PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Dispersion of Chemical Solutes in Chromatographs and Reactors

Vemuri Balakotaiah and Hsueh-Chia Chang

Phil. Trans. R. Soc. Lond. A 1995 **351**, 39-75
doi: 10.1098/rsta.1995.0025

Dispersion of chemical solutes in chromatographs and reactors

By Vemuri Balakotaiah[1] and Hsueh-Chia Chang[2]

[1] *Department of Chemical Engineering, University of Houston, Houston, TX 77204, U.S.A.*

[2] *Department of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556, U.S.A.*

Contents

The dispersion of a chemically active solute in unidirectional laminar flow in a channel of constant cross-sectional area is considered. Adsorption/desorption of the solute at the wall or the presence of a bulk or surface chemical reaction introduce additional timescales, in addition to the diffusive and convective ones, such that, under certain conditions, the asymptotic evolution of the cross-sectional mean concentration cannot be described by a one-dimensional Taylor–Aris model. We use the centre and invariant manifold theories to establish the proper time and length scale separations necessary for the existence of an effective transport equation and to determine the dependence of the effective transport coefficients on the kinetics of adsorption/desorption and reaction. For the case of classical Taylor–Aris dispersion with no reaction, we derive the effective transport equation

Phil. Trans. R. Soc. Lond. A (1995) **351**, 39–75
Printed in Great Britain

TEX Paper

to infinite order in the parameter, p, representing the ratio of the characteristic time for radial molecular diffusion to that for axial convection. We show that the infinite series in the effective transport model is convergent provided p is smaller than some critical value, which depends on the initial concentration distribution. We also examine the spatial evolution of time dependent inlet conditions and show that the spatial and temporal evolutions differ at third and higher orders.

It is shown that, except for slow reactions with a kinetic timescale of the same order as the transverse diffusion time, fast bulk reaction does not allow an asymptotic axial dispersion description. Slow bulk reactions do not affect dispersion but a correction to the apparent kinetics may arise due to nonlinear interaction among reaction, diffusion and convection. It is also shown that with a slow bulk reaction, steady-state dispersion due to a coupling of reaction and transverse velocity gradient can arise. Although this mechanism is distinct from the transient Taylor–Aris mechanism, the dispersion coefficient is identical to the classical unreactive Taylor–Aris coefficient. Surface reaction of any speed yields the proper asymptotic behaviour in time because the species still needs to diffuse slowly to the conduit wall. In the limit of fast surface reaction, the Taylor–Aris dispersion coefficient is reduced by a factor of 4.2, 7.1 and 4.0 for pipe, plane Poiseuille and Couette flows, respectively, as the slow-moving solutes near the wall are depleted. For the case of a linear surface reaction, we use the invariant manifold theory to derive the effective transport equation to infinite order. We also show that the radius of convergence of the invariant manifold expansion is approximately three times that of the no reaction case.

We demonstrate that if adsorption/desorption is as slow as transverse diffusion, an adsorption-induced dispersion, distinct from the Taylor–Aris shear dispersion, exists. While the total dispersion may increase because of the contribution of both, the Taylor–Aris component is reduced by a physical mechanism similar to surface reaction. The adsorption/desorption induced dispersion coefficient is shown to have a maximum when the adsorption equilibrium constant is exactly 2. Nonlinear Langmuir type adsorption at large concentration is shown to introduce a nonlinear drift term which causes non-Gaussian pulse responses with long tails. These tails are detrimental to separation chromatography since they cause overlaps which increase with the length of the chromatograph.

1. Introduction

Taylor (1953) first pointed out that a channel flow with non-zero transverse gradient can induce an effective axial dispersion of a solute at large time due to a combination of axial advection and transverse diffusion. The asymptotic cross-sectional mean concentration of the solute can be described by a one-dimensional advection-diffusion equation. If a finite amount of solute is released initially, the cross-sectional mean approaches a symmetric Gaussian distribution whose variance is related to the effective dispersion coefficient (Aris 1956). Several subsequent authors have refined and quantified this phenomenon and its various variants using several different analytical techniques. The moments method (Aris 1956, 1959; Brenner 1980) remains popular. Lungu & Moffat (1982) used a large time and small wave number expansion, after a Fourier transformation, to decipher the asymptotic behaviour. Pagitsas *et al.* (1980) have developed a projection operator formalism for the treatment of general dispersion phenomena. Very recently, Mercer and Roberts (1990) showed that the small wave number and large time expansion of Lungu & Moffat in the Fourier space can be more conveniently and systematically formalized by the centre manifold theory of dynamical systems (Carr 1981). They derived higher-order correction terms to the Taylor–Aris model of shear dispersion. The convergence of their expansion in the axial wave number essentially rigorizes the omission of higher moments at large time in the moments method. If this series fails to converge, a Taylor–Aris model for effective transport does not exist. Fortunately, this does not occur in the classical Taylor–Aris problem when the parameter, p, representing the characteristic time for radial molecular diffusion to that for axial convection is sufficiently small. The projection operator technique of Pagitsas *et al.* also allows derivation of higher order terms.

It was realized at an early stage that Taylor–Aris dispersion is important in many chemically active systems such as chromatographs and chemical reactors. There have been many attempts in the literature to extend the work of Taylor (1953, 1954) and Aris (1956, 1959) to systems with linear kinetics (Sankarasubramanian & Gill 1973; De Gance & Jones 1978; Smith 1983, 1988; Barton 1984; Dill & Brenner 1982; Shapiro & Brenner 1986; McNabb *et al.* 1993). The analysis of Lungu & Moffat (1982) can also be considered as Poiseuille flow with surface reaction even though heat transport with wall leakage was analysed. In fact, all the above authors, with the lone exception of Barton, have considered only an irreversible reaction for the bulk species at the surface which yields a mixed boundary condition of the form,

$$\nabla_* C \cdot \boldsymbol{n} + \phi_{\mathrm{s}}^2 C = 0, \tag{1.1}$$

where ∇_* is the gradient operator in the transverse directions, $\boldsymbol{n}$ is the unit normal and ϕ_{s}^2 is square of the surface Thiele modulus (ratio of diffusion timescale to surface reaction timescale). Because of the depletion on the boundary, an injected cloud of solute will diminish in its absolute mass as it convects and diffuses downstream. At large time, all the above work has shown, in various guises, that the solute concentration approaches an equilibrium shape $\psi_0(x, y)$ in the transverse directions where ψ_0 is the normalized leading eigenfuction of the transverse diffusion operator with mixed boundary condition,

$$C(x, y, z, t) \sim C_0(z, t)\psi_0(x, y). \tag{1.2}$$

The total solute mass decays in time as expected. However, $C_0(z, t)$ itself obeys an effective one-dimensional advection-diffusion equation with an apparent reaction term where the effective advection velocity is faster than the average velocity and the effective dispersion coefficient is smaller than Taylor–Aris's inert case. Both are due to depletion of slow moving solutes near the wall. (Note that $C_0(z, t)$ is not the cross-sectional mean concentration since ψ_0 is not a constant. However, an effective equation for the mean concentration can also be derived.)

In addition to the irreversible surface reaction, Barton (1984) included a linear bulk reaction $(-kC)$ in the advection-diffusion equation. However, he removed this term by the transformation $C = C' \exp(-kt)$ and considered only the transport equation for C' which is without a bulk reaction term. We shall use the invariant manifold theory to show that this treatment of bulk reaction is incorrect if k is sufficiently large (more precisely, if the characteristic time for bulk reaction is much smaller than the transverse diffusion time). Under this condition, the requisite separation of timescales between the dominant eigenmode and the remaining modes does not exist and one cannot derive an effective one-dimensional equation for the amplitude of the leading mode $C_0(z,t)$. Physically, if the reaction rate is so fast that the solutes do not have time to sample all the streamlines, they will be depleted before the convection component of the Taylor–Aris mechanism sets in. An asymptotic behaviour like (1.2) will then be impossible. It is also quite uninteresting since the reactants are exhausted within small boundary layers in time and at the inlet. The reactor simply is not well designed as most of its length is wasted. We derive here the proper order of the bulk kinetic rate constant that allows the derivation of an effective one-dimensional transport equation and delineate the dependence of effective dispersion coefficient on the kinetics (or equivalently, the Thiele modulus). Distortion of nonlinear kinetics by transverse diffusion and convection will also be analysed. An interesting steady-state dispersion mechanism due to a coupling between the transverse velocity gradient and reaction is introduced.

Unlike the bulk reaction, we show that surface reaction of any speed yields an effective one-dimensional equation for the amplitude of the leading mode $C_0(z,t)$. Timescale separation exists because the species still needs to diffuse slowly to the wall. The classical results of the previous work and some new results on the convergence of the effective transport models are derived by the invariant manifold theory. More importantly, we exploit the new approach to study some important open problems in chromatograph theory. A chromatograph functions on the principle that solutes are adsorbed onto the wall and because of their affinity for the wall, their effective velocity is reduced and not increased as in the case of irreversible surface reaction studied in earlier work. From classical chromatograph theory (Amundson & Aris 1973) with linear adsorption-desorption equilibrium constant K, the velocity varies as $(1+K)^{-1}$. We show that if equilibrium is not established, namely, if adsorption/desorption is fast but not infinitely fast compared to axial convection, the same affinity mechanism can induce an effective dispersion that is distinct from shear dispersion. (This dispersion mechanism exists even if the flow field is gradientless.) Physically, the bulk solute is being adsorbed and released to form a tail. This dispersion coefficient varies as $\langle u\rangle^2 K^2/[k_{\mathrm{a}}(1+K)^3]$, where k_{a} is the adsorption rate constant. We use this result to estimate the spread of solute pulses exiting a chromatograph. This dispersion is especially important if the chromatograph is used for separation purposes (Subramanian 1991); the residence time must be sufficiently long such that the 'tails' produced by dispersion do not cause the solute pulses to overlap. Also apparent in a high-concentration chromatograph effluent is the significant long tail and front steepening of a solute pulse which invalidates the Gaussian distribution predicted by an advection-diffusion equation. This symmetry breaking may be due to higher order odd derivative terms or, more likely, due to a nonlinear mechanism. At high solute concentrations, more common in reactors than chromatographs, the surface-coverage Langmuir effect renders the adsorption nonlinear. In a flow reactor, nonlinear reactions for the surface species, which is far more common than linear irreversible ones, also introduce similar nonlinear terms in the effective dispersion model. It is the treatment of these nonlinear problems that the efficiency and clarity of the centre/invariant manifold theory is most welcomed.

For nonlinear Langmuir adsorption kinetics, we derive an effective equation with a nonlinear drift term that introduces a long non-Gaussian tail to the asymptotic shape reminiscent of the anomalous behaviour detected in high-concentration chromatograph effluents. The measured velocity, dispersion and skewness can then be used to estimate the adsorption/desorption parameters. In general, however, the Langmuir effect is extremely undersirable in separation chromatographs. We also show that for the case of flat velocity profile, there exists an effective transport equation in the presence of adsorption, desorption and surface reaction of any speed. We use this simple example to derive explicit expressions for the dependence of the effective transport coefficients on the reaction rate constant. Finally, we show that the transverse velocity gradients do not affect the adsorption induced dispersion but the Taylor–Aris contribution is reduced by the adsorption and desorption at the wall.

We review in the next section some important results from centre/invariant manifold theory that are pertinent to this work. Sections 3, 4 and 5 deal with classical Taylor–Aris dispersion with bulk and surface chemical reactions. Section 6 deals with linear and nonlinear chromatography models. The contributions of this work are the extension of many of the classical results derived for linear problems to nonlinear kinetics, determination of effective transport coefficients for steady-state and spatially evolving systems, derivation of higher-order corrections as well as the identification of the proper range of convergence of the various effective transport models.

2. Centre/invariant manifold theory

Since many of the results derived in this work are based on the application of ideas from the theory of dynamical systems, in particular, centre/invariant manifold theories, we give here a brief review of some of these concepts. A more formal and detailed approach to these concepts may be found in the books by Carr (1981), Guckenheimer & Holmes (1986) and the articles by Coullet & Spiegel (1983) and Roberts (1989*a*, *b*).

We consider the following dynamical system defined by a pair of ordinary differential equations:

$$\frac{\mathrm{d}C_0}{\mathrm{d}t} = F_0(C_0, C_1) = -\lambda_0 C_0 + f_0(C_0, C_1), \tag{2.1}$$

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = F_1(C_0, C_1) = -\lambda_1 C_1 + f_1(C_0, C_1), \tag{2.2}$$

where the functions $f_i(C_0, C_1)$ $(i = 0, 1)$ are smooth (differentiable to all orders) and contain only quadratic or higher order terms in the variables C_0 and C_1. For simplicity, we assume that λ_0 is non-negative, λ_1 is real and positive and $0 \leqslant \lambda_0/\lambda_1 < 1$. We also assume that the origin is a simple zero of the functions F_i $(i = 0, 1)$, or equivalently, a hyperbolic fixed point of the dynamical system, equations (2.1) and (2.2). Then, it follows from the stable manifold theorem (Carr 1981) that there exist smooth local stable manifolds M_0, M_1 that are tangent to the eigenspaces E_0, E_1 of the linearized system. These manifolds are invariant in the sense that any initial condition that is on one of these manifolds will remain on it for all times. When $\lambda_0 = 0$, the invariant manifold is also termed a centre manifold since the direction of the flow on it cannot be determined when (2.1) and

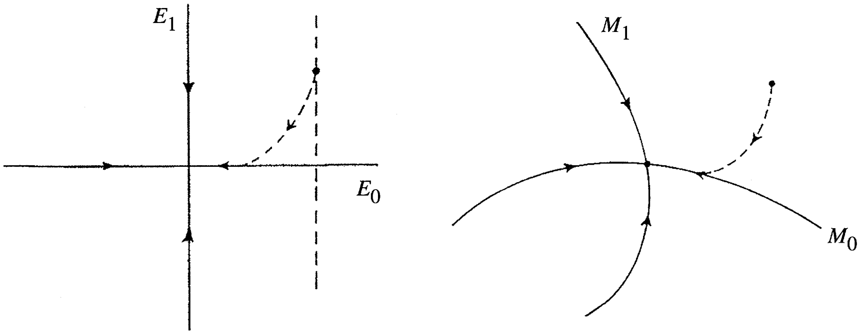

Figure 1. The approach of the trajectory to the eigenspace E_0 of the leading mode and its nonlinear extension, the centre or invariant manifold M_0.

(2.2) are truncated at the linear terms. It should be noted that centre/invariant manifolds are not unique but it is possible to find centre manifolds that are as smooth as the functions that appear on the right-hand side of (2.1) and (2.2). On the other hand, invariant manifolds, in general, are not analytic (Roberts 1989).

Of particular interest in our context is the decay of various initial conditions to the invariant manifolds M_0, M_1. This is shown schematically in figure 1. The left-hand diagram shows the invariant manifolds (eigenspaces) E_0, E_1 and a typical trajectory for the linearized equations while the right-hand diagram shows the same for the nonlinear system. It is clear from figure 1 that when $\lambda_0 \ll \lambda_1$, the C_1 component decays on a much faster timescale $(\lambda_1)^{-1}$ and after an initial transient, the trajectory approaches the invariant manifold E_0 corresponding to the slowly evolving component C_0. When nonlinear terms are included, this behaviour persists except that the invariant manifolds are not the eigenspaces but are tangent to them at the origin. Higher-order approximations to the invariant manifold M_0 can be obtained by writing

$$C_1 = G_0(C_0) = \sum_{i=2}^{\infty} \Delta_{0i} C_0^i. \tag{2.3}$$

(Note that G and its first derivative must vanish at the origin as M_0 is tangent to E_0.) The coefficients Δ_{0i} may be determined by substituting (2.3) in (2.1) and (2.2) and comparing the coefficients of various powers of C_0 in the following resulting equation:

$$\sum_{i=2}^{\infty} \Delta_{0i} C_0^{i-1} \left[-\lambda_0 C_0 + f_0 \left(C_0, \sum_{i=2}^{\infty} \Delta_{0i} C_0^i \right) \right] = -\lambda_1 \sum_{i=2}^{\infty} \Delta_{0i} C_0^i + f_1 \left(C_0, \sum_{i=2}^{\infty} \Delta_{0i} C_0^i \right). \tag{2.4}$$

When $\lambda_0 = 0$, it is always possible to solve for Δ_{0i} for any $i \geqslant 2$. However, for small but finite value of the ratio λ_0/λ_1, there is the possibility of zero divisors in the expressions for Δ_{0i}. It may be shown that the invariant manifold is unique only up to the smallest order at which this occurs (Roberts 1989). Thus, for $t \gg \lambda_1^{-1}$, the dynamics of (2.1) and (2.2) may be represented by the simplified system:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\lambda_0 s + f_0(s, G_0(s)), \tag{2.5a}$$

$$C_0 = s, \tag{2.5b}$$

$$C_1 = G_0(s). \tag{2.5c}$$

The variable C_1 is termed as the *slave* mode as its value is determined by C_0 through (2.5*c*). Equation (2.5*a*) is often termed the *effective equation* for the dynamics of the original system. Note that if the initial condition is on the invariant manifold M_0, the effective equation is valid for all $t > 0$. On the other hand, if the initial condition is on M_1, an effective equation for C_0 does not exist. Thus, the transient time after which the effective equation is valid depends not only on the eigenvalues of the linearized system but also on the initial conditions.

When λ_1 and λ_0 are of the same order but their ratio is still appreciably larger than unity, a separation of timescale still exists and an effective equation can still be derived but the transient time, after which the effective equation is valid, is increased. It is in the limit when λ_1 approaches λ_0 such that timescale separation no longer exists that the dynamics at large time can no longer be described by an effective equation. Note that it is also possible to determine higher-order approximations to the invariant manifold M_1 irrespective of the ratio λ_1 to λ_0. This can be done by writing

$$C_0 = G_1(C_1) = \sum_{i=2}^{\infty} \Delta_{1i} C_1^i. \tag{2.6}$$

The coefficients Δ_{1i} may be determined by substituting (2.6) in (2.1) and (2.2) and comparing the coefficients of various powers of C_1.

The centre/invariant manifold theory may be generalized to higher- (finite-) dimensional systems as well as to infinite-dimensional dynamical systems that have a discrete spectrum. In the applications considered in this work, C_0 and f_0 are r-dimensional vectors while C_1 and f_1 are N-dimensional vectors. (λ_0 and λ_1 are diagonal matrices with real eigenvalues that are well separated.) Once again, all the centre/invariant manifold calculations can be done by expanding the functions in Taylor series and comparison of the coefficients of various terms.

3. Classical Taylor–Aris dispersion

We consider the classical problem of dispersion of a chemically inactive tracer in unidirectional laminar flow in a channel of constant cross-sectional area. The local concentration of the tracer is described by the convective diffusion equation,

$$\frac{\partial C}{\partial t'} + \langle u \rangle f'(x', y') \frac{\partial C}{\partial z'} = D_{\mathrm{m}} \nabla^2 C, \tag{3.1}$$

where z' is the axial coordinate, $\langle u \rangle$ is the average velocity and D_{m} is the molecular diffusivity. The channel cross-section is denoted by Ω and its boundary by $\partial \Omega$; (x', y') are transverse coordinates in Ω and

$$\nabla^2 = \nabla_*^2 + \partial^2/\partial z'^2, \tag{3.2}$$

where ∇_*^2 is the Laplacian operator in Ω. In the transverse direction, (3.1) is subject to the boundary condition,

$$\nabla_* C \cdot \boldsymbol{n} = 0, \tag{3.3}$$

where $\boldsymbol{n}$ is the unit normal to $\partial\Omega$. We take a and L to be the characteristic lengths in the transverse and axial directions, respectively. (For example, for pipe flow, a is the radius of the pipe and L is its length.) Then, the three timescales associated with (3.1) are the timescale for radial molecular diffusion, $t_{\mathrm{D}} = a^2/D_{\mathrm{m}}$, the timescale for axial convection, $t_{\mathrm{C}} = L/\langle u\rangle$, and the timescale for axial diffusion, $t_{\mathrm{Z}} = L^2/D_{\mathrm{m}}$. These three time constants give rise to two dimensionless numbers p and ϵ, representing their ratios. The Taylor–Aris mechanism involves the coupling of a dominant transverse diffusion with weak convection and axial diffusion. The timescale t_{D} is then much smaller than the other two which will be considered to be of the same order ($\epsilon \sim O(p)$). Defining dimensionless variables:

$$\left.\begin{array}{c} x = x'/a, \quad y = y'/a, \quad z = z'/L, \quad f(x,y) = f'(ax, ay), \\ t = \dfrac{t'}{t_{\mathrm{D}}}, \quad \epsilon = \dfrac{a^2}{L^2} = \dfrac{t_{\mathrm{D}}}{t_{\mathrm{Z}}}, \quad p^* = \dfrac{D_{\mathrm{m}}}{\langle u\rangle L} = \dfrac{t_{\mathrm{C}}}{t_{\mathrm{Z}}}, \quad p = \dfrac{a^2\langle u\rangle}{D_{\mathrm{m}}L} = \dfrac{t_{\mathrm{D}}}{t_{\mathrm{C}}}. \end{array}\right\} \tag{3.4}$$

Equations (3.1) and (3.3) may be written as

$$\frac{\partial C}{\partial t} + pf(x,y)\frac{\partial C}{\partial z} = \nabla_*^2 C + \epsilon\frac{\partial^2 C}{\partial z^2}; \quad 0 < z < 1, \quad t > 0, \quad (x,y) \in \Omega, \tag{3.5a}$$

$$\nabla_* C \cdot \boldsymbol{n} = 0 \quad \text{on} \quad \partial\Omega. \tag{3.5b}$$

(Note that the same symbols are used for the dimensional as well as non-dimensional gradient and Laplacian operators.)

We have deliberately fixed the axial length scale (or equivalently, the distance downstream at which the concentration is measured) so that the convective timescale is clearly defined. The parameter p, which is the ratio of the characteristic time for radial molecular diffusion to that for axial convection, is assumed to be small. It plays the same role as that of the wave number in the approach of Lungu & Moffat (1982) and Mercer & Roberts (1990). We will carry out an expansion in p in our subsequent analysis of nonlinear mechanisms. The dimensionless parameter ϵ will be stipulated to be of order p or smaller.

(a) *Effective transport equation for cross-sectional mean concentration*

Let $\lambda_0 = 0$, λ_i ($i = 1, 2, \ldots$) be the eigenvalues and ψ_i ($i = 0, 1, \ldots$) be the respective orthonormal set of eigenfunctions of the self-adjoint eigenvalue problem:

$$\nabla_*^2\psi_i = -\lambda_i\psi_i \quad \text{in} \quad \Omega; \quad \nabla_*\psi_i \cdot \boldsymbol{n} = 0 \quad \text{on} \quad \partial\Omega. \tag{3.6}$$

We note that the leading master mode ψ_0 is a constant and simply represents a mode with no transverse variation. Due to the no-flux boundary condition, $\int_\Omega \psi_i \,\mathrm{d}\Omega = 0$ for $i \neq 0$, and these functions ψ_i represent the higher modes with transverse variation but zero transverse average. These are eigenfunctions of the dominant transverse diffusion operator in (3.5). When reaction terms are added, these functions will no longer be the eigenfunctions of the dominant operator. However, we shall still use them as bases and construct the true eigenfunctions in the projected space spanned by them. Writing

$$C(x,y,z,t) = \sum_{i=0}^{\infty} C_i(z,t)\psi_i(x,y), \tag{3.7}$$

it is clear that the leading mode C_0 is simply the cross-sectional mean concentration. Equation (3.5*a*) may be written in its component form in the projected space spanned by ψ_i

$$\frac{\partial C_0}{\partial t} = -p\alpha_{00}\frac{\partial C_0}{\partial z} - p\sum_{i=1}^{\infty}\alpha_{0i}\frac{\partial C_i}{\partial z} + p^*p\frac{\partial^2 C_0}{\partial z^2}, \tag{3.8}$$

$$\frac{\partial C_j}{\partial t} + \lambda_j C_j = -p\alpha_{j0}\frac{\partial C_0}{\partial z} - p\sum_{i=1}^{\infty}\alpha_{ji}\frac{\partial C_i}{\partial z} + p^*p\frac{\partial^2 C_j}{\partial z^2}, \tag{3.9}$$

where
$$\alpha_{ji} = \int_{\Omega} f\psi_i\psi_j\,\mathrm{d}\Omega \qquad (i,j = 0,1,\ldots) \tag{3.10}$$

and $p^* = D_{\mathrm{m}}/\langle u\rangle L$ is assumed to be of order unity or smaller. (Note that the normalization of the eigenfunctions implies $\alpha_{00} = 1$ and symmetry gives $\alpha_{ji} = \alpha_{ij}$.) It follows from (3.8) and (3.9) that when $p \ll 1$, and p^* is of order p^q $(q \geqslant 0)$, C_0 evolves on a timescale p^{-1} while C_j $(j \geqslant 1)$ evolves on a timescale λ_j^{-1}. When the trivial equation

$$\partial p/\partial t = 0 \tag{3.11}$$

is appended, (3.8), (3.9) and (3.11) describe a dynamical system that has two zero eigenvalues at $p = 0$. (Note that the right-hand sides of (3.8) and (3.9) are now quadratic in the variables.) In the language of the centre manifold theory, the modes C_j $(j = 1, 2, \ldots, \infty)$ are slave modes, i.e. they decay very rapidly to their equilibrium values determined by the evolution equation for C_0. Thus, a centre manifold exists and the flow on it may be described by a single evolution equation in terms of C_0 for large times $(t \gg \lambda_2^{-1})$. The form of (3.8), (3.9) and (3.11) dictates that the centre manifold must be of the form,

$$C_j = \sum_{n=1}^{\infty}\Delta_{jn}p^n\frac{\partial^n C_0}{\partial z^n} \qquad (j = 1,2,\ldots). \tag{3.12}$$

The constants Δ_{jn} may be determined by substituting (3.12) into (3.8), (3.9) and comparing the coefficients of various powers of p. After some algebra, one gets the following effective transport equation for C_0:

$$\frac{\partial C_0}{\partial t} + p\alpha_{00}\frac{\partial C_0}{\partial z} = p(p^* + \beta_1 p)\frac{\partial^2 C_0}{\partial z^2} + \sum_{n=2}^{\infty}\beta_n p^{n+1}\frac{\partial^{n+1}C_0}{\partial z^{n+1}}, \tag{3.13}$$

where

$$\beta_n = -\sum_{i=1}^{\infty}\alpha_{0i}\Delta_{in} \quad (n = 1,2,\ldots), \quad \lambda_j\Delta_{j1} = -\alpha_{0j}, \quad \lambda_j\Delta_{j2} = \Delta_{j1} - \sum_{i=1}^{\infty}\alpha_{ji}\Delta_{i1},$$

$$\lambda_j\Delta_{jn} = \Delta_{j,n-1} - \sum_{i=1}^{\infty}\alpha_{ji}\Delta_{i,n-1} + \sum_{i=1}^{\infty}\sum_{k=1}^{n-2}\alpha_{0i}\Delta_{ik}\Delta_{j,n-k-1}, \quad (n \geqslant 3, j \geqslant 1) \tag{3.14}$$

and the numerical constants β_n depend only on the geometry of Ω. Defining a new dimensionless time based on the convective scale t_{C},

$$\tau = pt = t'/t_{\mathrm{C}} \tag{3.15}$$

and noting that the cross-sectional mean concentration,

$$C_m(z,t) = \frac{1}{\Omega}\int_{\Omega} C(x,y,z,t)\,\mathrm{d}\Omega \tag{3.16}$$

is related to C_0 by $C_m(z,t) = C_0(z,t)\psi_0$, where ψ_0 is a numerical constant depending on the geometry of Ω, (3.13) may be reduced to the standard one-dimensional generalized convective diffusion equation:

$$\frac{\partial C_m}{\partial \tau} + \frac{\partial C_m}{\partial z} = (p^* + \beta_1 p)\frac{\partial^2 C_m}{\partial z^2} + \sum_{n=2}^{\infty} \beta_n p^n \frac{\partial^{n+1} C_m}{\partial z^{n+1}}. \tag{3.17a}$$

In dimensional form, (3.17a) may be written as

$$\frac{\partial C_m}{\partial t'} + \langle u\rangle \frac{\partial C_m}{\partial z'} = \sum_{n=2}^{\infty} D_n \frac{\partial^n C_m}{\partial z'^n} \qquad (t' > 0), \tag{3.17b}$$

where the dispersion coefficients D_n are defined by

$$D_2 = D_{\mathrm{m}} + \beta_1\langle u\rangle^2 a^2/D_{\mathrm{m}}; \quad D_i = \beta_{i-1}\langle u\rangle^i (a^2/D_{\mathrm{m}})^{i-1} \quad (i \geqslant 3). \tag{3.17c}$$

We note that D_2 is the classical Taylor–Aris dispersion coefficient having units of the diffusion coefficient while D_n ($n \geqslant 3$) having units of $[\text{length}]^n \cdot [\text{time}]^{-1}$ is the generalized Taylor–Aris dispersion coefficient.

The arguments leading to the effective dispersion (3.17a) indicate that it is valid only for $p \ll t \leqslant 1$, and p^* of order p^q ($q \geqslant 0$). The lower bound on τ is determined by the time required for the flow of (3.8) and (3.9) to approach the centre manifold ($\tau \sim 1/\lambda_1$ or equivalently, $\tau \sim p/\lambda_1$) while the upper bound is determined by the convective timescale (or equivalently, the axial distance downstream at which the concentration is measured).

The numerical constants β_i can be evaluated for any specific flow. The constant,

$$\beta_1 = \sum_{i=1}^{\infty} \frac{\alpha_{0i}^2}{\lambda_i}, \tag{3.18}$$

has already been calculated by several authors for some standard flows (Taylor 1953; Aris 1956; Dill & Brenner 1983). For example, for pipe flow, Ω is the unit disc ($0 \leqslant r < 1$) and λ_i ($i \geqslant 1$) are the roots of the equation,

$$\left.\begin{aligned} &J_1(\sqrt{\lambda_i}) = 0,\\ \text{and}\quad &\psi_0 = \sqrt{2}; \quad \psi_i = \sqrt{2}\frac{J_0(\sqrt{(\lambda_i)}r)}{J_0(\sqrt{\lambda_i})}; \quad f(r) = 2(1-r^2); \quad \alpha_{0i} = -\frac{8}{\lambda_i},\\ &\beta_1 = 64\sum_{i=1}^{\infty}\frac{1}{\lambda_i^3} = \frac{1}{48}. \end{aligned}\right\} \tag{3.19}$$

For plane Poiseuille flow, Ω is the open region $-1 < y < 1$ and

$$\left.\begin{aligned} &\lambda_i = \tfrac{1}{4}i^2\pi^2 \quad (i \geqslant 1); \quad \psi_0 = 1/\sqrt{2}; \quad \psi_i = \cos[\tfrac{1}{2}i\pi(1-y)],\\ &f(y) = \tfrac{3}{2}(1-y^2); \quad \alpha_{0i} = -12\sqrt{2}/i^2\pi^2 \quad (i \text{ odd}),\\ &\beta_1 = 18\sum_{i=1}^{\infty}\frac{1}{j^6\pi^6} = \frac{2}{105}. \end{aligned}\right\} \tag{3.20}$$

For plane Couette flow, Ω is the unit interval $0 < y < 1$ and

$$\left.\begin{aligned} \lambda_i = i^2\pi^2 \quad (i \geqslant 1); \quad \psi_0 = 1; \quad \psi_i = \sqrt{2}\cos(i\pi y), \\ f(y) = 2y; \quad \alpha_{0i} = -4\sqrt{2}/i^2\pi^2 \quad (i \text{ odd}), \\ \beta_1 = 32\sum_{i=1}^{\infty}\frac{1}{(2i-1)^6\pi^6} = \frac{1}{30}. \end{aligned}\right\} \tag{3.21}$$

It may be seen from (3.17*a*) that the inclusion of axial molecular dispersion adds only a single term on the right-hand side and does not affect the coefficients β_i $(i \geqslant 2)$. If (3.17*a*) is truncated at order p, it reduces to the standard one-dimensional convective diffusion equation,

$$\frac{\partial C_m}{\partial t} + \frac{\partial C_m}{\partial z} = \frac{1}{Pe}\frac{\partial^2 C_m}{\partial z^2}, \tag{3.22}$$

where

$$\frac{1}{Pe} = \frac{D_2}{\langle u\rangle L} = p^* + \beta_1 p. \tag{3.23}$$

It follows from (3.23) that the impact of axial molecular diffusion is negligible if p^* is of order p^2 or higher, while if p^* is of order p, both radial and axial molecular diffusion are equally important. When p^* is of order unity, the contribution of the Taylor dispersion term is negligible compared to the axial molecular diffusion.

The centre manifold approach may be used to show that the effective transport equation for any other weighted mean concentration is identical to (3.17*a*). This property is due to the linearity of (3.1) in C and may no longer be true for the case of nonlinear kinetics. We consider the weighted mean concentration defined by

$$C_w = \int_\Omega w(x,y)C\,\mathrm{d}\Omega \Big/ \int_\Omega w(x,y)\,\mathrm{d}\Omega \tag{3.24}$$

(where $w = f$ gives convected mean or mixing cup concentration; Ultman & Weaver 1979). Substituting from (3.7) and simplifying, we get

$$C_w = C_m + \sum_{i=1}^{\infty}\sum_{n=1}^{\infty}\Delta_{in}\mu_i p^n \frac{\partial^n C_m}{\partial z^n} = \mathsf{L}C_m, \tag{3.25}$$

where

$$\mathsf{L} = 1 + \sum_{i=1}^{\infty}\sum_{n=1}^{\infty}\Delta_{in}\mu_i p^n\frac{\partial^n}{\partial z^n}; \quad \mu_i = \int_\Omega \psi_i(x,y)w(x,y)\,\mathrm{d}\Omega \Big/ \int_\Omega \psi_0(x,y)w(x,y)\,\mathrm{d}\Omega. \tag{3.26}$$

Since L is a linear differential operator in z, operating both sides of (3.17*a*) by L gives an effective transport equation for C_w, which is identical to that for C_m.

(*b*) *Convergence of higher-order approximations*

In practice, the effective transport equation (3.17*a*) is often truncated at the second derivative term, which makes the dispersion Gaussian. However, retaining higher order terms introduces non-Gaussian effects and long tails. A natural question that arises is the convergence of the truncated effective equation to the 'exact' solution. As stated earlier this convergence for small but non-zero val-

Table 1. *Coefficients in the centre manifold expansion*

	β_i		
i	pipe flow	Couette flow	Poiseuille flow
1	0.20833E−01	0.33333E−01	0.19048E−01
2	−0.34722E−03	0.00000E 00	0.23088E−03
3	−0.15888E−04	−0.94596E−04	−0.28416E−04
4	0.11755E−05	0.00000E 00	−0.10523E−05
5	0.49257E−08	0.57487E−06	0.83626E−07
6	−0.36895E−08	0.00000E 00	0.56525E−08
7	0.10715E−09	−0.43935E−08	−0.27333E−09
8	0.93087E−11	0.00000E 00	−0.31659E−10
9	−0.72057E−12	0.37657E−10	0.78450E−12
10	−0.10244E−13	0.00000E 00	0.17838E−12
11	0.32220E−14	−0.34596E−12	−0.83503E−15
12	−0.75089E−16	0.00000E 00	−0.99276E−15
13	−0.10632E−16	0.33306E−14	−0.14396E−16
14	0.70908E−18	0.00000E 00	0.53764E−17
15	0.19357E−19	−0.33160E−16	0.18820E−18
16	−0.38083E−20	0.00000E 00	−0.27836E−19
17	0.57559E−22	0.35863E−18	−0.16666E−20
18	0.14781E−22	0.00000E 00	0.13388E−21
19	−0.81784E−24	−0.35275E−20	0.12758E−22
20	−0.35907E−25	0.00000E 00	−0.56201E−24

ues of p is crucial to the validity of the present approach. We now examine the convergence of the centre manifold expansion given by (3.17*a*).

We have used the expressions given by (3.14) to compute the first 100 coefficients in (3.17*a*). The first 20 of these are listed in table 1 for the three types of flows considered above. The first seven coefficients computed for Poiseuille flow agree with those reported by Mercer & Roberts (1990). In general, the coefficients decrease with increasing n, but there are some exceptions. For example, for Poiseuille flow, $|\beta_{12}| > |\beta_{11}|$ and $|\beta_{25}| > |\beta_{24}|$ while for pipe flow, $|\beta_{28}| > |\beta_{27}|$, $|\beta_{67}| > |\beta_{66}|$, and $|\beta_{89}| > |\beta_{88}|$. For Couette flow, all even coefficients vanish while the odd coefficients are strictly decreasing. The convergence of the infinite series on the right-hand side of (3.17*a*), may be examined by writing it as

$$\frac{\partial C_m}{\partial \tau}+\frac{\partial C_m}{\partial z}=\left[(p^*+\beta_1 p)\frac{\partial^2}{\partial z^2}+\frac{\partial \mathsf{S}}{\partial z}\right]C_m, \tag{3.27a}$$

where the linear differential operators S and η are defined by

$$\mathsf{S}=\sum_{n=2}^{\infty}\beta_n\eta^n;\qquad \eta=p\frac{\partial}{\partial z}=\frac{a^2\langle u\rangle}{D_\mathrm{m}}\frac{\partial}{\partial z'}. \tag{3.27b}$$

Since the coefficients β_n exhibit an approximate periodicity of four, the method described by Mercer & Roberts (1990) is most suitable for determining the radius of convergence of the infinite series S. Using the first 100 terms, we computed the critical radius to be $\eta_c = 13.80$, 11.87 and 9.05 for pipe, Poiseuille and Couette flows, respectively. Thus, the convergence of the centre manifold expansion depends not only on the magnitude of the parameter p, but also on the axial gradient, $\partial/\partial z$, of the initial conditions. If the initial conditions are such that the axial gradient is finite, the effective transport equation is valid for finite (non-zero) values of p and non-Gaussian effects can be quantified by solving the higher-order effective transport models.

Another way of establishing the convergence of the effective transport equation is to compare the solutions of the truncated equations at different orders. Since (3.17*b*) is invariant to translations in z', we may take the spatial domain to be $-\infty < z' < \infty$ and consider the solution to a pulse input

$$C_m(z', 0) = \delta(z'). \tag{3.28}$$

An exact solution of (3.17*b*) and (3.28) may be shown to be

$$C_m(z', t') = N C_{m\mathrm{G}}, \tag{3.29}$$

where $C_{m\mathrm{G}}$ is the Gaussian profile,

$$C_{m\mathrm{G}} = \frac{1}{\sqrt{(4\pi D_2 t')}} \exp\left[-\frac{(z' - \langle u \rangle t')^2}{4 D_2 t'}\right] \tag{3.30}$$

and N is the (nonlinear differential) operator defined by

$$N = \exp\left[t' \sum_{n=3}^{\infty} D_n \frac{\partial^n}{\partial z'^n}\right] = 1 + t' D_3 \frac{\partial^3}{\partial z'^3} + t' D_4 \frac{\partial^4}{\partial z'^4} + \ldots \tag{3.31}$$

We note that the infinite series appearing in N is identical to S and hence, the convergence of the series S also establishes the convergence of the solution given by (3.29). The operator N may be factored as

$$N = \prod_{j=3}^{\infty} N_j; \quad N_j = \exp\left[t' D_j \frac{\partial^j}{\partial z'^j}\right]. \tag{3.32}$$

This property may be used to compute the solution given by (3.29) to any desired degree of accuracy as well as establish the algebraic decay (in inverse powers of time) to the Gaussian profile. Thus, the higher-order terms in (3.17*b*) make the dispersion non-Gaussian at any finite time and only for $t' \to \infty$, the Gaussian profile is attained.

(*c*) *Spatial versus temporal evolution*

The above approach to determine the effective transport model is based on the temporal evolution of an initial pulse as it is advected downstream. This approach is not convenient for describing finite systems in which the dispersion is induced through temporal forcing at the inlet, as is the case in a chromatograph. Here, there will be a boundary layer at the inlet before the spatial centre manifold is approached. We now examine the spatial evolution of C towards the spatial centre manifold in the longitudinal direction and derive the effective equation for the mean concentration. For simplicity, we consider (3.1) without the axial molecular diffusion term.

Let $\mu_0 = 0$, μ_i $(i = 1, 2, \ldots)$ be the eigenvalues and Ψ_i $(i = 0, 1, \ldots)$ be the respective orthonormal set of eigenfunctions of the self-adjoint eigenvalue problem:

$$\nabla_*^2 \Psi_i = -\mu_i f(x,y) \Psi_i \quad \text{in} \quad \Omega; \qquad \nabla_* \Psi_i \cdot \boldsymbol{n} = 0 \quad \text{on} \quad \partial\Omega. \tag{3.33}$$

We note that unlike the temporal eigenfunctions, $\int_\Omega \Psi_i \, \mathrm{d}\Omega \neq 0$ for any i and hence the leading mode no longer represents the cross-sectional mean. Writing

$$C(x,y,z,t) = \sum_{i=0}^{\infty} c_i(z,t) \Psi_i(x,y), \tag{3.34}$$

the component form of (3.5) is

$$\frac{\partial c_0}{\partial Z} = -p\epsilon_{00} \frac{\partial c_0}{\partial \tau} - p \sum_{i=1}^{\infty} \epsilon_{0i} \frac{\partial c_i}{\partial \tau}, \tag{3.35}$$

$$\frac{\partial c_j}{\partial Z} + \mu_j c_j = -p\epsilon_{j0} \frac{\partial c_0}{\partial \tau} - p \sum_{i=1}^{\infty} \epsilon_{ji} \frac{\partial c_i}{\partial \tau}, \tag{3.36}$$

where

$$\epsilon_{ji} = \int_\Omega \Psi_i \Psi_j \, \mathrm{d}\Omega \qquad (i, j = 0, 1, \ldots), \tag{3.37}$$

$$Z = z/p. \tag{3.38}$$

(Note that $\epsilon_{00} = 1$ and $\epsilon_{ji} = \epsilon_{ij}$ and $\Psi_0 = \psi_0$.) A spatial centre manifold of (3.35) and (3.36) may be written as

$$c_j = \sum_{n=1}^{\infty} \delta_{jn} p^n \frac{\partial^n c_0}{\partial \tau^n}. \tag{3.39}$$

The constants δ_{jn} may be determined by substituting (3.38) into (3.35), (3.36) and comparing the coefficients of various powers of p. Since the form of (3.35) and (3.36) is identical to (3.11) and (3.12), δ_{jn} are given by (3.14) with λ_j, α_{ji} replaced by μ_j, ϵ_{ji}, respectively. Substitution of (3.38) into (3.35) gives the effective transport equation for c_0:

$$\frac{\partial c_0}{\partial \tau} + \frac{\partial c_0}{\partial z} = \sum_{n=1}^{\infty} \gamma_n p^n \frac{\partial^{n+1} c_0}{\partial \tau^{n+1}}, \tag{3.40}$$

where

$$\gamma_n = -\sum_{i=1}^{\infty} \epsilon_{0i} \delta_{in} \qquad (n = 1, 2, \ldots). \tag{3.41}$$

Equation (3.40) may also be written in terms of any weighted mean concentration. For example, the cross-sectional mean concentration is given by

$$C_m = \Psi_0[c_0 - \gamma_1 p \partial c_0 / \partial \tau + O(p^2)] = L^* c_0, \tag{3.42}$$

where L^* is a linear differential operator in τ. Operating both sides of (3.39) by L^* gives the same effective equation for C_m, which in dimensional form may be written as

$$\frac{\partial C_m}{\partial t'} + \langle u \rangle \frac{\partial C_m}{\partial z'} = \sum_{n=1}^{\infty} d_n \frac{\partial^{n+1} C_m}{\partial t'^{n+1}} \qquad (t' > 0), \tag{3.43}$$

where the effective spatial evolution constants d_n are defined by

$$d_n = \gamma_n (a^2/D_{\mathrm{m}})^n \qquad (n \geqslant 1). \tag{3.44}$$

(Note that d_n has units of $(\text{time})^n$.) The numerical values of γ_n can be found by solving the eigenvalue problem defined by (3.33) and evaluation of the integrals and sums given by (3.37) and (3.40). Alternatively, they can be related to the temporal evolution constants by relating the spatial and temporal differential operators appearing in (3.17*a*) and (3.39). It follows from (3.17*a*) that

$$\zeta \equiv p \frac{\partial}{\partial \tau} = -\eta + \sum_{n=1}^{\infty} \beta_n \eta^{n+1}, \tag{3.45}$$

while (3.39) implies that

$$\eta = p \frac{\partial}{\partial z} = -\zeta + \sum_{n=1}^{\infty} \gamma_n \zeta^{n+1}. \tag{3.46}$$

Inverting the power series in (3.44) gives the relationship between the two sets of constants β_n and γ_n. The first six of these are given by

$$\left.\begin{array}{c} \gamma_1 = \beta_1; \quad \gamma_2 = -(\beta_2 + 2\beta_1^2); \quad \gamma_3 = \beta_3 + 5\beta_2\beta_1 + 5\beta_1^3; \\ \gamma_4 = -(\beta_4 + 6\beta_3\beta_1 + 3\beta_2^2 + 21\beta_2\beta_1^2 + 14\beta_1^4); \\ \gamma_5 = \beta_5 + 7\beta_4\beta_1 + 84\beta_1^3\beta_2 + 7\beta_2\beta_3 + 28\beta_1\beta_2^2 + 28\beta_1^2\beta_3 + 42\beta_1^5; \\ \gamma_6 = -(\beta_6 + 8\beta_5\beta_1 + 8\beta_4\beta_2 + 36\beta_4\beta_1^2 + 4\beta_3^2 + 72\beta_1\beta_2\beta_3 + 120\beta_3\beta_1^3 \\ +12\beta_2^3 + 180\beta_2^2\beta_1^2 + 330\beta_2\beta_1^4 + 132\beta_1^6). \end{array}\right\} \tag{3.47}$$

It is interesting to compare the truncated forms of (3.39) with those of (3.17*b*) without the axial molecular dispersion term . At zero order, the two equations are hyperbolic and identical. At first order, both are nearly hyperbolic and the coefficient of the dispersion term is the same in both spatial and temporal formulations. This may be explained by the fact that Taylor–Aris dispersion corresponds to the spreading of a concentration profile along the characteristic z–τ. Consequently, the dispersion is Gaussian and may be described by either the spatial or the temporal formulation. However, at third and higher orders, the spatial and temporal evolutions differ. This distinction between the spatial and temporal evolutions at third order was first noted by Roberts (1992). The relations given by (3.46) show that the spatial and temporal formulations differ at all orders higher than three. Since most physical systems are of finite extent and are observed at finite times, one must combine the spatial and temporal evolution approaches to derive an effecive transport model, and the proper initial and boundary conditions to be used with that model. This is still an open problem that needs to be addressed.

4. Taylor–Aris dispersion with a bulk reaction

We now consider the classical Taylor–Aris problem (without axial molecular dispersion) with a nonlinear bulk or volumetric reaction term. As we discussed in the Introduction, a long-time or large-distance asymptotic behaviour described by an effective equation only exists for the bulk reaction case if the reaction timescale is not smaller than the transverse diffusion timescale t_{D} ($\phi^2 \sim O(1)$ in the notation to be introduced next). If the reaction timescale is as slow as t_{c} and t_z ($\phi^2 \sim O(p)$), transverse diffusion remains the dominant mechanism and $\{\psi_i\}$ of (3.9) are still the eigenfunctions of the dominant (leading order) operator. We then expect dispersion to be unaffected by reaction and vice versa. The most interesting case occurs for $\phi^2 \sim O(1)$ when transverse diffusion and reaction are equally fast. In this case, reaction begins to affect how the solutes are distributed along the streamlines and we shall show that the Taylor–Aris mechanism will distort the apparent kinetics. Equation (3.5*a*) is now modified to

$$\frac{\partial C}{\partial t} + pf(x,y)\frac{\partial C}{\partial z} = \nabla_*^2 C - \phi^2 r(C); \quad 0 < z < 1, \quad t > 0, (x,y) \in \Omega, \qquad (4.1a)$$

$$\nabla_* C \cdot \boldsymbol{n} = 0 \quad \text{on} \quad \partial\Omega, \qquad (4.1b)$$

where

$$\phi^2 = \frac{a^2}{D_{\mathrm{m}}}\frac{R(C_{\mathrm{R}})}{C_{\mathrm{R}}} = \frac{t_{\mathrm{D}}}{t_{\mathrm{R}}}, \quad r(C) = \frac{R(C_{\mathrm{R}}C)}{R(C_{\mathrm{R}})}, \quad t_{\mathrm{R}} = \frac{C_{\mathrm{R}}}{R(C_{\mathrm{R}})}, \quad Da = \frac{t_{\mathrm{C}}}{t_{\mathrm{R}}} = \frac{\phi^2}{p}. \qquad (4.2)$$

Here, ϕ^2 is the square of the Thiele modulus, the ratio between the characteristic time for radial molecular diffusion (t_{D}) to that for chemical reaction (t_{R}), and $r(C)$ is the dimensionless reaction rate normalized with respect to some reference concentration C_{R}. The Damköhler number, Da, is the ratio between the characteristic time for convection (t_{C}) to that for chemical reaction (t_{R}). It is assumed that the reaction rate $r(C)$ is a smooth function, i.e. differentiable to all orders in C. Equation (4.1) may be written in its component form,

$$\frac{\partial C_0}{\partial t} = -p\frac{\partial C_0}{\partial z} - p\sum_{i=1}^{\infty}\alpha_{0i}\frac{\partial C_i}{\partial z} - \phi^2\left\langle r\left(C_0\psi_0 + \sum_{i=1}^{\infty}C_i\psi_i\right), \psi_0\right\rangle, \qquad (4.3)$$

$$\frac{\partial C_j}{\partial t} + \lambda_j C_j = -p\alpha_{j0}\frac{\partial C_0}{\partial z} - p\sum_{i=1}^{\infty}\alpha_{ji}\frac{\partial C_i}{\partial z} - \phi^2\left\langle r\left(C_0\psi_0 + \sum_{i=1}^{\infty}C_i\psi_i\right), \psi_j\right\rangle, \quad (4.4)$$

where $\langle \cdot, \cdot \rangle$ denotes inner product. As noted earlier, if $\phi^2 \sim O(1)$, the linear kinetic terms in (4.3) and (4.4) will now introduce a coupling between the dominant diffusive mode C_0 and the slave modes C_j. This, in fact, will cause the true dominant mode to decay nearly as fast as the slave modes. However, if there is still an appreciable difference between the two rates, we can still capture the large time behaviour with the invariant manifold approach. The asymptotes, however, will take longer to reach.

(*a*) *Effective transport equation for a slow reaction* ($\phi^2 \sim O(p)$)

We first consider the case of a slow reaction for which ϕ^2 is of order p, or equivalently, $\phi^2 = p\,Da$, where Da is of order unity. Then, it is clear from (4.3) and (4.4) that C_0 evolves on a timescale p^{-1} while C_j ($j \geqslant 1$) evolves on a timescale λ_j^{-1}. Thus, for $p \ll 1$, a centre manifold exists and to first order in p, is given by

$$C_j = -\frac{p\alpha_{j0}}{\lambda_j}\frac{\partial C_0}{\partial z} + O(p^2) \qquad (j = 1, 2, \ldots). \tag{4.5}$$

Substitution of (4.5) into (4.3) and noting that $C_m = C_0\psi_0$, we get the following standard one-dimensional diffusion-convection-reaction model for the cross-sectional mean concentration:

$$\frac{\partial C_m}{\partial \tau} + \frac{\partial C_m}{\partial z} = \frac{1}{Pe}\frac{\partial^2 C_m}{\partial z^2} - Da\, r(C_m) + O(Pe^{-2}); \quad p \ll \tau < 1, p \ll z < 1, \tag{4.6}$$

where $Pe = 1/\beta_1 p$. Thus, for slow reaction ($t_{\mathrm{D}} \ll t_{\mathrm{R}}$), the effective dispersion coefficient is same as that for Taylor–Aris's inert case.

The effective transport equation (4.6) may also be written in terms of other weighted average concentrations. Combining (3.24), (3.25) and (4.6), we obtain

$$\frac{\partial C_w}{\partial \tau} + \frac{\partial C_w}{\partial z} = \frac{1}{Pe}\frac{\partial^2 C_w}{\partial z^2} - Da\, \mathsf{L}r(\mathsf{L}^{-1}C_w) + O(p^2), \tag{4.7}$$

where L^{-1} is the inverse of the linear differential operator defined by (3.26). Simple algebraic manipulations show that

$$\mathsf{L}r(\mathsf{L}^{-1}C_w) = r(C_w) + O(p^2). \tag{4.8}$$

Thus, (4.6) is valid for all weighted mean concentrations up to the order indicated. It may also be shown that the spatial and temporal formulations agree up to the same order.

The centre manifold approach may easily be generalized to cases in which the reaction rate constant is dependent on the transverse coordinates. Writing

$$r = g(x,y)R(C)\; \delta_i = \langle \psi_0 g(x,y), \psi_i(x,y)\rangle, \tag{4.9}$$

it may be shown that the effective transport equation is now modified to

$$\begin{aligned}&\frac{\partial C_m}{\partial \tau} + [1 + 2p\beta_3 Da\, R'(C_m)]\frac{\partial C_m}{\partial z}\\ &= \beta_1 p\frac{\partial^2 C_m}{\partial z^2} - Da\; \delta_0 R(C_m)[1 + p\beta_4 Da\, R'(C_m)] + O(p^2); \quad p \ll \tau < 1, p \ll z < 1,\end{aligned} \tag{4.10}$$

where

$$\beta_3 = -\sum_{k=1}^{\infty}\frac{\alpha_{0i}\delta_i}{\lambda_i}, \tag{4.11}$$

$$\beta_4 = \sum_{k=1}^{\infty}\frac{\delta_i^2}{\lambda_i\delta_0}. \tag{4.12}$$

Now, there is a drift correction term and also a source correction term. Both of these terms are of the same order of magnitude as the dispersion term and vanish if either the rate constant is independent of position or the reaction is of zero order.

(*b*) *Effective transport equation for fast reaction* ($\phi^2 \sim O(p^0)$)

It follows from (4.3) and (4.4) that if ϕ^2 is of order unity and $p \ll 1$, C_0 evolves on a timescale $(\phi^2)^{-1}$ while C_j ($j \geqslant 1$) evolves on a timescale $(\lambda_j + \phi^2)^{-1}$. From

(3.19) to (3.21), it is clear that there is still an appreciable separation between these two timescales. Thus an invariant manifold exists and it is still possible to derive an effective transport equation provided $p \ll 1$. After some algebra, the invariant manifold may be calculated to be

$$C_j = \Delta_{1j} p \frac{\partial C_0}{\partial z} + \Delta_{2j} p^2 \frac{\partial^2 C_0}{\partial z^2} + O(p^3) \qquad (j = 1, 2, \ldots), \tag{4.13}$$

where

$$\Delta_{1j} = -\alpha_{j0}/\lambda_j, \tag{4.14}$$

$$\Delta_{2j} = \frac{(\Delta_{3j}\partial^2 C_0/\partial z^2 - \Delta_{4j}\phi^2 r''(C_0\psi_0)(\partial C_0/\partial z)^2)}{\lambda_j \partial^2 C_0/\partial z^2 - \phi^2 r''(C_0\psi_0)(\partial C_0/\partial z)^2}, \tag{4.15}$$

$$\Delta_{3j} = \Delta_{1j} - \sum_{i=1}^{\infty} \alpha_{ji}\Delta_{1i}, \tag{4.16}$$

$$\Delta_{4j} = \frac{1}{2}\sum_{i=1}^{\infty}\sum_{k=1}^{\infty} \beta_{jik}\Delta_{1i}\Delta_{1k}, \tag{4.17}$$

$$\beta_{jik} = \langle \psi_i \psi_k, \psi_j \rangle \qquad (j = 0, 1, \ldots;\ i, k = 1, 2, \ldots), \tag{4.18}$$

and the primes on r denote differentiation with respect to C. The effective transport equation is now modified to

$$\frac{\partial C_m}{\partial \tau} + \frac{\partial C_m}{\partial z} = \frac{1}{Pe}\frac{\partial^2 C_m}{\partial z^2} - Da\, r(C_m) - \beta_2 \frac{Da}{Pe} r''(C_m)\left(\frac{\partial C_m}{\partial z}\right)^2 + O(Pe^{-2}); \tag{4.19}$$

$$\left(\frac{\phi^2}{\lambda_1 + \phi^2} \ll \tau < 1, \quad \frac{\phi^2}{\mu_1 + \phi^2} \ll z < 1\right),$$

where

$$\beta_2 = \frac{1}{2\beta_1}\sum_{i=1}^{\infty}\sum_{k=1}^{\infty} \beta_{0ik}\Delta_{1i}\Delta_{1k}. \tag{4.20}$$

We note that the effective diffusivity is still independent of the Thiele modulus but there is a nonlinear source term that is of the same order of magnitude as the dispersion term. This source terms vanishes only for the special case of linear kinetics. Since this small correction term is related to the gradient in C_m, it only occurs under transient conditions. (A similar result can be derived using the spatial evolution formulation and the spatial slave modes can be shown to be related to the time derivative of the spatial master mode.) Nevertheless, kinetic data are often deciphered from transient experiments and this correction will partly disguise the true kinetics. It will also affect the performance of unsteady reactors.

For the case of very fast reaction ($\phi^2 \gg O(p^0)$), the timescales for the evolution of C_0 and C_j ($j = 1, 2, \ldots$) are no longer separated and hence it is not possible to derive an effective transport equation. In this uninteresting case, boundary layers exist at $z = t = 0$ and most of the reactant is consumed in these boundary layers.

(c) *Higher-order corrections for first-order reaction*

It is straightforward to extend the centre manifold calculations to include higher-order terms in p. The algebraic manipulations for general rate expressions are tedious and will not be pursued here. Instead, we look at the special case of linear kinetics. For $r(C) = C$, (4.3) and (4.4) simplify to

$$\frac{\partial C_0}{\partial t} = -p\alpha_{00}\frac{\partial C_0}{\partial z} - p\sum_{i=1}^{\infty}\alpha_{0i}\frac{\partial C_i}{\partial z} - p\,Da\,C_0, \tag{4.21}$$

$$\frac{\partial C_j}{\partial t} + \lambda_j C_j = -p\alpha_{j0}\frac{\partial C_0}{\partial z} - p\sum_{i=1}^{\infty}\alpha_{ji}\frac{\partial C_i}{\partial z} - p\,Da\,C_j. \tag{4.22}$$

Writing the centre/invariant manifold as

$$C_j = \sum_{n=1}^{\infty}\Delta_{jn}p^n\frac{\partial^n C_0}{\partial z^n}, \tag{4.23}$$

after some algebra, one gets the following effective transport equation for C_m:

$$\frac{\partial C_m}{\partial \tau} + \frac{\partial C_m}{\partial z} = \sum_{n=1}^{\infty}\beta_n p^n\frac{\partial^{n+1} C_m}{\partial z^{n+1}} - Da\,C_m \quad \left(\frac{\phi^2}{\lambda_1+\phi^2} \ll \tau < 1,\ \frac{\phi^2}{\mu_1+\phi^2} \ll z < 1\right), \tag{4.24}$$

where β_n and Δ_{jn} are independent of ϕ^2 and are again given by (3.14)! Thus, for the special case of a first-order reaction, all the effective transport coefficients are independent of the reaction rate constant.

We note that (4.24) is valid for a slow as well as a fast reaction. As ϕ^2 increases from order p to order unity or higher, the transient time after which (4.24) is valid increases and approaches the convective timescale. As stated earlier, for $\phi^2 \gg 1$, most of the reactant is consumed during this transient period and the effective transport equation is no longer useful.

(*d*) *Effective dispersion equations for steady-state models*

We have seen that in the absence of a reaction, there is no steady-state Taylor–Aris dispersion. However, when a bulk reaction is present, a spatial centre manifold exists and there can be an effective transport equation for steady-state models. This is because of the fact that with reaction, even if the inlet concentration is constant over the entire cross section, a transverse gradient will exist at any down stream location since the residence time on each streamline is different and the solute is depleted by a different amount. This coupling between reaction and transverse velocity gradient is a steady-state one and hence different from the transient Taylor–Aris mechanism involving diffusion and transverse velocity gradient. However, like transient Taylor–Aris dispersion with a bulk reaction, care must be taken such that the depletion of solute in the entrance boundary layer before the spatial centre manifold is reached is avoided. This should be true for a well-designed reactor in which the reaction takes place over the entire length of the reactor and not just at the entrance. Consequently, we shall only examine the case of a reaction which is slow with respect to the transverse diffusion time ($\phi^2 \sim O(p)$ or equivalently, $\phi^2 = p\,Da$, where Da is of order unity). For the case of a nonlinear reaction, the relevant amplitude equations are

$$\begin{aligned}\frac{\mathrm{d}c_0}{\mathrm{d}Z} = {} & -p\,Da\,\langle r(c_0\psi_0), \psi_0\rangle - p\,Da\,r'(c_0\psi_0)\sum_{i=1}^{\infty}\epsilon_{0i}c_i \\ & -\tfrac{1}{2}p\,Da\,r''(c_0\psi_0)\sum_{i=1}^{\infty}\sum_{k=1}^{\infty}\beta_{0ik}c_ic_k + \dots,\end{aligned} \tag{4.25}$$

$$\frac{\mathrm{d}c_j}{\mathrm{d}Z}+\mu_j c_j=-p\,Da\langle r(c_0\psi_0),\psi_j\rangle-p\,Da\,r'(c_0\psi_0)\sum_{i=1}^{\infty}\epsilon_{ji}c_i$$
$$-\tfrac{1}{2}p\,Da\,r''(c_0\psi_0)\sum_{i=1}^{\infty}\sum_{k=1}^{\infty}\beta_{ijk}c_i c_k+\ldots \qquad (4.26)$$

Thus a spatial centre manifold exists provided ϕ^2 is of order p and $p \ll 1$. The latter condition also ensures that the effective equation is valid over much of the reactor length. The spatial centre manifold to first order in p is given by

$$c_j=-p\,Da\langle r(c_0\psi_0),\psi_j\rangle/\mu_j+O(p^2) \qquad (j=1,2,\ldots,\infty). \qquad (4.27)$$

Note that the slave modes are related to the master mode c_0 and not its gradient. This reflects the steady-state coupling between convection and kinetics. Substitution of (4.27) in (4.25) and rescaling the spatial coordinate gives the effective transport equation,

$$\frac{\mathrm{d}c_0}{\mathrm{d}z}=-Da\langle r(c_0\psi_0),\psi_0\rangle+\gamma_1 p\,Da^2\frac{r(c_0\psi_0)r'(c_0\psi_0)}{\psi_0}+O(p^2), \qquad (4.28a)$$

where $$\gamma_1=\sum_{i=1}^{\infty}\frac{\epsilon_{0i}^2}{\mu_i}. \qquad (4.28b)$$

We now show that the source correction term in (4.28*a*) has the same effect as adding a dispersion term to the right-hand side. Differentiating (4.28*a*) with respect to z and substituting for the first derivative, we obtain

$$\frac{\mathrm{d}^2c_0}{\mathrm{d}z^2}=Da^2\frac{r(c_0\psi_0)r'(c_0\psi_0)}{\psi_0}+O(p). \qquad (4.29)$$

Using this relation, the effective transport equation may be now be written as

$$\frac{1}{Pe}\frac{\mathrm{d}^2c_0}{\mathrm{d}z^2}-\frac{\mathrm{d}c_0}{\mathrm{d}z}-Da\frac{r(c_0\psi_0)}{\psi_0}+O(p^2)=0; \qquad p\ll z<1, \qquad (4.30)$$

where $$1/Pe=\gamma_1 p. \qquad (4.31)$$

Since $C_m=c_0\psi_0$, (4.30) is also valid for the cross-sectional mean concentration (or any other mean concentration up to the order indicated). Thus the effective diffusivity for the steady-state model is the same as that for the transient model (since $\gamma_1=\beta_1$). Since the spatial eigenfunctions Ψ_i in (3.33) do not have zero cross-sectional mean, the slave modes c_j $(j\neq 0)$ contribute to the mean concentration. Appropriate boundary conditions to the effective equation may be derived by analysing this steady-state reaction-induced boundary layer at the entrance. These conditions must also account for the transverse variation of the inlet condition as it determines how the spatial dynamics approach the spatial centre manifold. It is also possible to derive higher order corrections analogous to the previous cases, but this and the corresponding boundary conditions will be pursued in a subsequent manuscript.

5. Taylor–Aris dispersion with a surface reaction

In this section, we consider the classical Taylor–Aris problem with a linear surface reaction term. As stated in the Introduction, this problem was first considered by Sankarasubramanian & Gill (1973) and later by Lungu & Moffat (1982), Smith (1983), Barton (1984) and Shapiro & Brenner (1986). Here we extend their results by deriving the effective transport equation to infinite order by using the invariant manifold approach. We also determine the region of convergence of the invariant manifold expansion. Because diffusion and surface reaction occur in series, a timescale separation always exists and complete depletion of reactants in small boundary layers do not occur even for very fast reactions. This renders the surface reaction case most suitable for our analysis. The pertinent equations and boundary conditions are

$$\frac{\partial C}{\partial t} + pf(x,y)\frac{\partial C}{\partial z} = \nabla_*^2 C; \qquad 0<z<1, t>0, (x,y)\in\Omega, \tag{5.1a}$$

$$\nabla_* C \cdot \boldsymbol{n} + \phi_{\mathrm{s}}^2 C = 0 \quad \text{on} \quad \partial\Omega_1, \tag{5.1b}$$

$$\nabla_* C \cdot \boldsymbol{n} = 0 \quad \text{on} \quad \partial\Omega_2 \quad (\partial\Omega = \partial\Omega_1 + \partial\Omega_2), \tag{5.1c}$$

where $\phi_{\mathrm{s}}^2 = a^2 k_{\mathrm{r}}/D_{\mathrm{m}}$, ($k_{\mathrm{r}} = k_{\mathrm{s}} a_{\mathrm{v}}$; k_{s} is the surface rate constant, a_{v} reaction area per unit channel volume). Let λ_i $(i=0,1,2,\ldots)$ be the eigenvalues and ψ_i $(i=0,1,\ldots)$ be the respective orthonormal set of eigenfunctions of the self-adjoint eigenvalue problem:

$$\nabla_*^2\psi_i = -\lambda_i\psi_i \quad \text{in} \quad \partial\Omega; \quad \nabla_*\psi_i\cdot\boldsymbol{n} + \phi_{\mathrm{s}}^2\psi_i = 0 \quad \text{on} \quad \partial\Omega_1, \quad \nabla_*\psi_i\cdot\boldsymbol{n} = 0 \quad \text{on} \quad \partial\Omega_2. \tag{5.2}$$

Writing

$$C(x,y,z,t) = C_0(z,t)\psi_0(x,y) + \sum_{i=1}^{\infty} C_i(z,t)\psi_i(x,y), \tag{5.3}$$

equation (5.1) may be written in its component form:

$$\frac{\partial C_0}{\partial t} + p\alpha_{00}\frac{\partial C_0}{\partial z} + p\sum_{i=1}^{\infty}\alpha_{0i}\frac{\partial C_i}{\partial z} + \lambda_0 C_0 = 0, \tag{5.4}$$

$$\frac{\partial C_j}{\partial t} + p\alpha_{j0}\frac{\partial C_0}{\partial z} + p\sum_{i=1}^{\infty}\alpha_{ji}\frac{\partial C_i}{\partial z} + \lambda_j C_j = 0 \qquad (j=1,2,\ldots). \tag{5.5}$$

(Note that ψ_0 is not a constant, C_0 does not represent the mean concentration and α_{00} is no longer equal to unity.) It follows from (5.4) and (5.5) that for $p=0$, C_0 evolves on a timescale λ_0^{-1} while C_j $(j\geqslant 1)$ evolves on a timescale λ_j^{-1}. The spectrum changes with ϕ_{s}^2, but unlike the case of bulk reaction, remains discrete and well separated for all values of ϕ_{s}^2. For example, for plane Couette flow with reaction only on the top surface, λ_j $(j\geqslant 0)$ changes from $j^2\pi^2$ to $(j+\frac{1}{2})^2\pi^2$ as ϕ_{s}^2 changes from zero to infinity. Thus, for $p\ll 1$, an invariant manifold exists for the flow defined by the dynamical system, (5.4) and (5.5), for all ϕ_{s}^2. The invariant manifold may be calculated to be

$$C_j = \sum_{n=1}^{\infty}\Delta_{jn}p^n\frac{\partial^n C_0}{\partial z^n} \qquad (j=1,2,\ldots), \tag{5.6}$$

where the constants Δ_{jn} are given by

$$\left.\begin{aligned}(\lambda_j-\lambda_0)\Delta_{j1}&=-\alpha_{0j},\\(\lambda_j-\lambda_0)\Delta_{j2}&=\alpha_{00}\Delta_{j1}-\sum_{i=1}^{\infty}\alpha_{ji}\Delta_{i1},\\(\lambda_j-\lambda_0)\Delta_{jn}&=\alpha_{00}\Delta_{j,n-1}-\sum_{i=1}^{\infty}\alpha_{ji}\Delta_{i,n-1}+\sum_{i=1}^{\infty}\sum_{k=1}^{n-2}\alpha_{0i}\Delta_{ik}\Delta_{j,n-k-1}\\&\qquad(n\geqslant 3, j\geqslant 1).\end{aligned}\right\}\tag{5.7}$$

Substituting this result in (5.4), we get the effective transport equation,

$$\frac{\partial C_0}{\partial \tau}+\alpha_{00}\frac{\partial C_0}{\partial z}=\sum_{n=1}^{\infty}\beta_n p^n\frac{\partial^{n+1}C_0}{\partial z^{n+1}}-Da\,C_0,\tag{5.8}$$

where

$$Da=\lambda_0/p,\qquad \tau=pt,$$

$$\beta_n=-\sum_{i=1}^{\infty}\alpha_{0i}\Delta_{in}\qquad(n=1,2,\ldots).\tag{5.9}$$

As shown earlier, (5.8) is also valid for the cross-sectional mean concentration or any other weighted mean concentration. In dimensional form, (5.8) may be written as

$$\frac{\partial C_0}{\partial t'}+u_{\mathrm{e}}\frac{\partial C_0}{\partial z'}=\sum_{n=2}^{\infty}D_n\frac{\partial^n C_0}{\partial z'^n}-k_{\mathrm{e}}C_0\qquad(t'>0),\tag{5.10a}$$

where the effective velocity (u_{e}), rate constant (k_{e}) and the dispersion coefficients, D_n ($n\geqslant 2$), are defined by

$$u_{\mathrm{e}}=\alpha_{00}\langle u\rangle;\quad k_{\mathrm{e}}=\lambda_0 D_{\mathrm{m}}/a^2;\quad D_n=\beta_{n-1}\langle u\rangle^n(a^2/D_{\mathrm{m}})^{n-1}\quad(n\geqslant 2).\tag{5.10b}$$

Equations (5.7) and (5.9) provide the requisite formulas for the dependence of the effective transport coefficients on the surface Thiele modulus ϕ_{s}^2.

Tables 2, 3 and 4 show the variation of α_{00}, λ_0 and β_1 as a function of ϕ_{s}^2 for the three types of flows considered in the previous section. (Note that for the case of pipe and Poiseuille flows, $\partial\Omega_2$ is assumed to be empty while for Couette flow, $\partial\Omega_1$ is the top surface while $\partial\Omega_2$ is the bottom surface). For the case of a slow reaction (ϕ_{s}^2 is of order p), the numerical factor β_1 approaches the classical Taylor–Aris limit ($\frac{1}{48}, \frac{2}{105}, \frac{1}{30}$) for pipe, Poiseuille and Couette flows, respectively. For infinitely fast surface reaction ($\phi_{\mathrm{s}}^2\gg 1$), β_1 approaches another limit (*ca.* $\frac{1}{200}, \frac{1}{375}, \frac{1}{119}$). Thus, for the three geometries considered, the effective diffusivity, D_2, decreases by a factor 4.2, 7.1, 4.0, respectively.

For the case of pipe and Poiseuille flows, the coefficient α_{00}, giving the effective velocity increases from 1.00 (for $\phi_{\mathrm{s}}^2=0$) to 1.56 and 1.30, respectively (for $\phi_{\mathrm{s}}^2=\infty$). For the case of Couette flow, it decreases from 1.0 to 0.595. This decrease may be explained by the fact that we have taken the reaction plane to be the top surface at which the velocity is maximum. In order to examine the convergence of the invariant manifold expansion for the case of a fast surface reaction, we have computed the first 100 coefficients in (5.8) for $\phi_{\mathrm{s}}^2=\infty$. The first 20 of these are listed in table 5 for the three types of flows. From these numerical values, we

Table 2. *Effective transport coefficients for surface reaction (pipe flow)*

ϕ_s^2	β_1^{-1}	α_{00}	$\surd\lambda_0$
0.01	47.984	1.0017	0.14124
0.02	47.970	1.0033	0.19950
0.05	47.932	1.0083	0.31426
0.10	47.888	1.0164	0.44168
0.20	47.869	1.0325	0.61697
0.50	48.293	1.0778	0.94077
1.00	50.265	1.1440	1.2558
2.00	57.131	1.2446	1.5994
5.0	83.562	1.3938	1.9898
10.0	117.19	1.5461	2.3572
20.0	149.83	1.5189	2.2880
50.0	177.69	1.5461	2.3572
100.0	188.56	1.5551	2.3809
1000.0	199.01	1.5630	2.4024
∞	200.20	1.5638	2.4048

computed the radius of convergence of the invariant manifold expansion to be

$$\eta_c = \frac{a^2\langle u\rangle}{D_m}\frac{\partial}{\partial z'} = 37.7, 38.0, 24.3 \tag{5.11}$$

for pipe, Poiseuille and Couette flows, respectively. Comparison of these values with those of the centre manifold expansion shows that the radius of convergence increases by a factor three as ϕ_s^2 changes from zero to infinity.

6. Effective dispersion in chromatographic models

In this section, we consider some linear and nonlinear problems in chromatographic theory and derive effective dispersion models. As stated in the Introduction, a chromatograph functions on the principle that solutes are adsorbed onto the wall (or solid packing) and because of their affinity for the wall, their effective velocity is reduced. From classical equilibrium chromatograph theory (Amundson & Aris 1973) with linear adsorption–desorption equilibrium constant K, the velocity varies as $(1+K)^{-1}$. We first show that if equilibrium is not established, namely, if adsorption/desorption is fast compared to axial convection, but occurs at a finite rate, the affinity mechanism can induce an effective dispersion. Intuitively, one expects the adsorption/desorption process in a chromatograph to reduce the Taylor–Aris dispersion mechanism since, like surface reaction, it removes slow-moving solutes near the wall. However, unlike surface reaction, the solutes are released after a time lag related to the adsorption/desorption kinetics and the capacitance of the wall and one hence expects a new dispersion mechanism that can over compensate for the reduction in Taylor–Aris dispersion. One can also visualize this new mechanism as a special kind of Taylor–Aris dispersion by considering the wall as a streamline with zero velocity. The transverse

Table 3. *Effective transport coefficients for surface reaction (Poiseuille flow)*

ϕ_s^2	β_1^{-1}	α_{00}	$\surd\lambda_0$
0.01	52.640	1.0013	0.099833
0.02	52.782	1.0027	0.14095
0.05	53.212	1.0066	0.22176
0.10	53.949	1.0130	0.31105
0.20	55.489	1.0252	0.43284
0.50	60.584	1.0578	0.65327
1.00	70.266	1.1009	0.86033
2.00	91.885	1.1579	1.07687
5.0	153.494	1.2296	1.31384
10.0	220.565	1.2647	1.42887
20.0	281.832	1.2841	1.49613
50.0	333.341	1.2961	1.54000
100.0	353.490	1.3000	1.55524
1000.0	372.970	1.30357	1.56923
∞	375.213	1.30396	1.57079

Table 4. *Effective transport coefficients for surface reaction (Couette flow)*

ϕ_s^2	β_1^{-1}	α_{00}	$\surd\lambda_0$
0.01	30.050	0.99834	0.099833
0.02	30.101	0.99668	0.14095
0.05	30.256	0.99178	0.22176
0.10	30.524	0.98377	0.31105
0.20	31.093	0.96840	0.43284
0.50	33.013	0.92708	0.65327
1.00	36.686	0.87189	0.86033
2.00	44.612	0.79757	1.07687
5.0	64.695	0.70110	1.31384
10.0	83.407	0.65210	1.42887
20.0	98.577	0.62415	1.49613
50.0	110.335	0.60659	1.54000
100.0	114.744	0.60066	1.55525
1000.0	118.922	0.59531	1.56923
∞	119.399	0.59472	1.57079

gradient in the velocity field for the Taylor–Aris mechanism is then present even if the fluid velocity profile is flat. Instead of a diffusive mechanism to sample streamlines of different velocities, we replace it with the adsorption/desorption process, which like diffusion, is dependent on the concentration gradient (difference). However, unlike diffusion, for the same concentration difference, the flux in

Table 5. *Coefficients in the invariant manifold expansion (infinitely fast surface reaction)*

	β_i		
i	pipe flow	Couette flow	Poiseuille flow
1	0.49950E−02	0.83753E−02	0.26652E−02
2	0.49206E−04	−0.13878E−03	0.41154E−04
3	−0.11850E−06	0.14054E−06	0.42663E−06
4	−0.14514E−07	0.86498E−07	−0.10895E−08
5	−0.17859E−09	−0.25806E−08	−0.17021E−09
6	0.29071E−11	−0.65890E−11	−0.39339E−11
7	0.12584E−12	0.29462E−11	−0.31296E−13
8	0.77189E−15	−0.85853E−13	0.95547E−15
9	−0.48611E−16	−0.74572E−15	0.41724E−16
10	−0.12510E−17	0.13114E−15	0.69960E−18
11	0.33958E−20	−0.34068E−17	−0.16101E−20
12	0.74061E−21	−0.57887E−19	−0.41964E−21
13	0.11614E−22	0.65426E−20	−0.11410E−22
14	−0.20522E−24	−0.14467E−21	−0.10401E−24
15	−0.10470E−25	−0.41086E−23	0.33393E−26
16	−0.75539E−28	0.34625E−24	0.15934E−27
17	0.47550E−29	−0.62098E−26	0.28617E−29
18	0.13451E−30	−0.28144E−27	−0.66313E−32
19	−0.31584E−33	0.18930E−28	−0.18899E−32
20	−0.87563E−34	−0.25555E−30	−0.53658E−34

opposite directions can be different depending on the ratio between the adsorption and desorption rates, the adsorption equilibrium constant K. This asymmetry allows an interesting coupling with the velocity gradient to yield a maximum in dispersion with respect to K. Nevertheless, because this adsorption/desorption dispersion mechanism is like the Taylor–Aris mechanism in its physical origin, it is also a transient phenomenon. As a result, the spatial evolution problem, which is more consistent with the operation of a chromatograph, agrees with the temporal evolution problem up to second order. Here, we examine the simpler temporal problem only. We also exploit the nonlinear capability of our approach to show that at high solute concentrations where the surface-coverage Langmuir effect renders the adsorption nonlinear, the effective transport equation reduces to the Burger's equation which is responsible for non-symmetric pulse responses. The effects of molecular diffusion in the fluid phase, surface chemical reactions as well as that of the velocity profile is also considered.

(*a*) *Linear adsorption–desorption models with flat velocity profile*

We consider the classical problem of linear adsorption and desorption with a flat velocity profile. Neglecting transverse as well as longitudinal diffusion, the evolution equations describing the concentrations of the solute in the fluid and solid phases may be written as

$$\frac{\partial C_\mathrm{f}}{\partial t'} + \langle u \rangle \frac{\partial C_\mathrm{f}}{\partial z'} = -k_\mathrm{a} C_\mathrm{f} + k_\mathrm{d} C_\mathrm{s}, \tag{6.1}$$

$$\frac{\partial C_\mathrm{s}}{\partial t'} = k_\mathrm{a} C_\mathrm{f} - k_\mathrm{d} C_\mathrm{s}, \tag{6.2}$$

where k_a and k_d are adsorption and desorption rate constants, respectively. Note that since we are considering an infinitely thin wall phase, the capacitance for both equations are identical if the surface concentration is renormalized with respect to the fluid volume. The three timescales associated with (6.1) and (6.2) are that of axial convection ($t_\mathrm{C} = L/\langle u \rangle$), adsorption ($t_\mathrm{A} = 1/k_\mathrm{a}$) and desorption ($t_\mathrm{DE} = 1/k_\mathrm{d}$), or equivalently, the adsorption equilibrium constant, $K = k_\mathrm{a}/k_\mathrm{d}$. Defining dimensionless variables

$$t = k_\mathrm{a} t', \quad z = z'/L, \quad p_\mathrm{a} = \langle u \rangle / L k_\mathrm{a}. \tag{6.3}$$

Equations (6.1) and (6.2) may be written as

$$\partial \boldsymbol{c}/\partial t = \boldsymbol{A}\boldsymbol{c} + N(\boldsymbol{c}), \tag{6.4}$$

where

$$\boldsymbol{c} = \begin{pmatrix} C_\mathrm{f} \\ C_\mathrm{s} \\ p_\mathrm{a} \end{pmatrix}, \quad \boldsymbol{A} = \begin{pmatrix} -1 & K^{-1} & 0 \\ 1 & -K^{-1} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad N(\boldsymbol{c}) = \begin{pmatrix} -p_\mathrm{a} \partial C_\mathrm{f}/\partial z \\ 0 \\ 0 \end{pmatrix}. \tag{6.5}$$

In what follows, we shall assume that $p_\mathrm{a} \ll 1$ and K is of order unity, i.e. adsorption and desorption are rapid compared to axial convection. It is clear that the matrix $\boldsymbol{A}$ has two zero eigenvalues ($\lambda_1 = \lambda_2 = 0$) and one negative eigenvalue ($\lambda_3 = -1 - K^{-1}$). After a similarity transformation, (6.4) may be transformed to the canonical form,

$$\frac{\partial C_1}{\partial t} = -\frac{p_\mathrm{a}}{K+1}\left(\frac{\partial C_1}{\partial z} + \frac{\partial C_2}{\partial z}\right), \tag{6.6a}$$

$$\frac{\partial C_2}{\partial t} = -\left(1 + \frac{1}{K}\right) C_2 - \frac{p_\mathrm{a} K}{K+1}\left(\frac{\partial C_1}{\partial z} + \frac{\partial C_2}{\partial z}\right), \tag{6.6b}$$

$$\frac{\partial p_\mathrm{a}}{\partial t} = 0, \tag{6.6c}$$

where the canonical variables C_1 and C_2 are related to C_f and C_s by

$$C_1 = C_\mathrm{f} + C_\mathrm{s}, \quad C_2 = K C_\mathrm{f} - C_\mathrm{s}. \tag{6.7}$$

Note that C_1 is the total concentration of the solute under equilibrium conditions while C_2 measures the deviation from the equilibrium. The centre manifold of (6.6) may be calculated to be

$$C_2 = \sum_{n=1}^{\infty} \Delta_n \left(\frac{p_\mathrm{a}}{K+1}\right)^n \frac{\partial^n C_1}{\partial z^n}, \tag{6.8}$$

where

$$\left.\begin{aligned} \Delta_1 = -\frac{K^2}{1+K}, \quad \Delta_2 = -\frac{K(1-K)}{1+K}\Delta_1, \\ \Delta_m = -\frac{K(1-K)}{1+K}\Delta_{m-1} + \frac{K}{1+K}\sum_{i=1}^{m-2}\Delta_i\Delta_{m-i-1} \qquad (m \geqslant 3). \end{aligned}\right\} \tag{6.9}$$

(Note that when $K = 1$, $\Delta_{2j} = 0$, $j = 1, 2, \ldots$.) Substitution of (6.8) into (6.6*a*) gives the following effective transport equation,

$$\frac{\partial C_1}{\partial \tau} + \frac{1}{1+K}\frac{\partial C_1}{\partial z} = \sum_{n=1}^{\infty}\beta_n p_{\mathrm{a}}^n \frac{\partial^{n+1}C_1}{\partial z^{n+1}}, \tag{6.10a}$$

where $$\tau = p_{\mathrm{a}}t = \langle u\rangle t'/L; \quad \beta_n = -\Delta_n/(K+1)^{n+1}. \tag{6.10b}$$

Truncating (6.10*a*) at $n = 1$ gives the following convective diffusion equation,

$$\frac{\partial C_1}{\partial \tau} + \frac{1}{1+K}\frac{\partial C_1}{\partial z} = \frac{1}{Pe}\frac{\partial^2 C_1}{\partial z^2}, \tag{6.11a}$$

where $$\frac{1}{Pe} = \frac{p_{\mathrm{a}}K^2}{(1+K)^3}. \tag{6.11b}$$

Thus the effective velocity and dispersion coefficient are given by

$$u_{\mathrm{e}} = \frac{\langle u\rangle}{1+K}, \quad D_{\mathrm{e}} = \frac{\langle u\rangle^2}{k_{\mathrm{a}}}\frac{K^2}{(1+K)^3}. \tag{6.11c}$$

Note that D_{e} is a non-monotonic function of K and approaches zero when adsorption is much faster or slower than desorption ($K \ll 1$ or $K \gg 1$). In these two limits, complete retention or negligible adsorption occur and there is hence no mechanism for dispersion. The maximum value of D_{e} is attained when $K = 2$ and is given by

$$D_{\mathrm{e,max}} = \tfrac{4}{27}\langle u\rangle^2/k_{\mathrm{a}}. \tag{6.12}$$

This maximum at $K = 2$ is intriguing but we are unable to determine its precise physical origin. In fact, one would expect the diffusive analog K = 1 to yield the maximum dispersion. This is indeed the case for an analogous problem studied by Aris (1959). For the case of mass transfer between a fluid in a pipe with a thin porous wall, Aris has shown that the effective dispersion coefficient is given by

$$D_{\mathrm{e,max}} = \frac{a\langle u\rangle^2}{2k_{\mathrm{c}}}\frac{K^2}{(1+K)^4}, \tag{6.13}$$

where K is the equilibrium constant, a is the pipe radius and k_{c} is the mass transfer coefficient. It is clear that the maximum value of $D_{\mathrm{e,max}}$ occurs at $K = 1$ and is equal to $D_{\mathrm{e,max}} = a\langle u\rangle^2/32k_{\mathrm{c}}$. The difference between the two cases is that our model does not allow diffusion in the solid phase while (6.13) accounts for it.

The concentration C_1 is not an easily measurable concentration and it is preferable to write the effective equation (6.10*a*) in terms of the solute concentration in the fluid phase, C_{f}. This can be done by noting that

$$C_{\mathrm{f}} = \frac{C_1 + C_2}{1+K} = \frac{C_1}{1+K} + \frac{1}{1+K}\sum_{n=1}^{\infty}\Delta_n\left(\frac{p_{\mathrm{a}}}{K+1}\right)^n\frac{\partial^n C_1}{\partial z^n} = L^{**}C_1, \tag{6.14}$$

where L^{**} is a linear differential operator. Operating both sides of (6.10*a*) by L^{**} gives the effective equation for C_f, which is identical to that for C_1.

Equations (6.11*c*) may be used to estimate the length of the chromatograph needed so that the distance between the peaks of any two solute pulses exceeds the spread between them. The distance between peaks is given by

$$\Delta x_d = (t_1 - t_2)\langle u\rangle, \tag{6.15a}$$

where
$$t_1 = L/u_{1e}, \quad t_2 = L/u_{2e}, \tag{6.15b}$$

while the spread between the peaks is given by

$$\Delta x_s = 2(\surd(2D_{1e}t_1) + \surd(2D_{2e}t_2)). \tag{6.15c}$$

(The definition of the spread is based on 95.5% of the total area of the pulse, or equivalently, two standard deviations from the mean.) Thus Δx_d exceeds Δx_s if

$$\frac{L}{\langle u\rangle} > \frac{8}{(K_1 - K_2)^2}\left[\frac{1}{\surd k_{a1}}\frac{K_1}{1+K_1} + \frac{1}{\surd k_{a2}}\frac{K_2}{1+K_2}\right]. \tag{6.15d}$$

This equation may be simplified if one of the species adsorps/desorps much faster than the other. As expected, (6.15*d*) predicts that if $K_1 \neq K_2$, it is always possible to achieve the required separation by increasing the residence time. As noted by Aris (1959) for the mass transfer problem, the minimum residence timescales by a -2 power with respect to the difference in the two affinities.

It is interesting to determine the region of convergence of the effective model given by (6.10*a*) and compare it with that of the classical Taylor–Aris dispersion model. We have computed the first 100 coefficients in (6.10*a*) using the analytical expressions, (6.9) and (6.10*b*), for K values of 0.1, 0.5, 1.0, 2.0 and 10. For the special case of $K = 1$, all even β_n vanish and the odd coefficients are strictly decreasing with alternating signs. For all other values of K, the coefficients are non-monotonic and there is no definite pattern of signs. Application of the method of Mercer & Roberts (1990) showed that the centre manifold expansion in (6.10*b*) converges provided

$$p_a\frac{\partial}{\partial z} = \frac{\langle u\rangle}{k_a}\frac{\partial}{\partial z'} < \frac{K}{K+1}.$$

Thus, the largest region of convergence is obtained when the desorption rate constant is zero.

(*b*) *Effect of molecular diffusion in the fluid phase*

The above analysis may be extended to include axial molecular diffusion in the fluid phase. In this case, (6.6*a*) and (6.6*b*) are modified to

$$\frac{\partial C_1}{\partial t} = -\frac{p_a}{K+1}\left(\frac{\partial C_1}{\partial z} + \frac{\partial C_2}{\partial z}\right) + \frac{p^* p_a}{K+1}\left(\frac{\partial^2 C_1}{\partial z^2} + \frac{\partial^2 C_2}{\partial z^2}\right), \tag{6.16a}$$

$$\frac{\partial C_2}{\partial t} = -\left(1+\frac{1}{K}\right)C_2 - \frac{p_a K}{K+1}\left(\frac{\partial C_1}{\partial z} + \frac{\partial C_2}{\partial z}\right) + \frac{K p^* p_a}{K+1}\left(\frac{\partial^2 C_1}{\partial z^2} + \frac{\partial^2 C_2}{\partial z^2}\right), \tag{6.16b}$$

where $p^* = D_m/\langle u\rangle L$ is assumed to be of order unity or smaller. To leading order, the centre manifold is now given by

$$C_2 = -\frac{p_\mathrm{a}K^2}{(K+1)^2}\frac{\partial C_1}{\partial z} + \frac{K^2 p^* p_\mathrm{a}}{(K+1)^2}\frac{\partial^2 C_1}{\partial z^2} + O(p_\mathrm{a}^2) \qquad (6.17)$$

and the effective equation for C_1 is given by

$$\frac{\partial C_1}{\partial \tau} + \frac{1}{1+K}\frac{\partial C_1}{\partial z} = \left[\frac{p_\mathrm{a}K^2}{(K+1)^3} + \frac{p^*}{K+1}\right]\frac{\partial^2 C_1}{\partial z^2}$$
$$- \frac{2K^2 p^* p_\mathrm{a}}{(K+1)^3}\frac{\partial^3 C_1}{\partial z^3} + \frac{K^2 {p^*}^2 p_\mathrm{a}}{(K+1)^3}\frac{\partial^4 C_1}{\partial z^4} + O(p_\mathrm{a}^2). \qquad (6.18a)$$

When p^* is of order unity, the contribution of adsorption induced dispersion may be neglected compared to axial molecular diffusion. In this case (6.18a) reduces to the convective diffusion equation with the effective velocity and diffusivity reduced by a factor $(1+K)$. When p^* is of order p_a the contributions of adsorption induced dispersion and axial molecular dispersion are of equal order of magnitude. However, in this case the last two terms in (6.18a) are of higher order and may be neglected. The effective velocity is again reduced by a factor $(1+K)$ but the effective diffusivity is now given by

$$D_\mathrm{e} = \frac{D_\mathrm{m}}{1+K} + \frac{\langle u\rangle^2}{k_\mathrm{a}}\frac{K^2}{(1+K)^3}. \qquad (6.18b)$$

The effective diffusivity is a monotonic decreasing function of K if $D_\mathrm{m} > \langle u\rangle^2/3k_\mathrm{a}$. Otherwise, the curve D_e versus K has a minimum and a maximum and the adsorption/desorption mechanism can increase the overall dispersion. Finally, we note that when p^* is of order p_a^2, the contribution of axial molecular diffusion is negligible and (6.18a) reduces to (6.11a) upto leading-order terms.

(*c*) *Effective dispersion model with Langmuir adsorption*

At high concentrations of the solute, saturation effects (or surface coverage) becomes important and the rate of adsorption is not linear in the concentrations. We consider here the case of Langmuir adsorption for which (6.1) and (6.2), after proper normalization, may be written as

$$\frac{\partial C_\mathrm{f}}{\partial t} + p_\mathrm{a}\frac{\partial C_\mathrm{f}}{\partial z} = -C_\mathrm{f} + \frac{C_\mathrm{s}}{K} + C_\mathrm{f}C_\mathrm{s}, \qquad (6.19)$$

$$\frac{\partial C_\mathrm{s}}{\partial t} = C_\mathrm{f} - \frac{C_\mathrm{s}}{K} - C_\mathrm{f}C_\mathrm{s}. \qquad (6.20)$$

Note that the nonlinear saturation effect impedes adsorption while enhancing desorption. We here expect a nonlinear enhancement of the effective velocity, namely, a nonlinear drift term that accelerates the front edge. Since the linear terms are unchanged, (6.7) may again be used to write (6.19) and (6.20) in canonical variables:

$$\frac{\partial C_1}{\partial t} = -\frac{p_\mathrm{a}}{K+1}\left(\frac{\partial C_1}{\partial z} + \frac{\partial C_2}{\partial z}\right), \qquad (6.21a)$$

$$\frac{\partial C_2}{\partial t} = -\left(1+\frac{1}{K}\right)C_2 - \frac{p_\mathrm{a}K}{K+1}\left(\frac{\partial C_1}{\partial z}+\frac{\partial C_2}{\partial z}\right)+\frac{1}{1+K}[KC_1^2+(K-1)C_1C_2-C_2^2]. \tag{6.21b}$$

To leading order, the centre manifold is now given by

$$C_2 = -\frac{p_\mathrm{a}K^2}{(K+1)^2}\frac{\partial C_1}{\partial z}+\frac{K^2C_1^2}{(K+1)^2}+O(|p_\mathrm{a},C_1|^3) \tag{6.22}$$

and the effective equation for C_1 is

$$\frac{\partial C_1}{\partial \tau}+\frac{1}{1+K}\frac{\partial C_1}{\partial z} = \frac{p_\mathrm{a}K^2}{(K+1)^3}\frac{\partial^2 C_1}{\partial z^2} - \frac{2K^2}{(K+1)^3}C_1\frac{\partial C_1}{\partial z}+O(|p_\mathrm{a},C_1|^3). \tag{6.23}$$

Note the appearance of nonlinear convection terms that are associated with Langmuir adsorption. Equation (6.23) implies that a finite rate of adsorption/desorption is equivalent to adding a viscous term to the standard hyperbolic conservation laws used in equilibrium chromatography theory! Thus, the discontinuous solutions predicted by equilibrium chromatograph theory disappear if adsorption/desorption are assumed to occur at a finite rate. Equation (6.23) may be written in the conservative form,

$$\frac{\partial C_1}{\partial \tau}+\frac{\partial q}{\partial z}=0; \quad q=\frac{C_1}{1+K}+\frac{K^2}{(K+1)^3}C_1^2-\frac{p_\mathrm{a}K^2}{(K+1)^3}\frac{\partial C_1}{\partial z}, \tag{6.24a}$$

which gives the effective velocity and dispersion coefficient to be

$$u_\mathrm{e}=\frac{\langle u\rangle}{1+K}\left[1+\frac{K^2C_1}{(K+1)^2}\right], \quad D_\mathrm{e}=\frac{\langle u\rangle^2}{k_\mathrm{a}}\frac{K^2}{(1+K)^3}. \tag{6.24b}$$

Equation (6.24*b*) predicts that the effective velocity of the solute increases with the concentration. Thus, a pulse that is initially symmetric will develop a long tail toward the lower concentration. We further note that by defining the following variables in a moving coordinate Z,

$$c=\frac{2K^2C_1}{(K+1)^2}, \quad Z=z-\theta, \quad \theta=\frac{\tau}{1+K}, \quad \nu=\frac{p_\mathrm{a}K^2}{(K+1)^2}. \tag{6.25}$$

Equation (6.23) transforms to the Burgers' equation

$$\frac{\partial c}{\partial \theta}+c\frac{\partial c}{\partial Z}=\nu\frac{\partial^2 c}{\partial Z^2}. \tag{6.26}$$

Response of this equation to an arbitrary initial condition can be derived using the standard Cole–Hopf transformation (Whitham 1974). For large ν (large p_a or small k_a corresponding to slow adsorption), which is not consistent with our formulation, (6.25) would behave like the linear adsorption case, (6.11*a*) at large times. Its asymptotic behaviour would then be described by an effective convection-diffusion equation like (3.22). The asymptotic behaviour of (6.26) for the pertinent case of small ν, however, suggests anomalous transport for strong Langmuir adsorption. (Note that ν is always of order p_a regardless of the magnitude of K.) The asymptotic response to a delta function initial condition yields a right-angle triangular shock with the back edge fixed at the initial location of the delta function and the front edge moving forward at the speed of $\surd(2\theta)$. The slope of the triangle approaches $c \approx Z/\theta$ with the maximum at the front edge

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

decaying at the rate of $c_{\mathrm{max}} \approx \surd(2/\theta)$. A simple calculation of the moments for this response yields that the centre of mass moves at a speed of $2^{3/2}/(3\surd\theta)$ in the moving coordinate frame and the variance increases linearly in time, $\sigma^2 \approx \theta/9$. Although this seems like a diffusive asymptote in the moving frame at large θ, calculation of higher moments yields the result that the mth moment varies as $\theta^{m/2}$. This implies that the higher order terms quickly dominate the drift velocity and dispersion terms if an equation like (3.17*a*) is used to describe the response of (6.26). Consequently, Langmuir adsorption introduces an anomalous dispersion that can only be described by the Burger equation in (6.26). This nonlinear effect is extremely undesirable in separation chromatography since the long tails of the solution to Burger's equation will cause significant overlap between solute pulses. Unlike the dispersion-induced spread in the linear case, the nonlinear drift term introduces a front edge which accelerates away from the back edge (the location of the pulse if the Langmuir effect is absent). Since the speed of the front edge of a pulse increases by $\surd\theta$ while the back edge of another pulse in front of it moves at constant speed, overlap between the two will eventually occur. Hence, unlike the linear adsorption case, separation cannot be ensured with a sufficiently long chromatograph. The solution, in fact, involves choosing a chromatograph of appropriate length such that the separation has occured due to the linear hyperbolic terms of (6.23) and yet nonlinear acceleration has not caused significant asymmetry and overlap. This chromatograph must also be long enough to avoid overlap by dispersion spreading as dictated by (6.15*d*). If the linear dispersion term is the same order as the nonlinear drift term, which is often the case, the interval of appropriate chromatograph length may be small or even non-existent. One would then need to minimize the Langmuir effect by decreasing the solute concentrations, which is practically unsound, or by increasing the wall capacitance neglected in our study, namely, allow diffusion into the solid phase.

Higher-order correction terms to the effective transport (6.24) may easily be derived using the centre manifold approach. Inclusion of third-order terms modifies (6.24) to

$$\frac{\partial C_1}{\partial \tau} + \frac{\partial Q}{\partial z} = 0, \tag{6.27a}$$

$$\begin{aligned} Q = {} & \left[\frac{1}{1+K} + \frac{K^2}{(K+1)^3}C_1 + \frac{(K-1)K^3}{(K+1)^5}C_1^2\right]C_1 \\ & - \left[\frac{p_{\mathrm{a}}K^2}{(K+1)^3} - \frac{3p_{\mathrm{a}}K^2(1-K)}{(K+1)^5}C_1\right]\frac{\partial C_1}{\partial z} - \frac{p_{\mathrm{a}}^2K^3(1-K)}{(K+1)^4}\frac{\partial^2 C_1}{\partial z^2}. \end{aligned} \tag{6.27b}$$

Now, the effective velocity as well as diffusivity are concentration dependent. We also note that all the cubic terms in equation (6.27*b*) vanish for the special case of $K = 1$.

(*d*) *Effective dispersion with adsorption, desorption and surface reaction*

We now consider the effect of a linear surface reaction on the effective dispersion coefficient. In this case, (6.2) is modified to

$$\frac{\partial C_{\mathrm{s}}}{\partial t'} = k_{\mathrm{a}}C_{\mathrm{f}} - k_{\mathrm{d}}C_{\mathrm{s}} - k_{\mathrm{r}}C_{\mathrm{s}}, \tag{6.28}$$

where k_{r} is the surface reaction rate constant. For the case of a slow surface reaction, we write

$$\frac{k_{\mathrm{r}}}{k_{\mathrm{a}}} = K_{\mathrm{R}} = p_{\mathrm{a}} Da; \quad Da = \frac{k_{\mathrm{r}} L}{\langle u \rangle} \tag{6.29}$$

and assume that Da is of order unity. The analysis in § 6 *a* may be repeated and it is straightforward to show that the effective equation is given by

$$\frac{\partial C_1}{\partial \tau} + \frac{\partial C_1}{\partial z}\left[\frac{1}{1+K} + \frac{p_{\mathrm{a}} Da\, K^2}{(K+1)^3}\right] = \frac{p_{\mathrm{a}} K^2}{(K+1)^3}\frac{\partial^2 C_1}{\partial z^2} - \frac{Da\, K}{K+1} C_1 + O(p_{\mathrm{a}}^2). \tag{6.30}$$

It follows from (6.30) that the effective dispersion coefficient, velocity and rate constant are given by

$$D_{\mathrm{e}} = \frac{\langle u \rangle^2}{k_{\mathrm{a}}} \frac{K^2}{(1+K)^3} \quad u_{\mathrm{e}} = \frac{\langle u \rangle}{1+K}\left[1 + \frac{k_{\mathrm{r}}}{k_{\mathrm{a}}}\frac{K^2}{(1+K)^2}\right], \quad k_{\mathrm{e}} = k_{\mathrm{r}} \frac{K}{1+K}. \tag{6.31}$$

Thus there is a drift correction to the effective velocity, which is slightly higher than that predicted by equilibrium chromatograph theory.

When the reaction is fast (K_{R} is of order unity or larger), the matrix $\boldsymbol{A}$ in (6.5) is modified to

$$\boldsymbol{A} = \begin{pmatrix} -1 & K^{-1} & 0 \\ 1 & -K^{-1} - K_{\mathrm{R}} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{6.32}$$

The two non-zero eigenvalues of $\boldsymbol{A}$ are now given by

$$2\lambda_{1,2} = -(1 + K^{-1}) + K_{\mathrm{R}}) \pm \surd[(1 + K^{-1} + K_{\mathrm{R}})^2 - 4K_{\mathrm{R}}]. \tag{6.33}$$

For $K_{\mathrm{R}} = 0$, $\lambda_1 = 0$, $\lambda_2 = -(1+K^{-1})$ while for $K_{\mathrm{R}} \gg 1$, λ_1 approaches -1 and λ_2 approaches $(-K^{-1} - K_{\mathrm{R}})$. Thus the timescales are well separated for all values of K_{R} and an effective transport equation can be derived provided $p_{\mathrm{a}} \ll 1$. It may be shown that the flow on the invariant manifold is described by the effective transport equation,

$$\frac{\partial C_1}{\partial \tau} + \alpha_1 \frac{\partial C_1}{\partial z} = \beta_1 p_{\mathrm{a}} \frac{\partial^2 C_1}{\partial z^2} + \left(\frac{\lambda_1 C_1}{p_{\mathrm{a}}}\right) + O(p_{\mathrm{a}}^2), \tag{6.34a}$$

where

$$\alpha_1 = \frac{1}{1 + K(1+\lambda_1)^2}, \tag{6.34b}$$

$$\beta_1 = \frac{K(\lambda_2 + K^{-1} + K_{\mathrm{R}})2}{[1 + K(1+\lambda_1)^2][1 + K(\lambda_2 + K^{-1} + K_{\mathrm{R}})^2](\lambda_1 - \lambda_2)}. \tag{6.34c}$$

The effective dispersion coefficient, velocity and rate constant are now given by

$$D_{\mathrm{e}} = \beta_1 \langle u \rangle^2 / k_{\mathrm{a}}, \tag{6.35a}$$

$$u_{\mathrm{e}} = \alpha_1 \langle u \rangle, \tag{6.35b}$$

$$k_{\mathrm{e}} = -\langle u \rangle \lambda_1 / L p_{\mathrm{a}} = -\lambda_1 k_{\mathrm{a}}. \tag{6.35c}$$

For $K_{\mathrm{R}} \rightarrow 0$, these effective values approach the slow reaction limit (equation

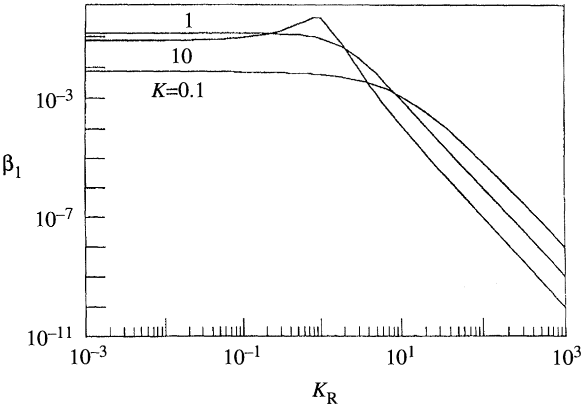

Figure 2. Dependence of the constant β_1 for effective dispersion coefficient on the dimensionless surface reaction rate K_R and the adsorption equilibrium constant K.

(6.31)) while for $K_R \gg 1$, they approach another asymptote

$$D_e = \frac{1}{KK_R^3}\frac{\langle u\rangle^2}{k_a}, \tag{6.36a}$$

$$u_e = \langle u\rangle, \tag{6.36b}$$

$$k_e = k_a. \tag{6.36c}$$

Thus the effective diffusivity approaches zero for a fast reaction. We show in figure 2 the variation of β_1 as a function of K_R for three typical values of K. For $K = 10$, the effective dispersion coefficient increases first and then decreases to zero. It may be shown that the effective velocity given by (6.35*b*) is a monotonic function of K_R for all values of K. It increases from $\langle u\rangle/(1+K)$ to $\langle u\rangle$ as K_R increases from zero to infinity. Similarly, the effective rate constant decreases monotonically from the value given by (6.31*c*) to that given by (6.36*c*) as K_R increases from zero to infinity.

(*e*) *Effect of transverse velocity gradients*

As a final example, we consider the classical Taylor problem with adsorption and desorption at the wall. This problem is analogous to the mass transfer problem studied by Aris (1959) using the moments technique but our results are different as we do not include diffusion on the wall. For the sake of simplicity, we treat here only the Couette flow case with adsorption and desorption at the top surface. The relevant mathematical model is given by

$$\frac{\partial C_f}{\partial t} + pf(y)\frac{\partial C_f}{\partial z} = \frac{\partial^2 C_f}{\partial y^2}, \tag{6.37}$$

$$\frac{\partial C_s}{\partial t} + \frac{\partial C_f}{\partial y} = 0; \quad y = 1, \tag{6.38}$$

$$\frac{\partial C_f}{\partial y} + \phi_s^2(C_f - C_s/K) = 0; \quad y = 1, \tag{6.39}$$

$$\frac{\partial C_{\mathrm{f}}}{\partial y}=0; \quad y=0, \tag{6.40}$$

where

$$p=\phi_{\mathrm{s}}^{2} p_{\mathrm{a}}, \qquad \phi_{\mathrm{s}}^{2}=a^{2} k_{\mathrm{a}} / D_{\mathrm{m}} \tag{6.41}$$

and all other parameters are as defined previously. As it is convenient to analyse (6.37)–(6.40) using the spatial centre manifold approach, we define $\tau=pt$, $Z=z/p$ and take Laplace transformation with respect to τ, so that we can eliminate C_{s} and obtain the following simplified model for the transformed variable $\hat{C}_{\mathrm{f}}(Z, y, s)$:

$$\frac{\partial \hat{C}_{\mathrm{f}}}{\partial Z}=\frac{1}{f(y)}\left[\frac{\partial^{2} C_{\mathrm{f}}}{\partial y^{2}}-s p \hat{C}_{\mathrm{f}}\right], \tag{6.42}$$

$$\frac{\partial \hat{C}_{\mathrm{f}}}{\partial y}=-\Phi^{2} \hat{C}_{\mathrm{f}}; \quad y=1, \tag{6.43}$$

$$\frac{\partial \hat{C}_{\mathrm{f}}}{\partial y}=0; \quad y=0, \tag{6.44}$$

where

$$\Phi^{2}=s p K \phi_{\mathrm{s}}^{2} /\left(s p K+\phi_{\mathrm{s}}^{2}\right). \tag{6.45}$$

Let Λ_{i} $(i=0,1,2, \ldots)$ be the eigenvalues and ψ_{i} $(i=0,1, \ldots)$ be the respective orthonormal set of eigenfunctions of the self-adjoint eigenvalue problem

$$\frac{\mathrm{d}^{2} \psi}{\mathrm{d} y^{2}}=-\Lambda f(y) \psi ; \quad \frac{\mathrm{d} \psi}{\mathrm{d} y}+\Phi^{2} \psi=0 \quad \text{at} \quad y=1 ; \quad \frac{\mathrm{d} \psi}{\mathrm{d} y}=0 \quad \text{at} \quad y=0. \tag{6.46}$$

Then, expanding $\hat{C}_{\mathrm{f}}$ as

$$\hat{C}_{\mathrm{f}}(Z, y, s)=\sum_{i=0}^{\infty} \hat{c}_{i}(Z, s) \psi_{i}(y), \tag{6.47}$$

it may be shown that the effective equation satisfied by $\hat{c}_{0}(z, s)$ is

$$\frac{\mathrm{d} \hat{c}_{0}}{\mathrm{d} z}=-\frac{\Lambda_{0}}{p} \hat{c}_{0}-s \epsilon_{00} \hat{c}_{0}+\hat{\beta}_{1} s^{2} p \hat{c}_{0}, \tag{6.48a}$$

where

$$\hat{\beta}_{1}=\sum_{i=1}^{\infty} \frac{\epsilon_{0 i}^{2}}{\Lambda_{i}-\Lambda_{0}}, \tag{6.48b}$$

$$\epsilon_{j i}=\int_{0}^{1} \psi_{i} \psi_{j} \,\mathrm{d} y \qquad (i, j=0,1, \ldots). \tag{6.48c}$$

We now consider some limiting cases of (6.48a). We first note that for $K=\infty$, $\Phi^{2}=\phi_{\mathrm{s}}^{2}$ which corresponds to the surface reaction case treated in § 5 (for $\phi_{\mathrm{s}}^{2}=0$, this further reduces to the classical Taylor–Aris limit). For a flat velocity profile with $p \rightarrow 0$ and $\phi_{\mathrm{s}}^{2} \rightarrow 0$ but the ratio $p / \phi_{\mathrm{s}}^{2}=p_{\mathrm{a}}$ remaining finite, we get

$$\frac{\Lambda_{0}}{p}=\frac{K s}{1+K s p_{\mathrm{a}}}=K s-K^{2} s^{2} p_{\mathrm{a}}+\ldots, \qquad \epsilon_{00}=1, \quad \epsilon_{0 i}=0 \quad (\hat{\beta}_{1}=0). \tag{6.49}$$

Substitution of these into (6.48a) and interchanging the spatial and time derivatives using the result

$$\frac{\partial}{\partial \tau} = -\frac{1}{1+K}\frac{\partial}{\partial z} + O(p_{\mathrm{a}}), \tag{6.50}$$

we recover the result given by (6.11).

When p and p_{a} are both small, but their ratio ϕ_{s}^2 is finite, (6.48a) may be simplified to

$$\frac{\partial c_0}{\partial \tau} + \frac{1}{1+K}\frac{\partial c_0}{\partial z} = \left[\frac{p_{\mathrm{a}}K^2}{(K+1)^3} + \frac{\beta_1 p_{\mathrm{a}}\phi_{\mathrm{s}}^2}{(K+1)^3}\right]\frac{\partial^2 c_0}{\partial z^2}, \tag{6.51}$$

where β_1 is given by (3.18). Thus, when the adsorption, desorption and transverse diffusion timescales are of the same order of magnitude but much smaller than the axial convective timescale, the effective dispersion coefficient is given by

$$D_{\mathrm{e}} = \frac{K^2}{(K+1)^3}\frac{\langle u\rangle^2}{k_{\mathrm{a}}} + \beta_1\frac{\langle u\rangle^2 a^2}{D_{\mathrm{m}}(K+1)^3}. \tag{6.52}$$

For $K \to 0$, this reduces to the Taylor–Aris limit while for $D_{\mathrm{m}} \to \infty$ (or for flat velocity profile, $\beta_1 = 0$), it reduces to the limit given by (6.11). However, we see from (6.52) that D_{e} is not a sum of these two limits. Thus adsorption and desorption reduce the Taylor–Aris contribution but there is always a contribution due to finite rate of adsorption. Analysis of (6.52) shows that the effective diffusivity is a monotonic decreasing function of K if $\beta_1\phi_{\mathrm{s}}^2 > \frac{1}{3}$. Similarly, if $\frac{1}{3} > \beta_1\phi_{\mathrm{s}}^2 > (2/\sqrt{3} - 1)$, D_{e} is a non-monotonic function of K but its global maximum is attained at $K = 0$. If $(2/\sqrt{3} - 1) > \beta_1\phi_{\mathrm{s}}^2 > 0$, the sum of the two contributions could be higher than the Taylor–Aris contribution. Finally, we note that when adsorption and desorption are much faster than transverse diffusion, the effective velocity and diffusivity are reduced by a factor $(1+K)$ and $(1+K)^3$, respectively.

7. Summary and conclusions

We have used the centre and invariant manifold theories to analyse a class of dispersion phenomena involving a chemically active solute. Some of our results are simply extension and validation of classical results. These include a complete derivation of diffusive eigenfunctions for some common channel geometries; the correct convergence arguments for higher order terms; the distinction between spatial and temporal evolution at higher orders and the proper time and space scalings to allow a dispersion description including an upper bound on the rate of the bulk reaction and the possibility of describing all surface reactions with arbitrary rates and how they reduce dispersion by removing solutes near the wall. There are, however, some new results. The possibility of inducing dispersions by an adsorption/desorption mechanism is introduced with a curious dependence on the adsorption equilibrium constant K. The maximum at $K = 2$ is especially intriguing. The explanation of anomalous dispersion in a chromatograph due to a nonlinear Langmuir adsorption mechanism is also demonstrated. The long tails induced by this mechanism severely limit the performance of separation chromatography. The distortion of apparent bulk reaction by a nonlinear coupling among bulk reaction, diffusion and convection is suggested. Finally, the possibility of inducing steady-state dispersion by a coupling between bulk reaction and transverse velocity gradient has very practical implications. The performance of chemical reactors, which are usually operated under steady conditions, is intimately related to the dispersion. The derivation of effective equations describing the steady-state distribution of the solute concentration will allow an accurate assessment of the overall conversion. These effective equations must, however, be accompanied by appropriate steady-state boundary conditions at the inlet and exit which require an analysis of at least the inlet boundary layer. We shall defer these results till a later manuscript.

We are grateful to Professor D. Leighton and Professor M. J. Roberts for many helpful comments. Special thanks are also to Mr Sudhakar Subramanian for his help with the numerical calculations reported in tables 2–4. The work of V.B. is partly supported by grants from the American Chemical Society Petroleum Research Fund and the Robert A. Welch Foundation. H.-C.C. is partly supported by NSF grant CTS 91-12977.

References

Amundson, N. R. & Aris, R. 1973 *Mathematical methods in chemical engineering*, vol. 2. Prentice-Hall.

Aris, R. 1956 On the dispersion of a solute in a fluid flowing through a tube. *Proc. R. Soc. Lond.* A **235**, 67–77.

Aris, R. 1959 On the dispersion of a solute by diffusion, convection and exchange between phases. *Proc. R. Soc. Lond.* A **252**, 538–550.

Barton, N. G. 1984 An asymptotic theory of dispersion of reactive contaminant in parallel flow. *Austral. math. Soc.* B **25**, 287–310.

Brenner, H. 1980 Dispersion resulting from flow through spatially periodic porous media. *Phil. Trans. R. Soc. Lond.* A **297**, 81–133.

Carr, J. 1981 *Applications of center manifold theory.* Springer.

Coullet, P. H. & Spiegel, E. A. 1983 Amplitude equations for systems with competing instabilities. *SIAM J. appl. Math.* **43**, 776–821.

De Gance, A. E. & Johns, L. E. 1978 The theory of dispersion of chemically active solutes in rectilinear flow field. *Appl. Sci. Res.* **34**, 189–225.

Dill, L. H. & Brenner, H. 1982 A general theory of Taylor dispersion phenomena. III. *J. Colloid Interface Sci.* **85**, 101–117.

Dill, L. H. & Brenner, H. 1983 A general theory of Taylor dispersion phenomena. VI. *J. Colloid Interface Sci.* **93**, 343–365.

Guckenheimer, J. & Holmes, P. 1983 *Nonlinear oscillations, dynamical systems, and bifurcations of vector fields.* Springer.

Lungu, E. M. & Moffat, H. K. 1982 The effect of wall conductance on heat diffusion in duct flow. *J. Engng Math.* **16**, 121–136.

McNabb, A., Parshotam, A. & Wake, G. 1993 Outputs and time lags for linear bioreactors. *Math. Computer Model.* **16**, 109–120.

Mercer, G. N. & Roberts, A. J. 1990 A center manifold description of contaminant dispersion in channels with varying flow properties. *SIAM J. appl. Math.* **50**, 1547–1565.

Pagitsas, M., Nadim, A. & Brenner, H. 1986 Projection operator analysis of macrotransport processes. *J. chem. Phys.* **84**, 2801–2807.

Roberts, A. J. 1989*a* The utility of an invariant manifold description of the evolution of a dynamical system. *SIAM J. appl. Math.* **20**, 1447–1458.

Roberts, A. J. 1989*b* Appropriate initial conditions for asymptotic descriptions of the long term evolution of dynamical systems. *J. Austral. math. Soc.* B **31**, 48–75.

Roberts, A. J. 1992 Boundary conditions for approximate differential equations. *J. Austral. math. Soc.* B **34**, 54–80.

Shapiro, M. & Brenner, H. 1986 Taylor dispersion of chemically reactive species: irreversible first order reactions in bulk and on boundaries. *Chem. Engng Sci.* **41**, 1417–1433.

Sankarasubramanian, R. & Gill, W. N. 1973 Unsteady convective diffusion with interphase mass transfer. *Proc. R. Soc. Lond.* A **333**, 115–132.

Smith, R. 1983 Effect of boundary adsorption upon longitudinal dispersion in shear flow. *J. Fluid Mech.* **134**, 161–177.

Smith, R. 1988 Entry and exit conditions for flow reactors. *IMA J. appl. Math.* **41**, 1–20.

Subramanian, G. 1991 *Preparative and process-scale liquid chromatography.* Ellis Horwood.

Taylor, G. I. 1953 Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. Lond.* A **219**, 186–203.

Taylor, G. I. 1954 Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion. *Proc. R. Soc. Lond.* A **225**, 473–477.

Ultman, J. S. & Weaver, D. W. 1979 Concentration sampling methods in relation to the computation of a dispersion coefficient. *Chem. Engng Sci.* **34**, 1170–1172.

Whitham, G. B. 1974 *Linear and nonlinear waves.* Wiley.

Young, W. R. & Jones, S. 1991 Shear dispersion. *Phys. Fluids* A **3**, 1087–1101.

Received 8 September 1992; revised 5 August 1993; accepted 18 October 1994