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Self-similar behaviour in the coagulation equations

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Abstract. This paper describes solutions to the Smoluchowski coagulation equations with power-law kernels in both constant-mass and constant-monomer cases. Exact solutions are obtained in special cases by a generating function approach. For more general kernels, the large-time behaviour is obtained by use of matched asymptotics. Numerical results are also given, which confirm the asymptotic analysis.

Key words: coagulation equations, asymptotics, self-similar solutions, Smoluchowski.

1. Introduction

The discrete coagulation-fragmentation equations were first derived, and for certain cases solved, by von Smoluchowski [1] in 1916. They are an infinite set of chemical rate equations for the cluster-size distribution $c_j(t)$, *i.e.* a mathematical model for the dynamics of cluster growth.

If $c_j(t) \geqslant 0,\ j = 1, 2, \ldots$ denotes the number of clusters per unit volume consisting of j particles (j-clusters), the discrete coagulation-fragmentation equations are, when no particles are introduced to or removed from the system,

$$\dot{c}_1 = -\sum_{k=1}^{\infty}(a_{k,1}c_kc_1 - b_{k,1}c_{k+1}),$$

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1}\left(a_{k,j-k}c_kc_{j-k} - b_{k,j-k}c_j\right) - \sum_{k=1}^{\infty}\left(a_{k,j}c_kc_j - b_{k,j}c_{k+j}\right), \quad j = 2, 3\ldots, \tag{1.1}$$

where the values of the $a_{j,k} = a_{k,j}$ are determined by the bonding behaviour of a cluster of size j with one of size k and the values of the $b_{j,k} = b_{k,j}$ by the fragmentation rate of a cluster of size $j + k$ into one of size j and one of size k. Such models are of interest in a number of fields, such as aerosols, red blood cells [2], polymerisation and the clustering of colloidal particles [3].

In this paper we shall look at coagulating systems in which no fragmentation occurs, so that $b_{j,k} = 0$. The coagulation kernel we shall mainly use is

$$a_{j,k} = \tfrac{1}{2}\left(j^{\alpha}k^{\beta} + j^{\beta}k^{\alpha}\right), \tag{1.2}$$

where α and β are nonnegative constants. Such kernels apply, for example, in situations where bond linking and interactions between large clusters are the dominant mechanisms, when $\alpha = \beta = 1 - 1/d$ and d is the dimension of the cluster [4, 5]. Different $a_{j,k}$ have been looked at in [5] and [3]. We thus study

$$\dot{c}_1 = -\tfrac{1}{2}\left(M_\alpha(t) + M_\beta(t)\right) c_1, \tag{1.3}$$

$$\dot{c}_j = \frac{1}{4}\sum_{k=1}^{j-1}\left((j-k)^\alpha k^\beta + k^\alpha (j-k)^\beta\right) c_k c_{j-k} - \tfrac{1}{2}\left(M_\alpha(t) j^\beta + M_\beta(t) j^\alpha\right) c_j, \quad j \geqslant 2, \tag{1.4}$$

where we define

$$M_p(t) = \sum_{k=1}^{\infty} k^p c_k(t). \tag{1.5}$$

M_0 therefore denotes the total number of clusters and M_1 the total number of particles within these clusters. We shall consider two sets of boundary and initial data, which we term the ‘constant mass’ and the ‘constant monomer’ cases.

The constant-mass case arises when the full system (1.3), (1.4) holds. We define the mass by

$$\varrho \equiv \sum_{k=1}^{\infty} k c_k = M_1. \tag{1.6}$$

Introducing

$$J_0 = 0, \qquad J_k = \sum_{j=1}^{k} \sum_{l=k+1-j}^{\infty} j a_{l,j} c_l c_j, \quad k = 1, 2, \ldots, \tag{1.7}$$

we may readily show for the coagulation equations with general kernels $a_{j,k}$ that

$$\frac{\mathrm{d}(k c_k)}{\mathrm{d}t} = J_{k-1} - J_k, \tag{1.8}$$

so, formally,

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = -\lim_{N\to\infty} J_N. \tag{1.9}$$

Hence mass is conserved when the right-hand side of (1.8) is zero. However, we shall term even the cases when it is nonzero as ‘constant mass’; in such circumstances mass is lost to a cluster of infinite size (the ‘superparticle’ [6–7] or ‘gel-particle’) in a process known as gelation. The growth rate of the gel can be determined from (1.8) and the total mass in the finite size clusters together with the gel is conserved. We investigate below circumstances under which gelation occurs.

Commonly adopted initial conditions for the constant mass case correspond to monodisperse data, whereby the system contains only free monomers at $t = 0$, so that

$$\text{at} \quad t = 0, \qquad c_1 = 1, \qquad c_r = 0 \quad \forall\, r \geqslant 2; \tag{1.10}$$

without loss of generality we thus take $\varrho = 1$ at $t = 0$. The monomers then react with each other to form larger particles as time increases.

For the constant monomer case [8–9] we keep the number of free monomers at a specific concentration for all time by continually introducing monomers into the system, so we replace (1.3) by $\dot{c}_1 = 0$ and take $c_1 = 1$, without loss of generality; the simplest initial conditions are again given by (1.10). The mass will not be constant in this case due to the input of monomers, so in particular gelation need not coincide with a decrease in M_1.

Ball and Carr [4] have considered issues of existence, uniqueness and density conservation for solutions to the coagulation-fragmentation equations, extending proofs developed for the Becker–Döring equations (the special case of (1.1) in which $a_{j,k} = \alpha_j \delta_{j1} + \alpha_k \delta_{k1}$ and $b_{j,k} = \beta_{j+1}\delta_{j1} + \beta_{k+1}\delta_{k1}$) to more general systems. Both Leyvraz and Tschudi [10] and Hendriks *et al*. [5] examine purely coagulating systems, with kernels $a_{j,k} = (Aj + B)(Ak + B)$ and $a_{j,k} = (jk)^\alpha$, respectively. For coagulation equations with reaction coefficients $a_{j,k} = (jk)^\alpha$ in which gelation occurs, after gelation the appropriate *ansatz* for large j is that

$$c_j(t) \sim K(t) j^{-\sigma} \qquad \text{as } j \to +\infty \quad \text{for } t > t_g, \tag{1.11}$$

for some constant σ and some $K(t)$, where t_g is the gelation time. Leyvraz and Tschudi [11] and Ziff *et al*. [14] discuss the relationship between α and σ for the case $\alpha = \beta$, both showing that $\sigma = \frac{3}{2} + \alpha$.

We note that the discrete system (1.4) has the continuous symmetries

$$c^*_{j^*} = \mu c_j, \quad M^*_p = \mu M_p, \quad j^* = j, \quad k^* = k, \quad t^* = t/\mu, \tag{1.12}$$

$$c^*_{j^*} = c_j, \quad M^*_p = M_p, \quad j^* = j, \quad k^* = k, \quad t^* = t + t_0; \tag{1.13}$$

these in fact exist for general coagulation kernels. Equation (1.12) implies the existence of the separable similarity reduction

$$c_j(t) = \frac{1}{t} f_j, \tag{1.14}$$

while steady states

$$c_j(t) = g_j \tag{1.15}$$

correspond to (1.13). As we shall see, both of these similarity reductions play a crucial role in describing the large time behaviour (the generalisation of (1.14) given by $c_j(t) = f(k + a \ln t)/t$ for constant a does not play a role here). Much of the asymptotic behaviour, however, while of self-similar form, does not correspond to an exact similarity reduction of (1.4). We also note a discrete symmetry of (1.4) (*cf*. [11]), namely

$$M^*_p = n^p M_p \quad j^* = nj, \quad k^* = nk, \quad t^* = t/n^{\alpha+\beta}, \tag{1.16}$$

and

$$c^*_{j^*} = \begin{cases} c_j & \text{if } j^* \text{ is a multiple of } n, \\ 0 & \text{otherwise,} \end{cases} \tag{1.17}$$

where n is a positive integer.

In Section 2 of this paper we give explicit solutions to the special cases $\alpha = \beta = 0$, $\alpha = 1$ with $\beta = 0$ and $\alpha = \beta = 1$ for the constant-mass case and investigate the behaviour of the constant-monomer case with the same values of α and β. Other values of α and β are considered in Section 3 for the constant mass case and in Section 4 for the constant-monomer case. Both these sections include numerical solutions of the system together with a detailed asymptotic analysis. The paper concludes with a discussion of our results.

There is substantial literature making use of scaling and similarity ideas in the analysis of the coagulation equations (in addition to the references already noted, see [12] and [13], for example) and we shall not attempt to review it here. Many of the results for constant mass derived below have appeared before, largely in the special case $\alpha = \beta$, but even in these cases our approach is somewhat different and we believe the results are in general more complete.

2. Exact solutions

For certain values of α and β (namely $\alpha, \beta = 0, 1$) the coagulation equations can be solved analytically in the constant-mass case. From our outline of these solutions it can be seen that for $\alpha = \beta = 0$ and $\alpha = 1$ with $\beta = 0$ the system does not gelate, but for $\alpha = \beta = 1$ mass is ultimately lost to the gel-particle, the system gelating within finite time. For the constant monomer case it can again be seen that with the first two sets of coagulation kernels the system does not gelate but for the third it does.

2.1. Constant mass

In this case the coagulation equations and initial conditions are defined by (1.3)–(1.4) and (1.10), so that

$$M_0(0) = M_1(0) = 1. \tag{2.1}$$

For the cases indicated above the system can be solved explicitly, as noted by Leyvraz and Tschudi [10] who solve for $\alpha = \beta = 0$ and $\alpha = \beta = 1$. A more concise way to obtain these exact solutions is to study the generating function

$$C(z, t) = \sum_{k=1}^{\infty} c_k(t) \exp(-kz), \tag{2.2}$$

for each integrable kernel, so that in particular

$$M_0 = C(0, t), \qquad M_1 = -\frac{\partial C}{\partial z}(0, t). \tag{2.3}$$

From (1.10) we thus have

$$C(z, 0) = \exp(-z). \tag{2.4}$$

2.1.1. *Case I: $\alpha = \beta = 0$*

For $\alpha = \beta = 0$, substituting the generating function in Equation (1.1) yields

$$\frac{\partial C}{\partial t} = \tfrac{1}{2} C^2(z, t) - M_0 C(z, t), \tag{2.5}$$

where $M_0 = C(0, t)$, the zeroth moment, can be determined by setting $z = 0$ in (2.5) to give $\dot{M}_0 = -\frac{1}{2} M_0^2$, with solution $M_0 = 2/(t + 2)$. Solving the Bernoulli equation (2.5), subject to (2.4), we have

$$C(z, t) = \frac{4}{(t + 2)^2 \exp(z) - t(t + 2)}, \tag{2.6}$$

which can be expanded to yield the solution

$$c_j(t) = \frac{4t^{j-1}}{(t + 2)^{j+1}} \quad t \geqslant 0. \tag{2.7}$$

No gelation occurs in this case, with $M_1 = 1$ holding for all time. The large-time behaviour of (2.7) is of the form

$$c_j \sim t^{-2} g\,(j/t) \quad \text{as } t \to \infty \quad \text{with } j = O(t), \tag{2.8}$$

with

$$g(\eta) = 4\,\mathrm{e}^{-2\eta}. \tag{2.9}$$

2.1.2. *Case II: $\alpha = 1,\ \beta = 0$*

The partial differential equation for the generating function is now

$$\frac{\partial C}{\partial t} = -\tfrac{1}{2} C \frac{\partial C}{\partial z} + \tfrac{1}{2} \frac{\partial C}{\partial z} M_0(t) - \tfrac{1}{2} M_1(t) C. \tag{2.10}$$

Assuming no gelation occurs, we have $M_1 = 1$ for all time. The zeroth moment can then be found by setting $z = 0$ in (2.10), which gives $M_0(t) = \mathrm{e}^{-t/2}$, so

$$\frac{\partial C}{\partial t} = \tfrac{1}{2} \left(\mathrm{e}^{-t/2} - C\right) \frac{\partial C}{\partial z} - \tfrac{1}{2} C. \tag{2.11}$$

We can solve this, subject to (2.4), in implicit form using the method of characteristics to give

$$\mathrm{e}^{-z} = C(z, t) \exp\left(1 + \tfrac{1}{2} t - \mathrm{e}^{-t/2}\right) \exp\left(\left(\mathrm{e}^{t/2} - 1\right) C(z, t)\right). \tag{2.12}$$

If we use Lagrange's expansion [15, Equations 3.6.6–3.6.7] the concentrations can then be shown to be

$$c_j(t) = \frac{1}{j!} j^{j-1}\, \mathrm{e}^{-t/2} \left(1 - \mathrm{e}^{-t/2}\right)^{j-1} \exp\left(-j\left(1 - \mathrm{e}^{-t/2}\right)\right), \tag{2.13}$$

confirming our assumption of no gelation.

The large time behaviour can easily be extracted from (2.13) as

$$c_j \sim \frac{j^{j-1}}{j!}\, \mathrm{e}^{-j}\, \mathrm{e}^{-t/2} \quad \text{as } t \to \infty \quad \text{with } j = O(1), \tag{2.14}$$

and, from Stirling's formula, as

$$c_j \sim \mathrm{e}^{-2t} g(j/\mathrm{e}^t) \quad \text{as } t \to \infty \quad \text{with } j = O(\mathrm{e}^t), \tag{2.15}$$

with

$$g(\eta) = \mathrm{e}^{-\eta/2}/(2\pi\eta^3)^{1/2}. \tag{2.16}$$

2.1.3. *Case III:* $\alpha = \beta = 1$
For $\alpha = \beta = 1$ we have

$$\frac{\partial C}{\partial t} = \frac{1}{2}\left(\frac{\partial C}{\partial z}\right)^2 + M_1(t)\frac{\partial C}{\partial z}. \tag{2.17}$$

The substitution $u = -\partial C/\partial z$ simplifies (2.17) to an equation of inviscid Burgers type

$$\frac{\partial u}{\partial t} = (M_1(t) - u)\frac{\partial u}{\partial z}. \tag{2.18}$$

Solving by the method of characteristics, subject to $u = \mathrm{e}^{-z}$ at $t = 0$, we have

$$z = tu - \log u - \int_0^t M_1(t')\,\mathrm{d}t', \tag{2.19}$$

so that

$$\frac{\partial u}{\partial z} = -\frac{u}{1 - tu}. \tag{2.20}$$

It remains to determine $M_1(t)$. Since $u(0,t) = M_1(t)$, it follows from (2.18) that the two possibilities are the following.

(i) $\dot{M}_1 = 0$, this being the pre-gelation case, $0 \leqslant t < t_g$. We then have $u(0,t) = M_1 = 1$, with $z = 0$ being a characteristic of (2.18), up until the gelation time $t = t_g$. Thus

$$z = tu - \log u - t \tag{2.21}$$

and (2.10), which implies that

$$M_2(t) = \frac{1}{1-t} \quad \text{for } t < 1, \tag{2.22}$$

blows up at $z = 0$ when $t = 1$, from which we deduce that $t_g = 1$. For $t > 1$, $u(z,t)$ as given by (2.21) is multi-valued in $z > 0$, implying the presence of a shock in the solution to (2.18).

(ii) $(\partial u/\partial z)(0,t)$ is unbounded, indicating the post-gelation case, $t > t_g = 1$. After gelation, we determine M_1 by requiring that the point at which $\partial u/\partial z$ is unbounded remain fixed at $z = 0$. This corresponds to

$$M_2(t) = -\frac{\partial u}{\partial z}(0,t) \tag{2.23}$$

being unbounded. Since M_0 and M_1, in particular, remain bounded after gelation, singularities in $z > 0$ are not permissible. It thus follows from (2.20) that for $t > 1$

$$1/t = u(0,t) = M_1(t). \tag{2.24}$$

Equation (2.19) then gives

$$\exp(-z) = \begin{cases} u\exp((1-u)t), & t \leqslant 1, \\ ut\exp(1-ut), & t \geqslant 1, \end{cases} \tag{2.25}$$

from which we can extract $u(z, t)$ using Lagrange's expansion [15, Equations 3.6.6–3.6.7], giving

$$u(z,t) = \begin{cases} \displaystyle\sum_{k=1}^{\infty} \frac{k^{k-1}t^{k-1}}{k!}\exp(-k(t+z)), & t \leqslant 1, \\ \displaystyle\sum_{k=1}^{\infty} \frac{k^{k-1}\exp(-k)}{k!t}\exp(-kz), & t \geqslant 1, \end{cases} \tag{2.26}$$

so that

$$c_j(t) = \begin{cases} \dfrac{j^{j-3}t^{j-1}e^{-jt}}{(j-1)!}, & t \leqslant 1, \\ \dfrac{j^{j-3}e^{-j}}{(j-1)!t}, & t \geqslant 1. \end{cases} \tag{2.27}$$

The post-gelation behaviour is thus exactly of the separable form [10],

$$c_j(t) = \frac{1}{t} f_j \tag{2.28}$$

with

$$f_j = \frac{j^{j-3}\,\mathrm{e}^{-j}}{(j-1)!}. \tag{2.29}$$

We note from (2.17) that

$$\frac{\mathrm{d}M_0}{\mathrm{d}t} = -\tfrac{1}{2}M_1^2 \tag{2.30}$$

so that

$$M_0 = \begin{cases} 1 - \tfrac{1}{2}t, & t \leqslant 1, \\ \dfrac{1}{2t}, & t \geqslant 1. \end{cases} \tag{2.31}$$

By applying Stirling's formula to (2.27), the large j behaviour can be written in the instructive form

$$\text{as } j \to +\infty \qquad c_j(t) \sim \begin{cases} \dfrac{\mathrm{e}^{-j(t-1-\log(t))}}{j^{5/2}t\sqrt{2\pi}} & \text{pre-gel}, \quad t < 1, \\ \dfrac{1}{j^{5/2}t\sqrt{2\pi}} & \text{post-gel}, \quad t \geqslant 1. \end{cases} \tag{2.32}$$

2.2. Constant monomer

While closed-form solutions are scarcer than in the constant mass case, valuable information can still be deduced by generating-function methods. We again adopt the initial conditions (1.10).

2.2.1. *Case I:* $\alpha = \beta = 0$

Again introducing (2.2), with $c_1 = 1$, we obtain

$$\frac{\partial C}{\partial t} = \tfrac{1}{2}C^2 - (C - \mathrm{e}^{-z})M_0, \tag{2.33}$$

where $M_0 = C(0, t)$ can be found by setting $z = 0$ in (2.33), giving $M_0 = 2/(1 + \mathrm{e}^{-t})$, and hence

$$\frac{\partial C}{\partial t} = \tfrac{1}{2}C^2 - \frac{2}{1 + \mathrm{e}^{-t}}C + \frac{2\mathrm{e}^{-z}}{1 + \mathrm{e}^{-t}}, \tag{2.34}$$

subject to (2.4). This is a Riccati equation which we can in the usual way transform to a linear second-order equation by writing $C(z, t) = -2(\partial w/\partial t)/w$. The further substitution $\tau = -\exp(t)$ leads to

$$\tau(1 - \tau)\frac{\partial^2 w}{\partial \tau^2} + (1 - 3\tau)\frac{\partial w}{\partial \tau} - \mathrm{e}^{-z}w = 0, \tag{2.35}$$

which is a hypergeometric equation. It does not seem possible to write the solution in a useful form; the behaviour as $t \to \infty$ is readily deduced as

$$w \sim W(z)(-\tau)^{-1+\sqrt{1-\mathrm{e}^{-z}}} \quad \text{as} \quad \tau \to -\infty, \tag{2.36}$$

for some $W(z)$, which corresponds to the steady state solution for C (*cf*. Section 4.1). The large time behaviour is discussed in more detail in Appendix A.

2.2.2. *Case II:* $\alpha = 1,\ \beta = 0$

In this case the generating function $C(z, t)$ satisfies

$$\frac{\partial C}{\partial t} = -\tfrac{1}{2}C\frac{\partial C}{\partial z} + \tfrac{1}{2}\left(\mathrm{e}^{-z} + \frac{\partial C}{\partial z}\right)M_0 + \tfrac{1}{2}\left(\mathrm{e}^{-z} - C\right)M_1. \tag{2.37}$$

This system does not gelate and two simultaneous equations for the zeroth and first moments can be gained by setting $z = 0$ in Equation (2.37) and its derivative with respect to z, namely

$$\frac{\mathrm{d}M_0}{\mathrm{d}t} = \tfrac{1}{2}\left(M_0 + M_1 - M_0 M_1\right), \tag{2.38}$$

$$\frac{\mathrm{d}M_1}{\mathrm{d}t} = \tfrac{1}{2}(M_0 + M_1). \tag{2.39}$$

The phase-plane for these equations is shown in Figure 1. From this it can be seen that mass (M_1) is monotonically increasing, but the number of clusters (M_0) reaches a maximum and then decreases, due to the average size of the clusters getting larger as time increases.

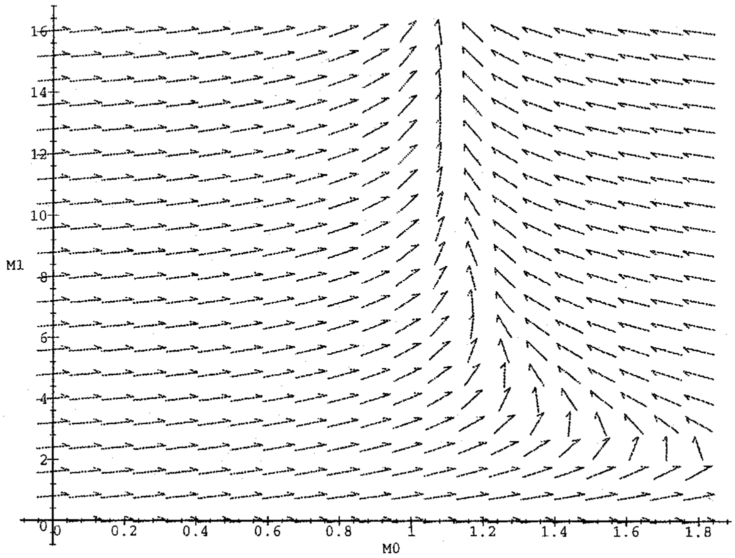

Figure 1. The phase portrait of the zeroth and first moments.

Clearly (2.38) implies $M_0 \to 1$ as $t \to \infty$ and then (2.39) implies that the mass diverges exponentially. To be more precise

$$\begin{aligned} M_0 &\sim 1 + \mathrm{e}^{-t/2}/A, \\ M_1 &\sim A\,\mathrm{e}^{t/2} - 1 \quad \text{as } t \to \infty, \end{aligned} \tag{2.40}$$

indicating that the number of clusters with aggregation numbers greater than unity decays exponentially with time. The constant A depends on the initial data. In fact we can solve (2.38) and (2.39) in closed form by introducing $\phi = M_0 + M_1 + M_1^2/2$, which satisfies

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \phi. \tag{2.41}$$

In view of (2.3) we have

$$\phi = \frac{5}{2}\,\mathrm{e}^t, \tag{2.42}$$

from which it follows that $A = \sqrt{5}$ when the initial data (1.10) holds. (2.42) can be used to give a Riccati equation for M_1 which can be solved in terms of modified Bessel functions.

The large time behaviour of this case is remarkably rich in structure and has some noteworthy features; it is outlined in Appendix B.

2.2.3. *Case III:* $\alpha = \beta = 1$

Gelation does not occur in the preceding two cases, but does in the current one. The equation

$$\frac{\partial C}{\partial t} = \frac{1}{2}\left(\frac{\partial C}{\partial z}\right)^2 + \left(\mathrm{e}^{-z} + \frac{\partial C}{\partial z}\right) M_1(t) \tag{2.43}$$

holds, from which it follows that $M_1 = \mathrm{e}^t$ before gelation. By again substituting $u(z,t) = -\partial C/\partial z$ we thus obtain prior to gelation that

$$\frac{\partial u}{\partial t} = \left(\mathrm{e}^t - u\right)\frac{\partial u}{\partial z} + \mathrm{e}^{t-z}. \tag{2.44}$$

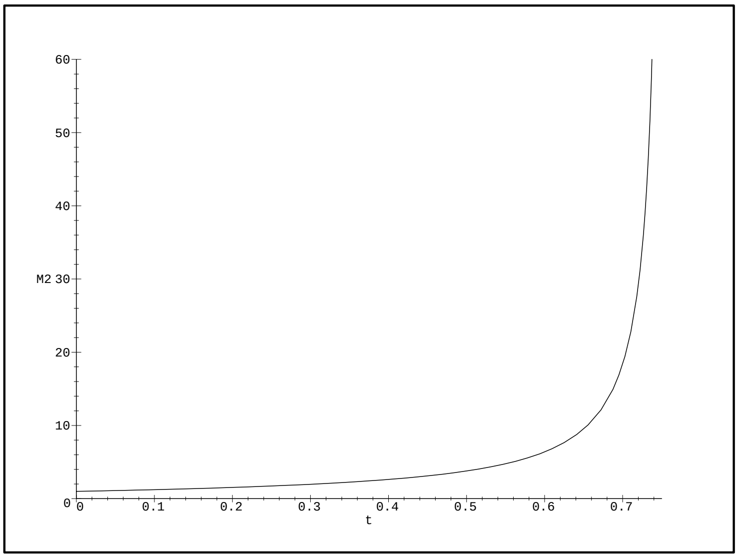

Figure 2. The second moment for the constant-monomer case with $\alpha = \beta = 1$.

We thus have along characteristics that

$$\frac{dz}{dt} = u - e^t, \qquad \frac{du}{dt} = e^{t-z}. \tag{2.45}$$

Further analytical progress with the full solution does not appear possible.

The gelation time can, however, be calculated. Differentiating (2.44) with respect to z and setting $z = 0$, we obtain

$$\frac{dM_2}{dt} = M_2^2 + e^t, \tag{2.46}$$

which is again a Riccati equation. Substituting $M_2 = -(d\kappa/dt)/\kappa$ and $\tau = 2\,e^{t/2}$ yields

$$\tau \frac{d^2\kappa}{d\tau^2} + \frac{d\kappa}{d\tau} + \tau\kappa = 0, \tag{2.47}$$

and, since $M_2 = 1$ at $t = 0$, we find that

$$M_2(t) = e^{t/2} \frac{(Y_0(2) - Y_1(2))\, J_1(2e^{t/2}) - (J_0(2) - J_1(2))\, Y_1(2e^{t/2})}{(Y_0(2) - Y_1(2))\, J_0\left(2e^{t/2}\right) - (J_0(2) - J_1(2))\, Y_0(2e^{t/2})}, \tag{2.48}$$

which is plotted in Figure 2. The gelation time, at which M_2 becomes unbounded, is approximately 0·754. It follows from the steady-state solution of Section 4.1 (which gives the large time behaviour) that $M_2 \to 2$ as $t \to \infty$, a slight decrease in the mass of finite clusters compared to its value at the gelation time.

Limited other information can also readily be deduced. For example, from (2.43) we have

$$\frac{dM_0}{dt} = M_1 - \tfrac{1}{2}M_1^2, \tag{2.49}$$

so that $M_0 = e^t + \frac{1}{4}(1 - e^{2t})$ for $t < t_g$. The other pre-gelation moments can be calculated sequentially, as can the c_j. We have

$$\frac{dM_n}{dt} = \frac{1}{2}\sum_{j=1}^{n-1} \frac{n!}{j!(n-j)!} M_{j+1}M_{n-j+1} + e^t. \tag{2.50}$$

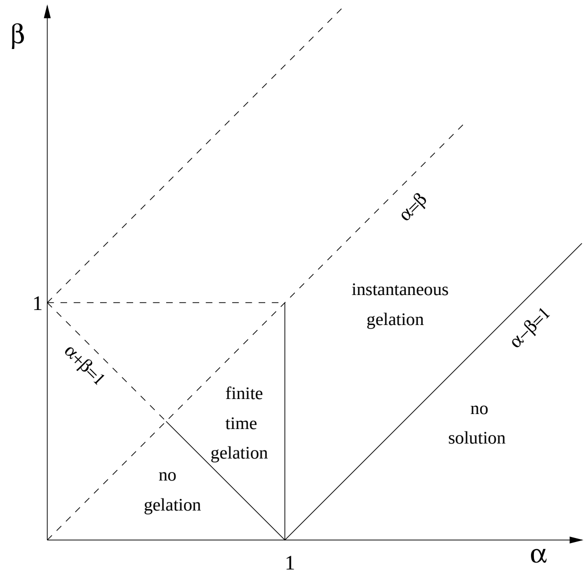

Figure 3. Gelation behaviour in the (α, β) plane.

3. The constant-mass case

3.1. Numerical results

3.1.1. *Formulation*

We shall now look at general (including noninteger) values of α and β, for which exact solutions cannot be found. Solutions to the coagulation equations fall into four categories depending on the value of α and β; without loss of generality we take $\alpha \geqslant \beta$ throughout. For values with $\alpha + \beta < 1$ no gelation occurs, while for $\alpha + \beta > 1$, $\alpha < 1$ gelation occurs at some finite time, $t_g > 0$. For $\alpha > 1$ gelation occurs instantaneously ($t_g = 0$), and if $\alpha - \beta > 1$ no solution exists, all of the mass being transferred into a gel (we term this 'complete gelation'). The situation is shown schematically in Figure 3 and the results given below indicate how the various dividing lines are deduced (the identification of the borderline between finite time and instantaneous gelation is beyond the scope of this paper, however); we shall not for the most part discuss the borderline cases. Because α and β are interchangeable Figure 3 is symmetric about $\alpha = \beta$.

A suite of Fortran 77 programs has been written to solve the various coagulation systems described in this paper. NAG routines for stiff systems of ordinary differential equations were used to solve a truncated form of the infinite system, namely

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1} a_{k,j-k} c_k c_{j-k} - \sum_{k=1}^{N-j} a_{k,j} c_k c_j \quad \text{for} \ \ j = 1, \ldots, N, \tag{3.1}$$

where we typically take $N = 200$ (the first sum is absent when $j = 1$ and the second when $j = N$). The density $\varrho = \sum_{k=1}^{N} k c_k$ is thus conserved for all time and all choices of coefficients $a_{j,k}$ and this is used as a test of accuracy of the programs. Various criteria for numerically identifying when gelation has occurred have been tested. The one most commonly used here is that if more than 5% of the total mass is present in the particles of size between 195–200 (for $N = 200$) by the final time step then gelation is said to have occurred. This approach

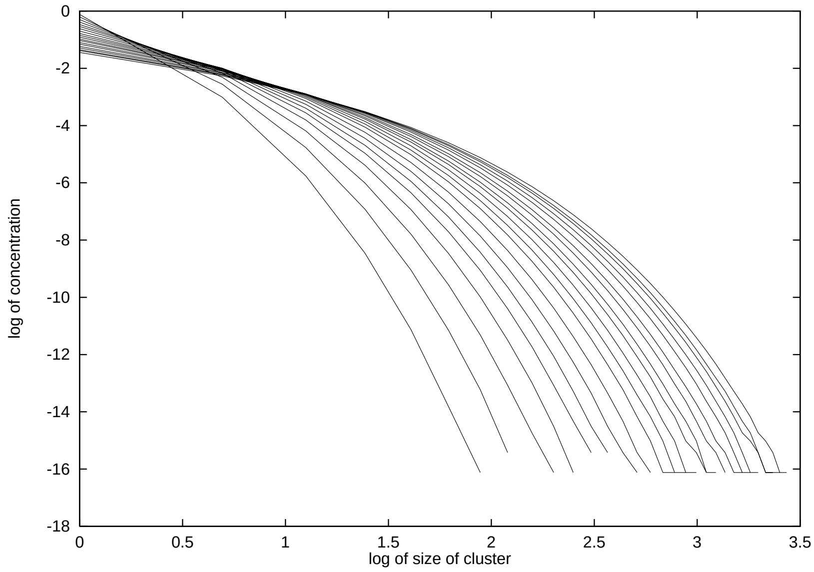

Figure 4. Plot of $\log c_j(t)$ against $\log j$ at times $t = 0{\cdot}1$ to $t = 2$, in steps of $0{\cdot}1$, for the case $\alpha = \beta = 0{\cdot}2$ with constant mass.

performs reasonably well, giving a value for t_g of around $0{\cdot}7$ for $\alpha = \beta = 1$ in the constant monomer case (*cf*. Section 2.2.3). Problems arise when a large percentage of the concentration is found in clusters of size larger than $N/2$, because the formulation (3.1) does not allow these clusters to react together. If this is the case the numerical results can be misleading.

Looking more specifically now at the case $\alpha = \beta$, we can see from Figure 3 that solutions split into three groups. It has been shown [10] that solutions exist for all α, but if $\alpha > \frac{1}{2}$ density conservation breaks down after a finite time – the gelation time t_g. If $\alpha > 1$ the gelation time is zero, *i.e*. density is lost to the gel from the start. We therefore split the numerics for the constant mass case into three ranges $\alpha \leqslant \frac{1}{2}$, $\frac{1}{2} < \alpha \leqslant 1$ and $\alpha > 1$. A fourth case arises when $\alpha - \beta < 1$, that of complete gelation.

3.1.2. *Results for* $\alpha = \beta \leqslant \frac{1}{2}$

In this case it is known that no gelation occurs, the coagulation kernel growing too slowly for large j to induce the formation of an infinite cluster. From the numerical solution it can be seen that few large clusters are formed, with Figure 4 showing plots of the log of concentration (c_j) against the log of cluster size (j). There is no build-up of mass towards the right-hand side of the graph, indicating the absence of gelation.

3.1.3. *Results for* $\frac{1}{2} < \alpha = \beta \leqslant 1$

From the results of a numerical solution for $\alpha = \beta = 0.8$ shown in Figure 5 it can be seen that there is a build-up of larger clusters after a certain time period, indicating that gelation occurs within finite time.

3.1.4. *Results for* $\alpha = \beta > 1$

We now turn to models where $a_{j,k}$ increases faster than jk; in applications [5], this corresponds to the effective surface area of a cluster growing more rapidly than the volume as its size increases.

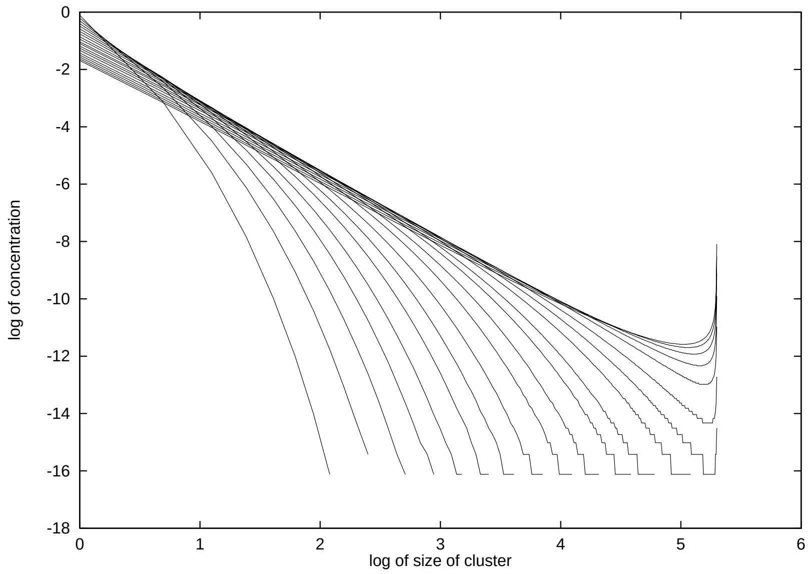

Figure 5. Plot of $\log c_j(t)$ against $\log j$ at times $t = 0{\cdot}1$ to $t = 2$, in steps of $0{\cdot}1$, for the case $\alpha = \beta = 0{\cdot}8$ with constant mass.

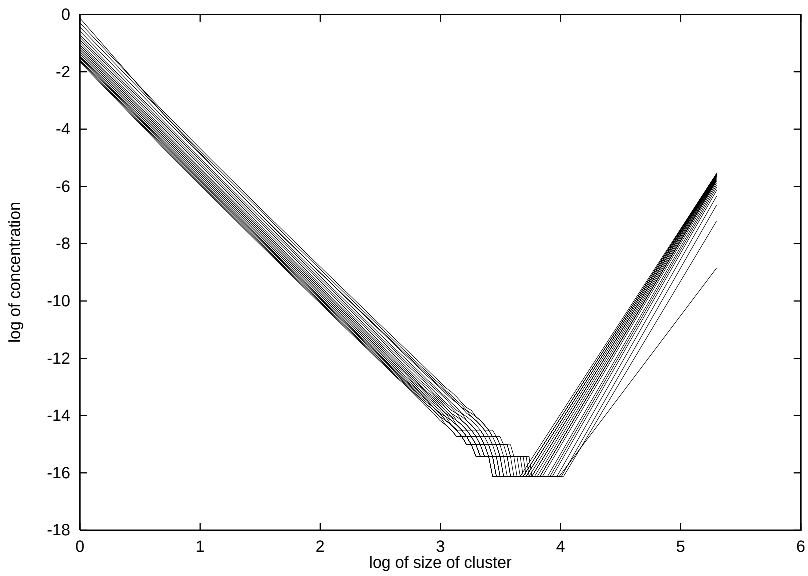

Figure 6. Plot of $\log c_j(t)$ versus $\log j$ at times $t = 0{\cdot}1$ to $t = 2{\cdot}0$, in steps of $0{\cdot}1$, for the case $\alpha = \beta = 2{\cdot}5$ with constant mass.

In the numerical simulations for $\alpha = \beta > 1$ gelation has occurred by $t = 0{\cdot}1$. From the results for $\alpha = \beta = 2{\cdot}5$ in Figure 6 it can be seen that even for $t = 0{\cdot}1$ there is a significant build up of large clusters, suggesting that in the full system of equations density would not be conserved. The behaviour to the right of the figure is an artifact of the feature of (3.1), noted earlier, that clusters of size $\frac{1}{2}N$ are not permitted to combine by the truncated form of the equations. It does nevertheless provide a clear indication of the presence of gelation.

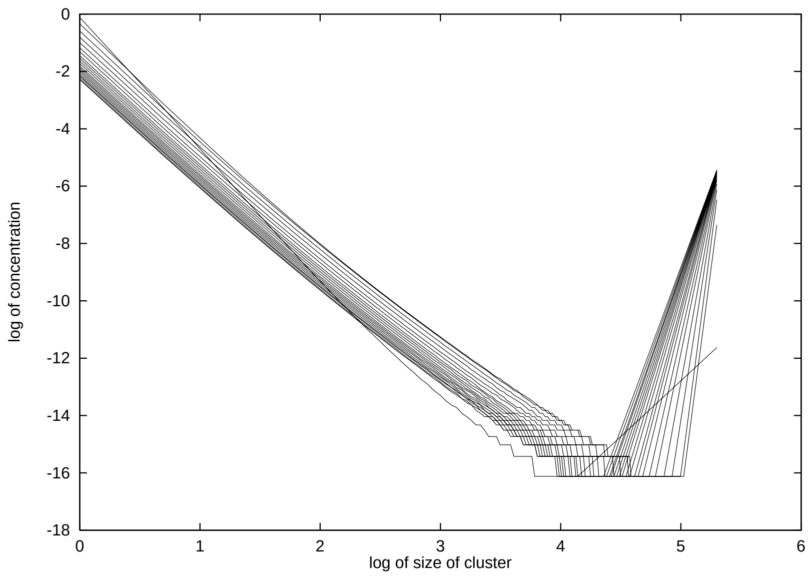

Figure 7. Plot of $\log c_j(t)$ against $\log j$ at times $t = 0{\cdot}1$ to $t = 2$, in steps of $0{\cdot}1$, for the case $\alpha = 2{\cdot}5$, $\beta = 1{\cdot}0$ with constant mass, showing the gel forming with larger particles than Figure 6.

3.1.5. *Results for* $\alpha - \beta < 1$

This is the only regime that cannot be illustrated with $\alpha = \beta$. In this case no solution exists – we conjecture that for the infinite system all of the mass coagulates into a gel. It is, however, possible, to obtain numerical results to the truncated system (3.1). It can be seen from Figure 7 that a significant amount of mass is within the large clusters after just a few time steps. This can be regarded as corresponding to instantaneous gelation of the majority of the mass in the truncated system, cluster sizes being significantly larger than in the instantaneous gelation regime of Section 3.1.5.

3.2. LARGE-TIME ASYMPTOTICS

If we consider concentrations c_j with large j values, it is often appropriate to take the continuum limit of the coagulation equations, in which we replace j by the continuous variable x and k by y; the leading-order balance can then be written in a number of equivalent forms, including

$$\frac{\partial c(x,t)}{\partial t} = \int_0^{x/2} c(y,t)[a(y,x-y)c(x-y,t) - a(y,x)c(x,t)]\,\mathrm{d}y$$
$$-c(x,t)\int_{x/2}^{\infty} a(y,x)c(y,t)\,\mathrm{d}y; \qquad (3.2)$$

as we shall see, the required solutions of (3.2) are typically singular as $x \to 0^+$. For $a(x,y) = \frac{1}{2}(x^\alpha y^\beta + x^\beta y^\alpha)$, Equation (3.2) possesses two rescaling invariants

$$c^* = \mu c, \qquad x^* = x, \qquad y^* = y, \qquad t^* = t/\mu, \qquad (3.3)$$

$$c^* = c, \qquad x^* = \nu x, \qquad y^* = \nu y, \qquad t^* = t/\nu^{\alpha+\beta+1}, \qquad (3.4)$$

as well as the translation invariant

$$c^* = c, \qquad x^* = x, \qquad y^* = y, \qquad t^* = t + t_0. \tag{3.5}$$

(3.3) and (3.5) are inherited from symmetries of the discrete problem (1.4), but (3.4) is an additional symmetry of the continuous approximation. In view of (3.3)–(3.5), Equation (3.2) therefore has the families of similarity solutions

$$c = t^{-p} g(\eta), \quad \eta = x/t^q, \quad \text{with } p - (\alpha + \beta + 1)q = 1, \tag{3.6}$$

$$c = \mathrm{e}^{-(\alpha+\beta+1)\lambda t} g(\eta), \quad \eta = x/\mathrm{e}^{\lambda t}, \tag{3.7}$$

where p and λ are arbitrary constants.

We are now in a position to discuss the asymptotic behaviour as $t \to \infty$. In the nongelating case $\alpha + \beta < 1$ this will comprise an 'outer' region, in which the leading order solution is governed by (3.2), and an 'inner' region $j = O(1)$. In the gelating case only the latter arises. The leading-order 'outer' solution in the nongelating cases is assumed to be a similarity solution to (3.2) of the form (3.6). This solution cannot in general be constructed explicitly and we shall concentrate on the large-time matching problem, which determines the values of p and q. We thus need to determine the large j behaviour in the inner region and the small η behaviour in the outer region.

(i) Gelating regime, $\alpha + \beta > 1$, $\alpha - \beta < 1$.
As $t \to \infty$, the uniformly valid large time solution is of the separable form

$$c_j(t) \sim \frac{1}{t} f_j \quad \text{as } t \to +\infty, \tag{3.8}$$

for some constants f_j, which can in principle be determined from (1.3)–(1.4). Some simple properties of the f_j, such as

$$\sum_{j=1}^{\infty} (j^\alpha + j^\beta) f_j = 2, \qquad \sum_{j=1}^{\infty} j^\alpha f_j \sum_{k=1}^{\infty} k^\beta f_k = 2 \sum_{l=1}^{\infty} f_l \tag{3.9}$$

are readily deduced from (1.3)–(1.4). In the gelating case, it follows from (1.9) that we require $J_N(t) \to J(t) > 0$ as $N \to \infty$ for some function $J(t)$. The behaviour as $j \to +\infty$ for all $t > t_g$ can then be deduced from (1.7), as follows. Assuming (1.11) and successively approximating the summations in (1.7) by integrals, as is appropriate in the limit $k \to \infty$, we find that

$$\begin{aligned} J(t) \;=\; \lim_{k\to\infty} \Bigg(& \tfrac{1}{2} K^2(t) B(\alpha + 2 - \sigma, \beta + 2 - \sigma) \\ & \times \left(\frac{1}{\sigma - \beta - 1} + \frac{1}{\sigma - \alpha - 1} \right) k^{\alpha+\beta+3-2\sigma} \Bigg), \end{aligned} \tag{3.10}$$

provided that

$$\sigma - 2 < \alpha, \quad \beta < \sigma - 1, \tag{3.11}$$

these being the conditions for existence of the integrals that arise; $B(m, n)$ is the Beta function. It follows immediately that $\sigma = (\alpha + \beta + 3)/2$ and, because of (3.11) and the finite mass requirement of $\sigma > 2$, the regions of existence of gelating solutions noted above, namely

$$\alpha + \beta > 1, \quad -1 < \alpha - \beta < 1, \tag{3.12}$$

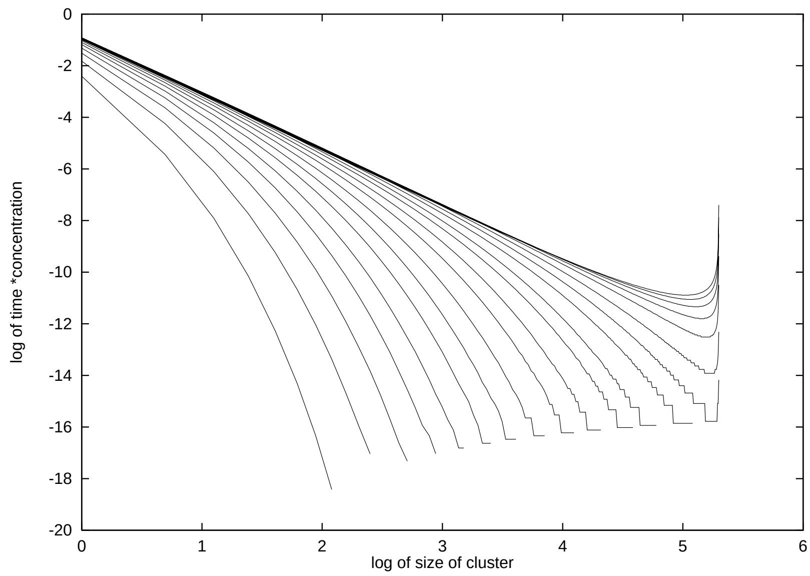

Figure 8. Plot of $\log tc_j(t)$ against $\log j$, showing the large time behaviour for $\alpha = \beta = 0{\cdot}8$; values of t are as in Figure 5.

are immediately identified; these conditions also ensure that M_α and M_β are bounded, as required. We arrive at

$$J(t) = 2\pi K^2(t)/(\alpha - \beta + 1)(\beta - \alpha + 1)\cos(\pi(\alpha - \beta)/2). \tag{3.13}$$

Such results generalise those of [11] and [14] in which $\alpha = \beta$ is considered. It follows from (3.8) that $K(t) \sim K_0/t$ as $t \to \infty$ for some constant K_0 and that the required separable solution has

$$f_j \sim K_0 j^{-(\alpha+\beta+3)/2} \quad \text{as} \quad j \to +\infty. \tag{3.14}$$

A numerical example showing the approach to a separable solution is given in Figure 8; here the slope $\approx 2{\cdot}3$ in the relevant regime, the agreement with (3.14) being excellent.

(ii) Non-gelating regime, $\alpha + \beta < 1$, with $\alpha, \beta > 0$.
The solution (3.8) does not conserve mass, so it cannot be uniformly valid in the nongelating case. It does, however, provide the asymptotic behaviour in the inner region $j = O(1)$. Before proceeding with the outer solution, it will prove helpful to the matching that we note an exact solution to the continuum limit

$$\begin{aligned}\frac{\partial c}{\partial t}(x,t) \;=\; & \frac{1}{2}\int_0^{x/2} c(y,t)([y^\alpha(x-y)^\beta + y^\beta(x-y)^\alpha]c(x-y,t) \\ & -(y^\alpha x^\beta + y^\beta x^\alpha)c(x,t))\mathrm{d}y - \tfrac{1}{2}c(x,t)\int_{x/2}^\infty (y^\alpha x^\beta + y^\beta x^\alpha)c(y,t)\,\mathrm{d}y,\end{aligned} \tag{3.15}$$

namely the separable solution

$$c(x,t) = 2\alpha\beta x^{-(\alpha+\beta+1)}/(\alpha+\beta)(1-(\alpha+\beta))B(1-\alpha, 1-\beta)t; \tag{3.16}$$

this solution exists if $\alpha+\beta < 1$, corresponding to the nongelating regime, provided $\alpha, \beta > 0$.

The outer solution is a similarity solution of the form (3.6). The values of p and q are specified by the conservation of mass constraint, i.e.

$$\int_0^\infty xc(x,t)\,\mathrm{d}x = 1, \tag{3.17}$$

which requires

$$p = 2/(1-(\alpha+\beta)), \qquad q = 1/(1-(\alpha+\beta)), \tag{3.18}$$

again confirming the condition $\alpha+\beta < 1$. The inner and outer solutions can be matched via (3.16), whereby in (3.6)

$$g(\eta) \sim 2\alpha\beta\eta^{-(\alpha+\beta+1)}/(1-(\alpha+\beta))(\alpha+\beta)B(1-\alpha, 1-\beta) \quad \text{as} \ \ \eta \to 0^+ \tag{3.19}$$

and for (3.8) we impose

$$f_j \sim 2\alpha\beta j^{-(\alpha+\beta+1)}/(1-(\alpha+\beta))(\alpha+\beta)B(1-\alpha, 1-\beta) \quad \text{as} \ \ j \to +\infty. \tag{3.20}$$

We note that the far-field behaviour of f_j differs from that in the gelating regime (see (3.14)).

4. The constant-monomer case

4.1. Steady-state solution

As $t \to \infty$ with $j = O(1)$ the concentrations $c_j(t)$ tend to a nonzero steady state, g_j. Writing $g_j = j^{-\beta} d_j$, we observe that this satisfies

$$d_1 = 1, \qquad \frac{1}{2}\sum_{k=1}^{j-1}(k^\gamma + (j-k)^\gamma)d_k d_{j-k} = d_j \sum_{k=1}^{\infty}(j^\gamma + k^\gamma)d_k, \quad j \geqslant 2 \tag{4.1}$$

where $\gamma = \alpha - \beta$, and $|\gamma| < 1$ is required for a solution to exist. This can be solved explicitly when $\alpha = \beta$, for which

$$\sum_{k=1}^{j-1} d_k d_{j-k} = 2d_j \sum_{k=1}^{\infty} d_k, \quad j \geqslant 2. \tag{4.2}$$

By analysing the generating function $D(z) = \sum_{k=1}^{\infty} \mathrm{d}_k\, \mathrm{e}^{-kz}$, we see that

$$D^2(z) - 2D(0)D(z) + 2\,\mathrm{e}^{-z} D(0) = 0, \tag{4.3}$$

implying that $D(0) = 2$ and $D(z) = 2(1 \pm \sqrt{1-\mathrm{e}^{-z}})$. We require that $D \to 0$ as $z \to \infty$, so the negative root must be taken, giving

$$D(z) = 2(1 - \sqrt{1-\mathrm{e}^{-z}}). \tag{4.4}$$

Expanding the square root, this yields

$$g_j = \frac{2(2j)!\,j^{-\alpha}}{j!\,j!\,2^{2j}(2j-1)}. \tag{4.5}$$

It can be confirmed numerically that general time-dependent solutions to the constant-monomer case approach this steady state solution at large times. The large j limit of (4.5) yields

$$g_j \sim j^{-(\alpha+\frac{3}{2})}/\sqrt{\pi} \quad \text{as} \quad j \to +\infty \tag{4.6}$$

consistent with previous studies of gelating systems [11, 14].

4.2. Asymptotic solutions

The steady-state solution is approached uniformly as $t \to \infty$ in the gelating regime $\alpha+\beta > 1$, $\alpha - \beta < 1$, with (*cf.* (3.14)

$$g_j \sim K_1 j^{-(\alpha+\beta+3)/2} \quad \text{as} \quad j \to +\infty, \tag{4.7}$$

for some constant K_1 which is depends only on γ; for $\alpha = \beta$ we have (4.5)–(4.6). In (3.13) we thus have $K(t) \to K_1$ as $t \to \infty$.

In the nongelating regime we again seek a similarity solution of the form (3.6) to describe the outer solution. The second relationship between p and q obviously cannot be derived by conservation of mass in this case, but follows from matching into the inner (steady state) solution which holds for $j = O(1)$. We note that the solution to (4.1) depends only on γ, so the far-field behaviour of the steady state is necessarily given by (4.7) in both gelating and nongelating regimes. The expression (4.7) implies finite mass for $\alpha+\beta > 1$ and infinite mass for $\alpha + \beta < 1$, clearly indicating the need for an outer solution in the non-gelating case. Matching with (4.7) requires that

$$g(\eta) \sim K_1 \eta^{-(\alpha+\beta+3)/2} \quad \text{as} \quad \eta \to 0^+ \tag{4.8}$$

and that

$$p = q(\alpha+\beta+3)/2, \tag{4.9}$$

which gives

$$p = \frac{\alpha+\beta+3}{1-(\alpha+\beta)}, \qquad q = \frac{2}{1-(\alpha+\beta)}, \tag{4.10}$$

again confirming the requirement of $\alpha + \beta < 1$.

4.3. Numerical results

The numerical results for this case are again obtained from (3.1) for $j \geqslant 2$. They can be split into the same categories of $\alpha + \beta \leqslant 1$ (no gelation), $\alpha + \beta > 1,\ \alpha,\ \beta > 1$ (finite-time gelation) and $\alpha - \beta < 1$ with α or $\beta > 1$ (instantaneous gelation). The complete gelation regime, where no solution exists, is also present, in this case almost all the mass in numerical solutions to the truncated system being in the form of monomers or 'gel'. Numerical results are given below for $\alpha = \beta$ in the two main cases $\alpha \leqslant \frac{1}{2}$ and $\frac{1}{2} < \alpha$.

4.3.1. *Results for $\alpha \leqslant \frac{1}{2}$*

It can be seen in Figure 9 (as in Figure 4), that there is no build-up of mass for larger particles and the system does not gelate; the approach to the steady state for $j = O(1)$ (the inner region) is also shown. Figure 10 shows $\log(c_j t^{(2\alpha+3)/(1-2\alpha)})$ plotted against $\log(j/t^{2/(1-2\alpha)})$,

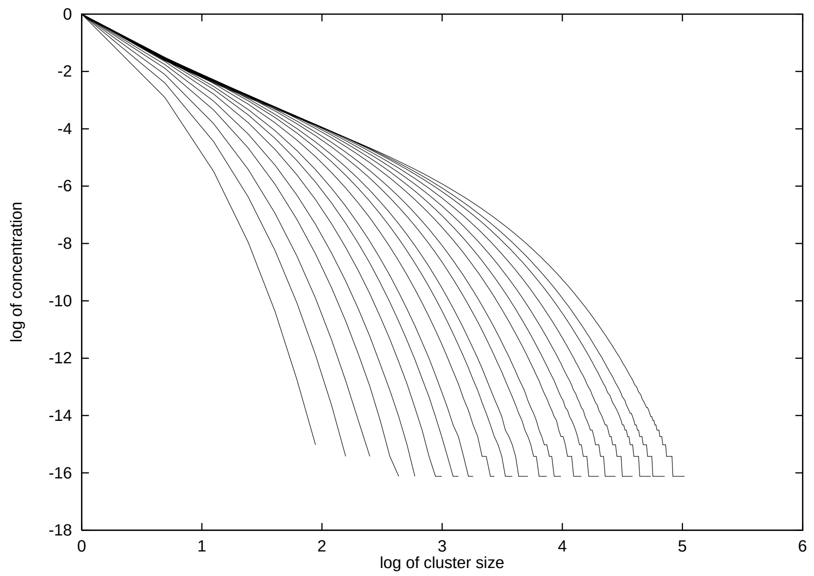

Figure 9. Plot of $\log c_j$ versus $\log j$ at times from $t = 0{\cdot}1$ to $t = 2{\cdot}0$, in steps of $0{\cdot}1$, for the case $\alpha = 0{\cdot}4$ with constant monomer concentration.

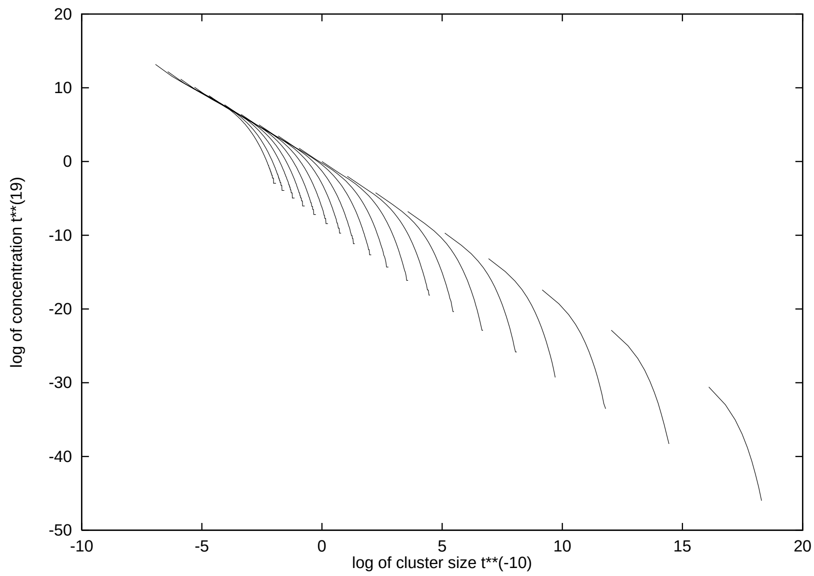

Figure 10. Plot of $\log(t^{(2\alpha+3)/(1-2\alpha)}c_j)$ against $\log(j/t^{2/(1-2\alpha)})$ for $\alpha = 0{\cdot}4$ showing approach to the large-time behaviour, the times shown being from $t = 0{\cdot}2$ to $t = 2{\cdot}0$, in steps of $0{\cdot}1$.

also for $\alpha = 0{\cdot}4$, with time increasing from right to left; these variables are chosen in view of the similarity exponents (4.10) (with $\alpha = \beta$) and the approach of the solution in the outer region to the postulated similarity solution is clearly illustrated. The relevant part of the profile approaches a straight line with a gradient of approximately $-1{\cdot}8$, in fair agreement with (4.8).

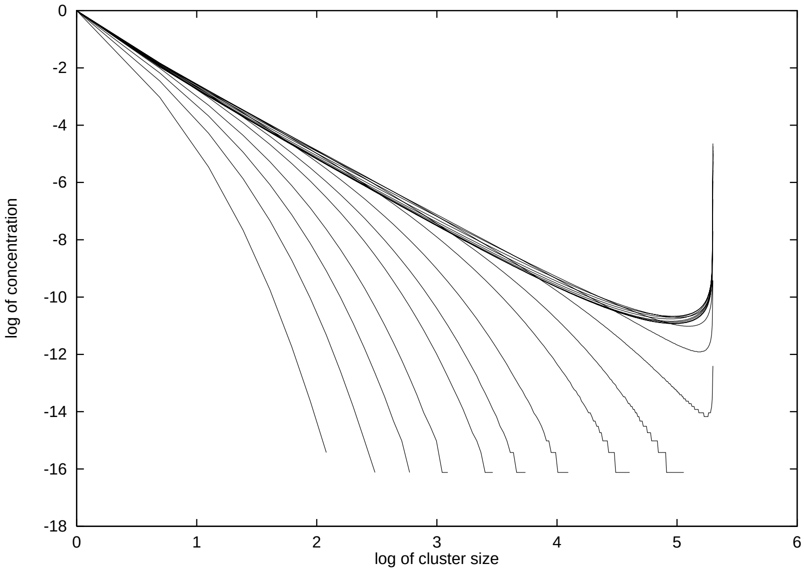

Figure 11. Plot of $\log c_j$ versus $\log j$ at times from $t = 0{\cdot}1$ to $t = 2{\cdot}0$, in steps of $0{\cdot}1$, for the case $\alpha = 0{\cdot}8$ with constant monomer concentration.

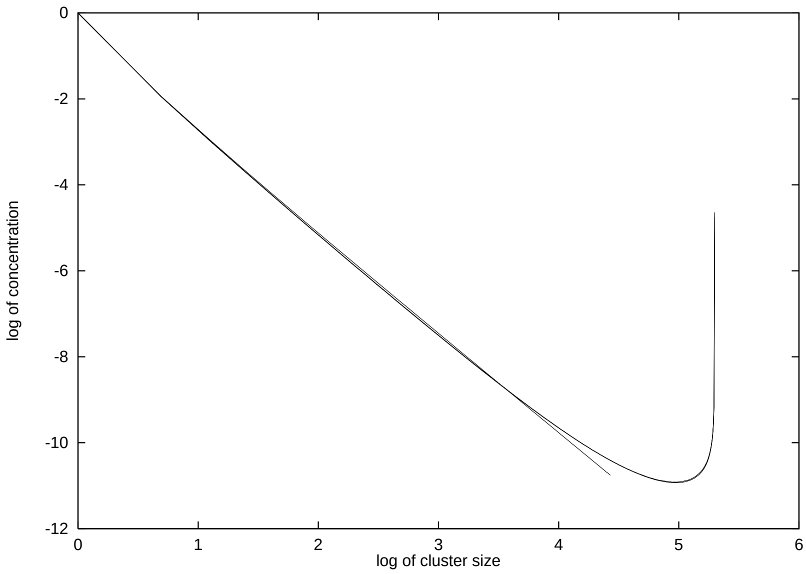

Figure 12. The profiles from Figure 11 at times $t = 1{\cdot}9$ and $t = 2{\cdot}0$ together with the steady-state solution. The steady-state solution is the lowest curve at large cluster size; the other two curves lie almost on top one another.

4.3.2. *Results for* $\frac{1}{2} < \alpha$

In this case the build up of mass to the right-hand side in Figure 11 indicates that the system gelates. The steady state solution (4.5) has been included in Figure 12 to show that it is approached uniformly for large time in this regime; the disagreement for large j arises because the numerical approach truncates the system at clusters of size 200, where mass accumulates.

5. Discussion

We start by noting some features of the special cases $\alpha = \beta = 0$, $\alpha = 1$ with $\beta = 0$ and $\alpha = \beta = 1$ discussed in Section 2. These are the most widely studied values because they are solvable via a generating function, for example (we further discuss their integrability below), but the results they give can be somewhat misleading with respect to the general case of (1.3)–(1.4). This is implicit in Figure 3, from which their special status in the (α, β) plane is apparent. Summarising we conclude that the large-time behaviour is instructive in this regard.

(i) $\alpha = \beta = 0$. In the constant mass case, (2.8) is of the form (3.6) with (3.18), but (3.19) is inapplicable and no inner region is present. However, in the constant-monomer case, with inner solution (A7) and outer solution (A11), the asymptotic structure is of the general nongelating form outlined in Section 4.2.

(ii) $\alpha = 1$, $\beta = 0$. This case is particularly significant because, as shown by Figure 3, it lies at the intersection of all of the different regimes. The large-time limit of the constant-mass case has outer solution (2.15), which is a similarity solution of the continuum limit ((3.7) with $\lambda = 1$) and can be regarded as a limit case of (3.6) with (3.18) as $p, q \to \infty$. That such a limit arises in this critical case is to be expected. The inner solution (2.14) is separable, but is of a quite different form from (3.8), decaying much more rapidly. The constant-monomer case is rather complicated, the most important results probably being (2.40), which shows that the total mass increases exponentially fast, and (B12), which shows how extremely small concentrations of extremely large clusters form. Since $\alpha = 1,\ \beta = 0$ lies on the boundary of, but not within, the 'no solution' regime, these large-time results provide clues as to what can be expected to happen in complete gelation cases, namely that for constant mass all the material is transferred into the gel (*cf.* the exponential decay in (2.14)), while with constant-monomer concentration the 'solution' is given by $c_1 = 1,\ c_j = 0$ for $j \geqslant 2$, with an infinite gel (*cf.* (B15), from which it follows that $c_j \propto 1/M_1^{j-1}$, which is exponentially small for $j \geqslant 2$). Some insight into the dependence on α and β can be given as follows. When α and β are both large, clusters of large size combine much more rapidly with each other than they do with small ones. There is thus a tendency for large clusters to combine (which they do faster and faster as they become larger) to form a gel, without the small clusters initially being substantially depleted. By contrast, when α is large but β is not, large clusters combine with small ones not much more slowly than they do with other large ones, giving the possibility of all the mass gelating at once.

(iii) $\alpha = \beta = 1$. For the constant mass case the large-time behaviour is of the separable form (2.28) and for constant monomer a steady state is approached, both in keeping with the general behaviour of gelating cases.

These three special cases can be regarded as integrable, having an infinite number of conservation laws for example. We give the details only in the simplest of case $\alpha = \beta = 0$ with constant mass, for which (2.5) with $M_0 = 2/(t+2)$ implies that $(1-2/(t+2)C(z,t))/(t+2)$ is independent of t. Insertion of (2.2) or (A1) then leads to a recursive system of conservation laws involving the concentrations or the moments. For values of α and β other than the three cases given above, the coupling of the moment equations implies that they cannot be solved sequentially. In particular, it is not possible in general to determine M_α and M_β in (1.3)–(1.4) *a priori*. Such comments provide further indications of the very special nature of the cases discussed in Section 2; as is typical, solving only the integrable versions of the system may fail to give a good indication of the generic behaviour.

The final feature of the special cases that we note is the following. Introducing the transformations

$\alpha = \beta = 0$:

$$c_j = \exp\left(-\int_0^t M_0(t')\,\mathrm{d}t'\right)\hat{c}_j, \qquad \hat{t} = \int_0^t \exp\left(-\int_0^{t'} M_0(t'')\,\mathrm{d}t''\right)\mathrm{d}t',$$

$\alpha = 1, \quad \beta = 0$;

$$c_j = \exp\left(-\frac{1}{2}\int_0^t (jM_0(t') + M_1(t'))\mathrm{d}t'\right)\hat{c}_j, \tag{5.1}$$

$$\hat{t} = \int_0^t \exp\left(-\frac{1}{2}\int_0^{t'} M_1(t'')\,\mathrm{d}t''\right)\mathrm{d}t',$$

$\alpha = \beta = 1$:

$$c_j = \exp\left(-j\int_0^t M_1(t')\,\mathrm{d}t'\right)\hat{c}_j, \quad \hat{t} = t,$$

(we note that these transformations are nonlocal because $M_p(t)$ depends on the unknowns c_k), we obtain

$$\frac{\partial \hat{c}_j}{\partial \hat{t}} = \frac{1}{4}\sum_{k=1}^{j-1}\left((j-k)^\alpha k^\beta + k^\alpha (j-k)^\beta\right)\hat{c}_k\hat{c}_{j-k}, \tag{5.2}$$

which has the further symmetry

$$\hat{c}^*_{j^*} = \mathrm{e}^{aj}\hat{c}_j, \quad j^* = j, \quad k^* = k, \quad \hat{t}^* = \hat{t}, \tag{5.3}$$

where a is a constant, so that similarity reductions include

$$\hat{c}_j(\hat{t}) = \exp(\lambda j \hat{t})\hat{f}_j, \tag{5.4}$$

$$\hat{c}_j(\hat{t}) = \exp((\lambda j - 1)\log \hat{t})\hat{g}_j. \tag{5.5}$$

In this framework the solutions of Section 2.1 are classical similarity reductions of the form (5.5) with $\lambda = 1$. Thus, for (2.7) we have

$$c_j = \frac{4}{(t+2)^2}\hat{c}_j, \qquad \hat{t} = \frac{2t}{t+2}, \qquad \hat{g}_j = \frac{1}{2^{j-1}}, \tag{5.6}$$

for (2.13)

$$c_j = \exp\left(-j(1-\mathrm{e}^{-t/2}) - t/2\right)\hat{c}_j, \qquad \hat{t} = 2(1-\mathrm{e}^{-t/2}), \qquad \hat{g}_j = (j/2)^{j-1}/j!, \tag{5.7}$$

and for (2.27)

$$c_j = \begin{cases} \exp(-jt)\hat{c}_j & t \leqslant 1, \\ \exp(-j(1+\log t))\hat{c}_j & t \geqslant 1, \end{cases} \qquad \hat{t} = t, \tag{5.8}$$

with

$$\hat{g}_j = j^{j-3}/(j-1)!. \tag{5.9}$$

This last case is particularly noteworthy since the solution takes the same similarity form both before and after gelation, which is why the post-gelation solution is exactly separable when (1.10) holds. Moreover, given (5.1), that (5.9) holds with $\lambda = 1$ (which is dictated by the initial conditions) and the fact that the solution decays as $j \to +\infty$ exponentially pre-gelation and algebraically post-gelation, we can immediately deduce, without using (5.8), the results

$$t_g = 1, \qquad -\int_0^t M_1(t')\,\mathrm{d}t' + \log t + 1 = 0, \quad t \geqslant 1. \tag{5.10}$$

This similarity between $\hat{g}_j$ in (5.7) and (5.9) is not coincidental. Writing (*cf.* [5]) $\hat{c}_j = \hat{C}_j/j,\ \hat{t} = \hat{T}/2$ maps (5.2) from $\alpha = \beta = 1$ to $\alpha = 1,\ \beta = 0$. There is thus an equivalence transformation between two of the integrable cases.

We are now in a position to summarise the various types of self-similar solution which arise. The inner solutions (3.8) and (4.5) are classical reductions of (1.3)–(1.4); the exact solutions (2.7), (2.13) and (2.27) can be viewed as nonlocal reductions; the outer solutions given by (3.18) and (4.10) are classical reductions of the continuum approximation (3.15); and (B12), for example, is an asymptotically self-consistent balance in (3.15), rather than being an exact similarity reduction. The exponential of an exponential dependence of (B12) is noteworthy. The problems discussed here are thus instructive in illustrating the role of a wide variety of types of self-similarity and asymptotic self-similarity in a discrete problem. A number of different continuum limits also occur; the most significant of these is the conventional one *i.e.* (3.2), but (B20) and (B27) (which is of Fokker–Planck type) also arises as continuum approximations. A continuous formulation (C3)–(C4) also results from applying generating function (or equivalently z-transform) methods, as described in Appendix C.

We can summarise our asymptotics by noting the behaviour of the following quantities as $t \to \infty$.

(a) Constant mass:

- (i) Gelating regime $M_0 \propto 1/t$, $M_1 = 1 -$ gel size $\propto 1/t$
- (ii) Nongelating regime $M_0 \propto 1/t,\ \ M_1 = 1$

(b) Constant monomer:

- (i) Gelating regime $M_0,\ M_1 \propto t^0$, gel size $\propto t$
- (ii) Nongelating regime $M_0 \propto t^0,\ M_1 \propto t$.

In the nongelating regime, M_0 is dominated in both cases by the inner region and M_1 by the outer. Some of these expressions are violated in the borderline cases such as $\alpha = 1,\ \beta = 0$.

While we have concentrated here on specific initial conditions, we expect our asymptotic results to provide the large-time (intermediate asymptotic) behaviour for large classes of initial data. Two important exceptions to this should be noted, however, in the constant-mass case. Firstly, with regard to borderline cases it is implicit from the fact that $\hat{t}$ remains bounded as $t \to \infty$ in (5.6) and (5.7) that important aspects of the large-time behaviour may depend on the initial data in these cases. For $\alpha = \beta = 0$, we have from (2.5) that $M_0 \sim 2/t$ as $t \to \infty$

for arbitrary initial data and, while (2.8) will always give the form of the outer solution, the inner solution is

$$c_j(t) \sim t^{-2} h_j \quad \text{as } t \to \infty \text{ with } j = O(1), \tag{5.11}$$

where h_j is almost completely arbitrary (in (2.7) we simply have $h_j = 4$); the summation term in (1.4) is negligible in this limit. Similarly, for $\alpha = 1, \ \beta = 0$ the outer solution is in general of the form (2.15) (though in (3.7) λ will be determined by the mass; we stick to the case $M_1 = 1$ here) but the inner will be

$$c_j(t) \sim \mathrm{e}^{-t/2} h_j \quad \text{as } t \to \infty \text{ with } j = O(1), \tag{5.12}$$

h_j again depending on the initial data. Similar comments apply in other borderline cases. Secondly, if the initial data is made up only of n-mers (with $n \geqslant 2$) then the clusters will for all time each contain exact multiples of n particles, unlike the large-time solutions derived above. This can easily be addressed via (1.16)–(1.17) (*cf.* [11]). If $c_j = C_j(t)$ is the solution when (1.10) holds then

$$c_j = \begin{cases} \dfrac{1}{n} C_{j/n}(n^{\alpha+\beta-1} t) & \text{if } j \text{ is a multiple of } n, \\ 0 & \text{otherwise}, \end{cases} \tag{5.13}$$

is the solution for the initial conditions

$$\text{at } t = 0, \qquad c_n = 1/n, \qquad c_j = 0, \qquad \forall j \neq n; \tag{5.14}$$

the nature of the time dependence in (5.13) as $n \to \infty$ can be used to identify $\alpha + \beta = 1$ as a critical case (*cf.* Figure 3). If all the initial clusters are of even size (say) then the large-time behaviour will in general correspond to (5.11) with $n = 2$; the evolution when only a very small proportion of the clusters is initially of odd size would be of interest.

In summary, we have applied similarity methods to the coagulation equations to obtain, in particular, new asymptotic results for both constant mass (particularly for $\alpha \neq \beta$) and constant monomer; the latter has been little studied before. Numerical solutions have been used to yield useful complementary information and to verify the asymptotic results; we are not aware of comparable earlier work of this type. The numerical results are expected to be accurate unless and until gelation occurs, in which case their interpretation requires care.

We have shown similarity methods to be highly applicable in the analysis of this type of discrete system. Possible extensions of the work are numerous. Here we note only that it generalises rather easily to other scale invariant kernels, notably

$$a_{k,j} = k^{\alpha+\beta} F(j/k) \quad \text{where } F(\sigma) = \sigma^{\alpha+\beta} F(1/\sigma), \tag{5.15}$$

and to kernels which take this form asymptotically for large cluster size $j, \ k \to \infty$; most cases of interest can thus readily be incorporated into the theory.

Appendix A. Large-time behaviour for $\alpha = \beta = 0$

A1. Introduction

This appendix concerns the constant-monomer case, the generating function satisfying (2.34). We start by noting some results for the moments.

Since

$$C(z,t) = \sum_{n=0}^{\infty} \frac{M_n}{n!}(-z)^n, \tag{A1}$$

it follows from (2.34) that

$$\begin{aligned} \frac{\mathrm{d}M_1}{\mathrm{d}t} &= \frac{2}{1+\mathrm{e}^{-t}}, \\ \frac{\mathrm{d}M_n}{\mathrm{d}t} &= \frac{1}{2}\sum_{j=1}^{n-1} \frac{n!}{j!(n-j)!} M_j M_{n-j} + \frac{2}{1+\mathrm{e}^{-t}} \quad \text{for } n \geqslant 2. \end{aligned} \tag{A2}$$

Hence, in particular,

$$\begin{aligned} &M_1 = 2\log\left(\left(1+\mathrm{e}^t\right)/2\right) + 1 \sim 2t \quad \text{as } t \to \infty, \\ &M_2 \sim \tfrac{4}{3}t^3 \quad \text{as } t \to \infty. \end{aligned} \tag{A3}$$

The c_j can also be constructed sequentially. In particular

$$\dot{c}_2 = \tfrac{1}{2} - \frac{2}{1+\mathrm{e}^{-t}} c_2, \tag{A4}$$

so that

$$c_2 = \left(t + 2(\mathrm{e}^t - 1) + \tfrac{1}{2}(\mathrm{e}^{2t} - 1)\right)/2(\mathrm{e}^t + 1)^2, \tag{A5}$$

implying exponential approach to steady state, with

$$c_2 \to \tfrac{1}{4} \quad \text{as } t \to \infty. \tag{A6}$$

A2. Asymptotic behaviour

As $t \to \infty$, the asymptotic behaviour divides into two regions. In the inner region $j = O(1)$, we have (*cf.* (4.5))

$$c_j \to \frac{2(2j)!}{j!j!2^{2j}(2j-1)} \quad \text{as } t \to \infty, \tag{A7}$$

consistent with (A6).

The outer solution is most easily addressed via (2.34). Guided by (A3), we seek a solution of the form

$$C(z,t) \sim \frac{2}{1+\mathrm{e}^{-t}} + t^{-1} f(\zeta), \quad \zeta = zt^2 \tag{A8}$$

as $t \to \infty$ with $z = O(t^{-2})$. While this is not an exact similarity reduction of (2.34), a self-consistent dominant balance as $t \to \infty$ is

$$-f + 2\zeta \frac{\mathrm{d}f}{\mathrm{d}\zeta} = \tfrac{1}{2} f^2 - 2\zeta. \tag{A9}$$

This can be written as a separable equation for $f/\sqrt{\zeta}$, with solution

$$f = -2\sqrt{\zeta}\tanh\sqrt{\zeta} \tag{A10}$$

since $f(0) = 0$; this is consistent with (A3).

It follows from (A8) that

$$c_j \sim t^{-3}g(\eta), \quad \eta = j/t^2 \tag{A11}$$

as $t \to \infty$ with $\eta = O(1)$, this being the outer expansion. From (2.3) we have that

$$\int_0^\infty e^{-\zeta\eta}\eta g(\eta)\,d\eta = -\frac{df}{d\zeta}. \tag{A12}$$

The inverse transform can be written in a number of ways; here we note only the asymptotic behaviour. We have

$$g(\eta) \sim 1/\sqrt{\pi\eta^3} \quad \text{as} \quad \eta \to 0^+, \tag{A13}$$

matching with (A7), the correction term to (A13) being exponentially small ($\sim 4\,e^{-1/\eta}/\sqrt{\pi\eta^5}$), consistent with the exponentially rapid approach to the steady state in the inner region. The large η behaviour can be determined by a residue calculation, giving

$$g(\eta) \sim \pi^2\eta\, e^{-\pi^2\eta/4} \quad \text{as} \quad \eta \to \infty, \tag{A14}$$

the correction terms again being exponentially smaller.

Appendix B. Large-time behaviour for $\alpha = 1$, $\beta = 0$

B1. Introduction

We are again concerned here with the constant monomer case, in which (2.37) governs the generating function. The large-time behaviour subdivides into a number of regions, the first of which (the outer region) is most easily addressed via (2.37) and the remainder using (1.4), which we write in the form

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1} kc_k c_{j-k} - \tfrac{1}{2}(M_1 c_j + M_0 j c_j). \tag{B1}$$

We restrict ourselves to giving a fairly brief summary of the results of what turns out to be a rather complicated asymptotic analysis.

Before proceeding with the various regions, it is helpful to note the behaviour of c_j for small j and of the moments. From (B1) we have

$$\begin{aligned} \dot{c}_2 &= \tfrac{1}{2} - \tfrac{1}{2}M_1 c_2 - M_0 c_2, \\ \dot{c}_3 &= \tfrac{3}{2}c_2 - \tfrac{1}{2}M_1 c_3 - \tfrac{3}{2}M_0 c_3, \end{aligned} \tag{B2}$$

etc., and in view of (2.40) it follows that

$$c_2 \sim 1/M_1, \qquad c_3 \sim 3/M_1^2 \quad \text{as} \quad t \to \infty, \tag{B3}$$

c_{j+1} being exponentially smaller than c_j for $j = O(1)$. From (A1) and (2.37) it follows that

$$\frac{\mathrm{d}M_n}{\mathrm{d}t} = \frac{1}{2}\left(\sum_{j=1}^{n-1}\frac{n!}{j!(n-j)!}M_j M_{n-j+1} + M_0 + M_1\right) \quad \text{for } n \geqslant 2, \tag{B4}$$

from which it can readily be deduced that

$$M_2 \sim \hat{B}\,\mathrm{e}^{\int_0^t M_1(t')\,\mathrm{d}t'} \quad \text{as } t \to \infty, \tag{B5}$$

for some constant $\hat{B}$ which we can determine by integrating (B4) for $n = 2$, while

$$M_n \sim K_n \hat{B}^{n-1}\,\mathrm{e}^{(n-1)\int_0^t M_1(t')\mathrm{d}t'}/M_1^{n-2} \tag{B6}$$

for $n \geqslant 3$, where a recurrence relation for K_n (which contains no arbitrary constants) can readily be obtained from (B4).

B2. The outer region

In view of (2.40), (A1) and (B6) we seek an asymptotic solution to (2.37) of the self similar form

$$C(z,t) \sim M_0(t) + \mathrm{e}^{2t}\mathrm{e}^{-2A\mathrm{e}^{t/2}} f(\zeta), \quad \zeta = z\,\mathrm{e}^{-3t/2}\,\mathrm{e}^{2A\mathrm{e}^{t/2}}, \tag{B7}$$

as $t \to \infty$ with $\zeta = O(1)$. Thus z is exponentially small; while this is an inner region for (2.37), we shall see that it corresponds to the outer region of (B1). In view of (2.40) and (B5), the initial conditions on f are

$$f'(0) = -A, \qquad f''(0) = 2B, \tag{B8}$$

where

$$B = \hat{B}\exp\left(\int_0^\infty \left(M_1(t) - A\,\mathrm{e}^{t/2} + 1\right)\mathrm{d}t - 2A\right). \tag{B9}$$

From (2.37) and (2.40) we find that to leading order

$$(f + 2A\zeta)\frac{\mathrm{d}f}{\mathrm{d}\zeta} = Af \tag{B10}$$

so, given (B8),

$$f(\zeta) = \frac{A^2}{2B}\left(1 - \left(1 + \frac{4B}{A}\zeta\right)^{1/2}\right). \tag{B11}$$

From this it can be shown that c_j is of the self similar form

$$c_j \sim \mathrm{e}^{7t/2}\mathrm{e}^{-4A\mathrm{e}^{t/2}} g(\eta), \qquad \eta = j\,\mathrm{e}^{3t/2}\,\mathrm{e}^{-2A\mathrm{e}^{t/2}}, \tag{B12}$$

as $t \to \infty$ with $\eta = O(1)$; this governs the large time behaviour of c_j for large j. Inverting the Laplace transform in (A12) we find that

$$g(\eta) = \frac{A^{3/2}}{2(\pi B)^{1/2}}\eta^{-3/2}\,\mathrm{e}^{-A\eta/4B}. \tag{B13}$$

In order to match, we shall need the behaviour of (B12)–(B13) as $\eta \to 0^+$, namely

$$c_j \sim \frac{A^{3/2}}{2(\pi B)^{1/2}}\, \mathrm{e}^{5t/4}\, \mathrm{e}^{-A\mathrm{e}^{t/2}}\, j^{-3/2}. \tag{B14}$$

There are four further regions and we now work with (B1) through successively increasing regimes for j.

B3. $j = O(1)$

The dominant balance in (B1) as $t \to \infty$ is (*cf.* (B3))

$$c_1 = 1, \qquad c_j \sim \frac{1}{M_1}\sum_{k=1}^{j-1} k c_k c_{j-k}, \quad j \geqslant 2, \tag{B15}$$

from which it can be shown that

$$c_j \sim \kappa j^{j+3/2}\, \mathrm{e}^{-j}/M_1^{j-1} \quad \text{as} \ \ j \to +\infty, \tag{B16}$$

for some constant κ which we can determine by iterating (B15) to large j. The next scaling has $j = \mathrm{e}^{t/2}\varrho$, so matching with (B16) requires

$$c_j \sim \kappa A \varrho^{3/2}\, \mathrm{e}^{\varrho/A} e^{5t/4} \exp\left(\mathrm{e}^{t/2}\varrho(\log\varrho - 1 - \log A)\right) \quad \text{as} \ \ \varrho \to 0^+, \tag{B17}$$

where we have used (2.40).

B4. $\varrho = O(1)$ WITH $0 < \varrho < A$

In view of (B17), as $t \to \infty$ with $\varrho = O(1)$ we adopt the WKB *ansatz*

$$c_k \sim a_0(\varrho, t) \exp(\mathrm{e}^{t/2}\omega(\varrho)) \tag{B18}$$

and (B1) yields

$$\begin{aligned}
&\omega - \varrho\frac{\mathrm{d}\omega}{\mathrm{d}\varrho} + A + \varrho = \varrho \exp\left(-\frac{\mathrm{d}\omega}{\mathrm{d}\varrho}\right), \\
&2\frac{\partial a_0}{\partial t} - a_0 + \frac{\varrho}{A}a_0 - \varrho\frac{\partial a_0}{\partial \varrho} \\
&\quad = \left(\tfrac{1}{2}\varrho a_0 \frac{\mathrm{d}^2\omega}{\mathrm{d}\varrho^2} - \varrho\frac{\partial a_0}{\partial\varrho}\right)\exp\left(-\frac{\mathrm{d}\omega}{\mathrm{d}\varrho}\right) + \frac{\varrho}{A}a_0 \exp\left(-2\frac{\mathrm{d}\omega}{\mathrm{d}\varrho}\right),
\end{aligned} \tag{B19}$$

only the first two terms in the sum in (B1) contributing to this order. Writing $\omega(\varrho) = \varrho\log\varrho - \varrho + \Omega(\varrho)$ transforms the first of (B20) to

$$\Omega - \varrho\frac{\mathrm{d}\Omega}{\mathrm{d}\varrho} + A = \exp\left(-\frac{\mathrm{d}\Omega}{\mathrm{d}\varrho}\right), \tag{B20}$$

which is of Clairaut's form, and the solution required to match with (B17) is simply

$$\omega(\varrho) = \varrho(\log\varrho - 1 - \log A). \tag{B21}$$

The second of (B20) now becomes

$$2\frac{\partial a_0}{\partial t} + (A-\varrho)\frac{\partial a_0}{\partial \varrho} = \left(\frac{3A}{2\varrho} + \frac{A-\varrho}{A}\right) a_0, \tag{B22}$$

which has in view of (B17), the solution

$$a_0 = \kappa (A-\varrho)\varrho^{3/2}\, \mathrm{e}^{\varrho/A}\, \mathrm{e}^{5t/4}. \tag{B23}$$

This vanishes at $\varrho = A$, which is a stationary point of (B21). These observations can be used to identify the next scaling as

$$\varrho = A + \sigma/\mathrm{e}^{t/4}, \tag{B24}$$

where from (B21) and (B23) we require in order to match that

$$c_j \sim \kappa(-\sigma)A^{3/2}\, \mathrm{e}^{1+t} \exp\left(-A\,\mathrm{e}^{t/2} + \sigma^2/2A\right) \quad \text{as } \sigma \to -\infty. \tag{B25}$$

We note that $\varrho \sim A$ corresponds to the point at which (B16) and (B21) are minimal (*cf.* optimal truncation). In terms of $C(z,t)$, this asymptotic structure is hidden beyond all orders of the large-time expansion.

B5. $\sigma = O(1)$

If we write

$$c_j \sim \exp(-A\,\mathrm{e}^{t/2})\phi(\sigma, t), \tag{B26}$$

then (B1) yields the leading-order balance

$$2\frac{\partial \phi}{\partial t} + \tfrac{1}{2}\sigma\frac{\partial \phi}{\partial \sigma} = \tfrac{1}{2}A\frac{\partial^2 \phi}{\partial \sigma^2} + \phi, \tag{B27}$$

and because of (B25) we have

$$\phi = \mathrm{e}^t\Phi(\sigma). \tag{B28}$$

Since we require $\Phi \to 0$ as $\sigma \to +\infty$ in order to match forward, it follows from (B25) that

$$\Phi(\sigma) = \frac{\kappa A^2\,\mathrm{e}}{\sqrt{2\pi}}\left(1 - \sqrt{\frac{\pi}{2A}}\sigma\, \mathrm{e}^{\sigma^2/2A}\mathrm{erfc}(\sigma/\sqrt{2A})\right). \tag{B29}$$

Hence

$$\Phi(\sigma) \sim \kappa A^3\,\mathrm{e}/\sqrt{2\pi}\sigma^2 \quad \text{as } \sigma \to +\infty. \tag{B30}$$

B6. $\varrho = O(1)$ WITH $\varrho > A$

This is the final region and (B18) and (B20) are again valid, but to match with (B30) we require the singular solution to (B20), giving $\omega(\varrho) = -A$ and

$$2\frac{\partial a_0}{\partial t} - a_0 = 0, \tag{B31}$$

so that

$$a_0 = e^{t/2}\Psi(\varrho). \tag{B32}$$

It does not seem possible to calculate the function $\Psi(\varrho)$ explicitly and, when general initial conditions are considered, it will depend on the initial data. However, in view of (B30) and (B14) we have

$$\begin{aligned} &\Psi(\varrho) \sim \kappa A^3\, e/\sqrt{2\pi}\,(\varrho - A)^2 \quad \text{as } \varrho \to A^+, \\ &\Psi(\varrho) \sim A^{3/2}/2(\pi B \varrho^3)^{1/2} \quad \text{as } \varrho \to +\infty, \end{aligned} \tag{B33}$$

the t dependence being consistent in the various regions; this completes the matching.

C. The generating-function approach

It is worthwhile to note briefly the application of the generating function (2.2) to the general class (1.3)–(1.4) (*cf.* [5, 11]). Introducing

$$\Phi_p(z,t) = \sum_{k=1}^{\infty} k^p c_k(t)\exp(-kz), \tag{C1}$$

so that

$$M_p(t) = \Phi_p(0,t) \tag{C2}$$

and $C(z,t) = \Phi_0(z,t)$, we have

$$\frac{\partial C}{\partial t}(z,t) = \tfrac{1}{2}\left(\Phi_\alpha(z,t)\Phi_\beta(z,t) - M_\alpha(t)\Phi_\beta(z,t) - M_\beta(t)\Phi_\alpha(z,t)\right). \tag{C3}$$

The relationship between the quantities appearing in (C3) can be written in a number of ways, including

$$\begin{aligned} C(z,t) &= \frac{1}{\Gamma(\alpha)}\int_0^\infty z'^{\alpha-1}\Phi_\alpha(z+z',t)\,dz' \\ &= \frac{1}{\Gamma(\beta)}\int_0^\infty z'^{\beta-1}\Phi_\beta(z+z',t)\,dz'; \end{aligned} \tag{C4}$$

when p is an integer we have

$$\Phi_p(z,t) = (-1)^p\frac{\partial^p C}{\partial z^p}(z,t). \tag{C5}$$

In view of (C2), the Equation (C3) is of a nonlocal type similar to that discussed in [16]; indeed, in the special case $\alpha = \beta = 2$, for instance, we have

$$\frac{\partial v}{\partial t} = \frac{\partial}{\partial z}\left((v - v_s)\frac{\partial v}{\partial z}\right), \tag{C6}$$

where $v(z,t) = \partial^2 C/\partial z^2$ and $v_s(t) = v(0,t) = M_2(t)$. Equation (C6) is to be solved subject to

$$\begin{aligned} &\text{at } z = 0 \qquad v = v_s(t), \\ &\text{as } z \to +\infty \qquad v \sim c_1(t)\, e^{-z}, \end{aligned} \tag{C7}$$

where v_s and c_1 are both unknown but are related via

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -v_s c_1. \tag{C8}$$

The formulation (C6)–(C7) is of some interest: in particular, (C6) is of backward diffusion type because $v < v_s$ for $z > 0$.

Returning to (C3)–(C4), we note that they could be regarded as an alternative continuum formulation of (1.3)–(1.4). In addition to the symmetries

$$\begin{aligned} &C^* = \mu C, \quad \Phi_p^* = \mu \Phi_p, \quad M_p^* = \mu M_p, \quad z^* = z, \quad t^* = t/\mu, \\ &C^* = C, \quad \Phi_p^* = \Phi_p, \quad M_p^* = M_p, \quad z^* = z, \quad t^* = t + t_0, \end{aligned} \tag{C9}$$

inherited from (1.12)–(1.13), it has the further rescaling invariant

$$C^* = C, \quad \Phi_p^* = \nu^p \Phi_p, \quad M_p^* = \nu^p M_p, \quad z^* = z/\nu, \quad t^* = t/\nu^{\alpha+\beta}. \tag{C10}$$

The continuum approximation to (2.2) is the Laplace transformation

$$C(z,t) = \int_0^\infty c(x,t)\, \mathrm{e}^{-xz}\, \mathrm{d}x \tag{C11}$$

and (C10) means that the symmetry (3.4) of the continuous approximation (3.15) is in fact shared by (C3)–(C4), which are an exact representation of the original system; (C10) is equivalent to the combination of (3.3) and (3.4) with $\mu = 1/\nu$. Nevertheless, the continuous symmetry (C10) does not apply to the discrete form (1.3)–(1.4); in particular, it requires setting $k^* = \nu k$ which is not in general an integer. In the special case in which $\nu = n$ is an integer we do, however, recover the discrete symmetry (1.14). Such comments may have fairly general implications for the application of symmetry methods to discrete systems.

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