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Coagulation processes with mass loss

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Abstract. Smoluchowski's coagulation equation, with reaction rate $K(x, y)$, describing the time evolution of a size distribution $c(x, t)$ is studied in the presence of a mass loss term $m(x) = mx (m > 0)$. For $K(x, y) = 1$, $c(x, t)$ is determined explicitly for arbitrary initial distributions. If $K(x, y) = xy$, we determine $c(x, t)$ explicitly for arbitrary initial distributions and describe the behaviour of $c(x, t)$ for large x, for all times. Here, we show that a phase transition occurs in a finite time $t_g = -(1/2m)\log_e(1 - 2m)$ provided $m < \frac{1}{2}$. An investigation into $K(x, y) = (xy)^\omega$ reveals that a phase transition occurs in a finite time t_g if and only if $\frac{1}{2} < \omega \leqslant 1$ and $m < \frac{1}{2}$. An estimate of the least upper bound for t_g is calculated, and the behaviour of $c(x, t)$ for large x with $t > t_g$ is presented.

1. Introduction

Coagulation is very important in a wide variety of physical, chemical and biological processes. Consequently, an understanding of its kinetics is of great interest in many problems ranging from colloidal polymer technology [1] to antigen–antibody aggregation [2] and cluster formation in galaxies [3].

Smoluchowski's equation for rapid coagulation describes the temporal 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. Such systems may, in general, be described by the kinetic equation

$$\frac{\partial}{\partial t}c(x, t) = \frac{1}{2}\int_0^x \mathrm{d}y\, K(y, x - y)c(y, t)c(x - y, t) - c(x, t)\int_0^\infty \mathrm{d}y\, K(x, y)c(y, t) \qquad (1.1)$$

where $c(x, t)$ represents the concentration of particles of size x at time t, and $K(x, y)$ is the rate at which particles of size x and y coagulate to form a particle of size $(x + y)$.

For sufficiently high coagulation rates the solution of (1.1) describes a phase transition (gelation), signalled by the divergence of some moment of the size distribution $c(x, t)$ at a definite (critical) point. This occurs when $K(x, y) = (xy)^\omega$ if and only if $\frac{1}{2} < \omega \leqslant 1$ [4–8].

We are interested in physical systems which do not conserve mass during coagulation. Systems in which oxidation, melting, or evaporation occur on the exposed surface of the particles during coagulation are typical examples. Here, the exposed surface of the particle recedes continuously, eventually leading to a total loss of the mass of the particle. The intention of this paper is to study coagulation with this particular type of mass loss using a

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nonlinear rate equation similar to (1.1) for such systems. The appropriate rate equation is

$$\frac{\partial}{\partial t}c(x,t) = \tfrac{1}{2}\int_0^x \mathrm{d}y\, K(y,x-y)c(y,t)c(x-y,t) - c(x,t)\int_0^\infty \mathrm{d}y\, K(x,y)c(y,t) + \frac{\partial}{\partial x}(m(x)c(x,t)) \tag{1.2}$$

where $m(x)$ is a continuous mass loss rate, defined so that $m(\mu(t)) = -\mathrm{d}\mu(t)/\mathrm{d}t$ for a particle of time-dependent size or mass $\mu(t)$, as first introduced in work on fragmentation by Edwards *et al* [9]. The third term on the left-hand side of (1.2) arises when mass is removed continuously from particles in the system at a rate determined by $m(x)$, through evaporation, melting, or oxidation at the surface of the coagulating particles.

For coagulation, the structure of mass removable terms corresponding to various processes has been given by Crump and Seinfeld [10] and Hendriks [11], using ‘sinks’. It is of interest to investigate the effect of $m(x)$, a novel alternative to ‘sinks’, on properties of the solution $c(x,t)$, such as critical exponents, the occurrence of phase transitions (gelation), and so on, and see how this mass removal mechanism compares and contrasts with the usual ‘sinks’. It must be emphasized that although $m(x)$ and the usual ‘sinks’ both describe mass removal from physical systems, $m(x)$ and ‘sinks’ differ in one important aspect. When a ‘sink’ is employed to remove mass from a system it removes mass by removing complete particles. However, when the mass removal mechanism is implemented by $m(x)$, mass disappears from the particles themselves, yet the particles will still remain behind, albeit in diminished form, in the system. This essential difference between $m(x)$ and ‘sinks’ enables one to describe mass removal processes in coagulating systems which are beyond the scope and physical capabilities of the usual ‘sinks’.

The mass, $M(t)$, of our system is given by

$$M(t) = \int_0^\infty \mathrm{d}x\, x c(x,t)\,. \tag{1.3}$$

Differentiating (1.3) with respect to t and using (1.2) gives

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = -\int_0^\infty \mathrm{d}x\, m(x)c(x,t) \tag{1.4}$$

before a phase transition (gelation), if it occurs, provided $c(x,t) \to 0$ as $x \to \infty$ sufficiently quickly, and $m(x)c(x,t) \to$ constant as $x \to 0$.

The mass balance equation (1.4) describes the rate at which mass is being removed from the system before the occurrence of a phase transition. Whether equation (1.4) holds, or not, is one important criteria which signals the occurrence of a phase transition, another being the divergence of some higher moment of the size distribution $c(x,t)$. In the system under investigation the manner in which mass is removed may be adopted as a defining property of the system. Of course, other definitions based on the rate of change of various other moments of the size distribution $c(x,t)$ may also be adopted. For example, the system may be defined in terms of the rate of change of its zeroth moment, i.e. the number of particles in the system.

When a system exhibits a phase transition one is usually interested in the behaviour of the mass of the system before and after the phase transition. The number of particles in the system and other higher moments of the size distribution $c(x,t)$ are not so important. For this reason, in our work, we choose to define a system in terms of the rate of change of its mass, i.e. by (1.4). Bearing this in mind, it seems natural to investigate systems in which the rate at which mass being removed from the system is proportional to the amount of mass present in the system. This suggests we use the following form for the mass removal term:

$$m(x) = mx \qquad m > 0\,. \tag{1.5}$$

In which case

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = -mM(t)\,. \tag{1.6}$$

One may also consider systems in which $m(x) = mx^{\alpha}$, with $\alpha = 0$ corresponding to a system in which the rate of mass removal is proportional to the number of particles, $M_0(t)$, present in the system. However, in this paper we restrict ourselves to $m(x)$ defined as in (1.5).

Define the nth moment, $M_n(t)$, by

$$M_n(t) = \int_0^{\infty} \mathrm{d}x\, x^n c(x, t)\,. \tag{1.7}$$

Differentiating $M_n(t)$ with respect to t and using (1.2) yields

$$\frac{\mathrm{d}M_n(t)}{\mathrm{d}t} = \tfrac{1}{2}\int_0^{\infty} \mathrm{d}x \int_0^{\infty} \mathrm{d}y\, [(x+y)^n - x^n - y^n] K(x, y) c(x, t) c(y, t) - mnM_n(t)\,. \tag{1.8}$$

2. $K(x, y) = 1$

In the case of constant coagulation rates, as in Smoluchowski's original coagulation equation [12], (1.2) becomes

$$\frac{\partial}{\partial t} c(x, t) = \tfrac{1}{2}\int_0^{x} \mathrm{d}y\, c(y, t) c(x-y, t) - c(x, t)\int_0^{\infty} \mathrm{d}y\, c(y, t) + m\frac{\partial}{\partial x}(xc(x, t))\,. \tag{2.1}$$

Define the Laplace transform, $\phi(p, t)$, of $c(x, t)$ with respect to x by

$$\phi(p, t) = \int_0^{\infty} \mathrm{d}x\, \mathrm{e}^{-px} c(x, t) \tag{2.2}$$

in which case $c(x, t)$ is given by the inverse Laplace transform

$$c(x, t) = \frac{1}{2\pi \mathrm{i}}\int_{\gamma - \mathrm{i}\infty}^{\gamma + \mathrm{i}\infty} \mathrm{d}p\, \mathrm{e}^{px}\phi(p, t) \tag{2.3}$$

and $\mathrm{Re}(p) > \gamma$ to ensure convergence. It can be shown that $\phi(p, t)$ satisfies

$$\frac{\partial \phi(p, t)}{\partial t} + mp\frac{\partial \phi(p, t)}{\partial p} = \tfrac{1}{2}\phi^2(p, t) - \phi(p, t)\phi(0, t) \tag{2.4}$$

where, of course,

$$\phi(0, t) = \int_0^{\infty} \mathrm{d}x\, c(x, t) = M_0(t)\,. \tag{2.5}$$

From equation (1.8) with $n = 0$ and $K(x, y) = 1$, one finds

$$\phi(0, t) = M_0(t) = \frac{M_0(0)}{(1 + M_0(0)t/2)}\,. \tag{2.6}$$

Consequently, we need to solve (2.4), subject to the initial condition

$$f(p) = \phi(p, 0) = \int_0^{\infty} \mathrm{d}x\, \mathrm{e}^{-px} c(x, 0) \tag{2.7}$$

with $\phi(0,t) = M_0(t)$ as in (2.6). A solution can be found via the method of characteristics and reads

$$\phi(p,t) = \frac{f(p\mathrm{e}^{-mt})}{(1+M_0(0)t/2)(1+M_0(0)t/2-\frac{1}{2}f(p\mathrm{e}^{-mt})t)}\,. \tag{2.8}$$

Then $c(x,t)$ may be found from (2.3).

As an example consider an initially mono-disperse distribution

$$c(x,0) = \delta(x-1)\,. \tag{2.9}$$

Then a short calculation yields

$$c(x,t) = \sum_{k=1}^{\infty} \frac{(t/2)^{k-1}}{(1+t/2)^{k+1}}\delta(x - k\mathrm{e}^{-mt})\,. \tag{2.10}$$

Then using (2.10)

$$M(t) = \int_0^\infty \mathrm{d}x\, x c(x,t) = \mathrm{e}^{-mt} \tag{2.11}$$

which is a solution of the mass balance equation (1.6) with $M(0) = 1$. Therefore, this model does not undergo a phase transition. It may be noted that in the $m \to 0$ limit, we recover the solution of Smoluchowski [12].

3. $K(x,y) = xy$

In this case (1.2) becomes

$$\frac{\partial c(x,t)}{\partial t} = \frac{1}{2}\int_0^x \mathrm{d}y\, y(x-y)c(y,t)c(x-y,t) - xc(x,t)\int_0^\infty \mathrm{d}y\, yc(y,t) + m\frac{\partial}{\partial x}(xc(x,t))\,. \tag{3.1}$$

From equation (1.8) the first three moment equations are

$$\frac{\mathrm{d}M_0(t)}{\mathrm{d}t} = -\frac{1}{2}M^2(t) \tag{3.2a}$$

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = -mM(t) \tag{3.2b}$$

$$\frac{\mathrm{d}M_2(t)}{\mathrm{d}t} = M_2(t)(M_2(t) - 2m)\,. \tag{3.2c}$$

The solution of (3.2c) with $M_2(0) = 1$ is

$$M_2(t) = \frac{2m}{(1+(2m-1)\mathrm{e}^{2mt})}\,. \tag{3.3}$$

There are two qualitatively distinct cases to consider here for non-zero and positive m. If $2m \geqslant 1$, $M_2(t)$ remains bounded for all times. This implies that the mass balance equation (1.6) is valid, so that a gel never forms. If $2m < 1$, however, $M_2(t)$ diverges within a finite time, t_g (gel point), at which point $M_2(t)$ becomes singular. The gel point corresponds to a zero of the denominator in (3.3), whence

$$t_\mathrm{g} = -\frac{1}{2m}\log_\mathrm{e}(1-2m)\,. \tag{3.4}$$

Thus, we get the formation of an infinite gel in a finite time, t_g, which depends on the mass loss term. The situation here is in contrast to the case for the purely coagulating system where a gel forms, without fail, in a finite time $t_\mathrm{g} = 1$, for $M_2(0) = 1$. We note that if

$2m \geqslant 1$, the mass removal from the system is strong enough to prevent the formation of an infinite gel cluster. If $2m < 1$, the mass removal is insufficient to prevent the formation of an infinite gel cluster, which forms in a finite time t_g given by (3.4). Notice, however, that the mass removal does slow down the process of gel formation, i.e. $t_g > 1$. Of course, $t_g \to 1$, as $m \to 0$.

We now investigate each case in turn. First, define the Laplace transform, $\psi(p, t)$, of $xc(x, t)$ by

$$\psi(p, t) = \int_0^\infty \mathrm{d}x\, \mathrm{e}^{-px} xc(x, t)\,. \tag{3.5}$$

It can be shown that $\psi(p, t)$ satisfies

$$\frac{\partial \psi(p, t)}{\partial t} = -\frac{\partial \psi(p, t)}{\partial p}(\psi(p, t) - \psi(0, t)) - m\frac{\partial}{\partial p}(p\psi(p, t)) \tag{3.6}$$

where

$$\psi(0, t) = \int_0^\infty \mathrm{d}x\, xc(x, t) = M(t) \tag{3.7}$$

and $c(x, t)$ is given by the inverse Laplace transform

$$xc(x, t) = \frac{1}{2\pi \mathrm{i}} \int_{\gamma - \mathrm{i}\infty}^{\gamma + \mathrm{i}\infty} \mathrm{d}p\, \mathrm{e}^{px} \psi(p, t) \tag{3.8}$$

where $\mathrm{Re}(p) > \gamma$ to ensure convergence.

3.1. $2m < 1$

In this case a phase transition occurs and we get the formation of an infinite gel cluster in a finite time t_g given by (3.4). Without loss of generality we will always assume that $M(0) = 1 = M_2(0)$, which may be achieved by choosing suitable units for x, t and $c(x, t)$. It then remains for us to solve (3.6) subject to the initial condition

$$\psi(p, 0) = f(p) \tag{3.9}$$

and $f(0) = 1 = -f'(0)$. The method of characteristics provides us with the following solution for $\psi(p, t)$:

$$\psi(p, t) = \mathrm{e}^{-mt} f\left(p\mathrm{e}^{-mt} - \psi(p, t)\frac{\sinh(mt)}{m} + I(m, t)\right) \tag{3.10}$$

where

$$I(m, t) = \int_0^t \mathrm{d}\tau\, \mathrm{e}^{-m\tau} M(\tau)\,. \tag{3.11}$$

The Laplace transform $\psi(p, t)$ is therefore given implicitly by (3.10) for any given initial distribution $\psi(p, 0) = f(p)$.

The solution (3.10) still contains the unknown mass of the particles in the solution, $M(t) = \psi(0, t)$, which can be determined self-consistently by setting $p = 0$ in (3.10). So

$$M(t) = \mathrm{e}^{-mt} f\left(I(m, t) - M(t)\frac{\sinh(mt)}{m}\right). \tag{3.12}$$

Differentiating (3.12) with respect to t gives

$$\left(\frac{\mathrm{d}M(t)}{\mathrm{d}t} + mM(t)\right)\left(1 + \mathrm{e}^{-mt}\frac{\sinh(mt)}{m} f'\left(I(m, t) - M(t)\frac{\sinh(mt)}{m}\right)\right) = 0\,. \tag{3.13}$$

This equation has two distinct solutions for all t, provided the first singularity of $f(p)$ in the complex p-plane with $\mathrm{Re}(p) < 0$ is: (i) located at a point $p_0 < 0$, a finite distance away from the origin, and (ii) has the property, $f'(0) = \infty$, i.e. the initial size distribution can be bounded by an exponential. So, we find

$$M(t) = \mathrm{e}^{-mt} \qquad t < t_{\mathrm{g}} \tag{3.14}$$

which agrees with formal mass loss in the pre-gelation regime, and

$$M(t) - \mathrm{e}^{-mt} f\left(I(m,t) - M(t)\frac{\sinh(mt)}{m}\right) = 0 \qquad t > t_{\mathrm{g}} \tag{3.15a}$$

$$1 + \mathrm{e}^{-mt} f'\left(I(m,t) - M(t)\frac{\sinh(mt)}{m}\right) = 0 \qquad t > t_{\mathrm{g}} \tag{3.15b}$$

in the post-gelation regime.

There occurs a phase transition (gelation) in a finite time t_{g}, called the gel point, given by (3.4). In the pre-gelation phase, $t < t_{\mathrm{g}}$, $M(t)$ decreases exponentially with time, as expected. In the post-gelation phase, $t > t_{\mathrm{g}}$, the loss of mass, starting at $t = t_{\mathrm{g}}$, is associated with the formation of an infinite cluster, or gel. It is a loss to infinity due to the cascading growth of larger and larger clusters.

Consider again the mono-disperse initial distribution $c(x,0) = \delta(x-1)$. Then it can be shown that

$$M(t) = \begin{cases} \mathrm{e}^{-mt} & t < t_{\mathrm{g}} \\ \dfrac{m}{\sinh(mt)} & t > t_{\mathrm{g}} \end{cases} \tag{3.16}$$

and

$$M_0(t) = \begin{cases} M_0(0) + \dfrac{1}{4m}(\mathrm{e}^{-2mt} - 1) & t < t_{\mathrm{g}} \\ \dfrac{m}{2}\coth(mt) + M_0(0) - 1 + \dfrac{m}{2} & t > t_{\mathrm{g}}\,. \end{cases} \tag{3.17}$$

In the $m \to 0$ limit, these results reduce to those of Ernst *et al* [13]. Notice that for large t $M(t) \sim \mathrm{e}^{-mt}$, in contrast to [13], where $M(t) \sim 1/t$ for large t. This means that after the phase transition has occurred the rate at which mass is removed from the system above is faster than that in [13], which is consistent with expectations of a system which includes a mass removal mechanism.

We are now in a position to derive the general expression for the size distribution $c(x,t)$, valid for all times using (3.8). First, introduce a new integration variable ξ defined by

$$\mathrm{e}^{mt}\psi(p,t) = f(\xi) \qquad p = \mathrm{e}^{mt}\left(f^{-1}(\psi(p,t)\mathrm{e}^{mt}) + \psi(p,t)\frac{\sinh(mt)}{m} - I(m,t)\right). \tag{3.18}$$

Then equation (3.8), after two integrations by parts with vanishing boundary terms, yields

$$c(x,t) = \frac{m\mathrm{e}^{-xJ(m,t)}}{(2\pi\mathrm{i})x^2\sinh(mt)}\int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty}\mathrm{d}\xi\;\mathrm{e}^{x(\mathrm{e}^{mt}\xi + f(\xi)\sinh(mt)/m)} \tag{3.19}$$

where

$$J(m,t) = \mathrm{e}^{mt}I(m,t)\,. \tag{3.20}$$

The contour is a straight line to the right of all singularities in $f(p)$. Equation (3.19) represents the solution of our coagulation equation for all times, and $J(m,t)$ is given accordingly, depending on whether $t < t_{\mathrm{g}}$ or $t > t_{\mathrm{g}}$.

As our first example, suppose

$$c(x,0)=\frac{\mathrm{e}^{-x}}{x}\,. \tag{3.21}$$

Then,

$$\psi(p,0)=f(p)=\frac{1}{(1+p)}\,. \tag{3.22}$$

In which case (3.19) gives

$$c(x,t)=\frac{m^{1/2}\mathrm{e}^{-mt/2-x\mathrm{e}^{mt}-xJ(m,t)}}{x^2(\sinh(mt))^{1/2}}I_1\left(2\mathrm{e}^{mt/2}\left(\frac{\sinh(mt)}{m}\right)^{1/2}x\right) \tag{3.23}$$

where

$$J(m,t)=\begin{cases}\dfrac{\sinh(mt)}{m} & t<t_{\mathrm{g}}\\ \mathrm{e}^{mt}\left(1+m^{1/2}\displaystyle\int_{t_{\mathrm{g}}}^{t}\mathrm{d}u\,\frac{\mathrm{e}^{-3mu/2}}{(\sinh(mu))^{1/2}}\right) & t>t_{\mathrm{g}}\end{cases} \tag{3.24}$$

$$M(t)=\begin{cases}\mathrm{e}^{-mt} & t<t_{\mathrm{g}}\\ \dfrac{m^{1/2}\mathrm{e}^{-mt/2}}{(\sinh(mt))^{1/2}} & t>t_{\mathrm{g}}\end{cases} \tag{3.25}$$

and $I_1(2x)$ is the modified Bessel function defined by

$$I_1(2x)=\frac{1}{2\pi\mathrm{i}}\int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty}\mathrm{d}p\,\mathrm{e}^{x(p+1/p)}\,. \tag{3.26}$$

Returning to (3.19), we may re-write this expression for $c(x,t)$ as a power series, namely,

$$c(x,t)=\frac{m\mathrm{e}^{-xJ(m,t)}}{x^2\sinh(mt)}\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{x\sinh(mt)}{m}\right)^k\int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty}\frac{\mathrm{d}\xi}{2\pi\mathrm{i}}\mathrm{e}^{x\mathrm{e}^{mt}\xi}(f(\xi))^k \tag{3.27}$$

which is a convenient form to illustrate our next example.

Suppose, we have a mono-disperse initial distribution $c(x,0)=\delta(x-1)$. Then we find that $M(t)$ and $M_0(t)$ are as given above by (3.16) and (3.17), respectively, and

$$c(x,t)=\frac{m\mathrm{e}^{-mt-xJ(m,t)}}{x^2\sinh(mt)}\sum_{k=1}^{\infty}\frac{1}{k!}\left(\frac{x\sinh(mt)}{m}\right)^k\delta(x-k\mathrm{e}^{-mt}) \tag{3.28}$$

where

$$J(m,t)=\begin{cases}\dfrac{\sinh(mt)}{m} & t<t_{\mathrm{g}}\\ \mathrm{e}^{mt}\left(1+\log_{\mathrm{e}}\left(\dfrac{\mathrm{e}^{2mt}-1}{\mathrm{e}^{2mt_{\mathrm{g}}}-1}\right)-2m(t-t_{\mathrm{g}})\right) & t>t_{\mathrm{g}}\,.\end{cases} \tag{3.29}$$

We conclude this subsection with a brief derivation of the behaviour of $c(x,t)$ at large x. It may be noticed that the integral representation (3.19) for $c(x,t)$ is most convenient for obtaining the asymptotic behaviour of $c(x,t)$ at large x, using the saddle-point method. To obtain an asymptotic expression for (3.19) choose γ such that

$$F(\xi)=\mathrm{e}^{mt}\xi+\frac{\sinh(mt)}{m}f(\xi) \tag{3.30}$$

is at a maximum when the contour crosses the real axis. Then, γ is determined by

$$F'(\gamma) = \mathrm{e}^{mt} + \frac{\sinh(mt)}{m} f'(\gamma) = 0\,. \tag{3.31}$$

Observe that (3.31) is equivalent to (3.15*b*). Consequently, using (3.15*a*) gives

$$M(t) = \mathrm{e}^{-mt} f(\gamma) \qquad t > t_{\mathrm{g}}\,. \tag{3.32}$$

Expanding $F(\xi)$ about γ with $\xi = \gamma + \mathrm{i}y$, and deforming the contour to ensure that it passes through the saddle point at $\xi = \gamma$ with $\mathrm{Re}\{F(\xi)\}$ largest at $\xi = \gamma$ and $\mathrm{Im}\{F(\xi)\}$ constant in the neighbourhood of $\xi = \gamma$ gives

$$c(x,t) \sim \left(\frac{m^3}{2\pi \sinh^3(mt) f''(\gamma)}\right)^{1/2} \frac{1}{x^{5/2}} \mathrm{e}^{-x(J(m,t)-F(\gamma))} \tag{3.33}$$

as $x \to \infty$. It can readily be shown that for $t < t_{\mathrm{g}}$,

$$\xi_0 = J(m,t) - F(\gamma) = \frac{\sinh(mt)}{m}(1 - f(\gamma)) - \mathrm{e}^{mt}\gamma \tag{3.34a}$$

$$\ddot{\xi}_0 - m^2\xi_0 = \frac{m^3}{\sinh^3(mt) f''(\gamma)} \tag{3.34b}$$

and for $t > t_{\mathrm{g}}$

$$\xi_0 = J(m,t) - F(\gamma) = 0 \tag{3.35a}$$

$$\frac{m^3}{\sinh^3(mt) f''(\gamma)} = -\dot{M}(t) - mM(t)\,. \tag{3.35b}$$

Hence, we now have,

$$c(x,t) \sim \begin{cases} \left(\dfrac{\ddot{\xi}_0 - m^2\xi_0}{2\pi}\right)^{1/2} x^{-5/2}\mathrm{e}^{-x\xi_0} & t < t_{\mathrm{g}} \\[2ex] \left(\dfrac{-(\dot{M}(t) + mM(t))}{2\pi}\right)^{1/2} x^{-5/2} & t > t_{\mathrm{g}} \end{cases} \tag{3.36}$$

as $x \to \infty$. From which we deduce that for all times past the transition time, t_{g}, the mass spectrum has a universal shape $x^{-\tau}$, where $\tau = \frac{5}{2}$, independent of the initial size distribution. Equation (3.36) is also very useful for analysing the behaviour of $c(x,t)$ as $x \to \infty$, near the gel point t_{g}.

It follows from equation (3.19) that the behaviour of $c(x,t)$ at large t and fixed x is similar to that at large x and fixed t with $t > t_{\mathrm{g}}$. One only needs to insert the large t behaviour of $M(t)$ for $t > t_{\mathrm{g}}$, from (3.15*a*) and (3.15*b*). Of course, in the $m \to 0$ limit, the results presented in this subsection reduce to those obtained for the pure Smoluchowski equation with $K(x,y) = xy$ [13].

3.2. $2m \geqslant 1$

In this case a phase transition does not occur, i.e. a gel never forms, and it can readily be shown that the first three moments $M_0(t)$, $M(t)$, and $M_2(t)$ are given by

$$M_0(t) = M_0(0) + \frac{1}{4m}(\mathrm{e}^{-2mt} - 1) \tag{3.37a}$$

$$M(t) = \mathrm{e}^{-mt} \tag{3.37b}$$

$$M_2(t) = \frac{2m}{(1 + (2m-1)\mathrm{e}^{2mt})} \tag{3.37c}$$

and the problem is reduced to solving the following partial differential equation

$$\frac{\partial\psi(p,t)}{\partial t} = -\frac{\partial\psi(p,t)}{\partial p}(\psi(p,t) - \mathrm{e}^{-mt} + mp) - m\psi(p,t) \tag{3.38}$$

subject to the initial condition

$$\psi(p,0) = f(p) \tag{3.39}$$

with $f(0) = -f'(0) = 1$.

A calculation of the type performed in subsection 3.1 gives

$$\psi(p,t) = \mathrm{e}^{-mt} f\left(p\mathrm{e}^{-mt} - \psi(p,t)\frac{\sinh(mt)}{m} + \mathrm{e}^{-mt}\frac{\sinh(mt)}{m}\right). \tag{3.40}$$

Therefore, as above, the Laplace transform $\psi(p,t)$ is given implicitly by (3.40) for any given initial distribution $\psi(p,0) = f(p)$.

We are now in a position to determine $c(x,t)$ via (3.8), obtaining, as in subsection 3.1,

$$c(x,t) = \frac{m\mathrm{e}^{-x\sinh(mt)/m}}{(2\pi\mathrm{i})x^2\sinh(mt)}\int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty}\mathrm{d}\xi\;\mathrm{e}^{x(\mathrm{e}^{mt}\xi+\sinh(mt)f(\xi)/m)} \tag{3.41}$$

where, again, the contour is a straight line to the right of all singularities in $f(p)$. Equation (3.41) represents the solution of our coagulation equation with mass loss for all times for any given initial distribution $\psi(p,0) = f(p)$, and $2m \geqslant 1$.

Expanding (3.41) as a power series, we obtain

$$c(x,t) = \frac{m\mathrm{e}^{-x\sinh(mt)/m}}{x^2\sinh(mt)}\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{x\sinh(mt)}{m}\right)^k\int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty}\frac{\mathrm{d}\xi}{2\pi\mathrm{i}}\mathrm{e}^{x\mathrm{e}^{mt}\xi}(f(\xi))^k. \tag{3.42}$$

As an example consider a mono-disperse initial distribution $c(x,0) = \delta(x-1)$. Then it is easily shown that

$$c(x,t) = \frac{m\mathrm{e}^{-mt-x\sinh(mt)/m}}{x^2\sinh(mt)}\sum_{k=1}^{\infty}\frac{1}{k!}\left(\frac{x\sinh(mt)}{m}\right)^k\delta(x-k\mathrm{e}^{-mt}). \tag{3.43}$$

Furthermore, as shown in subsection 3.1, the integral representation (3.41) for $c(x,t)$ readily yields an asymptotic expression for $c(x,t)$ as $x\to\infty$. As above, choose γ to be such that (3.30) is at a maximum when the contour crosses the real axis. Then, γ is determined by (3.31). By expanding $F(\xi)$ about γ, and writing $\xi = \gamma + \mathrm{i}y$, we find

$$c(x,t) \sim \left(\frac{m^3}{2\pi\sinh^3(mt)f''(\gamma)}\right)^{1/2}\frac{1}{x^{5/2}}\mathrm{e}^{-x\sinh(mt)/m+x\mathrm{e}^{mt}\gamma+x\sinh(mt)f(\gamma)/m} \tag{3.44}$$

as $x\to\infty$.

4. The coagulation rate $K(x,y) = (xy)^\omega$

The coagulation rate $K(x,y) = xy$ represents a reaction rate for coagulating particles which is proportional to their volumes. In many types of reaction the effective surface area of the particles determines their reaction rate, in which case one requires $K(x,y) \cong (xy)^{2/3}$. Further examples of coagulation rates $K(x,y)$ for specific coagulation processes can be found in [14, 15]. Here we will restrict ourselves to the study of a coagulation process in which the coagulation rate $K(x,y)$ is of the form

$$K(x,y) = (xy)^\omega \qquad \omega \leqslant 1. \tag{4.1}$$

Thus, coagulation rates $K(x, y)$ which are proportional to the volumes and surfaces areas of the reacting particles are included in (4.1). Smoluchowski's coagulation equation with mass loss term (1.2) now takes the form

$$\frac{\partial c(x,t)}{\partial t} = \frac{1}{2}\int_0^x \mathrm{d}y\,[y(x-y)]^\omega c(y,t)c(x-y,t) - x^\omega c(x,t)\int_0^\infty \mathrm{d}y\, y^\omega c(y,t) + m\frac{\partial}{\partial x}(xc(x,t)) \,. \tag{4.2}$$

When $m = 0$, it is well known that for $\frac{1}{2} < \omega \leqslant 1$ a phase transition occurs within a finite time t_g [13]. As shown above, a phase transition occurs for $K(x, y) = xy$ and $m(x) = mx(m > 0)$ in a finite time t_g given by (3.4), provided m is restricted to certain values. Thus, choosing m carefully gives one the option of preventing the onset of gelation. We suspect this to be the case for $K(x, y) = (xy)^\omega$ as well, and we therefore investigate how m affects gelation in this case.

Using $K(x, y) = (xy)^\omega$ in (1.8) gives the first three moment equations in the form

$$\frac{\mathrm{d}M_0(t)}{\mathrm{d}t} = -\tfrac{1}{2}M_\omega^2(t) \tag{4.3a}$$

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = -mM(t) \tag{4.3b}$$

$$\frac{\mathrm{d}M_2(t)}{\mathrm{d}t} = M_{1+\omega}^2(t) - 2mM_2(t) \,. \tag{4.3c}$$

If $c(x, t)$ is non-negative we may write

$$M_{1+\omega}(t) \leqslant M_2^\omega(t)M^{\omega-1}(t) \,. \tag{4.4}$$

Before gelation, $M(t) = \mathrm{e}^{-mt}(M(0) = 1)$, consequently, (4.3$c$) and (4.4) yield

$$\frac{\mathrm{d}M_2(t)}{\mathrm{d}t} \leqslant M_2^{2\omega}(t)\mathrm{e}^{-2m(\omega-1)t} - 2mM_2(t) \,. \tag{4.5}$$

From which it follows that a phase transition will occur if and only if $\omega > \frac{1}{2}$. So, as with the case of a purely coagulating system, i.e. $m = 0$, a phase transition (gelation) occurs if and only if

$$\tfrac{1}{2} < \omega \leqslant 1 \,. \tag{4.6}$$

We now present a brief account of the theory for the above coagulation rate $K(x, y) = (xy)^\omega$, and show that the size distribution $c(x, t)$ at and beyond the gel point t_g has the asymptotic power law

$$c(x,t) \sim Ax^{-\tau} \tag{4.7}$$

as $x \to \infty$, with exponent $\tau = \omega + \frac{3}{2}$ and time-dependent amplitude A. This behaviour can be found by studying the small p behaviour of the Laplace transform of the distribution function. We introduce,

$$\psi(p,t) = \int_0^\infty \mathrm{d}x\,\mathrm{e}^{-px}c(x,t) \tag{4.8a}$$

$$\phi(p,t) = \int_0^\infty \mathrm{d}x\,\mathrm{e}^{-px}x^\omega c(x,t) \,. \tag{4.8b}$$

It is then possible to show that $\psi(p, t)$ and $\phi(p, t)$ are related by the partial differential equation

$$\frac{\partial\psi(p,t)}{\partial t} + mp\frac{\partial\psi(p,t)}{\partial p} = \frac{1}{2}\phi^2(p,t) - \phi(p,t)M_\omega(t) \tag{4.9}$$

where

$$M_\omega(t) = \int_0^\infty \mathrm{d}x\, x^\omega c(x,t)\,. \tag{4.10}$$

From equation (4.9) we find

$$\phi(p,t) = M_\omega(t) - \left[M_\omega^2(t) + 2\left(\frac{\partial\psi(p,t)}{\partial t} + mp\frac{\partial\psi(p,t)}{\partial p}\right)\right]^{1/2} \tag{4.11}$$

where the solution of (4.9) with the minus sign is taken since $\phi(p,t)$ is a decreasing function of p.

In this case we can write, for small p,

$$\psi(p,t) = M_0(t) - pM(t) + \varepsilon(p,t) \qquad \varepsilon(p,t) = \mathrm{O}(p) \tag{4.12a}$$

$$\phi(p,t) = M_\omega(t) + \delta(p,t) \qquad \delta(p,t) = \mathrm{O}(1) \tag{4.12b}$$

since $M_0(t) < M_\omega(t) < M(t) < \infty$, as the total mass in our system must be finite. A short calculation, with the aid of (4.3*a*), now produces,

$$\phi(p,t) \sim (-2\dot{M}_0(t))^{1/2} - (-2(\dot{M}(t) + mM(t)))^{1/2}p^{1/2} \tag{4.13}$$

as $p \to 0$. Here, $\dot{M}(t) + mM(t) \neq 0$, i.e. formal mass balance does not hold in the post-gel regime. Then inverting (4.13) gives,

$$c(x,t) \sim \left(\frac{-(\dot{M}(t) + mM(t))}{2\pi}\right)^{1/2} x^{-\omega-3/2} \tag{4.14}$$

as $x \to \infty$. Thus, we have determined the behaviour of $c(x,t)$ for large x past the gel point t_g, where

$$\dot{M}(t) + mM(t) \neq 0 \tag{4.15}$$

and have expressed the time-dependent amplitude, A, in terms of the unknown mass loss rate. The behaviour of (4.14) must be consistent with the requirements on the existence of the moments in (4.12). For $M(t)$ to be finite we must have $\omega > \frac{1}{2}$.

Although it has been shown that the mass removal term does not affect the values of ω for which a phase transition occurs, it does affect the time at which these phase transitions (gelations) occur, if and when they occur, for certain values of m.

For $K(x,y) = (xy)^\omega$ with ω restricted by (4.6), we have not been able to solve for $c(x,t)$, or find the value of t_g at which a phase transition occurs. However, we have been able to calculate a least upper bound for t_g, which reads

$$t_g \leqslant \frac{1}{2m(1-2\omega)}\log_e\bigl(1 - 2mM_2^{1-2\omega}(0)\bigr)\,. \tag{4.16}$$

Setting $M_2(0) = 1$, as usual, gives

$$t_g \leqslant \frac{1}{2m(1-2\omega)}\log_e(1-2m)\,. \tag{4.17}$$

Again a phase transition only occurs, for a given value of ω, if $2m < 1$. It is easily verified that the results of this section, in the $m \to 0$ limit, reduce to those obtained from an investigation of the analogous case with the pure Smoluchowski equation [13].

5. Conclusions

In this paper we introduce a continuous mass removal term, $m(x)$, which is a novel alternative to the usual 'sinks' [10, 11]. As stated in the introduction, we stress more forcefully here, the distinction between the mass removal process discussed in this paper and the usual 'sinks' is as follows. A 'sink' would remove complete particles from the system, whilst the continuous mass loss process considered here removes mass from the particles themselves, yet leaves these particles behind in the system. We have investigated the effect of this mass removal term on the coagulation process. For a constant coagulation rate $K(x, y) = 1$ and $m(x) = mx$, with $m > 0$, we present an exact solution to the coagulation problem with mass removal for arbitrary initial distributions, which reduces to the solution of Smoluchowski [12] in the $m \to 0$ limit. When $K(x, y) = xy$ and $m(x) = mx$, with $m > 0$, we have obtained an exact solution of the coagulation problem with mass removal for arbitrary initial distributions. In this case we also show that when $m < \frac{1}{2}$ a phase transition occurs in finite time t_g, given by (3.4), and a gel forms. When $m \geqslant \frac{1}{2}$, a phase transition does not occur, and we do not get gelation. Similar results are obtained in [11] using 'sinks', where it is shown that if the mass removal process, i.e. 'sink', is sufficiently strong gelation never occurs. The situation here is in contrast to the case for a purely coagulating system where a phase transition always occurs, and a gel forms, without fail, in a finite time $t_g = 1$. We have demonstrated that if the mass removal term is sufficiently strong, i.e. when $m \geqslant \frac{1}{2}$, the occurrence of a phase transition may be prevented. Even when the mass removal term is relatively weak, i.e. when $m < \frac{1}{2}$, the onset of the phase transition is slowed down. We have also determined explicitly the mass, $M(t)$, of the particles in the solution both before and after the gel point t_g as in (3.14) and (3.15). We have illustrated our results with some examples using various initial distributions $c(x, 0)$.

For arbitrary initial distributions we have determined the behaviour of $c(x, t)$ as $x \to \infty$, both before and after the gel point t_g. We show that the mass spectrum is exponentially cut-off for $t < t_g$, and has an algebraic tail $x^{-5/2}$ for $t > t_g$ which is universal. The solution of (1.2) when $K(x, y) = xy$ and $2m \geqslant 1$, for arbitrary initial distributions, when a phase transition does not occur and mass balance holds, is also presented along with the behaviour of $c(x, t)$ for large x.

Finally, an investigation into $K(x, y) = (xy)^{\omega}$ with $m(x) = mx$, $(m > 0)$, reveals that a phase transition occurs in a finite time t_g if and only if $\frac{1}{2} < \omega \leqslant 1$ and $2m < 1$. Thus, the presence of the mass removal term does not affect the values of ω for which a phase transition is possible. In this case it is also demonstrated that in the post gelation regime $c(x, t) \sim Ax^{-\tau}$, for large x, where $\tau = \omega + \frac{3}{2}$ and the amplitude A depends on $M(t)$. As we were unable to determine t_g explicitly, an estimate for t_g based on the least upper bound is calculated.

The technical nature of the subject of our paper, unfortunately, has the effect of making the consequences of our equations obscure. We therefore consider some of the equations in this paper in an attempt to clarify their meaning and also provide an insight into the meaning of other equations presented here. Consider, for example (2.10). The meaning of (2.10) is fairly simple, namely that the concentration of particles having undergone k collisions is the same as in the case of the pure Smoluchowski equation [12] as a function of k. The reason why the concentration is the same as that in the analogous pure Smoluchowski case is that the particles are colliding, and therefore coagulating, at a constant rate $(K(x, y) = 1)$ independent of their sizes or masses. Consequently, the continuous mass loss from the particles cannot possibly influence the coagulation process via the reaction rate $(K(x, y) = 1)$, and hence the concentration of particles which have undergone k collisions is unaffected. However, the mass contained within the particles has diminished as a consequence of the mass loss process. It is interesting to note that particles which have undergone a large number of collisions, i.e. k is large, contain very little mass. This is a manifestation of the fact that by the time the concentration of such particles has become appreciable, their mass has already become negligible. This last remark is even more relevant to the case where a phase transition (gelation) occurs, namely in the case described by (3.28) and (3.29). Here, we have a loss of mass from the system to an infinite gel cluster, in addition to the continuous loss of mass from the particles themselves. Now consider (3.28) and (3.29). In this case, the concentration of particles which have undergone k collisions is not the same as in the analogous case of the pure Smoluchowski equation [13]. This difference is due to the fact that two colliding particles, apart from coagulating at a rate which depends on the product of their sizes or masses $(K(x, y) = xy)$, are now also continuously losing mass at a rate which depends on their size or mass as they coagulate. Consequently, the continuous mass loss from the particles can influence the coagulation process via the reaction rate $(K(x, y) = xy)$, and hence the concentration of particles which have undergone k collisions is different. Again, as in the case described by (2.10), the mass contained within the particles which have undergone k collisions has also diminished as a direct consequence of the continuous mass loss process. Finally, consider (4.14). In contrast with the analogous pure Smoluchowski case [13], the size distribution $c(x, t)$ at and beyond the gel point t_g has a time-dependent amplitude A which now depends on the (unknown) mass $M(t)$ as well as the (unknown) mass loss rate $\mathrm{d}M(t)/\mathrm{d}t$. This is perfectly reasonable. The dependency of A on $\mathrm{d}M(t)/\mathrm{d}t$ is due to the loss of mass to the infinite gel cluster and the dependency of A on $M(t)$ is due to a continuous loss of mass from the particles themselves. Again, we state that taking the $m \to 0$ limit of the work presented in this paper reduces to the results presented in [12, 13] for the analogous pure Smoluchowski equation, as expected and required.

In this work we have restricted ourselves exclusively to $m(x) = mx$, with $m > 0$, which represents a mass removal process in which the rate at which mass being removed from the system is proportional to the amount of mass already present in the system. It would be interesting to see how $m(x) = m$, with $m > 0$, affects the coagulation process. Here, we have a mass removal process in which the rate at which mass being removed from the system is proportional to the number of particles (clusters) already present in the system. Indeed, it would be worthwhile to investigate $m(x) = mx^{\alpha}$, in general. The inclusion of a 'source' term in (1.2) would allow for the possibility of steady-state solutions. It would be interesting to investigate the nature of these steady-state solutions and see how these results compare with the well known work of White [14] and Crump and Seinfeld [15]. Furthermore, it would also be instructive to compare general solutions of (3.1) with a 'source' term with those of Hendriks and Ziff [16], where the usual 'sources' and 'sinks' are considered. We propose to investigate these issues in subsequent work.

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