Time Scaling Regimes in Aggregation of Magnetic Dipolar Particles: Scattering Dichroism Results

Sonia Melle,[1] Miguel A. Rubio,[1] and Gerald G. Fuller[2]

[1]*Departamento Física Fundamental, UNED, Senda del Rey 9, Madrid 28040, Spain*
[2]*Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025*

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We report experimental results on the aggregation kinetics in magnetorheological fluids subject to a constant uniaxial magnetic field using the technique of scattering dichroism. We show that the number of aggregated particles displays a long-time power-law dependence with exponents that correspond to two different aggregation regimes. These regimes coincide with 3D and 1D-like aggregation. We also derive the values of both time exponents for the number of aggregated particles.

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The irreversible aggregation of particles has been the subject of wide interest over the last decades, both from a fundamental point of view, e.g., the study of reaction and diffusion limited aggregation of particles as a pattern formation problem (see [1] and references therein), and because of its practical applications. Magnetorheological (MR) fluids are colloidal suspensions of particles that acquire a magnetic dipole moment under the action of a magnetic field. After applying a magnetic field these suspensions experience a dramatic change in their mechanical and optical properties due to the aggregation of the particles, which form clusters of macroscopic size usually in the form of linear chains oriented in the direction of the field. This aggregation process is irreversible as long as the field is maintained: the chains grow longer and do not break as long as the magnetic field is present. Because of its irreversibility, the aggregation of magnetic dipolar particles provides an excellent model system for studies concerning the kinetics of irreversible cluster-cluster aggregation processes [2,3].

Several experimental and theoretical studies have focused on the kinetics of irreversible aggregation. The aggregation problem is usually described in terms of the *cluster size distribution*, $n_s(t)$, which is the number of clusters of size s per unit volume present in the system at time t, the density of clusters at time t, $n(t)$, and the *average cluster size*, $S(t)$. These are usually defined as

$$n(t) = \sum_s n_s(t); \qquad S(t) = \frac{\sum_s s^2 n_s(t)}{\sum_s s n_s(t)}.$$

A particularly interesting experimental finding in diffusion limited aggregation of suspended dipolar particles is the appearance of time invariant regimes in which $S(t) \sim t^z$. For instance, Fraden *et al.* [4] conducted a videomicroscopy study of aggregation in dielectric dipolar particles, obtaining $z = 0.60 \pm 0.02$. Also, videomicroscopy experiments of aggregation by magnetic dipolar particles yielded exponents ranging between 0.45 and 0.75 [5]. Moreover, the long-time coarsening regime of chains to form columns has also been experimentally investigated in dielectric particle suspensions, yielding an exponent $z \sim 0.4$ [6].

Chain aggregation is usually interpreted in the framework of the kinetics of the cluster size distribution, which is governed by the Smoluchowski equation [7] with a reaction kernel $K(s, s')$, giving the rate at which clusters of sizes s and s' join to form clusters of size $s + s'$.

$$\frac{dn_s(t)}{dt} = \sum_{i+j=s} K(i,j) n_i(t) n_j(t) - n_s(t) \sum_{i=1} K(s,i) n_i(t).$$

In the absence of hydrodynamic interactions, numerical studies [2,8] of rodlike cluster aggregation show a power-law behavior in $S(t)$ with $z = 1/2$, which differs from the values measured experimentally ($z \sim 0.6$) [4,5]. This discrepancy has been explained recently [8] by realizing that hydrodynamic interactions cause anisotropic diffusion of the rods along and normal to their axes and induces logarithmic corrections in the diffusion coefficient dependence on the cluster size [9]. Monte Carlo simulations incorporating this assumption [8] coincide remarkably well with the experimental results cited above.

Of particular interest here is the existence of a one-dimensional like (1D) aggregation regime found at long times in numerical simulations at large volume fractions [2,8] yielding $z \sim 1/3$. This regime was qualitatively observed by Fraden *et al.* [4] although, to our knowledge, no quantitative experimental measurement of the exponent in this regime has been reported.

All of these studies are focused on the behavior of the average chain length $S(t)$, which can be obtained in experiments by means of, e.g., light scattering or videomicroscopy techniques. However, other optical properties of the suspensions may be considered of interest, both from an application point of view and as tools for obtaining information on the state of aggregation of the suspensions. For example, studies on birefringence of ferrofluids [10], transmittance of electrorheological suspensions [11], and dichroism of MR suspensions [12] have been performed also.

Here we report on experimental scattering dichroism (SD hereafter) studies of the aggregation process in suspensions of magnetic dipolar particles under a uniaxial magnetic field. The SD technique yields a measurement of the number of aggregated particles, which is a useful indicator of 1D-like aggregation regimes. We show that two time invariant regimes appear depending on the values of the volume fraction, ϕ, and magnetic field, H. At low ϕ, the time exponent value is 0.43, while at large ϕ the exponent changes to 0.29. It is shown also that these exponents correspond to the 3D and 1D-like aggregation regimes, respectively, when the number of aggregated particles is measured.

The experiments were performed using aqueous suspensions of superparamagnetic particles, with mean diameter $2a = 0.9 \pm 0.3$ μm, manufactured by Prolabo (M1-180/20). All of the length scales discussed hereafter are made dimensionless with the particle diameter. The particles are formed by magnetite crystals (diameter 1–20 nm) dispersed in divinylbenzene monomers and polymerized by the emulsion process. Their surface is composed of carboxylic acid groups with a surfactant (sodium dodecyl sulfate) coating layer to stabilize the suspension. The magnetic content of the particle is 24.8% and a saturation magnetization of 21.1 emu/g. The fluid sample is sandwiched between two circular quartz windows held in place by a delrin attachment and separated by an annular delrin spacer 100 μm thick. All experiments were performed at a temperature of $T = 282 \pm 1$ K. The sample was located in between two electromagnets, and we used constant uniaxial magnetic fields up to 25 kA/m in the plane perpendicular to the optical path. The magnetic field spatial variation was smaller than 3% over the whole size of the sample. A full description of the SD technique can be found in [13], and the implementation here used has been reported in [12]. The magnetic field is applied by means of a Kepco BOP20-10M power amplifier, driven by a HP-FG3325A function generator. The field is applied in square pulses of appropriate duration, the rise time of the amplifier output being 60 μs. Typically, the SD signals are averaged over different magnetic field pulses on a given sample, taking care that the time separation between pulses is long enough for the formed chains to disappear, and over different samples.

When a uniaxial magnetic field, $\vec{H}$, is applied to the suspension, the field induces a magnetic dipole moment in the particles $\vec{m}$. A key dimensionless parameter is the ratio between the magnetic energy for two particles in contact and the thermal energy, $\lambda = \mu_0 m^2/16\pi a^3 k_B T$, where μ_0 is the vacuum magnetic permeability, and k_B the Boltzmann constant. For the range of fields used here [14] $[0.62 \leq H(\mathrm{kA/m}) \leq 24.8]$, $3.6 \leq \lambda \leq 1310$. Hence, the magnetic interaction will dominate over thermal fluctuations and the aggregation of particles is irreversible. An equilibrium dimensionless distance between thermal energy and dipolar interaction energy may be defined as $R_1 = \lambda^{1/3}$. Consequently, if the average dimensionless distance between particles at a given time is higher than R_1 the aggregation process can be considered as being limited by diffusion.

Because these chains have a preferred orientation the suspension exhibits optical anisotropy by way of a complex refractive index tensor, due to the polarization dependent scattering from oriented aggregates. Since the length scale of the scattering objects is larger than the laser wavelength, the SD, $\Delta n''$ (anisotropy of the imaginary part of the refractive index) will be larger than the induced birefringence $\Delta n'$ (anisotropy of the real part) [15]. Assuming that the chain can be represented as a long circular cylinder of length L and radius a, Mie's approximation for light scattering [15] shows that the SD in the forward direction generated by such a chain is

$$\Delta n''(L) = \frac{2L}{k^2}\left(\mathrm{Re}[T_2(\theta = 0)] - \mathrm{Re}[T_1(\theta = 0)]\right), \quad (1)$$

where k is the wave vector of the incident light, and $T_i(\theta = 0)$ are functions that depend only on k, a, and the isotropic refractive indexes of solvent and particles, and θ is the azimuthal angle in cylindrical coordinates aligned with the chain axis. Assuming that the scattered light from different chains is incoherent, the total SD is just the sum of the contributions from all chains located within the measurement volume. This means that $\Delta n'' \propto \frac{2}{k^2}\sum_j L_j$, and, therefore, the SD is proportional to the number of particles that are aggregated into chains, N_a, within the measurement volume. We performed videomicroscopy experiments at low ϕ that show chains with a cross section of only one particle and, therefore, support the interpretation that $\Delta n'' \propto N_a$ [16].

Figure 1 shows the average of 15 magnetic field pulses at $\phi = 0.105$ and $H = 12.4$ kA/m. In the absence of a magnetic field, the particles are not aggregated and the SD is zero, corresponding to an isotropic medium. According to [8], the average separation between neighboring aggregates can be estimated to be $\overline{R} \sim (S/\phi)^{1/d}$, where d is

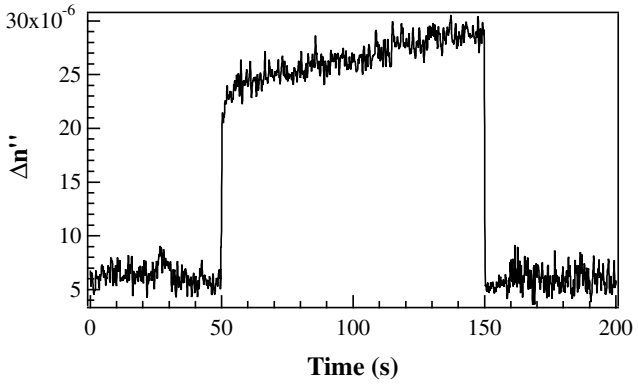

FIG. 1. SD response to a square magnetic field pulse at $\phi = 0.105$, $H = 12.4$ kA/m, averaged over 15 realizations.

the dimension of the system. When the magnetic field is applied, the dichroism rapidly increases due to the formation of chainlike structures aligned in the direction of the field. This is to be expected, because for these values of ϕ and H, the initial average distance between particles, $\overline{R}_0 \sim (1/\phi)^{1/d} = 2.1$, is smaller than $R_1 \sim 9$ and, therefore, initial fast magnetically driven aggregation should occur. Typically, following this fast initial regime a slow aggregation regime appears in which the SD increases slowly. When the magnetic field is switched off, the SD decays to zero.

Figures 2 and 3 show representative plots of $\Delta n''(t)$ at different values of ϕ and H. Each curve represents an average of over 10 magnetic field pulses. Power-law behavior ($\Delta n'' \propto t^{\beta}$) at long times appears in all cases. However, we have found two different values of β appearing systematically at experiments performed in different conditions.

Figure 2 corresponds to experiments performed at low ϕ; specifically $\phi = 0.0005$ and $H = 12.4$ kA/m (a), and $\phi = 0.005$ and $H = 0.62$ kA/m (b). The initial aggregation is clearly slower than in the case of Fig. 1. Because at these low volume fractions $\overline{R}_0 \gtrsim R_1$ the aggregation process is mainly diffusion limited from the very beginning. The exponent values obtained for the long-time power-law regime are $\beta = 0.440 \pm 0.008$ in (a) and $\beta = 0.42 \pm 0.01$ in (b).

Figure 3 shows plots of $\Delta n''(t)$ at high volume fraction, $\phi = 0.105$, for $H = 24.8$ kA/m (a), $H = 12.4$ kA/m (b), and $H = 3.1$ kA/m (c), respectively. In all cases fast initial aggregation is seen, which is caused by the initial average distance, $\overline{R_0} \sim 2.1$, being smaller than R_1, now being $5 \leq R_1 \leq 11$. Power-law fits at long times give $\beta = 0.29 \pm 0.01$ (a), $\beta = 0.290 \pm 0.006$ (b), and $\beta = 0.280 \pm 0.004$ (c), which are distinctly different from the values at low ϕ.

The different kinetic regimes appearing in dipolar particle aggregation experiments can be qualitatively understood by considering the interplay between several characteristic length scales. As argued above, if $\overline{R_0} > R_1$, as is the case in the experiments in Fig. 2, an initial diffusion driven aggregation regime should appear. Now, should this diffusion driven regime be 3D or 1D-like? The aggregation kinetics in the 1D-like regime involves mostly small clusters that follow linear paths in between parallel long chains to finally aggregate at a chain end when they reach it [2,4,8]. This observation can be translated into a geometrical condition for the 1D-like regime to appear, $S > \overline{R}$, so that the small cluster is effectively seeing chains that are longer than the average chain separation. Therefore, if the aggregation is initially diffusion driven a 3D aggregation regime should be expected. At long times this regime may cross over to 1D-like aggregation [because $\overline{R(t)} \sim (S)^{1/d}$], or lateral aggregation of chains into columns may start [17].

On the other hand, if $\overline{R_0} < R_1$, as is the case in the experiments in Fig. 3, the initial regime should be field driven. In this case, the lateral interaction between parallel short chains that overlap along the chain axis will be repulsive [17], provided $\overline{R_0} \geq 2$. Therefore, the aggregation goes on mainly by head to head field-driven aggregation of chains placed along the same line. Furthermore, as time goes on, the average distance between chains placed along the same line will grow like S and, after a short time, the average magnetic interaction energy between chains placed along the same line will drop below $k_B T$. Consequently, a crossover to 1D-like diffusion-driven aggregation should occur [18].

Now let us consider the exponent values. The SD is $\Delta n''(t) \propto N_a(t) = N - n_1(t)$, where N is the total number of particles and $n_1(t)$ is the time-dependent number of isolated particles. Now, the Smoluchowsky equation for $n_1(t)$, assuming irreversible aggregation, reads

$$\frac{dn_1(t)}{dt} = -n_1(t) \sum_{i=1} K(1,i) n_i(t) . \qquad (2)$$

The right-hand side (rhs) represents the rate at which isolated particles "disappear" by aggregation with chains

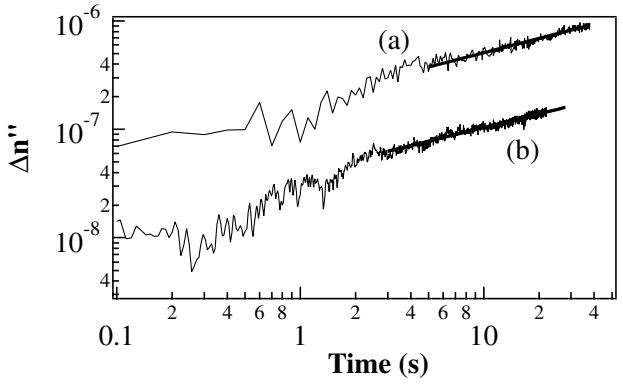

FIG. 2. (*a*) $\Delta n''(t)$ at $\phi = 0.0005$, $H = 12.4$ kA/m; $\beta = 0.440 \pm 0.008$. (*b*) $\Delta n''(t)$ at $\phi = 0.005$, $H = 0.62$ kA/m; $\beta = 0.42 \pm 0.01$.

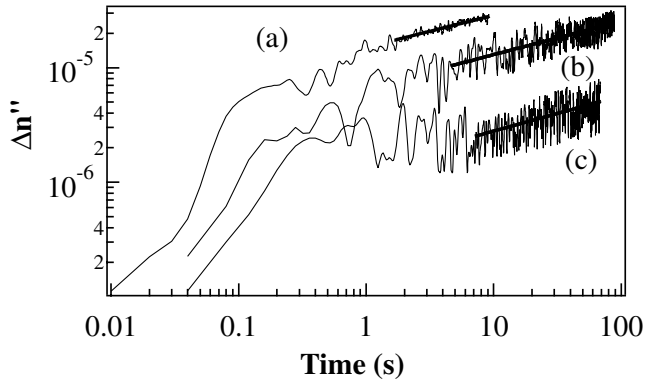

FIG. 3. $\Delta n''(t)$ at $\phi = 0.105$. (*a*) $H = 24.8$ kA/m; $\beta = 0.280 \pm 0.004$. (*b*) $H = 12.4$ kA/m; $\beta = 0.290 \pm 0.006$. (*c*) $H = 3.6$ kA/m; $\beta = 0.29 \pm 0.01$. (*b*) has been up-shifted by a factor of 3 to avoid plot overlapping.

of any length. In a crude approximation the sum in the rhs can be represented as a time-dependent inverse of the *lifetime* of a free particle $\tau(t)$. In 2D and 3D, the *lifetime* $\tau(S)$ is precisely the characteristic time for a single aggregation event evaluated in Ref. [8] with the only difference that here the diffusion coefficient D is the one corresponding to an isolated particle, i.e., $\tau(S) \propto 1/(Dn) \propto S/D\phi$. Assuming that the evolution of S is still ruled by the aggregation kinetics of large chains, the dependence $t(S)$ is known [see Eqs. (1.14) and (1.15) of Ref. [8]], and the preceding equation can be written in terms of S and integrated. Therefore, we arrive at

$$\frac{dn_1(S)}{dS} \sim -D\,\frac{2\ln S - 1}{(\ln S)^2}\,n_1(S)\,, \tag{3}$$

with a possible coefficient of order unity in the rhs. If D is small, which is usually the case with micron sized particles, it is easy to show numerically and analytically, that there is a large range in t in which $N_a(t) \propto t^{\beta}$, with an *effective* time exponent $\beta \approx 0.45$, which coincides remarkably well with the experimental value.

In the case of $d = 1$, and reasoning along the same lines supplied in Ref. [8], $\tau(S) \simeq \overline{R}^2/D$, where $\overline{R} \simeq S(t)/\phi$, and D is again the isolated particle diffusion coefficient. Repeating the same procedure as in the previous case, we arrive again at Eq. (3), with the only change being that the coefficient 2 in the numerator becomes a 3. Again, if D is small enough, $N_a(t)$ has a large range in t in which it behaves as a power law with an *effective* time exponent $\beta \approx 0.29$, which again coincides remarkably well with the experimental value.

In summary, we have shown that the SD technique is a valuable tool for the study of the aggregation kinetics of dipolar micron sized particles. The SD is proportional to the number of particles aggregated into chains and, therefore, it is complementary to techniques more adequate to measure the average chain length, such as light scattering or videomicroscopy. Turning to the aggregation kinetics, we have found two power-law regimes that correspond to the more commonly encountered 3D aggregation and 1D-like long-time aggregation in more concentrated suspensions. Both exponent values can be predicted considering the evolution equation for the density of isolated particles, within the approximations outlined in Ref. [8].

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[17] See, for instance, E. M. Furst and A. P. Gast, Phys. Rev. E **62**, 6916 (2000), and references therein. A calculation of the lateral interaction between a chain and a single particle located at the chains equatorial plane shows that for λ equal to 100 and 1300 the effective repulsive energy barrier is higher than $k_B T$ for chain lengths up to 20 and 70 particles, respectively.
[18] In the experiments reported here, lateral aggregation that would give rise to column formation does not play a significant role. Indeed, in experiments performed imposing the field during much longer times, lateral aggregation has been detected through a strong decrease in the dichroism signal, due to the lowering of the anisotropy of the aggregates.