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The statistical distribution of coagulating droplets

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Abstract. The statistical distribution of coagulating droplets is studied assuming that they form a Markovian system in continuous time. Only the total number density is studied, but the resulting probability balance equation can be solved exactly by means of generating function techniques. Thus for the first time we have available an exact solution showing how the probability evolves as time proceeds. We note that the variance changes from zero at the initial time through a maximum and back to zero as time tends to infinity: this is consistent with the deterministic initial and endpoint distribution functions. The accuracy of a closure scheme based upon quasi-normality is studied and shown to be acceptable for the initial stages of evolution when the values of the particle density are large.

1. Introduction

The statistical distribution of droplets in suspension is of interest in several important areas of engineering and physics. In particular, we note the need to understand droplet coalescence in warm clouds (Warshaw 1967) and aerosol coagulation in pollution studies (Hidy and Brock 1970). The fundamental problem is to calculate the conditional probability distribution of droplet volume; that is, to obtain $P_N(v_1, v_2, \dots, v_N; t)\, dv_1\, dv_2 \dots dv_N$, the probability that, given some initial droplet distribution at $t=0$, there will be N droplets at time t with volume in the ranges (v_1, v_1+dv_1), (v_2, v_2+dv_2), $\dots$, (v_N, v_N+dv_N). A number of approaches have been adopted to deal with this problem, but all suffer from the fundamental problem of closure, i.e. an inability to calculate the statistical averages of the distribution from a closed set of equations. To overcome this difficulty Warshaw assumed *a priori* a particular shape for the probability distribution with some adjustable parameters (in fact a binomial distribution). On the other hand, Scott (1967) used a closure approximation to obtain the mean value of the number of particles at time t and the corresponding variance. De Marcus (1965) has also made contributions to this subject via a probability balance equation for $P_N(\dots)$, but his equations are very complex and only in special cases can they be solved with any ease.

It is the purpose of the present paper to obtain an exact solution for a reduced probability distribution, namely $P(n, t)$, which is the total number of droplets at time t irrespective of their volume. Several assumptions are introduced to make the problem tractable. They are: (i) droplets are uniformly mixed in space; (ii) on collision, particles stick together; (iii) the collision cross section does not depend on the number of previous collisions (i.e. the effective size remains the same after each coalescence); and (iv) only binary collisions occur. These assumptions enable the problem to be regarded as a discrete Markov process in continuous time. The resulting probability distribution can be obtained exactly, and any number of statistical moments can thereby be generated. In view of the exact solutions, various closure schemes can be assessed for accuracy.

2. General theory

We shall follow the scheme suggested by Bartlett (1962) for constructing probability balance equations for Markov processes in continuous time. Thus let the population of individual droplets at time t be represented by the random variable $X(t)$. Let the increment in $X(t)$ during Δt be $\Delta X(t)$ such that $\Delta X(t) = X(t+\Delta t) - X(t)$ is either a positive or negative integer or zero. Then we assume that a finite number of transitions are possible in Δt such that

$$P(\Delta X(t) = j | X(t)) = f_j(X)\Delta t, \qquad j \neq 0,$$

where $f_j(X)$ are non-negative functions of X. Then it is shown that the probability generating function $F(x, t)$ for $P(n, t)$, i.e.

$$F(x, t) = \sum_{n=0}^{\infty} x^n P(n, t), \tag{1}$$

is given by the following differential equation (Bartlett 1962),

$$\frac{\partial F(x, t)}{\partial t} = \sum_{j \neq 0} (x^j - 1) f_j\left(x \frac{\partial}{\partial x}\right) F(x, t), \tag{2}$$

where j is a positive or negative integer corresponding to births or deaths.

In the case under consideration the only transitions which take place lead to deaths by coalescence. The associated transition probability is

$$f_{-1}(X) = \beta X(t)(X(t) - 1), \tag{3}$$

where β is the collision frequency. The reason for this form of quadratic product arises from the physical requirement that when $X = 1$ no further transitions can take place.

Inserting equation (3) into equation (2) and simplifying leads to the following differential equation for the generating function, with $\tau = \beta t$:

$$\partial F(x, \tau)/\partial \tau = (1 - x)x\, \partial^2 F(x, \tau)/\partial x^2. \tag{4}$$

The initial condition imposed on equation (4) arises from

$$P(n, 0) = \delta_{n,N}, \tag{5}$$

or from equation (1),

$$F(x, 0) = x^N. \tag{6}$$

Equation (4) may be solved easily by the method of separation of variables; thus, if we set

$$F(x, \tau) = T(\tau)G(x), \tag{7}$$

equation (4) can be rewritten as

$$T'(\tau)/T(\tau) = x(1 - x)G''(x)/G(x) = -\lambda, \tag{8}$$

where λ is a constant. Clearly

$$T(\tau)=\mathrm{e}^{-\lambda\tau} \tag{9}$$

and $G(x)$ satisfies

$$x(1-x)G''+\lambda G=0. \tag{10}$$

Now this equation is related to the hypergeometric equation. Thus taking into account the fact that $P(0,\tau)=0$ (cf equation (3)), we may write for the particular solution

$$G(x)=x\,{}_2F_1(\tfrac{1}{2}-\tfrac{1}{2}\sqrt{1+4\lambda},\tfrac{1}{2}+\tfrac{1}{2}\sqrt{1+4\lambda};2;x). \tag{11}$$

Let us now recall that the maximum number of droplets is N. Moreover, the coefficient of x^n in $F(x,t)$ gives the probability of there being just n droplets present at time t. Therefore we see that the hypergeometric function must be a polynomial in x of order not greater than $N-1$. For this to be so we must have

$$\tfrac{1}{2}-\tfrac{1}{2}\sqrt{1+4\lambda}=-k, \tag{12}$$

where k is an integer running from zero to $N-1$.

The general solution of equation (4) can now be written as

$$F(x,\tau)=x\sum_{k=0}^{N-1}d_k\,\mathrm{e}^{-k(k+1)\tau}\,{}_2F_1(-k,k+1;2;x), \tag{13}$$

where we have set $\lambda=k(k+1)$ from equation (12).

It is now necessary to calculate the expansion coefficients d_k. This may be done by means of the initial condition (6), i.e.

$$x^N=x\sum_{k=0}^{N-1}d_k\,{}_2F_1(-k,k+1;2;x). \tag{14}$$

To solve for the d_k it is convenient to write $x=(1-y)/2$ and to note that ${}_2F_1(\ldots)$ is related to the Jacobi polynomials $P_n^{(\alpha,\beta)}(y)$ as follows (Gradsteyn and Ryzhik 1965):

$$P_n^{(\alpha,\beta)}(y)=\binom{n+\alpha}{\alpha}{}_2F_1\left(-n,\alpha+\beta+n+1;\alpha+1;\frac{1-y}{2}\right). \tag{15}$$

Some simple orthogonality relations exist for the Jacobi polynomials. Use of these shows that for $k>0$

$$d_k=\frac{(-)^k(N-1)!N!(2k+1)}{(N-1-k)!(N+k)!}. \tag{16}$$

It may also be readily seen by examining $F(x,\infty)$ that $d_0=1$. Thus we may write the complete solution of equation (4) as

$$F(x,\tau)=x\sum_{k=0}^{N-1}\frac{(-)^k(N-1)!N!(2k+1)}{(N-1-k)!(N+k)!}\mathrm{e}^{-k(k+1)\tau}\,{}_2F_1(-k,k+1;2;x). \tag{17}$$

It is readily verified that $F(1,\tau)=1$ as we expect. The hypergeometric function is a polynomial in x which can be written concisely as

$${}_2F_1(-k,k+1;2;x)=1+\sum_{l=1}^{k}\frac{x^l}{l!(l+1)!}\prod_{m=1}^{l}(k+m)(m-1-k) \tag{18}$$

for $k>0$.

3. Probability distributions and averages

By definition the coefficient of x^l in equation (17) is $P(l, \tau)$, the probability that at time τ there are l droplets present. By reversing the order of summation we find that

$$P(1, \tau) = \sum_{k=0}^{N-1} \frac{(-)^k (N-1)! N! (2k+1)}{(N-1-k)!(N+k)!} e^{-k(k+1)\tau}, \tag{19}$$

and for $l > 0$

$$P(l+1, \tau) = \frac{1}{l!(l+1)!} \sum_{k=l}^{N-1} \frac{(-)^k (N-1)! N! (2k+1)}{(N-1-k)!(N+k)!} e^{-k(k+1)\tau} \prod_{m=1}^{l} (k+m)(m-1-k). \tag{20}$$

As an example we see that for $N = 3$

$$P(1, \tau) = 1 - \tfrac{3}{2} e^{-2\tau} + \tfrac{1}{2} e^{-6\tau}, \tag{21}$$

$$P(2, \tau) = \tfrac{3}{2} e^{-2\tau} - \tfrac{3}{2} e^{-6\tau}, \tag{22}$$

$$P(3, \tau) = e^{-6\tau}. \tag{23}$$

The statistical moments or averages of the distribution function are easily obtained by differentiating the generating function. Thus the mean value is

$$\bar{N}(\tau) = \frac{\partial}{\partial x} F(x, \tau) \bigg|_{x=1}, \tag{24a}$$

and the variance is

$$\overline{N^2(\tau)} - \bar{N}(\tau)^2 = \frac{\partial^2 F}{\partial x^2} + \frac{\partial F}{\partial x} - \left(\frac{\partial F}{\partial x}\right)^2 \bigg|_{x=1}. \tag{24b}$$

We see easily then that

$$\bar{N}(\tau) = 1 + \sum_{k=1}^{N-1} \frac{(-)^k (N-1)! N! (2k+1)}{(N-1-k)!(N+k)!} e^{-k(k+1)\tau} \times \left(1 + \sum_{l=1}^{k} \frac{1}{(l!)^2} \prod_{m=1}^{l} (m+k)(m-1-k)\right), \tag{25}$$

which for computational purposes is better written as

$$\bar{N}(\tau) = 1 + \sum_{k=1}^{N-1} (-)^k (2k+1) e^{-k(k+1)\tau} \prod_{l=1}^{k} \left(1 - \frac{k+1}{N+l}\right) \left[1 + \sum_{l=1}^{k} \prod_{m=1}^{l} \left(1 + \frac{k}{m}\right)\left(1 - \frac{1+k}{m}\right)\right].$$

Also we have

$$\overline{N^2(\tau)} - \bar{N}(\tau)^2 = \sum_{k=1}^{N-1} \frac{(-)^k (N-1)! N! (2k+1)}{(N-1-k)!(N+k)!} e^{-k(k+1)\tau} (xF)'', \tag{26}$$

where

$$(xF)'' = \sum_{l=1}^{k} \frac{1}{l!(l-1)!} \prod_{m=1}^{l} (k+m)(m-1-k). \tag{27}$$

As an example, for $N = 3$, we find

$$\bar{N}(\tau) = 1 + \tfrac{3}{2} e^{-2\tau} + \tfrac{1}{2} e^{-6\tau} \tag{28}$$

and

$$\overline{N^2(\tau)} - \bar{N}(\tau)^2 = \tfrac{3}{2}\,\mathrm{e}^{-2\tau} - \tfrac{9}{4}\,\mathrm{e}^{-4\tau} + \tfrac{5}{2}\,\mathrm{e}^{-6\tau} - \tfrac{3}{2}\,\mathrm{e}^{-8\tau} - \tfrac{1}{4}\,\mathrm{e}^{-12\tau}. \tag{29}$$

We note that for any N the variance tends to zero as $\tau \to \infty$, which is consistent with the number of droplets decreasing to the fixed value of unity as $\tau \to \infty$.

4. The closure problem

If only a few moments of the distribution are required, it is often convenient to bypass the complete solution and solve for the moments directly. Let us therefore consider equation (4) for the generating function and differentiate it with respect to x and set $x = 1$. We find the equation

$$\mathrm{d}\bar{N}(\tau)/\mathrm{d}\tau = -\overline{N^2(\tau)} + \bar{N}(\tau) \tag{30}$$

subject to $\bar{N}(0) = N$.

It is unfortunate that equation (30) contains two unknown quantities $\overline{N^2}$ and $\bar{N}$. We therefore differentiate equation (4) again to get

$$\mathrm{d}\overline{N^2(\tau)}/\mathrm{d}\tau = -2\overline{N^3(\tau)} + 3\overline{N^2(\tau)} - \bar{N}(\tau). \tag{31}$$

But again we note the existence of an additional unknown $\overline{N^3}$. This process continues and constitutes the well known problem of closure. In practice, when it is not possible to solve for the probability distribution directly, various closure schemes are adopted which attempt to relate higher moments to lower ones. In view of the fact that we have an exact solution, we are in a position to assess the accuracy of some of those schemes.

A frequently used method of closure consists of neglecting a certain-order cumulant. Thus if we define the cumulant generating function $K(\theta, \tau)$ by

$$K(\theta, \tau) = \ln F(\mathrm{e}^{\theta}, \tau) = \sum_{r=1}^{\infty} K_r(\tau)\frac{\theta^r}{r!}, \tag{32}$$

we see that equation (4) leads to the following equations for K_1 and K_2:

$$dK_1/\mathrm{d}\tau = -K_1{}^2 + K_1 - K_2 \tag{33}$$

and

$$\mathrm{d}K_2/\mathrm{d}\tau = K_1^2 - K_1 + 3K_2 - 4K_1K_2 - 2K_3. \tag{34}$$

In these equations we have by definition that $\bar{N} = K_1$ and $\overline{N^2} - \bar{N}^2 = K_2$. Now the simplest closure scheme for K_1 is to set $K_2 = 0$ in equation (33); then we have an equation which can be solved exactly, namely,

$$K_1(\tau) = N/[N - (N-1)\,\mathrm{e}^{-\tau}]. \tag{35}$$

On the other hand, if we assume that the probability law is close to Poisson, it would be better to set the variance K_2 equal to the mean K_1. In that case the solution of equation (33) becomes

$$K_1(\tau) = N/(1 + N\tau). \tag{36}$$

Although equation (35) satisfies the asymptotic condition $K_1(\infty) = 1$, equation (36) is closer to the accepted and experimentally measured time dependence of the mean. Numerical calculations of the exact result given by equation (25) indicate a behaviour which is intermediate between that of equations (35) and (36).

An improved solution can be obtained for K_1 and an initial estimate of K_2 obtained by using equation (34) and setting $K_3 = 0$. Then we have a pair of coupled nonlinear equations for K_1 and K_2 with initial conditions $K_1(0) = N$ and $K_2(0) = 0$. Further improvements can be made in an obvious manner.

Some illustrative numerical results are given in figure 1, which shows the relative variance K_2/K_1 as a function of particle number K_1. This is done for the approximate model of equations (33) and (34) with $K_3 = 0$ and for the exact solution. A general feature of the exact result is that the variance is zero at $\tau = 0$ ($K_1 = N$); increases due to the statistical variation of coagulating events; and tends to zero again as $\tau \to \infty$ ($K_1 \to 1$).

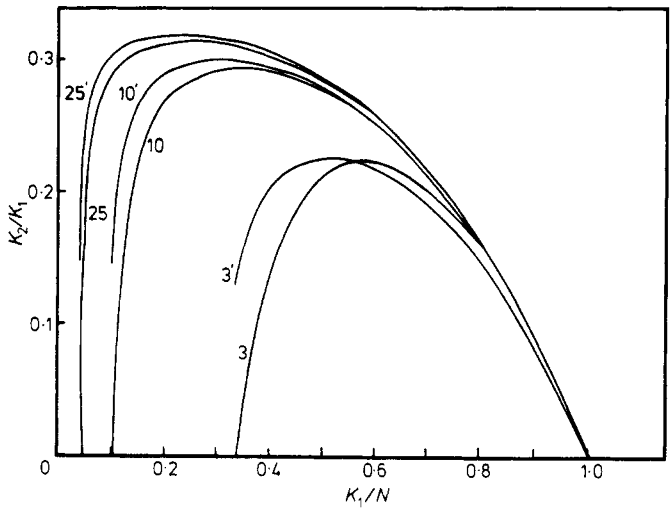

Figure 1. The normalised variance K_2/K_1 against the normalised number density K_1/N for various values of N. The values of N are marked on the curve. N denotes the exact curve and N' the approximate one. Note that time runs from right to left.

This corresponds to the deterministic starting and finishing points of the process. The approximation is seen to improve markedly as the initial concentration increases, particularly at early times. However, for long times, when the particle number is low, the quasi-normality approximation fails and large deviations are noted for small K_1/N. It does not seem possible to obtain any simple expressions for K_2 and K_1 or indeed the probability distribution $P(n, \tau)$. In practical situations N is likely to be very large, and hence a normal distribution for $P(n, \tau)$ seems a reasonable first approximation; however, we have not investigated the behaviour of higher moments K_n which may be markedly non-normal.

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