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# A version of Smoluchowski's coagulation equation with gelation

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**Abstract.** We assume the rate constants of Smoluchowski's coagulation equation to be of the form, $K_{i,j} = a(i) \cdot a(j)/[a(i) + a(j) - a(i + j)]$. If $a(i)/i > K > 0$ for all $i$ then the model will have gelation (provided the solution exists). If $a(i)/i \to 0$ as $i \to \infty$ it is then suggested that the model will not have gelation.

## 1. Introduction

In this article we shall consider Smoluchowski's coagulation equation

$$\dot{c}_i = \frac{1}{2} \sum_{j=1}^{i-1} K_{j,i-j} c_j c_{i-j} - c_i \sum_{j=1}^{\infty} K_{i,j} c_j \tag{1}$$

$(1 \leqslant i \leqslant \infty)$ under the assumption that the rate constants, $K_{i,j}$, are of the form

$$K_{i,j} = \frac{a(i)a(j)}{a(i) + a(j) - a(i + j)} \tag{2}$$

for some positive numbers $a(i) (i = 1, 2, \ldots)$ which satisfy

$$a(i + j) < a(i) + a(j) \qquad i \geqslant 1, \quad j \geqslant 1. \tag{3}$$

Clearly, equation (3) is necessary to ensure that the rate constants are positive and finite.

The main result is given in theorem 4, which states that the model will have gelation independent of the initial condition if $a(i)/i > K > 0$ for all $i$. Earlier, Van Dongen [1] considered rate constants of the form $K_{i,j} = (ij)^{\mu}(i + j)^{\nu-\mu} K^{(0)}(i, j)$ (where $K^{(0)}(i, j)$ only depends weakly on $i$ and $j$) and showed that one will get instant gelation if $\nu > 1$ and $\mu > \nu-1$. This result was strengthened by Carr and da Costa [2] who proved that one gets instant gelation if the rate constants satisfy $C_L(i^{\alpha} + j^{\alpha}) \leqslant K_{i,j} \leqslant C_U(ij)^{\beta}$ for some constants $C_L, C_U > 0$ and $\beta > \alpha > 1$. Buffet and Pulé [3] showed that one gets gelation in the diagonal model ($K_{i,j} = 0$ if $i \neq j$) if the rate constants satisfy a condition which implies that $K_{i,i}$ should increase slightly faster than $i$ as $i \to \infty$.

The form given by equation (2) is of course not the most natural form from a physical point of view. The reason for choosing it is purely mathematical. However, the form might be sufficiently flexible to be able to mimic some plausible forms of the rate constants. Rate constants of the form given by equation (2) were considered by Ziff [4]. However, he only considered $a(i) = i^n$ for $n$ integer. For $n > 1$ this implies that one should change the sign of the denominator in equation (2) and the direction of the inequality in (3). As we shall see in the following, the interesting part occurs when $0 \leqslant n \leqslant 1$ and $a(i)$ is of a more general form.

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## 2. Consequences of equation (3)

**Lemma 1.**

$$a(i) < i \cdot a(1). \tag{4}$$

*In other words $a(i)$ cannot grow faster than linearly.*

**Proof.** By induction on equation (3) in the form $a(i+1) < a(i) + a(1)$. □

**Lemma 2.** *The limit*

$$\lim_{i\to\infty} a(i)/i = \alpha \tag{5}$$

*exists.*

**Proof.** The sequence $\{a(i)/i : i = 1, 2, \ldots\}$, is clearly bounded (above by $a(1)$ and below by 0). Consequently, the following two limits exist:

$$\limsup_{i\to\infty} a(i)/i = \alpha_1$$
$$\liminf_{i\to\infty} a(i)/i = \alpha_0.$$

If $\alpha_1 > \alpha_0$ then we can choose $\epsilon$ less than 1, such that $(\alpha_1 - \alpha_0)/[3 \cdot (1 + a(1))] > \epsilon > 0$. We can then find $j$, such that $a(j)/j < \alpha_0 + \epsilon$. By an argument similar to the argument for lemma 1, we find $a(n \cdot j)/(n \cdot j) < \alpha_0 + \epsilon$ for any positive integer $n$. We next chose $k > j/\epsilon$ such that $a(k)/k > \alpha_1 - \epsilon$. For $0 < m \leqslant j$ we have

$$\begin{aligned} a(k-m)/(k-m) &> a(k)/(k-m) - m \cdot a(1)/(k-m) \\ &> (\alpha_1 - \epsilon) \cdot (1+\epsilon) - a(1)\epsilon(1+\epsilon) \\ &> \alpha_1 - \epsilon(1+\epsilon)(1+a(1)) > \alpha_0 + \epsilon. \end{aligned}$$

But among the numbers $k - j, k - j + 1, \ldots, k - 1$, there must be one which is of the form $n \cdot j$, which gives a contradiction. □

Otherwise, the consequences of the condition in equation (3) are limited. A monotone decrease of $a(i)/i$ would of course imply equation (3); but monotonicity of $a(i)/i$ is not necessary (see Hardy *et al* [5], section 103).

## 3. The main theorem

We define

$$A(t) = \sum_{i=1}^{\infty} a(i) \cdot c_i(t). \tag{6}$$

Lemma (1) implies that the sum in equation (6) converges if the sum defining the total monomer concentration, $\mu_1$, converges:

$$\mu_1(t) = \sum_{i=1}^{\infty} i \cdot c_i(t). \tag{7}$$

Since this sum is known to converge if a solution exists, $A(t)$ will also exist.

**Theorem 3.** *If equation (1) has a solution then it satisfies*

$$A(t) \leqslant A(0)/[1 + A(0) \cdot t/2]. \tag{8}$$

**Proof.** We shall consider the truncated version of $A(t)$:

$$A_N(t) = \sum_{i=1}^{N} a(i) \cdot c_i(t). \tag{9}$$

From equation (1) we get

$$\frac{\mathrm{d}}{\mathrm{d}t} A_N(t) \leqslant \frac{1}{2} \sum_{j=1}^{N} \sum_{i=1}^{N} K_{i,j} c_i c_j (a(i+j) - a(i) - a(j)) = -\frac{1}{2} A_N(t)^2. \tag{10}$$

Integrating equation (10) we get equation (8) with $A_N(t)$ in place of $A(t)$. Taking the limit $N \to \infty$ equation (8) is obtained. □

**Theorem 4.** *If equation (1) has a solution and $\alpha > 0$, then $\mu_1(t)$ goes to 0 as $t \to \infty$, i.e. the model has gelation.*

**Proof.** If $\alpha > 0$, then we can find a strictly positive constant $\beta$ such that $a(i)/i > \beta$ for all $i$. This implies $A(t) > \beta \cdot \mu_1(t)$ and theorem 4 is a consequence of theorem 3. □

One might wonder whether the opposite is true, that $\alpha = 0$ implies absence of gelation. This could be so, but it is certainly not true that $\alpha = 0$ implies the existence of a constant, $K$, such that $K_{i,j} < K \cdot (i + j)$ for all $i$ and $j$—in fact, a counter example will be presented in the next section. However, if $K_{i,j}$ is given by equation (2) and one has $K_{i,j} < K \cdot (i + j)$, then the results of White [6] together with theorem 4 would imply $\alpha = 0$ and the analysis of Heilmann [7] would imply that one has equality in equation (8).

Also the question of the existence of a solution is left open by the known results, although the results of Leyvraz and Tschudi [8] and Laurençot [9] do cover many cases.

## 4. Consequences of equation (2)

It is not easy to draw general consequences about the rate constants from equation (2), since it is possible to make the difference $a(i) + a(j) - a(i + j)$ arbitrarily small for some selected values of $i$ and $j$. However, one can examine some examples. The simplest possibility is

$$a(i) = 1 \tag{11}$$

which gives

$$K_{i,j} = 1. \tag{12}$$

This is one of the cases where the complete solution is known (Kreer *et al* [10]). The corresponding case with $\alpha > 0$:

$$a(i) = \alpha i + \beta \tag{13}$$

gives

$$K_{i,j} = \tfrac{1}{\beta}(\alpha i + \beta)(\alpha j + \beta). \tag{14}$$

This model has also been solved ([8, 11]) and one thus has that the present model for $K_{i,j}$, equation (2), covers the two cases where one knows the solution to the product form of $K_{i,j} (K_{i,j} = a(i) \cdot a(j))$.

The more general case

$$a(i) = i^{\gamma} \qquad 0 < \gamma < 1 \tag{15}$$

does not allow any general simplifications in the expression for $K_{i,j}$. One gets for $i$ large and $j$ fixed

$$K_{i,j} \approx a(i)/(1 - \gamma \cdot (j/i)^{1-\gamma}) \qquad (16)$$

and for $i$ large and $j = i \cdot (1 - \delta)$

$$K_{i,j} \approx a(i)/[(2 - 2^{\gamma})(1 + \delta\gamma/2)]. \qquad (17)$$

It is easy to see that one can find a constant, $K$, such that $K_{i,j} < K \cdot (i + j)$.

If one goes one step further and takes

$$a(1) = a(2) = 2 \qquad a(i) = i \cdot \exp[-\epsilon \ln(\ln i)] \qquad \text{for} \quad i \geqslant 3 \qquad (18)$$

then one gets for large $i$

$$K_{i,i} \approx i(\ln i)^{1-\epsilon}/[2\epsilon \ln 2]. \qquad (19)$$

In other words one can no longer find a constant, $K$, such that $K_{i,j} < K \cdot (i + j)$ if $\epsilon < 1$.

If we take

$$a(i) = \alpha i + i^{\gamma} \qquad 0 < \gamma < 1 \qquad (20)$$

then the denominator for $K_{i,j}$ becomes the same as for the case given by equation (15) and we get

$$K_{i,j} \approx (\alpha i + i^{\gamma})(\alpha j^{1-\gamma} + 1) \qquad \text{for} \quad j \leqslant i \qquad (21)$$

except for a factor which only depends weakly on $j$ and $i$.

## 5. Conclusion

In view of the ease with which the occurrence of gelation can be proven for the present model and the fact that both versions of a product model for which the solutions are known are included in the present model, then this model might be worth further investigation, at least from a mathematical viewpoint.

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