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HYPERBOLIC HOMOGENIZED MODELS FOR THERMAL AND SOLUTAL DISPERSION*

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Abstract. We formulate a general theory, based on a Lyapunov–Schmidt expansion, for averaging thermal and solutal dispersion phenomena in multiphase reactors, with specific attention to the important Taylor mechanism due to transverse intraphase and interphase capacitance-weighted velocity gradients. We show that the classical Taylor dispersion phenomena are better described in terms of low dimensional models that are hyperbolic and contain an effective local time or length scale in place of the traditional Taylor dispersion coefficient. This description eliminates the use of an artificial exit boundary condition associated with parabolic homogenized equations as well as the classical upstream-feedback and infinite propagation speed anomalies. Our approach is also applicable for describing steady dispersion in the presence of reaction and thermal generation or consumption. For two-phase systems, maximum dispersion is found to exist at an optimum fraction ϵ_f of the lower-capacitance phase. For the disparate phase capacities of most reactors, thermal or solutal dispersion is shown to have the scaling $\frac{\epsilon_f p^2}{(1-\epsilon_f)\Gamma}\alpha_f$, where α_f is the thermal diffusivity of the low-capacitance phase, Γ is the capacitance ratio, and p is the transverse Peclet number.

Key words. solutal dispersion, thermal dispersion, averaging, Liapunov–Schmidt reduction, multiphase reactors

AMS subject classifications. 76R05, 34C29, 34K60, 35B27

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1. Introduction.

A major goal of the discipline of chemical engineering known as reaction engineering is to combine the complex kinetics, flow fields, and geometries of multiphase reacting systems (such as a packed bed) into accurate low dimensional homogenized convection-diffusion-reaction models that contain all the pertinent transport and kinetic effects of the above complications. It was realized very early that flow turbulence, tortuosity of the interstitial streamlines, velocity gradient of the flowing phase, adsorption onto a stationary phase (as in a chromatograph), and accumulation near stagnation points or stagnant dead zones can give rise to anomalously high solutal dispersion, orders of magnitude higher than molecular diffusion, that must somehow be modeled and included in the homogenized model as a dispersion term $D_{eff}\frac{\partial^2 c}{\partial z^2}$ with the dispersion coefficient D_{eff}. That such a term stipulates that two boundary conditions be provided for the parabolic homogenized model has also introduced considerable confusion. The classical Danckwerts boundary conditions and many other inconsistent ones provide one boundary condition at each end of the reactor (Danckwerts (1953), Choi and Perlmutter (1976), Wehner and Wilhelm (1956)) and have recently been "justified" by Roberts (1989) using center manifold theory. There are, however, fundamental difficulties with this parabolic equation and the Danckwerts boundary conditions. This model introduces infinitely fast diffusive spreading of a

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localized concentration perturbation and upstream diffusive propagation (Hinduja, Sundaresan, and Jackson (1980), Sundaresan, Anderson, and Aris (1980)). Both phenomena are not observed experimentally as the flow-induced dispersion mechanisms are hyperbolic in nature (Hiby (1962), Chang (1982)). As a result, the homogenized parabolic equation and Danckwerts boundary conditions cannot describe the observed dispersion phenomena in finite length reactors.

Local turbulent dispersion can be estimated using classical homogeneous turbulent mixing theory. Dispersion in periodic as well as random velocity fields has been reviewed by Majda and Kramer (1999). These authors also present an excellent review of homogenization methods for the convective diffusion equation with periodic velocity fields.

In many applications such as chromatographs and reactors involving packed beds, the flow is laminar, and the more important larger scale dispersion effects that occur over several reactor radii are mostly due to a Taylor–Aris dispersion mechanism (Taylor (1953), Aris (1959), Brenner and Edwards (1993)). This mechanism occurs when a macroscopic transverse velocity gradient, like Poiseuille flow in a tube or macroscopic flow nonuniformity in a packed bed, induces longitudinal dispersion as transverse diffusion lands molecules onto streamlines or flow channels of different velocity. Adsorption onto a stationary solid phase also can trigger this effect as the solid phase has a velocity (zero) different from the flowing phase. Adsorption-induced Taylor–Aris dispersion is responsible for the dispersion of chromatograph signals (Balakotaiah and Chang (1995)). It is also a main problem in biochemical assays on chip-scale laboratories and reactors using microfluidics (Culbertson, Jacobson, and Ramsey (1998)).

Several theories have been developed to predict solutal Taylor–Aris dispersion in packed beds. In the limit of extremely high Peclet number p in an unbounded medium when diffusion is unimportant in the bulk of the flowing phase, Koch and Brady used a diffusive boundary layer cutoff to show that D_{eff} scales as $p \ln p$ (Koch and Brady (1985)). Roberts (1989) and Balakotaiah and Chang (1995) used center manifold theory to show that reaction can affect the dispersion coefficient in a long reactor whose length is much longer than its transverse dimension (radius) such that diffusion dominates in the transverse direction.

Another confusion concerning dispersion is whether a homogenized model remains valid at steady state and whether D_{eff} and its underlying dispersion mechanism are still in play at steady state. While Taylor's classical theory (Taylor, 1953), Koch and Brady's high-p dispersion mechanism in an unbounded medium, and Roberts's and Balakotaiah and Chang's reactive dispersion theory in a long reactor are clearly for transient dispersion, it seems physically intuitive that the same transverse gradient in longitudinal velocity can affect steady-state reactor conversion or performance (Chang, 1982). In fact, it is common practice to use the homogenized model for both steady and transient reactors (Westerterp, Dilman, and Kronberg (1995)). Steady dispersion, however, lacks theoretical justification. An apparent steady dispersion will be shown here to exist, but its description is fundamentally different from that of the transient one.

Even more important than solutal dispersion is thermal dispersion, a subject that is only recently being scrutinized in detail. It is well known in the reaction engineering literature (Balakotaiah (1996), Subramanian and Balakotaiah (1996)) that reactor dynamics and steady-state multiplicity are extremely sensitive to thermal dispersion. Empirical studies and recent analyses have shown that reactor ignition, extinction, hot spot formation, and thermal runaways of most important (and difficult to control) reactors for exothermic reactions are also extremely sensitive to thermal dispersion

(Balakotaiah, Kodra, and Nyugen (1995), Leighton and Chang (1995), and Keith, Leighton, and Chang (1999)). To compound the problem, thermal dispersion is more sensitive to packing and flow geometries and is far more difficult to estimate than solutal dispersion. Two major difficulties are that the thermal penetration depth into the solid phase is deeper than the solutal one, and that the stationary and mobile capacitances are more disparate. As a result, interphase dispersion due to discrepancies in the phase-averaged thermal velocities can enhance and even dominate the intraphase dispersion mechanism in the flowing phase due to transverse flow velocity gradient. The addition of interphase dispersion, distinct from Taylor's intraphase dispersion, renders the analysis more difficult. Vortmeyer and Schaefer (1974), Leighton and Chang (1995), and Balakotaiah and Dommeti (1999) obtained interphase dispersion coefficients based on lumped models with heat transfer coefficients. Leighton and Chang (1995) showed that the ignition location and light-off time of a catalytic converter is determined mostly by this thermal dispersion mechanism. Keith, Leighton, and Chang (1999) used metal inserts to enhance thermal dispersion of a reverse-flow reactor to prevent thermal runaway. Without including the intraphase dispersion mechanism due to flow nonuniformity, they found that an optimum void fraction of intermediate value and with maximum dispersion exists when the heat capacity ratio Γ is near unity, but none exists for realistic void fractions for disparate capacities. In fact, for the more common case of disparate capacities, a generic scaling seems to exist. This would be a significant general result as most reactors have disparate capacities and complex flow fields. It would be desirable to obtain general dispersion scalings insensitive to the flow fields. However, the omission of intraphase dispersion will be shown here to be valid only for disparate capacities. Greatly enhanced dispersion still exists near unit Γ and at an optimum flowing-phase fraction, but the actual dispersion coefficient must include intraphase dispersion and a detailed description of the macroscopic flow fields.

A general solutal/thermal Taylor–Aris dispersion theory will be formulated here to clearly delineate the intraphase and interphase contributions. The proper limit when the former can be omitted and the simpler lumped-phase models can be utilized is also defined. The theory also shows that dispersion phenomena are better described in terms of reduced (low dimensional) models that are hyperbolic in the longitudinal coordinate and time, and with an effective transfer or exchange time constant between the master (slowly varying) mode and slave (local) modes, in contrast to the traditional parabolic models with an effective dispersion coefficient. The reduced models derived based on the present theory eliminate the classical problems of upstream diffusion and infinite propagation speed associated with the parabolic-type averaged equations derived in the prior literature. The theory utilizes the Lyapunov–Schmidt reduction technique of classical bifurcation theory and is based on a perturbation expansion near zero eigenvalue(s).

2. Packed-bed heat transfer. To illustrate the concept of interphase dispersion (due to transfer or exchange between the phases) and some key ideas in our approach, we first consider a very simple model of a packed bed in which the solid is stationary and the fluid moves (Figure 1). The classical heat transfer model of this system ignores the (transverse) gradients within each phase as well as conduction in the axial direction in each phase. The model is described by the following pair of hyperbolic equations for the solid and fluid temperatures:

$$\epsilon_f\ (\rho c_p)_f \left[\frac{\partial T_f}{\partial t'} + u_0 \frac{\partial T_f}{\partial z'}\right] = h a_v (T_s - T_f), \tag{2.1a}$$

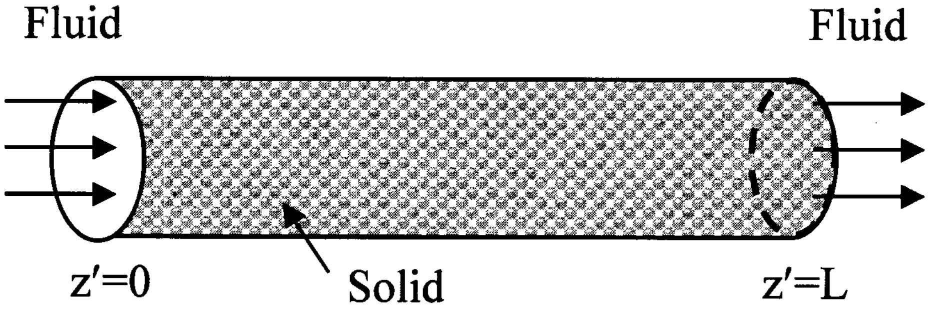

FIG. 1. *Schematic diagram of a packed-bed reactor in which solid and fluid phases interact.*

$$(1-\epsilon_f)(\rho c_p)_s \frac{\partial T_s}{\partial t'} = -h a_v (T_s - T_f), \tag{2.1b}$$

with initial and boundary conditions

$$T_f = f_0(t'), \qquad z' = 0,\ t' > 0, \tag{2.1c}$$

$$T_f = T_f^0(z'), \qquad t' = 0,\ z' > 0, \tag{2.1d}$$

$$T_s = T_s^0(z'), \qquad t' = 0,\ z' > 0. \tag{2.1e}$$

Here, u_0 (assumed to be a constant) is the interstitial fluid velocity, ϵ_f is the void fraction of the bed (available for flow), $(\rho c_p)_s$ ($(\rho c_p)_f$) is the solid (fluid) heat capacity per unit volume, h is the interphase heat transfer coefficient, and a_v is the (interphase) transfer area per unit bed volume. Assuming that the bed has a length L, we define

$$z = \frac{z'}{L}, \qquad t = \frac{u_0 t'}{L}, \qquad \Gamma = \frac{(\rho c_p)_s}{(\rho c_p)_f}, \qquad Pe = \frac{(\rho c_p)_f u_0}{L h a_v}, \tag{2.2}$$

and write (2.1a) and (2.1b) in dimensionless form as

$$A \begin{pmatrix} T_f \\ T_s \end{pmatrix} = Pe \begin{pmatrix} \frac{\partial T_f}{\partial t} + \frac{\partial T_f}{\partial z} \\ \frac{\partial T_s}{\partial t} \end{pmatrix}, \tag{2.3a}$$

where the matrix operator A is defined by

$$A = \begin{pmatrix} -\frac{1}{\epsilon_f} & \frac{1}{\epsilon_f} \\ \frac{1}{\Gamma(1-\epsilon_f)} & -\frac{1}{\Gamma(1-\epsilon_f)} \end{pmatrix}. \tag{2.3b}$$

(As shown later, A can be made symmetric by defining an inner product weighted with respect to the relative capacitances of the phases.) We note that the Peclet number Pe is the ratio of interphase transfer time ($\frac{(\rho c_p)_f}{h a_v}$) to the convection time ($\frac{L}{u_0}$), Γ is the ratio of solid to fluid heat capacities, and time is nondimensionalized with respect to the convection time. It is assumed that the Peclet number is small, or equivalently, that the interphase transfer time is much smaller compared to the convection time. The matrix A is singular with the following null eigenvector and slave eigenvector (with eigenvalue $-\frac{1}{\epsilon_f}-\frac{1}{\Gamma(1-\epsilon_f)}$):

$$\phi_0=\begin{pmatrix}1\\1\end{pmatrix},\qquad \phi_1=\begin{pmatrix}\Gamma(1-\epsilon_f)\\-\epsilon_f\end{pmatrix}. \tag{2.4}$$

Writing

$$\begin{pmatrix}T_f\\T_s\end{pmatrix}=\begin{pmatrix}1 & \Gamma(1-\epsilon_f)\\1 & -\epsilon_f\end{pmatrix}\begin{pmatrix}T_m\\T_d\end{pmatrix} \tag{2.5a}$$

or

$$\begin{pmatrix}T_m\\T_d\end{pmatrix}=\begin{pmatrix}\frac{\epsilon_f}{[\epsilon_f+\Gamma(1-\epsilon_f)]} & \frac{\Gamma(1-\epsilon_f)}{[\epsilon_f+\Gamma(1-\epsilon_f)]}\\ \frac{1}{[\epsilon_f+\Gamma(1-\epsilon_f)]} & \frac{-1}{[\epsilon_f+\Gamma(1-\epsilon_f)]}\end{pmatrix}\begin{pmatrix}T_f\\T_s\end{pmatrix}, \tag{2.5b}$$

we observe that T_m is the capacitance-weighted (average) temperature, while T_d is the local temperature difference. In terms of these variables, the model may be written as

$$[\epsilon_f+\Gamma(1-\epsilon_f)]\frac{\partial T_m}{\partial t}+\epsilon_f\frac{\partial T_m}{\partial z}=-\epsilon_f(1-\epsilon_f)\Gamma\frac{\partial T_d}{\partial z}, \tag{2.6a}$$

$$T_d=-\frac{Pe\epsilon_f(1-\epsilon_f)\Gamma}{[\epsilon_f+\Gamma(1-\epsilon_f)]^2}\left[\frac{\partial T_m}{\partial z}+\epsilon_f\frac{\partial T_d}{\partial t}+\Gamma(1-\epsilon_f)\left(\frac{\partial T_d}{\partial t}+\frac{\partial T_d}{\partial z}\right)\right]. \tag{2.6b}$$

For $Pe=0$, the solid and fluid temperatures are in equilibrium, and the average temperature evolves according to (2.6a) with its right-hand side set to zero. For small values of the Peclet number, we have from (2.6b)

$$T_d=-\frac{Pe\epsilon_f(1-\epsilon_f)\Gamma}{[\epsilon_f+\Gamma(1-\epsilon_f)]^2}\left(\frac{\partial T_m}{\partial z}\right)+O(Pe^2). \tag{2.7}$$

Thus, the temperature difference T_d is slaved to the average temperature. Substituting (2.7) into (2.6a) and writing the resulting averaged equation in dimensional form, we obtain

$$\frac{\partial T_m}{\partial t'}+\langle u\rangle\frac{\partial T_m}{\partial z'}=\alpha_{eff}\frac{\partial^2 T_m}{\partial z'^2}, \tag{2.8a}$$

$$\langle u\rangle=u_0\frac{\epsilon_f}{[\epsilon_f+\Gamma(1-\epsilon_f)]},\qquad \alpha_{eff}=\frac{u_0^2(\rho c_p)_f\,\Gamma^2\,\epsilon_f^2(1-\epsilon_f)^2}{ha_v[\epsilon_f+\Gamma(1-\epsilon_f)]^3}. \tag{2.8b}$$

Here, $\langle u\rangle$ and α_{eff} are the capacitance-weighted velocity and effective thermal diffusivity of the bed, respectively. From the above derivation, it is clear that the reduced model is valid only when $t'\gg\frac{(\rho c_p)_f}{ha_v}$ and $z'\gg u_0\frac{(\rho c_p)_f}{ha_v}$, i.e., when there is a short transient that escapes the effective equation. During this transient, the two phases equilibrate, and the appropriate initial condition for T_m is simply the capacitance-weighted average of the initial conditions of T_s and T_f,

$$T_m(t'=0)=\frac{\epsilon_f\;T_f(t'=0)+\Gamma(1-\epsilon_f)T_s(t'=0)}{[\epsilon_f\;+\Gamma(1-\epsilon_f)]}. \tag{2.8c}$$

This is valid even though $t' = 0$ on the two sides of (2.8c) corresponds to slightly different instants in time. The two boundary conditions for (2.8a) are more problematic, as the original equation only offers one boundary condition at $z' = 0$. Thus, one obvious one (from (2.1b) and (2.1c)) is that

$$T_m(z'=0,t') = f_0(t') + \frac{(\rho c_p)_s\ \Gamma(1-\epsilon_f)^2}{ha_v[\epsilon_f + \Gamma(1-\epsilon_f)]}\left(\frac{\partial f_0(t')}{\partial t'}\right). \tag{2.8d}$$

In the engineering and the Taylor dispersion theory literature (Danckwerts (1953), Vortmeyer and Schaeffer (1974), Roberts (1992)), the other boundary condition is imposed at the exit $z' = L$, and the often-used exit (Danckwerts) boundary condition is

$$\frac{\partial T_m}{\partial z'}(z'=L,t') = 0. \tag{2.8e}$$

This is clearly not acceptable since the original problem does not possess any boundary condition at the exit. There is also a more fundamental problem associated with the form of the reduced model given by (2.8a). In this form, the reduced model is a parabolic equation, and imposing an artificial exit boundary condition leads to infinite propagation speed for inlet signals. Again, this is certainly not true for the original equations (2.1a) and (2.1b), which may be combined to obtain a single hyperbolic equation for T_f, T_s, or any linear combination of these. For example, without any assumptions on the length or time scales, it is easily seen that the temperature T_i ($i = f, s$, or m) satisfies the hyperbolic equation

$$\frac{\partial T_i}{\partial t'} + \langle u\rangle \frac{\partial T_i}{\partial z'} + \frac{(\rho c_p)_s\ \epsilon_f(1-\epsilon_f)}{ha_v[\epsilon_f + \Gamma(1-\epsilon_f)]}\frac{\partial}{\partial t'}\left[\frac{\partial T_i}{\partial t'} + u_0\frac{\partial T_i}{\partial z'}\right] = 0. \tag{2.9}$$

For $i = m$, the initial and boundary conditions for (2.9) are the same as those defined by (2.8c) and (2.8d), respectively. Thus, the parabolic form of the reduced equation given by (2.8a) is not preferable as it leads to nonphysical phenomena such as upstream diffusion and infinite speed of propagation. This is certainly not true for the initial model, (2.9), which predicts finite propagation speed for all inlet and initial signals and no upstream diffusion. (This can be seen more clearly by comparing the analytical solutions of the exact and reduced equations for a unit step or impulse inputs. These analytical solutions can be expressed in terms of modified Bessel functions.) The origin of the second spatial derivative term in the reduced equation and the interpretation of the coefficient α_{eff} as an effective (Taylor) diffusivity can be traced back to the paper of Taylor on shear dispersion (Taylor (1953)). We present here an alternate form of the reduced equation (and interpretation of the local coefficients) that eliminates the above-mentioned inconsistencies of the classical Taylor dispersion theory.

We note that, when the interphase transfer time is small, the leading order approximation

$$\frac{\partial T_m}{\partial t'} = -\langle u\rangle \frac{\partial T_m}{\partial z'} + O\left(\frac{(\rho c_p)_f}{ha_v}\right) \tag{2.10}$$

may be used to write the reduced equation in three different forms: as a parabolic equation in z' (i.e., (2.8a)), a parabolic equation in t', or a hyperbolic equation in z' and t'. We also note that the local (2.7) written in terms of either $\frac{\partial T_m}{\partial t'}$ or $\frac{\partial T_m}{\partial z'}$ defines a characteristic time (that is proportional to $\frac{(\rho c_p)_f}{ha_v}$) for heat exchange between the slowly varying mode T_m and the slave (local) mode T_d. Thus, we write the averaged model as

$$\frac{\partial T_m}{\partial t'} + \langle u \rangle \frac{\partial T_m}{\partial z'} + \langle u \rangle \, t_H \frac{\partial^2 T_m}{\partial z' \partial t'} = 0, \tag{2.11}$$

where t_H is the characteristic local exchange time (between the two modes) defined by

$$t_H = \frac{(\rho c_p)_s \, (1-\epsilon_f)^2 \Gamma}{h a_v [\epsilon_f + \Gamma(1-\epsilon_f)]}. \tag{2.12}$$

We also define a local length scale as $\ell_H = \langle u \rangle \, t_H$ and note that the reduced model is valid for $z' \gg \ell_H$ and $t' \gg t_H$. In this form, the reduced model defines both the local length and time scales (their ratio being $\langle u \rangle$), and the local effective diffusivity is given by $\alpha_{eff} = \frac{\ell_H^2}{t_H} = \langle u \rangle^2 \, t_H$.

This hyperbolic form of the reduced equation is favored for the following reasons: (i) Since the initial model is hyperbolic, the reduced model should also be hyperbolic; (ii) writing the reduced model as a parabolic equation either in z' or t' requires an artificial boundary or initial condition; (iii) the hyperbolic (2.11) defines a characteristic initial value problem for T_m and hence only T_m needs to be specified along the characteristic curves $z' =$ constant and $t' =$ constant. (In contrast, for the general Cauchy problem, both the function and the normal derivative should be specified along a noncharacteristic curve.) The initial and boundary conditions for (2.11) are the same as those defined by (2.8c) and (2.8d), respectively. Now, no artificial boundary or initial conditions are required, and the reduced model does not lead to any nonphysical phenomena. This hyperbolic form of the reduced model also replaces the concept of an effective (Taylor) diffusivity by that of an effective local time or length scale.

The perturbation expansion can be carried out to higher orders in Pe, and the reduced model (with appropriate initial and boundary conditions) can be expressed in hyperbolic form, but we do not pursue this calculation here. The conditions under which the perturbation expansion converges may also be obtained (for this specific example) in terms of the spatial or time scales appearing in the initial and boundary conditions. We consider it only briefly here and refer to Balakotaiah and Dommeti (1999) for more details.

We note that the local equation (2.6b) may be written as

$$\left[1 + \frac{Pe \; \epsilon_f (1-\epsilon_f)\Gamma}{[\epsilon_f + \Gamma(1-\epsilon_f)]} \left(\frac{\partial}{\partial t} \right) \right] T_d = \frac{Pe \; (1-\epsilon_f)\Gamma}{[\epsilon_f + \Gamma(1-\epsilon_f)]} \left(\frac{\partial T_m}{\partial t} \right). \tag{2.13}$$

Thus, if we consider the special case in which only the inlet conditions are varied, then by taking a Laplace transform, we can reduce the local equation to a linear algebraic equation in terms of the forcing frequency. This equation has a convergent power series expansion in Pe, provided the dimensionless forcing frequency (ω) satisfies the criterion

$$\frac{Pe \; \epsilon_f \; (1-\epsilon_f)\Gamma\omega}{[\epsilon_f + \Gamma(1-\epsilon_f)]} < 1. \tag{2.14}$$

In dimensional terms, (2.14) may be written as

$$\omega' t_H < \frac{(1-\epsilon_f)\Gamma}{\epsilon_f}. \tag{2.15}$$

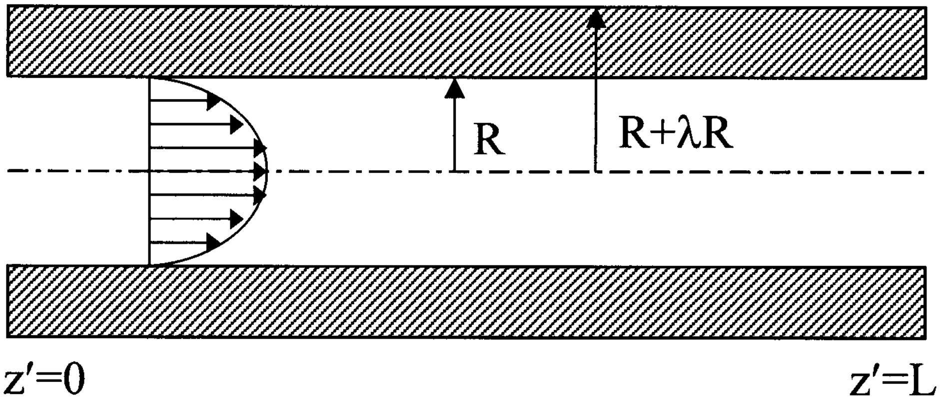

FIG. 2. *Schematic diagram illustrating the classical Taylor solutal dispersion in laminar flow in a circular tube.*

This convergence criterion has a simple physical meaning for the special case in which the volumetric heat capacities of the phases are equal (when the right-hand side of (2.15) is equal to unity): the reduced model exists only if the forcing frequency is less than that defined by the characteristic local exchange time ($\omega' < \frac{1}{t_H}$).

3. Taylor's solutal dispersion theory revisited. In this section, we consider the classical Taylor problem that illustrates intraphase dispersion due to transverse velocity gradients 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. Our approach also shows the similarity between the inter- and intraphase dispersion and the superiority of the hyperbolic models for describing these phenomena.

The dispersion of a nonreactive solute in a circular tube of constant cross section (see Figure 2 for notation) in which the flow is laminar is described by the convective-diffusion equation

$$\text{(3.1a)} \qquad \frac{\partial C}{\partial t'} + 2\langle u\rangle\left(1-\frac{r^2}{R^2}\right)\frac{\partial C}{\partial z'} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right), \; 0<r<R,\; z'>0,\; t'>0,$$

$$\text{(3.1b)} \qquad \frac{\partial C}{\partial r} = 0@r = 0, R,$$

$$\text{(3.1c)} \qquad I.C: C(z', r, 0) = f(z', r),$$

$$\text{(3.1d)} \qquad B.C: C(0, r, t') = g(r, t').$$

In writing (3.1a), it is assumed that longitudinal diffusion can be neglected (this assumption is relaxed later on). Here, $\langle u\rangle$ is the average velocity in the pipe, R is the radius, and D is the diffusivity of the species. Defining dimensionless variables

$$\text{(3.2)} \qquad z = \frac{z'}{L}, \qquad t = \frac{\langle u\rangle t'}{L}, \qquad \xi = \frac{r}{R}, \qquad Pe = \frac{R^2\langle u\rangle}{LD},$$

we can write (3.1a) and (3.1b) as

$$\text{(3.3)} \quad \pounds C \equiv \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial C}{\partial \xi}\right) = Pe\left[\frac{\partial C}{\partial t} + 2\left(1-\xi^2\right)\frac{\partial C}{\partial z}\right], \qquad \frac{\partial C}{\partial \xi} = 0@\xi = 0, 1.$$

We note that the transverse operator $\pounds$ 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 $\phi_0=1$. We define the mixing-cup (velocity weighted) and spatial average concentrations by

$$C_m=\int_0^1 4\xi(1-\xi^2)C(\xi,z,t)d\xi, \tag{3.4a}$$

$$\langle C\rangle=\int_0^1 2\xi C(\xi,z,t)d\xi. \tag{3.4b}$$

Transverse averaging of (3.3) gives

$$\frac{\partial\langle C\rangle}{\partial t}+\frac{\partial C_m}{\partial z}=0. \tag{3.5}$$

We note that when $Pe=0$, $\langle C\rangle=C_m$, and substitution of this into (3.5) gives the leading order evolution equation for the averaged concentration. Writing

$$C(\xi,z,t)=\langle C\rangle(z,t)+W(\xi,z,t),\qquad W\in\ker\ \pounds, \tag{3.6}$$

we can solve for the slave variable $W(\xi,z,t)$ in terms of $\langle C\rangle(z,t)$ using a perturbation expansion in Pe (and the Fredholm alternative):

$$\pounds W-Pe\left[\frac{\partial W}{\partial t}+2\left(1-\xi^2\right)\frac{\partial W}{\partial z}\right]=Pe\left[\frac{\partial\langle C\rangle}{\partial t}+2\left(1-\xi^2\right)\frac{\partial\langle C\rangle}{\partial z}\right], \tag{3.7a}$$

$$\frac{\partial W}{\partial\xi}=0@\xi=0,1. \tag{3.7b}$$

To leading order, we have

$$W(\xi,z,t)=Pe\frac{\partial\langle C\rangle}{\partial t}\left[\frac{1}{12}-\frac{\xi^2}{4}+\frac{\xi^4}{8}\right]+O(Pe^2). \tag{3.8}$$

Substitution of this into (3.6) and transverse averaging (after multiplying by the velocity profile) gives the local equation relating C_m and $\langle C\rangle$:

$$C_m-\langle C\rangle=\frac{Pe}{48}\frac{\partial\langle C\rangle}{\partial t}+O(Pe^2)=\frac{Pe}{48}\frac{\partial C_m}{\partial t}+O(Pe^2). \tag{3.9}$$

As in the packed-bed problem, this local equation (when written in dimensional form) defines a characteristic transfer time between the slowly evolving mode C_m(or $\langle C\rangle$) and the slave mode $C_m-\langle C\rangle$. Equations (3.5) and (3.9) complete the reduced model to leading order. In this form, the reduced model for intraphase diffusion is similar to the two-mode packed-bed model of interphase diffusion. We can combine the two equations to obtain a single equation for either C_m or $\langle C\rangle$. Since the mixing-cup concentration (which is often measured in experiments) is more relevant in applications, the reduced model in terms of C_m in dimensional form is given by

$$\frac{\partial C_m}{\partial t'}+\langle u\rangle\frac{\partial C_m}{\partial z'}+\langle u\rangle\ t_D\frac{\partial^2 C_m}{\partial z'\partial t'}=0,\qquad t'\gg t_D,\ z'\gg\ell_D, \tag{3.10}$$

where the local diffusion or mixing time is defined by

$$t_D = \frac{R^2}{48D}. \tag{3.11}$$

The corresponding length scale and local diffusivity are given by $\ell_D = \langle u \rangle \, t_D$, $D_{eff} = \langle u \rangle^2 t_D$. As noted earlier, in the Taylor dispersion literature, (3.10) is written as a parabolic equation with an effective dispersion coefficient D_{eff}, which requires an artificial boundary condition at the exit of the tube (Roberts (1992)). Below we present a solution of (3.10) for general inlet and initial conditions and show that it can describe dispersion for long times as well as the parabolic model. However, unlike the classical parabolic equation over an infinite domain, (3.10) can accommodate an inlet boundary condition. Once again, since (3.10) defines a characteristic initial value problem, to complete the model, we need to specify C_m only along the characteristic curves $z' = 0$ and $t' = 0$. Thus, the initial and boundary conditions for the reduced model are obtained by taking the mixing-cup averages of (13.c) and (13.d):

$$C_m(z', t' = 0) = \int_0^1 4\xi(1 - \xi^2) \; f(z', R\xi) d\xi \equiv f_m(z'), \tag{3.12a}$$

$$C_m(z' = 0, t') = \int_0^1 4\xi(1 - \xi^2) \; g(R\xi, t') d\xi \equiv g_m(t'). \tag{3.12b}$$

Equations (3.10) and (3.12) complete the hyperbolic model to order Pe. As in the packed-bed example, the perturbation expansion can be carried out to higher orders, and it can be shown that it converges, provided $t_D \omega_t' < 0.858$ and $\ell_D \omega_z' < 0.288$, where $\omega_t'(\omega_z')$ is the temporal (spatial) frequency contained in the inlet or initial conditions. (For details, see Chakraborty and Balakotaiah (2002), Balakotaiah and Chang (1995), and Mercer and Roberts (1990).)

The above analysis can be extended to the general case in which axial diffusion is included in (13.a). In this case, the reduced model may be shown to be

$$\frac{\partial \langle C \rangle}{\partial t'} + \langle u \rangle \frac{\partial C_m}{\partial z'} = D \frac{\partial^2 \langle C \rangle}{\partial z'^2}, \tag{3.13a}$$

$$\langle C \rangle - C_m = - \, t_D \frac{\partial \langle C \rangle}{\partial t'}. \tag{3.13b}$$

We can combine these equations to obtain a single hyperbolic equation for $\langle C \rangle$:

$$\frac{\partial \langle C \rangle}{\partial t'} + \langle u \rangle \frac{\partial \langle C \rangle}{\partial z'} + \langle u \rangle \; t_D \frac{\partial^2 \langle C \rangle}{\partial z' \partial t'} = D \frac{\partial^2 \langle C \rangle}{\partial z'^2}. \tag{3.14}$$

(We note that C_m or any other weighted average concentration also satisfies the same equation (3.14). This is due to the fact that the original conservation equation is linear in the concentration.) We note that when $D \ll \langle u \rangle^2 \; t_D$, or equivalently, the radial Peclet number $p = \frac{\langle u \rangle \, R}{D} \gg 6.93$, axial diffusion can be neglected. (Note that the perturbation Peclet number Pe, which is equal to p times the aspect ratio $\left(\frac{R}{L}\right)$, can be small even when $p \gg 6.93$, provided that the aspect ratio is sufficiently small. The conditions $p \gg 6.93$ and $Pe \ll 1$ are usually satisfied for well-designed reactors or chromatographic columns.)

3.1. Solution of the hyperbolic model. In this section, we present the solution of the hyperbolic model defined by (3.10) and (3.12) and compare these solutions to those of the classical parabolic model. We use the local time and length scales to nondimensionalize the variables and write the hyperbolic model in the following form:

$$\frac{\partial C_m}{\partial t} + \frac{\partial C_m}{\partial z} + \frac{\partial^2 C_m}{\partial z \partial t} = 0, \qquad t \gg 1,\ z \gg 1, \tag{3.15a}$$

$$C_m(z, t = 0) = f(z), \tag{3.15b}$$

$$C_m(z = 0, t) = g(t). \tag{3.15c}$$

(With this scaling, the reciprocal of the nondimensional time is the Peclet number.) The substitution

$$C_m = W \exp(-z - t) \tag{3.16a}$$

reduces (3.15a) to the canonical form

$$\frac{\partial^2 W}{\partial z \partial t} - W = 0. \tag{3.16b}$$

The fundamental solution (Riemann function) of (3.16b) is given by (see Garabedian (1964))

$$W_g(z, t, \xi, \eta) = I_0\left(2\sqrt{(z-\xi)(t-\eta)}\right), \tag{3.16c}$$

where I_0 is the modified Bessel function of order zero. Using this fundamental solution, we may express the solution of (3.15) as

$$\begin{aligned} C_m(z,t) = e^{-z-t} \Bigg\{ & c_0 I_0(2\sqrt{zt}) + \int_0^z \frac{dF(\xi)}{d\xi} I_0\left(2\sqrt{t(z-\xi)}\right) d\xi \\ & + \int_0^t \frac{dG(\eta)}{d\eta} I_0\left(2\sqrt{z(t-\eta)}\right) d\eta \Bigg\}, \end{aligned} \tag{3.17a}$$

where

$$F(z) = e^z f(z), \tag{3.17b}$$

$$G(t) = e^t g(t), \tag{3.17c}$$

$$c_0 = \frac{f(0) + g(0)}{2}. \tag{3.17d}$$

Below, we use this analytical solution to show that the solution of the hyperbolic model, (3.15a)–(3.15c), remains positive for arbitrary but positive inlet and initial conditions. We also compare the solutions of the hyperbolic model with those of the parabolic model for some special cases.

3.2. Positivity of the solutions to the hyperbolic model. We note that (3.15) as well as the general solution given by (3.17) have the permutational symmetry in z and t; i.e., they are invariant to the transformation $(z, t, f) \to (t, z, g)$. Thus, to prove the positivity of the solution of (3.15), it is sufficient to consider the case of $g(t) = 0$ and $f(z) \neq 0$. Now, for the special case of $f(z) = \delta(z - z_0)$ and $g(t) = 0$, the general solution given by (3.17) simplifies to

$$C_{mg}(z, z_0, t) = \begin{cases} I_1\left(2\sqrt{t(z-z_0)}\right) e^{z_0 - z - t}\sqrt{\frac{t}{z-z_0}}, & z > z_0, \\ 0, & z < z_0. \end{cases} \tag{3.18}$$

Since this Green's function is positive, the solution given by (3.17) remains positive for all positive inlet and initial conditions. In fact, an alternate form of the analytical solution to (3.15) makes this obvious:

$$C_m(z,t) = \begin{cases} \int_0^z I_1\left(2\sqrt{t(z-z_0)}\right) e^{z_0-z-t}\sqrt{\frac{t}{z-z_0}} f(z_0)dz_0 \\ \qquad + \int_0^t I_1\left(2\sqrt{z(t-t_0)}\right) e^{t_0-t-z}\sqrt{\frac{z}{t-t_0}} g(t_0)dt_0, & z > 0,\ t > 0, \\ 0, & z < 0 \text{ or } t < 0. \end{cases} \tag{3.19}$$

3.3. Comparison of the dispersion curves for parabolic and hyperbolic models. As stated earlier, it is of interest to determine how the solution of the hyperbolic model differs from that of the parabolic models used in the literature to describe solutal dispersion in nonreacting systems. In the engineering literature, the solution of the averaged model to a unit impulse (Delta function) input is known as the dispersion curve. For the parabolic model, this is the standard Gaussian curve given by

$$E_p(z,t) = \frac{1}{\sqrt{4\pi t}} \exp\left\{-\frac{(z-t)^2}{4t}\right\}. \tag{3.20}$$

Thus, the parabolic model predicts a peak in the dispersion curve at $z = t$ and a variance that increases linearly with time. The dispersion curve for the hyperbolic model is obtained by taking $z_0 = 0$ in (3.18):

$$E_h(z,t) = \begin{cases} e^{-z-t}\sqrt{\frac{t}{z}} I_1(2\sqrt{tz}), & z > 0, \\ 0, & z < 0. \end{cases} \tag{3.21}$$

Examination of this curve shows that it has a peak at $z = 0$ for $t \leq 2$. This is consistent with physical observation that, for short times, transverse diffusion has not acted on the initial delta function input and hence the peak should be at the injection point. For $t \gg 1$, (3.21) may be written as

$$E_h(z,t) \approx \left(\frac{t}{z}\right)^{\frac{3}{4}} \frac{1}{\sqrt{4\pi t}} \exp\left\{-\frac{(z-t)^2}{(\sqrt{t}+\sqrt{z})^2}\right\}. \tag{3.22}$$

Thus, the dispersion curves predicted by the two models are close to each other near $t = z$ (and $t \gg 1$), but the hyperbolic model predicts an asymmetric curve with a slightly higher peak at $z = t - \frac{3}{2}$. In addition, as noted earlier, the parabolic model predicts upstream diffusion (since $E_p(z,t)$ is not zero for $z < 0$) and infinite propagation speed. Neither of these nonphysical phenomena is present in the hyperbolic

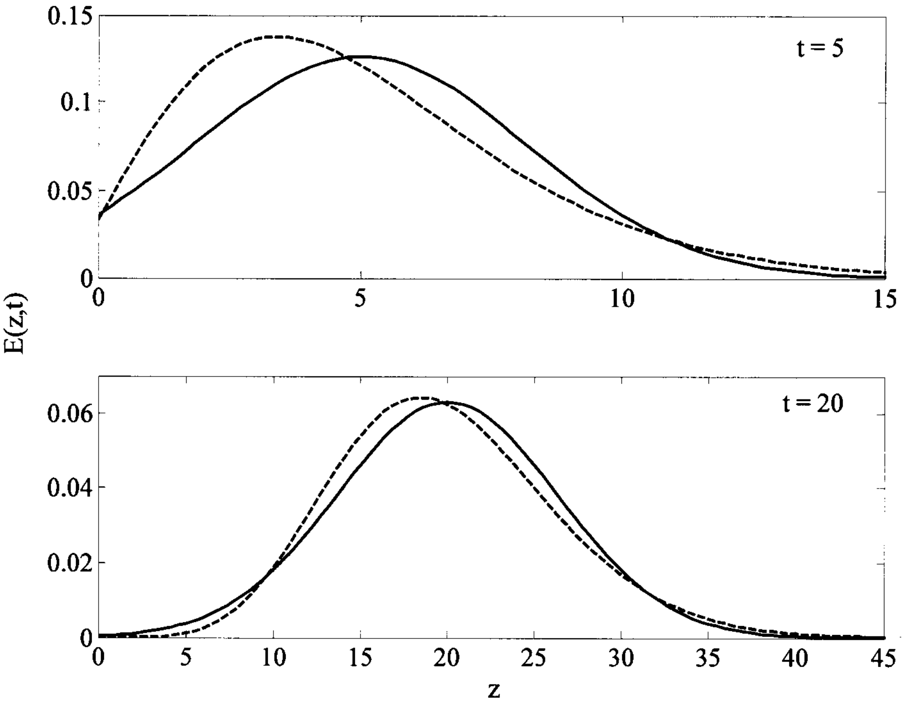

FIG. 3. *Comparison of the dispersion curves predicted by the parabolic and hyperbolic models at $t = 5$ and 20. The symmetric curve with peak at $t = z$ is for the parabolic model, while the asymmetric curve with peak at $z \approx t - \frac{3}{2}$ is for the hyperbolic model.*

model. Figure 3 compares the two solutions at two different times, $t = 5$ and $t = 20$. While the two curves are extraordinarily close for large times, they intersect three times (for all $t > 4.84$), and the dispersion curve predicted by the hyperbolic model has a nonzero skewness at all finite times. We note that this skewness can also be predicted by the parabolic-type models as done by Chatwin (1970), but higher order terms (like $\frac{\partial^3 C_m}{\partial z^3}$) have to be included in the perturbation expansion. The hyperbolic model captures the asymmetry at the lowest order.

4. General thermal/solutal dispersion theory. We now extend the theory to the general case of a multiphase system in which the individual phases may be stationary or moving and the capacitance varies with transverse coordinates; i.e., dispersion is due to combined inter- and intraphase mechanisms. We assume a long reactor with weak longitudinal variation of temperature or concentration (due to the small aspect ratio) and strong longitudinal (laminar) flow $w(x, y)$. We retain only transverse molecular solutal or thermal diffusion in x and y. Conversely, only longitudinal convection is appreciable to balance transverse diffusion. The general governing equation for the reactor temperature or concentration in dimensionless form is then

$$F(\theta, Pe) \equiv \frac{1}{\rho c_p}\nabla \cdot k\nabla\theta - Pe\left(\frac{\partial\theta}{\partial t} + w\frac{\partial\theta}{\partial z}\right) = 0, \tag{4.1}$$

where the ∇ operator is only for the transverse direction $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, 0)^T$ and both the dimensionless conductivity k and the heat or solutal capacity ρc_p are functions of the transverse coordinates x and y within the transverse cross section Ω. The Peclet number in (4.1) is again defined as the ratio of the transverse diffusion or local exchange time ($\frac{R^2}{\alpha_0}$) to the convection time ($\frac{L}{u_0}$). (We note here that the thermal conductivity, heat capacitance per unit volume, and the velocity are nondimensionalized using some reference values k_0, $(\rho c_p)_0$, and u_0, which can be chosen conveniently for each application. Here, $Pe = \frac{R^2 u_0}{L\alpha_0}$, where $\alpha_0 = \frac{k_0}{(\rho c_p)_0}$.) When $\rho c_p = 1$ is uniform throughout Ω, the transport problem (4.1) reduces to mass transport with uniform capacitance. However, the solutal diffusivity can vary from phase to phase and is hence a function of (x, y). Similarly, the transport coefficients w and k do not have to be constant within each phase but can vary continuously with respect to (x, y).

Equation (4.1) must be solved in the transverse direction with continuity in θ and $k\frac{\partial\theta}{\partial n}$ at the phase boundaries. We shall also impose a no-flux boundary condition at the transverse reactor boundary $\partial\Omega$,

$$\left.\frac{\partial\theta}{\partial n}\right|_{\partial\Omega} = 0. \tag{4.2}$$

It is then clear that, at $Pe = 0$, a particular solution to (4.1) is $\theta = \langle\theta\rangle$, the capacitance-weighted transverse average of θ, independent of the transverse coordinates x and y. We then seek correction to $\langle\theta\rangle$ for small Pe. To leading order, one obtains the linear operator in Ω,

$$D_\theta F(\langle\theta\rangle, 0) \cdot v = \frac{1}{\rho c_p}\nabla \cdot k\nabla v \equiv \pounds v, \tag{4.3}$$

with Neumann boundary conditions on the outer boundary $\partial\Omega$, $\frac{\partial v}{\partial n}|_{\partial\Omega} = 0$. This transverse diffusion operator contains a transverse-dependent conductivity k and capacitance ρc_p that change from phase to phase. The operator is self-adjoint with respect to the inner product

$$[u, v] = \frac{1}{\Omega_{cp}}\int_\Omega \rho c_p \; u \; v \; d\Omega, \tag{4.4a}$$

$$\Omega_{cp} = \int_\Omega \rho c_p \; d\Omega. \tag{4.4b}$$

It has a zero eigenvalue with a constant null eigenfunction ϕ_0, which can be chosen as unity. The other eigenfunctions $\phi_n(x, y)$ all have zero integral (transverse average) from a simple application of divergence theorem to $\pounds\phi_n = -\lambda_n\phi_n$ with the Neumann boundary condition to $\partial\Omega$:

$$[\phi_n, \phi_0] = \langle\phi_n\rangle = \frac{1}{\Omega_{cp}}\int_\Omega \rho c_p \phi_n d\Omega = 0. \tag{4.5}$$

(We point out that (4.5) defines the capacitance-weighted transverse average of any function. We also define $\langle\rho c_p\rangle = \Omega_{cp}/\,|\Omega|$.)

We expand θ in terms of $\{\phi_n\}_{n=0}^{\infty}$,

$$\theta = \langle\theta\rangle + \theta'(x, y, z, t), \tag{4.6}$$

where $\langle\theta\rangle$ represents the null eigenfunction ϕ_0 component without (x, y)-dependence, while $\theta' \perp \ker\pounds$ represents the complement spanned by the other eigenfunctions.

Since $\pounds$ is self-adjoint with respect to the Hilbert inner product and $\theta' \perp \ker \pounds$, we have

$$\langle \theta' \rangle = 0. \tag{4.7}$$

In the terminology of bifurcation theory, the equation satisfied by $\langle \theta \rangle$ is the so-called branching equation at a simple zero eigenvalue. (In the engineering literature, this is often referred to as the homogenized equation, reduced model, averaged equation, pseudohomogeneous model, etc.) This reduced equation can be obtained by applying the implicit function theorem to eliminate θ' from the equation $EF(\langle \theta \rangle + \theta', Pe) = 0$. (Here, E is the projection operator onto *range* $\pounds$.) This Lyapunov–Schmidt reduction can be done by expanding θ' in terms of the small parameter Pe and solving a linear equation at each order by using the Fredholm alternative. Writing

$$\theta' = Pe\theta_1 + Pe^2\theta_2 + \cdots , \tag{4.8}$$

the leading order equation is given by

$$\pounds\theta_1 - \left(\frac{\partial \langle \theta \rangle}{\partial t} + w \frac{\partial \langle \theta \rangle}{\partial z} \right) = 0. \tag{4.9}$$

Before we solve for θ' in terms of $\langle \theta \rangle$ to obtain the reduced model, we invoke a unique relationship between the capacitance-weighted average $\langle \theta \rangle$ and the mixing-cup average defined by

$$\theta_m = \frac{1}{\Omega_{cp}} \int_\Omega \rho c_p \; w \; \theta \; d\Omega = \frac{[w\theta, \phi_0]}{[w, \phi_0]} = \frac{\langle w\theta \rangle}{\langle w \rangle}, \tag{4.10a}$$

where $\langle w \rangle$ is the capacitance-weighted average dimensionless velocity, i.e.,

$$\langle w \rangle = \frac{1}{\Omega_{cp}} \int_\Omega \rho c_p \; w \; d\Omega. \tag{4.10b}$$

We note that, only in the degenerate case in which w is uniform over Ω, $\theta_m = \langle \theta \rangle$. In all other cases, $\theta_m \neq \langle \theta \rangle$. Integrating (4.1) over the transverse cross-section Ω and invoking the Neumann condition (4.2), one obtains

$$\frac{\partial \langle \theta \rangle}{\partial t} + \langle w \rangle \frac{\partial \theta_m}{\partial z} = 0. \tag{4.11}$$

This relationship is exact and is valid for all orders in Pe. A second relation between $\langle \theta \rangle$ and θ_m may be obtained by multiplying (4.6) by w and taking the inner product with the null eigenfunction ϕ_0:

$$\theta_m = \langle \theta \rangle + Pe \frac{[w\theta_1, \phi_0]}{\langle w \rangle} + O(Pe^2). \tag{4.12}$$

Thus, to leading order, the mixing-cup and capacitance-weighted average temperatures are equal, and the evolution equation (4.11) for $\langle \theta \rangle$ reduces to

$$\frac{\partial \langle \theta \rangle}{\partial t} + \langle w \rangle \frac{\partial \langle \theta \rangle}{\partial z} + O(Pe) = 0. \tag{4.13}$$

To obtain the evolution equation to order Pe, we insert (4.13) into (4.9) and define η as

$$\theta_1 \sim \eta \frac{\partial \langle \theta \rangle}{\partial z} \tag{4.14}$$

to reduce (4.9) to the following convenient form:

$$\pounds \eta = w - \langle w \rangle , \tag{4.15a}$$

with no-flux condition at $\partial\Omega$

$$\left.\frac{\partial \eta}{\partial n}\right|_{\partial\Omega} = 0 \tag{4.15b}$$

and the usual continuity of η and $k\frac{d\eta}{dn}$ at the phase boundaries within Ω. Substitution of (4.14) into (4.11) and (4.12) gives the reduced model

$$\frac{\partial \theta_m}{\partial t} + \langle w \rangle \frac{\partial \theta_m}{\partial z} + Pe\Lambda \frac{\partial^2 \theta_m}{\partial z \partial t} = 0, \tag{4.16}$$

where the numerical coefficient Λ is given by

$$\Lambda = - \frac{[w\eta, \phi_0]}{\langle w \rangle} = - \frac{\langle w\eta \rangle}{\langle w \rangle}. \tag{4.17}$$

In dimensional form, (4.16) becomes

$$\frac{\partial \theta_m}{\partial t'} + \langle u \rangle \frac{\partial \theta_m}{\partial z} + \ell_H \frac{\partial^2 \theta_m}{\partial z' \partial t'} = 0, \tag{4.18}$$

where $\langle u \rangle$ is the capacitance-weighted average velocity and the effective local length scale ℓ_H is defined by

$$\ell_H = \Lambda \frac{R^2 u_0}{\alpha_0}. \tag{4.19}$$

The corresponding time scale and the dimensional effective dispersion coefficient are given by $t_H = \frac{\ell_H}{\langle u \rangle}$ and $\alpha_{eff} = \frac{\ell_H^2}{t_H} = \Lambda \frac{R^2 u_0 \langle u \rangle}{\alpha_0}$, respectively. Again, we note that (4.18) is valid only for $t' \gg t_H$ and $z' \gg \ell_H$. Dispersion can still occur for $0 < t' < t_H$ or $0 < z' < \ell_H$ or even when w is uniform in Ω. However, in these higher order cases, the expansion must be carried to higher orders in Pe so that the averaged model can capture this early dispersion. Similarly, as pointed out by Mercer and Roberts (1990) and Young and Jones (1991), early dispersion effects due to point sources or sinks can be captured at order Pe^2 and higher. We shall not discuss these higher order special cases here as they are not very common in reactors and are also specific to each problem.

The initial and boundary conditions for the general equation (4.18) may be derived in the same manner as for the two specific examples illustrated earlier. We now consider the local equation and various special cases of thermal and solutal dispersion.

4.1. The local equation. As noted above, the local equation (4.15) must be solved before we can determine the numerical coefficient Λ and hence the effective local length or time scales. It is clear that the inhomogeneous term on the right-hand side of (4.15a) satisfies the solvability condition for the singular operator. Also, since $\eta \perp \ker \pounds$,

$$\langle \eta \rangle = 0, \tag{4.20}$$

which can be used to solve for η uniquely.

Multiplying (4.15a) by η, taking the inner product with the null eigenfunction, and using (4.20), one obtains

$$\begin{aligned} \Lambda &= -[\eta w, \phi_0] \\ &= -[\eta \pounds \eta, \phi_0] \\ &= -\tfrac{1}{\Omega_{cp}} \textstyle\int_\Omega \eta \nabla \cdot k \nabla \eta \; d\Omega. \end{aligned} \tag{4.21}$$

Using (4.15b) and the divergence theorem (integration by parts), (4.21) then yields

$$\Lambda = \frac{1}{\Omega_{cp}} \int_\Omega k \nabla \eta \cdot \nabla \eta \; d\Omega, \tag{4.22}$$

which is always positive. This quadratic form for Λ is more convenient for some of our derivations and could possibly be used in a variational numerical scheme for η.

In the case of single-phase thermal transport or multiphase solutal transport when ρc_p is uniform throughout Ω, (4.22) simplifies to

$$\Lambda = \frac{1}{|\Omega|} \int_\Omega \alpha \nabla \eta \cdot \nabla \eta \; d\Omega, \tag{4.23}$$

where α is the dimensionless local diffusivity. If, in addition, α is independent of the transverse coordinates (x, y) and is normalized to unity, then Λ depends on only the velocity profile and the geometry of Ω. This clearly shows that, for the single-phase limit and for uniform-capacitance solutal transport, dispersion occurs when a transverse gradient in the longitudinal velocity exists.

The interphase dispersion seen in the packed-bed example arises from the different thermal or capacitance-weighted velocities of each phase and hence contributes to dispersion even if the longitudinal velocity w_j is gradientless within each phase j. This limit is particularly interesting, as the local equation has the following algebraic form for each phase Ω_j in Ω:

$$\sum_j A_{ij} \; \eta_j = (w_i - \langle w \rangle), \tag{4.24a}$$

where A is the matrix defining the coupling between the phases. The numerical coefficient Λ takes the simple and explicit form

$$\Lambda = \frac{\sum_j w_j \eta_j \left(\rho c_p\right)_j \; \epsilon_j}{\sum_j \left(\rho c_p\right)_j \; \epsilon_j}, \tag{4.24b}$$

where ϵ_i is the volume fraction of phase i. For the two-phase example of section 2, with A defined by (2.3b) and $w_1 = 1, w_2 = 0$, we have

$$\begin{aligned} \eta &= \frac{\epsilon_f (1-\epsilon_f)\Gamma}{\left[\epsilon_f + (1-\epsilon_f)\Gamma\right]^2} \begin{pmatrix} -(1-\epsilon_f)\Gamma \\ \epsilon_f \end{pmatrix}, \\ \Lambda &= \frac{-w_1 \eta_1 \epsilon_f}{\left[\epsilon_f + (1-\epsilon_f)\Gamma\right]} = \frac{\epsilon_f^2 (1-\epsilon_f)^2 \Gamma^2}{\left[\epsilon_f + (1-\epsilon_f)\Gamma\right]^3}. \end{aligned} \tag{4.25}$$

This interphase dispersion mechanism arises as solutal or heat "molecules" are transported to different phases through transverse thermal random walks. Once arrived, molecules at each phase are caused to propagate longitudinally by different thermal or capacitance-weighted velocities. The proportion of molecules in each phase is determined by the local diffusivity and the size of Ω_i. Hence, the capacitance-weighted longitudinal phase thermal velocities (as defined by (4.24)) simply yield the thermal dispersion.

4.2. Thermal/solutal dispersion with diffusion into the wall. We next examine thermal and solutal dispersion in a cylindrical pipe of radius R with a solid wall of thickness λR ($\lambda > 0$); see Figure 2. The diffusivity in the wall (α_s) is assumed to be distinct from that in the fluid phase. Here, we take the pipe radius (R), the average fluid velocity ($\langle u_f \rangle$), the fluid heat capacitance $(\rho c_p)_f$, and fluid thermal diffusivity (α_f) to nondimensionalize the variables. The velocity field is now

$$w(\xi) = \begin{cases} 2\left[1-\xi^2\right] & \text{in} \quad \Omega_f,\ 0 < \xi < 1, \\ 0 & \text{in} \ \ \Omega_s,\ 1 < \xi < 1+\lambda, \end{cases} \tag{4.26}$$

with

$$\langle w \rangle = \frac{\epsilon_f}{\epsilon_f + \Gamma(1-\epsilon_f)},$$

$$\epsilon_f = \frac{1}{(1+\lambda)^2}.$$

The local equation is now

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \eta_f}{\partial \xi}\right) = w - \langle w \rangle \quad \text{in } \Omega_f, \tag{4.27a}$$

$$\frac{1}{\mu}\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \eta_s}{\partial \xi}\right) = w - \langle w \rangle \quad \text{in } \Omega_s, \tag{4.27b}$$

with boundary conditions

$$\frac{\partial \eta_f}{\partial \xi} = 0, \qquad \xi = 0, \tag{4.28a}$$

$$\frac{\partial \eta_s}{\partial \xi} = 0, \qquad \xi = (1+\lambda), \tag{4.28b}$$

$$\eta_f = \eta_s, \qquad \xi = 1, \tag{4.28c}$$

$$\frac{\Gamma}{\mu}\frac{\partial \eta_s}{\partial \xi} = \frac{\partial \eta_f}{\partial \xi}, \quad \xi = 1, \tag{4.28d}$$

where $\mu = \alpha_f/\alpha_s$ is the ratio between the diffusivities.

Some algebraic manipulation immediately yields

$$\eta_f = \left\{ \frac{1}{2}\xi^2 - \frac{1}{8}\xi^4 - \frac{\langle w\rangle}{4}\xi^2 + s_f \right\}, \tag{4.29a}$$

$$s_f = -\frac{5}{24}\epsilon_f - \frac{3}{8}(1-\epsilon_f) - \langle w\rangle \left\{ (\mu - 1)\frac{(1-\epsilon_f)}{4} - \frac{\epsilon_f}{8} + \frac{\mu}{2} f(\epsilon_f) \right\}, \tag{4.29b}$$

$$f(\epsilon_f) = \frac{\epsilon_f^2 + 2\epsilon_f - 3 - 2ln\epsilon_f}{4\epsilon_f}, \tag{4.29c}$$

$$\eta_s = \left(\frac{\mu}{2}\right) \langle w\rangle \left\{ (1+\lambda)^2 \ln(\xi) - \frac{1}{2}\xi^2 + s_s \right\}, \tag{4.29d}$$

$$s_s = \frac{1}{2} + \frac{s_f + \frac{3}{8} - \frac{1}{4}\langle w\rangle}{\frac{\mu}{2}\langle w\rangle}. \tag{4.29e}$$

Substituting into (4.17), we obtain

$$\Lambda = \frac{\beta_1 \epsilon_f}{\epsilon_f + \Gamma(1-\epsilon_f)} + \frac{(\Gamma - 1)\beta_2 \epsilon_f^2 (1-\epsilon_f)}{[\epsilon_f + \Gamma(1-\epsilon_f)]^2}, \tag{4.30}$$

$$\begin{aligned} \beta_1 = {} & \frac{11 - 8\epsilon_f}{48} + \left(\frac{\epsilon_f}{\epsilon_f + \Gamma(1-\epsilon_f)} \right) \left(\frac{6\epsilon_f - 8}{48} \right) \\ & + \frac{\mu}{4} \left(\frac{\epsilon_f}{\epsilon_f + \Gamma(1-\epsilon_f)} \right) (2f(\epsilon_f) + 1 - \epsilon_f), \end{aligned} \tag{4.31a}$$

$$\beta_2 = \frac{1}{6} + \frac{-\epsilon_f(1-\epsilon_f) + \mu(4\epsilon_f - \epsilon_f^2 - 3 - 2ln\epsilon_f)}{8(1-\epsilon_f)(\epsilon_f + \Gamma(1-\epsilon_f))}. \tag{4.31b}$$

Several limits are of interest. As $\epsilon_f \to 1$, we obtain Taylor's result $\Lambda = \frac{1}{48}$ for solutal dispersion. In the limit of $\Gamma(1-\epsilon_f) \gg \epsilon_f$, for intermediate ϵ_f values away from unity we obtain

$$\Lambda = \frac{\alpha_{eff}}{p^2 \alpha_f} = \frac{11}{48} \frac{\epsilon_f}{\Gamma(1-\epsilon_f)}, \tag{4.32}$$

where $p = \langle u_f\rangle R/\alpha_f$ is the transverse Peclet number. The coefficient 11/48 is also consistent with Leighton and Chang (1995), using the lumped-phase approach. (Note that $\frac{48}{11}$ is the asymptotic Nusselt number, Nu_∞, for laminar flow in a tube with a constant flux boundary condition on the tube wall.) In Figure 4 we plot the product of Γ and the normalized dispersion coefficient Λ given by (4.30) for Γ values of 100 and 1000, with μ varying from 10^{-1} to 10^2. It is obvious that all of them are independent of μ and collapse nicely into the specific scaling of (4.32) except near $\epsilon_f = 1$, where (4.32) is singular. Thus, the high-Γ limit yields a scaling that is insensitive to geometric and

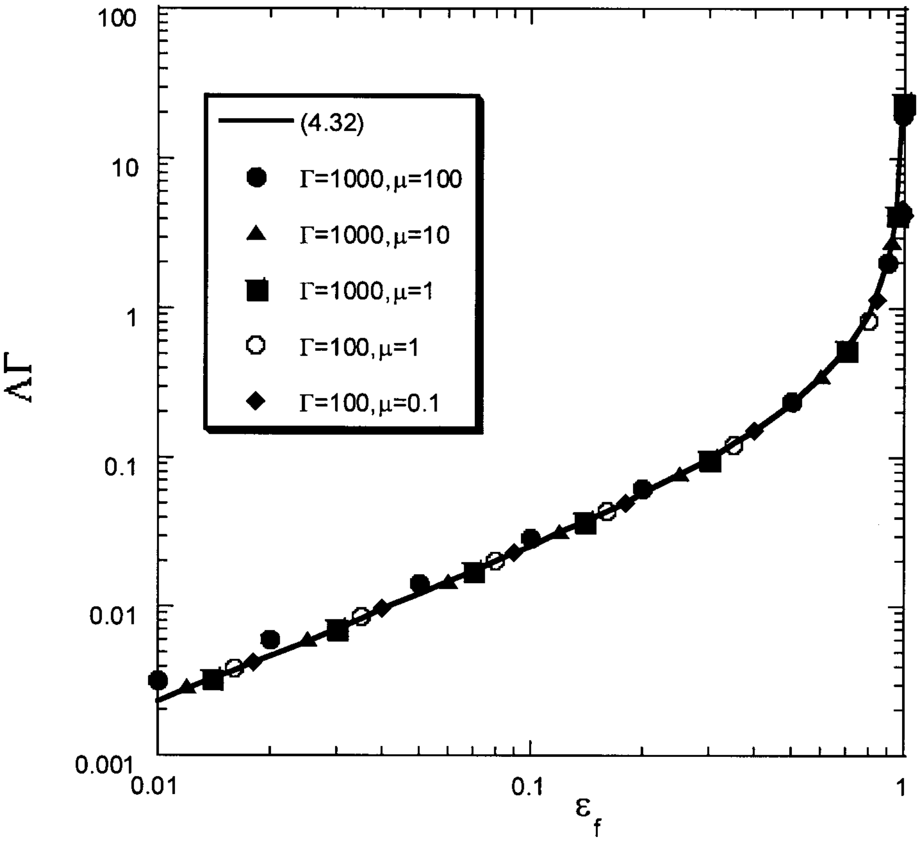

FIG. 4. *High-Γ dispersion for various values of diffusivity (μ) and capacitance ratio (Γ). The curves for various μ and Γ collapse nicely into the μ-independent limit of* (4.32).

flow details and is independent of α_s. The dispersion is small in this limit at $O(\Gamma^{-1})$ and increases sharply with ϵ_f.

For $\epsilon_f \ll 1$ and Γ of unit order, one can deduce from (4.30) that the flowfield-sensitive intraphase term with the β_1 coefficient dominates over the other interphase term. A simple calculation then yields

$$\frac{\alpha_{eff}}{p^2\alpha_f} = \left(\frac{\mu}{4\Gamma^2}\right)\epsilon_f \ln\left(\frac{1}{\epsilon_f}\right), \tag{4.33}$$

with a different Γ scaling from (4.32).

For ϵ_f close to unity, the interphase term becomes equally important as the intraphase term. The high effective dispersion near $\Gamma(1-\epsilon_f) \sim \epsilon_f$ is verified in Table 1, where we have used (4.30) to determine the optimum ϵ_f for various μ and Γ values. Figure 5 shows a plot of the maximum value of the normalized dispersion coefficient that can be obtained for the optimum volume fraction ϵ_f of the low capacitance phase. All these curves approach an asymptotic value for $\Gamma > 10$. This asymptote may be found from (4.30) in the limit of $\Gamma \gg 1$ and $\delta = \Gamma(1-\epsilon_f)$ finite. This simplification

TABLE 1

Optimum fraction of the low capacitance phase at which the dispersion coefficient is maximum.

Γ		$\varepsilon_{\max}$	
	$\mu = 0.1$	$\mu = 1$	$\mu = 10$
1	0.45	0.31	0.16
2	0.63	0.59	0.30
5	0.81	0.81	0.74
10	0.90	0.90	0.89
20	0.95	0.95	0.94
50	0.98	0.98	0.98

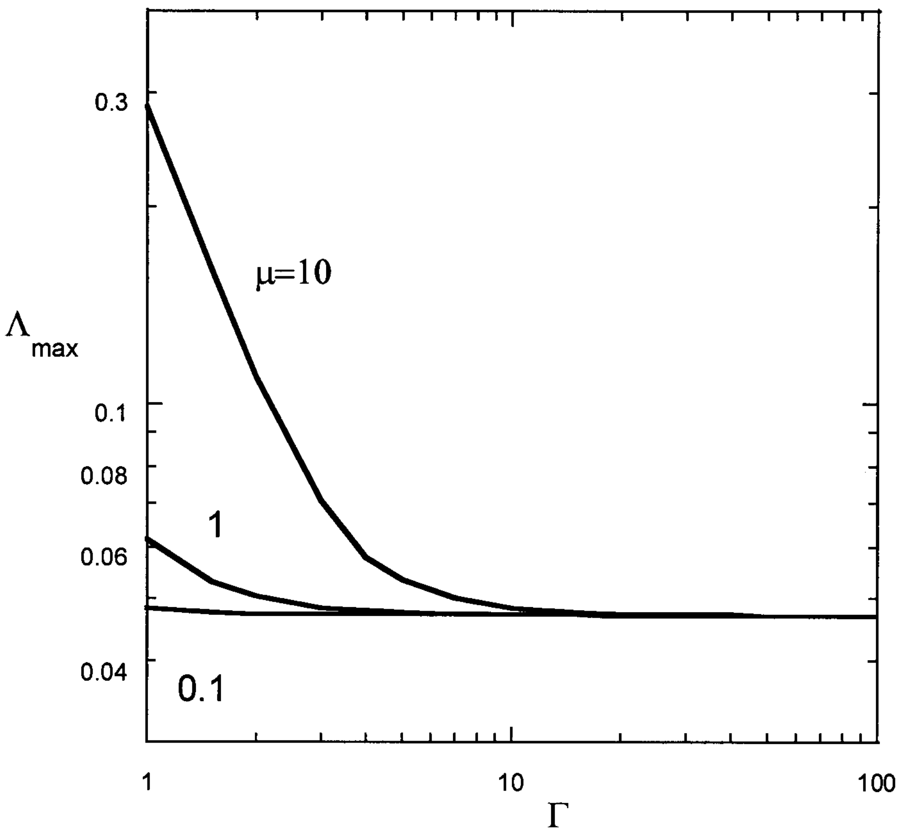

FIG. 5. *Maximum dispersion coefficient obtained at an optimum ϵ_f as a function of Γ for various μ values.*

gives

$$\Lambda = \frac{1 + 6\delta + 11\delta^2}{48(1+\delta)^3}. \tag{4.34}$$

This is the expression derived by Golay (1958) for capillary chromatography with a retentive layer. It follows from (4.34) that $\Lambda_{\max} = 0.047$ at $\delta = 1.15$. As is evident from Figure 5, the optimum normalized dispersion $\Lambda_{\max}$ relative to ϵ_f becomes independent of Γ and μ for Γ beyond 10, as is consistent with (4.30). However, this optimum dispersion is highest for Γ below 10, near unit order Γ. Hence, the largest dispersion occurs near unit order Γ with a dispersion magnitude that is 3 to 4 times the high Γ limit. Unfortunately, we cannot use the lumped model approach with heat transfer coefficients for these high dispersion reactors. Their dispersion coefficient is highly sensitive to flow distribution/packing, in contrast to the generic limit at high Γ.

Finally, we consider the case of $\Gamma = 1$, which corresponds to the solutal dispersion in a pipe and into the porous wall or particles as in a catalytic monolith or packed-bed reactor, respectively. Here, the phases have equal capacities and, as reasoned above, D_{eff} should be sensitive to details in geometry and flow. For $\Gamma = 1$, (4.30) simplifies to

$$\Lambda = \frac{1}{48} g_1(\epsilon_f) + \frac{\mu}{8} g_2(\epsilon_f), \tag{4.35a}$$

$$\begin{aligned} g_1(\epsilon_f) &= \epsilon_f (6\epsilon_f^2 - 16\epsilon_f + 11), \\ g_2(\epsilon_f) &= \epsilon_f (4\epsilon_f - \epsilon_f^2 - 3 - 2\ln(\epsilon_f)). \end{aligned} \tag{4.35b}$$

We note that the function $g_1(\epsilon_f)$ has a maximum value of 2.26 at $\epsilon_f = 0.465$, while $g_2(\epsilon_f)$ has a maximum value of 0.206 at $\epsilon_f = 0.15$. As μ increases from 0 to ∞, the optimum ϵ_f decreases from 0.465 to 0.206. This is verified in Figure 6, where we have plotted Λ as a function of ϵ_f for different μ values. As expected, Λ is sensitive to both μ and ϵ_f.

5. Reactive and steady dispersion. It is clear from (4.18) that, at steady state, the mixing-cup temperature θ_m remains constant along the reactor—dispersion disappears at steady state. However, steady dispersion can exist under reactive conditions. As transverse diffusion and a longitudinal velocity gradient can produce transient longitudinal dispersion, steady reactive conversion differences across streamlines due to the transverse velocity gradient can also trigger transverse steady diffusive flux. The latter can, in turn, alter the overall conversion and produce an apparent steady dispersion. We shall examine this case here for the simplest scalar case—a single step irreversible reaction for solutal transport or a zeroth order reaction (with excess reactants) for thermal transport valid under thermal ignition conditions (Zeldovich et al. (1985)). Equation (4.1) can then be modified to

$$F(\theta, Pe) \equiv \frac{1}{\rho c_p} \nabla \cdot k \nabla \theta - Pe \left(\frac{\partial \theta}{\partial t} + w \frac{\partial \theta}{\partial z} \right) - Pe K f(\theta) = 0, \tag{5.1}$$

where the Damköhler number $K(x, y, z, t)$ reflects the different activity in different phases (e.g., due to varying catalytic activity caused by nonuniform distribution of the catalytic agent and catalyst decay in time), and the nonlinear function $f(\theta)$ captures the temperature or concentration dependence of the reaction rate. (Note also that, unlike the previous cases, $F(\theta, Pe)$ is now nonlinear in θ.) Both $K(x, y, z, t)$ and $f(\theta)$ are of unit order with respect to Pe. The function $f(\theta)$ can be positive or negative, corresponding to solutal/thermal consumption or generation, respectively.

With this scaling, the transverse diffusion operator $\pounds$ remains the dominant linear operator. Moreover, the decomposition into a capacitance-weighted transverse average $\langle \theta \rangle$ and a θ' component, with $\langle \theta' \rangle = 0$, remains valid. However, the overall transverse balance now becomes

$$\frac{\partial \langle \theta \rangle}{\partial t} + \langle w \rangle \frac{\partial \theta_m}{\partial z} + \langle K f(\theta) \rangle = 0. \tag{5.2}$$

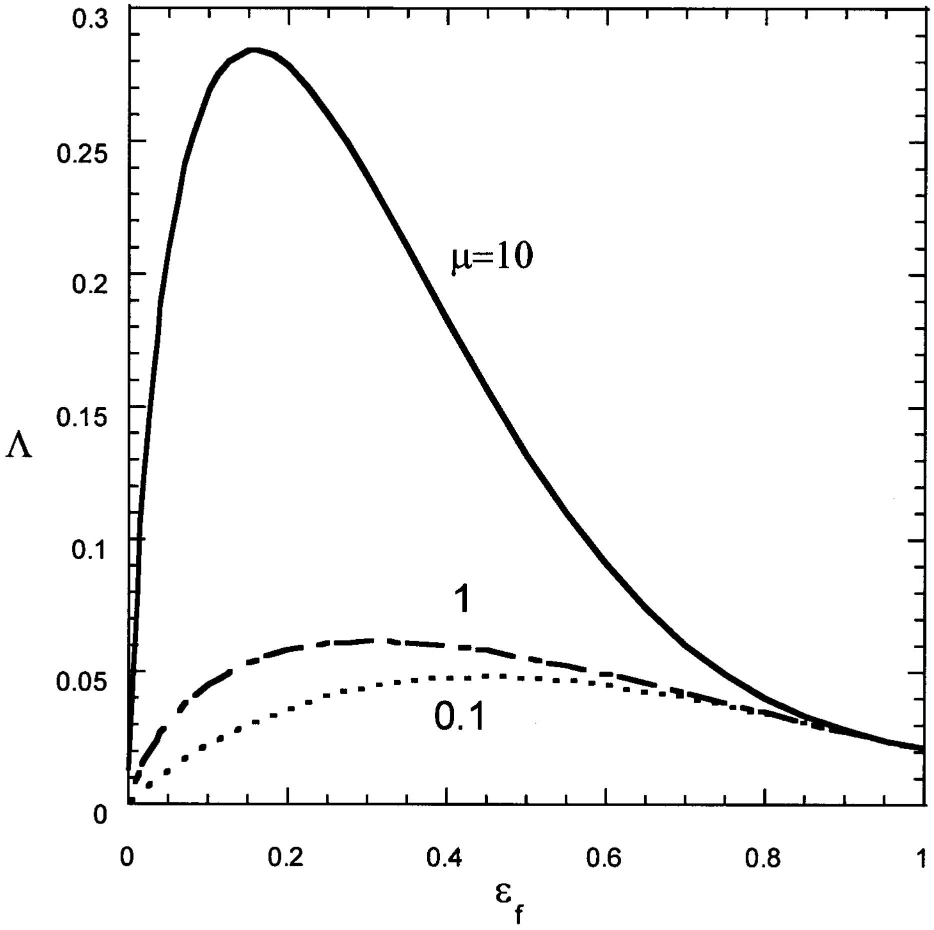

FIG. 6. *Unit order* Γ *dispersion as a function of* ϵ_f *for various* μ *values.*

To leading order, (5.2) reduces to

$$\frac{\partial \langle \theta \rangle}{\partial t} + \langle w \rangle \frac{\partial \langle \theta \rangle}{\partial z} + \langle K \rangle f(\langle \theta \rangle) + O(Pe) = 0. \tag{5.3}$$

The equation for θ' then becomes, to leading order in Pe,

$$\pounds\ \theta' = Pe(w - \langle w \rangle) \frac{\partial \langle \theta \rangle}{\partial z} + Pe(K - \langle K \rangle) f(\langle \theta \rangle). \tag{5.4}$$

We then require the decomposition of θ' into two components

$$\theta' = Pe \left[\eta \frac{\partial \langle \theta \rangle}{\partial z} + \chi f(\langle \theta \rangle) \right] + O(Pe^2); \tag{5.5}$$

the first term containing η is the transient dispersion contribution considered earlier. The reactive (source or sink) contribution is captured by χ as defined by

$$\pounds\ \chi = K - \langle K \rangle , \tag{5.6}$$

where $\langle\chi\rangle = 0$ as for η. The other boundary conditions are $\frac{\partial\chi}{\partial n} = 0$ on $\partial\Omega$ and continuity of χ and $k\frac{\partial\chi}{\partial n}$ across the phase boundaries $\partial\Omega_i$.

The homogenized model then becomes

$$\text{(5.7a)}\quad \frac{\partial\langle\theta\rangle}{\partial t} + \langle w\rangle \frac{\partial\theta_m}{\partial z} + \langle K\rangle f(\langle\theta\rangle) + Pe\ f'(\langle\theta\rangle)\left(\delta\frac{\partial\langle\theta\rangle}{\partial z} + \kappa f(\langle\theta\rangle)\right) = 0,$$

$$\text{(5.7b)}\quad \theta_m = \langle\theta\rangle - Pe\left[\Lambda\frac{\partial\langle\theta\rangle}{\partial z} + \gamma f(\langle\theta\rangle)\right],$$

where Λ is defined earlier by (4.17) and the new constants are

$$\gamma = -\frac{\langle w\chi\rangle}{\langle w\rangle}, \qquad \delta = \langle K\eta\rangle, \qquad \kappa = \langle K\chi\rangle.$$

We can combine (5.7a) and (5.7b) into a single equation for either $\langle\theta\rangle$ or θ_m. However, the coefficients that appear in the resulting equation are no longer constants but depend on the source function. As in the nonreactive case, representing the dispersion terms as second derivatives in z and interpretation of their coefficients as Taylor dispersion coefficients leads to further conceptual difficulties (in addition to the upstream diffusion, infinite propagation speed anomalies, and extra boundary or initial condition needed). Now, the capacitance-weighted average velocity and the dispersion coefficient are no longer constants but depend on the source function and its derivative. (They can be negative and hence lose their physical meaning!) Our approach based on the local length or times scales is still applicable here, the only difference being the additional length or time scales that appear due to the source or sink terms. Thus, in this case, it is preferable to leave the model in the two-mode form, the two modes being the mixing-cup and capacitance-weighted average temperature or concentration. The model is still hyperbolic as in the nonreactive case and reduces to (4.16) when the Damköhler number $K \equiv 0$. The initial and boundary conditions on (5.7) may also be derived in the same manner as in the nonreactive case.

We note that the reduced model now contains four effective local constants that are of the same order of magnitude. It can be seen that the two terms in (5.7b) (containing the constants Λ and γ) represent dispersion effects due to velocity gradients, while the two terms in (5.7a) (containing the constants δ and κ) represent dispersion effects due to a nonuniform reaction rate. The three new terms with coefficients γ, δ, and κ represent reactive dispersion effects (commonly known as mixing effects in the engineering literature), where as the nonreactive term with coefficient Λ may be interpreted as the traditional velocity gradient-induced dispersion. (This term may be interpreted as the so-called micromixing effect; see Chakraborty and Balakotaiah (2002) for more details.) We now examine various special cases.

The first case we consider is that in which $f(\theta)$ is a constant (say, $f(\theta) = -1$). This corresponds to the nonreactive situation, with a source term added to the classical Taylor problem or the thermal dispersion problem. For this case, three of the source-induced dispersion terms vanish, and (5.7) reduces to

$$\text{(5.8)}\quad \frac{\partial\theta_m}{\partial t} + \langle w\rangle\frac{\partial\theta_m}{\partial z} + \Lambda Pe\frac{\partial^2\theta_m}{\partial z\partial t} = \langle K\rangle.$$

Thus, the addition of a slowly varying source term simply adds its capacitance-weighted transverse average to the reduced model.

Next, we consider the case in which the Damköhler number K is constant (independent of transverse coordinates and time). Again, the three constants γ, δ, and κ vanish, and the model reduces to

$$\frac{\partial \theta_m}{\partial t} + \langle w \rangle \frac{\partial \theta_m}{\partial z} + \Lambda Pe \frac{\partial^2 \theta_m}{\partial z \partial t} = K\ f\left(\theta_m + \Lambda Pe \frac{\partial \theta_m}{\partial z}\right). \tag{5.9}$$

In this case, in addition to the transient dispersion term, we also have a source correction term, and the reduced model is different from the standard models used in the literature. These earlier literature models were obtained by just adding the source term to the nonreactive reduced model. Such models are clearly invalid as they exclude the correction term which appears in (5.9). (This was first noted by Balakotaiah and Dommeti (1999) using lumped resistance models. This correction term is also missing in the averaged models of Westerterp, Dilman, and Kronberg (1995) and Westerterp et al. (1995) using a heuristic approach.)

The third case we consider is that of a two-phase system in which the low capacitance fluid phase is moving and the solid phase is stationary. We also assume that $K = 0$ in the fluid phase and $K = 1$ in the solid phase. (This is a generalization of the packed-bed model with heat generation in the solid phase.) For this case, it may be seen that $\gamma > 0$, $\kappa > 0$, and $\delta < 0$. If $f'(\langle \theta \rangle) > 0$ (exothermic reaction), this corresponds to a decrease in the capacitance-weighted average velocity and an increase in the source strength in the reduced model.

The last case we consider is that of steady-state dispersion under reactive conditions. Now, since K is independent of t and since the time derivative in (5.2) is zero, we redo the Liapunov–Schmidt reduction. The reduced model is now given by the pair of equations

$$\langle w \rangle \frac{d\theta_m}{dz} + \langle K \rangle f(\langle \theta \rangle) + Pe\ \langle K\chi \rangle f'(\langle \theta \rangle) f(\langle \theta \rangle) = 0, \tag{5.10a}$$

$$\theta_m = \langle \theta \rangle + Pe\ \frac{\langle w\chi \rangle}{\langle w \rangle} f(\langle \theta \rangle), \tag{5.10b}$$

where χ is distinct from the transient version (5.6) and is now defined by

$$\pounds \chi = K - \frac{w}{\langle w \rangle} \langle K \rangle, \tag{5.11a}$$

$$\frac{\partial \chi}{\partial n} = 0 \qquad \text{on } \partial\Omega. \tag{5.11b}$$

The boundary condition to be used on (5.10) is

$$\theta = \theta_{m0} \qquad \text{at } z = 0. \tag{5.12}$$

The reduced model is a differential-algebraic system, and there is no second derivative term. (We note that the reduced model is not an initial value problem in z! For the case of an exothermic reaction, it is an index infinity differential-algebraic system and can have multiple (in fact, an infinite number of) solutions whenever the local equation (5.10b) has multiple solutions. This can happen when the kinetics is autocatalytic. For more details, see Chakraborty and Balakotaiah (2002).) The steady-state reactive correction/dispersion term $-\langle w\chi\rangle$ is different from the transient reactive and nonreactive dispersion coefficient $-\langle w\eta\rangle$. For the special case of uniform activity (K is independent of transverse coordinates) it is easily seen that

$$\chi = -\frac{K}{\langle w\rangle}\eta, \tag{5.13}$$

where η is as defined in the nonreactive case. For this special case, the steady-state model (5.10) simplifies to

$$\langle w\rangle \frac{d\theta_m}{dz} + K\ f(\langle\theta\rangle) = 0, \tag{5.14a}$$

$$\theta_m = \langle\theta\rangle - \ Pe\frac{K\Lambda}{\langle w\rangle^2} f(\langle\theta\rangle), \tag{5.14b}$$

with initial/boundary condition (5.12). This reduced model is very different from the standard pseudohomogeneous model with Danckwerts boundary conditions. We note that while the numerical coefficient Λ that appears in the above steady-state model is the same as that in the Taylor's transient solutal dispersion problem, there is also a correction to the source term containing the same coefficient (see also (5.9)). In addition, it should be emphasized again that the reduced model is a differential-algebraic system rather than a two-point boundary value problem as in the following classical Danckwerts model:

$$\Lambda\frac{d^2\theta_m}{dz^2} - \langle w\rangle \frac{d\theta_m}{dz} - K\ f(\theta_m) = 0, \tag{5.15a}$$

$$\langle w\rangle\, \theta_{m0} = \langle w\rangle\, \theta_m \ - \Lambda\ \frac{d\theta_m}{dz} \qquad \text{at } z = 0, \tag{5.15b}$$

$$\frac{d\theta_m}{dz} = 0 \qquad \text{at } z = L. \tag{5.15c}$$

In this model, the exit boundary condition (5.15c) is imposed rather than derived from the original two-dimensional model.

6. Discussion. We have shown in this work that dispersion caused by transverse gradients can be described by reduced models that are hyperbolic in the longitudinal coordinate and time and that contain an effective local length or time scale. Our method also overcomes the main deficiencies of the previous approaches to averaging based on the moments method and the center manifold theorem. The former is applicable only to linear problems, while the latter describes the asymptotic behavior close to a fixed point (such as a trivial solution $\theta(x, y, z, t) = 0$). In contrast, our method is based on expansion around a state $\langle\theta\rangle(z, t)$ that is only independent of the transverse coordinates and can be applied to both steady-state and transient problems.

We have presented here the averaged models to only the lowest order in Pe. However, the extension to obtain higher order averaged models is straightforward. For example, for the solutal/thermal dispersion problem, it is easily seen that the reduced model to all orders (in Pe or t_H) is of the form

$$\frac{\partial\langle\theta\rangle}{\partial t'} + \langle u\rangle \frac{\partial\theta_m}{\partial z'} = 0, \tag{6.1a}$$

$$\langle \theta \rangle - \theta_m + \sum_{i=1}^{\infty} \beta_i (t_H)^i \frac{\partial^i \langle \theta \rangle}{\partial t^i} = 0, \tag{6.1b}$$

where t_H is the local time scale and β_i are numerical constants that depend on the velocity profile $w(x, y)$ and the geometry of Ω. Appropriate inlet and initial conditions may also be derived for (6.1).

The present approach may also be extended in many ways. Instead of the no-flux outer wall, we can allow an isothermal wall or a mixed boundary condition with a wall heat transfer coefficient. In such cases, the operator $\pounds$ is no longer singular and $\langle \theta \rangle$ does not strictly correspond to the null eigenfunction. However, if the transverse gradient remains small (and $\pounds$ has a discrete spectrum), the invariant manifold approach of Roberts (1989) and Balakotaiah and Chang (1995) can be used to extend the Lyapunov–Schmidt technique presented here.

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