# Diffusive relaxation for a system of coagulating particles—interactions between the modes

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**Abstract.** A theoretical treatment is developed of the relaxation of a spatially inhomogeneous system of particles simultaneously undergoing diffusion and coagulation. It is shown in general that the effect of coagulation is such as to induce interactions between otherwise independent diffusive modes characterized by wavenumbers $k$ and $k'$, leading to the spontaneous creation of modes with wavenumber $K = k \pm k'$. The consequences of this are investigated quantatively for the situation when initially there exists a set of discrete modes, and numerical estimates are made of the effect.

## 1. Introduction

Consider a spatially inhomogeneous suspension of particles in a stationary fluid (aerosol or hydrosol). If the volume fraction of particulate matter $\varphi(r, t)$ 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

$$\frac{\partial \varphi}{\partial t} = D\nabla^2\varphi \tag{1}$$

where $D$ is the particle diffusion coefficient. On expressing $\varphi$ in the form

$$\varphi(r, t) = \int \varphi(k, t) \exp(ik \cdot r) \, dk \tag{2}$$

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

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

   The above description will remain true as long as the particles retain their individuality. However, the Brownian motion of the particles which causes them to diffuse will at the same time cause them to coagulate (Smoluchowski 1917), and the question then arises of what effect this will have on the simple diffusion picture outlined above. An initial attempt to tackle this problem was made by Simons and Simpson (1988) where it was shown that the time dependence of each Fourier component becomes modified due to the fact that the diffusion coefficient $D$ depends on the particle size, and thus changes as a result of coagulational growth, this change being greater in regions of greater $\varphi$ where growth is more rapid. The technique used by Simons and Simpson (1988) was to consider the solution of the equation governing

the number of particles as a function of position and time, taking into account both particle diffusion and coagulation in the formulation of the equation. However, in tackling the equation two approximations were used. The first was to assume a solution of the 'self-preserving' form (Friedlander and Wang 1966), and the second was to linearize the equation, corresponding to the situation where variations in $\varphi$ are small compared with the spatial mean value. With these approximations it was then shown that Fourier components of $\varphi$ decay independently with modified time dependence as outlined above.

The purpose of this paper is to consider afresh the equation governing the number of particles in the presence of both particle diffusion and coagulation, without making the above approximations. The main new result that emerges is that Fourier components of the particle number do not now decay independently. Rather, if at some time there exist Fourier components characterized by the wavenumbers $k$ and $k'$, then, with the passage of time, these will produce a new component with wavenumber $K$, given by

$$K = k \pm k'. \tag{4}$$

The production of this new component is a consequence of the quadratic form of the coagulation term in the equation, and the rate at which it is produced is proportional to the product of the number of particles in each of the $k$ and $k'$ modes. One important consequence of this concerns the situation when $|k - k'| \ll |k|$ or $|k'|$. Since the damping of each mode follows equation (3), at least approximately, the possibility exists of the created mode $K$ having a significantly greater lifetime than those of the modes $k$ and $k'$ which were initially present, and hence of the mode $K$ becoming the predominant mode after a sufficiently long time; this will be discussed in more detail in section 2. Another consequence of equation (4) is that if initially there was present only a single Fourier component $k$, then with the passage of time components with wavenumber $lk$, for any integer $l$, will be created.

## 2. Basic formulation

Consider an infinite volume of fluid, and let $n(v, r, t)\,dv$ be the number of particles with volumes lying between $v$ and $v + dv$ per unit volume of fluid at position $r$ and time $t$. Then the general equation governing $n$ takes the form

$$\frac{\partial n}{\partial t} = D(v)\nabla^2 n + \left(\frac{\partial n}{\partial t}\right)_{\text{coag}} \tag{5a}$$

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

$$\left(\frac{\partial n}{\partial t}\right)_{\text{coag}} = \tfrac{1}{2}\int_0^v P(u, v-u)n(u)n(v-u)\,du - n(v)\int_0^\infty P(u, v)n(u)\,du \tag{5b}$$

where $P(u, v)$ is the kernel describing the coagulation.

We begin by non-dimensionalizing equation (5a); to do this we define

$$T = t/\tau \qquad R = r/\mathscr{L}$$
$$U = u/W \qquad V = v/W \qquad N = \theta^2 n \tag{6}$$

where $\tau$ and $\mathscr{L}$ have the dimensions of time and length respectively while $W$ and $\theta$ both have the dimensions of volume. For all situations of interest (see Simons and Simpson 1988)

$$D(v) = \mu v^{-s} \tag{7a}$$

$$P(u, v) = \sigma G(u, v) \tag{7b}$$

where $\mu$ and $\sigma$ are physical constants and $G(u, v)$ is a homogeneous function of $u$ and $v$ with degree $\alpha$ satisfying

$$G(1, 1) = 1. \tag{7c}$$

We suppose $\alpha$ to be sufficiently small for gelling phenomena not to occur. On transforming equation $(5a)$ to the non-dimensional variables defined in equations (6), and imposing the conditions

$$\frac{\tau\mu}{W^s \mathscr{L}^2} = 1 = \frac{W^{1+\alpha}\tau\sigma}{\theta^2} \tag{8}$$

we find that equation $(5a)$ takes the form

$$\frac{\partial N}{\partial T} = V^{-s}\nabla_R^2 N + F[N, N] \tag{9}$$

where the operator $F$ is defined by

$$F[X, Y] = \tfrac{1}{2} \int_0^V G(U, V-U) X(U) Y(V-U) \, dU - X(V) \int_0^\infty G(U, V) Y(U) \, dU. \tag{10}$$

The basic technique we use to tackle equation (9) is to make a spatial Fourier analysis of the function $N(V, R, T)$, so we therefore express $N$ in the form

$$N(V, R, T) = \int M_k(V, T) \exp(ik \cdot R) \, dk \tag{11}$$

where the integration is taken over the whole of $k$ space. Since $N$ is real, $M$ must satisfy the condition

$$M_{-k}(V, T) = M_k^*(V, T). \tag{12}$$

It then readily follows from equations (9) and (11) that $M$ satisfies the relation

$$\frac{\partial M_K}{\partial T} + K^2 V^{-s} M_K = \int F[M_k, M_{K-k}] \, dk. \tag{13}$$

Equation (13) is the basic equation describing the combined effect of particle diffusion and coagulation; it yields a unique solution for $M_K(V, T)$ when supplemented by the value of $M_K(V, 0)$.

In the absence of coagulation the right-hand side of equations (13) is zero and the resulting equations are then uncoupled for all $V$ and $K$, leading to the usual exponential decay solutions. In the presence of coagulation, however, the existence of a non-zero right-hand side means that the equations (13) are coupled together for all $V$ and $K$ and this, of course, vastly complicates their solutions. We may note, however, that if equation (13) is multiplied by $V$ and then integrated with respect to $V$ from 0 to $\infty$, it follows from a standard result concerning the operator $F$ (Drake 1972) that the

right-hand side becomes zero. Equating the left-hand side to zero then gives the differential equation for the mass density $\varphi_K(T) = \int_0^\infty VM_K(V, T) \, dV$:

$$\frac{d\varphi_K}{dT} = -K^2 \int_0^\infty V^{1-s} M_K \, dV. \tag{14}$$

Finally, we note that if the function $N(V, R, T)$ is expressed as a sum over discrete modes of the form

$$N(V, R, T) = \sum_q M_{k_q}(V, T) \exp(ik_q \cdot R) \tag{15a}$$

(with $M_{-k_q}(V, T) = M_{k_q}^*(V, T)$) then it is readily shown that the analogue of equation (13) is

$$\frac{\partial M_K}{\partial T} + K^2 V^{-s} M_K = \sum_{k_q} F[M_{k_q}, M_{K-k_q}]. \tag{16}$$

It is worth pointing out at this stage that equation (15a) may be equivalently expressed in the real form

$$N(V, R, T) = 2 \sum_q' |M_{k_q}(V, T)| \cos[k_q \cdot R + \beta_{k_q}(V, T)] \tag{15b}$$

where $\beta \equiv \arg M$ and $\Sigma_q'$ implies a summation over all $k_q$ with positive component in a specified direction. It follows that $2|M_{k_q}|$ represents the actual number of particles in the real mode specified by $k_q$.

Before proceeding in the next section to a quantitative discussion of equations (13) and (16), we consider now some qualitative implications of these equations. Suppose that at some time $t$ there exists spatial sinusoidal variations in $N$ characterized by wavenumbers $k$ and $k'$; by reference to equation (15a) there will be non-zero $M$'s with subscript $\pm k, \pm k'$. In equation (16) the wavenumber appearing on the left-hand side is the sum of the wavenumbers on the right-hand side and hence there will be a non-zero right-hand side for $K = k \pm k'$. The structure of the equation shows that this non-zero right-hand side will act as a source term for $M_{k\pm k'}$, and thus, even if this $M$ is initially zero, it will become non-zero with the passage of time corresponding to the *creation of a new Fourier component of $N$ with wavenumber $K$* given by equation (4). An interesting general consequence of this concerns the situation when $K = |k \pm k'|$ is much less than $k$ or $k'$. We first note that $\int_0^\infty VM_k \, dV$ and $\int_0^\infty M_k \, dV$ are both finite, assuming that at $t = 0$, $\int_0^\infty n \, dv$ is finite. It follows that since $0 \le 1 - s \le 1$ in all cases of interest (see Simons and Simpson 1988), $\int_0^\infty V^{1-s} M_k \, dV$ is finite for all $K$; hence as $K \to 0$, the right-hand side of equation (14) tends to zero. Thus for sufficiently small $K$, the rate of decay of $\varphi_K$ will be less than that of $\varphi_k$ or $\varphi_{k'}$. Hence the possibility exists of the created mode $K$ having a greater lifetime than $k$ or $k'$, thus becoming the predominant mode after a sufficiently long time. One consequence of this concerns the situation where initially there exists a finite wavetrain of length $s(\gg \lambda = 2\pi/k)$. The Fourier analysis of this gives a continuous spectrum of wavenumbers, centred on $k$ and with width $\Delta k \sim s^{-1}(\ll k)$. The above discussion shows that with the passage of time new wavenumbers will be generated forming a continuous distribution in the neighbourhood of $K \approx \Delta k$, and corresponding to a wavelength $\lambda' \approx 2\pi/K \approx 2\pi s$. For $s \gg \lambda$, $K \ll k$ and hence these created modes may possess a much greater lifetime than the original wavetrain from which they were produced.

## 3. Development for a discrete spectrum

In order to develop the above approach quantitatively we now consider the situation where initially the spatial variation of $N$ is a linear combination of $n$ sinusoidal variations characterized by wavenumbers $p_1, p_2, \ldots, p_n$. Additionally there must exist a suitable spatially constant distribution for $N$ to be positive everywhere, and thus, in terms of equation (15a), the only non-zero $M$'s at $t = 0$ are those with subscripts $0, \pm p_1, \pm p_2, \ldots \pm p_n$. The discussion in the last section shows that these modes will interact to create new modes with wavenumbers of the form $p_r \pm p_q$ $(1 \leq r, q \leq n)$, and these will then interact further with each other leading in due course to the generation of modes with wavenumbers $K$ of the form

$$K_{l_1, l_2, \ldots, l_n} = \sum_{q=1}^{n} l_q p_q \qquad (17)$$

where $l_q$ $(1 \leq q \leq n)$ can take all positive and negative integer values. The set of quantities $l \equiv (l_1, l_2, \ldots, l_n)$ define a lattice in $n$-dimensional $l$ space, and if we use $M_l$ to denote $M$ with subscript $K_{l_1, l_2, \ldots, l_n}$, equation (16) takes the form

$$\frac{\partial M_l}{\partial T} + K^2 V^{-s} M_l = \sum_{m_1, \ldots, m_n = -\infty}^{\infty} F[M_m, M_{l-m}]. \qquad (18)$$

These equations are to be supplemented by the given initial conditions on $M$ at $t = 0$. To specify these, it is convenient to introduce $\pm L_r$ $(1 \leq r \leq n)$ to denote the $2n$ unit lattice vectors in $l$ space (given by $L_r = l$ with $l_r = +1$ and $l_q = 0$ $(q \neq r)$), together with $0$ to denote the null vector. Then the waves originally present correspond to $l = 0$ (the spatially constant distribution) and $l = \pm L_r$ $(1 \leq r \leq n)$ (the set of given sinusoidal waves). The initial conditions on $M$ are thus

$$M_l(V, 0) = 0 \qquad (l \neq 0, \pm L_r).$$

$M_0(V, 0)$ and $M_{\pm L_r}(V, 0)$ take specified non-zero values.

Equations (18) constitute an $n$-fold infinite set of nonlinear differential equations, and as such it is clear that little progress can be made with obtaining a general solution. Our approach is therefore to investigate whether any general properties of the $M$'s will allow a significant simplification in equations (18), and to do this we begin by looking for a power series expansion in $T$ of $M_l(V, T)$ of the form

$$M_l(V, T) = \sum_{s=0}^{\infty} C_{ls}(V) T^s \qquad (19a)$$

where

$$C_{ls} = (1/s!)[\mathrm{d}^s M_l(V, T)/\mathrm{d} T^s]_{T=0} \qquad (s \geq 1)$$
$$= M_l(V, 0) \qquad (s = 0). \qquad (19b)$$

This approach is motivated jointly by the possibility of differentiating equation (18) repeatedly to calculate $C_{ls}$ together with the fact that at $t = 0$, $M_l = 0$ except for $l = 0$, $\pm L_r$ $(1 \leq r \leq n)$. It may then be proved by induction that the leading non-zero term in the expansion (19a) is the one with $s = \sum_{q=1}^{n} |l_q| - 1$ $(l \neq 0)$; details are given in the appendix. This implies that initially $M$ increases more slowly with $T$ as the number of unit steps required to reach the lattice point $l$ from $0$ increases. This is to be expected physically since more steps to reach $l$ correspond to more interactions having to occur in order to create a mode with the corresponding $K$.

An important application of the above approach is in showing how $M_l(V, T)$ scales with the strength of the initial departure from spatial homogeneity for the case where this is small. Let us suppose that at $t = 0$

$$M_{\pm L_r}(V, 0) = \varepsilon_r J_{\pm r}(V) \qquad (1 \le r \le n) \qquad (20a)$$

where $J_{\pm r}$ is chosen so that

$$\left| \int_0^\infty J_{\pm r}(V) \, \mathrm{d}V \right| = \tfrac{1}{2} \int_0^\infty M_0(V, 0) \, \mathrm{d}V \qquad (1 \le r \le n). \qquad (20b)$$

The physical significance of equation (20b) is that $\varepsilon_r$ then equals the ratio of the initial total number of particles in each real relaxation mode to the initial total number in the spatially constant mode. We investigate in the appendix how the non-zero $C_{ls}$ depend on $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n$. The main result that emerges is that although the dependence of $C$ on the $\varepsilon$'s can be very complicated, depending on $s$, the leading term in $C_{ls}$ for small $\varepsilon$ scales with the $\varepsilon$'s as

$$\varepsilon_1^{|l_1|} \varepsilon_2^{|l_2|} \ldots \varepsilon_n^{|l_n|}. \qquad (21)$$

Since this is independent of $s$ it follows that for sufficiently small $\varepsilon$, $M_l$ will itself scale in this way. Scaling by this expression (21) is essentially the result of implementing a linearization-type procedure for the present situation whereby only the leading term is retained in an expansion of the $M$'s in terms of the $\varepsilon$'s. The fact that the power of $\varepsilon_r$ in expression (21) increases as $|l_r|$ increases follows from the quadratic nature of the right-hand side of equation (18) together with the larger number of interactions required to create a mode with greater $|l_r|$.

We now restrict our attention to the case of small $\varepsilon$ where $M_l$ scales according to the expression (21). We let

$$M_l = \varepsilon_1^{|l_1|} \varepsilon_2^{|l_2|} \ldots \varepsilon_n^{|l_n|} Q_l \qquad (22)$$

and introduce $Q_l$ into equation (18) retaining only terms of lowest power in the $\varepsilon$'s. On the right-hand side of equation (18), the power of $\varepsilon_p$ in $F[M_m, M_{l-m}]$ will be

$$A_p = |m_p| + |l_p - m_p|.$$

Now, if $m_p$ lies in the interval $[0, l_p]$, then $|l_p - m_p| = |l_p| - |m_p|$, while if $m_p$ lies outside this interval, $|l_p - m_p| > |l_p| - |m_p|$. Thus, if $m_p$ lies in the interval $[0, l_p]$, $A_p = |l_p|$, while if $m_p$ lies outside this interval, $A_p > |l_p|$. As we are currently retaining only the lowest power of $\varepsilon_p$ it follows that we need retain in the summation over $m_p$ only the contribution from $m_p$ within the interval $[0, l_p]$. The equation for $Q_l$ then takes the form

$$\frac{\partial Q_0}{\partial T} - F[Q_0, Q_0] = 0 \qquad (23a)$$

$$\frac{\partial Q_l}{\partial T} + K^2 V^{-s} Q_l - (F[Q_0, Q_l] + F[Q_l, Q_0]) = \sum_{m_1, \ldots m_n} F[Q_m, Q_{l-m}] \qquad (l \ne 0) \qquad (23b)$$

where the summation in equation (23b) now involves $m_p$ lying within the interval $0 \le m_p \le l_p$ for $l_p > 0$ and within the interval $l_p \le m_p \le 0$ for $l_p < 0$, with the exception of $m_p = 0$ (all $p$) and $m_p = l_p$ (all $p$). (These omitted terms are shown explicitly on the left-hand side of equation (23b).) Corresponding to equation (20a), the boundary condition on $Q$ is now

$$Q_{\pm L_r}(V, 0) = J_{\pm r}(V). \qquad (23c)$$

The change in the limits of the summation in equation (23*b*) as compared with equation (18) renders the former much easier to tackle for three reasons: firstly because the summation now involves only a finite number of terms rather than the *n*-fold infinite number that existed before; secondly, as a consequence of the fact that both $|m_p|$ and $|l_p - m_p|$ can never exceed $|l_p|$ the equations (23*b*) may be solved sequentially allowing a single component of *l* to increase by unity at each stage—in much the same way as a set of linear algebraic equations may be solved sequentially if the corresponding matrix is triangular; thirdly, in the implementation of this approach, the equation for $Q_l$ obtained at each stage is linear, except for $l = \mathbf{0}$.

Although the above derivation of equation (23*b*) has been given only for small $\varepsilon$'s, the equation will in fact be valid for all $\varepsilon$'s in the limit of small *T*. This follows from the fact that the omitted terms exhibit a higher power dependence on *T* than those which have been retained, as is readily seen from the result given earlier on the leading non-zero term in $M_l(V, T)$ for small *T*.

The above results clearly simplify when $n = 1$ corresponding to the existence initially of a single mode characterized by wavenumbers $\pm p$. The created modes then have wavenumbers $\mathbf{K} = l\mathbf{p}$ $(-\infty \leqslant l \leqslant +\infty)$, and equation (23*b*) takes the form

$$\frac{\partial Q_l}{\partial T} + l^2 p^2 V^{-s} Q_l - (F[Q_0, Q_l] + F[Q_l, Q_0]) = \sum_{m=1}^{l-1} F[Q_m, Q_{l-m}] \qquad (l > 1) \qquad (24)$$

and the same left-hand side with zero on the right-hand side when $l = 1$. We note that the approach used by Simons and Simpson (1988) for investigating the effect of coagulation on a single Fourier component was essentially through the approximate solution of equation (24) for the case of $l = 1$.

## 4. Constant diffusion coefficient *D* and coagulation kernel *P*

In general, both the diffusion coefficient *D* and the coagulation kernel *P* are functions of the particle volume *v*, the precise form of the functional relationship depending on the structure of the particle (compact or fractal) and on the value of *Kn*, the ratio of gas molecular mean-free path to particle size—see Simons (1988) for further details. As a result of this it is necessary to use numerical techniques in order to solve equations (23) accurately, and it is intended to follow this up in later work. Meanwhile, however, it was considered worthwhile tackling these equations under the assumption that both *D* and *P* are constant, independent of particle volume, as with this assumption analytic solutions can be obtained. This assumption of constant *P* and *D* is expected to give a reasonable, semi-quantitative description of the real situation since for the latter in the regime $Kn \ll 1$ both *P* and *D* are functions which vary relatively slowly with their respective variables as both are homogeneous functions of those variables with degree of homogeneity being respectively 0 and $\frac{1}{3}$. A further reason for exploring this option of constant *P* and *D* is that analytic solutions are very useful for validating computer programs designed to solve the equations with the correct volume-dependent *P* and *D*.

We begin by considering equations (23*b*) where, with the present assumption of constant *P* and *D*, $s = 0$, and

$$F[X, Y] = \tfrac{1}{2} \int_0^V X(U) Y(V - U) \, dU - X(V) \int_0^\infty Y(U) \, dU \qquad (25)$$

since $G = 1$. We now proceed to calculate $\mu_l$ the total number of particles in the Fourier component $e^{i\mathbf{K}\cdot\mathbf{R}}$ characterized by $l$. From equation (22), this is given by

$$\mu_l = \varepsilon_1^{|l_1|}\varepsilon_2^{|l_2|}\ldots\varepsilon_n^{|l_n|}q_l \tag{26a}$$

where

$$q_l(T) = \int_0^\infty Q_l(V, T)\,\mathrm{d}V. \tag{26b}$$

Integrating equations (23a, b) with respect to $V$ from 0 to $\infty$ then yields the following equation for $q_l$:

$$\frac{\partial q_0}{\partial T} + \tfrac{1}{2}q_0^2 = 0 \tag{27a}$$

$$\frac{\partial q_l}{\partial T} + (K^2 + q_0)q_l = -\tfrac{1}{2}\sum_{m_1,\ldots,m_n} q_m q_{l-m} \qquad (l \neq 0) \tag{27b}$$

where the $m$ summation is over the same interval as in equation (23). Equation (27a) is the standard equation for a spatially homogeneous aerosol, with the solution

$$q_0(T) = \frac{q_0(0)}{1 + \tfrac{1}{2}q_0(0)T}. \tag{28}$$

We now consider equation (27b) for the case where $l$ is a unit-lattice vector $\pm L_r$ (thus corresponding to one of the waves originally present in the aerosol) for which the right-hand side of the equation (27b) is zero. Making the use of equation (28), we readily obtain the solution of equation (27b) in the form

$$q_{\pm L_r}(T) = \frac{q_{\pm L_r}(0)\exp(-p_r^2 T)}{[1 + \tfrac{1}{2}q_0(0)T]^2}. \tag{29}$$

The exponential term in the numerator corresponds to the usual diffusive loss of particulate material due to relaxation, while the term in the denominator corresponds to the decrease in particle number arising from coagulation. We now consider the solution of equation (27b) when $l = L_r + L_s$; this of course corresponds to the simplest type of interaction of the waves originally present in the aerosol, with $K_l = p_r + p_s$. For $L_r \neq L_s$ the solution is

$$q_l(T) = \frac{-q_{L_r}(0)q_{L_s}(0)\exp(-K_l^2 T)}{[1 + \tfrac{1}{2}q_0(0)T]^2}\int_0^T \frac{\exp[2(p_r\cdot p_s)\tau]\,\mathrm{d}\tau}{[1 + \tfrac{1}{2}q_0(0)\tau]^2} \tag{30}$$

while when $L_r = L_s$ there is an additional factor of $\tfrac{1}{2}$ on the right-hand side. We simplify equation (30) by defining

$$\begin{aligned}
x &= \tfrac{1}{2}q_0(0)\tau & z &= \tfrac{1}{2}q_0(0)T \\
\alpha &= 4(p_r\cdot p_s)/q_0(0) & \beta &= 2(p_r + p_s)^2/q_0(0)
\end{aligned} \tag{31}$$

and thus obtain

$$q_l(z) = \left[\frac{-2q_{L_r}(0)q_{L_s}(0)}{q_0(0)}\right]F(\alpha, \beta, z) \tag{32a}$$

where

$$F(\alpha, \beta, z) = \frac{\exp(-\beta z)}{(1 + z)^2}\int_0^z \frac{\exp(\alpha x)\,\mathrm{d}x}{(1 + x)^2}. \tag{32b}$$

If $L_r = L_s$ the factor 2 in equation (32a) is omitted. Evaluating the integral in equation (32b) gives:

if $\alpha = 0$

$$F(0, \beta, z) = z \exp(-\beta z)/(1+z)^3 \tag{33a}$$

if $\alpha > 0$

$$F(\alpha, \beta, z) = \frac{\exp(-\beta z)}{(1+z)^2} \left\{ 1 - \frac{\exp(\alpha z)}{1+z} + \alpha \exp(-\alpha)[E_i[\alpha(1+z)] - E_i(\alpha)] \right\} \tag{33b}$$

if $\alpha < 0$

$$F(\alpha, \beta, z) = \frac{\exp(-\alpha - \beta z)}{(1+z)^2} \left\{ E_2(-\alpha) - \frac{E_2[-\alpha(1+z)]}{1+z} \right\} \tag{33c}$$

where the exponential integrals $E_i(x)$ and $E_2(x)$ are defined for $x > 0$ by

$$E_i(x) = P \int_{-\infty}^{x} \frac{e^t}{t} \, dt \qquad E_2(x) = \int_{1}^{\infty} \frac{e^{-xt}}{t^2} \, dt$$

with $P$ denoting the principal part (Abramowitz and Stegun 1965). We now express the total number of particles $\nu(\mathbf{R}, T) = \int_0^\infty N(V, \mathbf{R}, T) \, dV$ in the real form

$$\nu(\mathbf{R}, T) = \sum_l' \mathcal{N}_l(T) \cos[\mathbf{K}_l \cdot \mathbf{R} + \gamma_l(T)] \tag{34}$$

where $\sum_l'$ implies a summation over all $\mathbf{K}_l$ with positive component in a specified direction. It is then readily shown that $\gamma_l = \arg q_l$ and that

$$\mathcal{N}_l(T) = 2\varepsilon_1^{|l_1|}\varepsilon_2^{|l_2|} \ldots \varepsilon_n^{|l_n|}|q_l(T)| \qquad (l \neq 0) \tag{35a}$$

$$\mathcal{N}_0(T) = q_0(T). \tag{35b}$$

It is clear that $\mathcal{N}_l$ represents physically the total particle-number density in the real mode specified by $\mathbf{K}_l$. Equations (28), (29) and (32a) then yield

$$\mathcal{N}_0(z)/\mathcal{N}_0(0) = 1/(1+z) \tag{36a}$$

$$\mathcal{N}_{L_r}(z)/\mathcal{N}_0(0) = \varepsilon_r(1+z)^{-2} \exp(-bz) \tag{36b}$$

$$\mathcal{N}_l(z)/\mathcal{N}_0(0) = \varepsilon_r\varepsilon_s F(\alpha, \beta, z) \tag{36c}$$

where $b = 2p_r^2/q_0(0)$; if $L_r = L_s$ the right-hand side of equation (36c) is halved. We can use these results to illustrate the point made earlier that if $K_l < K_{L_r}$ and $K_{L_s}$ then as a consequence of the lifetime of the $l$ mode possibly becoming greater than that of the $L_r$ or $L_s$ modes, the value of $\mathcal{N}_l$ may eventually exceed that of $\mathcal{N}_{L_r}$ or $\mathcal{N}_{L_s}$. To show this explicitly we note that equations (36b, c) imply that

$$\mathcal{N}_l(z)/\mathcal{N}_{L_r}(z) = \varepsilon_s(1+z)^2 \exp(bz) F(\alpha < 0, \beta, z)$$

$$> \varepsilon_s \left[ \frac{\exp[(b-\beta)z]}{2-\alpha} - \frac{\exp(-b'z)}{(1+z)[1-\alpha(1+z)]} \right] \tag{37}$$

(where $b' = 2p_s^2/q_0(0)$) on using the explicit form (33c) for $F$, together with the inequality $(x+2)^{-1} < \exp x E_2(x) < (x+1)^{-1}$ (Abramowitz and Stegun 1965). Since we are currently taking $b > \beta$ (corresponding to $K_l < K_{L_r}, K_{L_s}$), it follows that for sufficiently large $z$, $\mathcal{N}_l(z)$ will exceed $\mathcal{N}_{L_r}(z)$.

Finally we make a rough estimate of the magnitude of $\mathcal{N}_t/\mathcal{N}_0$. Let $R$ be the mean particle radius, $\varphi$ the proportion of space occupied by the particulate matter and $\lambda_r$ the wavelength corresponding to the dimensionless wavenumber $p_r$. It then readily follows from previous work that

$$b = \left(\frac{2\pi^2}{3}\right)\left(\frac{R}{\lambda_r}\right)^2 \frac{1}{\varphi} \qquad \text{and} \qquad z = \frac{k\theta\varphi t}{\pi\eta R^3}$$

where $\theta$ and $\eta$ are respectively the temperature and viscosity of the fluid. We suppose the latter to be air at room temperature, and take $\varphi = 5 \times 10^{-8}$, $R = 10^{-4}$ mm and $\lambda_r = \lambda_s = 2.5$ mm. For $t = 5$ min, this gives $b \approx 0.2$ and $z \approx 1$. It then follows from equations (33c), (36a, c) that for $\lambda_t > 5$ mm,

$$\mathcal{N}_t(1)/\mathcal{N}_0(1) \approx 0.2\varepsilon_r\varepsilon_s$$

and thus if $\varepsilon_r \sim \varepsilon_s \sim 0.3$, $\mathcal{N}_t(1)$ will be about 2% of $\mathcal{N}_0(1)$. It is clear that although it would be very difficult to make experimental measurements of the particle number in the induced mode $K_t$ such measurements could nevertheless provide very useful information on particle diffusion and coagulation.

## Acknowledgment

## Appendix

With $C_{lr}$ defined in equation (19b) we proceed to prove that

$(a)$ $\qquad$ $C_{lr} = 0$ $\qquad$ for $\sum\limits_{q=1}^{n} |l_q| > r+1$

$$r = 0, 1, 2, \ldots$$

$\qquad\qquad$ $C_{lr} \neq 0$ $\qquad$ for $\sum\limits_{q=1}^{n} |l_q| \leq r+1$

$(b)$ If $C_{00}$ is independent of the $\varepsilon_q$ and $C_{\pm Ls}$ is proportional to $\varepsilon_s$, then for all $C_{lr} \neq 0$, the leading term in $\varepsilon$'s in $C_{lr}$ is proportional to

$$\varepsilon_1^{|l_1|}\varepsilon_2^{|l_2|} \ldots \varepsilon_n^{|l_n|}.$$

*Proof of (a).* Denoting $\mathrm{d}^r M_l(V, T)/\mathrm{d}T^r|_{T=0}$ by $M_l^{(r)}$ we obtain, by repeated differentiation of equation (18)

$$M_l^{(r+1)} + K^2 V^{-s} M_l^{(r)} = \sum_{s=0}^{r} \beta_{rs} \sum_{m_1,\ldots,m_n=-\infty}^{\infty} F[M_m^{(s)}, M_{l-m}^{(r-s)}] \qquad (A1)$$

for suitable non-zero constants $\beta_{rs}$. We now develop an inductive proof, assuming the proposition that $M_l^{(r)} \neq 0$ for $\sum_{q=1}^{n} |l_q| \leq r+1$ and $M_l^{(r)} = 0$ for $\sum_{q=1}^{n} |l_q| > r+1$ to hold for $r \leq k$, and proceed to show that it remains true for $r = k+1$.

Concerning the $M$ terms appearing on the right-hand side of equation (A1), it follows from the inductive hypothesis that

$$M_m^{(s)} \neq 0 \qquad \text{if} \qquad \sum_{q=1}^n |m_q| \leq s+1 \qquad (A2a)$$

$$M_m^{(s)} = 0 \qquad \text{if} \qquad \sum_{q=1}^n |m_q| > s+1 \qquad (A2b)$$

$$M_{l-m}^{(k-s)} \neq 0 \qquad \text{if} \qquad \sum_{q=1}^n |l_q - m_q| \leq k-s+1 \qquad (A3a)$$

$$M_{l-m}^{(k-s)} = 0 \qquad \text{if} \qquad \sum_{q=1}^n |l_q - m_q| > k-s+1. \qquad (A3b)$$

For the right-hand side of equation (A1) to give a non-zero contribution to $M_l^{(k+1)}$ there must exist suitable non-zero terms in both $M_m^{(s)}$ and $M_{l-m}^{(k-s)}$. That is, it must be possible to specify $m_q$ and $s$ ($\leq k$) so that the inequalities in (A2a) and (A3a) can hold simultaneously. Now, if $m_q$ lies in the interval $[0, l_q]$, $|l_q - m_q| = |l_q| - |m_q|$, while if $m_q$ lies outside this interval, $|l_q - m_q| > |l_q| - |m_q|$. To satisfy the inequality in (A3a) it is therefore necessary that the inequality

$$\sum_{q=1}^n (|l_q| - |m_q|) \leq k-s+1$$

should be satisfied, and adding this to the inequality (A2a) gives the following necessary condition for both to be satisfied

$$\sum_{q=1}^n |l_q| \leq k+2. \qquad (A4)$$

Thus if $\sum_{q=1}^n |l_q| > k+2$, no contribution to $M_l^{(k+1)}$ will arise from the right-hand side of equation (A1). Further, it follows directly from the inductive hypothesis that the second term on the left-hand side of equation (A2) will give no contribution to $M_l^{(k+1)}$ if $\sum_{q=1}^n |l_q| > k+1$, and thus if $\sum_{q=1}^n |l_q| > k+2$, $M_l^{(k+1)} = 0$. Further, for $\sum_{q=1}^n |l_q| \leq k+1$ the second term on the left-hand side of the equation (A2) will ensure that $M_l^{(k+1)} \neq 0$, and it therefore only remains to show that when $\sum_{q=1}^n |l_q| = k+2$, $m_q$ and $s$ can be specified to simultaneously satisfy inequalities (A2a) and (A3a). To do this we choose $m_q$ to lie in the interval $[0, l_q]$, when inequality (A3a) becomes equivalent to $\sum_{q=1}^n |l_q| - \sum_{q=1}^n |m_q| \leq k-s+1$ and thus, since $\sum_{q=1}^n |l_q| = k+2$, this is equivalent to $\sum_{q=1}^n |m_q| \geq s+1$. This can be satisfied at the same time as (A2a), if, and only if, we choose $m_q$ so that $\sum_{q=1}^n |m_q| = s+1$. This will have solutions for $m_q$ lying in the interval $[0, l_q]$ for all $s$; these will automatically satisfy the only other constraint on $m_q$, that $\sum_{q=1}^n |m_q| \leq \sum_{q=1}^n |l_q| = k+2$ since $s \leq k$. This completes the proof that if the inductive hypothesis holds for $r \leq k$, it will also hold for $r = k+1$. Now, the hypothesis is true for $k = 0$ where the only non-zero $M_l$ are those for which $\sum_{q=1}^n |l_q| \leq 1$. Hence it is true for all positive integers $r$.

*Proof of (b).* Here again we use an inductive proof, assuming the proposition that the leading term involving $\varepsilon$'s in non-zero $M_l^{(r)}$ is proportional to $\varepsilon_1^{|l_1|} \varepsilon_2^{|l_2|} \ldots \varepsilon_n^{|l_n|}$ to hold for $r \leq k$. We then proceed to show that it remains true for $r = k+1$.

With reference to equation (A1), it is clear from the inductive hypothesis that the proposition will hold for the contribution to $M_l^{(r+1)}$ arising from the second term on

the left-hand side. Regarding the right-hand side, a non-zero contribution to $M_l^{(r+1)}$ will be given by suitable non-zero $M_m^{(s)}$ and $M_{l-m}^{(r-s)}$, and making use of the inductive hypothesis the leading term in $\varepsilon$'s arising from these will be proportional to

$$\prod_{q=1}^{n} \varepsilon_q^{|m_q|+|l_q-m_q|}. \tag{A5}$$

Now as pointed out earlier $|l_q - m_q| \geq |l_q| - |m_q|$, the equality sign corresponding to $m_q$ lying in the interval $[0, l_q]$. It follows from expression (A5) that the lowest power of $\varepsilon_q$ that arises on the right-hand side of equation (A1) is $|l_q|$, and hence if the proposition is true for $r \leq k$, it will also be true for $r = k + 1$. Now, when $r = 0$ the proposition is true for all non-zero $M$'s, since $M_0^{(0)}$ is independent of the $\varepsilon$'s, and $M_{\pm L_r}^{(0)}$ is proportional to $\varepsilon_r$. Hence the proposition is true for all positive integers $r$.

# References

Abramowitz H and Stegun I A 1965 *Handbook of Mathematical Functions* (New York: Dover)
Drake R L 1972 *Topics in Current Aerosol Research* (New York: Pergamon) p 201
Friedlander S K and Wang C S 1966 *J. Colloid Interface Sci.* **22** 126-32
Simons S and Simpson D R 1988 *J. Phys. A: Math. Gen.* **21** 3523-36
Smoluchowski M 1917 *Z. Phys. Chem., Lpz.* **92** 129-68