Irreversible kinetic coagulations in the presence of a source

1987 J. Phys. A: Math. Gen. 20 L801

(http://iopscience.iop.org/0305-4470/20/12/009)

J. Phys. A: Math. Gen. **20** (1987) L801-L805. Printed in the UK

LETTER TO THE EDITOR

Irreversible kinetic coagulations in the presence of a source

Hisao Hayakawa
Department of Physics, Faculty of Science, Kobe University, Kobe 657, Japan

Received 6 May 1987

Abstract. The Smoluchowski equation with a source is analysed. Universal power-law distributions of cluster size are obtained in non-gelling and gelling systems.

Coagulation is an irreversible physical process in which a number of basic units (monomers) stick together to build clusters. There are two fundamental aspects in such processes: firstly the geometry, i.e. structures of aggregated clusters, and secondly the kinetics, such as time evolution of cluster size distribution. Recently, the first aspect has been very much studied (Witten and Sander 1981, Meakin 1983, Kolb *et al* 1983) due to the introduction of the mathematical concept of fractals (Mandelbrot 1982). However, we have few analytic results for this first aspect. The second aspect has an important role as a bridge between an analytic description by the kinetic equation and experimental data or numerical simulations.

In many cases, the coagulation process is controlled by diffusion and reaction: both having characteristic times, t_d and t_r respectively. The diffusion time t_d is the typical time needed for clusters to come close together. The reaction time t_r is the time taken to form a chemical bond between contacted clusters. If one of these timescales is much greater than the other, it is possible to find a simplified kinetic description on the timescale of the slower process. We refer to two extreme cases as the diffusion-limited cluster aggregation (DLCA) if $t_d \gg t_r$ and the reaction-limited cluster aggregation (RLCA) if $t_d \ll t_r$. In both cases, time evolution of clustering processes can be described by the Smoluchowski equation (Smoluchowski 1916, 1918). This equation has been widely used to describe kinetics of aggregation in many fields of science, for instance, coagulation of aerosol and colloid (Friedlander 1977), polymerisation (Ziff 1980), antigen-antibody aggregation (Johnston and Benedek 1984), cluster formation of galaxies (Silk and White 1978) and red blood cell aggregation (Samsel and Perelson 1982).

Coagulation processes with creation of monomers are often observed in aerosol systems (Drake 1972). Aerosols are created by various natural processes, such as smoke particles from fires, sand and dust storms, condensation of water vapours in the atmosphere, nucleation through chemical reactions and meteoritic dust. Although the Smoluchowski equation has been widely investigated (as reviewed by Ziff (1984) and Ernst (1985, 1986)), we have only a few results for the coagulation equation with injections (Klett 1975, Lushinikov and Piskunov 1976, Lushinikov *et al* 1981, White 1982, Crump and Seinfeld 1982). In this letter, we investigate a coagulation system with a permanent source by solving the Smoluchowski equation.

0305-4470/87/120801+05$02.50

The generalised Smoluchowski equation involving both source and sink is represented by

$$\dot{c}_k(t) = \tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i(t) c_j(t) - c_k(t) \sum_{j=1}^{\infty} K_{kj} c_j(t) + I_k - R_k c_k(t). \tag{1}$$

Here $c_k(t)$ denotes the number of clusters of size k (k-mers) per unit volume and K_{ij}, the coagulation kernel or rate coefficient, denotes the probability of coalescence of an i-mer and a j-mer in unit time. We introduce I_k and R_k as the permanent source and sink, respectively. The effect of the sink often appears in real physical processes, for instance, gravitational sedimentations where R_k is proportional to $k^{-2/3}$ (Klett 1975). When the sink term appears in equation (1), Crump and Seinfeld (1982) proved the following statement: if the coefficients of equation (1) satisfy the relations $K_{ij} \leqslant K(ij)^{\alpha+\beta}$, $R_k \geqslant Rk^{\beta}$, $R > 0$, $\beta > 0$ and $\alpha < \frac{1}{2}$, then the steady-state solution c_k has a tail that decays faster than any power of cluster size. In the absence of a sink, we know of a steady-state solution obeying a power law in the case of $K_{ij} = K(ij)^{\beta}$ (Klett 1975, White 1982). In this letter, we solve equation (1) with $K_{ij} = K(i^{\mu}j^{\nu} + i^{\nu}j^{\mu})$ and $R = 0$. When a sol–gel transition (or gelation) occurs, i.e. an infinite cluster emerges at a critical time, we obtain a self-consistent post-gel solution. If there is no gelation (in a non-gelling system), we derive a steady solution obeying a power law of cluster size.

Most of the coagulation kernels used in the description of physical phenomena are homogeneous functions of i and j, at least for large cluster sizes (Ernst 1985, 1986, van Dongen and Ernst 1984). We restrict ourselves to such kernels and we characterise K_{ij} by exponents μ and ν

$$K_{ij} \simeq i^{\mu} j^{\nu} \qquad j \geqslant i \tag{2a}$$

$$K_{ai,aj} \simeq a^{\lambda} K_{ij} \qquad \lambda = \mu + \nu,\ a = \text{constant}. \tag{2b}$$

Since the average number of reactive sites on a cluster cannot increase faster than its size, we impose the physical restrictions $\lambda \leqslant 2$ and $\nu \leqslant 1$ (van Dongen and Ernst 1984). In this case, some properties of $c_k(t)$ are determined by the parameter μ. Ernst (1985, 1986) distinguished three classes: $\mu > 0$ (class I), $\mu = 0$ (class II) and $\mu < 0$ (class III). A typical example of class I is RLCA, such as polymerisation, and an example of class III is DLCA, occurring in aerosol coagulation.

To simplify our discussion, we restrict ourselves to the simplest case satisfying (2a) and (2b). Then, K_{ij}, I_k and R_k are defined as

$$K_{ij} = K(i^{\mu}j^{\nu} + i^{\nu}j^{\mu}) \tag{3a}$$

$$I_k = I\delta_{k1} \tag{3b}$$

$$R_k = Rk^{\gamma} \tag{3c}$$

where K, I and R are constants. From equation (3a), a restriction $\nu \leqslant 1$ is replaced by $\max(\mu, \nu) \leqslant 1$.

First, we consider the asymptotic form of cluster size for a large time limit without gelation. As time goes to infinity, the time evolution of the cluster size distribution begins to cease, as the system approaches a steady state. Therefore, the Smoluchowski equation is reduced to the following form in a large time limit:

$$0 = \tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j + I_k - R_k c_k. \tag{4}$$

We substitute (2*a*) and (2*b*) into (4)

$$0 = K \sum_{i+j=k} i^\mu j^\nu c_i c_j - Kk^\mu c_k M_\nu - Kk^\nu c_k M_\mu + I\delta_{k1} - Rk^\gamma c_k \tag{5}$$

where M_n is the nth moment of c_k

$$M_n = \sum_k k^n c_k. \tag{6}$$

In order to solve equation (5), we introduce a generating function $f_n(x) = \Sigma_k\, k^n c_k\, \mathrm{e}^{-kx}$ which has the following behaviour for small x (Ziff *et al* 1982, Hendriks *et al* 1983):

$$f_n(x) \sim M_n + a(n)x^{\alpha(n)} \tag{7}$$

where $\alpha(n)$ is positive because of the continuity of the generating function at $x = 0$. We are interested in the case when $\alpha(n)$ is not equal to unity. In such a case, M_{1+n} is divergent and the second term of equation (7) expresses the leading singularity of $f_n(x)$ at $x = 0$. Multiplying e^{-kx} and 1 by equation (5) and summing them over all k and subtracting one from the other, we obtain

$$0 = K(f_\mu - M_\mu)(f_\nu - M_\nu) + I(\mathrm{e}^{-x} - 1) - R(f_\gamma - M_\gamma). \tag{8}$$

Substituting (7) into (8) we obtain

$$Ix \simeq Ka(\mu)a(\nu)x^{\alpha(\mu)+\alpha(\nu)} - Ra(\gamma)x^{\alpha(\gamma)}. \tag{9}$$

If R is not equal to zero, then $\alpha(\gamma) = 1$ for any $\alpha(\gamma) < \alpha(\mu) + \alpha(\nu)$. Thus $f_\gamma(x)$ contains no singularity in the second term of equation (7). The regularity of the generating functions and the convergence of all moments can be proved by the inductive method under the condition $\gamma \geqslant \max(\mu, \nu)$ (Hayakawa 1987). Namely, a solution of (4) does not obey any power of k, which is consistent with the result of Crump and Seinfeld (1982). If $R = 0$, then the generating functions are not regular and the following relations are derived:

$$\alpha(\mu) + \alpha(\nu) = 1 \qquad Ka(\mu)a(\nu) = I. \tag{10}$$

When $\alpha(n)$ is not unity, equation (7) is identical to (see Hendriks *et al* 1983, Robinson 1951)

$$k^n c_k \simeq a(n)k^{-\alpha(n)}/\Gamma(\alpha(n)) \qquad \text{as } k \to \infty \tag{11}$$

where $\Gamma(x)$ denotes a gamma function. From equation (11) for μ and ν, we can see that $\alpha(\mu) + \mu = \alpha(\nu) + \nu$. This result and equation (10) lead to

$$\begin{aligned} &\alpha(\mu) = \tfrac{1}{2}(1 + \nu - \mu) \equiv \alpha + \tfrac{1}{2} \qquad \alpha(\nu) = \tfrac{1}{2} - \alpha \\ &a(\mu) = a(\nu)\Gamma(-\alpha - \tfrac{1}{2})/\Gamma(\alpha - \tfrac{1}{2}). \end{aligned} \tag{12}$$

The distribution of cluster size finally yields

$$c_k \simeq \left(\frac{I(1 - 4\alpha^2)\cos \pi\alpha}{4\pi K}\right)^{1/2} k^{-(3+\mu+\nu)/2} \tag{13}$$

where $\alpha = \frac{1}{2}(\nu - \mu)$. There are some restrictions on μ and ν. The divergence of $a(\mu)$ and $a(\nu)$ leads to $\mu, \nu > -1$ and $|\mu - \nu| < -1$. A finite total number of clusters means that $\mu + \nu > -1$. By summarising the above restrictions, we can apply the expression of equation (13) to the inner region of the square in figure 1, i.e. $|\mu + \nu| < 1$ and $|\mu - \nu| < 1$. This square belongs to the non-gelling region according to the theorem of

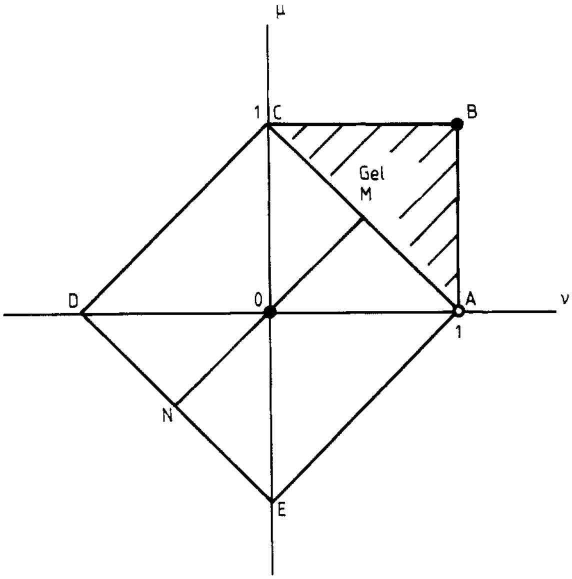

Figure 1. Our solutions in a parameter (μ, ν) space. Non-gelling steady-state solutions are inside the square ACDE in which border lines are not included. Self-consistent post-gel solutions are inside the triangle ABC where AB and BC are included and CA is excluded. Steady solutions on the straight line MN have already been obtained by White (1982). Time-dependent solutions at A, B and 0 were obtained by the Russian group (Lushnikov and Piskunov 1976, Lushnikov *et al* 1981) who proved that there is no steady-state solution at A.

White (1980). (White proves the existence of global initial solutions and the convergence of all moments at finite time in the case of $K_{ij} \leq K(i+j)$.) When there is no injection, i.e. $I=0$, we obtain only a trivial solution from equation (13). Therefore, we conclude that the balance between injection and coagulation leads to an asymptotic power-law distribution of cluster size. The Brownian coagulation in the continuum region with $K_{ij} = K(i^{1/3}+j^{1/3})(i^{-1/3}+j^{-1/3})$ (Chandrasekhar 1943) is the most important in colloidal and aerosol science. We can apply our method directly to this coagulation and obtain an asymptotic power law of cluster size as $c_k \sim k^{-3/2}$. In a time evolution of cluster size, the tail obeying the power law can be observed in the intermediate range of cluster size, because equation (4) holds approximately for suitable k.

We also get a self-consistent post-gel solution at finite time by the same method. We use two generating functions: $f_n(x, t) = \Sigma_k k^n c_k(t)\,\mathrm{e}^{-kx}$ and $g(x, t) = \Sigma_k c_k(t)\,\mathrm{e}^{-kx}$. If $R=0$, then we obtain the solution in the same manner:

$$c_k(t) \simeq \left(\frac{(\dot{M}_1 - I)(4\alpha^2-1)\cos \pi\alpha}{4\pi K}\right)^{1/2} k^{-(3+\mu+\nu)/2}. \tag{14}$$

A finite total mass of clusters at finite time leads to $\mu+\nu>1$. The conditions $\mu, \nu>0$ and $|\mu-\nu|<1$ are derived by the divergence $a(\mu)$ and $a(\nu)$. Equation (14) expresses a post-gel solution, because non-zero $\dot{M}_1 - I$ means a violation of mass conservation in the sol phase. This post-gel solution is essentially the same as that of no-injections obtained by Hendriks *et al* (1983).

We summarise our results. (i) The balance between injection and coagulation leads to an asymptotic power-law distribution of cluster size for the kernel $K_{ij} = K(i^\mu j^\nu + i^\nu j^\mu)$ in a non-gelling system. Our conclusion supports the results of a river model obtained by Takayasu and Nishikawa (1986) and a one-dimensional ballistic model by Hayakawa *et al* (1987). (ii) When gelation occurs, the effect of injection is not essential. We emphasise the result that $c_k \propto k^{-(3+\mu+\nu)/2}$ is a universal form in both (i) and (ii). There are many situations involving physical injections and negligible removals in nature. Our analysis suggests an origin of the often observed power-law distributions of cluster size. The power-law distribution represents one of the characteristic aspects of fractals. We believe our results to be a first step towards explaining why we often see fractals in nature.

The author is grateful to Dr H Takayasu for suggesting this problem and for Mr M Yamamoto for stimulating discussions. He also thanks Professor O Nagai for a critical reading of the manuscript.

References

Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
Crump J G and Seinfeld J H 1982 *J. Colloid Interface Sci.* **90** 469
Drake R L 1972 *Topics in Current Aerosol Research* vol 3, ed G M Hiddy and J R Brock (Oxford: Pergamon)
Ernst M H 1985 *Fundamental Problems in Statistical Mechanics* vol 6, ed E G D Cohen (Amsterdam: Elsevier)
—— 1986 *Fractals in Physics* ed L Pietronero and E Tosatti (Amsterdam: Elsevier)
Friedlander S K 1977 *Smoke, Dust and Haze* (New York: Wiley Interscience)
Hayakawa H 1987 unpublished
Hayakawa H, Yamamoto M and Takayasu H 1987 *Prog. Theor. Phys.* to be published
Hendriks E M, Ziff R M and Ernst M H 1983 *J. Stat. Phys.* **31** 519
Johnston D and Benedek L 1984 *Kinetics of Aggregation and Gelation* ed F Family and D P Landau (Amsterdam: Elsevier)
Klett J D 1975 *J. Atom. Sci.* **12** 380
Kolb M, Botet R and Jullien R 1983 *Phys. Rev. Lett.* **51** 1123
Lushnikov A A and Piskunov V N 1976 *Dokl. Phys. Chem.* **231** 1403
Lushnikov A A, Tokar Ya I and Tsitskishvili M S 1981 *Dokl. Phys. Chem.* **256** 1155
Mandelbrot B B 1982 *The Fractal Geometry of Nature* (San Francisco: Freeman)
Meakin P 1983 *Phys. Rev. Lett.* **51** 1119
Robinson J E 1951 *Phys. Rev.* **83** 678
Samsel R W and Perelson A S 1982 *Biophys. J.* **37** 493
Silk J and White S D 1978 *Astrophys. J.* **223** L59
Smoluchowski M V 1916 *Z. Phys.* **17** 557
—— 1918 *Z. Phys. Chem.* **92** 129
Takayasu H and Nishikawa I 1986 *Proc. 1st Int. Symp. on Science of Form* ed S Ishizaka (Tokyo: KTK Science Publisher)
van Dongen P G J and Ernst M H 1984 *Phys. Rev. Lett.* **54** 1396
White W H 1980 *Proc. Am. Math. Soc.* **35** 273
—— 1982 *J. Colloid Interface Sci.* **87** 204
Witten T A and Sander L M 1981 *Phys. Rev. Lett.* **47** 1400
Ziff R M 1980 *J. Stat. Phys.* **23** 241
—— 1984 *Kinetics of Aggregation and Gelation* ed F Family and D P Landau (Amsterdam: Elsevier)
Ziff R M, Hendriks E M and Ernst M H 1982 *Phys. Rev. Lett.* **49** 589