# Crossover region in the aggregation of colloids

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We study by means of dynamic light scattering the region in between the diffusion and the reaction limited regimes of cluster aggregation of colloidal solutions. We also study a simple model based on a suitably modified Smoluchowski equation for the intermediate regime. The comparison of the experimental data with the predictions of the Smoluchowski equation allows a satisfactory interpretation of the experimental data, a clarification of the crossing from the reaction to diffusion aggregation regime, and an estimate of the parameters of the interaction potential between monomers.

The aggregation process of colloidal particles from an initially stable suspension of monomers has been extensively studied in the past years, both experimentally and theoretically [1-8]. The existence of two distinct regimes of aggregation of colloidal particles has been proposed: (i) the slow or reaction limited cluster aggregation (RLCA) and (ii) the fast or diffusion limited cluster aggregation (DLCA). The difference between the two regimes is attributed to differences in the aggregation probability: In RLCA only a small fraction of encounters results in particles aggregation; a strong electrostatic repulsion between colloidal particles creates a high (order of tenth $k_BT$) interparticle potential barrier. In DLCA, the electrostatic repulsion is completely screened by salt and the diffusion of the colloidal particles becomes the only bottleneck in the aggregation process. The two regimes give rise to clusters of different fractal dimension $D$, to different cluster size distributions $c_k(t)$, and to different scaling law for the average cluster size $s(t)$ as a function of time $t$. In RLCA clusters of dimension $D \approx 2.1$ are formed, while $D \approx 1.8$ in the DLCA case. The concentration of clusters containing $k$ monomers $c_k(t)$ obeys the scaling $c_k(t) = [s(t)]^{-2} f(\frac{k}{s(t)})$, where $f(x)$ is a scaling function of the scaled variable $x = k/s(t)$. For DLCA $f(x) \approx e^{-x}$ and $s(t)$ scales with time according to a power law, $s(t) \approx t^z$ with $z$ close to 1, while for RLCA $f(x) \approx x^{-\tau} e^{-x}$ with $\tau \approx 1.5$ and $s(t)$ is an exponential function of time. While for DLCA a good agreement is observed between experimental results, theoretical predictions, and computer simulations, no clear consensus has been established on the RLCA regime as well as on the transition between the two extreme aggregation regimes. In particular, it is not clear if a true RLCA regime exists, i.e., if the RLCA is only an initial regime which crosses to DLCA after a certain aggregation time. Deviations from pure RLCA have been observed recently both in experiments [9,10] and in computer simulations [11-13]. The results indicate a time dependence of the cluster fractal dimension, a transition from the exponential to the power law for the growth of $s(t)$ [9,12], with exponents which depend on the salt concentration. In

order to shed light on the crossing between RLCA and DLCA we perform a series of experiments in a suspension of polystyrene particles where coagulation is induced by the addition of NaCl electrolyte. Changing electrolyte concentration allows us to modulate the height of the potential barrier between monomers. Thus, by varying the salt content we are able to cover the region in which the crossing between RLCA and DLCA is observed [14]. To measure $s(t)$ during the aggregation kinetics we perform dynamic light scattering experiments. We analyze the intensity correlation function by using the same approach as Lin *et al.* [7]. The time correlation function is written as the sum over a set of polydisperse fractal clusters

$$C(q, \Delta t, t) = \frac{\sum\limits_{k=1}^{\infty} c_k(t) k^2 S_k(q) e^{-D_k^{eff} q^2 \Delta t}}{\sum\limits_{k=1}^{\infty} c_k(t) k^2 S_k(q)}, \qquad (1)$$

where $\Delta t$ is the time difference in the correlations we are measuring and $q$ the momentum transfer in the scattering experiment. The normalized cluster structure factor $S_k(q)$ is here given by [15]

$$S_k(q) \approx \frac{\sin[(D-1)\arctan(qR_k)]}{(D-1)qR_k(1+q^2R_k^2)^{\frac{D-1}{2}}}, \qquad (2)$$

where $R_k = R_1 k^{\frac{1}{D}}$ is the radius of the cluster and $R_1$ the monomer radius. In order to take into account rotations of the clusters [7] we use the effective diffusion coefficient $D_k^{eff} = D_1 k^{-\frac{1}{D}}(1 + \frac{1}{2\rho^2})$, where $D_1$ characterizes monomer diffusion and $\rho$ is the ratio of the hydrodynamic radius to the radius of gyration of the cluster, a quantity of the order of one. The cluster distribution we use is $c_k(t) \approx \exp[-\frac{k}{bs(t)}]$, which has been shown to be appropriate for DLCA. In this case the form of the cluster distribution essentially amounts to a cutoff at $k \approx s$, the average number of particles in a cluster [16]. The parameter $b$ is fitted from the experimental data. We measure samples with NaCl concentration $c$ between $0.275M$ and $0.33M$, which show deviations from DLCA, and in the
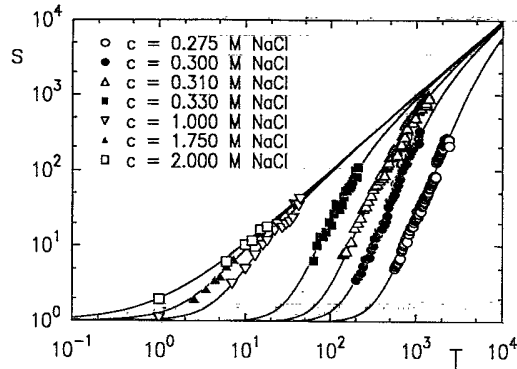
FIG. 1. The measured $s(T)$ for various concentration of the added salt $c$. The lines are calculated from Eq. ( 11), using $\epsilon = 1.4 \times 10^{-7}, 2.0 \times 10^{-6}, 1.2 \times 10^{-5}, 1.6 \times 10^{-4}, 2.7 \times 10^{-2}$, 0.155, and 1, as $c$ increases. The fitted parameters are $p_s = (0.9 \pm 0.3) \times 10^{-2}$ and $b = 0.9 \pm 0.4$.



FIG. 2. The scaling exponent $z$ as a function of the salt concentration $c$. The solid line is derived from the solution of our model.

vicinity of the pure DLCA behavior ($c$ varying from $1M$ to $2M$) [17]. Some typical results for the average cluster size as a function of time are reported in Fig. 1 in a double logarithmic plot. We note that (i) $s(t)$ displays a region with clear power law behavior for all the concentrations, with a well defined exponent $z$; (ii) the onset of the aggregation is strongly concentration dependent; and (iii) the value of the exponent $z$ is concentration dependent. The scaling exponent $z$ decreases toward the DLCA value on increasing the salt concentration, as shown in Fig. 2. The time dependence of $s(t)$ as well as the range of $z$ values reported in Fig. 2 are in perfect agreement with the values obtained in a recent simulation of aggregation in RLCA regime (see Fig. 2 in Ref. [12]). In these simulations, the power law region is preceded by a region of exponential growth, not seen in experiment due to the low scattering during the initial stage of the aggregation process. The experimental evidence we quoted together with the present measurements strongly suggest a crossover from RLCA at short times to DLCA asymptotically.

In the rest of this paper we solve the Smoluchowski rate equations [18] for a simple aggregation kernel and compare the prediction of the model with our data as well as with previously published data. The chosen kernel, despite its simplicity, allows us to describe theoretically the crossover from exponential to power law in the aggregation process and to shed light on the aggregation regimes at late stages. The rate equations take into account the creation of clusters from collisions of smaller ones and their annihilation due to the interactions leading to larger ones and are written

$$\frac{d}{dt} c_k(t) = \frac{1}{2} \sum_{i+j=k} c_i \, K_{i,j} \, c_j - c_k \sum_{j=1}^{\infty} K_{k,j} \, c_j, \qquad (3)$$

where $K_{i,j}$ are the rate constants of the processes of creation and destruction of clusters; their scaling properties give rise to the scaling behavior of the cluster distribution. For DLCA Smoluchowski originally assumed a diffusive motion of the clusters, from which he derived $K_{i,j} = 4\pi N(R_i + R_j)(D_i + D_j) \, p_{i,j}$ with $N$ the concen-
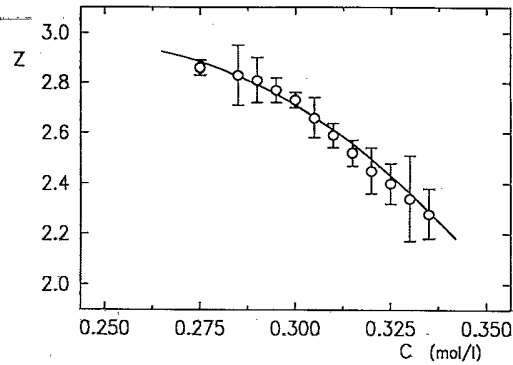
tration of the monomers initially present in the suspension and $D_i$ the diffusion coefficient of a size $i$ cluster. The function $p_{i,j}$ is the sticking probability, or inverse of the so-called stability ratio, defined by [19]

$$\frac{1}{p_{i,j}} = (R_i + R_j) \int_{R_i+R_j}^{\infty} dr \frac{e^{\frac{U_{ij}(r)}{k_B T}}}{r^2}, \qquad (4)$$

where $U_{ij}(r)$ is the interaction potential of two clusters a distance $r$ apart. In the original treatment the interaction was considered to be present only during the collisions, leading to $p_{i,j} = 1$, and the rate of aggregation turned out to be, to a first approximation, equal for any pair of clusters and given by the constant $16\pi R_1 D_1 N$. More generally, lacking the knowledge of the intercluster potential, one can take into account the interaction between aggregates by introducing an average sticking probability $p_s$.

In order to describe the transition region discussed above, we assume the following aggregation kernel:

$$K_{i,j} = \epsilon p_s \quad \text{for} \quad i = j = 1, \quad K_{i,j} = p_s \quad \text{for} \quad i, j \neq 1. \quad (5)$$

Such a kernel is meant to represent in a simple way the fact that small clusters (here described by $i = j = 1$) must meet several times before aggregating while larger clusters have a larger aggregation probability [20,21]. We are led to this assumption for energetic as well as kinetic reasons: (i) The monomer-monomer potential is the result of a short range screened electrostatic interaction plus an attractive dipole-induced dipole term. The effective cluster-cluster potential can be calculated by summing up all the pairs of interacting monomers of the two clusters. Such summing produces a potential with a progressively smaller activation energy barrier (Fig. 3). (ii) Large clusters have smaller diffusion coefficients. This slows down the process of coming in contact, but increases the number of attempts to overcome the barrier. Although the number of contact points between clusters remain small, due to the fractal nature of the aggregates, once two monomers meet, they stay close by for a time with scale with the inverse 3/2 power of the diffusion constant. (iii) Fractal clusters tend to fill the space quickly,
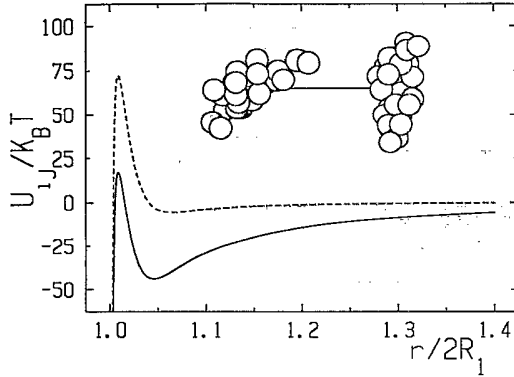
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FIG. 3. Cluster-cluster potential energy as a function of the cluster distance, for the two clusters shown in the inset (full line). Each cluster is composed by 32 monomers and the potential energy is built summing all the intercluster monomer-monomer pair interactions. The dashed line shows the corresponding DLVO potential energy.
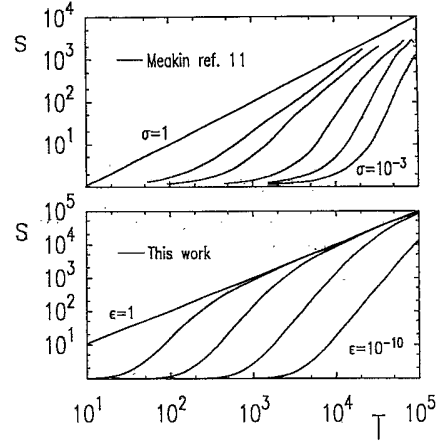


FIG. 4. The average number of particles in a cluster $s(t)$ vs scaled time. The parameter $\sigma$ of Ref. [11], related to the sticking probability, has the values 1,0.1,0.025,0.005,0.002,0.001. $\epsilon$ is $1, 10^{-4}, 10^{-6}, 10^{-8}$, and $10^{-10}$.

significantly reducing the mean free path between encounters.

Transforming the time $t$ into the scaled adimensional time $T = 16\pi p_s R_1 D_1 N t$, and using the kernel in Eq. (5), the rate equation for the number of clusters containing $k$ particles $c_k(T)$ becomes

$$\frac{d}{dT}c_k(T) = (\delta_{k,1} - \tfrac{1}{2}\delta_{k,2})(1-\epsilon)c_1^2$$

$$+\frac{1}{2}(1-\delta_{k,1})\sum_{j=1}^{k-1}c_j c_{k-j} - c_k\sum_{j=1}^{\infty}c_j \qquad (6)$$

for $k = 1,2,...,\infty$, where $\delta_{j,k}$ is the Kroenecker delta. The condition $\sum_{k=1}^{\infty}kc_k = 1$ holds and the time is scaled according to the original Smoluchowski equation. In particular the equation for $c_1(T)$ is

$$\frac{d}{dT}c_1(T) = (1-\epsilon)c_1^2 - c_1 N_c, \qquad (7)$$

where the total number of clusters is given by $N_c = \sum_{k=1}^{\infty}c_k$, and satisfies

$$\frac{d}{dT}N_c(T) = -\frac{1}{2}N_c^2 + \frac{1}{2}(1-\epsilon)c_1^2. \qquad (8)$$

Equations (7) and (8) can be solved to give

$$c_1(T) = \frac{4}{4+4\epsilon T + \epsilon T^2}, \quad N_c(T) = \frac{4(1+\frac{\epsilon}{2}T)}{4+4\epsilon T + \epsilon T^2}. \qquad (9)$$

$s(T) = \sum_{k=1}^{\infty}k^2 c_k(T)$ is the average number of particles and is easily shown to satisfy

$$\frac{d}{dT}s(T) = 1 - (1-\epsilon)c_1^2 \qquad (10)$$

with the solution

$$s(T) = \frac{4+2(1+4\epsilon)T + 6\epsilon T^2 + \epsilon T^3}{4+4\epsilon T + \epsilon T^2}$$

$$-\frac{1}{\sqrt{\epsilon(1-\epsilon)}}\arctan\frac{\sqrt{\epsilon(1-\epsilon)}T}{2+\epsilon T}. \qquad (11)$$

The same method of solution can be applied to the distribution of clusters $c_k(T)$, as we will report elsewhere.

The solution for $s(T)$, a function of the scaling time and of the parameter $\epsilon$, is shown in Fig. 1 (compared with our experimental data) and in Fig. 4 (compared with simulated data in RLCA regime by Meakin [11]). The agreement between the exact solutions of the rate equations and the experimental data support the soundness of the assumption made in writing the kernel [21]. We also note the following. (i) In the limit $\epsilon = 0$, i.e., no interaction among the monomers, we find $s(T) = 1$ and in the limit $\epsilon = 1$, i.e., the same interaction between monomers and clusters, $s(T) = 1+T$, the classical Smoluchowski result for DLCA. (ii) The Smoluchowski equation has been modified only through the change of the monomer-monomer aggregation rate. (iii) Independent from the value of $\epsilon$, for long times, $s(T) \approx T$, i.e., the same asymptotic behavior of DLCA. (iv) The onset of the power law region is $\epsilon$ dependent, as well as the value of the exponent $z$. (v) The comparison between the experimental and theoretical curves shown in Fig. 1 can be used to relate the salt concentration to the value of $\epsilon$ or, by using an effective potential and Eq. (4), to relate the salt concentration to the activation energy. Points (ii) and (iii) show that the scaling properties in the asymptotic time regime of the solution have not been changed. In other words, the long time properties of the equations are the same as those observed for DLCA. Thus our analysis suggests that the slow RLCA regime is only a transient regime, which crosses to the fast DLCA regime in the long time limit. Point (v) is expanded in the following for the case in which the monomer-monomer interaction potential is given by the classical Deriaguin-Landau-Verwey-Overbeek expression [22] for monovalent ions

$$U(x) = \frac{\epsilon_m R_1 \phi_d^2}{2K_B T}\ln[1 + e^{-2R_1 e\sqrt{\frac{8\pi N_A c}{\epsilon_m K_B T}}(x-1)}]$$

$$-\frac{A}{12K_B T}\left[\frac{1}{x^2-1} + \frac{1}{x^2} + 2\ln\left(1 - \frac{1}{x^2}\right)\right]. \qquad (12)$$

Here $x$ is the interparticle distance in units of $R_1$, $\epsilon_m$ is the dielectric constant of the medium, $\phi_d$ is the double layer diffusion potential, $A$ is the Hamacker constant, $N_A$ is the Avogadro number, and $K_B$ is the Boltzmann constant. Once the potential is fixed it is possible to evaluate $p_{1,1}$ and obtain $\epsilon$ in terms of $c$. The comparison between the measured values of $z$ and the ones derived from the theory is shown in Fig. 2 for $A = (0.47 \pm 0.02) \times 10^{-12}$ and $\phi_d = (0.260 \pm 0.005) \times 10^{-3}$, both in cgs units, values characteristic of colloidal systems of this type.

In conclusion, we investigate the approach to the fast DLCA regime of colloidal aggregation when starting from a situation in which the kinetics is slow. The parameter used to describe the crossover is the exponent $z$, which relates the average number of particles in a cluster to the aggregation time. We introduce a modified Smoluchowski equation that takes into account the fact that the reaction rate between small clusters is slower than the large cluster-cluster rate of aggregation. The exact solution of the equation shows, in a reasonable way, that the slowed-down monomer interaction is sufficient to explain the anomalously large values of the exponent $z$ observed in some situations. Last but not least, the model suggests that the RLCA regime is a transient regime characteristic of the initial stages of aggregation. It exists only up to a certain time, which depends on the monomer-monomer sticking probability. Finally, it is possible to relate the driving parameters of the crossover $z$ and $\epsilon$ to the parameters characterizing the interparticle potential.

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