

Depolarized dynamic light scattering from optically anisotropic reaction-limited aggregates

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We have used small-angle depolarized dynamic light scattering in conjunction with aggregates of (rather unique) optically anisotropic spherical particles. Pure rotational diffusion is observed, and all the relevant information on a reaction-limited aggregation has been derived as a function of time. We show that the asymptotic form of the cluster mass distribution is actually attained during the very early stages of the process. The value of the exponent τ characterizing the low-mass portion of the cluster distribution is derived.

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Cluster mass distribution is one of the most important issues in colloidal aggregation, and limited work has been produced so far, especially in connection with the particularly interesting case of reaction-limited cluster aggregation (RLCA) [1–5]. In the present work we have taken advantage of rather unique partially crystalline spherical particles that form clusters possessing intrinsic optical anisotropy. We present a depolarized dynamic light scattering (DDLS) study of the time evolution of cluster mass distribution during the aggregation process according to RLCA. The main emphasis of this work is to show *when* the mass distribution attains its scaling, time-independent form. The exponent τ characterizing the low-mass portion of the cluster size is thus determined under truly asymptotic conditions. The fractal dimension d_f of the aggregates and the typical cutoff mass m_c are also directly derived from the DDLS data as a function of time. We show that the evolution of all these quantities is in agreement with theoretical predictions once the cluster mass distribution has reached its steady-state form.

DDLS is much more efficient than conventional dynamic light scattering in providing size distributions of polydisperse samples. In fact, at small angles it probes *rotational* diffusion, which has a strong a^{-3} dependence (a being the particle radius), at variance with the weak a^{-1} dependence of the *translational* diffusion probed by polarized scattering. Moreover, DDLS from random clusters is an incoherent process and thus does not tend to overweigh large aggregates. The potentialities of this attractive technique can be fully exploited only by using partially crystalline particles having a low refractive-index mismatch with the solvent.

We find that the depolarized field correlation function $I_{VH}(t)$ always exhibits a stretched-exponential (SE) behavior at large values of the delay t , as expected on the basis of straightforward calculations. From the characteristic exponent of the SE and from its decay time constant we derive the fractal dimension d_f and the typical cluster mass m_c . Furthermore, from the short-time-delay analysis (first cumulant) of I_{VH} we derive the value of the

exponent τ characterizing the low- m behavior of the cluster mass distribution $N(m) \sim m^{-\tau} \exp(-m/m_c)$, where m is the number of monomers in a cluster and m_c is a time-dependent cutoff mass. The relevance of the actual value of τ can hardly be overemphasized. Indeed, should τ be larger than 2, all the static scattering data and therefore the estimates of the fractal dimension should be severely revised [6].

The correlation functions of the vertically (V) and horizontally (H) polarized field scattered by optically anisotropic particles for a vertical incident polarization are well known [7]. When such particles (monomers) aggregate into a cluster, their axes will in general be randomly oriented. Consequently the scattered field correlation functions for a cluster become

$$I_{VH}(q, t) \propto m (\Delta n)^2 \exp(-D_m q^2 t) \exp(-6\Theta_m t), \quad (1)$$

$$I_{VV}(q, t) \propto m^2 (n_p - n_s)^2 P(q) \exp(-D_m q^2 t) + \frac{4}{3} I_{VH}(q, t), \quad (2)$$

where q is the transferred momentum, n_p is the average monomer refractive index, n_s is the solvent refractive index, Δn is the intrinsic anisotropy of a monomer, D_m and Θ_m are the cluster translational and rotational diffusion coefficients, and $P(q)$ is the cluster form factor. Recalling the peculiar fractal nature of the clusters ($m \propto a^{d_f}$), their diffusion coefficients become $D_m = D_m^{-1/d_f}$, $\Theta_m = \Theta_m^{-3/d_f}$, where D and Θ are the monomer translational and rotational diffusion coefficients. We point out that while I_{VH} is completely incoherent (proportional to m), I_{VV} contains also a coherent term (proportional to m^2) which depends on the refractive index mismatch with the solvent.

The sample is made of an aqueous suspension of FEP, a polytetrafluoroethylene copolymer, graciously given to us by Ausimont (Bollate, Italy). The colloidal particles are spherical with a radius $a_0 = 45.8 \pm 3$ nm, as determined by polarized dynamic light scattering (DLS) and have $n_p = 1.3536$ and $\Delta n \simeq 10^{-2}$. The properties of these particles are unique. In fact, by judicious choice of the

solvent, the particle average index of refraction can be matched, while still retaining a strong depolarized scattering. They have been used for a number of relevant studies [8–10]. We found that the particles aggregate when salt is added to the solution. The monomer concentration was chosen high enough to make the reaction proceed at a reasonable rate, in spite of the low salt content necessary to produce RLCA. At the same time an upper bound to the concentration was imposed by the necessity to avoid close packing during the typical run duration. A volume fraction of 0.5% and NaCl 26-mM salt molarity were found to be appropriate. The duration of a run was typically 24 h, and measurements were taken every 2 h.

The sample was index matched by adding a 17.5% weight fraction of glycerol. Since $n_p - n_s \approx 0$, I_{VV} and I_{VH} are of the same order of magnitude. When collecting I_{VH} , stray leakage contributions of the coherent term are therefore greatly reduced.

In order to have the decay of I_{VH} controlled solely by the rotational diffusion, the condition $(q^2 D_m / 6\Theta_m) \ll 1$ must be satisfied [see Eq. (1)]. This implies that $(qa_{\max})^2 \ll 1$, where a_{\max} is the largest size to be attained by the clusters during the run. We selected $a_{\max} = 10a_0$, which roughly implies that the largest cluster should not contain more than 100 monomers. Accordingly, we have selected a scattering angle of 3° . Due to the rather small scattering angle, a 50-mm-long flat window cell was used, in order to eliminate stray light contributions from spots on the entrance and exit surfaces. The cell was cylindrical in shape, and filled so that no bubbles were left in the sample volume.

A crucial undesirable effect perturbing aggregation processes is the presence of gravity. Differential sedimentation causes clusters to drift with a size-dependent velocity. As a consequence the reaction rates are not controlled by diffusion and sticking probability only, as contemplated by the theory. In order to create an “effective” gravitation-free condition, we have kept the cell rotating around the horizontal axis at four rotations per hour. During measurements, however, the cell was kept stationary.

The raw data consist of a sequence of correlation functions taken at different times during the aggregation. The correlation function I_{VH} consists of a superposition of contributions due to clusters of different sizes, weighted by the cluster mass distribution $N(m)$. If we neglect the translational diffusion, we have

$$I_{VH}(t) \propto \frac{\sum_{m=1}^{\infty} m [m^{-\tau} \exp(-m/m_c)] \exp(-6\Theta m^{-3/d_f} t)}{\sum_{m=1}^{\infty} m [m^{-\tau} \exp(-m/m_c)]} \quad (3)$$

For large values of the delay time t , $I_{VH}(t)$ can be approximated (via the steepest-descent method) with a stretched exponential function [11]: $I_{VH}(t) \propto \exp[-(t/T_{SE})^\alpha]$, where

$$\alpha = d_f / (3 + d_f), \quad (4)$$

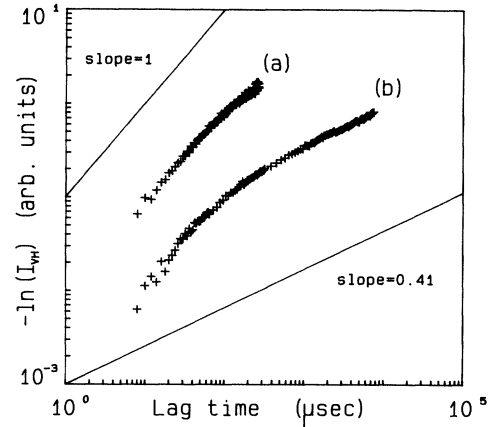


FIG. 1. Field correlation functions I_{VH} taken respectively 5 min (a) and 1085 min (b) after the aggregation process started. Notice that $-\ln[I_{VH}(t)]$ is plotted in a log-log scale as a function of delay. In this plot an ideal stretched exponential decay, $\exp[-(t/T_{SE})^\alpha]$, is a line with slope α . Both curves for short delay have a slope close to 1 and therefore the decay is nearly a simple exponential. However, for large delays, curve (b) attains a slope $\alpha=0.41$, thus indicating a SE behavior. The solid lines with slopes 1 and 0.41 are plotted for direct comparison with the curves.

$$T_{SE} = \frac{m_c^{3/d_f} d_f}{6\Theta} \left[\frac{3+d_f}{3} \right]^{-(3+d_f)/d_f} \quad (5)$$

Consequently from the experimentally determined values for these two variables, both the fractal dimension and the cutoff mass can be derived, once the monomer rotational diffusion coefficient Θ is also determined [12].

We report in Fig. 1 two correlation functions taken at the early stage [curve (a)] and at an intermediate stage [curve (b)] of the aggregation. Notice that $-\ln(I_{VH})$ is reported on a log-log plot as a function of delay. Both curves at short delay have a slope close to 1 and therefore the decay is nearly a simple exponential. For large delays, however, the slope decreases and SE behavior sets

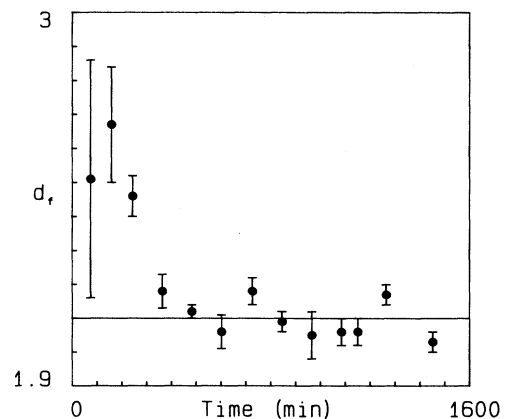
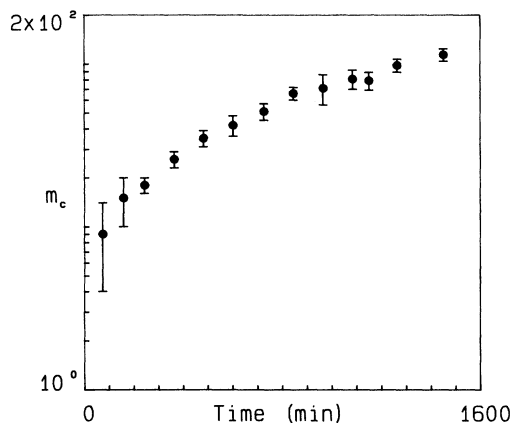


FIG. 2. The cluster's fractal dimension plotted vs the aggregation time. The solid line, corresponding to the typical RLCA value $d_f=2.1$, is also shown for convenience.


 FIG. 3. Time evolution of the cutoff mass m_c .

in. It should be noticed that the asymptotic slope value gives the SE characteristic exponent α , and for curve (b) $\alpha=0.41$. Incidentally, a similar behavior has also been observed for I_{VV} functions obtained from aggregating silica colloids [3].

The time evolution of the fractal dimension d_f and of the cutoff mass are reported in Figs. 2 and 3, respectively. The fractal dimension is found close to 2.1, the typical value reported for RLCA [3,4]. Actually, the first three data points at the earliest stages are somewhat off and affected by large errors (see later on the discussion on the early stages of the aggregation).

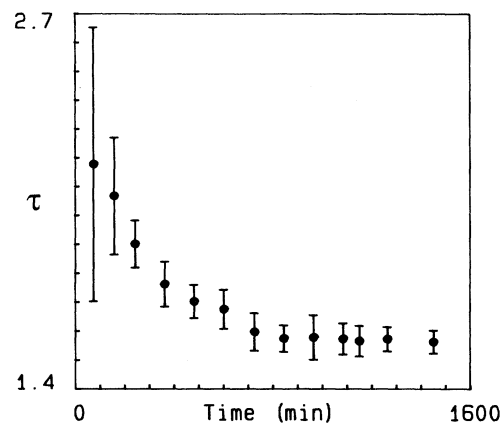
Figure 3 shows that the cutoff mass (which is proportional to the weight average cluster mass) has a rapid initial increase, followed by a slower rate of growth, compatible with an exponential growth. Similar results have been already reported for RLCA dynamics in conjunction with polystyrene spheres [4].

Additional and important information can be extracted from the small delay portion of the correlation function. The first cumulant is given by

$$\Gamma_{VH} = - \left. \frac{d}{dt} \{ \ln [I_{VH}(t)] \} \right|_{t=0}. \quad (6)$$

Γ_{VH} can be easily evaluated from I_{VH} at small delay times. From Eqs. (3) and (6) we can derive the dependence of Γ_{VH} on the parameters τ , d_f , m_c , and Θ :

$$\Gamma_{VH} = \frac{\sum_{m=1}^{\infty} m [m^{-\tau} \exp(-m/m_c)] 6 \frac{\Theta}{m^{3/d_f}}}{\sum_{m=1}^{\infty} m [m^{-\tau} \exp(-m/m_c)]}. \quad (7)$$


 FIG. 4. The exponent τ (characterizing the low- m power-law behavior of the mass distribution) vs the aggregation time.

Since we measure Γ_{VH} and we have already determined d_f , m_c , and Θ , we can insert these values into Eq. (7) and numerically solve for τ .

A plot of τ vs aggregation time is shown in Fig. 4. Notice that at the early stages the value of τ is affected by large error bars. We believe that this is due to the fact that the expression $N(m) \sim m^{-\tau}$ is a poor representation of the polydispersity at the early phases of the aggregation. Consequently, the forceful fitting with such an expression yields large error bars for τ . Later on, the data approach the value 1.5, and the error bars are substantially reduced. This result confirms the values reported in previous papers [1,2,4,5]. At variance with the techniques used in some of these works, however, DDLs neither requires sample manipulations nor sophisticated algorithms for the data analysis, the interpretation of the results being instead rather straightforward.

We point out that, by comparing Figs. 3 and 4, both curves approach the predicted theoretical behavior approximately at the same time. Consequently, we conclude that the exponential growth sets in only after the transient that is necessary to let the cluster mass distribution attain its asymptotic form. Incidentally, Figs. 3 and 4 also show that the cutoff mass m_c should roughly exceed 50 monomers.

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