

The Evolution of the Cluster Size Distribution in a Coagulation System

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The coagulation equation with kernel $K_{ij} = A + B(i + j) + Cij$ and arbitrary initial conditions is studied analytically and a simple expression for the solution is found. For monodisperse initial conditions, we recover the known size distribution expressed in terms of a degeneracy factor N_k , which is determined by a recursion relation. For polydisperse initial conditions, a similar solution form is found, which includes a degeneracy factor N_{kl} , also determined by a recursion relation. The physical meaning of N_{kl} and the recursion relation is given. A method to get explicit expressions for N_k and N_{kl} is illustrated. Finally, the pre-gel solution is given explicitly and a general method to get the post-gel solution is proposed.

KEY WORDS: Smoluchovski equation; polycondensation; Flory-Stockmayer theory, degeneracy factor; gelation; post-gel solution.

1. INTRODUCTION

In recent years, the Smoluchovski equation, which describes the evolution of the size distribution in coagulation systems, has attracted considerable attention.⁽¹⁾ The basic equation is

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

where $c_k(t)$ is the concentration at time t of clusters containing k units, which we refer to as k -mers. 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.

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Among the many fields where the coagulation equation can be used, polycondensation is the most prominent one. The statistical theory of the size distribution for a polycondensation system was established many years ago.^(2,3) For the f -functionality model, which is the most important, the details of the mathematics required to obtain the solution from the kinetic equation were given in 1979 by Dušek⁽⁴⁾ and in 1980 by Ziff and Stell.⁽⁵⁾ The earlier research work on the coagulation equation can be taken all the way back to 1916, when Smoluchovski⁽⁶⁾ solved the coagulation equation with equal K_{ij} . In 1962, McLeod⁽⁷⁾ gave the solution of the equation with $K_{ij} = ij$. The continuous version of the equation has been studied extensively in aerosol physics,⁽⁸⁾ using many different approximation methods. A continuous equation including both aggregation and fragmentation was studied in 1979 by Aizenman and Bak.⁽⁹⁾

Recent developments have mostly been concerned with the discrete kinetic equation (1). Some special models were solved,^(10,11) and the post-gel solution was discussed.^(12,13)

It is well known that the most probable size distribution for the condensation polymerization system due to Flory is based on a special choice of initial conditions, namely a monodisperse distribution. Most of the kinetic work mentioned above is unfortunately also limited to monodisperse initial conditions. The present knowledge of the solution of the coagulation equation (1) and the concept of the most probable size distribution are still almost completely limited to the case of monodisperse initial conditions, although some papers concerned with the discrete equation (1) and arbitrary initial conditions have been published. Ziff *et al.*⁽¹⁴⁾ studied the kinetic equation (1) with kernel $K_{ij} = ij$ and arbitrary initial conditions, and they nearly obtained the explicit expression of the size distribution. Recently, we solved the coagulation equation with kernel $K_{ij} = [(f-2)i+2][(f-2)j+2]$ and $K_{ij} = A(i+j) + B$ and arbitrary initial conditions.^(15,16)

In this paper, we obtain the general solution for the coagulation equation with a bilinear kernel $K_{ij} = A + B(i+j) + Cij$ and arbitrary initial conditions, and generalize the concept of the most probable size distribution from monodisperse initial conditions to arbitrary initial conditions. Starting from the kinetic equation, through a transformation, we obtain a simple solution for both monodisperse initial conditions and polydisperse initial conditions. In the case of monodisperse initial conditions, the most probable size distribution form is recovered, including a degeneracy factor N_k , which satisfies a recursion relation. For polydisperse initial conditions, a similar solution is found, including a factor N_{k_i} , which also satisfy a recursion relation. The physical meaning of N_{k_i} and the recursion relation is explained using terms from polymer science and the method

by which we get an explicit expression for N_k and N_{kl} is illustrated. We obtain the time-dependent part of the solution by solving the moment equation before gelation. After gelation, a general method to get the time-dependent part of the solution is proposed, and a method based on a generating function method is illustrated. The special model with kernel $K_{ij} = (E + Fi)(E + Fj)$, is solved as an example.

2. GENERAL SOLUTION FORM

We consider the kinetic equation

$$\begin{aligned} \frac{dc_k}{dt} = & \frac{1}{2} \sum_{i+j=k} [A + B(i + j) + Cij] c_i c_j \\ & - c_k \sum_{j=1}^{\infty} [A + B(k + j) + Ckj] c_j \end{aligned} \tag{2}$$

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

Define the n th moment as usual

$$M_n = \sum_{k=1}^{\infty} k^n c_k(t) \tag{3}$$

It satisfies the equation

$$\dot{M}_n = \frac{1}{2} \sum_{i,j}^{\infty} [(i + j)^n - i^n - j^n] [A + B(i + j) + Cij] c_i c_j \tag{4}$$

up to the “gel point,” where the second moment and higher moments diverge. To solve the kinetic equation (2), we introduce the transformation

$$c_k(t) = x_k(t) \exp \left\{ - \int_0^t [(A + Bk) M_0(t') + (B + Ck) M_1(t')] dt' \right\} \tag{5}$$

which includes $M_0(t)$ and $M_1(t)$ as parameters.

Substituting (5) into (2), we have

$$\begin{aligned} \dot{x}_k = & \frac{1}{2} \sum_{i+j=k} [A + B(i + j) + Cij] x_i x_j \\ & \times \exp \left\{ - \int_0^t [AM_0(t') + BM_1(t')] dt' \right\} \end{aligned} \tag{6}$$

To simplify (6), we introduce a new variable

$$\tau = \int_0^t \exp \left\{ - \int_0^{t'} [AM_0(t'') + BM_1(t'')] dt'' \right\} dt' \tag{7}$$

Substituting (7) into Eq. (6), we have

$$\frac{dx_k}{d\tau} = \frac{1}{2} \sum_{i+j=k} [A + B(i + j) + Cij] x_i x_j \tag{8}$$

Equation (8) has a simple form, and we can obtain its solutions by integrating successively from $k=1$. This process at the same time also shows the uniqueness of the solution.

For some special kernels, Eq. (8) can be solved by introducing a generating function as done in a previous paper.⁽¹⁵⁾ For the general kernel, however, the partial differential equation for the generating function is quite complicated, and in general the solution probably cannot be written in a compact form. Here we therefore proceed in another way, assuming the following form for the solution:

$$x_k = \sum_{l=1}^k N_{kl} \tau^{l-1} \tag{9}$$

The correctness of this form can be shown by direct integration of Eq. (9) from $k=1$. Substituting (9) into (8) and comparing the coefficients of the same powers of τ yields a recursion relation for N_{kl} ,

$$(l-1) N_{kl} = \sum_{\substack{i+j=k \\ p+q=l \text{ and } p \leq i, q \leq j}} N_{ip} N_{jq} [A + B(i + j) + Cij] \tag{10}$$

with $N_{kl} = c_k(0)$.

Using Eq. (10) and the initial condition, any N_{kl} can be determined.

The solution of the kinetic equation (2) hence can be written as

$$c_k(t) = \sum_{l=1}^k N_{kl} \tau^{l-1} \exp \left\{ - \int_0^t [(A + Bk) M_0(t') + (B + Ck) M_1(t')] dt' \right\} \tag{11}$$

where the parameters $M_0(t)$ and $M_1(t)$ can be obtained from the differential equation (4) for times smaller than the time for gelation.⁽⁸⁾ Hence we have a time-dependent M_0 and a constant M_1 ,

$$M_0(t) = \frac{2 - (B + C)t}{2 + (A + B)t}, \quad B^2 = AC \tag{12}$$

$$M_0(t) = \frac{(AC - B^2)^{1/2} - (B + C) \tan[(AC - B^2)^{1/2} t/2]}{(AC - B^2)^{1/2} + (A + B) \tan[(AC - B^2)^{1/2} t/2]}, \quad AC - B^2 > 0 \tag{13}$$

$$\begin{aligned}
 M_0(t) = & ((B^2 - AC)^{1/2} \{1 + \exp[-(B^2 - AC)^{1/2} t]\}) \\
 & - (B + C) \{1 - \exp[-(B^2 - AC)^{1/2} t]\}) \\
 & \times ((B^2 - AC)^{1/2} \{1 + \exp[-(B^2 - AC)^{1/2} t]\}) \\
 & + (A + B) \{1 - \exp[-(B^2 - AC)^{1/2} t]\})^{-1}, \quad B^2 - AC > 0
 \end{aligned} \tag{14}$$

where we take the initial conditions to be $M_0(0) = 1$ and $M_1(0) = 1$.

Substituting Eqs. (12)–(14) into Eqs. (11) and (7), we have the general solution before gelation for the kinetic equation (2).

It is interesting to write this solution in a slightly different form. By changing the variable of integration from t to $M_0(t)$ and noting that M_0 satisfies Eq. (4), one obtains from the integration of Eq. (7)

$$\tau = 2[M_0(0) - M_0(t)]/Q \tag{15}$$

with

$$Q = A + 2B + C \tag{16}$$

The integration in Eq. (5) can be carried out in the same way as before. We have

$$\begin{aligned}
 & \exp \left\{ - \int_0^t [(A + Bk) M_0(t) + (B + Ck)] dt' \right\} \\
 & = \left[\frac{AM_0^2 + 2BM_0 + C}{Q} \right]^{(B/A)k+1} \exp \left[-k \left(C - \frac{B^2}{A} \right) t \right]
 \end{aligned} \tag{17}$$

Substituting Eqs. (15) and (17) into (11), we then have

$$\begin{aligned}
 c_k = & \sum_{l=1}^k N_{kl} \exp \left[k \left(\frac{B^2}{A} - C \right) t \right] \left[\frac{2[M_0(0) - M_0(t)]}{Q} \right]^{l-1} \\
 & \times \left\{ \frac{AM_0^2 + 2BM_0 + C}{Q} \right\}^{k(B/A)+1}
 \end{aligned} \tag{18}$$

It is clear from this expression that when $B^2/A - C = 0$ the solution becomes a function of $M_0(t)$ only, and this makes a simple probability explanation possible.

3. THE SOLUTION OF THE COAGULATION EQUATION WITH MONODISPERSE INITIAL CONDITIONS

To understand the general expression for the size distribution for polydisperse initial conditions, we first discuss the simplest case, assuming

all initial particles to be monomers, which has been solved by van Dongen and Ernst.⁽¹³⁾ This case also has been studied using a statistical method.

We have

$$c_k(t=0) = \delta_{kl} \quad (19)$$

and in this case Eq. (8) has the solution

$$x_k = N_k \tau^{k-1} \quad (20)$$

Substituting Eq. (21) into Eq. (18), we have the recursion relation

$$(k-1) N_k = \sum_{i+j=k} [A + B(i+j) + Cij] N_i N_j \quad (21)$$

with $N_1 = 1$.

The solution before gelation then has the following form:

$$c_k(t) = N_k \exp \left[k \left(\frac{B^2}{A} - C \right) t \right] \{ 2[1 - M_0(t)] \}^{k-1} \\ \times [AM_0^2 + 2BM_0 + C]^{(B/A)k+1} Q^{-k(B/A+1)} \quad (22)$$

where M_0 is a function of t , as expressed in Eqs. (12)–(14).

The combinatorial explanation for Eq. (21) has been known for some years.^(17,18) N_k is the number of configurations in which k monomeric units are combined to form a k -mer. The kernel $K_{ij} = A + B(i+j) + Cij$ 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 number of ways a k -mer can be formed out of monomers repeated $k-1$ times. In the statistical theory of condensation polymerization⁽¹⁹⁾ N_k is a degeneracy factor. It is worthwhile to note that the parameter N_k originally came from equilibrium statistical theory, and that the appearance of the recursion relation (21) in that connection was assumed to be caused by the reversible polymerization system.⁽²⁾

The only thing we can do further with the general form of the size distribution (23) is to write N_k in an explicit form. For a general bilinear kernel, this is difficult and may be impossible. Using the generating function technique, for example, we obtain the differential equation

$$2 \left(\frac{\partial g}{\partial z} - g \right) = Ag^2 + 2B \frac{\partial g}{\partial z} g + C \left(\frac{\partial g}{\partial z} \right)^2 \quad (23)$$

with

$$g(z, t) = \sum_{k=1}^{\infty} N_k(t) e^{zk} \quad (24)$$

Equation (23) has a simple form, and we can obtain $\partial g/\partial z$ as a function of g , which yields a differential equation with separated variables. We have finally

$$z = \int \frac{dg}{2 - Bg \pm [g^2(B^2 - AC) - (B + 2C)g + 4]^{1/2}} \tag{25}$$

We have not succeeded in writing the solution of this equation in a simple form, however, in order to be able to use the Lagrange expansion to get an explicit expression for N_k .

At present, we therefore must be satisfied with the solution of the coagulation equation given by (22) containing the parameter N_k , which can be obtained from the recursion relation (21). In some special situations, N_k has a simple form. Some work in this direction has been done previously; here we just mention the work of van Dongen and Ernst,⁽¹⁰⁾ who gave the explicit expression for N_k for the coagulation kernel

$$K_{ij} = [(f - 1)i + 1][(g - 1)j + 1] + [(f - 1)j + 1][(g - 1)i + 1]$$

namely

$$N_k = \frac{f^k}{k[(f - 1)k + 1]} \sum_{m+n=k-1} \left(1 - \frac{g}{f}\right)^n \binom{-(f - 1)k}{n} \binom{(g + f - 1)k}{m} \tag{26}$$

This kernel corresponds to the important polymerization model in which the units are A_fRB_g and A connects with B only. In this paper we give the solution to another important model, with $K_{ij} = (E + Fi)(E + Fj)$, where E and F are not restricted to be integers. We give the explicit expressions for N_k using a generating function.

The recursion relation in this case is

$$(k - 1) N_k = \sum_{i+j=k} (E + Fi)(E + Fj) N_i N_j \tag{27}$$

Introducing the generating function

$$G = \sum_{k=1}^{\infty} (E + Fk) N_k z^k \tag{28}$$

we obtain the partial differential equation

$$\left(z \frac{\partial G}{\partial z} - G\right) = EG^2 + 2FG \frac{\partial G}{\partial z} \tag{29}$$

Solving (29) for $\partial G/\partial z$, we obtain

$$\frac{\partial G}{\partial z} = \frac{\frac{1}{2}EG^2 + G}{z(1 - FG)} \tag{30}$$

The solution of (30) is

$$z = \frac{CG}{\left(\frac{1}{2}EG + 1\right)^{2F/E+1}} \quad (31)$$

where C is an integration constant.

The Lagrange expansion gives

$$G = C \sum_k \frac{z^k}{k!} \left[\frac{d^{k-1}}{dG^{k-1}} (EG + 2)^{(2F/E+1)k} \right]_{G=0} \quad (32)$$

From (28) we have

$$(E + Fk) N_k = \frac{1}{k!} \left(\frac{\partial^k G}{\partial z^k} \right)_{z=0} \quad (33)$$

Hence, the configuration number N_k can be written in the following form:

$$N_k = \frac{1}{(E + Fk)!} \left(\frac{2F}{E} k + k \right) \left(\frac{2F}{E} k + k - 1 \right) \cdots \left(\frac{2F}{E} k + 2 \right) \left(\frac{E}{2} \right)^{k-1} \quad (34)$$

The pre-gel solution of the coagulation equation with kernel $K_{ij} = (E + Fi)(E + Fj)$ can now be written down explicitly,

$$\begin{aligned} c_k(t) &= \frac{(E + F)^k}{k! (E + Fk)} \left(\frac{2F}{E} k + k \right) \left(\frac{2F}{E} k + k - 1 \right) \cdots \left(\frac{2F}{E} k + 2 \right) \\ &\quad \times \left(\frac{E}{2} \right)^{k-1} t^{k-1} \left(\frac{2}{2 + E(E + F)t} \right)^{(2F/E+1)k+1} \end{aligned} \quad (35)$$

when $E = 2$, $F = f - 2$, this corresponds to the f -functionality polymerization model, for which we have the well-known result

$$c_k(t) = \frac{f^k [(f-1)k]!}{k! [(f-2)k+2]!} t^{k-1} \left(\frac{1}{1+ft} \right)^{(f-1)k+1} \quad (36)$$

4. SOLUTIONS FOR POLYDISPERSE INITIAL CONDITIONS

Generally, the coagulation equation with polydisperse initial conditions is assumed to be difficult to solve, and very few papers on the subject have been published. In this section, we analyze the new result of the pre-gel solution of the kinetic equation (1) with bilinear kernel and arbitrary initial conditions.

Actually, the solution given by Eq. (8), which we have obtained from the kinetic equation (2), is surprisingly simple. The parameter N_{ki} is the interesting quantity in this expression. Comparing with monodisperse

initial conditions, we can give a physical explanation for N_{kl} and the relation (10). Using terms from polymer science, N_{kl} is the number of ways of forming a k -mer out of l initial particles. The k -mer can be separated into initial particles at $l - 1$ places to give an i -mer formed out of p initial particles and a j -mer formed out of q initial particles, with $i + j = k$ and $p + q = l$. The left-hand side of (10) is the total number of ways in which we can separate the k -mer, and this is equal to the number of ways in which we can build up the k -mer out of l initial particles.

Not only does N_{kl} and relationship (10) have a physical explanation, a probability explanation can also be given to the size distribution, at least for some coagulation equations with polydisperse initial conditions. In a previous paper⁽¹⁵⁾ we generalized Flory's probability argument from monodisperse initial conditions to polydisperse initial conditions. From the expressions (18) and (22) we see that, if there is a probability explanation of the size distribution for some kernel and monodisperse initial conditions, there is a probability explanation of the size distribution for the same kernel and polydisperse initial conditions. The correspondence of N_k and N_{kl} and their physical explanations play an essential rule. The actual situation is, however, that only in the special cases for which $B^2 = AC$ is a probability argument possible, and of these Flory's probability argument was only applied to the simplest cases with $K_{ij} = (E + Fi)(E + Fj)$, particularly with $E = 2, F = f - 2$. Generally, the kinetic method is more difficult to carry out than the statistical method and the probability argument. Using the kinetic method, we can, however, easily go further than the statistical method and the probability argument permit. Taking the equation with monodisperse initial conditions as an example, it is difficult to write the solution (22) as a function only of M_0 and M_1 or p , the extent of reaction, and, as is known, both statistical theory and the probability argument are based on these functions.

In some special cases, N_{kl} can be written in a compact form; in this paper, we give an example for an f -functionality system. We then have

$$(l - 1) N_{kl} = \sum_{\substack{i+j=k \\ p+q=l \text{ and } p \leq i, q \leq j}} [(f - 2)i + 2][(f - 2)j + 2] N_{ip} N_{jq} \quad (37)$$

Introducing the generating function

$$g(z_1, z_2) = \sum_{k,l} N_{kl} z_1^{(f-2)k+2} \exp[z_2(l-1)] \quad (38)$$

we have the partial differential equation

$$\frac{\partial g}{\partial z_2} = \frac{1}{2} \exp z_2 \left(\frac{\partial g}{\partial z_1} \right)^2 \quad (39)$$

Setting

$$y = \partial g / \partial z_1 \quad (40)$$

one can obtain a linear partial differential equation:

$$\frac{\partial y}{\partial z_2} - \exp z_2 y \frac{\partial y}{\partial z_1} = 0 \quad (41)$$

Using the Lagrange–Charpid method, we obtain the general solution

$$y = u(z_1 + y \exp z_2) \quad (42)$$

where u is an arbitrary function.

From (38), when $z_2 \rightarrow -\infty$, we have

$$g(z_1, z_2) \rightarrow \sum_k c_k(0) z_1^{(f-2)k+2} \quad (43)$$

and

$$y \rightarrow \sum_k c_k(0) [(f-2)k+2] z_1^{(f-2)k+2} = \theta(z) \quad (44)$$

In (43), when $z_2 \rightarrow -\infty$, $y \exp z_2 \rightarrow 0$, and we have

$$y = \theta(z_1) \quad (45)$$

The solution that satisfies the boundary condition is

$$y = \theta(z_1 + y \exp z_2) \quad (46)$$

We further set

$$\xi = z_1 + y \exp z_2 \quad (47)$$

and

$$z_1 = \xi - y \exp z_2 = \xi - \theta(\xi) \exp z_2 \quad (48)$$

Using the Lagrange expansion on (48), treating z_2 as a parameter, we have

$$\xi = \sum_{k=1}^{\infty} \frac{z_1^k}{k!} \sum_{\{n_j\}} \frac{(k+m-1)!}{\prod_j n_j!} \exp(mz_2) \prod_j \left[\frac{\varphi^{(j)}}{j!} \right]^{n_j} \quad (49)$$

where

$$\varphi(\xi) = \frac{\theta(\xi)}{\xi} = \sum_{k=1}^{\infty} c_k(0) [(f-2)k+2] z_1^{(f-2)k} \quad (50)$$

From (38) it is obvious that

$$N_{kl} = \left[\frac{\partial^{(f-2)k+l} y}{\partial z_1^{(f-2)k+1} \partial (\exp z_2)^{l-1}} \right]_{\substack{z_1=0 \\ \exp z_2=0}} \frac{1}{(l-1)!} \frac{1}{[(f-2)k+2]!} \quad (51)$$

Noting that

$$y = (\xi - z_1) \exp(-z_2) \quad (52)$$

we have

$$N_{kl} = \frac{1}{[(f-2)k+2]!} \sum_{\{n_j\}} \frac{[(f-2)k+l]!}{\prod_j n_j!} \prod_j \{[(f-2)j+2] c_j(0)\}^{n_j} \quad (53)$$

The pre-gel solution for an f -functionality system can then be written as

$$c_k(t) = \frac{1}{[(f-2)k+2]!} \sum_{\{n_j\}} \frac{[(f-2)k+m]!}{\prod_j n_j!} \frac{t^{m-1}}{(1+\mu_0 t)^{(f-2)k+m+1}} \times \prod_j \{[(f-2)j+2] c_j(0)\}^{n_j} \quad (54)$$

where

$$\mu_0 = \sum [(f-2)k+2] c_k(0) \quad (55)$$

and the summation goes over all sets $\{n_j\}$ that satisfy the conditions

$$\sum_j j n_j = k, \quad \sum_j n_j = m \quad (56)$$

This result agrees with what we obtained earlier.⁽¹⁴⁾

5. POST-GEL SOLUTIONS

For coagulation equations with a bilinear kernel for which $c \neq 0$, the second moment and all higher moments will diverge at a critical time t_c , which corresponds to a sol-gel transition in polymer chemistry. Two models have been used to describe the behavior of the system after gelation, proposed by Flory and Stockmayer, respectively. According to Ziff and Stell,⁽⁵⁾ in Flory's model, all free functionalities can react with each other, and the form of the time-dependent size distribution remains unchanged. In Stockmayer's model, however, the sol cannot react with the gel. Kinetically, this corresponds to keeping the original kinetic equation unchanged. In this paper, we are interested in obtaining the solution of the

original equation (2) after $t > t_c$, and this obviously corresponds to Stockmayer's model.

The existence of the post-gel solution for the coagulation equation has been shown by some authors,⁽¹²⁾ but not the uniqueness of the solution. In this paper, we concentrate on building up equations for the functions $M_0(t)$ and $M_1(t)$ after gelation. When $M_0(t)$ and $M_1(t)$ are determined we then have the solution after gelation from (18) and (20). Just as we discussed in a previous paper,⁽¹⁴⁾ $M_0(t)$ and $M_1(t)$ are discontinuous at the gel point even though $M_0(t)$ and $M_1(t)$ are continuous. A direct way to get $M_0(t)$ and $M_1(t)$ is by using expression (11) to get $M_0(t)$ and $M_1(t)$ from (2), respectively, and then solve these equations to get $M_0(t)$ and $M_1(t)$ after gelation.

This is easy to say, but quite complicated to do. In special situations, for which the generating function method works, this procedure can, however, be used. In the following we illustrate the method with the kernel $K_{ij} = (E + Fi)(E + Fj)$ and monodisperse initial conditions. In this case we are dealing with the kinetic equation

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} (E + Fi)(E + Fj) c_i c_j - (E + Fk) c_k \sum_{j=1}^{\infty} (E + Fj) c_j \quad (57)$$

With the transformation

$$c_k(t) = x_k(t) \exp \left[- (E + Fk) \int_0^t \mu(t') dt' \right] \quad (58)$$

and

$$\tau = \int_0^t \exp \left[- \int_0^{t'} \mu(t'') dt'' \right] dt' \quad (59)$$

where

$$\mu(t) = \sum_k (E + Fk) c_k(t) \quad (60)$$

we have the differential equation

$$\dot{x}_k(\tau) = \frac{1}{2} \sum_{i+j=k} (E + Fi)(E + Fj) x_i x_j \quad (61)$$

We solve this equation directly by introducing the generating function

$$G = \sum_{k=1}^{\infty} (E + Fk) x_k(\tau) z^k \quad (62)$$

to get

$$\frac{\partial G}{\partial \tau} = Fz \frac{\partial G}{\partial z} G + \frac{E}{2} G^2 \tag{63}$$

The solution that satisfies the initial condition is

$$z = \frac{G}{E + F} \left[\frac{E\tau G}{2} + 1 \right]^{-(2F/E + 1)} \tag{64}$$

In (64) we set

$$z = \exp \left[-F \int_0^t \mu(t') dt' \right] \tag{65}$$

Hence

$$G |_{z = \exp[-F \int_0^t \mu(t') dt']} = \mu \exp \left[E \int_0^t \mu(t') dt' \right] \tag{66}$$

and we have

$$\begin{aligned} \exp \left[-F \int_0^t \mu(t') dt' \right] &= \frac{\mu \exp[E \int_0^t \mu(t') dt']}{E + F} \\ &\times \left\{ \frac{E\tau \mu \exp[E \int_0^t \mu(t') dt']}{2} + 1 \right\}^{-(2F/E + 1)} \end{aligned} \tag{67}$$

This is the equation we want to establish.

If we further set

$$\psi = \exp \frac{1}{2} F \int_0^t \mu(t') dt' \tag{68}$$

and hence

$$\dot{\psi} = \frac{1}{2} F \mu \psi \tag{69}$$

we can write Eq. (67) as

$$\psi = \left(\frac{E + F}{\mu \psi} \right)^{E/(2F + E)} \left(1 + \frac{E\mu\psi^2 \int_0^t \psi^{-2} dt'}{2} \right) \tag{70}$$

that is,

$$\frac{E(E + F)}{2} \dot{\psi}^{-1} = \left(\dot{\psi} \int_0^t \psi^{-2} dt + \psi^{-1} \right)^{-2F/E} \tag{71}$$

Differentiating this, we have

$$\begin{aligned} \frac{E(E+F)}{2} \dot{\psi}^{-2} \ddot{\psi} &= \frac{2F+E}{E} \left(\dot{\psi} \int_0^t \psi^{-2} dt + \psi^{-1} \right)^{-2F/E-1} \\ &\times \left(\dot{\psi} \psi^{-2} + \ddot{\psi} \int_0^t \psi^{-2} dt - \psi^{-2} \dot{\psi} \right) \end{aligned} \tag{72}$$

Noting that

$$\dot{\psi} \int_0^t \psi^{-2} dt = 1 + \int_0^t \left(\ddot{\psi} \int_0^{t'} \psi dt'' \right) dt \tag{73}$$

we see that $\ddot{\psi} = 0$, $\dot{\psi} = E(E+F)/2$ is a solution, which yields

$$\mu = 2\mu_0/(2 + E\mu_0 t) \tag{74}$$

corresponding to the pre-gel solution. After a lengthy calculating, we can also show that

$$\mu(t > t_c) = \frac{EM_0(t_c) + F}{1 + (E + F)\mu_0(t_c)(t - t_c)} \tag{75}$$

together with

$$\mu = 2\mu_0/(2 + E\mu_0 t) \quad (t \leq t_c) \tag{76}$$

is a solution of (67). It gives the post-gel solution

$$c_k(t > t) = \frac{c_k(t_c)}{1 + (E + F)\mu_0(t_c)(t - t_c)} \tag{77}$$

Equation (77) is a special case of the result of van Dongen and Ernst.⁽¹³⁾ The critical time t_c appearing above can easily be obtained from the moment equation given by Drake⁽⁸⁾ for the general bilinear kernel

$$\begin{aligned} t_c &= \frac{1}{B + CM_2(0)}, & AC &= B^2 \\ t_c &= \frac{1}{(AC - B^2)^{1/2}} \tan^{-1} \frac{(AC - B^2)^{1/2}}{B + CM_2(0)}, & AC &> B^2 \\ t_c &= \frac{1}{(B^2 - AC)^{1/2}} \ln \frac{B + CM_2(0) + (B^2 - AC)^{1/2}}{B + CM_2(0) + (B^2 - AC)^{1/2}}, & AC &< B^2 \end{aligned} \tag{78}$$

For the model with $k_{ij} = (E + Fi)(E + Fj)$, we have

$$t_c = 1/[EF + F^2M_2(0)] \tag{79}$$

6. CONCLUSIONS AND DISCUSSION

The solutions of coagulation equations with bilinear kernels can be written in a simple form both for monodisperse initial conditions and polydisperse initial conditions such as (18) and (22). The configuration number or degeneracy factor is N_k in the case of monodisperse initial conditions and N_{kl} in the case of polydisperse initial conditions, and they satisfy the recursion relations (21) and (19). The probability argument can only be used successfully for some special kernels, but it can be used both with monodisperse initial conditions and polydisperse initial conditions. The concept of a most probable size distribution can be used not only for monodisperse initial conditions, but also for polydisperse initial conditions, corresponding to different size distribution forms. Formally, the post-gel solution has the same form as the pre-gel solution, but the expressions for the time-dependent parameters that enter into it are much more difficult to obtain than those for the parameters in the pre-gel solutions. Whenever a generating function method works, an equation that determines the time-dependent part of the post-gel solution can, however, be established. In most cases, we use a coagulation equation with the kernel $K_{ij} = (E + Fi)(E + Fj)$ as an example, but for N_{kl} , we can only get an explicit expression for an f -functionality system.

It is still unknown if coagulation equations with other kinds of kernels have solutions of the same form as the most probable distribution, and, if so, what the degeneracy factors N_k and N_{kl} are.

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REFERENCES

1. R. M. Ziff, in *Proceedings of the International Topical Conference on the Kinetics of Aggregation and Gelation*, F. Family and D. P. Landau, eds. (North-Holland, Amsterdam, 1984).
2. P. G. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
3. W. H. Stockmayer, *J. Chem. Phys.* **11**:45 (1943).
4. K. Dušek, *Polymer Bull.* **1**:523 (1979).
5. R. M. Ziff and G. Stell, *J. Chem. Phys.* **73**:3492 (1980).
6. M. V. Smoluchovski, *Phys. Z.* **17**:557 (1916).
7. J. B. McLeod, *Q. J. Math.* **13**:119, 192, 283 (1962).
8. R. L. Drake, in *Topics in Current Aerosol Research*, Vol. 3, Hidy and Brock, eds. (Pergamon Press, New York), Part 2.

9. M. Aizenman and T. A. Bak, *Commun. Math. Phys.* **65**:203 (1979).
10. P. G. J. van Dongen and M. H. Ernst, *J. Phys. A: Math. Gen.* **17**:2281 (1984).
11. J. Spouge, *J. Phys. A: Math. Gen.* **16**:767 (1983).
12. F. Leyvraz and H. R. Tschudi, *J. Phys. A: Math. Gen.* **14**:3389 (1981).
13. P. G. J. van Dongen and M. H. Ernst, *J. Phys. A: Math. Gen.* **16**:L327 (1983).
14. R. M. Ziff, M. H. Ernst, and E. M. Hendricks, *J. Phys. A: Math. Gen.* **16**:2293 (1983).
15. T. A. Bak and Binglin Lu, *Chem. Phys.* **112**:189 (1987).
16. Binglin Lu, *J. Phys. A: Math. Gen.*, accepted for publication.
17. J. Spouge, *Macromolecules* **16**:831 (1983).
18. P. G. J. van Dongen and M. H. Ernst, *J. Stat. Phys.* **37**:301 (1984).
19. R. J. Cohen and G. B. Benedek, *J. Phys. Chem.* **86**:3696 (1982).
20. M. M. R. Williams, *J. Phys. A: Math. Gen.* **13**:1867 (1984).
21. E. M. Hendriks, *J. Phys. A: Math. Gen.* **17**:229 (1984).
22. T. A. Bak and Lu Binglin, *Lecture in Applied Mathematics*, Vol. 24 (American Mathematical Society, 1986).