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Hyperbolic Averaged Models for Describing Dispersion Effects in Chromatographs and Reactors

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Abstract−We show that dispersion effects due to local velocity gradients and transverse molecular diffusion in chromatographs and chemical reactors can be better described in terms of averaged models that are hyperbolic in the longitudinal coordinate and time, and with an effective local time or length scale in place of the traditional axial dispersion coefficient. This description not only eliminates the use of artificial exit boundary conditions but also inconsistencies such as upstream propagation and infinite speed of signals associated with the traditional parabolic averaged models. We also show that the hyperbolic models can describe dispersion effects accurately and have a much larger region of validity in the physical parameter space compared to the traditional parabolic models. Our method of obtaining averaged models from the governing partial differential equations is based on the Lyapunov-Schmidt technique of classical bifurcation theory and is rigorous. We illustrate our approach using three well known chemical engineering problems.

Key words: Dispersion, Multi-scale Averaging, Lyapunov-Schmidt Reduction, Chromatography, Chemical Reactors

INTRODUCTION

Mathematical models that describe the steady-state and transient behavior of chromatographs and reactors are obtained by combining the conservation laws (continuity, momentum, species, and energy balances) with the various constitutive equations for the transport and rate processes (adsorption, desorption, reaction, etc). Depending on the simplifications, or assumptions made and the level of detail included at various length and time scales, these models can vary in complexity as well as the number of physico-chemical parameters describing the phenomenon of interest. In addition, due to the strong coupling between the transport and rate processes and the dependence of the kinetic and transport rates on the state variables, the model equations are usually highly nonlinear and are known to exhibit a variety of complex spatio-temporal patterns. For most cases of practical interest, even with the present day computational power, it is impractical to solve such detailed models and explore all the different types of solutions that exist in the multi-dimensional parameter space. Even in cases where detailed solutions are obtained, the numerical results do not provide directly the results an engineer is usually interested in, such as the average exit conversion of a reactant or the propagation speed of a thermal or concentration front, unless some averaging or coarse-graining is done on the numerical results. Accurate low-dimensional models in terms of average and measurable variables, such as the cup-mixing temperature or concentration, are desired for the purpose of design, control and optimization of chemical processes.

The usual procedure in chemical engineering to develop low-dimensional or averaged models of reactors and chromatographs is to make certain *a priori* assumptions on the length and time scales of reaction, diffusion and convection and apply the conservation principles only at the macroscopic level. For example, under the assumption of perfect mixing or no spatial gradients, the model for a continuous-flow stirred tank reactor (CSTR) consists of ordinary differential equations describing the species and energy balances. Similarly, the model for a single solute adsorption column under the assumption of flat velocity profile, no radial diffusion and local equilibrium consists of a single hyperbolic equation describing the solute concentration in the fluid phase [Rhee et al., 1986]. The assumptions made in developing such simplified low-dimensional models usually ignore some important physics at small scales that can influence the macroscopic behavior (e.g., exit conversion or selectivity in a reactor). When the predictions of such ad-hoc models do not match with experimental results, the low-dimensional models are modified by expanding the degrees of freedom by using concepts such as residence time distribution, non-ideal flow and mixing, and introducing empirical constants such as effective axial dispersion coefficients. The short-comings of this approach (such as the dependence of the effective dispersion coefficients on the kinetic parameters and inconsistencies such as infinite propagation speed of signals even in convection dominated systems) have been recognized recently.

In this work, we demonstrate a systematic method for obtaining low-dimensional models by relaxing some of the *a priori* assumptions. We start with more detailed models based on the fundamental laws and take advantage of the separation of the length or time scales to average (or reduce the spatial degrees of freedom) to obtain low-dimensional averaged models. Our method of averaging is rigorous and is based on the Lyapunov-Schmidt technique of classical bifurcation theory. Intuitively speaking, our method of averaging is equivalent to an expansion of a more detailed fundamental model in terms of one or more small parameters representing separation of length or time scales in the original model. In such an

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expansion, the lowest order term is the simplified model while higher order corrections modify the model, just as the terms in the Taylor series expansion of a scalar function of single variable, by including the small but significant physical phenomena such as local velocity gradients and molecular diffusion, finite rate of adsorption, etc.

In the next section, we outline our spatial averaging technique. In section 3, we examine in some detail the classical Taylor-Aris problem of dispersion of a non-reactive solute in laminar flow in a tube. In section 4, we derive low-dimensional hyperbolic models for chromatographic columns. Section 5 presents low-dimensional models for tubular reactors with homogeneous or catalytic reactions. In the last section, we discuss some advantages and possible extensions of our approach.

THE LYAPUNOV-SCHMIDT METHOD FOR AVERAGING OF PDEs

The Lyapunov-Schmidt method is a well known and widely used technique for dimension reduction and bifurcation analysis near a zero eigenvalue [Golubitsky and Schaeffer, 1984; Balakotaiah et al., 1985]. However, only recently Balakotaiah and Chang [2003] showed that this method is also an excellent spatial averaging technique. Some examples of spatial averaging using the L-S method were presented by Balakotaiah and Chang [2003] and Chakraborty and Balakotaiah [2002] and Balakotaiah and Chakraborty [2003]. We review here the methodology of the L-S procedure briefly (and in a more general form) and refer the reader for further details to the cited references.

We consider a nonlinear partial differential equation of the form

$$F(c, p) \equiv \nabla^2 c - pf(x, y, z, t, c, p, \mathbf{p}^*) = 0, \qquad (1)$$

where c(x, y, z, t) is a concentration variable dependent on the local coordinates (x, y) as well as other independent variables z and t, ∇^2 is the diffusion (Laplacian) operator in the local coordinates x and y in a region Ω subject to either zero flux or periodic boundary conditions on the boundary ∂Ω. The parameter p is assumed to be small and is the ratio of local diffusion time to (global scale) convection time. f is a non-linear operator that accounts for large scale mixing (diffusion) and convection effects as well as the source/sink terms due to reaction, adsorption, etc. It is assumed that f has a Taylor series expansion in terms of p and the parameters $\mathbf{p}^*$ appearing in f are of order unity.

We note that the diffusion operator with Neumann boundary conditions is symmetric and has a simple zero eigenvalue with a constant eigenfunction. Equivalently, the eigenvalue problem

$$L\psi \equiv \nabla^2 \psi = -\mu\psi \text{ in } \Omega, \qquad (2)$$

$$\nabla\psi \cdot \mathbf{n} = 0 \text{ on } \partial\Omega \qquad (3)$$

is self-adjoint (L^*=adjoint operator=L) with a zero eigenvalue $\mu_0=0$ and a constant eigenfunction $\psi_0(x, y)=1$. Moreover, for j≥1, $\mu_j>0$ and for all j≥0, the eigenfunctions $\psi_j(x, y)$ can be chosen to satisfy the orthogonality condition

$$\langle \psi_i, \psi_j \rangle = \frac{1}{A_\Omega}\iint_\Omega \psi_i \psi_j dxdy = \delta_{ij} = \begin{cases} 0, i \neq j \\ 1, i = j. \end{cases} \qquad (4)$$

As shown below, these properties can be used to eliminate the spatial degrees of freedom in Eq. (1).

Averaging Eq. (1) over the domain Ω and use of divergence theorem gives

$$\langle f(x, y, z, t, c, p, \mathbf{p}^*), \psi_0 \rangle = 0. \qquad (5)$$

For obvious reasons, we shall refer to Eq. (5) as the *averaged model*. To write it in a more useful form, we express c as

$$c(x, y, z, t) = \langle c \rangle (z, t)\psi_0 + c'(x, y, z, t), \qquad (6)$$

where

$$\langle c \rangle = \frac{1}{A_\Omega}\iint_\Omega c(x, y, z, t)dxdy = \langle c, \psi_0 \rangle$$

is the spatially averaged concentration (over the domain Ω). It follows from Eq. (6) that

$$\langle c' \rangle = \langle c', \psi_0 \rangle = 0. \qquad (7)$$

For obvious reasons, c'(x, y, z, t) will be referred to as the *local variation*. The Lyapunov-Schmidt procedure uses orthogonal complementary spaces in the domain to split c as given by Eq. (6). Similarly, in the codomain, Eq. (1) is satisfied iff

$$EF(\langle c \rangle \psi_0 + c') = 0, \qquad (8)$$

$$(I - E)F(\langle c \rangle \psi_0 + c') = 0, \qquad (9)$$

where E is the projection operator onto *range* L. The complementary projection (onto *ker* L) is given by

$$(I - E)F = \langle F, \psi_0 \rangle \psi_0. \qquad (10)$$

Then, Eq. (9) is identical to Eq. (5), which may be written as

$$\langle f(x, y, z, t, \langle c \rangle \psi_0 + c', p, \mathbf{p}^*), \psi_0 \rangle = 0. \qquad (11)$$

Simplification of Eq. (8) gives

$$\begin{aligned} Lc' = {} & pf(x, y, z, t, \langle c \rangle \psi_0 + c', p, \mathbf{p}^*) \\ & - p\langle f(x, y, z, t, \langle c \rangle \psi_0 + c', p, \mathbf{p}^*), \psi_0 \rangle \psi_0. \end{aligned} \qquad (12)$$

We refer to this as the *local equation*. Since L : *range* L⟶*range* L is invertible, it follows from the implicit function theorem that the local equation (Eq. (12)) with the constraint given by Eq. (7) can be solved uniquely for c' in terms of ⟨c⟩. Substitution of this in Eq. (11) gives the reduced or averaged model.

The local equation may be solved perturbatively for c'. Writing

$$c' = \sum_{i=1}^{\infty} p^i c_i, \qquad (13)$$

we get

$$Lc_1 = f(\langle c \rangle \psi_0, 0, \mathbf{p}^*) - \langle f(\langle c \rangle \psi_0, 0, \mathbf{p}^*), \psi_0 \rangle \psi_0;\ \langle c_1 \rangle = 0, \qquad (14)$$

$$\begin{aligned} Lc_2 = {} & D_c f(\langle c \rangle \psi_0, 0, \mathbf{p}^*) \cdot c_1 + D_p f(\langle c \rangle \psi_0, 0, \mathbf{p}^*) \\ & - \langle D_c f(\langle c \rangle \psi_0, 0, \mathbf{p}^*) \cdot c_1 - D_p f(\langle c \rangle \psi_0, 0, \mathbf{p}^*), \psi_0 \rangle \psi_0 \\ = {} & 0;\ \langle c_2 \rangle = 0, \end{aligned} \qquad (15)$$

etc. Taylor series expansion of Eq. (11) gives

$$\left. \begin{aligned} & \langle f(\langle c \rangle \psi_0, 0, \mathbf{p}^*), \psi_0 \rangle + \langle D_c f(\langle c \rangle \psi_0, 0, \mathbf{p}^*) \cdot c', \psi_0 \rangle \\ & + p\langle D_p f(\langle c \rangle \psi_0, 0, \mathbf{p}^*), \psi_0 \rangle + \frac{1}{2!}\langle D_{cc}^2 f(\langle c \rangle, \psi_0, 0, \mathbf{p}^*) \cdot (c', c'), \psi_0 \rangle \\ & + p\langle D_{cp}^2 f(\langle c \rangle \psi_0, 0, \mathbf{p}^*) \cdot c', \psi_0 \rangle + \frac{1}{2!}p^2 \langle D_{pp}^2 f(\langle c \rangle \psi_0, 0, \mathbf{p}^*), \psi_0 \rangle + \ldots = 0 \end{aligned} \right\} \qquad (16)$$

[For simplicity of notation, we have written $f(x, y, z, t, \langle c\rangle \psi_0, 0, \mathbf{p}^*)$ as $f(\langle c\rangle \psi_0, 0, \mathbf{p}^*)$.] Thus, the averaged model to order p^2 is given by

$$\left.\begin{array}{c}\langle f(\langle c\rangle \psi_0, 0, \mathbf{p}^*), \psi_0\rangle + p\langle D_c f(\langle c\rangle \psi_0, 0, \mathbf{p}^*)\cdot c_1, \psi_0\rangle \\ + p\langle D_p f(\langle c\rangle \psi_0, 0, \mathbf{p}^*), \psi_0\rangle + \frac{p^2}{2!}\langle D^2_{cc} f(\langle c\rangle \psi_0, 0, \mathbf{p}^*)\cdot (c_1, c_1), \psi_0\rangle \\ + p^2\langle D^2_{cp} f(\langle c\rangle \psi_0, 0, \mathbf{p}^*)\cdot c_1, \psi_0\rangle + p^2\langle D_c f(\langle c\rangle \psi_0, 0, \mathbf{p}^*)\cdot c_2, \psi_0\rangle \\ + \frac{1}{2!}p^2\langle D^2_{pp} f(\langle c\rangle \psi_0, 0, \mathbf{p}^*), \psi_0\rangle + \ldots = 0\end{array}\right) \quad (17)$$

Here, $D_c f$, $D_p f$, $D^2_{cc} f$, $D^2_{cp} f$ are the Fréchet derivatives of the nonlinear operator f and $D^2_{cc} f\cdot(c_i, c_j)$, is a symmetric multilinear form.

The following observations may be made from the form of the averaged model given by Eq. (17): (i) The (zeroth order) first term is the averaged model to the lowest order and can be obtained by setting $c'=0$ and $p=0$ in Eq. (11); (ii) The second and third terms represent the order p corrections. The second term arises due to elimination of local spatial degrees of freedom. In physical terms, this is the combined effect of the interaction of local diffusion and convection/reaction. We shall refer it as the *Taylor dispersion* term. The third term is due to order p effect that is already present in the function f of the original model (We shall refer it to as the *Aris correction* term.). (iii) If the Taylor expansion of f in powers of p has terms up to order p^q ($q\geq 0$), then the averaged model has to be derived to order p^q so that all the physical phenomena present in the original detailed model are also represented in the averaged model. If this is not the case, then some of the physical phenomena represented in the original model are not important and can be ignored; (iv) when Eq. (17) is truncated at order p^q ($q\geq 1$), the truncation error arises from two sources, the first being the truncation of the Taylor series of the averaged Eq. (11), the second being the truncation error of the perturbation expansion Eq. (13) of the local equation. As we show in the following sections, the first truncation error may be zero in some practical cases (e.g. linear kinetics, wall reaction case, or solutal dispersion problems in which f is linear in c) and the averaged equation may be closed exactly, i.e., higher order Fréchet derivatives are zero and the Taylor expansion of f terminates at some finite order (usually after the linear and quadratic terms in most applications). In such cases, the only error is due to the truncation of the solution of the local equation.

While it is always possible to obtain a single averaged equation in terms of $\langle c\rangle$ to any order in p, this may not be useful or what is desired in applications. For example, in chemical reactors or chromatographs, it is not the spatially averaged concentration ($\langle c\rangle$) that is measured experimentally but the so called "cup-mixing" or velocity weighted concentration defined by

$$c_m = \langle c(x, y, z, t) g(x, y), \psi_0\rangle, \quad (18)$$

where $g(x, y)$ (with $\langle g\rangle = \langle g, \psi_0\rangle = 1$) is the local velocity profile. The relationship between c_m and $\langle c\rangle$ may be obtained from Eq. (6) as

$$c_m(z, t) = \langle c\rangle(z, t) + \langle g(x, y) c', \psi_0\rangle. \quad (19)$$

Now, the averaged model is defined in terms of c_m and $\langle c\rangle$ by the global Eq. (11) and the local Eq. (19), with c' defined by Eq. (13). This form of the reduced model, expressed in terms of two concentration variables will be referred to as the "*two-mode model*," and is convenient for physical interpretation of various limiting cases as well as to extend the range of validity by a procedure called *regularization.*

The above averaging procedure described for Neumann boundary conditions may be extended to Robin boundary conditions

$$\nabla c\cdot \mathbf{n} + p\,Da\, r_w(c) = 0 \text{ on } \partial\Omega, \quad (20)$$

where Da is a (reactor scale) Damköhler number (which is of order unity) and $r_w(c)$ is some nonlinear function describing reaction or adsorption at the wall. When $p\rightarrow 0$, the local gradients vanish and the leading order operator remains the same. Thus, the splitting given by Eq. (6) is again valid. However, for this case, the averaged equation as well as the local equation may contain extra terms that appear due to the inhomogeneous boundary condition at the wall.

A HYPERBOLIC AVERAGED MODEL FOR DISPERSION IN CAPILLARIES

As our first example, we consider the classical Taylor-Aris problem that illustrates dispersion due to transverse velocity gradients and molecular diffusion and show that the inconsistencies associated with the parabolic form of the reduced model can be removed by expressing the reduced model in a hyperbolic form. We also analyze the averaged hyperbolic model and show that it has a much larger range of validity than the standard parabolic model with Danckwerts' boundary conditions.

The dispersion of a non-reactive solute in a circular tube of constant cross-section in which the flow is laminar is described by the convective-diffusion equation

$$\frac{\partial C}{\partial t'} + 2\bar{u}\left(1 - \frac{r^2}{a^2}\right)\frac{\partial C}{\partial x} = \frac{D_m}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + C_m\frac{\partial^2 C}{\partial x^2};\ 0<r<a, x>0, t'>0 \quad (21a)$$

with the following boundary and initial conditions:

$$\frac{\partial C}{\partial r} = 0 @ r = 0, a \quad (21b)$$

$$\text{I.C}: C(x, r, 0) = f(x, r) \quad (21c)$$

$$\text{B.C}: C(0, r, t') = g(r, t') \quad (21d)$$

Here, $\bar{u}$ is the average velocity in the pipe, a is the radius and D_m is the molecular diffusivity of the species. Defining dimensionless variables

$$z = \frac{x}{L} \qquad t = \frac{\bar{u}t'}{L} \qquad \xi = \frac{r}{a} \qquad p = \frac{a^2\bar{u}}{LD_m} \qquad Pe_r = \frac{a\bar{u}}{D_m} \quad (22)$$

we can write Eq. (21a & b) as

$$LC \equiv \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial C}{\partial \xi}\right) = p\left[\frac{\partial C}{\partial t} + 2(1-\xi^2)\frac{\partial C}{\partial z} - \frac{p}{Pe_r^2}\frac{\partial^2 C}{\partial z^2}\right];$$
$$\frac{\partial C}{\partial \xi} = 0 @ \xi = 0, 1 \quad (23)$$

Here, p is the local (transverse) Peclet number, which is the ratio of transverse diffusion time to the convection time. Pe_r is the radial Peclet number (ratio of transverse diffusion time to a convection time based on pipe radius). We assume that $p\ll 1$ while Pe_r is of order unity. The parameter $Pe_r^2/p = \bar{u}L/D_m$ is also known as the axial

Peclet number. Also note that for any finite Pe_r or tube diameter, the axial Peclet number goes to infinity as p goes to zero. In physical terms, the conditions p□1 and Pe_r is of order unity imply that the transverse diffusion time ($t_D=a^2/D_m$) is much smaller compared to the convection time ($t_c=L/\bar{u}$) and the axial diffusion time ($t_z=L^2/D_m$). When such scale separation exists, we can average the governing equation over the transverse length scale using the L-S technique and obtain averaged model in terms of axial length and time scales.

We note that the transverse operator L is symmetric with respect to the inner product

$$(v,w)=\int_0^1 2\xi v(\xi)w(\xi)d\xi$$

It has a zero eigenvalue with normalized eigenfunction of unity. We define the mixing-cup (velocity weighted) and spatial average concentrations by

$$C_m=\int_0^1 4\xi(1-\xi^2)C(\xi,z,t)d\xi \tag{24a}$$

$$\langle C\rangle=\int_0^1 2\xi C(\xi,z,t)d\xi \tag{24b}$$

Transverse averaging of Eq. (23) gives

$$\frac{\partial\langle C\rangle}{\partial t}+\frac{\partial C_m}{\partial z}-\frac{p}{Pe_r^2}\frac{\partial^2\langle C\rangle}{\partial z^2}=0 \tag{25}$$

We note that when p=0, $\langle C\rangle=C_m$ and substitution of this into Eq. (25) gives the leading (or zeroth) order evolution equation for the averaged concentration:

$$\frac{\partial\langle C\rangle}{\partial t}+\frac{\partial\langle C\rangle}{\partial z}=0 \tag{26}$$

To obtain the averaged equation to order p, we write

$$C(\xi,z,t)=\langle C\rangle(z,t)+C'(\xi,z,t);\quad C'\in\ker L \tag{27}$$

and solve for the slave variable $C'(\xi, z, t)$ in terms of $\langle C\rangle(z, t)$ using the procedure outlined above. To leading order, we have

$$C'(\xi,z,t)=-p\frac{\partial\langle C\rangle}{\partial z}\left[\frac{1}{12}-\frac{\xi^2}{4}+\frac{\xi^4}{8}\right]+O(p^2) \tag{28}$$

Substitution of this in Eq. (27) and transverse averaging (after multiplying by the velocity profile) gives the local equation relating C_m and $\langle C\rangle$:

$$C_m-\langle C\rangle=-\frac{p}{48}\frac{\partial\langle C\rangle}{\partial z}+O(p^2)=-\frac{p}{48}\frac{\partial C_m}{\partial z}+O(p^2) \tag{29}$$

This local equation, when written in dimensional form, defines a characteristic transfer time between the slowly evolving mode C_m and the slave mode $C_m-\langle C\rangle$. Thus, the averaged model to order p is given by

$$\frac{\partial\langle C\rangle}{\partial t}+\frac{\partial C_m}{\partial z}-\frac{p}{Pe_r^2}\frac{\partial^2\langle C\rangle}{\partial z^2}=0 \tag{30a}$$

$$C_m-\langle C\rangle=-\frac{p}{48}\frac{\partial\langle C\rangle}{\partial z} \tag{30b}$$

We can combine these two equations to obtain a single equation either for C_m or $\langle C\rangle$. In this specific example, the model is linear in the concentration and hence both C_m and $\langle C\rangle$ satisfy the same equation, as they are linearly related. Since the cup-mixing concentration, which is often measured in experiments, is more relevant in applications, we write the reduced model in terms of C_m:

$$\frac{\partial C_m}{\partial t}+\frac{\partial C_m}{\partial z}+\frac{p}{48}\frac{\partial^2 C_m}{\partial z\partial t}-\frac{p}{Pe_r^2}\frac{\partial^2 C_m}{\partial z^2}+O(p^2)=0 \tag{31}$$

We note that this averaged model is hyperbolic. The third term in Eq. (31) represents the Taylor dispersion term, due to velocity gradients and transverse molecular diffusion, while the last term is the Aris correction term, representing the influence of axial molecular diffusion. In dimensional form, the reduced model may be written as

$$\frac{\partial C_m}{\partial t'}+\langle u\rangle\frac{\partial C_m}{\partial x}+\langle u\rangle t_D\frac{\partial^2 C_m}{\partial x\partial t'}-D_m\frac{\partial^2 C_m}{\partial x^2}=0;\ t'\gg t_D, x\gg\lambda_D, \tag{32}$$

where the local diffusion or mixing time is defined by

$$t_D=\frac{a^2}{48D_m} \tag{33}$$

The corresponding local length scale is given by $\lambda_D=\langle u\rangle t_D$ while the diffusivity may be written as $D_{eff}=\langle u\rangle^2 t_D$. We note that axial molecular diffusion can be neglected when $Pe_r^2\gg 48$. In such cases, Eq. (32) simplifies to

$$\frac{\partial C_m}{\partial t'}+\langle u\rangle\frac{\partial C_m}{\partial x}+\langle u\rangle t_D\frac{\partial^2 C_m}{\partial x\partial t'}=0 \tag{34}$$

In his famous paper, Taylor [1953] used the leading order approximation

$$\frac{\partial C_m}{\partial t'}=-\langle u\rangle\frac{\partial C_m}{\partial x}$$

to express the mixed derivative term as a dispersion term and Eq. (34) as

$$\frac{\partial C_m}{\partial t'}+\langle u\rangle\frac{\partial C_m}{\partial x}=D_{eff}\frac{\partial^2 C_m}{\partial x^2};\ D_{eff}=\langle u\rangle^2 t_D \tag{35}$$

In the literature, D_{eff} is also known as the Taylor dispersion coefficient. However, the approximation used by Taylor transforms a hyperbolic equation into a parabolic equation. In the chemical engineering literature, this approximation is made worse by the further requirement of an artificial boundary condition at the exit of the tube. During the past fifty years, the parabolic model with Danckwerts' boundary conditions is used extensively to describe dispersion effects in chromatographs and reactors. We show here that the hyperbolic form of the model is more accurate, retains the proper physics, can describe dispersion effects more accurately than the parabolic model and is valid in a much larger domain of the physical parameter space. A good analogy between the parabolic and hyperbolic models is the approximation of the function e^{-x} for small x by $f_p(x)=1-x$ and $f_h(x)=1/(1+x)$. Both approximations have the same accuracy for $x\rightarrow 0$ but the first approximation breaks down qualitatively for $x>1$ while the second approximation is valid qualitatively for all x. The second (Pade) approximation is a regularized version of the first function. This regularization is closely connected with how we write the local equation. Though the local equation is an infinite series in powers of p, we can truncate it (often at the first term) and rewrite it so that it is qualitatively valid for all values of p.

When the Taylor approximation is used in Eq. (32) the averaged model is again parabolic but now the effective dispersion coefficient is given by

$$D_{eff}=\langle u\rangle^2 t_D+D_m=\frac{a^2\langle u\rangle^2}{48D_m}+D_m$$

This result was first derived by Aris [1956] using the method of moments. While the resulting model now includes both the effects (axial molecular diffusion and dispersion caused by transverse velocity gradients and molecular diffusion) it has the same deficiency as the Taylor model, i.e. converting a hyperbolic model into a parabolic one.

We note that when $D_m \ll \langle u\rangle^2 t_D$, or equivalently, the radial Peclet number $Pe_r \gg 6.93$, axial diffusion can be neglected. The local Peclet number p, which is equal to Pe_r times the aspect ratio (a/L), can be small even when $Pe_r \gg 6.93$ provided the aspect ratio is sufficiently small. Thus, the conditions $Pe_r \gg 6.93$ and $p \ll 1$ are usually satisfied in most tubular reactors or chromatographic columns. In such cases, it is more appropriate to use the leading order approximation to modify the small axial dispersion term to a mixed derivative term and write the averaged model as

$$\frac{\partial C_m}{\partial t'}+\langle u\rangle\frac{\partial C_m}{\partial x}+\langle u\rangle\overline{t_D}\frac{\partial^2 C_m}{\partial x\partial t'}=0;\quad \overline{t_D}=t_D+\frac{D_m}{\langle u\rangle^2}=\frac{a^2}{48D_m}+\frac{D_m}{\langle u\rangle^2} \tag{36}$$

Now, the averaged hyperbolic model, Eq. (36) defines a characteristic initial value problem (Cauchy problem). To complete the model, we need to specify C_m only along the characteristic curves x'=0 and t'=0. Thus, the initial and boundary conditions for the averaged model are obtained by taking the mixing-cup averages of Eq. (21c) and (21d):

$$C_m(x,t'=0)=\int_0^1 4\xi(1-\xi^2)f(x,R\xi)d\xi\equiv f_m(x) \tag{37a}$$

$$C_m(x=0,t')=\int_0^1 4\xi(1-\xi^2)g(R\xi,t')d\xi\equiv g_m(t') \tag{37b}$$

When the assumption $Pe_r \gg 6.93$ is not valid, it is better to leave the averaged model in the more general hyperbolic form given by Eq. (31) or (32) with boundary and initial conditions given by Eq. (37). The important point to be made is the hyperbolic forms of the averaged model, either Eq. (32) or Eq. (36), have much larger domain of validity than the parabolic form as shown below.

The L-S method can be used to derive the averaged model to higher orders in p but we will not be pursue it here. In fact, since our averaged model at order p is also regularized, as explained earlier, higher order approximations are not necessary to see the qualitative behavior for all positive values of p.

Comparison of Solutions of Parabolic and Hyperbolic Models

We now present the solution of the hyperbolic model defined by Eqs. (36) and (37) and compare the solution to that of the classical parabolic model with Danckwerts boundary conditions. We use the axial length and convective time scales to non-dimensionalize the variables and write the hyperbolic model in the following form:

$$\frac{\partial C_m}{\partial t}+\frac{\partial C_m}{\partial z}+P\frac{\partial^2 C_m}{\partial z\partial t}=0;\quad t\gg P,\ z\gg P \tag{38a}$$

$$C_m(z,t=0)=f(z) \tag{38b}$$

$$C_m(z=0,t)=g(t) \tag{38c}$$

where P is now the effective local Peclet number defined by

$$P=\frac{\langle u\rangle\overline{t_D}}{L}=\frac{a^2\langle u\rangle}{48LD_m}+\frac{D_m}{\langle u\rangle L}=p\left[\frac{1}{48}+\frac{1}{Pe_r^2}\right]\equiv p\Lambda$$

and is the ratio of effective transverse diffusion time to the convection time. Hereafter, we shall refer to the parameter Λ as the dimensionless dispersion coefficient (The dimensional dispersion coefficient is $D_{eff}=\langle u\rangle^2\overline{t_D}$).

The exit concentration $C_m(z=1,t)$ for the case of a unit impulse (Delta function) input ($f(z)=0$, $g(t)=\delta(t)$) is known as the dispersion, or residence time distribution, curve. For the hyperbolic model, this can be found either by Laplace transformation or from the general solution of the model (see Balakotaiah and Chang, 2003 for a general analytical solution of Eqs. (38)). It is easily seen that the Laplace transform of the dispersion curve is given by

$$\overline{E(s)}=\mathrm{Exp}\left\{-\frac{s}{1+sP}\right\} \tag{39}$$

while the dispersion curve is given by

$$E_h(t)=C_m(1,t)=\mathrm{Exp}\left(-\frac{(1+t)}{P}\right)\left[\delta(t)+\frac{1}{P\sqrt{t}}I_1\left(\frac{2\sqrt{t}}{P}\right)\right] \tag{40}$$

We note that the second central moment (or the dimensionless variance) of the dispersion curve is given by

$$\sigma^2=2P \tag{41}$$

Thus, for P⟶0, the variance approaches zero and the behavior approaches that of plug flow. For P small, Eq. (40) may be simplified to

$$E_h(t)\approx\frac{1}{\sqrt{4\pi P t^{3/2}}}\mathrm{Exp}\left\{-\frac{(1-\sqrt{t})^2}{P}\right\} \tag{42}$$

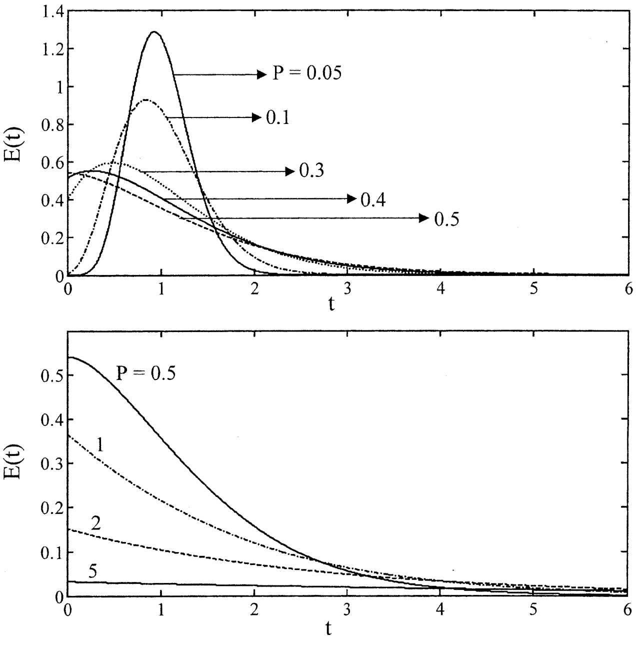

Fig. 1. Dispersion curves predicted by the hyperbolic model, Eq. (38) for various values of the effective local Peclet number, P.

Hence, the dispersion curve has a peak at t=1 and is slightly asymmetrical (but the deviation from the Gaussian curve is small). As P increases to 0.5, it can be shown by analyzing Eq. (40) that the peak moves to t=0 and for any P>0.5, the peak remains at t=0. For any P>0.5, the dispersion curve has a slow decaying (long) tail and the variance can exceed unity. Fig. 1 shows the dispersion curves for different values of P. For simplicity, the delta function of magnitude Exp(−1/P) at t=0 is not shown in the figure.

We now compare the solution of the hyperbolic model with that of the parabolic model used widely in the literature to describe dispersion in chromatographs and reactors. The parabolic model with Danckwerts boundary conditions, in dimensionless form, is given by

$$\frac{\partial C}{\partial t}+\frac{\partial C}{\partial z}=\frac{1}{Pe}\frac{\partial^2 C}{\partial z^2};\quad 0<z<1, t>0 \tag{43a}$$

$$\frac{1}{Pe}\frac{\partial C}{\partial z}-C=g(t)\quad @z=0 \tag{43b}$$

$$\frac{\partial C}{\partial z}=0\quad @z=1 \tag{43c}$$

$$C(z, t=0)=f(z) \tag{43d}$$

where Pe is the axial Peclet number. For the parabolic model with f(z)=0 and g(t)=δ(t), the dispersion curve is given by

$$E_p(t)=C(z=1,t)=\frac{2}{Pe}\sum_{n=1}^{\infty}\mathrm{Exp}\left\{\frac{Pe}{2}-\frac{Pe^2+4\lambda_n}{4Pe}t\right\}\frac{\sqrt{\lambda_n}\sin\sqrt{\lambda_n}(Pe^2+4\lambda_n)}{(Pe^2+4Pe+4\lambda_n)}, \tag{44}$$

where

$$\cot\sqrt{\lambda_n}=\frac{\sqrt{\lambda_n}}{Pe}-\frac{Pe}{4\sqrt{\lambda_n}};\quad n=1,2,\ldots$$

The dimensionless variance can be found more easily from the Laplace transform and is given by

$$\sigma^2=\frac{2}{Pe}-\frac{2}{Pe^2}(1-e^{-Pe}) \tag{45}$$

We note that the variance for the parabolic model is always bounded between zero (for Pe→∞ or plug flow) and unity (Pe→0 or ideal CSTR behavior). Thus, the parabolic model can only describe dispersion behavior that lies between these two extremes. In contrast, the hyperbolic model can describe the same behavior when P varies between 0 and 0.5 as well as the bypassing, stagnant region or solute retaining behavior (with long tails as in segregated laminar flow) when P>0.5. For very small P, the dispersion curves predicted by the two models are very close to each other but the hyperbolic model predicts an asymmetric curve with a slightly higher peak than the parabolic model. In addition, the parabolic model predicts upstream diffusion and infinite propagation speed. Both these non-physical phenomena are not present in the hyperbolic model which retains the qualitative behavior of the full model for all values of P. Thus, we conclude that the hyperbolic model describes dispersion effects better than the parabolic model and is valid over a wider range of the physical parameter space.

Before we close this section, we also present solutions of the full hyperbolic model

$$\frac{\partial C_m}{\partial t}+\frac{\partial C_m}{\partial z}+P\frac{\partial^2 C_m}{\partial z\partial t}-\lambda P\frac{\partial^2 C_m}{\partial z^2}=0;\quad \lambda=\frac{48}{Pe_r^2} \tag{46}$$

for the case of a unit impulse input. The Laplace transform of the dispersion curve is now given by

$$\overline{E(s)}=\mathrm{Exp}\left\{\frac{1+sP-\sqrt{s^2P^2+2sP(1+2\lambda)+1}}{2P\lambda}\right\} \tag{47}$$

from which we can obtain the second central moment (variance) as

$$\sigma^2=2\bar{P};\quad \bar{P}=P(1+\lambda) \tag{48}$$

This shows again that when λ is small (or equivalently, $Pe_r \gg 1$), we can combine the small axial dispersion term with the mixed derivative term and simplify the general hyperbolic model Eq. (46) to the simpler model Eq. (38a). However, for λ values of order unity or larger, this cannot be justified. The inverse transform of Eq. (47) can be found by integrating around the branch points but we will not pursue it here. Instead, we show in Figs. 2 and 3 the numerically determined (using Matlab) dispersion curves for P=0.1, 1 and various values of λ. As can be expected, for small λ values, the qualitative behavior of the full hyperbolic model Eq. (46) is similar to that of the simpler case of λ=0. Only for $\lambda\geq1$, the peak value changes and shifts to lower times.

HYPERBOLIC AVERAGED MODELS FOR DESCRIBING DISPERSION EFFECTS IN CHROMATOGRAPHS

We now extend the averaging method to derive hyperbolic models to describe dispersion effects in chromatographs. We consider the

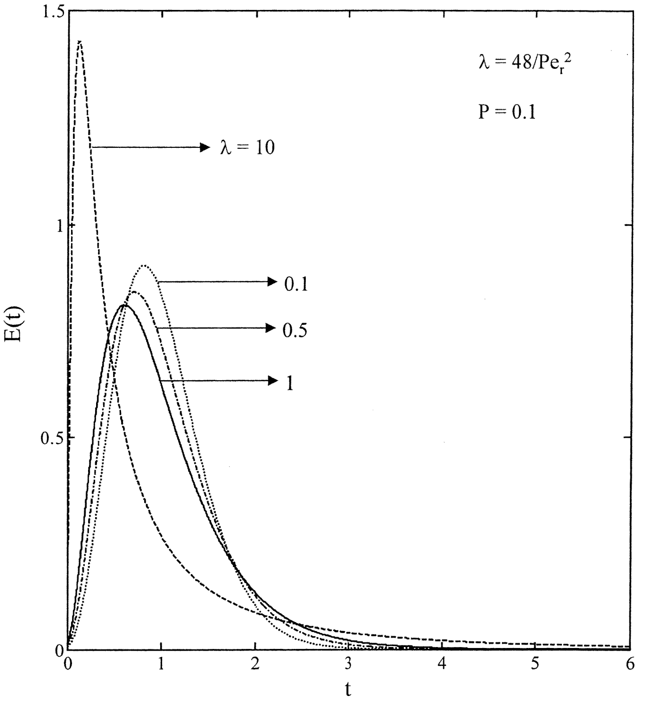

Fig. 2. Dispersion curves predicted by the full hyperbolic model, Eq. (46) for P=0.1.

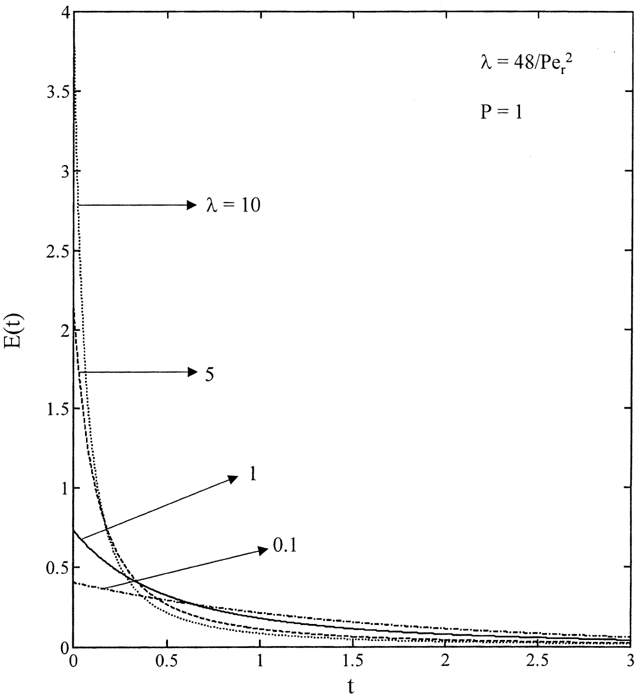

Fig. 3. Dispersion curves predicted by the full hyperbolic model, Eq. (46) for P=1.

case of a single solute being adsorbed on the wall of a tube in which the flow is laminar. Assuming Langmuir adsorption and neglecting axial molecular diffusion ($Pe_r \gg 1$), the governing partial differential equations (assuming azimuthal symmetry) may be written as

$$\frac{\partial C_A}{\partial t'} + 2\bar{u}\left(1-\frac{r^2}{a^2}\right)\frac{\partial C_A}{\partial x} = \frac{D_m}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right); \quad 0<r<a, x>0 \tag{49}$$

$$-D_m\frac{\partial C_A}{\partial r}(r=a,z,t) = k_a C_{Aw} C_s - k_d C_{As}; \quad \frac{\partial C_A}{\partial r}(r=0,z,t)=0 \tag{50}$$

$$\frac{\partial C_{As}}{\partial t'} = k_a C_{Aw} C_s - k_d C_{As} \tag{51}$$

$$C_{Aw} = C_A(r=a,z,t); \quad C_s + C_{As} = C_0 \tag{52}$$

with appropriate inlet and initial conditions. Here, k_a and k_d are the adsorption and desorption rate constants and C_{Aw} is the solute concentration at the wall and the other symbols have their usual meaning. Scaling the solute concentration using some reference inlet concentration (C_{A0}), adsorbed concentration by the total concentration of sites C_0(θ=C_{As}/C_0), time, radial and axial coordinates as in the Taylor problem (using convection time, tube radius and length, respectively) and defining dimensionless parameters

$$\Gamma = \frac{2\,C_0}{a\,C_{A0}} \qquad K = \frac{k_a C_{A0}}{k_d} \qquad Da_l = \frac{a^2 k_a C_{A0}}{D_m}, \tag{53}$$

the dimensionless model equations may be written as

$$LC \equiv \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial C}{\partial \xi}\right) = p\left[\frac{\partial C}{\partial t} + 2(1-\xi^2)\frac{\partial C}{\partial z}\right] \tag{54}$$

$$\frac{\partial C}{\partial \xi} = 0 \quad @\xi=0 \tag{55}$$

$$\frac{1}{Da_l}\frac{\partial C}{\partial \xi}(\xi=1,z,t) = -\frac{\Gamma}{2}\left[C_w(1-\theta) - \frac{\theta}{K}\right]; \quad C_w = C(\xi=1,z,t) \tag{56}$$

$$\frac{\Gamma}{Da_l}\frac{\partial \theta}{\partial t} = \left[C_w(1-\theta) - \frac{\theta}{K}\right] \tag{57}$$

with initial and inlet conditions

$$C(\xi, z, t=0) = C_0(\xi, z) \tag{58a}$$

$$\theta(z, t=0) = \theta_0(z) \tag{58b}$$

$$C(\xi, z=0, t) = C_{in}(\xi, t) \tag{59}$$

Here, $C(\xi, z, t)$ is the scaled solute concentration in the fluid phase, C_w is the solute concentration at the wall, θ is the normalized adsorbed concentration ($0 \le \theta \le 1$), K is the adsorption equilibrium constant, p is the transverse Peclet number, Γ represents the adsorption capacity (ratio of adsorption sites per unit tube volume to the reference solute concentration) and Da_l is the local Damköhler number (ratio of transverse diffusion time to the characteristic adsorption time). We shall assume that $p \ll 1$ while Γ and Da_l are order one parameters (In physical terms, this implies that transverse molecular diffusion and adsorption processes are much faster compared to the convection).

Transverse averaging of the above model using the procedure outlined in section 2 gives the following averaged model to order p:

$$\frac{\partial \langle C \rangle}{\partial t} + \frac{\partial C_m}{\partial z} + \Gamma\frac{\partial \theta}{\partial t} = 0 \tag{60}$$

$$p\frac{\partial \theta}{\partial t} = Da_l\left[C_w(1-\theta) - \frac{\theta}{K}\right] \tag{61}$$

$$C_w - \langle C \rangle = \frac{p}{8}\frac{\partial \langle C \rangle}{\partial t} + \frac{p}{6}\frac{\partial \langle C \rangle}{\partial z} \tag{62}$$

$$C_m - \langle C \rangle = -\frac{p}{24}\frac{\partial \langle C \rangle}{\partial t} - \frac{p}{16}\frac{\partial \langle C \rangle}{\partial z} \tag{63}$$

$$\begin{gathered}\langle C \rangle(z,t=0) = \langle C_0(\xi,z) \rangle; \quad \theta(z,t=0) = \theta_0(z); \\ C_m(z=0,t) = C_{m,in}(t)\end{gathered} \tag{64}$$

The averaged model is defined in terms of four variables (or four modes), namely, the fluid phase cup-mixing concentration (C_m), the fluid phase average concentration ($\langle C \rangle$), the solute concentration at the wall (C_w) and the adsorbed concentration (θ). Since the initial and boundary conditions for the averaged model are obtained in the same manner as the Taylor problem by taking transverse averages of Eqs. (58a) and (59), we do not consider them any further. We now consider various limiting cases of this model.

For the case of p=0, which corresponds to adsorption, desorption and transverse diffusion time scales going to zero, we have

$$C_m = C_w = \langle C \rangle; \quad \theta = \frac{K\langle C \rangle}{1+K\langle C \rangle} \tag{65a}$$

and the above model reduces to the widely used zeroth order hyperbolic model (with no dispersion) [Rhee et al., 1986]:

$$\frac{\partial \langle C \rangle}{\partial t} + \frac{\partial \langle C \rangle}{\partial z} + \Gamma\frac{\partial \theta}{\partial t} = 0 \tag{65b}$$

The first non-trivial case we consider is that of linear adsorption and desorption. For this case, we have $\theta \ll 1$ and the model becomes linear. For small p, we can use the leading order approximation to further simplify the model by eliminating the variables C_w and $\langle C\rangle$ and write it in terms of C_m:

$$\frac{\partial C_m}{\partial t}+\frac{1}{(1+\gamma)}\frac{\partial C_m}{\partial z}+p\Lambda\frac{\partial^2 C_m}{\partial z\partial t}=0 \tag{66a}$$

$$\Lambda=\frac{1}{48}\frac{1+6\gamma+11\gamma^2}{(1+\gamma)^2}+\frac{1}{\Gamma \mathrm{Da}_l}\frac{\gamma^2}{(1+\gamma)^2} \tag{66b}$$

$$\gamma=\Gamma K=\frac{2}{a}\frac{k_a C_0}{k_d} \tag{66c}$$

Since the model is linear for the special case considered, the same equation is also satisfied by the other three variables. The following observations may be made from Eq. (66b) that expresses the dimensionless dispersion coefficient Λ: (i) the first term describes dispersion effects due to velocity gradients when adsorption equilibrium exists at the interface. We note that this expression was first derived by Golay [1958] for capillary chromatography with a retentive layer. (ii) The second term corresponds to dispersion effects due to finite rate of adsorption, since this term vanishes if we assume that adsorption and desorption are very fast so that equilibrium exists at the interface. (iii) the effective dispersion coefficient reduces to the Taylor limit when the adsorption rate constant or the adsorption capacity is zero. (iv) As is well known [Rhee et al., 1986], the effective solute velocity is reduced by a factor $(1+\gamma)$. (v) For the case of irreversible adsorption ($\gamma\to\infty$ and $\mathrm{Da}_l\to\infty$), the dispersion coefficient is equal to eleven times the Taylor value. It is also equal to the reciprocal of the asymptotic Sherwood number for mass transfer in a circular channel with constant wall flux boundary condition. (vi) When the local Damkohler number is small (adsorption is slow or capacity is low), Λ can be large, leading to long tails in the dispersion curve.

The second limiting case we consider is that of Langmuir adsorption with equilibrium at the interface. In physical terms, this corresponds to adsorption and desorption being very fast compared to transverse diffusion and convection. This assumption is equivalent to assuming $\mathrm{Da}_l\to\infty$ and replacing Eq. (61) by

$$\theta=\frac{KC_w}{1+KC_w} \tag{67}$$

Combining Eqs. (62) and (63), we get

$$C_w=C_m+\frac{p}{6}\frac{\partial\langle C\rangle}{\partial t}+\frac{11p}{48}\frac{\partial\langle C\rangle}{\partial z}=C_m+\frac{p}{6}\frac{\partial C_m}{\partial t}+\frac{11p}{48}\frac{\partial C_m}{\partial z}+O(p^2) \tag{68}$$

Thus, we can obtain the following single evolution equation for the cup-mixing concentration:

$$\frac{\partial C_m}{\partial t}+\frac{\partial C_m}{\partial z}+\frac{p}{24}\frac{\partial^2 C_m}{\partial t^2}+\frac{p}{16}\frac{\partial^2 C_m}{\partial z\partial t}+\Gamma\frac{\partial}{\partial t}\left(\frac{KC_m+\frac{pK}{6}\frac{\partial C_m}{\partial t}+\frac{11pK}{48}\frac{\partial C_m}{\partial z}}{1+KC_m+\frac{pK}{6}\frac{\partial C_m}{\partial t}+\frac{11pK}{48}\frac{\partial C_m}{\partial z}}\right)=0 \tag{69}$$

This equation reduces to the zeroth order hyperbolic model (Eq. (65)) for p=0. It also reduces to the hyperbolic model treated in the previous section for either Γ=0 or K=0, after combining of the third and fourth terms using the leading order approximation. For finite p, Γ and K, this rigorously derived averaged model is quite different from the intuitively written models in the literature!

The last case we consider is that of a flat velocity profile with Langmuir adsorption. In this case, the dimensionless model equations are given by

$$\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(\xi\frac{\partial C}{\partial\xi}\right)=p\left[\frac{\partial C}{\partial t}+\frac{\partial C}{\partial z}\right] \tag{70}$$

$$\frac{\partial C}{\partial\xi}=0\quad @\xi=0 \tag{71}$$

$$\frac{1}{\mathrm{Da}_l}\frac{\partial C}{\partial\xi}(\xi=1,\ z,\ t)=-\frac{\Gamma}{2}\left[C_w(1-\theta)-\frac{\theta}{K}\right];\quad C_w=C(\xi=1,\ z,\ t) \tag{72}$$

$$p\frac{\partial\theta}{\partial t}=\mathrm{Da}_l\left[C_w(1-\theta)-\frac{\theta}{K}\right] \tag{73}$$

Now, because of flat velocity profile, the distinction between cup-mixing and averaged concentrations disappears and the averaged model to order p may be expressed in terms of only three variables (three-mode form) as

$$\frac{\partial\langle C\rangle}{\partial t}+\frac{\partial\langle C\rangle}{\partial z}+\Gamma\frac{\partial\theta}{\partial t}=0 \tag{74}$$

$$p\frac{\partial\theta}{\partial t}=\mathrm{Da}_l\left[C_w(1-\theta)-\frac{\theta}{K}\right] \tag{75}$$

$$C_w-\langle C\rangle=\frac{p}{8}\left(\frac{\partial\langle C\rangle}{\partial t}+\frac{\partial\langle C\rangle}{\partial z}\right) \tag{76}$$

For the special case of linear adsorption, we can combine these equations into a single hyperbolic equation

$$\frac{\partial\langle C\rangle}{\partial t}+\frac{1}{(1+\gamma)}\frac{\partial\langle C\rangle}{\partial z}+p\Lambda\frac{\partial^2\langle C\rangle}{\partial z\partial t}=0 \tag{77a}$$

$$\Lambda=\frac{1}{8}\frac{\gamma^2}{(1+\gamma)^2}+\frac{1}{\Gamma \mathrm{Da}_l}\frac{\gamma^2}{(1+\gamma)^2} \tag{77b}$$

Comparing Eqs. (66) and (77), we see that the adsorption induced dispersion is independent of the velocity profile. We also note that for the case of flat velocity profile, there is no dispersion when γ=0. When equilibrium is assumed at the wall, we can eliminate θ and C_w and write the averaged equation as

$$\frac{\partial\langle C\rangle}{\partial t}+\frac{\partial\langle C\rangle}{\partial z}+\Gamma\frac{\partial}{\partial t}\left(\frac{K\langle C\rangle+\frac{pK}{8}\frac{\partial\langle C\rangle}{\partial t}+\frac{pK}{8}\frac{\partial\langle C\rangle}{\partial z}}{1+K\langle C\rangle+\frac{pK}{8}\frac{\partial\langle C\rangle}{\partial t}+\frac{pK}{8}\frac{\partial\langle C\rangle}{\partial z}}\right)=0 \tag{78}$$

As expected, for p=0, this model reduces again to the zeroth order hyperbolic model, Eq. (65) but for any finite p, it does not simplify to any of the standard models in the literature.

The order p terms that appear in Eqs. (69) and (78) modify the leading order hyperbolic behavior by introducing dispersion (which is always present in real systems due to velocity gradients and/or finite rates of adsorption). As is well known in the literature, the leading order hyperbolic models may have discontinuous solution profiles [Rhee et al., 1986]. As stated in the introduction, in the literature, these models are often modified by adding a dispersion term and transforming them to a parabolic form. The above analysis shows that the parabolic form of the reduced model is not only a poor approximation but also cannot be justified based on physical grounds (and rigorous derivation). The Lyapunov-Schmidt method of averaging modifies the zeroth order hyperbolic models by adding order p corrections and gives the averaged models in multi-mode form. In some special cases (e.g., linear adsorption or equilibrium at the wall) it is possible to transform them to a single hyperbolic equation containing the dispersion effects. When this simplification is not possible, it is best to leave the averaged models in multi-mode form, which is more convenient for numerical solution.

HYPERBOLIC MODELS FOR DESCRIBING DISPERSION EFFECTS IN CHEMICAL REACTORS

In this section, we present hyperbolic low-dimensional averaged models for tubular homogeneous and catalytic reactors. Again, we skip algebraic details and focus on the results and their physical interpretation.

1. Homogeneous Tubular Reactors

As our third example, we consider the problem of fully developed laminar flow in a tube with a single homogenous reaction A→B. For a constant density system, assuming azimuthal symmetry, the scaled concentration c(ξ, z, t) of species A obeys the convection-diffusion-reaction equation:

$$\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(\xi\frac{\partial c}{\partial\xi}\right)=p\left[\frac{\partial c}{\partial t}-\frac{p}{\mathrm{Pe}_r^2}\frac{\partial^2 c}{\partial z^2}+2(1-\xi^2)\frac{\partial c}{\partial z}+\mathrm{Da}r(c)\right] \tag{79}$$

where Da is the reactor scale Damköhler number defined by

$$\mathrm{Da}=\frac{LR(C_R)}{\langle u_z\rangle C_R} \tag{80}$$

and other parameters have their usual meaning. Here, C_R is some reference concentration which may be taken as the inlet concentration. As in the previous problems, we assume that $p\ll 1$ while Da and Pe_r are order one parameters. The boundary and initial conditions on the model are given by

$$\frac{p}{\mathrm{Pe}_r^2}\frac{\partial c}{\partial z}=u(\xi)[c-c_{in}(\xi,t)]@z=0, \tag{81a}$$

$$\frac{\partial c}{\partial z}=0@z=1, \tag{81b}$$

$$\frac{\partial c}{\partial \xi}=0@\xi=0,\ 1 \tag{81c}$$

$$c(\xi,z,t=0)=c_0(\xi,z). \tag{81d}$$

Transverse averaging of the above model using the procedure outlined in section 2 gives the following two-mode model, involving the spatially averaged concentration $\langle c\rangle$ and the mixing-cup concentration c_m to order p:

$$\frac{\partial c_m}{\partial t}+\frac{\partial c_m}{\partial z}+\frac{p}{48}\frac{\partial^2 c_m}{\partial z\partial t}-\frac{p}{\mathrm{Pe}_r^2}\frac{\partial^2 c_m}{\partial z^2}+\mathrm{Da}r(\langle c\rangle)+O(p^2)=0, \tag{82}$$

$$\langle c\rangle-c_m=\frac{p}{48}\frac{\partial c_m}{\partial z}+O(p^2) \tag{83}$$

with boundary and initial conditions given by

$$\frac{p}{\mathrm{Pe}_r^2}\frac{\partial c_m}{\partial z}=c_m-c_{m,in}(t),\ \ @z=0, \tag{84a}$$

$$\frac{\partial c_m}{\partial z}=0,\ \ @z=1, \tag{84b}$$

$$c_m=c_{m0}(z),\ \ @t=0. \tag{84c}$$

We now consider some important limiting cases of this model. First, we note that for p=0, $\langle c\rangle=c_m$ and the model reduces to the zeroth order hyperbolic (plug flow) model. When axial molecular diffusion is negligible, it reduces to the hyperbolic model:

$$\frac{\partial c_m}{\partial t}+\frac{\partial c_m}{\partial z}+\Lambda_1 p\frac{\partial^2 c_m}{\partial z\partial t}+\mathrm{Da}r(\langle c\rangle)=0 \tag{85a}$$

$$\langle c\rangle-c_m=\Lambda_1 p\frac{\partial c_m}{\partial z} \tag{85b}$$

$$c_m=c_{m,in}(t)\ @\ z=0;\ c_m=c_{m0}(z),\ @\ t=0, \tag{86}$$

where Λ_1(=1/48) is now the dimensionless (local) mixing time. Under steady-state conditions, this two-mode model can be further simplified to

$$\frac{dc_m}{dz}=-\mathrm{Da}r(\langle c\rangle),\ \ \text{with } c_m|_{z=0}=c_{m,in} \tag{87a}$$

$$\langle c\rangle-c_m=\Lambda_1 p\frac{dc_m}{dz}=-\Lambda_1 p\mathrm{Da}r(\langle c\rangle), \tag{87b}$$

which in dimensional form may be written as

$$\langle u\rangle\frac{dC_{Am}}{dx}=-R(\langle C_A\rangle),\ \ \text{with } C_{Am}|_{x=0}=C_{m,in}, \tag{88a}$$

$$\langle C\rangle-C_m=-t_{mix}R(\langle C_A\rangle), \tag{88b}$$

where $t_{mix}=\Lambda_1(a^2/D_m)$ is the local mixing time. The solutions of the two-mode model given by Eq. (87) should be compared to the parabolic axial dispersion model with Danckwerts boundary conditions [Danckwerts,1953; Wehner and Wilhelm, 1973]:

$$\frac{1}{\mathrm{Pe}}\frac{d^2\langle c\rangle}{dz^2}-\frac{d\langle c\rangle}{dz}-\mathrm{Da}r(\langle c\rangle)=0;\ \ 0<z<1 \tag{89a}$$

$$\frac{1}{\mathrm{Pe}}\frac{d\langle c\rangle}{dz}=\langle c\rangle-\langle c_{in}\rangle\ \ @z=0;\ \ \frac{d\langle c\rangle}{dz}=0\ \ @z=1 \tag{89b}$$

As in the Taylor problem, the exit concentration predicted by the Danckwerts model is always bounded between the two limiting cases of plug flow (Pe=∞) and CSTR (Pe=0). This is not the case for the two-mode defined by Eqs. (87). While for p→0 the solution approaches the plug flow limit, as p increases the conversions can be below those obtained in a CSTR. This is the so-called mixing limited asymptote which is similar to the mass transfer controlled case for the case of catalytic reactions. The single mode Danckwerts model cannot describe (even qualitatively) this mixing- or micromixing-limited regime. Thus, we have shown that the hyperbolic two-mode model has a much larger region of validity than the parabolic model with Danckwerts boundary conditions.

2. Tubular Catalytic Reactors

The last case we consider is that of a single wall-catalyzed reaction A→B in a laminar flow tubular reactor (e.g., a catalytic monolith). The governing convection-diffusion-reaction (CDR) equation for species A is now given by

$$\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(\xi\frac{\partial c}{\partial\xi}\right)=p\left[\frac{\partial c}{\partial t}-\frac{p}{\mathrm{Pe}_r^2}\frac{\partial^2 c}{\partial z^2}+2(1-\xi^2)\frac{\partial c}{\partial z}\right] \tag{90}$$

The initial and boundary conditions are given by Eq. (81) as in the case of homogeneous reactors. However, as the reaction occurs on the tube wall instead of the bulk, the boundary condition at the tube wall is not Neumann as in homogeneous reactors, but of the form:

$$\left.\frac{\partial c}{\partial \xi}\right|_{\xi=1} = -p\frac{Da_s}{2}r_w(c_w). \qquad (91)$$

In the above equations, c_w is the surface/wall concentration of species A, $r_w(c_w)$ is the dimensionless intrinsic rate of surface reaction, Da_s is the reactor scale Damköhler number, which are given by

$$c_w = c|_{\xi=1} = \langle c\rangle + c'|_{\xi=1}$$
$$r_w(c_w) = \frac{R_w(C_{Aw})}{R_w(C_R)},$$
$$Da_s = \frac{2LR_w(C_R)}{\langle u\rangle aC_R}, \qquad (92)$$

while the other symbols retain their usual meanings. We assume that $p \ll 1$ while Pe_r and Da_s are order one parameters.

It may be noted that the above set of equations has a zero eigenvalue and a corresponding constant eigenfunction for p=0, making spatial averaging by L-S technique possible. Using the averaging theory outlined in section 2, we obtain c' as

$$c'(\xi,z,t) = p\frac{\partial\langle c\rangle}{\partial z}\left[-\frac{1}{12}+\frac{\xi^2}{4}-\frac{\xi^4}{8}\right]+pDa_s r_w(\langle c\rangle)\left[\frac{1}{8}-\frac{\xi^2}{4}\right]+O(p^2),$$
$$= p\frac{\partial\langle c\rangle}{\partial z}\left[-\frac{1}{12}+\frac{\xi^2}{4}-\frac{\xi^4}{8}\right]+pDa_s r_w(\langle c_w\rangle)\left[\frac{1}{8}-\frac{\xi^2}{4}\right]+O(p^2), \quad (93)$$

and the spatially averaged low-dimensional model to O(p) as

$$\frac{\partial\langle c\rangle}{\partial t}+\frac{\partial c_m}{\partial z}-\frac{p}{Pe_r^2}\frac{\partial^2\langle c\rangle}{\partial z^2}+Da_s r_w(c_w)=0, \qquad (94a)$$

$$c_w-\langle c\rangle = \frac{p}{24}\frac{\partial c_m}{\partial z}-\frac{p}{8}Da_s r_w(c_w)+O(p^2), \qquad (94b)$$

$$c_m-\langle c\rangle = -\frac{p}{48}\frac{\partial c_m}{\partial z}+\frac{p}{24}Da_s r_w(c_w)+O(p^2) \qquad (94c)$$

We note that the averaged model is now expressed in terms of three modes: the cup-mixing, spatial and wall concentrations. The cup-mixing and wall concentrations are necessary to describe the mass transfer between the bulk and the wall while the two modes c_m and $\langle c\rangle$ describe the micromixing that occurs in the fluid phase, due to transverse velocity gradients and transverse molecular diffusion. Traditional two-phase models of catalytic reactors that use only the wall and cup-mixing concentrations ignore this term which can be important in the transient operation of the reactor. The initial and boundary conditions for this averaged model are same as those in the case of homogeneous tubular reactor.

It should be noted that it is possible to eliminate $\langle c\rangle$ from Eq. (94) and write it in the following two-mode form:

$$\left[1-\frac{p}{24}Da_s\frac{dr_w}{dc}(c_w)\right]\frac{\partial c_m}{\partial t}+\frac{\partial c_m}{\partial z}+\frac{p}{48}\frac{\partial^2 c_m}{\partial z\partial t}-\frac{p}{Pe_r^2}\frac{\partial^2 c_m}{\partial z^2}+Da_s r_w(c_w)=0 \qquad (95a)$$

$$c_w-c_m = \frac{p}{16}\frac{\partial c_m}{\partial z}-\frac{p}{6}Da_s r_w(c_w) \qquad (95b)$$

In this form, the applicability of the model is limited to the parameter range in which the term in square bracket does not vanish. We now consider various limiting cases of this model.

The first limiting case we consider is that of steady-state limit with negligible axial diffusion ($Pe_r \gg 1$). For this case, Eqs. (94) or (95) reduce to the two-mode form

$$\frac{c_w-c_m}{\left(\frac{11p}{48}\right)} = \frac{dc_m}{dz} = -Da_s r_w(c_w), \text{ with } c_m|_{z=0}=c_{m,in}. \qquad (96)$$

In this form, the two-mode model is identical to the classical steady-state two-phase model of a tubular catalytic reactor with negligible axial dispersion. There is also a striking similarity between the two-mode models for homogeneous reactors and two-phase models of catalytic reactors in the practical limit of $Pe_r \gg 1$. This can be seen when the steady-state models are rewritten as

$$\frac{dc_m}{dz} = \frac{\langle c\rangle - c_m}{\Lambda_1 p} = -Dar(\langle c\rangle), \text{ with } c_m|_{z=0}=c_{m,in},$$

(Homogeneous Tubular Reactor) (97)

$$\frac{dc_m}{dz} = \frac{c_w - c_m}{\Lambda_2 p} = -Da_s r_w(c_w), \text{ with } c_m|_{z=0}=c_{m,in}.$$

(Tubular Catalytic Reactor) (98)

where $\Lambda_1=1/48$ and $\Lambda_2=11/48$. The reciprocals of these numbers are the asymptotic Sherwood numbers or dimensionless mass transfer coefficients for exchange between the two modes. We can now see the one-to-one correspondence between the two-mode models of homogeneous reactions and the two-phase models of catalytic reactions. For example, just as the reaction rate in the two-phase model is not evaluated at the mixing-cup concentration c_m but at the wall concentration c_w, similarly the reaction rate term in the two-mode model is evaluated at the spatially averaged concentration $\langle c\rangle$. Also, analogous to the dimensionless two phase transfer time (Λ_2) in the two-phase model is the dimensionless local mixing time (Λ_1) in the two-mode model.

The second limiting case we consider is that of linear kinetics with negligible axial diffusion ($Pe_r \gg 1$). For this case, the averaged model can be written in terms of the cup-mixing concentration as

$$\left[\frac{2}{3}+\frac{1}{3}\frac{1+\frac{\phi_s^2}{24}}{1+\frac{\phi_s^2}{6}}\right]\frac{\partial c_m}{\partial t}+\left[1+\frac{\frac{\phi_s^2}{16}}{1+\frac{\phi_s^2}{6}}\right]\frac{\partial c_m}{\partial z}+\frac{p}{48}\frac{1+\frac{\phi_s^2}{24}}{1+\frac{\phi_s^2}{6}}\frac{\partial^2 c_m}{\partial z\partial t}+\frac{Da_s}{1+\frac{\phi_s^2}{6}}c_m=0 \qquad (99)$$

where

$$\phi_s^2 = pDa_s \qquad (100)$$

is the local Damköhler number. For the case of $\phi_s^2 \to 0$ (slow wall reaction), Eq. (99) reduces to

$$\frac{\partial c_m}{\partial t}+\frac{\partial c_m}{\partial z}+\frac{p}{48}\frac{\partial^2 c_m}{\partial z\partial t}+Da_s c_m=0 \qquad (101)$$

while for the case of $\phi_s^2 \to \infty$ (infinitely fast wall reaction or the mass transfer controlled limit), it may be written as

$$\frac{\partial c_m}{\partial t}+\frac{11}{6}\frac{\partial c_m}{\partial z}+\frac{p}{144}\frac{\partial^2 c_m}{\partial z\partial t}+\frac{8}{p}c_m=0 \qquad (102)$$

Comparing this with the slow reaction case, we note that the effective velocity has increased (by a factor 1.83); the dispersion coefficient is reduced by a factor 3 while the apparent reactor scale Damköhler number changed from Da_s to 8/p.

The last limiting case we consider is the practical case of long tubes where the axial dispersion term may be neglected. For this case, it is more convenient to write the three model given by Eq. (94) in the following form

$$\frac{\partial\langle c\rangle}{\partial t} = -\frac{24}{p}[11\langle c\rangle - 8c_m - 3c_w] \tag{103a}$$

$$\frac{\partial c_m}{\partial z} = \frac{48}{p}[4\langle c\rangle - 3c_m - c_w] \tag{103b}$$

$$\frac{24}{p}[3\langle c\rangle - 2c_m - c_w] = Da_s r_w(c_w) \tag{103c}$$

with initial and boundary conditions

$$\langle c\rangle(z,t=0)=c_0(z);\;\; c_m(z,t=0)=c_{m0}(z);\;\; c_m(z=0,t)=c_{m,in}(t) \tag{103d}$$

This model reduces to the two-phase model given by Eq. (96) under steady-state conditions. However, for the general case of time varying inlet conditions this model retains all the qualitative features of the full partial differential equation model while the traditional two-phase model which does not distinguish between c_m and $\langle c\rangle$ ignores the dispersion effect in the fluid phase.

SUMMARY AND DISCUSSION

We have shown in this work that dispersion caused by transverse velocity gradients and molecular diffusion can be described by averaged models that are hyperbolic in the longitudinal coordinate and time and containing an effective local time (or length) scale. This description overcomes the main deficiencies of the literature approaches to describe dispersion by using parabolic averaged models. We have also shown that the hyperbolic models can describe the dispersion effects as well as the parabolic models, have a much larger domain of validity and retain the essential physics contained in the original more detailed models.

The rigorously derived multi-mode low-dimensional models of reactors and chromatographs in this work are quite different from the intuitively written and widely used models in the chemical engineering literature!

We have considered here only unidirectional velocity fields and straight channels. However, the main ideas and the averaging procedure can be extended to more general cases (e.g. dispersion in porous media or packed beds, non-isothermal systems and multiphase reactors). In addition, though we have derived the averaged models for chromatographs and reactors, we have not presented a detailed analysis or solutions of these models. This will be pursued in future work.

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