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An exact solution of the discrete Smoluchowski equation and its correspondence to the solution of the continuous equation

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Abstract. An exact, general solution of the discrete Smoluchowski equation for the kernel $K_{k,j} = A + B(k+j)$ is derived. Rules are given for taking the continuous limit of the discrete solution. The limit obtained is an exact, general solution of the continuous Smoluchowski equation. Examples of limits are given for specific initial distributions for the case of constant kernel.

1. Introduction

The Smoluchowski equation provides a theory for the time evolution of a size distribution of particles coagulating by two-body collisions [1, 2]. The equation in its original and simplest form expresses the conservation of the mass of a system of colliding particles. It was applied first to small, suspended particles which collide and coagulate by virtue of their Brownian motion and has subsequently been applied to many other physical systems where two-body collisions are the dominant physical process. The discrete form of the equation was derived first by Smoluchowski [1] and was given later in the continuous form by Müller [3]. The discrete equation gives the better theoretical description of a physical system since particles have discrete masses. However, the continuous equation has provided the setting for constructing Laplace transform solutions and Friedlander's self-preserving solutions and studying the temporal asymptotic behaviour of solutions [4–7]. A general review of the considerable amount of mathematical analysis devoted to both forms of the equation has been given by Drake [4].

In this work we consider the discrete equation with the collision matrix

$$K_{k,j} = A + B(k+j) \tag{1}$$

where A and B are constants. This particular collision matrix, here called the linear kernel, has been studied because of its mathematical simplicity and its application to physical systems. The linear kernel represents a certain kind of polymer formation [8], and also approximates a combination of Brownian and shear-flow coagulation [4]. An exact solution for a monodisperse initial distribution has been constructed by Lu [9], but a solution has not been given for general polydisperse initial distributions. In this work we construct the general solution. We then identify some special cases and consider an alternative form of the constant kernel equation.

The exact solution of the continuous equation for the linear kernel for general polydisperse initial distributions was given some time ago by Drake and Wright [10].

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Although exact solutions for both the discrete and continuous equations are known for the linear kernel and quadratic kernels as well, the correspondence between discrete and continuous solutions has not been studied. We consider the correspondence here. The continuous limit is taken to be the limit of the discrete solution as the smallest particle size in the initial discrete distribution goes to zero. We show that the continuous limit of the discrete solution is identical to the exact solution of the continuous equation given by Drake and Wright [10]. For the case of constant kernel, we consider two simple examples of initial discrete distributions. We generate two one-parameter families of discrete solutions which have limits that are well known solutions of the continuous equation.

In the appendix we confirm directly, by taking moments of the general solution for the linear kernel, that the second moment of the distribution is finite for $0 \leq t < \infty$.

2. Transformation of the Smoluchowski equation

The discrete equation is given by

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \frac{1}{2}\sum_{j=1}^{k-1} K_{k-j,j} n_{k-j} n_j - n_k \sum_{j=1}^{\infty} K_{k,j} n_j. \tag{2}$$

In (2) t is time and n_k is the spatial density of particles with volume v_k, where the discrete particle volumes are assumed to be integer multiples of some smallest volume v_1. The first term on the right-hand side of (2) gives the rate of increase of the concentration of particles with volume v_k due to collisions between particles with volumes v_{k-j} and v_j. The second term gives the decrease in concentration due to collisions between particles with volume v_k and all other particles.

The first step in constructing the solution is to transform the Smoluchowski equation to a simpler form. To make the transformation we need to consider the time dependence of the zeroth, first and second moments of the distribution. If the first three initial moments exist, we can take moments of the Smoluchowski equation and obtain the equations

$$\mathrm{d}N/\mathrm{d}t = -\tfrac{1}{2}(AN^2 + 2BM_1N) \tag{3a}$$

$$\mathrm{d}M_1/\mathrm{d}t = 0 \tag{3b}$$

$$\mathrm{d}M_2/\mathrm{d}t = AM_1^2 + 2BM_1M_2 \tag{3c}$$

where the moments are given by

$$N = \sum_{k=1}^{\infty} n_k \qquad M_1 = \sum_{k=1}^{\infty} kn_k \qquad M_2 = \sum_{k=1}^{\infty} k^2 n_k.$$

N is the total particle number and $v_1M_1 = V$ is the volume of the distribution. The integrals of (3) are

$$N = N_0 2\mu_1 B[\exp(-\mu_1 BN_0 t)][A + 2\mu_1 B - A\exp(-\mu_1 BN_0 t)]^{-1} \tag{4a}$$

$$M_1 = \text{constant} \tag{4b}$$

$$M_2 = N_0(1/2B)[(\mu_1 A + 2\mu_2 B)\exp(2\mu_1 BN_0 t) - \mu_1 A]. \tag{4c}$$

N_0 is the initial value of the total particle number, and μ_1 and μ_2 are the reduced first and second initial moments defined by

$$\mu_1 = M_1/N_0 = \langle v\rangle/v_1 \qquad \mu_2 = M_2(0)/N_0$$

where $\langle v\rangle = V/N_0$ is the average particle volume of the initial distribution. We see that M_2 is finite for $0 \leqslant t < \infty$, and M_1 is constant and $N \geqslant 0$ for $0 \leqslant t \leqslant \infty$.

For a monodisperse initial distribution μ_1 has the value unity and for polydisperse distributions μ_1 is greater than unity. It is one of the measures of the dispersity of the initial distribution. For example, for an initial bimodal distribution with concentrations $n_1(0) = N_0/2$, $n_2(0) = N_0/2$, we have

$$\mu_1 = \sum_{k=1}^{\infty} k n_k(0) \left(\sum_{k=1}^{\infty} n_k(0) \right)^{-1} = \tfrac{3}{2}.$$

Proceeding with the solution, we seek a transformation that will transform away the second term on the right-hand side of (2) without spoiling the convolution form of the first term. To this end we write the distribution in the form

$$n_k = N_0 g_k \exp(-f_k) \tag{5}$$

where g_k and f_k are functions of time and f_k is defined by

$$\frac{\mathrm{d}f_k}{\mathrm{d}t} = \sum_{j=1}^{\infty} K_{k,j} n_j .$$

The integral is

$$f_k = -\ln[(\mathrm{d}N/\mathrm{d}t)/(\mathrm{d}N(0)/\mathrm{d}t)] + k\phi \tag{6}$$

where

$$\mathrm{d}N(0)/\mathrm{d}t = -\tfrac{1}{2} N_0^2 (A + 2B\mu_1) \tag{7}$$

$$\phi = -\ln[(N/N_0 + 2B\mu_1/A)/(1 + 2B\mu_1/A)]^{2B/A}. \tag{8}$$

Substitution of (5) into the Smoluchowski equation yields

$$\frac{\mathrm{d}g_k}{\mathrm{d}t} = \tfrac{1}{2} N_0 [(\mathrm{d}N/\mathrm{d}t)/(\mathrm{d}N(0)/\mathrm{d}t)] \sum_{j=1}^{k-1} K_{k-j,j} g_{k-j} g_j$$

where, because of the linear dependence of f_k on k, the convolution form of the sum has not been spoiled. Finally we introduce the scaled time variable

$$\tau = 1 - N/N_0 \tag{9}$$

and obtain the reduced equation

$$\frac{\mathrm{d}g_k}{\mathrm{d}\tau} = \sum_{j=1}^{k-1} (A^* + B^* k) g_{k-j} g_j \tag{10}$$

where the dimensionless collision constants are defined by

$$A^* = A/(A + 2\mu_1 B) \qquad B^* = B/(A + 2\mu_1 B). \tag{11}$$

We denote the initial values of g_k by c_k, which are arbitrary except for the constraining conditions

$$\sum_{k=1}^{\infty} c_k = 1 \qquad \sum_{k=1}^{\infty} k c_k = \mu_1 \tag{12}$$

and μ_1 is assumed to be finite. The constraints on the zeroth and first moments ensure that the distributions have the initial number N_0 and the first moment M_1. The reduced equation (10) has been derived previously by Bak and Lu [11], and Lu [9] and, in a different context, by Kobraei and Duncan [12].

From (5), (6) and (8) and the scaled time variable $\tau = 1 - N/N_0$, we obtain the solution in the form

$$n_k = N_0(1-\tau)(1-A^*\tau)^{(1+2Bk/A)} g_k \tag{13}$$

where g_k is a solution of (10). We note that the distribution (13) depends only on the total number N (or τ) and contains no explicit dependence on the real time t.

3. Construction of the solution

We construct solutions of (10) by the generating function method, where the generating function is defined by the formal power series

$$G(\tau, s) = \sum_{k=1}^{\infty} g_k(\tau) s^k. \tag{14}$$

Differentiation of G with respect to τ and use of (10) yields

$$\frac{\mathrm{d}G}{\mathrm{d}\tau} = \left(A^* + B^* s \frac{\mathrm{d}}{\mathrm{d}s}\right) G^2. \tag{15}$$

Repeated differentiation of (15) yields

$$\frac{\mathrm{d}^n G}{\mathrm{d}\tau^n} = \prod_{j=1}^{n} \left(A^*(j+1) + 2B^* s \frac{\mathrm{d}}{\mathrm{d}s}\right)(n+1)^{-1} G^{n+1}.$$

Evaluating the derivatives of the generating function at $\tau = 0$ gives

$$\frac{\mathrm{d}G^n(0)}{\mathrm{d}\tau^n} = \sum_{k=1}^{\infty} \prod_{j=1}^{n} [A^*(j+1) + 2B^* k](n+1)^{-1} c_k^{(n+1)} s^k \tag{16}$$

where

$$c_k^{(n+1)} = \sum_{k_1+k_2+\ldots+k_{n+1}=k} c_{k_1} c_{k_2} \ldots c_{k_{n+1}} \tag{17}$$

is the notation used by Henrici [13] to denote the coefficients in the formal power series

$$G^{n+1}(0, s) = (c_1 s + c_2 s^2 + c_3 s^3 + \ldots)^{n+1}.$$

With (16) the generating function may be expressed as

$$G = \sum_{k=1}^{\infty} \left(c_k + \sum_{n=1}^{k-1} \frac{1}{(n+1)!} \prod_{j=1}^{n} [A^*(j+1) + 2B^* k] c_k^{(n+1)} \tau^n\right) s^k \tag{18}$$

where we used $c_k^{(n+1)} = 0$ for $n > k-1$. Comparison with (14) shows that

$$g_k = \sum_{n=0}^{k-1} \frac{1}{(n+1)!} A^*(2 + 2Bk/A)_n c_k^{(n+1)} \tau^n \tag{19}$$

where

$$(a)_n = a(a+1)(a+2)\ldots(a+n-1) = \Gamma(a+n)/\Gamma(a) \tag{20}$$

is the Pochhammer symbol, Γ is the gamma function and we use the convention $(a)_0 = 1$.

Substituting (19) into (13), we obtain

$$n_k = N_0(1-\tau)(1-A^*\tau)^{(1+2Bk/A)} \sum_{n=0}^{k-1} \frac{1}{(n+1)!} A^{*n}(2 + 2Bk/A)_n c_k^{(n+1)} \tau^n. \tag{21}$$

The scaled time is given in terms of the real time by

$$\tau = [1 - \exp(-\mu_1 BN_0 t)][1 - A^* \exp(-\mu_1 BN_0 t)]^{-1}. \tag{22}$$

The polynomial distribution given by (21) is an exact general solution of the Smoluchowski equation. After we consider some special cases of (21) we will compare the continuous limit of the solution (21) with the exact, general solution of the continuous equation given by Drake and Wright [10].

4. Special cases

There are a number of special solutions which are easily derived from the general solution. For the sake of completeness we show these solutions, show a calculation of the first moment of the solution for the sum kernel and give an alternative form of the constant kernel equation.

4.1. Linear kernel, Flory-Stockmayer polymerisation theory, polydisperse initial distribution

In the Flory-Stockmayer theory [14], if there are f functional sites of one kind per unit, then, according to Ziff [8], we have $A = 2K$, and $B = (f-1)K$, where K is a constant and $f = 1, 2, \ldots$. Substitution and simplification in (21) yields

$$\begin{aligned} n_k = {} & N_0(1-\tau)\{1 - \tau/[1 + \mu_1(f-1)]\}^{[1+(f-1)k]} \\ & \times \sum_{n=0}^{k-1} \{[1 + (f-1)\mu_1]^n [1 + (f-1)k]!(n+1)!\}^{-1} \\ & \times [n + 1 + (f-1)k]!\, c_k^{(n+1)} \tau^n \end{aligned} \tag{23}$$

where the Pochhammer symbol has been expressed in terms of factorials.

4.2. Linear kernel, monodisperse initial distribution

For a monodisperse distribution, we see from (12) that $\mu_1 = 1$, and from (17) we obtain $c_k^{(n+1)} = \delta_{k,n+1}$. Substitution into (21) yields

$$n_k = N_0(1-\tau)(1 - A^*\tau)^{(1+2Bk/A)}(1/k!)A^{*k-1}(2 + 2Bk/A)_{k-1}\tau^{k-1} \tag{24}$$

where τ is given by (22) with $\mu_1 = 1$ and $A^* = A/(A + 2B)$. This solution was given first by Lu [9].

4.3. Sum kernel, polydisperse initial distribution

Taking the limit $A \to 0$ in (21), we obtain the general solution for the kernel $K_{k,j} = B(k+j)$:

$$n_k = N_0(1-\tau)\exp(-k\tau/\mu_1) \sum_{n=0}^{k-1} \frac{1}{(n+1)!} c_k^{(n+1)}(k\tau/\mu_1)^n \tag{25}$$

where the scaled time is given by

$$\tau = 1 - \exp(-\mu_1 BN_0 t).$$

The solution (25) has been given first in a different form by Lu [9].

4.4. *Sum kernel, monodisperse initial distribution*

Taking the limit $A \to 0$ in (24) yields

$$n_k = N_0(1-\tau)\exp(-k\tau)(1/k!)k^{k-1}\tau^{k-1} \tag{26}$$

which is the solution first given by Ziff *et al* [15].

4.5. *Sum kernel, calculation of the first moment*

We can write the solution in another form by making use of the generating function. Let $C(s)$ denote the initial value of the generating function. We have

$$C(s) = \sum_{k=1}^{\infty} c_k s^k \tag{27}$$

$$C^n(s) = \sum_{k=1}^{\infty} c_k^{(n)} s^k \tag{28}$$

$$c_k^{(n)} = \frac{1}{2\pi \mathrm{i}} \oint C^n(s) s^{-k-1}\, \mathrm{d}s \tag{29}$$

where the contour in the complex s-plane encloses the singularity at the origin, but does not include singularities of $C^n(s)$. Substitution into (25) and extending the summation to infinity yields

$$n_k = N_0(1-\tau)\exp(-k\tau/\mu_1) \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \frac{1}{2\pi \mathrm{i}} \int C^{n+1}(s) s^{-k-1}\, \mathrm{d}s (k\tau/\mu_1)^n. \tag{30}$$

Carrying out the sum we obtain

$$n_k = N_0(1-\tau)(\mu_1/k\tau)\exp(-k\tau/\mu_1) \frac{1}{2\pi \mathrm{i}} \oint [\exp(kC(s)\tau/\mu_1) - 1] s^{-k-1}\, \mathrm{d}s \tag{31}$$

which is close to the form of the Laplace transformation solution of the continuous equation given in [4].

The above form of the solution is convenient for calculating moments. We calculate the first moment. From (31) we obtain

$$M_1 = N_0(1-\tau) \sum_{k=1}^{\infty} (\mu_1/\tau)\exp(-k\tau/\mu_1) \frac{1}{2\pi \mathrm{i}} \oint [\exp(kC(s)\tau/\mu_1) - 1] s^{-k-1}\, \mathrm{d}s.$$

If

$$F(s) = s^{-1}\exp[(1 - C(s))\tau/\mu_1] < 1$$

then the sum over k is a convergent geometric series. Taking the derivative of $F(s)$ shows that its minimum value occurs at $s = 1/\tau$. Since $F(1) = 1$, if we take the contour $s = r$, where $1 < r < \tau^{-1}$, $\tau < 1$, then $F(s) < 1$. Further, if all the moments of the initial distribution are finite this contour will not contain singularities of C^n. Making this assumption, we sum over k and obtain

$$\begin{aligned} M_1 = {} & N_0(1-\tau)(\mu_1/\tau) \\ & \times \frac{1}{2\pi \mathrm{i}} \oint s^{-1} \left(\frac{\exp[(-1 + C(s))\tau/\mu_1]}{\{s - \exp[(-1 + C(s))\tau/\mu_1]\}} \right. \\ & \left. - \frac{\exp(-\tau/\mu_1)}{[s - \exp(-\tau/\mu_1)]} \right) \mathrm{d}s \qquad \tau < 1. \end{aligned}$$

The sum of the residues of the integrand is $\tau/(1-\tau)$. Thus $M_1 = N_0\mu_1$, which confirms that the first moment is constant for $0 \leq \tau \leq 1$. In the calculation it has been assumed that all initial moments exist, whereas in the calculation of the moments from the three moment equations it was only necessary to assume that the first three initial moments exist. Shirvani and Stock [16] have proved a strong theorem which asserts that the particle volume is constant even if the second moment is initially infinite.

A direct calculation of the second moment using the general solution for the sum kernel with the hypothesis that all moments exist is given in the appendix. The result is

$$M_2 = N_0\mu_2/(1-\tau)^2$$

which is the same result obtained from the three moment equations with $A=0$.

As another check one may substitute the general solution for the sum kernel into the definition of the zeroth moment, carry out a residue calculation and obtain the desired identity, $N = N_0(1-\tau)$.

4.6. *Constant kernel, a linear equation for the reduced distribution*

For $B=0$ in (19) we obtain the solution for the constant kernel which is

$$g_k = \sum_{n=0}^{k-1} c_k^{(n+1)}\tau^n. \tag{32}$$

With (32), (13) becomes

$$n_k = N_0(1-\tau)^2 \sum_{n=0}^{k-1} c_k^{(n+1)}\tau^n. \tag{33}$$

For a monodisperse initial distribution we have $c_k^{(n+1)} = \delta_{k,n+1}$ and obtain the well known solution

$$n_k = N_0(1-\tau)^2\tau^{k-1} \tag{34}$$

first given by Smoluchowski [1].

We now derive an alternative form for the constant-kernel Smoluchowski equation. Writing out the first few terms of the sum in (32) gives

$$g_k = c_k + \tau \sum_{k_1+k_2=k} c_{k_1}c_{k_2} + \tau^2 \sum_{k_1+k_2+k_3=k} c_{k_1}c_{k_2}c_{k_3} + \dots$$

which may be written in the form

$$g_k = c_k + \tau \sum_{k_1=1}^{k-1} c_{k-k_1}\left(c_{k_1} + \tau \sum_{k_2+k_3=k_1} c_{k_2}c_{k_3} + \tau^2 \sum_{k_2+k_3+k_4=k_1} c_{k_2}c_{k_3}c_{k_4}\dots\right).$$

We thus have

$$g_k = c_k + \tau \sum_{j=1}^{k-1} c_{k-j}g_j. \tag{35}$$

Equation (35) shows that g_k satisfies a system of linear, inhomogeneous, algebraic equations. After specifying initial values, the solutions of (35) are the same as those of the nonlinear reduced equation (10) with $B=0$. The linear equation may thus be regarded as an alternative form of the reduced constant-kernel Smoluchowski equation. This form of the equation was first pointed out by Loos [17]. Equation (35) may be easily solved recursively or by standard matrix methods. Because of the convolution form of the sum, the matrix of coefficients is lower triangular. Further, the matrix of coefficients in (35) is non-singular, so existence and uniqueness are assured. Unfortunately, g_k satisfies the linear system of equations only for the special case of constant kernel.

5. The correspondence between solutions of the discrete and continuous Smoluchowski equations

The continuous equation is given by

$$\frac{\partial n(u,t)}{\partial t}=\frac{1}{2}\int_0^u K(u-v,v)n(u-v,t)n(v,t)\,\mathrm{d}v-n(u,t)\int_0^\infty K(u,v)n(v,t)\,\mathrm{d}v. \tag{36}$$

In (36), t is the real time, u and v denote the particle-cluster volumes, and $n(u,t)$ is the spatial density of particles per unit particle volume. $K(u,v)$ is a symmetric collision frequency function which is determined by the physical nature of the collision process. Drake and Wright [10] have derived a general solution of (36) for the continuous version of the linear kernel. We give this solution below in a form that is convenient for comparison with the discrete solution. The continuous kernel is given by

$$K(u,v)=a+b(u,v) \tag{37}$$

where a and b are constants. The solution of (36), obtained by Laplace transformation, is

$$n(v,\tau)=(N_0^2/V)(1-\tau)(1-a^*\tau)^{(1+2bv/a)}$$
$$\times\sum_{n=0}^{\infty}[1/(n+1)!]a^{*n}(2+2bv/a)_n L^{-1}[C^{n+1}(s)]\tau^n \tag{38}$$

where

$$a^*=a/(a+2\langle v\rangle b).$$

As in the discrete theory, V is the total volume of the distribution, $\langle v\rangle=V/N_0$ is the initial average particle volume, $\tau=1-N/N_0$ is the scaled time variable, and $(\ldots)_n$ is the Pochhammer symbol with $(\ldots)_0=1$. We use the same symbol we used for the generating function, but now $C(s)$ is the Laplace transform of a dimensionless, normalised, initial distribution $c(x)$, where $x=N_0v/V$ is a dimensionless particle volume. $L^{-1}[C(s)]$ is the inverse Laplace transform of $C(s)$.

Another form of the solution is obtained by carrying out the inverse Laplace transformation in (38). With the aid of the convolution theorem we have

$$L^{-1}[C^{n+1}(s)]=[c(x)]^{(n+1)}$$

where we use the notation

$$[c(x)]^{(n+1)}=\int_{x_1=0}^{x}\cdots\int_{x_{n+1}}^{x_n}c(x-x_1)c(x_1-x_2)\ldots c(x_{n+1})\,\mathrm{d}x_1\ldots\mathrm{d}x_{n+1}$$

for the convolution integrals. Thus, the general solution may be expressed as

$$n(v,\tau)=(N_0^2/V)(1-\tau)(1-a^*\tau)^{(1+2bv/a)}$$
$$\times\sum_{n=0}^{\infty}[a^{*n}/(n+1)!](2+2bv/a)_n[c(x)]^{(n+1)}\tau^n. \tag{39}$$

One expects that the continuous limit of the solution of the discrete equation will be equal to the solution of the continuous Smoluchowski equation, and this is indeed the case. We now give the rules which show the formal correspondence between the discrete and continuous solutions.

Let v_1 denote the smallest particle volume in the initial distribution, where it is assumed that all other particle volumes are integer multiples of this smallest volume. A continuous distribution is obtained by taking the limit $v_1 \to 0$, $k \to \infty$ with $kv_1 =$ constant. The correspondences to the continuous initial and the continuous time-dependent distributions are given by

$$c(x) = \lim_{v_1 \to 0} Vc_k/(v_1 N_0) \tag{40}$$

$$n(v, \tau) = \lim_{v_1 \to 0} n_k(\tau)/v_1 \tag{41}$$

where the initial distribution is normalised according to

$$\int_0^\infty c(x)\,\mathrm{d}x = 1 \qquad \int_0^\infty xc(x)\,\mathrm{d}x = 1.$$

The correspondence between the convolution sums and the convolution integrals is given by

$$\lim_{v_1 \to 0} [V/(v_1 N_0)]c_k^{(n)} = [c(x)]^{(n)}. \tag{42}$$

Finally, the collision kernel is invariant in the continuous limit if $A = a$ and $Bk = bv$. The latter condition implies that

$$\lim_{v_1 \to 0} B/v_1 = b. \tag{43}$$

Making the substitutions (40)–(43) into the discrete solution (21), and taking $k = \infty$ in the upper limit of the sum over powers of τ, one obtains the continuous distribution given by (39). The scaled time τ for the continuous distribution is obtained from (22), and is given by

$$\tau = 1 - N/N_0 = [1 - \exp(-Vbt)]/[1 - a^* \exp(-Vbt)].$$

6. Continuous limits of solutions of the constant-kernel equation

We give some examples of solutions for the case of the constant-kernel equation for specific initial conditions. We then use the rules given above to obtain continuous limits. We consider initial distributions of the form

$$c_k = pk^{m-1}q^k \tag{44}$$

where p and q are independent of k and $m = 1, 2, \ldots$. The initial values satisfy the constraints

$$\sum_{k=1}^{\infty} c_k = 1 \qquad \sum_{k=1}^{\infty} kc_k = \mu_1.$$

The constraints determine p and q as a function of the dispersity parameter μ_1 and the index m. In the limit $\mu_1 = \langle v \rangle / v_1 \to \infty$, the above initial distributions become the so-called gamma distributions considered in [4].

Substituting (44) into (12) and summing the series shows that p and q satisfy the polynomial equations

$$\begin{aligned} &p[q(\mathrm{d}/\mathrm{d}q)]^{m-1}[q/(1-q)]=1 \qquad m\geqslant 1 \\ &p[q(\mathrm{d}/\mathrm{d}q)]^{m}[q/(1-q)]=\mu_1. \end{aligned} \tag{45}$$

After calculating q, we can calculate p with either of the equations in (45). We will return to the solution of (45) after we construct the time-dependent solution of the constant-kernel Smoluchowski equation.

For the case of constant kernel we have $B=0$ in (15), and the generating function satisfies

$$\mathrm{d}G/\mathrm{d}\tau=G^2. \tag{46}$$

The general solution is

$$G(s,\tau)=C(s)/[1-C(s)\tau] \tag{47}$$

where $C(s)$ is the initial value of $G(s,\tau)$.

If $C(s)$ is analytic in a disc of radius r in the complex s-plane then the Cauchy residue theorem gives

$$g_k=\frac{1}{2\pi\mathrm{i}}\oint \{C(s)/[1-C(s)\tau]\}s^{-k-1}]\,\mathrm{d}s \tag{48}$$

where $s<r$. For initial values of the form (44) we have

$$C(s)=p(s\mathrm{d}/\mathrm{d}s)^{m-1}[qs/(1-qs)]. \tag{49}$$

The integral in (48) is easy to evaluate for small values of m. We give the calculations for $m=1$, and $m=2$.

6.1. $m=1$, $c_k=pq^k$

From the constraint equations (45) we obtain

$$p=1/(\mu_1-1) \qquad q=1-1/\mu_1 \tag{50}$$

where $1\leqslant\mu_1\leqslant\infty$. The initial value of the generating function is

$$C(s)=pqs/(1-qs)$$

and the reduced distribution is given by

$$g_k=pq^k\frac{1}{2\pi\mathrm{i}}\int z^{-k}[1-(1+p\tau)z]^{-1}\,\mathrm{d}z$$

where we have made the substitution $z=qs$ in the contour integral. The poles of the integrand are at

$$z=0 \qquad z_1=(1+p\tau)^{-1}.$$

Evaluating the integral with the residue theorem, we obtain

$$g_k=pq^kz_1^{-k+1} \tag{51}$$

where p and q are given by (50). With (50) amd (51) we have

$$n_k=N_0(1-\tau)^2(1/\mu_1)(1-1/\mu_1)^{k-1}[1+\tau/(\mu_1-1)]^{k-1}. \tag{52}$$

According to the rule given above we have

$$n(v) = \lim_{v_1 \to 0} n_k / v_1 .$$

Using

$$\exp(a) = \lim_{k \to \infty} (1 + a/k)^k$$

and $\tau = 1 - N/N_0$ in the expressions for n_k, we obtain the limit

$$n(v, \tau) = (N^2/V) \exp(-Nv/V). \tag{53}$$

We recognise (53) as the Friedlander self-preserving distribution.

The solution given by (52) is a one-parameter family of exact solutions. The solutions are labelled by the allowed values of μ_1, which are $1 \leqslant \mu_1 \leqslant \infty$. For large differences in μ_1 the solutions are quite different. For example, for μ_1 near unity the initial distributions are narrow and are not at all like the initial, exponential self-preserving distribution ($\mu_1 = \infty$). For the smallest allowed value $\mu_1 = 1$, c_k is monodisperse and (52) yields the Smoluchowski solution (34). Clearly this solution, at least in its early stage of temporal evolution, is quite different from the self-preserving distribution.

6.2. $m = 2$, $c_k = pkq^k$

Solving the constraint equations for $m = 2$ yields

$$q = (\mu_1 - 1)/(\mu_1 + 1) \qquad p = 4/[(\mu_1 - 1)(\mu_1 + 1)]. \tag{54}$$

The initial value of the generating function is

$$C(s) = pqs/(1 - qs)^2 \tag{55}$$

and

$$g_k = pq^k \frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}z}{(z^k[z^2 - (2 + p\tau)z + 1])} \tag{56}$$

where we have made the substitution $z = qs$. The poles in the integrand are at $z = 0$ and

$$\begin{aligned} z_+ &= 1 + \tfrac{1}{2}p\tau + [(1 + p\tau/2)^2 - 1]^{1/2} \\ z_- &= 1 + \tfrac{1}{2}p\tau - [(1 + p\tau/2)^2 - 1]^{1/2}. \end{aligned} \tag{57}$$

Using the residue theorem we obtain

$$\begin{aligned} n_k &= N_0(1 - \tau)^2 g_k \\ n_k &= N_0(1 - \tau)^2 pq^k (z_+ - z_-)^{-1}(1/z_-^k - 1/z_+^k). \end{aligned} \tag{58}$$

Setting $\tau = 0$ in (58) confirms that n_k has the correct initial values. Taking the limit $\mu_1 = \infty$ in (58), with $\mu_1/k = v/\langle v \rangle = \text{constant}$ yields

$$n(v, \tau) = (2N_0^2/V) \exp(-2v/\langle v \rangle)(1 - \tau)^2 \tau^{1/2} \sinh(2v\tau^{1/2}/\langle v \rangle). \tag{59}$$

The distribution (59) has the initial value

$$c(v) = 4(v/\langle v \rangle) \exp(-2v/\langle v \rangle) \tag{60}$$

which is the $m = 2$ gamma distribution. The distribution given by (59) has been shown by Drake [4] and Wayland [18] to be a solution of the continuous, constant-kernel Smoluchowski equation.

Equation (58) gives an exact solution for every allowed value of μ_1. Thus we have constructed another one-parameter family of solutions. Taking $\mu_1 = 1$ gives a monodisperse initial distribution for the $m = 2$ distribution, which is what we found for the $\mu_1 = 1$ member of the $m = 1$ family of solutions. Thus, the two families have the $\mu_1 = 1$ member in common. However, for $\mu_1 > 1$ the members of the two families are all different and, as we have seen, have different continuous limits.

7. Comments

We have constructed a general solution the discrete Smoluchowski equation for the linear kernel and shown its correspondence to the known continuous solution in the limit that the smallest particle size vanishes. Discrete and continuous general solutions for the branched polymer kernel

$$K_{k,j} = (\alpha + \beta k)(\alpha + \beta j)$$

are also known [9, 10]. It is not shown here, but the correspondence between the discrete and continuous solutions for the branched polymer kernel is essentially the same as for the linear kernel.

Simple explicit discrete or continuous solutions of the kind given for the linear and the branched polymer kernels are not known and may not exist for the general quadratic kernel

$$K_{k,j} = A + B(k + j) + Ckj$$

or the special cases

$$K_{k,j} = A + Ckj \qquad K_{k,j} = B(k + j) + Ckj.$$

However, a solution of the discrete equation for the general quadratic kernel which is a polynomial in the scaled time with recursively calculated coefficients has been given by Bak and Lu [10].

Since the Friedlander self-preserving solution does not exist for the linear kernel (or the sum kernel), and certain other kernels as well, different approaches are needed (see e.g. [19]) to study the temporal asymptotic behaviour of distributions. Possibly the general solution given here could be used to investigate the asymptotic behaviour of solutions for the linear kernel.

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Appendix. The existence of the second moment for the linear kernel

White [20] has shown that the second and higher moments for the sum kernel exist for $0 \leqslant \tau < 1$ if the initial moments are finite. We calculate the second moment of the distribution for general initial distributions for the sum kernel and then use it for a bound on the second moment of the distribution for the linear kernel. Let n_k^* denote the solution and let M_k^* denote the second moment for the sum kernel. Taking the second moment of n_k^*, given by (31), rearranging, and extending the upper limit to ∞, we obtain

$$M_2^* = N_0(1-\tau)\sum_{k=1}^{\infty} k^2 \exp(-k\tau/\mu_1) \times \sum_{n=0}^{\infty} \frac{1}{(n+1)!}\frac{1}{2\pi i}\oint C^{n+1}(s)s^{-k-1}\,ds(k\tau/\mu_1)^n. \tag{A.1}$$

Summation over n yields

$$M_2^* = N_0(1-\tau)\sum_{k=1}^{\infty}(\mu_1 k/\tau)\exp(-k\tau/\mu_1) \times \frac{1}{2\pi i}\oint [\exp(kC(s)\tau/\mu_1)-1]s^{-k-1}\,ds. \tag{A.2}$$

As we showed in subsection 4.5, if all the moments of the initial distribution are finite, the contour $s=r$, where $1<r<\tau^{-2}$, $\tau<1$, will not contain singularities of C^n and the geometric series in (A.2) is convergent. We then obtain

$$M_2^* = N_0(1-\tau)(\mu_1/\tau)\mu_1(d/d\tau)(2\pi i)^{-1} \times \oint s^{-1}\left(\frac{[1-C(s)]^{-1}\exp[(-1+C(s))\tau/\mu_1]}{s-\exp[(-1+C(s))\tau/\mu_1]} - \frac{\exp(-\tau/\mu_1)}{[s-\exp(-\tau/\mu_1)]}\right)ds \qquad \tau<1. \tag{A.3}$$

There are poles at the origin and $s=1$. We have $C(0)=0$ and $C(1)=1$. The contribution to the integral from the origin vanishes. To determine the residue from the pole at $s=1$ we note that the leading terms in the Taylor expansion of $C(s)$ are

$$C(s) = 1+\mu_1(s-1)+\tfrac{1}{2}(\mu_2-\mu_1)(s-1)^2+\dots$$

and hence

$$\exp[(1-C(s))\tau/\mu_1] = 1-\tau(s-1)+\tfrac{1}{2}[\tau^2+(\mu_2-\mu_1)\tau/\mu_1](s-1)^2\dots.$$

Computing the residues, we obtain

$$M_2^* = N_0\mu_2/(1-\tau)^2 \qquad \tau<1. \tag{A.4}$$

Let M_2 denote the second moment for the kernel $A+B(k+j)$. We find a bound for M_2 as follows. From the definitions of the Pochhammer symbol and the dimensionless collision constants A^* and B^* we see that

$$A^{*n}(2+2Bk/A)_n \leqslant k^n.$$

And, since $\tau<1$ and $\mu_1 \geqslant 1$, we have

$$(1-A^*\tau)^{2B/A} \leqslant \exp(1)\exp(-\tau/\mu_1).$$

With these inequalities, by inspection of the solution (21) for the linear kernel and the solution (30) for the sum kernel, we see by comparison that $n_k \leqslant \exp(1)n_k^*$, $\tau<1$. Thus, the second moment of the solution for the linear kernel is finite for $\tau<1$.

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