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1981 J. Phys. A: Math. Gen. 14 3389

(http://iopscience.iop.org/0305-4470/14/12/030)

J. Phys. A: Math. Gen. 14 (1981) 3389–3405. Printed in Great Britain

# Singularities in the kinetics of coagulation processes

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Received 11 November 1980, in final form 1 April 1981

**Abstract.** We consider a system of substances $A_j$ reacting according to the following scheme:

$$A_k + A_l \xrightarrow[R_{kl}]{} A_{k+l} \qquad (R_{kl} = R_{lk} \geqslant 0).$$

(The reaction is taken as irreversible.) We discuss the existence of global solutions of the kinetic equations derived for the concentrations. It is shown that we cannot expect the total number of monomers to remain constant. Rather, it can decrease as the result of the formation of infinite clusters (gelation). With this restriction, we obtain that a physically reasonable global solution exists if $R_{kl} \leqslant r_k r_l$ and $r_k = o(k)$. It is further conjectured that no gelation will take place if $r_k = o(\sqrt{k})$. The case $R_{jk} = (Aj + B)(Ak + B)$ is also solved explicitly and shown to exhibit gelation at $t = 1/A(A+B)$.

## 1. Introduction

The following model of reaction kinetics has been extensively studied, in the theory of polymerisation (in particular with respect to gelation), as well as in the theory of colloidal suspensions. For reviews on these and related topics see e.g. Tompa (1976), Peebles (1971), Drake (1972).

(1) We consider a system consisting of an infinite number of species $A_1, A_2, \ldots,$ where $A_k$ is to be thought of as consisting of $k$ particles $A_1$ bound together. We do not differentiate between any kinds of 'isomers'.

(2) The substances $A_1, A_2, \ldots$ react with each other according to the following scheme:

$$A_k + A_l \xrightarrow[R_{kl}]{} A_{k+l}. \tag{1.1}$$

$R_{kl}$ is a reaction constant (depending only on $k$ and $l$) with

$$R_{kl} = R_{lk} \geqslant 0.$$

A few remarks concerning this model are in order.

(i) Reaction (1.1) is entirely irreversible. This means that there is no equilibrium possible in this model. Alternatively, one may think of the system as being far from chemical equilibrium in the beginning. The model then only holds as long as the system is still sufficiently far from equilibrium.

(ii) We further disregard any reactions which might deactivate an $A_k$, say:

$$A_k + B_l \rightarrow B_{k+l} \qquad \text{or} \qquad A_k + B_l \rightarrow B_k + B_l$$

  

where the $B_k$ are otherwise inert molecules. This is a serious assumption. It can be hoped, however, that at least the structure of the singularities will remain unaltered.

(iii) We finally remark that the $R_{kl}$ are *given* coefficients which we shall in no way attempt to determine. Their determination is dependent on very particular models of the molecular processes involved, which we do not discuss. Instead we show what can happen if the $R_{kl}$ are chosen in a certain way. We shall discuss the case

$$R_{kl}=(Ak+B)(Al+B)$$

in particular detail, because it corresponds to the Flory–Stockmayer model of gelation and because, to our knowledge, the kinetic behaviour of the above system *after* gelation has not been discussed and even the very existence of a meaningful solution after gelation has been doubted (see e.g. McLeod 1962).

If we denote the volume concentration of $A_k$ by $c_k$, we obtain

$$\dot{c}_j=\tfrac{1}{2}\sum_{k=1}^{j-1}R_{k,j-k}c_kc_{j-k}-c_j\sum_{k=1}^{\infty}R_{jk}c_k \tag{1.2}$$

as kinetic equations describing the system.

If we limit ourselves to a system containing at most $N$ molecules of type $A_1$, no molecule of type $A_k$ can be formed for $k>N$. We therefore obtain

$$\dot{c}_{j,N}=\tfrac{1}{2}\sum_{k=1}^{j-1}R_{k,j-k}c_{k,N}c_{j-k,N}-c_{j,N}\sum_{k=1}^{N-j}R_{jk}c_{k,N}. \tag{1.3}$$

We consider (1.2) as a formal limit of (1.3) for large $N$, which appears to be physically reasonable. We shall later see how this can be made more rigorous.

We further note that for an arbitrary sequence of numbers $(g_j)_{j=1}^{N}$ the following relation holds:

$$\sum_{j=1}^{N}g_j\dot{c}_{j,N}=\tfrac{1}{2}\sum_{\substack{k,l=1\\k+l\leqslant N}}^{N}(g_{k+l}-g_k-g_l)R_{kl}c_{k,N}c_{l,N}. \tag{1.4}$$

This implies

$$\sum_{j=1}^{N}j\dot{c}_{j,N}=0. \tag{1.5}$$

This reflects conservation of the total number of $A_1$ molecules involved in a reaction of the type (1.1). It is not possible to show the analogue of (1.5) for the infinite system, as we shall see in an exactly solvable case. The reason for this is easy to understand: let us assume that

$$\lim_{N\to\infty}c_{j,N}(t)=c_j(t)$$

for all $j$ and all $t\geqslant 0$. This is clearly necessary if (1.2) is to be interpreted as a limit of (1.3). We then have

$$\begin{aligned}\sum_{j=1}^{\infty}jc_j&=\lim_{M\to\infty}\sum_{j=1}^{M-1}jc_j=\lim_{M\to\infty}\lim_{N\to\infty}\sum_{j=1}^{M-1}jc_{j,N}\\&=\lim_{M\to\infty}\lim_{N\to\infty}\left(1-\sum_{j=M}^{N}jc_{j,N}\right)=1-\lim_{M\to\infty}\lim_{N\to\infty}\sum_{j=M}^{N}jc_{j,N}.\end{aligned}$$

This last term, however, need not vanish. If the dynamics (1.3) can produce, in finite time, a finite quantity of clusters, the size of which goes to infinity as $N$ does, then clearly it will *not* vanish. This phenomenon is well known in chemistry as gelation.

As far as formula (1.4) is concerned, it is seen that for $N \to \infty$ the order of summation can be interchanged if the sums

$$\sum_{j=1}^{\infty} R_{jl} c_j, \qquad \sum_{j=1}^{\infty} |g_j| R_{jl} c_j, \qquad \sum_{j=1}^{\infty} |g_{j+l}| R_{jl} c_j,$$

are finite for all $l$. It follows that gelation can only occur if

$$\sum_{j=1}^{\infty} j R_{jl} c_j = \infty$$

for at least one $l$.

We now introduce some further assumptions on the nature of the system and on the constants $R_{kl}$. We assume that every $A_k$ has a certain number of reactive sites, say $r_k$. These are assumed to be equally reactive, independently of the size of the molecules they belong to. This leads in a straightforward way to the ansatz:

$$R_{kl} = r_k r_l. \tag{1.6}$$

Furthermore, it is geometrically obvious that the number of reactive sites on $A_k$ cannot grow more quickly than $k$, that is, there is a constant $C$ such that

$$r_k \leqslant Ck.$$

Indeed it is easily seen that linear growth of the $r_k$ (that is, $r_k \sim Ck$) is equivalent to the absence of cycles in the structure of $A_k$, i.e. we are essentially dealing with the Flory–Stockmayer model of gelation (see e.g. Stockmayer 1943, Flory 1941). The following model can be solved exactly:

$$R_{kl} = (Ak+B)(Al+B), \qquad A>0,\ B>-A.$$

This solution is shown in the next section. It is most simply stated in the case $B=0$, but similar results are obtained in the general case. We have

$$\begin{aligned} c_j(t) &= \frac{j^{j-3}}{(j-1)!}(A^2t)^{j-1}\exp(-A^2jt) \qquad \left(t \leqslant \frac{1}{A^2}\right) \\ &= \frac{j^{j-3}\,\mathrm{e}^{-j}}{(j-1)!A^2t} \qquad \left(t \geqslant \frac{1}{A^2}\right) \end{aligned} \tag{1.7}$$

as a solution of the equations

$$\dot{c}_j = \frac{A^2}{2}\sum_{k=1}^{j-1} k(j-k)c_k c_{j-k} - A^2 j c_j \sum_{k=1}^{\infty} k c_k, \qquad c_j(0) = \delta_{j1}. \tag{1.8}$$

We notice immediately that

$$\begin{aligned} \sum_{j=1}^{\infty} j c_j(t) &= 1 \qquad (t \leqslant 1/A^2) \\ &= 1/A^2 t \qquad (t \geqslant 1/A^2), \end{aligned}$$

i.e. gelation (in the sense given above) does occur at $t = 1/A^2$. It is readily seen that the solution given by (1.7) is continuously differentiable, and that the right-hand side of equation (1.8) always makes sense and is always equal to the derivative of the function. This would not be the case if we had taken the small-times solution for all $t$: the right-hand side would still always converge, but would be different from the left-hand side. (See e.g. McLeod 1962.) Actually the explicit construction of the solution in the general case ($B \neq 0$) proves that the solution to these equations is unique.

Since the assumptions on $R_{kl}$ in this model are quite severe, we wish to relax them somewhat and further assume that $r_k$ grows less quickly than $k$. This seems to be a reasonable way to account for the considerable amount of cross-linking, cyclisation and so on, which occurs in realistic large clusters. Indeed it can be reasonably argued that a reactive site must lie on the 'surface' of $A_k$, whereas $k$ is proportional to its 'volume'. This strongly indicates that

$$\lim_{k\to\infty} \frac{r_k}{k} = 0.$$

It is clear, however, that this is a very *ad hoc* way to deal with cyclisation. It has nothing of the detailed character of an analysis such as Stauffer's on percolation and gelation (see Stauffer 1976, 1979) or Gordon and Scantlebury's treatment (1966). It might nonetheless be argued that our approach has more generality and does not rely on any particular geometrical assumptions, and therefore allows the discussion of other modifications of the classical Flory–Stockmayer model, since the whole argument relies only on the asymptotic behaviour of reaction constants. We now have the following:

*Theorem 1.* Let $R_{kl} = R_{lk} \geqslant 0$ be such that

$$R_{kl} \leqslant r_k r_l, \qquad \lim_{k\to\infty} \frac{r_k}{k} = 0.$$

Then there exists a solution $(c_j(t))_{j=1}^{\infty}$ of the infinite system

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

$$c_j(0) \geqslant 0, \qquad \sum_{j=1}^{\infty} j c_j(0) = 1,$$

with the following properties.

(i) $c_j(t) \geqslant 0$, $\Sigma_{j=1}^{\infty} j c_j(t) \leqslant 1$ for all $t \geqslant 0$.

(ii) $c_j(t)$ is continuously differentiable for all $t \geqslant 0$.

(iii) There is a sequence $N_i \to \infty$ such that

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

for all $j$ and all $t \geqslant 0$. Furthermore, we have

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

The proof is given in § 3.

Under the hypotheses given above, this theorem settles the general existence theory of kinetic equations of the type of equation (1.2), up to two important problems:

(1) The theorem says nothing about uniqueness of the solution of the infinite system.

(2) The theorem does not assert that $\lim_{N\to\infty} c_{j,N}(t)$ exists. It is easily seen that once the existence of this limit is proved, we have

$$\lim_{N\to\infty} c_{j,N}(t) = c_j(t)$$

where $c_j(t)$ is a solution of (1.2) which in this case should clearly be considered as the physical solution. On the other hand, the proof of theorem 1 shows that if the solution of the infinite system is indeed unique, then $\lim_{N\to\infty} c_{j,N}(t)$ exists and is equal to this solution.

Those two problems are then closely interconnected. We know of no satisfactory answer to either. There is a uniqueness result by Melzak (1957) valid for all times but with the restriction

$$R_{kl} \leqslant C$$

for all $k$, $l$. Melzak also shows that under those circumstances no gelation can take place. There is another uniqueness result by McLeod (1962, p 193) under the hypothesis

$$R_{kl} \leqslant Ckl$$

which is, however, only valid for times so small that again gelation can be shown to be impossible. The difficulty appears to be that it is difficult to control the growth of a small initial error over times large enough to allow gelation (let alone arbitrary times!).

Another interesting problem would be to know under which conditions gelation can occur at all. Here we have the following

*Conjecture.* Let $R_{kl} \leqslant r_k r_l$, where

$$\lim_{k\to\infty} \frac{r_k}{\sqrt{k}} = 0.$$

Then gelation does not occur.

The conjecture can be proved—as shown in an Appendix—if it is true that increasing one or several $r_k$ does not increase the gelation time. Although we strongly believe this to be true, we are not able to prove it.

It is further not clear whether or not gelation will occur if

$$\lim_{k\to\infty} \frac{r_k}{k} = 0 \qquad \text{but} \qquad \lim_{k\to\infty} \frac{r_k}{\sqrt{k}} = \infty.$$

There are a few heuristic arguments in favour of gelation, which will be discussed elsewhere. There is, however, the following:

*Theorem 2.* Let $R_{kl} \geqslant r_k r_l$ where $r_k \geqslant Ck$ for some $C>0$. Then it cannot be true that

$$\sum_{j=1}^{\infty} jc_j(t) = 1 \qquad \text{for all } t \geqslant 0.$$

The proof is so short that we give it here.

*Proof.* Assume the contrary. Then

$$\sum_{j=1}^{\infty} \dot{c}_j = -\tfrac{1}{2} \sum_{j,k=1}^{\infty} R_{jk} c_j c_k \leqslant -\frac{C^2}{2}\left(\sum_{j=1}^{\infty} j c_j\right)^2 \leqslant -\frac{C^2}{2}$$

for all $t$. This implies that

$$\sum_{j=1}^{\infty} c_j(t) = \sum_{j=1}^{\infty} c_j(0) - \frac{C^2 t}{2} < 0$$

for $t > 0$ sufficiently large. The transformation

$$\phi_j(t) = c_j(t) \exp\left(\int_0^t \mathrm{d}t'\, S_j(t')\right)$$

with

$$S_j(t) = \sum_{k=1}^{\infty} R_{jk} c_k(t)$$

leads to

$$\dot{\phi}_j = \tfrac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} \exp\left(\int_0^t \mathrm{d}t'(S_j - S_k - S_{j-k})\right) \phi_k \phi_{j-k},$$

$$\phi_j(0) = c_j(0) \geqslant 0,$$

from which $\phi_j(t) \geqslant 0$ and therefore $c_j(t) \geqslant 0$ follows for all $t$ where the equations make sense. This is a contradiction and the theorem is proved.

Finally, it must be noted that the theorem does *not* state that $\Sigma_{j=1}^{\infty} j c_j(t) < 1$ at any finite time, since the existence of a global solution is not proven under the assumptions of the theorem.

## 2. The Flory–Stockmayer model

We want to solve the following system of equations:

$$\frac{\mathrm{d}c_j}{\mathrm{d}t} = \frac{1}{2} \sum_{k=1}^{j-1} r_k r_{j-k} c_k c_{j-k} - r_j c_j \sum_{k=1}^{\infty} r_k c_k,$$

$$c_j(0) = \delta_{j1}, \qquad r_k = Ak + B.$$

Let us make the following substitutions:

$$\tau = (A+B)^2 t, \qquad p_j = r_j c_j/(A+B).$$

This leads to

$$\frac{\mathrm{d}p_j}{\mathrm{d}\tau} = \dot{p}_j = \frac{r_j}{A+B}\left(\frac{1}{2}\sum_{k=1}^{j-1} p_k p_{j-k} - p_j \sum_{k=1}^{\infty} p_k\right)$$

$$= [(1-b)j + b]\left(\frac{1}{2}\sum_{k=1}^{j-1} p_k p_{j-k} - p_j \sum_{k=1}^{\infty} p_k\right).$$

In the following, the dot will always mean derivative with respect to $\tau$. Since $A>0$ and $B>-A$, we have

$$b=B/(A+B)<1.$$

We will also assume $b\neq 0$. The case $b=0$ can then be obtained by an adequate limiting process. We further define

$$K(\tau)=\sum_{k=1}^{\infty} p_k(\tau),$$

$$\phi_j(\tau)=p_j\exp\left([(1-b)j+b]\int_0^{\tau} K(\tau')\,\mathrm{d}\tau'\right)$$

and obtain

$$\dot{\phi}_j=\frac{(1-b)j+b}{2}\sum_{k=1}^{j-1}\phi_k\phi_{j-k}\exp\left(-b\int_0^{\tau}K(\tau')\,\mathrm{d}\tau'\right).$$

We now consider the generating function

$$G(z;\tau)=\sum_{k=1}^{\infty}\phi_k(\tau)z^k.$$

Obviously

$$\begin{aligned}&\exp\left(b\int_0^{\tau}K(\tau')\,\mathrm{d}\tau'\right)\frac{\partial G}{\partial\tau}-(1-b)zG\frac{\partial G}{\partial z}=\frac{bG^2}{2},\\ &G(z;0)=z.\end{aligned}\tag{2.1}$$

This is a quasilinear partial differential equation and can therefore be solved by Cauchy's method of characteristics (for a discussion see e.g. Courant and Hilbert (1968)). It then follows that the solutions of the system

$$\begin{aligned}&\frac{\mathrm{d}\tau}{\mathrm{d}s}=\exp\left(b\int_0^{\tau}\mathrm{d}\tau' K(\tau')\right),\\ &\mathrm{d}z/\mathrm{d}s=-(1-b)zG, \qquad \mathrm{d}G/\mathrm{d}s=\tfrac{1}{2}bG^2,\\ &\tau(0)=0, \qquad G(0)=z(0)=z_0,\end{aligned}\tag{2.2}$$

taken for all values of the parameter $z_0$, cover the entire surface representing the function $G(z;\tau)$.

We now proceed in two steps: first we determine the $\phi_j(s)$, which is a purely local problem, since it only involves the form of $G(z;s)$ around $z=0$. Next we determine $K(\tau)$ and therefore are able to work in the variables $(z;\tau)$, i.e. we can calculate $\phi_j(\tau)$ and finally $c_j(\tau)$.

Solving the equations (2.2) with the more general initial conditions

$$G(0)=G_0, \qquad z(0)=z_0,$$

we obtain

$$G(s)=G_0/(1-\tfrac{1}{2}bG_0s), \qquad z(s)=z_0(1-\tfrac{1}{2}bG_0s)^{2(1-b)/b}.\tag{2.3}$$

With our more special initial conditions we obtain

$$G_0=z_0=\zeta.$$

We have

$$G(s)=\sum_{j=1}^{\infty}\phi_j(s)z(s)^j \qquad \text{for all } \zeta.$$

Therefore by Cauchy's theorem

$$\phi_j(s)=\frac{1}{2\pi\mathrm{i}}\oint_C \mathrm{d}\zeta\frac{\zeta}{1-\frac{1}{2}b\zeta s}\,\frac{(\mathrm{d}/\mathrm{d}\zeta)[\zeta(1-\frac{1}{2}bs\zeta)^{2(1-b)/b}]}{[\zeta(1-\frac{1}{2}bs\zeta)^{2(1-b)/b}]^{j+1}}$$

where $C$ is a small circle around the origin. It follows that

$$\begin{aligned}\phi_j(s)&=\frac{s^{j-1}}{2\pi\mathrm{i}}\oint_C \mathrm{d}u\left(\frac{1}{1-\frac{1}{2}bu}+\frac{(b-1)u}{(1-\frac{1}{2}bu)^2}\right)[u(1-\tfrac{1}{2}bu)^{2(1-b)/2}]^{-j-1}\\&=\frac{1-b/2}{j-1}\left(-\frac{b}{2}\right)^{j-1}\binom{-[2(1-b)/b]j-2}{j-2}s^{j-1}.\end{aligned}$$

We now need to determine $K(\tau)$. Define

$$R(\tau)=\exp\left(-(1-b)\int_0^{\tau}\mathrm{d}\tau'\,K(\tau')\right).$$

We obtain

$$\begin{aligned}K(\tau)&=\sum_{j=1}^{\infty}\phi_j(\tau)R(\tau)^jR(\tau)^{b/(1-b)}\\&=G(R(\tau);\,\tau)R(\tau)^{b/(1-b)}.\end{aligned}$$

Differentiating $R(\tau)$ with respect to $\tau$ gives

$$\dot{R}(\tau)=-(1-b)K(\tau)R(\tau)=-(1-b)R(\tau)G(R(\tau);\,\tau)\,\mathrm{d}s/\mathrm{d}\tau.$$

Using equations (2.2), it follows that

$$\mathrm{d}R/\mathrm{d}s=-(1-b)G(R(s);\,s)R(s). \tag{2.4}$$

This is nothing else than the second of the equations (2.2). The equations (2.3) define a surface in the $(s, z, G)$ space by the map

$$(s,\zeta)\rightarrow(s,z(\zeta;s),G(\zeta;s))=\left(s,\zeta(1-\tfrac{1}{2}b\zeta s)^{2(1-b)/b},\frac{\zeta}{1-\frac{1}{2}b\zeta s}\right).$$

For an appropriate discussion of the function $R(s)$ we now investigate the nature of this surface, limiting ourselves to positive values of the parameters $s$, $\zeta$. We see that for a given $s$ the function $z(\zeta, s)$ cannot exceed the value

$$z_c(s)=\left(\frac{2(1-b)}{(2-b)}\right)^{2(1-b)/b}\frac{2}{(2-b)s}. \tag{2.5}$$

The corresponding value of $\zeta$ is

$$\zeta_c(s)=2/(2-b)s \tag{2.6}$$

and therefore

$$G(\zeta_c(s);\,s)=G_c(s)=1/(1-b)s. \tag{2.7}$$

It can further be shown that, for fixed $s$, $G(\zeta, s)$ is a monotonic function, at least up to a point beyond the critical curve $(s, z_c(s), G_c(s))$. This means that the surface $(s, z(\zeta, s), G(\zeta; s))$ covers the region

$$\{(s, z) : 0 \leqslant z \leqslant z_c(s)\}$$

twice. The two sheets meet smoothly along the critical curve. This means that the derivatives $(\partial G/\partial \tau)_z$ and $(\partial G/\partial z)_\tau$ do not exist on this curve. This can easily be verified analytically.

It follows from the above formulae that the second sheet does not represent a function analytic around zero. Since we have derived equation (2.4) for $R(s)$ under this assumption, we must be careful to solve (2.4) without ever reaching the second sheet. We have now

$$R(0) = 1.$$

Therefore, by equations (2.3),

$$R(s) = (1 - \tfrac{1}{2}bs)^{2(1-b)/b} \qquad (s < 2/(2-b) = s_c(1))$$

where $s_c(\zeta)$ is the inverse function of $\zeta_c(s)$. For $s > s_c(1)$ we would be on the second sheet, which immediately leads to a contradiction with equation (2.4). However, we note that the curves $(s, z(\zeta; s), G(\zeta; s))$ for fixed $\zeta$ are smooth in the neighbourhood of the critical curve. This means that the curves $(s, z(\zeta; s))$ will always be tangent to the curve $(s, z_c(s))$ at their intersection. Therefore the two curves satisfy the same differential equation, namely the second equation (2.2). The curve $(s, z_c(s))$ is the projection on the $(s, z)$ plane of the critical curve (where both sheets of the surface meet). Though $G(z; s)$ is no longer analytic in $z$ there, still equation (2.4) can be derived, since it is on the border of the domain of analyticity, by Abel's theorem. Therefore we can define $R(s)$ for all $s$ as follows:

$$\begin{aligned} R(s) &= (1 - \tfrac{1}{2}bs)^{2(1-b)/b} && (s \leqslant 2/(2-b)) \\ &= z_c(s) = \left(\frac{2(1-b)}{2-b}\right)^{2(1-b)/b} \frac{2}{(2-b)s} && \left(s \geqslant \frac{2}{2-b}\right). \end{aligned}$$

The first equation (2.2) can now be written as

$$\mathrm{d}\tau/\mathrm{d}s = R(s)^{-b/(1-b)}$$

which can be solved to yield

$$\begin{aligned} s &= \frac{2\tau}{2 + b\tau} && \left(\tau \leqslant \frac{1}{1-b}\right) \\ &= \left(\frac{2}{2-b}\right)\left(\frac{2(1-b)\tau - b}{2-b}\right)^{1-b} && \left(\tau \geqslant \frac{1}{1-b}\right). \end{aligned}$$

Using (2.3) for $s \leqslant 2/(2-b)$ and (2.7) otherwise, we obtain

$$\begin{aligned} G(R(s); s) &= \frac{1}{1 - \frac{1}{2}bs} && \left(s \leqslant \frac{2}{2-b}\right) \\ &= \frac{1}{(1-b)s} && \left(s \geqslant \frac{2}{2-b}\right). \end{aligned}$$

It follows that

$$
\begin{aligned}
K(\tau) &= G(R(s);\, s)R(s)^{b/(1-b)} \\
&= 1/(1+\tfrac{1}{2}b\tau) \qquad (\tau \leqslant 1/(1-b)) \\
&= \frac{2(1-b)}{2(1-b)\tau - b} \qquad \left(\tau \geqslant \frac{1}{1-b}\right).
\end{aligned}
$$

Define now

$$
C(\tau) = \sum_{j=1}^{\infty} c_j(\tau), \qquad M(\tau) = \sum_{j=1}^{\infty} jc_j(\tau).
$$

We have

$$
\begin{aligned}
&\mathrm{d}C/\mathrm{d}\tau = -\tfrac{1}{2}(K(\tau))^2, \\
&C(0) = 1, \qquad K(\tau) = (1-b)M(\tau) + bC(\tau).
\end{aligned}
$$

It follows that

$$
\begin{aligned}
M(\tau) &= 1 \qquad (\tau \leqslant 1/(1-b)) \\
&= \frac{2-b}{2(1-b)\tau - b} \qquad \left(\tau \geqslant \frac{1}{1-b}\right).
\end{aligned}
$$

That is, we do indeed get gelation at $\tau = 1/(1-b)$, i.e. at $t = 1/A(A+B)$. The expressions for the concentrations $c_j(\tau)$ can now be derived, but they are complicated and quite unnecessary to the understanding of the phenomena involved, so we shall not go to any more detail. We have also systematically eliminated discussion of the 'singular' case $b = 0$, since it can be derived by straightforward limiting processes. One obtains

$$
\begin{aligned}
\phi_j(s) &= \frac{j^{j-2}}{(j-1)!} s^{j-1}, \qquad s = \tau \qquad \text{for all } \tau, \\
c_j(\tau) &= \frac{j^{j-3}}{(j-1)!} \tau^{j-1}\, \mathrm{e}^{-j\tau} \qquad (\tau \leqslant 1) \\
&= \frac{j^{j-3}\, \mathrm{e}^{-j}}{(j-1)!} \frac{1}{\tau} \qquad (\tau \geqslant 1), \\
K(\tau) = M(\tau) &= 1 \qquad (\tau \leqslant 1) \\
&= 1/\tau \qquad (\tau \geqslant 1),
\end{aligned}
$$

and so on. Similar results can be obtained for more general initial conditions. The qualitative features remain the same, with the exception that if

$$
\sum_{j=1}^{\infty} j^2 c_j(0) = \infty
$$

then gelation occurs immediately, that is

$$
\sum_{j=1}^{\infty} jc_j(t) < 1 \qquad \text{for all } t > 0.
$$

Indeed it is not hard to show that the following formula holds for the gelation time $t_g$:

$$t_g = \frac{1}{A\,\Sigma_{j=1}^{\infty}\,(Aj+B)jc_j(0)}.$$

## 3. General existence theorem

We want to prove:

*Theorem 1.* Let $R_{kl} = R_{lk} \geq 0$ be such that

$$R_{kl} \leq r_k r_l, \qquad \lim_{k\to\infty} \frac{r_k}{k} = 0.$$

Then there exists a solution $(c_j(\tau))_{j=1}^{\infty}$ of the infinite system,

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1} R_{k,j-k}c_k c_{j-k} - c_j \sum_{k=1}^{\infty} R_{jk}c_k, \tag{3.1}$$

$$c_j(0) \geq 0, \qquad \sum_{j=1}^{\infty} jc_j(0) = 1,$$

with the following properties:

(i) $c_j(t) \geq 0$; $\Sigma_{j=1}^{\infty}\, jc_j(t) \leq 1$ for all $t \geq 0$.
(ii) $c_j(t)$ is continuously differentiable for all $t \geq 0$.
(iii) There is a sequence $N_i \to \infty$ such that

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

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

$$\lim_{N_i\to\infty} \sum_{j=1}^{N_i} r_j\, c_{j,N_i}(t) = \sum_{j=1}^{\infty} r_j\, c_j(t)$$

where the $c_{j,N}(t)$ are solutions of the finite system. The theorem will become obvious after the proof of a few lemmas.

*Lemma 1.* The system

$$\begin{aligned} \dot{c}_{j,N} &= \tfrac{1}{2}\sum_{k=1}^{j-1} R_{k,j-k}c_{k,N}c_{j-k,N} - c_{j,N}\sum_{k=1}^{N-j} R_{jk}c_{k,N}, \\ c_{j,N}(0) &= c_j(0) \geq 0, \end{aligned} \tag{3.2}$$

has a unique positive solution for all $t \geq 0$.

*Proof.* We have

$$\sum_{j=1}^{N} j\dot{c}_{j,N} = 0$$

and therefore

$$\sum_{j=1}^{N} jc_{j,N}(t) = \sum_{j=1}^{N} jc_j(0) = K \leqslant 1 \tag{3.3}$$

for all $t \geqslant 0$. Define

$$S_{j,N}(t) = \int_0^t \mathrm{d}t' \sum_{k=1}^{N-j} R_{jk} c_{k,N}(t'),$$

$$\phi_{j,N}(t) = c_{j,N}(t) \exp[S_{j,N}(t)].$$

We obtain

$$\dot{\phi}_{j,N} = \tfrac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} \exp(S_{j,N} - S_{k,N} - S_{j-k,N}) \phi_{k,N} \phi_{j-k,N},$$

$$\phi_{j,N}(0) = c_j(0) \geqslant 0.$$

From this it follows clearly that $\phi_{j,N}(t) > 0$ for all $t > 0$ and all $j$. This means that

$$c_{j,N}(t) \geqslant 0 \qquad \text{for all } j \text{ and all } t \geqslant 0.$$

Together with (3.3) this means that

$$0 \leqslant c_{j,N}(t) \leqslant K/j.$$

Since we are dealing with a finite system, standard theorems on ordinary differential equations prove the lemma.

We now define two sequence spaces, which will play a major role in the following:

$$l_{1,1} = \left\{ (a_j)_{j=1}^{\infty} : \sum_{j=1}^{\infty} j|a_j| < \infty \right\}, \qquad l_{1,r} = \left\{ (a_j)_{j=1}^{\infty} : \sum_{j=1}^{\infty} r_j|a_j| < \infty \right\},$$

with the corresponding norms

$$\|(a_j)_{j=1}^{\infty}\|_{1,1} = \sum_{j=1}^{\infty} j|a_j|, \qquad \|(a_j)_{j=1}^{\infty}\|_{1,r} = \sum_{j=1}^{\infty} r_j|a_j|.$$

In the following, $\boldsymbol{a}$ denotes the sequence $(a_j)_{j=1}^{\infty}$.

*Lemma 2.* Let $(\boldsymbol{a}_N)_{N=1}^{\infty}$ be a bounded sequence of elements of $l_{1,1}$, i.e.

$$\|\boldsymbol{a}_N\|_{1,1} \leqslant K \qquad \text{for all } N.$$

Then there exists a sequence $N_i \to \infty$ and an element $\boldsymbol{a}$ of $l_{1,1}$ such that

$$\lim_{N_i \to \infty} \|\boldsymbol{a}_{N_i} - \boldsymbol{a}\|_{1,r} = 0.$$

*Proof.* Let $\boldsymbol{a}_N = (a_{j,N})_{j=1}^{\infty}$. Since $\|\boldsymbol{a}_N\|_{1,1} \leqslant K$, we have

$$|a_{j,N}| \leqslant K/j \qquad \text{for all } N \text{ and } j.$$

From this, it is standard (see e.g. Reed and Simon 1972, theorem I.24) that there is a sequence $N_i \to \infty$ such that

$$\lim_{N_i \to \infty} a_{j,N_i} = a_j$$

for all $j$. We now drop the subscript $i$. Let $\varepsilon > 0$ be arbitrary and $M$ such that

$$\max_{k \geq M} \frac{r_k}{k} \leq \varepsilon.$$

Choose now $N_0$ so large that

$$\max_{k=1}^{M} |a_{k,N} - a_k| \leq \frac{\varepsilon}{M \max_{k=1}^{M} r_k} \qquad \text{for all } N \geq N_0.$$

It follows that

$$\begin{aligned}\|\boldsymbol{a}_N - \boldsymbol{a}\|_{1,r} &= \sum_{j=1}^{\infty} r_j |a_{j,N} - a_j| \\ &= \sum_{j=1}^{M} r_j |a_{j,N} - a_j| + \sum_{j=M+1}^{\infty} r_j |a_{j,N} - a_j| \\ &\leq \varepsilon(1+2K)\end{aligned}$$

for all $N > N_0$, from which the convergence in the sense stated in the lemma follows. It follows that $\boldsymbol{a} \in l_{1,1}$ by a reasoning already used in the Introduction:

$$\sum_{j=1}^{\infty} j|a_j| \leq K - \lim_{M\to\infty} \lim_{N\to\infty} \sum_{j=M}^{N} j|a_{j,N}| < \infty.$$

The lemma is thus proved.

The example $\boldsymbol{a}_N = ((1/N)\delta_{jN})_{j=1}^{\infty}$ shows that although

$$\|\boldsymbol{a}_N\|_{1,1} \leq 1 \qquad \text{for all } N$$

there is no subsequence convergent in $l_{1,1}$.

*Lemma 3.* The functions $(c_{j,N}(t))_{N=1}^{\infty}$ are uniformly equicontinuous, i.e. for every $\varepsilon > 0$ there exists a $\delta$ depending only on $j$ such that for all $t$, $t'$ with

$$|t - t'| < \delta$$

we have

$$|c_{j,N}(t) - c_{j,N}(t')| < \varepsilon \qquad \text{for all } N.$$

*Proof.* By the mean value theorem, it is enough to prove that

$$|\dot{c}_{j,N}(t)| < A_j \qquad \text{for all } N \text{ and } t \geq 0.$$

This follows by

$$|\dot{c}_{j,N}(t)| \leq \frac{1}{2} \sum_{k=1}^{j-1} r_k r_{j-k} |c_{k,N} c_{j-k,N}| + \left(\sum_{k=1}^{N-j} r_k |c_{k,N}|\right) r_j |c_{j,N}| \leq K^2 \left(\frac{1}{2} \sum_{k=1}^{j-1} \frac{r_k r_{j-k}}{k(j-k)} + \max_{k=1}^{\infty} \frac{r_k}{k} \frac{r_j}{j}\right)$$

which proves the lemma.

We are now ready to prove:

*Result 1.* Let

$$\boldsymbol{c}_N(t) = (c_{1,N}(t), \ldots, c_{N,N}(t), 0, \ldots).$$

Then there exists a sequence $N_i \to \infty$ and an element $\boldsymbol{c}$ of $l_{1,1}$ such that

$$\lim_{N_i \to \infty} \|\boldsymbol{c}_{N_i}(t) - \boldsymbol{c}(t)\|_{1,r} = 0$$

for all $t \geqslant 0$.

*Proof.* Since the $c_{1,N}(t)$ are uniformly equicontinuous, it is possible by Ascoli's theorem (see e.g. Reed and Simon 1972, theorem I.28) to choose a sequence $N_{i,1} \to \infty$ such that

$$\lim_{N_{i,1} \to \infty} c_{1,N_{i,1}}(t) = c_i(t)$$

uniformly in a given finite time interval, say $[0, T]$. Again, this can be refined to a sequence $N_{i,2} \to \infty$ such that both $c_{2,N_{i,2}}$ converge. Again using a standard procedure, we take $N_i = N_{i,1}$ and obtain

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

for all $j$ and $t \geqslant 0$. Now we have

$$\|\boldsymbol{c}_{N_i}(t)\|_{1,1} \leqslant 1 \qquad \text{for all } t \geqslant 0.$$

We now claim that

$$\lim_{N_i \to \infty} \|\boldsymbol{c}_{N_i}(t) - \boldsymbol{c}(t)\|_{1,r} = 0$$

for all $t \geqslant 0$. Let us assume this to be wrong. Then for a given time $t_0$ it is possible to refine the sequence $N_i \to \infty$ so that

$$\lim_{N'_i \to \infty} \|\boldsymbol{c}_{N'_i}(t_0) - \boldsymbol{d}\|_{1,r} = 0, \qquad \boldsymbol{d} \neq \boldsymbol{c}(t_0),$$

and therefore

$$\lim_{N'_i \to \infty} c_{j,N'_i} = d_j \qquad \text{for all } j,$$

from which we obtain, since $N'_i$ is a refinement of $N_i$, that

$$d_j = c_j(t_0)$$

for all $j$. This is a contradiction and the statement is proved.

We now obtain:

*Result 2.* Let $\boldsymbol{c}(t)$ be (as described above) a limit of a subsequence of $(\boldsymbol{c}_N(t))_{N=1}^{\infty}$. The components satisfy

$$c_j(t) = c_j(0) + \int_0^t \mathrm{d}t' \left( \frac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} c_k c_{j-k} - c_j \sum_{k=1}^{\infty} R_{jk} c_k \right).$$

*Proof.* If we drop the subscript $i$ in the sequence $N_i \to \infty$, we obtain

$$\begin{aligned} c_j(t) &= \lim_{N \to \infty} c_{j,N}(t) \\ &= \lim_{N \to \infty} \left[ c_j(0) + \int_0^t \mathrm{d}t' \left( \frac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} c_{k,N} c_{j-k,N} - c_{j,N} \sum_{k=1}^{N-j} R_{jk} c_{k,N} \right) \right] \end{aligned}$$

$$= c_j(0) + \lim_{N\to\infty} \int_0^t \mathrm{d}t' \left( \frac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} c_{k,N} c_{j-k,N} - c_{j,N} \sum_{k=1}^{N-j} R_{jk} c_{k,N} \right). \tag{3.4}$$

Furthermore

$$\lim_{N\to\infty} \sum_{k=1}^{j-1} R_{k,j-k} c_{k,N} c_{j-k,N} = \sum_{k=1}^{j-1} R_{k,j-k} c_k c_{j-k}$$

as well as

$$\begin{aligned}\lim_{N\to\infty} \left| \sum_{k=1}^{N-j} R_{jk} c_{k,N} - \sum_{k=1}^{\infty} R_{jk} c_k \right| &\leq \lim_{N\to\infty} \left( \sum_{k=1}^{N-j} R_{jk} |c_{k,N} - c_k| + \sum_{k=N-j+1}^{\infty} R_{jk} c_k \right) \\ &\leq r_j \lim_{N\to\infty} \|\mathbf{c}_N - \mathbf{c}\|_{1,r} + \lim_{N\to\infty} \sum_{k=N-j+1}^{\infty} R_{jk} c_k \\ &\leq r_j \lim_{N\to\infty} \max_{k>N-j} \frac{r_k}{k} \|\mathbf{c}\|_{1,1} = 0.\end{aligned}$$

Therefore

$$\lim_{N\to\infty} \sum_{k=1}^{N-j} R_{jk} c_{k,N} = \sum_{k=1}^{\infty} R_{jk} c_k.$$

It is further clear that the whole integrand is uniformly bounded in $N$ and $t$. Since we integrate only over a finite interval, we can interchange limit and integration, thereby proving the result.

*Result 3.* $c_j(t)$ is continuously differentiable for all $t \geq 0$ and satisfies

$$\dot{c}_j = \tfrac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} c_k c_{j-k} - c_j \sum_{k=1}^{\infty} R_{jk} c_k \tag{3.5}$$

and $\Sigma_{j=1}^{\infty} j c_j(t) \leq 1$ and is non-increasing for all $t \geq 0$.

*Proof.* In order to prove (3.5), it is sufficient, by result 2, to prove that the right-hand side of (3.5) is continuous in $t$. Since on any finite interval, $c_j(t)$ is the uniform limit of $(c_{j,N}(t))_{N=1}^{\infty}$ and since the $c_{j,N}(t)$ are continuous, so are the $c_j(t)$. Furthermore

$$\left| \sum_{k=1}^{N} R_{jk} c_k - \sum_{k=1}^{\infty} R_{jk} c_k \right| = \left| \sum_{k=N+1}^{\infty} R_{jk} c_1 \right| \leq r_j \left| \sum_{k=N+1}^{\infty} r_k c_k \right| \leq r_j \max_{k>N} \frac{r_k}{k} \|\mathbf{c}\|_{1,1}.$$

This shows that the functions

$$\sum_{k=1}^{N} R_{jk} c_k,$$

which are clearly continuous, converge uniformly to the infinite sum, which is therefore also continuous. This proves (3.5) and the continuity of its right-hand side.

To show that $\Sigma_{j=1}^{\infty} j c_j(t)$ is non-increasing, note that

$$\sum_{j=1}^{N} j \dot{c}_j = - \sum_{k=1}^{N} \sum_{l=N-k+1}^{\infty} k R_{kl} c_k c_l \leq 0,$$

that is, it is non-increasing. Since, however, we have

$$\lim_{N\to\infty} \sum_{j=1}^{N} jc_j(t) = \sum_{j=1}^{\infty} jc_j(t) \leq 1$$

the whole result is proved.

We have actually proved more than what is stated in the theorem: for example, given an arbitrary subsequence $(\boldsymbol{c}_{N_i}(t))_{N_i=1}^{\infty}$ of solutions of the finite system, we can clearly refine it so that it converges to a solution of the infinite system. This implies the different connections, stated in the Introduction, between the uniqueness problem for the infinite system and the convergence problem for $(\boldsymbol{c}_N(t))_{N=1}^{\infty}$.

The theorem can also be extended in a straightforward way to the more general dynamics:

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

$$c_j(0) \geq 0, \qquad \sum_{j=1}^{\infty} jc_j(0) = 1,$$

where $P(x, y)$ is an arbitrary function of two positive variables, such that
(i) $P(x, y) = P(y, x) \geq 0$ for all $x$, $y$ smaller than one;
(ii) $P(x, y) \leq Cxy$ for some $C > 0$;
(iii) $P$ is continuous.
A simple example is provided by

$$P(x, y) = (xy)^{\rho} \qquad (\rho > 1).$$

## Appendix

We here wish to prove the following:

*Theorem.* Let $(r_k)_{k=1}^{\infty}$ be an arbitrary sequence of positive numbers such that

$$\lim_{k\to\infty} \frac{r_k}{\sqrt{k}} = 0.$$

Then there exist sequences $(A_n)_{n=1}^{\infty}$, $(B_n)_{n=1}^{\infty}$ such that
(i) $r_k \leq A_n k + B_n$ for all $k$ and all $n$;
(ii) $\lim_{n\to\infty} A_n(A_n + B_n) = 0$.

*Proof.* Let $\varepsilon > 0$ be arbitrary. Choose $N(\varepsilon)$ such that

$$r_k \leq \varepsilon\sqrt{k} \qquad \text{for all } k \geq N(\varepsilon).$$

Consider now the points $(M, \varepsilon M^{1/2})$ and $(M+1, \varepsilon(M+1)^{1/2})$. Since the square root is a concave function, it follows that the straight line joining these two points lies above all points $(k, \varepsilon k^{1/2})$. This means that

$$\varepsilon k^{1/2} \leq \alpha_M k + \beta_M$$

where

$$\alpha_M = \varepsilon((M+1)^{1/2} - M^{1/2}), \qquad \beta_M = \varepsilon((M+1)M^{1/2} - M(M+1)^{1/2}).$$

It is easy to see that

$$\beta_M = \tfrac{1}{2}M^{1/2} + O(M^{-1/2}), \qquad \alpha_M(\alpha_M + \beta_M) = \tfrac{1}{4}\varepsilon^2 + O(M^{-1}).$$

Keeping $\varepsilon$ fixed, it is then clearly possible to choose $M(\varepsilon)$ such that

$$\max_{l=1}^{N(\varepsilon)} r_k \leqslant \beta_{M(\varepsilon)} \leqslant \alpha_{M(\varepsilon)}k + \beta_{M(\varepsilon)}.$$

But we have for all $k \geqslant N(\varepsilon)$

$$r_k \leqslant \varepsilon k^{1/2} \leqslant \alpha_{M(\varepsilon)}k + \beta_{M(\varepsilon)}$$

and from the two last inequalities it follows that

$$r_k \leqslant \alpha_{M(\varepsilon)}k + \beta_{M(\varepsilon)}$$

for all $k$. Now take

$$A_n = \alpha_{M(1/n)} \qquad B_n = \beta_{M(1/n)}.$$

The first part of the theorem follows by construction. Furthermore, since the numbers $M(\varepsilon)$ can always be chosen so as to satisfy

$$\lim_{\varepsilon \to 0} M(\varepsilon) = \infty$$

we obtain

$$\lim_{n\to\infty} A_n(A_n + B_n) = \lim_{n\to\infty} \left\{ \frac{1}{4n^2} + O\left[ M\left(\frac{1}{n}\right)^{-1} \right] \right\} = 0.$$

Since $A_n(A_n + B_n)$ is the inverse gelation time for $r_k = A_n k + B_n$, the theorem shows $r_k$ can be dominated by coefficients leading to arbitrarily large gelation times. This proves the conjecture.

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