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Time-dependent behavior and wall slip in concentrated shear thickening dispersions

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Synopsis

The viscosity of concentrated shear thickening dispersions was measured as a function of shear rate, Couette cylinder size, and time. The level of the low shear rate viscosity, which was found to be independent of system size and time, could be predicted by the equation of Frankel and Acrivos. At shear rates above the critical shear rate for shear thickening in highly concentrated ($\phi > 0.57$) dispersions of monodisperse particles strong viscosity instabilities were detected, together with a dependence on cylinder size. The instabilities are attributed to reversible order-disorder transitions, e.g., from strings to clusters. This dependence on cylinder size is due to wall slip, slipping planes in the dispersion, and even plug flow in the gap. With less concentrated or polydisperse dispersions the effects are much less severe but there is thixotropy, probably due to a reordering of the dispersion.

INTRODUCTION

In recent years considerable effort has been put into understanding the connection between the macroscopic rheological properties and the microstructure of a dispersion. It was discovered, for example, that an order-disorder transition can have a very pronounced effect on the viscosity of a dispersion (Hoffman, 1972).

The rheological behavior of dilute as well as concentrated dispersions has been the subject of several reviews. Experimental data were reviewed among others by Jinescu (1974) and Metzner (1985). The latter mainly dealt with suspensions in polymeric liquids. Other reviews include those by Jeffrey and Acrivos (1976), who considered experimental and theoretical work, by Mewis and Spaull (1976), who showed the
relation between rheology and colloidal stability, and a comprehensive review by Kamal and Mute1 (1985) on suspensions in Newtonian and non-Newtonian fluids.

In some studies on the rheology of concentrated dispersions, time-dependent behavior is reported. The phenomena associated with this behavior usually are called thixotropy or rheopexy, which are, respectively, the recoverable decrease and increase of the viscosity with time. An extensive review on thixotropy was written by Mewis (1979). Often this time-dependent behavior is related to the breakdown or buildup of structures in the dispersion, e.g., the disruption of aggregates, but in concentrated dispersions this behavior may originate from shear induced diffusion (Leighton and Acrivos, 1987), from the occurrence of stick-slip (Cheng and Richmond, 1978) of the dispersion in the measuring assembly or from flow blockage (Schreuder et al., 1986).

A special type of time-dependent behavior is encountered with dispersions which show shear thickening (or, more exactly, shear-rate thickening, also named rheological dilatancy, which is probably related to, but should not be confused with, volumetric dilatancy). A recent very broad review on shear thickening is given by Barnes (1989). Shear thickening dispersions usually show a gradual but distinct increase of the viscosity with increasing shear rate. With concentrated dispersions of monodisperse particles, however, a discontinuous jump in the viscosity can occur with increasing shear rate (Hoffman, 1972; Wagstaff and Chaffey, 1977; Boersma et al., 1990). Especially at shear rates in the neighborhood of this critical shear-rate rheopectic (Willey and Macosko, 1978) and thixotropic (Hoffman, 1982; Strivens, 1976) behavior have been observed. In measurements of flow curves this time dependency is sometimes avoided as much as possible by performing fast measurements (Hoffman, private communication).

It is now almost generally accepted that some kind of an order-disorder transition is responsible for the shear thickening behavior in concentrated dispersions of monodisperse particles (Hoffman, 1982). In this transition a free flowing, relatively ordered arrangement of the particles (for example, layers or strings) breaks up to form a disordered state, which can even consist of particle clusters. Such a layer–cluster transition may be responsible for the observed time-dependent behavior as well. However, shear induced diffusion or wall slip cannot be excluded beforehand as explanations of the time-dependent behavior. Therefore light and neutron scattering techniques are sometimes employed to get direct information on the structure of a flowing dispersion (Hoffman, 1972; Ackerson et al., 1986).
A way of studying suspension dynamics which became increasingly popular during the last ten years is computer simulation. These simulations offer a powerful tool for studying macroscopic properties of a dispersion (e.g., viscosity) while at the same time the evolution of the microstructure can be observed. Simulations can be performed dynamically as well as statically. A review on the application of computer simulations to the rheology of dense suspensions and their relation to experiments has been given by Barnes et al. (1987). Most computer simulations which are of interest for concentrated dispersions of interacting particles are nonequilibrium molecular dynamics simulations (NEMD) on simple liquids. In these simulations both shear thinning (Heyes, 1986; Loose and Hess, 1989) and shear thickening (Woodcock, 1984) have been observed.

For the simulation of colloidal dispersions the Stokesian dynamics method, as presented by Bossis and Brady (1984) and improved by Durlofsky et al. (1987) is of interest. In this method many-body hydrodynamic interactions as well as two-body interaction forces (e.g., electrostatic repulsion or van der Waals attraction) are taken into account. In these simulations order–disorder transitions, shear thickening (Brady and Bossis, 1985), and time-dependent effects (Durlofsky and Brady, 1989) have been observed.

In this study we present measurements of time-dependent viscosities of shear thickening dispersions at various shear rates and volume fractions. We also show the influence of polydispersity and discuss wall slip. We discuss which mechanisms are responsible for the reported behavior and compare our experimental results with other experiments and with computer simulations.

EXPERIMENT

Materials

Rheological measurements were performed with dispersions of polystyrene (PS) particles in water and in a glycerol/water mixture. Also some other dispersions were used. The preparation and characterization of all used dispersions were described elsewhere (Boersma et al., 1990).

In this investigation two batches of PS particles were used, with different particle sizes (diameters 1.61 μm, referred to further on as PS1, and 2.60 μm, referred to as PS2). The particle sizes were determined with a Coulter Counter ZM 256. From electron micrographs it could be seen that all particles were spherical. Their density was determined by pycnometry to be 1051 kg/m³ and the ratio of the weight
average to the number average diameter was in both cases smaller than 1.008, indicating a high degree of monodispersity. The particles were electrostatically stabilized, due to the presence of surfactant in their preparation (sodium dodecylsulfate).

In this investigation also dispersions of polyvinylchloride (PVC) particles in dioctylphtalate (DOP) and dispersions of glass particles in a glycerol/water mixture were used. Both size distributions were polydisperse. The number-average diameters for the PVC and glass particles were 1.4 and 2.4 μm, respectively, and the ratios of the weight-average to number average diameters were 1.41 and 2.08, respectively. The glass particles were electrostatically stabilized. The PVC particles can be electrostatically as well as sterically stabilized. For a more extended discussion of this fact see Boersma et al. (1990).

**Methods**

Rheological measurements were carried out with a Contraves Rheomat 115 shear-rate controlled rheometer, supplied with a personal computer both for reading torque values and for applying certain shear rates. Various concentric cylinder geometries were used in order to cover a wide range of shear stresses. The ratio between cup and bob diameter was, however, always the same. The dimensions of the various geometries are listed in Table I, with $R_b$ and $R_c$ being, respectively, the bob and cup radii, and $L_b$ being the length of the bob. The rheometer was kept at 20.0±0.1 or at 50.0±0.1 °C, using a thermostatic water circulation system. After the measuring system was filled, with care being taken not to include air in the system, the system was fitted in the rheometer. There it was first kept at rest for 30 min in order to equilibrate thermally. The system was closed with a Teflon cover in order to prevent evaporation of the dispersion medium. Three types of torque measurements were made: (1) a series of measurements at varying fixed

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**TABLE I. Dimensions of the different measuring systems.**

<table>
<thead>
<tr>
<th>System</th>
<th>$R_b$ (mm)</th>
<th>$R_c$ (mm)</th>
<th>$L_b$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN 140</td>
<td>22.5</td>
<td>24.4</td>
<td>80.3</td>
</tr>
<tr>
<td>DIN 125</td>
<td>12.5</td>
<td>13.5</td>
<td>44.7</td>
</tr>
<tr>
<td>DIN 114</td>
<td>7.0</td>
<td>7.6</td>
<td>25.0</td>
</tr>
<tr>
<td>DIN 108</td>
<td>4.0</td>
<td>4.35</td>
<td>14.3</td>
</tr>
</tbody>
</table>
shear rates ("flow curves"), the time between individual measurements being kept as short as possible (only with the PS1 in glycerol/water dispersions), (2) measurements at a range of fixed shear rates whereby every shear rate was measured in time for approximately 400 s after which the viscosity readings were averaged over all the measured values (only with the PS in water dispersions), and (3) measurements in time at a fixed shear rate (with all dispersions). With the latter type of measurement the dispersion in the system was gently stirred by hand with a spatula before each measurement.

An attempt was made to show the occurrence of wall slip by looking at the flow pattern at the top of the dispersion in the gap between the two concentric cylinders. The system was filled with the dispersion up to such a level that the gap between the cup and the bob was just filled. Then a small amount of carbon-black powder was gently pressed into the top layer of the dispersion. When the bob was then rotated the carbon powder flowed with the dispersion and the flow pattern of the dispersion could be observed. Although with this method exact determination of the slip velocity is not possible and although surface effects can slightly influence the local flow pattern, it is possible to obtain information about the type of flow taking place in the gap. Photographs of the flow pattern were taken via a mirror, because direct observation was difficult due to the presence of the thermostatic mantle of the rheometer, which also serves to center the system.

RESULTS AND DISCUSSION

Viscosity as a function of shear rate

Viscosities of polystyrene in water dispersions were measured using measuring procedure (2) at volume fractions between 0.44 and 0.6. Measurements were carried out in systems with different cup and bob diameters.

The characteristics of the batches of PS particles and of the dispersions prepared from them are summarized in Table II. In Fig. 1 typical results obtained with the different Couette sizes for a dispersion of PS2 with volume fraction 0.584 are shown. Lines through the data points have been drawn to guide the eye. The shear rate at which shear thickening starts ($\gamma_s$) is seen to be almost independent of the size of the measuring system for the largest two systems. Unfortunately for the smaller systems no data at lower shear rates could be measured in this dispersion, due to accuracy limitations. Other measurements, on dispersions with even higher volume fractions, indicated that in the smaller
systems the same low shear limit can probably be found and that shear thickening starts at approximately the same $\gamma_0$, but the data are too limited to draw definitive conclusions. Above $\gamma_0$, however, viscosities show a strong dependence on the measuring system. Later on we will indicate that this is probably due to wall slip. The dispersions with other volume fractions gave similar results, although at lower volume fractions the dependence on measuring system was less pronounced. Also the dispersions of PS1 showed a similar dependence of viscosity on shear rate.

In Fig. 2 “quick” flow curves [measuring procedure (1)] at two different temperatures are shown for a dispersion of PS1 in glycerol/water with a volume fraction of 0.585. The dependence of the viscosity on the measuring system is also indicated. Although less severe than with the polystyrene in water dispersions above $\gamma_0$, there is still a dependence on the radius of the cup (and thus bob), indicating wall slip.

Shear thickening in concentrated dispersions is generally associated with some kind of an order–disorder transition. Hoffman (1972) concluded from light scattering experiments on monodisperse polyvinylchloride dispersions which exhibit severe shear thickening, that at low shear rates particles flow in a two-dimensional ordered state of hexagonally packed layers. At a certain shear rate, corresponding to the

**FIG. 1.** Relative viscosities as a function of shear rate for a dispersion of PS2 in water ($\phi = 0.584$), measured in different systems at 20°C. Indication of peaks in the viscosity time trace. DIN140 (▲), DIN125 (●), DIN114 (■), DIN108 (+).
sudden rise in viscosity, the ordering disappears. At even higher shear rates he found that the order returns again. Ackerson et al. (1986), however, found with neutron scattering from charge-stabilized suspensions undergoing shear that at low shear rates an even higher, three dimensional, degree of order exists than that found by Hoffman. At the highest shear rates they did not observe layers anymore but concluded from their experiments that the particles can be arranged in strings. In view of the discrepancy of their results with light scattering results of, e.g., Hoffman, they suggest caution in interpreting shear induced order in dense colloidal suspensions based solely on light scattering experiments because surface induced effects can have a pronounced influence on the measurements. The dispersion with which they performed their experiments was, however, not very concentrated (14 wt % solids), and so it is not clear whether this dispersion showed shear thickening in the shear rate range observed. Laun (1988) mentions SANS (small angle neutron scattering) experiments on shear thickening dispersions and reports that below $\gamma_s$ no layer formation is detected but only the shear induced formation of particle strings. In the shear thickening regime SANS indicates only minor changes in the arrangement of adjacent particles but a strong increase of density fluctuations.
Although there is no general agreement about the exact structural changes that take place it can be concluded that there is a certain transition from a free-flowing structure to another structure which is much less regular, probably through the formation of shear induced aggregates. On the basis of this assumption we have recently deduced a criterion for the onset of shear thickening in a concentrated dispersion (Boersma et al., 1990). Like others in the past (Hoffman, 1974; Berezov et al., 1982) the starting point was a force balance between the different forces working on the particles. It was stated that when the shear forces overcome the repulsive interparticle forces there is a transition to shear thickening. For high volume fractions and thus small interparticle distances this leads to the following formula for the critical shear rate at which shear thickening starts:

$$\gamma_c = \frac{2 \pi \epsilon_0 \epsilon \psi_0^2 \kappa \eta h}{6 \pi \eta a}$$

where $\epsilon_r$ is the relative dielectric constant of the medium and $\epsilon_0$ is the permittivity of vacuum; $\psi_0$ is the surface potential, which in many cases can be approximated by the $\zeta$ potential of the particles in the medium; $\eta_0$ is the medium viscosity; $a$ is the particle radius; $1/\kappa$ is the Debye double layer thickness; and $h$ is the distance between the particles. Note that it is also possible to write this critical shear rate in the form of a dimensionless number $N_{HE} = (12 \pi \eta a^2 \gamma)/(2 \pi \epsilon_0 \epsilon \psi_0 \kappa h)$, which represents the balance between hydrodynamic and electrostatic forces. Shear thickening occurs when $N_{HE}$ becomes larger than order one. The ratio $h/a$ is a function of the volume fraction and can be determined from (Boersma et al., 1990)

$$h/a = \left( \frac{8 \pi}{3 \sqrt[3]{3 \phi}} \right)^{1/3}.$$  (2)

In the derivation of Eq. (1) we assumed constant surface potential on the particles.

As can be seen from Eq. (1) the critical shear rate for shear thickening depends on a number of parameters of a dispersion. A very important parameter is the volume fraction. As we showed, the volume fraction does not only influence the critical shear rate but has a pronounced influence on the amount of increase in viscosity as well. At lower volume fractions the increase is much less severe and eventually disappears completely. The volume fraction at which shear thickening disappears is dependent on the dispersion. Polydispersity also has a
large influence on the increase in viscosity. A larger degree of polydispersity decreases the severity of the rise in viscosity. Also the transition is more smooth and spread over a wider range of shear rates.

From Fig. 2 it can be seen that the change in temperature results in a horizontal shift of the flow curves, as is expected from Eq. (1). When using the data of Table II it is possible to calculate the shear rate at the onset of shear thickening, as predicted from Eqs. (1) and (2). In Table III these predictions are compared with the measured values. As can be seen the agreement is good, especially when taking into account the uncertainties in the parameters characterizing the dispersions. For other volume fractions the agreement between theory and experiment was found to be equally good.

A number of rheological phenomena which in principle may interfere with our results have to be discussed. One of them is wall slip, which will be discussed in a later section. The occurrence of Taylor vortices (Taylor, 1936), which would lead to apparent shear thickening, can be shown to be absent in all our measurements. It is also important that particle inertia can be neglected. This can be judged from the particle Reynolds number: \( \text{Re} = \frac{\rho v a^2}{\eta_0} \), where \( \rho \) is the density of the medium,

**TABLE II. Physical parameters of the dispersions.**

<table>
<thead>
<tr>
<th>Dispersion</th>
<th>( a ) (( \mu m ))</th>
<th>( \eta_0 ) (Pa s)</th>
<th>( \epsilon_r )</th>
<th>( \zeta (\approx \eta_0) ) (mV)</th>
<th>( C ) (mol m(^{-3}))</th>
<th>( \kappa ) (10(^3) m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1 in water</td>
<td>0.805</td>
<td>0.001</td>
<td>80.37</td>
<td>0.3</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>PS2 in water</td>
<td>1.3</td>
<td>0.001</td>
<td>80.37</td>
<td>0.2</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>PS1 in gly/wat 20°C</td>
<td>0.805</td>
<td>0.140</td>
<td>48.65</td>
<td>0.2</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>PS1 in gly/wat 50°C</td>
<td>0.805</td>
<td>0.0285</td>
<td>48.65</td>
<td>0.2</td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE III. Critical shear rates of the dispersions.**

<table>
<thead>
<tr>
<th>Dispersion</th>
<th>( \phi )</th>
<th>( \gamma_{\text{calc}} ) (s(^{-1}))</th>
<th>( \gamma_{\text{meas}} ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS2 in water</td>
<td>0.584</td>
<td>100</td>
<td>115</td>
</tr>
<tr>
<td>PS1 in gly/wat 20°C</td>
<td>0.585</td>
<td>0.81</td>
<td>1.1</td>
</tr>
<tr>
<td>PS1 in gly/wat 50°C</td>
<td>0.585</td>
<td>3.8</td>
<td>5</td>
</tr>
</tbody>
</table>
and $\dot{\gamma}$ is the shear rate. If $\text{Re} \ll 1$ inertia effects can be neglected. In our measurements the Reynolds number varies between $6.5 \times 10^{-10}$ (PS1 in glycerol/water dispersion at the lowest shear rate) and $1.7 \times 10^{-3}$ (PS2 in water dispersion at the highest shear rate). This means that inertia effects are completely negligible.

**Influence of Brownian movement**

In dispersions Brownian movement is always present. In the case of suppressed electrostatic forces Krieger (1972) showed that a reduced shear stress $\tau_r = a^3 \tau/k_B T$ could be defined where $k_B T$ is the thermal energy. Around $\tau_r = 1$ there is a shear thinning transition from a Brownian dominated to a hydrodynamically dominated regime. Van der Werff and de Kruif (1989) argued that the shear thinning transition is around $\mathrm{Pe} = 1$, where $\mathrm{Pe}$ is the Péclet number, $\mathrm{Pe} = a^2 \dot{\gamma}/D_0$. Here $D_0$ is the particle diffusion coefficient. In the case of spherical particles, introduction of the Stokes–Einstein result for $D_0$ leads to $\mathrm{Pe} = 6 \pi \eta a^2 \dot{\gamma}/k_B T$. The Pe number expresses the ratio between shear forces and Brownian forces. If $\mathrm{Pe} \gg 1$, Brownian motion can be neglected.

For our measurements the Péclet number varies between 17.0 for the dispersion of PS1 in glycerol/water ($20^\circ\text{C}$, lowest shear rate) to $> 10^4$ for the dispersion of PS2 in water at the highest shear rate. This means that in most of the measurements Brownian motion is negligible. Measurements by de Kruif et al. (1985) indicate that for hard spheres Brownian motion is still important at $\mathrm{Pe}$ up to approximately 100 but since in our dispersions the electrostatic forces are much stronger than the Brownian forces ($N_{EB} = (\text{electrostatic force}/\text{Brownian force}) \equiv 2\pi \varepsilon_0 \varepsilon_0 \dot{\gamma} a / k_B T > 500$) we expect that Brownian forces will not influence our viscosity results, even at the lowest measured shear rates.

When the Brownian forces dominate the electrostatic forces ($N_{EB} < 1$) the predicted critical shear rate for the onset of shear thickening is located below the shear thinning transition around $\mathrm{Pe} = 1$. Shear thickening will probably be very weak and may not be observable at all, because the equilibrium state of the dispersed particles is liquid-like. Only at very high volume fractions ($\phi > 0.585$) can the equilibrium state be a crystal. Unfortunately not many measurements have been reported on suitable dispersions in this range, but to our knowledge shear thickening has never been observed at Péclet numbers lower than one. In Fig. 3(a) we show some possible forms of the flow curve for this case.
FIG. 3. Possible flow curves for a concentrated dispersion when (a) the Brownian forces dominate the electrostatic forces and (b) the electrostatic forces dominate the Brownian forces.

The second possible case is when the electrostatic forces dominate the Brownian forces \( \left( N_{EB} \gg 1 \right) \). Here, the fundamental phenomenon is shear thickening at \( \gamma_s \) (or \( N_{HE} = 1 \)). This may be complemented by a shear thinning regime at lower \( \gamma \), where \( \text{Pe} \approx O(1) \). Possible shapes of the flow curve in this case are shown in Fig. 3(b). In our measurements no sign of shear thinning is found down to \( \text{Pe} \approx 20 \), but it is possible that
it occurs at lower shear rates. The flow behavior reported by Laun (1988) in his Fig. 9 is an example of a flow curve with two transitions that may be due to this specific behavior. The onset of shear thickening in that figure can be explained with our model if one assumes a value of $\phi_0$ in the order of 50 mV. The Pe number at which shear thinning occurs decreases by approximately two decades with increasing volume fraction, starting at Pe = $O(1)$ for low $\phi$. Qualitatively this drop in critical Pe number is in accordance with the results of van der Werff and de Kruif (1989) who investigated systems with $N_{EB} \to 0$.

It is unclear what the form of the flow curve is at shear rates above the shear thickening transition, because, as we will indicate in the section about time-dependent behavior, it is very difficult to perform reliable experiments in this range.

For each Newtonian plateau it is possible to plot the relative viscosity as a function of volume fraction. These different Newtonian plateaus may give rise to different maximum packing fractions $\phi_{max}$ (van der Werff and de Kruif, 1989).

**Low shear-rate viscosities as a function of volume fraction**

For all the measured flow curves it is possible to determine a Newtonian region at low shear rates. The values of the relative viscosities at low shear rates for the investigated dispersions of polystyrene are plotted against the volume fraction in Fig. 4. The agreement between the results with different particle sizes and medium viscosities is remarkably good.

For concentrated suspensions of spheres Frankel and Acrivos (1967) derived an expression for the relative viscosity as a function of volume fraction. Only hydrodynamic interactions were taken into account. Although the assumptions they made have been criticized (Marrucci and Denn, 1985), their result compares very well with many experimental data. Their equation reads

$$\eta_r = \frac{9}{8} \left[ \frac{(\phi/\phi_{max})^{1/3}}{1 - (\phi/\phi_{max})^{1/3}} \right].$$

Here $\eta_r$ is the relative viscosity of the dispersion and $\phi$ is the volume fraction of the dispersion. They used the concept of a maximum packing fraction at which flow is still possible, $\phi_{max}$. In this equation it is assumed that the viscosity of a dispersion is independent of shear rate. In experiments this is often not the case. Newtonian regions may, however, be
FIG. 4. Low shear-rate relative viscosity as a function of volume fraction. PS1 in water (○), PS2 in water (▲), PS1 in glycerol/water (86.1% w/w) (■). Low Pe (filled cross) and high Pe (+) data of van der Werff and de Kruijff (1989), \( a = 110 \text{ nm} \). The dotted line is the equation of Frankel and Acrivos with \( \phi_{\text{max}} = 0.605 \).

found at low and high shear rates. In such cases, the above-mentioned equation is usually applied to either the low or high shear rate limit of the viscosity.

In Fig. 4, for comparison, Eq. (3) is also plotted (the dotted line). We used a maximum packing fraction, \( \phi_{\text{max}} \), of 0.605, which is the volume fraction for a cubically stacked hexagonal packing. It can be seen that the equation compares very well with the data. In previous work (Schreuder and Stein, 1988) on concentrated dispersions the same maximum packing fraction was found.

For comparison the low and high shear relative viscosities of hard sphere dispersions of Van der Werff and de Kruijff (1989) have also been plotted in Fig. 4. These are the plateau values on both sides of the shear thinning transition around \( Pe = 1 \) [see Fig. 3(a)]. It can be seen that
our viscosities lie in between their high and low Peclet level. If we increase our particle radius by the double layer thickness \((1/\kappa)\) and calculate our volume fractions with this new particle radius our data and their high shear data show good agreement.

**Time-dependent viscosity behavior**

If viscosities (or torques) are measured at shear rates slightly above the shear rate at which shear thickening starts very strong time effects can be found. In our measurements these time effects occurred especially with highly concentrated dispersions of monodisperse particles. As an example, in Fig. 5 the viscosity evolution with time is given for the PS2 in water dispersion with \(\phi = 0.584\) at different shear rates. When \(\dot{\gamma} = 131 \text{ s}^{-1}\) [Fig. 5(a)] the shear rate is just below \(\dot{\gamma}_c\) and no time effects are found. At a slightly higher shear rate \((144 \text{ s}^{-1})\), however, the viscosity–time trace starts to show peaks in time [Fig. 5(b)]. The number and height of the peaks increase with increasing shear rate. The maximum value of the viscosity of a peak can be more than twenty times the value of the low viscosity. When the shear rate is again slightly higher \((156 \text{ s}^{-1})\), in some cases a transition to a steady high viscosity level occurs after shearing for a few minutes [Fig. 5(c)]. This high viscosity level is immediately reached at a still higher shear rate \((158 \text{ s}^{-1})\), as is shown in Fig. 5(d). Note the difference in vertical scaling between Figs. 5(a) and 5(b) and Figs. 5(c) and 5(d). The large structural changes in the dispersion, suggested by the described flow behavior, take place in a narrow range of shear rates: \(\gamma\) changes only by a factor of 1.2.

In these measurements we stirred the dispersion by hand with a spatula before each measurement at a certain shear rate. This was done to ensure that no effects from a previous measurement would interfere with the present one. The reproducibility of the measurements was very good (except for the places of the peaks, which were random). The same sequence of results with varying shear rate was also found with other volume fractions (between 0.57 and 0.60) and with dispersions of PS1 in water, all at their own critical shear rates. The results shown here are all for cup and bob system DIN 125. In the other geometries qualitatively the same behavior was shown. Only the shear rate at which the peaks appeared shifted to higher values at smaller cup and bob diameters. This was probably due to wall slip. In Fig. 1 the regions of the flow curves where peaks could be observed are indicated for the dispersion of PS2 in water with volume fraction 0.584.
FIG. 5. Time dependence of the relative viscosity of a dispersion of PS2 in water \( (\phi = 0.584) \) at 20 °C in system DIN125. (a) \( \gamma = 131 \, s^{-1} \), (b) \( 144 \, s^{-1} \), (c) \( 156 \, s^{-1} \), (d) \( 158 \, s^{-1} \).
In order to check the influence of the medium viscosity and to get a confirmation of the measured phenomena, time-dependent experiments were also performed with dispersions of PS1 in glycerol/water at 20 and 50 °C. These measurements were performed in the same way as the measurements on PS in water. Some typical results are shown in Fig. 6 for a dispersion with \( \phi = 0.585 \) at 20 °C. In Figs. 6(a) and 6(b) it can be seen how a very small increase in shear rate gives a quite large increase in peak frequency and peak height. As can be seen the occurrence of peaks resembles that of the PS2 in water systems, only the time scale is much larger. However, in terms of deformation, the scales are of the same magnitude. Similarity in terms of amount of deformation was also found at 50 °C, where the viscosity of the glycerol/water is approximately a factor of 5 lower.

The observed behavior can be explained in terms of an order-disorder transition, accompanied by the formation of large clusters, which sometimes span the whole cell width. When the viscosity is at its low "base" level there is some type of ordered flow. This is due to the fact that below \( \gamma_s \), electrostatic stabilization dominates the hydrodynamic forces. Although we see the peaks slightly above \( \gamma_s \), it is very well possible that there is also ordered flow there. This can still be due to the electrostatic stabilization, but even with only hydrodynamic forces in theory perfectly regular ordered flow is possible (Nunan and Keller, 1984). Due to some type of instability the order can break up and there is a sudden severe rise in viscosity. This rise can be due to cluster
FIG. 6. Time dependence of the relative viscosity of a dispersion of P51 in glycerol/water (86.1% w/w) with $\phi = 0.585$ at 20°C in system DIN125. (a) $\gamma = 1.45 \text{ s}^{-1}$, (b) $1.5 \text{ s}^{-1}$.

formation, which is well known to occur in dispersions with only hydrodynamic interactions (Brady and Bossis, 1985; Bouillot et al., 1982; Graham and Bird, 1984). Then the dispersion possibly orders again, leading to the low viscosity after some time.

Considering the measurements presented above, it seems reasonable to assume that the same mechanism can be used to obtain a general explanation of shear thickening in concentrated dispersions. At shear rates below $\gamma_2$ there is some kind of regular flow, possibly layers or strings. At shear rates around $\gamma_2$ the regular flow breaks up and clusters start to form due to the hydrodynamic forces. These clusters cause a higher energy dissipation and this then gives a higher viscosity. They
also can increase the effective volume fraction by enclosing dispersion medium. This can give rise to the dramatic increase in viscosity found in some shear thickening dispersions. Finally, when the clusters become very large, they can even be cell spanning and severe wall slip can occur at shear rates above $\dot{\gamma}_b$ (see below). Hereby the viscosity is too large to measure and meaningful experiments cannot be performed anymore.

**Thixotropic behavior and shifting of $\dot{\gamma}_b$**

When starting a measurement at a shear rate slightly above $\dot{\gamma}_b$, it was observed that first the viscosity decreased to some steady level (see, e.g., Fig. 6). This level usually was the base level for the peaked time trace. Thixotropy was especially seen with the PS1 in glycerol/water dispersions. The same behavior was seen at the other medium viscosities, but the decrease was faster at lower viscosities. This behavior is probably due to a slow ordering of the dispersion. When the measurement is started the dispersion is in a disordered state, due to the stirring before the measurement and the introduction of the bob into the cup containing the dispersion. Under shear the dispersion slowly orders into layers or strings sliding parallel to each other. When the base level is reached there is ordered flow, just as at shear rates below $\dot{\gamma}_b$. The only way to obtain confirmation of these structural changes would be, however, to perform light or neutron scattering experiments, together with rheological measurements, on suitable dispersions.

Leighton and Acrivos (1987) reported on the decrease with time of the viscosity of a concentrated dispersion of polystyrene spheres in silicone oil. After shearing, for in some cases as long as 20 h, the viscosity decreased by approximately a factor of 2. They showed that this was due to shear induced migration of the particles from the gap between the cylinders in their Couette geometry to the reservoir below the cylinders. We checked for shear induced diffusion by sealing the gap below the bob with a layer of mercury. This had no influence at all on the reported behavior of the viscosity. Also the height of filling above the bob was of no influence on the results. From this it can be concluded that migration phenomena are not important in these dispersions. This is confirmed by an estimation of the diffusion time for shear induced migration. Since the shear induced diffusion coefficient scales with $a^2\gamma$, the diffusion rate of our smaller particles is more than a factor of a hundred slower than the diffusion rate of the particles of Leighton and Acrivos. And since the decrease they measured took several hours, for
our particles this would mean several weeks, which is much longer than the time scale in which we noticed a decrease in viscosity.

Our measurements indicated that the amount of thixotropy could be influenced by the measuring procedure. In the “fast” measuring procedure, in which one scans the total shear-rate range in quick equidistant (on log scale) steps, the system is not allowed to develop any thixotropy. However, if the system is sheared long enough then it attains, after a period of thixotropy, a low equilibrium viscosity. If the shear rate is then slightly increased the viscosity shows a large increase followed by thixotropic behavior. This maximum viscosity is, however, lower than the corresponding value in the fast procedure, until finally the viscosity becomes too high to measure in the specific system. Measuring like this we were able to measure the PS1 in glycerol/water dispersion at 20 °C up to a shear rate of 2.4 s⁻¹, instead of the 1.7 s⁻¹ that can be reached when measuring as fast as possible or with stirring the dispersion before every new shear rate. This indicates that when measuring shear thickening dispersions measuring procedures have to be specified with great care. Also this phenomenon can be explained with a slow reordering of the dispersion and the breakup of clusters.

Wall slip

In order to explain the strong dependence of the viscosity on the size of the measuring system at shear rates above γₑ we checked for the occurrence of wall slip by using the carbon-black method described before. The Couette system was rotated at a certain shear rate and photographs were taken during a certain time (typically about 30 s). This procedure was applied to the dispersion of PS1 in glycerol/water at 20 °C in system DIN 125 at several shear rates.

Typical results at two shear rates are shown in Figs. 7 and 8. In Fig. 7 the shear rate is 0.572 s⁻¹ and within the limited accuracy the velocity profile is linear from wall to wall, indicating that no wall slip takes place, as is also expected from the measurements. In Fig. 8 the shear rate is 1.676 s⁻¹ and a slipping plane in the dispersion can be observed. Also on the inside of the slipping plane there is a strong indication that plug flow takes place. At even higher shear rates we observed slip both at inner and outer cylinders and also plug flow over the whole gap was visible. These results confirm the behavior expected from the viscosity measurements and indicate that when measuring concentrated dispersions which show severe shear thickening great care has to be taken when measuring at shear rates above γₑ.
In Fig. 1, we estimated, from our measurements, the probable form of the apparent flow curves in the different Couette systems. This form was also indicated by measurements on dispersions with different volume fractions, where a wider shear-rate range was covered for the smaller Couette geometries. If the formulas derived by Yoshimura and Prud’homme (1988) are used to calculate the wall slip velocity and to correct the shear rate (and thus viscosity) from these estimated curves, this leads to very high slip velocities, almost equal to the angular velocity of rotation. Sometimes the equations even give negative values for the angular deformation in the fluid, which is unrealistic. This is probably due to inaccuracies in the measurements. It can also be due to the
FIG. 8. Time trace of the flow in the Couette gap of system DIN125 for a dispersion of PSI in glycerol/water (86.1% w/w) with $d = 0.585$ at 20$^\circ$C. The shear rate is 1.676 s$^{-1}$.

(a) $t = 0$ s. (b) $t = 6$ s. (c) $t = 9$ s. The cup and bob walls are drawn in the photographs for clarity. The slipping plane is indicated by an arrow.
fact that the theory is not applicable if slip occurs over a finite-thickness slip layer. But also a nonhomogeneous Couette flow theory [e.g., Cameron (1989)] seems not applicable because the plug flow is probably caused by large clusters which press against the walls of the system. The slip layer will then be very thin. This also excludes the occurrence of radial migration away from the walls. In this light a quantitative discussion of the results is not possible, but one can state that the largest systems always give the best results and that measurements at shear rates above \( \dot{\gamma}_s \) are very sensitive to wall slip because of the extremely high viscosities. These high viscosities are probably due to the formation of large clusters, which can even be cell spanning. The latter then induce plug flow.

**Measurements on dispersions with lower volume fractions or on dispersions of polydisperse particles**

Measurements were carried out with dispersions of PS1 in water at volume fractions down to \( \phi = 0.45 \) and with dispersions of PS1 in water at \( \phi = 0.57 \). Dispersions of polydisperse PVC in dioctylphthalate were measured up to \( \phi = 0.60 \) and dispersions of polydisperse glass in glycerol/water up to \( \phi = 0.585 \) [for some of the measurements, see Boersma et al. (1990)]. These dispersions showed much weaker time dependency of the viscosities than that reported above.

The dependence of the torque-angular velocity curves on the measuring geometry indicates wall slip also with the polydisperse and with the less concentrated monodisperse systems, but this slip was much less severe than with the highly concentrated monodisperse dispersions. The shear rate at which any slip could be observed with the carbon-black method was far above \( \dot{\gamma}_s \) (more than twice as high) and there is only a slight dependence on measuring geometry.

A decrease of the viscosity in time was observed with all polydisperse and less concentrated monodisperse dispersions at shear rates above \( \dot{\gamma}_s \). As an example in Fig. 9 an \( \eta(t) \) curve is given for a dispersion of glass in glycerol/water at 20 °C with volume fraction \( \phi = 0.57 \). The applied shear rate was \( 4.92 \text{ s}^{-1} \), while \( \dot{\gamma}_s \) for this dispersion is around \( 1.8 \text{ s}^{-1} \). The viscosity decreases to approximately half of its starting value. It was checked that no shear induced diffusion occurred. Also it can be calculated that heating effects due to viscous dissipation are negligible at the shear rates applied. The thixotropy is considerable but will not interfere too much when a flow curve is taken as fast as possible. Also the decrease in viscosity is by far not as strong as the increase due
FIG. 9. Time dependence of the relative viscosity of a dispersion of glass in glycerol/water (86.1% w/w) with $\phi = 0.57$ at 20°C in system DIN125. The shear rate is $4.92 \, \text{s}^{-1}$.

to shear thickening, which is in most cases more than a decade. We think that the decrease in viscosity is again due to a slow reordering of the dispersion, even at these shear rates far above $\gamma_p$.

The measurements indicate that with polydisperse dispersions and with less concentrated monodisperse dispersions small perturbations of the ordered regular flow probably have a less drastic influence on their surroundings in the dispersion and are restored more easily. At shear rates above $\gamma_s$ there is a more gradual transition from the ordered flow to a disordered flow with clusters and large density fluctuations. This is not unexpected as, at a given volume fraction, there is simply more free volume in the dispersion, and a small degree of disorder is then less effective in blocking the flow. Moreover, the cell spanning cluster can be expected to disappear below a critical volume fraction. Polydispersity breaks the spanning cluster by placing small particles between large ones, thereby disrupting the connection between the aggregates.

Comparison with previously reported results

Almost all of the results presented in this paper can be explained with the concept of an order–disorder transition. However, the exact state of the order (layers or strings) is not clear. Recently scattering experiments indicated that string formation takes place in a sheared dispersion, while layer formation could not be detected (Laun, 1988; Lindner
et al., 1988). In other experiments, however, both string and layer formation were detected (Ackerson et al., 1986). The latter behavior was also reported in NEMD computer simulations (Heyes, 1986; Loose and Hess, 1989; Hess, 1985). Unfortunately, one has to take care in interpreting the simulation results, because some of them may result from the procedures used to equilibrate the system thermally (Hanley et al., 1988).

The disordered state is probably characterized by the formation of large clusters in the dispersion. This has been observed experimentally (Bouillot et al., 1982; Graham and Bird, 1984), as well as with computer simulations (Durlofsky and Brady, 1989). Laun (1988) indicates that with SANS measurements large density fluctuations were observed. We think that in a Couette gap sometimes even cell spanning clusters can form, leading to large instabilities and wall slip or plug flow. This behavior also resulted from Stokesian dynamics computer simulations (Durlofsky and Brady, 1989; Brady and Bossis, 1988). NEMD simulations recently showed wall slip and plug flow to appear in dense fluids (Hess and Loose, 1989).

Flow instabilities in shear thickening dispersions have also been reported by other authors. Strivens (1976) reported that different rheometers gave different results and that unstable stress readings interfered with his measurements. In view of our results this was probably due to wall slip and cluster formation. Willey and Macosko (1978) mentioned that they observed time-dependent shear thickening in PVC dispersions in various plasticizers, but give no data, so it is difficult to judge their results. Plug flow and wall slip have been observed in a number of other experiments on concentrated dispersions. However, these observations were mainly done in capillary flows (Yilmazer and Kalyon, 1989).

Finally, Heyes noted that in NEMD simulations on the Lennard-Jones liquid shear thickening can be seen. He also found that the shear rate at which shear thickening is first observed depends on the rate of change of shear rate up to that point (Heyes, 1986). If the system has more time for a structural recorganization the shear rate at which shear thickening occurs will be higher. This is in agreement with our experimental findings of the shifting of \( \gamma_c \).

CONCLUSIONS

The electrostatically stabilized dispersions investigated exhibit, at shear rates below the critical shear rate for shear thickening, a Newtonian plateau, the level of which can be described by the relation of
Frankel and Acrivos. At the critical shear rate there is some kind of an order–disorder transition, probably from ordered layers or strings to disordered clusters.

Above the critical shear rate in highly concentrated ($\phi > 0.57$) dispersions of monodisperse particles severe time-dependent effects and thixotropy can be observed, due to cluster formation and structural reordering. The strong dependence of the angular velocity of the measuring system size, at a fixed torque, indicates wall slip. The occurrence of slip was confirmed by photographs, which also indicated slipping planes in the dispersion and plug flow. Calculations showed that the slip velocities are very high and indicated that measurements can best be performed in larger systems. Still, care has to be taken in interpreting the results.

With dispersions of polydisperse particles or with dispersions of monodisperse particles at lower volume fractions ($\phi < 0.57$), viscosity fluctuations are almost absent and wall slip is much less pronounced. Considerable thixotropy still takes place, leading in some cases to a reduction of viscosity with time by a factor of 2. This is probably due to structural reordering.

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NOMENCLATURE

- $a$: particle radius, m
- $C$: concentration of electrolyte, mol m$^{-3}$
- $D_0$: particle diffusion coefficient, m$^2$ s$^{-1}$
- $h$: distance between two particles, m
- $k_B$: Boltzmann's constant, $1.38 \times 10^{-23}$ J K$^{-1}$
- $L_b$: bob length
- $R_b$: bob radius
- $R_c$: cup radius
- $t$: time, s
- $T$: temperature, K

Greek letters

- $\gamma'$: shear rate, s$^{-1}$
- $\gamma_s'$: shear rate at which shear thickening starts, s$^{-1}$
- $\varepsilon_0$: permittivity of vacuum, $8.854 \times 10^{-12}$ C V$^{-1}$ m$^{-1}$
- $\varepsilon_r$: relative dielectric constant
$\zeta$  
zeta potential, mV  

$\eta_0$  
viscosity of the dispersion medium, Pa s  

$\eta_r$  
relative viscosity  

$\kappa$  
reciprocal Debye double layer thickness, m$^{-1}$  

$\rho$  
density, kg m$^{-3}$  

$\tau$  
shear stress, Pa  

$\tau_r$  
reduced shear stress  

$\phi$  
volume fraction  

$\phi_{\text{max}}$  
volume fraction at maximum packing  

$\psi_0$  
surface potential of sphere, here equal to z potential, mV  

References


