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New exactly solvable models of Smoluchowski's equations of coagulation

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Abstract. The Smoluchowski equations of coagulation are solved analytically in two cases involving a finite cut-off of the system: the constant kernel set to zero for any $j > N$ on the one hand, and the general three-particle case on the other. Both are seen to exhibit rather unusual large-time behaviour. The first model can be used to account for large particles precipitating out of a system and its behaviour is therefore of particular interest.

1. Introduction

The kinetics of irreversible coagulation have been the object of considerable study. In particular the following rate equations for the concentrations c_j of clusters of size j:

$$\dot{c}_j = \frac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} c_k c_{j-k} - c_j \sum_{k=1}^{\infty} R_{jk} c_k$$

(where R_{jk} is the reaction rate between j-clusters and k-clusters) have been quite extensively studied. However, while much work of qualitative or numerical character exists, the only exactly solved case is:

$$R_{kl} = A + B(k+l) + Ckl$$

(see e.g. Drake (1972) and Hendriks *et al* (1983) for the solution for $C \neq 0$ and arbitrary times). Furthermore, the following cases can be solved exactly:

$$R_{jk} = R$$

where an arbitrary monomer production term is added to the equations (see Leyvraz and Tschudi 1980), and equilibrium solutions for $R_{jk} = j^{\beta} k^{\beta}$ if a constant monomer source is added (see White 1982). For more details on exact solutions see e.g. Hendriks *et al* (1983).

It is the aim of this paper to solve exactly the following two kernels:

$$\begin{aligned} R_{jk} &= 1 \qquad &&\text{for } \max(j, k) \leqslant N \\ &= 0 &&\text{otherwise} \end{aligned}$$

and

$$\begin{aligned} R_{11} &= 1; \qquad && R_{12} = R_{21} = a > 0 \\ R_{jk} &= 0 && (j + k > 3). \end{aligned}$$

The first is a cut-off of the ordinary Smoluchowski kinetics. It is of some interest in its own right since such cut-offs are frequently used in numerical work: the exact solution for finite N should then make it possible to discriminate between the error introduced by the cut-off and the purely numerical error.

Further, such a cut-off can be used to model the effect of particles above a certain size precipitating from the system or becoming highly non-reactive by some other, unspecified mechanism. The solution is given by:

$$t = \int_0^x \mathrm{d}y \exp\left(2 \sum_{k=1}^{N} \frac{1}{k}\left(\frac{y}{2}\right)^k\right)$$

$$c_j(t) = \left(\frac{x}{2}\right)^{j-1} \exp\left(-2 \sum_{k=1}^{N} \frac{1}{k}\left(\frac{x}{2}\right)^k\right)$$

which is seen to be valid for N finite or infinite. The most striking difference is that, for N finite, $x(t)$ goes to infinity for large times, whereas for N infinite, $x(t)$ is always less than two. This means that

$$c_j/c_1 = (x/2)^{j-1}$$

will behave totally differently in the two cases. The behaviour occurring for infinite N:

$$\lim_{t\to\infty} c_j/c_1 = 1$$

is also familiar from many other systems (Leyvraz 1984), whereas the behaviour for finite N is rather new and unexpected. Furthermore, one finds for N finite that $c_1(t) \sim (Nt \ln t)^{-1}$ for large times, in contrast to the classical $1/t^2$ behaviour. At finite times, of course, this effect disappears as N is increased, which might make numerical observation difficult. The reason for this anomaly is not quite clear, but it should be noted that for any kernel of the form:

$$R_{jk} = j^\omega k^\omega, \qquad R_{jk} = j^\omega + k^\omega$$

the large-time behaviour has been analysed (Leyvraz 1984) and in the limit $\omega \to 0$ yields a $1/t$-behaviour. It would therefore appear that the constant kernel is, in this respect, somewhat exceptional.

The second kernel represents the reaction scheme:

$$A_1 + A_1 \underset{1}{\rightarrow} A_2, \qquad A_1 + A_2 \underset{a}{\rightarrow} A_3.$$

It is primarily interesting because of its long-time behaviour: $c_1(t)$ either falls off exponentially or as $1/t$, while $c_2(t)$ either saturates to a constant non-zero value or also falls off as $1/t$. Clearly the only reason c_2 can saturate at all is because no reaction of A_2 with itself is possible. Equally clearly if c_2 does saturate to a non-zero value it will cause exponential decrease of all concentrations of such clusters as can react with A_2. The above example shows explicitly that such a situation can indeed arise, even when $c_j(0) = \delta_{j1}$.

It has been pointed out by Lushnikov (1973–1975) and later in a somewhat different manner by Leyvraz (1984) that if

$$R_{jk} > R_{1k} \qquad \text{for all } j \geq 2$$

then

$$c_j/c_1 \rightarrow a_j \qquad (t \to \infty).$$

The following is meant to illustrate the rich variety of large-time behaviours when the above condition on the reaction kernel is violated. I will now proceed to show the exact solutions and discuss their large-time behaviour in detail.

2. Finite Smoluchowski kinetics

The system considered is

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1} c_k c_{j-k} - c_j \sum_{k=1}^{N} c_k \qquad (1 \leq j \leq N)$$

$$c_j(0) = \delta_{j1}.$$

Define

$$S(t) = \sum_{k-1}^{N} c_k(t), \qquad \phi_j(t) = c_j(t)/c_1(t), \qquad x = \int_0^t \mathrm{d}t'\, c_1(t').$$

Clearly

$$\frac{\mathrm{d}\phi_j}{\mathrm{d}x} = \frac{1}{2}\sum_{k=1}^{j-1} \phi_k \phi_{j-k}, \qquad \phi_j(0) = \delta_{j1},$$

and hence $\phi_j(x) = a_j x^{j-1}$ where

$$(j-1)a_j = \frac{1}{2}\sum_{k=1}^{j-1} a_k a_{j-k} \qquad a_1 = 1$$

implying $\phi_j(x) = (x/2)^{j-1}$. It follows that

$$S(x) = \sum_{j=1}^{N} \phi_j(x) c_1 = \sum_{j=1}^{N} \left(\frac{x}{2}\right)^{j-1} \frac{\mathrm{d}x}{\mathrm{d}t}.$$

However

$$S(x) = -(\mathrm{d}\dot{c}_1/\mathrm{d}c_1) = (-\mathrm{d}^2x/\mathrm{d}t^2)(\mathrm{d}x/\mathrm{d}t)$$

and hence

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = \sum_{j=1}^{N} \left(\frac{x}{2}\right)^{j-1} \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2, \qquad x(0) = 0, \qquad \dot{x}(0) = 1.$$

Introducing $p = \dot{x}(x)$, it follows that

$$p\frac{\mathrm{d}p}{\mathrm{d}x} = -\sum_{k=1}^{N} \left(\frac{x}{2}\right)^{k-1} p^2 \qquad p(0) = 1$$

and solving this yields

$$p(x) = \exp\left[-2\sum_{k=1}^{N} \frac{1}{k}\left(\frac{x}{2}\right)^k\right]$$

and hence

$$t = \int_0^x \frac{\mathrm{d}y}{p(y)} = \int_0^x \mathrm{d}y \exp\left[2\sum_{k=1}^{N} \frac{1}{k}\left(\frac{y}{2}\right)^k\right].$$

Therefore

$$c_j(x) = \phi_j(x)\,\mathrm{d}x/\mathrm{d}t$$
$$= \left(\frac{x}{2}\right)^{j-1} \exp\left[-2\sum_{k=1}^{N}\frac{1}{k}\left(\frac{x}{2}\right)^{k}\right].$$

Clearly we have $c_j/c_1 = (x/2)^{j-1} \to \infty$ as $t \to \infty$. This is not so, however, if N is taken to be infinite because the sum $\Sigma_{j=1}^{\infty}(1/j)(x/2)^{j-1}$ diverges at $x=2$, thus limiting the range of x to numbers smaller than 2. This is a strong indication that there is something slightly singular about the fact that

$$c_1(t) \sim 1/t^2 \qquad (t \to \infty)$$

in the classical case. It has been conjectured (Leyvraz 1984) that for the kernels

$$R_{jk} = j^{\omega}k^{\omega} \qquad \text{(product kernel)}$$
$$= j^{\omega} + k^{\omega} \qquad \text{(sum kernel)}$$

we would have

$$c_1(t) \sim 1/t \qquad \text{(product kernel)}$$
$$\sim t^{-[2-\omega/(2-2\omega)]} \qquad \text{(sum kernel)}$$

which both give the same (wrong) result for $\omega = 0$. This is not very surprising, since this case cannot be treated by the methods developed there. For the case of finite N, however, one has for large t (i.e. large x)

$$\sum_{k=1}^{N}\left(\frac{x}{2}\right)^{k-1} \sim \left(\frac{x}{2}\right)^{N-1}$$

and hence

$$\dot{c}_1 = -c_1^2\sum_{k=1}^{N}\left(\frac{x}{2}\right)^{k-1} \sim -c_1^2\left(\frac{x}{2}\right)^{N-1}.$$

However,

$$\ln t \sim 2\sum_{k=1}^{N}\frac{1}{k}\left(\frac{x}{2}\right)^{k} \sim \frac{2}{N}\left(\frac{x}{2}\right)^{N}$$

implying $\dot{c}_1 \sim (N/2)\ln t c_1^2$ and hence $c_1 \sim [Nt(\ln t - 1)]^{-1}$ for large times. This clearly shows that the behaviour predicted for $\omega = 0$ does indeed occur if the finite system is considered but that the size of that asymptotic effect goes to zero as $N \to \infty$. It is, however, difficult to say whether or not this is just a coincidence, since the other main prediction of Leyvraz (1984) that $c_j/c_1 \to a_j \sim j^{-1}$ is still false even for the finite system.

3. General three-molecule system

Consider the system

$$\dot{c}_1 = -c_1^2 - ac_1c_2 \qquad \dot{c}_2 = \tfrac{1}{2}c_1^2 - ac_1c_2$$
$$\dot{c}_3 = ac_1c_2 \qquad c_1(0),\ c_2(0)\ \text{arbitrary}.$$

Clearly the third equation is redundant.

$$\phi = c_2/c_1 \qquad \tau = \ln|c_1|$$

implying

$$d\phi/d\tau = \phi + (1-2a\phi)/(2a\phi+2).$$

The zeros of the right-hand side are

$$\phi_\pm = (1/2a)\{a-1\pm[(a-1)^2-2a]^{1/2}\}.$$

Clearly these are imaginary if

$$2-\sqrt{3} < a < 2+\sqrt{3}$$

and real otherwise. Further it is clear that

$$\phi + (1-2a\phi)/(2a\phi+2) < 0 \qquad \text{if } \phi_- < \phi < \phi_+$$

and larger than zero otherwise. This clearly means that

$$\lim_{\tau\to\infty} \phi(\tau) = \phi_- \qquad (\phi(0) < \phi_+)$$

$$= \infty \qquad (\phi(0) > \phi_+).$$

To obtain the complete solution by quadrature, we remark that

$$\ln c_1 = \ln c_1(0) - \int_{\phi(0)}^{\phi(c_1)} d\phi \bigg/ \left(\phi + \frac{1-2a\phi}{2a\phi+2}\right)$$

and that further

$$\dot{c}_1 = -c_1^2(1+a\phi)$$

yielding

$$t = -\int_{c_1(0)}^{c_1} \frac{dc}{c^2(1+a\phi(0))}.$$

Consider the case where $\phi(t)$ tends to a limit (namely ϕ_-) as $\tau\to\infty$. Clearly, for large times

$$t \sim -\int_{c_1(0)}^{c_1} \frac{dc}{(1+a\phi_-)c^2}$$

and hence

$$c_1 \sim [(1+a\phi_-)t]^{-1}, \qquad c_2 \sim \phi_-/(1+a\phi_-)t.$$

In the opposite case (i.e., in particular when $2-\sqrt{3} < a < 2+\sqrt{3}$) one has

$$\ln c_1 \sim \ln c_1(0) - \int_{\phi(0)}^{\phi(c_1)} \frac{d\phi}{\phi}$$

so that $c_1 \sim c_1(0)/\phi$, implying that

$$t = -\int_{c_1(0)}^{c_1} \frac{dc}{c^2(1+ac_1(0)/c)}$$

$$\sim -[ac_1(0)]^{-1} \ln c_1$$

and therefore $c_1 \sim \exp(-ac_1(0)t)$, leading to

$$c_2 \sim \phi c_1 \sim c_1(0) = 0(1) \qquad (t \to \infty)$$

so that c_2 saturates to a non-zero value.

4. Conclusion

Two new exactly solvable cases of the Smoluchowski equations of coagulation were discussed. These were

$$R_{jk} = R \qquad \max(j, k) \leq N$$
$$= 0 \qquad \text{otherwise}$$

and

$$R_{11} = 1 \qquad R_{12} = R_{21} = a$$
$$R_{jk} = 0 \qquad \text{otherwise}$$

All these kernels violate the condition

$$R_{jk} > R_{1k} \qquad \text{for all } j \geq 2$$

under which the large-time behaviour can be described by saying that the ratios of $c_j(t)$ to $c_1(t)$ approach an equilibrium value.

For these exactly solvable models the large-time behaviour was shown to be sensitively dependent on rather detailed features of the system, thus making it difficult to make any precise suggestions for the large-time behaviour of more general systems violating the above condition on the reaction kernels.

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