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The exact solution of the coagulation equation with kernel $K_{ij} = A(i+j)+B$

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Abstract. The Smoluchowski coagulation equation with the kernel $K_{ij} = A(i+j)+B$ is solved exactly for arbitrary initial conditions. We obtain a compact form of the size distribution for monodisperse initial conditions. For polydisperse initial conditions, a simple form of the size distribution, including a parameter N_{kl} determined by a recursive relation, is obtained. In the special case with $K_{ij} = i+j$, we obtain the compact form of the size distribution for arbitrary initial conditions.

1. Introduction

Smoluchowski's coagulation equation

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} K_{ij}c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj}c_j \tag{1}$$

describes the evolution of the size distribution of particles in systems where coagulation or aggregation takes place. This equation has been widely used in many fields of physics (Drake 1972, Friedlander 1977). Using terms from polymer science, $c_k(t)$ is the concentration of clusters containing k units (k-mers) at time t. The two terms in the equation are the usual gain and loss terms and K_{ij} is a rate constant for the irreversible reaction between i-mers and j-mers to form $(i+j)$-mers.

Equation (1) has been studied extensively using the bilinear kernel

$$K_{ij} = A + B(i+j) + Cij \tag{2}$$

where A, B and C are constant. However, the number of exact solutions, which can be written down explicitly, has been quite limited. For monodisperse initial conditions, Smoluchowski (1916) obtained the solution for constant K_{ij}. McLeod (1962) gave the solution of the coagulation equation with kernel $K_{ij} = ij$. Dušek (1979) and Ziff and Stell (1980) gave the details of the mathematics required to get the general expression of $c_k(t)$ for an f functionality system, which agrees with the result obtained by the statistical method (Stockmayer 1943, Flory 1953). Starting from the equilibrium size distribution form, van Dongen and Ernst (1984b) obtained the solution of the equation with kernel $K_{ij} = [(f-1)i+1][(g-1)j+1]+[(g-1)i+1][(f-1)j+1]$ which was previously studied by Spouge (1983a) who gave the solution in implicit form. Spouge (1983a) also obtained the solution in implicit form for the general kernel (2), starting from the form of the equilibrium size distribution.

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The coagulation equation with polydisperse initial conditions has, however, been studied for the continuous version of the equation. Scott (1968) solved the coagulation equation with kernel $K_{ij} = i + j$ which is a special case of the general kernel $K_{ij} = A(i+j) + B$. To solve the continuous equation, a Laplace transformation and a conformal transformation was used and the result is in an implicit form including a contour integral. Drake (1972) wrote the general form of the implicit solution for kernel (2).

For the discrete coagulation equation with arbitrary initial conditions, Ziff *et al* (1983) studied equation (1) with kernel $K_{ij} = ij$ and they nearly obtained the explicit expression for $c_k(t)$. Recently, Bak and Lu (1986, 1987) solved the coagulation equation with $K_{ij} = [(f-2)i+2][(f-2)j+2]$ and arbitrary initial conditions, corresponding to the most important polymerisation model in physical chemistry. We obtain an explicit form of the solution before gelation and an implicit form of the solution after gelation.

In this paper, we concentrate on solving the coagulation equation with kernel $K_{ij} = A(i+j) + B$ and arbitrary initial conditions.

The evolution of the moments shows that this system is a non-gelling system and mass conservation is valid for all times. Starting from the kinetic equation itself, and using a generating function and Lagrange expansion, the form of the size distribution for monodisperse initial conditions is obtained. For polydisperse initial conditions, a simple form of the size distribution, including a parameter N_{kl} known by a recursion relation, is obtained. For the special case of $K_{ij} = i + j$, we obtain explicit expressions for arbitrary initial conditions. According to the connection between model $K_{ij} = A(i+j) + B$ and $K_{ij} = (Ai+B)(Aj+B)$, we have solved the latter model before gelation. The method which we have used in this paper can be easily generalised to an open system (Williams 1984, Hendriks 1984, Bak and Lu 1986, 1987).

2. Moment equation

First we study the following kinetic equation:

$$\frac{dc_k}{dt} = \tfrac{1}{2} \sum_{i+j=k} [A(i+j)+B]c_i c_j - c_k \sum_{j=1}^{\infty} [A(k+j)+B]c_j \tag{3}$$

with

$$c_k(t=0) = c_k(0).$$

To find the fundamental behaviour of the system, the moment equation is useful.

We define the moment as usual:

$$M_n = \sum_{k=1}^{\infty} k^n c_k(t). \tag{4}$$

At the initial state, $M_n(t=0) = M_n(0)$. We assume $M_1(0) = 1$, which can be done by choosing a suitable unit. Multiplying (2) by k^n, summing over all possible k and rearranging the terms, we have

$$\frac{dM_n}{dt} = \tfrac{1}{2} \sum_{i,j} [(i+j)^n - i^n - j^n][A(i+j)+B]c_i c_j \tag{5}$$

which is valid up to the gel point, where the second moment is divergent and mass conservation is no longer valid. The evolution of the second moment can be obtained from the equation

$$dM_2/dt = 2AM_2 + B. \tag{6}$$

Here we first assume $M_1 = 1$.

The solution of (6) is

$$M_2 = (1/2A)[(2AM_2(0) + B)\exp(2At) - B]. \tag{7}$$

It is obvious that $M_2(t)$ is a monotonically increasing function, and when $t \to \infty$, $M_2 \to \infty$. So in this system, there is no gelation phenomena. For all times we have

$$M_1(t) = M_1(0) = 1. \tag{8}$$

The evolution of the number of total molecules can be obtained by solving the differential equation

$$dM_0/dt = -AM_0 - \tfrac{1}{2}BM_0^2. \tag{9}$$

The solution of this equation is

$$M_0 = \frac{AM_0(0)\,e^{-At}}{A + \frac{1}{2}BM_0(0)(1 - e^{-At})}. \tag{10}$$

The main purpose of this paper is to get an explicit expression for the size distribution. We consider the case of monodisperse initial condition first.

3. Size distribution with monodisperse initial conditions

The monodisperse initial condition is the simplest case one can have. We consider

$$\frac{dc_k}{dt} = \tfrac{1}{2}\sum_{i+j=k}[A(i+j)+B]c_ic_j - c_k\sum_{j=1}^{\infty}[A(k+j)+B]c_j \tag{11}$$

with

$$c_k(0) = \delta_{kl}.$$

To solve the equation we use the following transformation

$$c_k(t) = x_k(t)\exp\left(-\int_0^t [(Ak+B)M_0 + A]\,dt\right). \tag{12}$$

Substituting (12) into (11) we have a differential equation for $x_k(t)$:

$$\frac{dx_k(t)}{dt} = \tfrac{1}{2}\sum_{i+j=k}[A(i+j)+B]x_ix_j\exp\left(-\int_0^t (BM_0 + A)\,dt'\right). \tag{13}$$

We can further set

$$\tau = \int_0^t \exp\left(-\int_0^{t'} (BM_0 + A)\,dt''\right)dt'. \tag{14}$$

A simpler equation is then obtained:

$$\frac{dx_k}{d\tau} = \tfrac{1}{2}\sum_{i+j=k}[A(i+j)+B]x_ix_j. \tag{15}$$

The generating function method is useful in solving this equation. We introduce

$$g(z,\tau)=\sum_{k=1}^{\infty}x_k(\tau)z^k. \tag{16}$$

It gives

$$x_k=\frac{1}{k!}\left(\frac{\partial^k g}{\partial z^k}\right)_{z=0} \tag{17}$$

The initial condition is

$$g(z,0)=\sum_{k=1}^{\infty}x_k(0)z^k=z. \tag{18}$$

Multiplying (15) by z^k and summing over all possible k, one obtains

$$\frac{\partial g}{\partial \tau}=\frac{1}{2}\left(Bg^2+2Az\frac{\partial g}{\partial z}g\right). \tag{19}$$

This is a first-order partial differential equation. We can use the Lagrange-Charpid method to get the general solution. The differential equations for the characteristics are

$$\mathrm{d}\tau=\frac{\mathrm{d}z}{-Azg}=\frac{\mathrm{d}g}{\frac{1}{2}Bg^2}. \tag{20}$$

The solution of (20) is

$$\begin{aligned} &zg^{2A/B}=\text{constant}\\ &\tfrac{1}{2}B\tau+1/g=\text{constant}. \end{aligned} \tag{21}$$

The general solution of the partial differential equation (19) is

$$zg^{2A/B}=u(\tfrac{1}{2}B\tau+1/g) \tag{22}$$

where u is an arbitrary function determined by the initial condition. In our case, when $\tau=0$, $t=0$, we have

$$u(1/z)=z^{2A/B+1}=(1/z)^{-(2A/B+1)}. \tag{23}$$

The general solution is

$$zg^{2A/B}=(\tfrac{1}{2}B\tau+1/g)^{-(2A/B+1)}. \tag{24}$$

It gives

$$z=g^{-2A/B}(\tfrac{1}{2}B\tau+1/g)^{-(2A+B)/B}. \tag{25}$$

To obtain the size distribution, we use the Lagrange expansion

$$g=\sum_{k=1}^{\infty}\frac{z^k}{k!}\left[\frac{\mathrm{d}^{k-1}}{\mathrm{d}g^{k-1}}\left(\frac{B\tau g}{2}+1\right)^{(2A+B)k/B}\right]_{g=0}. \tag{26}$$

It is not difficult to carry out the differentiation, which yields

$$g=\sum_{k=1}^{\infty}\frac{z^k}{k!}\left(\frac{2A}{B}+1\right)k\left[\left(\frac{2A}{B}+1\right)k-1\right]\cdots\left(\frac{2A}{B}k+2\right)\left(\frac{B\tau}{2}\right)^{k-1}. \tag{27}$$

From (17), it is obvious that

$$x_k(\tau)=\frac{1}{k!}\left(\frac{2A}{B}k+k\right)\left(\frac{2A}{B}k+k-1\right)\ldots\left(\frac{2A}{B}k+2\right)\left(\frac{B\tau}{2}\right)^{k-1}. \tag{28}$$

From (14) and (10), we can obtain an explicit form for τ

$$\tau=\frac{1-e^{-At}}{A+\frac{1}{2}BM_0(0)(1-e^{-At})}. \tag{29}$$

The compact form of the solution of equation (11) is thus obtained:

$$c_k(t)=\frac{1}{k!}\left(\frac{2A}{B}k+k\right)\left(\frac{2A}{B}k+k-1\right)\ldots\left(\frac{2A}{B}k+2\right)\left(\frac{B}{2}\right)^{k-1}e^{-At}(1-e^{-At})^{k-1}$$
$$\times[A+\tfrac{1}{2}BM_0(0)(1-e^{-At})]^{-[(2A/B+1)k+1]} \tag{30}$$

which is a new result.

4. Size distribution with arbitrary initial conditions

To solve equation (12) with arbitrary initial conditions, in principle, the foregoing method can be used. At least, we can formally write an expression for $x_k(\tau)$. But in reality, it is difficult to ascertain the detailed form of the solution for arbitrary initial conditions. Even if one can write the general form of $c_k(t)$, it turns out to be quite complicated and not as transparent as (28). Instead of doing that, we propose a method which gives a relatively simple expression, including a parameter determined by a recursive relation.

As we have done in the case of monodisperse initial conditions, through transformation (12)-(14), we have the same equation as (15) in the case of polydisperse initial conditions.

We assume (15) has the solution

$$x_k(\tau)=\sum_{l=1}^{k}N_{kl}\tau^{l-1}. \tag{31}$$

The correctness of this assumption can be shown by direct integration of equation (15) from c_1 to a general c_k. Substituting (31) into (15) and comparing coefficients of powers of τ yields a recursive relation of N_{kl} which has the following form:

$$2(l-1)N_{kl}=\sum_{\substack{i+j=k\\ p+q=l}}{}^{\text{and}}{}_{\substack{p\leqslant i\\ q\leqslant j}}[A(i+j)+B]N_{ip}N_{jq} \tag{32}$$

with

$$N_{k1}=c_k(0). \tag{33}$$

From (32) and (33) any N_{kl} is known.

The general expression of $c_k(t)$ can be written as

$$c_k(t)=\sum_{l=1}^{k-1}N_{kl}\left(\frac{1-e^{-At}}{A+\frac{1}{2}BM_0(0)(1-e^{-At})}\right)^{l-1}$$
$$\times\exp(-At)[A+\tfrac{1}{2}BM_0(0)(1-e^{-At})]^{-2(Ak+B)/B} \tag{34}$$

where as before we have used (9), (11) and (28) to calculate the corresponding quantity.

Equation (32) is a very interesting result. For monodisperse initial conditions, it reduces to

$$2(k-1)N_k = \sum_{i+j=k} K_{ij} N_i N_j \tag{35}$$

where we have used the general kernel K_{ij}. Equation (35) has a combinatorial explanation in polymer science which has been known for some years (Spouge 1983c, van Dongen and Ernst 1984a). N_k is the number of configurations in which k monomeric units are combined to form a k-mer. The kernel K_{ij} is the number of ways of bonding an i-mer and a j-mer together. The number of ways to build an i-mer and a j-mer and then combine them together is equal to the configurations of the k-mer out of monomer repeated $(k-1)$ times. In the equilibrium statistical theory of polycondensation (Cohen and Benedek 1982) N_k is the degeneracy factor. Now in the case with polydisperse initial conditions, from the kinetic equation we find N_{kl} and the relationship (32) which includes N_k and the relation (35) as a special case. This finding will change the usual view about the standard equilibrium theory of polycondensation, which claims that the equilibrium theory and the most probable size distribution are valid only for the case of monodisperse initial conditions.

Evidently, N_{kl} and relation (35) have a similar explanation to N_k and relation (32). Here we consider the configuration number of k-mer out of l initial particles. The details will be discussed elsewhere.

5. The model with $K_{ij} = i + j$

The model with $K_{ij} = i + j$ was studied by Scott (1968) in the continuous version. Obviously, this is a special case of $K_{ij} = A(i+j) + B$ with $B = 0$ and $A = 1$. To obtain the explicit form of $c_k(t)$, we must proceed in a manner slightly different from the one we used above.

The kinetic equation in this case is

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = \frac{1}{2} \sum_{i+j=k} (i+j) c_i c_j - c_k \sum_{j=1}^{\infty} (k+j) c_j \tag{36}$$

with

$$c_k(t=0) = c_k(0).$$

By the argument used in § 2, we have the moments

$$M_0 = M_0(0)\, \mathrm{e}^{-t} \tag{37}$$

$$M_1 = M_1(0) \tag{38}$$

$$M_2 = M_2(0)\, \mathrm{e}^{2t}. \tag{39}$$

Similarly, we set

$$c_k(t) = x_k(t) \exp\left(-\int_0^t (kM_0 + 1)\, \mathrm{d}t \right) \tag{40}$$

and obtain a differential equation for x_k:

$$\frac{\mathrm{d}x_k}{\mathrm{d}t} = \frac{1}{2} \sum_{i+j=k} (i+j) x_i x_j \tag{41}$$

where

$$\tau = 1 - e^{-t}. \tag{42}$$

Introducing the generating function

$$g = \sum_{k=1}^{\infty} x_k(t)\, e^{kz} \tag{43}$$

which is different from (16), we have the partial differential equation

$$\frac{\partial g}{\partial \tau} = \left(\frac{\partial g}{\partial z}\right) g \tag{44}$$

with the solution

$$g = u(z + g\tau) \tag{45}$$

where u is an arbitrary function.

From the initial condition

$$g(z, 0) = \sum_{k=1}^{\infty} c_k(0)\, e^{kz} = \phi(z) \tag{46}$$

and (45) for $\tau = 0$, we have the solution

$$g = \phi(z + g\tau). \tag{47}$$

To expand g in a power series of e^z, we write it in parametric form

$$z = s - \tau\phi(s) \tag{48}$$

$$g(z, t) = \phi(s). \tag{49}$$

We introduce

$$\xi = e^z \tag{50}$$

which is a new variable and we have

$$\bar{g}(\xi, t) = g(z, t) = \sum_{k=1}^{\infty} x_k(t)\xi^k \tag{51}$$

$$\bar{\phi}(\xi) = \xi(z) = \sum_{k=1}^{\infty} c_k(0)\xi^k. \tag{52}$$

The general solution can be written as

$$\xi = y \exp(-\tau\bar{\phi}(y)) \tag{53}$$

$$\bar{g} = \bar{u}(y) \tag{54}$$

where we have introduced

$$y = e^s. \tag{55}$$

The Lagrange expansion at the vicinity of $\xi = 0$ and $y_0 = 0$ is

$$g(\xi, t) = \sum_{k=1}^{\infty} \frac{\xi^k}{k!}\left[\left(\frac{d}{dy}\right)^{k-1} [\exp(\tau k\phi(y))]\right]_{y=0}. \tag{56}$$

According to the rule of differentiation of composite functions, we have

$$g(\xi, t) = \sum_{k=1}^{\infty} \frac{\xi^k}{k!} \sum_{\{n_j\}} \frac{(k-1)!}{\Pi_j n_j!} (k\tau)^m \prod_j (c_j(0))^{n_j} \tag{57}$$

where the summation goes over all possible sets of $\{n_j\}$, which satisfy the conditions $\Sigma_j j n_j = k-1$ and $m = \Sigma_j n_j$. From (56), we can easily obtain x_k

$$x_k = \frac{1}{k} \sum_{\{n_j\}} \frac{(k\tau)^m}{\Pi_j n_j!} \prod_j [c_j(0)]^{n_j}. \tag{58}$$

Hence $c_k(t)$ can be obtained

$$c_k(t) = \frac{1}{k} e^{-t} \exp[-M_0(0)k(1-e^{-t})] \sum_{\{n_j\}} \frac{k^m (1-e^{-t})^m}{\Pi_j n_j!} \prod_j [c_j(0)]^{n_j} \tag{59}$$

where the summation goes over all possible sets of $\{n_j\}$, which satisfy the conditions $\Sigma_j j n_j = k-1$ and $m = \Sigma_j n_j$.

It includes the monodisperse initial conditions as a special case

$$c_k(t) = \frac{e^{-t} k^{k-1}}{k!} (1-e^{-t})^{k-1} \exp[-k(1-e^{-kt})]. \tag{60}$$

Equation (59) is a new result. Equation (60) was obtained by Ziff *et al* (1984), using the transformation linking the models $K_{ij} = (Ai+B)(Aj+B)$ and $K_{ij} = A(i+j)+B$, where the explicit solution of the special case $K_{ij} = ij$ is well known (McLeod 1962).

6. The connection with the model $K_{ij} = (Ai+B)(Aj+B)$

The coagulation equation with kernel $K_{ij} = (Ai+B)(Aj+B)$ was investigated qualitatively by Leyvraz and Tschudi (1981), but they did not give the explicit expression for the size distribution even for the monodisperse initial conditions. Ziff *et al* (1984) have found the transformation linking the models $K_{ij} = A(i+j)+B$ and $K_{ij} = (Ai+B)(Aj+B)$. Our method reveals this connection clearly. For the latter model, we are concerned with the following kinetic equation:

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} (Ai+B)(Aj+B) c_i c_j - c_k \sum_{j=1}^{\infty} (Ak+B)(Aj+B) c_j \tag{61}$$

using the transformation

$$c_k(t) = x_k(t) \exp\left(-\sigma_k \int_0^t \mu(t')\, dt'\right) \tag{62}$$

$$\tau = \int_0^t \exp\left(-\int_0^t B\mu(t')\, dt''\right) dt' \tag{63}$$

where

$$\mu = \sum_k (Ak+B) c_k \qquad \sigma_k = Ak+B. \tag{64}$$

The kinetic equation (61) becomes

$$\frac{dx_k}{dt} = \tfrac{1}{2} \sum_{i+j=k} (Ai+B)(Aj+B) x_i x_j. \tag{65}$$

A further transformation

$$n_k = (Ak + B)x_k \tag{66}$$

reduces (65) to the form

$$\frac{dn_k}{d\tau} = \tfrac{1}{2} \sum_{i+j=k} [A(i+j) + B]n_i n_j \tag{67}$$

which is the same as (15).

The system described by $K_{ij} = (Ai + B)(Aj + B)$ is a gelling system. In spite of the fact that the pre-gel solution can be obtained in the same way as we have done in this paper, the post-gel solution should be determined separately.

For monodisperse initial conditions, the pre-gel solution of the coagulation equation with kernel $K_{ij} = (Ai + B)(Aj + B)$ is

$$c_k(t) = \frac{(A+B)^k}{k!(Ak+B)} \left(\frac{2A}{B}k + k\right)\left(\frac{2A}{B}k + k - 1\right) \ldots \left(\frac{2A}{B}k + 2\right)\left(\frac{B}{2}\right)^{k-1} \times t^{k-1}\left(\frac{2}{2 + B\mu_0 t}\right)^{(2A/B+1)k+1} \tag{68}$$

When $A = f - 2$, $B = 2$, expression (68) has the following form:

$$c_k(t) = \frac{f^k[(f-1)k]!}{k![(f-2)k+2]!} t^{k-1}\left(\frac{1}{1+ft}\right)^{(f-1)k+1} \tag{69}$$

corresponding to the important f functionality system in polymer science.

The details of the mathematics for the solution of the model

$$K_{ij} = (Ai + B)(Aj + B)$$

will be given later.

7. Conclusion

The coagulation equation with kernel $K_{ij} = A(i+j) + B$ is an important model in applied science (Drake 1972). We solve the discrete equation with arbitrary initial conditions, which has not been studied previously. We obtain the explicit expression of the size distribution written in compact form as (30). For arbitrary initial conditions, a simple form solution including a parameter N_{kl} can be written as (34). For the coagulation equation with kernel $K_{ij} = i + j$, the solution is written in an explicit compact form as (59) for arbitrary initial conditions. We also give the pre-gel solution of the coagulation equation with the kernel $K_{ij} = (Ai + B)(Aj + B)$ and monodisperse initial conditions as (68).

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