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**LETTER TO THE EDITOR**

# On the expectation value of particle coagulation times

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**Abstract.** It is shown that for a stochastic system of coalescing particles with coagulation probability independent of particle size, the expectation value of the time for the number of particles to change by a specified amount is identical with the time given by the solution of the relevant deterministic equation. For the stochastic problem an estimate is made of the standard deviation of the coagulation time. A brief discussion is given of how these results are modified when particle coalescence and removal occur simultaneously.

Two approaches have conventionally been used for the quantitative discussion of coagulation phenomena. The first, pioneered by Smoluchowski, assumes a system containing an infinite number of particles and formulates the deterministic equation governing the temporal development of $n(v, t)$, the number density of particles with volume $v$. This equation takes the form

$$\partial n/\partial t = \frac{1}{2}\int_0^v P(u, v-u)n(u)n(v-u)\,\mathrm{d}u - n(v)\int_0^\infty P(u, v)n(u)\,\mathrm{d}u \qquad (1)$$

where $P(u, v)$ is the relevant coagulation kernel. Although equation (1) cannot be solved analytically for general $P$, it can be tackled for the case of constant $P$, which is a good approximation for Brownian coagulation. Letting $\mathcal{N}(t)$ $(=\int_0^\infty n(v, t)\,\mathrm{d}v)$ be the total number of particles per unit volume, it is then readily shown that for constant $P$, equation (1) leads to

$$\mathrm{d}\mathcal{N}/\mathrm{d}t = -\tfrac{1}{2}P\mathcal{N}^2. \qquad (2)$$

The second approach to coagulation has been to consider a system containing in total a finite number of particles $N$ and to deal with this stochastically, formulating a master equation whose solution gives the probability of there being a specified number of particles in each of the allowed volume states; from this probability the expectation value of the number of particles in each such volume state $\langle n(v)\rangle$ may be obtained. Now, in the limit as the number of particles tends to infinity it is to be expected on physical grounds that $\langle n(v)\rangle$ should tend towards the value of $n(v)$ as given by the deterministic approach sketched above and various attempts have been made to show this to be so. Among these are Hendriks *et al* (1985) who deal with the case of $P=$ constant (apart from other specific forms of $P$) and Donoghue (1982) who tackles the problem in the context of gelation theory. Other authors dealing with finite systems of particles for the case of constant $P$ include Williams (1979) and Arcipiani (1980).

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The aim of the present communication is to calculate the time $t$ for the total number of particles $N$ to change by a specified amount and we do this using in turn the deterministic and stochastic approaches sketched above. We confine our attention to the case of a constant coagulation kernel and proceed to show that the expectation value of $t$ when the problem is treated stochastically is identical to the value of $t$ given by the deterministic approach and that this is so, not only as $N \to \infty$ (as would be expected), but for all values of $N$. In addition, we are able to calculate $\sigma$, the standard deviation of $t$, in the stochastic approach.

To develop the stochastic approach we begin by noting that since the coagulation of the particles forms a discrete Markov process, the probability $P_2(\tau)$ of a specified pair not coalescing after time $\tau$ will satisfy

$$P_2(\tau+\tau') = P_2(\tau)P_2(\tau') \tag{3}$$

whence

$$P_2(\tau) = \exp(-K\tau) \tag{4}$$

for some constant $K$. It follows that the probability of there being no collisions after time $\tau$ for a set of $N$ particles is given by

$$P_N(\tau) = \exp[-\tfrac{1}{2}KN(N-1)\tau]. \tag{5}$$

We can now derive the corresponding deterministic equation for the system by noting that if $N(t)$ is the particle number at time $t$, then the change $\delta N$ after time $\delta t$ is given by

$$\delta N = -[P_N(0) - P_N(\delta t)] \tag{6}$$

since in each collision $N$ decreases by unity. Thus

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \left.\frac{\partial P_N}{\partial \tau}\right|_{\tau=0} = -\tfrac{1}{2}KN(N-1) \tag{7}$$

yielding for $N \gg 1$,

$$\mathrm{d}N/\mathrm{d}t = -\tfrac{1}{2}KN^2. \tag{8}$$

If $V$ is the total volume of space occupied by the particles, we note that equation (8) becomes identical with equation (2) on letting $N = \mathcal{N}V$ and $K = P/V$. This is, of course, to be expected since both equations reflect a deterministic approach to essentially the same system, although their derivation has followed somewhat different paths. The solution of equation (8) is clearly

$$N^{-1} - n^{-1} = \tfrac{1}{2}Kt \tag{9}$$

where $n$ is the initial number of particles at $t = 0$.

We now return to the stochastic treatment of the problem. Since $P_N(\tau)$ is given by equation (5), it follows that the expectation value of the time interval $t_p$ for which exactly $p$ particles exist is given by

$$\langle t_p \rangle = -\int_0^\infty \tau(\partial P_p/\partial\tau)\,\mathrm{d}\tau = \frac{2}{Kp(p-1)}. \tag{10}$$

Thus the expectation value of the total time for the number of particles to decrease from $n$ to $N$ is

$$\langle t \rangle = \sum_{p=N+1}^{n} \langle t_p \rangle = \frac{2}{K}\left(\frac{1}{N} - \frac{1}{n}\right). \tag{11}$$

It is clear that this relation is identical to the solution (9) of the deterministic equation if $t$ in the latter is replaced by its expectation value $\langle t\rangle$. Further, the standard deviation $\sigma_p$ associated with the time interval $t_p$ is given by

$$\sigma_p^2 = -\int_0^\infty \tau^2(\partial P_p/\partial\tau)\,\mathrm{d}\tau - \langle t_p\rangle^2 = \frac{4}{K^2p^2(p-1)^2}. \tag{12}$$

Since the time intervals $t_p$ are uncorrelated, it follows that the standard deviation $\sigma$ associated with the total time $t$ is given by

$$\sigma^2 = \sum_{p=N+1}^{n} \sigma_p^2 = \frac{4}{K^2} \sum_{p=N+1}^{n} \frac{1}{p^2(p-1)^2}. \tag{13}$$

The summation in equation (13) can be estimated by the Euler–Maclaurin summation formula (Abramowitz and Stegun 1965), which yields

$$\sum_{p=N+1}^{n} \frac{1}{p^2(p-1)^2} = \frac{1}{3}\left(\frac{1}{N^3} - \frac{1}{n^3}\right) - \frac{1}{15}\left(\frac{1}{N^5} - \frac{1}{n^5}\right) + \dots \tag{14}$$

and hence

$$\sigma \approx \frac{2}{3^{1/2}K}\left(\frac{1}{N^3} - \frac{1}{n^3}\right)^{1/2}. \tag{15}$$

Equations (11) and (15) give

$$\frac{\sigma}{\langle t\rangle} \approx \left[\frac{n^2 + Nn + N^2}{3Nn(n-N)}\right]^{1/2}. \tag{16}$$

Thus for $n \gg 1$, $\sigma/\langle t\rangle$ will initially be close to unity (for $n - N \sim 1$) before decreasing as $(n-N)^{-1/2}$ with the passage of time and decreasing $N$. $\sigma/\langle t\rangle$ then passes through a minimum [at $N/n = \frac{1}{2}(\sqrt{3}-1)$] before finally increasing as $N^{-1/2}$ when $N$ approaches one. That $\sigma/\langle t\rangle$ is close to unity for $n - N \sim 1$ and for $N \sim 1$ is physically due to the fact that for both of these situations $\langle t\rangle$ is essentially governed by relatively few coagulations.

Finally, we consider briefly the situation when in addition to coagulation there exists a removal mechanism (for example, deposition of particles on the walls of the container) whose effectiveness is assumed to be independent of particle size. Then the probability of a single particle not being removed after time $\tau$ is

$$Q(\tau) = \exp(-R\tau)$$

for some constant $R$, and thus the probability of a set of $N$ particles remaining unchanged after time $t$ when both coagulation and removal are operative is given by

$$S_N(\tau) = \exp[-(\tfrac{1}{2}KN(N-1) + RN)\tau]. \tag{17}$$

Following the approach developed earlier, expression (17) gives the deterministic equation for the system in the form

$$\mathrm{d}N/\mathrm{d}t = -\tfrac{1}{2}KN^2 - RN \tag{18}$$

with solution

$$t = \frac{1}{R}\ln\left(\frac{1+\alpha N^{-1}}{1+\alpha n^{-1}}\right) \tag{19}$$

where $\alpha = 2R/K$. On pursuing the stochastic treatment of the problem along the lines outlined above, it transpires that

$$\langle t \rangle = \frac{2}{(1-\alpha)K} \sum_{p=N+1}^{n} \left( \frac{1}{p+\alpha-1} - \frac{1}{p} \right). \tag{20}$$

It is clear that for $\alpha \neq 0$ the right-hand side of (19) is different from the right-hand side of (20) and thus the introduction of a removal mechanism spoils the $\langle t \rangle = t$ equality which applies for coagulation acting alone. However, by first performing the summation in (20) using the Euler–Maclaurin summation formula, and then considering the form taken by $t$ (19) and $\langle t \rangle$ (20) for $N$, $n \gg 1$ it may be shown that, in this limit, $t = \langle t \rangle$.

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