

Solute dispersion and weak second-order recombination at large times in parallel flow

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This work is concerned with the parallel-flow shear dispersion of a solute which undergoes a second-order recombination reaction. The primary goal of the work is to provide background theory for the determination of the coefficient of diffusion of reactive-gas-phase species. Approximations are sought for large time and weak combination. At first, dispersion dominates recombination, and a modification of the Chatwin (1970) asymptotic expansion gives the concentration distribution as a regular perturbation expansion in ϵ and $t^{-1/2}$, where ϵ is a dimensionless parameter characterizing recombination and t is dimensionless time. The regular expansion breaks down for dimensionless times t of $O(\epsilon^{-2})$ when dispersion and recombination are of the same importance. At these times, the governing equation is nonlinear and this regime is analysed by a numerical method. Finally, a similarity solution is derived for the concentration of solute when $\epsilon^2 t$ is large. Overall, the major effect of second-order recombination on dispersion is to flatten the peak of the dominant Gaussian concentration distribution. The speed of the centre of mass of the solute cloud is not affected at leading order by recombination.

1. Introduction

In a recent paper, Plumb, Ryan & Barton (1983) have accurately determined the coefficient of diffusion for a mixture of gases using Taylor's (1953) shear-dispersion theory for solutes injected into flowing solvent. A knowledge of diffusion coefficients for gas species is required for a variety of technological processes; and the work of Plumb *et al.* and Barton (1984*a*) is adequate for the case when the gaseous solute is chemically inert, or if it undergoes a first-order chemical reaction either within the flow or at the boundary. Other sorts of chemical reactions lead to hitherto unstudied complications of the dispersion process however. The present paper is concerned with just such a case encountered by Plumb & Ryan (private communication), specifically, when a gaseous solute undergoing shear dispersion also takes part in a second-order chemical reaction by recombining with itself. In this case, the familiar advection-diffusion equation for the concentration of solute is modified to include a nonlinear recombination term, and the established literature gives no results for the properties of the concentration distribution.

This paper is concerned with the shear dispersion in parallel flow of a solute which undergoes a weak recombination reaction. Mathematically, 'weak' means that the dimensionless reaction rate ϵ , defined in §2, is such that $0 < \epsilon \ll 1$. Five natural timescales may then be distinguished for dispersion from a δ function or other reasonably localized source:

- (a) $t \ll 1$, (b) t of $O(1)$, (c) $1 \ll t \ll \epsilon^{-2}$, (d) t of $O(\epsilon^{-2})$, (e) $1 \ll \epsilon^2 t$,

where t denotes dimensionless time (see §2). In regimes (a), (b) and (c), recombination effects represent a regular perturbation to the basic dispersion process. Regime (a) is not investigated in this paper, but could be handled by suitable modification of one of the analytical short-time approximations such as those of Chatwin (1977), Barton (1978) or Smith (1981*b*). Numerical procedures, such as those described by Barton & Stokes (1985), were developed for regime (b), but are not included in this paper.

Regime (c) requires quite complicated mathematical manipulations which are presented in some detail in §3. The theory involves a regular perturbation in ϵ of the Chatwin (1970) large-time approximation, and the results are useful provided $(Mt)^{\frac{1}{2}} \ll \epsilon^{-1}$ where M is a dimensionless constant. The key features of the solution are that recombination flattens the peak of the dominant (Gaussian) term of the concentration distribution, whilst not affecting at leading order the speed of the centre of mass of the solute cloud. All the constants involved in the theory for regime (c) could be determined, in principle, by matching onto the numerical results for regime (b) and by enforcing suitable behaviour on the perturbation solution. Regime (c) is important practically, and successful fits of the theory to data gathered by Plumb & Ryan (private communication) have been made (Barton 1984*b*). Unfortunately, Plumb & Ryan found it difficult to gather good experimental data when the process is dispersion-dominated with weak recombination; thus the data analysed in Barton (1984*b*) is not consistent enough to warrant open publication.

Regime (d) is concerned with times such that $(Mt)^{\frac{1}{2}}$ is of $O(\epsilon^{-1})$ when the problem becomes inherently nonlinear and the regular perturbation expansion derived in §3 breaks down. Standard singular-perturbation techniques were not able to analyse this regime, and it was therefore examined in §4 by applying a numerical method to the appropriately simplified form of the advection-diffusion-recombination equation (2.1*a*). The theory derived in §3 provides initial conditions for the numerical work of §4. The results for regime (d) are again simple and show that the mean speed of the solute cloud is unaffected, whilst there is a continued flattening of the peak of the concentration distribution by recombination. Numerical results for the total amount of solute remaining are presented in this section.

Finally, §5 is concerned with regime (e) in which $\epsilon^2 t$ is large. A similarity solution is applicable for these times, and it is shown that the two key parameters in the similarity solution could be determined by matching onto the numerical solution derived in §4. The general properties of the similarity solution are investigated briefly, and the specific determination of the key parameters is attempted but found to involve prohibitive amounts of computer time. Regime (e) is not relevant to the laboratory experiments which motivated the present work.

2. Mathematical preliminaries

The object of the paper is to investigate the large- t and small- ϵ behaviour of the solution $C(x, y, z, t, \epsilon, P)$ of the problem

$$\frac{\partial C}{\partial t} + Pu(y, z) \frac{\partial C}{\partial x} = \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] C - \epsilon C^2 \quad \text{in } \Omega, \quad (2.1a)$$

$$\hat{n} \cdot \nabla C = 0 \quad \text{at } \partial\Omega, \quad (2.1b)$$

$$C(x, y, z, 0, \epsilon, P) = C_0(x, y, z), \quad (2.1c)$$

$$C \text{ finite, } \left| x^n \frac{\partial C^m}{\partial x^m} \right| \rightarrow 0 \text{ for } m, n = 0, 1, 2, \dots \tag{2.1d}$$

These equations describe the behaviour of a cloud of soluble material undergoing a second-order recombination reaction whilst being dispersed in the parallel flow $(u(y, z), 0, 0)$ through the cross-sectional region Ω with boundary $\partial\Omega$. The problem has been written in dimensionless variables, and dimensional constants and variables (denoted by asterisks) may be recovered using the definitions

$$[x^*, y^*, z^*] = a^*[x, y, z], \tag{2.2a}$$

$$t^* = \frac{a^{*2}t}{\kappa^*}, \quad u^* = U^*u, \tag{2.2b}$$

$$C^* = \frac{Q^*C}{a^{*3}|\Omega|}, \quad \epsilon^* = \epsilon \left[\frac{\kappa^*}{a^{*2}} \right] \left/ \left[\frac{Q^*}{|\Omega|a^{*3}} \right] \right., \tag{2.2c}$$

where κ^* is the diffusion coefficient for the solute and solvent, U^* is the mean value of u^* over Ω^* , a^* is typical cross-sectional length, Q^* is the initial amount of solute, and $|\Omega|$ is the dimensionless cross-sectional area of the flow. The solute undergoes Fickian diffusion with dimensionless diffusive flux given by $-\nabla C$ and $P = U^*a^*/\kappa^*$ is the Péclet number of the flow. The inclusion of the factor $|\Omega|$ in the non-dimensionalization of C^* conveniently ensures that $\iiint C \, dV = |\Omega|$ initially, and the variable u has unit cross-sectional mean,

$$\bar{u} = \frac{1}{|\Omega|} \iint_{\Omega} u(y, z) \, dy \, dz = 1.$$

The term $-\epsilon C^2$ on the right-hand side of (2.1a) represents the effect of solute recombining with itself through a second-order reaction. It should be remarked that, if $\epsilon = 0$, a great deal is known about the asymptotic large-time properties of the solution of problem (2.1): in particular, Taylor (1953), Aris (1956), Gill & Sankarabramanian (1970), Chatwin (1970) and Smith (1981a) have presented successful asymptotic theories based on different approaches. Asymptotic theories also exist for reactive contaminant dispersion. For example, De Gance & Johns (1978a, b), Smith (1983) and Barton (1984a) examine the case when the no-diffusive-flux boundary condition (2.1b) is replaced by the following one describing (possibly catalysed) boundary reactions,

$$\hat{n} \cdot \nabla C = -\beta C \text{ at } \partial\Omega.$$

First-order reactions in the bulk of the flow are also known not to present mathematical difficulties (Barton 1984a). In contrast, very little is known about the effect of second-order reactions on contaminants undergoing shear dispersion.

It was pointed out in the introduction that problem (2.1) requires different methods of solution for each of five timescales. The first two regimes are not investigated in this paper; rather we commence with a motivation for regime (c) – the large-time, weak-recombination limit described by $1 \ll (Mt)^{\frac{1}{2}} \ll \epsilon^{-1}$. This regime is defined by the requirement that the recombination effects represent a regular perturbation to the simple large-time approximation due to Chatwin (1970). Chatwin’s direct expansion employs the coordinates

$$X = \frac{(x - \gamma Pt)}{PT}, \quad Y = y, \quad Z = z, \quad T = (Mt)^{\frac{1}{2}}, \tag{2.3}$$

where γ and M are constants whose values are fixed by the theory and it is known that, for passive contaminants, the leading solution at large time is

$$C = \alpha_{1,0} T^{-1} \exp\{-\frac{1}{2}X^2\}. \quad (2.4)$$

If the recombination is weak, that is $0 < \epsilon \ll 1$, the term (2.4) will provide a forcing term for a perturbation calculation. An estimate of this perturbation suggests that it is necessary and consistent to look for a solution in the form

$$C = C_0(X, Y, Z, T) + \epsilon C_1(X, Y, Z, T) + \epsilon^2 C_2(X, Y, Z, T) + \dots, \quad (2.5)$$

where each C_n can be expressed as a power series in $1/T$ as follows:

$$C_0(X, Y, Z, T) = \frac{1}{T} C_{0,1}(X, Y, Z) + \frac{1}{T^2} C_{0,2}(X, Y, Z) + \frac{1}{T^3} C_{0,3}(X, Y, Z) + \dots, \quad (2.6a)$$

$$C_1(X, Y, Z, T) = C_{1,0}(X, Y, Z) + \frac{1}{T} C_{1,1}(X, Y, Z) + \frac{1}{T^2} C_{1,2}(X, Y, Z) + \dots, \quad (2.6b)$$

$$C_2(X, Y, Z, T) = TC_{2,-1}(X, Y, Z) + C_{2,0}(X, Y, Z) + \frac{1}{T} C_{2,1}(X, Y, Z) + \dots \quad (2.6c)$$

(Note that the Péclet-number dependence of all coefficient functions is no longer mentioned explicitly.) A regular perturbation calculation is used in the next section to determine the coefficient functions $C_{m,n}$. It is clear that the expansions (2.6) become singular for times T of $O(1/\epsilon)$, and this regime is considered in §4.

3. Regular perturbation calculation for $(Mt)^{\frac{1}{2}} \ll \epsilon^{-1}$

This section contains the most difficult mathematics of the paper: the analysis for regime (c). We begin by establishing equations for the coefficients $C_{m,n}$ mentioned in the perturbation approximations (2.6a, b, c). Chatwin's (1970) results for the coefficients $C_{0,n}$ are then summarized, and this is followed by a calculation of the important term $C_{1,0}$ which represents the leading effect at large time of the recombination reaction. Readers who wish to skip some of the analysis are advised that (3.8) and (3.9) contain the main results of the section, and, indeed, of the paper.

In terms of the coordinates X, Y, Z, T defined by (2.3), the basic problem (2.1a) becomes

$$\frac{M}{2T} \frac{\partial C}{\partial T} + \left[\frac{u-\gamma}{T} - \frac{XM}{2T^2} \right] \frac{\partial C}{\partial X} = \frac{1}{P^2 T^2} \frac{\partial^2 C}{\partial X^2} + \Delta C - \epsilon C^2 \quad \text{in } \Omega, \quad (3.1a)$$

where ΔC is given by

$$\Delta C = \left[\frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right] C.$$

This problem (3.1a) is to be solved under the boundary conditions

$$\hat{n} \cdot \left[\frac{\partial C}{\partial X}, \frac{\partial C}{\partial Y}, \frac{\partial C}{\partial Z} \right] = 0 \quad \text{at } \partial\Omega. \quad (3.1b)$$

If the expansions (2.5) and (2.6) are substituted into equation (3.1a), the following hierarchy of problems are to be solved under the boundary condition (3.1b).

$O(\epsilon^0)$ terms

$$O(\epsilon^0 T^{-1}): \Delta C_{0,1} = 0, \tag{3.2a}$$

$$O(\epsilon^0 T^{-2}): \Delta C_{0,2} = (u - \gamma) \frac{\partial C_{0,1}}{\partial X}, \tag{3.2b}$$

$$O(\epsilon^0 T^{-n}): \Delta C_{0,n} = (u - \gamma) \frac{\partial C_{0,n-1}}{\partial X} - \frac{1}{2} M \left\{ \frac{2}{MP^2} \frac{\partial^2 C_{0,n-2}}{\partial X^2} + X \frac{\partial C_{0,n-2}}{\partial X} + (n-2) C_{0,n-2} \right\} \quad (n \geq 3). \tag{3.2c}$$

$O(\epsilon)$ terms

$$O(\epsilon T^0): \Delta C_{1,0} = 0, \tag{3.3a}$$

$$O(\epsilon T^{-1}): \Delta C_{1,1} = (u - \gamma) \frac{\partial C_{1,0}}{\partial X}, \tag{3.3b}$$

$$O(\epsilon T^{-n}): \Delta C_{1,n} = (u - \gamma) \frac{\partial C_{1,n-1}}{\partial X} - \frac{1}{2} M \left\{ \frac{2}{P^2 M} \frac{\partial^2 C_{1,n-2}}{\partial X^2} + X \frac{\partial C_{1,n-2}}{\partial X} + (n-2) C_{1,n-2} \right\} + \sum_{q=1}^{n-1} C_{0,q} C_{0,n-q} \quad (n \geq 2). \tag{3.3c}$$

$O(\epsilon^2)$ terms

$$O(\epsilon^2 T): \Delta C_{2,-1} = 0, \tag{3.4a}$$

$$O(\epsilon^2 T^0): \Delta C_{2,0} = (u - \gamma) \frac{\partial C_{2,-1}}{\partial X}, \tag{3.4b}$$

$$O(\epsilon^2 T^{-n}): \Delta C_{2,n} = (u - \gamma) \frac{\partial C_{2,n-1}}{\partial X} - \frac{1}{2} M \left\{ \frac{2}{MP^2} \frac{\partial^2 C_{2,n-2}}{\partial X^2} + X \frac{\partial C_{2,n-2}}{\partial X} + (n-2) C_{2,n-2} \right\} + 2 \sum_{q=1}^n C_{0,q} C_{1,n-q} \quad (n \geq 1). \tag{3.4c}$$

It is possible to solve (3.2), (3.3) and (3.4) sequentially to determine the coefficient functions $C_{m,n}$. For the purposes of the present work, the analysis is taken far enough to determine the leading correction forced by the recombination reaction, and to ensure that the expansion procedure is consistent.

In fact, the problems (3.2a-c) for the $O(\epsilon^0)$ terms have been completely studied by Chatwin (1970) who showed that the coefficient functions $C_{0,1}$, $C_{0,2}$ and $C_{0,3}$ are (with slight changes of notation)

$$\begin{aligned} C_{0,1} &= \alpha_{1,0} \phi_1 H_0(X) \exp\{-\frac{1}{2}X^2\}, \\ C_{0,2} &= [(\alpha_{2,0} \phi_1 - \alpha_{1,0} \phi_2) H_1(X) + \alpha_{2,1} \phi_1 H_3(X)] \exp\{-\frac{1}{2}X^2\}, \\ C_{0,3} &= [(\alpha_{3,0} \phi_1 - \alpha_{2,0} \phi_2 + \alpha_{1,0} \phi_3) H_2(X) + (\alpha_{3,1} \phi_1 - \alpha_{2,1} \phi_2) H_4(X) \\ &\quad + \alpha_{3,2} f_1 H_6(X)] \exp\{-\frac{1}{2}X^2\}. \end{aligned}$$

Here, the $H_n(X)$ are Hermite polynomials defined by

$$H_n(X) \exp\{-\frac{1}{2}X^2\} = \left(-\frac{d}{dX}\right)^n \exp\{-\frac{1}{2}X^2\},$$

and the functions $\phi_n(Y, z)$ are the finite solutions of the equations

$$\Delta\phi_1 = 0, \quad \bar{\phi}_1^2 = 1, \quad (3.5a)$$

$$\Delta\phi_2 = (u - \gamma)\phi_1, \quad \bar{\phi}_2 = 0, \quad (3.5b)$$

$$\Delta\phi_3 = (u - \gamma)\phi_2 - \overline{(u - \gamma)\phi_2\phi_1}\phi_1, \quad \bar{\phi}_3 = 0, \quad (3.5c)$$

subject to the boundary conditions (3.1b). Each of these problems possess a unique solution and the function ϕ_1 is, in fact, identically unity. The constant γ is found by a solvability requirement (see below) to be

$$\gamma = \bar{u}, \quad (3.6a)$$

and the solution has the stated concise form provided that the constant M is

$$M = 2 \left(\frac{1}{P^2} - \overline{(u - \gamma)\phi_2} \right). \quad (3.6b)$$

Also the constants $\alpha_{p,0}$ ($p = 1, 2, 3$) are to be determined by matching onto regime (b), and the remaining constants $\alpha_{2,1}$, $\alpha_{3,1}$, $\alpha_{3,2}$ depend on the $\alpha_{p,0}$. Chatwin (1970) gives expressions for all of these constants.

The foregoing provides a direct three-term approximation for the case when $\epsilon = 0$. The results depend crucially on the solvability requirement that the equation $\Delta\psi = R$ under boundary conditions (3.1b) possess a solution provided only that $\bar{R} = \bar{R\phi_1} = \bar{\phi_1\Delta\psi} - \bar{\psi\Delta\phi_1} = 0$ (by integration by parts and boundary conditions).

It is now possible to calculate the $O(\epsilon)$ terms, the first of which gives the dominant correction forced by the recombination reaction. The solutions of (3.3a, b) are

$$C_{1,0} = f_0(X),$$

$$C_{1,1} = \phi_2 \frac{df_0}{dX} + f_1(X),$$

with ϕ_2 determined by (3.5b) and $f_0(X)$, $f_1(X)$ as yet arbitrary. Equation (3.3c) with $n = 2$ yields

$$\begin{aligned} \Delta C_{1,2} &= (u - \gamma) \frac{\partial C_{1,1}}{\partial X} - \frac{1}{2} M \left\{ \frac{2}{P^2 M} \frac{\partial^2 C_{1,0}}{\partial X^2} + X \frac{\partial C_{1,0}}{\partial X} \right\} + \alpha_{1,0}^2 \exp\{-X^2\} \\ &= (u - \gamma) \frac{df_1}{dX} + \left[(u - \gamma)\phi_2 - \frac{1}{P^2} \right] \frac{d^2 f_0}{dX^2} - \frac{1}{2} M X \frac{df_0}{dX^2} + \alpha_{1,0}^2 \exp\{-X^2\}, \end{aligned}$$

and, since the property $\gamma = \bar{u}$ has been established, the solvability requirement provides the ordinary differential equation (ODE)

$$\frac{d^2 f_0}{dX^2} + X \frac{df_0}{dX} = \frac{2}{M} \alpha_{1,0}^2 \exp\{-X^2\}, \quad (3.7)$$

for $f_0(X)$ upon using the definition (3.6b) for M .

Equation (3.7) describes the leading effect of the second-order recombination reaction and it has the general solution

$$f_0(X) = A \int_0^X e^{-\frac{1}{2}t^2} \int_0^t e^{-\frac{1}{2}s^2} ds dt + c_1 \int_0^X e^{-\frac{1}{2}t^2} dt + c_2$$

with $A = 2\alpha_{1,0}^2/M$. The constants c_1 and c_2 are determined by ensuring that $f_0(X)$ decays to zero for $|X|$ large; this gives

$$c_1 = 0,$$

$$c_2 = -A \int_0^\infty e^{-\frac{1}{2}t^2} \int_0^t e^{-\frac{1}{2}s^2} ds dt = -\frac{1}{4}A\pi,$$

whence $f_0(X)$ can be more conveniently expressed as

$$f_0(X) = -A \int_X^\infty e^{-\frac{1}{2}t^2} \int_0^t e^{-\frac{1}{2}s^2} ds dt$$

or

$$f_0(X) = \frac{1}{4}A\pi \{\text{erf}^2(X/2^{\frac{1}{2}}) - 1\},$$

under the usual definition of the error function,

$$\text{erf } z = \frac{2}{\pi^{\frac{1}{2}}} \int_0^z e^{-t^2} dt.$$

The principal goal of the present work has thus been achieved. That is, the injected cloud of solute takes the approximate form

$$C = \frac{\alpha_{1,0}}{T} \left[e^{\frac{1}{2}X^2} - \frac{2}{M} \epsilon T \alpha_{1,0} \frac{1}{4}\pi \left(1 - \text{erf}^2 \left(\frac{X}{2^{\frac{1}{2}}} \right) \right) \right] + O(T^{-2}, \epsilon T^{-1}, \epsilon^2 T) \tag{3.8}$$

for T large and ϵ small where, formally, the terms designated $O(T^{-2}, \epsilon T^{-1}, \epsilon^2 T)$ in the approximation (3.8) are small compared with the displayed terms provided that $\epsilon^{-\frac{1}{2}} \ll T \ll 1/\epsilon$. In the expression (3.8), the constant $\alpha_{1,0}$ is known to be $1/P(2\pi)^{\frac{1}{2}}$ since the initial dimensionless amount of solute is $|\Omega|$. Moreover, if the definitions (2.3) are recalled and if $\frac{1}{2}P^2M$ is defined to be D (the dimensionless shear dispersion coefficient), approximation (3.8) can be re-written

$$C = (4\pi Dt)^{-\frac{1}{2}} e^{-(x-Pt)^2/4Dt} - \frac{\epsilon}{8D} \left[1 - \text{erf}^2 \left(\frac{x-Pt}{(4Dt)^{\frac{1}{2}}} \right) \right] + O(t^{-1}, \epsilon t^{-\frac{1}{2}}, \epsilon^2 t^{\frac{1}{2}}). \tag{3.9}$$

One- and two-term plots of the approximation (3.9) are given in figure 1 for representative values of (t, ϵ, P) when the basic flow is Poiseuille flow in a tube. In this case, the constant M is known to be $M = 2(P^{-2} + \frac{1}{48})$, and the values of (t, ϵ, P) are chosen so that the second term in (3.9) is small compared with the first. The plots are simple in form: the major effect of the weak recombination is to flatten the peak of the dominant Gaussian distribution.

A partial justification of the representations (2.5) and (2.6) was made by examining some of the neglected terms in the result (3.8). Of these, the $O(T^{-2})$ term has already been described, and the $O(\epsilon T^{-1})$ and $O(\epsilon^2 T)$ terms were found to involve the solutions of second-order inhomogeneous ODEs. These ODEs satisfied certain (secondary) solvability conditions and there was no reason to suspect that their solutions could not be found; that is, there was no indication that $\log_e T$ terms were required in the representations (2.5) and (2.6). The cumbersome details of the consistency checks are omitted.

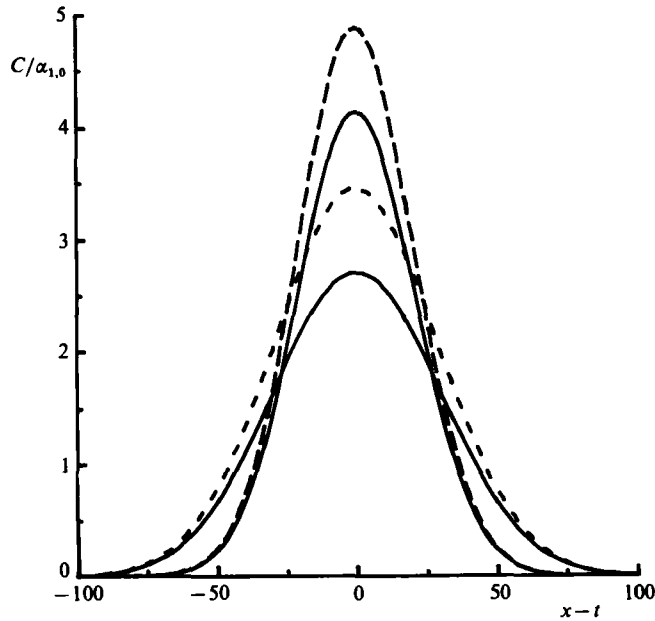


FIGURE 1. One- and two-term plots of approximation (3.9) for Poiseuille flow at dimensionless times $t = 1, 2$ as a function of dimensionless distance x : ----, one-term approximation; —, two-term approximation. The parameters P and ϵ are $P = 100, \epsilon = 5$.

4. The numerical solution for t of $O(\epsilon^{-2})$

The regular perturbation expansion (3.8) is not applicable to regime (*d*), in which T is of $O(\epsilon^{-1})$ or, equivalently, t is of $O(\epsilon^{-2})$. A number of attempts were made using singular perturbation techniques (such as the method of multiple scales and the method of strained coordinates, Nayfeh 1973), to derive approximations for the concentration in this regime. All the attempts led to failure, however, and the complicated details are again suppressed. At these times, it appears that the effects of shear dispersion and of recombination are of comparable importance in (2.1 *a*), and the problem becomes inherently nonlinear.

Accordingly, a numerical solution has to be found for (2.1 *a*) for time t of order $O(\epsilon^{-2})$. At these large times, the solute is fully mixed over the cross-section of the parallel flow and, in dimensionless coordinates (x, t) moving at the discharge speed of the flow, the dominant equation reduces to

$$\frac{\partial \bar{C}}{\partial t} = D \frac{\partial^2 \bar{C}}{\partial x^2} - \epsilon \bar{C}^2, \tag{4.1}$$

where D is the appropriate dimensionless shear dispersion coefficient (for example, $D = 1 + (\frac{1}{48}P^2)$ for solute dispersion in Poiseuille flow). Equation (4.1) can be reduced to the simple form

$$\frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial \xi^2} - \phi^2, \tag{4.2}$$

by introducing the natural scales

$$\tau = \frac{\epsilon^2 t}{D}, \quad \xi = \frac{\epsilon x}{D}, \quad \phi = \frac{D \bar{C}}{\epsilon}, \tag{4.3}$$

whilst an initial condition on (4.2) can be obtained by re-writing (3.9) using (4.3). The resultant equation is

$$\phi(\xi, \tau) \sim (4\pi\tau)^{-\frac{1}{2}} e^{-\xi^2/4\tau} - \frac{1}{8}[1 - \text{erf}^2 \xi/(4\tau)^{\frac{1}{2}}] \quad \text{as } \tau \rightarrow 0, \tag{4.4}$$

and this represents the matching condition between regimes (c) and (d).

For the computational purposes of the present section, (4.4) is replaced by the one-term approximate expression

$$\phi(\xi, 0) = \left[\frac{\beta}{\pi} \right]^{\frac{1}{2}} e^{-\beta\xi^2} \quad (\beta \text{ large}), \tag{4.5a}$$

and the auxiliary condition $\phi \rightarrow 0$ as $|\xi| \rightarrow \infty$ (4.5b)

is applied so as to obtain a well-posed problem for $\phi(\xi, \tau)$. To introduce the numerical technique, it is observed that, for a fixed β and in the absence of recombination, (4.3) and (4.5) would have the solution

$$\phi(\xi, \tau) = \left[4\pi \left(\tau + \frac{1}{4\beta} \right) \right]^{-\frac{1}{2}} \exp \left\{ -\frac{\xi^2}{4 \left(\tau + \frac{1}{4\beta} \right)} \right\}. \tag{4.6}$$

This suggests that it would be advantageous to look for a solution in terms of the new variables (ζ, η) ,

$$\zeta = \xi \left(\tau + \frac{1}{4\beta} \right)^{-\frac{1}{2}}, \quad \eta = \tau. \tag{4.7}$$

If $\phi(\xi, \tau)$ is identified as $\psi(\zeta, \eta)$, the full problem for ψ is found to be

$$\frac{\partial \psi}{\partial \eta} = \left(\eta + \frac{1}{4\beta} \right)^{-1} \left\{ \frac{1}{2} \zeta \frac{\partial \psi}{\partial \zeta} + \frac{\partial^2 \psi}{\partial \zeta^2} \right\} - \psi^2, \tag{4.8a}$$

$$\psi(\zeta, 0) = \left(\frac{\beta}{\pi} \right)^{\frac{1}{2}} e^{-\frac{1}{4}\zeta^2}, \tag{4.8b}$$

$$\psi \rightarrow 0 \quad \text{as } |\zeta| \rightarrow \infty. \tag{4.8c}$$

The particular utility of the variables (ζ, η) lies in the fact that the solution ψ does not spread with ζ as η is increased. In fact, for the computations, condition (4.8c) was replaced by

$$\psi = 0 \quad \text{at } |\zeta| = 8, \tag{4.9}$$

and it was expected that ψ was less than $(\beta/\pi)^{\frac{1}{2}} \exp(-16)$ for ζ outside this range.

Equations (4.8a, b) and (4.9) pose a parabolic problem for $\psi(\zeta, \eta)$ and the method of lines is ideally suited for its solution. Thus the software interface PDEONE (Sincovec & Madsen 1975) was used to convert equation (4.8a) to a set of ODEs in η which were solved using the package GEARB (Hindmarsh 1975). For most of the computations described subsequently, the parameter NPTS in PDEONE was set to be 201. This means that central-difference expressions on a uniformly spaced mesh of 201 ζ values in $-8 \leq \zeta \leq 8$ were used to replace the ζ derivatives in (4.8a).

To present some numerical results, we revert to the variables (ξ, τ) and fix the value of β in the initial condition (4.5a) to $\beta = 2$. (This value of β is too small for the initial condition (4.5a) to be a good approximation to the matching condition (4.4); however, the form of the results for large τ is insensitive to the value of β , whilst numerical calculations are quicker for β of $O(1)$.) Figure 2 shows the concentration $\phi(\xi, \tau)$ as a function of ξ at $\tau = 1$ and $\tau = 10$; dashed lines in this figure show

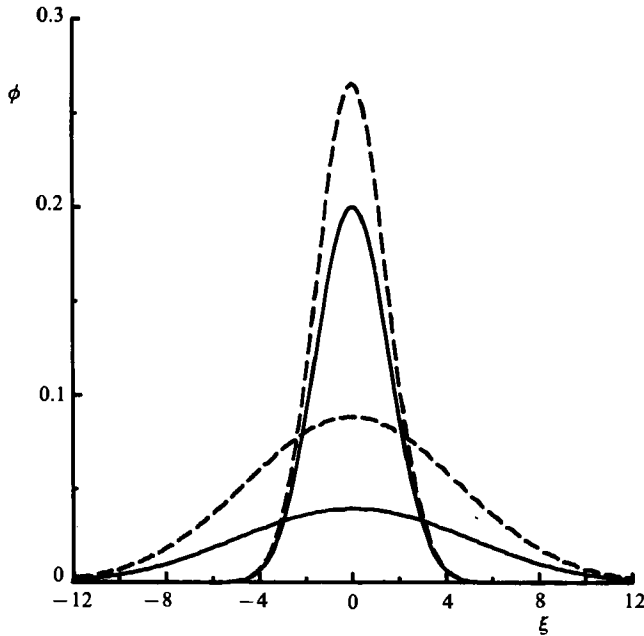


FIGURE 2. Numerical solutions of (4.3) at $\tau = 1$ and $\tau = 10$; dashed lines show equivalent results when the recombination term in (4.3) is omitted.

equivalent results when the recombination term in (4.3) is neglected. The concentration plots are again simple in form, and it is clear that the effect of the recombination is to flatten the peaks of the distribution without affecting the speed of the solute cloud. Figure 3 shows the total quantity of solute,

$$m(\tau) = \int_{-\infty}^{\infty} \bar{C} dx = \int_{-\infty}^{\infty} \phi d\xi,$$

as a function of τ , and includes short- and large- τ approximations which may be derived independently. The large- τ approximation is given by (5.4) in the next section and the short- τ approximation was obtained as follows.

The expression (3.9) applies when a delta function of unit strength is injected at $t = 0$ and it may be integrated to give the total mass of solute:

$$\int_{-\infty}^{\infty} \bar{C} dx = 1 - \frac{\epsilon}{8D} \int_{-\infty}^{\infty} [1 - \text{erf}^2(s)] (4Dt)^{\frac{1}{2}} ds + \dots,$$

or (4.10)

$$m(\epsilon, t) = 1 - 0.39894\tau^{\frac{1}{2}} + \dots,$$

on identifying $\epsilon^2 t/D$ as τ and evaluating the definite integral. In contrast, the numerical work of this section has used the initial condition (4.5a) with $\beta = 2$. This initial condition is approximately equivalent to a delta function of strength q (say) injected at $\tau = -\frac{1}{4}\beta$, since the dispersion process is dominant at small times and it takes a time $\frac{1}{4}\beta$ for an initial delta function to diffuse to the form (4.5a). If the delta function injected at $-\frac{1}{4}\beta$ had strength q , the mass of solute would be given by the following modified form of (4.10),

$$m(\epsilon, t) = q \left[1 - 0.39894 q \left(\tau + \frac{1}{4\beta} \right)^{\frac{1}{2}} + \dots \right].$$

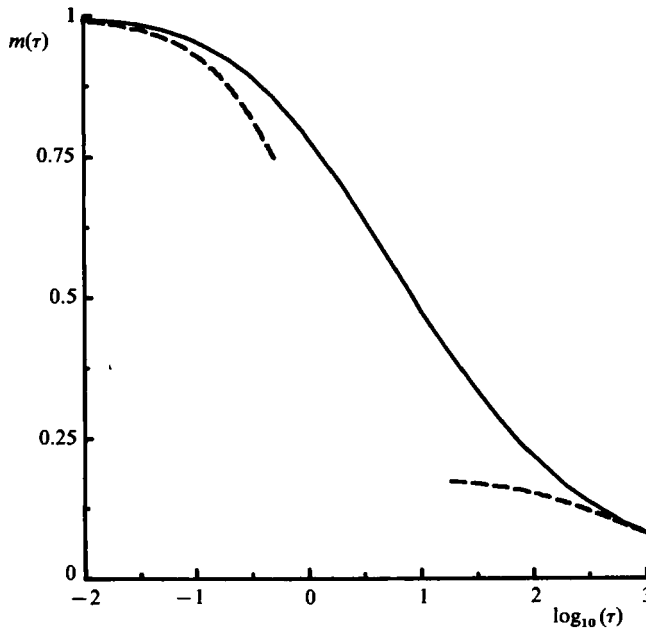


FIGURE 3. Numerical results for the total amount of solute $m(\tau) = \int_{-\infty}^{\infty} \phi \, d\xi$ when the initial condition is given by (4.5a) with $\beta = 2$. Dashed lines show the small- and large- τ approximations, equations (4.11) and (5.4).

Hence, if the total mass of solute is to be unity at $\tau = 0$ with $\beta = 2$, q will be approximately given by the quadratic equation

$$1 = q[1 - 0.39894q(\frac{1}{8})^{\frac{1}{2}}].$$

This has the applicable root $q = 1.2047$, so the appropriate short-time expression for the mass is

$$m(\epsilon, t) = 1.2047(1 - 0.48060[\tau + \frac{1}{8}]^{\frac{1}{2}} + \dots) \tag{4.11}$$

and this expression is plotted in figure 3.

5. A similarity solution for $\epsilon^2 t$ large

This section contains an investigation of regime (e) in which $\tau = \epsilon^2 t$ is large and there is still an inherent balance between shear dispersion and recombination terms in (2.1a). In this regime, (2.1a), or its appropriately simplified form (4.1), possesses a similarity solution

$$\phi(\xi, \tau) = \frac{1}{\tau + \tau_0} f(\eta), \quad \eta = \xi[2(\tau + \tau_0)]^{-\frac{1}{2}}, \tag{5.1a, b}$$

where $f(\eta)$ satisfies the ODE $f'' + \eta f' + 2f = 2f^2$, (5.2a)

and is subject to the conditions

$$f'(0) = 0, \quad f(\eta) \rightarrow 0 \quad \text{as } \eta \rightarrow 0. \tag{5.2b, c}$$

(A physical constraint which must also be satisfied is that $f(\eta)$ is always positive.) The key parameters which must be specified independently are τ_0 and $f(0)$, and these

Central τ of data	$\beta = 0.5$		$\beta = 2.0$	
	a_1	a_2	a_1	a_2
3000	64.5 ± 1.6	0.6697 ± 0.0004	73.0 ± 1.8	0.6671 ± 0.0004
5000	86.9 ± 1.4	0.6735 ± 0.0002	102 ± 2	0.6719 ± 0.0002
7000	111 ± 2	0.6761 ± 0.0002	126 ± 2	0.6748 ± 0.0002
9000	126 ± 3	0.6774 ± 0.0002	139 ± 8	0.6758 ± 0.0006
11000	149 ± 4	0.6789 ± 0.0002	172 ± 14	0.6780 ± 0.0008
13000	163 ± 7	0.6797 ± 0.0004	197 ± 18	0.679 ± 0.0001
15000	170 ± 14	0.6799 ± 0.0006	224 ± 55	0.681 ± 0.002
17000	200 ± 13	0.6812 ± 0.0006	237 ± 45	0.681 ± 0.002
19000	208 ± 23	0.6815 ± 0.0008	241 ± 75	0.681 ± 0.002

TABLE 1. The coefficients a_1 and a_2 in the representation of $1/\phi(0, \tau)$ by $(\tau + a_1)/a_2$ for $\beta = 0.5$ and $\beta = 2$. The key parameters τ_0 and $f(0)$ are equivalent to a_1 and a_2 . The coefficients were determined by a least-squares fit to $1/\phi(0, \tau)$ at 21 evenly spaced values in the interval $[\tau - 1000, \tau + 1000]$. Approximate 95% confidence limits are also shown.

could be found, in principle, by using the numerical procedures of the previous section to compute $\phi(\xi, \tau)$ for large values of τ and then matching with (5.1a).

Suppose that a value of β has been fixed in the initial condition (4.5a). Then the similarity solution (5.1) is applicable when a plot of $1/\phi(0, \tau)$ against τ has the straight-line asymptote $(\tau + \tau_0)/f(0)$. Unfortunately, however, it is necessary to compute $\phi(0, \tau)$ for very large values of τ before this procedure is possible. This point is illustrated in table 1, which describes the result of a least-squares fit of the form $(\tau + a_1)/a_2$ to $1/\phi(0, \tau)$ where the data consist of 21 evenly spaced points in the interval $[\tau - 1000, \tau + 1000]$. It is clear from this table that, even for modest values of β , it is impossible to determine the parameters τ_0 and $f(0)$ unless the time integration is pursued quite a lot further than $\tau = 20000$. Bearing in mind that $\tau = \epsilon^2 t$, this amounts to computations at unrealistically large values of the dimensionless time t . Another point is the computing time involved: the numerical method introduced in the previous section is particularly convenient for computations at large values of τ , yet it still took about 1 hour's c.p.u. time on a VAX 11/750 to compute out to $\tau = 20000$ with a mesh of 201 evenly spaced ζ points. For the purposes of this paper, an accurate determination of τ_0 and $f(0)$ is not worth the expense it would entail. (In passing, it is noted that another numerical algorithm based on a spectral method was also used to solve (4.3). The algorithm would have taken much longer to produce the results in table 1, and it was regarded as inferior to the algorithm described in §4.)

It is of interest to examine the properties of $f(\eta)$ as a function of $f(0)$. Problem (5.2) was written in the form

$$\frac{d}{d\eta} \begin{bmatrix} f \\ g \end{bmatrix} = \begin{bmatrix} g \\ -\eta g - 2f(1-f) \end{bmatrix}, \quad (5.3a)$$

and this was integrated numerically from the initial condition

$$f(0) = A, \quad g(0) = 0, \quad (5.3b)$$

to give results for various values of A as shown in figures 4 and 5. The phase plane plot in figure 4 shows that $f(\eta)$ becomes negative for large values of ζ if A lies in the range $0 < A < 0.6899$, and these values of A therefore lead to physically unrealistic solutions. Values of A in the range $0.6899 < A < 1$ all lead to positive solutions which decay as $\eta \rightarrow \infty$, whilst values of A greater than 1 lead to physically unrealistic

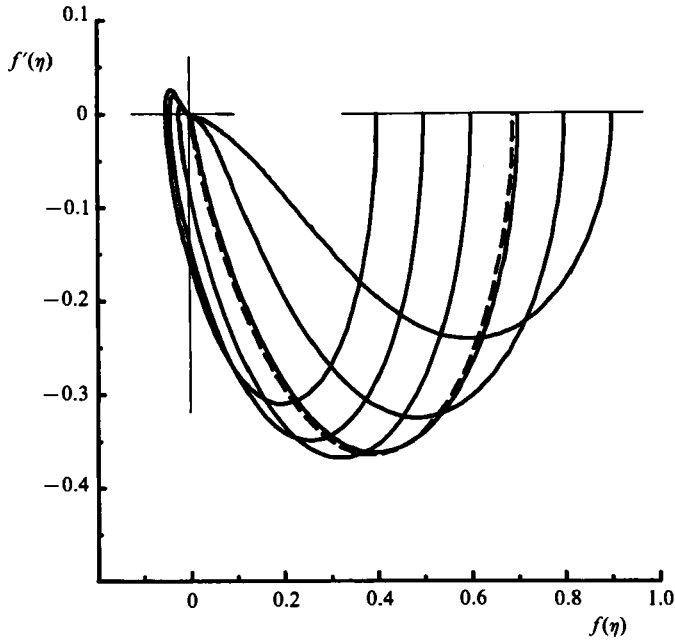


FIGURE 4. Phase plane plots of $g = f'$ against f for various values of A in the initial condition (5.3*b*). The dashed line shows the solution trajectory for $A = 0.6899$.

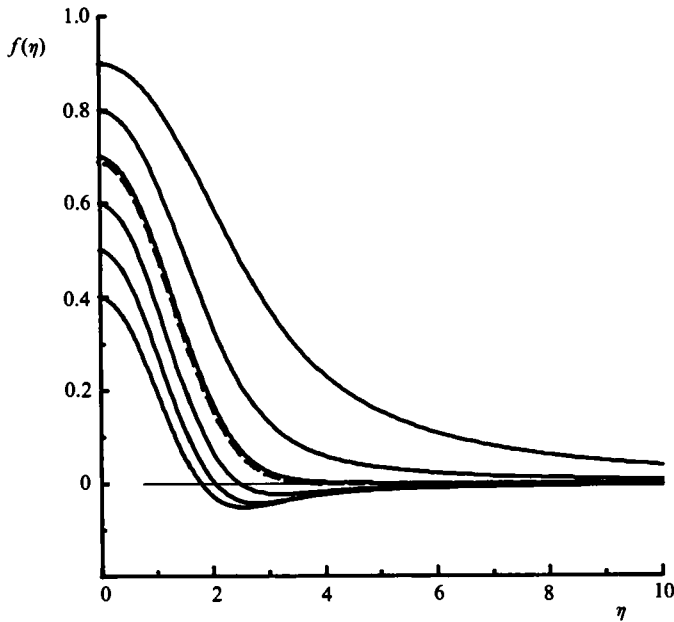


FIGURE 5. Plots of $f(\eta)$ against η for various values of A in the initial condition (5.3*b*). The dashed line shows the solution for $A = 0.6899$.

growing solutions as η is increased. These points are borne out by the plots of $f(\eta)$ against η in figure 5.

It may be seen that the values of $f(0) = a_2$ described in table 1 are all just below the critical value 0.6899. Presumably, the main cause of this physically unreasonable result is truncation error in the central-difference expressions for the ζ derivatives in (4.8a). It is speculated that high-accuracy computations would give the critical value 0.6899 for $f(0) = a_2$ independent of the value of β chosen in (4.5a). The value of $\tau_0 = a_1$ should be dependent on β however. It is reasonable to assume that τ_0 should tend to a limiting value as β is taken very large and (4.5a) becomes a good representation of a δ function. On the other hand, for β of $O(1)$, there is quite a mismatch between the initial condition (4.5a) and the requirements (of balance between diffusion and recombination) for the similarity solution. Hence it takes some time for the solute distribution to reach the similarity form, and this is reflected in a smaller positive value for $\tau_0 = a_1$. (That is, the virtual origin of the similarity solution is still negative, but becomes less negative as β is decreased.)

Finally, the amount of solute remaining at very large values of the time is considered. By (5.1a, b), this is given by

$$\begin{aligned} m(\tau) &= \int_{-\infty}^{\infty} \phi(\xi, \tau) d\xi \\ &= 2^{\frac{1}{2}}(\tau + \tau_0)^{-\frac{1}{2}} \int_{-\infty}^{\infty} f(\eta) d\eta. \end{aligned}$$

The integral in this expression is found to be 2.0532 if $f(0)$ is set to the critical value 0.6899. Further, an examination of table 1 shows that a reasonable value for τ_0 is $\tau_0 = 260$ when $\beta = 2$. Thus, the large-time expression for the mass (for $\beta = 2$) is

$$m(\tau) = 2.904(\tau + 260)^{-\frac{1}{2}} \quad (5.4)$$

and this expression is plotted in figure 3.

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REFERENCES

- ARIS, R. 1956 On the dispersion of a solute in a fluid flowing through a tube. *Proc. R. Soc. Lond. A* **235**, 67–77.
- BARTON, N. G. 1978 The initial dispersion of soluble matter in three-dimensional flow. *J. Austral. Math. Soc. B* **20**, 265–279.
- BARTON, N. G. 1984a An asymptotic theory for dispersion of reactive contaminants in parallel flow. *J. Austral. Math. Soc. B* **25**, 287–310.
- BARTON, N. G. 1984b The determination of diffusion coefficients of gas species with one recombining species: a preliminary report. *CSIRO Div. Maths and Stats Consulting Rep. NSW* 84/12/NGB4.
- BARTON, N. G. & STOKES, A. N. 1986 A computational method for shear dispersion in parallel flow. *Proc. CTAC-85, Computational Techniques and Applications Conference*, (ed. J. Noye & R. May), pp. 345–356. North-Holland.
- CHATWIN, P. C. 1970 The approach to normality of the concentration distribution of a solute in a solvent flowing along a straight pipe. *J. Fluid Mech.* **43**, 321–352.

- CHATWIN, P. C. 1977 The initial development of dispersion in straight tubes. *J. Fluid Mech.* **80**, 33–48.
- DE GANCE, A. E. & JOHNS, L. E. 1978*a* The theory of dispersion of chemically active solutes in a rectilinear flow field. *Appl. Sci. Res.* **34**, 189–225.
- DE GANCE, A. E. & JOHNS, L. E. 1978*b* On the dispersion coefficients for Poiseuille flow in a circular cylinder. *Appl. Sci. Res.* **34**, 227–258.
- GILL, W. M. & SANKARASUBRAMANIAN, R. 1970 Exact analysis of unsteady convective diffusion. *Proc. R. Soc. Lond. A* **316**, 341–350.
- HINDMARSH, A. C. 1975 GEARB: solution of ordinary differential equations having banded Jacobian. *Lawrence Livermore Laboratory Rep.* UCID 30059.
- NAYFEH, A. H. 1973 *Perturbation Methods*. Wiley.
- PLUMB, I. C., RYAN, K. R. & BARTON, N. G. 1983 Method for the measurement of diffusion coefficients of labile gas phase species: the diffusion coefficient of O(³P) in He at 294 K. *Intl J. Chem. Kin.* **15**, 1081–1097.
- SINCOVEC, R. F. & MADSEN, N. K. 1975 Software for nonlinear partial differential equations. *ACM Trans. Math. Software* **1**, 232–260.
- SMITH, R. 1981*a* A delay-diffusion description for contaminant dispersion. *J. Fluid Mech.* **105**, 469–486.
- SMITH, R. 1981*b* The early stages of contaminant dispersion in shear flow. *J. Fluid Mech.* **111**, 107–122.
- SMITH, R. 1983 Effect of boundary absorption upon longitudinal dispersion in shear flows. *J. Fluid Mech.* **134**, 161–177.
- TAYLOR, G. I. 1953 Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. Lond. A* **219**, 186–203.