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A Generalization of the Smoluchowski Coagulation Equation*

by P.C. Hemmer

Institute of Physics, Norwegian University of Science and Technology, N 7491 Trondheim, Norway

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The Smoluchowski equation for irreversible coagulation is generalized by taking both two- and three-particle aggregations into account. The effects of three-particle events are studied through the exact solution of a special model.

Key words: aggregation, coagulation, gelation

Coagulation phenomena occur in many fields of science and technology, for instance in colloid and polymer chemistry, in aerosol science, in biology (red blood cells) and in food technology. The usual decription of the coagulation kinetics is via a set of rate equations for the concentrations $c_k(t)$ of aggregates consisting of k units:

$$\frac{dc_n}{dt} = \frac{1}{2}\sum_{i+j=n} K_{ij}c_i c_j - c_n \sum_{i=1}^{\infty} K_{ni}c_i \qquad n = 1,2,... \tag{1}$$

Equation (1) is known as the Smoluchowski coagulation equation [1]. The dependence of the rate constants K_{ij} on the sizes i and j of the two aggregates that form an n-mer will necessarily be different for different chemical and physical processes. As examples, for Brownian coagulation $K_{ij} \propto (i^{1/3} + j^{1/3})(i^{-1\backslash 3} + j^{-1/3})$ is appropriate [1,2], for coagulation in shear flow $K_{ij} \propto (i^{1/3} + j^{1/3})^3$ has been used [3], and $K_{ij} \propto ij$ has been used for growth of branched polymers [4]. The Smoluchowski coagulation equation is well studied and comprehensive reviews of its properties have been given [5,6].

Several assumptions underly equation (1). Fragmentation is assumed to be absent, and spatial fluctuations and correlations are neglected. The present note is concerned with the assumption of binary collisions, that the kinetics consists solely of two-body aggregation events. At low densities the binary collision assumption obviously is well-founded, but at higher densities clustering events with more than two particles must become important. The first corrections to pair aggregation evidently come from three-particle events, and to include these the Smoluchowski equation (1) is generalized to

$$\frac{dc_n}{dt} = \frac{1}{2}\sum_{i+j=n} K_{ij}c_i c_j - c_n \sum_{i=1}^{\infty} K_{ni}c_i + \frac{1}{3}\sum_{i+j+k=n} L_{ijk}c_i c_j c_k - c_n \sum_{i,j} L_{ijn}c_i c_j \tag{2}$$

* Dedicated to Prof. Jan Stecki on the occasion of his 70th birthday.

for $n = 1, 2, 3, \ldots$. The kinetic cefficients K_{ij} and L_{ijk} are symmetric in the indices.

We will now study some properties of this generalized coagulation equation.

Moments of the size distribution: Mass conservation requires that the first moment of the statistical distribution $c_n(t)$,

$$\mathrm{M}_1 = \sum_{n=1}^{\infty} n\, c_n(t) \tag{3}$$

is constant in time. By multiplication of (2) with n, and summation over n, one easily finds $dM_1/dt = 0$, as should be, at least in the pregelation stage (see below). In the following it is convenient to normalize the total mass to $M_1 = 1$.

The zeroth moment of the statistical distribution,

$$\mathrm{M}_0 = \sum_{n=1}^{\infty} c_n(t) \tag{4}$$

is the number of aggregates, which essentially determines the osmotic pressure. Summing equation (2) over n, one deduces that the number of aggregates decays according to

$$\frac{dM_0}{dt} = -\frac{1}{2}\sum_{ij} K_{ij} c_i c_j - \frac{2}{3}\sum_{ijk} L_{ijk} c_i c_j c_k \tag{5}$$

The presence of the three-particle events obviously speeds up the reduction of the number of aggregates.

The most spectacular property of the Smoluchowski coagulation equation (1) is that for a class of kinetic coefficients K_{ij} gelation occurs. Characteristic for this phase transition is that an initial monomer distribution, say, produces an infinite cluster after a finite time t_g, the gelation time. An alternative characterization is that the second moment

$$M_2(t) = \sum_n n^2 c_n(t) \tag{6}$$

important for transport and scattering properties, diverges at $t = t_g$. The presence of three-body aggregation naturally should reduce the gelation time. One may ask, however, whether the presence of three-body aggregation influences the exponent characterizing the divergence of M_2 when $t \to t_g$, the behaviour with time of the loss of finite clusters to the infinite cluster (the gel), and, more generally, the behaviour of the statistical size distribution both in the pregelation and the postgelation stage. We will now answer some of these questions through an exactly soluble model.

Exact model solution: It is reasonable to assume that the kinetic coefficients increase with the size of the coagulating aggregates. The simplest model is to assume strict proportionality,

$$K_{ij} \propto ij; \qquad L_{ijk} \propto ijk \tag{7}$$

corresponding to the kinetic equation

$$\frac{dc_n}{dt} = \frac{1}{2}\sum_{i+j=n} ijc_i c_j - nc_n + \frac{1}{3}\rho \sum_{i+j+k=n} ijk c_i c_j c_k - nc_n \rho \tag{8}$$

$n = 1, 2, \ldots$. The proportionality constant in K_{ij} has been absorbed into the unit of time, while the remaining constant in L_{ijk} has been denoted ρ as a reminder that the three-particle events are expected to be one order higher in the density. For $\rho = 0$ the model equals the Flory model for high functionality. This model with binary collisions only was solved exactly in the pregelation regime by McLeod [7]. In order to solve (8) we introduce the generating function

$$G(x, t) = \sum_{n=1}^{\infty} n c_n(t) e^{nx} \tag{9}$$

Differentiating G with respect to time and using (8) we find

$$\frac{\partial G}{\partial t} = (G + \rho G^2 - 1 - \rho)\frac{\partial G}{\partial x} \tag{10}$$

The solution of this partial differential equation is given implicitly as follows

$$G(x, t) = g(x + t[G + \rho G^2 - 1 - \rho]) \tag{11}$$

with an arbitrary function g, as is easily verified by insertion. Since $G(x, 0) = g(x)$, one naturally specifies the arbitrary function g by the initial size distribution $c_n(0)$.

Let us consider the pregelation regime, and let for simplicity the initial distribution consist of monomers only: $c_1(0) = 1$, $c_n(0) = 0$ for $n > 1$. Then

$$g(x) = G(x,0) = e^x \tag{12}$$

and (11) takes the form

$$G(x, t) = e^{x + t(G + \rho G^2 - 1 - \rho)} \tag{13}$$

By expanding in (13) the generating function G in powers of $z = e^x$ one finds, according to (9), $c_n(t)$ for small n. In particular we obtain

$$c_1(t) = e^{-(1+\rho)t} \tag{14}$$

$$c_2(t) = \frac{1}{2} t e^{-2(1+\rho)t} \tag{15}$$

$$c_3(t) = \left(\frac{1}{3}\rho t + \frac{1}{2}t^2\right) e^{-3(1+\rho)t} \tag{16}$$

That the size-three distribution c_3, for $\rho = 0$ proportional to t^2 for early times reflecting a two-step aggregation process, now starts increasing proportional to time, is expected.

In order to find the complete size distribution, we express first G, given by (13), as a power series in z = e^x by means of Lagrange's theorem:

$$G = \sum_{k=1}^{\infty} \frac{z^k}{k!} \left[\frac{d^{k-1}}{dG^{k-1}} e^{kt(G+\rho G^2-1-\rho)} \right]_{G=0} = e^{-kt(1+\rho)} e^{-kt/(4\rho)} \left[\frac{d^{k-1}}{dy^{k-1}} e^{\rho kt(G+1/2\rho)^2} \right]_{G=0} \tag{17}$$

By (9) the coefficient of z^k is $kc_k(t)$. Thus,

$$c_k(t) = \frac{1}{k \cdot k!} e^{-k(1+\rho)t} \left[e^{-\rho kty^2} \frac{d^{k-1}}{dy^{k-1}} e^{\rho kty^2} \right]_{y=(2\rho)^{-1}}$$

where we have introduced $y = G + 1/(2\rho)$. Using the Rodrigues formula for the Hermite polynomials,

$$H_n(x) = e^{x^2} \left(-\frac{d}{dx} \right)^n e^{-x^2}$$

we find finally the exact solution for the kinetics:

$$c_k(t) = \frac{1}{k \cdot k!} \left(i\sqrt{\rho kt} \right)^{k-1} H_{k-1}\left(-i\sqrt{kt/4\rho} \right) e^{-(1+\rho)kt} \tag{18}$$

As a check we take the limit $\rho \to 0$ (no threebody events), using the asymptotic behaviour $H_n(x) \simeq 2^n x^n$ for large x, with the result

$$\lim_{\rho \to 0} c_k(t) = \frac{k^{k-2}}{k!} t^{k-1} e^{-kt} \tag{19}$$

first derived in [7].

In the opposite limit of only three-body aggregation, we introduce the scaled time variable $\hat{t} = t\rho$ and take the limit of large ρ afterwards. The result is

$$\lim_{\rho \to \infty} c_k(\hat{t}) = \begin{cases} 0 & \text{for } k = 2p = \text{even} \\ \dfrac{(1+2p)^{p-2}}{p!} \hat{t}^{\,p} e^{-(1+2p)\hat{t}} & \text{for } k = 2p+1 = \text{odd.} \end{cases} \tag{20}$$

The vanishing of all even size distribution functions is clearly due to the choice of an initial situation with merely monomers present.

Gelation: The second moment (6) of the size distribution is determined by the generating function (9),

$$M_2(t) = \left(\frac{dG(x,t}{dx} \right)_{x=0} \tag{21}$$

For our model differentiation of both sides of (13) with respect to x, and use of the conservation law $G(0, t) = 1$ in the sol phase, gives

$$M_2 = 1 + t(M_2 + 2\rho M_2) \tag{22}$$

Thus

$$M_2 = \frac{1}{1 - t(1 + 2\rho)} \tag{23}$$

diverging at time

$$t_g = \frac{1}{1 + 2\rho} \tag{24}$$

This is interpreted as the onset of gelation. At times $t > t_g$ an infinite cluster is present, constituting the gel phase, while the finite clusters make up the sol phase. One therefore expects the total mass of the finite clusters to decrease steadily in this post-gelation regime, violating the pre-gelation conservation law $M_1 = 1$.

The model is not fully defined until one specifies how the gel phase enters the kinetics [4]. We use here the simplest alternative, based on the assumption that the loss terms in the kinetic equation are the same in the pre- and postgelation stage, the socalled Flory model. This assumption implies, that for a k-mer the decrease in the number of coagulation events with finite-sized aggregates is precisely compensated by the number of coagulation events with the gel.

In order to calculate how the mass M_1 of the sol fraction decreases, we note that $M_1(t) = G(0, t)$. By (13), therefore,

$$M_1 = e^{t(M_1 + \rho M_1^2 - 1 - \rho)} \tag{25}$$

This nonlinear equation obviously has the solution $M(t) = 1$, relevant for the pregelation stage $t \le t_g$. However, for $t > t_g$ another solution $M_1(t) < 1$ exists, to be associated with the sol fraction in the postgelation stage. Fig. 1 shows how the sol mass decreases with time. The asymptotic behaviour for short and long times is easily deduced from (25):

$$M_1(t) = \begin{cases} 1 - \dfrac{2 + 4\rho}{1 + 4\rho}\left(\dfrac{t}{t_g} - 1\right) & \text{for } 0 < t - t_g << t_g \\ \exp\left(-\dfrac{1 + \rho}{1 + 2\rho}\dfrac{t}{t_g}\right) & \text{for } t >> t_g \end{cases} \tag{26}$$

From these expressions, as well as from Fig. 1, one observes that although the gelation time t_g is shortened by three-body aggregation events, the gel mass at twice the gelation time, say, is less than in the absence of three-body aggregation.

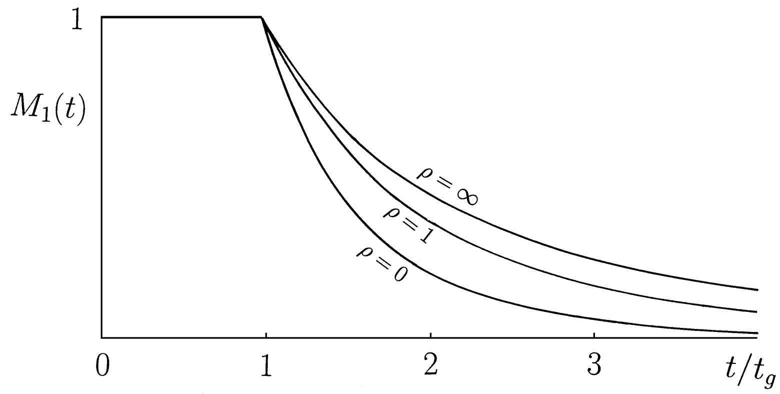

Figure 1. The sol mass M_1 as function of dimensionless time. The gel mass is $1 - M_1$. Here t_g is the time at the onset of gelation.

The number of aggregates, M_0, can be determined from (5) with the result

$$\frac{dM_0}{dt} = -\frac{1}{2} - \frac{2}{3}\rho$$

At the onset of gelation this gives

$$M_0(t_g) = \frac{3 + 8\rho}{6 + 12\rho} \tag{27}$$

For $\rho = 0$ the number of aggregates at the onset of gelation has been reduced to one half the original number, with $\rho > 0$ the number of aggregates is larger than this, somewhere between 1/2 and 2/3 of the original number of aggregates (monomers).

For binary collision models scaling in the form of similarity solutions for long times and for large clusters were studied by several authors (early references for continuous sizes are [8] and [9]). We investigate here for the present simple model the scaling properties for large clusters near the onset of gelation, t_g. The scaling hypothesis is the assumption, that in the limit where $k \to \infty$ and $t \to t_g$, the size distribution has the form

$$c_k(t) \simeq k^{-\tau}\Phi\,(k|1 - t/t_g|^{1/\sigma}) \tag{28}$$

characterized by two exponents τ and σ, and a scaling function $\Phi(x)$.

For the $\rho = 0$ size distribution (19), with gel point $t_g = 1$, the well-known scaling properties [10] are characterized by $\sigma = 1/2$, $\tau = 5/2$ and $\Phi(x) = (2\pi)^{-1/2}e^{-x/2}$. For the other extreme $\rho \to \infty$, (20) yields

$$c_k(t) \simeq (2\pi)^{-1/2}\, k^{-5/2} e^{-k(1 - t/t_g)^{2/4}} \tag{29}$$

again with $\sigma = 1/2$ and $\tau = 5/2$, but with $\Phi(x) = e^{-x/4}$. Thus, the scaling function $\Phi(x)$ depends upon the amount of three-body events present, while the critical indices τ and σ apparently do not.

Summary: The natural generalization of the Smoluchowski coagulation equation to include three-body aggregation events is formulated and studied. For the special case of kinetic coefficients corresponding to the Flory model, the time evolution of the size distribution, initially monodisperse, can be followed exactly also in the presence of three-particle aggregation. The three-particle events influence results in ways that are easily understood, *e.g.* by shortening the gelation time. Universal features like critical indices characterizing the distribution of large clusters near the onset of gelation are, however, the same as for two-particle aggregation kinetics.

REFERENCES

1. Smoluchowski M. von, *Z. Phys. Chem.*, **92**, 129 (1917); *Phys. Z.*, **17**, 585 (1916).
2. Drake R.L., in *Topics in Current Aerosol Research*, Vol. 3, part 2, Hidy G.M. and Brock J.R., *Eds*., Pergamon Press, NY (1972).
3. Friedlander S.K., *Smoke*, *Dust and Haze*, Wiley, NY (1972).
4. Ziff R.M. and Stell G., *J. Chem. Phys*., **73**, 3492 (1980).
5. ZifF R.M., in *Kinetics of Aggregation and Gelation*, Family F. and Landau D.P., *Eds*., Elsevier, Amsterdam (1984).
6. Ernst M.H., in *Fractals in Physics*, Pietronero L. and Tosatti E., *Eds*., Elsevier, Amsterdam (1985).
7. McLeod J.B., *Quart. J. Math. Oxford*, **13**, 119, 192, 283 (1962).
8. Swift D.L. and Friedlander S.K., *J. Coll. Interf. Sci*., **19**, 621 (1964).
9. Friedlander S.K. and Wang C.S., *J. Coll. Interf. Sci*., **22**, 126 (1966).
10. Ziff R.M., Ernst M.H. and Hendriks E.M., *J. Phys. A: Math. Gen*., **16**, 2293 (1983).