Transition from Semiorder to Disorder in the Aggregation of Dense Colloidal Solutions

Marina Carpineti and Marzio Giglio
Dipartimento di Fisica, Università di Milano, via Celoria 16, Milano 20133, Italy

(Received 28 December 1992)

By using low-angle static light scattering we study the aggregation of dense colloidal solutions under diffusion limited (DLCA) and reaction limited cluster aggregation (RLCA) conditions. While it has been recently shown that DLCA surprisingly leads to a semiordered state, we show here that any order is lost under RLCA conditions. While in the first case a scattering peak at finite wave vector q is observed, in the second the scattered peak always occurs at $q=0$.

PACS numbers: 82.70.Gg, 05.40.+j, 64.75.+g, 82.70.Dd

Colloidal solutions can be made unstable by decreasing the repulsive interaction between the solute particles to the extent that upon encounter the probability that a bound cluster is formed is finite [1]. Under these circumstances, colloidal monomers undergo Brownian motion until small clusters are formed, and in turn clusters themselves diffuse to form yet larger clusters and so on. Two limiting modes of aggregation have been identified, according to whether the sticking probability is equal to one or close to zero. These modes have been recognized to be endowed of universal character [2–4], and have been named diffusion limited and reaction limited cluster aggregation, respectively (DLCA and RLCA).

Both modes have been intensively studied, but almost invariably in the *dilute* regime. Although theory predicts and experiments show that the two modes are quite different in terms of cluster morphology and kinetics of growth, dilute-regime studies clearly indicate that the two modes share at least one feature in common, namely, that during their growing process the clusters are randomly positioned in space, and no correlation is established between them at any time. In fact, light scattering data invariably show that the structure factor is peaked at $q=0$ where $q=2(2\pi/\lambda)\sin(\theta/2)$, λ being the wavelength of light in the medium and θ the scattering angle.

In a recent study [5], it has been shown that aggregation in *dense* colloidal polystyrene spheres solutions does produce some kind of ordering between the clusters. In fact the scattered intensity distribution displays a pronounced peak at a finite q vector. The position of the peak $q_{\max}$ moves to smaller and smaller values as the reaction proceeds, while the peak intensity increases. Accordingly, the clusters grow by draining material from their immediate neighborhood, thus creating depletion volumes around them. Also, it has been conjectured that they are approximately of the same size, so that the juxtaposition of clusters and depletion regions leads to a density modulation with a wavelength of the order of the clusters' average distance. The data were taken at rather low salt content, so to reduce the sticking probability and hence slow down the reaction. In spite of this, it is likely that the mode of aggregation was still similar to DLCA, since for this regime the cluster size distribution is predicted to be monodisperse, while for RLCA a markedly polydisperse distribution is expected. Similar surprising results have been recently reported for completely different physical systems [6–8].

In this Letter we will show that, again very surprisingly, the spatial ordering in the aggregation of dense colloidal solutions occurs only if the reaction proceeds with sufficiently large sticking probability. If the reaction is initiated at very low salt content, the peak at finite q vectors disappears, and the scattered intensity distribution has the typical shape observed in structureless dilute systems. In order to clearly demonstrate the existence of this transition, runs with samples with the same type of colloid and at the same concentration have been used, the salt content being changed from run to run to vary the sticking probability. Low-angle static light scattering has been used, and the setup is the same as described in Ref. [9]. A parallel beam 8 mm in diameter falls onto a flat window, 2 or 1 mm optical path cuvette, and the scattered light is collected by a lens. A multielement sensor is placed in the focal plane and the individual elements are shaped in the form of concentric annuli, their average radii scaling according to a geometric sequence. Consequently each element collects light scattered at a given angle, and the range of q vectors spans between 3.06×10^{-5} and 2.86×10^{-3} nm^{-1}. The rather generous size of the incoming beam has been chosen so that the number of coherence areas falling onto the smallest sensing element is large enough to reduce the statistical noise below 4% (larger elements are accordingly affected by smaller noise).

The sample consists of a solution of polystyrene spheres 0.019 μm in diameter, provided by Interfacial Dynamics Corporation. The solvent was a mixture of water and heavy water adjusted so as to match the polystyrene sphere density. Differential sedimentation problems are thus avoided. The aggregation was induced by adding $MgCl_2$.

In Fig. 1 a plot of the scattered intensity as a function of q is reported for a run at 6 mM $MgCl_2$ salt content, and $c=8.25\times10^{14}$ cm^{-3} (a factor of 10 higher than in Ref. [5]), corresponding to a volume fraction $\Phi\sim2.96\times10^{-3}$. This curve refers to the terminal time-inde-

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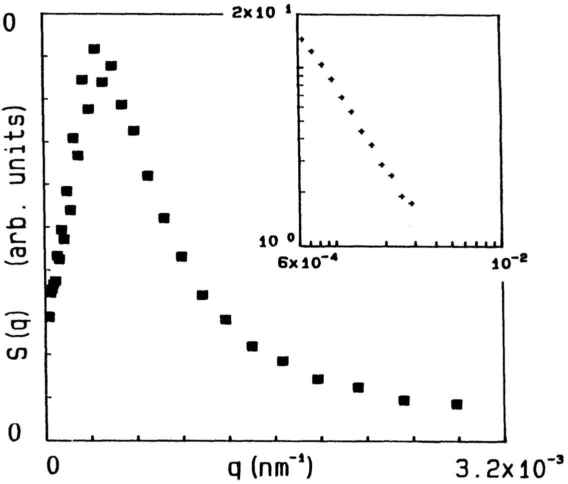

FIG. 1. Scattered intensity distribution at the terminal state for monomer concentration $c_0 = 8.25 \times 10^{14}$ cm^{-3}, and salt content 6 mM MgCl$_2$. The tail of the distribution is shown in a log-log plot in the inset.

pendent state described in Ref. [5]. Because of the higher monomer concentration, this state is achieved in about 20 min. It has been suggested that this state occurs when all the volume available is filled with close-packing clusters, and the sample attains a continuously connected structure. At this stage, the system can still flow, but the speckles in the scattered field appear stationary under visual inspection, thus indicating that the system has attained a close-packed configuration. The finite-q peak indicates that all the clusters have approximately the same size and are fairly regularly spaced, their distance being approximately $q_{\max}^{-1}$.

In order to verify that the terminal state coincides with close packing, we have performed a series of measurements at the same salt content but varying the monomer concentration. Because of its fractal nature, a cluster made up of n monomers of radius R_0 (in this case $R_0 = 0.0095$ μm) has a radius $R_g = R_0 n^{1/d_f}$, where d_f is the fractal dimension. Under close-packing conditions, the volume fraction of the clusters is equal to unity. Consequently, assuming a monodisperse distribution the terminal cluster radius is given by

$$R_{\max} = \frac{R_0}{\frac{1}{3}(4\pi c_0 R_0^3)/(3-d_f)}, \tag{1}$$

which, if $d_f \cong 2$, assumes the simple form $R_{\max} \approx 1/4c_0R_0^2$.

In Fig. 2 we plot the terminal $q_{\max}$ value as a function of c_0. The solid line represents the curve $q_{\max} = AR_0^2c_0$ with $A = 6.0$, the best fit of the experimental points. It is worth pointing out that in spite of the very rudimentary calculation, the numerical agreement between the data and the theoretical line is surprisingly good taking $q_{\max} = 1/R_{\max}$. With the assumption that the terminal state is made of nearly equal size, close-packing clusters seem therefore quite tenable. It should be mentioned that similar calculations have already been presented for gels generated by aggregation of silica colloids [10]. As indicated in the paper, these gels exhibit a fractal dimension equal to 2.1, a value typical of RLCA. No finite-q peak was observed during the evolution of the reaction, and the terminal scattered intensity distributions at gelation consistently exhibit no structure. We felt it was interesting to investigate the scattered intensity distribution in the polystyrene sample at reduced salt content, so to approach the RLCA mode in order to prove that the very same sample could be switched between a structured and a nonstructured terminal configuration just by operating on the aggregation conditions.

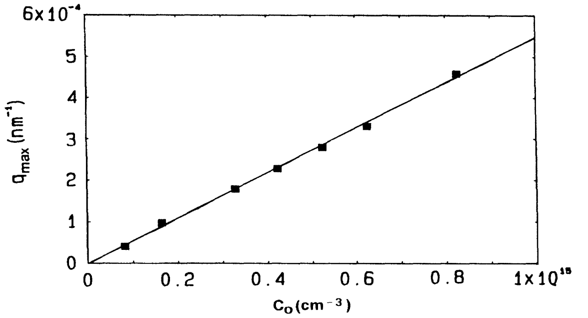

FIG. 2. Monomer concentration dependence of the terminal-state scattering peak position. The data do confirm that the terminal state is due to close packing of colloidal fractal clusters.

We report in Fig. 3 a plot of the scattered intensity at the terminal stage of the aggregation for the same sample

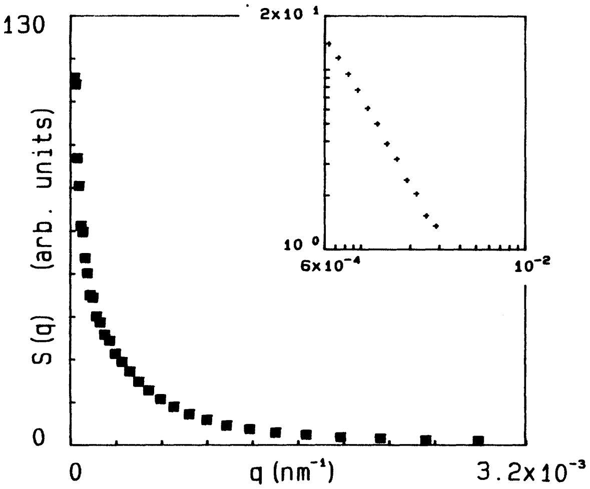

FIG. 3. Scattered intensity distribution at the terminal state for the same monomer concentration of Fig. 1, but salt content 2 mM of MgCl$_2$. The peak at finite wave vector has disappeared. The behavior in the tail (shown in the inset) is the same as in Fig. 1.

of Fig. 1, but with a salt content of 2 mM $MgCl_2$. Because of the reduced salt content, the time scale is now much slower and the terminal state is reached after about 54 h. Strongly at variance with Fig. 1, the curve no longer shows a peak at finite q. Also, although not shown here, during the entire process the curves do show a rolloff, but peaks like those in Fig. 1 are never observed. The lack of the scattering peak mirrors the lack of a well-defined wavelength for the density modulation, and therefore it strongly suggests that the sizes of the clusters and of void spaces are widely distributed. It should be emphasized that both in Fig. 1 and in Fig. 3 the sample turbidity is very high, and typically sample attenuation is of the order of 60%. In order to ascertain the influence of multiple scattering, the measurements have occasionally been performed with a 1 mm optical path cell. Very minor changes in the actual shape were observed, and therefore we claim that the conclusions drawn here are not affected by the presence of multiple scattering.

By a direct comparison between Fig. 1 and Fig. 3 it can be noticed that both curves merge at high q onto two asymptotic power-law lines (see insets in both figures). If one ignores slight changes between the actual values of the exponents (1.9 and 2.1, respectively), the two lines are numerically very close, and the data are virtually superimposable. This implies that if slight changes in the fractal dimension are disregarded, the two types of aggregates appear very much the same when examined on the scale of their finer texture.

No peak is observed in Fig. 3, but one could argue that in this final state a peak might possibly exist in a much lower range of q values than those explored in this measurement. In fact, the mass distributions for DLCA and RLCA are so different that the characteristic final cluster size could be very different in spite of the fact that the monomer concentration is the same in the two runs. We have therefore calculated the size of the cutoff cluster for the RLCA mass distribution under close-packing conditions and for the same monomer concentration as in Fig. 1. We assume, as customary, that the cluster size distribution is given by [11-14]

$$N(n) \approx n^{-\tau}\exp(-n/n_c)\,, \tag{2}$$

where n_c is the cutoff size, the typical largest cluster in the distribution, and for the exponent τ we take the commonly accepted value of 1.5. The following equations yield n_c (and therefore $R_{\max}$) under close-packing conditions:

$$\Phi = c_0 \frac{\sum_{n=1}^{\infty} N(n)V(n)}{\sum_{n=1}^{\infty} nN(n)} = 1\,, \tag{3}$$

where Φ is the volume fraction and $V(n)$ is the volume of the cluster of size n. By solving these calculations with $d_f = 2$ we find

$$R_{\max} \approx \frac{1}{2c_0R_0^2}\,, \tag{4}$$

where we have used the relation $n_c = (R_{\max}/R_0)^{d_f}$.

The actual value for the radius of the cutoff size cluster under RLCA conditions therefore differs by approximately a factor of 2 from the average value for the DLCA case [see Eq. (1)]. Assuming that the reciprocal of this radius gives the position of the hypothetical RLCA peak, one should then definitely observe it within the range of q explored here. Indeed in Fig. 2 the close-packing value of $c_0 = 8.25\times10^{14}$ cm^{-3} corresponds to the point in the upper right corner. The plot shows that even an increase of a factor of 10 in cluster size should be detectable if the close packing would lead to a semiordered structure typical of the DLCA. Of course the calculation is very crude, and it can be relied upon only to a limited extent.

Although the data presented so far refer to two salt concentrations, preliminary measurements have also been performed at intermediate salt content, namely, 2.5, 3, 3.5, 4, and 5 mM of $MgCl_2$. The data show that the transition between peaked curves and nonpeaked ones is fairly smooth. As the salt concentration is reduced, the emergence of a peaked feature becomes progressively less evident, until it is ultimately completely frustrated. All these intermediate salt runs lack the presence of a finite-q peak in the early stages of the aggregation. A peak eventually appears, but as the salt content is reduced its emergence is delayed and the peak position $q_{\max}$ at which it is first observed moves to smaller values. Finally for salt content below 3 mM, the peak never appears. Tentatively, the picture that emerges is the following. In due time all the samples will eventually reach the close-packing condition, and the system will attain a time-independent morphology. On the other hand it is known [15,16] that RLCA conditions will eventually revert to DLCA. The crucial question is whether the time required to cross over to DLCA is short or long compared to the time required to attain the time-independent regime. While the crossover may occur at somewhat larger salt content, under RLCA conditions the transition just does not have a chance to materialize. It would be highly desirable to compare these results with numerical simulations. Unfortunately to our knowledge no new results along these lines are available.

This work has been supported by grants from the Ministero dell'Università e della Ricerca Scientifica (MURST) and the Consiglio Nazionale delle Richerche (CNR).

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