The effect of particle coagulation on the diffusive relaxation of a spatially inhomogeneous aerosol

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Abstract. It is pointed out that during the diffusive relaxation of a spatially inhomogeneous aerosol, the difference in particle coagulation growth rates in regions with different particulate volume fractions will result in a modification of the corresponding local particle diffusion coefficients. This in turn will lead to a decrease in the rate of relaxation of the aerosol, and results are derived for this modified relaxation, for aerosol particles with both compact and fractal structures in the regimes $Kn \ll 1$ and $Kn \gg 1$. In the case of fractal particles with $Kn \gg 1$, the modification is sufficiently strong for a spatial inhomogeneity in volume fraction to increase with the passage of time over a restricted time interval. A calculation of numerical values suggests that, if experimental difficulties could be overcome, measurement of aerosol relaxation could provide useful information on particle structure and coagulation effects.

1. Introduction

Consider an initially spatially inhomogeneous suspension of particles in a stationary fluid (aerosol or hydrosol). If the volume fraction of particulate matter $\phi(x, t)$ is increased in some finite region of the fluid then this increase will decay, as the particles diffuse away, in accordance with the diffusion equation

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} \tag{1}$$

where D is the particle diffusion coefficient. On expressing ϕ in the form

$$\phi(x, t) = \int_{-\infty}^{\infty} \phi(k, t) \, e^{ikx} \, dk \tag{2}$$

it immediately follows from equation (1) that each Fourier component $\phi(k, t)$ decays monotonically with time, with

$$\phi(k, t) = \phi(k, 0) \exp(-Dk^2 t). \tag{3}$$

Now, the Brownian motion of the particles in the fluid which causes them to diffuse will at the same time cause them to coagulate (Smoluchowski 1917), so that the mean particle size will become progressively larger. Since the diffusion coefficient D decreases as the particle size increases (see table 1), coagulation will cause D to decrease continually with the passage of time. If we consider the situation where the spatial variations in ϕ are small compared with the mean value of ϕ, then the standard theory

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Table 1. Expressions and values for $D(v)$, $P(u, v)$, s, α and R for compact and fractal structure particles in the regimes $Kn \ll 1$ and $Kn \gg 1$. Here, ρ', η, m and a are the gas density, viscosity, molecular mass and accommodation coefficient respectively. ρ is the density of particulate matter and v_0, R_0 are respectively the volume and radius of the elementary spherules which form the basis of the fractal structure. $\delta (=0.56)$ is the reciprocal of the fractal dimension.

	$D(v)$	$P(u, v)$	s	α	R
(a) Compact structure					
$Kn \ll 1$	$\dfrac{0.086kT}{\eta v^{1/3}}$	$\dfrac{2kT}{3\eta}\left[2 + \left(\dfrac{u}{v}\right)^{1/3} + \left(\dfrac{v}{u}\right)^{1/3}\right]$	$\tfrac{1}{3}$	0	$\dfrac{1.4kT}{\eta}$
$Kn \gg 1$	$\dfrac{0.39(mkT)^{1/2}}{\rho'(1+\pi a/8)v^{2/3}}$	$1.9\left(\dfrac{kT}{\rho}\right)^{1/2}\left(\dfrac{1}{u}+\dfrac{1}{v}\right)^{1/2}(u^{1/3}+v^{1/3})^2$	$\tfrac{2}{3}$	$\tfrac{1}{6}$	$6\left(\dfrac{kT}{\rho}\right)^{1/2}$
(b) Fractal structure					
$Kn \ll 1$	$\dfrac{0.053kT}{\eta R_0}\left(\dfrac{v_0}{v}\right)^\delta$	$\dfrac{2kT}{3\eta}\left[2 + \left(\dfrac{u}{v}\right)^\delta + \left(\dfrac{v}{u}\right)^\delta\right]$	0.56	0	$\dfrac{1.4kT}{\eta}$
$Kn \gg 1$	$\dfrac{0.15(mkT)^{1/2}}{\rho'(1+\pi a/8)R_0^2}\left(\dfrac{v_0}{v}\right)$	$5.0\left(\dfrac{kT}{\rho}\right)^{1/2}\dfrac{R_0^2}{v_0^{2\delta}}\left(\dfrac{1}{u}+\dfrac{1}{v}\right)^{1/2}(u^\delta+v^\delta)^2$	1	0.62	$6\left(\dfrac{kT}{\rho}\right)^{1/2}\dfrac{1}{v_0^{0.45}}$

of coagulational growth (Friedlander 1977) can be used to calculate the time variation of the mean particle size and hence the time dependence of the diffusion coefficient $D(t)$. Equation (1) may then be used to give the analogue of equation (3) in the form

$$\phi(k, t) = \phi(k, 0) \exp\left(-k^2 \int_0^t D(t)\, dt\right). \tag{4}$$

Since D decreases with time, the above considerations imply that the effect of coagulation will be to slow down the exponential decrease of $\phi(k, t)$ with time.

Now, apart from the effect of coagulation in modifying $D(t)$ as described in the previous paragraph, there is another mechanism by which coagulation affects the rate of relaxation of ϕ. Thus, consider two small regions A and B, separated by distance l, such that the value of ϕ in A is greater than that in B. As a result of this larger value of ϕ the particle coagulational growth in A will exceed that in B and thus A will contain 'large' particles and B will contain 'small' particles. Hence the net particulate flux from A to B may be considered to consist of the sum of two components. The first is that of the 'large' particles which have $\phi = \phi_A$ in A and $\phi = 0$ in B while the second is that of the 'small' particles which have $\phi = 0$ in A and $\phi = \phi_B$ in B. The net particulate flux from A to B is thus given by

$$J = l^{-1}(D_l\phi_A - D_s\phi_B)$$
$$= l^{-1}[D_l(\phi_A - \phi_B) - (D_s - D_l)\phi_B] \tag{5}$$

where D_l and D_s are the respective diffusion coefficients for 'large' and 'small' particles.

Now, since D decreases with increasing particle size, $D_s > D_l$ and thus

$$J < l^{-1}D_l(\phi_A - \phi_B). \tag{6}$$

The spatial variation in D produced by the spatially varying coagulation rates is thus such as to decrease the magnitude of the net particle flux below what it would otherwise be, and this effect will be present wherever there is a spatial variation in ϕ (which will produce greater particle coagulation growth in a region of greater ϕ, and in turn will

modify D in a way which lessens the net particulate flux into regions of smaller ϕ). This effect will operate in addition to the one described in the previous paragraph to decrease the rate of relaxation of ϕ. The calculation of this effect is, however, significantly more difficult than the calculation outlined in the previous paragraph. In order to tackle it we begin in the next section by considering the general equation which describes simultaneous diffusion and coagulation of suspended particulate matter. Finally we remark with reference to equation (5) that, if $(D_s - D_l)\phi_B > D_l(\phi_A - \phi_B)$, then $J < 0$ and the net particle flux would be in the direction of increasing ϕ, and as such would tend to increase $\phi_A - \phi_B$ rather than decrease it. Such an effect has been noted previously (Simons 1987a, b) and we shall see later situations where it can occur in the present work.

This paper is a continuation of previous work (Simons 1986a, b, 1987a, b) concerned with the simultaneous effects of spatial diffusion and coagulation. Simons (1986a, b) dealt with an aerosol initially localised within a finite region and showed how, as the aerosol spread out, the root mean square particle displacement increased with time less rapidly than $t^{1/2}$ due to the increase in particle size resulting from coagulation. Simons (1987a, b) was concerned with investigating the explicit spatial dependence of particulate matter for the time-independent situation arising as a result of steady-state diffusive flow. The present paper is essentially a generalisation of this latter work to the situation where the distribution of particulate matter can vary both in space and time. Following Simons (1987a, b), we shall confine our attention to the case of particle diffusion in one dimension. However, there exists the possibility of extending the technique to two or three dimensions if subsequent work should warrant this.

2. Basic formulation

Let $n(v, x, t)\,\mathrm{d}v$ be the number of particles with volumes lying between v and $v + \mathrm{d}v$ per unit volume of fluid at position x and time t. Then the general equation governing n takes the form

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

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

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

where $P(u, v)$ is the kernel describing the coagulation. We shall consider in §5 explicit forms for $D(v)$ and $P(u, v)$; meanwhile we note that for the various situations of interest

$$D(v) = \mu v^{-s} \tag{9}$$

$$P(\lambda u, \lambda v) = \lambda^\alpha P(u, v) \tag{10}$$

for arbitrary λ, where μ, s and α take specific values (considered later) for each situation of interest.

In order to tackle equation (7) we shall now assume a solution for n of the 'self-preserving' form (Friedlander and Wang 1966). This has been successfully used

in spatially dependent problems by Simons (1986a, b, 1987a, b), and takes the form

$$n(v, x, t) = \frac{\phi(x, t)}{V^2(x, t)} g\left(\frac{v}{V(x, t)}\right) \tag{11}$$

where $V(x, t)$ is the mean particle volume at position x and time t. $g(w)$ is a function which increases monotonically from zero as w increases from zero, before passing through a single maximum and then decreasing monotonically to zero as $w \to \infty$. It satisfies the relations

$$\int_0^\infty g(w) \, dw = \int_0^\infty wg(w) \, dw = 1. \tag{12}$$

We now substitute from (11) into (7) and proceed to take the zeroth and first moments with respect to v of the latter. Making use of equations (9) and (10) this yields the following pair of equations for $\phi(x, t)$ and $V(x, t)$:

$$\frac{\partial \phi}{\partial t} = \mu C_{1-s} \frac{\partial^2}{\partial x^2}\left(\frac{\phi}{V^s}\right) \tag{13}$$

$$\frac{\partial}{\partial t}\left(\frac{\phi}{V}\right) = \mu C_{-s} \frac{\partial^2}{\partial x^2}\left(\frac{\phi}{V^{1+s}}\right) - \frac{R\phi^2}{V^{2-\alpha}} \tag{14}$$

where

$$C_m = \int_0^\infty w^m g(w) \, dw \tag{15a}$$

and

$$R = \tfrac{1}{2} \int_0^\infty \int_0^\infty P(w, w')g(w)g(w') \, dw \, dw'. \tag{15b}$$

In order to make (13) and (14) non-dimensional we now introduce the mean values over x at time $t = 0$ of $\phi(x, t)$ and $V(x, t)$, and denote these means by ϕ_0 and V_0 respectively (clearly ϕ_0 will be the mean value of ϕ for all t). We then define

$$\tau = \frac{t}{V_0^{1-\alpha}/R\phi_0} \qquad X = \frac{x}{(\mu C_{1-s} V_0^{1-\alpha-s}/R\phi_0)^{1/2}} \tag{16a}$$

$$\phi^*(X, \tau) = \phi(x, t)/\phi_0 \qquad V^*(X, \tau) = V(x, t)/V_0 \tag{16b}$$

when (13) and (14) take the form

$$\frac{\partial \phi^*}{\partial \tau} = \frac{\partial^2}{\partial X^2}\left(\frac{\phi^*}{V^{*s}}\right) \tag{17}$$

$$\frac{\partial}{\partial \tau}\left(\frac{\phi^*}{V^*}\right) = \beta \frac{\partial^2}{\partial X^2}\left(\frac{\phi^*}{V^{*1+s}}\right) - \frac{\phi^{*2}}{V^{*2-\alpha}} \tag{18}$$

with $\beta = C_{-s}/C_{1-s}$. In order to obtain an equation for $dV^*/d\tau$ to supplement equation (17), we now consider (17) minus V^* times (18). After a little manipulative algebra this yields

$$\frac{\partial V^*}{\partial t} = (1 - \beta)\frac{V^{*2}}{\phi^*}\frac{\partial^2}{\partial X^2}\left(\frac{\phi^*}{V^{*1+s}}\right) + \frac{2V^*}{\phi^*}\frac{\partial V^*}{\partial X}\frac{\partial}{\partial X}\left(\frac{\phi^*}{V^{*1+s}}\right) + \frac{1}{V^{*s}}\frac{\partial^2 V^*}{\partial X^2} + \phi^* V^{*\alpha}. \tag{19}$$

Now consider the situation at a given time t when ϕ^* varies with X, but V^* is independent of X (this corresponds to a typical spatially inhomogeneous suspension when it is initially formed at $t = 0$, with $V^* = 1$ everywhere). At this instant the second and third terms on the right-hand side of equation (19) are zero and the equation therefore becomes

$$\frac{\partial V^*}{\partial \tau} = (1 - \beta) \frac{V^{*2}}{\phi^*} \frac{\partial^2}{\partial X^2} \left(\frac{\phi^*}{V^{*1+s}} \right) + \phi^* V^{*\alpha}. \tag{20}$$

The second term on the right-hand side is the expected contribution to $\partial V^*/\partial \tau$ arising from coagulation, and the first term represents the contribution arising from diffusion. However, it is clear on physical grounds that a non-zero contribution to $\partial V^*/\partial \tau$ due to diffusion can only exist if V^* varies with X. For the present situation, where V^* is independent of X, the diffusional contribution to $\partial V^*/\partial \tau$ must be identically zero, and this can only be achieved if the function $g(w)$ is such that $\beta = 1$, corresponding to $C_{1-s} = C_{-s}$. If s were zero, this equality would be satisfied automatically (equation (12)); for s non-zero it corresponds to an additional constraint on $g(w)$. Since $\beta = 1$, the first term on the right-hand side of equation (19) vanishes identically, and this equation becomes

$$\frac{\partial V^*}{\partial \tau} = \frac{1}{\phi^*} \frac{\partial V^{*2}}{\partial X} \frac{\partial}{\partial X} \left(\frac{\phi^*}{V^{*1+s}} \right) + \frac{1}{V^{*s}} \frac{\partial^2 V^*}{\partial X^2} + \phi^* V^{*\alpha}. \tag{21}$$

Equations (17) and (21) form the required pair of non-linear coupled equations for $\phi^*(X, \tau)$ and $V^*(X, \tau)$.

3. The linear approximation

In order to progress further with the solution of equations (17) and (21), it is now necessary to restrict consideration to the situation where at time τ the variations of ϕ^* and V^* with X are small compared with the corresponding spatial mean values. We shall denote these spatially constant mean values by $\overline{\phi^*}(\tau)$ and $\overline{V^*}(\tau)$; they satisfy equations (17) and (21) with all spatial derivatives equated to zero. Thus

$$\frac{d\overline{\phi^*}}{d\tau} = 0 \tag{22a}$$

$$\frac{d\overline{V^*}}{d\tau} = \overline{\phi^*}\ \overline{V^{*\alpha}} \tag{22b}$$

with $\overline{\phi^*}(0) = \overline{V^*}(0) = 1$. From equation (22a), $\overline{\phi^*}(\tau) = 1$ (as expected), and thus equation (22b) becomes

$$\frac{d\overline{V^*}}{d\tau} = \overline{V^{*\alpha}}. \tag{23}$$

This equation is equivalent to the standard equation describing particle growth in a spatially homogeneous suspension and has the solution

$$\overline{V^*}(\tau) = [1 + (1-\alpha)\tau]^{1/(1-\alpha)} \qquad (\alpha \neq 1). \tag{24}$$

We now let

$$\phi(x, t) = \phi_0[1 + \phi'(x, t)] \qquad V(x, t) = \bar{V}(t)[1 + V'(x, t)]$$

so that

$$\phi^*(X, \tau) = 1 + \phi'(X, \tau) \qquad V^*(X, \tau) = \overline{V^*}(\tau)[1 + V'(X, \tau)]. \tag{25}$$

We substitute these forms into equations (17) and (21), retaining terms linear in ϕ' and V'. With the help of equation (23), this yields

$$\frac{\partial \phi'}{\partial \tau} = \frac{1}{\overline{V^*}^s} \left(\frac{\partial^2 \phi'}{\partial X^2} - s \frac{\partial^2 V'}{\partial X^2} \right) \tag{26a}$$

$$\frac{\partial V'}{\partial \tau} = \frac{1}{\overline{V^*}^s} \frac{\partial^2 V'}{\partial X^2} + \frac{\phi' - (1 - \alpha) V'}{\overline{V^*}^{1-\alpha}}. \tag{26b}$$

These equations may be simplified by changing the dimensionless time variable from τ to u given by

$$u = \frac{[1 + (1 - \alpha)\tau]^{(1-\alpha-s)/(1-\alpha)}}{1 - \alpha - s}. \tag{27}$$

They then take the form

$$\frac{\partial \phi'}{\partial u} = \frac{\partial^2 \phi'}{\partial X^2} - s \frac{\partial^2 V'}{\partial X^2} \tag{28a}$$

$$\frac{\partial V'}{\partial u} = \frac{\partial^2 V'}{\partial X^2} + \frac{\phi' - (1 - \alpha) V'}{(1 - \alpha - s)u}. \tag{28b}$$

To tackle these equations we express $\phi'(X, u)$ and $V'(X, u)$ as Fourier integrals of the form

$$\phi'(X, u) = \int_{-\infty}^{\infty} \Gamma(K, u) \exp(iKX) \, dK \tag{29a}$$

$$V'(X, u) = \int_{-\infty}^{\infty} Q(K, u) \exp(iKX) \, dK. \tag{29b}$$

We then change the independent variable from u to

$$z = K^2 u - \frac{K^2}{1 - \alpha - s} = \left(\frac{K^2}{1 - \alpha - s} \right) \{[1 + (1 - \alpha)\tau]^{(1-\alpha-s)/(1-\alpha)} - 1\} \tag{30}$$

and find that $\theta(K, z) \equiv \Gamma(K, u)$ and $W(K, z) \equiv Q(K, u)$ satisfy

$$\frac{d\theta}{dz} = -\theta + sW \tag{31a}$$

$$\frac{dW}{dz} = -W + \frac{\theta - (1 - \alpha) W}{(1 - \alpha - s)z + K^2}. \tag{31b}$$

We now consider the interval in which z lies and the corresponding boundary conditions to be imposed on θ and W. Let us suppose that the suspension is initially formed at $t = 0$ and we are interested in its development for $0 \leq t \leq \infty$. For all cases of interest, $\alpha < 1$ (see §5), and we can then distinguish between $\alpha + s < 1$ and $\alpha + s > 1$. If $\alpha + s < 1$, it follows from equation (30) that as t increases from 0 to ∞, z also increases from 0 to ∞. If $\alpha + s > 1$, then as t increases from 0 to ∞, z increases from 0 to $K^2/(\alpha + s - 1)$. The suspension is normally initially formed with the same particle

size distribution everywhere, and thus $V'(X, 0) = 0$. Corresponding to the specified initial spatial variation in the aerosol volume fraction, we suppose that

$$\phi'(X, 0) = \phi_0'(X) = \int_{-\infty}^{\infty} \theta_0(K) \exp(\mathrm{i}KX)\, \mathrm{d}K$$

and the boundary conditions to be applied to equations (31) are then

$$W(K, 0) = 0 \tag{32a}$$

$$\theta(K, 0) = \theta_0(K). \tag{32b}$$

To simplify equations (31) and (32), we now define $\sigma(K, z)$ and $Y(K, z)$ by

$$\theta(K, z) = \theta_0(K)\, \mathrm{e}^{-z} \sigma(K, z) \tag{33a}$$

$$W(K, z) = \theta_0(K)\, \mathrm{e}^{-z} Y(K, z). \tag{33b}$$

σ and Y then satisfy

$$\frac{\mathrm{d}\sigma}{\mathrm{d}z} = sY \tag{34a}$$

$$\frac{\mathrm{d}Y}{\mathrm{d}z} = \frac{\sigma - (1 - \alpha)Y}{(1 - \alpha - s)z + K^2} \tag{34b}$$

combined with boundary conditions

$$Y(K, 0) = 0 \tag{35a}$$

$$\sigma(K, 0) = 1. \tag{35b}$$

It may be readily shown that, if the right-hand side of equation (34a) is put equal to zero so that $\sigma = 1$ for all z, then the solution for θ given by equation (33a) ($\theta = \theta_0\, \mathrm{e}^{-z}$) corresponds to the result for diffusive relaxation if one considers only the first of the two mechanisms that were given in the introduction for the modifying effect of coagulation on relaxation; for convenience we shall refer to this mechanism in the remainder of the paper as 'mechanism A'. The correction to this constant value of σ given by the full solution of equations (34) and (35) will therefore correspond to the modifying effect of the second mechanism given in the introduction; in the remainder of the paper we shall refer to this as 'mechanism B'.

4. Formal solution of the linearised equations

Since we are principally interested in $\sigma(K, z)$, we eliminate Y in equations (34) to give

$$[(1 - \alpha - s)z + K^2]\frac{\mathrm{d}^2\sigma}{\mathrm{d}z^2} + (1 - \alpha)\frac{\mathrm{d}\sigma}{\mathrm{d}z} - s\sigma = 0 \tag{36a}$$

combined with boundary conditions that

$$\sigma(K, 0) = 1 \qquad \sigma'(K, 0) = 0. \tag{36b}$$

At this stage it is instructive to consider the limiting values of K corresponding to no coagulation and to infinite coagulation. If $\phi'(x, t)$ were expressed in the form

$$\phi'(x, t) = \int_{-\infty}^{\infty} \nu(k, t) \exp(\mathrm{i}kx)\, \mathrm{d}k$$

it readily follows from equations (16a) and (29a) that

$$K = \left(\frac{\mu C_{1-s} V_0^{1-\alpha-s}}{R\phi_0}\right)^{1/2} k \tag{37}$$

and hence in the limit of no coagulation where $R = 0$, $K = \infty$. For this value of K, equation (36a) becomes $\mathrm{d}^2\sigma/\mathrm{d}z^2 = 0$, and in view of the boundary conditions (36b) this has the solution $\sigma(K, z) = 1$ for all z as expected. It may then be readily shown from equations (30) and (33a) that the solution for θ corresponds to the solution given by equation (3). In the opposite limit of infinite coagulation, it is clear that the appropriate form for σ is given by the solution of equation (36a) with $K = 0$.

Now, the general solution of equation (36a) may be expressed in terms of the modified Bessel functions $I_\nu(x)$ and $K_\nu(x)$ which are linearly independent solutions of the equation

$$x^2 \frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + x \frac{\mathrm{d}y}{\mathrm{d}x} - (x^2 + \nu^2)y = 0$$

(Magnus *et al* 1966). It transpires that the general solution of equation (36a) is, for $\alpha + s < 1$,

$$\sigma(K, z) = w^{-p/2}[A(K)I_p(2p^{1/2}w^{1/2}) + B(K)K_p(2p^{1/2}w^{1/2})] \tag{38a}$$

where $w = z + (1 - \alpha - s)^{-1}K^2$ and $p = s/(1 - \alpha - s)$; while for $\alpha + s > 1$,

$$\sigma(K, z) = v^{+q/2}[A(K)I_q(2q^{1/2}v^{1/2}) + B(K)K_q(2q^{1/2}v^{1/2})] \tag{38b}$$

where $v = (\alpha + s - 1)^{-1}K^2 - z$ and $q = s/(\alpha + s - 1)$. The boundary conditions (36b) may then be used to determine $A(K)$ and $B(K)$ in terms of particular values of the modified Bessel functions and their derivatives. In general the resulting formulae are rather unwieldly and a direct numerical solution of equations (34) and (35) is more rewarding. However, for the important case of $p = \frac{1}{2}$ (to be considered in the next section) the modified Bessel functions may be expressed in terms of elementary functions to yield useful results.

The analytic results (38) are also useful in predicting general behaviour of σ in the limit of $t \to \infty$. Taking first the case of $\alpha + s < 1$, this limit corresponds to the result (38a) as $z \to \infty$. Here, the standard asymptotic forms for the modified Bessel functions (Magnus *et al* 1966) yields the result that, as $t \to \infty$,

$$\sigma(K, z) \to \text{constant} \times \frac{\exp(2p^{1/2}z^{1/2})}{z^{(2p+1)/4}}. \tag{39}$$

Although σ is thus an increasing function of z, it is clear that $\theta(K, z) = \theta_0 e^{-z}\sigma(K, z)$ will be a decreasing function of z for large z and will tend to zero as t (and z) tend to infinity. This means that, for $\alpha + s < 1$, the effect of mechanism B on diffusive relaxation will be such as to decrease the rate at which relaxation occurs, but not to reverse it. For the case of $\alpha + s > 1$, the limit of $t \to \infty$ corresponds to $z \to K^2/(\alpha + s - 1)$. This means that, if we consider only the modifying effect on relaxation of mechanism A (whereby $\theta/\theta_0 = e^{-z}$), then θ decreases monotonically but tends to a positive non-zero value as $t \to \infty$. This result is equivalent to the term

$$\int_0^\infty D(t)\,\mathrm{d}t$$

in equation (4) being finite, and corresponds physically to particle growth being sufficiently rapid for the diffusion coefficient to effectively become zero before all

spatial variations in θ have been 'ironed out'. To assess the effect of mechanism B we note that the limit of $t \to \infty$ corresponds to v tending to 0 in equation (38b). Using the leading terms in the standard power series expansions for the modified Bessel functions (Magnus *et al* 1966), we then obtain the result that, as $t \to \infty$,

$$\sigma(K, z) \to \text{constant} \times \left[1 - \frac{sv}{1 - \alpha}\right] \tag{40a}$$

and

$$e^{-z}\sigma(K, z) \to \text{constant} \times \left[1 - \frac{(\alpha + s - 1)v}{1 - \alpha}\right]. \tag{40b}$$

This means that, as t increases (and correspondingly v decreases), not only does σ increase, but also $e^{-z}\sigma$ increases (since $\alpha + s > 1$). This in turn implies that for sufficiently long times the effect of mechanism B on diffusive relaxation will be such as to reverse the direction of the net diffusive flux and to cause the initially decreasing $\theta(K, z)/\theta_0$ to ultimately increase and tend to a finite non-zero value as $t \to \infty$. The discussion in the introduction suggests that it is to be expected on physical grounds that this reversal of the usual behaviour should be associated with a strong variation with particle volume of both the coagulation rate and diffusion coefficient. This is in accordance with the above result that such reversal only occurs if $\alpha + s$ exceeds unity.

5. Application to particle regimes

We begin by noting that in order for formulae with the structure given by equations (9) and (10) to apply to particle diffusion and coagulation it is necessary that the particle size should either be significantly greater or significantly less than the gas molecular mean free path l. These two situations correspond respectively to the Knudsen number Kn satisfying $Kn \ll 1$ and $Kn \gg 1$. A further distinction concerns the internal particle structure. Until fairly recently it was assumed that particles possessed a compact structure with constant density and that the effect of coagulation of two particles with radii R_1 and R_2 was to produce a compound particle of radius $(R_1^3 + R_2^3)^{1/3}$. However, recent work has shown that this assumption may well be incorrect and that the internal structure of coagulating particles is probably of a fractal form rather than the compact form assumed hitherto (Stanley and Ostrowsky 1986, Sander 1986, Jullien and Botet 1987). In view of this, we proceed to consider the application of our work to both compact and fractal structure particles, in each case considering both $Kn \ll 1$ and $Kn \gg 1$. The relevant formulae for $D(v)$ and $P(u, v)$ are given by Friedlander (1977) for the case of compact structure, while analogous expressions for the case of fractal structure are obtained in Simons (1986b). We list all these formulae in table 1, together with the corresponding values of α and s; for fractal structures we have taken the generally accepted value of 1.8 for the dimension. As regards the appropriate form to be taken for R (equation (15b)), this has been discussed previously by Simons (1986a, b) who showed that the detailed expression for R did not depend critically on the form taken for $g(w)$ as long as this satisfied the conditions given after equation (11). The relevant expressions for R derived in the above papers are given in table 1.

 We begin by considering the case of compact particles in the regime $Kn \ll 1$ as this is the only situation in which simple analytic results can be obtained. Here the result

(38a) is applicable with $p = \frac{1}{2}$. Two linearly independent modified Bessel functions are then $y(x) = e^x/x^{1/2}$ and $e^{-x}/x^{1/2}$. On incorporating the boundary conditions (36b), we then obtain from equation (38a) that

$$\sigma(K, z) = f^{-1}\{\cosh[\sqrt{3}K(f-1)] + (\sqrt{3}K)^{-1}\sinh[\sqrt{3}K(f-1)]\} \qquad (41)$$

where $f = [1 + (2z/3K^2)]^{1/2} = (1 + \tau)^{1/3}$. In the limit of $z \gg 1$, this gives

$$\sigma(K, z) \approx \left(\frac{\sqrt{3}}{2}K + \frac{1}{2}\right)\frac{\exp(2z)^{1/2}}{(2z)^{1/2}}$$

and so $\theta(K, z)/\theta_0 \propto z^{-1/2}\exp[-z + (2z)^{1/2}]$. As regards the K variation of $\sigma(K, z)$, we note that for $K = \infty$, $\sigma = 1$ for all z (as expected), and in the limit as $K \to 0$, $\sigma(K, z) \to (2z)^{-1/2}\sinh(2z)^{1/2}$. Thus in the limit of very large coagulation,

$$\theta(K, z)/\theta_0 = (2z)^{-1/2}\exp(-z)\sinh(2z)^{1/2}.$$

For all four cases of interest (compact and fractal structures, each with $Kn \ll 1$ and $Kn \gg 1$), the form for σ as a function of z was obtained by the direct numerical solution of equations (34) for various values of K. The results are exhibited for the three cases where $\alpha + s < 1$ in figures 1, 2 and 3 which correspond respectively to compact with $Kn \ll 1$, compact with $Kn \gg 1$ and fractal with $Kn \ll 1$. In each case graphs are given of $\ln[\theta(K, z)/\theta(K, 0)] = -z + \ln[\sigma(K, z)]$ as a function of z for different values of K. As expected, $\theta(K, z)$ is always a monotonically decreasing function of z and, in each of the cases, $\theta(K, z)$ decreases less rapidly with z as K decreases corresponding to an increase in the effect of coagulation and hence in the modifying effect of mechanism B. A more unexpected result is that the curves in figures 1, 2 and 3 may all be approximated, to a greater or lesser extent, by straight lines which implies that the effect of mechanism B is such as to yield the approximate result

$$\theta(K, z) = \theta(K, 0)\exp(-\beta z) \qquad (42)$$

where β decreases below unity as the effect of coagulation becomes more important and K decreases. It is readily seen that in the limit when $K \to 0$ the curves in figures
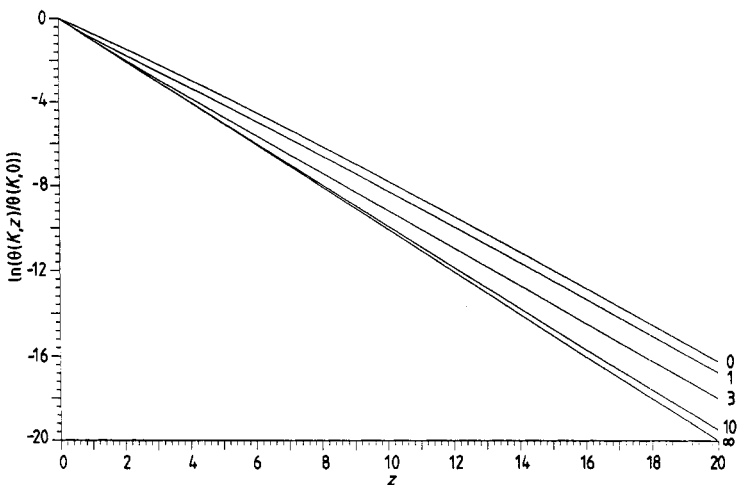

Figure 1. $\ln(\theta(K, z)/\theta(K, 0))$ as a function of z for compact particles with $Kn \ll 1$. The value of K is shown against each plot.
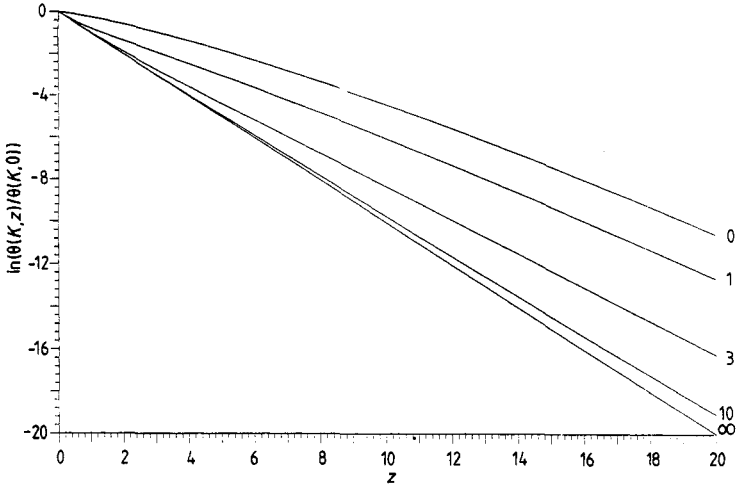
Figure 2. $\ln(\theta(K, z)/\theta(K, 0))$ as a function of z for compact particles with $Kn \gg 1$. The value of K is shown against each plot.
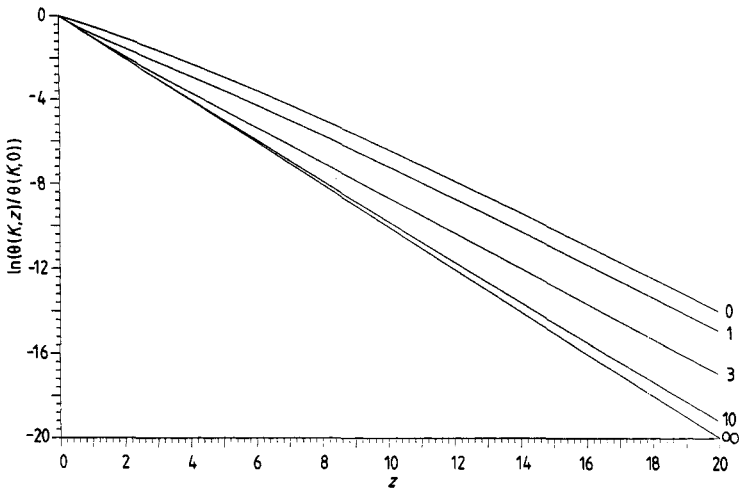

Figure 3. $\ln(\theta(K, z)/\theta(K, 0))$ as a function of z for fractal particles with $Kn \ll 1$. The value of K is shown against each plot.

1, 2, and 3 correspond respectively to limiting values of β in the intervals 0.7–0.8, 0.4–0.5 and 0.6–0.7.

A rather different picture is presented by the case of fractal structure with $Kn \gg 1$, where $\alpha + s > 1$. Here, as t increases from 0 to ∞, z increases from 0 to $K^2/0.62$ $(\alpha + s - 1 = 0.62)$, and we have therefore given in figure 4 graphs of $W = (0.62/K^2)\ln[\theta(K, z)/\theta(K, 0)] = (0.62/K^2)\{-z + \ln[\sigma(K, z)]\}$ as a function of $w = 0.62z/K^2$ for different values of K. For each finite value of K, W initially decreases before passing through a minimum and then increasing towards a certain value as $w \to 1$. This is in agreement with the discussion after equations (40) which predicted just this type of behaviour with the effect of mechanism B being such as to eventually reverse the initial direction of diffusive flux, and it is seen that this reversal is greatest
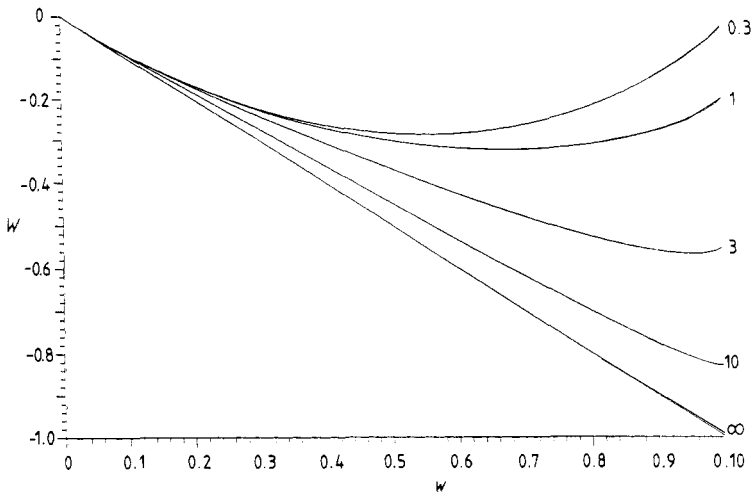
Figure 4. $W = (0.62/K^2) \ln((K, z)/\theta(K, 0))$ as a function of $w = (0.62/K^2)z$ for fractal particles with $Kn \gg 1$. The value of K is shown against each plot.

for low values of K, becoming progressively weaker as K increases. It should be noticed that, despite this reversal, $\theta(K, z)$ never reaches its initial value $\theta(K, 0)$, and hence this effect cannot give rise to greater localisation of particulate matter than existed initially. However, as $t \to \infty$ the limiting value of $\theta(z)/\theta(0)$ can be substantially greater than it would have been in the absence of mechanism B. Thus, if we let $\theta(K^2/0.62)/\theta(0) = \exp(-z)$ and $\exp(-\beta z)$ in the absence and presence respectively of mechanism B, we find that for $K = 3.0$, 1.0 and 0.3, the values of β are respectively 0.54, 0.19 and 0.02.

6. Numerical values

In this section we consider numerical estimates of the effects calculated above, primarily in order to assess their importance in typical practical situations, but also with a view to deciding whether experimental measurements may be possible. We consider first the situation where $\alpha + s < 1$ (that is, particles with a compact structure, or fractal structure in the regime $Kn \ll 1$), and it is clear from figures 1, 2 and 3 that the proportional effect of mechanism B will increase as z increases. If we assume that initially $\theta(K) \lesssim 0.2$ (for the linear approximation to be valid), it is reasonable (on the basis of equation (42) and the subsequent comments) to expect experimental measurements to be possible up to a value for z of about 3 and we therefore take $z = 3$ in the present discussion. Further, the effect of mechanism B will be maximised by choosing as small a value as possible for K, but here there is an important constraint arising from the relation

$$z = \left(\frac{K^2}{1 - \alpha - s}\right)\{[\overline{V^*(\tau)}]^{1-\alpha-s} - 1\} \tag{43}$$

which follows from equations (24) and (30). For given z, the value of K will be minimised by choosing $V^*(\tau)$ as large as possible, but there exist limits on $V^*(\tau)$ arising from the fact that throughout the particle's growth it must lie entirely in one

regime—either $Kn \ll 1$ or $Kn \gg 1$. For the regime $Kn \ll 1$, we take the minimum effective particle radius as 2×10^{-5} cm (following Simons (1986a), since the molecular mean free path for air is about 7×10^{-6} cm) and the maximum radius as 10^{-4} cm, since for larger particles differential sedimentation will modify particle coagulation. For the regime $Kn \gg 1$, we take the minimum radius as 10^{-6} cm, since this is the radius of a typical elementary smoke spherule, and the maximum radius as 2×10^{-6} cm in view of the magnitude of the molecular mean free path (Simons 1987a). For each of the regimes under consideration it is then possible to obtain from equation (43) the minimum value (K_{min}) that K can take, together with the corresponding value of τ from equation (24). Finally, if we then choose a value for ϕ_0, equations (16a) and (37) can be used to give values of t and k. The results of this approach are shown in table 2, where for each of the regimes under consideration the values are given of t and λ ($=2\pi/k$) corresponding to $z = 3$, the relevant K_{min} and a specified ϕ_0. For other ϕ_0 the values of t and λ are readily obtainable since $t \propto \phi_0^{-1}$ and $\lambda \propto \phi_0^{-1/2}$. We also tabulate the value of $\sigma(K_{min}, 3)$ which gives for $K = K_{min}$ and $z = 3$ the ratio of the value of ϕ' (see equation (25)) to what it would have been in the absence of mechanism B.

Table 2. The values of K_{min} and $\sigma(K_{min}, z)$ for $z = 3$, together with the values of λ and t for the stated ϕ_0. Results are given for compact and fractal structure particles in the regimes $Kn \ll 1$ and $Kn \gg 1$.

	K_{min}	ϕ_0	λ (mm)	t	$\sigma(K_{min}, 3)$
(a) Compact structure					
$Kn \ll 1$	0.29	2×10^{-7}	4	17 h	2.2
$Kn \gg 1$	1.10	10^{-11}	14	35 min	2.8
(b) Fractal structure					
$Kn \ll 1$	0.72	7×10^{-10}	4	20 h	2.7
$Kn \gg 1$	1.86	3×10^{-12}	16	37 min	2.9

We now deal with the case of particles with a fractal structure in the regime $Kn \gg 1$, where $\alpha + s > 1$. Perhaps the main point of interest here is to consider whether the time interval during which ϕ' increases with time is accessible. We see from the graphs in figure 4 that for this interval to be accessible we require $w = [(\alpha + s - 1)/K^2]z$ to be able to significantly exceed 0.5, while from equations (24) and (30), we have

$$w = 1 - [\overline{V^*}(\tau)]^{-(\alpha + s - 1)}. \tag{44}$$

As explained above, we take the minimum and maximum particle radii in this regime to be 10^{-6} and 2×10^{-6} cm respectively, and assuming the fractal dimension to be 1.8, we then obtain from equation (44) that the maximum value of w is 0.54. This suggests that there is little likelihood of experimentally observing an increase in the spatial inhomogeneity of ϕ, unless particles can be produced with an initial radius significantly less than 10^{-6} cm. As regards estimating the effect of mechanism B, we can combine the minimum and maximum radii given above with the value of $z = 3$ to yield a value for K_{min} and hence to complete the entries in table 2 for a fractal structure in the regime $Kn \gg 1$.

Finally, we consider the feasibility of making experimental measurements of the effects discussed in this paper. Practically there are difficulties: firstly, in setting up

an experimental arrangement in which the physical parameters characterising the aerosol are accurately known; secondly, in ensuring that particle transport is due solely to diffusion without any contribution from convective or turbulent motion of the air; and, thirdly, in the measurement of ϕ. If these experimental difficulties could be overcome, it is clear that measurements of the spatial relaxation of aerosols could be of value both in elucidating the structure of aerosol particles and also in verifying the basic coagulation theory.

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