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Aggregation processes with n-particle elementary reactions

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Abstract. We study aggregation processes of n-particle coalescence by means of a generalized Smoluchowski equation. For a model of constant reaction rates, an exact general solution is obtained and the scaling behaviour for the cluster-mass distribution is observed. A model with sum-kernel reaction rates is also studied and an exact solution for a monodisperse initial distribution is found.

1. Introduction

Aggregation processes have attracted considerable interest in many apparently unrelated fields of science and technology. Examples can be found in such diverse subjects as colloid science, polymerization, cloud dynamics, aerosol physics, biology, dairy research and astrophysics. Consequently, it is of great practical and theoretical interest to possess mathematical prediction concerning the evolution of aggregating systems. Typically, such processes are described by the binary reaction scheme

$$A_i + A_j \xrightarrow{K(i,j)} A_{i+j}$$

where A_j denotes an aggregate consisting of j monomers (j-mer) and $K(i,j)$ is the rate at which reaction proceeds. This last depends on the respective sizes i and j of the reacting aggregates in a way that is essentially model dependent.

It is, however, quite clear that in a variety of physical and chemical applications aggregation by n-body collisions can also take place. The goal of the present study is to investigate these types of reactions symbolized as

$$A_{i_1} + \ldots + A_{i_n} \xrightarrow{K(i_1,\ldots,i_n)} A_{i_1+\ldots+i_n}.$$

We believe that a thorough study of n-tuple coalescence will contribute towards a better understanding of general aggregation processes.

The kinetics in the mean-field limit, where spatial fluctuations in cluster density and cluster shape are neglected, is adequately described by Smoluchowski's coagulation equation for the systems aggregating by two-body collisions [1-3]. A similar equation describes the aggregation by n-body collision [4]:

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = \sum_{i_1+\ldots+i_n=k} K(i_1,\ldots,i_n) C_{i_1}\ldots C_{i_n} - nC_k \sum_{i_1,\ldots,i_{n-1}} K(k,i_1,\ldots,i_{n-1}) C_{i_1}\ldots C_{i_{n-1}}. \tag{1}$$

In (1) t is time and C_k is the concentration of k-mers. The gain terms on the right-hand side describe a formation of k-mers out of smaller clusters by n-body collisions and the loss terms describe a removal of k-mers due to reactions with other aggregates.

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For the usual Smoluchowski equation, exact solutions have been constructed for three types of reaction rates: constant kernel $K(i,j)=$ constant, sum kernel $K(i,j)=i+j$ and product kernel $K(i,j)=ij$ (see e.g [2, 3, 5] and references therein). It is therefore natural to look for similar solutions of the generalized Smoluchowski equation (1). The exact solutions for the product kernel with a monodisperse initial distribution have recently been found by Yu Jiang and Hu Gang [4] (see also very recent papers [6, 7]). In this work we consider the generalized Smoluchowski equation with two other types of the reaction kernel and construct the general solutions.

2. Constant kernel

We start our study with the simplest model of constant reaction rates, $K(i_1,\ldots,i_n)=1$. In this case we have

$$\frac{dc_k}{dt}=\sum_{i_1+\ldots+i_n=k} C_{i_1}\ldots C_{i_n}-nC_kN^{n+1} \tag{2}$$

where

$$N=\sum_{k=1}^{\infty} C_k \tag{3}$$

is the total number of the clusters in the system. Summing all equations (2) we obtain

$$\frac{dN}{dt}=-(n-1)N^n. \tag{4}$$

The solution of this equation is

$$N(t)=N_0[1+N_0^{n-1}(n-1)^2t]^{-1/(n-1)} \tag{5}$$

where N_0 is the initial value of the total number of clusters.

Proceeding with the solution to the kinetic equation (2) we introduce the generating function

$$g(y,t)=\sum_{k=1}^{\infty} C_k(t)\exp(ky) \tag{6}$$

and transform equation (2) into the following:

$$\frac{\partial g}{\partial t}=g^n-ngN^{n-1}. \tag{7}$$

Solving (7) yields

$$g(y,t)=N(t)\left[1+\frac{f(g)}{N(t)}\right]^{-1/(n-1)} \tag{8}$$

where $N(t)$ is given by (5) and $f(y)$ is defined from the initial conditions

$$f(y)=N_0\left(\left[\frac{N_0}{g(y,0)}\right]^{n-1}-1\right). \tag{9}$$

For the monodisperse distribution

$$C_k(0)=\delta_{k1} \tag{10}$$

we recast the solution (5) and (8) into the form

$$N(t) = [1 + (n-1)^2 t]^{-1/(n-1)} \tag{11a}$$

$$g(y, t) = N^{n/(n-1)} \exp(y)\{1 - (1-N)\exp[(n-1)y]\}^{-1/(n-1)}. \tag{11b}$$

Inversing (11*b*) one can find the cluster-size distribution

$$C_{1+k(n-1)}(t) = N^{n/(n-1)}(1-N)^k \Gamma\left(k + \frac{1}{n-1}\right)\left[\Gamma\left(\frac{1}{n-1}\right)\Gamma(k+1)\right]^{-1}. \tag{12}$$

Here Γ is the gamma function. All the concentrations $C_k(t)$ with $k \neq 1 \pmod{n-1}$ are trivial due to our choice of the initial conditions (10).

In many recent studies of aggregation phenomena, only one characteristic size $S(t)$ in a system has been observed (for a review, see e.g. Frielander [3]). This rather naturally leads to the scaling behaviour

$$C_k(t) = S^{-2}\phi(k/S(t)). \tag{13}$$

Furthermore, it was observed as a quite general fact that $S(t)$ increases as a power law, $S(t) \sim t^z$.

The distribution (12) belongs to the scaling class. Actually, we have

$$S = N^{-1} \sim t^z \tag{14}$$

with the scaling exponent $z = (n-1)^{-1}$. In the scaling limit

$$k \to \infty \qquad t \to \infty \qquad x = k/S = kN = \text{finite} \tag{15}$$

we can rewrite (12) as follows:

$$C_{1+k(n-1)}(t) \simeq N^2\left[\Gamma\left(\frac{1}{n-1}\right)\right]^{-1} x^{(2-n)/(n-1)} \exp(-x) \tag{16}$$

which proves the scaling nature of the solution (12) and yields the precise expression for the scaling function $\phi(x)$ in (13).

Furthermore, the general solution (8) also belongs to the scaling class. To prove this, we first note that the scaling limit (15) corresponds to

$$t \to \infty \qquad y \to -0 \qquad u = (-y)S = \text{finite} \tag{17}$$

in (t, y) variables. Then we expand $g(y, 0)$ and $f(y)$ in the vicinity of $y = 0$ and find

$$\begin{aligned} g(y, 0) &= N_0 + M_0 y + \dots \\ f(y) &= M_0(n-1)(-y) + \dots \end{aligned} \tag{18}$$

where M_0 is the first moment of distribution, i.e. the total mass of the system

$$M = \sum_{k=1}^{\infty} kC_k(t) = M_0 = \text{constant}. \tag{19}$$

Substituting (18) into the general solution (8), we obtain

$$g = S^{-1}[1 + M_0(n-1)u]^{-1/(n-1)} \tag{20}$$

in the scaling limit (17). Here $S = N^{-1}$ as previously. Combining (6) and (13) and replacing the sum in (6) by the integral, we derive another formula for $g(y, t)$ in the scaling limit

$$g = S^{-1}\int_0^{\infty} dx\, \phi(x) \exp(-xu). \tag{21}$$

Comparing these formulae, we arrive at the following exact solution for the scaling function:

$$\phi(x)=[M_0(n-1)]^{-1/(n-1)}\left[\Gamma\left(\frac{1}{n-1}\right)\right]^{-1}x^{(2-n)/(n-1)}\exp\left[-\frac{x}{M_0(n-1)}\right]. \tag{22}$$

Thus the asymptotic behaviour of the solutions of the generalized Smoluchowski equation with constant reaction rates is essentially independent of any features of initial conditions and evolves into the universal scaling form (22).

3. Sum kernel

We now turn to a model of aggregation by n-body collisions with the sum kernel

$$K(i_1,\ldots,i_n)=i_1+\ldots+i_n. \tag{23}$$

Substitution of (23) into the generalized Smoluchowski equation (1) yields

$$\frac{dC_k}{dt}=k\sum_{i_1+\ldots+i_n=k}C_{i_1}\ldots C_{i_n}-nC_k[kN^{n-1}+(n+1)M_0N^{n-2}]. \tag{24}$$

The total number of clusters obeys the following equation:

$$\frac{dN}{dt}=-n(n-1)M_0N^{n-1}. \tag{25}$$

The solution of this equation is

$$N(t)=N_0[1+n(n-1)(n-2)M_0t]^{-1/(n-2)}. \tag{26}$$

We see that the total number of clusters decreases algebraically as a function of time for $n>2$, rather than exponentially as for $n=2$. Thus the model of aggregation by n-body collisions with the sum kernel at $n>2$ is much less reactive than the corresponding binary model.

Proceeding with the solution of (24), we seek a transformation that will transform away the second term on the right-hand side without spoiling the convolution form of the first term. To this end we write the distribution in the form

$$C_k(t)=a_k(t)\exp\left\{-n\int_0^t[kN^{n-1}+(n-1)M_0N^{n-2}]\,dt\right\}. \tag{27}$$

Substitution of (27) into (24) yields

$$\frac{da_k}{dt}=k\sum_{i_1+\ldots+i_n=k}a_{i_1}\ldots a_{i_n}\exp\left\{-n(n-1)^2M_0\int_0^t dt'[N(t')]^{n-2}\right\}. \tag{28}$$

Finally we introduce the scaled time variable

$$T=\int_0^t dt'\exp\left\{-n(n-1)^2M_0\int_0^{t'}dt''[N(t'')]^{n-2}\right\} \tag{29}$$

and after simple calculations we obtain the reduced equation

$$\frac{da_k}{dT}=k\sum_{i_1+\ldots+i_n=k}a_{i_1}\ldots a_{i_n}. \tag{30}$$

The generating function method is useful in solving the system (30). We introduce

$$G(y, T) = \sum_{k=1}^{\infty} a_k(T) \exp(ky) \tag{31}$$

then multiply (30) by $\exp(ky)$, sum over all k and find

$$\frac{\partial G}{\partial T} = nG^{n-1} \frac{\partial G}{\partial y}. \tag{32}$$

To solve (32) we introduce the inverse function $y = Y(G, T)$ and find a simple equation

$$\frac{\partial Y}{\partial T} = -nG^{n-1}. \tag{33}$$

One can find the implicit general solution of this equation

$$G(y, T) = G(y + nTG^{n-1}, 0). \tag{34}$$

For the monodisperse initial conditions, $G(y, 0) = \exp(y)$, we reduce (34) to

$$G(y, T) = \exp(y + nTG^{n-1}). \tag{35}$$

To obtain the cluster-size distribution, we use the Lagrange expansion of G in a power of $\exp(y)$. After some algebra, one can obtain the non-zero concentrations

$$a_{1+k(n-1)}(T) = nT([1 + k(n-1)]nT)^{k-1}/k!. \tag{36}$$

Substitution of (26) at $N_0 = M_0 = 1$ into (27) and (29) yields

$$C_k = a_k N \exp(-knT) \tag{37}$$

$$T = \frac{1 - N}{n(n-1)}. \tag{38}$$

Thus for the monodisperse distribution we arrive at the exact solution

$$C_{1+k(n-1)}(T) = nNT \exp(-[1 + k(n-1)]nT)([1 + k(n-1)]nT)^{k-1}/k! \tag{39}$$

with N and T given by (26) and (38), respectively. This cluster-size distribution belongs to the scaling class. Actually, in the scaling limit

$$k \to \infty \qquad t \to \infty \qquad x = kN^2/2 = \text{finite} \tag{40}$$

we can rewrite (39) as follows:

$$C_{1+k(n-1)} \simeq \frac{N^4}{4\sqrt{\pi}(n-1)} x^{-3/2} \exp(-x). \tag{41}$$

In deriving (41) we employed the relation (38) and Stirling's approximation.

4. Discussion and conclusions

We have presented an idealized aggregation model of particles coagulating by n-body collisions. The model reduces to the usual aggregation process at $n = 2$.

In the mean-field limit, n-particle aggregation processes are described by the generalized Smoluchowski equation. For the constant kernel, we obtained a general solution to this equation and observed the universal scaling behaviour. For the sum kernel, we found an implicit general solution and also an explicit exact solution for the monodisperse distribution.

Much attention has recently been paid to the definition of conditions under which systems aggregating by binary collisions are correctly described by the corresponding mean-field rate equations [8-14]. The discussion has focused on the value of the upper critical dimension d_c. For $d > d_c$ the mean-field description is valid at all times; for $d < d_c$ different behaviour is to be expected at $t \to \infty$. For the simple chemical reactions $A + A \to$ inert and $A + A \to A$, the result is $d_c = 2$ [8-11]. Kang and Redner [12] observed that the simplest model $K(i, j) =$ constant, with constant diffusion coefficients $D(k) = D$, reduces to the reaction scheme $A + A \to A$ if one considers only the number of clusters. Hence, $d_c = 2$ also for this aggregation model.

We now discuss the simplest constant rate n-particle aggregation model with constant diffusion coefficients. In the same fashion, we map this model to the chemical reaction $A + \ldots + A \to A$ and then find the upper critical dimension for this process by appropriate generalization of simple dimensional arguments by Toussaint and Wilczek [10]. To this end we write the rate equation for the particle density $a(t)$

$$\frac{da}{dt} = -Ka^n \tag{42}$$

which has the solution

$$a(t) = a_0[1 + (n-1)Ka_0^{n-1}t]^{-1/(n-1)}$$
$$\to [(n-1)Kt]^{-1/(n-1)} \qquad \text{at } t \to \infty.$$

The reaction rate K depends on the diffusion constant D and the size R of particles, $K = K(D, R)$. A simple dimensional analysis gives

$$K \sim DR^{d(n-1)-2}. \tag{44}$$

Combining (43) and (44) leads to

$$a(t) \sim R^{[2/(n-1)]-d}(Dt)^{-1/(n-1)} \qquad \text{at } t \to \infty. \tag{45}$$

On the physical ground, the particle density must be the decreasing function of the particle size, i.e. (45) is valid only at $d > 2(n-1)^{-1}$. Hence

$$d_c = \frac{2}{n-1} \tag{46}$$

for n-particle aggregation processes with constant reaction rates. Notice, that at $d < d_c$ the particle density does not depend on R at $t \to \infty$. Therefore $a = a(D, t)$ and dimensional analysis yield the universal (i.e. independent of n) asymptotical behaviour at $d < d_c$ and $t \to \infty$:

$$a(t) \sim (Dt)^{-d/2}. \tag{47}$$

We see that the mean-field results of section 2 are valid at all times and at all dimensions $d \geqslant 1$ for n-particle constant reaction kernel when $n \geqslant 3$, with possible logarithmic corrections at $d = 1$ and $n = 3$.

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References

[1] Smoluchowski M V 1917 *Z. Phys. Chem.* **92** 129, 155
[2] Drake R L 1972 *Topics of Current Aerosol Research* vol III, part 2, ed G M Hidy and J R Brook (Oxford: Pergamon)
[3] Frielander S K 1977 *Smoke, Dust and Haze: Fundamentals of Aerosol Behaviour* (New York: Wiley)
[4] Yu Jiang and Hu Gang 1989 *Phys. Rev.* B **39** 4659
[5] Treat R P 1990 *J. Phys. A: Math. Gen.* **23** 3003
[6] Yu Jiang and Hu Gang 1989 *Phys. Rev.* B **40** 661
[7] Yu Jiang, Hu Gang and Ma B K 1990 *Phys. Rev.* B **41** 9424
[8] Kang K and Redner S 1985 *Phys. Rev.* A **32** 435
[9] Bramson M and Griffeath D 1980 *Ann. Prob.* **8** 183
[10] Toussaint D and Wilczek F 1983 *J. Chem. Phys.* **78** 2642
[11] Peliti L 1986 *J. Phys. A: Math. Gen.* **19** L135
[12] Kang K and Redner S 1984 *Phys. Rev.* A **30** 2833
[13] van Dongen P G J 1989 *Phys. Rev. Lett.* **63** 1281
[14] ben-Avraham D and Redner S 1986 *Phys. Rev.* A **34** 501