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LETTER TO THE EDITOR

The effect of coagulation on the diffusive spread of aerosol particles with a fractal structure

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Abstract. The treatment of Simons concerning the effect of Brownian coagulation on particle diffusive spread is extended to cover the case of particles with a fractal structure. A novel result is that in the regime $Kn \gg 1$, the particulate matter in most cases cannot diffuse outside a certain finite region. For $1-D$ diffusion when $Kn \ll 1$, it is shown that after sufficiently long times the root mean square particle displacement is proportional to t^n with $n \approx 0.3$, to be contrasted with the cases of coagulating compact particles and non-coagulating particles where $n = 0.4$ and 0.5, respectively. In a typical situation the diffusion time for fractal particles is predicted to be greater than that for compact particles by a factor of about five, and this suggests that experimental measurements on diffusive spread could provide useful evidence about the fractal structure of particles.

Recent work by Simons (1986, hereafter referred to as S) was concerned with modifications to the Brownian diffusive spread of a localised aerosol arising from the mutual coagulation of the solid aerosol particles. It was shown there that the effect of coagulation was to yield a modified mean square particle displacement $\overline{r^2}$ which in general increases less rapidly with time than the linear variation characteristic of non-interacting particles, and that the change from linearity increased as the number of dimensions in which the diffusion was occurring decreased from three to one. Analytic results were obtained for $\overline{r^2}(t)$ for one, two and three dimensions in the regimes $Kn \ll 1$ and $Kn \gg 1$ where Kn is the Knudsen number l/R (l being the gas molecular mean free path and R the particle radius). However, it was assumed in this work that throughout the coagulational growth of the particles the particle density remained constant, and that the effect of coagulation of particles with radii R_1 and R_2 was to produce a compound particle of radius $(R_1^3+R_2^3)^{1/3}$. Now, recent work has shown that this assumption is incorrect and that aerosol particles produced by Brownian coagulation exhibit a fractal structure rather than the compact structure previously assumed (see, for example, papers in Family and Landau (1984) and Stanley and Ostrowsky (1986)). The effect of this is that while the general approach used in S remains valid, the input into the calculation of specific formulae for the particle diffusion coefficient and coagulation kernel as functions of particle volume requires modification, and as we shall see this can lead to a considerable change in the final forms for $\overline{r^2}$ as a function of t.

The general form we shall take for the fractal particle structure is that given by the simulation work of Mountain and Mulholland (1984) and Mountain *et al* (1986). They found that, starting with initially identical spherules, the effect of coagulating k spherules was to yield a structure whose radius of gyration R_g was proportional to k^δ

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where δ (the reciprocal of the fractal dimensionality d) was found by their simulation technique to always lie in the interval 0.53–0.59 (corresponding to d in the interval 1.7–1.9). In order to progress with our calculation we shall model the fractal structures by spheres of effective radius R. If R_0 and v_0 are the radius and volume of a single spherule respectively, then the above relation between R_g and k shows that, if a compound particle contains a total volume v of spherule material, then

$$R = R_0(v/v_0)^{\delta}. \tag{1}$$

In order to implement the approach of S for fractal particles, we now need to obtain expressions for the diffusion coefficient $D(v)$ and coagulation kernel $P(u, v)$ for the cases of $Kn \ll 1$ ('large' particles) and $Kn \gg 1$ ('small' particles). In general $D = kT/f$ where fw is the frictional resistance to particle motion when moving through the gas with speed w. For a solid spherical 'large' particle of radius R the gas behaves as a continuum, leading to $f = 6\pi\eta R$ where η is the gas viscosity. This, with R given by equation (1), will therefore be the appropriate formula for our fractal model if it is assumed that the fluid in the interstices of the fractal structure is effectively trapped and moves with the particle rather than modifying the resistance to motion by moving relative to the particle. The conclusion of Mountain *et al* (1986) is that this assumption is probably justified, and we therefore take for

$$Kn \ll 1 \qquad D(v) = \frac{kT}{6\pi\eta R_0}\left(\frac{v_0}{v}\right)^{\delta}. \tag{2}$$

At the other extreme, when $Kn \gg 1$, the resistance to motion for a single particle is obtained by summing the impacts on it of individual gas molecules. Following Epstein (1924) this gives for a single spherule of radius R_0, $f = \frac{8}{3}R_0^2\rho'(2\pi kT/m)^{1/2}(1+\frac{1}{8}\pi\alpha)$ where ρ' and m are the gas density and molecular mass respectively and α is the accommodation coefficient. Now in our model, since the fractal dimensionality d is less than 2 there will be very little effective shielding against molecular impact of one spherule by another, and thus the value of f we require is simply the above value times the number of spherules in a single particle. This gives for

$$Kn \gg 1 \qquad D(v) = \frac{3}{8}\left(\frac{mkT}{2\pi}\right)^{1/2}\frac{1}{\rho'(1+\frac{1}{8}\pi\alpha)R_0^2}\left(\frac{v_0}{v}\right). \tag{3}$$

We now consider appropriate expressions to use for the coagulation kernel $P(u, v)$. In the limit of $Kn \ll 1$, the form for solid spherical particles is $P(u, v) = 4\pi[D(u)+D(v)][R(u)+R(v)]$, obtained by considering the mutual diffusion of particles with radii $R(u)$ and $R(v)$. We apply this result to our fractal particles, using equations (1) and (2) for R and D. This gives for

$$Kn \ll 1 \qquad P(u, v) = (2kT/3\eta)(u^{\delta}+v^{\delta})(u^{-\delta}+v^{-\delta}). \tag{4}$$

At the other extreme of $Kn \gg 1$, P is obtained by considering the number of collisions between the particles, each being considered as a free particle in thermal equilibrium. For solid particles of radius R we have $P(u, v) = [8\pi kT\rho^{-1}(u^{-1}+v^{-1})]^{1/2}[R(u)+R(v)]^2$ where ρ is the density of particulate matter. The first term in this product corresponds to a thermal velocity and will be unchanged when we consider a fractal structure. The second term derives from a cross-sectional area, and the R–v relationship will therefore be given by equation (1) for a fractal particle. This gives for

$$Kn \gg 1 \qquad P(u, v) = \left(\frac{8\pi kT}{\rho}\right)^{1/2}\frac{R_0^2}{v_o^{2\delta}}\left(\frac{1}{u}+\frac{1}{v}\right)^{1/2}(u^{\delta}+v^{\delta})^2. \tag{5}$$

On the basis of equations (2)-(5) we can now proceed to consider $\overline{r^2}$ as a function of t. In view of the assumptions made in deriving these equations we may reasonably expect the functional form of $r^2(t)$ that we shall obtain to be substantially correct, although the accuracy of the coefficients appearing in it is less certain. In support of this claim we may quote the results of Mountain *et al* (1986) who, having obtained the u and v dependence of equations (2), (4) and (5), derived from these for the case of spatially homogeneous coagulation the asymptotic value of p as $t \to \infty$ in the relation $v(t) \sim t^p$. Their results agreed well with those given by detailed simulation techniques.

We begin by noting that equations (2) and (3) can both be expressed in the form

$$D(v) = \mu v^{-s} \tag{6}$$

where $s = \delta$ and 1 for 'large' and 'small' particles respectively. Further, the forms (4) and (5) both satisfy

$$P(\lambda u, \lambda v) = \lambda^{\alpha} P(u, v) \tag{7}$$

where $\alpha = 0$ and $2\delta - \frac{1}{2}$ for 'large' and 'small' particles respectively. The general formulation and treatment of the problem then follows exactly the approach developed in S and yields equations for $X(t)$ and $V(t)$, where $X^2 = \overline{r^2}$ and $V(t)$ is the mean value of v taken over all particles at time t. If $\beta (= 1, 2 \text{ or } 3)$ is the number of dimensions in which the diffusion takes place and quantities depending on the number of dimensions have this number specified by the subscript β, then these equations take the form

$$\mathrm{d}X/\mathrm{d}t = \beta \mu V^{-s} X^{-1} \tag{8}$$

$$\mathrm{d}V/\mathrm{d}t = \tfrac{1}{2} C_\beta \phi_\beta \bar{P} V^{\alpha} X^{-\beta}. \tag{9}$$

Here $C_1 \approx 0{\cdot}28$, $C_2 \approx 1{\cdot}0$, $C_3 \approx 1{\cdot}4$, ϕ_1 is the total volume of spherule material in a column of unit cross section oriented in the direction along which diffusion occurs, ϕ_2 is the total volume of spherule material in a slab of thickness $1/2\pi$ with faces parallel to the plane in which diffusion occurs and ϕ_3 is $1/4\pi$ times the total volume of spherule material. $\bar{P}$ is a certain weighted mean over u and v of $P(u, v)$, given by

$$\bar{P} \approx 2{\cdot}7\, kT/\eta \qquad (Kn \ll 1) \tag{10a}$$

$$\bar{P} = 11 \left(\frac{kT}{\rho}\right)^{1/2} \frac{1}{v_0^{(2\delta - 2/3)}} \qquad (Kn \gg 1). \tag{10b}$$

From equations (8) and (9) we obtain

$$\mathrm{d}V/\mathrm{d}X = \kappa V^{1-n} X^{1-\beta} \tag{11}$$

where $\kappa = C_\beta \phi_\beta \bar{P}/2\beta\mu$ and $n = 1 - \alpha - s$. Equation (11) may be readily integrated to give V in terms of X, making use of the boundary condition that at $t = 0$, $V = V_0$ and $X = X_0$. Substituting this into equation (8), followed by a further integration, then yields t as a function of X. For arbitrary values of n this procedure can be implemented to give t explicitly in terms of X only for diffusion in one dimension. For that case we let

$$X^* = \frac{X}{X_0} \qquad t^* = \frac{\mu t}{\kappa^{(s/n)} X_0^{2+(s/n)}} \tag{12}$$

and obtain

$$t^* = \{[A + n(X^* - 1)]^{1+(s/n)}[(s+n)X^* + n - A] - A^{1+(s/n)}(s + 2n - A)\}/(s+n)(s+2n) \tag{13}$$

where $A = V_0^n/\kappa X_0$. Now, the behaviour of t^* as X^* increases depends on whether $n > 0$ or $n < 0$. For $n > 0$ (and bearing in mind that $s > 0$), it is clear that t^* increases monotonically as X^* increases beyond 1, tending to infinity as $X^* \to \infty$. Further, for $X^* \gg 1$ and A we have

$$X^*(t^*) \approx \frac{(s+2n)^{(n/2n+s)}}{n^{(n+s/2n+s)}} t^{*(n/2n+s)} \tag{14}$$

which corresponds to $X(t) \propto t^p$ where $p = 0{\cdot}29$–$0{\cdot}32$ for 'large' particles. This should be compared with the values for p of 0·50 for non-interacting particles and 0·40 obtained in S for coagulating compact spherical particles. On the other hand, if we consider the case of 'small' particles where $n < 0$ and $n + s > 0$ the behaviour of $t^*(X^*)$ is very different. As X^* increases, t^* increases but tends to infinity as $X^* \to X_\infty^*$ where $X_\infty^* = (A/|n|) + 1$. This behaviour, whereby the particles take an infinite time to reach $X^* = X_\infty^*$ and cannot diffuse beyond this, did not occur in S since there n was always positive. In order to understand the reason for this new type of behaviour we consider again the integration of equation (11). It is readily shown that this gives rise to a form for $V(X)$ such that $V \to \infty$ as $X \to X_\infty^*$ if $n < 0$. Once V has become infinite, the diffusion coefficient D (equation (6)) drops to zero and thus the particles cannot get beyond X_∞. The physical reason for this new behaviour is that, compared with 'large' particles, 'small' particles undergo a greater increase in coagulation during their growth ($\alpha \sim 0{\cdot}6$ compared with $\alpha = 0$) and a greater decrease in diffusion coefficient ($s = 1$ compared with $s \sim 0{\cdot}55$). The combined effect of $\alpha + s$ exceeding unity is to cause V to become infinite at a finite value of X. Of course, in practice this behaviour will not occur since, once V has increased sufficiently, the particles will have become 'large' ones for which X can increase without limit. However, it is clear that as long as the particles remain 'small' X must be less than X_∞.

Although for the case of two dimensions one cannot obtain an explicit form for $X(t)$, it can be shown that the qualitative behaviour is the same as in one dimension. Thus for 'large' particles with $n > 0$, it transpires that after sufficiently long times

$$X(t) \propto t^{1/2}[\ln(Bt)]^{-q} \tag{15}$$

where $q \sim 0{\cdot}6$ and this can be compared with the result of S for compact particles which took the form (15) with $q = 0{\cdot}25$. On the other hand, for 'small' particles with $n < 0$, X can only increase up to a finite value X_∞, which is readily shown to be given by $X_\infty = X_0 \exp(V_0^n/|n|\kappa)$.

For diffusion in three dimensions the general behaviour is somewhat different from that in one and two dimensions. In the latter cases for 'large' particles with $n > 0$, $V(X)$ increased monotonically with X and tended to infinity as $X \to \infty$. However, for the three-dimensional situation $V(X)$, while increasing with X, tends to a finite value V_∞, given by $V_\infty^n = V_0^n + (n\kappa/X_0)$, as $X \to \infty$. This means that, for sufficiently large t, $X(t) \propto t^{1/2}$ with a constant of proportionality corresponding to the diffusion of particles with constant volume V_∞. This behaviour is qualitatively similar to that obtained in S, albeit with a different value for V_∞. For $n < 0$, however, the situation becomes slightly more complicated. Integration of equation (11) gives

$$V_0^n - V^n = |n|\kappa(X_0^{-1} - X^{-1}) \tag{16}$$

and thus V increases with X. If $(|n|\kappa/X_0) > V_0^n$, V becomes infinite at $X_\infty = [X_0^{-1} - (V_0^n/|n|\kappa)]^{-1}$ and so no diffusion can occur beyond this point. On the other hand, if $|n|\kappa/X_0 < V_0^n$ then X can increase without limit, with V remaining finite

throughout and tending to the value $V_\infty = [V_0^n - (|n|\kappa/X_0)]^{1/n}$ as $X \to \infty$. This corresponds to a situation similar to that for $n > 0$, with $X(t) \propto t^{1/2}$ for sufficiently large t.

Apart from our conclusion that for $Kn \gg 1$ particulate matter in most cases cannot diffuse outside a certain region, the main result of this letter concerns diffusion in one dimension for $Kn \ll 1$. Here we showed that, for sufficiently long times, $X \propto t^p$ with $p = 0{\cdot}30 \pm 0{\cdot}02$, in contrast with $p = 0{\cdot}40$ for coagulating compact particles. This suggests that experimental results on diffusive spread could provide useful evidence about the fractal nature of coagulating particles. This suggestion is borne out by the following illustrative example which shows that quite large differences can exist between the diffusion times for fractal and compact particles even before the limiting form $X \propto t^p$ is reached. Following S we calculate the time for the value of X for particles with initial radius 2×10^{-5} cm to increase from 1 to 2 mm. We consider both fractal particles built up from spherules with $R_0 = 10^{-6}$ cm and also compact particles and take $\phi_1 = 7 \times 10^{-10}$ in both cases. The above equations then predict that for the compact particles the mean radius only increases by about 10% during the diffusion process, the time for which is only a few per cent greater than that for non-coagulating particles. On the other hand, for the fractal particles the mean radius increases by a factor of ten and the diffusion time is about six times larger than that for the compact particles.

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