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1983 J. Phys. A: Math. Gen. 16 2861

(http://iopscience.iop.org/0305-4470/16/12/032)

J. Phys. A: Math. Gen. 16 (1983) 2861–2873. Printed in Great Britain

Existence and properties of post-gel solutions for the kinetic equations of coagulation

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Received 13 December 1982

Abstract. The kinetic equations of coagulation with kernels R_{ij} are studied for both factorisable ($R_{ij}=r_ir_j$) and diagonal ($R_{ij}=A_i\delta_{ij}$) kernels. It is rigorously shown that they allow solutions of the type $c_j(t)=a_j/t$ for suitably chosen a_j. These solutions are further shown to have finite mass if $R_{ij}\sim j^d$ for $d>1$. The asymptotic behaviour of the a_j is also studied and found to agree with numerous previous findings.

1. Introduction

Some interest has recently arisen in the following model for polymerisation: polymers react irreversibly by the bonding of reactive sites, the number of which is assumed to grow at most as fast as the size of the polymer. More simply, if A_j denotes a j-mer:

$$A_j+A_k \xrightarrow[R_{jk}]{} A_{j+k} \qquad R_{jk}\leqslant r_jr_k \qquad r_j/j \text{ bounded for } j\to\infty$$

(kernels violating these conditions will not be discussed here, as they are not physically meaningful). This leads to the following kinetic equations:

$$\dot{c}_j=\tfrac{1}{2}\sum_{k=1}^{j-1} R_{k,j-k}c_kc_{j-k}-c_j\sum_{k=1}^{\infty} R_{jk}c_k \tag{1}$$

where $c_j(t)$ is the concentration of A_j at time t. In the case

$$R_{jk}=(Aj+B)(Ak+B)$$

corresponding to the Flory–Stockmayer model of gelation, an exact solution of equations (1) could be found for all times (Ziff and Stell 1980, Leyvraz and Tschudi 1981). In particular it was found that after a certain finite time all concentrations decrease and therefore the quantity representing total mass

$$\sum_{j=1}^{\infty} jc_j(t)$$

is not conserved any more. This indicates the presence of an infinite cluster of finite total mass. This, however, makes it difficult to say whether this solution is physically significant and whether the infinite system (1) retains its validity after gelation. This question has been extensively discussed by Ziff (1980) and it is fairly clear that adding an interaction term between finite molecules and the infinite cluster is perfectly justifiable and can modify the nature of the solution quite deeply. If, however,

$$R_{jk} \leq r_j \cdot r_k \qquad r_j/j \to 0 \quad (j \to \infty) \tag{2}$$

then it has been shown that the infinite system (1)—without further sol–gel interaction—is physically relevant in the following sense: the finite systems

$$\dot{c}_j^{(N)} = \tfrac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} c_k^{(N)} c_{j-k}^{(N)} - c_j^{(N)} \sum_{k=1}^{N-j} R_{jk} c_k^{(N)} \tag{3}$$

are kinetic equations for the polymerisation process described previously but limited in size to polymers no larger than N. These contain interaction between 'small' and 'large' molecules, i.e., between what will in the limit of large N become sol and gel respectively. To consider the behaviour of

$$\lim_{N\to\infty} c_j^{(N)}(t)$$

appears therefore to be the most natural way to account for sol–gel interaction within the framework of the kinetic theory. But it was shown by Leyvraz and Tschudi (1981) that this limit is always a solution of the infinite system (1) if conditions (2) are fulfilled.

What is now unanswered is the question whether gelation can occur under these conditions. Ziff (1980) has suggested the following: if

$$R_{jj} \sim j^d$$

then gelation occurs if $d > 1$ and not otherwise. This would in particular imply that

$$R_{jk} = j^\alpha k^\alpha$$

leads to gelation if $\alpha > \frac{1}{2}$ and not otherwise. It has been rigorously shown (White 1980) that no kernel satisfying

$$R_{ij} \leq i + j$$

can lead to gelation. This corresponds roughly to saying that no physically meaningful kernel with $d \leq 1$ can lead to gelation. Ziff (1980) has further shown that for the three types of kernels

$$R_{ij} = \frac{Aij}{(i+j)^n - i^n - j^n};\; A\frac{i^n j + ij^n}{(i+j)^n - i^n - j^n};\; A\frac{i^n j^n}{(i+j)^n - i^n - j^n} \qquad (n \text{ real arbitrary})$$

some moment of the c_j's becomes infinite in finite time if n is so chosen that $d > 1$. It is the aim of this note to prove rigorously that solutions with finite mass violating mass conservation exist for the following kernels if their diagonal exponent d is larger than one:

$$\begin{aligned} R_{jk} &= j^d \delta_{jk} && \text{(diagonal kernel)} \\ &= j^\alpha k^\alpha && \text{(factorisable kernel).} \end{aligned}$$

While it is fairly clear that the diagonal kernel has no physical realisation, it has been argued that the second describes branched polymerisation if α is taken to be some measure of the rate of growth of effective external area with size. It is not the purpose of this paper to discuss the possible validity of such assumptions: they are at best dubious, since it is, for example, not obvious that a small cluster 'sees' the same area of a large cluster as another large cluster. It must therefore be realised that the choice of factorisable kernels is a matter of mathematical convenience far more than of physical necessity.

In this respect the diagonal kernel is now interesting, as clearly any kernel with diagonal exponent larger than one is larger (i.e. contains more possible reactions) than the corresponding diagonal kernel. It will be shown, however, that this kernel always leads to violation of mass conservation in finite time. Hence on a qualitative level it appears likely that the criterion using the diagonal exponent is most probably correct for arbitrary reasonable kernels. It must, however, be noted that this argument is not rigorous, since the additional reactions could actually be unfavourable for gelation, since they destroy the extreme 'streamlining' effect of diagonal kinetics. One has in this case the following theorem.

Theorem 1. Let $R_{jk} = A_j\delta_{jk}$ with $A_j > Bj^d$ $(d > 1)$. Then:

(i) there are numbers $a_j \geq 0$ such that

$$\sum_{j=1}^{\infty} ja_j < \infty$$

and

$$c_j(t) = a_j/(t + C)$$

is a solution of (1);

(ii) for monodisperse initial conditions gelation occurs at finite time, that is, mass conservation is violated after finite time.

This result is of course far too limited to be of any practical value. It does however indicate that reactions limited to polymers of comparable size are sufficient to bring about gelation.

A more general type of kernel is

$$R_{jk} = r_j r_k.$$

For such kernels it has been hypothesised that the first part of theorem 1 can be carried over if

$$r_j \geq Bj^{\alpha} \qquad (\alpha > \tfrac{1}{2})$$

(see e.g. Hendriks *et al* 1983, Leyvraz and Tschudi 1982). This will be proved rigorously in the following.

Theorem 2. Let $R_{jk} = r_j r_k$, where

$$r_j > r_1 \qquad (j \geq 2) \qquad r_j \geq Bj^{\alpha} \quad (\alpha > 0).$$

Then there exist numbers $\alpha_j \geq 0$ such that

$$c_j(t) = \alpha_j/(t + C)$$

is a solution of (1). Further, if $\alpha > \frac{1}{2}$,

$$\sum_{j=1}^{\infty} j\alpha_j < \infty.$$

Hence the existence of finite mass, non-mass-conserving solutions of (1) is proved if $\alpha > \frac{1}{2}$, that is if $d > 1$. In contradistinction to theorem 1, however, I cannot prove that from realistic initial conditions (monodisperse or exponentially decaying in j) mass conservation will be violated in finite time. For this it would be easiest to prove (as is possible in the case of theorem 1) that

$$c_j(t) \leq D\alpha_j/t \tag{4}$$

for some constant D.

If the validity of (4) is assumed for $r_j = j^\alpha$, it is plausible to reason as follows. In the proof of theorem 2, it will be seen that

$$\sum_{j=1}^{N} j\alpha_j = \mathrm{o}(N^{1-2\alpha+\varepsilon}) \qquad (\alpha \leq \tfrac{1}{2})$$

$$= \sum_{j=1}^{\infty} j\alpha_j - \mathrm{o}(N^{(1-2\alpha+\varepsilon)/2}) \qquad (\alpha > \tfrac{1}{2})$$

for every $\varepsilon > 0$. It is easy to see that if t_N is defined by

$$\left|\frac{\mathrm{d}}{\mathrm{d}t}\sum_{j=1}^{N} jc_j(t_N)\right| = K > 0$$

then one obtains

$$t_N = t_\infty - \mathrm{o}(N^{(1-2\alpha+\varepsilon)/2}) \qquad (\alpha > \tfrac{1}{2}).$$

It is easily verified that these scaling laws do indeed hold for $\alpha = 1$. It is also easy to see that

$$t_N \sim \ln N$$

for $R_{ij} = i + j$, which has $d = 1$, similarly to $\alpha = \frac{1}{2}$. It should be noted that the above results are exactly consistent with the following estimate on the order of magnitude of α_j:

$$\alpha_j \sim j^{-2\alpha-1} \qquad (\alpha \leq \tfrac{1}{2})$$

$$\sim j^{-\alpha-3/2} \qquad (\alpha > \tfrac{1}{2}).$$

For $\alpha > \frac{1}{2}$ these were obtained, among others, by Hendriks *et al* (1983) and Leyvraz and Tschudi (1982). Stationary solutions of the equations (1) with a monodisperse source were shown by White (1982) to behave as $j^{-\alpha-3/2}$ for all $\alpha > 0$. The reason for the different behaviour for $\alpha < \frac{1}{2}$ is not obvious.

As a final remark, it should be noted that the scaling behaviour of the times t_N may be the reason for the discrepancy between numerical estimates of gelation times and theoretical estimates: Hendriks and Ernst (1982) and the author independently had found gelation times approximately 1.65 for $\alpha = 0.8$ and $N = 200$, in clear violation of an inequality proved in Hendriks *et al* (1983):

$$(2^{2\alpha-1} - 1)^{-1} \leq t_\infty \qquad \text{(equation (5.26))}$$

leading to

$$t_\infty > 1.93.$$

It should be noted, however, that $t_\infty - t_N$ is of the order $N^{-0.3}$, which is about 0.2 for $N = 200$.

The rest of this paper will be devoted to proving theorems 1 and 2, as well as the various assertions concerning the large-j behaviour of the α_j's.

2. Proof of theorem 1

For the kernel

$$R_{jk} = A_j\delta_{jk}$$

and for monodisperse initial conditions one has

$$c_j(t) = 0 \qquad (j \neq 2^k).$$

Define

$$\gamma_k(t) = c_j(t) \qquad \alpha_k = A_j \qquad (j = 2^k, k = 0, 1, \ldots).$$

It follows that

$$\dot{\gamma}_k = \tfrac{1}{2}\alpha_{k-1}\gamma_{k-1}^2 - \alpha_k\gamma_k^2. \tag{5}$$

Putting the ansatz

$$\gamma_k(t) = \lambda_k/t$$

in (5), the time dependence drops out and I get

$$\lambda_k = \alpha_k\lambda_k^2 - \tfrac{1}{2}\alpha_{k-1}\lambda_{k-1}^2, \qquad \lambda_0 = \alpha_0^{-1}. \tag{6}$$

Clearly

$$\alpha_k \geqslant B2^{dk}$$

and

$$\lambda_k = (2\alpha_k)^{-1}[1 + (1 + 2\alpha_k\alpha_{k-1}\lambda_{k-1}^2)^{1/2}] \geqslant (\alpha_{k-1}/2\alpha_k)^{1/2}\lambda_{k-1}.$$

Therefore

$$\alpha_k\lambda_k \geqslant (\alpha_k/2\alpha_{k-1})^{1/2}\alpha_{k-1}\lambda_{k-1} \geqslant (\alpha_k/2^k\alpha_0)^{1/2}.$$

Hence

$$\sum_{k=0}^{\infty} \frac{1}{\alpha_k\lambda_k} \leqslant C \sum_{k=0}^{\infty} 2^{(1-d)k/2} < \infty. \tag{7}$$

But from (6) one obtains

$$\frac{\lambda_k}{\lambda_{k-1}} = \frac{\alpha_{k-1}\lambda_{k-1}}{2(\alpha_k\lambda_k - 1)} = \frac{\alpha_{k-1}\lambda_{k-1}}{2\alpha_k\lambda_k[1 - (\alpha_k\lambda_k)^{-1}]}$$

and, multiplying out,

$$\frac{\lambda_k}{\lambda_0} = \frac{\alpha_0\lambda_0}{2^k\alpha_k\lambda_k}\left[\prod_{n=1}^{k}\left(1 - \frac{1}{\alpha_n\lambda_n}\right)\right]^{-1}.$$

But because of (7)

$$\prod_{n=1}^{k}\left(1 - \frac{1}{\alpha_n\lambda_n}\right) \geqslant \prod_{n=1}^{\infty}\left(1 - \frac{1}{\alpha_n\lambda_n}\right) > 0$$

i.e.

$$\lambda_k \leqslant C'/2^k\alpha_k\lambda_k$$

implying

$$\sum_{k=0}^{\infty} 2^k \lambda_k \leqslant C' \sum_{k=0}^{\infty} \frac{1}{\alpha_k \lambda_k} < \infty.$$

The first part of theorem 1 is therefore proved: there exist solutions of finite mass violating mass conservation. It now remains to prove that monodisperse initial conditions will lead to such a violation in finite time.

Denote the solution of (5) with monodisperse initial conditions by $\gamma_k(t)$. I claim that

$$\gamma_k(t) \leqslant \lambda_k/(t+\alpha_0^{-1}) \tag{8}$$

for all $t>0$.

For $\gamma_0(t)$ this is obvious, since the equality sign actually holds. Now assume (8) for all $l<k$. It follows that

$$\dot{\gamma}_k = \tfrac{1}{2}\alpha_{k-1}\gamma_{k-1}^2 - \alpha_k \gamma_k^2 \leqslant \alpha_{k-1}\lambda_{k-1}^2/2(t+\alpha_0^{-1})^2 - \alpha_k\gamma_k^2.$$

Define

$$\dot{\varphi}_k(t; a_0) = \frac{\alpha_{k-1}\lambda_{k-1}^2}{2(t+\alpha_0^{-1})^2} - \alpha_k \varphi_k(t; a_0)^2 \qquad \varphi_k(0; a_0) = a_0.$$

Clearly

$$\gamma_k(t) \leqslant \varphi_k(t; 0) \leqslant \varphi_k(t; \alpha_0\lambda_k) = \lambda_k/(t+\alpha_0^{-1})$$

proving (8) for all $t>0$ and for all k. This implies

$$\sum_{j=1}^{\infty} j c_j(t) \leqslant \frac{1}{t+\alpha_0^{-1}} \sum_{k=0}^{\infty} 2^k \lambda_k \to 0 \qquad (t\to\infty)$$

thus proving all of theorem 1.

3. Proof of theorem 2

I now turn to the equations

$$\dot{c}_j = \tfrac{1}{2}\sum_{k=1}^{j-1} r_k r_{j-k} c_k c_{j-k} - r_j c_j \sum_{k=1}^{\infty} r_k c_k. \tag{9}$$

Putting the ansatz

$$c_j(t) = \alpha_j/t$$

in (9) one obtains

$$\alpha_j = r_j\alpha_j \sum_{k=1}^{\infty} r_k\alpha_k - \tfrac{1}{2}\sum_{k=1}^{j-1} r_k r_{j-k}\alpha_k\alpha_{j-k}. \tag{10}$$

I first prove the following lemma.

Lemma 1. Let r_j satisfy

(i) $\quad r_j > r_1 \qquad (j \geqslant 2)$

(ii) $\quad \lim_{j\to\infty} r_j^{-1} = 0.$

Then equations (10) have a positive solution.

Proof. Define

$$a_j = r_j \alpha_j.$$

Equations (10) become

$$a_j = r_j\left(a_j \sum_{k=1}^{\infty} a_k - \tfrac{1}{2}\sum_{k=1}^{j-1} a_k a_{j-k}\right)$$

or, written otherwise,

$$a_j = \frac{1}{2(r_1^{-1} - r_j^{-1})} \sum_{k=1}^{j-1} a_k a_{j-k} \qquad (j \geq 2) \tag{11a}$$

$$\sum_{k=1}^{\infty} a_k = r_1^{-1}. \tag{11b}$$

Equation (11a) determines the whole sequence $(a_j)_{j=1}^{\infty}$ once a_1 is known, which must then be so chosen as to fulfil (11b). To show that this is possible, recast the problem as follows: define

$$\beta_j(b) = \frac{1}{2b(r_1^{-1} - r_j^{-1})} \sum_{k=1}^{j-1} \beta_k(b)\beta_{j-k}(b) \qquad (j \geq 2)$$

$$\beta_1(b) = 1.$$

Clearly

$$a_j' = \beta_j(b)/b$$

satisfy (11a) for all b and (11b) if

$$\sum_{j=1}^{\infty} \beta_j(b) = r_1^{-1} b. \tag{12}$$

It is therefore enough to show the existence of a number of b satisfying (12). To this end define

$$C_N^{-1} = \max_{k \geq N} r_k^{-1}, \qquad \gamma_j^{(N)}(b) = \beta_j(b) \quad (j \leq N)$$

$$\gamma_j^{(N)}(b) = \frac{1}{2b(r_1^{-1} - C_N^{-1})} \sum_{k=1}^{j-1} \gamma_k^{(N)}(b)\gamma_{j-k}^{(N)}(b) \qquad (j \geq N)$$

$$F_N(z\,;b) = \sum_{j=1}^{\infty} \gamma_j^{(N)}(b) z^j$$

$$P_N(z\,;b) = \sum_{j=1}^{N} (r_j^{-1} - C_N^{-1})\gamma_j^{(N)}(b) z^j = \sum_{j=1}^{N} (r_j^{-1} - C_N^{-1})\beta_j(b) z^j.$$

Clearly

$$F_N^2 - 2b(r_1^{-1} - C_N^{-1})F_N + 2bP_N = 0$$

or otherwise

$$F_N = b(r_1^{-1} - C_N^{-1})\{1 - [1 - 2P_N/b(r_1^{-1} - C_N^{-1})^2]^{1/2}\}. \tag{13}$$

Now define b_N as the number such that $F_N(z\,;b_N)$ has exactly convergence radius one in the variable z. Such a number exists, since

$$\gamma_j^{(N)}(b)=\gamma_j^{(N)}(1)b^{1-j} \tag{14}$$

and $F_N(z;1)$ has a finite, non-zero convergence radius. From (13) it follows that

$$F_N(1;b_N)=b_N(r_1^{-1}-C_N^{-1}) \qquad P_N(1;b_N)=\tfrac{1}{2}b_N(r_1^{-1}-C_N^{-1})^2 \tag{15}$$

since $F_N(z;b_N)$, having only positive coefficients, has a singularity at $z=1$.

From the definitions of $\gamma_j^{(N)}(b)$ it follows immediately that

$$\beta_j(b)\leq\gamma_j^{(N)}(b)$$

for all j and N. From this follows

$$\gamma_j^{(N+1)}(b)\leq\gamma_j^{(N)}(b)$$

for all j and N. Therefore the convergence radius of $\gamma_j^{(N)}(1)$ can only increase and therefore b_N only decrease with N. Since $b_N>0$ one obtains that

$$b_\infty=\lim_{N\to\infty}b_N$$

exists. Remark now that

$$r_1^{-1}b_\infty=\lim_{N\to\infty}(r_1^{-1}-C_N^{-1})b_N=\lim_{N\to\infty}F_N(1;b_N)=\lim_{N\to\infty}\sum_{j=1}^{\infty}\gamma_j^{(N)}(b_N)$$

$$=\sum_{j=1}^{M-1}\beta_j(b_\infty)+\lim_{N\to\infty}\sum_{j=M}^{\infty}\gamma_j^{(N)}(b_N)=\sum_{j=1}^{\infty}\beta_j(b_\infty)+\lim_{M\to\infty}\lim_{N\to\infty}\sum_{j=M}^{\infty}\gamma_j^{(N)}(b_N)$$

and hence

$$\sum_{j=1}^{\infty}\beta_j(b_\infty)\leq r_1^{-1}b_\infty<\infty.$$

I now prove that

$$\lim_{N\to\infty}P_N(z;b_\infty)=P(z) \tag{16}$$

uniformly for $0\leq z\leq 1$. Indeed

$$\max_{0\leq z\leq 1}|P_N(z)-P_M(z)|$$

$$\leq\sum_{j=M+1}^{N}|r_j^{-1}-C_N^{-1}|\beta_j(b_\infty)+\sum_{j=1}^{M}|C_M^{-1}-C_N^{-1}|\beta_j(b_\infty)$$

$$\leq\max_{M<j\leq N}|r_j^{-1}-C_N^{-1}|\sum_{k=M+1}^{N}\beta_k(b_\infty)$$

$$+|C_M^{-1}-C_N^{-1}|\sum_{j=1}^{\infty}\beta_j(b_\infty)\to 0 \qquad (M,N\to\infty)$$

thus proving that $(P_N(z))_{N=1}^{\infty}$ is a Cauchy sequence in the space of continuous functions with the supremum norm proving (16).

From (14), (15) and (16) it follows that

$$r_1^{-2}\frac{b_\infty}{2}=\lim_{N\to\infty}P_N(1;b_N)=\lim_{N\to\infty}\frac{b_N}{b_\infty}P_N\left(\frac{b_\infty}{b_N};b_\infty\right)=P(1). \tag{17}$$

From (16) it follows equally that

$$P(z)=\sum_{j=1}^{\infty} r_j^{-1}\beta_j(b_\infty)z^j \qquad (0\leqslant z\leqslant 1)$$

and

$$\lim_{N\to\infty} F_N(z;b_\infty)=r_1^{-1}b_\infty[1-(1-2P(z)/r_1^{-2}b_\infty)^{1/2}],$$

for all z so small that $F_N(z;b_\infty)$ exists for all N. It then follows that

$$F(z)=\sum_{j=1}^{\infty}\beta_j(b_\infty)z^j=r_1^{-1}b_\infty[1-(1-2P(z)/r_1^{-2}b_\infty)^{1/2}] \tag{18}$$

for z sufficiently small. However, since $F(z)$ is an analytic function with positive coefficients, its first singularity will be on the positive real axis. By (17), clearly $z=1$ is a possibility, and since $P(z)$ is a monotonic function in z analytic in $|z|<1$, no singularity is possible for $z<1$. Hence (18) is valid for $z<1$ and by Abel's theorem for $z=1$

$$F(1)=\sum_{j=1}^{\infty}\beta_j(b_\infty)=r_1^{-1}b_\infty \tag{19}$$

proving that b_∞ is a solution of (12) and hence proving the lemma.

I now need the following, purely technical result.

Lemma 2. Let the a_j be positive numbers such that

$$f(z)=\sum_{j=1}^{\infty} a_j z^j$$

has convergence radius one. Define

$$s_j=\sum_{k=1}^{j} a_k$$

and let $\lambda>0$ be arbitrary. Then the statements

(i) $\quad s_n=o(n^\lambda) \qquad (n\to\infty)$

(ii) $\quad f(z)=o[(1-z)^{-\lambda}] \qquad (z\to 1)$

are equivalent.

The proof is given in the appendix. With this lemma I now prove the following.

Lemma 3. Let the r_j satisfy the following conditions:

(i) $\quad r_j>r_1 \qquad (j\geqslant 2)$

(ii) $\quad r_j\geqslant Bj^\alpha.$

Then the solution α_j of (10) (shown to exist by lemma 1) satisfy

$$\sum_{j=1}^{\infty} j\alpha_j < \infty \qquad (\alpha > \tfrac{1}{2})$$

$$\sum_{j=1}^{N} j\alpha_j = o(N^{1-2\alpha+\varepsilon}) \qquad (\alpha \leqslant \tfrac{1}{2})$$

for any positive ε.

Proof. In the notation of lemma 1, what I want to investigate is the behaviour of

$$s_j = \sum_{k=1}^{j} k r_k^{-1} a_k. \tag{20}$$

Defining

$$f(z) = \sum_{j=1}^{\infty} a_j z^j \qquad g(z) = \sum_{j=1}^{\infty} r_j^{-1} a_j z^j$$

one obtains from (18)

$$f(z) = r_1^{-1}[1-(1-2r_1^2 g(z))^{1/2}]$$

or using (17) and (19)

$$(f(z)-f(1))^2 = 2r_1^2(g(1)-g(z)). \tag{21}$$

Now define

$$\sigma_j = \sum_{k=1}^{j} k a_k.$$

I have

$$s_j \leqslant B \sum_{k=1}^{j} k^{1-\alpha} a_k \leqslant B j^{1-\alpha} \sum_{k=1}^{j} a_k \leqslant B' j^{1-\alpha} = o(j^\lambda) \tag{22}$$

if $\lambda > 1-\alpha$. From lemma 2 we get $g'(z) = o[(1-z)^{-\lambda}]$ implying

$$g(1)-g(z) = \int_z^1 g'(t)\,dt = o(1)\int_z^1 (1-t)^{-\lambda}\,dt = o[(1-z)^{1-\lambda}]$$

and from (21) it follows that

$$f(z)-f(1) = o[(1-z)^{(1-\lambda)/2}]$$

and since $f(z)$ has positive coefficients

$$f'(z) \leqslant (f(1)-f(z))/(1-z) = o[(1-z)^{-(\lambda+1)/2}]$$

and therefore, by lemma 2,

$$\sigma_j = o(j^{(\lambda+1)/2})$$

implying

$$s_j \leq B \sum_{k=1}^{j} k^{1-\alpha} a_k = B \sum_{k=1}^{j} k^{-\alpha}(\sigma_k - \sigma_{k-1})$$

$$= Bj^{-\alpha}\sigma_j + B \sum_{k=1}^{j} [k^{-\alpha} - (k+1)^{-\alpha}]\sigma_k$$

$$= \mathrm{o}(j^{(1+\lambda-2\alpha)/2}) + \sum_{k=1}^{j} \mathrm{o}(k^{(\lambda-1-2\alpha)/2}). \tag{23}$$

Now two different cases appear.

Case (*a*). $1+\lambda-2\alpha<0$. Then (23) implies immediately

$$s_j = \mathrm{O}(1)$$

and the statement of the lemma is proved.

Case (*b*). $1+\lambda-2\alpha>0$. Then (23) implies

$$s_j = \mathrm{o}(j^{(1+\lambda-2\alpha)/2}).$$

This statement, however, is identical to (22) except that λ is replaced by

$$\lambda_1 = \tfrac{1}{2}(1+\lambda-2\alpha).$$

This process can be iterated, giving

$$\lambda_n = \tfrac{1}{2}(1+\lambda_{n-1}-2\alpha).$$

As long as $\lambda_n > 0$, I can state

$$s_j = \mathrm{o}(j^{\lambda_n}).$$

However, it is easy to see that

$$\lim_{n\to\infty} \lambda_n = \lambda_\infty = 1-2\alpha.$$

Hence, if $\alpha > \frac{1}{2}$, case (a) is found to hold after finitely many iterations. If $\alpha \leq \frac{1}{2}$, I have for any $\varepsilon > 0$

$$\lambda_n < 1-2\alpha+\varepsilon$$

for some n, thereby proving the whole lemma and theorem 2.

Further, if $\alpha > \frac{1}{2}$, I can clearly assume (22) for $\lambda = \varepsilon > 0$ arbitrary, since the s_j are in fact bounded. The whole procedure then leads to (see (23))

$$s_j = \mathrm{O}(1) + \mathrm{o}(j^{(1-2\alpha+\varepsilon)/2})$$

as was said in § 1.

4. Conclusion

The kinetic equations defined by the kernels

$$R_{ij} = i^d \delta_{ij} \text{ and } R_{ij} = i^\alpha j^\alpha$$

were examined for the case $1<d<2$ and $\frac{1}{2}<\alpha<1$. Under those conditions it is well known that the solutions exist for all positive times (Leyvraz and Tschudi 1981). It could be shown of both kernels that they allowed finite-mass, mass-non-conserving solutions of the type

$$c_j(t)=\alpha_j/(t+C)$$

and in the case

$$R_{ij}=i^d\delta_{ij}$$

it could even be shown that from monodisperse initial conditions mass conservation must be violated at finite time. While this could not be proved in the second case, it remains highly plausible. Under very plausible assumptions it was found possible to derive the scaling behaviour of 'gelation times' observed on the first N concentrations as a function of N.

Acknowledgments

I would like to thank M H Ernst and E M Hendriks for many valuable discussions, as well as H R Tschudi for a critical reading of the proof of theorem 2.

Appendix

I want to prove the following.

Lemma 2. Let the a_j be positive numbers such that

$$f(z)=\sum_{j=1}^{\infty} a_j z^j$$

has convergence radius one. Define

$$s_j=\sum_{k=1}^{j} a_k$$

and let $\lambda>0$ be arbitrary. Then the statements

(i) $\quad s_n=\mathrm{o}(n^\lambda) \qquad (n\to\infty)$

(ii) $\quad f(z)=\mathrm{o}[(1-z)^{-\lambda}] \qquad (z\to 1)$

are equivalent.

Proof. Assume first $s_n=\mathrm{o}(n^\lambda)$. If

$$\sum_{n=1}^{\infty} s_n<\infty$$

then the lemma is trivial. Else for every M and every $\varepsilon>0$ exists a $z<1$ such that

$$\left(\sum_{j=M}^{\infty} s_j z^j\right)\Big/\left(\sum_{j=1}^{\infty} s_j z^j\right)\geqslant 1-\varepsilon.$$

Choose M so large that

$$s_j \leqslant \varepsilon \left| \binom{-\lambda-1}{j} \right| = \varepsilon\, \mathrm{O}(j^\lambda).$$

It follows that

$$\sum_{j=1}^{\infty} s_j z^j \leqslant \frac{1}{1-\varepsilon} \sum_{j=M}^{\infty} s_j z^j \leqslant \frac{\varepsilon}{1-\varepsilon} \sum_{j=M}^{\infty} \left| \binom{-\lambda-1}{j} \right| z^j$$
$$\leqslant [\varepsilon/(1-\varepsilon)](1-z)^{-\lambda-1}$$

and hence

$$\sum_{j=1}^{\infty} a_j z^j = (1-z) \sum_{j=1}^{\infty} s_j z^j = \mathrm{o}[(1-z)^{-\lambda}].$$

Assume now that

$$f(z) = \mathrm{o}[(1-z)^{-\lambda}].$$

It follows that

$$s_j = \sum_{k=1}^{j} a_k \leqslant \left(1-\frac{1}{j}\right)^{-j} \sum_{k=1}^{j} a_k \left(1-\frac{1}{j}\right)^{k} \leqslant 4f\left(1-\frac{1}{j}\right) = \mathrm{o}(j^\lambda)$$

thus proving the whole lemma.

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