Dynamic Scaling in Colloidal Aggregation: Comparison of Experimental Data with Results of a Stochastic Simulation

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A stochastic simulation method is used to recover the scaling behavior and the complete time evolution of an experimental system of colloidal aggregation of polystyrene particles under both diffusion-limited aggregation and reaction-limited aggregation conditions. Several hypotheses about the underlying kinetics and the scaling properties of the aggregation process are tested by comparing numerical with experimental results.

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Colloidal aggregation systems of gold [1], polystyrene [2,3], and silica [4–6] are extensively studied in the literature. In experimental systems two limiting growth processes can be observed: (a) diffusion-limited aggregation (DLA), i.e., every collision between clusters results in a reaction, and (b) reaction-limited aggregation (RLA), i.e., many collisions between clusters take place before a reaction occurs. These processes are usually treated within the scaling approach of the Smoluchowski equation [7,8]. Nevertheless, this description is often unsatisfactory since its validity is restricted to the scaling limit of long times and large clusters whereas in experiments small clusters and short times are often of interest. Thus, a description of the complete time evolution of each cluster is desirable.

In this Letter we show that a stochastic simulation method [9–11] based on a master equation is an ideal tool for the investigation of the kinetics and dynamic scaling properties of colloidal aggregation experiments. With the stochastic simulation method a hypothesis about the appropriate kinetics of the aggregation process can easily be tested by comparison of numerical results with experimental data.

Our Letter is organized as follows. We begin with a description of the usual deterministic treatment of aggregation processes within the scaling approach of the Smoluchowski equation. Furthermore, we briefly discuss the corresponding stochastic formulation of the problem. The results and the interpretation of the experimental system in the context of the scaling theory are described in the second part. The stochastic simulation results are discussed in the last part of this Letter. There we compare the simulation results with the predictions of the scaling theory and the experimentally observed data.

In general, a colloidal aggregation process can be described by the following reaction scheme:

$$A_i + A_j \xrightarrow{k(i,j)} A_{i+j}, \tag{1}$$

where A_i denotes a cluster of i unit masses and $k(i,j)$ is the mass dependent rate coefficient or kernel of the irreversible reaction. The kinetics of the aggregation system is determined by this kernel. In the usual deterministic approach, this process is described by the well-known deterministic Smoluchowski equation,

$$\frac{\partial c_m(t)}{\partial t} = \frac{1}{2}\sum_{i+j=m} k(i,j)c_i(t)c_j(t) - c_m(t)\sum_{j=1}^{\infty} k(m,j)c_j(t), \tag{2}$$

where $c_m(t)$ denotes the concentration of clusters of mass m at time t. For convenience, the dynamics of the Smoluchowski equation (2) is often formulated in dimensionless variables defined by the transformations $X_m(T) = c_m(T)/c_0$, $T = t/t_{\mathrm{agg}}$, and $K(i,j) = 2k(i,j)/k(1,1)$, where $c_0 = \sum_{m=1}^{\infty} mc_m$ is a constant and $t_{\mathrm{agg}} = 2/c_0k(1,1)$. The Smoluchowski equation is analytically solvable only for very few kernels; for example, if $K(i,j) = i+j$ then the so-called sum kernel solution is given by $X_m(T) = (1-u)(mu)^{m-1}\exp(-mu)/m!$, where $u = 1-\exp(-T)$ for monodisperse initial conditions.

The kinetics of the process (1) predicted by the Smoluchowski equation (2) can be characterized by the well-known classification scheme of van Dongen and Ernst [7,8]. In this theory it is assumed that the cluster-size distributions approach the form

$$X_m(T) \longrightarrow s^{-\Theta}\Phi(m/s(T)) \tag{3}$$

in the scaling limit $m \to \infty, s(T) \to \infty$ with $x = m/s(T)$ constant. Here Θ is a kinetic exponent, $s(T)$ is some measure for the average cluster size, and $\Phi(x)$ is the scaling function. The scaling properties of the solutions $X_m(T)$ depend on two exponents λ and μ which characterize homogeneous kernels. These exponents are defined by

$$k(ai,aj) = a^{\lambda}k(i,j) \quad \text{and} \quad k(i,j) \sim i^{\mu}j^{\lambda-\mu} \quad (i \ll j).$$

Here we consider only kernels with $\lambda \leq 1$ describing nongelling aggregation kinetics for which $\Theta = 2$ can be derived. The scaling function $\Phi(x)$ is bell shaped for kernels with $\mu < 0$ and $s(T) = \bar{n}_n \overset{\text{def}}{=} c_0/\sum_i c_i(T)$. Solutions to

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kernels with $\mu \geq 0$ show a different kinetic behavior. In this case $\Phi(x)$ decreases monotonically for increasing x and $s(T) = (\bar{n}_n)^{1/(1-\lambda)}$ for $\lambda < 1$. These properties can be seen in the experimental system considered here as shown later.

Before presenting the results of the experimental study let us discuss the essentials of the stochastic simulation method. The numerical algorithm is described in detail elsewhere [11–14]. The master equation according to the stochastic process (1) describes the evolution of the joint probability distribution $P(\mathbf{N}, t)$:

$$\frac{\partial P(\mathbf{N},t)}{\partial t} = \frac{1}{2}\sum_{i,j}\frac{k(i,j)}{V}[(N_i+1)(N_j+1+\delta_{ij})P(\mathbf{N}^+_{i,j},t) - N_i(N_j-\delta_{ij})P(\mathbf{N},t)]. \quad (4)$$

Here $P(\mathbf{N};t)$ denotes the probability that the system with volume V is at time t in the state $\mathbf{N} = (N_1, N_2, \ldots)$, where N_i is the number of clusters A_i. The state $\mathbf{N}^+_{i,j}$ is given by

$$\mathbf{N}^+_{i,j} = \begin{cases} (\ldots, N_i+1, \ldots, N_j+1, \ldots, N_{i+j}-1, \ldots) & \text{if } i \neq j, \\ (\ldots, N_i+2, \ldots, N_{2i}-1, \ldots) & \text{if } i = j. \end{cases}$$

The quotient $k(i,j)/V$ is the rate that a cluster of mass i reacts with a cluster of mass j and the kernel $k(i,j)$ is taken from the Smoluchowski equation (2). The expectation values of the stochastic process and the concentrations $X_m(t)$ which can be measured experimentally are related via

$$\frac{\langle N_m(t)\rangle}{c_0 V} = X_m(t). \quad (5)$$

As an initial condition for the numerical algorithm we assume in the following that at time $t = 0$ the system consists of $N_1 = 2 \times 10^5$ monomers whereas the numbers $N_i, i = 2, 3, \ldots$, are taken to be zero. The magnitude of the fluctuations is estimated by performing 200 realizations of the stochastic process. The approximate CPU time on a 486 PC is, in the simulations presented here, 1 h for 100 realizations of the stochastic process. We checked that our numerical results do not vary when the initial number of monomers is enlarged.

Let us now describe the experimental system which was investigated by Broide and Cohen [2,3]. It consists of an aqueous suspension of surfactant-free charged polystyrene microspheres with a radius of 0.258 μm. Irreversible aggregation was induced by the addition of salt ($MgCl_2$). The experiment was performed under both DLA and RLA conditions. In the experimental system only clusters with masses 1 to 20 were measured.

The experiment is interpreted in the context of the scaling theory describing the evolution of $s(T)$, $\Phi(x)$, and $X_n(T)$. In Figs. 1(a), 2(a), 3(a), and 4(a) some of the experimental results of the DLA study with parameters $c_0 = 1.6 \times 10^8/\text{cm}^3$ and $t_{\text{agg}} = 0.60$ h and of the RLA study with $c_0 = 1.6 \times 10^{10}/\text{cm}^3$ and $t_{\text{agg}} = 1.4$ h are presented. In Fig. 1(a) the evolution of $\bar{n}_n$ is shown for the DLA measurements (solid circles) and the RLA measurements (open circles). It is seen that $\bar{n}_n$ increases approximately linearly after a certain time for both processes. If $\Phi(x) = s(T)^2 X_m(T)$ is plotted versus $x = m/s(T)$ at different times T, one observes a data collapse on a single master curve. This can be seen in Fig. 2(a) for DLA data in the time interval $1.7 \leq T \leq 89$ and in Fig. 3(a) for RLA data in the time interval $1.2 \leq T \leq 39$. These results demonstrate that the scaling assumption (3) is a well suited description of the experimental data, which is somewhat surprising since the experimental data do not represent the scaling limes, i.e., long times and large clusters. The dependence of X_n from T is shown in Fig. 4(a) exemplified for clusters with masses $n = 1$, $n = 5$, and $n = 20$. These experimentally observed features of the aggregation systems for DLA and RLA can be used to determine the kinetics, i.e., the correct kernel $k(i,j)$ of the reaction system.

From the form of the scaling plot Fig. 2(a) Broide and

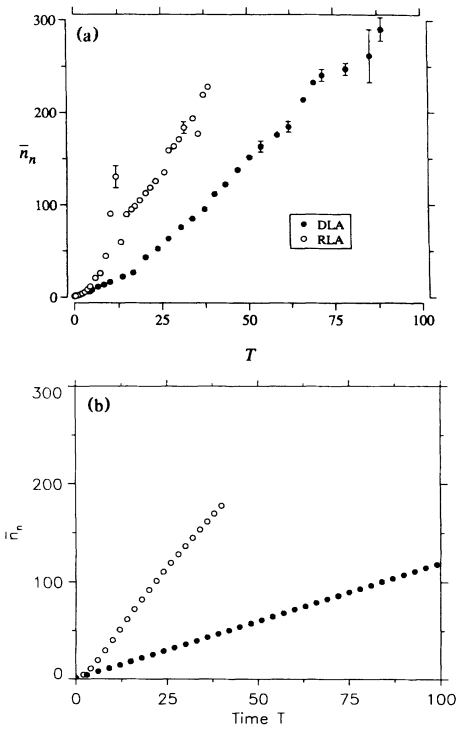

FIG. 1. (a) The average cluster size $\bar{n}_n$ as a function of the dimensionless time T for DLA (•) and RLA (○) as obtained from the experimental study [2]. (b) Temporal evolution of $\bar{n}_n$ for DLA (•) and RLA (○) as obtained from the stochastic simulation of the kernels $K_D(i,j)$ and $K_R(i,j)$.

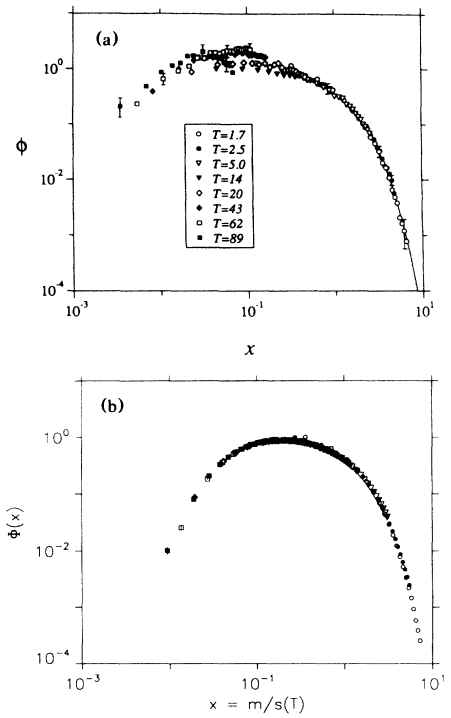

FIG. 2. (a) Scaling function $\Phi(x) = X_m \bar{n}_n^2$ versus the parameter $x = m/\bar{n}_n$ taken from the experimental study of DLA [2] showing alignment of distributions measured at different times. (b) Dynamic scaling plot $\Phi(x)$ versus $x = m/\bar{n}_n$ for the stochastic simulation of the kernel $K_D(i,j)$ describing DLA.

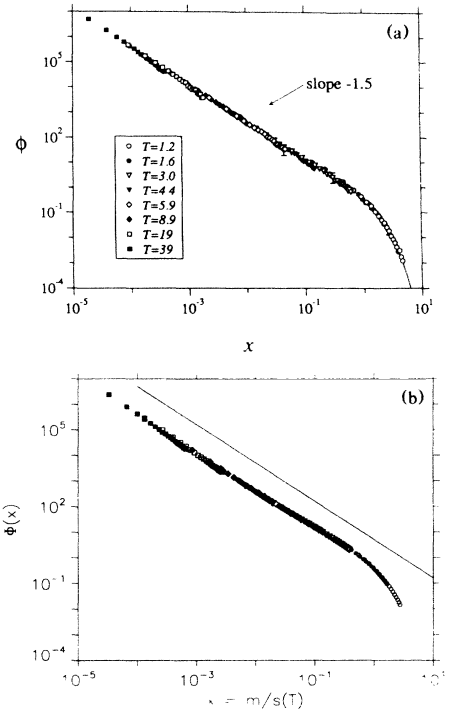

FIG. 3. (a) Scaling function $\Phi(x) = X_m \bar{n}_n^4$ versus the parameter $x = m/\bar{n}_n^2$ taken from the experimental study of RLA [2] showing alignment of distributions measured at different times. (b) Dynamic scaling plot for the stochastic simulation of the kernel $K_R(i,j)$ describing RLA.

Cohen suggest that the following kernel should describe DLA: $k_D(i,j) = k_0(i^{1/d_f} + j^{1/d_f})(i^{-1/d_H} + j^{-1/d_H})$. Here d_f is the fractal dimension of the aggregates, d_H is the hydrodynamic fractal dimension of the clusters, k_0 is a constant factor, and the subscript "D" stands for DLA. From the experimental data they deduced $d_f \approx d_H$. Other experiments [1] show that for diffusion-limited aggregation $d_f = 1.75$, so we finally arrive at the kernel

$$K_D(i,j) \stackrel{\text{def}}{=} \frac{2k_D(i,j)}{k_D(1,1)} = \frac{1}{2}(i^{1/1.75} + j^{1/1.75})(i^{-1/1.75} + j^{-1/1.75}),$$

which should describe the DLA measurements.

On the other hand, a simple assumption for the form of the kernel describing RLA is $k_R(i,j) \sim (ij)^{\lambda/2}$. The value of λ should be $\lambda = 0.5$ for the following reason. A slope $\tau = 1.5$ of the scaling function $\Phi(x)$ is observed experimentally, as can be seen from Fig. 3(a), and in the scaling theory of the Smoluchowski equation the slope τ and the value of λ are related via $\tau = 1 + \lambda$ for this class of kernels.

Let us now compare the experimental data with the stochastic simulation results to the DLA and RLA processes. We simulate the process with the same monodisperse initial condition as in the experimental system. We show the results of the stochastic simulation for the same quantities as experimentally observed.

The results of the simulation of DLA governed by the kernel $K_D(i,j)$ with initially 2×10^5 monomers are shown in Figs. 1(b), 2(b), and 4(b). In Fig. 1(b) it can

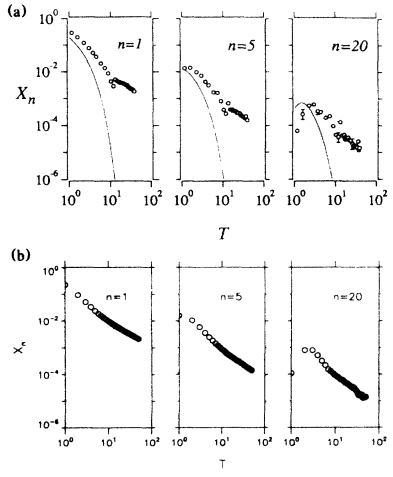

FIG. 4. (a) Temporal evolution of X_1, X_5, and X_{20} for the experimental system of RLA [3]. The solid lines are the sum kernel predictions. (b) Temporal evolution of X_1, X_5, and X_{20} as obtained by the stochastic simulation of RLA.

be seen that $\bar{n}_n$ (solid circles) increases linearly in time T but much slower than the experimentally measured value of $\bar{n}_n$ [Fig. 1(a)]. Nevertheless, the graph $\Phi(x)$ obtained by the stochastic simulation [Fig. 2(b)] agrees perfectly with the one observed experimentally [Fig. 2(a)] for large values of x. For small values of x, the agreement of the graphs is only qualitative in the sense that they both show a bell-shaped form. These findings agree well with those obtained by the diffusion-limited cluster-cluster aggregation model [15] with diffusion coefficient $D(m) \sim m^{-1/1.75}$.

Discrepancies between the results of the stochastic simulation and those of the experiment may be explained by gravitational settling of large clusters [16]. Gravitational settling would have two effects on the kinetics of the experimental system. The first one is an underestimation of the total concentration since large clusters are not measured. Since $\bar{n}_n$ is determined in the experiment by the quotient of c_0 and the total concentration, this leads to an overestimation of $\bar{n}_n$. This may explain the discrepancy of Figs. 1(a) and 1(b). This overestimation of $\bar{n}_n$ also affects the scaling plots $\Phi(x)$ versus x in Figs. 2(a) and 2(b), and 3(a) and 3(b) since $x = m/\bar{n}_n$ and $\Phi(x) = X_m \bar{n}_n$. The second effect of gravitational settling is that the purely Brownian kernel $K_D(i,j)$ has to be modified in such a way that large clusters have a higher collision rate since they move faster than assumed in Brownian motion.

However, we have also simulated the kinetics of the RLA system with the kernel

$$K_R(i,j) \stackrel{\text{def}}{=} \frac{2k_R(i,j)}{k_R(1,1)} = 2(ij)^{\lambda/2}$$

for several values of λ. The best agreement of the stochastic simulation results with the experimental data is given for $\lambda = 0.8$ and not for $\lambda = 0.5$ as predicted by the scaling theory of the Smoluchowski equation. In addition we find that $s(T) = \bar{n}_n^2$ leads to a data collapse of $\Phi(x)$ whereas other exponents such as $s(T) = \bar{n}_n^5$ as predicted by the scaling theory do fail to align on a single master curve. In Fig. 1(b) the temporal evolution of $\bar{n}_n$ (open circles) is shown. In this model $\bar{n}_n$ increases approximately linearly in the time interval $3 \leq T \leq 40$ but slightly slower than experimentally observed [Fig. 1(a)]. The reason for the slower growth of $\bar{n}_n$ in the experimental RLA system could also be an overestimation of $\bar{n}_n$ caused by gravitational settling as discussed above in the DLA experiment. The scaling function $\Phi(x)$ agrees perfectly with the experimental data as can be seen from Figs. 3(a) and 3(b). This scaling is not the asymptotic one predicted by the scaling theory of the Smoluchowski equation, since this would imply a value of $\tau = 1.8$ for $\lambda = 0.8$. However, in the stochastic simulation we observe a value of $\tau = 1.5$ as it is also measured experimentally. From this example it is seen that the asymptotic predictions of the scaling theory are not sufficient to describe the complete time behavior of experimental systems. We exemplify the temporal evolution of our RLA model by presenting the stochastic simulation results of the evolution of X_1, X_5, and X_{20} in Fig. 4(b). This shows a good agreement with the experimental data plot in Fig. 4(a).

To conclude, we have shown that the stochastic simulation method is an ideal tool to test hypotheses about the reaction kinetics for an aggregation process observed experimentally. The method can easily be extended so that fragmentation processes or three particle interactions can also be included.

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