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Post-gelation solutions to Smoluchowski's coagulation equation

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Abstract. It is proven how the post-gelation behaviour originally suggested by Flory can be obtained as a result of a limiting process, passing from a finite to an infinite system. In a previous paper by the authors it was shown how the post-gelation behaviour first suggested by Stockmayer can be obtained by passing to the limit of an infinite system in a different way. It is thus demonstrated that different post-gelation solutions of Smoluchowski's coagulation equation can be obtained by different limiting processes.

1. Introduction

The general form of Smoluchowski's coagulation equation is

$$\dot{c}_k = \frac{1}{2} \sum_{j=1}^{k-1} K_{j,k-j} c_j c_{k-j} - c_k \sum_{j=1}^{\infty} K_{k,j} c_j \quad (1)$$

where k runs from 1 to ∞ . It is well known that if the kernel, $K_{j,k}$, is of the form

$$K_{j,k} = (Aj + B)(Ak + B) \quad (2)$$

then the solution to (1) will exhibit an abnormal behaviour at some finite time, t_g , known as the gelation point [1–7]. After this point, mass conservation appears to be violated, a fact which is commonly connected with the formation of an infinitely large component, the gel, which contains the missing monomers. The solution of (1) for $t \leq t_g$ with K_{kj} given by (2) is generally agreed upon. In fact, Kokholm [8] proved rigorously the uniqueness of the solution in the case $A = 1$, $B = 0$ by a proof which clearly can be generalized to the general case $A > 0$, $B \geq 0$.

As it stands, the solution of (1) is still unique past the gelation point when K_{kj} is given by (2) (this has also been proved rigorously by Kokholm [8] in the case $A = 1$, $B = 0$). However, as discussed by Ziff [2] and Ziff and Stell [3] this is not the only possible choice for the coagulation equation in the post-gelation state. The problem is that equation (1) does not include any reaction between the molecules in the sol and the gel. After the gelation point such reactions cannot necessarily be neglected.

In the present article we shall focus our attention on the case $A = 1$, $B = 0$ in order to avoid unnecessary complications, i.e. we take

$$K_{j,k} = jk. \quad (3)$$

Ziff [2] and Ziff and Stell [3] discuss three different models for the post-gelation kinetics, one model without any interaction between the sol and the gel and two models with interactions between sol and gel. However, with the simplification introduced by using (3) the two models with reaction of the sol with the gel coalesce into one.

With the usual initial condition

$$c_k(0) = \delta_{k,1} \quad (4)$$

the solution without reaction between sol and gel and $K_{j,k}$ given by (3) is [4]

$$c_k(t) = \frac{k^{k-2}}{k!} t^{k-1} \exp(-kt) \quad (5)$$

for $0 \leq t \leq 1$, while the solution for $t \geq 1$ is given by

$$c_k(t) = \frac{k^{k-2}}{k!} \exp(-k)t^{k-1}. \quad (6)$$

(This is the result originally suggested by Stockmayer [9].) In the model with reaction between the gel and the molecules in the sol it is assumed that the monomer units of the gel have the same reactivity as in the sol. When (3) is inserted in (1), one obtains

$$\dot{c}_k = \sum_{j=1}^{k-1} j(k-j)c_j c_{k-j} - kM_1 c_k \quad (7)$$

where M_1 is given by

$$M_1 = \sum_{j=1}^{\infty} j c_j. \quad (8)$$

Clearly, M_1 is equal to the total number of monomer units in the sol. If the monomer units of the gel are included, then M_1 should remain unchanged as the point of gelation is passed, since the total number of monomer units must be conserved. The initial condition (4) implies $M_1 = 1$ and we obtain the following kinetic equation

$$\dot{c}_k = \sum_{j=1}^{k-1} j(k-j)c_j c_{k-j} - kc_k. \quad (9)$$

It is easily seen that the solution to (9) is given by (5) for all values of t . This is the behaviour which Flory [10] has proposed. Since equation (9) for c_k involves only c_j with $1 \leq j \leq k$ the system of differential equations can be treated as an ordinary system with a finite number of species, for which the uniqueness of the solution is easily inferred.

In a previous article [1] we showed how the solution given by (5) for $t \leq 1$ and by (6) for $t \geq 1$ can be obtained in a natural way as the limit of a finite system of equations. It is the main object of the present article to show the solution given by (5) for all values of t can also be obtained as the limit of a finite system. We shall, in fact, consider two very different approaches which both produce this result.

In section 4 we prove a theorem which indicates that the post-gelation behaviour considered in this article is peculiar for kernels which behave like equation (2) for large j and k .

2. A truncated model

The model we shall consider here is a truncated version of (7) and (8), where molecules which have more than N monomer units are allowed to react only with molecules which do not have more than N monomer units; i.e. in (1) we take

$$K_{j,k} = \begin{cases} jk & \text{if } j \leq N \text{ or } k \leq N \\ 0 & \text{if } j > N \text{ and } k > N. \end{cases} \quad (10)$$

This model satisfies

$$K_{j,k} \leq N(j+k) \quad (11)$$

for all j and k and is therefore covered by the theorems proved by Heilmann [11], from which we conclude that with the initial condition (4) the model has a unique solution which is analytical for positive values of t , and that furthermore all the moments are analytical functions too. In particular, the first moment is constant and equal to 1. This implies that for $k \leq N$ the behaviour of c_k is governed by (9) and the solution given by (5) is valid for all $t \geq 0$. When we take the limit $N \rightarrow \infty$ this is clearly what we obtain for all k .

3. A finite Markov model

One way to try to understand the behaviour of a macroscopic model is to create a corresponding microscopic model which contains only a finite number of particles and obtain the macroscopic model as a limit of an infinite number of particles ('the thermodynamic limit').

We assume that we start with M free monomer units at time $\tau = 0$. At later times they combine to larger molecules according to the following Markov process: at each positive integral value of τ two different monomer units are chosen at random; if they belong to different molecules the two molecules are joined together to form one larger molecule.

We shall not attempt a complete solution of this model. Rather, we shall focus our attention on the time dependence of the average value of the number of free monomer units. If we at time τ have ν free monomer units, then at time $\tau + 1$ we have ν , $\nu - 1$ or $\nu - 2$ free monomer units with probability, respectively

$$\binom{M-\nu}{2} / \binom{M}{2} \quad \nu(M-\nu) / \binom{M}{2} \quad \text{and} \quad \binom{\nu}{2} / \binom{M}{2}$$

i.e. the probability distribution for the number of free monomer units $p_1(\nu; \tau)$ (= the probability of having precisely ν free monomer units at time τ) satisfies the recurrence relation

$$p_1(\nu; \tau + 1) = \left[\binom{M-\nu}{2} p_1(\nu; \tau) + (\nu+1)(M-\nu-1) p_1(\nu+1; \tau) + \binom{\nu+2}{2} p_1(\nu+2; \tau) \right] / \binom{M}{2}. \quad (12)$$

The average value of the number of free monomer units at time τ is given by

$$\langle \nu_1; \tau \rangle = \sum_{\nu=0}^M \nu p_1(\nu; \tau). \quad (13)$$

From (12) one easily derives

$$\langle v_1; \tau + 1 \rangle = \frac{M - 2}{M} \langle v_1; \tau \rangle \quad (14)$$

or

$$\langle v_1; \tau \rangle = (1 - 2/M)^\tau M. \quad (15)$$

When one takes the limit $M \rightarrow \infty$ one should remember to scale the unit of time correctly. If one takes

$$\tau = Mt/2 \quad (16)$$

where t is measured in a physical unit of time then a monomer unit reacts on average once per physical unit of time. We find that

$$c_1(t) = \lim_{M \rightarrow \infty} \langle v_1; Mt/2 \rangle / M = \lim_{M \rightarrow \infty} \exp[\frac{1}{2}Mt \ln(1 - 2/M)] = \exp(-t). \quad (17)$$

Once more we have an analytical behaviour for all times—admittedly only for c_1 ; but this should be sufficient to indicate what to expect if one tries to find c_2 , c_3 , etc. However, in order to convince the sceptical reader, we have included the computations for c_2 in an appendix.

4. A general theorem

The truncation introduced in section 2 can, of course, be applied generally; i.e. for some kernel $K_{j,k}$ the corresponding truncated kernel, $K_{j,k}^{(N)}$, is defined by

$$K_{j,k}^{(N)} = \begin{cases} K_{j,k} & \text{if } j \leq N \text{ or } k \leq N \\ 0 & \text{if } j > N \text{ and } k > N. \end{cases} \quad (18)$$

We shall be interested in this truncation in connection with kernels which satisfies the following condition (Leyvraz and Tschudi [4]):

Condition 1. A kernel $K_{j,k}$ is said to satisfy this condition if $K_{j,k} = K_{k,j}$ and one can find constants, r_1, r_2, \dots , such that

$$K_{j,k} \leq r_j r_k \quad \lim_{k \rightarrow \infty} \frac{r_k}{k} = 0. \quad (19)$$

Clearly, if the constants, r_1, r_2, \dots , satisfy the limiting condition above then we can find a constant A , such that

$$r_k \leq Ak \quad k = 1, 2, \dots \quad (20)$$

This implies that if $K_{j,k}$ satisfies condition 1 and we use the truncation given by (18) then

$$K_{j,k}^{(N)} \leq A^2 N(j+k) \quad (21)$$

i.e. as in section 2, the truncated model is covered by the article by Heilmann [11] and we can conclude that the truncated model has a unique, analytical solution where all the moments are analytical functions of time, t , for t real and positive. In particular the first moment, M_1 , is constant. We shall denote the solution to (1) using the truncated kernel by $c_{j,N}$.

Leyvraz and Tschudi [4] also consider kernels which satisfy condition 1. They use a truncation to a finite system and prove some very important results about the existence of a convergent subsequence ([4], theorem 1). However, in their proof they do not actually use the finiteness of the truncated models, but only properties of the solution to the truncated models which, by the above statements, are also satisfied by the truncation given by (18). Therefore, the proof given by Leyvraz and Tschudi [4] remains valid if the present truncation is used and we conclude that we have the following theorem.

Theorem 1. Let $K_{j,k}$ be a kernel which satisfies condition 1 and let $c_{j,N}$ be the solution to (1) with the truncated kernel given by (18) and initial conditions which satisfy

$$c_{j,N}(0) = c_j(0) \geq 0 \quad \sum_{j=1}^{\infty} j c_j(0) = 1 \quad (22)$$

then there exists a solution to (1) with the kernel $K_{j,k}$ and the same initial condition with the following properties

- (i) $c_j(t) \geq 0$, $\sum_{j=1}^{\infty} j c_j(t) \leq 1$ for all $t \geq 0$
- (ii) $c_j(t)$ is continuously differentiable for all $t \geq 0$
- (iii) there is a sequence $N_i \rightarrow \infty$ such that

$$\lim_{N_i \rightarrow \infty} c_{j,N_i}(t) = c_j(t)$$

for all j and $t \geq 0$. We even have

$$\lim_{N_i \rightarrow \infty} \sum_{j=1}^{\infty} r_j c_{j,N_i}(t) = \sum_{j=1}^{\infty} r_j c_j(t). \quad (23)$$

5. Discussion

In the truncated model considered here, the molecules with more than N monomer units play the role of the gel, just as they did in our first article [1]. The difference being that in the previous article the molecules with more than N monomer units were not allowed to react at all, while in the present work we prohibit reactions only between two molecules which both contain more than N monomers. Viewed this way, the model considered here is a model with reaction between the sol and the gel in contrast to the finite model which we considered earlier [1] which did include reactions between the sol and the gel. The limiting results obtained in section 2 confirm the interpretation given by Ziff and Stell [3] that the post-gelation solution given by (6) obtains when the gel cannot react with the sol, while a post-gelation solution given by (5) is a possibility if the gel is allowed to react with the sol.

The behaviour of the Markov model is perhaps more surprising. The Markov model does not appear to have any built-in sol-gel interaction. A clue to the explanation might be the single molecule with more than $M/2$ monomer units which eventually is created during the process. This molecule can react only with smaller molecules and in that sense it acts as the gel. Perhaps a more detailed solution of the model could illuminate this point further.

Another aspect of the results of the present article, when taken together with our previous article [1] on the same subject, is the demonstration of the problems connected with taking the limit of an infinite system. It can produce rather different results even if the finite system looks very similar. One should therefore not take the matter of choosing the right version of the finite system lightly.

Finally, the theorem in section 4 shows that the above is peculiar to kernels which behave like equation (2) at least for large values of j and k . If there the kernel satisfies condition 1 and thus grows more slowly with j and k then the truncation given by (18) will give a sequence with a convergent subsequence which converges to a solution to (1). This should not be surprising since, if the kernel satisfies condition 1 and the reactivity of the gel obtained as the limiting behaviour of large molecules in the sol, then the reactivity of the gel should be zero. Consequently, it should have no effect to allow the gel to react with the sol. If one wants an interesting reaction between the sol and the gel, then an independent hypothesis about the reaction between the sol and the gel is called for.

Appendix

In this appendix we prove that the Markov model considered in section 3 does indeed give the expected limiting behaviour of the dimer concentration, $c_2(t)$. We start with simultaneous distribution of the number of monomers and the number of dimers, $p_2(v, \mu; \tau)$ (= the probability of having exactly v monomers and μ dimers at time τ). It satisfies the following recurrence relation (analogous to (12)):

$$\begin{aligned}
 p_2(v, \mu; \tau + 1) = & \left[\left\{ \binom{M - v - 2\mu}{2} + \mu \right\} p_2(v, \mu; \tau) \right. \\
 & + \binom{\mu + 2}{2} p_2(v + 2, \mu - 1; \tau) + (v + 1)(M - v - 2\mu - 1) p_2(v + 1, \mu; \tau) \\
 & + 2(\mu + 1)(M - v - 2\mu - 2) p_2(v, \mu + 1; \tau) + 4 \binom{\mu + 2}{2} p_2(v, \mu + 2; \tau) \\
 & \left. + 2(v + 1)(\mu + 1) p_2(v + 1, \mu + 1; \tau) \right] / \binom{M}{2}. \quad (\text{A.1})
 \end{aligned}$$

The average number of dimers at time τ is given by

$$\langle \mu; \tau \rangle = \sum_{\mu=0}^{M/2} \sum_{v=0}^{M-2\mu} \mu p_2(v, \mu; \tau). \quad (\text{A.2})$$

From (A.1) one obtains

$$\langle \mu; \tau + 1 \rangle = \left(\left[\binom{M-2}{2} + 1 \right] / \binom{M}{2} \right) \langle \mu; \tau \rangle + \left\langle \binom{v}{2}; \tau \right\rangle / \binom{M}{2} \quad (\text{A.3})$$

where

$$\left\langle \binom{v}{2}; \tau \right\rangle = \sum_{v=0}^M \binom{v}{2} p_1(v; \tau). \quad (\text{A.4})$$

Equation (12) yields the recurrence relation

$$\left\langle \binom{v}{2}; \tau + 1 \right\rangle = \left[\binom{M-2}{2} / \binom{M}{2} \right] \left\langle \binom{v}{2}; \tau \right\rangle \quad (\text{A.5})$$

which implies

$$\left\langle \binom{v}{2}; \tau \right\rangle = \left[\binom{M-2}{2} / \binom{M}{2} \right]^\tau \binom{M}{2}. \quad (\text{A.6})$$

When this is combined with (A.3) one obtains

$$\langle \mu; \tau \rangle = a \left[\left\{ \binom{M-2}{2} + 1 \right\} / \binom{M}{2} \right]^\tau - \binom{M}{2} \left[\binom{M-2}{2} / \binom{M}{2} \right]^\tau \quad (\text{A.7})$$

where a is a constant, which is determined by the initial condition

$$\langle \mu; 0 \rangle = 0. \quad (\text{A.8})$$

The final result for $\langle \mu; \tau \rangle$ is

$$\langle \mu; \tau \rangle = \binom{M}{2} \left(\left[1 + 1 / \binom{M-2}{2} \right]^\tau - 1 \right) \cdot \left[\binom{M-2}{2} / \binom{M}{2} \right]^\tau. \quad (\text{A.9})$$

When the limit $M \rightarrow \infty$ is taken the expected result for $c_2(t)$ obtains:

$$\begin{aligned} c_2(t) &= \lim_{M \rightarrow \infty} \langle \mu; Mt/2 \rangle / M \\ &= \lim_{M \rightarrow \infty} \frac{M-1}{2} \left\{ \exp \left[\frac{1}{2} Mt \ln \left(1 + 1 / \binom{M-2}{2} \right) \right] - 1 \right\} \\ &\quad \times \exp \left[\frac{1}{2} Mt \ln \left(\frac{(M-2)(M-3)}{M(M-1)} \right) \right] \\ &= \lim_{M \rightarrow \infty} \frac{M-1}{2} \{ \exp[t/M + O(M^{-2})] - 1 \} \exp \left[\frac{1}{2} Mt \ln(1 - 4/M + O(M^{-2})) \right] \\ &= \frac{1}{2} t \exp(-2t). \end{aligned} \quad (\text{A.10})$$

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