Universal Kinetics in Reaction-Limited Aggregation

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Reaction-limited cluster aggregation is modeled with the kinetic rate (Smoluchowski) equations, with a kernel determined intrinsically by the clusters' fractal geometry. The kernel scales with cluster mass as $M_1 M_2^{\lambda-1}$ ($M_1 \gg M_2$), and M^{λ} ($M_1 \approx M_2$), with $\lambda = 1$ in three dimensions, resulting in exponential kinetics and a cluster mass distribution $C_M \sim M^{-\tau}$, with $\tau = \frac{3}{2}$, in excellent accord with experiments. The singular nature of this solution forces the adjustment of the cluster fractal dimension, d_f, thereby determining its value.

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The observation that the structure of the clusters produced by kinetic aggregation of colloidal particles can be characterized as fractal has sparked renewed interest in the description of the physics of the kinetic aggregation process itself.[1] To date, two distinct classes of kinetic aggregation have been investigated. One class is diffusion-limited aggregation of clusters, where the aggregation rate is limited solely by the time taken for clusters to collide via Brownian diffusion.[2-4] The other class is reaction-limited aggregation (RLA), where the reaction rate is limited by the probability of forming a bond upon collision of two clusters. This class of aggregation has been observed experimentally in several colloid systems,[5-10] and has been modeled by computer simulation.[11,12] In this paper we discuss a theoretical interpretation of this regime based on the Smoluchowski equation.[13-18]

The Smoluchowski equation describes kinetic aggregation in terms of the reaction probability for clusters of mass M_1 and M_2. This reaction kernel, $K(M_1,M_2)$, is assumed to have some average functional dependence on M_1 and M_2; thus these equations are a mean-field approach to the aggregation dynamics. The solution to the equations provides no information on the structure of the aggregates; instead the structure must be included in the determination of the correct kernel. In this paper we describe a geometric prescription for the appropriate RLA kernel for fractal clusters, and we present a scaling argument to determine its functional form. The solutions to the Smoluchowski equations obtained with this kernel are in excellent accord with the experimental data. Furthermore, when extended to higher spatial dimensionalities, they suggest a sharp transition between the exponential kinetics observed in few dimensions and gelling kinetics in more dimensions. Surprisingly, the cluster fractal dimension appears to be discontinuous at this transition.

The experimentally observed features[5-10] of RLA include clusters which have $d_f \approx 2.1 \pm 0.1$; exponential growth kinetics of the characteristic cluster mass, $M_c \sim e^{t/\tau_M}$, where τ_M is a sample-dependent time constant; and a power-law cluster mass distribution, $C_M \sim M^{-\tau}$, with $\tau \approx 1.5 \pm 0.15$. We show that these observations can be accounted for with use of the rate equations and the reaction kernel determined here, the scaling of which is $K(M_1,M_2) \sim M_1 M_2^{\lambda-1}$, provided $\lambda = 1$. Mathematically, values of λ even slightly different from 1 give qualitatively very different behavior. Physically, λ is determined by d_f and the cluster structures and we will argue that the system resists a singular change in its behavior by the adjustment of d_f to give $\lambda = 1$ in $d = 3$. Thus we show that the value of d_f is uniquely determined by the controlling physics in the reaction-limited aggregation process. This establishes a causal relationship between the geometric structure of the aggregates, as characterized by d_f, and the aggregation process, through the cluster mass distribution.

The rate of two single particles in a colloidal suspension sticking is given by $k \sim \nu \exp(-V_b/k_B T)$, where V_b is the repulsive barrier between two approaching particles. The attempt frequency, ν, is determined by the diffusive motion of the particles, as well as by their radius and concentration. When two floc clusters approach each other closely on Brownian trajectories, there will typically be many single-particle contacts, and the probability P of the two clusters sticking will increase rapidly with cluster mass. Reaction-limited kinetics typically occurs when $V_b \geq k_B T$, making k sufficiently small that there is a significant range of cluster size with $P \ll 1$, even though the attempt frequency, determined by diffusion, remains high. If P does approach 1 the diffusion-limited and reaction-limited rates become equal and there is a crossover to the diffusion-limited regime.

The key feature of the reaction-limited regime is that the number of diffusion-induced collisions before aggregation of two clusters succeeds is sufficiently large to allow clusters to sample all possible mutual bonding con-

figurations without bias.[11,12] The probability of two clusters sticking is then directly proportional to the fraction of the phase space (of the assembly of rigid clusters) for which they are in bondable contact, ϕ_c, and their rate of sticking per unit time is $k\phi_c$. We define two clusters to be in bondable contact if they are within a microscopic distance, w, of touching, and not overlapping. The width of the repulsive barrier can define a natural value for w which is typically no larger than a single-particle radius in flocculating systems, and thus is significantly less than the cluster size.

At low concentrations, so that three-cluster effects can be ignored, the phase-space fraction is given by $\phi_c = V_c/V$, where V_c is the volume of distinct space over which the center of the first cluster can be positioned so that the two clusters are in bondable contact, and V is the total volume of the system. For small w, V_c/w is the area of the contact surface of two given clusters, defined by the center of cluster 1 as it is scraped all round cluster 2, as illustrated in Fig. 1. The contact surface can in general be fractal and is a mutual but intrinsic property of the two clusters and their structure. We obtain ϕ_c for clusters with given mass by averaging the contact surface over all configurations, including rotations.

For fixed cluster masses M_1 and M_2, we assume that the variation in ϕ_c is not too great and we can replace it by the average over all such pairs in the distribution. Thus, the rate coefficient for reaction-limited sticking between two particular clusters is given simply by $K(M_1,M_2) = k\phi_c V = kV_c$ so that if the two species occur in concentrations C_1 and C_2 the total aggregation rate per unit volume is $K(M_1,M_2)C_1C_2$. We now consider the scaling of the kernel in the two regimes $M_1 \approx M_2$ and $M_1 \gg M_2$, which is sufficient to determine the behavior of the aggregation rate equation.

For solid spheres of radii R_1 and R_2, we have $V_c = 4\pi(R_1+R_2)^2 w$ in $d=3$ for $w \ll R_1, R_2$, giving $K(M_1,M_2) \sim (M_1^{1/3}+M_2^{1/3})^2$. For any two objects which can be characterized by a dimension, it is natural to expect a power law,

$$K(M_1,M_2) \sim M^{\lambda}, \quad M_1 \approx M_2 = M, \tag{1}$$

where for spheres (and other solid objects), $\lambda = (d-1)/d$. For fractal clusters of similar radius, we expect V_c to be larger than for spheres because their mutual contact surface must be at least slightly rough. It can be bounded by

$$wR^{d-1} \le V_c \le R^d \text{ or } (d-1)/d_f \le \lambda \le d/d_f, \tag{2}$$

provided only that $2d_f > d$, so that the clusters cannot totally interpenetrate. If they can, we expect $\lambda = 2$, but for flocculation this requires unphysically high space dimensionality. In general, we expect λ to decrease with higher d_f, because more compact clusters will interpenetrate less, making the mutual contact surface less rough, as reflected in the bounds on λ stated above.

We now consider V_c for two fractal clusters of similar structure but very different masses $M_1 \gg M_2$. If we consider the larger cluster as M_1/M_2 blobs of mass M_2, then for $d_f < d$ the smaller cluster can freely penetrate within the overall cluster of blobs, but not within each blob. Thus the reaction surface is additive over blobs giving

$$K(M_1,M_2) \sim M_1 M_2^{\lambda-1}, \quad M_1 \gg M_2. \tag{3}$$

The scaling properties of Eqs. (1) and (3) for $K(M_1,M_2)$ suffice to determine the behavior of the rate equation for the cluster mass distribution,[16,17]

$$\frac{\partial}{\partial t} C_M(t) = \sum_{P+Q=M} K(P,Q) C_P(t) C_Q(t) [\delta(P+Q,M) - \delta(P,M) - \delta(Q,M)]. \tag{4}$$

This equation has been extensively analyzed and there are three qualitatively distinct cases for the present form of kernel,[17,18] $\lambda < 1$, $\lambda = 1$ (which, for example, corresponds to the sum-of-masses kernel), and $\lambda > 1$.

For $\lambda < 1$, $C_M(t)$ goes to zero at large and small masses with a peak that has a power-law time dependence, $M_c(t) \sim t^{1/(1-\lambda)}$. In contrast, for $\lambda \ge 1$, C_M has a power-law form, $C_M \sim M^{-\tau}$, with $\tau = \frac{3}{2}$ for $\lambda = 1$ and $\tau = (3+\lambda)/2 > 2$ for $\lambda > 1$, up to a cutoff mass. The time dependence of the cutoff is exponential, $M_c(t) \sim e^{t/\tau_M}$ for $\lambda = 1$, while for $\lambda > 1$, gelation occurs at a finite time, t_g, and the cutoff mass diverges as $M_c(t) \sim (1-t/t_g)^{-2/(\lambda-1)}$. Thus $\lambda = 1$ is a quite singular case. Surprisingly, it is this special case which agrees with experimental results in $d=3$, particularly $\tau = \frac{3}{2}$ and exponential kinetics.

It is the extreme singularity of the solution at $\lambda = 1$ that actually stabilizes the system, by forcing the adjust-

FIG. 1. The contact surface traced out by the center of cluster B as it is scraped around cluster A, keeping the cluster orientations fixed. Expanded to a shell of width w, this gives the volume V_c within which the center of B must lie for sticking reactions to be attempted. In the RLA limit, where the attempt frequency is low enough for all of V_c to be sampled, the sticking rate is then proportional to V_c.

ment of λ through the adjustment of d_f. Qualitatively, this can be seen by our imagining the effect of increasing λ from 1. This produces relatively more small clusters as a result of the increased τ of the distribution. The greater number of small clusters will be able to penetrate within the large, tenuous clusters. Then the dominant reaction event is a small cluster reacting with a large cluster. Since the small cluster can freely penetrate within the larger, this reaction event will tend to increase the mass of the larger cluster without changing its radius. This will increase d_f and hence force λ down. Similarly, if λ is decreased from 1, the cluster mass distribution becomes more nearly monodisperse. Then the dominant reaction event is that of two clusters of equal size. These clusters will interpenetrate substantially less than for $\lambda=1$, and the resulting clusters will be more open and have smaller d_f, tending to increase λ. Thus, the system can force λ to 1 by the adjustment of d_f.

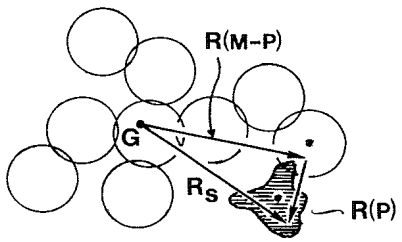

FIG. 2. The aggregation of a small cluster of mass P onto a much larger one of mass $M-P$. The latter is viewed as a cluster of equally accessible blobs of radius $R(P)$. The mean-square radius of gyration R_s^2 of the added material about the center of mass G of the larger cluster is then given by Eq. (7) if the direction of local attachment is uncorrelated with the vector from G.

In a more quantitative fashion, we can show that the system is not stable for λ just above unity by investigating the effect of λ on d_f near $\lambda=1$. The fractal dimension is controlled by the average squared radius $R^2(M)$ for clusters of a given mass M. However, d_f is also related to λ through the dynamics. The reaction with $P+Q=M$ makes clusters of size $R^2(P,Q)$, which depend on $R^2(P)$ and $R^2(Q)$. Then $R^2(M)$ is simply the average squared radius of all the M clusters produced in a time Δt,

$$R^2(M)=\sum_{P,Q}\delta(P+Q-M)C_PC_QK(P,Q)R^2(P,Q)\Big[\sum_{P,Q}\delta(P+Q-M)C_PC_QK(P,Q)\Big]^{-1}. \tag{5}$$

If λ approaches 1, the dominant contribution to $R^2(M)$ comes from $P\ll M$. To see this, we divide the sums above into $\sum_{P\ll M}+\sum'$. Noting that $\tau=(3+\lambda)/2$ and using $C_M\sim M^{-(3+\lambda)/2}$ and $K(P,Q)\sim QP^{\lambda-1}$, we obtain

$$M^{-(1+\lambda)/2}\sum_{P\ll M}P^{(\lambda-5)/2}[R^2(P,M-P)-R^2(M)]+\sum{}'C_PC_QK(P,Q)[R^2(P,M-P)-R^2(M)]=0. \tag{6}$$

While the second term remains finite for fixed M as $\lambda\to 1$, the first term has the potential of diverging because of the factor $P^{(\lambda-5)/2}$. Thus the cluster sizes are dominated by reactions where P is progressively smaller relative to Q, and we must investigate the behavior of $R^2(P,Q)$ in this limit.

As long as $d_f<d$, the small P cluster may stick to the large Q cluster throughout its interior. The mean squared distance, R_s^2, from the center of the large cluster to the small one has the form (see Fig. 2)

$$R_s^2=R^2(M-P)+R^2(P). \tag{7}$$

Then $R^2(P,Q)$ is a mass-weighted average of this R_s^2 with $R^2(M-P)$:

$$R^2(P,M-P)=R^2(M-P)+C_1\left(\frac{P}{M}\right)R^2(P)+C_2\left(\frac{P}{M}\right)^2, \tag{8}$$

where C_1 and C_2 are constants of order unity. Since $R\sim M^{d_f}$, we have

$$[R^2(P,M-P)-R^2(M)]=R^2(M)\left[-\frac{2}{d_f}\left(\frac{P}{M}\right)+C_3\left(\frac{P}{M}\right)^{1+2/d_f}+C_4\left(\frac{P}{M}\right)^2\right]. \tag{9}$$

When $\lambda\cong 1$, the first term in the brackets makes a diverging contribution to the sum in Eq. (6); this must be canceled by the second term. This, in turn, requires $d_f\sim(\lambda-1)^{-1/2}$, as one verifies by substituting Eq. (9) into Eq. (6).

Evidently, if $\lambda\to 1$ from above, then d_f cannot remain less than d. But even if $d_f=d$, λ cannot be larger than 1, for this would violate the bound in Eq. (2). There is therefore a range of λ just above 1 which is physically unattainable; it is this extreme lack of continuity between $\lambda=1$ and $\lambda>1$ that provides a physical mechanism to stabilize the system at $\lambda=1$ by adjustment of d_f.

The system might also stabilize at $\lambda<1$. However, in this case the mass distribution is well peaked and λ would be expected to approach its value for a monodisperse aggregation, determined by Jullien and Kolb[11]; in $d=3$, this results both in $\lambda>1$ (1.16), and in clusters with a somewhat lower d_f (2.00) than is measured experimentally. Thus for $d=3$,

we expect d_f to be pulled up and $\lambda=1$. Similarly, for $d=4$, the monodisperse λ is greater than 1 (1.44), and we predict $\lambda=1$ as for $d=3$. In contrast, in $d=2$, the monodisperse λ is less than 1, and we expect it to remain stable below 1.

The solutions to the rate equations with our predicted kernel with $\lambda=1$ account for all the salient experimental observations reported to date for reaction-limited aggregation, including exponential kinetics[8,10] and $C_M \sim M^{-\tau}$ with $\tau=\frac{3}{2}$ (Refs. 5 and 9). Further, a computer simulation[12] of RLA in $d=3$ found that true polydispersity decreased λ to 1.06 ± 0.02 and increased d_f to 2.1 ± 0.03 as compared to monodisperse simulations. These results are in excellent accord with experiment and consistent with our theory.

There are several additional tests of our predictions that should be carried out. Experimentally the prediction of power-law kinetics for slow flocculation in $d=2$ should be investigated. For computer simulation, an outstanding crucial test is what happens in $d=4$, where we predict exponential kinetics, with $\lambda=1$ and $\tau=\frac{3}{2}$. Finally, given our form of the reaction-limited rate coefficient we predict the crossover to diffusion-limited control at $kM_c^{\lambda} \approx k_B T/\eta_0$ with $\lambda=1$, where η_0 is the fluid viscosity.

We conclude with speculation about higher dimensionalities. Either exponential kinetics with $\lambda=1$ persists indefinitely, in which case $d_f \geq d-1$, or there is a kinetic critical dimension at which λ "escapes" from 1 to distinctly higher values. If there is a kinetic critical dimension, it should correspond to a discontinuity of the cluster fractal dimension, because the exponent $\tau+1-\lambda$ which governs the distribution of ratio of masses will be discontinuous. Thus either $d_f \geq d-1$ or it is discontinuous with space dimension.[19]

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[19]If λ jumps from 1 to 2, δ is continuous, but $\lambda=2$ corresponds to transparent clusters with $d_f \leq d/2$ which is discontinuous with $d_f \geq d-1$ for $d>2$.