Coagulation Processes with a Phase Transition

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Smoluchowski's coagulation equation with a collection kernel $K(x, y) \sim (xy)^{\omega}$ with $\frac{1}{2} < \omega \leqslant 1$ describes a gelation transition (formation of an infinite cluster after a finite time t_c (gel point)). For general ω and $t > t_c$ the size distribution is $c(x, t) \sim x^{-\tau}$ for $x \to \infty$ with $\tau = \omega + 3/2$. For $\omega = 1$, we determine $c(x, t)$ and the time dependent sol mass $M(t)$ for arbitrary initial distribution in pre- and post-gel stage, where $c(x, t) \sim x^{-5/2} \exp(-x/x_c)$ for large x and $t < t_c$; $c(x, t) \sim (-\dot{M})^{1/2}x^{-5/2}$ for large xt and $t > t_c$. Here x_c is a critical cluster size diverging as $(t - t_c)^{-2}$ as $t \uparrow t_c$. For initial distributions such that $c(x, 0) \sim x^{p-2}$ as $x \to 0$, we find $M(t) \sim t^{-p/(p+1)}$ as $t \to \infty$. New explicit post-gel solutions are obtained for initial gamma distributions, $c(x, 0) \sim x^{p-2}e^{-px}$ $(p > 0)$ in the form of a power series (convergent for *all* t), and reducing for $p = \infty$ to the solution for monodisperse initial conditions. For $p = 1$, the solution is found in closed form.

1. INTRODUCTION

Smoluchowski's equation for rapid coagulation (1) describes the evolution of a system of particles which are continuously growing as a result of pairs of particles coming into contact and adhering or bonding to form clusters. Examples include the coagulation of aerosols and colloidal suspensions, and the formation of polymers. These systems may, in general, be described by the kinetic equation:

$$c_t(x, t) = \frac{1}{2}\int_0^x dyK(y, x-y)c(y, t)c(x-y, t) - c(x, t)\int_0^\infty dyK(x, y)c(y, t), \quad [1.1]$$

where $c(x, t)dx$ represents the number of clusters with size in $(x, x + dx)$ at time t. A subscript, as in c_t, denotes a partial derivative. The two terms represent the gain and loss of x-clusters, the rate at which x_1-clusters x_2-clusters combine to form $(x_1 + x_2)$-clusters being given by $K(x_1, x_2)c(x_1, t)c(x_2, t)dx_1dx_2$. The coagulation kernels of interest in this paper are of the general form $K(x, y) = K_0(xy)^{\omega}$.

First we consider the special case $\omega = 1$. It was believed for a long time (1–6) that solutions of Smoluchowski's coagulation equation with the collection kernel $K(x, y) \sim xy$ exist only for small times. This belief was based upon the behavior of the moments, which in general are defined by

$$M_n(t) = \int_0^\infty dxx^n c(x, t). \quad [1.2]$$

At some point, M_2 becomes infinite, and at a later time, M_0 seems to become negative. However, it turns out that past the point where M_2 is infinite, the formally derived moment equations are no longer valid, and there exists solutions for which M_0 (the number of clusters) remains positive for all time. In the case of discrete mass distributions, Ziff *et al.* (7, 8) and Leyvraz and Tschundi (9) have recently given the explicit global solution for a monodisperse initial distribution and discuss the ensuing phase transition (gelation); Leyvraz and Tschudi have proved the existence of solutions for all times, and Ziff *et al.* (10) have given the explicit global solutions for arbitrary initial distributions, and extensively analyzed the singularities occurring in the size distri-

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bution and its moments near the transition time.

In this paper we will discuss the case of general continuous initial mass spectra, $c(x, 0)$, for the coagulation kernel $K(x, y) = K_0xy$. Here some properties of the solution differ strongly from those in the discrete case, in particular the long time properties. Note that we may set $K_0 = M_1(0) = M_2(0) = 1$ without loss of generality by choosing proper units for x, t and $c(x, t)$: $M_2(0)/M_1(0)$, $1/K_0M_2(0)$, and $M_1(0)^3/M_2(0)^2$, respectively. For the kernel $K(xy) = xy$ we make a preliminary investigation of the moment equations (1):

$$\dot{M}_n(t) = \frac{1}{2}\int_0^\infty dx \int_0^\infty dy[(x+y)^n - x^n - y^n] \times xyc(x, t)c(y, t). \quad [1.3]$$

These can be derived from the coagulation equation if one assumes that orders of integration can be freely interchanged.

For $n = 1$ it follows that the total mass of all clusters $M(t) \equiv M_1(t)$ is conserved:

$$\dot{M}_1 = 0 \quad \text{or} \quad M_1(t) = M(t) = 1 \quad [1.4]$$

provided $M_2(t) < \infty$. This condition is necessary to give a well-defined meaning to [1.3], as the right-hand side equals $M_1(M_2 - M_2)$. When $c(x, t)$ is such that $M_2 = \infty$, the determination of $\dot{M}$ requires more care, as discussed below.

For $n = 0$ one finds

$$\dot{M}_0 = -\tfrac{1}{2}M^2. \quad [1.5]$$

As long as $M(t) = 1$, the general solution of [1.5] is

$$M_0(t) = M_0(0) - \tfrac{1}{2}t, \quad [1.6]$$

where $M_0(0)$ is the number of clusters at the initial time. Note the unphysical prediction by [1.6] that $M_0(t)$ becomes negative for $t > t_0 = 2/M_0(0)$.

For $n = 2$ one finds $\dot{M}_2 = M_2^2$, provided $M_3(t) < \infty$. This yields

$$M_2(t) = M_2(0)(1 - tM_2(0))^{-1} = (1 - t)^{-1}, \quad [1.7]$$

where $M_2(t)$ approaches infinity within a finite time $t_c = 1/M_2(0) = 1$. (Recall that units are chosen such that $M_1(0) = M_2(0) = 1$.)

For $n = 3$ one finds

$$M_3(t) = M_3(0)(1 - t)^{-3}, \quad [1.8]$$

provided $M_4(t) < \infty$.

Similar peculiar properties become manifest for the somewhat different situation, where $c(x, 0) = 0$ and where clusters of size x are generated by a source of strength $Q(x)$, for convenience taken to be time independent (4, 11–17). After adding the source term $Q(x)$ to the right-hand side of the coagulation equation [1.1], one finds

$$M_0(t) = J_0t - \frac{1}{6}t^3; \quad M(t) = M_1(t) = t$$

$$M_2(t) = \tan t;$$

$$M_3(t) = J_3(\cos t)^{-3}\left\{\sin t - \frac{1}{3}(\sin t)^3\right\}, \quad [1.9]$$

where the moments of the source are defined as $J_n = \int_0^\infty dx x^n Q(x)$. Here we have chosen units such that $K_0 = J_1 = J_2 = 1$. The results [1.9] for $M_n(t)$ are valid provided $M_{n+1}(t) < \infty (n \geq 1)$. We note again that $M_0(t)$ becomes negative for $t > t_0 = (6J_0)^{1/2}$; and $M_2(t)$ diverges at $t = t_c = \pi/2$, with $t_c < t_0$.

In Sections 2 and 3 we will obtain the solution of the coagulation equation [1.1] (without a source term) with $K(x, y) = xy$ for *all times* and for *general initial conditions,* and show that they are physically meaningful for all times. The above results for $M_n(t)$ will appear to be valid only for $t < t_c = 1$. We will further see (Section 2) that for $t > 1$ the total mass $M(t)$, contained in the clusters of finite size (sol particles) is no longer conserved, implying the formation of an infinite cluster (gel, superparticle), which contains a finite fraction of the total mass in the system. In other words, at time t_c there occurs a phase transition, known as gelation in polymer science.

In the absence of sources the size distribution (see Section 3) past the transition point $(t > 1)$ is found to have an algebraic tail $c(x, t) \sim x^{-\tau}$ with $\tau = 5/2$ independent of the initial size distribution, as in Junge's law (33).

The Smoluchowski equation [1.1] with $K(x, y) = xy$ excludes for $t > t_c$ the possibility that finite clusters or sol particles coalesce with the infinite cluster or gel (8, 10). A modified coagulation equation, which accounts for sol–gel interactions, is discussed in Section 4.

In Section 5 we will briefly discuss coagulation kernels of the form $K(x, y) = (xy)^\omega$. If ω satisfies the inequalities $\frac{1}{2} < \omega < 1$ a similar phase transition occurs (18–21). Past the transition point the size distribution has an algebraic tail with an exponent $\tau = \omega + 3/2$. The results are summarized in Section 6.

For the case of a stationary source it is well known (4, 11, 13, 16, 17) that the coagulation equation with $K(x, y) = (xy)^\omega$ admits stationary solutions $c(x, \infty) \sim x^{-\tau}$ with $\tau = \omega + 3/2$, and it was pointed out (21, 17) that this corresponds for $\frac{1}{2} < \omega < 1$ to the formation of an infinite cluster.

In this paper we discuss the coagulation equation without source terms. In a separate paper the effects of sources on coagulation and gelation will be considered (22).

2. TIME DEPENDENCE OF THE SOL MASS

By calculating the mass flux across a certain mass L, and by taking the limit as $L \to \infty$, we show the possibility of a nonvanishing mass flux for $L \to \infty$, indicating the appearance of an infinite cluster or gel at the gel point t_c. From the general solution of the coagulation equation, a functional equation for the (time dependent) total mass $M(t)$ of sol particles is derived, and applied to examples of special initial distributions. Finally, we determine the asymptotic properties of $M(t)$ as $t \to t_c$ and as $t \to \infty$.

Violation of Mass Conservation

In order to understand what is happening at $t_c = 1$ we reconsider the derivation of the law of mass conservation. Call $M^{(L)}$ the total mass of sol particles with size $x < L$, i.e.,

$$M^{(L)}(t) = \int_0^L dx x c(x, t), \qquad [2.1]$$

then the loss of mass from smaller clusters with $x < L$ to larger clusters can be calculated from the coagulation equation [1.1] with $K(x, y) = xy$ as

$$\dot{M}^{(L)}(t) = -\int_0^L dx x^2 c(x, t) \int_{L-x}^{\infty} dy y c(y, t) \qquad [2.2]$$

and it follows that $\dot{M} = 0$ only if the right-hand side vanishes in the limit $L \to \infty$. The value of $\dot{M}^{(L)}(t_c)$ at large L depends on the large x-behavior of $c(x, t_c)$. The first factor on the right-hand side of [2.2] is part of $M_2(t)$, which diverges at t_c; the second factor is part of M_1, which remains finite at t_c. If we represent the large x-behavior of $c(x, t_c)$ by $x^{-\tau}$ then τ must satisfy the inequalities $2 < \tau < 3$. Simple power counting predicts that $\dot{M}^{(L)}(t_c) \sim L^{5-2\tau}$ for $L \to \infty$. For $\tau > 5/2$ the limit of $\dot{M}^{(L)}(t_c)$ as $L \to \infty$ vanishes, and the total mass of sol particles is still conserved at t_c. If, however, $\tau \leqslant 5/2$, then $\dot{M}^{(L)}(t_c)$ approaches for $L \to \infty$ a (finite or infinite) negative value, indicating that there is a loss of mass from finite size clusters (sol particles) to the infinite cluster (gel, or super particle).

In the next section we will solve the coagulation equation and determine the large x-behavior of $c(x, t)$. It will turn out to yield $c(x, t_c) \sim x^{-5/2}$, indicating that a phase transition occurs at the point $t_c = 1$ with a *finite* mass loss rate of sol particles.

General Solution

In order to solve $M(t)$ we consider first the equation of motion for the Laplace transform of the mass distribution $xc(x, t)$, defined as

$$f(z, t) = \int_0^\infty dx x c(x, t) e^{-zx}. \qquad [2.3]$$

After multiplying [1.1] with x and taking the Laplace transform we obtain

$$f_t = -f_z(f - M). \qquad [2.4]$$

It is a quasilinear partial differential equation which has to be solved subject to the initial condition:

$$f(z, 0) \equiv u(z) \quad (u(0) = -u'(0) = 1). \qquad [2.5]$$

This equation can be solved by introducing the inverse function, $z(f, t)$. Using $f_z = (z_f)^{-1}$ and $f_t = -z_t/z_f$ we see that z satisfies $z_t = f - M(t)$, with the initial condition $z(f, 0) = u^{-1}(f)$, the solution of which is given by

$$z = u^{-1}(f) + ft - T \qquad [2.6a]$$

or

$$f = u(z - ft + t) = f(z, t) \qquad [2.6b]$$

where

$$T = \int_0^t d\tau M(\tau). \qquad [2.6c]$$

The function u^{-1} is the inverse of u. The Laplace transform $f(z, t)$ is implicitly given by [2.6] as a function of (z, t) for a given initial distribution $f(z, 0) = u(z)$.

The equation of motion [2.4] and the general solution [2.6] for the Laplace transform $f(z, t)$ of the continuous size distribution $c(x, t)$, and for the generating function $f(z, t) = \sum_{k=1}^{\infty} c_k(t)e^{-kz}$ in the case of discrete masses are identical (10). However, the initial value $f(z, 0) = u(z)$ is an ordinary Laplace transform for continuous mass spectra and a discrete transform for discrete mass spectra. The properties of the functions $u(z)$ are markedly different at large z, resulting from the differences in the initial mass spectra (between the continuous and the discrete case) at the fine grained side of the spectrum.

Functional Equation for M(t)

The solution [2.6] still contains the unknown mass of sol particles, $M(t) = f(0, t)$, which may be determined self-consistently by putting $z = 0$ to yield the functional equation

$$M = u(T - tM). \qquad [2.7]$$

It can be solved by differentiating [2.7] with respect to time:

$$\dot{M} = -t\dot{M} \cdot u'(T - tM). \qquad [2.8]$$

This equation has two solutions for *all* t, provided the first singularity of $u(z)$ in the complex z-plane with $Re z < 0$ is (i) located at a point $z_0 < 0$, a finite distance away from the origin, and (ii) has the property $u'(z_0) = \infty$ (10), i.e., the initial size distribution can be bounded by an exponential. At the end of Section 3 more general initial distributions will be considered.

Returning to [2.8] we have a constant solution:

$$M_a(t) = M(0) = 1, \qquad [2.9]$$

and a time-dependent solution, parametrically given by

$$M_b = u(s)$$

$$t^{-1} = -u'(s) \qquad [2.10]$$

with $s > z_0$.

The two solutions indicate that $f(z, t)$ is a double valued function of z. The *physical branch* of $f(z, t)$—being a Laplace transform of a positive function $xc(x, t)$—is a *monotonically decreasing function of* z, and vanishes as $z \rightarrow +\infty$. Therefore, the physically relevant root of [2.8] is the smaller one of M_a and M_b. From a graphical solution of [2.10], using the property that $u(z)$ is monotonically decreasing (with $u(0) = 1$ and $u'(0) = -1$), it follows that $M_b(t) > 1$ for $t < 1$ and $M_b(t) < 1$ for $t > 1$. Therefore the sol mass is given by

$$M(t) = \min\{M_a, M_b\}$$

$$= \begin{cases} 1 & (t < 1) \\ M_b(t) & (t > 1). \end{cases} \qquad [2.11]$$

There occurs a phase transition (gelation) at the gel point $t_c = 1$. In the sol phase $(t < 1)$ $M(t)$ is constant; in the gel phase $(t > 1)$ $M(t)$ decreases to zero as time progresses. The loss of mass, starting at $t = 1$, is associated with the formation of an infinite cluster (gel, superparticle). It is a loss to infinity due to the cascading growth of larger and larger clusters, where the process accelerates, as the clusters grow larger, since the rate is given by $K(x, y) = xy$. The mass deficit, $G(t) = 1 - M(t)$, is called the gel fraction, which is only nonvanishing past the gel point $t_c = 1$.

Examples of Initial Distribution

For *monodisperse initial conditions*, $c(x, 0) = \delta(x - 1)$, it follows from [2.3] and [2.5] that

$u(z) = e^{-z}$. One deduces from [2.10] and [2.11] that the sol mass is

$$M(t) = \begin{cases} 1 & (t < 1) \\ t^{-1} & (t > 1). \end{cases} \quad [2.12]$$

The corresponding result for the total number of clusters follows from [1.5]:

$$M_0(t) = \begin{cases} M_0(0) - \tfrac{1}{2}t & (t < 1) \\ M_0(0) - 1 + 1/(2t) & (t > 1). \end{cases} \quad [2.13]$$

If the initial mass distribution is a *gamma-distribution* $xc(x, 0) = p^p x^{p-1} e^{-px}/\Gamma(p)$ with $p > 0$, then $u(z) = (p/(z + p))^p$. The sol mass is given by

$$M(t) = \begin{cases} 1 & (t < 1) \\ t^{-p/(p+1)} & (t > 1), \end{cases} \quad [2.14]$$

and the corresponding total number of clusters is

$$M_0(t) = \begin{cases} M_0(0) - \tfrac{1}{2}t \quad (t < 1) \\ M_0(0) - \dfrac{p}{p-1} + \dfrac{1}{2}\left(\dfrac{p+1}{p-1}\right) t^{-(p-1)/(p+1)} \\ \qquad (t > 1). \end{cases} \quad [2.15]$$

Note that the gamma distribution in the large p-limit reduces to the monodisperse initial condition, as can be seen most easily from the relation $\lim_{p\to\infty} (1 + z/p)^{-p} = e^{-z}$.

The initial gamma distributions have physical significance for $p > 0$, although $c(x, 0) \sim x^{p-2}e^{-px}$ with $p > 2$ becomes infinite as $x \to 0$. For $p > 1$ the total amount of particles, $M_0(0)$, contained in $c(x, 0)$, is still finite, but for $p \leqslant 1$ there is an infinite amount of grit (minute particles of size $x \cong 0$), so that $M_0(0) = \infty$. However, the corresponding *mass* distribution $xc(x, 0)$—which is the physically significant distribution—contains a *finite* amount of material, $M_1(0)$ as long as $p > 0$. Consequently initial gamma distributions with $0 < p < 1$ are physically meaningful, but $M_0(t)$ is undefined (infinite).

Asymptotic Properties of M(t)

We discuss the behavior near $t = t_c$ and $t = \infty$, starting with the first case.

For the class of initial distributions considered, the behavior of the sol mass for $t \downarrow t_c = 1$ can be obtained by expanding the right-hand side of both equations in [2.10] about $s = 0$, yielding

$$M(t) = 1 - G(t)$$
$$\cong 1 - (t - 1)/M_3(0) \quad (t \downarrow 1), \quad [2.16]$$

where the relation $u''(0) = M_3(0)$ has been used. The corresponding behavior of $M_0(t)$ follows from [1.5]

$$M_0(t) \cong M_0(0) - \tfrac{1}{2}t + (t - 1)^2/2M_3(0) \quad (t \downarrow 1). \quad [2.17]$$

For $t \to \infty$ the relevant mass is given by [2.10], in which the parameter $s \to \infty$. Thus we need $u(s)$ and $u'(s)$ for $s \to \infty$, corresponding to the small x-behavior of the initial size distribution. If $c(x, 0) \cong Ax^{p-2}/\Gamma(p)$ (with $p > 0$) for $x \to 0$, then $u(s) \cong As^{-p}$ for $s \to \infty$, and the resulting sol mass decreases asymptotically as

$$M(t) \cong A(Apt)^{-p/(p+1)} \quad (t \to \infty). \quad [2.18]$$

If the initial size distribution $c(x, 0) = 0$ for $x < x_0$, one finds asymptotically

$$M(t) \cong (x_0 t)^{-1} \quad (t \to \infty). \quad [2.19]$$

This result is similar to the discrete mass case. If the mass spectrum is continuous down to $x = 0$, the sol mass decreases more slowly due to the abundance of grit. The explicit examples of [2.12] and [2.14] are special cases of [2.19] and [2.18], respectively. The long time behavior of $M_0(t)$ can be inferred from [1.5] and [2.18–19].

3. SIZE DISTRIBUTION

In this section we derive the general expression for the size distribution, valid for all times, and apply it to the monodisperse and the gamma initial distributions. Next we determine the large x-behavior of $c(x, t)$ by means of the saddle point method, and study in particular its behavior near the gel point t_c. The effects of initial distributions with algebraic tails on the pre- and post-gelation behavior of $c(x, t)$ is also briefly discussed. We finish with the long time behavior of $c(x, t)$.

General Form and Examples

Having determined $M(t)$ we take the inverse Laplace transform of $f(z, t)$ in [2.6b] to find the mass distribution:

$$xc(x, t) = (2\pi i)^{-1} \int_{s-i\infty}^{s+i\infty} dz e^{xz} f(z, t), \quad [3.1]$$

where the contour is a straight line parallel to the imaginary axis and to the right of all singularities in $f(z, t)$. After introducing a new integration variable ζ, such that

$$f = u(\zeta); \quad z = \zeta + tu(\zeta) - T, \quad [3.2]$$

and calculating the Jacobian $dz = (1 + tu'(\zeta)d\zeta)$, we obtain from [3.1] after performing two partial integrations with respect to ζ (boundary terms are vanishing):

$$c(x, t) = (x^2 t) e^{-xT} (2\pi i)^{-1} \times \int_{s-i\infty}^{s+i\infty} dz \exp[x(z + tu(z))]. \quad [3.3]$$

The contour is a straight line to the right of all singularities in $u(z)$. Equation [3.3] represents the solution of our coagulation equation for *all* times, and $T(t)$ is given through [2.6c] and [2.11].

As an example we consider first $xc(x, 0) = e^{-x}$, i.e., the gamma distribution for $p = 1$, so that $u(z) = (z + 1)^{-1}$. With the help of the following integral representation of the modified Bessel function (23):

$$I_1(2x) = (2\pi i)^{-1} \int_{s-i\infty}^{s+i\infty} dz \exp[x(z + z^{-1})]$$
$$= (1/\pi) \int_0^{\pi} d\theta \cos\theta \exp(2x \cos\theta), \quad [3.4]$$

we obtain the solution:

$$c(x, t) = e^{-(1+T)x} I_1(2x\sqrt{t})/x^2\sqrt{t} \quad [3.5a]$$

where, according to [2.6c] and [2.14],

$$1 + T = \begin{cases} 1 + t & (t < 1) \\ 2\sqrt{t} & (t > 1). \end{cases} \quad [3.5b]$$

For $t \leqslant 1$ this solution has been obtained before by McLeod (3). For $t \geqslant 1$ it represents a new solution to the coagulation equation.

The general solution [3.3] can also be represented in the form of a series expansion:

$$c(x, t) = \frac{e^{-xT}}{x^2 t} \sum_{k=0}^{\infty} \frac{(xt)^k}{k!} \int_{s-i\infty}^{s+i\infty} \frac{dz}{2\pi i} (u(z))^k e^{xz}. \quad [3.6]$$

For the initial gamma distribution (see above [2.14]), $u(z) = [p/(z + p)]^p$, and [3.6] yields the solution:

$$c(x, t) = \frac{e^{-(p+T)x}}{x^2} \sum_{l=0}^{\infty} \frac{(xt)^l (px)^{p(l+1)}}{(l + 1)!\Gamma(p(l + 1))}. \quad [3.7a]$$

This series converges for all t. We further have

$$p + T = \begin{cases} p + t & (t < 1) \\ (p + 1)t^{1/(p+1)} & (t > 1) \end{cases} \quad [3.7b]$$

on account of [2.6c] and [2.14]. For $p = 1$ it reduces to the previous example [3.5], where [3.7a] is the series expansion of I_1. This solution for $t < 1$ is known (1, 3); the solution for $t > 1$ is new. Its large x- and t-behavior is discussed below. One may also formulate these results in terms of the variable M_0 instead of t, using [2.15], as has been done in (1).

Another example is supplied by the monodisperse initial condition, where $u(z) = e^{-z}$ (see above [2.12]). The series expansion [3.6] yields in this case

$$c(x, t) = \frac{e^{-xT}}{x} \sum_{k=1}^{\infty} \frac{(xt)^{k-1}}{k!} \delta(x - k), \quad [3.8a]$$

where, according to [2.12] and [2.6c],

$$T = \begin{cases} t & (t \leqslant 1) \\ 1 + \log t & (t \geqslant 1). \end{cases} \quad [3.8b]$$

It is actually the solution for the discrete mass case, where

$$c_k(t) = e^{-kt}(kt)^{k-1}/kk! \quad (t \leq 1)$$
$$= e^{-k}k^{k-2}/tk! \quad (t \geq 1). \quad [3.9]$$

For $t \leq 1$ the solution has been known for a long time (2, 24, 25); for $t \geq 1$ this solution has been recently given by Ziff *et al.* (7, 10) and Leyvraz and Tschudi (9).

Saddle Point Method

The integral representation [3.3] for $c(x, t)$ is very convenient to derive the asymptotic behavior of $c(x, t)$ at large x, using the saddle point method. To obtain an asymptotic expression for the integral in [3.3] we choose s such that $F(z) \equiv z + tu(z)$ is at a maximum when the contour crosses the real axis. Then, s is determined as the solution of

$$F'(s) = 1 + tu'(s) = 0. \quad [3.10]$$

Observe that [3.10] is identical to the second equation of [2.10]. Hence $u(s) = M_b(t)$.

By expanding $F(z)$ about s and writing $z = s + iy$ we find that [3.3] at large x is approximated by

$$c(x, t) = (2\pi x^2 t)^{-1} e^{-xT} \int_{-\infty}^{\infty} dy$$
$$\times \exp[xF(s) - \tfrac{1}{2}xy^2F''(s)]$$
$$\cong (2\pi t^3 u''(s))^{-1/2} x^{-5/2}$$
$$\times \exp[x(F(s) - T)]. \quad [3.11]$$

In this expression we have for $t \leq 1$

$$z_0 \equiv T - F(s) = t(1 - u(s)) - s$$
$$\ddot{z}_0 \equiv (t^3u''(s))^{-1}, \quad [3.12a]$$

where Eqs. [2.6c], [2.11], and [3.10] have been used. For $t \geq 1$ we have according to [2.6c] and [2.10]

$$z_0 = -\int_1^t d\tau \tau \dot{M}(\tau) - s = 0, \quad [3.12b]$$

since $d\tau = \tau^2 u''(s)ds$ and $\dot{M}(\tau) = -(\tau^2 u''(s))^{-1}$. In summary, we have for *large* x:

$$c(x, t) \cong \begin{cases} (\ddot{z}_0/2\pi)^{1/2} x^{-5/2} e^{-xz_0} & (t \leq 1) \\ (-\dot{M}/2\pi)^{1/2} x^{-5/2} & (t \geq 1). \end{cases} \quad [3.13]$$

As an example we take the initial gamma distribution, where z_0 follows from [2.6c], [3.10], and [3.12] as

$$z_0(t) = p + t - (p + 1)t^{1/(p+1)} \quad (t < 1) \quad [3.14a]$$

and

$$\ddot{z}_0(t) = -\dot{M}(t)$$
$$= [p/(p + 1)]t^{-(2p+1)/(p+1)}. \quad [3.14b]$$

Note that for times past the transition time, $t_c = 1$, the mass spectrum has a universal shape $\sim x^{-\tau}$ with $\tau = 5/2$, independent of the initial size distribution. Similar long tailed distributions occur in Junge's power low distributions for atmospheric aerosols (1, 4), although the typical τ- values[1] given in (1) are smaller than 5/2.

For an analysis of the behavior of [3.14] in the close vicinity of the gel point $t_c = 1$ we need the behavior of $z_0(t)$, which is parametrically given by [3.12] and [3.10]. By expanding [3.10] about $s = 0$ and using $u(0) = -u'(0) = 1$ and $u''(0) = M_3(0)$, we find $s \cong (t - 1)/M_3(0)$ as $t \uparrow 1$. Subsequent expansion of [3.12] about $s = 0$ and $t = 1$ yields finally: $z_0(t) \cong (t - 1)^2/2M_3(0)$ as $t \uparrow 1$. The behavior of [3.14] *past* the gel point depends on $\dot{M}(t)$, which has been calculated in [2.16]. Hence the asymptotic behavior for the size distribution $c(x, t)$ in the coupled limit $x \to \infty$ and $t \to t_c = 1$ with $x(t - t_c)^2 =$ fixed is given by

$$c(x, t) = (2\pi M_3(0))^{-1/2} x^{-5/2}$$
$$\times \begin{cases} \exp[-x(t - t_c)^2/2M_3(0)] & (t < t_c) \\ 1 & (t > t_c). \end{cases} \quad [3.15]$$

Therefore, the size distribution for $t < 1$ (sol phase) decreases exponentially at large x, so that all moments $M_n(t)$ remain finite for $t < 1$. For $t \geq 1$ (gel phase) the size distribution decays algebraically at large x, $c(x, t) \sim x^{-\tau}$ with $\tau = 5/2$, so that all moments with $n > 3/2$ are divergent, whereas the sol mass, $M_1(t)$, starts to decrease at a finite rate, as

[1] The relation between τ and the exponent β in Junge's power law is $\beta = 3\tau - 3$ [see (1)].

indicated in the beginning of Section 2. For $t < t_c$ the crossover from exponential to $x^{-5/2}$-behavior occurs at a critical cluster-size x_c with $x_c \cong M_3(0)(t - t_c)^{-2}$ as $t \uparrow t_c$. For $x \gg x_c$ we have $c(x, t) \sim x^{-\tau} \exp(-x/x_c)$, while in the intermediate range $0 \ll x \ll x_c$ we have $c(x, t) \sim x^{-\tau}$. As $t \uparrow t_c$, $x_c \to \infty$, and the $x^{-\tau}$-behavior extends to infinity for all $t \geq t_c$.

The results obtained so far apply to initial distributions, $c(x, 0)$, decaying exponentially at large x (see below [2.8]). A general discussion of the effects of initial distributions with algebraic tails has been given in (10). Here we only quote the results for a typical example, namely, $c(x, 0) \sim x^{-2-\lambda}$ with $1 < \lambda < 2$. At any fixed $t < 1$ the algebraic tail, $c(x, t) \sim Ax^{-2-\lambda}(x \to \infty)$, remains, but as $t \to 1$ the amplitude, A, diverges as $(1 - t)^{-\lambda-1}$; at the transition point $t = 1$ one finds $c(x, t) \sim x^{-2-1/\lambda}$ with a nonvanishing amplitude; and for $t > 1$ one finds $c(x, t) \sim x^{-5/2}$ with an amplitude, vanishing like $(t - 1)^{\gamma}$ as $t \downarrow 1$ with $\gamma = (1 - \frac{1}{2}\lambda)/(\lambda - 1)$.

If the initial distribution has an exponent λ in the range $0 < \lambda < 1$, so that $M_2(0) = \infty$, then $u'(0) = \infty$, and the gelation transition occurs instantaneously.

Large Time Behavior of c(x, t)

It follows from [3.3] that the behavior of $c(x, t)$ at large t and fixed x is similar to that at large x and fixed t with $t > 1$, as given in [3.14]. One only needs to insert the large t-behavior of $M(t)$ from [2.18–19].

An illustrative example is provided by the initial gamma distributions. Here we have on account of [2.14] and [3.13]:

$$c(x, t) \cong [2\pi(p + 1)/p]^{-1/2}x^{-5/2}t^{-(2p+1)/2(p+1)}$$
$$(t \to \infty, x \text{ fixed}). \qquad [3.16]$$

It reduces in the limit $p \to \infty$ to the well-known result for monodisperse initial conditions (9, 10). For general initial conditions, as discussed below [2.17], the same long time behavior [3.16] is found with a different multiplicative constant with a t-exponent depending on the shape of $c(x, 0)$. This behavior differs strongly from the corresponding result in the *discrete mass* case, where $c_k(t) \propto k^{-5/2}t^{-1}(t \to \infty)$ for general initial conditions. The abundance of grit at the fine grained end of the *continuous* initial mass spectrum is slowing down the coagulation and gelation reactions.

4. MODIFIED COAGULATION EQUATION

In this section we discuss a different coagulation problem with a phase transition, in which the loss term in the kinetic equation is modified past the transition point. We determine the Laplace transform of the size distribution and the time dependence of the sol mass. The ensuing behavior of $c(x, t)$ and $M_n(t)$ with $n \geq 2$ is quoted. Consider the loss term, $-xc(x, t)M(t)$, in the coagulation equation [1.1] for the kernel $K(x, y) = xy$. For $t < 1$ it is proportional to the *total mass* in the system, ($M(t) = 1$). For $t > 1$, the loss term only contains sol particles, with $M(t) < 1$. Therefore, in the coagulation process, described by [1.1] with $K = xy$, sol particles are only allowed to coalesce with other finite clusters, but not with the infinite cluster or superparticle. This corresponds to the situation in which the infinite cluster is continuously removed from the coagulating sol system (e.g., through precipitation).

One may also envisage the situation in which the finite clusters in the system can coalesce both with other finite clusters *and* with the infinite cluster; i.e., all mass, $M_1(0)$, initially present in the system, whether bonded in sol or gel, remains available for bonding sol particles. Therefore, the quantity $M_1(t)$ in the *loss term* of the kinetic equation for $K = xy$ equals unity at all times before and past t_c. The above model is described by the *modified coagulation equation:*

$$c_t(x, t) = \frac{1}{2}\int_0^x dyy(x - y)$$
$$\times\, c(y, t)c(x - y, t) - xc(x, t). \qquad [4.1]$$

For $t < t_c = 1$ this equation is identical to [1.1] with $K = xy$. In the case of discrete masses the modified coagulation equation has been discussed by Dusek (26) and Ziff *et al.* (7, 10) in connection with the gelation transition in reacting polymer systems. In polymer physics the modified coagulation equation [4.1] corresponds to Flory's theory (24) of gelation, and the usual coagulation equation with $K = xy$ to Stockmayer's (25), as discussed in (8, 10). Both theories yield different results only in the gel phase ($t \geq t_c$). In the former theory sol–gel interactions are allowed; in the latter theory such interactions are absent.

In the aerosol physics the gelation transition has been discussed by Lushnikov and coworkers (14, 27, 28). Following the method of Marcus [see (1), Section 2.4] a master equation is constructed for the probability distribution $P(c_1 c_2 \cdots c_k \cdots; t)$, in which the transition probabilities are constructed from the coagulation rates $K_{ij} = ij$ in Smoluchowski's coagulation equation. Here $\{c_k\}$ are the (fluctuating) numbers of k-clusters per unit volume, and the macroscopic size distribution is then an average $\bar{c}_k(t)$. At and past the gel point the fluctuations become of macroscopic size, and modify the average rate equations to yield effectively [4.1]. This procedure looks very different from the arguments leading to [4.1]. However, Ziff *et al.* (10) have shown for the case of discrete masses that Lushnikov procedure yields results, identical to those obtained from [4.1].

In the case of a continuous initial mass spectrum the modified coagulation equation can be discussed along the same lines as in the discrete case. However, the time dependence of the sol mass for $t > 1$ differs qualitatively from the discrete case. (Similar differences occur in the solutions of the usual coagulation equation, as already discussed in Section 2). This will be briefly elucidated.

The Laplace transform of [4.1] is given by [2.4] with M put equal to unity for all t. Hence, its solution for all t is

$$f(z, t) = u(z - tf + t). \qquad [4.2]$$

This follows from [2.6]. In the present case the mass of sol particles, $M(t) = f(0, t)$, can be obtained from [4.2] by setting $z = 0$, and yields the functional equation:

$$M = u(t - tM). \qquad [4.3]$$

This equation has two solutions: a constant solution $M_a(t) = 1$, and a solution $M_c(t)$, that decreases with increasing t. The physical mass of sol particles is again the smaller one of the two, i.e, $M(t) = \min(1, M_c(t))$. The large t-behavior is given by $M(t) \simeq u(t)$, where $u(z)$ at $z \to \infty$ is determined by the small x behavior of $c(x, 0)$.

The different behavior of $M(t) = 1 - G(t)$ in the usual and modified coagulation equation is best illustrated by the example of the initial gamma distributions with $u(z)$ given below [2.13]. The mass deficit or gel fraction, $G = 1 - M$, is according to [4.3] determined by

$$G = 1 - (1 + tG/p)^{-p} \qquad [4.4]$$

and leads to the long time behavior:

$$M(t) = 1 - G(t) \cong (p/t)^p \quad (t \to \infty). \qquad [4.5]$$

This result should be compared with the sol mass [2.14] in the usual coagulation equation, which has a slower decay at large t. The reason is the larger loss rate of sol particles in the modified coagulation equation due to the bonding of sol particles by the gel.

The discrete mass case with monodisperse initial conditions can be obtained by taking $p \to \infty$ in [4.4] with the result

$$G = 1 - \exp(-tG). \qquad [4.6]$$

This relation was first obtained by Flory (24) and Lushnikov (27). The large t-behavior of $G(t)$ in [4.6] decays exponentially:

$$M(t) = 1 - G(t) \simeq e^{-t} \qquad [4.7]$$

to be compared with the algebraic decay [2.12]. For an extensive comparison of results from the usual and modified coagulation equation we refer to (10).

The size distribution from the modified coagulation for $t > 1$ has the same function form as for $t < 1$; and is found by setting $T = t$ in Eqs. [3.3–8]. It always decays exponentially at large x, except at the transition point $t_c = 1$, where the size distribution has an algebraic tail $c(x, t_c) \propto x^{-5/2}$ as $x \to \infty$. Therefore, all moments $M_n(t)$ with $n \geqslant 2$ in the solution of the modified coagulation equation exist for $t \neq t_c = 1$, and behave in the close vicinity of the gel point as

$$M_2(t) \propto |t - 1|^{-1};$$
$$M_3(t) \propto |t - 1|^{-3} \quad (t \to 1). \qquad [4.8]$$

5. COAGULATION KERNELS $K(x, y) = (xy)^\omega$

The coagulation coefficient $K(x, y) = xy$ represents a reaction rate for coalescing clusters, proportional to their volumes. In many types of reactions the effective surface area of the reacting clusters determines their reaction rate so that we have typically $K(x, y) \simeq (xy)^{2/3}$. Some further examples of coagulation kernels for selected coagulation processes can be found in (1, 16, 17). Here we will study coagulation processes in which the coagulation rates have the general form $K(x, y) = (xy)^\omega$ with $\omega < 1$. Smoluchowski's coagulation equation takes the form

$$\partial_t c(x, t) = \frac{1}{2}\int_0^x dy[y(x-y)]^\omega c(y, t)c(x-y, t) - x^\omega c(x, t)\int_0^\infty dy y^\omega c(y, t). \qquad [5.1]$$

From the extensive literature on the subject it is known that the asymptotic dependence of $K(x, y)$ on the cluster size at large x and y is of crucial importance for the x- and t-dependence (1, 16, 29, 30), and in particular for the occurrence of a gelation transition within a finite time (21). For kernels $K(x, y) \leqslant c(xy)^{1/2}$ all moments remain bounded on bounded time intervals (31), thus excluding the occurrence of gelation within a finite time. For kernels $K(x, y) = (xy)^\omega$ with $\frac{1}{2} < \omega < 1$ the occurrence of gelation has been established in (18–21) for the case of discrete masses. Here we present a brief account of the theory for the continuous mass spectra and we will show that the size distribution $c(x, t)$ at and past the gel point t_c has asymptotically a power law behavior:

$$c(x, t) \simeq Ax^{-\tau} \quad (x \to \infty) \qquad [5.2]$$

with an exponent $\tau = \omega + 3/2$. This behavior can be found by studying the small z behavior of the Laplace transform of the distribution function. We, therefore, introduce

$$g(z, t) = \int^\infty dxc(x, t)e^{-zx}$$
$$f(z, t) = \int_0^\infty dxx^\omega c(x, t)e^{-zx} \qquad [5.3]$$

and take the Laplace transform of [5.1], which yields

$$g_t = \tfrac{1}{2}f^2 - fM_\omega. \qquad [5.4a]$$

Here M_ω is defined in [1.2]. Alternatively we may write

$$f = M_\omega - [M_\omega^2 + 2g_t]^{1/2}, \qquad [5.4b]$$

where the root with the minus sign is chosen because $f(z, t)$ is a decreasing function of z. If we write f and g as

$$g(z, t) = M_0 - zM_1 + \Delta(z, t)$$
$$f(z, t) = M_\omega + \delta(z, t), \qquad [5.5]$$

then $\Delta = 0(z)$ and $\delta = 0(1)$ for small z, since $M_0 < M_\omega < M_1 < \infty$ as the total mass of the system is finite. Furthermore, by setting $z = 0$ in [5.4a] it follows that

$$g_t(0, t) = \dot{M}_0 = -\tfrac{1}{2}M_\omega^2. \qquad [5.6]$$

To discuss the solution at and past the gel point t_c, it is necessary to look for solutions in which the total mass of sol particles, $M_1(t)$, depends upon time, so that $g_t \simeq \dot{M}_0 - z\dot{M}_1 + \cdots$. Combination of this result with [5.6] yields through [5.4b]

$$f(z, t) \simeq M_0 - (-2\dot{M}_1 z)^{1/2} \quad (z \to 0), \qquad [5.7]$$

where $\dot{M}_1$ is negative. The dominant small z singularity in $f(z, t)$ is a square root branch point, implying an algebraic tail $\sim x^{-3/2}$ in the inverse Laplace transform, so that (18, 19)

$$c(x, t) \cong (-\dot{M}_1/2\pi)^{1/2} x^{-\omega-3/2} \quad (x \to \infty). \qquad [5.8]$$

Thus, we have determined the large x-behavior of the size distribution past the gel point, where $\dot{M}_1 \neq 0$, and we have expressed the amplitude A in [5.2] in terms of the (unknown) mass loss rate. The behavior [5.8] must be consistent with the requirements on the existence of the moments in [5.5]. For M_1 to be finite we must have $\omega > 1/2$. Therefore, only for $\omega > 1/2$ can the coagulation equation [5.1] have (post-gelation) solutions with a time dependent M_1. For the kernels with $1/2 < \omega < 1$ we have neither been able to determine the sol mass $M_1(t)$, nor the gel point t_c. Estimates, or more precisely, lower bounds on t_c can be derived by studying the moments. A lower bound on $M_\alpha(t)$ with $\alpha > 1$, diverging at t_0, provides a lower bound: $t_c > t_0$. Our best lower bound for the gel point is

$$t_c > [(2^{2\omega-1} - 1)M_{2\omega}(0)]^{-1}, \qquad [5.9]$$

as has been derived in (20, 21).

The solution [5.8] is very similar to the steady-state solutions with gelation ($1/2 < \omega \leqslant 1$) (16, 17, 21) or without gelation ($\omega < 1/2$) (32), found in coagulating systems with sources. In case of a stationary monomer source, $q(x) = q\delta(x - 1)$, one simply replaces the mass loss rate $(-\dot{M}_1)$ in [5.8] by the source strength to obtain the stationary solution.

6. SUMMARY AND CONCLUSIONS

The coagulation equation with a rate constant $K(x, y) = (xy)^\omega$ with $1/2 < \omega < 1$ shows a phase transition, which manifests itself for times larger than a critical time t_c (gel point) through a violation of mass conservation. The violation of this conservation law is interpreted as the appearance of an infinite cluster or gel, which accounts for the mass deficit. For $t < t_c$ the sol mass is constant, and it starts to decrease for $t > t_c$.

For the special case $\omega = 1$ we have obtained the explicit solution of the coagulation equation for arbitrary initial distributions. The explicit form of the sol mass $M_1(t)$ is given parametrically by [2.9–11]. If the initial distribution is monodisperse or a gamma distribution a closed expression for $M_1(t)$ is given in [2.12] or [2.14]. The *long time* behavior [2.18] of $M_1(t) \sim t^{-p/(p+1)}$ with $p > 0$ for continuous mass spectra is markedly different from $M_1(t) \sim t^{-1}$ in the discrete case. This difference is caused by an abundance of minute particles of size $x \cong 0$ in the continuous case, which slow down the coagulation process. The size distribution $c(x, t)$ for an arbitrary initial distribution $u(z) = f(z, 0)$, defined in [2.5], is obtained in the form of an integral, which may be expanded in powers of t (see [3.6]). For the initial distribution $c(x, 0) = x^{-1}\exp(-x)$ we have obtained a global solution [3.5] in the form of a modified Bessel function. For the family of initial gamma distributions with parameter p we have obtained a global solution in the form of an infinite series [3.7] which converges for all t. For $p = 1$ the modified Bessel function is recovered; for $p = \infty$ one recovers the pre- and post-gelation solutions for monodisperse initial conditions. These explicit results constitute new solutions to the coagulation equation with the kernel $K(x, y) = xy$.

For general initial distributions we have calculated the large x-behavior [3.14] of $c(x, t)$ in the sol and gel phase. The mass spectrum is exponentially cut-off in the sol phase, and has an algebraic tail $\sim x^{-5/2}$ in the gel phase. The size distribution at large x and times close to $t = t_c$ or close to $t = \infty$, is given in [3.15] and [3.16]. The coagulation equation [1.1] with $K(x, y) = xy$ corresponds to Stockmayer's theory of the gelation transition in reacting polymer systems. The modified coagulation equation [4.1] corresponds to Flory's theory of gelation, in which sol and gel are allowed to interact. Such interactions are absent in Stockmayer's theory and, likewise, in [1.1] with $K(x, y) = xy$. The solution $c(x, t)$ of the modified coagulation equation decays exponentially for all $t \neq t_c$. Only at t_c has the size distribution $c(x, t_c)$ an algebraic tail $x^{-5/2}$. The modified coagulation equation is also equivalent to Lushnikov's coagulation theory (27) with a gelation transition. For coagulation kernels $K(x, y) = (xy)^{\omega}$ with $1/2 < \omega < 1$ we have obtained post-gelation solutions [5.8] in the form $c(x, t) \sim x^{-\tau}$ with $\tau = \omega + 3/2$, the amplitude of which depends on the function $M_1(t)$. We have neither been able to determine the sol mass $M_1(t)$, nor the gel point t_c. For the latter quantity we have given an estimate.

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