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# The effect of coagulation on the diffusive spread of aerosol particles

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**Abstract.** It is pointed out that the Brownian diffusive spread of a gaseous suspension of particles ('aerosol') will be decreased due to the mutual coagulation of the particles, which gives rise to a continually decreasing effective particle diffusion coefficient. This leads to a modified mean-square particle displacement which in general increases less rapidly with time than the linear variation characteristic of non-interacting particles, and analytic results are obtained for this displacement in the regimes  $Kn \ll 1$  and  $Kn \gg 1$  for diffusion in one, two and three dimensions. The effects of coagulation, both on particle displacement and particle growth, become less important as the number of dimensions increases, and in the 3D case it is shown that despite coagulation growth, particle sizes cannot exceed a certain maximum. Calculation of numerical values suggests that measurements of the modified spread could provide useful experimental data on coagulation effects.

## 1. Introduction

It is well known that the distribution of particulate matter suspended in a stationary gas and undergoing Brownian motion is described by the standard diffusion equation. The solution of this equation then gives rise to an expression for the mean-square particle displacement  $\overline{r^2}$  after time  $t$ , and in one dimension this takes the form

$$\overline{r^2} = \overline{r_0^2} + 2Dt \quad (1)$$

where  $D$  is the particle diffusion coefficient and  $\overline{r_0^2}$  is the value of  $\overline{r^2}$  at  $t = 0$  (Friedlander 1977, hereafter referred to as F). Thus for large values of  $t$ ,

$$(\overline{r^2})^{1/2} \propto t^{1/2}. \quad (2)$$

The above results assume that the particles retain their individual identity throughout the diffusive process, but in practice the random Brownian motion which gives rise to diffusion will also lead to collision and coagulation of the particles (Smoluchowski 1917). The resulting increase in particle size will modify the effects of diffusion since  $D$  is a function of the particle volume, and it is this modification which we are currently concerned with investigating. The problem is somewhat complicated as it involves both particle coagulation and diffusive flow, and while considerable work has been done on these aspects separately, very little has been done on any real physical problem involving coagulation together with a spatial variation. The reason is simply that the equation for the complete particle distribution ((7) and (8) below) is very difficult to tackle directly owing to its complicated mathematical structure. In view of this we shall confine our attention to the way in which equations (1) and (2) become modified

by the existence of coagulation, and in particular, we shall show that by making certain plausible assumptions, relatively simple analytic results may be obtained.

We note at this stage that the problem may be tackled in one, two or three dimensions. In one dimension we consider a particle distribution which spatially varies with  $x$  but which is independent of  $y$  and  $z$  ( $-\infty \leq y, z \leq +\infty$ ). In two dimensions we suppose the distribution to exhibit cylindrical symmetry, varying only with  $\rho = (x^2 + y^2)^{1/2}$  and being independent of  $z$  ( $-\infty \leq z \leq +\infty$ ), while in three dimensions the spatial distribution is taken to exhibit spherical symmetry, depending only on  $r = (x^2 + y^2 + z^2)^{1/2}$ .

Now, in general the effect of coagulation will be to decrease the diffusive spread since  $D$  decreases with increasing particle volume (see equations (12) below), and hence decreases with increasing time. This decrease in diffusive spread will be coupled to the particle growth through a sort of feedback mechanism. Thus, consider a second situation in which an identical aerosol is suspended in a different gas whose particle diffusion coefficient is less than that of the first gas. This smaller diffusion coefficient will result at any later time in a smaller spatial spread for the second aerosol, and this will give rise to greater growth for particles of the second aerosol, since the coagulation growth rate varies quadratically with the particle concentration. The greater size of the particles in the second aerosol will further limit their spatial spread compared with the first aerosol, and this in turn will further increase their relative growth and decrease their relative mobility. The net effect of coagulation therefore is that with the passage of time it tends to enhance the localising effect of an initially smaller diffusion coefficient. Further, since the particle coagulation growth rate increases with the particle concentration it is to be expected that the above effects will be more pronounced for diffusion in one dimension, where the concentration varies with time as  $(r^2)^{-1/2}$ , than in two and three dimensions where it varies respectively as  $(r^2)^{-1}$  and  $(r^2)^{-3/2}$ . In accordance with this, we shall see later that even in the presence of coagulation the relation (2) still applies in three dimensions after a sufficiently long time, though with a modified constant of proportionality, while in two dimensions, and even more in one dimension, the functional form of  $r^2(t)$  corresponds to a slower than linear increase in  $t$ .

It is clear from the above discussion that for sufficiently short times and low particle concentrations the effects of coagulation are negligible and the usual results of diffusion theory apply. A conservative estimate of the maximum time for this to be so is readily obtained by considering coagulation particle growth, assuming no diffusive spread. For the situation where the particle size is greater than the gas molecular mean free path  $l$ , the standard theory of Brownian coagulation gives (Twomey 1977)

$$\partial N / \partial t = -(4kT/3\eta)N^2 \quad (3)$$

where  $N$  is the total particle number density and  $\eta$  is the coefficient of gas viscosity. If  $\Phi$  is the proportion of space occupied by particulate matter of mean particle volume  $V$ ,  $N = \Phi/V$  and equation (3) yields

$$dV/dt = 4kT\Phi/3\eta. \quad (4)$$

If the particle volume increases from  $V$  to  $V + \Delta V$  in time  $t$ , then coagulation can be neglected if  $\Delta V/V \ll 1$ , and hence from equation (4) we find that coagulation can be neglected if

$$t \ll \pi\eta R^3/kT\Phi \quad (5)$$

where  $R$  is the mean particle radius. Applying this to air at  $T = 300$  K then gives

$$t \ll 10^{10} R^3/\Phi. \quad (6)$$

For typical aerosols  $R$  lies in the interval  $10^{-6}$ - $10^{-3}$  cm† and  $\Phi$  in the interval  $10^{-11}$ - $10^{-5}$ . The right-hand side of equation (6) can thus lie in the interval  $10^{-3}$ - $10^{12}$  s. Although at the upper end of this range inequality (6) will obviously be satisfied for all times of interest, at the lower end this will certainly not be so. This gives a clear motivation for the approach we develop in this paper.

In order to carry through our programme it is necessary to have simple analytic expressions for the particle diffusion coefficient and coagulation kernel. Such expressions only exist in the limits of  $Kn \ll 1$  and  $Kn \gg 1$  (where  $Kn = l/R$ ), and our work will therefore be confined to these two limiting situations. For convenience we shall refer to particles lying in these two size regimes as ‘large’ and ‘small’ respectively, and the basic equations we shall derive ((13) and (26)) will only be valid for these size limits.

In §§ 2 and 3 we obtain respectively equations for  $d\bar{r}^2/dt$  and  $dV/dt$  in terms of  $\bar{r}^2$  and  $V$ , where  $V$  is the mean particle volume. The solution of this pair of coupled equations is dealt with in § 4, leading to expressions for  $\bar{r}^2$  as a function of  $t$  for various cases of interest. It will be seen that these expressions are in agreement with the results of the physical discussion given above.

## 2. Calculation of $d\bar{r}^2/dt$

For the sake of clarity of exposition we shall develop the detailed argument for the one-dimensional problem, noting as we proceed how the results are modified for the cases of two and three dimensions.

Let  $n(v, x, t) dv$  be the number of particles with volumes lying between  $v$  and  $v + dv$  per unit volume of gas at position  $x$  and time  $t$ . Then the general equation governing  $n$  takes the form (F)

$$\frac{\partial n}{\partial t} = D(v) \frac{\partial^2 n}{\partial x^2} + \left( \frac{\partial n}{\partial t} \right)_{\text{coag}} \tag{7}$$

where  $D(v)$  is the volume dependent particle diffusion coefficient. Here  $(\partial n/\partial t)_{\text{coag}}$  represents the rate of change of  $n$  due to Brownian coagulation, being given by

$$\left( \frac{\partial n}{\partial t} \right)_{\text{coag}} = \frac{1}{2} \int_0^v P(u, v-u) n(u) n(v-u) du - n(v) \int_0^\infty P(u, v) n(u) du \tag{8}$$

where  $P(u, v)$  is the kernel describing the coagulation. The form taken by  $P(u, v)$  depends on the size of the particles. For ‘large’ particles, we have (F)

$$P(u, v) = (2kT/3\eta)(u^{1/3} + v^{1/3})(u^{-1/3} + v^{-1/3}) \tag{9a}$$

while for ‘small’ particles

$$P(u, v) = (3/4\pi)^{1/6} (6kT/\rho)^{1/2} (u+v)^{1/2} (u^{1/3} + v^{1/3})^2 (uv)^{-1/2} \tag{9b}$$

where  $\rho$  is the particle density.

Now, the mean-square displacement of the particulate matter in the  $x$  direction is given by

$$\bar{r}^2(t) = \phi_1^{-1} \int_{-\infty}^\infty \int_0^\infty vn(v, x, t) x^2 dv dx \tag{10a}$$

† Although at the lowest end of this interval  $R < l$ , it may be shown from the relevant formulae for this latter regime that the greatest change to the right-hand side of equation (5) is to decrease it by a factor  $\sim 3$ .

where

$$\phi_1 = \int_{-\infty}^{\infty} \int_0^{\infty} vn(v, x, t) dv dx. \quad (10b)$$

$\phi_1$  is clearly independent of  $t$  as it represents the total volume of particulate matter contained in a column of unit cross sectional area extending from  $x = -\infty$  to  $+\infty$ , and this is unaffected by both diffusion and coagulation. Thus

$$\frac{d\bar{r}^2(t)}{dt} = \phi_1^{-1} \int_{-\infty}^{\infty} \int_0^{\infty} vx^2 \frac{\partial n}{\partial t} dv dx.$$

We substitute for  $\partial n/\partial t$  from equation (7), when the contribution arising from  $(\partial n/\partial t)_{\text{coag}}$  is zero corresponding to the conservation of particle volume during coagulation. In the contribution arising from the diffusion term of equation (7) we integrate twice 'by parts' with respect to  $x$ , when the boundary terms vanish and we finally obtain

$$\frac{d\bar{r}^2(t)}{dt} = \frac{2}{\phi_1} \int_{-\infty}^{\infty} \int_0^{\infty} vD(v)n(v, x, t) dv dx. \quad (11)$$

Now, the form for  $D(v)$  depends on whether the particles are 'large' or 'small'. In the former case

$$D(v) = (2/3^{1/2}\pi)^{2/3}(kT/6\eta)v^{-1/3} \quad (12a)$$

while in the latter,

$$D(v) = \left( \frac{2^{5/6}3^{1/3}\pi^{1/6}}{8} \right) \frac{(mkT)^{1/2}}{\rho'[1+(\pi\alpha/8)]} v^{-2/3} \quad (12b)$$

where  $\rho'$  is the gas density,  $m$  is the mass of a gas molecule and  $\alpha$  is the accommodation coefficient (F). Thus  $D(v) \propto v^{-s}$  with  $s = \frac{1}{3}$  or  $\frac{2}{3}$ , and hence we obtain from equation (11)

$$d\bar{r}^2(t)/dt = 2D(W) \quad (13)$$

where

$$W^{-s} = \bar{v}^{1-s}/\bar{v} \quad (14)$$

with  $\bar{v}^n$  being the mean value of  $v^n$  taken over all the particles. We note that in the absence of coagulation equation (13) implies equation (1) with  $D$  evaluated for the volume  $W$  given above.

For the two- and three-dimensional problems described in the introduction  $r$  refers respectively to the particle displacements from the  $z$  axis and the origin. By following through the analogues of the above arguments for these two cases it is readily shown that  $d\bar{r}^2(t)/dt = 2\beta D(W)$  where  $\beta = 2$  and  $3$  respectively for two and three dimensions.

### 3. Calculation of $dV/dt$

The differential equation (13) for  $\bar{r}^2(t)$  involves the weighted mean particle volume  $W$  which is an as yet unknown function of  $t$ . In order therefore to obtain  $\bar{r}^2(t)$  it is necessary to supplement equation (13) with an equation which effectively determines  $W(t)$ . To do this we begin by considering the mean particle size  $V$ , given by

$$V = \phi_1/N(t) \quad (15)$$

where

$$N = \int_{-\infty}^{\infty} \int_0^{\infty} n(v, x, t) dv dx. \tag{16}$$

As pointed out in § 2,  $\phi_1$  is independent of  $t$ , and so

$$\frac{dV}{dt} = -\frac{\phi_1}{N^2} \frac{dN}{dt}. \tag{17}$$

We substitute for  $(\partial n/\partial t)$  from equation (7) in the expression for  $dN/dt$ , when the contribution from the diffusive term vanishes as  $\partial n/\partial x \rightarrow 0$  as  $x \rightarrow \pm\infty$ . Thus we obtain (Twomey 1977)

$$\frac{dV}{dt} = \frac{\phi_1}{2N^2} \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} P(u, v)n(u, x, t)n(v, x, t) du dv dx. \tag{18}$$

To progress further we now define the total number of particles  $m$  and mean particle volume  $\bar{v}$  at  $(x, t)$  by

$$m(x, t) = \int_0^{\infty} n(v, x, t) dv \tag{19a}$$

$$\bar{v}(x, t) = \int_0^{\infty} vn(v, x, t) dv/m(x, t) \tag{19b}$$

and express  $n(v, x, t)$  in the form

$$n(v, x, t) = \frac{m(x, t)}{\bar{v}(x, t)} g\left(\frac{v}{\bar{v}(x, t)}, x, t\right). \tag{20}$$

In the case of spatially independent coagulation, it is known that if the transformation (20) is used (with  $x$  suppressed throughout), then the variation in  $n$  with increase in  $t$  is mainly described by a decrease in  $m(t)$  and an increase in  $\bar{v}(t)$ . The change in the function  $g(w, t)$  is relatively small, where  $w = (v/\bar{v})$ , and indeed as  $t \rightarrow \infty$ ,  $g$  tends to a limiting form, the so-called ‘self-preserving distribution’ (Friedlander and Wang 1966). In accordance with this picture, we shall now assume in our spatially dependent problem that in equation (20),  $g$  depends on  $x$  only through  $[v/\bar{v}(x, t)]$ , and does not exhibit any explicit  $x$  dependence. This is, of course, equivalent to assuming that the *shape* of  $n(v, x, t)$  is independent of  $x$ , and while this will not hold exactly, it would appear to be a reasonable assumption in our work, where we are only concerned with calculating a particular average over the distribution  $\bar{r}^2(t)$ , rather than the detailed form of  $n(v, x, t)$ .  $m(x, t)$ , on the other hand, will vary with  $x$ , corresponding to the spatial variation in the aerosol distribution, while  $\bar{v}(x, t)$  will also exhibit a potentially significant  $x$  dependence, since smaller particles will have diffused further from the original region in which the aerosol was localised and therefore  $\bar{v}$  may be expected to decrease as we move away from this region.

We now substitute the form (20) for  $n(v, x, t)$  into equation (18), noting that the expressions for  $P(u, v)$  given in equations (9) both satisfy  $P(\lambda u, \lambda v) = \lambda^\alpha P(u, v)$ , where  $\alpha = 0$  and  $\frac{1}{6}$  respectively for (9a) and (9b). On introducing

$$f(x, t) = m(x, t)/N \tag{21}$$

we then obtain

$$dV/dt = \frac{1}{2}\phi_1 BE \tag{22}$$

where

$$B = \int_0^\infty \int_0^\infty P(w, w')g(w, t)g(w', t) dw dw' \tag{23}$$

$$E = \int_{-\infty}^\infty [\bar{v}(x, t)]^\alpha [f(x, t)]^2 dx. \tag{24}$$

We note that it readily follows from equations (20) and (21) that

$$\int_0^\infty g(w, t) dw = \int_0^\infty wg(w, t) dw = 1 \tag{25a}$$

$$\int_{-\infty}^\infty f(x, t) dx = 1. \tag{25b}$$

To simplify the above expression for  $E$ , we first remark that the power of  $\bar{v}$  (0 or  $\frac{1}{6}$ ) in the integral is much less than the power of  $f$  (2). This suggests that even if the  $x$  variation of  $\bar{v}$  and  $f$  are of the same order, a satisfactory approximation would be to replace  $[\bar{v}(x, t)]^\alpha$  by the  $x$  independent value  $[V(t)]^\alpha$ , since  $V(t)$  is the mean over  $x$  of  $\bar{v}(x, t)$  weighted with factor  $f(x, t)$ . This procedure is clearly exact if  $\alpha = 0$ , and even for  $\alpha = \frac{1}{6}$ , a detailed numerical check along the lines followed later in this section shows that with plausible assumptions about the form of  $v(x)$  and  $f(x)$ , the error incurred in this replacement is at most a few per cent. This approximation therefore allows equation (22) to be expressed in the form

$$dV/dt = \frac{1}{2}AB\phi_1 V^\alpha \tag{26}$$

where

$$A = \int_{-\infty}^\infty [f(x, t)]^2 dx. \tag{27}$$

To tackle  $A$  we shall suppose that  $f(x, t)$  corresponds to a pulse centred at the origin, i.e.  $f(x, t)$  is an even function, with a maximum at  $x = 0$ , which decreases monotonically as  $|x|$  increases and becomes effectively zero for large  $|x|$ . We shall also assume that with the passage of time this pulse becomes progressively wider, but essentially retains the same shape so that  $f(x, t)$  may be expressed in the form

$$f(x, t) \propto S[x/a(t)] \tag{28}$$

where  $S$  is a specified function of  $[x/a(t)]$  and  $a(t)$  is an arbitrary function of  $t$  with the dimension of length. The constant of proportionality in relation (28) is defined through equation (25b), and the form (28) then corresponds to assuming that a change in  $t$  is equivalent to a change in scale of  $x$ . We note that in the absence of coagulation such a form for  $f$  satisfies equation (7) if  $a(t) = 2D^{1/2}t^{1/2}$  and  $S(\theta) = \exp(-\theta^2)$ . It is shown in appendix 1 that if the form (28) is used in equation (27), we obtain the result

$$A(t) = C_1/X(t) \tag{29}$$

where

$$X(t) = [\bar{r}^2(t)]^{1/2} \tag{30}$$

and

$$C_1 = \int_{-\infty}^\infty [S(\theta)]^2 d\theta \left( \int_{-\infty}^\infty \theta^2 S(\theta) d\theta \right)^{1/2} \left( \int_{-\infty}^\infty S(\theta) d\theta \right)^{-5/2}. \tag{31}$$

It is clear that the same value for  $C_1$  is given by  $S(\theta)$  and  $aS(b\theta)$  ( $a$  and  $b$  constants), and we might reasonably expect the value of  $C_1$  not to depend critically on the precise form of  $S(\theta)$ , for any  $S(\theta)$  which corresponds to the pulse shape described above. This is borne out by a calculation of the value of  $C_1$  for the following cases.

- (i)  $S(\theta) = \exp(-\theta^2)$ ;  $C_1 = 0.28$
- (ii)  $S(\theta) = 1$  for  $|\theta| < 1$ ,  $S(\theta) = 0$  for  $|\theta| > 1$ ;  $C_1 = 0.29$
- (iii)  $S(\theta) = 1 - \theta^2$  for  $|\theta| < 1$ ,  $S(\theta) = 0$  for  $|\theta| > 1$ ;  $C_1 = 0.27$
- (iv)  $S(\theta) = (1 + \theta^2)^{-2}$ ;  $C_1 = 0.40$ .

We note that the value of  $C_1$  for case (iv) is rather larger than that for cases (i), (ii) and (iii), which among themselves are in close agreement. This disparity corresponds to the fact that in case (iv) the value of  $S(\theta)$  is relatively large in the 'wings' of the pulse, i.e. for  $\theta \gg 1$ . This in turn suggests that the first three values probably form more realistic estimates of  $C_1$ , since in practice one is generally dealing with a spatial distribution which is effectively zero outside some region.

We now proceed to consider  $B$ , given by equation (23). We note that the function  $g(w)$  is always non-negative ( $0 \leq w \leq \infty$ ) and satisfies the two equations (25a). For such a function these latter two conditions act as powerful constraints which drastically limit any possible variation in the value of  $B$ . Thus if  $P(u, v)$  is given by equation (9a) we have

$$B = \frac{4kT}{3\eta} \left( \int_0^\infty g(w) dw \int_0^\infty g(w') dw' + \int_0^\infty w^{1/3} g(w) dw \int_0^\infty w^{-1/3} g(w) dw \right). \quad (32)$$

It is seen from equations (25a) that  $\int_0^\infty w^n g(w, t) dw$  is independent of  $t$  for  $n = 0, 1$  and this implies not only that the first product of integrals in equation (32) is certainly independent of  $t$ , but also that the  $t$  variation of the second product would be expected to be small. This is supported by the fact that the qualitative behaviour of  $g(w)$  is generally of a standard form: as  $w$  increases from zero,  $g(w)$  increases monotonically from zero before passing through a single maximum and then decreasing monotonically to zero as  $w \rightarrow \infty$ . This conclusion, that any variation in  $B$  would be expected to be small, is further borne out quantitatively by a detailed calculation of  $B$  using for  $g(w)$  the standard gamma distribution which is known to give a reasonable representation of the particle size spectrum (Levin 1954, Scott 1968, Williams 1986). This distribution takes the form

$$g(w) = Cw^q \exp(-Dw) \quad (33)$$

where the constants  $C$  and  $D$  are given in terms of the parameter  $q$  by the conditions (25a). The quantity in brackets (' $J$ ') in equation (32) will thus be given as a function of  $q$ , and consideration can then be given as to how  $J(q)$  varies with  $q$ ; since  $g(0)$  must be finite, we are only interested in  $q \geq 0$ . The details are given in appendix 2 where it is shown that as  $q$  increases from 0 to  $\infty$ ,  $J$  decreases monotonically from 2.21 to 2.00. This implies that even if substantial variations in  $q$  occur with the passage of time, the effect on  $B$  will be minimal.

For  $P(u, v)$  given by equation (9b) we have

$$B = G \int_0^\infty \int_0^\infty (uv)^{-1/2} (u+v)^{1/2} (u^{1/3} + v^{1/3})^2 g(u)g(v) du dv \quad (34a)$$

where

$$G = (3/4\pi)^{1/6} (6kT/\rho)^{1/2}. \quad (34b)$$



Although the double integral in (34a) cannot be expressed as the sum of products of single integrals (owing to the  $(u + v)^{1/2}$  term), nevertheless the above discussion suggests that since the powers of  $u$  and  $v$  in the integrand lie in the interval  $[0, 1]$  it would be expected that the temporal variation of  $B$  would be small. This is borne out by a calculation of  $B$  using the gamma distribution (33). The details are given in appendix 2 where it is shown that as  $q$  increases from 0 to  $\infty$ ,  $B$  decreases monotonically from  $7.0G$  to  $5.7G$ . Finally we make the point that, although according to the above discussion small temporal variations in  $B$  may occur initially, we can reasonably expect that after a certain time even these small variations may well vanish if  $g$  tends to a 'self-preserving distribution' when  $t \rightarrow \infty$ , as it does in the spatially independent situation.

On the basis of the discussion in the previous two paragraphs we shall assume that  $C_1$  and  $B$  are independent of time. Making use of equation (29) this then allows us to express equation (26) in the form

$$dV/dt = \Gamma_1 V^\alpha X^{-1} \tag{35a}$$

where

$$\Gamma_1 = \frac{1}{2}BC_1\phi_1. \tag{35b}$$

The analogue of the above development for the cases of two and three dimensions may be carried through without any difficulties. For two dimensions we deal with  $n(v, \rho, t)$  and all integrals of the form  $\int_{-\infty}^{\infty} dx$  above are now replaced by  $\int_0^{\infty} \rho d\rho$ . The final result thus obtained is

$$dV/dt = \Gamma_2 V^\alpha X^{-2} \tag{36}$$

where

$$\Gamma_2 = \frac{1}{2}BC_2\phi_2. \tag{37}$$

Here  $\phi_2$  is the total volume of particulate matter contained in a slab with parallel faces extending throughout the  $xy$  plane and with thickness  $(1/2\pi)$  in the  $z$  direction,

$$C_2 = \int_0^{\infty} \theta[S(\theta)]^2 d\theta \int_0^{\infty} \theta^3 S(\theta) d\theta \left( \int_0^{\infty} \theta S(\theta) d\theta \right)^{-3}. \tag{38}$$

In view of the comments made earlier in the one-dimensional situation we evaluate  $C_2$  for the first three forms of  $S(\theta)$  given there, and obtain respectively the values 1.0, 1.0 and 0.9.

For three dimensions we deal with  $n(v, r, t)$  and all earlier integrals of the form  $\int_{-\infty}^{\infty} dx$  are now replaced by  $\int_0^{\infty} r^2 dr$ . The final result obtained is

$$dV/dt = \Gamma_3 V^\alpha X^{-3} \tag{39a}$$

where

$$\Gamma_3 = \frac{1}{2}BC_3\phi_3. \tag{39b}$$

Here  $\phi_3$  is  $(1/4\pi)$  times the total volume of particulate matter, and

$$C_3 = \int_0^{\infty} \theta^2[S(\theta)]^2 d\theta \left( \int_0^{\infty} \theta^4 S(\theta) d\theta \right)^{3/2} \left( \int_0^{\infty} \theta^2 S(\theta) d\theta \right)^{-7/2}. \tag{40}$$

Calculation of  $C_3$  for the first three forms of  $S(\theta)$  given earlier yields respectively the values 1.5, 1.4 and 1.2.

#### 4. Expressions for $X$ and $V$

The basic equations derived above for the one-dimensional problem are (13), which gives  $dr^2/dt$  in terms of a certain time-dependent mean particle volume  $W$ , and (35) which describes the time variation of  $W$  through an expression for  $dV/dt$ . We now proceed to express equation (13) in terms of  $V$  instead of  $W$ . Noting that equations (12) both take the form

$$D(v) = \mu v^{-s} \quad (41)$$

it is readily shown by following the transformations of the last section that

$$D(W) = \gamma D(V) \quad \text{where} \quad \gamma = \int_0^\infty w^{1-s} g(w) dw. \quad (42)$$

The discussion of the last section based on the constraints (25a) suggests that  $\gamma$  should be effectively constant, with a value close to unity, and a detailed evaluation using the gamma distribution (33) shows that for both  $s = \frac{1}{3}$  and  $\frac{2}{3}$ ,  $\gamma$  increases monotonically from 0.9 to 1.0 as  $q$  increases from 0 to  $\infty$ . It then follows from equations (30), (41) and (42) and the remarks at the end of § 2 that in general equation (13) may be expressed in the form

$$dX/dt = \Delta V^{-s} X^{-1} \quad (43)$$

where  $\Delta = \beta\gamma\mu$ ,  $\beta$  being the number of dimensions. This equation is to be supplemented by the relevant equation for  $dV/dt$  ((35), (36) or (39)), and these can all be expressed in the form

$$dV/dt = \Gamma_\beta V^\alpha X^{-\beta}. \quad (44)$$

Equations (43) and (44) constitute a pair of coupled first-order non-linear differential equations for  $X(t)$  and  $V(t)$  and a unique solution will exist if these are supplemented by boundary conditions that at  $t=0$ ,  $X = X_0$  and  $V = V_0$ . We are, of course, primarily interested in  $X$ , and therefore proceed to eliminate  $V$  by first dividing equation (44) by (43). This gives

$$dV/dX = \kappa V^{1-n} X^{1-\beta} \quad (45)$$

where  $\kappa = \Gamma_\beta/\Delta$  and  $n = 1 - \alpha - s$ . We recall that  $\alpha$  and  $s$ , respectively, are essentially a measure of how rapidly  $P$  and  $D$  vary with  $v$ , with positive values of  $\alpha$  and  $s$  corresponding to larger particles coagulating more rapidly and being less mobile than smaller ones. The fact that the power of  $V$  in equation (45) is  $\alpha + s$  is thus physically plausible.

Equation (45) may be readily integrated to give  $V$  in terms of  $X$ . Substituting this into equation (43), followed by a further integration, yields  $t$  explicitly as a function of  $X$ . In general it is only possible to obtain  $X$  and  $V$  explicitly as functions of  $t$  in the limit of large  $t$ , when  $X \gg X_0$ . We therefore give below in table 1 the general forms for  $t(X)$ , together with  $X(t)$  and  $V(t)$  for  $X \gg X_0$ . Results are tabulated for one, two and three dimensions, for both 'small' and 'large' particles.

We proceed to compare the  $t$  variation of  $X$  for  $X \gg X_0$  with the case of non-coagulating particles given at the end of table 1. It is clear that for both one and two dimensions the  $t$  variation of  $x$  is less rapid than the  $t^{1/2}$  form characteristic of non-coagulating particles. Further, it is seen that the extent by which  $X(t)$  departs

**Table 1.** Relationship between diffusive spread, mean particle volume and time for 'large' and 'small' particles in one, two and three dimensions.

One dimension	$K_n \ll 1$	General X	$t = (3\kappa^{1/2}/5\Delta)\{[\frac{2}{3}(X - X_0) + Y]^{3/2}(X + \frac{2}{3}X_0 - Y) - Y^{3/2}(\frac{2}{3}X_0 - Y)\}$ where $Y = V_0^{2/3}/\kappa$
		$X \gg X_0, Y$	$X = 1.564\Delta^{3/5}\Gamma_1^{-1/5}t^{2/5}$ $V = 1.065\Delta^{-3/5}\Gamma_1^{6/5}t^{3/5}$
	$K_n \gg 1$	General X	$t = (6\kappa^4/5\Delta)\{[\frac{1}{6}(X - X_0) + Y]^5(\frac{2}{6}X + \frac{1}{6}X_0 - Y) - Y^5(X_0 - Y)\}$ where $Y = V_0^{1/6}/\kappa$
		$X \gg X_0, Y$	$X = 4.451\Delta^{5/6}\Gamma_1^{-2/3}t^{1/6}$ $V = 0.167\Delta^{-1}\Gamma_1^2t$
	$K_n \ll 1$	General X	$t = \Delta^{-1}(\frac{2}{3}\kappa)^{1/2} \int_{X_0}^X X[\ln(X/X')]^{1/2} dX$ where $V_0^{2/3} = \frac{2}{3}\kappa \ln(X_0/X')$
		$X \gg X_0$	$X = Et^{1/2}[\ln(Et^{1/2}/X')]^{-1/4}$ $V = (\frac{2}{3}\kappa)^{3/2}[\ln(Et^{1/2}/X')]^{3/2}$ where $E = 6^{1/4}\Delta^{3/4}\Gamma_2^{-1/4}$
Two dimensions	$K_n \gg 1$	General X	$t = (4\Delta)^{-1}(\kappa/6)^4[X^2F(X/X') - X_0^2F(X_0/X')]$ where $F(u) = 2(\ln u)^4 - 4(\ln u)^3 + 6(\ln u)^2 - 6 \ln u + 3$ and $V_0^{1/6} = \frac{1}{6}\kappa \ln(X_0/X')$
		$X \gg X_0$	$X = Et^{1/2}[\ln(Et^{1/2}/X')]^{-2}$ $V = (\frac{1}{6}\kappa)^6[\ln(Et^{1/2}/X')]^6$ where $E = 36\sqrt{2}\Delta^{5/2}\Gamma_2^{-2}$
	$K_n \ll 1$	General X	$t = \Delta^{-1}(\frac{2}{3}\kappa)^{1/2}X^{13/2}[H(X/X') - H(X_0/X')]$ where $H(u) = \frac{1}{2}(u - \frac{1}{2})(u^2 - u)^{1/2} - \frac{1}{8} \ln[u - \frac{1}{2} + (u^2 - u)^{1/2}]$ and $(2\kappa/3X') = (2\kappa/3X_0) + V_0^{2/3}$
Three dimensions	$K_n \gg 1$	General X	$X = (6X'/\Gamma_3)^{1/4}\Delta^{3/4}t^{1/2}$ $V = (2\kappa/3X')^{3/2}$
		$X \gg X_0$	$t = \Delta^{-1}(\kappa/6)^4X'^{-2}[J(X/X') - J(X_0/X')]$ where $J(u) = \frac{1}{2}u^2 - 4u + 6 \ln u + (4/u) - (1/2u^2)$ and $(\kappa/6X') = (\kappa/6X_0) + V_0^{1/6}$
	$K_n \ll 1$	$X \gg X_0$	$X = 36\sqrt{2}\Delta^{5/2}\Gamma_3^{-2}X'^2t^{1/2}$ $V = (\kappa/6X')^6$
Non-coagulating particles	$K_n \ll 1$		$X = (2\Delta)^{1/2}V_0^{-1/6}t^{1/2}$
	$K_n \gg 1$		$X = (2\Delta)^{1/2}V_0^{-1/3}t^{1/2}$
	All $K_n$		$V = V_0$

from a  $t^{1/2}$  variation is greater in each case for 'small' particles than it is for 'large' ones. This arises physically from the fact that compared with 'large' particles, 'small' particles undergo a greater increase in coagulation during their growth ( $\alpha = \frac{1}{6}$  compared with  $\alpha = 0$ ) and a greater decrease in diffusion coefficient ( $s = \frac{2}{3}$  compared with  $s = \frac{1}{3}$ ). The combined effect is to increase the particle growth rate (compare the relevant expressions for  $V$ ) and, as explained in the introduction, this will lead to a less rapid increase in  $X$  for 'small' particles. Regarding the dimensional dependence of the  $t$  variation of  $X$ , we note that for both 'large' and 'small' particles, the extent by which  $X(t)$  falls below a  $t^{1/2}$  variation is less in the 2D case than it is in the 1D case due to the relatively slow variation of the logarithmic term. This is in agreement with the discussion given in § 1 where it was pointed out that since coagulation effects vary quadratically with the particle concentration, they would be expected to be more pronounced in the 1D case where the concentration is proportional to  $X^{-1}$  than in the 2D case where it is proportional to  $X^{-2}$ , and therefore falls off more rapidly for large times. In accordance with this, it would be expected that in the 3D case any departure from a  $t^{1/2}$  variation for  $X$  would be even less than in the 2D case and indeed we see from table 1 that in the 3D case for  $X \gg X_0$ ,  $X$  exhibits exactly a  $t^{1/2}$  dependence. This corresponds to the fact that, unlike the 1D and 2D cases where  $V \rightarrow \infty$  as  $t \rightarrow \infty$ , the  $t$  variation of  $V$  in the 3D case is such that as  $t \rightarrow \infty$ ,  $V$  tends to a finite value  $V_\infty$ . This occurs essentially because the smaller particle concentration in the 3D case ( $\propto X^{-3}$ ) means that coagulation effects are effectively 'frozen out' at sufficiently long times, and  $V$  cannot therefore exceed a certain finite maximum value,  $V_\infty$ . Indeed, for  $X \gg X_0$  the form for  $X(t)$  is precisely that corresponding to particles with  $V = V_\infty$ .

The discussion in the introduction suggests that since coagulation increases with particle concentration an increase in particle concentration should lead to larger  $V$  and smaller  $X$ . This is clearly exhibited by all the results in table 1 for  $X \gg X_0$ , where the expressions for  $V$  have positive powers of  $\Gamma$ , while those for  $X$  have negative powers.

Finally, we refer to the point made in the introduction that one result of coagulation is to enhance the localising effect of a smaller diffusion coefficient  $D$ . For  $X \gg X_0$ , this is apparent in all the forms for  $X$  given in table 1, where the power of  $\Delta$  is always greater than the value of  $\frac{1}{2}$ , characteristic of non-coagulating particles.

## 5. Numerical values

In this section we list numerical results showing the effect of coagulation on diffusive spread. In calculating these it is necessary to bear in mind that the formulae derived in the last section are only valid if  $Kn \gg 1$  or  $Kn \ll 1$ , and this means that during the growth of the particles they must lie throughout in one or other of these two regimes. For 'small' particles, the initial particle dimensions cannot be less than a few times  $10^{-7}$  cm, while the final dimensions must be significantly less than  $l$ , the molecular mean free path for air, which is about  $7 \times 10^{-6}$  cm. For 'large' particles, the initial size must be significantly greater than  $l$ , while the final dimensions cannot exceed a few times  $10^{-4}$  cm, at which value differential sedimentation of the particles becomes important and our theory thus becomes inapplicable. For given initial particle size we let  $t$  and  $t'$  be the times for  $X$  to change from  $X_0$  to  $X_1$  in the presence and absence, respectively, of coagulation. We examine situations which maximise  $t/t'$ , and it is clear that these will correspond to choosing that aerosol density which yields maximum

particle growth consistent with the particles remaining throughout in one or other of the above two size regimes.

In table 2 we give for one and three dimensions, and for the two size regimes, suitable values for  $R_0$  and  $R_1$ , the initial and final particle radii, and for  $X_0$  and  $X_1$ . We also tabulate  $t'$  and  $t/t'$ , calculated from our earlier equations, together with  $\Phi$ , the initial proportion of space occupied by particulate matter, assuming that the initial spatial aerosol distribution is a square pulse. We note that all values of  $t/t'$  lie in the interval 3-7 and that the required values of  $\Phi$  range from  $\sim 3 \times 10^{-5}$  for 'large' particles in three dimensions down to a value of  $\sim 4 \times 10^{-11}$  for 'small' particles in one dimension.

Table 2. Values of  $t/t'$  and  $\Phi$  for aerosols and hydrosols in one and three dimensions.

			$R_0$ (cm)	$R_1$ (cm)	$X_0$ (mm)	$X_1$ (mm)	$t'$	$t/t'$	$\Phi$
One dimension	Aerosol	$K_n \ll 1$	$2 \times 10^{-5}$	$2 \times 10^{-4}$	1	2	7 h	7	$9 \times 10^{-7}$
		$K_n \gg 1$	$5 \times 10^{-7}$	$2.5 \times 10^{-6}$	3	6	5 min	6	$4 \times 10^{-11}$
	Hydrosol		$2 \times 10^{-6}$	$4 \times 10^{-3}$	1	2	35 h	350	$2 \times 10^{-5}$
Three dimensions	Aerosol	$K_n \ll 1$	$2 \times 10^{-5}$	$2 \times 10^{-4}$	1	2	2.3 h	6	$3 \times 10^{-5}$
		$K_n \gg 1$	$5 \times 10^{-7}$	$2.5 \times 10^{-6}$	3	6	1.7 min	3	$7 \times 10^{-11}$
	Hydrosol		$2 \times 10^{-6}$	$1 \times 10^{-3}$	1	2	12 h	350	$1 \times 10^{-3}$

Although the present work was designed primarily to deal with aerosols, an identical theory may also be used for the simultaneous coagulation and diffusion of hydrosols. As regards the requirement of maximising  $t/t'$ , this latter context is advantageous, since there is nothing analogous to the 'small' particle regime of aerosols, and the 'large' particle aerosol equations may be applied to arbitrarily small particles. Further, the effects of coagulation due to differential sedimentation may be minimised by using particles whose density is close to that of water. We therefore give in table 2 results for hydrosols in both one and three dimensions. Compared with aerosols these results correspond to substantially larger values of  $t/t'$ , and owing to the viscosity of water being greater than that of air by a factor of about 50, the actual values of  $t'$  are greater for water.

Experimental measurements of the variation of diffusive spread with particle concentration are difficult owing to the requirement that a localised aerosol should be generated and that its subsequent development should be unaffected by convective fluid currents throughout the time  $t$ . If this problem were overcome it is clear that the values of  $\Phi$  tabulated above are experimentally realisable and that the corresponding magnitudes of  $t/t'$  are sufficiently large to be experimentally measurable. Such measurements could provide useful information on the relationship between coagulation effects and particle size and concentration. In particular they would offer a way by which the effects of coagulation could be investigated by *macroscopic* observations of the spread of a localised aerosol, rather than *microscopic* observations of particle size and number.

It should again be emphasised that in order to derive the numerical results given above from the earlier analytic formulae it was necessary that particle growth should take place entirely within a single size regime. In order to perform the calculation

when growth spans the transition region between the two regimes it would be necessary to use expressions for  $D(v)$  and  $P(u, v)$ , containing the so-called Cunningham factors, which are valid in this region. Such expressions are given by F and Silberberg (1979), but since they no longer correspond to mathematically homogeneous functions of  $u$  and  $v$ , a numerical computation would be required, rather than the analytic approach developed above. If experimental results warranted it, such work would probably be justified since larger values of  $t/t'$  could then be obtained and a wider range of physical parameters could be used.

## 6. Conclusions

We have investigated the effects of particle coagulation on the diffusive spread of aerosols, and have obtained explicit analytic formulae in the regimes  $Kn \ll 1$  and  $Kn \gg 1$  for one, two and three dimensions. Our results are in agreement with what would be expected on physical grounds for variation with particle size and concentration, number of dimensions and strength of diffusion coefficient and coagulation kernel. The numerical values obtained suggest that if experimental difficulties were overcome, measurement of the effect could provide a useful probe for the investigation of particle coagulation by macroscopic observations. Further computational work spanning the two above size regimes might then be justified.

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## Appendix 1

We proceed to prove that if the form (28) is used in equation (27), then the results (29) and (31) are obtained.

Taking

$$f(x, t) = ZS(x/a) \quad (\text{A1.1})$$

we immediately obtain from equation (25b)

$$Za \int_{-\infty}^{\infty} S(\theta) d\theta = 1. \quad (\text{A1.2})$$

Also

$$X^2 = \overline{r^2} = \int_{-\infty}^{\infty} x^2 f(x, t) dx \quad (\text{A1.3})$$

in view of equation (25b). Using equation (A1.1) then gives

$$X^2 = Za^3 \int_{-\infty}^{\infty} \theta^2 S(\theta) d\theta. \quad (\text{A1.4})$$

Further, using equation (A1.1) in equation (27) yields

$$A = Z^2 a \int_{-\infty}^{\infty} (S(\theta))^2 d\theta. \tag{A1.5}$$

Equations (A1.2) and (A1.4) are readily solved to obtain  $Z$  and  $a$  in terms of  $X$  and integrals with respect to  $\theta$ . Substituting for  $Z$  and  $a$  into equation (A1.5) then gives equations (29) and (31).

**Appendix 2**

On applying the constraints (25a) to determine  $C$  and  $D$ , the distribution (33) takes the form

$$g_q(w) = [(q + 1)^{q+1}/q!] w^q \exp[-(q + 1)w] \tag{A2.1}$$

with

$$\int_0^{\infty} w^s g_q(w) dw = (q + s)!(q + 1)^{-s}/q!. \tag{A2.2}$$

Equation (32) then gives

$$B = (4kT/3\eta) \{1 + [(q + \frac{1}{3})!(q - \frac{1}{3})!/(q!)^2]\}. \tag{A2.3}$$

As  $q$  increases from zero to infinity the quantity  $J$  in braces in equation (A2.3) decreases monotonically from 2.21 to 2.00. The latter value corresponds to the situation where all particles have the same volume, since

$$\lim_{q \rightarrow \infty} g_q(w) = \delta(w - 1).$$

Denoting the double integral in equation (34a) by  $I$ , and using the above form (A2.1) for  $g$ , we have

$$I = \frac{(q + 1)^{2(q+1)}}{(q!)^2} \int_0^{\infty} \int_0^{\infty} (u + v)^{1/2} (u^{1/3} + v^{1/3})^2 (uv)^{q-1/2} \times \exp[-(q + 1)(u + v)] du dv. \tag{A2.4}$$

To evaluate the integral we transform the variables from  $u, v$  to  $\sigma, \theta$  defined by

$$u = [\sigma/(q + 1)] \cos^2 \theta \quad v = [\sigma/(q + 1)] \sin^2 \theta \tag{A2.5}$$

and obtain

$$I = \frac{4}{(q!)^2 (q + 1)^{1/6}} \int_0^{\infty} \sigma^{2q+7/6} e^{-\sigma} d\sigma \times \int_0^{\pi/2} (\cos^{2q+2/3} \theta \sin^{2q+2/3} \theta + \cos^{2q+4/3} \theta \sin^{2q} \theta) d\theta. \tag{A2.6}$$

Making use of the result

$$\int_0^{\pi/2} \sin^l \theta \cos^m \theta d\theta = \left(\frac{l-1}{2}\right)! \left(\frac{m-1}{2}\right)! \left[2 \left(\frac{l+m}{2}\right)!\right]^{-1}$$

(Abramowitz and Stegun 1965), we finally obtain

$$I = \left( \frac{2(2q + \frac{7}{6})!}{(q!)^2(q+1)^{1/6}(2q + \frac{2}{3})!} \right) \{ [(q - \frac{1}{6})!]^2 + (q - \frac{1}{2})!(q + \frac{1}{6})! \}.$$

As  $q$  increases from zero to infinity  $I$  decreases monotonically from 7.0 to 5.7.

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