Rheology of concentrated coagulating suspensions in non-aqueous media

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Abstract: The rheology of concentrated coagulating suspensions is analysed on the basis of the following model: (i) at low shear rates, the shear is not distributed homogeneously but limited to certain shear planes; (ii) the energy dissipation during steady flow is due primarily to the overcoming of viscous drag by the suspended particles during motion caused by encounters of particles in the shear planes. This model is called the "giant floc" model.

With increasing shear rate the distance between successive shear planes diminishes, approaching the suspended particles' diameter at average shear stresses of 88–117 Pa in suspensions of 78 μm particles (glass ballotini coated by a hydrophobic layer) in glycerol–water mixtures, at solid volume fractions between 0.35 and 0.40. Smaller particles form a more persistent coagulation structure. The average force necessary to separate two touching 78 μm particles is too large to be accounted for by London-van der Waals forces; thus coagulation is attributed to bridging connections between polymer chains protruding from the hydrophobic coatings.

The frictional ratio of the glass particles in these suspensions is of the order of 10. Coagulation leads to build-up of larger structural units at lower shear rates; on doubling the shear rate the average distance between the shear planes decreases by a factor of 0.81 to 0.88.

Key words: Suspension, coagulation, giant floc model, shear plane, glass sphere

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>inter-shear plane distance</td>
</tr>
<tr>
<td>A'</td>
<td>Hamaker constant</td>
</tr>
<tr>
<td>b</td>
<td>radius of primary particles</td>
</tr>
<tr>
<td>f</td>
<td>frictional ratio</td>
</tr>
<tr>
<td>F_A</td>
<td>attractive force between two particles</td>
</tr>
<tr>
<td>g</td>
<td>acceleration due to gravity</td>
</tr>
<tr>
<td>H</td>
<td>distance between the surfaces of two particles</td>
</tr>
<tr>
<td>K</td>
<td>proportionality constant in power law</td>
</tr>
<tr>
<td>l</td>
<td>fraction of distance by which a moving particle entrains its neighbours</td>
</tr>
<tr>
<td>l'</td>
<td>effective length of inner cylinder in the rheometer</td>
</tr>
<tr>
<td>M</td>
<td>torque experienced by inner cylinder during measurements</td>
</tr>
<tr>
<td>n</td>
<td>exponent in power law</td>
</tr>
<tr>
<td>n0, n1, n2</td>
<td>constants in extended power law</td>
</tr>
<tr>
<td>NC_hex</td>
<td>number of contacts, per mm², between particles in adjacent layers with an average degree of occupation, assuming a hexagonal arrangement of the particles within the layers</td>
</tr>
<tr>
<td>NC_cub</td>
<td>as NC_hex, but with a cubical arrangement</td>
</tr>
<tr>
<td>p(τ)dt</td>
<td>increase of slippage probability when the shear stress increases from τ to τ + dt</td>
</tr>
<tr>
<td>q</td>
<td>average coordination number of a particle in a coagulate</td>
</tr>
<tr>
<td>R_i</td>
<td>radius of inner cylinder of rheometer</td>
</tr>
<tr>
<td>R_o</td>
<td>radius of outer cylinder of rheometer</td>
</tr>
<tr>
<td>t_i</td>
<td>time during which particle i moves</td>
</tr>
<tr>
<td>t_0</td>
<td>time during which a particle bordering a shear plane moves from its rectilinear course, on meeting another particle</td>
</tr>
<tr>
<td>u</td>
<td>angle between the direction of motion, and the line connecting the centers of two successive particles bordering a shear plane</td>
</tr>
<tr>
<td>y_0, z_0</td>
<td>y, z value of a particle meeting another particle, when both are far removed from each other</td>
</tr>
<tr>
<td>y_0, z_0</td>
<td>spread in y_0 values</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>-2/n</td>
</tr>
<tr>
<td>z_0</td>
<td>capture efficiency</td>
</tr>
<tr>
<td>(\dot{\gamma})</td>
<td>shear rate</td>
</tr>
<tr>
<td>(\dot{\gamma}_{\text{ave}})</td>
<td>average shear rate calculated for a Newtonian liquid</td>
</tr>
<tr>
<td>(\delta_i)</td>
<td>distance by which a particle bordering a shear plane moves from its rectilinear course, when it encounters another particle</td>
</tr>
<tr>
<td>(\delta_0)</td>
<td>distance by which a particle bordering a shear plane moves from its rectilinear course, when it encounters another particle</td>
</tr>
<tr>
<td>(A)</td>
<td>square root of area occupied by a particle bordering a shear plane, in this plane</td>
</tr>
<tr>
<td>(\varepsilon_c)</td>
<td>energy dissipated during one encounter of two particles bordering a shear plane</td>
</tr>
<tr>
<td>(\varepsilon_p)</td>
<td>energy dissipated by one particle</td>
</tr>
</tbody>
</table>
1. Introduction

The rheological properties of concentrated coagulating suspensions are interesting from both a practical and a theoretical point of view. An example of practical interest is the blockage of flow by coagulation, and its prevention or enhancement. A theoretical aspect is that rheology is one of the few methods for learning something about particle arrangement and interaction in concentrated suspensions.

In recent years, Hunter and coworkers (see e.g. [1–6]) have developed the “elastic floc” model for analysing the energy dissipation during steady flow in dilute suspensions, where separate flocs can be discerned. The starting point of this model is that the energy dissipation related to the flow is caused predominantly by the viscous drag experienced by particles moving within flocs, and by the internal movement of liquid within the flocs when they change their volume or shape. Compared to these effects, the energy dissipation through formation and subsequent breaking of bonds between the suspended particles, and the elastic energy required to stretch bonds between primary particles are of minor importance.

The present authors regard the elastic floc model as a major advance in the rheology of suspensions. Its basic idea seems to be sound, although some assumptions need verification. We mention the following:

1) The solid volume fractions within the flocs is an important parameter in the calculations. It has been determined by Hunter from the effective solid volume fraction in the Dougherty-Krieger relation [7]:

\[
\eta_{PL} = \eta_0 (1 - \eta_{eff}/\varphi_{max})^{[\eta]/\varphi_{max}}
\]

where \(\eta_{PL}\) is \([\lim (\tau/\gamma)]_{\gamma \to \infty}\), \(\tau\) the shear stress, \(\gamma\) the shear rate, \(\varphi_{max}\) the effective maximum solid volume fraction permitting flow and \([\eta]\) the intrinsic viscosity. Hunter used \([\eta] = 2.5\) and \(\varphi_{max} = 0.60\). It should be noted that this rest on the assumption that an increase in solid volume fraction \(d\varphi\) results in an increase in viscosity \(d\eta_{PL} = 2.5 \eta_{PL} d\varphi/(1 - \varphi/\varphi_{max})\). Especially for suspensions with non-Newtonian rheological behaviour (as is usual in coagulating suspensions) this assumption is open to doubt [8, 9]. In addition, the general validity of \(\varphi_{max} = 0.60\) for suspensions with aggregates of different sizes must be doubted as well.

2) Distinguishing between the energy needed for motion of suspended particles in the flocs and the energy needed for moving the liquid between the particles in the flocs is not logical. Thus, the work necessary for moving a single spherical particle through an infinite liquid as calculated from the Stokes equation includes the work for displacing part of the liquid.

3) Hunter sets both \(\zeta_0\) (the capture efficiency for coagulation by shear) and the frictional ratio \(f\) (the ratio of the friction experienced by a particle in the suspension to that experienced by an isolated particle) equal to 1. For irregularly shaped particles, the former is one to two orders of magnitude too high [10, 11], whereas the latter seems to be rather low.

In view of these uncertainties a model was developed in our laboratory for treating the rheology of coagulating suspensions [12, 13] in which the number of assumptions involved was reduced. In order to avoid the use of the Dougherty-Krieger relation, we restrict ourselves to suspensions of such high concentrations that separation of discrete flocs is not observed. Use of the overall solid volume fraction for describing the surroundings of a particle then introduces a negligible error. When such a “giant floc” is subjected to a shear stress, the shear will not develop homogeneously at low stresses; the shear will occur in preferential shear planes only. In the model, these shear planes are idealised as flat planes parallel to the direction of flow (figure 1), with an average separation of \(\Lambda\). A shear plane separates two domains in which a given particle remains surrounded essentially by the same neighbours. A suspended particle bordering a shear plane occupies, on the average, an area \(\Lambda^2\) in this plane; this area is shaded in figure 1.

When shear occurs in a shear plane, a particle bordering this plane meets particles from the adjacent domain. In the direction of motion, two such particles approaching each other are separated on the average by a distance \(\Lambda \cos u\) (where \(u\) is the angle between the direction of motion and the line connecting the centers of the two particles). When such a collision is imminent,
the particles involved are forced out of their way over a certain distance $\delta_0$. Because of hydrodynamic interaction the particles do not really collide in most cases; nevertheless the process is here termed a “collision”. In the model, the distance $\delta_0$ is more important than whether or not a real collision occurs. Thus the present model is insensitive towards the value of the capture efficiency $\alpha_0$.

Since the colliding particles are bound to $q - 1$ neighbours in their own domains (where $q$ is the average number of neighbours of a particle within a domain), they entrain these neighbours each over a distance $\delta_0 l$ (with $0 < l < 1$). These neighbours entrain their $q - 1$ other neighbours over a distance $\delta_0 l^2$ etc.

The energy dissipated by a particle moving over a distance $\delta_0$ in time $t_i$ is given by

$$\varepsilon_p = \text{force} \cdot \text{distance} = 6 \pi \eta_0 b f(\delta_0/t_i) \cdot \delta_0$$

(2)

where $b$ is the particle radius, $\eta_0$ the viscosity of dispersing medium, and $f$ the frictional ratio.

Thus, one collision is accompanied by an energy dissipation:

$$\varepsilon_c = 2 \cdot 6 \pi \eta_0 b f(\delta_0/t_0 + (q - 1) l^2 \delta_0^2/t_0$$

$$+ (q - 1)^2 l^4 \delta_0^2/t_0 + \ldots)$$

$$= 12 \pi \eta_0 b f(\delta_0^2/t_0) \frac{1}{1 - (q - 1) l^2}.$$

(3)

Here use is made of the fact that the time during which the particles move is equal to $t_0$ for all particles entrained during one collision.

The energy dissipated per unit volume and time is then obtained by multiplying $\varepsilon_c$ by the number of particles in shear planes per unit volume ($= 2/(A d^2)$) divided by 2 (because we counted two particles in adjacent planes in relation (3)), and divided by the time between two successive collisions ($d \cos \bar{u}/(\dot{\gamma} A)$). In addition, $t_0 = \delta_0/(\dot{\gamma} A \cos \bar{u})$. We then obtain:

$$\dot{\varepsilon} = 12 \pi \eta_0 b \frac{\delta_0 A}{\dot{\gamma} A} \frac{f}{A} \frac{1}{1 - (q - 1) l^2}.$$

(4)

This would correspond with Newtonian behaviour if all parameters were independent of $\dot{\gamma}$. However, especially $A$ is expected to decrease with increasing shear rate and shear stress: a region able to withstand a small shear stress may break down on application of a larger one. Thus, at low $\dot{\gamma}$ values not all potential shear planes are operational.

In a previous paper [12], a preliminary version of this model was applied to suspensions of Ca(OH)$_2$ in water. In the present paper, the model is applied to systems better conforming with its basic concepts: suspensions of spherical particles with a narrow size distribution. Comparison with experimental data will then give information on the parameters of the model.

Coagulation was effected by using a suspension of particles coated by a non-polar layer [10, 14] in a polar liquid (glycerol-water mixture). In such suspensions absence of sedimentation is observed for solid volume fractions $\varphi \geq 0.350$.

2. Experimental

2.1 Materials

The suspended particles were glass ballotini (Tamsman, Zoetermeer). The original sample was divided into fractions by sedimentation. Coating by a hydrophobic layer was achieved by treatment with a solution of dimethyl-dichlorosilane in hexane [10, 14]. Three coated samples were used; their characteristics are shown in table 1. For comparison, some data for sample III before the coating application are mentioned in sec-
Table 1. Characteristics of glass samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass average particle diameter $\phi_{\text{avg}}/\mu m$</td>
<td>28.32</td>
<td>52.56</td>
<td>78.32</td>
</tr>
<tr>
<td>Number average particle diameter $\phi_{\text{n}}/\mu m$</td>
<td>26.64</td>
<td>48.71</td>
<td>75.38</td>
</tr>
<tr>
<td>Ratio $\phi_{\text{avg}}/\phi_{\text{n}}$</td>
<td>1.063</td>
<td>1.079</td>
<td>1.039</td>
</tr>
<tr>
<td>Thickness of polymer layer/nm</td>
<td>1.0</td>
<td>3.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Specific mass</td>
<td>2.69</td>
<td>2.83</td>
<td>2.84</td>
</tr>
</tbody>
</table>

2.2 Apparatus

A Contraves Rheomat 15 was used with measuring system C, a Couette geometry with rotating inner cylinder: radius of inner cylinder $R_i = 6.77$ mm; radius of outer cylinder $R_o = 10.00$ mm; effective length 46.2 mm.

The largest centrifugal acceleration used was $0.933g$, where $g$ is the acceleration due to gravity. Torques which can be measured vary between $3.56 \cdot 10^{-4}$ and $3.56 \cdot 10^{-3}$ N.m.

2.3 Procedure

Pastes were prepared on a mass basis. After thorough homogenisation by hand with a spatula, a mechanical homogenisation step was applied in order to break down agglomerates. This step consisted of stirring for 2 minutes at a stirring speed of 3,500 rpm in a 100 ml glass vessel of 43 mm internal diameter. The stirrer's head had dimensions $27 \times 11 \times 1$ mm$^3$ and made an angle of about $30^\circ$ with the horizontal plane.

After homogenisation the sample was introduced as fast as possible into the rheometer, and measurements were started immediately. A series of measurements performed on one sample consisted of 3–4 angular velocity scans. Each scan started at the highest angular velocity permitting torque measurement. Then the angular velocity was decreased stepwise to the lowest angular velocity permitting torque measurement (10% of the total torque scale). Then the angular velocity was increased again. The parts of a scan with decreasing and increasing $\dot{\gamma}$ are indicated as “initial” and “later” parts, respectively. The high limit of the angular velocity usually was $36.8$ rad $\cdot$ s$^{-1}$ (in some cases $27.9$ rad $\cdot$ s$^{-1}$); the low limit varied between 0.79 and $3.5$ rad $\cdot$ s$^{-1}$. Generally nine to ten different angular velocities were covered in a scan. Between successive scans, the suspension was homogenized by hand. Each scan took less than one minute to complete.

Measurements were performed at $293.2 \pm 0.2$ K. No sedimentation was observed during the measurements or within a few days afterwards; neither was any air introduction observed.

A check was made for the occurrence of wall slippage with similar but non-coagulating suspensions (uncoated glass in glycerol-water mixtures) according to the Rautenbach-Schlegel method [15]. No wall slippage was found.

3. Results

Figure 2a shows a typical scan of apparent relative viscosity $(\tau/\eta N \eta_0)$ versus apparent shear rate $\dot{\gamma}_N$, i.e. the average shear rate as calculated for a Newtonian liquid.

In all cases, at a given angular velocity of the inner cylinder, a larger apparent viscosity was measured in the initial part of a scan (with decreasing $\dot{\gamma}$) than in the later part of a scan (with $\dot{\gamma}$ increasing). This effect was, however, nearly absent in suspensions with 78 gm particles, especially at $\dot{\gamma} = 0.350$. Thus, sedimentation and/or centrifugal separation of the suspended particles cannot be held responsible for this effect. Neither is the effect consistent with a progressive breakdown of a coagulation structure during a scan. It is true that during the initial part of a scan a coagulation structure builds up which is destroyed again on increasing $\dot{\gamma}$ during the later part of the scan. But any hysteresis in this respect should lead to higher apparent viscosities at a given angular velocity of the inner cylinder, during the later part of a scan. The effect is ascribed to alignment of shear planes (see Discussion).

The apparent viscosity increases with decreasing $\dot{\gamma}$, indicating shear thinning behaviour. Average shear rates were then calculated by treating the suspension as
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20

20

40

80

40

80

0.350

0.375

0.400

0.425

Φ/µm

0.350

0.375

0.400

0.425

0.756

0.756

0.770

0.760

0.720

0.694

0.636

0.644

0.794

0.779

0.789

0.789

0.792

0.772

0.762

0.779

Table 2. Constant n for power-law description of data

(τ = Kγ^n)

γ vs. M (S⁻¹)

γ = (R₂⁻ - R₁⁻) (R₂₀ - R₁₀) Ωj

with ζ = -2/n.

The data, though represented well enough by relation (5) for calculating an average shear rate, showed systematic deviations from this relation necessitating representation by an extended power law:

log M = n₀ + n₁ log Ωj + n₂ (log Ωj)²

for calculating d log η_app/d log γ (see Discussion). For calculating γ, relation (5) was considered accurate enough, since the influence of n on the calculated γ values, though perceptible, was only a second-order effect.

4. Discussion

4.1 General remarks

One remarkable feature of the data is that the apparent viscosities, at a given angular velocity of the inner cylinder, are lower on going from low to high γ values than in the reverse direction. Since sedimentation and centrifugal separation of suspended particles, and hysteresis in the building-up and breakdown of a coagulation structure can be excluded, as mentioned above, we interpret this effect as an alignment of shear planes during a scan.

No disorder arises on reducing γ because of Brownian motion: the time necessary for a particle to diffuse over a distance equal to its own radius, in the pure dis-
persion medium is much longer (270–5,700 hours) than the time covered by a scan (± 1 min). Thus, alignment of shear planes progressively builds up during a scan. In the following, therefore, data obtained during the later part of a scan (with $\gamma$ increasing) are used in the calculations, as corresponding better with the assumptions of the “giant floc” model.

4.2 Analysis of behaviour at high shear rates

In the giant floc model, shear thinning in coagulating suspensions is ascribed predominantly to a decrease of the inter-shear plane separation $A$ (relation (4)), because regions able to withstand a small shear stress may break down on application of a larger one. It appears from figure 2b that at the highest shear stresses realized in the present work the apparent viscosity has not yet become constant. This is also seen in figure 3, showing typical results for the differential relative viscosity:

$$\frac{\eta_{\text{diff}}}{\eta_0} = \frac{\left(\frac{d\tau}{d\gamma}\right)_{\text{suspension}}}{\left(\frac{d\tau}{d\gamma}\right)_{\text{medium}}}.$$  \hspace{1cm} (8)

When plotted versus the logarithm of $\bar{\gamma}$, a linear relation is obtained up to the highest shear rates. No sign of levelling-off corresponding to complete breakdown ($A = 2b$) is seen.

Nevertheless, though complete breakdown of the coagulation structure is not achieved in the present investigation, the following arguments indicate that it is approached at the highest shear rates, for the suspensions with 78 $\mu$m particles:

1) The differential relative viscosity is in this case (in contrast with suspensions of smaller particles) nearly equal to that found in suspensions of uncoated particles in glycerol-water mixtures, with the same size distribution. In such suspensions, no rheologically measurable coagulation is found [8]. The values of $\eta_{\text{diff}}/\eta_0$ for $\gamma \to \infty$, obtained in those cases [9], are mentioned in the caption to figure 3.

2) The course of the differential viscosity vs. $\log_{10}\bar{\gamma}$ plots at various solid volume fractions would lead to a crossing of the curves at $\eta_{\text{diff}}/\eta_0 \approx 4$ if the linear relations were to continue. At such a crossing point the differential viscosity would become independent of the solid volume fraction. At higher $\bar{\gamma}$ values even a decreasing differential viscosity with increasing $\Phi$ would prevail. Since this is very improbable, a levelling-off of the curves at $\eta_{\text{diff}}/\eta_0 \approx 4.5$ is indicated.

If we assume that at the highest $\bar{\gamma}$ employed complete breakdown of the coagulation structure is achieved ($A = 2b$) in suspensions with 78 $\mu$m particles, but not in suspensions with 28 $\mu$m particles, we can calculate the force necessary for separating two touching particles. In table 3, the average number of contacts between particles in adjacent layers, per mm$^2$, is men-

![Fig. 3. Differential relative viscosity versus $\log_{10}\bar{\gamma}$. $\Phi = 78.32$ $\mu$m, $\varphi = 0.400$, $\bigcirc$ $\varphi = 0.375$, $\square$ $\varphi = 0.350$. For non-coagulating suspensions, $\lim (\eta_{\text{diff}}/\eta_0)\gamma \to \infty$ is 6.38, 5.29 and 4.66, respectively](image)

<table>
<thead>
<tr>
<th>$n/\mu$m</th>
<th>$\Phi = 0.350$</th>
<th>$\Phi = 0.375$</th>
<th>$\Phi = 0.400$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hexagonal</td>
<td>cubical</td>
<td>hexagonal</td>
</tr>
<tr>
<td></td>
<td>$F/10^{-7}$ N</td>
<td>$F/10^{-7}$ N</td>
<td>$F/10^{-7}$ N</td>
</tr>
<tr>
<td>28.32</td>
<td>483</td>
<td>1.89</td>
<td>557</td>
</tr>
<tr>
<td>52.26</td>
<td>140</td>
<td>5.71</td>
<td>162</td>
</tr>
<tr>
<td>78.32</td>
<td>63</td>
<td>9.88</td>
<td>73</td>
</tr>
</tbody>
</table>
tioned for suspensions with volume fractions and particle sizes comparable to those investigated experimentally. The distance between two adjacent layers was taken to be \(2b\), such as to enable the layers to slide past each other. Both a hexagonal and a cubical arrangement of the particles within the layers was introduced. Full occupation corresponds with \(\varphi = 0.6046 \) and \(0.5236\), respectively, in these cases. If a random distribution of vacancies over the available sites is assumed, the average number of contacts between two adjacent layers becomes:

\[
N_{C_{\text{hexagonal}}} = \left(\frac{\varphi}{0.6046}\right)^2 \frac{1}{(2b)^2 \sin 60^\circ}, \tag{9}
\]

\[
N_{C_{\text{cubical}}} = \left(\frac{\varphi}{0.5236}\right)^2 \frac{1}{(2b)^2}. \tag{10}
\]

By using the average shear stress at the highest values applied \(\tau_n\) to calculate the force available per particle pair in the direction of separation of the particles concerned \(F = \tau_n \cos (\pi/4)/NC\), we obtain values which are independent of the solid volume fraction (see table 3). If, on the other hand, we start from the assumption that when \(\tau = \tau_n\) the shear stress is equivalent with the force necessary to separate the touching particles at a constant (i.e., \(\varphi\) independent) occupation of the layers, we obtain \(F\) values which are dependent on the solid volume fraction \(\varphi\). This refers to the case of 78 and 28 \(\mu m\) particles; the 53 \(\mu m\) particles show a different behaviour (see below). Since a \(\varphi\) dependent force between suspended particles cannot be reconciled with current theories about particle interactions, we reject the later hypothesis.

The approach to complete structure breakdown \((A = 2b)\) in the case of the 78 \(\mu m\) particles, but not in the case of smaller particles, can then be explained by assuming that in the latter case the average force available per particle pair is too small to separate two adjacent planes with an average degree of occupation, while with larger particles it is sufficient. This leads to the conclusion that a force of \(1 \cdot 10^{-6} N\) suffices to separate two touching 78 \(\mu m\) particles, while a force of \(1.8 \cdot 10^{-7} N\) is not large enough to separate two touching 28 \(\mu m\) particles.

It may be criticized that there will be parts of the coagulation structure with a larger number of contacts between adjacent planes than the average number. This is undoubtedly true. But during shear the stress concentrates on these regions. The use of the average shear stress when \(A \to 2b\), for calculating the force necessary to separate two touching particles is equivalent to the assumption that, when the average shear stress suffices to separate neighbouring planes with an average degree of occupation, stress concentration takes into account regions with a larger number of bonds between particles.

The \(F\) values mentioned in table 3 provide insight into the coagulation mechanism. The absence of coagulation in suspensions of untreated glass in glycerol-water, while silanized glass is subject to pronounced coagulation, can be due to three different mechanisms:

a) The London-van der Waals attraction between the polymer coatings in glycerol-water is much larger than that between glass in glycerol-water. In colloid chemical terminology: the Hamaker constant in the case of polymer/glycerol-water/polymer is significantly larger than that of the case of glass/glycerol-water/glass.

b) The London-van der Waals attraction suffices for coagulation, for both silanized and untreated glass in glycerol-water. Untreated glass, however is, electrostatically stabilized by dissociation of surface Si-OH or Sii-ONa groups.

c) Polymer chains protruding from the coatings in the case of silanized glass form bridges.

In case (a), the attractive energy between two nearly touching spherical particles, is given by [16]:

\[
V_A = -\frac{A' b}{12 H}, \tag{11}
\]

with \(A'\) the Hamaker constant and \(H\) the distance between the surfaces of the particles.

The attractive force is found by differentiating relation (11):

\[
F_A = \frac{A' b}{12 H^2}. \tag{12}
\]

For polymer/glycerol-water/polymer, \(A' \approx 10^{-19} J\) (cf. the case of carbon in water [17]). For glass/glycerol-water/glass, \(A' \approx 10^{-20} J\) (cf. the case of SiO2 in water [17]).

However, in reality we deal with the case glass/polymer/glycerol-water/polymer/glass. For this case the attraction is determined by an effective Hamaker constant

\[
A'_{\text{eff}} = A' \left[1 + \frac{1}{\left(1 + 2 \frac{\delta}{H}\right)^2} - \frac{2}{\left(1 + \frac{\delta}{H}\right)^2}\right] \tag{13}
\]

if the contribution of the glass particles to the attractive energy is neglected \((A'_2 \approx 0)\). Here, \(\delta\) designates the thickness of the polymer layers. This relation can be derived from the expression for attraction between flat plates [18].

From relation (13) it follows that \(A'_{\text{eff}}\) is larger than \(0.5 A'\) only if \(\delta/H > 0.7\). Thus, the Hamaker constant of
the polymer chains will predominate only if the particles are very close together \( H \approx 2 \text{ nm} \). Since the irregularities on the surfaces (see figure 4) are much larger than this, two particles can approach each other only to distances at which the glass/glycerol-water/glass Hamaker constant determines the attraction. Thus, alternative (a) can be rejected.

With \( A' \approx 10^{-20} \text{ J} \) and \( F_A = 10^{-6} \text{ N} \), we calculate \( H \approx 2 \times 10^{-10} \text{ m} \). This means, however, that the assumption (b) must be rejected as well, since this distance again is much smaller than the irregularities of the surface.

We are left, then, with bridge formation between polymer chains protruding into the liquid medium as the cause of coagulation.

From the conclusion that \( A = 2b \) at \( \bar{\gamma} \approx 90 \text{ s}^{-1} \) in 78 \( \mu \text{m} \) particle suspensions, we obtain:

\[
\frac{\eta_{\text{diff}}}{\eta_0} = 24 \pi \left( \frac{b}{A} \right)^3 \frac{\delta_0}{b} \frac{f}{1 - (q - 1)b^2} = 4.5 \, . \tag{14}
\]

In this formula, several parameters can be estimated:

i) From a comparison with crystal structures, \( b/A \) can be found. This is based on the idea that particle surroundings in a suspension are comparable to those in a crystal. Quite generally, \( b/A \) is proportional to \( \phi^{1/3} \), while the proportionality constant varies between 0.49 and 0.62 for various crystal structures and shear planes (table 4). Because in flowing suspensions different types of particle arrangements and shear planes occur, we used an average value of 0.562 \( \phi^{1/3} \) for \( b/A \).

ii) \( \delta_0/b \) is estimated as follows: The particles are thought to be ordered at high \( \bar{\gamma} \) values in layers, with a distance between the centres in successive layers of \( 2b \) (figure 5). There is a certain spread of the particles about their ideal positions, expressed by a Gaussian type distribution of the \( y \) coordinate of their centres, with standard deviation \( \sigma \) (\( y \) designates the direction of the velocity gradient, \( x \) the direction of flow and \( z \) the direction perpendicular to \( x \) and \( y \)).

Consider now some particles in layer 2, threatening to collide with one particular particle in layer 1 (figure 5). The particles in layer 2 are still far removed from the particle in layer 1, their \( y \) coordinate is \( y_0 = 2b + A y_0 \), with \(-b < A y_0 < +b\), and the prob-

![Fig. 4. Typical scanning electron micrograph of silanized glass particle](image)

![Fig. 5. Schematic view of particles approaching a certain particle in layer 1. The shaded area represents the range of \( y_0 \) and \( z_0 \) values employed for calculating \( (\delta_0/b)^3 \)](image)

Table 4. Values \( b/\Delta \) for some possible shear planes in crystal structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>Shear plane</th>
<th>( b/\Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>100</td>
<td>0.6083 ( \phi^{1/3} )</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>0.5115 ( \phi^{1/3} )</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>0.5939 ( \phi^{1/3} )</td>
</tr>
<tr>
<td>Simple cubic</td>
<td>100</td>
<td>0.6204 ( \phi^{1/3} )</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>0.5217 ( \phi^{1/3} )</td>
</tr>
<tr>
<td>BCC</td>
<td>100</td>
<td>0.4924 ( \phi^{1/3} )</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>0.5855 ( \phi^{1/3} )</td>
</tr>
</tbody>
</table>
ability of one particular \( AY_0 \) value described by a Gaussian distribution with standard deviation \( \sigma \). Those particles in layer 2, which are displaced appreciably by interaction with the particle in layer 1 considered, are thought to be restricted to those with \(-b < z_0 < +b\). An average value of \( \delta_0/b \) can then be calculated by:

\[
(\delta_0/b) = \frac{\int_{z_0=-b}^{+b} \int_{y_0=-b}^{+b} \frac{\delta}{b} \exp \left[ -\frac{(y_0-2b)^2}{(\sigma \sqrt{2})^2} \right] dy_0 dz_0}{\int_{z_0=-b}^{+b} \int_{y_0=-b}^{+b} \exp \left[ -\frac{(y_0-2b)^2}{(\sigma \sqrt{2})^2} \right] dy_0 dz_0}
\]

\[
(\delta_0/b) = \frac{+b}{z_0=b} \int_{y_0=-b}^{+b} \int_{y_0=-b}^{+b} \exp \left[ -\frac{(y_0-2b)^2}{(\sigma \sqrt{2})^2} \right] dy_0 dz_0
\]

\[
\delta_0/b \quad \text{as a function of } y_0 \text{ and } z_0 \text{ was introduced on the basis of two hypotheses: (a) on the basis of the Batchelor and Green trajectories [19] (table 5, column 2); (b) on the basis the rectilinear motion, except when direct steric overlap with the particle in layer 1 would occur (table 5, column 3). These are the two extremes with reality somewhere between, since the particles are not free to follow the Batchelor and Green trajectories which refer to very dilute suspensions.}

We are then able to calculate the parameter combination \( f/[1-(q-1)/2]^2 \). In columns 4 and 5 of table 5, some values are mentioned calculated by relation (14), with the \( \delta_0/b \) values in column 2. Values from column 3 would lead to proportionally larger values of \( f/[1-(q-1)/2]^2 \). The largest uncertainty is caused by our ignorance of the degree of order under high shear rate, i.e. by ignorance of \( \sigma/b \). \( f/[1-(q-1)/2]^2 \) seems to be of the order of 10. In view of the fact that there is no significant difference between \( \lim (\eta_{diff}/\eta_0) \rightarrow \infty \) in coagulating suspensions, and \( \eta_{PL} \) in non-coagulating ones, the large value of \( f/[1-(q-1)/2]^2 \) is ascribed to a large value of \( f \) rather than to small value of the denominator. A large value of \( f \) is, indeed, expected because the effects of all deviations from rectilinear motion in a very dilute suspension, including rotation, are combined in this parameter.

### Table 5. Parameters in the high shear rate region

<table>
<thead>
<tr>
<th>( \alpha/b )</th>
<th>( \sigma_0/b )</th>
<th>( f/[1-(q-1)/2]^2 ) on the basis of the Batchelor trajectories ( \delta_0/b ) values</th>
</tr>
</thead>
<tbody>
<tr>
<td>from Batchelor trajectories</td>
<td></td>
<td></td>
</tr>
<tr>
<td>from rectilinear motion unless direct overlap would occur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \phi = 0.350 )</td>
<td>( \phi = 0.400 )</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.036</td>
<td>0.024</td>
</tr>
<tr>
<td>0.4</td>
<td>0.080</td>
<td>0.065</td>
</tr>
<tr>
<td>0.6</td>
<td>0.104</td>
<td>0.087</td>
</tr>
<tr>
<td>0.8</td>
<td>0.110</td>
<td>0.093</td>
</tr>
</tbody>
</table>

4.2 The build-up of structure at lower shear rates

At lower shear rates, \( \eta_{app}/\eta_0 \) increases (figure 2). If all other parameters remain constant, \( \eta_0/\eta_{app} \) is a measure for \( 1/A \) (cf. relation (4)), while

\[
A = \frac{2b}{\int_{\tau=0}^{\tau} p(\tau) \, d\tau}
\]

In relation (16), \( p(\tau) \, d\tau \) designates the increase of slippage probability, at a given potential shear plane, when the shear stress increases from \( \tau \) to \( \tau + d\tau \).

A typical graph is shown in figure 6. A large number of shear planes (about 1/2-1/3 of the total) is operative already at the lowest \( \tau \) values applied here, but further breakdown of the structure is difficult.

In order to abstract from parameters which remain constant when the shear rate and shear stress change, \( d\ln \eta_{app}/d\ln \gamma \) is plotted in figure 7 for various concentrations and particle sizes. A distinct difference is seen between the 28 and 78 \( \mu \)m particle suspensions on the one hand, and the 53 \( \mu \)m particle suspension on the other. This difference is apparent also from other data:

1) \( \eta_{app}/\eta_0 \) increases more strongly with decreasing \( \gamma \), for the suspensions with 53 \( \mu \)m particles than for those with 28 \( \mu \)m particles (cf. the crossing of the respective curves in figure 2 b; this was even more pronounced at higher concentrations).

2) The power law index \( n \) indicating the degree of shear thinning character, is approximately equal and
independent of concentration for the 28 μm and 78 μm particle suspensions. It is smaller and decreases with increasing concentration for the 53 μm particle suspensions (see table 5).

The fact that \( n \) does not vary with concentration in the suspensions with 28 μm and 78 μm particles suggests that in these cases the parameters which depend strongly on concentration (\( A, f, q \)) do not significantly influence \( n \) or \( d \ln \eta_{\text{app}} / d \ln \dot{\gamma} \) (the latter parameter also is determined by the shear thinning characteristics).

Thus, in these cases \( d \ln \eta_{\text{app}} / d \ln \dot{\gamma} \) is determined primarily by a change in the inter-shear plane distance \( A \) with increasing \( \dot{\gamma} \). The values of \( d \ln \eta_{\text{app}} / d \ln \dot{\gamma} \) shown in figure 7 vary from 0.20 to 0.33; they are consistent with a decrease of \( A \) by a factor 0.88 to 0.81 on doubling the shear rate.

Suspensions with 53 μm particles behave differently. This difference is not due to a lack of reproducibility of the suspension preparation (see table 2). Therefore the best way to account for it is that the treatment of the glass particles with (CH\(_3\))\(_2\)SiCl\(_2\) in the case of the 53 μm particles lead to a different surface coating with a more “sticky” surface, than in the case of the 28 μm and 78 μm particles. This accounts for the fact that \( \eta_{\text{app}} \) at low \( \dot{\gamma} \) values is higher for the 53 μm particles, at a given solid volume fraction, than for the 28 μm particles (cf. figure 2b). The more sticky surface of the 53 μm particles leads to a rapid build-up of a coagulation structure on decreasing \( \dot{\gamma} \); this structure, however is not able to withstand increasing shear stresses.

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