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On the stochastic approach to cluster size distribution during particle coagulation: I. Asymptotic expansion in the deterministic limit

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Abstract. Consideration is given to the stochastic problem of the coagulation of particles for the case of a size-independent coagulation kernel, and expressions are derived for the expectation value, variance and covariance of the cluster size distribution function, for both a discrete and a continuous spectrum of cluster sizes. We develop an asymptotic expansion in V^{-1} of these quantities (where V is the spatial volume), showing that as $V \to \infty$ the above expectation value tends to the deterministic result, and obtaining an explicit form for the first-order deviation from this expression for large (but finite) V. Analogous results are derived for the variance and covariance in the limit of large V. A discussion is given of the extent to which stochastic effects can produce significant changes to the deterministic results.

1. Introduction

Consider a number N_0 of identical particles, each of volume v_0 distributed homogeneously in a spatial volume V with number density $\mathcal{N}_0$ $(=N_0/V)$. We postulate that with the passage of time the particles coagulate, producing clusters of varying sizes, and two approaches have conventionally been used for the quantitative discussion of this phenomenon. The first, pioneered by Smoluchowski, takes V to be infinite and proceeds to formulate the relevant deterministic equations for $\mathcal{N}^{\mathrm{d}}(t)$, the total cluster density (number per unit volume) at time t, and for $\mathcal{N}_r^{\mathrm{d}}(t)$, the density of clusters containing r of the original particles. Assuming the coagulation kernel Q to be constant (a reasonable approximation for Brownian coagulation), it then transpires that

$$\mathcal{N}^{\mathrm{d}}(\tau)=(\mathcal{N}_0^{-1}+\tau)^{-1} \tag{1}$$

and

$$\mathcal{N}_r^{\mathrm{d}}(\tau)=\mathcal{N}_0\frac{(\mathcal{N}_0\tau)^{r-1}}{(1+\mathcal{N}_0\tau)^{r+1}} \tag{2}$$

where $\tau=\frac{1}{2}Qt$ (Friedlander 1977).

The second approach to coagulation is a stochastic one and early work using this technique includes that of Scott (1967), Warshaw (1967) and Marcus (Hidy and Brock

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1972). These workers were all basically concerned with placing the standard general coagulation equation for an infinite medium on a better theoretical foundation. However, as they acknowledge in their papers, each of their treatments required them to make assumptions in order to reach the desired results. These assumptions were physically plausible in some, though not all, situations, but mathematically they were unproved. Thus, Scott and Marcus assumed that the cluster distribution was uncorrelated in order to circumvent the well known closure problem, while Warshaw's assumption was that certain variables were multinomially distributed. The essential criticism of this early stochastic work is thus that it is characterized by a lack of mathematical rigour.

The next stage in implementing the stochastic approach is typified by the work of Williams (1979) and Arcipiani (1980) who developed a mathematically rigorous approach to the stochastic problem associated with the total number of clusters arising in a coagulating system of particles. They obtained somewhat complicated general expressions for the expectation value and variance of the total cluster number, but did no attempt to show how these expressions gave rise to the deterministic result (1) in the appropriate limit. Nor were they concerned with the number of clusters of a specified size. Following on this came the work of Hendriks *et al* (1985) and Merkulovich and Stepanov (1986). They considered $\langle N(t)\rangle$, the expectation value of $N(t)$, the total number of clusters at time t, and showed rigorously that if $V\to\infty$ keeping $\mathcal{N}_0$ constant, then $\langle\mathcal{N}(t)\rangle$ $[=V^{-1}\langle N(t)\rangle]$ tends to the result (1). Let us now consider the situation when V is large but finite. It is then possible to develop an expression for $\langle\mathcal{N}(t)\rangle$ as a power series in V^{-1}, the leading term of the series being the result (1) and the next term (proportional to V^{-1}) giving the dominant correction to this deterministic result in the limit of large but finite V. Additionally the corresponding series for $\mathrm{Var}(\mathcal{N})$ can also be obtained, and for this the leading term is proportional to V^{-1}. Detailed calculations of these quantities with a V^{-1} dependence (which measure the initial departure from a deterministic regime) have been carried out independently by Merkulovich and Stepanov (1986) and by Simons (1991).

The purpose of the present work is to develop a stochastic treatment, analogous to that outlined above, for $\mathcal{N}_r$ the number density of clusters of r particles, and for which the deterministic result is embodied in (2). That is, we will show by a mathematically rigorous stochastic approach that in the limit of $V\to\infty$ with $\mathcal{N}_0$ constant, $\langle\mathcal{N}_r\rangle$ tends to the result (2) and we will obtain the first order correction to this for large but finite V, together with the corresponding terms of $\mathrm{Var}(\mathcal{N}_r)$ and $\mathrm{Cov}(\mathcal{N}_q, \mathcal{N}_r)$—these all being proportionally to V^{-1}. A calculation of these corrections is of value for the following reasons. Firstly, it yields a simple analytic result for the relevant quantity, showing explicitly how the $V=\infty$ limit is approached. This should be contrasted with a complete calculation for general V (see the paper of Williams (1979)) where the complex dependence on N_0 and t prevents any easy understanding of this behaviour. Secondly, the correction formulae may be used to estimate quantitatively the differences between the stochastic and deterministic results for finite V, and hence to decide on the regime where stochastic effects may become significant. We shall return to this point later in the discussion of section 4.

In our treatment we first deal with a non-zero value for our initial particle size v_0 and a finite value for the initial particle density $\mathcal{N}_0$. Subsequently we consider the limiting form of the analysis when $v_0\to 0$ and $\mathcal{N}_0\to\infty$ with $\phi=v_0\mathcal{N}_0$ finite. This allows the formulation to be given in terms of a continuous variable v which specifies the amount of particulate material in a cluster.

2. Basic theory

2.1. Discrete case

We consider the following stochastic model for the coagulation of an initial collection of N_0 particles. Denote by $N(t)$ the number of clusters present at time t and for convenience label the clusters $a_1, \ldots, a_{N(t)}$ in an arbitrary way. We suppose that as $\delta \to 0$

$$\text{P(clusters } a_i \text{ and } a_j \text{ coagulate during } (t, t+\delta) | N(t) = k) = 2\delta + O(\delta^2)$$

$$i, j = 1, \ldots, k, \; i \neq k$$

that these events for different pairs of clusters are independent and further are independent of the past history of the process. Note that the above expression for P corresponds to a coagulation rate which is independent of cluster size. We begin by calculating $\langle N_r(t)\rangle$, the expectation value of $N_r(t)$ the number of clusters containing r of the original particles at time t. To do this we label the original particles $1, 2, \ldots, N_0$ and define

$$\begin{aligned} \chi_i^r(t) &= 1 \quad \text{if at time } t \text{ particle labelled } i \text{ is in a cluster of size } r \\ &= 0 \quad \text{otherwise.} \end{aligned}$$

Then

$$N_r(t) = r^{-1} \sum_{i=1}^{N_0} \chi_i^r(t) \tag{3}$$

leading to

$$\begin{aligned} \langle N_r(t)\rangle &= r^{-1} \sum_{i=1}^{N_0} \langle \chi_i^r(t)\rangle \\ &= (N_0/r)\langle \chi_1^r(t)\rangle \end{aligned} \tag{4}$$

since, by symmetry, each of the random variables $\chi_i^r(t)$ has the same distribution. Further, since χ_i^r only takes the values 0 and 1, it follows that

$$\langle N_r(t)\rangle = (N_0/r)\mathrm{P}(\chi_1^r(t) = 1) \tag{5}$$

where $\mathrm{P}(\chi_1^r(t) = 1)$ is the probability that the particle labelled 1 is in a cluster of size r at time t.

The dynamics of the stochastic model for coagulation considered here are identical (subject to a time scaling) to those of a process called the n-coalescent which arises in mathematical genetics (Kingman (1982) with $n = N_0$ in our notation). The N_0-coalescent is a process whose values are equivalence relations or partitions of the set $\{1, 2, \ldots, N_0\}$ with initial value being the partition with N_0 classes $\{1\}, \{2\}, \ldots, \{N_0\}$, and for which each existing pair of classes coalesces at rate 1. If the initial particles in the coagulation model are labelled $1, 2, \ldots, N_0$, the correspondence between the processes is that a class $\{i_1, \ldots, i_r\}$ in the N_0-coalescent at time t is equivalent to a cluster in the coagulation model at time t which is of size r and consists of exactly the particles labelled $i_1, \ldots, i_r$. We can thus translate results about the N_0-coalescent into results about the coagulation system. In particular, given that there are k clusters, the probability that there are m_r clusters of size r ($r = 1, 2, \ldots, N_0$, $m_r \geq 0$, $m_1 + \ldots + m_{N_0} = k$, $m_1 + 2m_2 + \ldots + N_0 m_{N_0} = N_0$) is

$$\frac{k!}{m_1! m_2! \ldots m_{N_0}!} \Big/ \binom{N_0 - 1}{k - 1}$$

(see, for example, Tavaré (1984)), and this probability does not depend on the time at which the k clusters occur. It is a straightforward combinatorial exercise to check that this distribution of cluster sizes is the same as that which would be obtained if the N_0 particles were arranged on a circle with k 'barriers' being inserted in the N_0 spaces between the particles, with all $\binom{N_0}{k}$ possible choices of locations being equally likely and with the cluster sizes being given by the number of particles between each of the k pairs of neighbouring 'barriers'. From this it follows by another easy combinatorial argument that

$$\begin{aligned} \mathrm{P}(\chi_1^r(t)=1|N(t)=k) &= \mathrm{P}(\text{particle labelled 1 in cluster of size } r|N(t)=k) \\ &= r\binom{N_0-r-1}{k-2}\bigg/\binom{N_0}{k} \qquad 2\leqslant k\leqslant N_0-r+1 \\ &= \frac{rk(k-1)(N_0-k)(N_0-k-1)\ldots(N_0-k-r+2)}{N_0(N_0-1)\ldots(N_0-r)} \qquad 2\leqslant k\leqslant N_0-r+1. \end{aligned}$$

Averaging over all values of k, we thus obtain from (5) that the expectation value of $N_r(t)$ is given by

$$\begin{aligned} \langle N_r(t)\rangle &= \sum_{k=1}^{N_0} \mathrm{P}(N(t)=k)\,\frac{k(k-1)(N_0-k)\ldots(N_0-k-r+2)}{(N_0-1)\ldots(N_0-r)} \\ &= \frac{\langle N(t)[N(t)-1][N_0-N(t)][N_0-N(t)-1]\ldots[N_0-N(t)-r+2]\rangle}{(N_0-1)(N_0-2)\ldots(N_0-r)}. \end{aligned} \tag{6}$$

This result holds for $r\leqslant N_0-1$ corresponding to the above conditions on k. For $r=N_0$, we have

$$\langle N_{N_0}(t)\rangle = \mathrm{P}(N(t)=1). \tag{6$'$}$$

We now consider the variance of $N_r(t)$ for which we require to calculate $\langle[N_r(t)]^2\rangle$. It follows from (3) and (4) that

$$\begin{aligned} \langle N_r^2\rangle &= \left\langle\left(r^{-1}\sum_{i=1}^{N_0}\chi_i^r\right)^2\right\rangle = r^{-2}\sum_{i=1}^{N_0}\langle\chi_i^r\rangle + r^{-2}\sum_{i\neq j}\langle\chi_i^r\chi_j^r\rangle \\ &= (N_0/r^2)\langle\chi_i^r\rangle + r^{-2}N_0(N_0-1)\langle\chi_1^r\chi_2^r\rangle \\ &= r^{-1}\langle N_r\rangle \\ &\quad + r^{-2}N_0(N_0-1)\mathrm{P}(\text{particles 1 and 2 in same cluster of size } r) \\ &\quad + r^{-2}N_0(N_0-1)\mathrm{P}(\text{particles 1 and 2 in different clusters of size } r). \end{aligned} \tag{7}$$

Now, it follows from (5) that

$$\mathrm{P}(\text{particles 1 and 2 in same cluster of size } r) = \frac{r(r-1)\langle N_r\rangle}{N_0(N_0-1)}$$

and hence that

$$\langle N_r^2\rangle = \langle N_r\rangle + r^{-2}N_0(N_0-1)\mathrm{P}(\text{particles 1 and 2 in different clusters of size } r). \tag{8}$$

Similarly we obtain that for $p\neq q$,

$$\langle N_pN_q\rangle = p^{-1}q^{-1}N_0(N_0-1)\mathrm{P}(\text{particle 1 in cluster of size } p \text{ and particle 2 in cluster of size } q). \tag{9}$$

Now it is clear that for all p and q such that $p+q<N_0$, the probability that particle 1 is in a cluster of size p and particle 2 is in a different cluster of size q will be the product of the probabilities that particle 1 is in a cluster of size p, that particle 2 is not in the same cluster as particle 1, and that particle 2 is in a cluster of size q chosen from the remaining N_0-p particles. Thus if there exists a total of k clusters, it follows from (8) and (9) that for all p and q such that $p+q<N_0$,

$$\langle N_pN_q\rangle=\langle N_p\rangle\delta_{pq}+\frac{N_0(N_0-1)}{pq}p\frac{\binom{N_0-p-1}{k-2}}{\binom{N_0}{k}}\frac{(N_0-p)}{(N_0-1)}q\frac{\binom{N_0-p-q-1}{k-3}}{\binom{N_0-p}{k-1}}$$

$$=\langle N_p\rangle\delta_{pq}+\frac{k(k-1)^2(k-2)(N_0-k)(N_0-k-1)\dots(N_0-k-p-q+3)}{(N_0-1)(N_0-2)\dots(N_0-p-q)}. \qquad (10)$$

On averaging this over all values of k, using the same technique as was employed above for $\langle N_r\rangle$, we obtain the result that for $p+q<N_0$, the expectation value of N_pN_q, whatever the value of k, is given by

$$\langle N_pN_q\rangle=\langle N_p\rangle\delta_{pq}+\frac{\langle N(N-1)^2(N-2)(N_0-N)(N_0-N-1)\dots(N_0-N-p-q+3)\rangle}{(N_0-1)(N_0-2)\dots(N_0-p-q)}. \qquad (11)$$

This result requires modification if $p+q=N_0$, corresponding to $N=2$. We then obtain

$$\langle N_pN_q\rangle=\langle N_p\rangle\delta_{pq}+\frac{2pq}{N_0(N_0-1)^2}\mathrm{P}(N=2). \qquad (11')$$

If $p+q>N_0$, $\langle N_pN_q\rangle=0$ unless $p=q\leqslant N_0$. For that situation $\langle N_p^2\rangle=\langle N_p\rangle$.

From the above results we may readily calculate

$$\mathrm{Var}(N_r)=\langle N_r^2\rangle-\langle N_r\rangle^2$$

and

$$\mathrm{Cov}(N_p, N_q)=\langle N_pN_q\rangle-\langle N_p\rangle\langle N_q\rangle.$$

2.2. Continuous case

This corresponds to the situation $N_0\to\infty$ and $v_0\to 0$ so that possible cluster volumes form a continuum. We then specify the cluster volume by a variable x defined as the ratio of the actual cluster volume to the total volume of particulate material. The expectation value of the cluster size distribution is now specified by a function $f(x, t)$; this is defined by $f(x, t)\,\mathrm{d}x$ being the expectation value of the number of clusters each containing a fraction of the total material in the interval x to $x+\mathrm{d}x$. Since $r=xN_0$, it follows from (6) that as N is finite for $t>0$,

$$f(x)=\lim_{N_0\to\infty}N_0\langle N_r\rangle$$

$$=\lim_{N_0\to\infty}\left\langle N(N-1)\left(\frac{N_0}{N_0-1}\right)\frac{(N_0-r-1)\dots[N_0-r-(N-2)]}{(N_0-2)\dots[N_0-(N-1)]}\right\rangle$$

$$=\lim_{N_0\to\infty}\left\langle N(N-1)\left(\frac{1}{1-N_0^{-1}}\right)\frac{(1-x-N_0^{-1})\dots[1-x-(N-2)N_0^{-1}]}{(1-2N_0^{-1})\dots[1-(N-1)N_0^{-1}]}\right\rangle$$

$$=\langle N(N-1)(1-x)^{N-2}\rangle=\frac{\mathrm{d}^2\langle(1-x)^N\rangle}{\mathrm{d}x^2}. \qquad (12)$$

For the calculation of variance and covariance of the cluster numbers a similar approach to that used above may be employed, whereby the limit as $N_0 \to \infty$ of the relevant formula in section 2.1 is considered. Let M_A be the number of clusters with proportional volume x lying in the interval $[a_1, a_2]$ and let M_B be the number of clusters with proportional volume y lying in the interval $[b_1, b_2]$. Further, let R be the rectangle in the x-y plane defined by $R = \{(x, y), a_1 < x < a_2, b_1 < y < b_2\}$, S the triangle defined by $S = \{(x, y), 0 < x < 1, 0 < y < 1 - x\}$ and T the line segment defined by $T = \{(x, y), 0 < x < 1, y = x\}$. Then the basic result that follows from the above limiting procedure is that

$$\langle M_A M_B \rangle = \int_{T \cap R} f(x, t)\, \mathrm{d}x + \iint_{S \cap R} g(x, y, t)\, \mathrm{d}x\, \mathrm{d}y + 2ZP(N=2) + \delta_{a_2 1}\delta_{b_2 1} P(N=1) \tag{13}$$

where

$$g(x, y, t) = \langle N(N-1)^2(N-2)(1-x-y)^{N-3} \rangle = -\partial^3 \langle (N-1)(1-x-y)^N \rangle / \partial x^3 \tag{14}$$

and Z is the length of the interval in x intercepted along the line $y = 1 - x$ by R.

3. Asymptotic expansion

3.1. Discrete case

We proceed to consider how the results of the last section yield the deterministic equation (2) in the appropriate limit, and to this end we follow Van Kampen (1981) in developing an expansion of the various quantities in powers of V^{-1}. We therefore suppose the clusters to be homogeneously distributed within spatial volume V, and rewrite (6) in terms of $\mathcal{N} = V^{-1}N$ and $\mathcal{N}_r = V^{-1}N_r$. This yields

$$\langle \mathcal{N}_r(t) \rangle = \frac{\langle [\mathcal{N}(t) - V^{-1}]\mathcal{N}(t)[\mathcal{N}_0 - \mathcal{N}(t)][\mathcal{N}_0 - \mathcal{N}(t) - V^{-1}] \ldots [\mathcal{N}_0 - \mathcal{N}(t) - (r-2)V^{-1}] \rangle}{(\mathcal{N}_0 - V^{-1})(\mathcal{N}_0 - 2V^{-1}) \ldots (\mathcal{N}_0 - rV^{-1})}. \tag{15}$$

We expand the explicit V dependent terms here as a power series in V^{-1}, retaining the first two terms. This gives

$$\begin{aligned}\langle \mathcal{N}_r(t) \rangle = {} & \mathcal{N}_0^{-r} \langle \mathcal{N}^2(\mathcal{N}_0 - \mathcal{N})^{r-1} \rangle - V^{-1}\mathcal{N}_0^{-r}[\langle \mathcal{N}(\mathcal{N}_0 - \mathcal{N})^{r-1} \rangle \\ & + \tfrac{1}{2}(r-1)(r-2)\langle \mathcal{N}^2(\mathcal{N}_0 - \mathcal{N})^{r-2} \rangle - \tfrac{1}{2}r(r+1)\mathcal{N}_0^{-1}\langle \mathcal{N}^2(\mathcal{N}_0 - \mathcal{N})^{r-1} \rangle].\end{aligned} \tag{16}$$

The various expectation values appearing here depend implicitly on V. It is shown in appendix 1 that if $g(\mathcal{N})$ is any polynomial in $\mathcal{N}$, then expansion of $\langle g(\mathcal{N}) \rangle$ as a power series in V^{-1} yields

$$\langle g(\mathcal{N}) \rangle = g(\mathcal{N}^{\mathrm{d}}) + \frac{1}{6V}\left[\frac{1}{\mathcal{N}^{\mathrm{d}}} - \frac{(\mathcal{N}^{\mathrm{d}})^2}{(\mathcal{N}_0)^3}\right] \frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left((\mathcal{N}^{\mathrm{d}})^2 \frac{\mathrm{d}g}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\right) + \ldots \tag{17}$$

and this allows us to obtain the first two terms of a power series expansion in V^{-1} for each expectation value occurring above. We use both terms of (17) for the first term of (16) and the first term of (17) for the remaining terms of (16). Making use of (1) in the form $\mathcal{N}^{\mathrm{d}}(\tau) = \mathcal{N}_0/(1+X)$, where $X = \mathcal{N}_0\tau$, gives us finally the result

$$\langle \mathcal{N}_r(\tau) \rangle = \frac{X^{r-1}}{(1+X)^{r+1}}\left\{\mathcal{N}_0 + V^{-1}\frac{[rX^2 - \tfrac{1}{3}(r^2 - 6r - 1)X - \tfrac{1}{2}r(r-1)]}{(1+X)^2}\right\}. \tag{18}$$

The first term on the right-hand side is the deterministic result (2), while the remainder of the expression gives the first order correction to this, proportional to V^{-1}; it is thus clear that

$$\lim_{V\to\infty} \langle \mathcal{N}_r(\tau)\rangle = \mathcal{N}_r^{\mathrm{d}}(\tau).$$

Let

$$\langle \mathcal{N}_r\rangle = \mathcal{N}_r^{\mathrm{d}} + \Delta\mathcal{N}_r.$$

Then for $r>1$ the sign of $\Delta\mathcal{N}_r$ changes as X increases, being negative for small X and positive for large X. It also follows from (18) that in general $|\Delta\mathcal{N}_r|$ increases with increasing r, the r dependence being approximately quadratic for small X and linear for large X. The mode of derivation of (18) shows it to be valid only if $|\Delta\mathcal{N}_r| \ll \mathcal{N}_r^{\mathrm{d}}$ and this gives a lower limit on V for the equation to hold, this limit increasing as r increases. For $r\gg 1$, $|\Delta\mathcal{N}_r|/\mathcal{N}_r^{\mathrm{d}}$ has its maximum value $\approx r^2/2\mathcal{N}_0 V$ at $X=0$ and thus the lower limit on V will be $\gg r^2/2\mathcal{N}_0$. Alternatively, for given V (18) will hold for $r^2 \ll 2\mathcal{N}_0 V = 2N_0$. Finally we note that for $X\ll 1$,

$$\langle \mathcal{N}_1(\tau)\rangle = \mathcal{N}_0 - 2(\mathcal{N}_0 - V^{-1})X \tag{19a}$$

$$\langle \mathcal{N}_r(\tau)\rangle = X^{r-1}[\mathcal{N}_0 - \tfrac{1}{2}r(r-1)V^{-1}] \qquad r\geq 2 \tag{19b}$$

while for $X\gg r$,

$$\langle \mathcal{N}_r(\tau)\rangle = X^{-2}(\mathcal{N}_0 + rV^{-1}). \tag{20}$$

We now consider the variance of $\mathcal{N}_p$ and covariance of $\mathcal{N}_p$ and $\mathcal{N}_q$. We begin with

$$\mathrm{Cov}(\mathcal{N}_p, \mathcal{N}_q) = \langle \mathcal{N}_p\mathcal{N}_q\rangle - \langle \mathcal{N}_p\rangle\langle \mathcal{N}_q\rangle \tag{21}$$

and use (11) to give

$$\langle \mathcal{N}_p\mathcal{N}_q\rangle = Y_{pq} + V^{-1}\langle \mathcal{N}_p\rangle\delta_{pq} \tag{22}$$

where

$$Y_{pq} = \frac{\begin{array}{l}\langle \mathcal{N}^4(\mathcal{N}_0-\mathcal{N})^{s-2}(1-\mathcal{N}^{-1}V^{-1})^2(1-2\mathcal{N}^{-1}V^{-1}) \\ \qquad\qquad \times[1-(\mathcal{N}_0-\mathcal{N})^{-1}V^{-1}]\ldots[1-(s-3)(\mathcal{N}_0-\mathcal{N})^{-1}V^{-1}]\rangle\end{array}}{\mathcal{N}_0^s(1-\mathcal{N}_0^{-1}V^{-1})(1-2\mathcal{N}_0^{-1}V^{-1})\ldots(1-s\mathcal{N}_0^{-1}V^{-1})} \tag{23}$$

with $s=p+q$. We expand the explicit V dependent terms here as a power series in V^{-1}, retaining the first two terms. This yields

$$\begin{aligned}Y_{pq} = \mathcal{N}_0^{-s}\langle \mathcal{N}^4(\mathcal{N}_0-\mathcal{N})^{s-2}\rangle - V^{-1}\mathcal{N}_0^{-s}[4\langle \mathcal{N}^3(\mathcal{N}_0-\mathcal{N})^{s-2}\rangle \\ +\tfrac{1}{2}(s-3)(s-2)\langle \mathcal{N}^4(\mathcal{N}_0-\mathcal{N})^{s-3}\rangle - \tfrac{1}{2}s(s+1)\mathcal{N}_0^{-1}\langle \mathcal{N}^4(\mathcal{N}_0-\mathcal{N})^{s-2}\rangle].\end{aligned} \tag{24}$$

The various expectation values appearing here depend implicitly on V, and hence employing the same approach as that used above in the treatment of $\langle \mathcal{N}_r\rangle$ allows us to obtain an explicit form for the first two terms of a power series expansion in V^{-1} of Y_{pq}. After some manipulative algebra, this finally takes the form

$$Y_{pq} = \frac{\mathcal{N}_0 X^{s-2}}{(1+X)^{s+2}}\left\{\mathcal{N}_0 - V^{-1}\frac{[2X^3-(4s-5)X^2+s(s-8)X+\tfrac{3}{2}s(s-1)]}{3(1+X)^2}\right\}. \tag{25}$$

We then obtain from (21) that for $p\neq q$,

$$\mathrm{Cov}(\mathcal{N}_p, \mathcal{N}_q) = -\left(\frac{\mathcal{N}_0 X^{p+q-2} V^{-1}}{3(1+X)^{p+q+4}}\right) \times [2X^3 - (p+q-5)X^2 + 2(p-1)(q-1)X + 3pq] \tag{26}$$

while for $p = q$,

$$\mathrm{Var}(\mathcal{N}_p) = \frac{\mathcal{N}_0 X^{p-1} V^{-1}}{(1+X)^{p+1}} \times \left\{1 - \frac{X^{p-1}}{3(1+X)^{p+3}}[2X^3 - (2p-5)X^2 + 2(p-1)^2 X + 3p^2]\right\}. \tag{27}$$

We note that $\mathrm{Cov}(\mathcal{N}_p, \mathcal{N}_q)$ and $\mathrm{Var}(\mathcal{N}_p)$ both exhibit a V^{-1} dependence and therefore tend to zero as $V \to \infty$. Further, apart from small X values for $p = 1$, the value of $\mathrm{Var}(\mathcal{N}_p)$ is dominated by the constant term inside $\{\ldots\}$, and thus in general, $\mathrm{Var}(N_p) \sim N_p^{\mathrm{d}}$. It is clear that $\mathrm{Cov}(\mathcal{N}_p, \mathcal{N}_q) < 0$ for sufficiently small X and also for sufficiently large X. If $p + q \leqslant 5$, $\mathrm{Cov}(\mathcal{N}_p, \mathcal{N}_q) < 0$ for all X and the same will be true for $p, q \gg 1$ if $\beta \geqslant p/q \geqslant \beta^{-1}$ where $\beta = 7 + 4\sqrt{3} \approx 14$. For values of p/q outside this interval $\mathrm{Cov}(\mathcal{N}_p, \mathcal{N}_q) > 0$ for some X.

3.2. *The continuous case*

In considering the asymptotic limit of the continuous case we wish to make contact with the conventional mode of description for the corresponding deterministic situation. We therefore specify the cluster size distribution by a function $n(v)$ such that $n(v)\,\mathrm{d}v$ is the number of clusters per unit volume of space whose volumes lie between v and $v + \mathrm{d}v$. The expectation value of the number of clusters for the whole system whose volumes lie between v and $v + \mathrm{d}v$ is thus $V\langle n(v)\rangle\,\mathrm{d}v$ which may be equated to $f(x)\,\mathrm{d}x$ where $f(x)$ is defined in (12). To connect v and x we introduce ϕ, the proportion of space occupied by particulate matter, when it follows that

$$v = V\varphi x \tag{28}$$

and hence

$$\langle n(v)\rangle = f(x)/V^2\phi = \varphi \frac{\mathrm{d}^2}{\mathrm{d}v^2}\left\langle\left(1 - \frac{v}{V\varphi}\right)^{V\mathcal{N}}\right\rangle. \tag{29}$$

We obtain the first two terms of a power series expansion in V^{-1} of $y = (1 - v/V\varphi)^{V\mathcal{N}}$ by considering

$$\ln y = V\mathcal{N} \ln\left(1 - \frac{v}{V\varphi}\right) = \frac{-v\mathcal{N}}{\varphi} - \frac{v^2\mathcal{N}}{2V\varphi^2} + \ldots$$

which gives

$$y = \exp\left(\frac{-v\mathcal{N}}{\varphi}\right) - \frac{v^2\mathcal{N}}{2V\varphi^2}\exp\left(\frac{-v\mathcal{N}}{\varphi}\right) + \ldots. \tag{30}$$

Equation (17) may then be used to evaluate the first two terms of a power series expansion in V^{-1} of $\langle y \rangle$. This yields

$$\left\langle \left(1-\frac{v}{V\varphi}\right)^{V\mathcal{N}} \right\rangle = \exp\left(\frac{-v}{\varphi\tau}\right) - \frac{v}{3V\varphi}\left(1+\frac{v}{\varphi\tau}\right)\exp\left(\frac{-v}{\varphi\tau}\right) \tag{31}$$

since $\mathcal{N}^{\mathrm{d}}(\tau)=1/\tau$ as $\mathcal{N}_0=\infty$. Equation (29) now gives

$$\langle n(v) \rangle = \frac{\exp(-v/\varphi\tau)}{\varphi\tau^2} + \frac{v}{V\varphi^2\tau^2}\left(1-\frac{v}{3\varphi\tau}\right)\exp(-v/\varphi\tau). \tag{32}$$

The first term here is the deterministic result $n^{\mathrm{d}}(v)$ as derived in appendix 2 and the second term is the first-order correction to this, proportional to V^{-1}. We note that (32) can be expressed more concisely if we define a dimensionless volume $w=v/\bar{v}$, where $\bar{v}=\phi/\mathcal{N}^{\mathrm{d}}=\varphi\tau$, and let $m(w)\,\mathrm{d}w$ be the number of clusters per unit volume of space whose dimensionless volumes lie between w and $w+\mathrm{d}w$. We then obtain

$$\langle m(w) \rangle = \mathcal{N}^{\mathrm{d}}\,\mathrm{e}^{-w} + V^{-1}w(1-\tfrac{1}{3}w)\,\mathrm{e}^{-w}. \tag{33}$$

The correction term $V^{-1}w(1-\frac{1}{3}w)\,\mathrm{e}^{-w}$ will be positive for $w<3$ and negative for $w>3$. For $w \gg 1$, the ratio of the magnitude of this term to the deterministic result will be $\sim w^2/3N^d$, and hence for (33) to be valid it is necessary that

$$w^2 \ll 3N^{\mathrm{d}}. \tag{34}$$

To calculate the asymptotic limit of the covariance and variance in the continuous case we begin by defining L_{A} and L_{B} as the numbers of clusters per unit volume of space whose own volumes lie respectively within the interval $[\alpha_1, \alpha_2]$ and within the interval $[\beta_1, \beta_2]$. Now, it follows from the earlier definition that $w=N^{\mathrm{d}}x$ and hence the above condition (34) for the asymptotic theory to hold yields

$$x \ll (3/N^{\mathrm{d}})^{1/2} \ll 1. \tag{35}$$

It then follows from the previous discussion, together with (13), that for the situation where the intervals $[\alpha_1, \alpha_2]$ and $[\beta_1, \beta_2]$ are disjoint,

$$\mathrm{Cov}(L_{\mathrm{A}}, L_{\mathrm{B}}) = \int_{\beta_1}^{\beta_2}\int_{\alpha_1}^{\alpha_2} F(u,v)\,\mathrm{d}u\,\mathrm{d}v \tag{36a}$$

where

$$F(u,v) = V^{-4}\varphi^{-2}\left[g\left(\frac{u}{V\varphi},\frac{v}{V\varphi}\right) - f\left(\frac{u}{V\varphi}\right)f\left(\frac{v}{V\varphi}\right)\right]. \tag{36b}$$

We employ the techniques used above to expand $F(u,v)$ as a power series in V^{-1}, and after some manipulative algebra obtain as the leading term

$$F(u,v) = -\frac{\exp[-(u+v)/\varphi\tau]}{3V\varphi^2\tau^3}\left[2-\frac{u+v}{\varphi\tau}+\frac{2uv}{\varphi^2\tau^2}\right]. \tag{37}$$

From (13) and (32) we also obtain the result

$$\mathrm{Var}(L_{\mathrm{A}}) = V^{-1}\left[\int_{\alpha_1}^{\alpha_2} G(v)\,\mathrm{d}v + \int_{\alpha_1}^{\alpha_2}\int_{\alpha_1}^{\alpha_2} F(u,v)\,\mathrm{d}u\,\mathrm{d}v\right] \tag{38}$$

where $G(v)=\exp(-v/\phi\tau)/\phi\tau^2$. To evaluate the above integrals we introduce the corresponding dimensionless cluster volumes $w=v/\phi\tau$, $w'=u/\phi\tau$, when letting $c_1=\alpha_1/\phi\tau$, $c_2=\alpha_2/\phi\tau$, $d_1=\beta_1/\phi\tau$, $d_2=\beta_2/\phi\tau$ we finally obtain

$$\begin{aligned}\mathrm{Cov}(L_A, L_B)=&-(\mathcal{N}^d/3V)[(2c_1d_1+c_1+d_1+2)\,\mathrm{e}^{-(c_1+d_1)}+(2c_2d_2+c_2+d_2+2)\,\mathrm{e}^{-(c_2+d_2)}\\&-(2c_1d_2+c_1+d_2+2)\,\mathrm{e}^{-(c_1+d_2)}-(2c_2d_1+c_2+d_1+2)\,\mathrm{e}^{-(c_2+d_1)}]\end{aligned} \tag{39}$$

$$\begin{aligned}\mathrm{Var}(L_A)=&(\mathcal{N}^d/V)\{(\mathrm{e}^{-c_1}-\mathrm{e}^{-c_2})-\tfrac{2}{3}[(c_1^2+c_1+1)\,\mathrm{e}^{-2c_1}+(c_2^2+c_2+1)\,\mathrm{e}^{-2c_2}\\&-(2c_1c_2+c_1+c_2+2)\,\mathrm{e}^{-(c_1+c_2)}]\}.\end{aligned} \tag{40}$$

Since $F(u, v)<0$ for all $u>\frac{1}{2}\phi\tau$, $v>\frac{1}{2}\phi\tau$ it follows that $\mathrm{Cov}(L_A, L_B)$ is always negative if $c_1\geqslant\frac{1}{2}$ and $d_1\geqslant\frac{1}{2}$.

4. Discussion

We have shown in this paper that a rigorous stochastic approach yields in the limit of $V\to\infty$ the standard deterministic results for cluster size distribution in a system of coagulating particles. In addition we have obtained for finite V explicit forms for the leading terms of expressions measuring the departure from this deterministic behaviour. We now proceed to consider to what extent these departures can lead to conclusions significantly different from those given by the usual deterministic approach, and to do this we deal with the total number of clusters of r particles lying within V. According to the deterministic approach this number will be given by $N_r^d(\tau)=V\mathcal{N}_r^d(\tau)$ with $\mathcal{N}_r^d(\tau)$ defined in (2), and this will represent the exact number of clusters of r particles at time τ. That is, if we repeat the measurement of $N_r(\tau)$ on a set of systems each with the same V and initial N_0, we would expect to obtain exactly the same result $N_r^d(\tau)$ in each case. According to the present stochastic approach, however, no prediction is made about the result of a single measurement of $N_r(\tau)$—rather, the theory predicts a value for $\langle N_r(\tau)\rangle$, the mean of a large number of such measurements made on initially identical systems. Further, in the stochastic approach a prediction is made of $\mathrm{Var}(N_r(\tau))$ which measures the extent to which individual measurements are likely to deviate from their mean value $\langle N_r(\tau)\rangle$. Now, it was shown in section 3.1 that apart from small values of X for $r=1$, $\mathrm{Var}(N_r)=\gamma N_r^d$ where γ is close to unity. Further, we will show presently that for N_r^d significantly greater than unity $\langle N_r\rangle\approx N_r^d$, and hence for such a situation our stochastic theory predicts the mean of a large number of measurements to be close to N_r^d, but with any individual measurement deviating from this value by an amount $\sim(N_r^d)^{1/2}$.

We now consider under what circumstances the value of $\langle N_r\rangle$ can differ significantly from N_r^d, and to do this we begin with the result (obtained from (18)),

$$\langle N_r(\tau)\rangle=\frac{X^{r-1}}{(1+X)^{r+1}}\left\{N_0+\frac{[rX^2-\frac{1}{3}(r^2-6r-1)X-\frac{1}{2}r(r-1)]}{(1+X)^2}\right\}. \tag{41}$$

Initially we suppose N_0 and r to be given and choose for X the value $\frac{1}{2}(r-1)$ which maximizes $N_r^d[=N_0X^{r-1}/(1+X)^{r+1}]$. For this value of X we then have

$$\langle N_r(\tau)\rangle=\frac{4}{(r+1)^2}\left(\frac{r-1}{r+1}\right)^{r-1}\left[N_0+\frac{(r-1)(r+2)}{3(r+1)}\right]. \tag{42}$$

We consider the situation when $\langle N_r(\tau)\rangle$ differs from N_r^d by at least 10%, and it is clear from (42) that this corresponds to $r \geqslant N_0/3$. Since $N_0 \leqslant 3r$, it then follows that

$$N_r^d \leqslant \frac{12r}{(r+1)^2}\left(\frac{r-1}{r+1}\right)^{r-1} \tag{43}$$

which is less than unity for $r \geqslant 1$. This in turn implies the result quoted above that for N_r^d significantly greater than one, the difference between $\langle N_r\rangle$ and N_r^d is very small. This difference can only become significant (in excess of about 10%) when $\langle N_r\rangle < 1$ which corresponds to a situation in which the stochastic properties of the system are already apparent in that successive measurements of N_r at time τ on initially identical systems can lead to significantly differing results. As a simple numerical illustration of this we consider $N_0 = 10$, $r = 5$. For $X = 2$ (the value which maximizes N_5^d) we then have $N_5^d = 0.220$ and $\langle N_5\rangle = 0.254$, the difference between the two values being about 15%. For such a situation most observations at $X = 2$ will yield no clusters of the specified size, about 1 in 4 observations will give a single cluster and a much smaller proportion will yield 2 clusters. If we choose for r and N_0 values much larger than these, then the corresponding values of N_r^d and $\langle N_r\rangle$ will both be much less since the expression (43) for N_r^d behaves as $1.62/r$ for $r \gg 1$. The final point to make in this connection is that for small values of X the proportional difference between N_r^d and $\langle N_r\rangle$ can be considerably greater, but this will correspond to a much smaller value for both quantities. Thus for $N_0 = 10$, $r = 5$ and $X = 0.1$, we obtain $\langle N_5\rangle \approx 0.2 N_5^d$ with $N_5^d \approx 6 \times 10^{-4}$.

The main point emerging from the above discussion is that quantitative differences between the stochastic and deterministic approaches can only become significant for a given cluster size when the expected number of clusters of that size within the system is $\leqslant 1$. Although in most practical aerosol or hydrosol problems this will not be the case, it may be so for very large clusters or for laboratory situations in which N_0 is relatively small.

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Appendix 1

We proceed to prove that if $g(\mathcal{N})$ is any polynomial in $\mathcal{N}$ and if $\langle g(\mathcal{N})\rangle$ is expanded as a power series in V^{-1}, then

$$\langle g(\mathcal{N})\rangle = g(\mathcal{N}^d) + \frac{1}{6V}\left[\frac{1}{\mathcal{N}^d} - \frac{(\mathcal{N}^d)^2}{\mathcal{N}_0^3}\right]\frac{d}{d\mathcal{N}^d}\left((\mathcal{N}^d)^2 \frac{dg}{d\mathcal{N}^d}\right) + \ldots \tag{A1.1}$$

Let $P(N, \tau')$ be the probability of there being N clusters in the whole system after time $\tau' = \frac{1}{2}Qt/V = \tau/V$. Then the master equation for P takes the form (Simons 1991)

$$\frac{dP(N, \tau')}{d\tau'} = -N(N-1)P(N, \tau') + N(N+1)P(N+1, \tau'). \tag{A1.2}$$

Let $f(N)$ be any function of N with $f(0)$ and $f(1)$ finite. Then multiplying equation (A1.2) by $f(N)$ and summing over all values of N in the interval $1 \leq N \leq \infty$ yields

$$\frac{\mathrm{d}\langle f(N)\rangle}{\mathrm{d}\tau'} = \langle N(N-1)[f(N-1)-f(N)]\rangle$$

provided that all expectation values are finite. We now change the variables N and τ' to $\mathcal{N} = V^{-1}N$ and $\tau = V\tau'$, letting $f(N) = g(\mathcal{N})$. This gives

$$\frac{\mathrm{d}\langle g(\mathcal{N})\rangle}{\mathrm{d}\tau} = V\langle \mathcal{N}(\mathcal{N}-V^{-1})[g(\mathcal{N}-V^{-1})-g(\mathcal{N})]\rangle$$

and on expanding the right-hand side as a power series in V^{-1} we obtain

$$\frac{\mathrm{d}\langle g(\mathcal{N})\rangle}{\mathrm{d}\tau} = -\left\langle \mathcal{N}^2 \frac{\mathrm{d}g(\mathcal{N})}{\mathrm{d}\mathcal{N}}\right\rangle + \frac{1}{2V}\left\langle \frac{\mathrm{d}}{\mathrm{d}\mathcal{N}}\left(\mathcal{N}^2\frac{\mathrm{d}g}{\mathrm{d}\mathcal{N}}\right)\right\rangle + \dots \tag{A1.3}$$

We now prove (A1.1) by induction and to this end we let g_k denote a general polynomial of degree k. We assume (A1.1) to hold for $k \leq s$ and proceed to show it to hold for $k = s+1$. To do this we note that any polynomial of degree $s+1$ can be expressed in the form

$$g_{s+1}(\mathcal{N}) = \mathcal{N}^2[\mathrm{d}g_s(\mathcal{N})/\mathrm{d}\mathcal{N}] + a\mathcal{N} + b$$

for suitable choice of g_s and constants a, b. Equation (A1.3) then yields to terms of order V^{-1}

$$\langle g_{s+1}\rangle = \left\langle \mathcal{N}^2\frac{\mathrm{d}g_s}{\mathrm{d}\mathcal{N}}\right\rangle + a\langle\mathcal{N}\rangle + b = -\frac{\mathrm{d}\langle g_s\rangle}{\mathrm{d}\tau} + \frac{1}{2V}\left\langle\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}}\left(\mathcal{N}^2\frac{\mathrm{d}g_s}{\mathrm{d}\mathcal{N}}\right)\right\rangle + a\langle\mathcal{N}\rangle + b.$$

Now g_s, $\mathrm{d}/\mathrm{d}\mathcal{N}(\mathcal{N}^2\,\mathrm{d}g_s/\mathrm{d}\mathcal{N})$ and $\mathcal{N}$ are all polynomials of degree $\leq s$ to which the inductive hypothesis (A1.1) may be applied, giving

$$\langle g_{s+1}\rangle = -\frac{\mathrm{d}g_s(\mathcal{N}^{\mathrm{d}})}{\mathrm{d}\tau} - \frac{1}{6V}\frac{\mathrm{d}}{\mathrm{d}\tau}\left[\left(\frac{1}{\mathcal{N}^{\mathrm{d}}} - \frac{(\mathcal{N}^{\mathrm{d}})^2}{\mathcal{N}_0^3}\right)\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left((\mathcal{N}^{\mathrm{d}})^2\frac{\mathrm{d}g_s}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\right)\right]$$
$$+\frac{1}{2V}\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left((\mathcal{N}^{\mathrm{d}})^2\frac{\mathrm{d}g_s}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\right) + a\mathcal{N}^{\mathrm{d}} + \frac{a}{3V}\left(1-\frac{(\mathcal{N}^{\mathrm{d}})^3}{\mathcal{N}_0^3}\right) + b$$

to term of order V^{-1}. Further, for any function $\theta(\mathcal{N}^{\mathrm{d}})$

$$\frac{\mathrm{d}\theta(\mathcal{N}^{\mathrm{d}})}{\mathrm{d}\tau} = -(\mathcal{N}^{\mathrm{d}})^2\frac{\mathrm{d}\theta}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}$$

as $\mathrm{d}\mathcal{N}^{\mathrm{d}}/\mathrm{d}\tau = -(\mathcal{N}^{\mathrm{d}})^2$, and so

$$\langle g_{s+1}\rangle = (\mathcal{N}^{\mathrm{d}})^2\frac{\mathrm{d}g_s(\mathcal{N}^{\mathrm{d}})}{\mathrm{d}\mathcal{N}^{\mathrm{d}}} + a\mathcal{N}^{\mathrm{d}} + b + \frac{(\mathcal{N}^{\mathrm{d}})^2}{6V}\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left[\left(\frac{1}{\mathcal{N}^{\mathrm{d}}} - \frac{(\mathcal{N}^{\mathrm{d}})^2}{\mathcal{N}_0^3}\right)\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left((\mathcal{N}^{\mathrm{d}})^2\frac{\mathrm{d}g_s}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\right)\right]$$
$$+\frac{1}{2V}\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left((\mathcal{N}^{\mathrm{d}})^2\frac{\mathrm{d}g_s}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\right) + \frac{a}{3V}\left(1-\frac{(\mathcal{N}^{\mathrm{d}})^3}{\mathcal{N}_0^3}\right)$$
$$= g_{s+1}(\mathcal{N}^{\mathrm{d}}) + \frac{(\mathcal{N}^{\mathrm{d}})^2}{6V}\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left[\left(\frac{1}{\mathcal{N}^{\mathrm{d}}} - \frac{(\mathcal{N}^{\mathrm{d}})^2}{\mathcal{N}_0^3}\right)\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}(g_{s+1}(\mathcal{N}^{\mathrm{d}}) - a\mathcal{N}^{\mathrm{d}} - b)\right]$$
$$+\frac{1}{2V}\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}(g_{s+1}(\mathcal{N}^{\mathrm{d}}) - a\mathcal{N}^{\mathrm{d}} - b) + \frac{a}{3V}\left(1-\frac{(\mathcal{N}^{\mathrm{d}})^3}{\mathcal{N}_0^3}\right)$$
$$= g_{s+1}(\mathcal{N}^{\mathrm{d}}) + \frac{1}{6V}\left(\frac{1}{\mathcal{N}^{\mathrm{d}}} - \frac{(\mathcal{N}^{\mathrm{d}})^2}{\mathcal{N}_0^3}\right)\frac{\mathrm{d}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\left((\mathcal{N}^{\mathrm{d}})^2\frac{\mathrm{d}g_{s+1}}{\mathrm{d}\mathcal{N}^{\mathrm{d}}}\right)$$

after a little algebra. Also result (A1.1) holds for $s=1$ since it is shown in Simons (1991) that

$$\langle \mathcal{N} \rangle = \mathcal{N}^{\mathrm{d}} + \frac{1}{3V}\left[1 - \left(\frac{\mathcal{N}^{\mathrm{d}}}{\mathcal{N}_0}\right)^3\right]$$

and hence result (A1.1) holds for any polynomial $g_k(\mathcal{N})$.

Appendix 2

We consider here the limiting form of (2) as $N_0 \to \infty$ with the initial particle volume $v_0 \to 0$ such that $N_0 v_0$ remains constant at a finite non-zero value. This value will be ϕ, the proportion of space occupied by particulate matter. Under these circumstances the volume of a single cluster is defined by a continuous variable v and the cluster size distribution is given by a function $n^{\mathrm{d}}(v)$ such that $n^{\mathrm{d}}(v)\,\mathrm{d}v$ is the number of clusters per unit volume of space whose volumes lie between v and $v+\mathrm{d}v$.

To obtain the required limiting form we begin by rewriting (2) as

$$\mathcal{N}_r^{\mathrm{d}}(\tau) = \frac{1}{\mathcal{N}_0 \tau^2 [1 + (1/\mathcal{N}_0 \tau)]^{r+1}}. \qquad \text{(A2.1)}$$

Now, $r = v/v_0 = v\mathcal{N}_0/\phi$ and hence in the interval $\mathrm{d}v$ there will be $\mathrm{d}r = (\mathcal{N}_0/\varphi)\,\mathrm{d}v$ possible cluster sizes. The number of clusters per unit volume of space whose volumes lie in the interval v to $v+\mathrm{d}v$ is thus

$$\mathcal{N}_r^{\mathrm{d}}(\tau)(\mathcal{N}_0/\varphi)\,\mathrm{d}v = \frac{\mathrm{d}v}{\varphi\tau^2[1+(1/\mathcal{N}_0\tau)]^{(v\mathcal{N}_0/\varphi+1)}}$$

from equation (A2.1), and on identifying this with $n^{\mathrm{d}}(v)\,\mathrm{d}v$ we obtain

$$n^{\mathrm{d}}(v) = \varphi^{-1}\tau^{-2}[1+(1/\mathcal{N}_0\tau)]^{-(v\mathcal{N}_0/\varphi)-1}.$$

On letting $N_0 \to \infty$, this finally gives

$$n^{\mathrm{d}}(v) = \frac{\exp(-v/\varphi\tau)}{\varphi\tau^2}.$$

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