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On the Occurrence of a Gelation Transition in Smoluchowski's Coagulation Equation

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It has been conjectured by Lushnikov and Ziff that Smoluchowski's coagulation equation describes a gelation transition, i.e., the mean cluster size diverges within a finite time t_c (gelpoint) if the coagulation rate constants $K(i, j)$ have the property $K(ai, aj) = a^{\lambda}K(i, j)$, with $\lambda > 1$. The existing evidence was based on self-consistency arguments. Here we prove this conjecture for an appropriate class of physically acceptable rate constants by constructing a finite upper bound for t_c and a nonvanishing lower bound. Apart from the exactly solved case $K(i, j) = ij$ this result provides the first solid proof of the occurrence of a gelation transition in a description based on Smoluchowski's coagulation equation.

KEY WORDS: Smoluchowski's equation; coagulation; aggregation; gelation; kinetic phase transition.

INTRODUCTION

The purpose of this note is to prove that Smoluchowski's coagulation equation, for certain classes of rate constants, leads to a gelation transition at a finite time t_c, (gelpoint). The property characterizing the gelation transition is the formation of an infinite cluster (gel) at a finite time t_c, where the mean cluster size (mass average degree of polymerization) grows beyond all bounds.

All previous evidence for the occurrence of gelation was based on an exactly solvable model or, for more general models, on self-consistency arguments. Here we prove for certain classes of rate constants that some measure for the mean cluster size becomes infinite at a finite nonvanishing

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time t_c. This phenomenon is identified here as the occurrence of a gelation transition.

Smoluchowski's coagulation equation[1] is a coupled set of rate equations for the cluster size distribution, i.e., for the concentrations $c_k(t)$ of clusters of size k ($k = 1, 2,...$). If $K(i, j)$ is the rate constant for the clustering of an i- and a j-mer, then Smoluchowski's equation has the following form

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

It was first recognized by Lushnikov[2] and, more recently, by Ziff,[3] that for certain choices of the reaction rates, Smoluchowski's equation describes a gelling system, i.e., a system going through a gelation transition at a finite time t_c. This time-dependent phase transition has been studied in great detail[4] in the exactly soluble model $K(i, j) = ij$. For this particular model one observes the following interesting phenomena

(i) As $t \uparrow t_c$, the weight average cluster size diverges

$$\bar{k}_w(t) = \sum k^2 c_k \Big/ \sum k c_k = (t_c - t)^{-1} \to \infty (t \uparrow t_c) \tag{2}$$

The value of t_c is given by $1/\bar{k}_w(o)$. For all $t < t_c$, the sol mass $M_1(t) = \sum_{k=1}^{\infty} k c_k(t)$, i.e., the concentration of monomeric units contained in finite size clusters (sol), is conserved: $\dot{M}_1(t) = 0$ or $M_1 =$ constant. The unit of volume is chosen such that $M_1 = 1$ for $t \leqslant t_c$.

(ii) For $t \geqslant t_c$ the mass conservation law, $\dot{M}_1 = 0$, is violated. This may be seen by calculating the mass flux $-J(L, t)$ from clusters with size $k \leqslant L$ to clusters with $k > L$. This yields, with the help of (1)

$$J(L, t) = \sum_{k=1}^{L} k \dot{c}_k = -\sum_{i=1}^{L} \sum_{j=L-i+1}^{\infty} iK(i, j)\, c_i c_j \tag{3}$$

For $t < t_c$, where $c_k(t)$ decays exponentially, $J(L, t)$ vanishes as $L \to \infty$. Hence the sol mass is conserved: $\dot{M}_1(t) = J(\infty, t) = 0$. However, at t_c, $c_k(t)$ decays algebraically, $c_k(t) \sim k^{-5/2}$ ($k \to \infty$), and a mass flux occurs from finite clusters (sol) to the gel, viz. $J(L, t) \propto L^0 =$ const. as $L \to \infty$. In this interpretation, the gel is identified as the infinite cluster.

The results (i), (ii) apply to the special model $K(i, j) = ij$. It is of interest to investigate whether other functional forms of the coagulation kernel $K(i, j)$ lead to a similar phase transition in a finite time.

Concerning the possible occurrence of a gelation transition, the following results are known. For $K(i, j) \leqslant (i + j)$, White[5] proves absence of gelation for all finite $t > 0$. Intuitive arguments for the occurrence of gelation have been given for a model describing surface interaction,[6] viz. $K(i, j) = (ij)^{\omega}$ provided $\frac{1}{2} < \omega \leqslant 1$, and also[7] for the model $K(i, j) = i^{\alpha} j^{\beta} + j^{\alpha} i^{\beta}$ provided $\alpha + \beta > 1$ and $|\alpha - \beta| < 1$. For the surface interaction model, there also exists numerical evidence for the occurrence of gelation.[8] Furthermore, Leyvraz[9] has shown that gelation occurs for the diagonal kernel $K(i, j) = j^{\lambda} \delta_{ij}$ with $\lambda > 1$. Ziff[3] has suggested that gelation occurs if $K(j, j) \sim j^{\lambda}$ with $\lambda > 1$ and is absent otherwise.

On the basis of intuitive arguments the following more general criterium[7,10] for the occurrence of gelation has been formulated concerning homogeneous kernels $K(ai, aj) = a^{\lambda} K(i, j)$ with a degree of homogeneity λ: gelation occurs for $\lambda > 1$ and is absent for $\lambda \leqslant 1$.

The purpose of this paper is to provide a rigorous proof of the occurrence of a gelation transition in Smoluchowski's coagulation equation for a class of coagulation kernels $K(i, j)$ with $1 < \lambda \leqslant 2$.

METHOD

We do not have a rigorous proof of this criterion for *general* homogeneous kernels with $\lambda > 1$ but only for a *subset* of such kernels, to be specified below. The point of this note is to prove the occurrence of gelation for this subset and to give an estimate of the gelpoint t_c.

We proceed as follows. As no explicit solutions are known in general, one has to develop other tests to decide on the occurrence of gelation; e.g., one may be able to demonstrate that one of the characteristic phenomena (i), (ii) does or does not occur. In particular, we study the possible divergence of some of the moments $M_{\alpha}(t) \equiv \sum_{k=1}^{\infty} k^{\alpha} c_k(t)$, which provide a measure for the mean cluster size, such as $M_2(t) = \bar{k}_w(t)$. We construct, in fact, rigorous bounds for the gelpoint t_c, where the mean cluster size becomes infinite. Upper bounds on t_c must be finite, lower bounds nonvanishing. We recall that lower bounds have been obtained before, and that lower bounds alone give no evidence whatsoever about the occurrence of gelation. No gelation (i.e., $t_c = \infty$) is also consistent with a lower bound.

The appropriate method is to construct upper and lower bounds on $M_{\alpha}(t)$ and to investigate whether these bounds do or do not diverge at a finite time, as illustrated in Fig. 1. The fact that one can construct a lower bound on M_{α} that diverges within a finite time t_1 (see Fig. 1c), shows that gelation has occurred at some time $t_c \leqslant t_1$. On the other hand, divergence of an upper bound on M_{α} yields a lower bound on the geltime, and gelation may or may not occur (see Fig. 1b). An upper bound, remaining finite for all finite times, proves the absence of gelation (see Fig. 1a).

The plan of this paper is as follows. We specify the subset of kernels to be considered and show that a gelation transition takes place at a finite

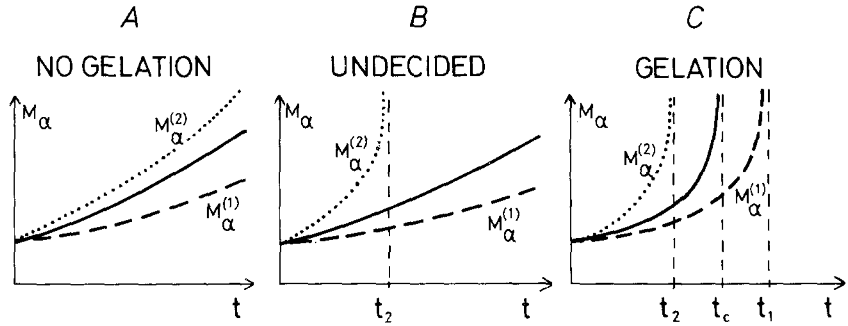

Fig. 1. Schematic behavior of $M_\alpha(t)$ (solid line) together with an upper bound (dotted line) and a lower bound (dashed line). If $\lambda \leqslant 1$ (Fig. 1a) there exists a finite upper bound on $M_\alpha(t)$ for all finite t, and gelation does not occur. In the undecided case (Fig. 1b: $\lambda > 1$, $\nu < 1$) gelation may occur with $t_c \geqslant t_2$. In the gelling case (Fig. 1c: $\lambda > 1$, $\nu = 1$) one has $t_2 \leqslant t_c \leqslant t_1$.

time t_c if $\lambda > 1$. Next, we calculate upper and lower bounds on the geltime and conclude with a discussion.

Specification of $K(i, j)$

We start by specifying the subset of coagulation kernels to be considered. We first recall that homogeneous kernels may be specified by two exponents

$$K(i, j) \simeq i^\mu j^\nu \qquad (j \gg i; \lambda = \mu + \nu) \tag{4a}$$

$$K(ai, aj) = a^\lambda K(i, j) = a^\lambda K(j, i) \tag{4b}$$

where we impose[10] the physical restrictions $\lambda \leqslant 2$ and $\nu \leqslant 1$. On account of the restrictions (4a, b) on $K(i, j)$, we may introduce a kernel $K^{(o)}(i, j)$, as follows

$$K(i, j) \equiv (ij)^\mu \, (i+j)^{\nu-\mu} K^{(o)}(i, j) \tag{5a}$$

where now $K^{(o)}(i, j)$ is a homogeneous function with zero degree of homogeneity. We assume that $K^{(o)}(i, j)$ is bounded and nonvanishing, i.e., that there exist constants K_1 and K_2 such that for all $i, j = 1, 2,...$

$$0 < K_1 \leqslant K^{(o)}(i, j) \leqslant K_2 < \infty \tag{5b}$$

The requirement that $K^{(o)}(i, j)$ is nonvanishing is imposed in order to exclude kernels with $K(j, j) = 0$ for which a monodisperse distribution would be stationary.[2] The criterion of boundedness, $K^{(o)}(i, j) \leqslant K_2$, is trivially fulfilled if $K^{(o)}(i, j)$ is a continuous function of the cluster sizes.

[2] An example is coagulation under gravitational settling, where $K(i, j) = (i^{1/3} + j^{1/3})^2 \, |i^{1/3} - j^{1/3}|$.

Since we are interested in the possible occurrence of a gelation transition, we consider only kernels $K(i, j)$ with a degree of homogeneity $\lambda > 1$. The reason is that kernels with $\lambda \leqslant 1$ may be bounded from above by $i + j$ as may be seen from eqs. (5a, b)

$$K(i, j) \leqslant 2^{-\mu} K_2 (i+j)^{\lambda} \leqslant 2^{-\mu} K_2 (i+j)$$

For such kernels it immediately follows from White's theorem that there does not occur a gelation transition (see Fig. 1a).

Upperbound on t_c

The *special subset* of homogeneous kernels to be considered is specified by eqs. (4) and (5) with $\lambda > 1$ and $\nu = 1$. Here one may obtain an *upper bound* for the geltime, if the gelpoint is identified as the earliest time at which some of the moments diverge. This upper bound is obtained as follows. The moment equation for the α-th moment

$$\dot{M}_{\alpha} = \frac{1}{2} \sum_{i,j} K(i,j)\, c_i c_j [(i+j)^{\alpha} - i^{\alpha} - j^{\alpha}] \tag{6}$$

may be written in the form

$$\dot{M}_{\alpha} = \frac{1}{2} \sum_{i,j} (ij)^{\lambda}\, (i^{\alpha - \lambda} + j^{\alpha - \lambda})\, \chi(i, j)\, c_i c_j \tag{7a}$$

with

$$\chi(i, j) \equiv K(i, j)[(i+j)^{\alpha} - i^{\alpha} - j^{\alpha}]/[(ij)^{\lambda}\, (i^{\alpha - \lambda} + j^{\alpha - \lambda})] \tag{7b}$$

From its definition it follows that $\chi(i, j)$ is a homogeneous function of i and j, with zero degree of homogeneity. The behavior of $\chi(i, j)$ for $j \gg i$ and $\alpha > 1$ may be obtained from (4b) as

$$\chi(i, j) \simeq \alpha (i/j)^{1-\nu} \qquad (j \gg i) \tag{8}$$

i.e., $\chi(i, j) \simeq \alpha$ for $j \gg i$ if $\nu = 1$. Thus $\chi(i, j)$ is bounded and nonvanishing if $j \gg i$ (or $i \gg j$) and hence, on account of (5a, b), for all i and j. We conclude that there exist constants $\chi_1(\alpha) > 0$ and $\chi_2(\alpha) < \infty$ such that

$$\chi_1(\alpha) \leqslant \chi(i, j) \leqslant \chi_2(\alpha) \tag{9}$$

for all i and j. Hereafter it is understood that $\chi_1(\alpha)$ and $\chi_2(\alpha)$ represent the largest, respectively smallest, number for which the inequality (9) holds.

The upper bound on t_c follows from the first inequality in (9). The special choice $\alpha = \lambda$ in eq. (7a) yields an inequality for the λ-th moment

$$\dot{M}_\lambda \geqslant \chi_1(\lambda)(M_\lambda)^2 \tag{10a}$$

or

$$M_\lambda(t) \geqslant M_\lambda(o)[1 - \chi_1(\lambda)\, M_\lambda(o)\, t]^{-1} \equiv M_\lambda(o)(1 - t/t_1)^{-1} \tag{10b}$$

For general $\alpha > \lambda$, one finds first an equation for the α-th moment

$$\dot{M}_\alpha \geqslant \chi_1(\alpha)\, M_\alpha(t)\, M_\lambda(t) \tag{11a}$$

which may be solved with the use of (10b)

$$\begin{aligned} M_\alpha(t) &\geqslant M_\alpha(o) \exp\left[\chi_1(\alpha) \int_0^t dt'\, M_\lambda(t')\right] \\ &= M_\alpha(o)(1 - t/t_1)^{-\beta(\alpha)} \end{aligned} \tag{11b}$$

with $\beta(\alpha) \equiv \chi_1(\alpha)/\chi_1(\lambda)$. Thus, we find the upper bound $t_c \leqslant t_1 \equiv [\chi_1(\lambda)\, M_\lambda(o)]^{-1}$.

Lower bound on t_c

The *lower bound* on the gelpoint follows from the second inequality in eq. (9). The choice $\alpha = \lambda$ in (7a) now gives

$$\dot{M}_\lambda \leqslant \chi_2(\lambda)(M_\lambda)^2 \tag{12a}$$

or

$$M_\lambda(t) \leqslant M_\lambda(o)(1 - t/t_2)^{-1} \tag{12b}$$

where we have defined $t_2 \equiv [\chi_2(\lambda)\, M_\lambda(o)]^{-1}$. We conclude that $M_\lambda(t)$ is finite for all $t \leqslant t_2$. Similarly one finds for general $\alpha > \lambda$ that

$$\dot{M}_\alpha \leqslant \chi_2(\alpha)\, M_\alpha(t)\, M_\lambda(t) \tag{13a}$$

or

$$M_\alpha(t) \leqslant M_\alpha(o)(1 - t/t_2)^{-\gamma(\alpha)} \tag{13b}$$

where the exponent γ is given by $\gamma(\alpha) = \chi_2(\alpha)/\chi_2(\lambda)$. We conclude that all moments $M_\alpha(t)$ are bounded for $t < t_2$, so that $J(L, t) \to 0$ as $L \to \infty$. This shows that t_2 is a lower bound for the geltime, $t_c \geqslant t_2$.

Thus, we have constructed diverging upper and lower bounds on the moments $M_\alpha(t)$ if $\nu = 1$, as illustrated in Fig. 1c. In particular, divergence of the bounds on the mean cluster size $M_2(t)$ implies that gelation takes place at a finite time t_c, with $t_2 \leqslant t_c \leqslant t_1$.

DISCUSSION

As an example with $\nu = 1$, consider the kernel $K(i, j) = ij^\omega + ji^\omega$, with $0 < \omega < 1$. One finds upper and lower bounds for the geltime, as follows

$$[\chi_2(\lambda)\, M_\lambda(o)]^{-1} \leqslant t_c \leqslant [\chi_1(\lambda)\, M_\lambda(o)]^{-1} \tag{14}$$

where $\chi_2(\lambda)$ may be calculated explicitly

$$\chi_2(\lambda) = \max\{\lambda/2, 2^\lambda - 2\} \tag{15a}$$

and furthermore

$$\begin{aligned} \chi_1(\lambda) &= \lambda/2 \qquad & (\lambda \geqslant \tfrac{3}{2}) \\ \chi_1(\lambda) &\geqslant 2(1 - 2^{1-\lambda}) \qquad & (\lambda \leqslant \tfrac{3}{2}) \end{aligned} \tag{15b}$$

We note that for the special case of monodisperse initial conditions, one has $M_\lambda(o) = 1$.

Next consider coagulation kernels with $\nu < 1$ but still $\lambda > 1$. The equation for the α-th moment may again be written in the form (7a, b), with $\chi(i, j)$ for $j \gg i$ given by (8). For kernels with $\nu < 1$ it follows that for all $\alpha > 1$, $\chi(i, j) \to 0$ as $i/j \to 0$. Therefore $\chi_1(\alpha) = 0$ in this case. As a consequence one finds that the upper bound on the geltime, $t_1 = [\chi_1(\lambda)\, M_\lambda(o)]^{-1}$ diverges for $\nu < 1$. Thus we are not able to prove with the help of the present methods that gelation actually occurs for $\nu < 1$. However, it is possible to construct lower bounds for the gelpoint, since $\chi_2(\alpha)$ is finite also for $\nu < 1$. In this case the same results are found as for $\nu = 1$.

Next, we want to stress that the homogeneity requirement (4a, b), (5a, b) has been imposed for convenience only. In fact, if one finds a lower bound t_2 on the geltime for some homogeneous kernel $K(i, j)$ with $\lambda > 1$, then clearly $t_c \geqslant t_2$ for any coagulation kernel K_{ij} satisfying $K_{ij} \leqslant K(i, j)$. Similarly, if t_1 sets an upper bound to the geltime for some homogeneous kernel $K(i, j)$ with $\lambda > 1$ and $\nu = 1$, then $t_c \leqslant t_1$ for any kernel K_{ij} with $K_{ij} \geqslant K(i, j)$ for all i and j.

We have imposed the *physical* requirements $\lambda \leqslant 2$ and $\nu \leqslant 1$ on the coagulation kernels considered in this paper. Inspection shows that our results are equally valid for models with $\lambda > 2$, provided one maintains the restriction $\nu \leqslant 1$. This shows that no *mathematical* problems, such as instantaneous gelation ($t_c = 0$), arise if $\lambda > 2$. However, for certain models with $\nu > 1$, there exists numerical evidence[11,8] that a gelation transition takes place already at $t=0$. In fact one can show also analytically[2] that for any model with $\nu > 1$, gelation occurs instantaneously.

Our definition of gelation, viz. the divergence of the mean cluster size, or, equivalently, of some moment $M_\alpha(t)$, is perhaps *physically not the most appropriate one*. In principle, it remains possible that $M_\alpha(t)$ for $\alpha > \lambda$ diverges as $t \uparrow t_c$, but that $\lim_{L \to \infty} J(L, t_c) \equiv J(\infty, t_c)$ is vanishing, i.e., that at the gelpoint t_c there is no finite flux of mass from the sol (finite size clusters) to the gel (infinite cluster). In that case the fraction of monomeric units, contained in the gel, which should be the order parameter of this gelation transition, would still be vanishing for $t \geqslant t_c$, and the divergence of some moment cannot be identified with a gelation transition. However, if one accepts the scaling hypothesis, this possibility is excluded, since it then follows that the occurrence of a gelation transition at t_c coincides with the divergence of all moments $M_\alpha(t)$ with $\alpha > (\lambda + 1)/2$.

Finally we mention that we have not attempted to calculate the sharpest possible upper or lower bounds on the gelpoint. Our primary goal was to show that such upper and lower bounds exist, and may in principle be calculated. In fact, it turns out that in certain special cases sharper lower bounds on t_c are obtained if Jensen's inequality is applied to eq. (13a).[7] In general, it depends upon the coagulation kernel under consideration which method gives the best estimate of the geltime t_c.

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