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Unique large-time behaviour for solutions to Smoluchowski's coagulation equation

Ole J Heilmann

Department of Chemistry, H C Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

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Abstract. It is proven that the diagonal version of Smoluchowski's coagulation equation has a unique behaviour for large times, independent of the initial condition. Roughly speaking, the concentration then goes to zero as b_m/t, where b_m is a constant which depends only on the size of the polymer (and the rate constants). If the rate constants increase sufficiently fast with molecular size, then the total number of monomer units in solution also goes to zero as $1/t$.

1. Introduction

In this paper we shall concentrate on a rather special restriction of Smoluchowski's coagulation equation

$$\dot{c}_m = \tfrac{1}{2} K_{m/2,m/2} c_{m/2}^2 - K_{m,m} c_m^2 \tag{1}$$

where m runs from 1 to ∞ (with $K_{m/2,m/2} = 0$ if m is odd). Leyvraz [1] was the first to notice that this class of Smoluchowski's coagulation equation has some interesting mathematical properties; in particular the existence of a stable distribution where all concentrations decayed as $1/t$, provided the rate constants $K_{m,m}$ increased sufficiently rapidly with m. It is the object of this paper to show that this solution represents the large-time behaviour of any solution to (1) provided the initial concentrations are non-negative. We shall also give explicit solutions to (1) for c_2 and c_4. The solution for c_2 will drop out during the proof of the main theorem (see equations (33)–(37)), while the solution for c_4 will be deferred to the appendix. The solution for c_4 is rather complicated; however, it does reveal the long-time behaviour in more detail than theorem 2 below.

The only other case where the general long-time behaviour of Smoluchowski's coagulation equation is known seems to be

$$\dot{c}_k = \frac{1}{2} \sum_{j=1}^{k-1} c_j c_{k-j} - c_k \sum_{j=1}^{\infty} c_j \tag{2}$$

(Kreer and Penrose [2]). For the similar case where the index k (and j) is considered to be a continuous variable, Friedlander and Wang [3] have proven an analogous result; however, their proof is only valid for a limited class of initial distributions. For the additive kernel

$$\dot{c}_k = \frac{1}{2} \sum_{j=1}^{k-1} (r_j + r_{k+j}) c_j c_{k-j} - c_k \sum_{j=1}^{\infty} (r_j + r_k) c_j \tag{3}$$

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Carr and da Costa [14] have proved the non-existence of solutions if $r_j \geqslant j^\alpha$ with $\alpha > 1$, which is of course also quite definitive.

So even if the restriction imposed by (1) makes the model quite unrealistic, the results still seem to be worthwhile, showing how solutions to Smoluchowski's coagulation equation might behave. Also the reactions where an m-mer reacts with another m-mer are important in the general case because these reactions ensure that all concentrations go to zero irrespective of the initial conditions.

The outline of this paper is that the main results are reported in the following section in the form of two lemmas and two theorems, together with the definitions which are needed to formulate the results. The proofs are given in section 3. Some of the results used during the proofs of the main theorems are stated as independent lemmas in order to clarify the structure of the proofs.

2. Main result

First we notice that the system of equations given by (1) falls into separate parts, one for each odd integer. If we start with $m = 2n + 1$, then the only possible products are those with the number of monomers equal to $(2n + 1) \cdot 2^k$, $k = 0, 1, \ldots$. Each of these separate systems of equations have the same structure, i.e. if we know how to handle one system, we can then deal with them all. We shall consequently concentrate on the equations where $m = 2^k$, $k = 0, 1, \ldots$.

For $m = 1$ equation (1) reads

$$\dot{c}_1(t) = -K_{1,1}c_1(t)^2 \tag{1a}$$

with the initial condition $c_1(0) = c_1^0$. (We shall always assume $c_1^0 > 0$; if $c_1^0 = 0$ then the problem could be reformulated.) The solution to (1a) is

$$c_1(t) = \frac{1}{K_{1,1}t + 1/c_1^0}. \tag{4}$$

It turns out that the notation becomes simpler if we change the variable to

$$x = K_{1,1}t + 1/c_1^0 \tag{5}$$

and introduce

$$\gamma_k(x) = c_{2^k}(t) \tag{6}$$

$$\alpha_k = K_{2^k,2^k}/K_{1,1} \tag{7}$$

where k runs from 0 to ∞. With this notation we get the following form of the differential equation (1)

$$\frac{\mathrm{d}\gamma_k(x)}{\mathrm{d}x} = \frac{1}{2}\alpha_{k-1}\gamma_{k-1}(x)^2 - \alpha_k\gamma_k(x)^2 \tag{8}$$

with the initial condition

$$\gamma_k(1/c_1^0) = \gamma_k^0 = c_{2^k}(0) \geqslant 0. \tag{9}$$

The solution given by equation (4) becomes

$$\gamma_0(x) = 1/x. \tag{10}$$

We define numbers λ_k recursively by

$$\lambda_0 = 1 \qquad \lambda_k = \frac{1 + [1 + 2\alpha_{k-1}\alpha_k\lambda_{k-1}^2]^{1/2}}{2\alpha_k} \qquad k = 1, 2, 3, \ldots. \tag{11}$$

It is easily seen that the set of functions

$$\gamma_k(x) = \lambda_k/x \qquad k = 0, 1, 2, \ldots \tag{12}$$

together constitute a consistent solution to (8) (Leyvraz [1]). It will not generally satisfy the initial conditions given by (9), but we shall prove that (12) gives the limiting large-time behaviour in any case.

Condition 1. If the sum

$$\sum_{k=0}^{\infty}[2^k/\alpha_k]^{1/2} \tag{13}$$

is finite, then we shall say that condition 1 is satisfied.

The importance of condition 1 is shown by the following lemma.

Lemma 1. Condition 1 is a necessary and sufficient condition for the sum

$$\sum_{k=0}^{\infty} 2^k\lambda_k = \Lambda_0 \tag{14}$$

to be finite. If condition 1 is satisfied then the behaviour of λ_k for large k is related to the behaviour of α_k by

$$\lambda_k^2 = \frac{\Lambda_0}{\alpha_k 2^k}(1-\epsilon_k) \tag{15}$$

where ϵ_k goes to zero as $k \to \infty$. More precisely

$$\epsilon_k = \frac{1}{\Lambda_0}\sum_{j=k+1}^{\infty} 2^j\lambda_j. \tag{16}$$

We shall give the proof in the next section. Leyvraz [1] used the condition

$$\alpha_k \geqslant C2^{k+k\delta} \tag{17}$$

for some strictly positive constants C and δ to secure that the sum in equation (14) is finite. It is easily seen that this condition implies condition 1.

Condition 2. If the sum

$$\sum_{k=0}^{\infty}[2^k/\alpha_k]^{1/2}\ln k \tag{18}$$

is finite, then we shall say that condition 2 is satisfied.

Theorem 2. We have for all k and all initial conditions (9)

$$\lim_{x\to\infty}|x\gamma_k(x) - \lambda_k| = 0. \tag{19}$$

If condition 2 is satisfied then the convergence is uniform in k.

We define the generating function, $f(y, x)$, by

$$f(y, x) = \sum_{k=0}^{\infty} y^k\gamma_k(x). \tag{20}$$

The nth moment of the distribution is given by $f(2^n, x)$. In particular, the total number of monomer units is equal to $f(2, x)$.

Theorem 3. If condition 1 is satisfied then

$$\lim_{x\to\infty} |xf(2,x) - \Lambda_0| = 0. \tag{21}$$

We shall give the proofs of theorem 2 and 3 in the next section. Buffet and Pulé [5] proved that condition 1 is sufficient for gelation using a technique which is very different from the method used in this paper.

If we define t_c as the gelation time, the time where $f(2,x)$ starts to decay, then we have the following lemma.

Lemma 4. If $K > 0$ and $y_0 > 2$ are chosen such that $\alpha_k \leqslant K y_0^k$ for $k = 0, 1, 2, \ldots,$ then

$$t_c \geqslant \frac{1}{K_{1,1} K f(y_0, 1/c_1^0)(\frac{1}{2}y_0 - 1)}. \tag{22}$$

3. Proofs of lemma 1, theorems 2 and 3 and lemma 4

Proof of lemma 1. We obtain from equation (11)

$$\lambda_k \geqslant \left[\frac{\alpha_{k-1}}{2\alpha_k}\right]^{1/2} \lambda_{k-1} \tag{23}$$

and by repeated application of (23)

$$\lambda_k \geqslant 2^{-k/2}\alpha_k^{-1/2}. \tag{24}$$

This clearly shows that condition 1 is necessary if the sum in equation (14) is finite.

To prove the sufficiency of condition 1 we write

$$\lambda_k \leqslant \frac{1}{\alpha_k} + \left[\frac{\alpha_{k-1}}{\alpha_k}\right]^{1/2} \lambda_{k-1}. \tag{25}$$

Repeated application of this inequality yields

$$\lambda_k \leqslant \sum_{j=0}^{k} [2^{k-j}\alpha_k\alpha_j]^{-1/2}.$$

Substituting into (14) we get

$$\sum_{k=0}^{\infty} 2^k\lambda_k \leqslant \sum_{k=0}^{\infty} [2^k/\alpha_k]^{1/2} \sum_{j=0}^{k} [2^j/\alpha_j]^{1/2} \leqslant \sum_{k=0}^{\infty} [2^k/\alpha_k]^{1/2} \sum_{j=0}^{\infty} [2^j/\alpha_j]^{1/2}.$$

We have thus proved that condition 1 is sufficient.

To prove the estimate in equation (15) we write equation (11) as

$$-\lambda_k = \frac{1}{2}\alpha_{k-1}\lambda_{k-1}^2 - \alpha_k\lambda_k^2.$$

Multiplying with y^k and summing on k gives

$$-\sum_{k=0}^{\infty} y^k\lambda_k = \left(\frac{1}{2}y - 1\right) \sum_{k=0}^{\infty} y^k\alpha_k\lambda_k^2.$$

The left-hand side certainly converges if $|y| < 2$ and condition 1 is satisfied. Consequently, this is also the case for the right-hand side. Dividing both sides by $(\frac{1}{2}y - 1)$, expanding $(1 - \frac{1}{2}y)^{-1}$ in powers of y and equating equal powers of y on both sides we obtain

$$2^{-k} \sum_{j=0}^{k} \lambda_j 2^j = \alpha_k\lambda_k^2$$

which easily produces the desired result. □

Lemma 5. *(General properties of the differential equation (8)).* Consider the differential equation

$$\frac{\mathrm{d}f(x)}{\mathrm{d}x} = g(x)^2 - a^2 f(x)^2 \qquad f(x_0) = f_0 \geqslant 0 \tag{26}$$

for $x \geqslant x_0$. Assuming that $g(x)$ is uniformly bounded for $x \geqslant x_0$, we have the following.

(i) The solution $f(x)$ exists and is unique, non-negative and uniformly bounded for $x \geqslant x_0$.

(ii) Let $f_1(x)$ be the solution to (26) with $g_1(x)$ in place of $g(x)$. If $g_1(x)^2 \leqslant g(x)^2$ for $x \geqslant x_0$ then $f_1(x) \leqslant f(x)$ for $x \geqslant x_0$. If $g_1(x)^2 \geqslant g(x)^2$ for $x \geqslant x_0$ then $f_1(x) \geqslant f(x)$ for $x \geqslant x_0$.

(iii) Let $f_2(x)$ be the solution to (26) with the initial condition $f_2(x_0) = b \geqslant 0$. If $b > f_0$, then $f_2(x) > f(x)$. If $b < f_0$, then $f_2(x) < f(x)$.

Proof. The local existence and uniqueness of the solution is standard from the theory of differential equations. That the solution is bounded and stays non-negative follows trivially from the form of the differential equation. The fact that f is bounded in turn implies that the solution can be extended to all higher x. (iii) follows trivially from the uniqueness and (ii) follows easily from the form of the differential equation. □

Lemma 6. The solution to the differential equation

$$\frac{\mathrm{d}f(x)}{\mathrm{d}x} = b^2/x^2 - a^2 f(x)^2 \qquad f(x_0) = f_0 \geqslant 0 \tag{27}$$

is given by

$$f(x) = \frac{\zeta_+ + A\zeta_-(x_0/x)^\xi}{x[1 + A(x_0/x)^\xi]} \tag{28}$$

where

$$\zeta_\pm = \frac{1 \pm [1 + 4a^2b^2]^{1/2}}{2a^2} \tag{29}$$

$$\xi = [1 + 4a^2b^2]^{1/2} \tag{30}$$

and

$$A = (\zeta_+ - x_0 f_0)/(x_0 f_0 - \zeta_-). \tag{31}$$

Proof. It is easily seen that $f(x)$ given by equation (28) satisfies the initial condition. To see that it also satisfies the differential equation one can start by writing $f(x) = g(x)/x$. The differential equation for g is then solved by noticing that $\zeta_\pm$ are the solutions to the following quadratic equation

$$a^2z^2 - z - b^2 = 0. \tag{32}$$

□

Corollary. One has

$$c_2(t) = \frac{\lambda_1 + \lambda_{-1}(K_{1,1}c_1^0 t + 1)^{-\nu} A_1}{(K_{1,1}t + 1/c_1^0)[1 + (K_{1,1}c_1^0 t + 1)^{-\nu} A_1]} \tag{33}$$

where

$$\lambda_1 = \frac{K_{1,1} + [K_{1,1}^2 + 2K_{1,1}K_{2,2}]^{1/2}}{2K_{2,2}} \tag{34}$$

$$\lambda_{-1} = \frac{K_{1,1} - [K_{1,1}^2 + 2K_{1,1}K_{2,2}]^{1/2}}{2K_{2,2}} \tag{35}$$

$$\nu = [1 + 2K_{2,2}/K_{1,1}]^{1/2} \tag{36}$$

and

$$A_1 = \frac{\lambda_1 c_1^0 - c_2^0}{c_2^0 - \lambda_{-1} c_1^0}. \tag{37}$$

Lemma 7. Put $\eta_0 = 1/c_1^0$ and define recursively for $k = 1, 2, \ldots$

$$\eta_k = \begin{cases} \eta_{k-1} & \text{if } \gamma_k^0 = 0 \\ \min\{\eta_{k-1}, \lambda_k/\gamma_k^0\} & \text{if } \gamma_k^0 > 0. \end{cases} \tag{38}$$

Then for all $x \geqslant 1/c_1^0$ and $k \geqslant 0$

$$\gamma_k(x) \leqslant \lambda_k/(x - \eta_0 + \eta_k). \tag{39}$$

Proof. For $k = 0$ it follows from equations (10) and (11) that one has equality in (39). We proceed by induction on k. If (39) holds for $k = j - 1$ and we solve

$$\frac{\mathrm{d}g(x)}{\mathrm{d}x} = \frac{1}{2}\alpha_{j-1}\left[\frac{\lambda_{k-1}}{(x - \eta_0 + \eta_{j-1})}\right]^2 - \alpha_j g(x)^2 \tag{40}$$

for $g(x)$ with the initial condition

$$g(1/c_1^0) = \gamma_j^0$$

then by lemma 5 part (ii) we shall get an upper bound on $\gamma_j(x)$. The definition (38) implies that this is not changed if we change η_{j-1} to η_j in (40). If we change the initial condition to

$$g(1/c_1^0) = \max\{\gamma_j^0, \lambda_j/\eta_{j-1}\}$$

then lemma 5 part (iii) implies that g remains an upper bound on $\gamma_j(x)$. But now we have transformed the problem such that the solution is

$$g(x) = \lambda_j/(x - \eta_0 + \eta_j).$$

Thus, the inequality (39) holds for $k = j$ if it holds for $k = j - 1$. □

Corollary.

$$x\gamma_k(x) - \lambda_k \leqslant \lambda_k/(K_{1,1}c_1^0 t). \tag{41}$$

Proof.

$$x\gamma_k(x) - \lambda_k \leqslant \frac{x\lambda_k}{x - \eta_0 + \eta_k} - \lambda_k \leqslant \frac{x\lambda_k}{x - \eta_0} - \lambda_k = \frac{\lambda_k \eta_0}{x - \eta_0}.$$

□

Lemma 8. For any $\epsilon > 0$ and any $n \geqslant 0$ one can find an x_n such that

$$\lambda_n - x\gamma_n(x) \leqslant \lambda_n \epsilon \tag{42}$$

for $x > x_n$. If condition 2 is satisfied then x_n can be chosen independent of n.

Proof. We start by choosing ϵ'

$$\epsilon' = 6\epsilon/\pi^2 \tag{43}$$

and

$$x_0 = 1/c_1^0 \qquad a_0 = 1. \tag{44}$$

We then define ϕ_k, ϕ_{-k}, ν_k, x_k and a_k recursively for $k = 1, 2, \ldots$ by

$$\phi_k = \frac{1 + [1 + 2\alpha_{k-1}\alpha_k a_{k-1}^2]^{1/2}}{2\alpha_k} \tag{45}$$

$$\phi_{-k} = \frac{1 - [1 + 2\alpha_{k-1}\alpha_k a_{k-1}^2]^{1/2}}{2\alpha_k} \tag{46}$$

$$\nu_k = [1 + 2\alpha_{k-1}\alpha_k a_{k-1}^2]^{1/2} \tag{47}$$

$$x_k = x_{k-1}[k^2/\epsilon']^{1/\nu_k} \tag{48}$$

$$a_k = \phi_k(1 - \epsilon'/k^2). \tag{49}$$

Finally, we define functions, f_k and $g_k (k = 1, 2, \ldots)$

$$f_k(x) = \begin{cases} 0 & x \leqslant x_{k-1} \\ \dfrac{\phi_k[1 - (x_{k-1}/x)^{\nu_k}]}{x[1 - (\phi_k/\phi_{-k})(x_{k-1}/x)^{\nu_k}]} & x > x_{k-1} \end{cases} \tag{50}$$

$$g_k(x) = \begin{cases} 0 & x < x_k \\ a_k/x & x \geqslant x_k. \end{cases} \tag{51}$$

First we want to show that $g_k(x) \leqslant f_k(x)$ for all x. For $x < x_k$ this is trivial. It follows from equation (46) that ϕ_{-k} is negative. Consequently, we have for $x \geqslant x_k$

$$f_k(x) \geqslant \phi_k[1 - (x_{k-1}/x_k)^{\nu_k}]/x = \phi_k[1 - \epsilon'/k^2]/x = a_k/x$$

where we have used equations (48) and (49). This proves that $g_k(x) \leqslant f_k(x)$. It follows from lemma 5 and equations (45)–(47) that f_k is the solution to

$$\frac{\mathrm{d}f_k(x)}{\mathrm{d}x} = \frac{1}{2}\alpha_{k-l} g_{k-1}(x)^2 - \alpha_k f_k(x)^2$$

with the initial condition $f_k(1/c_1^0) = 0$ for $k > 1$ and that $f_l(x) = \gamma_l(x)$ if the initial condition is $\gamma_l^0 = 0$. Combining it all with lemma 5 we find that

$$g_k(x) \leqslant f_k(x) \leqslant \gamma_k(x) \qquad \text{for } x \geqslant 1/c_1^0.$$

The next step is to get a bound on a_k. We introduce ϵ_k by

$$a_k = \lambda_k(1 - \epsilon_k) \tag{52}$$

and obtain (using the shorthand notation $b = \lambda_{k-l}\sqrt{2\alpha_{k-l}\alpha_k}$)

$$\begin{aligned} \phi_k &= \lambda_k \frac{1 + [1 + b^2(1 - \epsilon_{k-1})^2]^{1/2}}{1 + [1 + b^2]^{1/2}} \\ &= \lambda_k \left[1 - \frac{b^2(1 - (1 - \epsilon_{k-1})^2)}{(1 + [1 + b^2]^{1/2})([1 + b^2]^{1/2} + [1 + b^2(1 - \epsilon_{k-1})^2]^{1/2})}\right] \end{aligned}$$

$$\geqslant \lambda_k \left[1 - \frac{b^2\epsilon_{k-1}(2-\epsilon_{k-1})}{b(b+b(1-\epsilon_{k-1}))}\right] = \lambda_k[1-\epsilon_{k-1}]$$

or

$$\epsilon_k \leqslant \epsilon_{k-1} + \epsilon'/k^2.$$

Iterating this we get

$$\epsilon_k \leqslant \sum_{j=1}^{k} \epsilon'/j^2 \leqslant \epsilon. \tag{53}$$

This proves the first half of the lemma.

Taking equations (47), (52), (53) and (23) together we find

$$\nu_k \geqslant a_{k-1}\sqrt{2\alpha_{k-1}\alpha_k} \geqslant (1-\epsilon)\lambda_{k-1}\sqrt{2\alpha_{k-1}\alpha_k} \geqslant 2(1-\epsilon)\sqrt{\alpha_k/2^k}.$$

We can iterate equation (48), using the above

$$\ln x_k = \ln(1/c_1^0) + 2\sum_{j=1}^{k}\frac{1}{\nu_j}\ln j - \ln\epsilon'\sum_{j=1}^{k}\frac{1}{\nu_j}$$
$$\leqslant \ln(1/c_1^0) + \frac{1}{1-\epsilon}\sum_{j=1}^{\infty}\ln j[2^j/\alpha_j]^{1/2} - \frac{\ln\epsilon'}{2(1-\epsilon)}\sum_{j=1}^{\infty}[2^j/\alpha_j]^{1/2}.$$

If condition 2 is satisfied then the two sums in the last line are finite and we can use the value of this line to get a value for $\ln x_k$ which is independent of k. □

The corollary to lemma 7 together with lemma 8 implies theorem 2.

Proof of theorem 3. If condition 2 is satisfied then the uniform convergence assured by theorem 2 implies theorem 3. If we only have condition 1, we use lemma 1 to secure that we can find an n such that

$$\sum_{k=n+1}^{\infty} 2^k\lambda_k \leqslant \epsilon/2$$

and then use theorem 2 to determine x_n such that

$$|x\gamma_k - \lambda_k| \leqslant \frac{1}{2}\epsilon/\Lambda_0$$

for $k \leqslant n$ and $x \geqslant x_n$. This will then ensure that for $x \geqslant x_n$

$$|x\mu_1(x) - \Lambda_0| \leqslant \epsilon.$$

□

Proof of lemma 4. We start by defining truncated generating functions

$$f_m(y,x) = \sum_{k=0}^{m} y^k\gamma_k(x) \tag{54}$$

$$g_m(y,x) = \sum_{k=0}^{m} y^k\alpha_k[\gamma_k(x)]^2. \tag{55}$$

Multiplying equation (8) with y^k and summing from 0 to m we obtain

$$\frac{\mathrm{d}f_m(y,x)}{\mathrm{d}x} = \frac{1}{2}yg_{m-1}(y,x) - g_m(y,x) \leqslant \left(\frac{1}{2}y - 1\right)g_m(y,x). \tag{56}$$

Using the conditions of the lemma we have

$$g_m(y,x) \leqslant K \sum_{k=0}^{m} (yy_0)^2 |\gamma_k(x)|^2 \leqslant K \left[\sum_{k=0}^{m} (yy_0)^{k/2} \gamma_k(x) \right]^2 . \tag{57}$$

Choosing $y = y_0$ and combining the two inequalities we get

$$\frac{\mathrm{d}f_m(y_0,x)}{\mathrm{d}x} \leqslant K \left(\frac{1}{2} y_0 - 1 \right) [f_m(y_0,x)]^2 .$$

Integrating this inequality yields

$$\frac{1}{f_m(y_0, 1/c_1^0)} - \frac{1}{f_m(y_0,x)} \leqslant K \left(\frac{1}{2} y_0 - 1 \right) \left(x - \frac{1}{c_1^0} \right) .$$

Re-ordering this we obtain

$$f_m(y_0,x) \leqslant \left[\frac{1}{f_m(y_0, 1/c_1^0)} - \left(\frac{1}{2} y_0 - 1 \right) K \left(x - \frac{1}{c_1^0} \right) \right]^{-1} .$$

Assuming $f(y_0, 1/c_1^0)$ to be finite we can take the limit $m \to \infty$ on the right-hand side, and then, since the right-hand side now is independent of m, we can also take the limit on the left-hand side. As a result we find that $f(y_0,x)$ is bounded if

$$(x - 1/c_1^0) < \left[f(y_0, 1/c_1^0) K \left(\frac{1}{2} y_0 - 1 \right) \right]^{-1} .$$

If $f(y_0,x)$ is bounded, then it follows from equation (57) that $g(y_0,x)$ is bounded. Since $y_0 > 2$ we find that $g(2,x)$ is finite. If we take the limit $m \to \infty$ in equation (56) with $y = 2$ we finally find that $f(2,x)$ is constant. □

4. Discussion

The most remarkable result is theorem 2, which states that the large t behaviour is completely independent of the initial condition to the leading order in t^{-1}. We have not proved, but we believe that the left-hand side of equation (19) goes to zero faster than t^{-1} as is the case with $c_2(t)$ (equation (33)) and $c_4(t)$ (equation (A23)). The initial monomer concentration enters only as a shift of the time axis (equation (5)). It should be emphasized that the limiting t^{-1} behaviour holds for all values of the rate constants, i.e. also when there is no gelation. The difference between the models with and without gelation comes only in the uniformity in polymer size of the convergence as stated in the last line of theorem 2. It is not clear to the author whether the necessity for introducing condition 2 is just technical or there actually is a small region (between condition 1 and condition 2) where one has gelation, but not the uniform convergence.

Buffet and Pulé [5] proved that one has no gelation if the sum

$$\sum_{k=0}^{\infty} 2^k / \alpha_k \tag{58}$$

is finite. This is slightly better than the result by White [6], which requires that α_k is bounded by $A \cdot 2^k$ for some constant A. However, it still leaves a small undecided gap up to condition 1. In view of lemma 1, it seems most likely that condition 1 is both sufficient and necessary for gelation.

The result in lemma 4 is similar to the result obtained by Hendriks *et al* [7] for some other classes of Smoluchowski's coagulation equation. It should, in particular, be noticed that it excludes instant gelation irrespective of the initial condition for all values of the rate constant for the diagonal version of Smoluchowski's coagulation, in contrast to the result by Carr and da Costa [4] for some other versions.

Appendix

In this appendix we shall find the explicit solution $c_4(t)$. Our starting point is equation (8)

$$\frac{\mathrm{d}}{\mathrm{d}x}\gamma_2(x) = \frac{1}{2}\alpha_1\gamma_1(x)^2 - \alpha_2\gamma_2(x)^2 \tag{A1}$$

with $\gamma_1(x)$ given by the corollary to lemma 5

$$\gamma_1(x) = \frac{\lambda_1 + \lambda_{-1}A_1(c_1^0 x)^{-\nu}}{x(1 + A_1(c_1^0 x)^{-\nu})}. \tag{A2}$$

$$\nu = \sqrt{1+2\alpha_1} \qquad \lambda_{\pm 1} = (1 \pm \nu)/(2\alpha_1). \tag{A3}$$

If $A_1 = 0$, then the problem is the same as when we solved for γ_1. We shall therefore assume that $A_1 \neq 0$. We start by changing the variable to y

$$y = -A_1(c_1^0 x)^{-\nu} \tag{A4}$$

and introduce two new functions g_1 and g_2

$$g_1(y) = x\gamma_1(x) = \frac{\lambda_1 - \lambda_{-1}y}{1 - y} \tag{A5}$$

$$g_2(y) = x\gamma_2(x). \tag{A6}$$

This leads to the following differential equation in place of (A1)

$$\frac{\mathrm{d}}{\mathrm{d}y}g_2(y) = \frac{1}{\nu y}\left[\alpha_2 g_2(y)^2 - g_2(y) - \frac{1}{2}\alpha_1 g_1(y)^2\right]. \tag{A7}$$

Equation (A7) is a differential equation of the Ricatti type (see Kamke [8], section 4.9). It can be transformed into a linear, second-order homogeneous differential equation

$$\frac{\mathrm{d}^2u(y)}{\mathrm{d}y^2} + \frac{1+\nu}{\nu}\frac{1}{y}\frac{\mathrm{d}u(y)}{\mathrm{d}y} - \frac{\alpha_2\alpha_1}{2\nu^2 y^2}g_1(y)^2 u(y) = 0 \tag{A8}$$

where the relation between u and g_2 is such that if $u(y)$ is any solution to (A8), then one can find a solution to (A7) by

$$g_2(y) = -\left[\frac{\mathrm{d}u(y)}{\mathrm{d}y}\right] \Big/ \left[u(y)\frac{\alpha_2}{\nu y}\right]. \tag{A9}$$

Equation (A8) can be transformed into a differential equation for hypergeometric functions by the substitution

$$u(y) = y^p(1-y)^q h(y) \tag{A10}$$

with the right choice of p and q. The desired form is (Erdélyi *et al* [9] equation (2.1.1))

$$y(1-y)\frac{\mathrm{d}^2h(y)}{\mathrm{d}y^2} + [c - (a+b+1)y]\frac{\mathrm{d}h(y)}{\mathrm{d}y} - abh(y) = 0. \tag{A11}$$

This obtained, we require

$$p(p-1) + \frac{1+\nu}{\nu}p - \frac{\alpha_2\alpha_1\lambda_1^2}{2\nu^2} = 0 \tag{A12}$$

$$q(q-1) - \frac{\alpha_2}{2\alpha_1} = 0. \tag{A13}$$

We choose the solutions

$$p = -\frac{1}{2\nu}(1 + [1 + 2\alpha_1\alpha_2\lambda_1^2]^{1/2}) \tag{A14}$$

$$q = \frac{1}{2} + \frac{1}{2}[1 + 2\alpha_2/\alpha_1]^{1/2}. \tag{A15}$$

This leads to the following differential equation for h:

$$y(1-y)\frac{d^2h(y)}{dy^2} + \left[2p(1-y) - 2qy + \frac{1+\nu}{\nu}(1-y)\right]\frac{dh(y)}{dy} - \left[2pq + \frac{1+\nu}{\nu}q + \frac{\alpha_1\alpha_2}{\nu^2}\lambda_1(\lambda_1 - \lambda_{-1})\right]h(y) = 0. \tag{A16}$$

Comparing with equation (A11) we obtain, using equation (A3),

$$c = 1 - \frac{1}{\nu}\left[1 + \alpha_2\frac{\nu+1}{\nu-1}\right]^{1/2} \tag{A17}$$

$$a + b = 2p + 2q + 1/\nu = c + [1 + 2\alpha_2/\alpha_1]^{1/2} \tag{A18}$$

$$ab = qc + \alpha_2\lambda_1/\nu \tag{A19}$$

$$\left.\begin{matrix} a \\ b \end{matrix}\right\} = \frac{1}{2} + \frac{1}{2}[1 + 2\alpha_2/\alpha_1]^{1/2} - \frac{1}{2\nu}\left[1 + \alpha_2\frac{\nu+1}{\nu-1}\right]^{1/2} \pm \frac{1}{2\nu}\left[1 + \alpha_2\frac{\nu-1}{\nu+1}\right]^{1/2}. \tag{A20}$$

In general it is possible, but not necessary, that one or more of the numbers a, b, c, $c-a$ and $c-b$ are integers. In order not to complicate the situation, we shall assume that none of them are integers. In that case the full solution to (A16) can be written (Erdélyi *et al* [9] equation (2.3.1))

$$h(y) = B_1F(a, b; c; y) + B_2y^{1-c}F(a-c+1, b-c+1; 2-c; y) \tag{A21}$$

where B_1 and B_2 are two arbitrary constants. The derivative is given by (Erdélyi *et al* [9] equation (2.1.7))

$$\frac{dh(y)}{dy} = B_1\frac{ab}{c}F(a+1, b+1; c+1; y) + B_2(1-c)y^{-c}F(a-c+1, b-c+1; 2-c; y) + B_2\frac{(a-c+1)(b-c+1)}{2-c}y^{1-c}F(a-c+2, b-c+2; 3-c; y). \tag{A22}$$

Using equations (A6), (A9), (A10) and $\lambda_2 = -\nu p/\alpha_2$ we obtain

$$\gamma_2(x) = \frac{1}{x}\left[\lambda_2 + \frac{q\nu}{\alpha_2}\frac{y}{1-y} - \frac{\nu}{\alpha_2}\frac{y\,dh(y)/dy}{h(y)}\right]. \tag{A23}$$

The ratio B_1/B_2 is fixed by the initial condition (9), using equation (A4) which implies that $x = 1/c_1^0$ corresponds to $y = -A_1$. The behaviour for $t \to \infty$ (or $x \to \infty$) is according to equation (A4) given by the behaviour for $y \to 0$. The first term in (A23) is the term expected from theorem 2. The second term goes to zero as $x^{-\nu}$ and that will also be the case for the third term if $c < 0$ (unless $B_1 = 0$, which will make the third term decay faster than the second term). If $c > 0$, then the third term goes to zero as $x^{-\nu_2}$, where ν_2 is given by

$$\nu_2 = [1 + 2\alpha_1\alpha_2\lambda_1^2]^{1/2} \tag{A24}$$

unless $B_2 = 0$ (in which case the decay as $x^{-\nu}$ is retained). If $c = 0$, then the solution given by equations (A21) and (A22) can no longer be used. A more detailed analysis (Erdélyi *et al* [9] chapter 2; in particular, equations (2.3.6), (2.3.7), (2.1.7) and (2.3.2)) reveals that the third term behaves as $x^{-\nu}\ln(x)$ (again with a possible exception caused by the initial condition which could make the logarithmic term drop out).

References

[1] Leyvraz F 1983 *J. Phys. A: Math. Gen.* **16** 2861
[2] Kreer M and Penrose O 1994 *J. Stat. Phys.* **75** 389
[3] Friedlander S K and Wang C S 1966 *J. Colloid Interface Sci.* **22** 126
[4] Carr J and da Costa F P 1992 *Z. Angew. (Math) Phys.* **43** 974
[5] Buffet E and Pulé J V 1989 *Nonlinearity* **2** 373
[6] White W H 1980 *Proc. Am. Math. Soc.* **80** 273
[7] Hendriks E M, Ernst M H and Ziff R M 1983 *J. Stat. Phys.* **31** 519
[8] Kamke E 1959 *Differentialgleichungen. Lösumgsmethoden und Lösungen* (New York: Chelsea)
[9] Erdélyi *et al* 1953 *Higher Transcendental Functions* vol I (New York: McGraw-Hill)