

EXACT SOLUTIONS TO THE COAGULATION EQUATION

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Explicit post-gelation solutions are presented for Smoluchowski's coagulation equation with factorizable transition kernels $K_{ij} = s_i s_j$, when $s_k = k^\omega$ ($\omega > 1/2$) and $s_k = \exp[\alpha(k-1)]$ ($\alpha > 0$). In such solutions the total mass of sol (finite clusters) is not conserved in time, as the sol is loosing mass to the gel (infinite cluster). For the kernels $K_{ij} = i\mu_j^\nu + j\mu_i^\nu$ ($\mu = 0, 1, \nu$ general) Smoluchowski's equation can be solved sequentially in terms of a transformed time variable.

In coagulation processes Smoluchowski's equation describes the time evolution of the size distribution function $c_k(t)$, denoting the concentration of clusters of size k :

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

where the coagulation kernel K_{ij} models the coalescence mechanism of an i - and a j -cluster. Here we neglect fragmentation, source and sedimentation terms which are frequently added in studies of aerosol coagulation.

The exact solution for a given initial distribution $c_k(0)$ is only known for kernels of the general form $K_{ij} = A + B(i+j) + C_{ij}$ [1-4]. If $C \neq 0$, the solution $c_k(t)$ undergoes a phase transition, called gelation; viz. before the gelpoint t_c the total mass of finite size clusters (sol), $M_1(t) = \sum k c_k(t)$, is constant; at t_c an infinite cluster (gel) appears causing $M_1(t)$ to decrease for $t \geq t_c$, as the sol is loosing mass to the gel.

The purpose of the present letter is to show (i) that explicit post-gelation solutions, with $\dot{M}_1(t) \neq 0$, can

be found for factorizable kernels $K_{ij} = s_i s_j$ under some further restrictions on s_k , and (ii) that for a few other kernels the coagulation equation can be solved sequentially. Details will be published elsewhere [5].

A special post-gelation solution of the coagulation equation is suggested by the exact solution for a monodisperse initial distribution in the cases $s_k = (f-2)k + 2$ with $f \geq 3$ [2], and $s_k = k$ [3]. Past the gel point the size distribution is simply given by:

$$c_k(t) = c_k(t_c) [1 + b(t - t_c)]^{-1} \quad (t \geq t_c). \quad (2)$$

In the former case $t_c = 1/f(f-2)$ and $b = f^2(f-2)/(f-1)$ and in the latter case $t_c = b = 1$. Up to the gel point the mass is conserved ($M_1 = 1$), and past the gel point $M_1(t) = [1 + b(t - t_c)]^{-1}$. Therefore we investigate whether a post-gelation solution of the form (2) [satisfying $M_1(t_c) = 1$] is possible for the models $K_{ij} = s_i s_j$. On substituting (2) into (1) we find that the time part cancels, and we obtain a recursion relation for $c_k(t_c)$, where consistency for $k=1$ requires $b = \sum s_k c_k(t_c)$ (a proper choice of time unit gives $s_1 = 1$). By introducing $n_k = c_k(t_c)/b$ it takes the simple form:

$$(s_k - 1)n_k = \frac{1}{2} \sum_{i+j=k} s_i s_j n_i n_j, \quad (3)$$

which has to be solved subject to the condition:

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$$\sum s_k n_k = 1, \quad \text{or} \quad \sum n_k = \frac{1}{2}. \quad (4)$$

For a given n_1 , (3) determines all n_2, n_3, \dots . Choosing n_1 such that (4) is satisfied, one can then in principle find b from $M_1(t_c) = 1$ through $b^{-1} = \sum k n_k$. The solution will be obtained by introducing generating functions:

$$G(x) = \sum_k n_k e^{kx}, \quad F(x) = \sum_k s_k n_k e^{kx}. \quad (5)$$

If $1/s_k$ can be written as a Laplace transform, i.e.

$$1/s_k = \int_0^\infty dy \, \sigma(y) \exp(-ky),$$

then F and G are related by

$$G(x) = \int_0^\infty dy \, \sigma(y) F(x-y),$$

and it follows from the recursion relation (3) that

$$F - G = \frac{1}{2} F^2, \quad \text{or} \quad F = 1 - (1 - 2G)^{1/2}, \quad (6a)$$

or

$$F(x) - \frac{1}{2} F^2(x) = \int_0^\infty dy \, \sigma(y) F(x-y). \quad (6b)$$

We discuss two classes of models: $s_k = k^\omega$, where $\sigma(y) = y^{\omega-1}/\Gamma(\omega)$ [when ω is a positive integer F and G are simply related by differentiation: $F = (d/dx)^\omega G$], and $s_k = \exp[\alpha(k-1)]$, where $\sigma(y) = e^\alpha \delta(y-\alpha)$.

In the case, $s_k = k^2$, where $F = G'' = \sum k^2 n_k e^{kx}$, (6a) reduces to a differential equation, which can be solved to yield:

$$e^x = \frac{(\sqrt{3}+1)(\sqrt{3}-r)}{(\sqrt{3}-1)(\sqrt{3}+r)} \exp[\sqrt{3}(r-1)], \quad (7)$$

where $r = \sqrt{3 - 2F}$. The n_k follow by expanding $F(x)$ in powers of e^x , using Lagrange's expansion [6]. n_1 is obtained as:

$$n_1 = \lim_{x \rightarrow -\infty} e^{-x} F(x) = 6(2 - \sqrt{3})e^{\sqrt{3}-3}, \quad (8)$$

and the higher n_k are:

$$n_k = n_1^k \sum_{l=0}^{k-1} \frac{(k+l+1)(k-1)!}{l!(k-l+1)!(k-l-1)!} \left(\frac{-1}{6}\right)^l. \quad (9)$$

From $G'(0) = b^{-1}$ we obtain $b = M_2(t_c) = \sqrt{3}$. The large- k dependence of this solution is:

$$n_k \sim (2\pi\sqrt{3})^{-1/2} [k^{-7/2} + (3\sqrt{3}/8)k^{-9/2} + \dots]. \quad (10)$$

Thus we have determined all parameters (except t_c) in the post-gelation solution (2) for the model $s_k = k^2$, and obtained what constitutes a new solution to the coagulation equation.

In the general case $s_k = k^\omega$, post-gelation solutions only exist for $\omega > 1/2$ [7,8], and the quantities b and n_1 have been determined numerically [5]. Analytically only a few limiting properties can be calculated: viz.

(i) the small- x behavior of F is $F(x) \approx 1 - (-2x/b)^{1/2} + \dots$, implying $n_k \sim (2\pi b)^{-1/2} k^{-\omega-3/2} + \dots$ at large k , and (ii) for large ω

$$k^\omega n_k \approx -(-\frac{1}{2})_k / k! + \frac{1}{4} 2^{-\omega} (-3/2)_k / [3(k-1)!],$$

$$b \approx \left(\sum k n_k \right)^{-1} \approx 2 - \frac{1}{2} 2^{-\omega} + \dots,$$

$$\sum k^\alpha n_k \approx \frac{1}{2} + 1/8(2^\alpha - 1)2^{-\omega} + \dots \quad (\alpha \ll \omega), \quad (11)$$

where $(a)_k = \Gamma(a+k)/\Gamma(a)$.

In the case $s_k = \exp[\alpha(k-1)]$ post-gelation solutions only exist for $\alpha > 0$. The integral equation (6b) reduces to a difference equation:

$$F(x) - \frac{1}{2} F^2(x) = e^\alpha F(x-\alpha), \quad (12)$$

to be solved subject to $F(0) = 1$. The relevant quantities can be determined as follows:

$$\lim_{x \rightarrow -\infty} e^{-x} F(x) = n_1,$$

and all n_k are calculated from (3). Since $F(0) = \sum s_k n_k < \infty$, all moments exist, and

$$b^{-1} = e^\alpha F'(-\alpha); \quad \sum k^l n_k = e^\alpha F^{(l)}(-\alpha), \quad (13)$$

where $F^{(l)}(x)$ denotes the l th derivative. The solution is determined by defining numbers $p_k = e^{k\alpha} F(-k\alpha)$, which obey the recursion relation

$$p_{k+1} = p_k (1 - \frac{1}{2} e^{-k\alpha} p_k) \quad (p_0 = 1). \quad (14)$$

The limiting value gives $p_\infty = n_1$. For $\alpha > 0$ the p_k constitute a monotonically decreasing sequence of positive numbers, implying the existence of p_∞ , and the post-gelation solution (2) exists. (For $\alpha \leq 0$ no post-gelation solutions are possible). If α is not too small, (14) has the solution:

$$p_\infty = \frac{1}{2}(1 - \frac{1}{4}e^{-\alpha} - \frac{1}{4}e^{-2\alpha} - e^{-3\alpha}/8 + \dots), \quad (15)$$

and the n_k can be determined as a power series in $e^{-\alpha}$.

To obtain b we introduce another set of numbers $q_k = e^{k\alpha}F'(-\alpha)$, where $q_\infty = p_\infty = n_1$. A recursion relation for q_k is obtained by differentiating (12):

$$q_{k+1} = q_k(1 - e^{-k\alpha}p_k) \quad (q_\infty = n_1), \quad (16)$$

so that

$$b = (q_1)^{-1} = (n_1)^{-1} \prod_{k=1}^{\infty} (1 - e^{-k\alpha}p_k). \quad (17)$$

In general the recursion relations (14) and (16) must be solved numerically, yielding n_1 and b as a function of the parameter α [5]. The large- k behavior is given by

$$n_k \sim (2\pi b)^{-1/2} k^{-3/2} \exp[(1-k)\alpha] + \dots$$

The limiting case $\alpha \gg 1$ is completely analogous to the large- ω case, and the corresponding results are obtained from (11) by replacing $k^\omega n_k$ on the first line by $e^{(k-1)\alpha} n_k$, and $2^{-\omega}$ everywhere by $e^{-\alpha}$.

The question arises [5,8] whether the special solution (2) evolves from a monodisperse initial distribution, as is the case in the exactly solvable models. Although the solution to the initial value problem is not known, we can give a definite and negative answer to this question for the cases: $s_k = k^\omega$ with $\omega \gtrsim 1.1$ and $s_k = \exp[\alpha(k-1)]$ for $\alpha > \log 2$ by using inequalities. For the remaining range of α - and ω -values (except $\omega = 1$) we expect also a negative answer, but the question has not been settled.

In the second part of this letter we discuss the models $K_{ij} = ij^\mu + ji^\mu$ and $K_{ij} = i^\lambda + j^\lambda$, for which the coagulation equation can be solved sequentially. As far as gelation is concerned the following is known about these models. If $K_{ij} \leq C(i+j)$ (here $\mu \leq 0$ and $\lambda \leq 1$), White [9] has shown that the coagulation equation does not show a gelation transition. If $\mu > 0$ and $\lambda > 1$ gelation occurs [10]; possible pre-gelation solutions ($t < t_c$) have the scaling form

$$c_k(t) \sim k^{-\tau} \Phi(k(t_c - t)^{1/\sigma})$$

as $t \uparrow t_c$ and $k \rightarrow \infty$ with $x = k(t_c - t)^{1/\sigma}$ fixed; and possible post-gelation solutions have the form $c_k(t) \sim k^{-\tau} A(t)$ for large k . In the first model with $\mu > 0$ (where existence of global solutions follows from the work of Leyvraz and Tschudi [8] for $\mu \leq 1$) we found $\tau = 2 + \frac{1}{2}\mu$ and $\tau + \sigma = \mu + 2$. The second model with $\lambda > 1$ is only meaningful in the pre-gelation stage, where the exponents σ and τ in the scaling form are related as $\sigma + \tau = \lambda + 1$. At a finite time t_c the system undergoes a gelation transition. Post-gelation solutions do not exist, since the coagulation equation is no longer well-defined beyond the gel point, as it contains divergent quantities.

The coagulation equation for the first model $K_{ij} = ij^\mu + ji^\mu$ reads:

$$\dot{c}_k = \sum_{i+j=k} ij^\mu c_i c_j - k c_k M_\mu - k^\mu c_k M_1, \quad (18)$$

where $M_\alpha \equiv \sum k^\alpha c_k$. It has been solved by Lushnikov and Piskunov [11] for $\mu < 0$, where $M_1(t) = 1$ for all $t \geq 0$. Their method can be trivially extended to obtain pre-gelation solutions for the case $\mu > 0$ (where $M_1(t) = 1$ for $t \leq t_c$). With the help of the substitution

$$c_k(t) = \nu_k(t) \exp[kM_0(t)]$$

and the moment equation $\dot{M}_0 = -M_\mu$ (valid in the pre-gelation stage), the coagulation equation can be transformed into:

$$\dot{\nu}_k = \sum_{i+j=k} ij^\mu \nu_i \nu_j - k^\mu \nu_k. \quad (19)$$

The solution of (19) is given in ref. [11], where the unknown $M_0(t)$ can be determined from the transcendental equation:

$$1 = \sum k c_k = \sum k \nu_k \exp[kM_0(t)].$$

The above substitution does not lead to any simplifications in the post-gelation stage, neither does it enable us to locate the gel point exactly. However, in the range $0 < \mu \leq 1$ we have found [5,10] the lower bound $t_b = [2\mu M_2^H(0)]^{-1}$ for t_c . For $\mu \geq 1$ the lower-bound changes into an upperbound.

The coagulation equation for the second model $K_{ij} = i^\lambda + j^\lambda$, reading:

$$\dot{c}_k = \sum_{i+j=k} i^\lambda c_i c_j - c_k M_\lambda - k^\lambda c_k M_0, \quad (20)$$

can also be solved sequentially, as follows: we introduce new variables by the transformation (reminiscent of Lushnikov's transformation [12] where $M_0(t)$ is replaced by $c_1(t)$):

$$\tau = \int_0^t dt' M_0(t'); \quad \nu_k(\tau) = c_k(t)/M_0(t), \quad (21)$$

and with the help of the moment equation $\dot{M}_0 = -M_0 M_\lambda$ we transform (20) into:

$$d\nu_k(\tau)/d\tau = \sum_{i+j=k} i^\lambda \nu_i \nu_j - k^\lambda \nu_k, \quad (22)$$

to be solved subject to the condition, $\sum \nu_k = 1$. Once all $\nu_k(\tau)$ have been determined the function $M_0(t) \equiv \mu_0(\tau)$ can be found as a function of τ from $\sum k \nu_k = 1/\mu_0(\tau) = 1/M_0(t)$ and the original t -variable can be recovered by differentiating $\tau(t)$ in (21) and solving for t with the result

$$t = \int_0^\tau d\tau' [\mu_0(\tau')]^{-1}.$$

For a monodisperse initial distribution where $\nu_k(0) = \delta_{k1}$, the first few ν_k read explicitly:

$$\begin{aligned} \nu_1(\tau) &= e^{-\tau}, \\ \nu_2(\tau) &= (2^\omega - 2)^{-1} [\exp(-2\tau) - \exp(-2^\omega \tau)], \\ \nu_3(\tau) &= -(2^\omega - 2)^{-1} (3^\omega - 2^\omega - 1)^{-1} (2^\omega + 1) \\ &\quad \times \{ \exp[-(2^\omega + 1)\tau] - \exp(-3^\omega \tau) \} + (2^\omega - 2)^{-1} \\ &\quad \times (3^\omega - 3)^{-1} (2^\omega + 1) [\exp(-3\tau) - \exp(-3^\omega \tau)]. \end{aligned} \quad (23)$$

For the case $\lambda \leq 1$ the present method can be used for all t . For the case $\lambda > 1$ the kinetic equation is only well-defined below the gel point. We have not been able to determine t_c exactly, but only obtained the bound

$$t_c \leq [2(\lambda - 1)M_2^{\lambda-1}(0)]^{-1}.$$

Furthermore, without an intervening gelation transition, $M_0(t)$ would become negative within a finite time t_0 , obeying $t_c < t_0 \leq [M_0(0)]^{\lambda-1}/(\lambda - 1)$, so that there would not exist a one-to-one relationship between t and τ .

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