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LETTER TO THE EDITOR

On the relationship between the stochastic and deterministic approach to particle coagulation—asymptotic expansion of $\langle N \rangle$

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Abstract. Consideration is given to the solution of the stochastic equation governing the coagulation of particles for the case of a size-independent coagulation probability. The corresponding expression for the expectation value of particle number $\langle N \rangle$ is developed in the form of an asymptotic series valid for $N \gg 1$, the first term being the solution of the relevant deterministic equation. The next term, giving the first-order correction to this result, is obtained explicitly, together with an estimate of the corresponding standard deviation of N.

Two approaches have conventionally been used for the quantitative discussion of coagulation phenomena. The first, pioneered by Smoluchowski assumes a spatially homogeneous distribution of particles within an infinite volume. The distribution is characterized by the total number of particles per unit volume, $\mathcal{N}$, and for the case of the coagulation probability between two particles being independent of their size (a reasonable approximation for Brownian coagulation), Smoluchowski showed that $\mathcal{N}$ satisfies the equation

$$\mathrm{d}\mathcal{N}/\mathrm{d}t = -\tfrac{1}{2}Q\mathcal{N}^2 \tag{1}$$

where Q is the relevant coagulation kernel.

The second approach to coagulation has been to consider a finite number of particles N distributed homogeneously throughout a finite volume V. A proper treatment of this situation requires a stochastic approach, leading to a calculation of the expectation value of $Z(\langle Z \rangle)$, where Z is any physical quantity defined by the particle coagulation. Now if both N and V tend to infinity, maintaining the ratio $\mathcal{N} = N/V$ constant, it is to be expected that the limiting value of $\langle Z \rangle$ should correspond to the solution of the deterministic equation (1), and a discussion of this for the case where Z is the time for N to change by a specified amount has been given recently by Simons (1990). Of probably greater interest is the situation where Z is taken to be N, considered as a function of t, and a proof that the limiting value of $\langle N(t) \rangle$ does indeed correspond to the solution of equation (1) has been provided by Hendriks *et al* (1985). The purpose of the present communication is to supplement this latter work by showing how the approach of Hendriks may be extended to develop an asymptotic expansion of $\langle N(t) \rangle$, valid for $N \gg 1$. The leading term in this expansion corresponds to the solution of equation (1), while the next term (required for finite V) gives the first-order correction to this deterministic result. In addition we evaluate the leading term in σ, the standard deviation of $N(t)$. The approach we employ is a relatively simple one and allows comparison with some of the results obtained by Merkulovich and Stepanov (1986). These authors tackled coagulation systems of greater generality than ours using different and more complex techniques. For the situation we are concerned with, our results are identical with theirs.

We consider an initial assembly of n particles lying within a volume V and coagulating together with probability independent of particle size. We non-dimensionalize the time t by letting $\tau = \frac{1}{2}Qt/V$, and define $P(N, \tau)$ as the probability of there existing N particles ($N < n$) after time τ. Following the approach of Van Kampen (1981) the master equation for P then takes the form

$$\partial P(N,\tau)/\partial\tau = -N(N-1)P(N,\tau) + N(N+1)P(N+1,\tau) \qquad (N<n) \tag{2}$$

with initial condition $P(N, 0) = 0$. The approach of Hendriks *et al* (1985) then yields the solution of equation (2) in the form

$$P(N,\tau) = \sum_{p=N}^{n} A_{Np} \exp[-p(p-1)\tau] \tag{3a}$$

where

$$A_{Np} = \frac{(-1)^{p-N} n!(n-1)!(p+N-2)!(2p-1)}{N!(N-1)!(p-N)!(n-p)!(n+p-1)!}. \tag{3b}$$

It follows immediately from equations (3) that

$$\begin{aligned}\langle N\rangle &= \sum_{N=1}^{n} NP(N,\tau)\\ &= \sum_{p=1}^{n}\sum_{N=1}^{p} \frac{(-1)^{p-N}(2p-1)n!(n-1)!(p+N-2)!\,\mathrm{e}^{-p(p-1)\tau}}{[(N-1)!]^2(p-N)!(n-p)!(n+p-1)!}\\ &= \sum_{p=1}^{n} \frac{(2p-1)n!(n-1)!\,\mathrm{e}^{-p(p-1)\tau}}{(n-p)!(p+n-1)!}\end{aligned} \tag{4}$$

on making use of the result that

$$\sum_{N=1}^{p} \frac{(-1)^{p-N}(p+N-2)!}{[(N-1)!]^2(p-N)!} = 1 \tag{5}$$

(obtained by equating coefficients of x^{p-1} on both sides of the identity $(1-x)^{p-1}(1-x)^{-p} \equiv (1-x)^{-1}$).

In order to develop our asymptotic expansion for $\langle N\rangle$, we now proceed to employ the Euler-Maclaurin formula (Abramowitz and Stegun 1965), which transforms the summation in (4) into an integral, together with correction terms. In order to make a change of variable in this integral (as will be explained later) we wish to maintain the factor $(2p-1)$ positive throughout the integration interval, and we therefore begin by separating off the contribution to $\langle N\rangle$ arising from $p = 1$. We also separate off the terms arising from $p = n-1$, n so that Stirling's formula may be subsequently used for all expressions of the form $z!$ appearing in the integral, with $z > 0$. We therefore write

$$\langle N\rangle = 1 + X + \sum_{p=2}^{n-2} \frac{n!(n-1)!(2p-1)\,\mathrm{e}^{-p(p-1)\tau}}{(n-p)!(n+p-1)!} \tag{6}$$

where X is the contribution to $\langle N\rangle$ arising from $p=n-1$ and n. It is readily shown that $X \leqslant n^3/4^n$ which tends to zero as $n\to\infty$ more rapidly than n^{-s} for finite s, and thus X may be neglected in developing our asymptotic expansion. Letting $g(p)$ denote the summand in equation (6), we now apply the Euler–Maclaurin formula, which gives

$$\langle N\rangle = 1+\int_1^{n-1} g(p)\,\mathrm{d}p - \frac{1}{2}[g(1)+g(n-1)] \\ -\frac{1}{12}[g'(1)-g'(n-1)]+\frac{1}{120}[g'''(1)-g'''(n-1)]+\ldots \tag{7}$$

and it is readily shown that the terms involving g and its derivatives at $p=n-1$ may be neglected.

To progress further we now use the Stirling approximation in the form

$$\ln(x!)\approx\left(x+\frac{1}{2}\right)\ln x - x+\frac{1}{2}\ln(2\pi)+\frac{1}{12x}$$

to represent the factorials in the integrand in (7). That is, we let

$$F=\frac{n!(n-1)!}{(n-p)!(n+p-1)!} \tag{8a}$$

leading to

$$\ln F\approx\left(n-\frac{1}{2}\right)\ln\left(1-\frac{1}{n}\right)-\left(n-p+\frac{1}{2}\right)\ln\left(1-\frac{p}{n}\right) \\ -\left(n+p-\frac{1}{2}\right)\ln\left(1+\frac{p-1}{n}\right)-\frac{(2n-1)(p^2-p)}{12n(n-1)(n-p)(n+p-1)}. \tag{8b}$$

We now expand the logarithmic terms as power series in n^{-1}, retaining all terms in F up to n^{-3}. This yields

$$\ln F\approx\frac{-(p^2-p)}{n}-\frac{(p^2-p)^2}{6n^3} \tag{9}$$

with the term in n^{-2} vanishing identically. This, in turn, gives

$$g(p)=(2p-1)\exp\left[-(p^2-p)\left(\tau+\frac{1}{n}\right)-\frac{(p^2-p)^2}{6n^3}\right]. \tag{10}$$

To evaluate the integral in equation (7), we now let $x=(\tau+n^{-1})(p^2-p)$, when

$$\int_1^{n-1} g(p)\,\mathrm{d}p=\frac{1}{\tau+n^{-1}}\int_0^X \exp\left(-x-\frac{x^2}{6n^3(\tau+n^{-1})^2}\right)\mathrm{d}x \tag{11}$$

where $X\sim n$. Since the integrand behaves as e^{-x} at the upper limit, we may take this upper limit to be ∞. Further since we are looking for an asymptotic series in V^{-1} for $\langle N\rangle$, we can express equation (11) in the form

$$\int_1^{n-1} g(p)\,\mathrm{d}p=\frac{1}{\tau+n^{-1}}\int_0^\infty \mathrm{e}^{-x}\left(1-\frac{x^2}{6n^3(\tau+n^{-1})^2}\right)\mathrm{d}x \\ =\frac{1}{\tau+n^{-1}}-\frac{1}{3(n\tau+1)^3} \tag{12}$$

these two terms being respectively proportional to V and V^0. Finally, we consider the terms in equation (7) involving $g(1)$, $g'(1)$ etc. The highest power of V appearing in these terms is V^0, and if we neglect powers of V lower than this, we have $g(1)=1$, $g'(1)=2$, $g^{(q)}(1)=0$ for $q\geqslant 2$. Hence we obtain from equation (7)

$$\langle N\rangle=\frac{1}{\tau+n^{-1}}+\frac{1}{3}\left[1-\frac{1}{(n\tau+1)^3}\right]. \tag{13a}$$

Now, the deterministic equation for the present situation is $\mathrm{d}N/\mathrm{d}\tau=-N^2$, with solution $N(\tau)=(\tau+n^{-1})^{-1}$, and thus equation (13$a$) may be equivalently expressed as

$$\langle N\rangle=N+\frac{1}{3}\left[1-\left(\frac{N}{n}\right)^3\right]. \tag{13b}$$

The term $\frac{1}{3}[1-(N/n)^3]$ is the first-order correction to N and it is clear that this is initially zero when $N=n$ (as expected) and increases to a maximum value of $\frac{1}{3}$ for $N\ll n$. Since the result (13) corresponds to the first two terms of an asymptotic series it will be valid for $N\gg 1$, corresponding to $n\gg 1$ and $\tau\ll 1$.

We now calculate the standard deviation of N, and begin this by multiplying both sides of equation (2) by N and then summing over all values of N. This yields

$$\mathrm{d}\langle N\rangle/\mathrm{d}\tau=-\langle N^2\rangle+\langle N\rangle. \tag{14}$$

Hence

$$\begin{aligned}\langle N^2\rangle&=\langle N\rangle-\mathrm{d}\langle N\rangle/\mathrm{d}\tau\\&=\frac{1}{(\tau+n^{-1})^2}+\frac{1}{(\tau+n^{-1})}\left[1-\frac{1}{(n\tau+1)^3}\right]\end{aligned} \tag{15}$$

making use of equation (13a) and retaining terms proportional to V^2 and V. Retaining the leading term in σ then gives

$$\begin{aligned}\sigma&=(\langle N^2\rangle-\langle N\rangle^2)^{1/2}\\&=3^{-1/2}\left[1-\left(\frac{N}{n}\right)^3\right]N^{1/2}\end{aligned} \tag{16}$$

valid for $N\gg 1$. As expected this result corresponds to $\sigma=0$ initially (when $N=n$), and also $\sigma\sim N^{1/2}$ for $N\ll n$.

Finally we make the point (referred to earlier) that equations (13) and (16) are in exact agreement with the corresponding results of Merkulovich and Stepanov (1986) as expressed (albeit in a less concise fashion) in equation (24) of their paper.

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