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# Fractal aggregates and gels in shear flow

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We consider the steady-state rheology of aggregating colloidal suspensions, where cluster size is limited by the imposed shear. Brittle versus work-hardening behavior of the clusters is distinguished. For brittle clusters at large shear rates we predict a scaling law for their size and corresponding viscosity increment, $\Delta\eta \sim \dot{\gamma}^{-(3-D)/3}$, where $D$ is their fractal dimension. At low shear rates the system will gel due to cluster interpenetration and we discuss a crossover from brittle to work-hardening behavior at large length scales, and the corresponding yield stress. Above this yield stress we find a power-law creep regime with viscosity $\eta \sim \sigma^{-2/3}$. The predictions are compared with experimental results.

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Colloidal suspensions show a variety of nonlinear rheological properties, such as yield stress, shear thinning, shear thickening, thixotropy, and rheopexy [1–3]. Particle interactions and hydrodynamic coupling together with the Brownian motion and an imposed flow field lead to spatial correlation between particles, which in turn determines the nonlinear rheological behavior of the suspension. While a repulsive interaction leads for sufficiently high particle concentrations to an ordered liquidlike structure, an attractive interaction may lead to fractal clusters and continuous networks [4–8]. The latter case will be addressed in this paper.

Tenuous, fractal clusters are formed when initially dispersed colloidal particles undergoing Brownian motion undergo attractive interactions strong enough for bonding to be thermally irreversible [9]. The imposition of shear flow leads to two additional effects. First, as we show below, the imposed flow may dominate over Brownian motion in the rate of encounter (and hence aggregation) between clusters. Second, the elastic clusters [10,11] are deformed and may rupture under the shear stress, which is distributed over the cluster sites in a multifractal manner [12–14]. The continuous deformation of clusters may lead to energy dissipation via pumping of solvent inside the cluster [15–17]. For larger stresses we distinguish two regimes: *work hardening* where clusters are deformed until branches touch each other, leading to loops and more compact and rigid structures [11,18], or *brittle* in which clusters break before branches touch each other, leading to a maximum stable cluster size [19,20]. We will show that for large enough clusters and/or low enough stresses the work hardening regime is obtained, up to a yield stress. However, the brittle regime at large stresses also accounts for a wide range of parameters of practical interest.

Concentration imposes a further limit on the size that clusters can grow without interpenetration (and beyond which we would not expect them to be fractal), and thus a further distinction between regimes. For simplicity we will focus on the combination where the transition from brittle to work hardening falls in the interpenetrating regime, so that isolated clusters are always brittle.

Some aspects of these regimes have been investigated in recent years. It has been shown via computer simulations with zero shear [21,22] that diffusion-limited (dilute) cluster aggregation with bond breaking (thus to some extent mimicking our brittle regime) still yields fractal aggregates. However, in a simulation [23,24] with shear flow (though without hydrodynamic interactions), in which the clusters can deform, rupture, and aggregate, compact clusters are found, which form loose networks as the volume fraction increases, and the viscosity increment depends on the shear rate in form of a power law, independent of the volume fraction. A mean-field theory of aggregation and rupture of clusters in shear flow has been proposed [19], finding Newtonian behavior of the suspension above a yield stress with power-law dependence of the yield stress on the volume fraction. Experimental results show a decreasing of viscosity with increasing shear rate in form of a power law [19,25], which we explain below and a power-law dependence of the yield stress on the volume fraction [19].

In our model of the dilute and brittle regime, particles and clusters move in a fluid due to Brownian motion and an imposed shear flow. Clusters stick together at first contact, form fractal structures, and a distribution of cluster sizes evolves [9]. These clusters are elastic [10,11] and therefore are deformed in the applied shear stress, but break before branches can touch. Thus the system evolves towards a maximum stable cluster size, determined by the applied shear rate and a breaking condition. In the large shear rate regime only small clusters are stable. We approximate aggregation and fragmentation processes to be instantaneous in the sense that averaged over a characteristic time the clusters behave independently in the fluid. In the spirit of the Kirkwood approximation [26] we take the aggregates to behave hydrodynamically like compact spheres, for which the radius scales like the radius of gyration, and for a small cluster volume fraction the viscosity is determined by Einstein's equation for a dilute suspension of spheres. In the second part of this paper we turn to the low shear rate regime, in which big clusters are stable and the cluster volume fraction is of order one. In this regime cluster-cluster aggregates are not independent anymore, but connected into larger entities.

First we shall estimate the range of material parameters

 

for which the brittle regime can prevail for dilute clusters. Dilute cluster-cluster aggregation leads to fairly loopless clusters [27], thus we will assume that the aggregates behave elastically like contorted rigid chains [11] for which the displacement $\delta$ under an applied force $f$ costs an elastic energy [10]

$$f\delta \simeq \frac{K}{AR^2}\delta^2 , \tag{1}$$

where $K$ is the force constant for a pair of particles, $R$ the distance between the points where the force is applied, and $A$ the average number of particles in the connecting path between these points. A pair of forces $f$ applied to the tips of a cluster of linear size $R$ yields a bending moment

$$\Gamma \simeq fR \simeq \frac{K}{A}\frac{\delta}{R} . \tag{2}$$

Estimating the condition of branches to touch by $\delta/R \simeq 1$, we find that for $\Gamma < K/A$ branches do not touch. Taking the condition for breaking to be $\Gamma > \Gamma_b$, where $\Gamma_b$ is determined by the binding energy between particles, the "break before touch" regime prevails for

$$\Gamma_b < K/A . \tag{3}$$

For particles with 1000 atoms $K$ has been estimated [11] to be $K \simeq 1000$ eV. Taking $\Gamma_b \simeq 1$ eV the break before touch regime allows for clusters up to $A \simeq 1000$, where $A$ is the average number of particles in the connecting path between tips of the cluster.

At nonzero concentration the clusters will only be fractal out to a length scale $\xi$ and we will refer to units of this size as *blobs*. On larger length scales the distribution of blobs will be roughly space filling, but without elastic bending their connectivity will still be treelike as before and the elasticity and rupture conditions (1) and (2) still apply. However, the condition for branches to touch becomes $\delta/\xi \simeq 1$ and hence the limit of the brittle regime becomes

$$\Gamma_b < \frac{K}{A}\frac{\xi}{R} . \tag{4}$$

We will return to the consequences of this condition below.

For isolated clusters we have excluded the possibility of loop formation. This is justified when cluster bonding is fairly rigid and brittle, whereupon the probability for two clusters to encounter a multiply bonding configuration is very low. However, such configurations once found are expected to be much more stable than singly bonded ones and therefore we anticipate a slow build up in their numbers and a trend towards more compact aggregates at long times. In this sense, the results of this paper might be interpreted as applying to only an intermediate range of time.

Now we will relate the cluster size to the shear rate in the dilute cluster regime. An aggregate of size $R$ in a solvent with viscosity $\eta_0$, shear rate $\dot{\gamma}$, and shear stress $\sigma \simeq \eta_0\dot{\gamma}$ experiences on its surface a force $F \sim R^2\sigma$. This force exerts a bending moment $\Gamma \sim RF$ on the internal structure and for

$$\Gamma > \Gamma_b \sim R^3\eta_0\dot{\gamma} \tag{5}$$

the cluster breaks. This breaking condition relates the maximum stable cluster size $R$ to the solvent viscosity and shear rate

$$R \sim (\eta_0\dot{\gamma})^{-1/3} , \tag{6}$$

which is consistent with experimental data (Fig. 12 in Ref. [20]) for the hydrodynamic radius measured with polystyrene latexes for $\dot{\gamma}$ in the range 800–1600 $s^{-1}$. Clusters aggregate until they reach the size $R$ and then break. This leads to a cluster size distribution peaked around $R$ in the steady state. The characteristic size decreases with increasing shear rate in form of a power law.

This result enables us to estimate the relative importance of diffusion and shear flow to the encounter of clusters in the steady state [4]. The appropriate time scale for diffusion $t_D$ is given that for a cluster of radius $R$ to diffuse a distance equal to its radius, $t_D \sim \eta_0 R^3/kT$, to be compared with the time scale $t_S$ of shear flow given by the reciprocal of the shear rate. Their ratio is

$$\frac{t_D}{t_S} \sim \frac{\eta_0\dot{\gamma}R^3}{kT} \sim \frac{\Gamma_b}{kT} , \tag{7}$$

where Eq. (5) has been used on the right-hand side (rhs). Therefore if the aggregates are to have any thermal stability ($\Gamma_b/kT \gg 1$), the contribution of shear flow to the encounter of clusters always dominates in the steady state, independent of the shear rate.

Since the aggregates in the fluid act hydrodynamically like compact spheres, screening the fluid in the interior from the outside, the *cluster-volume fraction* $\Phi$ relates the cluster structure to the viscosity. Let $n$ be the number of primary particles per unit volume and $a$ the radius of these particles: Then the particle volume fraction is $\psi = n(4\pi/3)a^3$. Let $N$ be the number of clusters per unit volume and let all clusters have reached the maximum cluster size $R$, then the number of particles per cluster is $(n/N) \sim R^D$, where $D$ is the fractal dimension of the clusters. Finally the cluster-volume fraction is

$$\Phi = N\frac{4\pi}{3}R^3 \simeq \psi\left(\frac{R}{a}\right)^{3-D} \tag{8}$$

and with Eq. (6)

$$\Phi \simeq \psi\left(\frac{\eta_0\dot{\gamma}a^3}{\Gamma_b}\right)^{-(3-D)/3} . \tag{9}$$

In the large shear rate regime $\Phi$ is small and we can use Einstein's result [28] for the viscosity of a dilute suspension of hard spheres, $\eta = \eta_0(1+\frac{5}{2}\Phi) \equiv \eta_0 + \Delta\eta$. The viscosity *increment* then takes the form

$$\Delta\eta \simeq \psi\left(\frac{\eta_0\dot{\gamma}a^3}{\Gamma_b}\right)^{-(3-D)/3} . \tag{10}$$

For fractal clusters we find shear thinning in a power-law form, while for compact clusters the suspension is Newtonian. This result is a direct consequence of the hydrodynamic screening of the interior of fractal clusters, for which the volume fraction scales like $R^{3-D}$ and thus, since $n = \text{const}$, is bigger for "few and big" clusters than for "many and small" clusters, where the fragmentation

in shear flow pushes towards the latter situation. Note that except for compact clusters breaking up there would be no change in the cluster volume fraction and so no shear thinning. The fractal dimension of clusters in sheared suspensions has been measured to be $D \simeq 1.8$ [20]. Thus in the range of validity of Einstein's equation, i.e., $\Delta\eta \ll \eta_0$ or $\Phi \ll 1$, we expect a power-law exponent for the viscosity increment $\Delta\eta$ vs $\dot{\gamma}$ of about $-0.4$. Finally it should be noted that all of this calculation, based on the assumption of isolated clusters, can only yield a modest correction to the background Newtonian viscosity $\eta_0$.

Now we turn to the low shear rate, or large cluster volume fraction regime where the clusters have the structure of dilute aggregates only up to the blob size $\xi$. Beyond this length scale we will assume that they are space filling, but out to a length scale $\xi_{\text{touch}}$ is still treelike because of formation by sticking at one contact. We assume that the brittle regime applies at least up to length scale $\xi$.

For length scales $\xi_{\text{touch}} > r > \xi$ we write the elastic compliance of the gel as

$$C_g(r) \simeq \left(\frac{r}{\xi}\right)^{Z_g} C_c , \tag{11}$$

where $C_c \sim \xi^{Z_c}$ is the compliance of a blob and we expect $Z_c \simeq 3$ and $Z_g \simeq 4$. The criterion to form new bonds in the gel is that the elastic displacement is of order $\xi$

$$\xi \simeq f(r) C_g(r) \simeq \sigma r^2 (r/\xi)^{Z_g} C_c . \tag{12}$$

Therefore at stress $\sigma$ we expect new bonds on scales larger than $\xi_{\text{touch}} \simeq \xi(\sigma C_c \xi)^{-1/(2+Z_g)}$. On the other hand, the breaking condition $\sigma \xi_{\text{break}}^3 \simeq \Gamma_b$ remains, giving $\xi_{\text{break}} \sim \sigma^{-1/3}$. These two lengths match at

$$\sigma_y \sim \xi^{-3(1+Z_g-Z_c)/(Z_g-1)} \sim \psi^{3(1+Z_g-Z_c)/(Z_g-1)(3-D)} , \tag{13}$$

which may be interpreted as the yield stress, since for $\sigma > \sigma_y$ bonds break and we enter a "creeping-gel" regime (see below). If we assume that $Z_c = 3$, $Z_g = 4$ then Eq. (13) simplifies to

$$\sigma_y \sim \psi^{2/(3-D)} , \tag{14}$$

which we note is different from the corresponding result obtained by assuming simply that $\xi_{\text{touch}} \simeq \xi$ leading to an exponent of $3/(3-D)$.

What happens below the yield stress calculated above depends on the past history of the sample, but is essentially a work hardening behavior. Starting from a treelike structure out to very large scales, applied stress leads to new contacts and greater rigidity up to the yield point. We hope to return to this regime in a later paper.

In the *creeping-gel regime* strain and stress build up locally, until rupture on some scale $r$ followed by elastic recovery leading to new contacts and repetition of the process (see Fig. 1). At the moment of rupture the elastic strain is $\gamma(r) \simeq C(r)\sigma r^2 1/r$ and we estimate the strain rate from the rate at which this elastic strain is spontaneously recovered after rupture. For a drag coefficient $\alpha(r) \sim r^s$ the relaxation time is given by $\tau(r) = C(r)\alpha(r)$

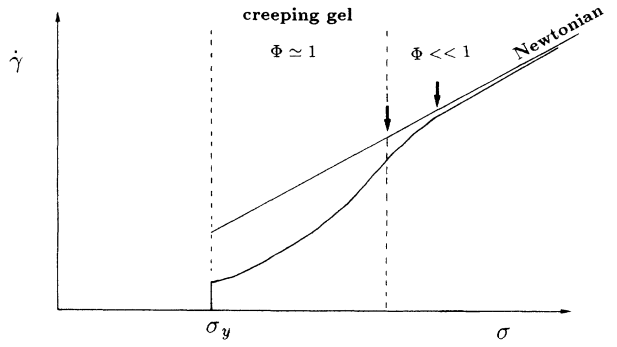


FIG. 1. Schematic picture of shear rate $\dot{\gamma}$ vs shear stress $\sigma$. The scaling of the yield stress $\sigma_y$ with particle volume fraction is described by Eq. (13). The creeping-gel regime is modeled by Eq. (16) and between the two arrows where the suspension contains fractal clusters but the volume fraction is small, we anticipate Eq. (10). Finally for larger shear rates the clusters break up into monomers and the suspension behaves Newtonian-like.

leading to

$$\eta = \frac{\sigma}{\dot{\gamma}} \simeq \frac{\sigma\tau(r)}{\gamma(r)} \simeq \frac{\alpha(r)}{r} \sim r^{s-1} \tag{15}$$

and with the breaking condition $\sigma r^3 \sim \Gamma_b$ we find

$$\eta \sim \sigma^{-(s-1)/3} \sim \sigma^{-2/3} \sim \dot{\gamma}^{-2/5} , \tag{16}$$

where on the rhs the gel is compact for $r > \xi$ and we expect $s = d = 3$ because flow inside a space-filling gel should be screened. Shear thinning in a power-law form has been measured for colloidal suspensions with attractive particle interaction, yielding a power-law exponent for $\eta$ vs $\dot{\gamma}$ of about $-1/3$ [19,25].

The one regime which we have not addressed is where the work hardening to brittle transition occurs within the regime of isolated fractal clusters. This is difficult because one needs to model clusters which are significantly reinforced elastically by the presence of loops and which are fractal rather than space filling as above. Some attempts toward this have been described in Ref. [18].

In summary we propose a model of aggregation and fragmentation for colloidal suspensions in shear flow. We contemplate two regimes distinguished by the cluster-volume fraction, which is determined by the shear rate. In the large-shear-rate regime, i.e., small cluster-volume fraction, clusters are deformed under shear and we estimate the range of material parameters for which a cluster breaks before its branches touch each other. Via a cluster-breaking condition the cluster size is related to the shear rate. The viscosity is related to the cluster size and structure via the hydrodynamical screening of the interior fluid of the cluster and the breaking condition, yielding $\Delta\eta \sim \dot{\gamma}^{-(3-D)/3}$. In the large-cluster-volume-fraction regime, we have a crossover from work hardening to brittle behavior at a yield stress $\sigma_y \sim \psi^{2/(3-D)}$. Above this stress the balance between rupture and local elastic recovery leads to a shear thinning rheology with $\eta \sim \sigma^{-2/3}$ in agreement with experiment. This creeping-gel regime obtains until the cluster size falls below that for overlap and the isolated cluster, high shear rate regime takes over.

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