Dynamic Scaling in the Kinetics of Clustering

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In irreversible aggregation processes without a gelation transition the cluster size distribution approaches a scaling form, $c_k(t) \sim s^{-2}\phi(k/s)$. Usking Smoluchowski's coagulation equation we determine the exponents in the mean cluster size $s(t) \sim t^z$ $(t \to \infty)$ and in the small- and large-x behavior of the scaling function $\phi(x)$. Depending on certain characteristics of the coagulation coefficients, $\phi(x) \sim x^{-\tau}$ $(x \to 0)$ or $\phi(x) \sim \exp(-x^{\mu})$ $(x \to 0)$ with μ some negative constant. In aggregation processes with gelation a similar scaling form is obtained as t approaches the gel point.

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To study the kinetics of irreversible aggregation and clustering phenomena, in particular the time evolution of the cluster size distribution $c_k(t)$, Smoluchowski's coagulation equation is one of the few available, and also one of the most widely used, theoretical tools in many fields of physics, astronomy, polymer physics, colloid chemistry, atmospheric physics, biology, and technology.[1–5] It reads

$$\dot{c}_k = \tfrac{1}{2}\sum_{i+j=k} K(i,j)\,c_i c_j - c_k \sum_{j=1}^{\infty} K(k,j)\,c_j, \tag{1}$$

where the coagulation kernel $K(i,j)$ represents the rate coefficient for a specific clustering mechanism between clusters of sizes i and j. We distinguish gelling and nongelling mechanisms. In the former the mean cluster size $s(t)$ diverges as t approaches the gel point t_c; in the latter $s(t)$ keeps increasing with time.

It is known from exact solutions,[1] coagulation experiments,[2] and computer simulations[6] that the size distribution approaches a scaling form, $c_k(t) \sim s^{-\tau}\phi(k/s)$, as soon as $s(t)$ becomes large compared to the characteristic size at the initial time. The important point is that the k and t dependence of $c_k(t)$ is given through a universal function of a single variable, $k/s(t)$, that does not depend on the initial distribution. For a limited number of coagulation mechanisms, all belonging to class III (see below), Friedlander's[2] theory of self-preserving spectra (SPS theory) gave a satisfactory explanation of the experimental observations on Brownian coagulation in the hydrodynamic and molecular regime, although the experimental data at large k and t are rather poor.

By generalizing the SPS theory we can give a unifying description of the scaling behavior occurring in gelling and nongelling systems, described by Smoluchowski's equation. Our generalization covers all coagulation kernels $K(i,j)$ that are homogeneous functions of i and j, and includes large classes of models, for which the original SPS theory is not valid, e.g., $K(i,j) = i + j$.

Since Smoluchowski's equation with a homogeneous kernel is invariant under a group of similarity transformations, it admits exact similarity or scaling solutions,[2,3] that can be solved from a nonlinear integral equation and whose properties are analyzed in this Letter. The basic assumption of our method is that the solutions for general initial distributions indeed approach the special similarity solution. With the help of the integral equation we can determine scaling functions and related exponents, analytically or numerically, and we are able to investigate many conflicting results in the literature.

A strong motivation for our investigations came from the explicit results for the complete scaling function and related exponents found in recent computer simulations of diffusion limited cluster-cluster aggregation.[6] In view of the success of the SPS theory one should also attempt to explain these data with the help of Smoluchowski's equation. However, to analyze these computer experiments a theoretical understanding of the collision rates $K(i,j)$ of large fractal clusters of sizes i and j would have to be found, or the $K(i,j)$ values should be measured in the same computer experiments,[7] and used as input to solve the nonlinear integral equation for the scaling function numerically.

Most coagulation coefficients used in the literature are homogeneous functions of i and j, at least for large i and j.[5] Thus, we restrict ourselves to such kernels and characterize $K(i,j)$ by two exponents, describing their i and j dependence at large i and/or j:

$$K(ai,aj) = a^{\lambda}K(i,j) = a^{\lambda}K(j,i),$$
$$K(i,j) \simeq i^{\mu}j^{\nu} \quad (j \gg i;\ \lambda = \mu + \nu), \tag{2}$$

with $\mu > 0$ (class I), $\mu = 0$ (class II), and $\mu < 0$ (class III). There exist two physical restrictions on the exponents: For two large interpenetrable clusters $K(j,j) \sim j^2$, which is an upper bound for all $K(j,j)$ as $j \to \infty$, and thus $\lambda \leq 2$. By similar arguments it is required that $\nu \leq 1$, but no restrictions are imposed on μ. In class I and III the rate constants for reactions of large with large and respectively large with small clusters are dominant. In the intermediate class II the rate constants $K(i,j)$ for aggregation of large with large and small with large clusters are of equal size. Nongelling systems correspond to $\lambda \leq 1$, and gelling systems to

$\lambda > 1$.

Criteria for gelation.—We first discuss the criteria for gelation.[5a,5b] To investigate which aggregation mechanisms lead to gelation we consider the mass loss rate $\dot{M}^{(k)}(t)$ across a certain cluster size k, which follows from Eq. (1) as

$$\dot{M}^{(k)}(t) \equiv \sum_{j=1}^{k} j\dot{c}_j = -\sum_{i=1}^{k}\sum_{j=k-i+1}^{\infty} iK(i,j)c_i c_j. \quad (3)$$

If $\dot{M}^{(\infty)}(t) = 0$ for all times, then the sol mass is conserved, $M(t) = \sum_k kc_k(t) = M$, and the system is nongelling. The property $\dot{M}^{(\infty)}(t) \neq 0$ for all $t \geq t_c$ is interpreted as the occurrence of gelation, since there is a nonvanishing mass flux of finite-size particles (sol) to the infinite cluster (gel). The right-hand side of Eq. (3) can only be nonvanishing if $c_k(t)$ has a sufficiently slow (algebraic) decay at large k, i.e., $c_k(t) \sim k^{-\tau}$ ($k \to \infty$). This *Ansatz* gives in combination with Eqs. (2) and (3) that $\dot{M}^{(\infty)}(t) \neq 0$ and is bounded for *all* $t \geq t_c$ if $\tau = \frac{1}{2}(\lambda + 3)$. A further requirement is that the total sol mass $M(t)$ is bounded for $t \geq t_c$, implying $\tau > 2$. Consequently, homogeneous coagulation kernels $K(i,j)$ of degree λ describe *gelling systems* if $\lambda > 1$ and *nongelling systems* if $\lambda \leq 1$ [where no consistent solutions of the form $c_k(t) \sim k^{-\tau}$ can be found].

Nongelling systems.—Next we consider *nongelling systems* ($\lambda \leq 1$), and we look for similarity solutions to Eq. (1) of the general form $c_k(t) \sim g(t)\phi(k/s(t))$. Here conservation of sol mass, $\sum kc_k(t) = M$, implies $g(t) \simeq M/s^2(t)$, so that

$$c_k(t) \simeq Ms^{-2}\phi(k/s) \equiv Mk^{-2}\psi(k/s). \quad (4)$$

To determine $s(t)$ and $\phi(x)$ the *Ansatz* (4) is inserted into Eq. (1) and gives the following integral equation:

$$-w[x\phi'(x) + 2\phi(x)] = \lim_{\epsilon \downarrow 0}\left[\tfrac{1}{2}\int_{\epsilon x}^{(1-\epsilon)x} dy\, K(y, x-y)\phi(y)\phi(x-y) - \phi(x)\int_{\epsilon x}^{\infty} dy\, K(x,y)\phi(y)\right]. \quad (5)$$

Here w is a separation constant for the x and t dependence, so that $\dot{s}s^{-\lambda} = Mw$ or $s(t) = [C + (1-\lambda)Mwt]^z$, with $z = 1/(1-\lambda)$ and C an integration constant. The mean cluster size increases asymptotically as $s(t) \sim t^z$ ($t \to \infty$), and we have determined the dynamic exponent z for all homogeneous coagulation kernels with $\lambda < 1$. On the border line $\lambda = 1$ the mean cluster size grows faster than any power of t. This special case ($\lambda = 1$) will be discussed elsewhere.

The constant w and the moments of the scaling function, defined as $p_\alpha = \int_0^\infty dx\, x^\alpha \phi(x)$, are related as

$$(\alpha - 1)p_\alpha w = \tfrac{1}{2}\int_0^\infty dx \int_0^\infty dy\, K(x,y)\phi(x)\phi(y)\{(x+y)^\alpha - x^\alpha - y^\alpha\}, \quad (6)$$

as follows after multiplication of Eq. (5) with x^α and integration over x, where α must be sufficiently large that the integrals in Eq. (6) exist at the lower limit of integration.

The solution $\phi(x)$ of Eq. (5) contains two arbitrary constants (a,b), since for any given solution $\phi(x)$ also $\bar{\phi}(x) = b\phi(ax)$ is a solution. One constant is fixed by the requirement of mass conservation $\sum kc_k(t) = M\int dx\, x\phi(x) = M$ or $p_1 = 1$. The other constant can be chosen such that $w = 1$, but we leave it arbitrary here. If the separate integrals in Eq. (5) are convergent, then ϵ may be set equal to zero. This appears to be the case in class III, whereas in classes I and II both terms contain canceling infinities. A representation of the $\phi(x)$ equation, free of canceling infinities, follows from Eq. (3):

$$wx^2\phi(x) = \int_0^x dy \int_{x-y}^\infty dz\, yK(y,z)\phi(y)\phi(z), \quad (7)$$

where consistency requires that $x^2\phi(x) \to 0$ as $x \to 0$. In our arguments we use the more convenient form (5).

We are interested in *solutions* $\phi(x)$ with exponential decay *at large* x. This restriction is motivated by a theorem of White,[8] applicable to kernels with $K(x, 1-x) \leq K_0$ so that $K(i,j) \leq K_0(i+j)^\lambda \leq K_0(i+j)$ $(i,j = 1, 2, \ldots)$, stating that $c_k(t)$ $(k = 1, 2, \ldots)$ at any finite time decays faster than any power of k. We find, in fact, $\phi(x) \simeq Ax^{-\lambda}e^{-ax}$ $(x \to \infty)$, which is valid for *all gelling and nongelling* coagulation kernels with $\nu < 1$.

To study the *small-x behavior* the three classes are considered separately. In *class I* one verifies by direct substitution that Eq. (5) admits algebraic solutions

$$\phi(x) \simeq Bx^{-\tau} \quad (x \to 0), \quad (8a)$$

$$\tau = 1 + \lambda, \quad B = (1-\lambda)w/L(1+\lambda), \quad (8b)$$

where mass conservation ($p_1 = 1$) implies $\tau < 2$ and $L(\tau)$ is defined as

$$L(\tau) = \tfrac{1}{2}\int_0^1 dx\, K(x, 1-x)[x(1-x)]^{-\tau}\{x^{2\tau-\lambda-2} + (1-x)^{2\tau-\lambda-2} - 1\} \quad (8c)$$

and converges for $\mu > 0$ (class I). Equation (8c) also shows that the dominant small-x contributions to $\phi(x)$ come from gain *and* loss terms in Smoluchowski's equation. We can further show that a leading behavior (3a) with

$\tau = \frac{1}{2}(\lambda + 3)$ is excluded if the sol mass is to be finite. Also note that $\phi(x) = Bx^{-1-\lambda}$ is an exact solution, which is unphysical as it contains an infinite mass $(p_1 \to \infty)$.[4]

In *class II* $(\mu = 0, \nu = \lambda)$ the small-x behavior is still of the form (8a), but Eqs. (8b) and (8c) are no longer valid since $L(1+\lambda)$ diverges logarithmically at $x = 0$ and $x = 1$. Analysis shows that the dominant small-x contributions come from the loss term in Eq. (5), and the result for class II is $\tau = 2 - p_\lambda / w$ where τ must satisfy the consistency requirement, $\tau < 1 + \lambda$. Since τ is given in terms of integrals over $\phi(x)$ [see Eq. (6)], it can only be determined after solution of the $\phi(x)$ equation. This result suggests that the τ exponent in class II systems depends on the specific form of the coagulation kernel.

In *class III* systems $(\mu < 0)$ the dominant small-x behavior is again determined by the loss term. Here Eq. (5) reduces to $-x\phi'(x) \sim \phi(x) x^{-|\mu|}$ so that $\phi(x) \sim \exp(-x^{-|\mu|})$ vanishes exponentially fast for $x \to 0$ [$\phi(x)$ has a bell-shaped curve]. This property is in strong contrast with the typical behavior (8a) in classes I and II. Much more detailed results follow from the explicit form of the kernels, e.g., (a) $K(x,y) = (xy)^{-\alpha}$ $(\alpha > 0)$, (b) $K(x,y) = x^{-\alpha} + y^{-\alpha}$ $(\alpha > 0)$, and (c) $K(x,y) = (x^{-\alpha} + y^{-\alpha})(x^{\alpha} + y^{\alpha})$ (in the last case $\alpha = \frac{1}{3}$ corresponds to Brownian coagulation) give respectively the following small-x behavior

$$\phi(x) \simeq Cx^{-2} \exp[-2x^{-\alpha} p_0 / \alpha p_{-\alpha}], \tag{9a}$$

$$\phi(x) \simeq Cx^{-1} \exp[-x^{-\alpha} p_0 / \alpha p_{-\alpha}], \tag{9b}$$

$$\phi(x) \simeq Cx^{-\tau'} \exp[-(x^{-\alpha} p_\alpha / \alpha w) + (x^{\alpha} p_{-\alpha} / \alpha w)], \tag{9c}$$

where τ' and w can be expressed in moments of the scaling function,

$$p_0 w = p_0^2 + p_\alpha p_{-\alpha}, \quad \tau' = 2 p_\alpha p_{-\alpha} / p_0 w. \tag{10}$$

The result $\phi(x) \simeq Bx^{-\tau}$ $(x \to 0)$ in classes I and II implies that the k and t dependence of $c_k(t)$ factorizes as $t \to \infty$. Thus, $c_k(t)/c_1(t) \sim k^{-\tau}$ $(t \to \infty)$ and $c_k(t) \sim c_1(t) \sim s^{\tau-2} \sim t^{-\delta}$ $(t \to \infty)$, where $\delta = 1$ in class I and $\delta = (2-\tau)/(1-\lambda)$. In class III $(\mu < 0)$, on the other hand, $c_k(t)/c_1(t) \to \infty$ as $t \to \infty$. If μ is very small $(|\mu| \to 0)$ there exists an intermediate x range, $1 >> x >> x_0 \equiv \exp(-1/|\mu|)$, where kernels in classes I and III show typical class II behavior with crossover to respectively class I and class III behavior at $x \sim x_0$.

Gelling systems.—Next, we return to *gelling systems*, where $1 < \lambda \leq 2$. It follows from the discussion around Eq. (3) that the size distribution in the postgel stage $(t \geq t_c)$ has the form

$$c_k(t) \simeq B(t) k^{-\tau} \quad [k \to \infty, \tau = \tfrac{1}{2}(\lambda + 3)]. \tag{11a}$$

In order to study the size distribution in the pregel stage, we consider the scaling form, supposedly valid for sufficiently large k and sufficiently close to the gelpoint $(t \to t_c^-)$, with $\psi(0)$ finite:

$$c_k(t) \simeq Mk^{-\tau} \psi(k/s) = Ms^{-\tau} \phi(k/s). \tag{11b}$$

Here $s(t)$ is a measure of the mean cluster size, which diverges as $t \to t_c^-$. Below we shall see that the pregel exponent equals the postgel exponent in $\tau = \frac{1}{2}(\lambda + 3)$. To determine the scaling function we insert the *Ansatz* (11b) into Smoluchowski's equation and obtain Eq. (5) with the factor of 2 on the left-hand side replaced by τ. The mean cluster size $s(t)$ is determined by $Mw = \dot{s} s^{\tau - 2 - \lambda}$, so that

$$s(t) = [C - wMt/\sigma]^{-1/\sigma} = s_0 (t_c - t)^{-1/\sigma}, \tag{12}$$

with $\sigma = \frac{1}{2}(\lambda - 1)$. Here we have anticipated that $\tau = \frac{1}{2}(\lambda + 3)$ also below the gelpoint. The mean cluster size is an increasing function of time. It diverges as $t \to t_c^- = \sigma C / (wM)$, where t_c has a finite value in gelling systems $1 < \lambda \leq 2$.

The small-x behavior of $\phi(x)$ is found by inserting the *Ansatz* (8a) into the $\phi(x)$-equation. The pregel τ-exponent is found by solving the transcendental equation, $L(\tau) = 0$, where $L(\tau)$ is defined in Eq. (8c). Its solution is easily seen to be $\tau = \frac{1}{2}(\lambda + 3)$.

In summary, we have for the size distribution in *gelling systems* $(1 < \lambda \leq 2)$ in the pregel stage

$$c_k(t) \simeq k^{-\tau} \psi(k(t_c - t)^{1/\sigma}) \quad (t \to t_c^-, k \to \infty), \tag{13a}$$

where the scaling function has the form

$$\phi(x) = x^{-\tau} \psi(x) \simeq Bx^{-\tau} + B_1 x^{-\tau x_1} + \ldots \quad (x \to 0), \tag{13b}$$

with $\sigma = \frac{1}{2}(\lambda - 1)$, $\tau = \frac{1}{2}(\lambda + 3)$, and $\tau_1 = \tau - \mu$. It can be shown further that $B \sim [-\dot{M}^{(\infty)}(t_c)]^{1/2}$. In the postgel stage $(t \geq t_c)$ the size distribution is given by Eq. (11a).

We discuss the relation of our results to those known in the literature and their relevance for the recent computer simulations. In classes I and II our large- and small-x results for homogeneous kernels with $\lambda < 1$ generalize previous results of Lushnikov and Piskunov[4] for the product kernel $K(x,y) = (xy)^{\omega}$ $(0 < \omega < \frac{1}{2}$; class I) and for the sum kernel $K(x,y) = x^{\omega} + y^{\omega}$ $(0 < \omega < 1$; class II). The result $\tau = 1 + 2\omega$ for the product kernel was rederived by Leyvraz,[9] using a recursion relation for the time-independent constants, $b_k \simeq c_k(t)/c_1(t)$ $(t \to \infty)$. For the sum kernel one finds that $\tau = 2 - p_\omega p_2 / (2 p_{\omega+1} p_1)$, as already shown in Ref. 4. This τ value differs from $\tau_R = 1 + \frac{1}{2}\omega$, derived in Ref. 9. The exponent τ_R has no bearing on the asymptotic properties of $\phi(x)$, as has been shown elsewhere.[10]

Class III kernels for several cases of Brownian coagulation[2a,2b] have been studied both analytically and numerically in connection with the theory of self-preserving spectra. The results[9,10] are new results for kernels of class III, which generalize previous results; e.g., in the case of Brownian coagulation [case 9c with $\alpha=\frac{1}{3}$] Friedlander and Wang[2b] have numerically evaluated the constants in Eq. (9c) using the normalization $p_1=p_0=1$, and obtained the value $\tau'=1.06$ for the exponent in Eq. (10), which is independent of the chosen normalizations.

The results[11-13] for gelling systems generalize the results[5] for the product kernel $K(x,y)=(xy)^{\omega}$ with $\frac{1}{2}<\omega\leq 1$.

For all gelling and nongelling kernels one can determine higher-order corrections of algebraic type to the dominant small-x behavior of $\phi(x)$. An exception is formed by certain nongelling class I kernels, such as $K(x,y)=(xy)^{\omega}$ $(0<\omega<\frac{1}{2})$, for which we have not been able to determine the analytic structure of the first correction to the leading term in Eq. (8a). This fact may be related to the question of *existence* of physically acceptable scaling solutions of Smoluchowski's equation. We cannot exclude the possibility that the exact solution $\phi_0(x)=Bx^{-1-\lambda}$, which has infinite mass, is the only solution for certain class I models, i.e., that for such models physically acceptable scaling solutions may not exist.

As already discussed in the introduction, our theory may possibly explain in a quantiative way the scaling behavior observed in recent computer simulations, after some theoretical or numerical data on the rate constants $K(i,j)$ become available. However, in a qualitative way one can understand the observed effect of a size-dependent diffusion coefficient on the scaling function. It was found that for a size-dependent diffusion coefficient, $D_k\sim k^{\gamma}$, with γ sufficiently large (e.g., $\gamma>\gamma_c\simeq -0.5$ in 3 dimensions), the scaling function $\phi(x)$ decreases monotonically, viz., $\phi(x)\sim x^{-\tau}$ $(x\to 0^+)$ and $\phi(x)\ll 1$ $(x\to\infty)$, where τ depends in a continuous manner on γ. If γ decreases below γ_c, the shape of $\phi(x)$ exhibits crossover from monotonic decrease to a bell-shaped curve. If one assumes that $K(i,j)$ has the same structure as in Brownian coagulation, i.e., $K(i,j)\simeq(D_i+D_j)(R_i+R_j)$, where $R_k\sim k^{\nu}$ $(k\to\infty)$ is the radius of gyration of a cluster of size k and $D_k\sim k^{\gamma}$ its diffusion coefficient, then one observes a similar crossover from class III $(\gamma<0)$, where $\phi(x)$ has a bell-shaped curve, to class II $(\gamma\geq 0)$, where $\phi(x)\sim x^{-\tau}$ $(x\to 0^+)$ decays monotonically.

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