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Instantaneous gelation in the generalized Smoluchovski coagulation equation

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Abstract. We study the possible intantaneous gelation in n-tuple coagulation processes with a pairwise coalescence mechanism. This reaction mechanism, which is characteristic of the many-body aggregation model, and is not shared by the usual binary coagulation, may increase the reaction rate and so make instantaneous gelation a physically possible process for the n-tuple coagulation model. We show that the generalized Smoluchovski coagulation equation (GSE) predicts instantaneous gelation if the reaction kernels behave as $K(i_1, i_2, \ldots, i_n) \simeq i_1^{\mu} i_2 \cdots i_{n-1})^{\mu'} i_n^{\nu}$ as $i_n \to \infty$, with an exponent ν satisfying $\nu > 1$. This type of reaction kernel is related to the multiple-site n-tuple coagulation process, and corresponds to possible physical systems, in contrast to the case of binary coagulation where such kernels do not occur in the corresponding physical systems. We also study the structure of gel solutions of the GSE. We found that, if $\mu > \nu - 1$, the cluster size distribution $c_k(t)$ approaches a universal form at large times ($t \to \infty$).

1. Introduction

The kinetics of cluster growth and its critical properties have been the object of considerable interest. In the study of the kinetics of irreversible aggregation and clustering phenomena, Smoluchovski's coagulation equation proved to be one of the few available theoretical tools in many fields of physics, atmospheric physics, colloidal chemistry, biology, and technology [1–5]. In Smoluchovski theory, clusters are assumed to grow purely through the process of binary coalescence, because the concentration of the growing clusters is assumed to be sufficiently low that many-body collisions can be neglected. Describing the system by a set of concentrations $c_k(t)$ of k-particle clusters, the time evolution of the cluster concentration is determined by the following kinetic equation [6–10]:

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

where the coagulation kernel $K(i, j)$ represents the rate coefficient for a specific clustering mechanism between clusters of sizes i and j. The first sum gives the increase of $c_k(t)$ as a result of the coalescence of clusters satisfying the condition $i + j = k$ while the second term accounts for the decrease of $c_k(t)$ due to the binary collision of the k-particle clusters with clusters of any size. In this mean-field kinetic theory the spatial fluctuations in the cluster distribution and the geometrical structure of the growing clusters are completely ignored. Therefore, Smoluchovski coagulation theory is applicable only to dilute, idealized aggregation systems, where only binary collision is appreciable. It is, however, obvious

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that in a variety of physical and chemical coagulation processes, clusters may be formed by binary, ternary, or generally n-tuple collisions, as a result of high concentration of the aggregates, correlations between the growing clusters, or specific coagulation mechanisms, etc. For example, if we assume that the reaction force which binds two aggregating clusters is finite, in respect of the relative motion between two clusters, then it is reasonable to assume that the clusters formed by a ternary collision may be structurally more stable than those formed by a binary collisions. This phenomenon is more likely to occur in ballistic aggregation [11, 12], especially when the velocities of the aggregates are large. Under certain conditions, it is also possible that a specific coagulation mechanism may favour a particular n-tuple aggregation, where a special structure (say, a ramified ring) is required to maintain the biological activity of the clusters thus formed. Here we would like to stress that we are not interested in the concrete chemical or biophysical processes, where the use of Smoluchovski coagulation theory is not justified. What we would like to know is to what extent a Smoluchovski-like mean-field theory for aggregation is relevant when the aggregation system deviates from the dilute, idealized conditions for which Smoluchovski kinetic theory is valid. It should be noted that in any aggregation process, as long as clusters can be formed by binary collision, binary aggregation prevails. If this is the case, we wish to know what the effects are of the high-order (n-tuple) aggregation on the properties of the whole aggregating system. It therefore seems to be relevant to study first the process of purely n-tuple aggregation, and it is expected that a better understanding of purely many-body coagulation may help us gain insight into complicated, mixed multiple coagulation.

Recently we proposed a generalized Smoluchovski coagulation theory to study purely n-tuple aggregation processes [13–15]. In this theory, the clusters aggregate through the following scheme:

$$A_{i_1} + A_{i_2} + \cdots + A_{i_n} \rightarrow A_{i_1+i_2+\cdots i_n}$$

where the time evolution of the cluster size distribution is assumed to be described by the generalized Smoluchovski equation

$$\dot{c}_k = \frac{1}{n!} \sum_{i_1+i_2+\cdots+i_n=k} K(i_1, i_2, \ldots, i_n) c_{i_1} c_{i_2} \cdots c_{i_n}$$

$$- c_k \sum_{i_1,i_2,\ldots,i_{n-1}=1}^{\infty} K(i_1, i_2, \ldots, i_{n-1}, k) c_{i_1} c_{i_2} \cdots c_{i_{n-1}}. \tag{2}$$

Here the coagulation kernel $K(i_1, i_2, \ldots, i_n)$ represents the reaction rate for a special clustering mechanism between n clusters of sizes $i_1, i_2, \ldots, i_n$, and i_n. In all previous studies of n-tuple aggregation, the aggregating clusters are assumed to react with one another through one reaction site, which is a straightforward generalization of binary coagulation. Therefore, the solution to the generalized Smoluchovski equation shows a similar structure to that of the classical Smoluchovski equation. However, it is obvious that in n-tuple aggregation there are many different ways through which clusters can react with one another and produce large clusters. For example, the clusters can coalesce through 'end-to-end' sticking. Hence, the reaction mechanism can actually be divided into two main classes, according to the number of the reaction sites involved. That is, single-site and multiple-site reaction mechanisms. Of course, the probability that a multiple-site reaction occurs in n-tuple aggregation is generally greater than that of a single-site reaction.

In this work we shall study the properties of n-tuple aggregation with a multiple-site reaction mechanism. It should be noted that since the reaction can take place at different parts of different clusters in multiple-site n-tuple aggregation, it may need an

appropriate definition of the reaction time for n-tuple aggregation, because a set of sequential pairwise binary reactions are more likely to happen than a simultaneous many-body reaction. However, the sequential binary collisions within a very short time period would undermine the idealized conditions under which the Smoluchovski theory is valid, since the clusters are not uniformly distributed in this case. This is just another aggregation model system for which we would like to find an approximate theory to describe its kinetic behaviour. Our aim is to seek a mean-field description for the time evolution of the cluster size distribution in n-tuple aggregation, without going into the details of the concrete physical or chemical reaction processes.

The outline of the paper is as follows. In section 2 we show that for homogeneous reaction rates with $\nu > 1$ the gelation transition can take place instantaneously. This instantaneous gelation is a result of a special choice of the multiple-site n-tuple reaction mechanism. In section 3 we study the structure of gel solution to the generalized Smoluchovski equation, and in section 4 we discuss our results.

2. Pre-gel behaviour of the moments

In multiple-site n-tuple aggregation, there exist a large number of ways that the aggregating clusters can coalesce with one another. Since the reaction rate $K(i_1, i_2, \ldots, i_n)$ is assumed to represent the coagulation rate for a specific clustering mechanism, one expects that, by choosing an appropriate reaction rate, multiple-site n-tuple aggregation will show much richer behaviour than single-site n-tuple aggregation. One notable feature of multiple-site n-tuple aggregation is that instantaneous gelation is a physically possible transition, if we assume that every A_k has a certain number of reactive sites, say s_k, which are equally active, independent of the size of the molecules to which they belong. It is geometrically obvious that the number of reactive sites on A_k cannot grow faster than k, i.e. $s_k < k$. In binary coagulation models, two clusters coalesce through one reaction unit. The linear growth of the s_k (that is, $s_k \sim Ck$) in this model is equivalent to the absence of cycles in the structure of A_k, corresponding to the Flory–Stockmayer model of gelation [3, 4]. However, in multiple-site n-tuple aggregation, there exist various ways for coalescence to occur between n molecules. For example, in a triple coagulation process, three polymers may bond together through one same reaction site to form a star-like cluster, or through two different reaction sites to form a chain-like cluster, and or through three different reaction sites to form a ring-like structure. The kinetic behaviour for 'star-like' aggregation has been studied extensively by using the generalized Smoluchovski equation [13–15]. It is clear that the instantaneous gelation transition does not occur for physical systems for single-site n-tuple aggregation.

In this work we are concerned with the kinetic behaviour of the 'chain-like', or multiple-site n-tuple aggregations, in which some of the n clusters coalesce in a pairwise manner. Since in this aggregation model it is not necessary that a n-tuple reaction take place on one reaction site, the possibility of such reactions is enhanced by the increase in the combinatorial ways that n clusters are linked to one another. It is not our purpose to determine the reaction rates for concrete physical and chemical processes; what we are interested in is the study of the effects of such a multiple-site reaction mechanism on the kinetic behaviour of the cluster size distribution.

The assumption of pairwise coalescence mechanism leads to the following ansatz:

$$K(i, j) = s_i s_j \tag{3}$$

$$K(i, j, k) \sim s_i s_j s_j s_k + s_j s_i s_i s_k + s_j s_k s_k s_i \tag{4}$$

$$\vdots$$

$$K(i_1, i_2, \ldots, i_n) \sim \sum_{k=1}^{n-1} \Pi_{i=i_k, j=i_{k+1}} s_i s_j. \tag{5}$$

If we further assume that

$$s_k \sim k^{\mu}$$

then equation (5) can be written as

$$K(i_1, i_2, \ldots, i_n) \sim i_1^{\mu_1} i 2^{\mu_2} \cdots i_n^{\mu_n} \tag{6}$$

and one finds that it is possible that $\mu_i > 1$ for some i. We recall that for binary coagulation models, coagulation kernels defined by (6) with $\mu_i > 1$ do not occur in physical systems. However, for n-tuple coagulation, the reaction kernels given by (6) do correspond to certain coagulation processes of physical systems.

To simplify our discussion, we will be concerned with the following homogeneous kernels:

$$K(ai_1, ai_2, \ldots, ai_n) = a^{\lambda} K(i_1, i_2, \ldots, i_n). \tag{7}$$

Following the standard scaling theory of the Smoluchovski equation [6], we further assume that

$$\begin{aligned} K(i_1, i_2, \ldots, i_n) &\sim K_0(i_1, i_2) K_1(i_3, \ldots, i_n) \\ &\sim i_1^{\mu} (i_2 i_3 \cdots i_{n-1})^{\mu'} i_n^{\nu} \qquad i_n \gg i_1 \quad \lambda = \mu + \nu + (n-2)\mu' \end{aligned} \tag{8}$$

with $\mu > 0$ corresponding to class I systems, $\mu = 0$ to class II, and $\mu < 0$ to class III. There are two physical restrictions on the exponents: for n large interpenetrable clusters $K(j, j, \ldots, j) \sim j^n$, which is an upper bound for all $K(j, j, \ldots, j)$ as $j \to \infty$, and thus $\lambda \leqslant n$. Since a j-mer contains at most j monomers, we require that $\nu \leqslant 1$. We stress that the reaction kernels considered in this work are actually characterized by two exponents. The case where the reaction kernels are characterized by more than two exponents will be discussed elsewhere. It should be noted that in class I (III) the rate constants for reactions of at least two large clusters involved (at least one large and one small cluster involved) are dominant, irrespective of the sizes of the other $n - 2$ clusters. In class II the rate constants are equal for aggregation of clusters of different sizes. By a similar argument, it has been shown that non-gelling systems correspond to $\lambda \leqslant n - 1$, and gelling systems to $n - 1 \leqslant \lambda \leqslant n$ [13].

The gelation transition can be studied by analyzing the moments M_α of the cluster size distribution, which are defined by

$$M_\alpha(t) = \sum_{k=1}^{\infty} k^{\alpha} c_k(t). \tag{9}$$

The time dependence of M_α is described by the moment equations, which may be derived from the generalized Smoluchovski equation if both sides of (2) are multiplied by k^α and summed over all k:

$$\begin{aligned} \dot{M}_\alpha = \frac{1}{n!} \sum_{i_1=1}^{\infty} \sum_{i_2=1}^{\infty} \cdots \sum_{i_n=1}^{\infty} K(i_1, i_2, \ldots, i_n) c_{i_1} c_{i_2} \cdots c_{i_n} \big[(i_1 + i_2 + \cdots + i_n)^{\alpha} \\ - i_1^{\alpha} - i_2^{\alpha} - \cdots - i_n^{\alpha} \big]. \end{aligned} \tag{10}$$

It should be noted that the moment equations are valid only if all moments M_α are finite. This requires that $c_k(t)$ falls off sufficiently fast as $k \to \infty$. In what follows we shall show that for a specially chosen reaction kernel (8), the cluster size distribution $c_k(t)$ is exponentially bounded as $k \to \infty$. First let us derive an upper bound for the mass $M^{(k)}(t)$ contained in clusters of size $j \geqslant k$:

$$M^{(k)}(t) = \sum_{j=k}^{\infty} j c_j(t). \tag{11}$$

It follows that

$$c_k(t) \leqslant k^{-1} \sum_{j=k}^{\infty} j c_j(t) \tag{12}$$

thus, if we can show that $\sum_{j=k}^{\infty} j c_j(t)$ is exponentially bounded, the desired ineqality follows.

Assume that for $t < t_c$ the sol mass is conserved, i.e. $\dot{M}(t) = \sum j \dot{c}_j(t) = 0$. In combination with (2) we find that

$$\dot{M}^{(k)}(t) = \frac{1}{(n-1)!} \sum_{i_1=1}^{k-1} \sum_{i_2=1}^{\infty} \cdots \sum_{i_n=1}^{\infty} i_1 K(i_1, i_2, \ldots, i_n) c_{i_1} c_{i_2} \cdots c_{i_n}$$

$$- \frac{1}{(n-1)!} \sum_{i_1=1}^{k-1} \sum_{i_2=1}^{k-i_1+1} \sum_{i_2=1}^{k-i_1-i_2+1} \cdots \sum_{i_n=1}^{k-i_1-i_2-\cdots-i_{n-1}+1} i_1 K(i_1, i_2, \ldots, i_n) c_{i_1} c_{i_2} \cdots c_{i_n}. \tag{13}$$

Since $c_k(t) \geqslant 0$ and all moments are finite, then after rearranging equation (13) and neglecting some irrelevant positive terms we obtain

$$\dot{M}^{(k)}(t) \geqslant \frac{1}{(n-1)!} \sum_{i_1=1}^{k-1} \sum_{i_2=1}^{\infty} \cdots \sum_{i_n=k-i_1-i_2-\cdots-i_{n-1}}^{\infty} i_1 K(i_1, i_2, \ldots, i_n) c_{i_1} c_{i_2} \cdots c_{i_n}. \tag{14}$$

Now we assume that $c_j(0) = 0$ for $1 \leqslant j \leqslant l-1$, but $c_l(0) \neq 0$. Since $K(l, l, \ldots, i_n) \sim l^{\nu} (i_2 i_3 \cdots i_{n-1})^{\mu'} i_n^{\nu}$ if $i_n >> l$, on account of (8), there must be some finite constant $k_0 \geqslant l+1$, such that for all $i_n \geqslant k_0$

$$K(l, l, \ldots, i_n) \geqslant l^{\nu} (i_2 i_3 \cdots i_{n-1})^{\mu'} i_n^{\nu}. \tag{15}$$

Substitution of (15) in equation (14) yields

$$\dot{M}^{(k)}(t) \geqslant a_l c_l(t) k^{\nu-1} M_{\mu'}^{n-2}(t) M^{(k)}(t) \qquad k \geqslant k_0 \tag{16}$$

where $a_l = l^{1+\mu}$. Straightforward integration of (16) from time t to t_c yields the following inequality for $M^{(k)}(t)$:

$$M^{(k)}(t) \leqslant \exp\left(-a_l k^{\nu-1} \int_t^{t_c} \mathrm{d}t' \; c_l(t') M_{\mu'}^{n-2}(t') \right). \tag{17}$$

It follows that $c_k(t)$ is exponentially bounded for $t < t_c$. As a result, all moments are finite and the moment equations are valid for $t < t_c$.

3. Instantaneous gelation

In this section we show that the generalized Smoluchovski equation predicts an instantaneous gelation transition, if the relatively large clusters coagulate with small clusters through multiple-site reaction mechanism (which means the reactivity of relatively large clusters increases faster than their size).

The gelation transition manifests itself by the 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 (2) by 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:

$$J(L,t) = \dot{M}^{(L+1)}(t).$$

If $J(L,t) = 0$ for all times, then the sol mass is conserved, and one has $M(t) = 1$. On the other hand, if $J(L,t) \neq 0$, for all $t \geqslant t_c$, then gelation transition occurs at t_c, since there is a non-vanishing mass flux of finite-size particles (sol) to the infinite cluster (gel).

In order to show that generalized Smoluchovski equation predicts an instantaneous gelation transition for $\nu > 1$, we assume that, for some initial distribution $c_k(0) \geqslant 0$ with $\sum k c_k(0) = 1$ and some time interval $0 \leqslant t < t_c$, there exists a continuously differentiable solution $c_k(t)$ of the GSE, with the property that the sol mass is conserved: $M(t) = 1$ for all $t < t_c$. Thus, we can use moment equations to discuss the critical behaviour near the gelation transition. Then we show that at any fixed time $t > 1$ the moment equations predict a divergence of some of the moments $M_m(t)$, which contradicts the assumption. This implies that there is no pre-gelation solution of GSE for $\nu > 1$, and gelation occurs instantaneously.

Here it is assumed that $c_k(t)$ falls off sufficiently fast as $k \to \infty$, such that all moments $M_m(t)$ are finite. We use the moment equations (10) for integer numbers to obtain a lower bound for the moment $M_m(t)$. It can be shown that the lower bound diverges at some finite time $t_m > 0$, with $t_m \to 0$ as $m \to \infty$. Since all moments $M_m(t)$ are finite for $t < t_c$, clearly t_m sets an upper bound to the gel time t_c, i.e. $t_c \leqslant t_m$ for all values of m. Thus, $t_c = 0$ if $t_n \to 0$ as $m \to \infty$.

First let us calculate a lower bound for the reaction kernels (8). Since it is assumed that the reaction kernels can be factorized as

$$K(i_1, i_2, \ldots, i_n) \sim K_0(i_1, i_2) K_1(i_3, \ldots, i_n)$$

and the property of $K_0(i, j)$ determines the behaviour of the system under consideration, we consider only a lower bound of $K_0(i, j)$, which is given by

$$K_0(i, j) \geqslant K'(i^\beta j^\nu + j^\beta i^\nu) \tag{18}$$

where $\beta = \min\{\mu, \nu\}$ and K' is a constant.

Substitution of the lower bound for $K_0(i, j)$ in (8), one finds

$$K(i_1, i_2, \ldots, i_n) \geqslant K' i_1^\beta (i_2 i_3 \cdots i_{n-1})^{\mu'} i_n^\nu. \tag{19}$$

Inserting equation (19) in the moment equations yields

$$\dot{M}_m \geqslant \frac{1}{n!} \sum_{i_1=1}^{\infty} \sum_{i_2=1}^{\infty} \cdots \sum_{i_n=1}^{\infty} c_{i_1} c_{i_2} \cdots c_{i_n}$$

$$\times \sum_{n_1=0}^{m} \sum_{n_2=0}^{m-n_1} \cdots \sum_{n_n=0}^{m-n_1-n_2-\cdots-n_{n-1}} \binom{m}{n_1} \binom{m-n_1}{n_2} \binom{m-n_1-n_2}{n_3}$$

$$\cdots \binom{m-n_1-n_2-\cdots-n_{n-1}}{n_n} i_1^{\beta+n_1} i_2^{\mu'+n_2} \cdots i_{n-1}^{\mu'+n_{n-1}} i_n^{\nu+m-n_1-n_2-\cdots-n_n}. \tag{20}$$

In the next approximation, we take into account only the term of $n_1 = 1$ and $n_2 = n_3 = \cdots n_n = 0$; then from (14) we obtain

$$\dot{M}_m \geqslant \frac{K'}{n!} M_{\mu'}^{n-2} M_{1+\beta} m M_{m+\nu-1}. \tag{21}$$

Since $M_{\mu'}$ and $M_{1+\beta}$ are finite for $0 \leqslant t \leqslant t_c$ we may transform to a new time variable $\tau(t)$, which is defined by

$$\tau(t) = \frac{K'}{n!} \int_0^t \mathrm{d}t' \; M_{1+\beta}(t') M_{\mu'}^{n-2}(t'). \tag{22}$$

Then equation (21) becomes

$$\frac{\mathrm{d}M_m}{\mathrm{d}\tau} \geqslant m M_{m+\nu-1}. \tag{23}$$

By using Jensen's inequality, one can obtain an equation in terms of $M_m(\tau)$ only. If we define the average value of some function $A(k)$ of the cluster size k by

$$E[A(k)] \equiv \sum_{k=1}^{\infty} k A(k) c_k \tag{24}$$

then Jensen's inequality [16] states that for any non-negative function $f(k)$ and any convex function $\phi(x)$ the following relation holds:

$$E[\phi(f(k))] \geqslant \phi(E[f(k)]). \tag{25}$$

As a immediate consequence we have

$$M_{n-\nu-1} = E[\phi(k^{n-1})] \geqslant \phi(E[k^{n-1}]) = \phi(M_n) \tag{26}$$

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

Substitution in (23) of the inequality (26) finally gives an equation in terms of $M_m(\tau)$ alone:

$$\frac{\dot{M}_m}{d\tau} \geqslant m M_m^{1+\gamma} \qquad \gamma = \frac{\nu-1}{n-1}. \tag{27}$$

Integrating equation (27) gives the result

$$M_m(\tau) \geqslant \frac{1}{(M_m(0)^{-\gamma} - \gamma m \tau)^{1/\gamma}}. \tag{28}$$

It follows that $M_m(\tau)$ diverges at, or before, the time τ_m, which is defined by

$$\tau_m = \frac{1}{m\gamma M_m(0)^{\gamma}}.$$

Since all moments $M_m(\tau)$ are finite for $\tau < \tau_c$, τ_m clearly sets an upper bound to τ_c. If one assumes that for $m \geqslant 3$, $M_m(0) \geqslant 1$, then for $\nu > 1$ one finds that

$$\tau_c \leqslant \tau_m \leqslant \frac{1}{m\gamma} \to 0 \qquad m \to \infty. \tag{29}$$

This implies that $t_c = 0$, contradicting the assumption $t_c > 0$. We therefore conclude that pre-gel solutions of the GSE do not exist for $\nu > 1$. Physically this means that, irrespective of the initial condition, gelation occurs instantaneously.

Now let us discuss the structure of solutions of GSE for the homogeneous coagulation kernels (8) with $\mu > 1$. It has been shown [13] that the generalized Smoluchovski equation allows an exact post-gel solution of the form

$$c_k(t) = c_1(t)b_k \qquad t \geqslant t_c \tag{30}$$

where b_k is constant and $c_1(t)$ is given by

$$c_1(t) = c_1(t_c)/[1 + b(t - t_c)]^{n-1}. \tag{31}$$

The parameter b in (31) may be determined through substitution of (30) and (31) in (2) for $k = 1$. The result is $b = c_1(t_c)E_1$, where in general E_k is defined as

$$E_k = \sum_{i_1=1}^{\infty}\sum_{i_2=1}^{\infty}\cdots\sum_{i_{n-1}=1}^{\infty} K(k, i_1, i_2, \ldots, i_{n-1})b_{i_1}b_{i_2}\cdots b_{i_{n-1}}. \tag{32}$$

It should be noted that the solution (30) is consistent only if $E_k < \infty$ for all k. Furthermore, by substituting equation (30) in the GSE, it is found that the factors b_k satisfy the following equation for all $k \geqslant 2$:

$$E_1\sum_{j=1}^{k} i b_j = \frac{1}{(n-1)!}\sum_{i_1=1}^{k-n+1}\sum_{i_2=1}^{\infty}\cdots\sum_{i_{n-1}=1}^{\infty}\sum_{i_n=k-i_1-i_2-\cdots-i_n+1}^{\infty} i_1 K(i_1, i_2, \ldots, i_n)b_{i_1}b_{i_2}\cdots b_{i_n} \tag{33}$$

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

In order to determine whether solutions of the form (30) are also allowed for $\nu > 1$, we calculate the asymptotic behaviour of the solution b_k of (33). We assume that the asymptotic behaviour of b_k is of the form

$$b_k \sim Bk^{-\tau} \qquad k \to \infty. \tag{34}$$

The requirement that at $t_c = 0$, the sol mass is finite, i.e. $M(0) = 1$ necessarily implies that $\tau > 2$. Substitution of ansatz (34) in (33), and approximation of the sum on the right-hand side of (33) by an integral, gives a consistent solution only if

$$\tau = (\lambda + n + 1)/n \tag{35}$$

$$B = \left(E_1\sum_{j=1}^{\infty} I(\tau)\right)^{1/n} \tag{36}$$

where the integral $I(\tau)$ is defined as

$$I(\tau) = \frac{1}{(n-1)!}\int_0^1 \mathrm{d}x_1\int_0^{\infty}\mathrm{d}x_2\cdots\int_0^{\infty}\mathrm{d}x_{n-1}\int_{1-x_1-x_2-\cdots-x_{n-1}}^{\infty}\mathrm{d}x_n\; x_1$$
$$\times K(x_1, x_2, \ldots, x_n)(x_1x_2\cdots x_n)^{-\tau}. \tag{37}$$

The finiteness of the infinite sums E_k requires that

$$\mu > (n-1)(\nu - 1) + (n-2)(1 - \mu') \tag{38}$$

and

$$\mu' > \tfrac{1}{2}(1 + \mu + \nu) \tag{39}$$

which yields the following restriction:

$$\mu > \nu - 1. \tag{40}$$

Under this condition $I(\tau)$ is also finite. We conclude, therefore, that the solutions of the form (30) are allowed for all models with $\nu > 1$, provided that $\mu > \nu - 1$.

It is worth pointing out that the conclusions drawn from the above discussion come as a result of the specific choice of the reaction kernels (8). For general reaction kernels, it is expected that instantaneous gelation can take place under certain restrictions other than (40), which is similar to that of binary coagulations.

4. Conclusions

We have investigated the structure of the solutions of the generalized Smoluchovski equation for the homogeneous coagulation kernels (8) with $\nu > 1$, i.e. for systems where the reactivity of large clusters increases faster than their size. We found that for all solutions of the generalized Smoluchovski equation, gelation occurs instantaneously, this being is attributed to the multiple-site reactions occurring in n-tuple aggregation processes. In contrast to binary coagulation, instantaneous gelation can take place in physical systems which undergo multiple-site n-tuple aggregation. We have also studied the gel solutions to the GSE and found that, if $\mu > \nu - 1$, all solutions of the GSE have the same asymptotic behaviour, i.e. $c_k(t) \sim A(t)k^{-\tau}$ with $\tau = (\lambda + n + 1)/n$. It should be noted that the coagulation kernels (8) are actually characterized by two exponents, μ and ν, so it is not surprising that the solutions of the GSE exibit qualitatively similar behaviour to those of the Smoluchovski coagulation equation. However, if more involved coagulation kernels are considered, it is expected that the general properties of solutions of the GSE may be distinct from those predicted by the Smoluchovski coagulation equation.

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