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Coagulation and fragmentation in cluster–monomer reaction models

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Abstract. We study aggregation kinetics for a model in which both coagulation and fragmentation processes are present. The coagulation kernel is restricted to processes involving monomer–cluster reactions, and only fragmentation processes with monomer break-off are allowed. We consider one model in which both coagulation and fragmentation processes scale with cluster size; in another model, fragmentation is subject to a cut-off at a certain critical size. This resembles physical processes in which a critical nucleus exists. Both sourceless and with-source evolution are considered. The scaling behaviour, steady-state size distributions, and growth exponents are discussed.

1. Introduction

Aggregation processes are of widespread interest in many branches of physics, chemistry and biology. A key quantity is the cluster size distribution $N_s(t)$. Smoluchowski's coagulation equation [1] provides a widely used approach to the time evolution of $N_s(t)$ within a mean field description:

$$dN_s/dt = \tfrac{1}{2}\sum_{i+j=s} K_{ij}N_iN_j - N_s\sum_j K_{sj}N_j \tag{1.1}$$

where the coagulation kernel, K_{ij}, is the rate constant for the merging of clusters of sizes i and j, and its functional form will depend on the diffusive behaviour of the clusters and on the details of the interactions between clusters.

Much of the recent work has addressed the scaling properties of the aggregation kinetics. An analysis of solutions for kernels that have the homogeneity property, $K(ai, aj) = a^\lambda K(i, j)$, has been given by van Dongen and Ernst [2]. Growth exponents and scaling functions were studied for the non-gelling regime ($\lambda \leqslant 1$). For $\lambda > 1$ the mean cluster size diverges at a finite time t_c known as the gel point. Van Dongen [3] has shown that, in some circumstances, gelation takes place instantaneously.

The limiting cases known as diffusion-limited cluster aggregation (DLCA) [4–6] and reaction-limited cluster aggregation (RLCA) [7] correspond to $\lambda = 0$ and 1, respectively. In addition to computer simulations of various aggregation models, there have been attempts [8–11] to relate the scaling predictions to experimental observations on colloidal aggregation. Droplet growth (as opposed to the fractal cluster growth of DLCA and RLCA) on a surface has also been studied by computer simulation [12] and by

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experiment [13]; the former has been related to scaling behaviour as predicted by the Smoluchowski equation.

The use of the Smoluchowski equation assumes that spatial fluctuations can be neglected. This is justified for systems with spatial dimensions larger than the upper critical dimensionality d_c. Although for certain models $d_c=2$, for others it can be arbitrarily large. The model dependence of d_c has been studied by van Dongen [14]. Other developments in the solution of the Smoluchowski equation include a power series approach [15] and generalizations to higher-order kernels [16]. For certain physical problems alternative rate equations to that of Smoluchowski have been proposed [17].

The work listed above is concerned with irreversible aggregation. If dissociation (fragmentation) of the clusters is allowed, reversible aggregation can be studied. Scaling laws in irreversible aggregation have been investigated by a number of authors [18–21] and, in particular, exponents have been obtained that relate the steady state distributions to the details of the coagulation and fragmentation kernels. The upper critical dimensionality appears to be reduced from its value in the fragmentation-free case. An alternative model in which fragmentation involves only monomers has also been investigated [22].

A slightly different model has been investigated by ourselves [23, 24] and independently by Brilliantov and Krapivsky [25] and, for special parameters, by Hendriks and Ernst [26]. In this it is assumed that only monomers are mobile and the aggregation process always involves monomers. Our motivation was to obtain an understanding of dimensional effects on scaling during the early stages of thin film deposition. We made predictions about the growth exponents for island formation on thin films which proved consistent with experimental observations [24]. Most of the work concerned irreversible aggregation though a brief mention of reversible processes was also made. Brilliantov and Krapivsky [25] consider sourceless aggregation as well. The purpose of the present paper is to explore more fully reversible aggregation in the limit in which monomers dominate entirely both the forward and the reverse processes. We shall consider two models for the reverse process and study the behaviour both in the absence and in the presence of a source.

Our basic equations are, for monomer evolution,

$$\mathrm{d}N_1/\mathrm{d}t = R - 2K_1N_1^2 - N_1\sum_{s\geqslant 2} K_sN_s + 2N_2/\tau_2 + \sum_{s\geqslant 3} N_s/\tau_s \tag{1.2}$$

and, for s-mers,

$$\mathrm{d}N_s/\mathrm{d}t = N_1(K_{s-1}N_{s-1} - K_sN_s) - N_s/\tau_s + N_{s+1}/\tau_{s+1}. \tag{1.3}$$

The K_s are the aggregation kernels and the dissociation process is characterized by a size-dependent decay time τ_s. The source term, R, allows the injection of monomers into the system. As stated, we shall consider both the sourceless case ($R=0$) and also the deposition of monomers at a constant rate ($R=$ constant).

2. Models and units

It is convenient to rewrite equations (1.2) and (1.3) in dimensionless units. We consider two different models for the dissociation process.

2.1. Scaled dissociation

The model considers both the aggregation and the dissociation processes scaling with cluster size

$$K_s = K_1 s^p \qquad \tau_s = \tau s^q \tag{2.1}$$

where p and q are arbitrary exponents. The previous work [23–25] considered aggregation kernels that scaled as equation (2.1) but the fragmentation terms were not included. We use the following dimensionless units:

$$K_s \to K_1 K_s \qquad N_s \to N_s/(K_1\tau) \qquad t \to \tau t \qquad \tau_s \to \tau\tau_s \qquad R \to R/(K_1\tau^2). \tag{2.2}$$

In these units, equations (1.2) and (1.3) become

$$\mathrm{d}N_1/\mathrm{d}t = R - 2N_1^2 - N_1 \sum_{s\geqslant 2} s^p N_s + 2N_2/2^q + \sum_{s\geqslant 3} N_s/s^q \tag{2.3}$$

$$\mathrm{d}N_s/\mathrm{d}t = N_1\{(s-1)^p N_{s-1} - s^p N_s\} - N_s/s^q + N_{s+1}/(s+1)^q \tag{2.4}$$

where R is set equal to zero for the sourceless case.

2.2. Truncated dissociation

In this model, the aggregation process is as in equation (2.1), but dissociation is completely absent for clusters larger than size m; that is

$$1/\tau_s = 0 \qquad \text{for } s > m. \tag{2.5}$$

No restrictions or assumptions about scaling with size are put on the τ_s for $s \leqslant m$. Such a model would be relevant to a situation in which there was a critical nucleus, with clusters of smaller size being unstable and larger ones experiencing negligible dissociation.

We again use units defined by equation (2.2), but now τ has the meaning of the smallest (and therefore dominant) of the τ_s. The expressions are similar to equations (2.2) and (2.3), but with the τ_s being left in a more general form:

$$\mathrm{d}N_1/\mathrm{d}t = R - 2N_1^2 - N_1 \sum_{s\geqslant 2} s^p N_s + 2N_2/\tau_2 + \sum_{s\geqslant 3} N_s/\tau_s \tag{2.6}$$

$$\mathrm{d}N_s/\mathrm{d}t = N_1\{(s-1)^p N_{s-1} - s^p N_s\} - N_s/\tau_s + N_{s+1}/\tau_{s+1}. \tag{2.7}$$

R is again zero for the sourceless case and the τ_s are subject to the cut-off defined by equation (2.5).

2.3. Moments and scaling

We note some standard expressions in this subsection. It is usual to express the cluster growth in terms of moments defined by

$$M_n = \sum_s s^n N_s. \tag{2.8}$$

The mean number of clusters is just the zeroth moment, M_0, while the mean cluster size is given by

$$S = M_2/M_1. \tag{2.9}$$

At certain points in the development it will be appropriate to introduce a scaling function to describe the cluster distribution. The canonical form is

$$N_s(t) = s^{-\theta} f(s/t^z). \tag{2.10}$$

The moments are then immediately expressible in terms of growth exponents

$$M_n = t^{z(n-\theta+1)} \int x^{(n-\theta)} f(x)\, \mathrm{d}x. \tag{2.11}$$

For the sourceless models, the total mass $\Sigma s N_s = M$ ($=M_1$, the first moment) is conserved. With the constant source, $M_1 = Rt$.

3. Scaled dissociation—sourceless

We seek first of all the steady state solutions ($R=0$) to equations (2.3) and (2.4). Partial zeroth moments are defined as

$$M_0(n) = \sum_{s \geqslant n} N_s \tag{3.1}$$

and their equations of motion, for $n \geqslant 2$, are trivially obtained from equation (2.4),

$$\mathrm{d}M_0(n)/\mathrm{d}t = (n-1)^p N_1 N_{n-1} - N_n n^{-q}. \tag{3.2}$$

In the steady state, assuming no gelation, each of the $M_0(n)$ is a constant. Hence, from the hierarchy of equations (3.2), in the $t \to \infty$ limit

$$N_s = s^q [(s-1)!]^{p+q} N_1^s. \tag{3.3}$$

This is a detailed balance condition. We refer to a discussion by Ernst and van Dongen [20] about the applicability of detailed balance in homogeneous kernel models. From equation (2.8), the moments can be written,

$$M_n = \sum_s s^{n+q} [(s-1)!]^{p+q} N_1^s. \tag{3.4}$$

The types of solution depend on the sign of $p+q$. We consider $p+q=0$ first, for which scaling solutions occur.

3.1. $p+q=0$

Since, from equation (3.4),

$$M_n = \sum_s s^{n-p} N_1^s \tag{3.5}$$

analytic solutions are possible in terms of standard series for a range of integer values of p. A few of these are examined prior to considering the general case.

$p=0$. For $p=0$, we easily obtain $M_0=N_1(1-N_1)^{-1}$, $M_1=N_1(1-N_1)^{-2}$, $M_2=N_1(1+N_1)(1-N_1)^{-3}$, and, using the boundary condition $M_1=M$, one gets

$$N_1=[1+1/(2M)]-[1/M+1/(4M^2)]^{1/2} \tag{3.6a}$$

$$M_0=(M+\tfrac{1}{4})^{1/2}-\tfrac{1}{2} \tag{3.6b}$$

$$S=(4M+1)^{1/2}. \tag{3.6c}$$

Thus, in the small-M limit,

$$N_1\to M \qquad M_0\to M \qquad S\to 1 \tag{3.7}$$

while, for large M, and using equation (3.3),

$$N_1\to 1-M^{-1/2}\approx\exp(-1/M^{1/2}) \tag{3.8a}$$

$$N_s\to\exp(-s/M^{1/2}) \tag{3.8b}$$

$$M_0\to M^{1/2} \tag{3.8c}$$

$$S\to 2M^{1/2}. \tag{3.8d}$$

Evidently the behaviour is most interesting when there is a large initial concentration of monomers (large-M limit). It is instructive to summarize analytic results for a couple of other values of p.

$p=1$. The following exact expressions are obtained:

$$N_1=M/(1+M) \tag{3.9a}$$

$$M_0=\ln(1+M) \tag{3.9b}$$

$$S=1+M. \tag{3.9c}$$

The small-M limit is as in the $p=0$ case (see equation (3.7)) while, for large M,

$$N_1\to\exp(-1/M) \tag{3.10a}$$

$$N_s\to s^{-1}\exp(-s/M) \tag{3.10b}$$

$$M\to\ln M \tag{3.10c}$$

$$S\to M. \tag{3.10d}$$

The appearance of logarithmic terms suggests that $p=1$, $q=-1$ is a critical case.

$p=-1$. Again at small M, the results of equation (3.7) apply. In the large-M limit,

$$N_1\to\exp[-(2/M)^{1/3}] \tag{3.11a}$$

$$N_s\to s\exp[-s(2/M)^{1/3}] \tag{3.11b}$$

$$M_0\to(M/2)^{2/3} \tag{3.11c}$$

$$S\to 3(M/2)^{1/3}. \tag{3.11d}$$

$p<1$. Equation (3.7) appears to represent the small-M limit generally, and we will not explore that case any further. We present a general development for the large-M behaviour in the $p<1$ regime. As a generalization of equations (3.9*a*), (3.10*a*), and (3.11*a*), it is assumed that we can write

$$N_1=1-\phi\approx\exp(-\phi) \tag{3.12}$$

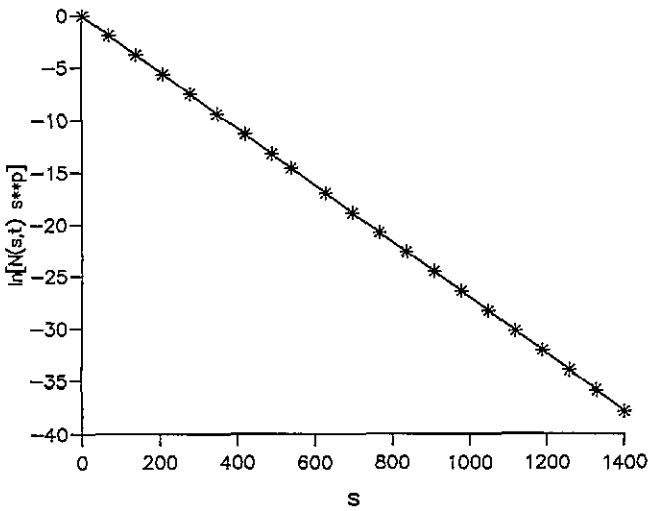

Figure 1. Plot of $\ln[N_s(t)s^{1/2}]$ against s for the parameters $p=0.5$, $M=200$, $t=5000$. Data points are from numerical integration of rate equations. The full line represents equation (3.16*a*). All units are dimensionless.

where ϕ is a small quantity that scales as some negative power of M. Thus, from equations (3.3 and 3.5)

$$M_n=\sum_s s^{n-p}\exp(-s\phi) \tag{3.13}$$

and, replacing the sum by an integral,

$$M_n=\phi^{p-n-1}\int_0^\infty \psi^{n-p}\exp(-\psi)\,\mathrm{d}\psi. \tag{3.14}$$

The integral in equation (3.14) is the gamma function and so we can write

$$M_n=\Gamma(n-p+1)(1-N_1)^{-(n+1-p)}. \tag{3.15}$$

Hence, from equations (3.3) and (3.15) and the condition $M_1=M$, we obtain the following results for the large-M limit:

$$N_s\rightarrow s^{-p}\exp[-s\{\Gamma(2-p)/M\}^{1/(2-p)}] \tag{3.16a}$$

$$M_n\rightarrow[\Gamma(n+1-p)/\Gamma(2-p)^{\{(n+1-p)/(2-p)\}}]M^{\{(n+1-p)/(2-p)\}} \tag{3.16b}$$

and, specifically,

$$M_0\rightarrow[\Gamma(1-p)/\Gamma(2-p)^{\{(1-p)/(2-p)\}}]M^{\{(1-p)/(2-p)\}} \tag{3.16c}$$

$$S\rightarrow[\Gamma(3-p)/\Gamma(2-p)^{\{(3-p)/(2-p)\}}]M^{\{1/(2-p)\}}. \tag{3.16d}$$

The equations reduce in the appropriate limit to the special cases discussed. N_s exhibits scaling behaviour (equation (3.16*a*)) with the total number of particles, M, taking the place of time in the canonical scaling form (equation (2.10)). To demonstrate this, the rate equations have been solved numerically (to a sufficiently high level in the hierarchy for a cut-off not to affect the outcome) and the results are shown in figure 1 for $p=0.5$ and $M=200$. The data points are displayed for $t=5000$, by which

time we are very close to the asymptotic limit. Equation (3.16*a*) is represented by the full line with negative slope of magnitude $\{\Gamma(2-p)/M\}^{1/(2-p)}$; the value is 0.02698 for the parameters used.

If we write $(2-p)^{-1}=y$ and return to the original units (see equation (2.2)), we obtain $M_0 \sim (K_1\tau)^{-y} M^{1-y}$ and $S \sim (K_1\tau)^y M^y$. This can be compared with the scaling form obtained with the homogeneous coagulation and fragmentation kernels (see equation (20) of [18], for example).

$1<p<2$. Equations (3.16*a*) and (3.16*c*) are still valid when the exponent p lies between 1 and 2. Care has to be taken, however, in evaluating M_0 because the integral in equation (3.14) is divergent at the lower limit for $n=0$. From equations (3.13) and (3.16*a*), terms can be regrouped to give

$$M_0 = \sum_s s^{-p}\{1-[1-\exp[-s\{\Gamma(2-p)/M\}^{1/(2-p)}]]\}. \tag{3.17}$$

The first term in this expression is the Riemann zeta function, and the remaining part can be written as a well-behaved integral:

$$M_0 = \zeta(p) - \{\Gamma(2-p)/M\}^{(p-1)/(2-p)} \int_0^\infty \psi^{-p}[1-\exp(-\psi)]\,\mathrm{d}\psi. \tag{3.18}$$

The integral in equation (3.18) can be written in terms of a gamma function, yielding

$$M_0 = \zeta(p) - \Gamma(2-p)^{1/(2-p)}/[(p-1)M^{(p-1)/(2-p)}]. \tag{3.19}$$

$p=2$. One immediately obtains $M_2 = N_1/(1-N_1)$ and $M_1 = -\ln(1-N_1)$, so that

$$N_1 = 1-\exp(-M) \tag{3.20*a*}$$

$$S = [\exp(M)-1]/M \tag{3.20*b*}$$

and, from the series for M_0, to leading order in M,

$$\mathrm{d}M_0/\mathrm{d}M = M\exp(-M).$$

Integrating this expression and noticing that M_0 is a zeta function in the $M\to\infty$ limit, the final expression for M_0 in the large-M limit is

$$M_0 = \zeta(2) - M\exp(-M). \tag{3.20*c*}$$

$p=1$ marks a critical point in the dissociation-free model as reported by Brilliantov and Krapivsky [25], and for larger values of p instantaneous gelation takes place. The behaviour is somewhat different when dissociation is present and it appears that $p=2$ is the corresponding critical value in this case. The regime $1<p\leqslant 2$ is an unstable one, however. The solutions just discussed for this regime are indeed steady state solutions, but they are not stable. A monodisperse initial distribution does not approach the steady state in the asymptotic limit (unlike in the $p<1$ regime), nor is a system prepared with a distribution matching the steady state stable against small perturbations. Although there are steady state solutions, their instability appears to lead to a violation of mass conservation after a time interval that depends on both p and M. This will be explored in more detail elsewhere.

3.2. $p+q<0$

To make progress with the evaluation of equation (3.4) for negative $(p+q)$ in the

large-M limit, we assume that it is possible to develop an expansion about the largest term in the summation. This is a reasonable procedure if $N_1 \to \infty$ as $M \to \infty$. The analysis, in fact, yields an N_1 which varies as a power of $\ln M$ so justifying the method *a posteriori*.

Using Stirling's formula on equation (3.4)

$$M_n \approx (2\pi)^{-|p+q|/2} \sum_{s=1}^{\infty} e^{|p+q|s} N_1^s s^{q+n-|p+q|(s-1/2)}. \tag{3.21}$$

Let us denote the largest term in the summation as T_0; it occurs at $s = s_0$, where

$$s_0 = N_1^{1/|p+q|}. \tag{3.22}$$

Expanding about s_0, the summation in equation (3.21) can be written as a Gaussian integral,

$$M_n \approx (2\pi)^{-|p+q|/2} T_0 \int ds \exp[-|p+q|(s-s_0)^2/2s_0] \tag{3.23}$$

which gives

$$M_n = (2\pi)^{-(|p+q|-1)/2} |p+q|^{-1/2} e^{\alpha} N_1^{\beta} \tag{3.24}$$

where

$$\alpha = |p+q| N_1^{1/|p+q|} \qquad \beta = \tfrac{1}{2} + (\tfrac{1}{2} + q + n)/|p+q|. \tag{3.25}$$

Examining the dominant behaviour of the moments, we obtain finally for the large-M limit

$$N_1 \to [\ln M/|p+q|]^{|p+q|} \tag{3.26a}$$

$$M_0 \to |p+q| M/\ln M \tag{3.26b}$$

$$S \to \ln M/|p+q|. \tag{3.26c}$$

3.3. $p+q>0$

In this regime there are no values of N_1 that provide a solution to equation (3.4) with a finite value for the first moment. This implies the absence of steady state solutions. Gelation takes place with the formation of an infinite cluster. Note this is a behaviour that is distinct from that occurring in the $p+q=0$, $1<p<2$ regime. In that case, there are steady state solutions but they are not stable; here no steady state solutions exist.

4. Scaled dissociation—with source

As in the sourceless case, the balance between coagulation and fragmentation when $p+q=0$ leads to scaling solutions, but here time t rather than M is one of the scaling variables.

4.1. $p+q=0$

An equation for the zeroth moment can be obtained from equations (2.3) and (2.4):

$$dM_0/dt = R - N_1 M_p - N_1 + M_p. \tag{4.1}$$

Assuming that M_p varies as a positive power of t, the second and fourth terms on the right-hand side of the equation are dominant asymptotically. This requires that $N_1 \to 1$. Now, to get a condition on the other N_s a partial moment equation is formed like equation (3.2):

$$dM_0(n)/dt = (n-1)^p N_1 N_{n-1} - n^p N_n \tag{4.2}$$

Since $N_1 \to 1$, this equation provides the general asymptotic behaviour:

$$N_s \to s^{-p}. \tag{4.3}$$

It is convenient to write N_s at arbitrary time in the form of a product of the asymptotic limit and some time-dependent function:

$$N_s = \Delta_s s^{-p} \tag{4.4}$$

where $\Delta_s = 0$ at $t = 0$ and $\Delta_s \to 1$ as $t \to \infty$. Then equation (2.4) can be expressed in the tidy form

$$s^{-p}\, d\Delta_s/dt = \Delta_1(\Delta_{s-1} - \Delta_s) - (\Delta_s - \Delta_{s+1}). \tag{4.5}$$

Considering Δ_s as a continuous function of s and retaining leading terms, we can rewrite this as

$$s^{-p}\partial\Delta_s/\partial t = (1-\Delta_1)\partial\Delta_s/\partial s + \tfrac{1}{2}(1+\Delta_1)\partial^2\Delta_s/\partial s^2 \tag{4.6}$$

Now, assume that Δ_1 approaches 1 as a power of t

$$\Delta_1 = 1 - \alpha/t^r \tag{4.7}$$

where α is a complicated function of R. We discuss the behaviour for a specific value of p later. Then to leading order

$$s^{-p}\partial\Delta_s/\partial t = \alpha/t^r \partial\Delta_s/\partial s + \partial^2\Delta_s/\partial s^2. \tag{4.8}$$

This is an equation that admits scaling solutions and so Δ_s is written in the standard scaling form

$$\Delta_s = s^{-\theta} f(s/t^z) \tag{4.9}$$

from which one obtains the following equation for the scaling function $f(x)$:

$$\frac{d^2 f}{dx^2} + (\alpha + z x^{1-p} - 2\theta x^{-1})\frac{df}{dx} + \theta[(\theta+1)x^{-1} - \alpha]x^{-1} f = 0. \tag{4.10}$$

In forming this equation the following scaling relation has been used:

$$z = r = (2-p)^{-1}. \tag{4.11}$$

A further scaling relation arises when we employ the boundary condition, $M_1 = Rt$,

$$\theta = 0. \tag{4.12}$$

The moments are again given by equation (2.11) and so, from equations (4.4), (4.11) and (4.12),

$$M_n \sim t^{(n+1-p)/(2-p)} \tag{4.13}$$

with, specifically,

$$M_0 \sim t^{(1-p)/(2-p)} \tag{4.14a}$$

$$S \sim t^{1/(2-p)}. \tag{4.14b}$$

For p equal to 1 the zeroth moment varies like ln t.

Since $\theta=0$, equation (4.10) simplifies to

$$\frac{d^2f}{dx^2}+(\alpha+zx^{1-p})\frac{df}{dx}=0 \tag{4.15}$$

which can be integrated to give

$$\frac{df}{dx}=A\exp[-(\alpha x+z^2x^{2-p})] \tag{4.16}$$

where A is a constant whose value is determined by boundary conditions. To satisfy the asymptotic limit, we require that $f(0)=1$ while, to deal with the small-t limit as well, it is necessary that $f(\infty)=0$. There are two cases where $f(x)$ can be obtained analytically.

$p=1$. From the scaling relation (4.11), $z=1$, and equation (4.16) has the trivial solution

$$f(x)=\exp[-(\alpha+1)x]. \tag{4.17}$$

The constants of integration have been chosen to satisfy the $f(0)$ and $f(\infty)$ limits.

$p=0$. In this case, $z=\frac{1}{2}$ from the scaling relations, and equation (4.16) is in a standard form for an error function solution. Again the $f(0)$ and $f(\infty)$ limits are satisfied, with the result

$$f(x)=\operatorname{erfc}(x/2+\alpha)/\operatorname{erfc}(\alpha). \tag{4.18}$$

Let us explore this case in greater detail. The moments can be written as $M_n=Q_nt^{(n+1)/2}$ where $Q_n=2^{n+1}\int_0^\infty x^nf(x)\,dx$. Now, there are conditions that the first two moments must satisfy. The first moment is determined by the rate at which particles are injected, and so $Q_1=R$. In addition to obtaining the leading term in N_1 from equation (4.1), that expression also leads to the condition $Q_0\alpha+R-1=0$ when $p=0$. Using equation (4.18), it can be shown that both of the conditions are satisfied if

$$R=1+2\alpha^2-2\alpha\pi^{-1/2}\exp(-\alpha^2)/\operatorname{erfc}(\alpha). \tag{4.19}$$

Thus, consistency is demonstrated and equation (4.19) enables one to relate α to R. The results are illustrated in figure 2. We have solved the hierarchy of rate equations numerically, and have plotted the data obtained as N_s versus $s/t^{1/2}$ for a number of different times. The results fall on a good universal curve and fit well to the functional form of equation (4.18).

4.2. $p+q\neq 0$

It will be noticed that, for $p+q=0$, the M dependence of the moments in the without-source case and their t dependence in the with-source case (see equations (3.16) and (4.14)) are of the same functional form. By analogy, we adapt equations (3.26) for the with-source case in the $p+q<0$ regime as follows:

$$N_1\rightarrow[\ln t/|p+q|]^{|p+q|} \tag{4.20a}$$

$$M_0\rightarrow|p+q|t/\ln t \tag{4.20b}$$

$$S\rightarrow\ln t/|p+q|.$$

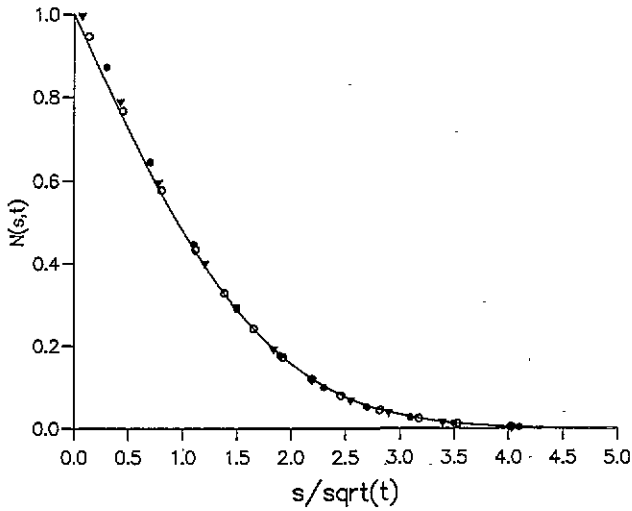

Figure 2. Plot of $N_s(t)$ against $s/t^{1/2}$ for the parameters $p=0$, $R=1$. Data points are from numerical integration of the rate equations. Three different times are represented: filled circles, $t=100$; filled triangles, $t=200$; open circles, $t=500$. The continuous curve is that given by equation (4.18) with α set equal to zero in accordance with equation (4.19). All units are dimensionless.

Their validity has been checked by numerical solution of the hierarchy of the rate equations. Similar considerations apply in the $p+q>0$ regime to those already discussed in section 3.3.

5. Truncated dissociation—sourceless

The behaviour discussed in section 3 where the distribution function and moments were scaling functions of M (see equations (3.16)) is a consequence of aggregation and fragmentation processes both being present in the rate equations for all sizes of cluster. When aggregation alone occurs, both the N_s and the moments scale simply linearly with M. This also occurs with truncated dissociation as we shall now demonstrate—but only in the limit of large M. First let us consider the dissociation-free case to see the reason for the trivial linear scaling.

The time evolution (for $s \geqslant 2$) is governed in the fragmentation-free case by the equation

$$dN_s/dt = N_1\{(s-1)^p N_{s-1} - s^p N_s\}. \tag{5.1}$$

In the absence of a natural unit of time like τ, we can regard t as the true time rather than a rescaled dimensionless unit as in equation (2.2). Now the cluster distribution is a function of time and the initial conditions, $N_s = N_s(t, M)$ where $N_s(t=0, M) = M\delta_{s1}$. A rescaling of the variables, $N_s \to \lambda N_s$, $M \to \lambda M$, $t \to t/\lambda$, leaves both equation (5.1) and also the equation for dN_1/dt invariant. Thus we obtain the relation

$$N_s(t/\lambda, \lambda M) = \lambda N_s(t, M). \tag{5.2}$$

In the large-time limit, $N_s(t \to \infty, \lambda M) = \lambda N_s(t \to \infty, M)$, demonstrating that the steady state distribution function and consequently also the moments scale simply with the number of particles in the system.

In the case of truncated dissociation, the equations governing the evolution are equations (2.6) and (2.7). The cluster distribution now depends on $\tau_s (2 \leqslant s \leqslant m)$, and the relation that is equivalent to equation (5.2) is

$$N_s(t/\lambda, \lambda M, \{\tau_s/\lambda\}) = \lambda N_s(t, M, \{\tau_s\}) \tag{5.3}$$

which is not particularly helpful.

Instead, let us consider partial zeroth moments as defined in equation (3.1). The equation, for $2 \leqslant n \leqslant m$ (from equation (2.7)) is

$$dM_0(n)/dt = (n-1)^p N_1 N_{n-1} - N_n/\tau_n \tag{5.4}$$

while, for $n > m$, the second term on the right-hand side is absent. For a steady state solution, the partial moments approach a constant value and so the left-hand side of equation (5.4) goes to zero in the large-time limit. For $n > m$, this implies that $N_1 N_{n-1}$ also approaches zero. This has to be a result of the behaviour of N_1, so $N_1 \to 0$. Then, using equation (5.4) for $n = 2$, we obtain $N_2 \to 0$ in the asymptotic limit and so on for successive values of n while $n \leqslant m$. So in the large-time limit, $N_s \to 0$ for $s \leqslant m$, while the N_s appoach constant values for $s > m$. The steady state moments are determined by the clusters larger than m.

The time evolution can be considered in two stages. In stage 1, if the initial value of N_1 (namely M) is large, then the coagulation terms in equation (2.7) will dominate over the fragmentation terms. By large, we mean $M \gg \tau^{-1}$. So during this stage (which lasts for a time, call it t_0, of order $\ln M$ in the dimensionless units used), the development follows the fragmentation-free behaviour and equation (5.2) holds. At the end of the stage, N_1 has been reduced from M to a value of order τ^{-1}, and the other N_s $(s > 1)$ are $O(M)$; let us denote their values by Mn_s where n_s where n_s is O(1). In fact, the n_s are essentially the asymptotic values for real fragmentation-free aggregation [25].

Now we focus on stage 2 (starting at t_0), during which the N_s $(s \leqslant m)$ reduce to zero, while the N_s $(s > m)$ approach their final asymptotic value. Consider the partial zeroth moment $M_0(m+1)$. Its value at t_0 is Mn_0 where

$$n_0 = \sum_{s \geqslant m+1} n_s \tag{5.5}$$

and integrating equation (5.4) between t_0 and ∞,

$$M_0 - Mn_0 = Mm^p \int_{t_0}^{\infty} N_1 n_m \, dt. \tag{5.6}$$

$M_0(m+1)$ is just M_0 is the asymptotic limit. Both N_1 and n_m are O(1) at t_0 reducing to zero at ∞ and have very weak dependence on M. We have demonstrated, therefore, that M_0 scales linearly with M. Note, the argument relies on $M \gg \tau^{-1}$, because it is necessary to be able to set up a cluster distribution scaling linearly with M at the end of stage 1.

The scaling of the moments with M is illustrated in figure 3 by means of numerical solutions of the rate equations. M_2/M and M/M_1 are plotted against time for three values of M. It can be seen that the asymptotic values are approaching a constant limit as M is increased. Having established the behaviour, the sourceless model will not be pursued further.

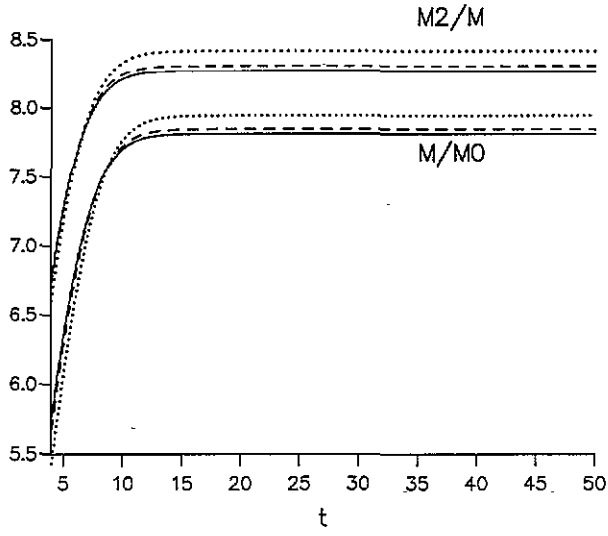

Figure 3. Plots of M_2/M and M/M_0 against t for parameters $p=0$, $m=4$, $\tau_2=\tau_3=\tau_4=1$. Full lines, $M=1500$; broken lines, $M=1000$; dotted lines, $M=500$. All units are dimensionless.

6. *Truncated dissociation—with source*

A preliminary report of this case was given earlier [23]. We develop the discussion more fully here, particularly with regard to the logarithmic time dependence occurring at a critical value of p. Let use assume that asymptotically the monomer distribution falls off algebraically with time, $N_1 \sim t^{-r}$. Now, from equation (2.7) for N_2,

$$dN_2/dt = N_1^2 - K_2 N_1 N_2 - N_2/\tau_2 + N_3/\tau_3 \tag{6.1}$$

it can be seen that to leading order in t^{-1}, $N_2 \sim t^{-2r}$, or $N_2 = \tau_2 N_1^2$. Similarly, from equation (2.7) for arbitrary s ($\leqslant m$), we obtain, to dominant powers of t^{-1}, the relation $N_s = K_{s-1}\tau_s N_1 N_{s-1}$, and so for $s \leqslant m$,

$$N_s \sim t^{-sr} \tag{6.2}$$

To obtain an expression for the zeroth moment, we sum equation (2.7) over all values of s greater than m and add the remaining terms to complete the series:

$$dM_0/dt = K_m N_1 N_m + \sum_{s \leqslant m} dN_s/dt. \tag{6.3}$$

The first term dominates at large t if $mr < 1$ (it will be seen shortly that this condition is fulfilled over a certain range of p). Assuming that a scaling form for $N_s(t)$ applies asymptotically, we obtain from equations (2.11) and (6.3) the scaling relation

$$(m+1)r = 1 - z(1-\theta). \tag{6.4}$$

The first moment, M_1, is equal to Rt for the source model used so that, from equation (2.11),

$$z(2-\theta) = 1. \tag{6.5}$$

The final equation needed is one for the general moment. Again it is obtained from equation (2.7) and, if only leading terms are retained, it takes the form

$$dM_n/dt \approx nN_1 M_{n+p-1}. \tag{6.6}$$

An expansion in powers of s^{-1} has been done, and terms like $s^n\, dN_s/dt$ have been neglected for the same reason that similar terms were discarded from equation (6.3). Now, using equation (2.11), this gives the final scaling relation

$$z(1-p)=1-r. \tag{6.7}$$

Thus from equations (6.4), (6.5) and (6.7) we get values for the three exponents

$$z=(m+1)[(m+2)-(m+1)p]^{-1} \tag{6.8a}$$

$$\theta=m/(m+1)+p \tag{6.8b}$$

$$r=[(m+2)-(m+1)p]^{-1}. \tag{6.8c}$$

The validity of equation (6.2) required that $mr<1$; it can be seen that this is true, at least for $p<2/(m+1)$. From equation (2.11) we can now write the moments generally and the cluster density and size in particular in the asymptotic limit as

$$M_n \rightarrow t^{[(m+1)n+1-(m+1)p]/[(m+2)-(m+1)p]} \tag{6.9}$$

$$M_0 \rightarrow t^{[1-(m+1)p]/[(m+2)-(m+1)p]} \tag{6.10a}$$

$$S \rightarrow t^{(m+1)/[(m+2)-(m+1)p]} \tag{6.10b}$$

These exponents agree with those obtained in the disssociation-free limit [23].

These relations are valid for $p<1/(m+1)$. At that limit the exponent in equation (6.10*a*) goes to zero. This is, in fact, indicative of logarithmic behaviour and it is necessary to consider that regime $p \geqslant 1/(m+1)$ separately. The $p>1(m+1)$ regime is examined first. The main point is that M_0 is approaching a constant value and so we make the assumption that we can write

$$M_0 = \text{constant} - a/t^w \tag{6.11}$$

where w is another exponent and a is some constant. The conditions necessary for the validity of equations (6.5) and (6.7) are unaffected, but the new form of M_0 leads to a different scaling relation to equation (6.4). First, we require

$$z(1-\theta)=0 \tag{6.12}$$

to satisfy equation (2.11). The exponents are now

$$\theta=z=1 \tag{6.13a}$$

$$r=p. \tag{6.13b}$$

Using equation (6.3), and matching leading powers of t^{-1}, one obtains conditions for w, namely $(q+1)=(m+1)r$ if $(m+1)r<(r+1)$, or $q=r$ otherwise. This leads to

$$w=(m+1)p-1 \qquad \text{if} \qquad (m+1)^{-1}<p<m^{-1} \tag{6.13c}$$

$$w=p \qquad \text{if} \qquad m^{-1}<p<1. \tag{6.13d}$$

The moments for $p>1/(m+1)$ are, therefore, simple power laws in order of the moment

$$M_n \rightarrow t^n. \tag{6.14}$$

The final situation to address is the critical value $p=1/(m+1)$ itself. We are dealing with logarithmic corrections and so start with the assumption that we can write

$$N_1 \sim t^{-1/(m+1)}(\ln t)^{\phi} \tag{6.15}$$

$$M_n \sim t^n(\ln t)^{\psi(n)}. \tag{6.16}$$

From equations (6.6) and (6.3) we get the relations

$$\psi(n)=\psi(n-m/(m+1))+\phi \tag{6.17}$$

$$\psi(0)-1=(m+1)\phi \tag{6.18}$$

and, from $M_1=t$,

$$\psi(1)=0. \tag{6.19}$$

Equation (6.17) suggests that one can write

$$\psi(n+\delta)=\psi(n)+\phi\delta(m+1)/m \tag{6.20}$$

and, to obtain consistency with equations (6.18) and (6.19),

$$\phi=-m/(m+1)^2 \tag{6.21}$$

Thus

$$\psi(n)=(1-n)/(m+1) \tag{6.22}$$

and the cluster density and size can be written asymptotically as

$$M_0 \sim (\ln t)^{1/(m+1)} \tag{6.23a}$$

$$S \sim t(\ln t)^{-1/(m+1)}. \tag{6.23b}$$

Again the dissociation-free limit [23] is obtained by setting $m \to 1$.

7. Conclusion

We have studied scaling behaviour in models based on the Smoluchowski equation in which monomers play a primary role in both aggregation and dissociation processes. In the first model the reaction kernels scale as some power of cluster size, while in the second no dissociation processes occur in clusters larger than a certain critical size. When a source is present, growth exponents are found in both models for a range of parameters that admit scaling solutions. Non-scaling solutions are also examined. Both scaling and non-scaling solutions (with particle density as one scaling parameter) are found in the sourceless version of the first model.

The models provide an interesting alternative limit to the extensively studied ones with homogeneous kernels and cluster–cluster interactions on all size scales.

There are some important issues that need addressing as a follow-up to this work. As stated in the paper, there is a certain range of parameters where one encounters breakdown of mass conservation. Although these are not in the physically interesting parameter range, the regime merits exploration as a mathematical example of a situation producing gelation. Finally, the work reported here uses mean field equations and it is not clear under what conditions fluctuations can be neglected; the upper critical dimensionality needs to be determined. We intend to report on these matters later.

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