

Some results for a cluster - monomer model of aggregation with fragmentation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys. A: Math. Gen. 30 6615

(<http://iopscience.iop.org/0305-4470/30/19/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.110

The article was downloaded on 02/06/2010 at 06:01

Please note that [terms and conditions apply](#).

Some results for a cluster–monomer model of aggregation with fragmentation

Francisco Chávez†, Michel Moreau‡ and Luis Vicente‡§

† Departamento de Física y Química Teórica, Facultad de Química, UNAM, 04510 México, DF

‡ Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

Received 6 February 1997, in final form 15 May 1997

Abstract. We study analytic and numerical solutions for a model for the dynamics of cluster growth with fragmentation. The model is restricted to a process involving a monomer–cluster reaction and the cluster of N particles cannot adsorb particles, it can only split up, that is, the X_N cluster is unstable, and for mathematical convenience we propose that it is split up mainly into monomers. In this model both coagulation and fragmentation processes scale with cluster size. Both sourceless and with-source evolutions are discussed. Our analysis shows that in the with-source case the final evolution for the concentrations is of the form $t^{1/2}$ for $X_n (n < N)$ and linear on t for X_N . By comparison, when there is no restriction to the maximum size for polymers and no dissociation the evolution goes asymptotically as $X_n \sim e^{-\tau} = 1/t$.

1. Introduction

Aggregation of macromolecular units into larger structures is of wide interest in many biological, chemical and physical processes which include organic polymer reactions, formation of droplets of water in clouds, etc. Traditionally, one approach for studying the problem has been through the Smoluchowski equation [1], which provides the evolution of the cluster-size distribution within a mean-field description. If dissociation (fragmentation) of the clusters is allowed, reversible aggregation can be studied.

The process of aggregation–fragmentation can be schematically represented by:



where X_p represents both a cluster or polymer containing p elementary units or p -mers and the concentration at time t . K_{ij} and \bar{K}_{ij} are the forward and reverse rate coefficients representing the aggregation and fragmentation rates, respectively, also called kernels. The kinetic equation which describes the evolution of the cluster size distribution, the so-called generalized Smoluchowski equation [2–7] is:

$$\frac{dX_p}{dt} = \frac{1}{2} \sum_{q+r=p} [K_{q,r} X_q X_r - \bar{K}_{q,r} X_p] - \sum_{q=1}^{\infty} [K_{q,p} X_q X_p - \bar{K}_{q,p} X_{p+q}]. \tag{1.2}$$

In (1.2) the first two terms represent the rate of change of the p -cluster due to the coalescence of smaller clusters and its break-up into smaller ones. The next two terms represent the

§ Author to whom correspondence should be addressed.

change of rate due to the coalescence of the p -cluster with others and the break-up of larger cluster into p -clusters. A general solution of the above equation is not possible but some analytical results have been obtained for special combinations of the kernels [8–10] and simulations of the process are also available [11].

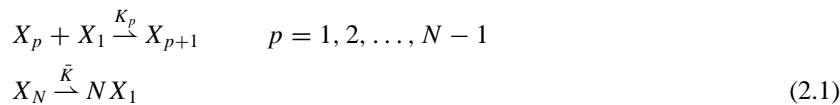
Much of the interest in pure aggregation has addressed the scaling properties of the kinetics. Scaling laws in reversible aggregation have also been studied by a number of researchers [12–14] and exponents that relate the steady-state distributions to the details of the kernels have been obtained. Recently, Blackman and Marshall [15] studied reversible aggregation in the limit in which monomers entirely dominate the process. They considered aggregation and dissociation processes that scale as some power of cluster size and found growth exponents for a range of parameters that admit scaling solutions.

In this paper we also study a model based on the Smoluchowski equation in which monomers play a primary role in both aggregation and dissociation processes. In our model the cluster of N particles cannot adsorb particles, they can only split up, that is, the X_N cluster is unstable, and for mathematical convenience we propose that it is split up mainly into monomers. Besides both coagulation and fragmentation processes scale with cluster size. Both sourceless and with-source evolution are considered.

2. Model and units

We consider a model for the cluster–monomer reaction where dissociation is absent for clusters smaller than a critical size. Such a model could be useful in situations in which there is a critical nucleus, with clusters of smaller size being stable until they reach the critical size. Furthermore, we assume that the decomposition is such that the cluster of size N is broken into monomers.

The process of aggregation–fragmentation can be schematically represented by:



where X_p represents both a cluster or polymer containing p elementary units or p -mers and the concentration at time t . K_i and \bar{K} are rate coefficients representing the aggregation and fragmentation rates, respectively.

The kinetic equations which describe the evolution of the cluster-size distribution is, for monomer evolution

$$\frac{dX_1}{dt} = A - 2K_1X_1^2 - X_1 \sum_{s=2}^{N-1} K_s X_s + \bar{K}NX_N \quad (2.2a)$$

and, for s -mers:

$$\frac{dX_s}{dt} = -K_s X_1 X_s + K_{s-1} X_1 X_{s-1} \quad s = 2, \dots, N-1 \quad (2.2b)$$

and

$$\frac{dX_N}{dt} = -\bar{K}X_N + K_{N-1}X_1X_{N-1} \quad (2.2c)$$

where the source term A allows the injection of monomers into the system. We will consider a scaled dissociation model [14], where the aggregation and dissociation rates are supposed to be proportional to the size of the clusters:

$$K_s = K_1 s \quad \bar{K} = N/\tau. \quad (2.3)$$

Here τ denotes the decay time. Using the following dimensionless units:

$$X_s \rightarrow X_s/(K_1\tau) \quad t \rightarrow \tau t \quad A \rightarrow A/(K_1\tau^2) \quad (2.4)$$

equations (2.2a)–(2.2c) become:

$$\frac{dX_1}{dt} = A - 2X_1^2 - X_1 \sum_{s=2}^{N-1} sX_s + N^2X_N \quad (2.5a)$$

$$\frac{dX_s}{dt} = X_1[(s-1)X_{s-1} - sX_s] \quad s = 2, \dots, N-1 \quad (2.5b)$$

$$\frac{dX_N}{dt} = (N-1)X_1X_{N-1} - NX_N. \quad (2.5c)$$

3. Sourceless case

3.1. Stationary solution

In this case $A = 0$. In this sourceless model the total mass $\sum sX_s = M$ is conserved. As can be seen from the equations, there are two kinds of stationary solutions:

(a)

$$X_1^0 = X_N^0 = 0$$

X_s^0 depending on the initial conditions for $1 < s < N$ and

(b)

$$\begin{aligned} X_s^0 &= \frac{X_1^0}{s} \quad s = 2, \dots, N-1 \\ X_N^0 &= \frac{(X_1^0)^2}{N} \end{aligned} \quad (3.1.1)$$

X_1^0 being solution of

$$(X_1^0)^2 + (N-1)X_1^0 - M = 0$$

which yields

$$X_1^0 = \frac{1}{2} \left(\sqrt{(N-1)^2 + 4M} + 1 - N \right). \quad (3.1.2)$$

3.2. Stability analysis

To determine the local stability of the stationary states we consider the fluctuations around those states, i.e. we will study the linearized equations. Let

$$X_s = X_s^0 + Y_s \quad (3.2.1)$$

where Y_s is the deviation of X_s with respect to its equilibrium value. From equations (2.5a)–(2.5c) we obtain a set of differential equations for Y_s . The set of equations can be written in matrix form:

$$\frac{d\mathbf{Y}}{dt} = \mathbf{R}\mathbf{Y} \quad (3.2.2)$$

where $\mathbf{Y} = (Y_1, \dots, Y_N)$, and $\mathbf{R} = (A_p^q)$ is the ‘reaction matrix’. In terms of components, (3.2.2) can be written as:

$$\frac{dY_s}{dt} = \sum_q A_s^q Y_q. \quad (3.2.3)$$

If \mathbf{R} can be diagonalized, the solution of (3.2.3) is

$$Y_s(t) = \sum_{\eta \neq 0} C_\eta U_s^\eta e^{\eta t} \quad (3.2.4)$$

where η are the different eigenvalues and U_s^η the different eigenvectors.

The explicit form of the reaction matrix for the stationary solutions (a) is

$$\mathbf{R} = \begin{pmatrix} -M & 0 & 0 & \cdots & N^2 \\ -2X_2^0 & 0 & 0 & \cdots & 0 \\ 2X_2^0 - 3X_3^0 & 0 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ (N-1)X_{N-1}^0 & 0 & 0 & \cdots & -N \end{pmatrix}. \quad (3.2.5)$$

It is easily seen that the eigenvectors $(x_i)_{i=1,\dots,N}$ of \mathbf{R} corresponding to the eigenvalue λ satisfy

$$A_1^1 x_1 + A_1^N x_N = \lambda x_1 \quad (3.2.6)$$

$$A_N^1 x_1 + A_N^N x_N = \lambda x_N$$

$$A_s^1 x_1 = \lambda x_1 \quad (3.2.7)$$

$\lambda = 0$ is obviously an eigenvalue of \mathbf{R} , corresponding to the $(N-2)$ -dimensional eigenspace defined by $x_1 = x_N = 0$. If x_1 and x_N are not both 0, (3.2.6) defines λ as a solution of

$$\lambda^2 - \lambda(A_1^1 + A_N^N) + A_1^1 A_N^N - A_N^1 A_1^N = 0$$

the discriminant of which is

$$\Delta = (A_1^1 - A_N^N)^2 + 4A_N^1 A_1^N.$$

Since A_1^1, A_N^N are negative and A_N^1, A_1^N are positive, the solutions are always real and distinct (except in exceptional cases) and this sum is negative. Then (3.2.6) and (3.2.7) define the corresponding eigenvector.

If

$$A_1^1 A_N^N - A_N^1 A_1^N = MN - N^2(N-1)X_{N-1}^0 = N[M - (N-1)X_{N-1}^0] \geq 0$$

(M = total mass as before) then both eigenvalues are ≤ 0 and the stationary states (a) are stable in the sense of Lyapounov, but not asymptotically stable (a point is asymptotically stable if all trajectories starting sufficiently near it tend to it asymptotically for $t \rightarrow \infty$) [16, 17] since the components of the perturbation in the $(N-2)$ -dimensional null space are invariant.

If

$$A_1^1 A_N^N - A_N^1 A_1^N < 0$$

one eigenvalue is negative and one eigenvalue is positive and the stationary state is unstable.

The stationary solution (b), (3.1.2), has a more complicated reaction matrix given by:

$$\mathbf{R} = \begin{pmatrix} -4X_1^0 - \sum_{s=2}^{N-1} sX_s^0 & -2X_1^0 & -3X_1^0 & \cdots & -(N-1)X_1 & N^2 \\ X_1^0 & -2X_1^0 & 0 & \cdots & 0 & 0 \\ 0 & 2X_1^0 & -3X_1^0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ X_1^0 & 0 & 0 & \cdots & (N-1)X_1 & -N \end{pmatrix}. \quad (3.2.8)$$

A general analytic analysis of the eigenvalues is not possible in this case and we turn next to a numerical analysis.

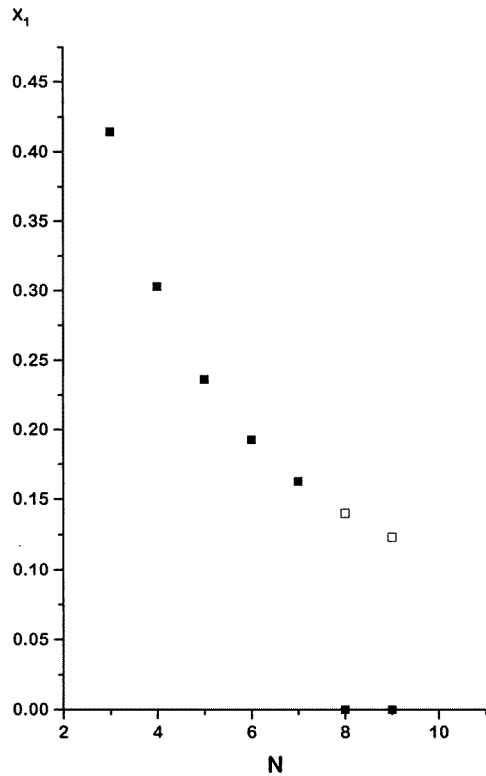


Figure 1. Stationary solution for X_1^0 , the full squares indicate the stable solution, the open squares are the continuation of solution (b).

3.3. Numerical solution of the kinetic equations and stability

The set of coupled nonlinear differential equations, equations (2.5a)–(2.5c), has been solved numerically for different values of $3 < N < 100$ and the total mass was normalized, $M = \sum_{s=1}^N X_s = 1$.

The numerical results show that for the important case where only monomers are initially present, i.e.

$$X_i(0) = \begin{cases} 1 & \text{if } i = 1 \\ 0 & \text{otherwise} \end{cases} \tag{3.3.1}$$

the stationary solution is (a) for $N > 8$ and is (b) for $N < 8$. Figure 1 shows the stable solution X_1^0 as N is increased for this situation.

Another feature to be noted with the numerical calculations is that as N increases the stationary values attain a limit (independent of N). This allows us to consider the next approximation.

3.4. Analytic solution of an approximation to the kinetic equations

If N is large enough and if $M = \sum_{s=1}^N sX_s$ is finite, it may be assumed that $X_N \ll 1$. Let us suppose that $N^2X_N \ll X_1$ and consider the following approximation to the kinetic equations, obtained by neglecting N^2X_N in (2.5a):

$$\frac{dX_1}{dt} = -X_1^2 - X_1M \tag{3.4.1a}$$

and, for s -mers:

$$\frac{dX_s}{dt} = -X_1((s-1)X_{s-1} - sX_s) \quad s = 2, \dots, N-1. \quad (3.4.1b)$$

Using the scaled variables

$$X_1 \rightarrow MX_1 \quad t \rightarrow M^{-1}t$$

it is always possible to take $M = 1$ in (3.4.1a). Defining a new time θ such that

$$X_1 dt = d\theta \quad (3.4.2)$$

we obtain:

$$\frac{dX_1}{d\theta} = -X_1 - 1 \quad (3.4.3a)$$

and, for s -mers:

$$\frac{dX_s}{d\theta} = -((s-1)X_{s-1} - sX_s) \quad s = 2, \dots, N-1 \quad (3.4.3b)$$

where N should be considered to be infinite in order that $\sum sX_s$ should be constant.

The solution for the set of equations is of the form:

$$X_s(\theta) = \sum_{k=1}^s a_k e^{-k\theta}. \quad (3.4.4)$$

If we consider again the initial conditions given by (3.1.1) the explicit solution is:

$$X_s(\theta) = (1 - e^{-\theta})^{s-1} \left(\left(1 + \frac{1}{s}\right) e^{-\theta} - \frac{1}{s} \right). \quad (3.4.5)$$

Furthermore, because of (3.4.2) we have $\theta = \log(2 - e^{-t})$ and we obtain

$$\lim_{t \rightarrow \infty} X_s(t) = \frac{1}{2^s} \left(1 - \frac{1}{s}\right). \quad (3.4.6)$$

Figure 2 displays the approach to equilibrium of $X_1(t)$ and $X_2(t)$ obtained numerically (full curve) and by (3.4.5) (broken curve) for $N = 10$. As can be seen, the approximation used in (3.4.5) is very accurate. In fact, for $N > 10$ they are practically indistinguishable. The plots for all $X_i(t)$, $i \neq 1$ (only shown in figure 2 for $X_2(t)$) exhibit the typical behaviour where they grow at the expense of $X_1(t)$ until a stationary value is reached and the monomers are exhausted. This solution was also obtained in [19].

The different moments, defined by

$$M_n = \sum_s s^n X_s$$

can also be calculated from (3.4.5). The zeroth moment (mean number of clusters) is

$$M_0 = 1 - \theta = 1 - \log(2 - e^{-t}) \quad (3.4.7)$$

which decreases with t and tends to the stationary value

$$M_0^0 = \sum_s X_s^0 = 1 + \log\left(\frac{1}{2}\right) = 0.307.$$

The mean cluster size is given by:

$$S = M_1/M_0 = (1 - \theta)^{-1}$$

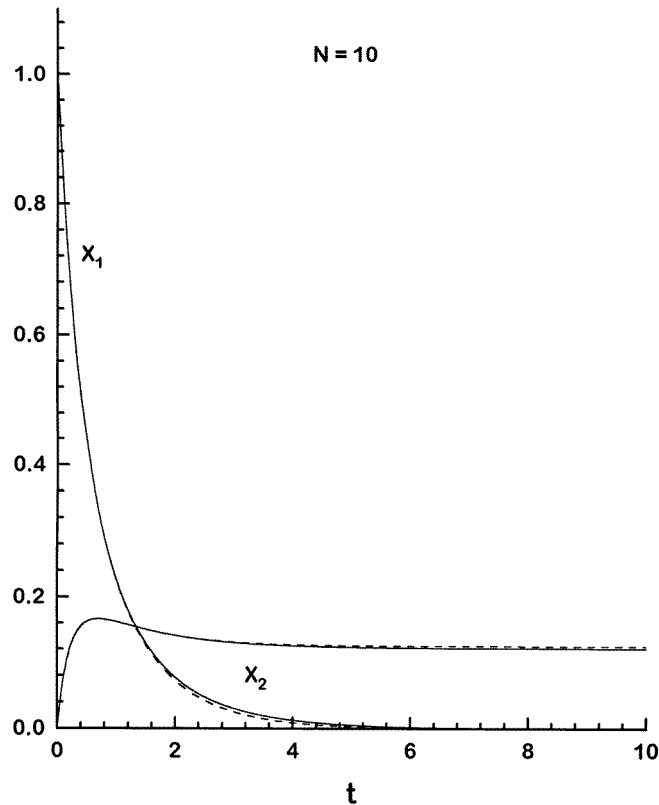


Figure 2. Monomer and dimer concentrations $X_1(t)$, $X_2(t)$ as a function of time. The full curves are the results of the numerical computation of the kinetic equations. The broken curves refer to approximation (3.15).

and tends to

$$S^0 \approx 3.25.$$

It is found that the mean square fluctuation of this size is

$$\sigma^2 = \frac{M_2}{M_0} - \left(\frac{M_1}{M_0} \right)^2 = (1 - \theta)^{-1} e^{2\theta} - (1 - \theta)^{-2}.$$

As a result, the relative fluctuation $\frac{\sigma}{S}$ at first increases with time, then it decreases to the asymptotic value $\frac{\sigma^0}{S^0} \sim 0.5$. Thus, the fluctuation of the cluster size, although not very small remains moderate, and it can be understood that this approximation is accurate for $N > 10$, as shown by the numerical results. As an illustration, figure 3 shows the relative fluctuation σ/S as a function of time for $N = 20$.

As stated before, equation (3.4.5) shows an excellent agreement for $N > 10$ for all $X_i(t)$, $i \neq N$. By solving numerically the complete set of kinetic equations one can see that the evolution of $X_N(t)$, shows a maximum whose location varies as N is increased, as it is depicted in figure 4. The height of this maximum only has an important value for small N values (for $N = 10$ is of order 10^{-4}).

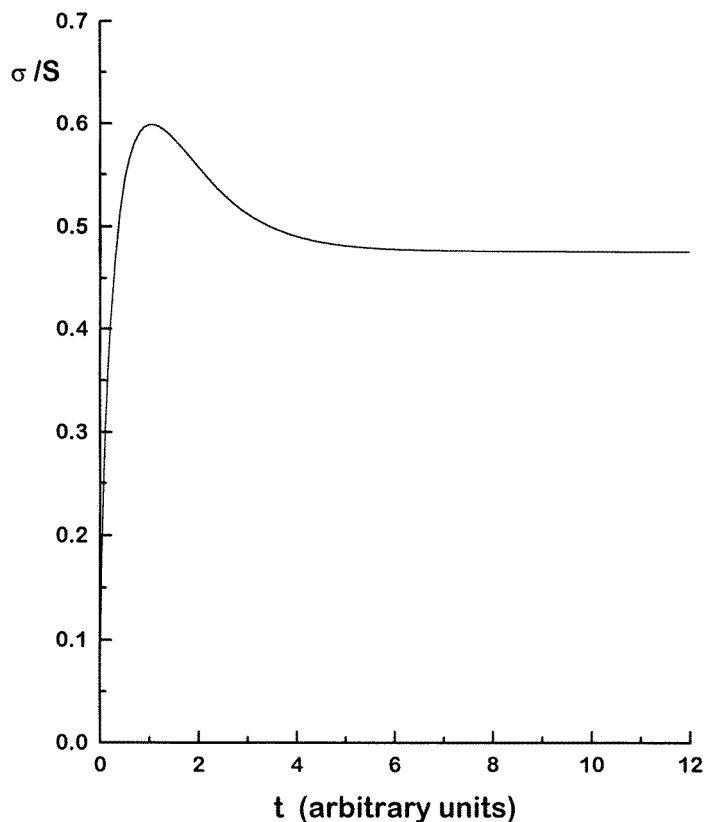


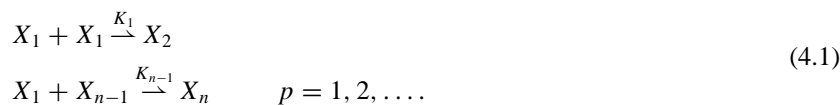
Figure 3. Relative fluctuation σ/S as a function of time for $N = 20$. σ^2 is the mean square fluctuation and S is the mean cluster size.

4. Effect of a source

The presence of a source completely modifies the behaviour of the X_k in time. The source is modelled by adding a constant term, A , in (2.5a), which means the (continuous) deposition of monomers at a constant rate. In order to obtain some analytic insight into this case we next consider an infinite polymerization [19,20] and then compare it with the finite polymerization we have been studying so far.

4.1. Infinite polymerization

Let us consider the polymerization scheme:



We neglect all dissociation, and assume that there is no maximum size for the polymers. If we have no monomers and no polymers of any size at time $t = 0$, we consider the case of a source which introduces monomers at a constant rate A into the system. Then the kinetic equations for the concentrations can easily be written in terms of A and K_i . Let us again

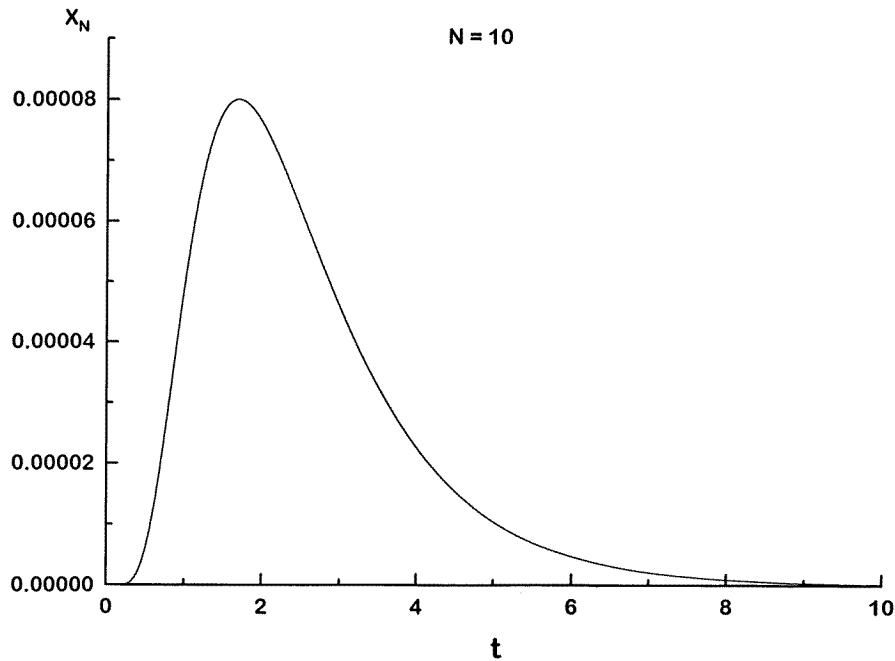


Figure 4. N -mer concentration $X_N(t)$ as a function of time ($N = 10$). For a larger value of N , $X_N \ll 1$.

assume that

$$K_n \propto n$$

then the equations, after renormalizing the concentrations and time, are conveniently expressed by means of the new variables

$$y_n = nX_n.$$

They read:

$$\frac{dy_1}{dt} = -y_1^2 - y_1M + a \quad (4.2a)$$

$$\frac{dy_n}{dt} = n(y_{n-1} - y_n)y_1 \quad n \geq 2 \quad (4.2b)$$

with $a = \text{constant}$ (source term) and

$$M(t) = \sum_{n \geq 1} nX_n(t) = \sum_{n \geq 1} y_n(t). \quad (4.3)$$

Obviously, we have from (4.2)

$$\frac{dM}{dt} = a$$

so that $M(t)$ is the total concentration of monomers introduced at t :

$$M = at. \quad (4.4)$$

4.1.1. *Solution for monomers.* Equation (4.2a) is closed and can be solved exactly. As a matter of fact, let us write

$$\frac{y_1}{M(t)} = z_1. \quad (4.1.1)$$

Clearly, when $t \rightarrow 0$, $z_1(t) \rightarrow 1$, since at very small times the system only contains the monomers which have been introduced by the source.

Let us define

$$\theta(t) = \frac{1}{2}at^2 \quad (4.1.2)$$

so that

$$d\theta = M dt \quad M = (2a\theta)^{\frac{1}{2}}.$$

Dividing (4.2a) by M^2 we obtain

$$\frac{1}{M} \frac{dM}{d\theta} z_1 + \frac{dz_1}{d\theta} = -z_1^2 - z_1 + \frac{1}{a\theta^2}. \quad (4.1.3)$$

Noting that

$$\frac{1}{M} \frac{dM}{d\theta} = \frac{1}{2\theta} = \frac{1}{a\theta^2}$$

we have

$$\frac{1}{2\theta} z_1 + \frac{dz_1}{d\theta} = -z_1^2 - z_1 + \frac{1}{2\theta} \quad (4.1.4)$$

we now write

$$z_1 = \frac{1}{2\theta} + u \quad (4.1.5)$$

$$u = \frac{1}{v} \quad (4.1.6)$$

so that we successively obtain

$$\frac{du}{d\theta} + u^2 + u \left(1 + \frac{3}{2\theta}\right) = 0 \quad (4.1.7)$$

$$\frac{dv}{d\theta} = v \left(1 + \frac{3}{2\theta}\right) + 1 \quad (4.1.8)$$

and

$$\begin{aligned} v &= \theta^{3/2} e^{\theta} \left(C + \int^{\theta} e^{-\theta'} \theta'^{-3/2} d\theta' \right) \\ &= \theta^{3/2} e^{\theta} \left(C - 2\theta^{-1/2} e^{-\theta} - \int_0^{\theta} e^{-\theta'} \theta'^{-1/2} d\theta' \right). \end{aligned} \quad (4.1.9)$$

Since $z_1 \rightarrow 1$ when $t \rightarrow 0$, or $\theta \rightarrow 0$, v should be equivalent to -2θ when $\theta \rightarrow 0$, which implies $C = 0$. Finally, we have

$$z_1 = \frac{1}{2\theta} \left(1 - \frac{1}{1 + \theta^{1/2} e^{\theta} \int_0^{\theta} e^{-\theta'} \theta'^{-1/2} d\theta'} \right)$$

or

$$z_1 = \frac{1}{2\theta} \frac{X}{1 + X} \quad (4.1.10)$$

with

$$X = \theta^{1/2} e^\theta \int_0^\theta e^{-\theta' \theta'^{-1/2}} d\theta'. \tag{4.1.11}$$

It can be easily checked that z_1 as given by (4.1.10) and (4.1.11) actually tends to 1 if $\theta \rightarrow 0$. As a matter of fact,

$$\int_0^\theta e^{-\theta' \theta'^{-1/2}} d\theta' = 2\theta^{1/2} e^{-\theta} + \mathcal{O}(\theta^{3/2})$$

so that

$$X \sim 2\theta \quad \text{when } \theta \rightarrow 0 \tag{4.1.12a}$$

on the other hand

$$X \sim \theta^{1/2} e^\theta \Gamma(\frac{1}{2}) = \sqrt{\pi\theta} e^\theta \quad \text{if } \theta \rightarrow \infty. \tag{4.1.12b}$$

Finally,

$$y_1 = M(t)z_1 = \frac{1}{t} \frac{X}{1+X} \tag{4.1.13}$$

from which it is seen that

$$\begin{aligned} y_1 &\sim at && \text{if } t \rightarrow 0 \\ y_1 &\sim \frac{1}{t} && \text{if } t \rightarrow \infty. \end{aligned}$$

Clearly $y_1(t)$ has a maximum for a positive value of t . It can be shown that this maximum is unique and corresponds to $\theta \simeq 0.6$.

4.1.2. *Solution for polymers.* Let us define

$$\tau = \int_0^t y_1(t') dt' = \int_0^\theta z_1(\theta') d\theta'. \tag{4.1.14}$$

Then equations (4.2) can be written

$$\frac{dy_n}{d\tau} = n(y_{n-1} - y_n) \quad (n \geq 2) \tag{4.1.15}$$

which gives, since $y_n(0) = 0$:

$$y_n(\tau) = n \int_0^\tau e^{-n(\tau-\tau')} y_{n-1}(\tau') d\tau' \tag{4.1.16a}$$

and

$$y_n(\tau) = y_{n-1}(\tau) - \int_0^\tau e^{-n(\tau-\tau')} \frac{dy_{n-1}(\tau')}{d\tau'} d\tau'. \tag{4.1.16b}$$

Obviously $\frac{d}{d\tau} y_n(t) \geq 0$ for very small values of $\tau > 0$. Let us denote τ_n the smallest value of $\tau > 0$ such that

$$\frac{d}{d\tau} y_n(\tau_n) = 0 \tag{4.1.17}$$

which by 4.1.15 is equivalent to

$$y_{n-1}(\tau_n) - y_n(\tau_n) = 0 \tag{4.1.18}$$

τ_n is finite. As a matter of fact, if $y_{n-1}(\tau) \rightarrow 0$ when $\tau \rightarrow \infty$, (4.1.16a) shows that $y_n(\tau) \rightarrow 0$ when $\tau \rightarrow \infty$, so that by induction this is true for all n . It results from (4.1.16b) that

$$\tau_n > \tau_{n-1}$$

since

$$\frac{d}{d\tau} y_{n-1}(\tau) > 0 \text{ for } 0 < \tau < \tau_{n-1}$$

which implies

$$y_{n-1}(\tau) - y_n(\tau) > 0$$

and by (4.1.15)

$$\frac{d}{d\tau} y_n(\tau) > 0 \text{ for all } 0 < \tau \leq \tau_{n-1}.$$

To estimate $\tau_n - \tau_{n-1}$, we write

$$\frac{d}{d\tau} y_n(\tau_n) \simeq \frac{d}{d\tau} y_n(\tau_{n-1}) + \frac{d^2}{d\tau^2} y_n(\tau_{n-1})(\tau_n - \tau_{n-1}) = 0. \tag{4.1.19}$$

By (4.1.15), we have

$$\begin{aligned} \frac{d^2}{d\tau^2} y_n(\tau_{n-1}) &= n \frac{d}{d\tau} y_n(\tau_{n-1}) - n \frac{d}{d\tau} y_n(\tau_{n-1}) \\ &= -n \frac{d}{d\tau} y_n(\tau_{n-1}). \end{aligned}$$

So that by (4.1.19)

$$\tau_n - \tau_{n-1} \simeq \frac{1}{n}. \tag{4.1.20}$$

Thus $\tau_n \sim \log n$ if $n \rightarrow \infty$ and we have

$$\begin{aligned} y_n(\tau) < y_{n-1}(\tau) \text{ and } \frac{d}{d\tau} y_n > 0 & \text{ if } \tau < \tau_n \\ y_n(\tau) > y_{n-1}(\tau) \text{ and } \frac{d}{d\tau} y_n < 0 & \text{ if } \tau > \tau_n. \end{aligned}$$

In order to relate τ to the former variables θ and t explicitly, we use (4.1.14),

$$\tau = \int_0^\theta z_1(\theta') d\theta'$$

with z_1 given by equations (4.1.10) and (4.1.11). It results from this last equation that

$$\frac{1}{X} \frac{dX}{d\theta} = \frac{1}{2\theta} + 1 + \frac{1}{X}$$

which gives

$$\frac{1}{X+1} \frac{dX}{d\theta} = \frac{1}{2\theta} \frac{X}{1+X} + 1 = z_1 + 1. \tag{4.1.21}$$

Finally we obtain

$$\tau = \log(X+1) - \theta \tag{4.1.22}$$

so that by using equations (4.1.12) we obtain

$$\tau \simeq \theta = \frac{1}{2}at^2 \quad \text{as } t \rightarrow 0 \tag{4.1.23a}$$

$$\tau \simeq \frac{1}{2} \log \theta \sim \log t \quad \text{as } t \rightarrow \infty. \quad (4.1.23b)$$

Writing t_n for the time corresponding to τ_n , we see that

$$t_n \propto n \quad \text{for } n \gg 1. \quad (4.1.24)$$

Furthermore, it is seen by induction from (4.1.16) and (4.1.23) that

$$\begin{aligned} y_n &\propto t^{2n-1} && \text{if } t \rightarrow 0 \\ y_n &\propto n e^{-\tau} = n/t && \text{if } t \rightarrow \infty. \end{aligned} \quad (4.1.25)$$

As a conclusion, it can be roughly said that the polymer of order n is mainly present at times of the order of t_n : its concentration is very low if $t \ll t_n$ or $t \gg t_n$.

At t_n the concentration X_n is stationary ($dX_n/dt = 0$) and

$$nX_n(t_n) \equiv y_n(t_n) = y_{n-1}(t_n) \equiv (n-1)X_{n-1}(t_n) \quad (4.1.26)$$

and all other y_k are smaller.

4.2. Finite polymerization

We now assume that there is a maximum size N for the polymers: the polymer X_N is unstable and spontaneously dissociates into N monomers X_1 . The reaction scheme is that given by (2.1) and we again consider the case where $K_n \propto n$. The monomer is still introduced into the system with a constant rate and the equations, with a convenient renormalization of time and concentrations can be written:

$$\frac{dy_1}{dt} = -y_1^2 - y_1 M + (y_1 + N)y_N + a \quad (4.2.1)$$

$$\frac{dy_n}{dt} = n(y_{n-1} - y_n)y_1 \quad 2 \leq n \leq N-1 \quad (4.2.2)$$

$$\frac{dy_N}{dt} = N(y_1 y_{N-1} - y_N) \quad (4.2.3)$$

with, as before

$$M(t) = \sum_{n=1}^N y_n(t) = at. \quad (4.2.4)$$

If $t \ll t_N$, t_N being the time defined in the previous section, the evolution of the polymers of order $n < N$ is practically identical to the evolution described in the previous section, since $y_N \ll 1$. However, for $t \simeq t_N$, the unstable N polymer begins to produce, and its decomposition gives rise to a large, fresh production of monomers. They will in turn trigger all the reaction, mainly the formation of polymers of higher orders, which are faster, until the N -mer temporarily disappears, while smaller polymers begin to be produced. There is clearly an oscillatory regime, the oscillations being due to the strong feedback of monomers caused by the decomposition of the N -mer, which itself enhance, then exhaust, the production of N -mers.

By numerically solving (4.2.1)–(4.2.3) for the initial condition (3.3.1) with $A = 0.001$ and $N = 12$ one obtains the behaviour shown in figure 5 for $X_1(t)$. We initially have a decay for a while until a critical time where the concentration begins to oscillate. The behaviour for the other $X_i(t)$'s is quite similar: there is a short initial period during which $X_i(t)$ growth from zero to their appropriate pseudosteady values. After a certain time, the

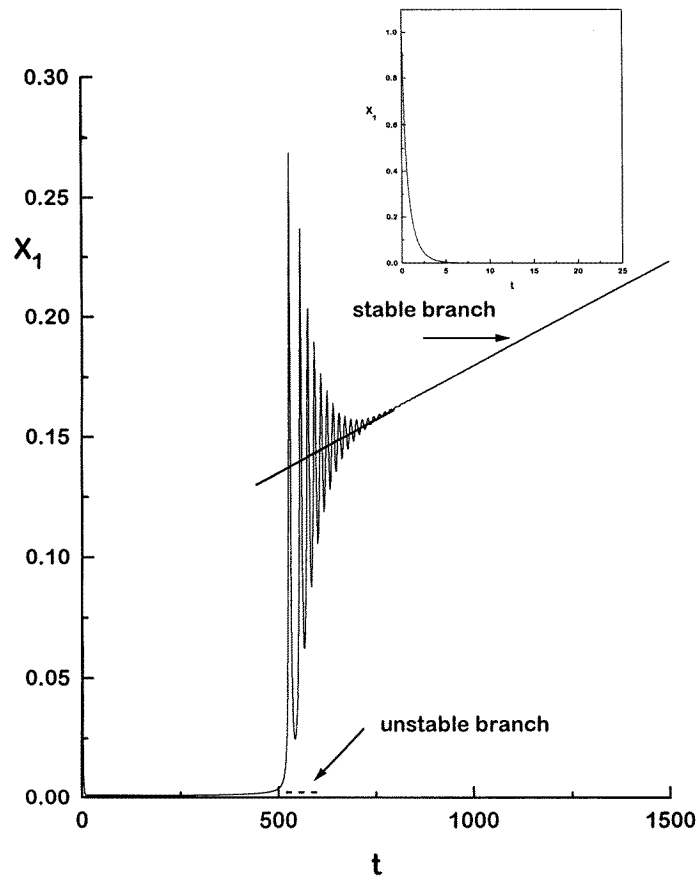


Figure 5. $X_1(t)$ with-source evolution. The inset shows the behaviour for the initial time. The line crossing the oscillations is the continuation of the 'stable branch'.

system moves spontaneously away from the pseudosteady curves and oscillatory behaviour develops. The oscillations eventually die out and there is a damped oscillatory approach to another branch, 'stable branch' (see figure 5). The numerical analysis with different values of N and A shows the same qualitative behaviour, the number of oscillations depending on A (less of them as A increases) and the time for the onset of oscillations is shorter. The same thing happens if we consider a small number of monomers initially present: as we decrease $X_1(0)$ the number of oscillations is smaller. Following Gray and Scott [18] we may think of the first state as being unstable or, in some sense 'repulsive' in contrast to the stability or 'attractiveness' of the other branch. Thus, we have a bifurcation to oscillatory responses.

The numerical simulations show us that the oscillations are progressively damped out, while all concentrations begin to increase regularly. Let us assume that in this final regime

$$y_n \sim c_n t^{\alpha_n} \quad (4.2.5)$$

with $\alpha_n > 0$. Then (4.2.2) implies

$$\begin{aligned} \alpha_1 &= \alpha_2 = \dots = \alpha_{N-1} = \alpha \\ c_1 &= c_2 = \dots = c_{N-1} = c \end{aligned} \quad (4.2.6)$$

and (4.2.3) implies

$$\begin{aligned} \alpha_N &= 2\alpha \\ c_N &= c^2 \end{aligned} \tag{4.2.7}$$

so that (4.2.4) permits us to conclude that

$$\begin{aligned} \alpha_N &= 1 & \alpha &= \frac{1}{2} \\ c_N &= a & c &= a^{1/2}. \end{aligned} \tag{4.2.8}$$

This analysis can be pursued by writing

$$y_n = c_n t^{\alpha_n} + d_n t^{\beta_n} + \tag{4.2.9}$$

with $0 \leq \beta_n \leq \alpha_n$.

Using (4.2.2) and (4.2.4) again finally gives

$$y_n = (at)^{1/2} - (N - 1)/2 + \mathcal{O}(t) \quad 1 \leq n \leq N - 1 \tag{4.2.10a}$$

$$y_N = at - (N - 1)(at)^{1/2} + \mathcal{O}(t) \tag{4.2.10b}$$

with $\mathcal{O}(t) \rightarrow 0$ if $t \rightarrow \infty$.

We can now compare this approximation with the numerical results obtained by numerically solving (4.2.1)–(4.2.3) with initial condition $X_i(0) = 0$ for all i . In this case the oscillations are not as pronounced as in figure 5. The results are shown in figures 6 and 7 and only the behaviour for very long time is shown.

In figure 6 the full curve is the numerical result for $X_1(t)$, the broken curve is the approximation with only the first term in (4.2.10a) and the dotted curve is the approximation with both terms. Figure 7 shows the results for $X_N(t)$. As it can be seen, the agreement is satisfactory.

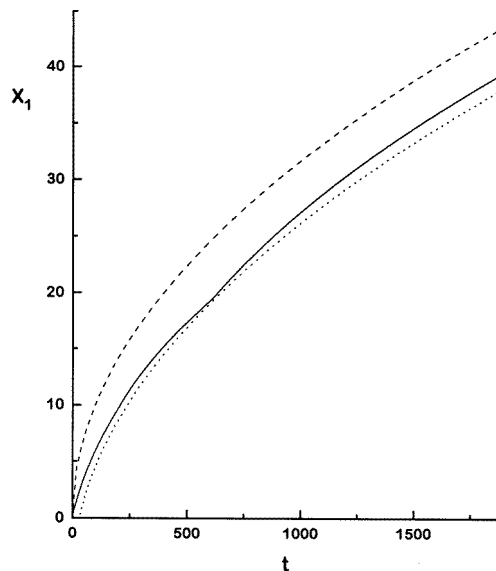


Figure 6. Comparison between numerically solving (4.2.1)–(4.2.3) (full curve) and the approximation with only the first term in (4.2.9) (broken curve) and using the two terms (dotted curve).

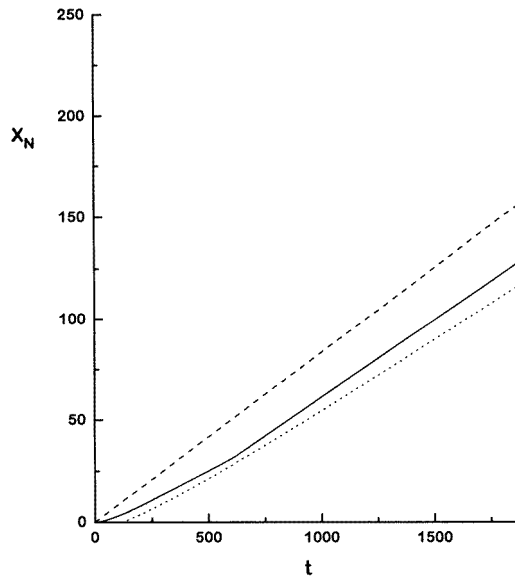


Figure 7. As figure 6 but for X_N .

5. Conclusions

We have studied the behaviour of a model based on the Smoluchowski equation in which the aggregation involves monomer cluster reactions and the cluster of N particles cannot adsorb particles, but can only split up, that is, the X_N cluster is unstable, and for mathematical convenience we propose that it is split up mainly into monomers. In the sourceless case the stability analysis showed that two stationary solutions exist where the trajectories tend, the attraction basin of each one being determined by N , the maximum size of the cluster. Besides, for N large the problem is similar to the addition problem without a source [19] and an approximate solution is found, with very fair agreement with the numerical solutions.

The other issue addressed in this paper was the consideration of a source A of monomers. In this case the model can have two parameters, N and A , and within a certain range of parameters one encounters oscillatory behaviour. A numerical analysis with different values of N and A showed that the number of oscillations depends on A (less of them as A increases) and the time for the onset of oscillations is shorter. The system jumps from an unstable state ('repulsive') to a stable one. This is a bifurcation to oscillatory responses. The oscillations eventually die out and there is a damped oscillatory approach to the stable branch. Our analysis shows that the final evolution for the concentrations is of the form $t^{1/2}$ for $X_n (n < N)$ and linear on t for X_N . In contrast, when there is no restriction to the maximum size for polymers and no dissociation the evolution goes asymptotically as $X_n \sim e^{-\tau} = 1/t$ in agreement with the result by Brilliantov [19].

Acknowledgment

We thank Dr Gleb Oshanin for helpful discussions.

References

- [1] Smoluchowski M V 1917 *Z. Phys. Chem.* **92** 124
A review is given Chandrasekhar S 1954 *Noise and Stochastic Systems* ed N Wax (New York: Dover)
- [2] Blatz P J and Tobolsky A V 1945 *J. Phys. Chem.* **49** 77
- [3] Barrow J D 1981 *J. Phys. A: Math. Gen.* **14** 729
- [4] van Dongen P G J and Ernst M H 1984 *J. Stat. Phys.* **37** 301
- [5] Ernst M H 1983 *Non-equilibrium Phenomena I, The Boltzmann Equation* ed J L Lebowitz and E W Montroll (Amsterdam: North-Holland)
- [6] Ziff R M and McGray E D 1985 *J. Phys. A: Math. Gen.* **18** 3027
Ziff R M and McGray E D 1980 *J. Stat. Phys.* **23** 241
- [7] Family F, Meakin P and Deutch J M 1986 *Phys. Rev. Lett.* **57** 727
- [8] Ziff R M 1980 *J. Stat. Phys.* **23** 241
- [9] Ball J M and Carr J 1989 *J. Stat. Phys.* **61** 203
- [10] Costas M E, Moreau M and Vicente L 1995 *J. Phys. A: Math. Gen.* **28** 2981
- [11] Kolb M 1986 *J. Phys. A: Math. Gen.* **19** L263
- [12] Meakin P and Ernst M H 1988 *Phys. Rev. Lett.* **60** 2503
- [13] Sorensen C M, Zhang X H and Taylor T W 1987 *Phys. Rev. Lett.* **58** 363
- [14] Ernst M H and van Dongen P G J 1987 *Phys. Rev. A* **36** 435
- [15] Blackman J A and Marshall A 1994 *J. Phys. A: Math. Gen.* **27** 725
- [16] Nicolis G and Prigogine I 1977 *Self-Organization in Nonequilibrium Systems* (New York: Wiley)
- [17] Nicolis G 1995 *Introduction to Nonlinear Science* (Cambridge: Cambridge University Press)
- [18] Gray P and Scott S K 1994 *Chemical Oscillations and Instabilities* (Oxford: Oxford University Press)
- [19] Brilliantov N V and Krapivsky P L 1991 *J. Phys. A: Math. Gen.* **24** 4787
- [20] Lyshnikov A A and Kulmala M 1995 *Phys. Rev. E* **52** 1658