Scaling theory for multipolymer coagulation

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We study the scaling behavior of the n-tuple coalescence process, described by the generalized Smoluchovski equations (GSE). It is found that, for a specific class of homogeneous reaction kernels, the cluster size distribution approaches a scaling form, $c_k(t) \sim s^{-2}\phi(k/s)$, with the mean cluster size behaving as $s(t) \sim t^z$ as $t \to \infty$. The dynamic exponent z and the small- and large-x behaviors of the scaling function $\phi(x)$ are derived from the GSE. For large x, it is found that $\phi(x) \approx Ax^{-\lambda}e^{-ax}$ $(x \to \infty)$ $[\Lambda = \mu + (n-1)\nu]$, which is valid for all gelling and nongelling coagulation kernels with $\nu < 1$. While for small x, $\phi(x) \sim x^{-\tau}$ or $\phi(x) \sim \exp(-x^{\mu})$ with $\mu < 0$, depending on certain characteristics of the coagulation kernels.

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I. INTRODUCTION

The kinetics of irreversible aggregation and clustering phenomena, in particular, the time evolution of cluster size distribution $c_k(t)$ has been studied extensively by using the Smoluchovski coagulation equation:

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

where the coagulation kernel $K(i,j)$ represents the rate coefficient for a specific clustering mechanism between clusters of sizes i and j. In the gelling mechanism the mean cluster size $s(t)$ diverges as t approaches the gel point t_c, while in nongelling mechanism $s(t)$ keeps increasing with time. It is known from the exact solution [1], coagulation experiments [2], and computer simulations [3] that the cluster-size distribution approaches a scaling form as soon as the typical size $s(t)$ becomes large compared to the characteristic size at initial time. A dynamic scaling theory has been developed to account for the scaling behavior occurring in gelling and nongelling systems, described by the Smoluchovski equation [4–6]. Recently, the n-tuple coagulation process has been studied by introducing a generalized Smoluchovski coagulation equation (GSE) [7–10]:

$$\dot{c}_k = \frac{1}{n!}\sum_{i_1+i_2+\cdots+i_n=k} K(i_1,i_2,\ldots,i_n)c_{i_1}c_{i_2}\cdots c_{i_n} - c_k \sum_{i_1,i_2,\ldots,i_{n-1}=1}^{\infty} K(i_1,i_2,\ldots,i_{n-1},k) \times c_{i_1}c_{i_2}\cdots c_{i_{n-1}} \ , \tag{2}$$

where the coagulation kernel $K(i_1,i_2,\ldots,i_n)$ represents the rate coefficient for a specific clustering mechanism among n clusters of sizes i_1, $i_2,\ldots,i_n$, and i_n. It is remarked that $K(i_1,i_2,\ldots,i_n)$ are given coefficients which we shall in no way attempt to determine. Their determination depends on very particular models of the molecular processes involved, and may be obtained by using the relevant fluid theories for some simplified model systems.

The most commonly used reaction kernels in the literature are constant kernels, sum kernels, and product kernels. The sum kernel may be obtained by the following consideration. Suppose that the clusters move ballistically, then the collision probability of such n clusters is obviously proportional to the sum of the cross section of each cluster. The cross section of the cluster of size k is given by

$$s_k \sim k^{1/3} \ .$$

Thus, the corresponding coagulation kernel is given by

$$K(i_1,i_2,\ldots,i_n) = s_{i_1} + s_{i_2} + \cdots + s_{i_n} \ .$$

In order to obtain the product kernel, let us consider the following chemical reaction mechanism. Suppose that the monomers are the basic reaction units. Clusters can be coalesced through the reaction among those constituent reaction units. Suppose that s_k is the effective number of such reaction units of a given cluster with k monomers, then the reaction probability is given by the so-called factorial kernel

$$K(i_1,i_2,\ldots,i_n) = s_{i_1}s_{i_2}\cdots s_{i_n} \ .$$

For factorial coagulation kernel with $s_k = Ak + B$, the exact solution of the GSE has been derived for the monodispersion initial condition $c_k(0) = \delta_{k,1}$ [9]. It has been shown that a gelation transition occurs at a finite time t_c. For product kernel

$$K(i_1,i_2,\ldots,i_n) = (i_1 i_2 \cdots i_n)^{\omega} \ ,$$

different critical properties have been found, which are qualitatively similar to the behaviors predicted from Smoluchovski equation for a binary coagulation process.

In this paper, we develop a scaling theory for the n-tuple coagulation process by using GSE. We show that for a class of special coagulation kernels the solution of GSE approaches a scaling form. In Sec. II, we derive an integral equation for the scaling function, starting from the GSE. The dynamic exponent can also be obtained by using a scaling ansatz. In Sec. III, we discuss the asymptotic behavior of the scaling function for different classes

of the coagulation kernels. Finally, in Sec. IV, some conclusions are given.

II. THE INTEGRAL EQUATION FOR SCALING FUNCTION $\phi(x)$

Since GSE is structurally similar to the Smoluchovski equation, it is expected that GSE with a homogeneous kernel is invariant under a group of similarity transformations. It is, therefore, expected that GSE may admit exact similarity or scaling solutions [4], that can be solved from a nonlinear integral equation. In principle, one can study the scaling behavior of GSE for a general homogeneous kernel such as

$$K(i_1,i_2,\ldots,i_n)=\frac{1}{n!}\sum_{P(i_1 i_2\cdots i_n)} i_1^{\mu_1} i_2^{\mu_2}\cdots i_n^{\mu_n} ,$$

where the summation is over all the possible permutation among n clusters. In order to study the large-cluster-size behavior of the concentration from GSE, it is convenient to distinguish the reaction processes into different dominant processes. There are, of course, various ways to do so. One may, for example, assume that the reaction among $n-1$ large clusters and a small one, or $n-2$ large clusters and two small ones, etc., is the dominant process at large-cluster-size limit. However, at present stage, it is still not clear whether GSE admits scaling solutions. Therefore, as a first step towards a complete understanding of the problem under consideration, we restrict ourselves to the following specific homogeneous kernels:

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

$$K(i_1,i_2,\ldots,i_n)\simeq(i_1 i_2\cdots i_{n-1})^{\nu} i_n^{\mu} \quad [i_1,i_2,\ldots,i_{n-1}\gg i_n,\ \lambda=(n-1)\nu+\mu] , \tag{3}$$

which correspond to the case of reaction among $n-1$ large clusters and a small one and are closely related with the standard classification for binary reaction kernel. In fact, this kernel reduces to the binary reaction kernel for the standard Smoluchovski equation if $n=2$. It is noted that $\mu>0$ corresponds to class I, $\mu=0$ to class II, and $\mu<0$ to class III. Note also that 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 $\lambda\le n$. Since a j-mer contains at most j monomers, it is required that $\nu\le 1$. There is no restriction imposed on μ except $\mu\le\lambda-(n-1)\nu$. In class I and III the rate constants for reactions of one large sample with other $n-1$ small and large samples are dominant, respectively. In class II, the reaction rates are the same for large-large and large-small clusters reactions. Nongelling systems correspond to $\lambda\le n-1$, and gelling systems to $n-1\le\lambda\le n$ [7].

To study which aggregation mechanisms lead to gelation, we consider the mass loss rate $\dot{M}_k(t)$ across a certain cluster size k, which is defined by

$$\dot{M}_k(t)=\sum_{j=1}^{k} j\dot{c}_j .$$

From Eq. (2), one finds

$$\dot{M}_k(t)=-\sum_{i_1=1}^{k}\sum_{i_2=k-i_1+1}^{\infty}\cdots\sum_{i_n=k-i_1-i_2-\cdots-i_n+1}^{\infty} i_1 K(i_1,i_2,\ldots,i_n)c_{i_1}c_{i_2}\cdots c_{i_n} . \tag{4}$$

If $\dot{M}_k(t)=0$ for all times, then the sol mass is conserved, and the system is nongelling. The property $\dot{M}_k(t)\neq 0$ for all $t\ge t_c$ is interpreted as the occurrence of gelation, since there is a nonvanishing mass flux of finite-size particles (sol) to the infinite cluster (gel). The right-hand side of Eq. (4) can only be nonvanishing if $c_k(t)$ has sufficiently slow (algebraic) decay at large k, i.e., $C_k(t)\sim k^{\tau}$ as $k\to\infty$. This ansatz gives in combination with Eqs. (3) and (4) that $\dot{M}^{(\infty)}(t)\neq 0$ and is bounded for all $t\ge t_c$ if $\tau=(n+1+\lambda)/n$. A further requirement is that the total sol mass $M(t)$ is bounded for $t\ge t_c$, implying $\tau>2$. Consequently, homogeneous coagulation kernels $K(i_1,i_2,\ldots,i_n)$ of degree λ describe gelling systems if $\lambda>n-1$ and nongelling systems if $\lambda\le n-1$.

For nongelling systems, we are looking for a similarity solution to Eq. (2) of the general form,

$$c_k(t)\sim g(t)\phi(k/s(t)) . \tag{5}$$

Since the sol mass is conserved in nongelling systems, we consider the following scaling ansatz:

$$c_k(t)\simeq M s^{-2}\phi(k/s) . \tag{6}$$

To determine the mean cluster size $s(t)$ and the scaling function $\phi(x)$, we insert the scaling ansatz (6) into Eq. (2) and obtain

$$\begin{aligned}-w[x\phi'(x)+2\phi(x)]=&\frac{1}{n!}\int_0^x dx_1\int_0^{x-x_1} dx_2\cdots\int_0^{x-x_1-x_2-\cdots-x_{n-2}} dx_{n-1}\\ &\times K(x_1,x_2,\ldots,x_{n-1},x-x_1-x_2-\cdots-x_{n-1})\\ &\times\phi(x_1)\phi(x_2)\cdots\phi(x_{n-1})\phi(x-x_1-x_2-\cdots-x_{n-1})\\ &-\frac{\phi(x)}{(n-1)!}\int_0^{\infty} dx_1 dx_2\cdots dx_{n-1}K(x_1,x_2,\ldots,x_{n-1},x)\phi(x_1)\phi(x_2)\cdots\phi(x_{n-1}) .\end{aligned} \tag{7}$$

Here, w is a separation constant for the x and t dependence, so that

$$\dot{s}s^{n-2-\lambda}=Mw \ . \tag{8}$$

Therefore, the mean cluster size $s(t)$ increases asymptotically as

$$s(t)\sim t^{z} \quad (t\to\infty) \ , \tag{9}$$

where the dynamic exponent z for all homogeneous coagulation kernels with $\lambda<(n-1)$ is given by

$$z=\frac{1}{(n-1-\lambda)} \ . \tag{10}$$

The result (10) shows that the larger n is, the slower $s(t)$ increases, as predicted in the previous study [7]. The special case of $\lambda=n-1$ is more involved and will be discussed elsewhere [11].

Note that in the derivation of Eq. (7), we have implicitly assumed that the separate integrals are convergent. If it is not the case, the integrals may contain canceling infinities [4]. A representation of integral equation for scaling function $\phi(x)$ without canceling infinities can be obtained from Eq. (4),

$$wx^{2}\phi(x)=\int_{0}^{x}dx_{1}\int_{x-x_{1}}^{\infty}dx_{2}\cdots\int_{x-x_{1}-x_{2}-\cdots-x_{n-1}}^{\infty}dx_{n}x_{1}K(x_{1},x_{2},\ldots,x_{n})\phi(x_{1})\phi(x_{2})\cdots\phi(x_{n}) \ , \tag{11}$$

where consistency requires that $x^{2}\phi(x)\to 0$ as $x\to 0$. The constant w and the moments of the scaling function, defined as

$$m_{\alpha}=\int_{0}^{\infty}dx^{\alpha}\phi(x) \ ,$$

are related as

$$\begin{aligned}(\alpha-1)p_{\alpha}w=\frac{1}{(n-1)!}\int_{0}^{\infty}dx_{1}\int_{0}^{\infty}dx_{2}\cdots\int_{0}^{\infty}dx_{n}K(x_{1},x_{2},\ldots,x_{n})\\ \times\phi(x_{1})\phi(x_{2})\cdots\phi(x_{n})[(x_{1}+x_{2}+\cdots+x_{n})^{\alpha}\\ -x_{1}^{\alpha}-x_{2}^{\alpha}-\cdots-x_{n}^{\alpha}] \ ,\end{aligned} \tag{12}$$

where α must be sufficiently large that the integrals exist at the lower limit of integration.

III. ASYMPTOTIC BEHAVIORS OF THE SCALING FUNCTION

In this section, we study the large-x and small-x behaviors of the scaling function $\phi(x)$ by analyzing the integral equations obtained in the previous section. It is noted that the solution $\phi(x)$ of Eq. (7) contains a pair of arbitrary constants (a,b), since for any given function $\phi(x)$ also $\bar{\phi}(x)=b\phi(ax)$ is a solution. One constant is fixed by the requirement of mass conservation $p_{1}=1$. The other constant can be chosen such that $w=1$.

For large x, we are interested in finding solutions $\phi(x)$ with exponential decay. It can be verified that the integral equation (7) admits an exponential decay solution,

$$\phi(x)\simeq Ax^{-\lambda_{n}}\exp(-ax) \ , \tag{13}$$

where λ_{n} is given by

$$\lambda_{n}=\frac{\lambda+n-2}{n-1} \ . \tag{14}$$

This solution is valid for all gelling and nongelling coagulation kernels with $\nu<1$.

The small-x behavior of the scaling function $\phi(x)$ can be obtained by studying GSE separately for the three classes. In class I, we found that Eq. (7) admits algebraic solutions,

$$\phi(x)\sim Bx^{\tau} \quad (x\to 0) \ , \tag{15}$$

$$\tau=1+\frac{\lambda}{n-1} \quad [\lambda=\mu+(n-1)\nu] \ , \tag{16}$$

$$B=\frac{(2-\tau)w}{L(\tau)} \ , \tag{17}$$

where the mass conservation in nongelling systems requires that $\tau<2$. The integral equation $L(\tau)$ is defined as

$$\begin{aligned}L(\tau)=&\frac{1}{(n-1)!}\int_{0}^{\infty}dx_{1}dx_{2}\cdots dx_{n-1}K(x_{1},x_{2},\ldots,x_{n-1},1)(x_{1}x_{2}\cdots x_{n-1})^{-\tau}\\ &-\frac{1}{n!}\int_{0}^{1}dx_{1}\int_{0}^{1-x_{1}}dx_{2}\cdots\int_{0}^{1-x_{1}-x_{2}-\cdots-x_{n-2}}dx_{n-1}K(x_{1},x_{2},\ldots,x_{n-1},1-x_{1}-x_{2}-\cdots-x_{n-1})\\ &\times(x_{1}x_{2}\cdots x_{n-1})^{-\tau}(1-x_{1}-x_{2}-\cdots-x_{n-1})^{-\tau} \ .\end{aligned} \tag{18}$$

In view of the specific reaction kernel (3), the second integral in Eq. (18) can be written as (see Appendix)

$$I=\prod_{i=0}^{n-2} S(\lambda_i) , \tag{19}$$

where $S(\lambda_i)$ is given by

$$S(\lambda_i)=\int_0^1 dx\, K(x,1-x;\lambda_i)x^{-\tau}(1-x)^{-\tau} . \tag{20}$$

Thus, $L(\tau)$ can be written as

$$L(\tau)=\frac{1}{(n-1)!}\int_0^\infty dx_1 dx_2\cdots dx_{n-1}K \times(x_1,x_2,\ldots,x_{n-1},1) \times(x_1x_2\cdots x_{n-1})^{-\tau}-\frac{1}{n!}\prod_{i=0}^{n-2} S(\lambda_i) . \tag{21}$$

Therefore, the small-x behavior, determined by the convergence of the integral equation (18), can be deduced from properties of the binary coagulation equation (21), which has been studied in great detail in Ref. [4].

In class II [$\mu=0,\nu=1/(n-1)$], the small-x behavior is still characterized by a power-law decay solution. It can be shown that the dominant small-x contributions come from the loss term in Eq. (2). Thus, the result for class II is

$$\phi(x)\sim x^{-\tau} ,$$
$$\tau=2-\frac{(p_\nu)^{n-1}}{w} . \tag{22}$$

Since τ is given in terms of integrals over $\phi(x)$, the small-x behavior of class II depends on the specific form of the coagulation kernel. For class III, the small-x behavior is again governed by the loss term in GSE. HEnce, Eq. (7) reduces to

$$-x\phi'(x)\sim\phi(x)x^{-|\mu|} , \tag{23}$$

so that

$$\phi(x)\sim\exp(-|\mu|) , \tag{24}$$

indicating that $\phi(x)$ has a bell-shaped curve and vanishes exponentially fast as $x\to 0$.

In gelling systems ($n-1<\lambda\le n$), the cluster-size distribution in the postgel stage ($t\ge t_c$) is assumed to be

$$c_k(t)\simeq Ms^{-\tau}\phi(k/s) , \tag{25}$$

where the mean cluster size $s(t)$ diverges as $t\to t_c^-$. By inserting the scaling ansatz (6) into GGE, we obtain

$$Mw=\dot{s}s^{(n-1)\tau-n-\lambda} ,$$

so that

$$s(t)=s_0(t_c-t)^{-1/\sigma} , \tag{26}$$

where $\sigma=(1+\lambda-n)/n$. From Eq. (26), it is seen that the mean cluster size is an increasing function of time and diverges as $t\to t_c$, where t_c has a finite value for gelling systems.

IV. CONCLUSIONS

In summary, we have studied dynamic scaling properties of n-tuple coagulation process for specific homogeneous reaction kernel defined by Eq. (3). For nongelling systems, we found that the cluster-size distribution approaches a scaling form, $c_k(t)\sim s^{-2}\phi(k/s)$. The mean cluster size behaves as $s(t)\sim t^z (t\to\infty)$ with $z=1/(n-1-\lambda)$. The small-x behaviors of the scaling function are found to be $\phi(x)\sim x^{-\tau}$ for class I and class II kernels, and $\phi(x)\sim\exp(-x^{-\tau})$ for class III kernel. For gelling systems, the size distribution in the pregel stage is found to be given by

$$c_k(t)\sim k^{-\tau}\psi(k(t_c-t)^{1/\sigma}) \quad (t\to t^-, k\to\infty) , \tag{27}$$

with $\sigma=(1+\lambda-n)/n$ and $\tau=(n+1+\lambda)/n$.

For a binary coagulation one can recover all corresponding results by setting $n=2$ in our GSE. It should ben noted that in this paper, we have concentrated only on a specific homogeneous coagulation kernel, which are characterized by two exponents. In more complicated cases, where the coagulation kernels are specified by j exponents ($2<j<n$), GSE will certainly show much diverse behaviors, which might be qualitatively different from the binary-collision coagulation process.

APPENDIX

The second integral in Eq. (18) reads

$$I=\int_0^1 dx_1\int_0^{1-x_1} dx_2\cdots\int_0^{1-x_1-x_2-\cdots-x_{n-2}} dx_{n-1}K(x_1,x_2,\ldots,x_{n-1},1-x_1-x_2-\cdots-x_{n-1}) \times(x_1x_2\cdots x_{n-1})^{-\tau}(1-x_1-x_2-\cdots-x_{n-1})^{-\tau} . \tag{A1}$$

Defining

$$y=x_{n-1}/X,\quad X=1-x_1-x_2-\cdots-x_{n-2} , \tag{A2}$$

and inserting (A2) into (A1), one gets

$$I=\int_0^1 dx_1\int_0^{1-x_1} dx_2\cdots\int_0^{1-x_1-x_2-\cdots-x_{n-3}} dx_{n-2}(x_1x_2\cdots x_{n-2})^{-\tau}(1-x_1-x_2-\cdots-x_{n-2})^{-\tau}F , \tag{A3}$$

where F is defined as

$$F=\int_0^1 dy\, K(x_1,x_2,\ldots,x_{n-1},1-x_1-x_2-\cdots-x_{n-1})X^{-\tau+1}[y(1-y)]^{-\tau} . \tag{A4}$$

In view of the asymptotic form of the coagulation kernel defined in Eq. (3), one obtains

$$F \simeq (x_1 x_2 \cdots x_{n-2})^{\nu}(1-x_1-x_2-\cdots-x_{n-2})^{1+\mu+\nu-\tau}\int_0^1 dy\, K_0(y,1-y)[y(1-y)]^{-\tau}\ , \tag{A5}$$

where

$$K_0(ax,ay)=a^{\lambda_0}K_0(x,y)\quad \lambda_0=\mu+\nu\ . \tag{A6}$$

Defining

$$K_1(x_1,x_2,\ldots,x_{n-2},1-x_1-x_2-\cdots-x_{n-2}) \simeq (x_1 x_2 \cdots x_{n-2})^{\nu}(1-x_1-x_2-\cdots-x_{n-2})^{\mu_1}\ , \tag{A7}$$

and

$$S(\lambda_i)=\int_0^1 dx\, K(x,1-x;\lambda_i)x^{-\tau}(1-x)^{-\tau}\ , \tag{A8}$$

with $K_i(ax,ay)=a^{\lambda_i}K_i(x,y)$ and $\lambda_i=\mu_i+v$, and introducing

$$\mu_0=\mu\ ,$$

$$\mu_i=i\mu-\frac{\mu}{n-1}\ , \tag{A9}$$

one can write F as

$$F=K_1(x_1,x_2,\ldots,x_{n-2},1-x_1-x_2-\cdots-x_{n-2})S(\lambda_0)\ . \tag{A10}$$

Finally, one obtains

$$I=S(\lambda_0)\int_0^1 dx_1\int_0^{1-x_1} dx_2\cdots\int_0^{1-x_1-x_2-\cdots-x_{n-2}} K_1(x_1,x_2,\ldots,x_{n-2},1-x_1-x_2-\cdots-x_{n-2}) \times (x_1 x_2 \cdots x_{n-2})^{-\tau}(1-x_1-x_2-\cdots-x_{n-2})^{-\tau}\ . \tag{A11}$$

By repeating the above procedure one finds

$$I=\prod_{i=0}^{n-2} S(\lambda_i)\ . \tag{A12}$$

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