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## Some analytical and numerical solutions for colloidal aggregation with fragmentation

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**Abstract.** We study the kinetic equation which describes the evolution of cluster-size distribution of the aggregation–fragmentation problem, the so-called generalized Smoluchowski equation for several dynamics of cluster growth. By using the method of the generating function we find analytical solutions for some cases. Besides, numerical solutions are found for the time evolution of clusters where the aggregation and fragmentation kernels do not allow a complete analytical solution.

### 1. Introduction

Colloidal science is a very important area of research both theoretically and experimentally. It concerns systems within dimensions of nanometres ( $10^{-9}$  m) to micrometres ( $10^{-6}$  m). Examples of systems which are colloidal are aerosols, cements, cosmetics, emulsions, foams, paints, and plastics, and processes which rely on the applications of properties of colloidal systems are, for example, adhesion, detergency, grinding, emulsion polymerization, etc [1]. Because of their small size, colloidal particles undergo Brownian motion just as molecules do. This results in collisions between particles in colloidal suspensions. The stability of colloidal dispersions depends on whether such collisions lead to aggregation. For example, for a lyophobic colloid, there is always an attractive (van der Waals) force between the particles and if they get close enough this force will dominate so that the particles become linked together. The system appears to be stable for some time only if some other force is able to reduce the approaching of other particles in the course of their Brownian motion. They are still thermodynamically unstable, however, and the barrier to coagulation is merely a kinetic one.

The classical understanding of coagulation was given by Smoluchowski at the beginning of this century [2]. He made the assumption that collisions are binary and fluctuations in density are small in order that collisions occur at random. The case of coagulation with fragmentation has been studied less. This case is important because many real systems involve both processes occurring simultaneously to lead to an equilibrium. The modelling of systems with this process arise not only in colloidal science but in a wide variety of situations, examples include astrophysics, atmospheric physics, biology, polymer science, etc. The approaches to solving the kinetic equation associated with this last problem have been scaling and numerical simulations [3–6]. To our knowledge, there are few exact results [7–14]. For a recent theoretical and experimental review see [15, 16].

In this paper we discuss some models for the dynamics of cluster growth. We solve the generalized Smoluchowski rate equation for different combinations of fragmentation

and aggregation kernels, constant and/or additive, by using the method of the generating function. A constant kernel means that the rates of aggregation or fragmentation do not depend on the size of the clusters. This is the simplest and most studied case. Constant aggregation rates occur, for example, for linear polymers which can only react at their extremities. In the case of aggregates which can react at all, or a number of sites, their aggregation rates will increase with the size of the reactants, and in the simplest model they can be assumed to be roughly additive. This assumption is relevant if two linear rods or respective lengths  $p$  and  $q$ , can stick with equal probability when the extremity of one of them touches any site on the other: then the aggregation rate should be proportional to  $p+q$ .

If the clusters reorganize as soon as they are formed to adopt a given form, for example spherical, the collision cross section of two clusters of sizes  $p$  and  $q$  is likely to be  $\sim(p^{\frac{d-1}{d}} + q^{\frac{d-1}{d}})$ ,  $d$  being the dimension of the space. However, we will not consider this case here, but only the limiting constant and additive cases.

As for fragmentation, a constant fragmentation rate is relevant for linear polymers which can be fragmented if a solvent molecule breaks any of its bonds with equal probability. The same assumption holds if a nonlinear cluster can be dissociated under the action of an external agent with any of its  $p$  elementary units, to give any of the  $p-1$  possible pairs  $X_q, X_r$  with  $q+r=p$ . However, if the fragmentation of an aggregate is due to, or enhanced by, some internal instability, the total probability of fragmentation can increase nonlinearly with the size  $p$  of the cluster; if, for instance, it is assumed to be roughly proportional to the number  $p(p-1)/2$  of existing interactions, each possible fragmentation occurs with a probability proportional to  $p$ .

Obviously these models are rather crude, and realistic treatments should be adapted to specific cases. Here we just study some simple examples which can be reasonable approximations of actual phenomena, and permit us to obtain analytical results. We solve the equations numerically and the results are compared with the analytical ones.

## 2. Analytical results

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 [3-8], is

$$\begin{aligned} \frac{dX_p}{dt} = & \sum_{q=1}^{[p/2]} K_{q,p-q} X_q X_{p-q} - \sum_{q=1}^{m-p} K_{q,p} (1 + \delta_{pq}) X_q X_p \\ & - \sum_{q=1}^{[p/2]} \bar{K}_{q,p-q} X_p + \sum_{q=1}^{m-p} \bar{K}_{q,p} (1 + \delta_{pq}) X_{p+q} \end{aligned} \quad (2)$$

with  $p = 1, 2, \dots, m$  and where  $[p/2]$  denotes the greater integer less or equal to  $p/2$ . In equation (2) the first and third terms represent the rate of change of the  $p$ -cluster due

to the coalescence of smaller clusters and its breakup into smaller ones. The other terms represent the change of rate due to the coalescence of the  $p$ -cluster with others and the breakup of larger cluster into  $p$ -clusters. This is a mean-field rate equation and neglects spatial fluctuations in cluster density. For information about this, see [17, 18]. In general, it is not possible to solve this equation but for very special situations. In the following we discuss some examples where analytical results can be found.

2.1. Example A

The size of the clusters is not limited ( $m = \infty$ ) and the reaction rates are constant [7, 12, 13].

Let

$$\begin{aligned} K_{p,q} &= 2k & p \neq q \\ K_{p,p} &= k \end{aligned}$$

and

$$\begin{aligned} \bar{K}_{p,q} &= 2\bar{k} & p \neq q \\ \bar{K}_{p,p} &= \bar{k}. \end{aligned}$$

In this case equation (2) becomes

$$\frac{dX_p}{dt} = \sum_{q+r=p} (kX_qX_r - \bar{k}X_p) - 2 \sum_{q=1}^{\infty} (kX_pX_q - \bar{k}X_{p+q}). \tag{3}$$

Let

$$F(t, z) = \sum_{p=1}^{\infty} X_p z^{p-1}$$

be the generating function for the  $X_p$ . For simplicity in the following the dependence of  $F$  on  $t$  and  $z$  will be dropped. By multiplying each side of (3) by  $z^{p-1}$  and summing over  $k$  we obtain the evolution equation for  $F$ :

$$\frac{\partial F}{\partial t} = k(zF^2 - 2F_1 F) - \bar{k}z \frac{\partial F}{\partial z} + 2\bar{k} \frac{F - F_1}{z - 1} \tag{4}$$

where

$$F_1 \equiv F(z = 1) = \sum_p X_p.$$

This example has been studied extensively, and it can be solved completely [13]. Here we only recall two interesting properties: there is an equilibrium stationary solution satisfying the detailed balance, and there is a particular time-dependent solution where each elementary reaction (1) has the same time-dependent chemical affinity.

2.1.1. *Particular solution.* A particular solution for (3) has the form

$$X_p = v^2(1 - v)^{p-1} \quad (5)$$

where the total concentration of monomers,  $\sum pX_p = \gamma$ , is constant and normalized to 1 ( $\gamma = 1$ ).

Indeed, in this case

$$F = \frac{v^2}{1 - (1 - v)z} \quad F_1 = v$$

and (4) is verified if  $v$  satisfies

$$\frac{\partial v}{\partial t} = -kv^2 + \bar{k}(1 - v)$$

the solution of which is

$$v = \frac{a + bce^{-\delta t}}{1 - ce^{-\delta t}} \quad (6)$$

where  $a$ ,  $b$ ,  $c$  and  $\delta$  are easily expressed as functions of  $k$  and  $\bar{k}$ .

It is clear that the solution considered is only valid for certain initial conditions which are determined by satisfying (6). They include the important case where only monomers are initially present, i.e.  $v(0) = 1$  and in this case the constants are

$$\begin{aligned} a &= \frac{-\bar{k} + \sqrt{\bar{k}^2 + 4\bar{k}k}}{2k} & b &= \frac{\bar{k} + \sqrt{\bar{k}^2 + 4\bar{k}k}}{2k} \\ c &= \frac{2k + \bar{k} - \delta}{2k + \bar{k} + \delta} & \delta &= \sqrt{4\bar{k}k + \bar{k}^2}. \end{aligned}$$

It should be noticed that each one of reactions (1) has the same affinity, since

$$\frac{\bar{k}X_{p+q}}{kX_pX_q} = \frac{1 - v}{v^2} \frac{\bar{k}}{k}.$$

When  $t \rightarrow \infty$ ,  $v \rightarrow a$ , and the asymptotic value reached by the aggregate of  $p$ -mers is

$$X_p \rightarrow a^2(1 - a)^{p-1} \quad (7)$$

and the detailed balance condition

$$kX_pX_q = \bar{k}X_{p+q}$$

is satisfied.

2.1.2. *Stationary solution.* In this case it is easily verified that an equilibrium stationary solution, where every reaction (1) is equilibrated, exists:

$$kX_p^e X_q^e = \bar{k}X_{p+q}^e \tag{8}$$

where  $X_p^e$  is the concentration of molecules of the  $p$ -mer at equilibrium. Considering  $q = 1$  and by an inductive argument we get

$$X_p^e = a_p (X_1^e)^p \tag{9}$$

where

$$a_p = \left(\frac{k}{\bar{k}}\right)^{p-1}.$$

This stationary state is stable and unique, as can be seen from the decreasing function

$$f(X_1^e) = \gamma - \sum_p p a_p (X_1^e)^p$$

which is positive if  $X_1^e = 0$  and negative if  $X_1^e \rightarrow \infty$ . Thus there exists an equilibrium unique point, defined by the total concentration of monomers  $\gamma$ , and  $k/\bar{k}$ , where the function  $f(X_1^e)$  vanishes.

### 2.2. Example B

The size of the clusters is not limited ( $m = \infty$ ) and additive coagulation and constant fragmentation kernels are considered.

These kernels are defined by

$$K_{ij} = k(i + j) \quad \bar{K}_{ij} = \bar{k}.$$

As was mentioned before, the additive form arises if we assume that binary interactions of clusters occur randomly with a rate proportional to the total surface area of the clusters. In this case the evolution equation is

$$\frac{dX_p}{dt} = \sum_{q+r=p} [k(q+r)X_q X_r - \bar{k}X_p] - 2 \sum_{q=1}^{\infty} [k(p+q)X_p X_q - \bar{k}X_{p+q}]. \tag{10}$$

Let us consider

$$\phi(t, \omega) = \sum_p e^{\omega p} X_p \tag{11}$$

which is related to  $F$  by

$$\phi(t, \ln z) = zF(t, z).$$

By multiplying each side of (10) by  $e^{\omega p}$  and summing over  $p$  we obtain the equation for  $\phi$ :

$$\frac{\partial \phi}{\partial t} = k(\phi^2)' - 2k(\phi' \phi_0 + \phi \phi_0') - \bar{k}(\phi' - \phi) + \frac{2\bar{k}}{1 - e^{-\omega}} (e^{-\omega} \phi - \phi_0) \tag{12}$$

where  $\phi' = \frac{\partial \phi}{\partial \omega}$  and  $\phi_0 = \phi(t, \omega = 0)$ .

2.2.1. *Total concentration of particles.* The total concentration of particles is

$$\sum_p X_p = \phi_0 \quad (13)$$

which satisfies the equation

$$\frac{\partial \phi_0}{\partial t} = -2k\phi_0\phi'_0 - \bar{k}(\phi_0 - \phi'_0). \quad (14)$$

Noting that the total concentration of monomer units is conserved:

$$\phi'_0 = \sum_p pX_p = \text{constant} = \gamma \quad (15)$$

equation (14) transforms into

$$\frac{\partial \phi_0}{\partial t} = -(2k\gamma + \bar{k})\phi_0 + \bar{k}\gamma \quad (16)$$

whose solution for the initial condition  $X_1 = \gamma$  at  $t = 0$  (only monomers present) is

$$\phi_0(t) = \frac{\gamma}{2k\gamma + \bar{k}} (2k\gamma e^{-(2k\gamma + \bar{k})t} + \bar{k}). \quad (17)$$

From this equation it is seen that the total number of particles decays exponentially and the asymptotic value is

$$\phi_0(\infty) = \frac{\gamma\bar{k}}{2k\gamma + \bar{k}}. \quad (18)$$

Then the average of polymers is

$$\langle p \rangle = \frac{\sum_p pX_p}{\sum_p X_p} = \frac{\gamma}{\phi_0(t)}. \quad (19)$$

As  $t \rightarrow \infty$ ,  $\langle p \rangle$  increases from 1 to

$$1 + \frac{2k\gamma}{\bar{k}}. \quad (20)$$

2.2.2. *Solution.* It is remarkable that the hierarchy (10) can be solved exactly, although we are not able to find a general analytical expression for this solution. As a matter of fact, because of (13) and (15), equation (10) can be written as

$$\frac{dX_p}{dt} = -X_p[2k(\gamma + p\phi_0) + (p+1)\bar{k}] + kp \sum_{q+r=p} X_q X_r + 2\bar{k} \left[ \phi_0 - \sum_{q=1}^{p-1} X_q \right]. \quad (21)$$

Thus, the last term in the right-hand side of (21) only contains the functions  $X_q$  for  $q < p$ , and the known function  $\phi_0$ : equation (21) is a linear, non-homogeneous first-order equation in  $X_p$ , and the hierarchy can easily be solved at all successive orders.

At first order we have

$$\frac{dX_1}{dt} = -X_1[2k(\gamma + \phi_0) + 2\bar{k}] + 2\bar{k}\phi_0 \tag{22}$$

with the following solution, if  $X_1(0) = \gamma$ :

$$X_1 = \gamma \exp\left(-\int_0^t [2k(\gamma + \phi_0) + 2\bar{k}] dt'\right) + \int_0^t 2\bar{k}\phi_0(t') \exp\left(-\int_{t'}^t [2k(\gamma + \phi_0) + 2\bar{k}] dt''\right) dt'. \tag{23}$$

This can also be written

$$X_1 = \frac{\bar{k}}{k} + \left(\gamma - \frac{\bar{k}}{k}\right)\psi(t) - 2\bar{k}\left(\gamma + \frac{\bar{k}}{k}\right)\psi(t) \int_0^t \frac{1}{\psi(t')} dt' \tag{24}$$

with

$$\psi(t) = \exp\left(-\int_0^t [2k(\gamma + \phi_0) + 2\bar{k}] dt'\right). \tag{25}$$

When  $t \rightarrow \infty$ ,

$$\psi(t) \sim \exp(-At)$$

with

$$A = 2k\left(\gamma + \frac{\bar{k}\gamma}{2k\gamma + \bar{k}}\right) + 2\bar{k} \tag{26}$$

and it is found that .

$$X_1 = \frac{2\bar{k}}{aA}\bar{k}\gamma + \frac{2\bar{k}}{aA}\left(\gamma + \frac{\bar{k}}{k}\right)\frac{(2k\gamma)^2}{A-a}e^{-at} + \dots \tag{27}$$

with

$$a = 2k\gamma + \bar{k}. \tag{28}$$

Obviously the asymptotic values of  $X_1, X_2, \dots$  can be obtained successively from (21). It has to be noted that in this case the detailed balance condition is not satisfied.

### 2.3. Example C

The size of the clusters is not limited ( $m = \infty$ ) and additive coagulation and size-dependent fragmentation kernels are considered.

These kernels are defined by

$$K_{ij} = k(i + j) \quad \bar{K}_{ij} = \bar{k}(i + j).$$



In this case the evolution equation is

$$\frac{dX_p}{dt} = \sum_{q+r=p} [k(q+r)X_qX_r - \bar{k}pX_p] - 2 \sum_{q=1}^{\infty} [k(p+q)X_pX_q - \bar{k}(p+q)X_{p+q}]. \quad (29)$$

Let us consider again the function  $\phi(t, \omega)$  given by (11). In this case the equation for  $\phi$  is

$$\frac{\partial \phi}{\partial t} = k(\phi^2)' - 2k(\phi'\phi_0 + \phi\phi_0') - \bar{k}(\phi'' - \phi') + \frac{2\bar{k}}{1 - e^{-\omega}}(e^{-\omega}\phi - \phi_0) \quad (30)$$

where as before the prime indicates the derivative with respect to  $\omega$  and,  $\phi_0 = \phi(t, \omega = 0)$

Then, the equation for  $\phi_0$ , which is the total number of particles, is

$$\frac{\partial \phi_0}{\partial t} = -2k\phi_0\phi_0' + \bar{k}(\phi_0'' - \phi_0') \quad (31)$$

or, using the conservation of mass

$$\frac{\partial \phi_0}{\partial t} = -2k\gamma\phi_0 - \bar{k}\gamma + \bar{k}\phi_0'' \quad (32)$$

A solution cannot be found for  $\phi_0(t)$  unless  $\phi_0''$  is given.

Thus it is generally impossible to solve the hierarchy of equations (29) in a closed form, except if a truncation is adopted, for instance by assuming that there is a maximum size for the aggregates.

**2.3.1. Equilibrium.** It should be pointed out that an equilibrium stationary solution, with detailed balance for all equation (1), again exists.

As a matter of fact this condition now reads

$$k(p+q)X_p^e X_q^e = \bar{k}(p+q)X_{p+q}^e$$

and gives, as in 2.1.2,

$$X_p^e = \left(\frac{k}{\bar{k}}\right)^{p-1} (X_1^e)^p = \frac{\phi_0^e}{1 + \kappa\phi_0^e} \left(\frac{\kappa\phi_0^e}{1 + \kappa\phi_0^e}\right)^{p-1}$$

with  $\kappa = k/\bar{k}$ , and

$$\phi_0^e = \sum X_p^e = (1 - \kappa X_1^e)^{-1} X_1^e$$

$\phi_0$  being uniquely determined by

$$\gamma = \sum_p p X_p^e = \phi_0^e (1 + \kappa\phi_0^e).$$

Although an equilibrium solution exists, it is easily seen that there is no exact time-dependent solution in the form of a geometrical series, similar to the solution (5) of case A described in 2.1.1. However, we will now study an approximation which assumes that the polymer distribution remains nearly a geometric series all the time.

2.3.2. *Approximate solution.* A simple approximation, if the dispersion of the size of the polymers is low, consists of assuming that the relation

$$\langle p^2 \rangle - \langle p \rangle^2 = \langle p \rangle (\langle p \rangle - 1)$$

which holds at time 0 (if there are only monomers initially) and at  $t = \infty$ , is always approximatively verified. Thus

$$\frac{\sum p^2 X_p}{\sum X_p} \simeq 2 \left( \frac{\sum p X_p}{\sum X_p} \right)^2 - \frac{\sum p X_p}{\sum X_p}$$

or

$$\phi_0'' = \sum_p p^2 X_p \simeq 2 \frac{\gamma^2}{\phi_0} - \gamma. \tag{33}$$

Then equation (32) becomes

$$\frac{\partial \phi_0}{\partial t} = -2k\gamma\phi_0 - 2\bar{k}\gamma + \frac{2\bar{k}\gamma^2}{\phi_0} \tag{34}$$

the solution of which (if  $\phi_0(0) = \gamma$ ) is given by

$$\phi_+ \ln \frac{\phi_0 - \phi_+}{\gamma - \phi_+} - \phi_- \ln \frac{\phi_0 - \phi_-}{\gamma - \phi_-} = -\frac{2k\gamma}{c} t \tag{35}$$

with

$$c = \left[ \frac{\bar{k}}{k} \left( \frac{\bar{k}}{k} + 4\gamma \right) \right]^{1/2} \quad \phi_{\pm} = -\frac{\bar{k}}{2k} \pm \frac{c}{2}. \tag{36}$$

It can be shown that  $\gamma > \phi_+ > 0 > \phi_-$ , and that (35) has a unique solution  $\phi_0(t) > \phi_+$  for all  $t > 0$ . When  $t \rightarrow \infty$ ,  $\phi_0 \rightarrow \phi_+$ , which is the equilibrium value calculated in 2.3.1. It is seen that  $\phi_0$  tends to  $\phi_+$  as  $\exp(-\frac{2k\gamma}{c\phi_+} t)$ .

Once  $\phi_0$  is estimated, all  $X_p$  can be calculated successively from (29), using the method of section 2.1.2.

The result of this approximation for  $X_1$  is compared to the numerical solution of the kinetic equations in figure 1, curve C. It is seen that the approximation is quite accurate.

### 3. Numerical method

Equation (2) is a set of coupled nonlinear first-order differential equations. We used the Euler method to solve this set of equations, cut by setting the limit to the maximum value  $q$  of the cluster  $X_q$ . This  $q_{max}$  was usually taken as 100; the results are not affected by this choice of relatively small system size, as we checked it by comparing with the numerical data produced by a higher value of  $q_{max}$ . So, we follow the evolution of the population  $X_k(t)$  with an initial distribution of 100 monomers. For simplicity we take  $k = \bar{k} = 1$ . The time step was taken so as to ensure that the results were independent of that step. We also calculated the zero and first moments,

$$M_0 = \sum_q X_q(t), \quad M_1 = \sum_q q X_q(t)$$

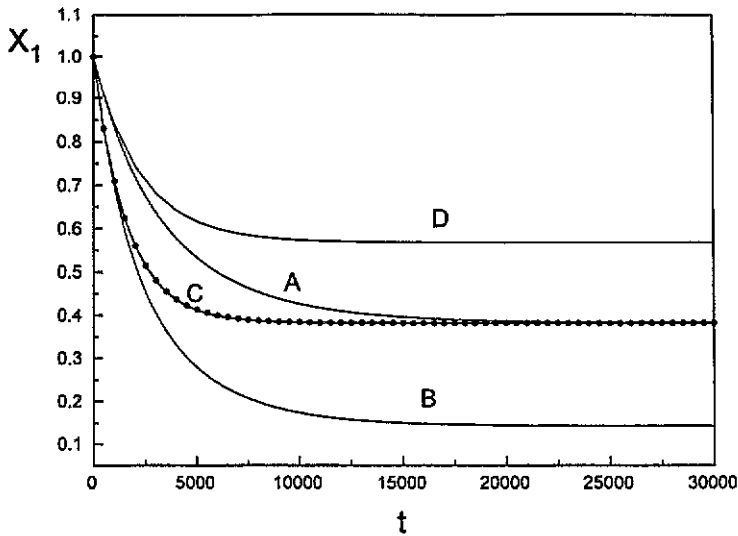


Figure 1. Monomer concentration values  $X_1(t)$  as a function of time for the different kernel combinations indicated as A, B, C and D in table 1. The full circles are the results from the approximation used in example C. Note that the numerical and analytical results for case C lie on top of each other.

which are the total number of clusters and the total mass.  $M_1$  is conserved with time and this constancy was a check for our calculations.

As is shown in [8] two basic models of the Flory–Stockmayer theory of polymerization can be described in terms of rate equations with the following coagulation rates:  $K_{ij} \sim 1$ ,  $K_{ij} \sim (i + j)$ . So, we used them as the aggregation kernels and choose those listed in table 1 for the fragmentation kernels. Cases A, B and C are the same as we dealt with in the previous section and checking them numerically indicated to us that the approximations were good enough. Case D is the inverse of example B, that is, constant coagulation and additive fragmentation. It is possible to write an equation as (21) for every  $X_p$ , but the equations for the monomers and  $\phi_0$  are

$$\frac{dX_1}{dt} = -X_1(2k\phi_0 + 2\bar{k}) + 2\bar{k}\gamma \quad \frac{d\phi_0}{dt} = -k\phi_0^2 - 2\bar{k}\gamma + \frac{2\bar{k}\gamma^2}{\phi_0}.$$

Table 1. Aggregation and fragmentation kernels.

Case	$K_{ij}$	$\bar{K}_{ij}$
A	1	1
B	$(i + j)$	1
C	$(i + j)$	$(i + j)$
D	1	$i + j$

#### 4. Results

Figure 1 displays the approach to equilibrium of  $X_1(t)$  for the different kernel combinations. In all cases  $X_1(t)$  decays monotonically with time from  $c_0$  at  $t = 0$ , since larger aggregates

are formed at the expenses of primary particles. As can be seen, the asymptotic value for cases A (constant aggregation and fragmentation kernels) and C (additive aggregation and constant kernels) is the same. The reason for this can be seen from (8), where equality of the aggregation and fragmentation kernels results in (9). But the initial decrease is different for every case. In fact the decrease for case C, whose kernels are area-dependent, is less steep than for case A whose kernels are constant. This same figure also shows that the approximation used in 2.3.2 (example C) is very accurate (plotted with full circles).

The asymptotic value for case B is different. For a comparison, from (27) we obtain the asymptotic value for  $X_1 \sim 0.14285$ , while the numeric value is 0.14293. The mechanism for case D implies the conservation of a larger number of monomers at equilibrium. Using the equations for  $X_1$  and  $\phi_0$  given above we also obtain a very accurate result, compared with the numerical solution. So, in this case the asymptotic value is  $X_1 \sim 0.57172$ , while the numeric value is  $X_1 \sim 0.57348$ .

At the same time the number of higher-order particles, which is zero at the beginning, increases at the expenses of the lower-order particles. For mechanisms B and C the number of dimers reaches a maximum, after which it begins to decrease owing to the formation of particles of a still higher order (see figure 2). This maximum is attained at (arbitrary units) time 8600 for case A and at time 2000 for case B. For cases C and D there is no maximum. The occurrence of a maximum for the evolution of the different  $k$ -mers depends only of the chosen values for  $k$  and  $\bar{k}$ . So, for the special choice  $k = \bar{k} = 1$  we see from (5) that the condition for a maximum is  $a < \frac{2}{3}$ , which is fulfilled only for dimers but not for higher-order-mers. Instead, if we choose  $k = 1, \bar{k} = 2$  and  $a = 0.222$  which fulfils the condition  $a < \frac{1}{3}$  valid for six-mers. Now, from figure 2 we also see that the number of dimers at equilibrium is greater for mechanism D and less for mechanism B. So this last mechanism is less able to preserve dimers and favours the formation of trimers and tetramers, as can be seen in figures 3 and 4, respectively.

Finally, figure 5 shows the average  $\langle p \rangle$  as a function of time. Note that for case B this value reaches the limit given by (20).

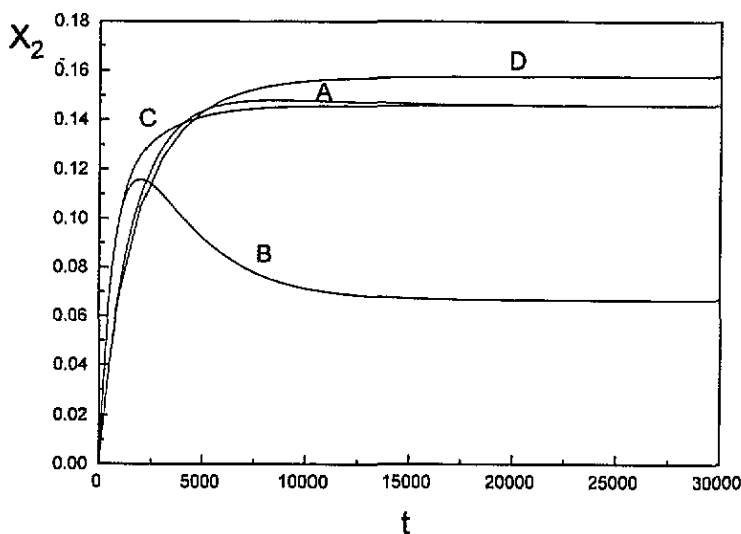


Figure 2. Dimer concentration values  $X_2(t)$  as a function of time for the different kernel combinations of table I.

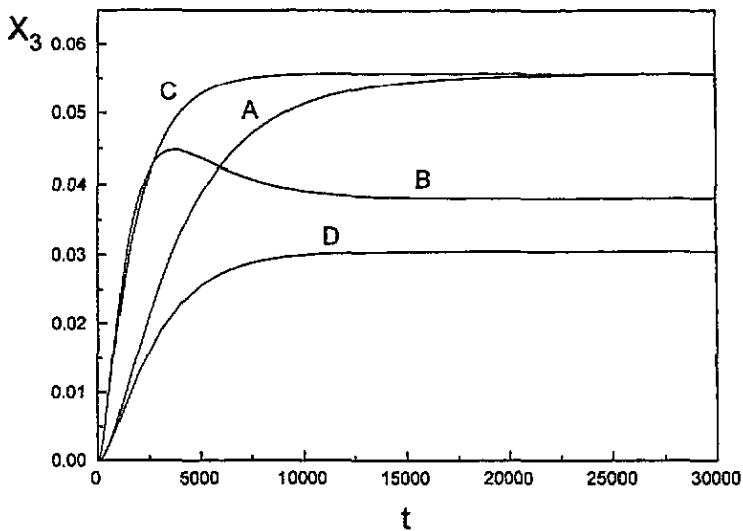


Figure 3. Trimer concentration values  $X_3(t)$  as a function of time for the different kernel combinations of table 1.

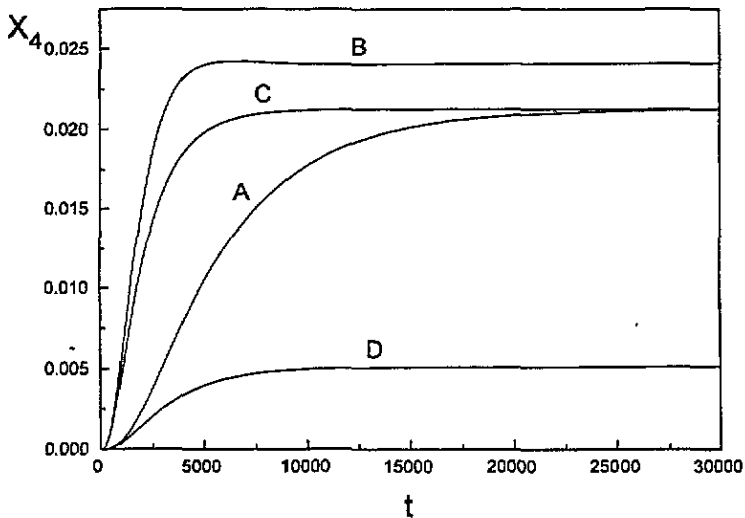


Figure 4. Tetramer concentration values  $X_4(t)$  as a function of time for the different kernel combinations of table 1.

## 5. Conclusions

In conclusion, the technique of the generating function can be applied to solve analytically the Smoluchowski rate equation including both aggregation and fragmentation, which we have exemplified in three cases. In the well known case A, the kernel is constant and the generating function allows us to obtain the complete solution to the problem. The technique applied to case B, additive coagulation kernel and constant fragmentation kernel, allows us to obtain only the solution for the total number of particles. When applied to more

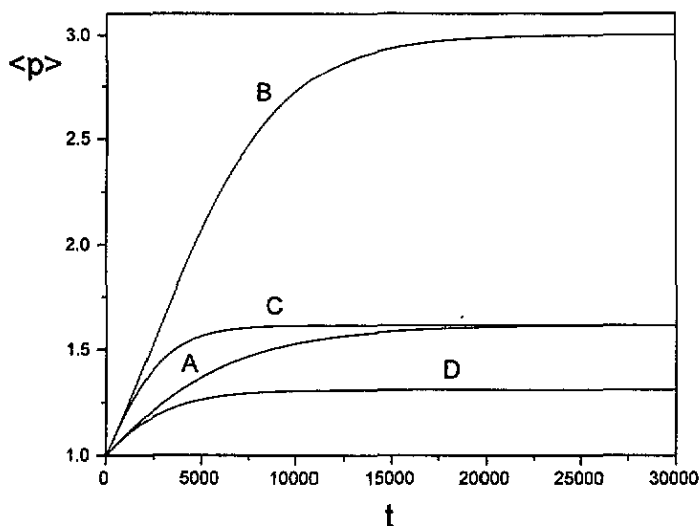


Figure 5. Average value  $\langle p \rangle$  as a function of time for the different kernel combinations of table 1.

complicated kernels, for example, with the fragmentation size-dependent, the method allows us to obtain solutions for  $\phi_0(t)$  provided an assumption is made on the second moment. In cases B and C, it is then possible to solve successively the evolution equations of the system.

Numerical results for the foregoing kernels plus case D were also found. The result is that cases A and C give the same asymptotic behaviour but differ in the initial growing. In these cases the condition of detailed balance is satisfied and a true stationary solution exists. With respect to cases B and D they give different equilibrium values for the  $k$ -mers and also show a different time evolution. They illustrate the role of the assumptions on the kinetic coefficients, and comparing with experimental results could give insight about the true mechanism of evolution for rapid coagulation.

It would naturally be interesting to extend the present analysis by taking into account the diffusion of polymers [19]. In this case the diffusion constants are likely to decrease with the size of the polymers. This should lead to a competition between reaction and diffusion and probably to non-classical time behaviour. Work in this direction is in progress.

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