A.5 Binder viscosity

As only three different binder liquids were used in the framework of this thesis, no systematic investigation on the impact of the binder viscosity on critical pressures can be presented. Nevertheless a few trends could be found (Figure A.5).

The critical pressures of wet Spheriglass powders bound by binders with Nutriose concentrations of 60 %, 63 % and 70 % (\(\eta=0.7\) Pas, 1.4 Pas and 11.3 Pas) are illustrated. Three different ram velocities (0.05 mm/s, 0.2 mm/s and 1 mm/s) and two pre-compaction pressures (16 bar and 255 bar) were applied. The differences between the critical pressures are moderate. At the slowest ram velocity of 0.05 mm/s there is within the commonly observed fluctuations no impact of the binder viscosity on the critical pressure. At the two higher ram velocities, the critical pressures of the materials with the lowest viscosity (0.7 Pas) lies above those with the two higher viscosities. These observations support, that the binder viscosity does not affect shear stresses at small deformation rates. At higher ram velocities, the worse lubricating properties of the low viscous binder might be an explanation for the higher critical pressures. Highly viscous binders feature better lubricating properties because they form thicker films on the particle surfaces.
### A.6 μCT analyses

The air volume fraction and the saturation as a function of the radius for ram velocities of 0.05 mm/s and 1 mm/s are illustrated in Figure A.6.

Figure A.6: Air volume fraction and saturation of a dried extrudate at distances of 1 cm, 4 cm and 7 cm from the extrudate front. μCT measurement (Sepasil B 5/63, $\phi_m=75 \%$, $d_{die}=12 \text{ mm}$, $l_{die}=15 \text{ mm}$, $p_c=32 \text{ bar}$).
A.7 Matlab code for the calculation of stress fields

clear global all

global theta apexdist rho_0

% angle of wall friction:
phi_x=19.758; % /degree

% barrel diameter:
D=20; % /mm

% height of the conical part at the beginning:
x_inlet=5; %/mm

% die diameter:
d_die=12; % /mm

% cone angle according to measurement:
theta=atan((20-d_die)/2/x_inlet)*180/pi; % /degree

% height of the cone including the apex:
x_cone=20/2/tan(theta*pi/180); % /mm

% cone apex:
x_apex=x_cone-x_inlet; % /mm

% height of the cylindrical part (distance between the ram and the
die at the beginning - x_inlet):
x_cyl_0=70.001-x_inlet; % /mm ENTER VALUE ACCORDING TO MEASUREMENT!

% number of volume elements:
n_0=200; % /

% total powder volume at the beginning:
\[V_{\text{total}_0} = \frac{\pi}{4}D^2x_{\text{cyl}_0} + \frac{1}{3}\pi\left(\frac{D}{2}\right)^2x_{\text{cone}} - \frac{1}{3}\pi\left(\frac{d_{\text{die}}}{2}\right)^2x_{\text{apex}}; \quad \text{/mm}^3\]

% volume of one slice element at the beginning:
\[V_{i_0} = V_{\text{total}_0}/n_0; \quad \text{/mm}^3\]

% precompaction pressure:
\[\sigma_v_{\text{start}} = 1000/(\pi/4\times(20\times10^{-3})^2); \quad \text{/Pa}\]

% bulk density at this stress:
\[\rho_0 = \text{density}_82(\sigma_v_{\text{start}}); \quad \text{/g/ccm}\]

% mass of one slice element:
\[m_{i_0} = \rho_0\times V_{i_0}\times 10^{-3}; \quad \text{/g}\]

% lower bound of the first slice (=die inlet):
\[x(1,1) = x_{\text{cone}} - x_{\text{inlet}};\]

% i is the slice number, x an auxiliary variable (0 or 1)
% Initialization:
\[i = 1;\]
\[x = 0;\]

% calculation of the heights \(h(i,1)\) and the lower bounds \(x(i,1)\) of the volume elements
% all \(n_0\) slice elements have the same volume \(V_{0_i}\)
% \(x(i,1)\) is related to the fictitious cone apex:

% distance of the cone apex from the origin (=0 at the beginning):
\[\text{apexdist} = 0;\]

while \(x(i,1) < x_{\text{cyl}_0} + x_{\text{cone}}\)
    if \(x(i,1) < x_{\text{cone}}\)

% \(h(i,1)\) is calculated in such a manner that
\[V_{i_0\_func}(h(i,1), x(i,1)) = V_{i_0}\]
% initial value is 1:
[h(i,1),resnorm,residual,exitflag,iterations] = lsqcurvefit(@V_i_0_func,1,x(i,1),V_i_0);
    x(i+1,1)=x(i,1)+h(i,1);
    i=i+1;
else
% when x(i,1)>x_cone for the first time (x==0): x(i,1) is recalculated
% considering the transition from the cone to the cylinder:
    if x==0
        V_limit=1/3*pi*tan(theta/180*pi)^2*x_cone^3-1/3*pi*tan(theta/180*pi)^2*x(i-1)^3;
    end;
end;
end;
end;

% calculation of the horizontal and wall stresses after precompaction:
sigma_v0=sigma_v_start;
% time step j=1 (t=0s):

j=1;
sigma_v(n_0+1,j)=0;
% all slice elements i:
for i=1:1:n_0
    sigma_v(i,j)=sigma_v_start;
    rho_b(i,j)=rho_0;
end;

% in the cylindrical part the horizontal stress ratio
lambda=sigma_h/digma_v at
% uniaxial compaction is valid as it is assumed that the compaction was made
% slice by slice, wall friction can be neglected % therefore no wall shear stress is existing at j=0:
    if x(i)>=x_cone
        sigma_w(i,j)=lambda(sigma_v(i,j))*sigma_v(i,j);
        sigma_h(i,j)=sigma_w(i,j);
        tau_w(i,j)=0;
    else
    % the factor K follows from a simple consideration of the Mohr stress circle
    % it is used to calculate the wall normal and shear stresses along
    % the cone wall developing during the extrusion % vertical and horizontal stresses are principal stresses:
        K(i,j)=sin(theta*pi/180)^2+lambda(sigma_v(i,j))*cos(theta*pi/180)^2;
        sigma_w(i,j)=K(i,j)*sigma_v(i,j);
        sigma_h(i,j)=lambda(sigma_v(i,j))*sigma_v(i,j);
        tau_w(i,j)=-sigma_v(i,j)*(1-lambda(sigma_v(i,j)))/2*sin(2*theta*pi/180);
    end;
end;

% the system starts to flow
% sigma_v_vorg ist the vertical stress applied by the ram:

% angle of internal friction at steady-state flow (in this version assumed to be constant):
\[ \phi_x^2 = 25.44 \text{ /degree} \]

\[ j = 2; \]
\[ \sigma_v(n_0+1,j) = \sigma_v_{\text{vorg}}(70.001); \] % ENTER VALUE ACCORDING TO MEASUREMENT!
\[ \rho_b(n_0+1,j) = \text{density}_{82}(\sigma_v(n_0+1,j)); \]
\[ x(n_0+1) = x(n_0) \times 2 - x(n_0-1); \]
\[ \text{for } i = n_0 : -1 : 1 \]
\[ \text{if } x(i) \geq x_{\text{cone}} \]

% the horizontal stress ratio is assumed to be constant within one slice element
% from a balance of forces and an integration from the upper bound of an element
% to its lower bound the vertical stress is calculated
% the horizontal stress ratio in the element \( i \) which is a function of the vertical stress
% is assumed to approximately correspond to the vertical stress in the slice
% element \( i+1 \) (alternatively an integration could be made with the Simpson rule
% and the function \( \lambda(\sigma_v) \):

\[ \sigma_v(i,j) = \sigma_v(i+1,j) \times \exp\left( \frac{2}{D/2} \times \tan(\phi_x \times \pi/180) \times \lambda(\sigma_v(i+1,j)) \right) \times (x(i) - x(i+1)) \]
\[ \rho_b(i,j) = \text{density}_{82}(\sigma_v(i,j)); \]
\[ \sigma_w(i,j) = \sigma_v(i,j) \times \lambda(\sigma_v(i,j)); \]
\[ \tau_w(i,j) = \sigma_w(i,j) \times \tan(\phi_x \times \pi/180); \]
\[ \sigma_h(i,j) = \sigma_w(i,j); \]

else

% conical part, the ratio of the horizontal shear stress to the horizontal normal stress close to the wall is equal to the tangens
% of the effective angle of friction (Motzkus' model):

\[ \text{my} \_\text{ie}(i,j) = \tan(\phi_e(\rho_b(i+1,j)) \times \pi/180); \]

% the horizontal stress ratio close to the wall follows from the assumption
% that the Mohr stress circle close to the wall touches the effective
% yield locus (passive plastic stress state) and that the boundary point
% corresponds to the horizontal stress plane
% this follows from experimental observations
% eventually 0.9*\phi_e gives better results:

\[
\lambda_{ie}(i,j) = \frac{1 - \sin(\phi_e(\rho_b(i+1,j))\pi/180)^2}{1 + \sin(\phi_e(\rho_b(i+1,j))\pi/180)^2};
\]

% to have identical vertical stresses close to the wall and at the wall
% the factor K must be identical, too
% as a consequence the shear stresses in horizontal direction are
% the same and the horizontal stress ratio at the wall can be shown to be:

\[
\lambda_e(i,j) = \frac{(\tan(\theta\pi/180) - 1 + \tan(\phi_x2\pi/180)) - \tan(\phi_x2\pi/180) \cdot \lambda_{ie}(i,j) \cdot (1 + \tan(\phi_x2\pi/180)^2 - (\tan(\theta\pi/180) - 1 + \tan(theta\pi/180)^2))^2)}{\tan(\theta\pi/180) - 1 + \tan(theta\pi/180)^2};
\]

% it follows from the equity of the shear stresses close to the wall and at the wall:

\[
\gamma_e = \frac{90 + \phi_x2 - \phi_e(\rho_b(i+1,j)) + \arcsin(\sin(\phi_x2\pi/180)/\sin(\phi_e(\rho_b(i+1,j))\pi/180))*180/\pi}{2};
\]

if \((90-\theta) > \gamma_e\)

\[
K(i,j) = \frac{(1 + \lambda_{ie}(i,j)) \cdot 2 + (\lambda_{ie}(i,j)-1)/2 \cdot \cos(2*\theta\pi/180)+\lambda_{ie}(i,j) \cdot \gamma_e(i,j) \cdot \sin(2*\theta\pi/180)}{\tan(\theta\pi/180)/2};
\]

\[n(i,j) = 2 \cdot \gamma_e(i,j) \cdot \lambda_{ie}(i,j)/\tan(\theta\pi/180/\pi);
\]

\[\lambda_h(i,j) = \lambda_e(i,j);
\]

else

\[
K(i,j) = \frac{(1 + \lambda_{ie}(i,j)) \cdot 2 + (\lambda_{ie}(i,j)-1)/2 \cdot \cos(2*\theta\pi/180)+\lambda_{ie}(i,j) \cdot \gamma_e(i,j) \cdot \sin(2*\theta\pi/180)}{\tan(\theta\pi/180)/2};
\]

\[n(i,j) = 2 \cdot \gamma_e(i,j) \cdot \lambda_{ie}(i,j)/\tan(\theta\pi/180/\pi);
\]

\[\lambda_h(i,j) = \lambda_e(i,j);
\]
n(i,j)=2*my_ie(i,j)*lambda_ie(i,j)/tan(theta*180/pi);
        lambda_h(i,j)=lambda_ie(i,j);
    end;

    % calculation of the vertical stress in the cone resulting from a balance of forces
    % the factor K is assumed to be constant within an element
    % again it is calculated from the bulk density of the element above the considered element
    % instead of the angle of wall friction the angle of internal friction at steady-state flow is used as the material slides along the static wet powder:

        sigma_v(i,j)=sigma_v(i+1,j)*(x(i)/x(i+1))^n(i,j);

        % per definitionem the factor K is the ratio of the wall normal stress and the vertical stress:

        sigma_w(i,j)=K(i,j)*sigma_v(i,j);
        tau_w(i,j)=sigma_w(i,j)*tan(phi_x2*pi/180);
        rho_b(i,j)=density_82(sigma_v(i,j));
        sigma_h(i,j)=lambda_h(i,j)*sigma_v(i,j);
    end;

    % In the following the same calculations are made for j>2
    % after each time step
    % the actual bottom element is removed and the other slices are displaced downwards
    % while maintaining their volume:

    for j=1:1:2
        for i=1:1:n_0
            x_new(i,j)=x(i,1);
            h_new(i,j)=h(i,1);
        end;
        x_new(n_0+1,j)=x(n_0+1,1);
        h_new(n_0+1,j)=h_new(n_0,1);
    end;

    % at j=3 the first slice has left the cone
    % at j=n_0+1 only one slice is left in the cone
for i=1:1:n_0
    masse(i,1:1:3)=m_i_0;
end;
d_die_0=d_die;
x_cone_new=x_cone;
for j=3:1:n_0+1
    x_new(1,j)=x_apex;
    x=0;
% calculation of the heights h(i,1) and the lower bounds x(i,1) of
% the volume elements
% at time step j
% use of the bulk density at the precedent time step:
    for i=1:1:(n_0-(j-2))
        if x_new(i,j)<x_cone_new
            V_i=masse(i+1,j-1)*1e3/rho_b(i+1,j-1);
            [h_new(i,j),resnorm,residual,exitflag,iterations]=lsqcurvefit(@V_i_0_func,1,x_new(i,j),V_i);
            x_new(i+1,j)=x_new(i,j)+h_new(i,j);
        else
            if x==0
                V_limit(1)=1/3*pi*tan(theta/180*pi)^2*(x_cone_new-apexdist)^3-1/3*pi*tan(theta/180*pi)^2*(x_new(i-1,j)-apexdist)^3;
                V_rest(1)=masse(i,j-1)/rho_b(i,j-1)*1e3-V_limit(1);
                h_rest(1)=V_rest(1)/(pi/4*D^2);
                x_new(i,j)=x_cone_new+h_rest(1);
            end;
        end;
    end;
    h_new(i,j)=x_cone_new+h_rest(1);
end;
for i=1:1:n_0     masse(i,1:1:3)=m_i_0; end; d_die_0=d_die; x_cone_new=x_cone;  for j=3:1:n_0+1          ...                 h_new(i,j)=x_new(i+1,j)-x_new(i,j);                     end;         end;     end;
for i=n_0-(j-2)+2:1:n_0
    x_new(i,j)=0;
end;
if x_new(n_0+1-(j-2),j)-x_apex<28.076 % ENTER VALUE ACCORDING TO MEASUREMENT (stop criterion)
    j_ende=j-1;
    break;
end;

% the cone moves upwards (theta=constant)
% the function inlet(distance) describes this relationship based
% on experimental data:

theta_alt=theta;
x_cone_new=x_apex+inlet(x_new(n_0-(j-2),j)+h_new(n_0-(j-2),j)-(x_apex));
apexdist=x_cone_new-x_cone;

% the die diameter virtually changes

d_die=D-2*(D-d_die_0)/2*(x_cone_new-x_apex)/x_inlet;
x=0;
for i=1:1:n_0-(j-2)
    if x_new(i,j)<x_cone_new
        R_frustum=0.5*(d_die+2*tan(theta*pi/180)*(x_new(i+1,j)-(x_apex)));
        r_frustum=0.5*(d_die+2*tan(theta*pi/180)*(x_new(i,j)-(x_apex)));
        vol(i,j)=1/3*pi*(x_new(i+1,j)-x_new(i,j))*(R_frustum^2+R_frustum*r_frustum+r_frustum^2);
        masse(i,j)=rho_b(i+1,j-1)/1000*vol(i,j);
    else
        if x==0
            V_limit(1)=1/3*pi*tan(theta/180*pi)^2*(x_cone_new-apexdist)^3-1/3*pi*tan(theta/180*pi)^2*(x_new(i-1,j)-apexdist)^3;
            V_rest(1)=masse(i,j-1)/rho_b(i,j-1)*1e3-V_limit(1);
            R_frustum=D/2;
            r_frustum=0.5*(d_die+2*tan(theta*pi/180)*(x_new(i-1,j)-(x_apex)));
            vol(i-1,j)=1/3*pi*(x_cone_new-x_new(i-1,j))*(R_frustum^2+R_frustum*r_frustum+r_frustum^2)+V_rest(1);
            masse(i-1,j)=rho_b(i,j-1)/1000*vol(i-1,j);
            masse(i,j)=m_i_0;
x=1;
else
    masse(i,j)=m_i_0;
end;
end;
end;

% the vertical stress on the top slice is:
sigma_v(n_0+1-(j-2),j)=sigma_v_vorg(x_new(n_0+1-(j-2),j)-
x_apex);
rho_b(n_0+1-(j-2),j)=density_82(sigma_v(n_0+1-(j-2),j));

% calculation of the stresses in the cylindrical part:
for i=n_0-(j-2):-1:1
    if x_new(i,j)>=x_cone_new

        sigma_v(i,j)=sigma_v(i+1,j)*exp(2/(D/2)*tan(phi_x*pi/180)*lambda(sigma_v(i+1,j))*(x_new(i,j)-x_new(i+1,j)));
        rho_b(i,j)=density_82(sigma_v(i,j));
        sigma_w(i,j)=sigma_v(i,j)*lambda(sigma_v(i,j));
        tau_w(i,j)=sigma_w(i,j)*tan(phi_x*pi/180);
        sigma_h(i,j)=sigma_w(i,j);
    else

        % calculation of the stresses in the cone:
        my_ie(i,j)=tan(phi_e(rho_b(i+1,j))*pi/180);
        lambda_ie(i,j)=(1-
            sin(phi_e(rho_b(i+1,j))*pi/180)^2)/(1+sin(phi_e(rho_b(i+1,j))*pi/180)^2);
        lambda_e(i,j)=((tan(theta_alt*pi/180)^-1-
            tan(phi_x2*pi/180))-my_ie(i,j)*lambda_ie(i,j)*(1+tan(phi_x2*pi/180)^2-...
\[
\left(\tan(\theta_{alt}\pi/180)^{-1}-1\right)^2 \div \left(\tan(\theta_{alt}\pi/180)^{-1} \tan(\phi_{x2}\pi/180)\right);
\]

\[
\text{my}_e(i,j) = \text{my}_ie(i,j) \times \text{lambda}_ie(i,j) / \text{lambda}_e(i,j);
\]

\[
\gamma_e = (90 + \phi_{x2} - \phi_e(\rho_{b(i+1,j)}) + \arcsin(\sin(\phi_{x2}\pi/180)/\sin(\phi_e(\rho_{b(i+1,j)})\pi/180))) \times 180/\pi / 2;
\]

\[
\text{if} \ (90 - \theta_{alt}) > \gamma_e \\
\text{K}(i,j) = (1 + \text{lambda}_e(i,j)) / 2 + (\text{lambda}_e(i,j) - 1) / 2 \times \cos(2 \times \theta_{alt} \pi/180) + \text{lambda}_e(i,j) \times \text{my}_e(i,j) \times \sin(2 \times \theta_{alt} \pi/180);
\]

\[
\text{n}(i,j) = 2 \times \text{my}_e(i,j) \times \text{lambda}_e(i,j) / \tan(\theta_{alt} \times 180/\pi);
\]

\[
\text{K}_2(i,j) = (1 - \text{lambda}_e(i,j)) / 2 \times \sin(2 \times \theta \pi/180) + \text{my}_e(i,j) \times \text{lambda}_e(i,j) \times \cos(2 \times \theta \pi/180);
\]

\[
\lambda_h(i,j) = \text{lambda}_e(i,j);
\]

\[
\%	ext{ fprintf('sliding fracture! \\
\n');}
\text{else}
\]

\[
\text{K}(i,j) = (1 + \text{lambda}_ie(i,j)) / 2 + (\text{lambda}_ie(i,j) - 1) / 2 \times \cos(2 \times \theta_{alt} \pi/180) + \text{lambda}_ie(i,j) \times \text{my}_ie(i,j) \times \sin(2 \times \theta_{alt} \pi/180);
\]

\[
\text{n}(i,j) = 2 \times \text{my}_ie(i,j) \times \text{lambda}_ie(i,j) / \tan(\theta_{alt} \times 180/\pi);
\]

\[
\text{K}_2(i,j) = (1 - \text{lambda}_ie(i,j)) / 2 \times \sin(2 \times \theta \pi/180) + \text{my}_ie(i,j) \times \text{lambda}_ie(i,j) \times \cos(2 \times \theta \pi/180);
\]

\[
\lambda_h(i,j) = \text{lambda}_ie(i,j);
\]

\[
\%	ext{ fprintf('material failure! \\
\n');}
\text{end};
\]

\[
\sigma_v(i,j) = \sigma_v(i+1,j) \times ((x_{new}(i,j) - \text{apexdist}) / (x_{new}(i+1,j) - \text{apexdist}) \times n(i,j));
\]

\[
\sigma_w(i,j) = K(i,j) \times \sigma_v(i,j);
\]

\[
\tau_w(i,j) = \sigma_v(i,j) \times K_2(i,j);
\]

\[
\rho_b(i,j) = \text{density}_82(\sigma_v(i,j));
\]

\[
\sigma_h(i,j) = \lambda_h(i,j) \times \sigma_v(i,j);
\]

\[
\%	ext{ fprintf('end');}
\]

\[
\%	ext{ for j=3:1:n_0+1}
\]
% end of calculations

for j=2:1:j_ende
    i_9(j)=1;
    i_10(j)=1;
    i_11(j)=1;
    for i=1:1:n_0-(j-2)

    if abs(x_new(i,j)-(x_apex+11.5))<abs(x_new(i_10(j),j)-(x_apex+11.5))
        i_10(j)=i;
    end;
    if abs(x_new(i,j)-(x_apex+10.0))<abs(x_new(i_9(j),j)-(x_apex+10.0))
        i_9(j)=i;
    end;
    if abs(x_new(i,j)-(x_apex+13))<abs(x_new(i_11(j),j)-(x_apex+13))
        i_11(j)=i;
    end;

    x_piston(j)=x_new(n_0-(j-2),j)+h_new(n_0-(j-2),j)-(x_apex);

    if abs(x_new(i_10(j),j)-(x_apex+11.5))<0.3
        sigma_v10(j)=sigma_v(i_10(j),j);
        sigma_w10(j)=sigma_h(i_10(j),j);
        sigma_w9(j)=sigma_h(i_9(j),j);
        sigma_w11(j)=sigma_h(i_11(j),j);
        sigma_w10(j)=1/3*(sigma_w9(j)+sigma_w10(j)+sigma_w11(j));
        tau_w10(j)=tau_w(i_10(j),j);
    else
        sigma_v10(j)=0;
        sigma_w10(j)=0;
        tau_w10(j)=0;
    end;
end;
x_piston(1)=x_new(n_0,1)+h_new(n_0,1)-x_apex;

% plotting:

i=1:1:n_0;

figure(2)
figure1 = figure(2);

j=1:20:j_ende;
% Create axes
axes('Parent',figure1,'FontSize',14,'FontName','times new roman');
box('on');
hold('all');
axis([0 1e7 0 x_piston(1)-(x_apex)]);

% Create plot
plot(sigma_w(i,j), x_new(i,j)-(x_apex),'LineWidth',2,'Color',[0 0 0]);
plot(tau_w(i,j), x_new(i,j)-(x_apex),'LineWidth',2,'Color','blue');
plot(sigma_v(i,j),x_new(i,j)-(x_apex),'LineWidth',2,'Color','red');

xlabel('Stress /Pa','FontWeight','bold','FontSize',14,...
'FontName','Times New Roman');
ylabel('Height /mm','FontWeight','bold','FontSize',14,...
'FontName','Times New Roman');

figure1 = figure(3);
for j=1:1:j_ende
sigma_w10_exp(j)=sigma_w_exp(x_new(n_0-(j-2),j)+h_new(n_0-(j-2),j)-(x_apex));
sigma_v_exp(j)=sigma_v_vorg(x_piston(j));
end;

YMatrix1=[sigma_v_exp; sigma_w10_exp; sigma_w10];
X1=x_piston;

% Create axes
axes1 = axes('Parent',figure1,'FontSize',14,'FontName','Times New Roman');
hold('all');

% Create multiple lines using matrix input to plot
plot1 = plot(X1,YMatrix1,'LineWidth',2);
set(plot1(1),'DisplayName','\sigma_{v,ram} exp');
% function density_82=density_82(sigma_v)
% global rho_0
% density_82=-3.89055+8.5692e-5*(sigma_v*1e-5)+5.87978*(1-exp(-sigma_v*1e-5)/0.897048));
% if density_82<rho_0
%     density_82=rho_0;
% end;
%
% sigma_v in Pa
% density_82 in g/ccm
%
% function inlet=inlet(distance)
% x=[100 80 50 30];
% y=[5 9 12 13];
% inlet=interp1(x,y,distance,'spline');
%
% function lambda=lambda(sigma_v)
% sigma_v=sigma_v/1e5;
% lambda=-0.0862+2.057e-4*sigma_v+0.2091*(1-exp(-sigma_v/2.3919));
% if lambda<0
%     lambda=0;
% function phi_e=phi_e(rho_b)
% % rho_b in g/ccm
% if rho_b>1.9
% phi_e=21.8;
% else
% phi_e=476.03*exp(-1.623*rho_b);
% end;
%
% function sigma_v_vorg=sigma_v_vorg(distance)
% x= [...]
% y= [...]
% sigma_v_vorg=interp1(x,y,distance)*1e5-0/(pi/4*(2.004e-2)^2);
%
% function sigma_w_exp=sigma_w_exp(x)
% x1= [...]
% y= [...]
% sigma_w_exp=interp1(x1,y,x)*1e5;
%
% function V_i_0_func=V_i_0_func(h,x)
% global theta apexdist
% x=x-apexdist;
% V_i_0_func=1/3.*pi.*tan(theta/180.*pi).^2.*(x.^3+2.*x.^2.*h+h.^2.*x+x.^2.*h+2.*x.*h.^2+h.^3-x.^3);
Curriculum Vitae

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Date of birth
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Education
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Research scientist at the Nestlé Research Centre, Lausanne, Switzerland

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Studies of Chemical Engineering, University of Karlsruhe (TH), Germany

1990 - 1999
Gymnasium, Saarbrücken, Germany