FLUID IMMOBILIZATION – A STRUCTURE-RELATED KEY MECHANISM FOR THE VISCOUS FLOW BEHAVIOR OF CONCENTRATED SUSPENSION SYSTEMS

Erich J. Windhab

Swiss Federal Institute of Technology Zürich (ETH), Institute of Food Science (ILW)
Laboratory of Food Process Engineering
Fax: x41.1.6321155
E-mail: windhab@ilw.agrl.ethz.ch

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ABSTRACT
The role of fluid immobilization (FIM) is not only of great importance for solid food systems with respect to their stability, but is also a crucial factor for the rheological behaviour of suspension systems [1]. Besides the fluid binding mechanisms known for porous solids an additional hydro-dynamically induced fluid immobilization (HIFI) is of importance for suspensions in flow. The contribution of the HIFI-mechanism is taken into account by a particle or aggregate shape factor, which for non-spherical or non-cube-like shapes depends additionally on the orientation in the flow field. In many food suspension systems sphere- or cube-like particles with hydrophilic or hydrophobic surface properties build aggregates in the watery and/or fat continuous phases. Such particle aggregates are characterised by different surface and volume FIM-properties. The fluid fraction which is immobilized at the surface \( f_{\text{sif}} \) depends on surface characteristics like fluid adhesion, interfacial tension and roughness. The volume related immobilized fluid fraction \( f_{\text{vif}} \) depends on porosity, pore size distribution or packing density.

ZUSAMMENFASSUNG

RÉSUMÉ
Le rôle de l’immobilisation de fluide (FIM) sur les propriétés de stabilité des systèmes alimentaires à l’état solide est non seulement important, mais aussi, est un facteur crucial sur le comportement rhéologique des suspensions [1]. En plus des mécanismes de fluides liants connus dans le cas des solides poreux, une immobilisation de fluide induite hydrodynamiquement (HIFI) additionnelle tient une place importante dans l’écoulement des suspensions. La contribution du mécanisme HIFI est prise en compte par un facteur de forme de la particule ou de l’agrégat, qui pour des formes non sphériques ou non cubiques, dépend de manière additionnelle de l’orientation dans le champ d’écoulement. Dans beaucoup de suspensions alimentaires, des particules sphériques ou cubiques, avec des surfaces hydrophiles ou hydrophobes, construisent des agrégats dans les phases continues acqueuses ou huileuses. De tels agrégats de particules sont caractérisés par des propriétés FIM de surface et de volume différentes. La fraction de fluide qui est immobilisée à la surface \( f_{\text{sif}} \) dépend des caractéristiques surfaciques telles que l’adhérence de fluide, la tension interfaciale et la topologie. La fraction volumique relative de fluide immobilisé \( f_{\text{vif}} \) dépend de la porosité, de la distribution en taille des pores ou de la densité de remplissage.

KEY WORDS: Suspension, fluid immobilization, rheology-structure relation

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1 INTRODUCTION

In stationary laminar flow fields most suspension systems build particle aggregates of an equilibrium size or size distribution which depends on the shear and normal stresses acting in the flow field. The competition of attractive inter-particle forces and hydrodynamic forces leads in general to a reduced aggregate size at increased shear or elongational rates in related flow fields. However, there can also be a flow-induced build-up of aggregate superstructures [2-4].

As shown in detail for viscous flow properties within the presented work, depending on the ratio of surface- and volume-immobilized fluid fractions, suspensions of solid particles in Newtonian continuous fluids can develop distinct non-Newtonian suspension flow behaviour, including shear thinning and shear thickening flow curve domains (shear rate dependency) as well as thixotropy and rheopexy (shear time dependency). A related rheological fluid immobilization (FiM) model is introduced. This model includes also the kinetics of micro-structural changes like aggregation and deaggregation. Typical food suspension viscosity functions can be simulated with this FiM model. Furthermore, it gives a good estimate for structure-rheology relationships of real food suspension systems, such as chocolates, sauces, protein-based liquid and semisolid foods as well as emulsion-based products, but it is not restricted to food suspension systems.

Fluid movability and migration are key words for food scientists who deal with stability of multiphase food systems. In general, the movability of a fluid phase within the microstructure of a multiphase system mirrors the fluid binding properties of the solid phase. In solid or semisolid porous food systems one can subdivide into four "binding classes", which are chemically bound fluid [5], physically bound fluid in the polymer network and micro capillaries [6], capillary fluid [7] and finally free fluid in coarse capillaries and at the surface [8]. These four fluid binding classes and related mechanisms are taken into account if the movability of liquid components is investigated with respect to stability, adsorption (during wetting), desorption (during drying) and transport phenomena. As soon as the fluid saturation of a porous solid product exceeds 100 percent, the system transfers from a solid or semi-solid into a suspension. From the point of view of water binding or water immobilization respectively, suspensions are commonly treated as another "material category". This means that for suspensions in general, the water binding properties of the solid disperse particles or aggregates are no longer a main aspect considered as important for suspension behaviour. However, this does not reflect reality.

2 FLUID IMMOBILIZATION MECHANISMS IN SUSPENSIONS

As will be shown in this article, fluid binding or immobilization mechanisms can also dominate the rheological characteristics of suspensions. Beside the well-known water binding mechanisms described before, there is one additional mechanism in flows, which is the hydrodynamic fluid immobilization. This mechanism occurs if solid particles or aggregates move within the continuous fluid phase in such a way (e.g. by rotation) that a certain fluid portion $\phi_{\text{hifi}}$ is excluded from contributing to the continuous fluid phase flow. Such fluid is regarded as "dynamically immobilized" at the solid particle or aggregate. If this is the case, the hydrodynamically immobilized fluid fraction has to be regarded as a contribution to the disperse phase, thus increasing the effective solid volume fraction $\phi_{\text{eff}}$.

$$
\phi_{\text{eff}} = \phi_s + \phi_{\text{fr}} + \phi_{\text{hr}} + \phi_{\text{hifi}}
$$

1

In the following, it will be demonstrated that the fluid binding mechanisms denoted before, have such a significant impact on the rheological behaviour of suspension systems, that the related fluid immobilization can be responsible for a strongly developed non-Newtonian suspension flow behaviour, even if the continuous fluid phase itself is a Newtonian fluid. If concentrated suspension systems are processed in a way that the particle size or aggregate size distribution is reduced, like in milling or dispersing apparatus, different changes in the rheological behaviour can be observed. In most cases reduced particle size causes an increase in viscosity. But there are also suspension systems where the opposite effect is found compared in the same applied shear rate range. On the other hand side it is known that concentrated suspensions
behave in general shear-thinning, but also shear-thickening depending on the shear rate or shear stress range in which they are treated. It is obvious that this type of different viscous flow behaviour is closely related to the microstructure of the disperse solid particle phase. A flow process related build-up or destruction of particle structures allows to explain the viscous flow characteristics. For a detailed understanding of particle structuring mechanisms in suspensions flow, beside the flow characteristics the solid particle properties have to be considered as well.

Particle characteristics which are expected to have an impact on the structuring behaviour in shear flows are: particle size, size distribution, size distribution width, shape, particle morphology (surface roughness, porosity, pore size) and interfacial properties between solid particle and surrounding liquid phase (interfacial tension, surface charge, surfactant layer). It is assumed that all particle-particle and particle-fluid interaction properties which influence the structuring behaviour in shear flow have an impact on the degree of continuous fluid phase immobilization within the volume of particle aggregates, \( \phi_{\text{eff}} \) or at their surface, \( \phi_{\text{SIF}} \). In the following it will be demonstrated that changes in fluid immobilization related to particle structuring in shear flow fields are key characteristics for the structure rheology relationships of suspensions.

In the case of structural changes caused by increasing shear stresses or related shear rates leading to a reduction of the immobilized fluid fraction, shear thinning behaviour will be detected. Consequently, the increase of the immobilized fluid fraction will lead to shear thickening (dilatant) shear flow behaviour. If such structural changes are related to time (at constant stresses/shear rates) thixotropic or rheopectic (antithixotropic) behaviour will result.

In the present work for suspensions with sphere- or cube-like particles and particle aggregates two fluid immobilization mechanisms were considered: surface immobilization (SIF) and volume immobilization of fluid (VIF) (see fig. 1). Surface immobilization (SIF) does in principle always exist, whereas in the minimal case only a monolayer of the continuous liquid phase molecules are immobilized at the considered surface. This case will only appear if the particle surfaces are ideally smooth and liquid molecule interaction and liquid viscosity are negligible. Real molecular interactions between solid interfaces and a liquid phase as well as between the molecules of the liquid phase will in general lead to a larger number of liquid molecule layers which can be regarded as immobilized at the particle surface. The (inner) volume immobilization (VIF) is related to particle cavities and pores as well as to inner voids in particle aggregates. Volume immobilization will increase with the inner porosity \( \varepsilon \) of particles or particle aggregates. Depending on the amount of immobilized continuous fluid phase the effective solid volume fraction \( \phi_{\text{eff}} \) can be generally determined by Eq. 1. For spherical or cube-like particles and particle aggregates, \( \phi_{\text{SIF}} \) is assumed to be approximately independent from shear stress or shear rate respectively, because there is no shear induced orientation and resulting structure anisotropy. Depending on the shear stress related structural changes of the solid particle microstructure, e.g. during aggregation and deaggregation the effective volume fraction \( \phi_{\text{eff}} \) will be a function of shear stress \( \tau \) or shear rate \( \gamma \) respectively but also of the shearing time \( t_S \) until a structural equilibrium is reached.

3 SUSPENSION RHEOLOGY

It has been shown in previous work that the shear viscosity dependency from solid volume fraction can be accurately described by an equation of the form

\[
\eta(\phi) = \left[ 1 + \frac{\phi}{\phi_{\text{c,max}}} \right]^{-n_{\text{K-D}}}
\]

Equations found by Krieger-Dougherty [9], Maron & Pierce [10], Eilers [11] and Quemada [12] fit to this form. It has been further shown that the Krieger-Dougherty equation gives the highest degree of freedom in describing the viscosity functions of solid particle suspensions, which are not in an equilibrium structural state. The three
parameters of the Krieger-Dougherty equation which are the solid volume fraction $\phi_v$, the maximum solid packing fraction $\phi_{v,max}$ and the shape factor $k = [\eta]$ (intrinsic viscosity factor) are physically meaningful. Consequently this equation is chosen for implementing the effective volume fraction $\phi_{eff}$. The maximum packing fraction $\phi_{v,max}$ is assumed to be constant for spherical or cube-like particle shapes, and dependent on the degree of orientation for non-isotropic particle shapes like fibres and platelet structures. The shape factor is also assumed to be constant at the value of $[\eta] = 2.5$ if the particles or build-up aggregates are spherical. Aggregation and deaggregation as a structuring mechanism in solid particle suspensions have been investigated in further detail according to the fluid immobilization approach described before. For this structuring mechanism Fig. 1 shows qualitatively the influences of surface parameters and aggregate structure parameters (influencing the volume-related immobilized fluid fraction) depending on the degree of aggregation, deaggregation and aggregate size, respectively.

From Fig. 1 it is obvious that the deaggregation of loose aggregates with large inner void volume (large porosity) will decrease an effective solid volume fraction $\phi_{eff}$ because more immobilized (void entrapped) fluid is removed from the broken voids than will be immobilized by the new surface which is generated. In the opposite case of dense aggregate breakage (deaggregation), the effective solid volume fraction $\phi_{eff}$ will increase due to the large amount of new interface and little entrapped fluid fraction.

Examples are given in Fig. 2, where the shear viscosity functions of model suspensions of silicon oil (AK 1000) with limestone particles (Fig. 2a) or limestone aggregates (Fig. 2b) are compared. For constant solid volume fraction the viscosity functions of non aggregated limestone particles are shifted to larger viscosities with decreasing mean particle size and approximately constant size distribution width ($x_{90,0}/x_{10.0} = 5$) as a consequence of an increased fluid immobilising particle surface (see Eq. 4). In the case of limestone aggregates (Fig. 2a) which have been formed on a roller refiner, the viscosity decreases dramatically if the deaggregation is applied by a high shear treatment within a helical ribbon stirring device. This is due to the release of fluid which had been immobilized in the void volume of the aggregates. Thus aggregate diameter changes during aggregation or deaggregation will determine the effective solid volume fraction and of related viscosity changes. If the aggregate size dependency on shear rate $\dot{\gamma}$ and shearing time $t_s$ is known, the coupling between structural, rheological and flow processing characteristics is possible.

4. A FLUID IMMOBILIZATION MODEL

4.1 BASIC ASSUMPTIONS

If one denotes the changes in surface- and volume-immobilized fluid volume before and after aggregation or deaggregation with $\Delta V_{fi}$ and $\Delta V_{fv}$, the ratio $\psi$ defined according to Eq. 3 characterises the impact of the structural change on the availability of free fluid.

Consequently, $\psi$ determines whether particle aggregation leads to shear-thinning and thixotropy if $\psi > 1$, or to shear-thickening and rheopexy if $\psi < 1$, or reverse in the case of deaggregation.

$$\psi = \frac{\Delta V_{fi}}{\Delta V_{fv}}$$

If $\psi$ is equal to 1, no net change of the available free fluid is caused by the structural change. Tab. 1 shows possible ranges for $\psi$, related structural interpretations and rheological consequences. The latter are given in Tab. 1 for a Newtonian suspension basis fluid. The volume specific particle or aggregate surface $S_P$ is reverse
proportional to the mean diameter $x_{50r}$ if the particles or aggregates are approximately sphere-like

$$S_r = \frac{1}{x_{50r}}$$

Based on the assumption of mono-disperse spherical particles and aggregates, one can derive the expression given by Eq. 5 for the effective solid volume fraction $\phi_{eff}$. $\phi_{eff}$ depends on aggregate packing density $\rho_a$ (or porosity $\epsilon$ respectively) and on surface which are integrally considered by $\psi$, as well as on the mean number of primary particles $n$ forming the aggregates.

$$\phi_{eff} = \phi_i + \frac{1 - \phi_{max}}{\phi_{max}} \left[ 1 + (\psi - 1) \frac{2}{4} n^{-1} \phi_{max} \right]$$

Shear rate $\gamma$ and shear time $t_s$ dependencies are related to a shear rate and/or time-dependent number of primary particles per aggregate $n(\gamma, t_s)$. Experimental studies have been undertaken to investigate the dependency of aggregate sizes and aggregate size distribution from shear rate and shear time.

### 4.2 EXPERIMENTS

Such experiments were carried out with glass sphere model systems having hydrophilic or hydrophobic surfaces suspended in oil- or water-based liquid continuous phases. Furthermore, the applied systems of sugar crystal and limestone aggregates suspended in oils were investigated. In particular for the latter two systems a measuring routine based on laser diffraction spectroscopy was worked out allowing for measuring aggregate size distributions after various aggregation/deaggregation treatment.

The mechanical shear treatment was done under various apparent shear rate conditions with helical ribbon mixing or $\sigma$-kneading geometries. These experimental set-ups allowed to satisfy the continuum boundary condition much better than a rheometric shear gap geometry. In the latter wall slipage, which is related to partial demixing at the gap walls, had a strong impact on the shear stress acting on the particle aggregates. The helical ribbon stirrer was used within a concentric cylinder rheometer system (Rheometric Scientific: DSR (stress controlled) or ARES (deformation controlled)) what allowed direct measurement of the rotational velocity and the applied shear stress during stirring.

If aggregates were shear treated, e.g. in a silicon oil (AK 1000) as continuous fluid phase, emulsifiers (e.g. lecithin) were added in order to avoid re-aggregation after the shear treatment. During deaggregation the new interface is rapidly covered by the emulsifier molecules. Fig. 3 shows sugar aggregates in diluted silicon oil suspensions ($\phi_s = 0.1$) before and after gentle shear.
treatment ($\dot{\gamma} = 10 \, 1/s$) in a Petri dish.

It is not possible to measure aggregate formation and size of concentrated suspension systems within shear flow fields directly. Consequently, the preparation procedure for particle aggregates after shear treatment in order to measure their size distribution by laser diffraction spectroscopy has to guarantee that the aggregate size is not significantly influenced. Otherwise only artefacts were investigated.

For the rather dense and mechanically stable sugar aggregates which were been built-up before in the gaps between rollers of a roller refiner, this presumption could be satisfyingly fulfilled. Fig. 4 shows primary particle and aggregate size distributions measured by laser diffraction spectroscopy before and after intensive concentrated suspension ($\phi_s = 0.65$) shear treatment in a kneading device (model conche, Brabender) with narrow shear gaps ($= 2 \, \text{mm}$). From such aggregate size distribution measurements before and after shear treatment, typical curves for shear rate and time dependency of the sugar aggregate mean diameter have been roughly approximated as qualitatively shown in Fig. 5. A related calculation was carried out with Eq. 6.

### 4.3 SHEAR RATE AND TIME DEPENDENCIES

The shear rate dependency of the aggregate mean diameter as demonstrated in Fig. 5 (top) allows to assume, that a certain shear rate/shear stress has to be exceeded in order to initiate deaggregation. This gets more and more efficient with increasing shear rate/shear rate and finally at high shear rates reaches an approximately constant aggregate size or a single particle level in the case of total deaggregation. If a simple superposition of aggregation and deaggregation kinetics (Eq. 7) with a shear rate- or shear stress-related dynamic equilibrium structure state is assumed, the shear rate dependency can be described by Eqs. 7 and 8.

$$\frac{dn}{dt} = k_a (n_\infty - n) - k_d (n - n_\infty)$$

$$n_{eq} = \frac{n_\infty + n - k_d}{1 + \frac{k_d}{k_a}}$$

$$k_{a,d} = k_{a,d} (\gamma) \left[ 1 + (t_\infty \dot{\gamma})^{\alpha \times \delta} \right]$$

The related time dependency at constant shear rate $\dot{\gamma}$ is described by Eq. 9

$$n(\dot{\gamma}, t) = \frac{k_a + k_d \exp \left( - (k_a + k_d) t \right)}{k_a + k_d}$$

For the example of concentrated sugar/oil suspensions as confirmed experimentally, a first order deaggregation kinetics can be assumed in the presence of lecithin emulsifier (negligible re-aggregation), thus leading to the exponential aggregate size decrease with shear time shown in Fig. 5 (bottom).

Ongoing research work is dealing with the experimental determination of the kinetic constants $k_a$ and $k_d$. For approximation of the shear

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**Figure 4:** Sugar aggregate size distributions from concentrated sugar silicon oil (AK 1000) suspensions (shear treated in a Brabender $s$-kneeder ($\phi_s \approx 0.65, \dot{\gamma} = 120 \, 1/s, 25^\circ \text{C}$) presence of lecithin emulsifier, [13]).

**Figure 5:** Dependencies of aggregate size from shear rate and shear time approximated from measurements and qualitatively described with a kinetic model for aggregation/deaggregation.

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rate and time dependencies the following Eqs. 10 and 11 were also found to give satisfying results

\[ n(\dot{\gamma}, t) = n_0 \left( 1 + C_1 C_2 (\dot{\gamma}/\gamma_0)^a \right) \left( 1 - n C_1 C_2 (\dot{\gamma}/\gamma_0)^a \right)^n \]

\[ n(\dot{\gamma}, t) = n_0 + (1 - \exp(C_1 C_2 (\dot{\gamma}/\gamma_0)^a)) (n(\dot{\gamma}, t) - n_0) \]

Eqs. 10 and 11 assume that increasing shear rate or shear stress respectively as well as increasing shear time under constant shear rate/shear stress conditions will decrease the aggregate size. For \( \psi < 1 \) this represents shear thinning and tixotropic suspensions. Shear thickening or rheopectic flow behaviour occurs if \( \psi > 1 \). In case of the reverse structuring mechanism which means increasing particle aggregate size with increasing shear rate/shear stress and shear time, only the constants \( C_1, C_2 \) and the system parameters \( n_0, n_1 \) and \( n(\dot{\gamma}, t) \) will change.

### 4.4 CALCULATED RHEOLOGICAL FUNCTIONS (FIM)

From Eqs. 8, 9 or 11, the coupled dependency of the solid particle aggregate size on shear stress/shear rate and time \( n(\dot{\gamma}, t) \) can be derived and implemented into Eq. 5. Coupling Eq. 5 with Eq. 2 leads to Eq. 12 for the shear viscosity calculation as shown below.

\[ \eta(\phi, \gamma, t) = \eta_0 \left( 1 - \frac{\varphi_{\text{vol}}(\phi, \gamma, t) - \eta_0}{\varphi_{\text{vol}, \text{max}}(\phi, \gamma, t)} \right) \]

The additional parameter \( \delta \) in Eq. 12 denotes a degree of orientation in the case non-spherical or non cube-like particle shapes (e.g. needles, fibres, platelets). In such a case \( \varphi_{\text{vol}, \text{max}} \) depends also on \( \delta, \gamma \) and \( t \). Based on Eq. 7 calculations for various parameter sets were carried out as demonstrated in Figs. 6-9. In Figs. 6-8 the main dependencies of the viscosity function from shear rate/shear stress, solid volume fraction \( \varphi \) and shear time \( t \) are demonstrated. Figure 9 shows the influence of the surface to volume immobilization ratio \( \psi \).

### 5 HIGH SHEAR INDUCED STRUCTURERS

Whether increasing shear rates or shear stresses respectively will lead to a decrease or increase in aggregate size, depends on the competition of hydrodynamic forces acting on aggregates in shear flows, and forces interacting between the particles like attractive Van der Waals forces, repulsive electrostatic forces and/or hydrophilic/hydrophobic interactions. For the sugar/limestone-silicon oil suspensions investigated, the hydrophilic particles build up large aggregates in the state of rest due to attractive hydrophilic and Van der Waals forces. In the sur-
rounding hydrophobic fluid (oil) such aggregates are reduced in size at increasing shear rates and shear stresses respectively, as well as with shear time under constant shear stress/shear rate conditions. Within suspensions of hydrophilic particles in a hydrophobic fluid no reaggregation phenomena during increasing shear rates or shear stresses, and thus no dilatant or rheopectic behaviour was found. For the case of hydrophilic particles within a hydrophilic fluid like native starch particles in corn syrup/water systems which were investigated as well, shear thinning behaviour is observed in the low shear rate range. A short upper Newtonian viscosity plateau was followed by a clearly pronounced shear thickening shear stress/shear rate domain (Fig. 10). It can be assumed that between hydrophilic starch particles there is some attractive interaction which forms loose aggregates in the state of rest, which are dispersed at increasing shear stresses/rates thus generating shear-thinning and thixotropic flow properties.

For the particle-aggregate suspensions, like the limestone/silicon oil system as well as the starch/glucose syrup suspensions investigated, there are immobilization ratios $\psi < 1$ leading to shear thinning and thixotropic behaviour in the case of deaggregation and reverse (shear thickening and rheopectic) for aggregation (shown for the starch/glucose syrup system).

In these cases the aggregates contain voids in which a certain amount of fluid is immobilized (entrapped), and the surface immobilization does not compensate the void volume effect. An example demonstrating also the influence of immobilization ratios $\psi > 1$ is limestone /silicon oil suspensions with refined particles of different mean size and approximately constant particle size distribution width. As demonstrated in Fig. 2b, the mean particle size reduction leads to an increased shear viscosity at constant volume fraction ($\phi = 0.3$) even at very high shear rates ($\dot{\gamma} \approx 1000 \, \text{s}^{-1}$), where all aggregates are dispersed. In the low shear rate range deaggregation has an additional non-negligible impact on the flow behaviour. In the case of $\psi = 1$ and Newtonian suspension fluid phase behaviour, the suspension had to behave also like a Newtonian fluid.

Figure 8 (left): Calculated shear time dependency of viscosity functions from FIM model.

Figure 9: Calculated viscosity functions for various immobilization ratio $\psi$ from FIM model.

Figure 10: Measured viscosity functions for starch particle/glucose syrup suspensions with dilatant shear flow behavior (25°C, [15]).
6 STRUCTURE VISCOSITY FUNCTIONS

Consequently structure viscosity functions ("virtual" viscosity function for non-changing suspension structure) have to be iso-viscosity lines. As shown in Fig. 11 such structure viscosity functions cross the equilibrium viscosity function [15].

In the crossing points the suspension structure is in an equilibrium (equilibrium aggregate size distribution) at the related shear rates. If shear rate steps from \( \dot{\gamma}_1 \) to \( \dot{\gamma}_2 \) are executed after structure equilibrium at \( \dot{\gamma}_1 \), the related equilibrium structure \( \Theta_{\dot{\gamma}_1} \) is still existing right after the shear rate step is carried out, but then develops towards the new equilibrium structure \( \Theta_{\dot{\gamma}_2} \). If \( \dot{\gamma}_1 > \dot{\gamma}_2 \) and particle aggregates are dispersed at increased shear rates, then the equilibrium structure development at \( \dot{\gamma}_2 \) will generate rheopctic behaviour for \( \psi < 1 \) (see Fig. 11) or thixotropic behaviour for \( \psi > 1 \) (see Fig. 12). The reverse relationships will be found if larger aggregates are built at increasing shear rates.

7 FLUID IMMOBILIZATION BY HYDRODYNAMICS

As already shown up in the discussion of main contributions of fluid immobilization (see Eq. 2) a hydrodynamically induced immobilized fluid fraction, \( \phi_{\text{hifi}} \), effects the efficient solids fraction, \( \phi_{\text{eff}} \), as well. \( \phi_{\text{hifi}} \) is assumed to be small for a single spherical particle in uniaxial shear or elongational flow fields, but increases strongly for non-spherical particles or aggregates.

In the case of fibre- or plate-like disperse structures, there is an enhanced dependency on orientation in the flow field. This is demonstrated in Fig. 13 for a fibre, rotating in a uniaxial shear flow field and \( \phi_{\text{hifi}} \) will be a periodic function of time. The frequency of the rotation can be calculated from the shear rate and the fibre length/diameter ratio \( l/d \). The minima in \( \phi_{\text{hifi}} \) correspond to fibre orientation in flow direction. Accordingly, the maxima stand for fibre orientation in gradient direction. In the case of concentrated suspensions of fibres or other non-spherical particles and aggregate structures, a free rotation is no longer possible. In shear flow fields such structuring units will orient in plains parallel to the flow direction and keep this orientation, if the flow field does not change. The resulting shear rate and time dependencies of viscosity functions for concentrated fibre systems mirror the fibre orientation dynamics and related changes in \( \phi_{\text{hifi}} \) (Figs. 14 and 15). For suspension systems with particles or aggregates with large dimensions into one or two axis directions (e.g. fibres, platelets) the effective volume fraction \( \phi_{\text{eff}} \) and the maximum packing fraction \( \phi_{\text{v,max}} \) will depend on the orientation state of such structuring units. This is already considered in Eq. 7 by the orientation factor \( \delta \).
For the sugar/oil suspension system investigated, an initial solid mean particle size of $x_{50,0} = 3 \text{mm}$ was measured. From such particles and silicon oil aggregates with a mean diameter of $x_{50,0} = 52 \text{mm}$ were formed using a 3-roller mill. With these aggregates a concentrated suspension was mixed ($f_S = 0.3$) which was subsequently sheared in a kneader.

In the most strongly shear treated state of these aggregates (representative shear rate $\gamma_r \approx 100 \text{s}^{-1}$) an aggregate mean diameter of 30 microns was detected (see Fig. 4). Knowing the primary particle mean diameter one can estimate the number of primary particles forming an aggregate, which leads to about 5000 primary particles per aggregate for the non-sheared aggregates and about 1000 primary particles for the strongly dispersed final state. It was shown that the related measured viscosity functions are in good agreement with calculated curves (FIM model, Eq. 7) from the same model data sets, just varying the aggregate size according to the measured values (Fig. 16). These results confirm that the rheological behaviour of concentrated suspension systems can be related to the immobilization of a certain fluid fraction, which is shear rate/shear stress and time dependent and reflects related changes in the disperse structure properties. The shear rate and time dependent aggregate size provides further information on the aggregation and deaggregation kinetics within investigated shear flow fields. Structure flow functions allow for defining microstructure-rheology relation-ships which do explain the shear rate/shear stress, time and solid volume fraction dependencies of measured viscosity functions for real suspension systems.

In future work experiments will be set up in order to evaluate the relevance of the introduced fluid immobilization model (FIM) for various structural characteristics of particles and aggregates like their surfaces, shapes and inner morphology. Furthermore the influence of the type of flow on the fluid immobilization characteristics are of particular interest, with special regard of elongational and mixed shear-/elengational flow fields in processing unit operations.
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