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# On the possible occurrence of instantaneous gelation in Smoluchowski's coagulation equation

P G J van Dongen

Institute for Theoretical Physics, Princetonplein 5, PO Box 80 006, 3508 TA Utrecht, The Netherlands

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**Abstract.** We consider possible solutions of Smoluchowski's coagulation equation if the rate constants $K(i,j)$ behave as $K(i,j) \sim i^\mu j^\nu$ as $j \to \infty$, with an exponent $\nu$ satisfying $\nu > 1$. We find that, for such rate constants, Smoluchowski's equation predicts the instantaneous occurrence of a gelation transition. Thus the gel time $t_c = 0$ in such models. This result confirms recent speculation in the literature. We also study the structure of post-gel solutions of Smoluchowski's equation, if they exist. For a given value of $\nu$, the results depend on the value of the exponent $\mu$. If $\mu > (\nu - 1)$, one finds that the cluster size distribution $c_k(t)$ approaches a universal form at large times $(t \to \infty)$. No solutions exist if $\mu \leqslant (\nu - 1)$. Physically this means that the sol phase is depleted instantaneously.

## 1. Introduction

The purpose of this paper is to show that Smoluchowski's coagulation equation predicts the occurrence of a gelation transition within infinitesimal time for certain classes of rate constants. This result confirms recent speculation, based on analytical indications (Hendriks *et al* 1982, Ziff 1984) and Monte Carlo simulations (Domilovskii *et al* 1978, Spouge 1985).

Smoluchowski's coagulation equation (for a review see Drake 1972 or Ernst 1986) is an infinite set of chemical rate equations for the cluster size distribution, i.e. for the concentrations $c_k(t)$ of clusters of size $k$, or $k$-mers $(k = 1, 2, \ldots)$. If the rate constant for the reaction of an $i$- and $j$-mer is given by $K(i,j)$, then Smoluchowski's equation has the following form:

$$\dot{c}_k(t) = \tfrac{1}{2} \sum_{i+j=k} K(i,j) c_i(t) c_j(t) - c_k(t) \sum_{j=1}^{\infty} K(k,j) c_j(t). \tag{1.1}$$

The gain and loss term on the right describe the formation of $k$-mers out of smaller clusters and the loss of $k$-mers due to reactions with other polymers respectively.

In recent years it has been noticed, e.g. by Lushnikov (1977a, b) and, more recently, by Ziff (1980), that, for certain choices of the rate constants, Smoluchowski's equation predicts the occurrence of a gelation transition at a finite time $t_c$ (gel point). The gel point $t_c$ is marked by a divergence of the mean cluster size and by the onset of a mass flux from the finite-size clusters (sol particles) towards the clusters of infinite size or gel.

The mass flux from the sol to the gel phase may be calculated as follows. Multiplication of equation (1.1) with $k$ and summation over all $k \leqslant L$ gives an equation for the mass flux $J(L, t)$ from clusters of size $k \leqslant L$ to clusters larger than $L$:

$$J(L, t) \equiv -\sum_{k=1}^{L} k\dot{c}_k = \sum_{i=1}^{L} \sum_{j=L-i+1}^{\infty} iK(i, j)c_i c_j. \tag{1.2}$$

The flux towards the infinite clusters, i.e. the rate of gel formation, as is seen for instance in the exactly solvable model $K(i, j) = ij$ (Ziff *et al* 1983), takes place as follows. In the pre-gel stage ($t < t_c$), where the mean cluster size is finite and large clusters are relatively rare, one finds that the mass flux $J(L, t)$ vanishes as $L \to \infty$, i.e. $J(\infty, t) = 0$. It follows that for $t < t_c$ the sol mass is conserved ($\Sigma\, k\dot{c}_k = 0$) and is equal to the total mass $M$ per unit volume:

$$M(t) \equiv \sum_{k=1}^{\infty} kc_k(t) = M = 1. \tag{1.3}$$

The constant $M$ may be set equal to unity by an appropriate choice of the unit of volume. At the gel point $t_c$, and in general for all $t \geqslant t_c$, $c_k(t)$ falls off algebraically, in such a way that $J(L, t)$ approaches a finite, non-vanishing limit as $L \to \infty$. Thus, for $t \geqslant t_c$, there exists a non-vanishing mass flux $J(\infty, t) = -\dot{M}(t)$ from the sol to the gel phase and the conservation law (1.3) is replaced by

$$M(t) + G(t) = 1 \tag{1.4}$$

where $G(t)$ represents the mass of the gel.

The possible occurrrence of a gelation transition within a finite time $t_c$ has been demonstrated for various special choices of the rate constants $K(i, j)$ (see e.g. Hendriks *et al* 1982, Leyvraz and Tschudi 1983, Leyvraz 1983), and in general for homogeneous kernels $K(ai, aj) = a^{\lambda}K(i, j)$ if the degree of homogeneity satisfies $\lambda > 1$ (van Dongen and Ernst 1985a, b, 1986a, b). White (1980) has shown that gelation does not occur if $K(i, j) \leqslant (i + j)$ for all $i$ and $j$.

Various authors have speculated that for certain forms of the reaction rates gelation may take place instantaneously ($t_c = 0$). Analytical arguments supporting this view have been given by Hendriks *et al* and by Ziff (1984). For rate contants $K(i, j) = (ij)^2$ and monodisperse initial conditions, $c_k(0) = \delta_{k1}$ these authors consider the moments $M_\alpha(t) \equiv \Sigma_{k=1}^{\infty} j^\alpha c_k(t)$ of the cluster size distribution. The second moment $M_2(t)$ is then expanded in a Taylor series about $t = 0$ and the coefficients are calculated from the moment equations for $M_\alpha(t)$. Numerically this series appears to be divergent for all $t > 0$, and one concludes that 'the possibility remains that no pre-gelation solutions exist for the kernels $K(i, j) = (ij)^\omega$ with $\omega > 1$' (Hendriks *et al* 1982). Similar conclusions hold for $K(i, j) = i^\omega + j^\omega$ with $\omega > 1$.

Different evidence, supporting the possible occurrence of an instantaneous gelation transition, comes from Monte Carlo simulations of random coagulation processes. Domilovskii *et al* (1978) investigate the behaviour of a finite system, starting from monodisperse initial conditions, with $K(i, j) = (ij)^3$. They find that their estimate of the gel time tends to zero as the system size is increased. Similarly, Spouge (1985) considers coagulation processes with $K(i, j) = (ij)^\omega$ and $\omega > 1$, and he gives as a first conjecture that in such models gelation occurs instantaneously.

This paper addresses the question of existence of instantaneous gelation in Smoluchowski's equation for certain choices of the rate constants. In order to simplify the discussion, we restrict ourselves to kernels $K(i, j)$ that are homogeneous functions of the cluster sizes $i$ and $j$ and we introduce exponents $\mu$ and $\nu$ to specify the behaviour of $K(i,j)$ for $j \gg i$:

$$K(ai, aj) = a^{\lambda} K(i,j) = a^{\lambda} K(j, i) \tag{1.5a}$$

$$K(i,j) \sim i^{\mu} j^{\nu} \qquad j \to \infty,\ i \text{ fixed};\ \lambda = \mu + \nu. \tag{1.5b}$$

On account of the restrictions (1.5$a$) and (1.5$b$) imposed on $K(i,j)$, we may introduce a new function $K^{(0)}(i,j)$, as follows:

$$K(i,j) \equiv (ij)^{\mu}(i+j)^{\nu-\mu} K^{(0)}(i,j). \tag{1.6}$$

The kernel $K^{(0)}(i,j)$ has zero degree of homogeneity, $K^{(0)}(ai, aj) = K^{(0)}(i,j)$. Moreover, it follows from (1.5$b$) that $K^{(0)}(i,j) \to 1$ as $i/j \to \infty$ or 0. We assume that $K^{(0)}(i,j)$ is a continuous, non-vanishing function of $i$ and $j$, such that for some positive constant $K_1$:

$$K^{(0)}(i,j) \geq K_1 > 0 \qquad i,j = 1, 2, \ldots. \tag{1.7}$$

Some of our results will be valid also for non-homogeneous kernels, as will be discussed in § 4.

The main result of this paper is that instantaneous gelation occurs if and only if the exponent $\nu$, defined in (1.5$b$), satisfies $\nu > 1$. Instantaneous gelation will certainly not occur if $\nu \leq 1$. For homogeneous kernels with $\nu \leq 1$ and $\lambda \leq 1$ it follows from White's theorem (White 1980) that gelation does not occur. Alternatively, if $\nu \leq 1$ and $\lambda > 1$, gelation may occur, but there exists a non-vanishing lower bound on the gel time, implying that $t_c > 0$ (van Dongen and Ernst 1986a). Since we are interested in the possible occurrence of instantaneous gelation, therefore, we consider only kernels $K(i,j)$ with an exponent $\nu > 1$.

It must be remarked that in physical systems, coagulation kernels with $\nu > 1$ do not occur. The reason is that the number of active sites on a cluster cannot increase faster than its size, i.e. that $K(i,j)/j$ is bounded as $j \to \infty$. In the literature, certain homogeneous kernels with $\nu > 1$ have been quoted as a model for physical systems. For instance, Domilovskii *et al* claim that gradient coagulation in a turbulent stream is described by the following kernel:

$$K(i,j) = (i^{1/3} + j^{1/3})^2 |i^{2/3} - j^{2/3}|. \tag{1.8a}$$

Secondly, Ziff (1980) quotes the following model for gravitationally attracting randomly distributed particles with a Maxwellian velocity distribution:

$$K(i,j) = (ij)^{1/2}(i+j)^{1/2}(i^{1/3} + j^{1/3}). \tag{1.8b}$$

Both kernels (1.8$a$) and (1.8$b$) have an exponent $\nu = \frac{4}{3} > 1$. In view of the above argument that $K(i,j)/j$ should be bounded as $j \to \infty$, such models cannot be considered as physically acceptable coagulation kernels.

Our results are of interest for the following reasons. Firstly, they provide an answer to speculations in the literature about the possible occurrence of instantaneous gelation in Smoluchowski's equation. Secondly, they reveal the structure of solutions of equation (1.1) for general homogeneous kernels with $\nu > 1$. Finally, our present results for $\nu > 1$, in combination with the results of van Dongen and Ernst (1985a, b, 1986a, b) for $\nu \leq 1$, show that Smoluchowski's equation for different rate constants may describe three types of coagulating systems: (i) non-gelling systems ($t_c = \infty$) if $\nu \leq 1$ and $\lambda \leq 1$, (ii) gelling systems with $0 < t_c < \infty$ if $\nu \leq 1$ and $\lambda > 1$, and (iii) systems showing instantaneous gelation ($t_c = 0$) if $\nu > 1$. Thus our results for $\nu > 1$ complement the previous work for $\nu \leq 1$.

The layout of this paper is as follows. In § 2 we show for homogeneous reaction rates with $\nu > 1$ that pre-gel solutions of equation (1.1) do not exist, i.e. that such rate constants lead to gelation within infinitesimal time ($t_c = 0$). Next we investigate the structure of possible post-gel solutions of equation (1.1). This is done in § 3. Finally we discuss our results (§ 4).

## 2. Instantaneous gelation

In this section we show that Smoluchowski's equation predicts an instantaneous gelation transition ($t_c = 0$), if the reactivity of relatively large clusters increases faster than their size ($\nu > 1$). This is done as follows. In order to show that there exist no solutions of equation (1.1) that conserve the sol mass, we assume the opposite ($t_c > 0$) and we derive a contradiction. More precisely, we assume that, for some initial distribution $c_k(0) \geq 0$, with $\Sigma\, kc_k(0) = 1$, and some time interval $0 \leq t < t_c$, there exists a (continuously differentiable) solution $c_k(t)$ of Smoluchowski's equation, with the property that the sol mass is conserved: $M(t) = 1$ for all $t < t_c$.

An important tool in our arguments are the moments $M_\alpha(t)$ of the cluster size distribution, which are defined by

$$M_\alpha(t) \equiv \sum_{k=1}^{\infty} k^\alpha c_k(t). \tag{2.1}$$

The time dependence of $M_\alpha(t)$ is described by the moment equations, which may be derived from equation (1.1) if both sides are multiplied by $k^\alpha$ and summed over all $k$:

$$\dot{M}_\alpha(t) = \tfrac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} K(i,j) c_i(t) c_j(t)[(i+j)^\alpha - i^\alpha - j^\alpha]. \tag{2.2}$$

In the derivation of equation (2.2) it is assumed that $c_k(t)$ falls off sufficiently fast as $k \to \infty$, such that all moments $M_\alpha(t)$ are finite. If this condition is not fulfilled, then (2.2) may not be valid for all values of $\alpha$. This point is also discussed in § 4.

This section is organised as follows. First we show (§ 2.1) that the assumed conservation of sol mass for $0 \leq t < t_c$ implies that, during this time interval, $c_k(t)$ is exponentially bounded as $k \to \infty$. It follows that all moments $M_\alpha(t)$ are finite, so that the moment equations (2.2) are valid for all $\alpha < \infty$ and all $t < t_c$. In § 2.2 we show that at any fixed time $t > 0$, the moment equations predict a divergence of some of the moments $M_\alpha(t)$, which is a contradiction. The conclusion is that the basic assumption, that sol mass conserving solutions exist for some time interval $0 \leq t < t_c$, is incorrect.

### *2.1. Finiteness of all moments ($0 \leq t < t_c$)*

In order to show that the cluster size distribution $c_k(t)$ is exponentially bounded as $k \to \infty$, we derive first an upper bound for the mass $M^{(k)}(t)$ contained in clusters of size $j \geq k$,

$$M^{(k)}(t) \equiv \sum_{j=k}^{\infty} jc_j(t). \tag{2.3}$$

It then follows from (2.3) that $c_k(t)$ is bounded by

$$c_k(t) \leqslant k^{-1} \sum_{j=k}^{\infty} jc_j(t) \tag{2.4}$$

which gives us the desired result.

Before deriving an inequality for $M^{(k)}(t)$, we remark that in (2.4) it has been tacitly assumed that $c_k(t) \geqslant 0$ for all $k$ and for all $t < t_c$, i.e. that solutions of Smoluchowski's equation conserve positivity. Physically this is obvious. Mathematically it may be seen as follows. If we define

$$\sigma_i(t) \equiv \sum_{j=1}^{\infty} K(i,j)c_j(t) \tag{2.5a}$$

$$S_i(t) \equiv \int_0^t \mathrm{d}t' \, \sigma_i(t') \tag{2.5b}$$

then equation (1.1) may be formally integrated to yield

$$c_k(t) = \exp[-S_k(t)]\left( c_k(0) + \tfrac{1}{2} \sum_{i+j=k} K(i,j) \int_0^t \mathrm{d}t' \, c_i(t')c_j(t') \exp[S_k(t')] \right). \tag{2.6}$$

Since we assume that $c_k(0) \geqslant 0$, it may readily be proved by induction that all factors on the right of (2.6) are non-negative, i.e. that for all $t < t_c$, $c_k(t) \geqslant 0$.

The desired inequality for $M^{(k)}(t)$ may now be obtained from Smoluchowski's equation in the form (1.2). The assumption that for $t < t_c$ the sol mass is conserved, $\Sigma \, k\dot{c}_k = 0$, implies in combination with (1.2):

$$\dot{M}^{(k)}(t) = J(k-1, t) = \sum_{i=1}^{k-1} \sum_{j=k-i}^{\infty} iK(i,j)c_ic_j. \tag{2.7}$$

The right-hand side of equation (2.7) may be estimated as follows. Since we have not specified the initial distribution $c_k(0)$, it may happen that some of the smaller polymers do not occur in the system. Let us assume that $c_j(0) = 0$ for $1 \leqslant j \leqslant l-1$, but $c_l(0) > 0$. Since $K(l,j) \sim l^\mu j^\nu$ if $j \gg l$, on account of (1.5$b$), there must be some finite constant $k_0 \geqslant l+1$, such that for all $j \geqslant k_0$:

$$K(l,j) \geqslant \tfrac{1}{2} l^\mu j^\nu \qquad \text{all}\, j \geqslant k_0. \tag{2.8}$$

Substitution of (2.8) into equation (2.7) shows that for $k \geqslant k_0$:

$$\begin{aligned} \dot{M}^{(k)}(t) &\geqslant \tfrac{1}{2} l^{1+\mu} c_l(t) \left( \sum_{j=k}^{\infty} j^\nu c_j \right) \\ &\geqslant a_l c_l(t) k^{\nu-1} M^{(k)}(t) \qquad k \geqslant k_0 \end{aligned} \tag{2.9}$$

with $a_l \equiv \frac{1}{2} l^{1+\mu}$. We have used that $j^\nu \geqslant k^{\nu-1} j$ if $j \geqslant k$.

Straightforward integration of equation (2.9) from time $t$ to $t_c$ yields the following inequality for $M^{(k)}(t)$:

$$\begin{aligned} M^{(k)}(t) &\leqslant M^{(k)}(t_c) \exp\left( -a_l k^{\nu-1} \int_t^{t_c} \mathrm{d}t' \, c_l(t') \right) \\ &\leqslant \exp\left( -a_l k^{\nu-1} \int_t^{t_c} \mathrm{d}t' \, c_l(t') \right) \qquad k \geqslant k_0. \end{aligned} \tag{2.10}$$

In the last step of (2.10) we have used that $M^{(k)}(t_c)$ is bounded from above by unity, i.e.

$$M^{(k)}(t_c) \equiv \lim_{t\uparrow t_c} M^{(k)}(t) \leq \lim_{t\uparrow t_c} M(t) = 1. \tag{2.11}$$

The notation $t\uparrow t_c$ indicates that in the limit $t\to t_c$, the gel point $t_c$ is approached from *below*.

Equations (2.10) and (2.4) have, as an immediate consequence, that for all $t<t_c$, $c_k(t)$ is bounded by the following exponential:

$$c_k(t) \leq k^{-1} \exp\left(-a_l k^{\nu-1} \int_t^{t_c} \mathrm{d}t'\, c_l(t')\right) \qquad k \geq k_0. \tag{2.12}$$

It follows that, for $t<t_c$, all moments $M_\alpha(t)$ are finite, and hence that the moment equations (2.2) are valid.

We add the following remark. In order that (2.12) sets an exponential bound to $c_k(t)$ for all $t<t_c$, it is essential that the $l$-mer concentration $c_l(t)$ is non-vanishing ($0\leq t<t_c$). To see that this is the case, consider equations (2.5$a$) and (2.5$b$). The existence of a well defined solution $c_k(t)$ of equation (1.1) requires that the integrals $S_i(t)$ are finite for all $t<t_c$ and all $i=1,2,\ldots$. Thus we infer from equation (1.1) for $k=l$ that $c_l(t)$ is indeed non-vanishing for $t<t_c$:

$$c_l(t) = c_l(0)\exp[-S_l(t)] > 0 \qquad 0\leq t<t_c. \tag{2.13}$$

In the derivation of (2.13) we have used the initial condition $c_j(0)=0$ ($j\leq l-1$).

### 2.2. *Instantaneous divergence of some moments ($t_c=0$)*

In this section we use the moment equations (2.2) for integer values of $\alpha$,

$$\begin{aligned}\dot{M}_n &= \tfrac{1}{2}\sum_{i,j} K(i,j)c_ic_j[(i+j)^n - i^n - j^n] \\ &= \tfrac{1}{2}\sum_{l=1}^{n-1}\binom{n}{l}\left(\sum_{i,j} K(i,j) i^l j^{n-l} c_i c_j\right) \qquad n=1,2,\ldots\end{aligned} \tag{2.14}$$

to obtain a lower bound $m_n(t)$ for the moment $M_n(t)$. We find that the lower bound diverges at some finite time $t_n>0$, with $t_n\to 0$ as $n\to\infty$. Since all moments $M_n(t)$ are finite for $t<t_c$, clearly $t_n$ sets an upper bound to the gel time $t_c$, i.e. $t_c\leq t_n$ for all values of $n$. The fact that $t_n$ vanishes as $n\to\infty$ then shows that $t_c=0$.

As a first step, we calculate a lower bound for the reaction rates $K(i,j)$ in (2.14). We distinguish kernels with $\mu\geq\nu$ and kernels with $\mu<\nu$. If $\mu\geq\nu$, the requirement (1.7) that $K^{(0)}(i,j)$ is bounded from below implies, in combination with (1.6),

$$K(i,j) \geq K_1(ij)^\mu (i+j)^{\nu-\mu} \geq 2^{\nu-\mu} K_1(ij)^\nu \qquad \mu\geq\nu \tag{2.15$a$}$$

where we have used that $(i+j)\leq 2ij$ for all $i,j=1,2,\ldots$. Alternatively, if $\mu<\nu$, $K(i,j)$ is bounded from below by

$$K(i,j) \geq K_1(ij)^\mu (i+j)^{\nu-\mu} \geq K_2(ij)^\mu (i^{\nu-\mu} + j^{\nu-\mu}) \qquad \mu\leq\nu \tag{2.15$b$}$$

where we have introduced

$$K_2 \equiv K_1(\max\{1, 2^{1-\nu+\mu}\})^{-1}. \tag{2.16$a$}$$

Combination of equations (2.15$a$) and (2.15$b$) yields an expression for $K(i,j)$, valid for all values of $\mu$ and $\nu$:

$$K(i,j) \geq K_2(i^\beta j^\nu + j^\beta i^\nu) \tag{2.16b}$$

where $\beta \equiv \min\{\mu, \nu\}$ and $K_2$ has been defined in (2.16$a$).

Substitution of the lower bound (2.16$a$) and (2.16$b$) into the moment equations (2.14) gives an inequality in terms of moments only:

$$\dot{M}_n \geq K_2 \sum_{l=1}^{n-1} \binom{n}{l} M_{n-l+\nu} M_{l+\beta}. \tag{2.17}$$

The next approximation is that we take into account only the terms for $l = 1$ and $l = 2$. If, moreover, we use that $M_{2+\beta} \geq M_{1+\beta}$, it follows from (2.17) for $n \geq 3$ that

$$\dot{M}_n \geq K_2 M_{1+\beta}[nM_{n+\nu-1} + \tfrac{1}{2}n(n-1)M_{n+\nu-2}] \qquad n \geq 3. \tag{2.18}$$

Since, according to § 2.1, $M_{1+\beta}(t)$ is finite for $0 \leq t < t_c$, we may transform to a new time variable $\tau(t)$, which is defined by

$$\tau(t) = K_2 \int_0^t \mathrm{d}t' \, M_{1+\beta}(t'). \tag{2.19}$$

The result is

$$\mathrm{d}M_n/\mathrm{d}\tau \geq nM_{n+\nu-1} + \tfrac{1}{2}n(n-1)M_{n+\nu-2} \qquad n \geq 3. \tag{2.20}$$

A convenient starting point for further calculations is obtained if, in (2.20), we reorganise the terms on the right, as follows:

$$\mathrm{d}M_n/\mathrm{d}\tau \geq \tfrac{1}{2}nM_{n+\nu-1} + \tfrac{1}{2}n \sum_{k=1}^{\infty} k^n b_n(k) c_k \qquad n \geq 3 \tag{2.21a}$$

$$b_n(k) \equiv k^{\nu-1} + (n-1)k^{\nu-2}. \tag{2.21b}$$

Thus the second term on the right in (2.21$a$) is a linear combination of both terms in the RHS of (2.20).

In order to obtain an equation in terms of $M_n(\tau)$ only, we use Jensen's inequality to estimate the first term in the RHS of (2.21$a$). If we define the average value of some function $A(k)$ of the cluster size $k$ by

$$E[A(k)] \equiv \sum_{k=1}^{\infty} kA(k)c_k \tag{2.22a}$$

then Jensen's inequality (see e.g. Gradshteyn and Ryzhik 1980) states that for any non-negative function $f(k)$ and any convex function $\phi(x)$ it holds that

$$E[\phi(f(k))] \geq \phi(E[f(k)]). \tag{2.22b}$$

As an immediate consequence we have

$$M_{n+\nu-1} = E[\phi(k^{n-1})] \geq \phi(E[k^{n-1}]) = \phi(M_n) \tag{2.23}$$

provided that we choose $\phi(x) = x^{(n+\nu-2)/(n-1)}$. This choice for $\phi(x)$ is clearly convex, since $\nu > 1$.

The second term on the right in (2.21$a$) may also be expressed in $M_n(\tau)$, as follows. If $\nu \geqslant 2$, then $b_n(k)$ attains a minimum for $k=1$, i.e. $b_n(k) \geqslant b_n \equiv n$. Alternatively, for $1<\nu<2$, the factor $b_n(k)$ diverges for small and for large values of $k$, and has a unique minimum $b_n=(k_0)^{\nu-1}/(2-\nu)$ at $k_0=(2-\nu)(n-1)/(\nu-1)$. Thus, for all values of $\nu>1$, the function $b_n(k)$ is bounded from below by some constant $b_n$,

$$b_n(k) \geqslant b_n \qquad \text{all } k=1,2,\ldots \tag{2.24$a$}$$

and the behaviour of the lower bound $b_n$ for large values of $n$ is given by

$$\begin{aligned} b_n &= n && \nu \geqslant 2 \\ b_n &\propto n^{\nu-1} && 1<\nu<2;\ n\to\infty. \end{aligned} \tag{2.24$b$}$$

Substitution into (2.21$a$) of the inequalities (2.23) and (2.24$a$) finally gives an equation in terms of $M_n(\tau)$ only:

$$\mathrm{d}M_n/\mathrm{d}\tau \geqslant \tfrac{1}{2}n(M_n)^{(n+\nu-2)/(n-1)}+\tfrac{1}{2}nb_nM_n \qquad n\geqslant 3. \tag{2.25}$$

Equation (2.25) is to be solved for general initial conditions $M_n(0)$.

The lower bound on $M_n(\tau)$ is determined as follows. Consider the function $m_n(\tau)$ which is defined as the solution of (2.25) if the equal sign holds, i.e.

$$\mathrm{d}m_n/\mathrm{d}\tau = \tfrac{1}{2}n(m_n)^{(n+\nu-2)/(n-1)}+\tfrac{1}{2}nb_nm_n \qquad m_n(0)=M_n(0). \tag{2.26}$$

Since the right-hand side of equation (2.25) is strictly positive for all $\tau<\tau_c \equiv \tau(t_c)$, it follows that

$$M_n(\tau) \geqslant m_n(\tau) \qquad 0 \leqslant \tau < \tau_c \tag{2.27}$$

i.e. $m_n(\tau)$ sets a lower bound to $M_n(\tau)$. The differential equation (2.26) for $m_n(\tau)$ is a special case of Bernoulli's differential equation (see e.g. Ince 1956). The method of solution is standard. We give only the result:

$$m_n(\tau)=\exp(nb_n\tau/2)\{M_n(0)^{-\gamma}-[\exp(\gamma nb_n\tau/2)-1]/b_n\}^{-1/\gamma} \tag{2.28}$$

where the exponent $\gamma$ is defined as $\gamma=(\nu-1)/(n-1)$.

It follows from (2.27), in combination with (2.28), that $M_n(\tau)$ diverges at, or before, the time $\tau_n$, which is given by

$$\tau_n=(\gamma nb_n/2)^{-1}\log(1+b_nM_n(0)^{-\gamma}). \tag{2.29}$$

Since all moments $M_n(\tau)$ are finite for $\tau<\tau_c$, clearly $\tau_n$ sets an upper bound to $\tau_c$. An upper bound on $\tau_c$ independent of the initial conditions $M_n(0)$ is obtained if we use that for $n\geqslant 3$, $M_n(0)\geqslant 1$, or $M_n(0)^{-\gamma}\leqslant 1$.

The result is

$$\tau_c \leqslant \tau_n \leqslant (\gamma nb_n/2)^{-1}\log(1+b_n)\to 0 \qquad n\to\infty. \tag{2.30}$$

The right-hand side of (2.30) vanishes as $n\to\infty$ on account of the definition of $\gamma$. This implies that $\tau_c=0$ or $t_c=0$ contradicting the assumption $t_c>0$ at the beginning of this section. We conclude that for $\nu>1$, pre-gel solutions of Smoluchowski's equation do not exist. Physically this means that, irrespective of the initial condition, gelation occurs instantaneously.

## 3. Post-gel solutions

We discuss briefly the structure of (post-gel) solutions of Smoluchowski's equation for homogeneous coagulation kernels with $\nu > 1$. We remark that, since $t_c = 0$ for such models, the epithet 'post-gel' is superfluous and will be dropped from now on. Within the class of models with $\nu > 1$, exact solutions for general initial conditions are, to our knowledge, unknown. For this reason, our method will rest essentially on exact solutions for special initial conditions and on self-consistency arguments.

First we recall the result of Hendriks *et al* (1982) and of van Dongen and Ernst (1985b), that for all gelling models with $\nu \leqslant 1$, and also for a special case with $\nu > 1$, namely, $K(i, j) = (ij)^2$, Smoluchowski's equation allows an exact post-gel solution of the form

$$c_k(t) = c_1(t) b_k \qquad t \geqslant t_c \tag{3.1a}$$

where $b_k$ is constant and $c_1(t)$ falls off algebraically as $t \to \infty$. More precisely,

$$c_1(t) = c_1(t_c)/[1 + b(t - t_c)]. \tag{3.1b}$$

The parameter $b$ in (3.1$b$) may be determined through substitution of (3.1) into equation (1.1) for $k = 1$. The result is $b = c_1(t_c) E_1$, where in general $E_k$ is defined as

$$E_k \equiv \sum_{j=1}^{\infty} K(k, j) b_j. \tag{3.2}$$

The solution (3.1) is consistent only if $E_k < \infty$ for all $k$. Furthermore, substitution of (3.1) into Smoluchowski's equation in the form (1.2) shows that the factors $b_k$ satisfy the following equation for all $k \geqslant 2$:

$$E_1 \sum_{j=1}^{k} j b_j = \sum_{i=1}^{k} \sum_{j=k-i+1}^{\infty} i K(i, j) b_i b_j \tag{3.3}$$

which is to be solved with the initial condition $b_1 = 1$.

In order to determine whether solutions of the form (3.1$a$) and (3.1$b$) are allowed also for $\nu > 1$, we calculate the asymptotic behaviour of the solution $b_k$ of (3.3). Following the method of van Dongen and Ernst (1985b), we assume that the asymptotic behaviour of $b_k$ is of the form

$$b_k \sim B k^{-\tau} \qquad k \to \infty. \tag{3.4}$$

The requirement that at $t_c = 0$, the sol mass is finite, i.e. $M(0) = c_1(0) \sum_{j=1}^{\infty} j b_j = 1$ implies that, necessarily, $\tau > 2$. Substitution of the ansatz (3.4) into (3.3), and approximation of the sum on the right of (3.3) by an integral, gives a consistent solution only if

$$\begin{aligned} \tau &= (\lambda + 3)/2 \\ B &= \left( E_1 \sum_{j=1}^{\infty} j b_j / I(\tau) \right)^{1/2} \end{aligned} \tag{3.5}$$

where we have introduced the integral $I(\tau)$ which is defined as

$$I(\tau) \equiv \int_0^1 \mathrm{d}x \int_{1-x}^{\infty} \mathrm{d}y \, x K(x, y)(xy)^{-\tau}. \tag{3.6}$$

The requirement that for the value of $\tau$ given in (3.5) the infinite sums $E_k$ should be finite, imposes the restriction $\mu > (\nu - 1)$. Under this condition, $I(\tau)$ is also finite. We conclude that solutions of the form (3.1) are allowed for all models with $\nu > 1$, provided that $\mu > (\nu - 1)$. For the special model $K(i, j) = (ij)^2$, which has $\mu = \nu = 2$, our results agree with the results of Hendriks *et al.*

The exact solution (3.1) is of interest for two reasons. First, if $\mu > (\nu - 1)$ all solutions of equation (1.1) have the same asymptotic ($k \to \infty$) form as the exact solution. This may be seen from equation (1.2). As $L \to \infty$, the LHS of equation (1.2) approaches a constant value $J(\infty, t) = -\dot{M}(t)$ for all $t > 0$. If we assume that the cluster size distribution has the form

$$c_k(t) \sim A(t) k^{-\tau} \qquad k \to \infty \tag{3.7a}$$

then the right-hand side of (1.2) approaches a finite value only if $\tau = (\lambda + 3)/2$. Moreover, one finds that $A(t)$ is related to the mass flux $\dot{M}(t)$ by

$$A(t) = [-\dot{M}(t)/I(\tau)]^{1/2} \tag{3.7b}$$

with $I(\tau)$ given by (3.6). Secondly, along the lines of van Dongen and Ernst (1985b), § 3, one may show that all solutions approach the exact solution as $t \to \infty$, i.e.

$$c_k(t)/c_1(t) \to b_k \qquad t \to \infty \tag{3.8}$$

provided, of course, $c_1(0) > 0$ and $\mu > (\nu - 1)$. This reveals the structure of the solutions of Smoluchowski's equation for $\nu > 1$ and $\mu > (\nu - 1)$.

We add a remark concerning possible solutions of equation (1.1) if $\mu \leqslant (\nu - 1)$. For homogeneous kernels with $\mu \leqslant (\nu - 1)$ one may show (see the appendix) that solutions of equation (1.1) with a well defined mass flux from the sol to the gel do not exist. In this context, the mass flux at time $t$ is well defined if the limit $J(\infty, t) = \lim_{L \to \infty} J(L, t)$ exists and $J(\infty, t) < \infty$. It follows that either the mass flux $J(L, t)$ does not converge as $L \to \infty$, or alternatively $J(\infty, t) = \infty (t > 0)$. The former possibility can be excluded, since non-convergence of $J(L, t)$ on some time interval $t_1 \leqslant t \leqslant t_2$ implies that also the sol mass $M(t) = 1 - \int_0^t \mathrm{d}t' \, J(\infty, t')$ is not defined. The only remaining possibility, $J(\infty, t) = \infty$ $(t > 0)$ implies that for $\mu \leqslant (\nu - 1)$, the system gels instantaneously and completely, i.e. that $c_k(t) = 0$ for all $k$ and all $t > 0$.

## 4. Summary and discussion

We start with a summary of our results. We have investigated the structure of solutions of Smoluchowski's coagulation equation for homogeneous coagulation kernels (1.5) with an exponent $\nu > 1$, i.e. for systems where the reactivity of large clusters increases faster than their size. As a first result, we have found that

(i) for all solutions of Smoluchowski's equation, gelation occurs instantaneously ($t_c = 0$).

Next we have examined the structure of the (post-gel) solutions of equation (1.1) if $\nu > 1$. Our results are drastically different for coagulating kernels with an exponent $\mu$ satisfying $\mu > (\nu - 1)$ and for models with $\mu \leqslant (\nu - 1)$. Our second result is that

(ii) if $\mu > (\nu - 1)$, the size distribution $c_k(t)$ has the form $c_k(t) \sim A(t) k^{-(\lambda+3)/2}$ as $k \to \infty$ for all $t > 0$. The prefactor $A(t)$ is related to the mass flux from the sol to the gel: $A(t) \propto [-\dot{M}(t)]^{1/2}$.

For large times ($t \to \infty$) one finds that the ratio $c_k(t)/c_1(t)$ approaches a constant value $b_k > 0$, independent of the initial conditions, with $c_1(t) \propto t^{-1}$ as $t \to \infty$. There exists also an exact solution of the form $c_k(t)=b_k c_1(t)$, with $c_1(t)=c_1(0)/(1+bt)$. Alternatively,

(iii) if $\mu \leqslant (\nu-1)$, solutions with a finite mass flux $\dot{M}(t)$ do not exist.

This result suggests that in such models, gelation occurs instantaneously and completely, i.e. $c_k(t)=0$ for all $t>0$.

Concerning the self-consistent arguments in § 3, leading to (ii), we make the following proviso. The result (i) implies that gelation occurs instantaneously for all initial distributions, provided that for such initial conditions Smoluchowski's equation has a solution. The existence of solutions for special initial distributions is demonstrated by the exact solution (3.1). However, the existence of solutions for general initial conditions has not been proved in this paper. Moreover, the method for obtaining the structure of solutions for $t>0$ is based on self-consistency and hence one cannot rigorously exclude the possibility of completely different behaviour.

One of the implications of the present work is that the moment equations (2.2) for $M_\alpha(t)$ are invalid for all $t>0$ if $\alpha \geqslant 1$. In order to see this, we examine the derivation of equation (2.2) in some detail. If equation (1.1) is multiplied with $k^\alpha$ and summed over all $k \leqslant L$ one finds the following result:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{k=1}^{L} k^\alpha c_k\right)=\tfrac{1}{2}\sum_{j=1}^{L}\sum_{i=1}^{L-j} K(i,j)c_i c_j[(i+j)^\alpha - i^\alpha - j^\alpha] - J_\alpha(L,t) \qquad (4.1a)$$

where we have defined

$$J_\alpha(L,t) \equiv \sum_{i=1}^{L}\sum_{j=L-i+1}^{\infty} i^\alpha K(i,j)c_i c_j. \qquad (4.1b)$$

If $J_\alpha(L,t)\to 0$ as $L\to\infty$, one obtains the usual expression (2.2) for the time evolution of $M_\alpha(t)$. For models with $\nu>1$, equations (4.1$a$) and (4.1$b$) have the following implications. We consider only kernels with $\mu>(\nu-1)$. In this case it follows from (ii) that $J_\alpha(L,t)\propto L^{\alpha-1}(L\to\infty)$. As a consequence $J_\alpha(L,t)$ vanishes as $L\to\infty$ only if $\alpha<1$ and hence the moment equations are invalid if $\alpha\geqslant 1$. As an aside, we remark that the same argument applies for all gelling models with $\lambda>1$ and $\nu\leqslant 1$. In this case the moment equations for $M_\alpha(\alpha\geqslant 1)$ are invalid for all $t>t_c$.

In § 1 it was mentioned that, assuming that the moment equations are correct, Hendriks *et al* (1982) and Ziff (1984) have studied the Taylor series of the second moment $M_2(t)$ for $K(i,j)=(ij)^2$. Numerically this series seems to diverge for all $t>0$ and these authors conjecture that gelation occurs instantaneously. The present paper shows that the moment equations are invalid, so that the observed divergence of $M_2(t)$ is not necessarily correct. In fact, $M_2(t)$ remains finite for all $t>0$, as may be seen from (ii) where $\lambda=4$ implies that $c_k(t)\propto k^{-7/2}$. The conclusion of Hendriks *et al* and of Ziff, that gelation occurs instantaneously, is nonetheless correct.

Next we discuss the relevance of Smoluchowski's equation (1.1) as a model for the coexistence of a sol and a gel phase. Smoluchowski's equation describes the interaction amongst finite-size clusters and the interaction between the sol and the gel is not taken into account. Therefore, one possible interpretation of equation (1.1) is that for some reason the gel is unreactive and another interpretation is that large clusters, say clusters larger than some size $k_\mathrm{p}$, precipitate and disappear from the system. The latter model reduces to equation (1.1) in the limit $k_\mathrm{p}\to\infty$.

In the presence of a reactive gel, Smoluchowski's equation would not necessarily give an appropriate description of the cluster size distribution. Qualitatively, this may be seen as follows. If we consider the gel as a set of large clusters, with size $k_\mathrm{G}$ and concentration $c_G$, then sol–gel interactions may be modelled by an extra term on the right of equation (1.1), of the form

$$-k^{\mu}(k_G)^{\nu}c_kc_G = -k^{\mu}(k_G)^{\nu-1}c_kG \tag{4.2}$$

where $G = k_Gc_G = 1 - M$ represents the gel fraction, i.e. the fraction of all units contained in the gel. Since, in the Smoluchowski theory, the gel is identified with an infinite cluster ($k_G = \infty$), one finds from equation (4.2) that sol–gel interactions yield a finite, non-vanishing contribution to Smoluchowski's equation only if $\nu = 1$. For $\nu < 1$, the gel term (4.2) is zero, implying that equation (1.1) gives the proper description of the combined sol–gel system, as was found by Spouge (1985). Finally for $\nu > 1$ the gel term is infinite, implying that in the presence of a reactive gel it would hold that $\dot{c}_k(t)/c_k(t) = -\infty$ for $t > t_c$. Since in such systems a gel is formed instantaneously ($t_c = 0$), it follows that $c_k(t) = 0$ for all $t > 0$, i.e. that for all positive times, the sol phase is empty.

Next we discuss the relevance of our work for the computer experiments of Domilovskii *et al* and Spouge. These authors have simulated the master equation for coagulating systems with a large but finite number of particles and reaction rates $K(i, j) = (ij)^{\omega}$ with $\omega > 1$. Such systems differ from equation (1.1) in two respects. First, since the number of particles in the simulation is finite, the deterministic equation (1.1) gives only an approximate description of the actual stochastic coagulation process. An exact description of finite systems is given only by the master equation (Spouge 1985) for the probability $P(\{n_k\}, t)$ for the presence at time $t$ of $n_k$ $k$-mers ($k = 1, 2, \ldots$). Secondly, since in the computer simulations also the largest clusters are reactive (no precipitation), these systems are qualitatively described by equation (1.1) with a term of the form (4.2) added.

The implications from our work for the simulations of finite systems are the following. Firstly, it follows from our result (i) that, in the limit of an infinite system, the computer experiments would show an instantaneous gelation transition. This can be seen as follows. In the pre-gel stage, the master equation may be expanded in powers of the inverse system size, and equation (1.1) is the dominant term in this expansion (for a review of the general method see van Kampen (1981)). The fact that the macroscopic law (1.1) does not allow sol mass conservation then implies that there is no pre-gel stage, i.e. that $t_c = 0$. A second implication is that gelation, once it has occurred, is complete, i.e. that the sol phase is empty for all $t > t_c$. This follows from the discussion around equation (4.2). Thus we conclude that the conjectures of Domilovskii *et al* and Spouge, stating that in their simulations for $K(i, j) = (ij)^{\omega}$ with $\omega > 1$, gelation occurs instantaneously and completely, are correct.

As a final remark we add that our present results are valid also for some non-homogeneous kernels. For instance, result (i), derived in § 2, is valid for all reaction rates $K(i, j)$ that can be bounded from below by a homogeneous coagulation kernel with $\nu > 1$, provided that the condition (1.6), (1.7) is fulfilled. Furthermore, the results of § 3 are valid, as a rule, if the kernel $K(i, j)$ is homogeneous at large cluster sizes, i.e. if the function $\psi(i, j) = \lim_{a\to\infty}[a^{-\lambda}K(ai, aj)]$ is homogeneous with the properties (1.5)–(1.7). Our results are not necessarily valid if the condition (1.6), (1.7), that the reaction rates $K(i, j)$ are strictly positive, is not fulfilled. This condition excludes e.g. kernels with $K(i, i) = 0$, for which a monodisperse distribution is stationary. An interesting example is the kernel (1.8*a*), quoted by Domilovskii *et al* as a model for gradient coagulation in a turbulent stream. For a non-monodisperse initial distribution, these authors find that their estimate of the gel time slightly decreases as the system size is increased. This suggests that for kernels with $\nu > 1$ and $K(i, i) = 0$, as in (1.8$a$), instantaneous gelation may or may nor occur, depending on the initial conditions.

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**Appendix**

In this appendix we show for homogeneous coagulation kernels with $\nu > 1$ and $\mu \leqslant (\nu - 1)$ that Smoluchowski's equation (1.1) does not allow for solutions with a finite mass flux from the sol to the gel. In order to prove that such solutions are forbidden, we show that the assumption that they exist is contradictory.

In order to obtain a contradiction, we make the following assumption: that there exists, for some interval $0 \leqslant t \leqslant t_1$, a solution $c_k(t)$ of equation (1.1) with $\Sigma\, kc_k(0) = 1$, such that for all $t > 0$ the mass flux $J(k, t)$, defined in (1.2), converges to a finite limit $J(\infty, t) = -\dot{M}(t)$ as $k \to \infty$. From this assumption we infer (see below) that necessarily $\dot{M}(t) = 0$, i.e. that the sol mass is conserved. However, according to § 2, this is impossible. The conclusion therefore is that our assumption is wrong.

We start with a few remarks. First, the finiteness of the mass flux $J(k, t)$ requires that the infinite sum in (1.2), i.e. $\sigma_i = \Sigma\, K(i, j)c_j$, is finite for all $i$. The finiteness of $\sigma_i(t)$ is equivalent to the finiteness of $M_\nu(t)$ on account of (1.5$b$). Furthermore, since we assume that $\mu \leqslant (\nu - 1)$, we infer also that $M_{1+\mu}(t)$ is finite:

$$M_{1+\mu}(t) \leqslant M_\nu(t) < \infty \qquad 0 \leqslant t \leqslant t_1. \tag{A1}$$

Our proof depends crucially on the finiteness of $M_{1+\mu}(t)$ and $M_\nu(t)$. The proof breaks down for models with $\mu > (\nu - 1)$, since in this case $M_{1+\mu}(t) = \infty$ for all $t > 0$. A second remark is that it will be used repeatedly that $c_k(t) \geqslant 0$. The non-negativity of $c_k(t)$ is obvious from (2.6), provided that $c_k(0) \geqslant 0$ for all values of $k$. The smallest cluster size for which $c_k(0) > 0$ will be denoted by $l$. It follows from (2.6) that $c_l(t) > 0$ for all $t \leqslant t_1$.

Consider the mass flux $J(k, t)$ defined in (1.2). In order to construct an upper bound on $J(k, t)$, we separate the double sum on the right of (1.2) in two parts, one with $j \geqslant k/2$ and one with $j < k/2$, as follows:

$$J(k, t) \equiv \Sigma_1(k, t) + \Sigma_2(k, t) \tag{A2}$$

with

$$\Sigma_n(k, t) \equiv \sum_{A(n)} iK(i, j)c_i(t)c_j(t) \qquad n = 1, 2. \tag{A3}$$

In the sum $\Sigma_n$, the summation indices $(i, j)$ run over all possible values in the set $A(n)$, which is defined by

$$A(1) = \{1 \leqslant i \leqslant k; j \geqslant \max(k/2, k-i+1)\}$$
$$A(2) = \{(1+k/2) < i \leqslant k; (k-i+1) \leqslant j < k/2\}. \qquad \text{(A4)}$$

In the sum $\Sigma_1$ we have $j \geqslant i/2$ for all possible values of $i$ and $j$. Similarly, for $\Sigma_2$, one has $j < i$. Consequently it follows from the requirements (1.5)-(1.7) imposed on the kernel $K(i,j)$ that there exist finite constants $C_1$ and $C_2$ such that

$$K(i,j) \leqslant C_1 i^\mu j^\nu \qquad \text{if } (i,j) \in A_1$$
$$K(i,j) \leqslant C_2 i^\nu j^\mu \qquad \text{if } (i,j) \in A_2. \qquad \text{(A5)}$$

The inequalities (A5), in combination with (A3), enable us to calculate upper bounds on the value of the sums $\Sigma_1$ and $\Sigma_2$.

First consider the sum $\Sigma_1$, defined in (A3). Substitution into (A3) of the inequality (A5) for $(i,j) \in A_1$ shows that

$$0 \leqslant \Sigma_1(k, t) \leqslant C_1 \sum_{i=1}^{k} i^{1+\mu} c_i \sum_{j=k/2}^{\infty} j^\nu c_j$$
$$\leqslant C_1 M_{1+\mu} \sum_{j=k/2}^{\infty} j^\nu c_j \to 0 \qquad k \to \infty. \qquad \text{(A6)}$$

On the second line of (A6) we have used that for models with $\mu \leqslant (\nu - 1)$, the moments $M_{1+\mu}$ and $M_\nu$ are finite. Equation (A6) shows that the sum $\Sigma_1(k, t)$ vanishes as $k \to \infty$.

Next we consider the sum $\Sigma_2(k, t)$. Insertion into (A3) of (A5) for $(i,j) \in A_2$, and interchange of the summation order, gives

$$0 \leqslant \Sigma_2(k, t) \leqslant C_2 \sum_{j=1}^{k/2} j^\mu c_j \sum_{i=k-j+1}^{k} i^{1+\nu} c_i$$
$$\leqslant C_2 \sum_{j=1}^{\infty} j^\mu c_j a(k,j) \qquad \text{(A7)}$$

where we have introduced

$$a(k,j) \equiv \sum_{i=k-j+1}^{k} q_i \qquad q_i(t) \equiv i^{1+\nu} c_i(t). \qquad \text{(A8)}$$

In equation (A8) it is understood that $a(k,j) = a(k,k)$ if $j > k$.

In order to obtain an upper bound on $\Sigma_2(k, t)$ for large $k$, we derive bounds on $q_i(t)$ and $a(k,j)$. The first step is to show that all $q_i(t)$ are bounded, i.e. that there exists some finite number $u(t)$ such that

$$q_i(t) \leqslant u(t) < \infty \qquad i = 1, 2, \ldots. \qquad \text{(A9)}$$

This follows from (1.2), since the inequality $J(i, t) \geqslant iK(l, i) c_l c_i$ reduces for large values of $i$ to $q_i(t) \leqslant J(\infty, t)/l^\mu c_l(t)$. Thus $q_i(t)$ is bounded for large $i$, implying that $u(t) = \max_i \{q_i(t)\}$ is finite.

Secondly, we show that $a(k,j)$ must be arbitrarily small for certain values of $k$. More precisely: for any given $\delta > 0$ and any $N < \infty$, we prove that there exists an infinite sequence $\{k_\alpha\}$, with $k_{\alpha+1} > k_\alpha$, such that

$$a(k_\alpha, N) \leqslant \delta \qquad \alpha = 1, 2, \ldots. \qquad \text{(A10)}$$

To see this, assume that the statement is not correct. In that case there exists a number $k_0 \geqslant N$ such that for all $k \geqslant k_0$: $a(k, N) > \delta$. It follows that for all $k \geqslant k_0$:

$$b(k, N) \equiv \sum_{j=k-N+1}^{k} j^{\nu} c_j = \sum_{j=k-N+1}^{k} q_j/j \geqslant k^{-1} a(k, N) > \delta k^{-1}.$$

This, however, implies that $M_\nu = \infty$, in contradiction with (A1):

$$M_\nu \geqslant \sum_{k=k_0-N+1}^{\infty} k^{\nu} c_k = \sum_{n=0}^{\infty} b(k_0 + nN, N) > \delta \sum_{n=0}^{\infty} (k_0 + nN)^{-1} = \infty.$$

We conclude that the infinite sequence $\{k_\alpha\}$, with the property (A10), exists.

We are now in a position to calculate an upper bound on the sum $\Sigma_2(k_\alpha, t)$. Combination of (A9) and (A10) gives an upper bound for $a(k_\alpha, j)$ in (A8), as follows:

$$\begin{aligned} &a(k_\alpha, j) \leqslant a(k_\alpha, N) \leqslant \delta && j \leqslant N \\ &a(k_\alpha, j) \leqslant u(t) j && j > N. \end{aligned} \tag{A11}$$

Substitution of (A11) into (A7) shows that

$$\begin{aligned} \Sigma_2(k_\alpha, t) &\leqslant C_2 \left( \sum_{j=1}^{N} j^{\mu} c_j a(k_\alpha, j) + \sum_{j=N+1}^{\infty} j^{\mu} c_j a(k_\alpha, j) \right) \\ &\leqslant C_2 \left( \delta M_\mu(t) + u(t) \sum_{j=N+1}^{\infty} j^{1+\mu} c_j(t) \right). \end{aligned} \tag{A12}$$

Thus $\Sigma_2(k_\alpha, t)$ is uniformly bounded for all $\alpha$.

Finally we show that $J(k, t)$ vanishes as $k \to \infty$. Since we assume that for $k \to \infty$, $J(k, t)$ converges to a finite limit $J(\infty, t)$, we may choose $k = k_\alpha$ and take the limit $\alpha \to \infty$. Combination of (A2), (A6) and (A12) shows that for $\alpha \to \infty$:

$$0 \leqslant J(\infty, t) \leqslant C_2 \left( \delta M_\mu(t) + u(t) \sum_{j=N+1}^{\infty} j^{1+\mu} c_j \right). \tag{A13}$$

Since, in (A13), the constant $\delta$ may be chosen arbitrarily small and $N$ may be chosen arbitrarily large it follows that necessarily $J(\infty, t) = 0$. In § 2 we have shown that this is impossible. We conclude that the assumption made at the beginning of this appendix is incorrect. Apparently solutions of Smoluchowski's equation with a finite mass flux from the sol to the gel do not exist if $\nu > 1$ and $\mu \leqslant (\nu - 1)$.

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