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The dispersion of chemically active solutes in parallel flow

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The irreversible loss of chemically active solutes by reactions at the boundary and the reversible adsorption on the flow boundary have been observed experimentally. Removal of solutes at the boundary alone reduces the rate of longitudinal shear dispersion; in contrast, the retention of solutes in the region close to the flow boundary alone increases the rate of longitudinal shear dispersion. Here an extension is given of the method of moments for chemically active solute dispersion to encompass this class of complications. Expressions are derived for the longitudinal shear dispersion coefficient and skewness. The results are applied to the practical example of a chemical flow reactor to quantify the effect of flow boundary retention when there exists reaction at the pipe wall.

1. Introduction

As understanding has advanced concerning the dispersion of passive (chemically inert) solutes, there has been increasing interest in the case of chemically active solutes. Plumb, Ryan & Barton (1983) have determined experimentally the rate of diffusion of oxygen atoms in flowing helium using a modification of Taylor's (1953) dispersion theory for the case of passive solutes injected into flowing solvent. Evans & Kenney (1966) have calculated empirically the rate of diffusion of nitrogen gas injected into flowing hydrogen gas under conditions in which the nitrogen gas can also be exchanged by diffusion with a retentive layer of stagnant gas held within a porous solid structure. The significance of reversible adsorption of chemically active solutes on the flow boundary was observed by Clifford *et al.* (1982), when studying the diffusion of hydrogen atoms in flowing nitrogen and flowing argon; and it was noted that when an atom is adsorbed on the pipe wall, not only can it be lost by reaction, but it also has a high probability of returning back to the gas phase. Based on these laboratory investigations, Boddington & Clifford (1983) have emphasized both these important effects of irreversible loss of chemically active solutes by reactions at the flow boundary, and their reversible adsorption onto and desorption from the flow boundary.

One obstacle to a general theory of the dispersion of chemically active solutes is the existence of various forms of boundary conditions used in representing processes occurring near the flow boundary. Purnama (1988*b*) has proposed a generalized boundary condition of the form

$$\kappa \boldsymbol{n}\cdot\nabla c = -\beta c - \partial_t \int_0^t \mathrm{d}\tau\, J(\tau)\, c(t-\tau) \quad \text{on} \quad \partial A. \tag{1.1}$$

The first term on the right-hand side represents an irreversible boundary reaction which reflects the effect of solute removal. (The case when $\beta = 0$ is usually referred to as the dispersion of passive solutes.) The second term represents the effect of flow boundary retention, which measures the amount of solute held in the stagnant region close to the flow boundary (this region will be referred to as the retentive layer). The kernel $J(t)$ determines the diffusive effect of the time lag between the solutes across the retentive layer. Some expressions for $J(t)$ are discussed in the Appendix.

Removal of chemically active solutes via boundary reactions alone causes a small amount of slow-moving solute near the flow boundary to be left far behind as an extended tail, i.e. a tendency to develop a skewness towards the rear (Smith 1983). Similar features have also been observed for the dispersion of passive solutes, due to the effects of flow boundary retention (Purnama 1988*a*). Since such deviations from Gaussianity cannot be described by Taylor's (1953) approach, the method considered here is to determine the values of the integral moments of the chemically active solute concentration c. This technique has been widely used (Barton 1984; Boddington & Clifford 1983) since knowledge of the first few moments of c gives great deal of information about c itself. For the dispersion of passive solutes, the method of moments (Aris 1956) gives rigorous justification for Taylor's (1953) heuristic approach to shear dispersion.

2. Advection diffusion equation

We start our analysis with the advection diffusion equation

$$\partial_t c + u\partial_x c - \nabla \cdot (\kappa \nabla c) = 0, \tag{2.1}$$

with the condition (1.1) at the flow boundary ∂A. Here $u(y,z)$ is the longitudinal velocity along the x-axis, $\kappa(y,z)$ the transverse diffusivity tensor, ∇ the transverse gradient operator $(0, \partial_y, \partial_z)$, and $\boldsymbol{n}$ the outward normal. We have ignored the effect of longitudinal diffusion, on the assumption that after a short distance downstream it is dominated by shear dispersion (Taylor 1953). The loss of chemically active solutes by a first-order reaction in the flowing region can be included by adding a term $-\gamma c$ on the right-hand side of (2.1). However, this term may be removed by transforming to $c = c' \exp(-\gamma t)$, and so we can set $\gamma = 0$ without loss of generality (Boddington & Clifford 1983).

If we ignore the effect of flow boundary retention ($J(t) = 0$), then at steady state, (2.1) admits an exponentially decaying solution $\exp(-\lambda x)$. The combined effects of diffusion and flow boundary reaction are to erode the concentration variations towards the (non-negative) asymptotic profile $\psi(y,z)$, which satisfies

$$\nabla \cdot (\kappa \nabla \psi) + \lambda u \psi = 0, \tag{2.2a}$$

with

$$\kappa \boldsymbol{n} \cdot \nabla \psi = \beta \psi \quad \text{on} \quad \partial A, \tag{2.2b}$$

and

$$\overline{\psi^2} = 1, \tag{2.2c}$$

where the decay rate λ, which determines the amount of solutes remaining in the flow, is given by

$$\lambda = \frac{\overline{\kappa(\nabla\psi)^2} + (1/A)\oint \beta\psi^2}{\overline{u\psi^2}}. \tag{2.3}$$

$\oint$ denotes an integration around the flow boundary, the overbars denote the cross-sectional average values, and A is the cross-sectional flow area.

In order to examine the effect of flow boundary retention when there exists reaction at the flow boundary, we make a change of dependent variable:

$$c = C\psi(y,z)\exp(-\lambda x). \tag{2.4}$$

In the axes moving with the bulk velocity $\tilde{U}$, (4.6), the new variable C satisfies

$$\psi^2\partial_t C + \psi^2(u-\tilde{U})\partial_x C - \nabla\cdot(\psi^2\kappa\nabla C) = 0, \tag{2.5a}$$

with
$$\psi^2\kappa\boldsymbol{n}\cdot\nabla C = -\psi^2\partial_t\Gamma + \psi^2\tilde{U}\partial_x\Gamma \quad \text{on} \quad \partial A, \tag{2.5b}$$

where Γ represents the trapped solutes in the retentive layer

$$\Gamma = \int_0^t \mathrm{d}\tau\, J(t-\tau)\, C(x+\tilde{U}\tau, y, z, \tau). \tag{2.5c}$$

In order to determine the large-time behaviour, we shall for simplicity restrict our attention to the case of an initial discharge with distribution ψ across the flow: at $t = 0$ a unit amount of solute is released at the plane $x = 0$. We will also consider the retentive layer to be stagnant; as shown in the Appendix this is a good approximation to the Boddington & Clifford (1983) model.

3. Some notation and the method of moments

As shown by Purnama (1988*a*) for the dispersion of passive solutes, and by using an appropriate composite cross-sectional averaging, the effects of the flow boundary retention can be incorporated into the conventional (no retention) Aris (1956) method of moments. Here we define the corresponding composite cross-sectional average value for the dispersion of chemically active solutes, which includes averaging over the retentive layer, as

$$\tilde{C} = \frac{\overline{\psi^2 C} + (1/A)\oint \psi^2\Gamma}{1+J_0}, \tag{3.1a}$$

where
$$J_0 = \frac{1}{A}\oint\psi^2\int_0^\infty \mathrm{d}\tau\, J(\tau). \tag{3.1b}$$

The x-derivative in (2.5*a*, *b*) could be eliminated if we introduce the moments

$$C_m = \int_{-\infty}^{\infty} \mathrm{d}x\, x^m C, \tag{3.2a}$$

with the composite cross-sectionally averaged moments

$$M_m = \int_{-\infty}^{\infty} \mathrm{d}x\, x^m \tilde{C} \quad (m = 0, 1, 2, \ldots). \tag{3.2b}$$

Taking moments of (2.5*a*–*c*), we obtain a hierarchy of equations for successive C_m:

$$\psi^2\partial_t C_m - \nabla\cdot(\psi^2\kappa\nabla C_m) = m\psi^2(u-\tilde{U})\, C_{m-1}, \tag{3.3a}$$

with
$$\psi^2\kappa\boldsymbol{n}\cdot\nabla C_m = -\psi^2\partial_t\Gamma_m - m\psi^2\tilde{U}\Gamma_{m-1} \quad \text{on} \quad \partial A, \tag{3.3b}$$

where
$$\Gamma_m = \int_0^t \mathrm{d}\tau\, J(t-\tau)\left[C_m(\tau) + \sum_{r=1}^{m}(-1)^r\frac{m!}{r!(m-r)!}(\tilde{U}\tau)^r C_{m-r}(\tau)\right], \tag{3.3c}$$

and
$$C_0 = 1, \quad C_1 = C_2 = \ldots = C_m = 0 \quad \text{at} \quad t = 0. \tag{3.3d}$$

The successive M_m evolve in accordance with

$$d_t M_m = m\widetilde{\psi^2(u-\tilde{U})\,C_{m-1}}, \tag{3.4}$$

where the tilde denotes the composite cross-sectional averaging defined in (3.1*a, b*). Indeed, what has been achieved through the introduction of the composite cross-sectional averaging is the elimination of any explicit occurrence of terms associated with the retentive layer at the flow boundary. The considerable advantage of using the composite cross-sectional averaging is that many of the results from the conventional method of moments for the dispersion of passive solutes with no flow boundary retention can be transferred directly simply by replacing an overbar by a tilde (weighted with ψ^2). Thus, as has been done by Purnama (1988*a*) for the dispersion of passive solutes, we can straightforwardly adapt any result of the conventional method of moments with no flow boundary retention. For example, if $\overline{\overline{C}}_{1\infty}$ denotes the asymptotic value of the first moment calculated using the conventional method of moments, then (cf. Smith 1981, equation (3.1))

$$\overline{\overline{M}}_2 = 2t\overline{(u-\bar{u})\overline{\overline{C}}_{1\infty}} + 2\int_0^t \mathrm{d}\tau\,\overline{(u-\bar{u})(\overline{\overline{C}}_1-\overline{\overline{C}}_{1\infty})}. \tag{3.5a}$$

The analogy with the dispersion of chemically active solutes (a tilde, weighted with ψ^2, replacing an overbar) permits us to infer that

$$M_2 = 2t\widetilde{\psi^2(u-\tilde{U})\,C_{1\infty}} + 2\int_0^t \mathrm{d}\tau\,\widetilde{\psi^2(u-\tilde{U})(C_1-C_{1\infty})}, \tag{3.5b}$$

4. First moment

The use of composite cross-sectional averaging ensures that the pattern of calculation proceeds as in the conventional method of moments for the dispersion of passive solutes with no flow boundary retention. For large times $\overline{C}_0 = 1$ and the first moment is formulated by the conventional method of moments as (cf. Smith 1981, equation (4.1))

$$\overline{\overline{C}}_{1\infty}(y) = g(y), \tag{4.1}$$

which satisfies the equation

$$\partial_y(\kappa\partial_y g) = \bar{u}-u, \tag{4.2a}$$

with

$$\kappa\partial_y g = 0 \quad \text{on} \quad \partial A, \tag{4.2b}$$

and

$$\bar{g} = 0. \tag{4.2c}$$

By analogy with the above results, we can infer that at large times C_0 remains uniform across the flow and has the constant value $M_{0\infty} = 1$. The corresponding form of the asymptotic first moment is given by

$$C_{1\infty}(y,z) = G(y,z), \tag{4.3}$$

which satisfies the equation

$$\nabla\cdot(\psi^2\kappa\nabla G) = -\psi^2(u-\tilde{U}), \tag{4.4a}$$

with

$$\psi^2\kappa\boldsymbol{n}\cdot\nabla G = -\psi^2\tilde{U}\int_0^\infty \mathrm{d}\tau\,J(\tau) \quad \text{on} \quad \partial A, \tag{4.4b}$$

and

$$\overline{\psi^2 G} = 0. \tag{4.4c}$$

Next (4.3) also implies that, for large t,

$$d_t M_{1\infty} = 0, \tag{4.5}$$

that is, in axes moving with the bulk velocity $\tilde{U}$, the centroid of the solute cloud remains stationary. Hence, from (3.4) with $m = 1$, the bulk velocity can readily be determined by

$$\tilde{U} = \frac{\overline{u\psi^2}}{1+J_0}, \tag{4.6}$$

since the flow within the retentive layer is stagnant.

The effect of chromatographic retention of chemically active solutes was first reported by Clifford *et al.* (1982) when measuring the diffusion coefficient of hydrogen atoms in flowing nitrogen and flowing argon. However, in their analysis of the experimental results (Clifford *et al.* 1982, equation (5)), they took $\bar{u}$, the mean gas carrier velocity, instead of $\overline{u\psi^2}$, which means that the bulk velocity $\tilde{U}$ does not depend on the irreversible loss of the hydrogen atoms by reaction on the pipe wall. In the absence of the flow boundary retention ($J(t) = 0$), this is only true when $\beta = 0$ (passive solutes), and for the case of $\beta \neq 0$ Sankarasubramanian & Gill (1973, figure 3) pointed out that the centroid distribution moves along at a velocity higher than the average velocity of the flow, $\bar{u}$ (Smith 1983, figure 2; Barton 1984, figure 2).

Plumb *et al.* (1983) reported that there was no evidence for a chromatographic effect when studying the diffusion of oxygen atoms in flowing helium. The value for the rate of loss of oxygen atoms by reactions at the walls is found typically to be 1.5 s^{-1} (Plumb *et al.* 1983). Following the non-dimensionalization procedure used by Barton (1984), the value of β equivalent to Barton's (1984) is found to be of the order 10^{-3}. In contrast, following the work of Boddington & Clifford (1983, equation (1.6)), we deduce that a value of β equivalent to Barton's of 2 must have been used in the Clifford *et al.* (1982) analyses of their experimental results. As an illustrative example (§7), the value of β in the present work equivalent to Barton's is 4.

5. Longitudinal shear dispersion

By analogy with the conventional case of dispersion of passive solutes, the coefficient of $2t$ in (3.5*b*) gives us a formula for the longitudinal shear dispersion coefficient

$$D = \widetilde{\psi^2(u-\tilde{U})\,C_{1\infty}}, \tag{5.1a}$$

and from the definition of the tilde averaging (3.1*a*, *b*), we find

$$(1+J_0)\,D = \overline{\psi^2(u-\tilde{U})\,G} - \frac{1}{A}\oint \psi^2 \tilde{U} G \int_0^\infty \mathrm{d}\tau\, J(\tau) + \tilde{U}^2 J_1, \tag{5.1b}$$

where

$$J_1 = \frac{1}{A}\oint \psi^2 \int_0^\infty \mathrm{d}\tau\, \tau J(\tau). \tag{5.1c}$$

If we multiply (4.4*a*) by $G(y,z)$ and integrate over the flow, then we can derive the identity

$$\overline{\psi^2(u-\tilde{U})\,G} - \frac{1}{A}\oint \psi^2 \tilde{U} G \int_0^\infty \mathrm{d}\tau\, J(\tau) = \overline{\psi^2 \kappa (\nabla G)^2}. \tag{5.2}$$

Thus, we can show that

$$(1+J_0)\,D = \overline{\psi^2 \kappa (\nabla G)^2} + \tilde{U}^2 J_1. \tag{5.3}$$

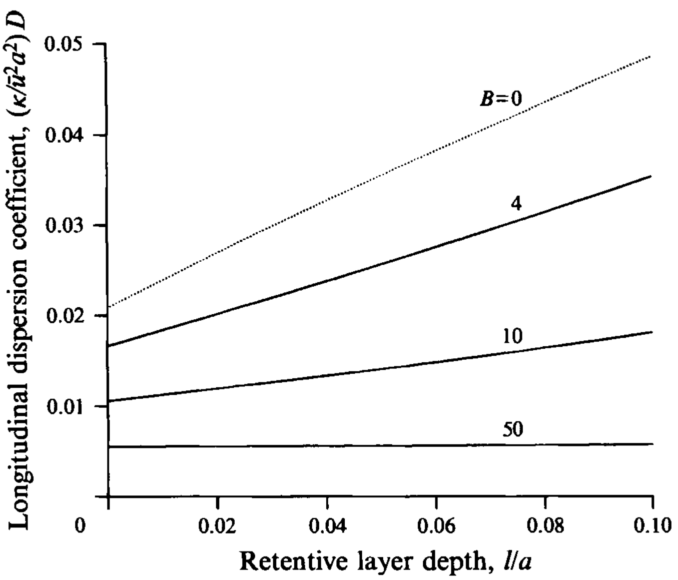

FIGURE 1. The longitudinal dispersion coefficient D for Poiseuille pipe flow.

This is strictly non-negative. For the dispersion of passive solutes ($\beta = 0; \psi = 1$) with no flow boundary retention ($J(t) = 0$), it reduces to the well-known Taylor (1953) longitudinal shear dispersion coefficient.

For Poiseuille pipe flow with a radius a (§7) we obtain a formula for D, which only involves the velocity $u(r)$, diffusivity $\kappa(r)$, and asymptotic concentration profile $\psi(r)$:

$$\begin{aligned}(1+J_0)^2D = {} & 2a^2\int_0^1 \mathrm{d}R\frac{1}{R\psi^2\kappa}\left(\int_0^R \mathrm{d}R'\,R'\psi^2(u-\overline{u\psi^2})\right)^2 \\ & +J_0\left(2a^2\int_0^1 \mathrm{d}R\frac{1}{R\psi^2\kappa}\left\{\int_0^R \mathrm{d}R'\,R'u\psi^2\right\}^2\right) \\ & -\frac{\overline{(u\psi^2)}^2J_0}{1+J_0}\left(2a^2\int_0^1 \mathrm{d}R\frac{1}{R\psi^2\kappa}\left\{\int_0^R \mathrm{d}R'\,R'\psi^2\right\}^2\right)+\frac{\overline{(u\psi^2)}^2J_1}{1+J_0}. \qquad (5.4a)\end{aligned}$$

Here, (3.1b) and (5.1c) reduce to

$$J_0 = \frac{1}{a}\psi^2(1)\int_0^\infty \mathrm{d}\tau\,J(\tau), \quad J_1 = \frac{1}{a}\psi^2(1)\int_0^\infty \mathrm{d}\tau\,\tau J(\tau). \qquad (5.4b, c)$$

A similar result for the exchange between phases (gas and liquid) flowing in a pipe and its surrounding annulus has been formulated by Aris (1959) and Davidson & Schroter (1983). Using (7.7) and (7.8), (5.4a) becomes (Davidson & Schroter 1983, equation (B 13))

$$D = \frac{\bar{u}^2a^2}{\kappa}\left[\breve{R}\left(\frac{11-16\breve{R}+6\breve{R}^2}{48}\right)+(1-\breve{R})\,\breve{R}^2\left(\frac{b^4\ln b}{2(b^2-1)}-\frac{3b^2-1}{8}\right)\right], \qquad (5.4d)$$

which may be obtained from Aris (1959, equations (17), (21) and (22)), where

$$\breve{R} = 1/(1+J_0) \quad \text{and} \quad b = 1+l/a.$$

Figure 1 show the dependence of D in Poiseuille pipe flow (§7) upon l/a for the stagnant layer model (see the Appendix) with $\kappa_l = \kappa$. Note that the value of $D(l/a = 0)$ decreases as the (dimensionless) wall reaction coefficient B increases. As was noted by Sankarasubramanian & Gill (1973, figure 4), Smith (1983, figure 7) and Barton (1984, figure 3), the effect of removing solutes at the flow boundary is to reduce the rate of shear dispersion. For very large B, this value is finally reduced to less than one-fifth of Taylor's value.

In contrast, the effect of flow boundary retention alone at the pipe wall is to increase the rate of shear dispersion (Purnama 1988*a*, figure 3), and this dominant effect supresses the effect of flow boundary reaction provided B is not very large. For $B = 4$ in Poiseuille pipe flow (§7) using the stagnant layer model (see the Appendix) with $\kappa_l = \kappa$, the longitudinal shear dispersion coefficient D is 55% greater than the value of $D(l/a = 0)$ for $l/a = 0.05$. For large B, the effect of flow boundary retention is negligible. This is expected since, as shown in figure 3, there is so little solute close to the flow boundary.

As an aid to the skewness calculation given in the next section, we proceed to the equation for C_2. The form of the second moment can be made more precise at large t in the conventional case of the method of moments (cf. Daish 1985, equation (3.6)):

$$\overline{C}_{2\infty} = 2\overline{D}t + 2g_2 - 2\overline{g^2}, \tag{5.5}$$

where $g_2(y)$ satisfies

$$\partial_y(\kappa \partial_y g_2) = \overline{(u-\overline{u})g} - (u-\overline{u})g, \tag{5.6a}$$

with

$$\kappa \partial_y g_2 = 0 \quad \text{on} \quad \partial A, \tag{5.6b}$$

and

$$\overline{g_2} = 0. \tag{5.6c}$$

Again by analogy with these results, replacing an overbar by a tilde (weighted with ψ^2), the corresponding form of the asymptotic second moment is given by

$$C_{2\infty} = 2Dt + 2G_2 - 2\widetilde{\psi^2 G^2}, \tag{5.7}$$

where the corresponding $G_2(y, z)$ satisfies the equation

$$\nabla \cdot (\psi^2 \kappa \nabla G_2) = \psi^2(\widetilde{\psi^2(u-\tilde{U})G} - (u-\tilde{U})G), \tag{5.8a}$$

with

$$\psi^2 \kappa \boldsymbol{n} \cdot \nabla G_2 = -\psi^2(D+\tilde{U}G)\int_0^\infty \mathrm{d}\tau\, J(\tau) + \psi^2 \tilde{U}^2 \int_0^\infty \mathrm{d}\tau\, \tau J(\tau) \quad \text{on} \quad \partial A, \tag{5.8b}$$

and

$$\overline{\psi^2 G_2} = 0. \tag{5.8c}$$

6. Skewness

A linear growth of the variance with time is not sufficient to ensure that the distribution of solute concentration is Gaussian. Purnama (1988*a*, figure 9) has shown for the dispersion of passive solutes that the flow boundary retention alone is responsible for the skewness of concentration distributions.

Now proceeding to the calculation of the higher-order moments, with $m = 3$ in (3.4) and from (5.7), at large t, finally we have

$$d_t M_{3\infty} = 6S, \tag{6.1a}$$

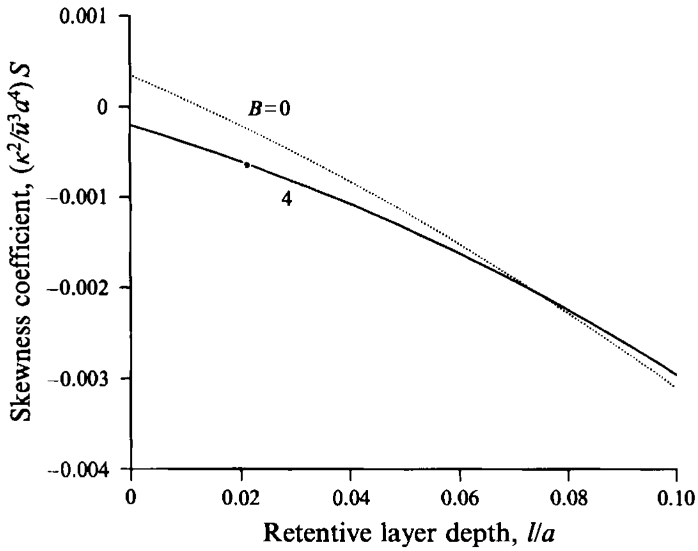

FIGURE 2. The skewness coefficient S for Poiseuille pipe flow.

where the skewness coefficient S is given by

$$(1+J_0)\,S=\overline{\psi^2(u-\tilde{U})\,G_2}-\frac{1}{A}\oint\psi^2\tilde{U}G_2\int_0^\infty \mathrm{d}\tau\,J(\tau)$$

$$+\frac{1}{A}\oint\psi^2\tilde{U}(\tilde{U}G-D)\int_0^\infty \mathrm{d}\tau\,\tau J(\tau)-\tfrac{1}{2}\tilde{U}^3J_2, \quad (6.1\,b)$$

$$J_2=\frac{1}{A}\oint\psi^2\int_0^\infty \mathrm{d}\tau\,\tau^2J(\tau). \quad (6.1\,c)$$

The increase in complexity of $G_2(y,z)$ deters us from continuing the analysis to even higher-order moments. The usefulness of (6.1*b*) depends upon the ease with which we can manipulate $G(y,z)$. From (4.4*a–c*) and (5.8*a–c*), we can derive the identity

$$\overline{\psi^2(u-\tilde{U})\,G_2}=\overline{\psi^2(u-\tilde{U})\,G^2}-\frac{1}{A}\oint\psi^2[G(\tilde{U}G+D)-\tilde{U}G_2]\int_0^\infty \mathrm{d}\tau\,J(\tau)$$

$$+\frac{1}{A}\oint\psi^2\tilde{U}^2G\int_0^\infty \mathrm{d}\tau\,\tau J(\tau). \quad (6.2)$$

This enables us to eliminate $G_2(y,z)$ in (6.1*b*):

$$(1+J_0)\,S=\overline{\psi^2(u-\tilde{U})\,G^2}-\frac{1}{A}\oint\psi^2G(\tilde{U}G+D)\int_0^\infty \mathrm{d}\tau\,J(\tau)$$

$$+\frac{1}{A}\oint\psi^2\tilde{U}(2\tilde{U}G-D)\int_0^\infty \mathrm{d}\tau\,\tau J(\tau)-\tfrac{1}{2}\tilde{U}^3J_2. \quad (6.3)$$

The skewness S_3, defined by (Boddington & Clifford 1983, equation (7.10))

$$S_3=6St/(2Dt)^{3/2}, \quad (6.4)$$

eventually decays at the slow rate of $t^{-1/2}$. Figure 2 shows the dependence of S in Poiseuille pipe flow (§7) upon l/a for the stagnant layer model (see the Appendix) with

$\kappa_l = \kappa$. In the absence of the flow boundary retention ($J(t) = 0$), Smith (1983) pointed out that for Poiseuille pipe flow, the effect of flow boundary reaction alone is to reduce and change the sign of the skewness. Similar features have also been observed for the dispersion of passive solutes, due to the effects of flow boundary retention (Purnama 1988*a*). For very large B, we expect that the effect of flow boundary retention is negligible; since removal of solutes at the boundary increases $\overline{u\psi^2}$, the variation of $u-\overline{u\psi^2}$ across the flow tends to be decreased (figure 4).

7. Poiseuille pipe flow

An application for the present work is to the flow reactor, a device for measuring reaction rates for chemical reactions taking place in a mixture of fluids (Clifford *et al.* 1982; Plumb *et al.* 1983). The flow reactor consists of a circular pipe of radius a through which a fluid flows. The main flow velocity profile takes the form

$$u(R) = 2\bar{u}(1-R^2), \tag{7.1}$$

where $R = r/a$.

The asymptotic concentration profile equation (2.2*a*, *b*) transforms to

$$\frac{1}{R}\partial_R(R\,\partial_R\,\psi)+2\lambda\frac{\bar{u}a^2}{\kappa}(1-R^2)\,\psi = 0, \tag{7.2a}$$

with

$$2\frac{\kappa}{a}\partial_R\,\psi = -\beta\psi \quad \text{on} \quad R = 1. \tag{7.2b}$$

For simplicity, we will take the (dimensionless) pipe wall reaction coefficient B such that

$$B \equiv a\beta/\kappa = 4. \tag{7.3}$$

A convenient feature of this special case is that there are simple explicit formulae for $\psi(R)$, λ, and $\tilde{U}$:

$$\psi(R) = \left(\frac{2e^2}{e^2-1}\right)^{1/2}\exp(-R^2), \quad \lambda = 2\frac{\kappa}{a^2\bar{u}}, \quad \tilde{U} = \bar{u}\frac{e^2+1}{e^2-1}\frac{1}{(1+J_0)}. \tag{7.4}$$

The asymptotic concentration profile $\psi(R)$ is shown in figure 3. The effect of the efficient removal of solutes at the flow boundary is to bring the concentration close to zero at the pipe wall (Sankarasubramanian & Gill 1973; Smith 1983).

To quantify the effect of flow boundary retention when there exists reaction at the pipe wall, we need to evaluate $G(R)$. Unfortunately, it is not possible to express $G(R)$ in closed form:

$$\begin{aligned}(1+J_0)\,G(R)-[g(0)+J_0 f(0)] = {} & -\frac{\bar{u}a^2}{\kappa}\left[\tfrac{1}{4}R^2+\int_0^R \mathrm{d}R'\,\frac{1-\exp(2R'^2)}{2(e^2-1)\,R'}\right] \\ & -J_0\frac{\bar{u}a^2}{\kappa}\left[\tfrac{1}{4}R^2-\frac{1}{4}\int_0^R \mathrm{d}R'\,\frac{1-\exp(2R'^2)}{R'}\right],\end{aligned} \tag{7.5}$$

where

$$g(0) = \frac{\bar{u}a^2}{\kappa}\left[\frac{1}{8}\left(\frac{e^2-3}{e^2-1}\right)-\frac{1}{2}\int_0^1 \mathrm{d}R\,\frac{1-\exp(2R^2)}{(e^2-1)^2\,R}+\frac{e^2}{2}\int_0^1 \mathrm{d}R\,\frac{\exp(-2R^2)-1}{(e^2-1)^2\,R}\right], \tag{7.6a}$$

$$f(0) = \frac{\bar{u}a^2}{\kappa}\left[\frac{1}{8}\left(\frac{e^2-3}{e^2-1}\right)+\frac{1}{2}\int_0^1 \mathrm{d}R\,\frac{1-\exp(2R^2)}{(e^2-1)\,R}-\frac{e^2}{2}\int_0^1 \mathrm{d}R\,\frac{\exp(-2R^2)-1}{(e^2-1)\,R}\right]. \tag{7.6b}$$

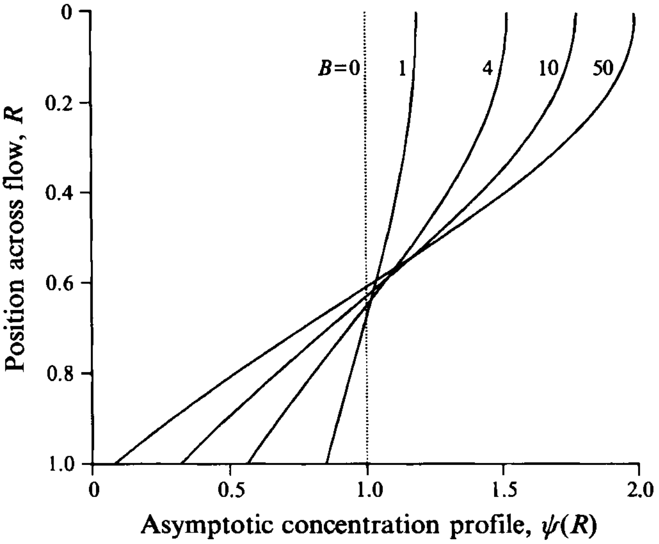

FIGURE 3. The asymptotic concentration profile ψ across the flow for Poiseuille pipe flow.

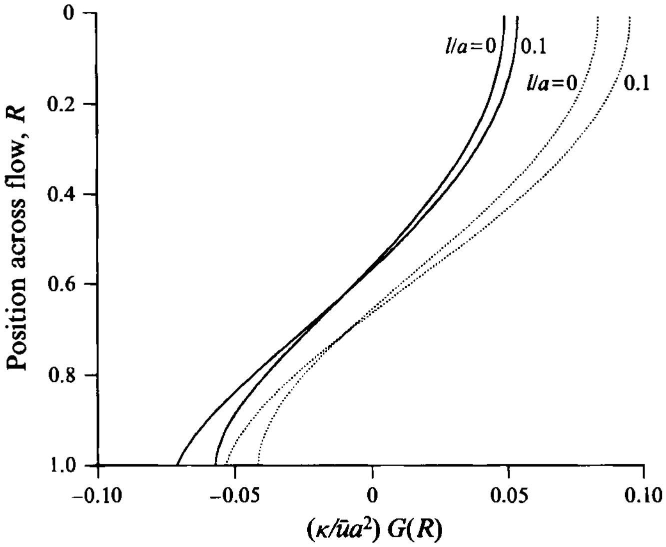

FIGURE 4. The profile of G across the flow for Poiseuille pipe flow with $B = 4$ (——) and $B = 0$ (⋯⋯).

However, we can evaluate (7.6) numerically:

$$g(0) = \frac{\bar{u}a^2}{\kappa}(0.04873), \quad f(0) = \frac{\bar{u}a^2}{\kappa}(0.20451).$$

For comparison, the corresponding result for the dispersion of passive solutes with flow boundary retention is

$$(1+J_0)\,G(R) = \frac{\bar{u}a^2}{24\kappa}(2-6R^2+3R^4)+J_0\frac{\bar{u}a^2}{24\kappa}(5-12R^2+3R^4). \tag{7.7}$$

For the stagnant layer model with $\kappa_l = \kappa$, we have from the Appendix

$$J_0 = \tfrac{1}{2}\psi^2(1)\frac{l}{a}\left(2+\frac{l}{a}\right), \tag{7.8a}$$

$$J_1 = \frac{a^2}{\kappa}\psi^2(1)\left[\frac{1}{4}\left(1+\frac{l}{a}\right)^4 \ln\left(1+\frac{l}{a}\right)-\frac{1}{8}\left(\frac{l}{a}\right)^2\left(2+\frac{l}{a}\right)^2\right], \tag{7.8b}$$

$$J_2 = \frac{1}{2}\left(\frac{a^2}{\kappa}\right)^2\left[2\left(1+\frac{l}{a}\right)^2 \ln\left(1+\frac{l}{a}\right)-\frac{l}{a}\left(2+\frac{l}{a}\right)\right]J_1. \tag{7.8c}$$

Figure 4 shows the variation of $G(R)$ across the flow. For chemically active solutes, the effect of flow boundary retention is supressed by the removal of solutes at the boundary because the variation of $u-\overline{u\psi^2}$ across the flow decreases as B increases.

8. Concluding remarks

We have generalized the method of moments to account for dispersion of chemically active solutes in the presence of both reactions and retention at the flow boundary. The effect of flow boundary retention is represented by the kernel $J(t)$, which embodies the totality of motion and mixing within the retentive layer. We have showed that the longitudinal shear dispersion coefficient D is increased and the skewness S_3 is decreased as the retentive layer depth increases, provided that the effect of chemical reaction at the flow boundary is not very large.

Although the widely used method of moments gives a great deal of information about the distribution of solute concentration across the flow as it disperses, it has the disadvantage that it does not give a direct expression for C or $\overline{\psi^2 C}$. For chemically active solutes, Barton (1984) has shown that we can also use the large-time Chatwin (1970) asymptotic expansion for $\overline{\psi^2 C}$. Again by analogy with the results of Smith (1981, appendix), we infer that, at large time,

$$\overline{\psi^2 C} = \frac{\exp\left(-\tfrac{1}{2}Z^2\right)}{(4\pi D t)^{1/2}}\left[1+\frac{S_3 He_3}{6}+\frac{S_3^2 He_6}{72}+O(t^{-3/2})\right], \tag{8.1}$$

with
$$Z = (x-\tilde{U}t)/(2Dt)^{1/2}, \tag{8.2}$$

and He_3 and He_6 are Hermite polynomials defined by

$$He_3(Z) = Z^3-3Z, \quad He_6(Z) = Z^6-15Z^4+45Z^2-15. \tag{8.3}$$

The series (8.1) is believed to be asymptotic rather than convergent, and unfortunately it may give negative values (figures 5 and 6), particularly near the tails where higher-order terms decrease in a somewhat irregular manner. The first term is the Gaussian function, and the succeeding terms describe the departure from the Gaussian profile.

Conventionally, the asymptotic form is achieved after 3e-folding times, the time for cross-sectional mixing. By analogy with the results of Purnama (1988*a*, §7), the e-folding time T_e can be formulated as

$$T_e = \frac{\widetilde{\psi^2 G^2}}{\widetilde{\psi^2 (u-\tilde{U})G}}, \tag{8.4a}$$

and the corresponding e-folding distance for the decay of transverse concentration variation is given by

$$Z_e = \tilde{U}T_e. \tag{8.4b}$$

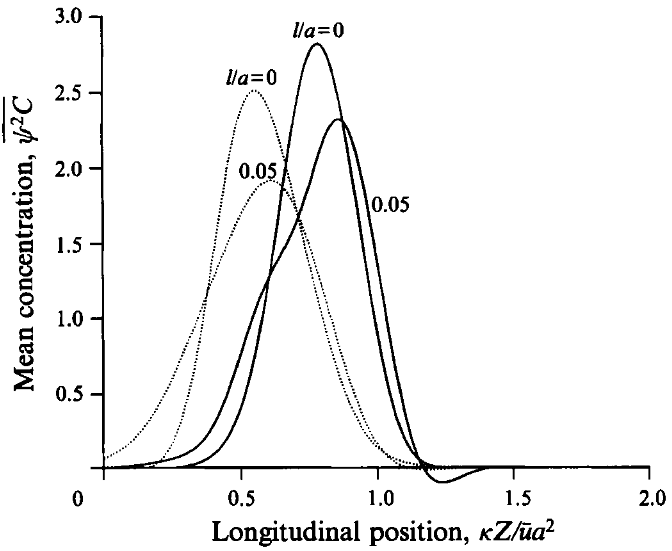

FIGURE 5. The mean concentration $\overline{\psi^2 C}$ for Poiseuille pipe flow at $t = 9\overline{\overline{T}}_e$ with $B = 4$ (——) and $B = 0$ (······).

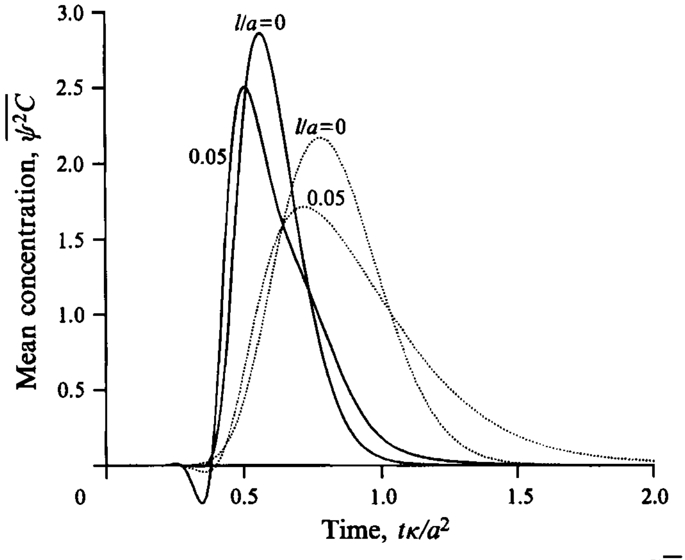

FIGURE 6. The mean concentration $\overline{\psi^2 C}$ for Poiseuille pipe flow at $Z = 9\tilde{U}\overline{\overline{T}}_e$ with $B = 4$(——) and $B = 0$ (······).

In the absence of flow boundary retention ($J(t) = 0$), Smith (1983) shows that for Poiseuille pipe flow, $T_e(l/a = 0)$ is a decreasing function of β; and at $\beta = 0$, $\overline{\overline{T}}_e(l/a = 0) = \frac{1}{15}$.

The asymptotic profiles of $\overline{\psi^2 C}$ in Poiseuille pipe flow (§7) at $9\overline{\overline{T}}_e(l/a = 0)$ and at $9\tilde{U}\overline{\overline{T}}_e(l/a = 0)$ are shown in figures 5 and 6 respectively for the stagnant layer model (see the Appendix) with $\kappa_l = \kappa$. As the retentive layer depth is increased the extended tail becomes more and more pronounced.

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Appendix. Kernel $J(t)$ for the stagnant layer model

In their study of the dispersion of hydrogen atoms in a flowing gas along the tube, Boddington & Clifford (1983, equations (1.6) and (1.7)) formulated the boundary condition at the tube wall as

$$\kappa \partial_r c = -\beta c - \partial_t c_s, \tag{A 1a}$$

where the wall concentration c_s changes at a rate given by

$$\partial_t c_s = k_1 c - k_2 c_s. \tag{A 1b}$$

Here k_1 and k_2 are the rate of adsorption on and desorption from the tube wall, respectively. On integrating (A 1*b*), we can rewrite (A 1*a*):

$$\kappa \partial_r c = -\beta c - k_1 \partial_t \int_0^t \mathrm{d}\tau\, c(t-\tau) \exp(-k_2 \tau). \tag{A 2a}$$

Hence, from (1.1), we deduce that, for the Boddington & Clifford (1983) model,

$$J(t) = k_1 \exp(-k_2 t). \tag{A 2b}$$

In the stagnant layer (annulus) of depth l surrounding a pipe of radius a, the solute concentration c_l satisfies

$$\partial_t c_l - (1/r)\partial_r(\kappa_l r \partial_r c_l) = 0, \tag{A 3a}$$

with

$$c_l = c \quad \text{on} \quad r = a, \tag{A 3b}$$

and

$$\partial_r c_l = 0 \quad \text{on} \quad r = a+l, \tag{A 3c}$$

and, initially,

$$c_l = 0, \quad t = 0. \tag{A 3d}$$

For the case of constant molecular diffusivity κ_l, the solution can be found using Laplace transforms:

$$\hat{c}_l \equiv \int_0^\infty \mathrm{d}t\, c_l(t) \exp(-pt).$$

By taking the Laplace transform of (A 3*a–d*), we obtain

$$\left.\begin{aligned} \hat{c}_l &= \hat{c}\frac{I_0(qr)\,K_1(q(a+l)) + I_1(q(a+l))\,K_0(qr)}{I_0(qa)\,K_1(q(a+l)) + I_1(q(a+l))\,K_0(qa)}, \\ q^2 &= p/\kappa_l, \end{aligned}\right\} \tag{A 4}$$

where $I_{0,1}(qr), K_{0,1}(qr)$ are modified Bessel functions, and we have used the recurrence relations (Abramowitz & Stegun 1965, equation (9.6.27))

$$I_0'(r) = I_1(r), \quad K_0'(r) = -K_1(r). \tag{A 5}$$

At $r = a$, we also have the boundary condition

$$\kappa \partial_r c = -\beta c + \kappa_l \partial_r c_l,$$

thus

$$\kappa_l \partial_r \hat{c}_l = p\hat{c}\frac{1}{q}\left(\frac{I_1(qa)\,K_1(q(a+l)) - K_1(qa)\,I_1(q(a+l))}{I_0(qa)\,K_1(q(a+l)) + K_0(qa)\,I_1(q(a+l))}\right).$$

On comparison with the Laplace transform of (1.1), we deduce that

$$\hat{J}(p) = -\frac{1}{q}\left(\frac{I_1(qa)\,K_1(q(a+l)) - K_1(qa)\,I_1(q(a+l))}{I_0(qa)\,K_1(q(a+l)) + K_0(qa)\,I_1(q(a+l))}\right). \tag{A 6}$$

As our limited concern here is to determine the form of the kernel at large times, we shall extract the small-p behaviour from (A 6). Using the series expansion for the modified Bessel functions (Abramowitz & Stegun 1965, equations (9.6.12) and (9.6.13)), (A 6) reduces to

$$\hat{J}(p) = -(\rho + \sigma p)/(1 + \omega p),$$

where

$$\left.\begin{aligned} \rho = -\tfrac{1}{2}l(2+l/a), \quad \sigma = (a^3/4\kappa_l)\,(1+l/a)^2 \ln(1+l/a), \\ \omega = (a^2/4\kappa_l)\,[2(1+l/a)^2 \ln(1+l/a) - (l/a)(2+l/a)]. \end{aligned}\right\} \tag{A 7}$$

Using the Inversion theorem, we have, for the stagnant layer model,

$$J(t) = \left(-\frac{\rho}{\omega} + \frac{\sigma}{\omega^2}\right)\exp\left(-\frac{t}{\omega}\right) - \frac{\sigma}{\omega}\delta(t), \tag{A 8}$$

with

$$\int_0^\infty \mathrm{d}\tau\, J(\tau) = -\rho, \quad \int_0^\infty \mathrm{d}\tau\, \tau J(\tau) = -\rho\omega + \sigma, \quad \int_0^\infty \mathrm{d}\tau\, \tau^2 J(\tau) = -2(\rho\omega^2 - \sigma\omega). \tag{A 9}$$

To determine the stagnant layer depth l, we seek to approximate k_1 and k_2 from the Boddington & Clifford (1983) model. If the bulk velocity and longitudinal shear dispersion coefficient are to be correctly reproduced, then the integrals

$$\int_0^\infty \mathrm{d}\tau\, J(\tau) \quad \text{and} \quad \int_0^\infty \mathrm{d}\tau\, \tau J(\tau)$$

need to be correct:

$$k_1 = -\rho k_2, \quad k_2 = \rho/(\rho\omega - \sigma). \tag{A 10}$$

Next, using the experimental parameters obtained by Clifford *et al.* (1982, tables 2 and 3),

$$\frac{2k_1}{ak_2} \approx 0.11,$$

we estimated that, from (A 7) and (A 10), the equivalent stagnant layer has a depth of

$$l/a \approx 0.05.$$

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