Chemically Reactive Generalized Taylor Dispersion Phenomena

Generalized Taylor dispersion theory for nonreactive solutes (Brenner 1980a; 1982) undergoing convection and diffusion is extended to include irreversible first-order volumetric and surface chemical reactions possessing position-dependent reactivity coefficients at the microscale. For sufficiently long times the equivalent chemical kinetic description of the rate of solute depletion at the macroscale is shown to manifest itself as a single constant reactivity coefficient $\bar{K}^*$ characterizing an apparent first-order irreversible volumetric reaction. Subtraction of this gross solute depletion rate from the original microscale transport equation permits the resulting Taylor dispersionlike problem to be resolved by a solution scheme closely paralleling that for the comparable nonreactive case. This allows a straightforward determination of the mean global solute velocity vector $\bar{\boldsymbol{U}}^*$ and dispersivity dyadic $\bar{\mathbf{D}}^*$ appearing in the macroscale convection-diffusion-reaction equation describing the local-space averaged mean transport process. By way of example, these three coefficients are explicitly calculated for reacting and diffusing solute particles sedimenting from a solvent flow occurring between two parallel plates onto the reactive surface of one of these plates.

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Introduction

The problem of solute dispersion accompanying fluid flow and molecular diffusion in capillary tubes was originally solved for passive (i.e., neutrally buoyant and chemically inert) solutes (Taylor, 1953, 1954; Aris, 1956) in the "long-time" limit. Within the last fifteen years much work has been done to include a first-order irreversible reaction occurring on the tube surface; Aris (1980) provides a review. As in the original works of Taylor (1953, 1954), the objectives of these investigations were to effect a purely axial, i.e. cross-sectionally averaged, description of the chemically reactive system, in which the area-averaged solute concentration is governed by an asymptotically long-time dispersion model characterized by effective axial transport phenomenological coefficients. In addition to the usual mean solute velocity $\bar{U}^*$ and dispersivity $\bar{D}^*$, these now also included a mean volumetric reactivity coefficient $\bar{K}^*$ characterizing the asymptotic long-time diminution via chemical reaction of the total amount of solute present.

Sankarasubramanian and Gill (1973) were the first to formulate a pertinent cross-sectional eigenfunction expansion for the irreversible first-order wall reaction problem. The three global phenomenological coefficients arising from their analysis were expressed in terms of infinite sets of cross-sectional eigenfunctions and eigenvalues. This approach was further developed by DeGance and Johns (1978a, b; 1980) who generalized it to cylinders of arbitrary cross-sectional geometry. They introduced a cross-sectionally weighted average solute concentration, demonstrating that the three asymptotically long-time effective axial transport coefficients were independent of the choice of the weight function. The leading eigenfunction was shown to be the mathematically preferred weight function for effecting the cross-sectional averaging, in the sense that the resulting short-time effective axial transport coefficients thereby achieved their simplest representations.

Barton (1984) applied Aris' (1956) method of moments scheme to this same problem, obtaining identical asymptotically long-time results. For large dimensionless times he proposed a direct asymptotic expansion (of the local solute concentration) of the type used by Chatwin (1970) for the nonreactive case.

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Other studies investigated dispersion accompanied by simultaneous surface reaction, adsorption, and desorption (Boddington and Clifford, 1983), as well as dispersion in multicomponent systems (DeGance and Johns, 1985; Wang and Stewart, 1982; Hatton and Lightfoot, 1984a, b).

The asymptotic long-time Taylor dispersion model with time-independent transport coefficients is valid for times much longer than the characteristic time scale t_s characterizing the cross-sectional-space solute transport process. This time t_s is, however, much smaller than the characteristic time t_L associated with the solute transport process parallel to the cylinder axis. Nevertheless, many studies have focused on short-time dispersion models, i.e., those valid for times comparable with t_s. Sankarasubramanian and Gill (1973), DeGance and Johns (1978a, b) and Barton (1984) developed such models, thereby obtaining time-dependent effective axial transport coefficients. Sankarasubramanian and Gill and DeGance and Johns further included higher order axial derivatives in their dispersion approximations. Smith (1983) proposed a different treatment, describing the short-time axial solute transport by a delay-diffusion equation with constant phenomenological coefficients and a time-dependent integral term, retaining memory of the initial stages of the dispersion process.

These short-time dispersion models are not independent of the initial solute spatial distribution. In contrast, the present contribution deals with an asymptotically long-time classical Taylor dispersion model that possesses this property of independence.

Recently, Shapiro and Brenner (1986) generalized convective-diffusive-reactive Taylor dispersion phenomena occurring in unidirectional, rectilinear duct flows to comparable reactive solute transport in more general curvilinear local (bounded) and global (unbounded) domains. They also included external forces exerted upon solute molecules, as well as both surface and volumetric first-order irreversible reactions. In the absence of local-space convective transport, the pertinent local-space eigenvalue problem that results is self-adjoint, thus assuring completeness of the local-space eigenfunctions in terms of which the global transport coefficients may be expressed. However, when local-space convection is present, this self-adjointness property disappears, whereupon the validity of such eigenfunction expansions cannot generally be substantiated. This is especially true for the dispersion of chemically reactive species in porous media (Shapiro and Brenner, 1987), where the convective solute transport cannot generally be decomposed into separate local and global contributions.

The present study is thus aimed at developing a solution scheme that resolves the general problem treated by Shapiro and Brenner (1986), but which—in contrast—does not hinge upon assuming the set of local-space eigenfunctions to be complete. Without thus utilizing the method of eigenfunction expansions, our subsequent treatment will closely parallel the generalized Taylor dispersion analysis for the comparable nonreactive case (Brenner, 1982). By way of example, the general scheme developed here will later be applied to study the Brownian motion and sedimentation of reactive solute particles from the flow between two parallel plates onto one of the plate surfaces, upon which the reaction actually occurs.

Problem Formulation

With subscript r denoting reaction, we begin with the equation (Shapiro and Brenner, 1986) for the transport and temporal evolution of the solute tracer's conditional probability density $P_r(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}')$ in the form

$$\frac{\partial P_r}{\partial t} + \nabla_Q \cdot \boldsymbol{J}_r + \nabla_q \cdot \boldsymbol{j}_r = -K(\boldsymbol{q})P_r + \delta(\boldsymbol{Q})\delta(\boldsymbol{q} - \boldsymbol{q}')\delta(t) \quad (1)$$

with local-space ($\boldsymbol{j}_r$) and global-space ($\boldsymbol{J}_r$) fluxes given respectively by

$$\boldsymbol{j}_r = \boldsymbol{\mathcal{J}} P_r \quad (2)$$

$$\boldsymbol{J}_r = \boldsymbol{U}(\boldsymbol{q})P_r - \mathbf{D}(\boldsymbol{q}) \cdot \nabla_Q P_r \quad (3)$$

and $\boldsymbol{\mathcal{J}}$ a vector-valued $\boldsymbol{q}$-space partial differential operator (functionally dependent only upon $\boldsymbol{q}$) defined such that

$$\boldsymbol{\mathcal{J}}\xi = \boldsymbol{u}(\boldsymbol{q})\xi - e^{-E(\boldsymbol{q})}\mathbf{d}(\boldsymbol{q}) \cdot \nabla_q(e^{E(\boldsymbol{q})}\xi) \quad (4)$$

for any function ξ of arbitrary tensorial order.

Boundary conditions imposed are, respectively,

$$\boldsymbol{n} \cdot \boldsymbol{j}_r = kP_r \quad \text{on } \partial \boldsymbol{q}_o \quad (5)$$

on the local-space boundaries $\partial \boldsymbol{q}_o$ (with $\boldsymbol{n}$ the unit outer normal vector), and

$$|\boldsymbol{Q}|^m\{P_r, \boldsymbol{J}_r\} \rightarrow \{0, \boldsymbol{0}\} \quad \text{as } |\boldsymbol{Q}| \rightarrow \infty \quad (m = 0, 1, 2, \ldots) \quad (6)$$

on the infinitely extended global-space boundary $\partial \boldsymbol{Q}_\infty$. The respective volumetric and surface reactivity coefficients $K(\boldsymbol{q})$ and $k(\boldsymbol{s})$ are assumed to be nonnegative in their respective domains, i.e.

$$K(\boldsymbol{q}) \geq 0 \quad \text{in } \boldsymbol{q}_o \quad (7a)$$

$$k(\boldsymbol{s}) \geq 0 \quad \text{on } \partial \boldsymbol{q}_o \quad (7b)$$

where $\boldsymbol{s}$ is a point lying on the surface $\partial \boldsymbol{q}_o$ bounding $\boldsymbol{q}_o$ space. The nonnegativity of the volumetric and surface reactivities assures that solute will be depleted rather than produced by the reaction (cf. Eq. 11).

The problem in Eqs. 1–6 constitutes a well-posed mathematical problem, which may in principle be solved for P_r for prescribed values of the local- and global-space velocities $\boldsymbol{u}(\boldsymbol{q})$, $\boldsymbol{U}(\boldsymbol{q})$ and molecular diffusivities $\mathbf{d}(\boldsymbol{q})$, $\mathbf{D}(\boldsymbol{q})$, respectively, local-space external force potential $E(\boldsymbol{q})$, and kinetic coefficients $K(\boldsymbol{q})$ and $k(\boldsymbol{s})$. We are, however, not interested in the exhaustive pointwise description furnished by P_r, but rather in the less-detailed averaged conditional probability density

$$\overline{P}_r = \int_{\boldsymbol{q}_o} P_r(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}')\, d\boldsymbol{q} \quad (8)$$

Moreover, it is not $\overline{P}_r$ itself that lies at the focus of our attention, but rather the global-space phenomenological coefficients appearing in the macrotransport equation (Shapiro and Brenner, 1986)

$$\frac{\partial \overline{P}_r}{\partial t} + \overline{\boldsymbol{U}}^* \cdot \nabla_Q \overline{P}_r - \overline{\mathbf{D}}^*:\nabla_Q\nabla_Q \overline{P}_r + \overline{K}^* \overline{P}_r = 0 \quad (9)$$

governing its temporal and spatial evolution. Physically, these three coefficients represent the mean solute velocity vector $\bar{\boldsymbol{U}}^*$ (which is not generally the same as the mean fluid velocity vector $\bar{\boldsymbol{V}}$), the dispersivity dyadic $\bar{\mathbf{D}}^*$, and the mean volumetric reactivity coefficient $\bar{K}^*$.

Define the total moments

$$M_{rm}(t|\boldsymbol{q}') = \int_{Q_\infty} d\boldsymbol{Q}\,\boldsymbol{Q}^m \int_{q_o} P_r(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}')\,d\boldsymbol{q} \quad (m = 0, 1, 2, \ldots) \tag{10}$$

of the probability density P_r. Integrate both sides of Eq. 1 over $\boldsymbol{q}_o \oplus \boldsymbol{Q}_\infty$ space, and use the local- and global-space divergence theorems along with the boundary conditions of Eqs. 5 and 6 to obtain the equation

$$\frac{dM_{r0}}{dt} = -\int_{Q_\infty} d\boldsymbol{Q}\left(\int_{q_o} KP_r\,d\boldsymbol{q} + \int_{\partial q_o} kP_r\,ds\right) \tag{11}$$

governing the temporal evolution of the conditional survival probability $M_{r0}(t|\boldsymbol{q}')$, i.e., the probability of finding the tracer particle anywhere within the domain $\boldsymbol{q}_o \oplus \boldsymbol{Q}_\infty$ at time t, given its original introduction into the system at the point $(\boldsymbol{0}, \boldsymbol{q}')$. Since the righthand side of Eq. 11 entails nonnegative integrands, it follows that M_{r0} decays monotonically with time due to the irreversible bulk and surface reactions that deplete the solute. This behavior is in marked contrast with that of nonreactive systems (where $K = k = 0$), for which M_{r0} represents a conserved property.

Method of Moments

The problem posed in Eqs. 1–6 will be solved by the method of moments. Prior to solution, introduce the modified conditional probability density

$$P(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}') \overset{\text{def.}}{=} \frac{\exp(\bar{K}t)}{A(\boldsymbol{q}')} P_r(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}') \tag{12}$$

where the constant $\bar{K}$ and nonnegative function $A(\boldsymbol{q}')$ will be chosen later. Explicitly, we propose to determine $\bar{K}$ such that the correspondingly modified form M_0' (cf. Eq. 18) of the total survival probability M_{r0} will eventually attain a constant nonzero value for asymptotically long times. P is easily shown to satisfy the transport equation

$$\frac{\partial P}{\partial t} + \nabla_q \cdot \boldsymbol{j} + \nabla_Q \cdot \boldsymbol{J} = [\bar{K} - K(\boldsymbol{q})]P + \frac{1}{A(\boldsymbol{q}')}\delta(\boldsymbol{Q})\delta(\boldsymbol{q} - \boldsymbol{q}')\delta(t) \tag{13}$$

with fluxes $\boldsymbol{j}$ and $\boldsymbol{J}$ given by

$$\{\boldsymbol{j}, \boldsymbol{J}\} = \frac{\exp(\bar{K}t)}{A(\boldsymbol{q}')}\{\boldsymbol{j}_r, \boldsymbol{J}_r\} \tag{14}$$

subject to the respective local- and global-space boundary conditions

$$\boldsymbol{n} \cdot \boldsymbol{j} = kP \quad \text{on } \partial\boldsymbol{q}_o \tag{15}$$

$$|\boldsymbol{Q}|^m\{P, \boldsymbol{J}\} \to \{0, \boldsymbol{0}\} \quad \text{as } |\boldsymbol{Q}| \to \infty \quad (m = 0, 1, 2, \ldots) \tag{16}$$

similar to Eqs. 5 and 6.

Physically, the transformation in Eq. 12 represents a superimposed first-order volumetric reaction with constant coefficient $\bar{K} \geq 0$ (by means of which solute is produced), so chosen as to globally balance the solute depletion arising from the prescribed surface and volumetric reactions, at least for asymptotically long times. Introduction of a $\boldsymbol{q}'$-dependent function into Eq. 12 reflects the fact that the average (reactive) probability density $\bar{P}_r$ will generally depend upon the initial tracer location $\boldsymbol{q}'$ within the local space, even for asymptotically long times. Indeed, if the tracer starts its chaotic trajectory from a point $\boldsymbol{q}'$ where the reactivity coefficient $K(\boldsymbol{q}')$ is relatively large, its long-time survival probability will be significantly less than in the converse case where the tracer was initially introduced into a region of small reactivity.

Define the local polyadic moments of the probability density P as

$$\boldsymbol{P}_m(\boldsymbol{q}, t|\boldsymbol{q}') \doteq \int_{Q_\infty} \boldsymbol{Q}^m P(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}')\,d\boldsymbol{Q} \tag{17}$$

($m = 0, 1, 2, \ldots$), along with comparable total polyadic moments

$$\boldsymbol{M}'_m(t|\boldsymbol{q}') = \int_{q_o} \boldsymbol{P}_m(\boldsymbol{q}, t|\boldsymbol{q}')\,d\boldsymbol{q} \tag{18}$$

In addition to Eq. 18 it will prove useful to define the modified total moments

$$\boldsymbol{M}_m(t|\boldsymbol{q}') = \int_{q_o} \boldsymbol{P}_m(\boldsymbol{q}, t|\boldsymbol{q}')\,A(\boldsymbol{q})\,d\boldsymbol{q} \tag{19}$$

with $A(\boldsymbol{q})$ the weight function appearing in Eq. 12.

Equations governing the spatial and temporal transport of the local moments $\boldsymbol{P}_m$ are obtained upon multiplication of both sides of Eqs. 13 and 15 by $\boldsymbol{Q}^m d\boldsymbol{Q}$ followed by their integration over global space, $\boldsymbol{Q}_\infty$. Subsequent use of the global-space divergence theorem, together with the boundary conditions of Eq. 16, eventually yields

$$\frac{\partial \boldsymbol{P}_m}{\partial t} + \nabla_q \cdot (\boldsymbol{\mathcal{J}}\boldsymbol{P}_m) - [\bar{K} - K(\boldsymbol{q})]\boldsymbol{P}_m = \boldsymbol{\Gamma}_m + \frac{1}{A(\boldsymbol{q}')}\delta_{m0}\delta(\boldsymbol{q} - \boldsymbol{q}')\delta(t) \quad \text{in } \boldsymbol{q}_o \tag{20}$$

$$\boldsymbol{n} \cdot \boldsymbol{\mathcal{J}}\boldsymbol{P}_m = k\boldsymbol{P}_m \quad \text{on } \partial\boldsymbol{q}_o \tag{21}$$

in which the polyadics $\boldsymbol{\Gamma}_m(\boldsymbol{q}, t|\boldsymbol{q}')$ are (Brenner, 1980a; Shapiro and Brenner, 1986)

$$\boldsymbol{\Gamma}_0 = 0 \tag{22a}$$

$$\boldsymbol{\Gamma}_1 = \boldsymbol{U}P_0 \tag{22b}$$

$$\boldsymbol{\Gamma}_2 = 2\,\text{sym}\,(\mathbf{D}P_0 + \boldsymbol{U}\boldsymbol{P}_1), \text{etc.} \tag{22c}$$

Zero-order moments

Consider the problem posed for P_0, rewritten in the form

$$\frac{\partial P_0}{\partial t} - \mathcal{L}P_0 = \frac{1}{A(\boldsymbol{q}')}\delta(\boldsymbol{q} - \boldsymbol{q}')\delta(t) \quad \text{in } \boldsymbol{q}_o \tag{23}$$

$$\boldsymbol{n} \cdot \boldsymbol{\mathcal{D}}P_0 = kP_0 \quad \text{on } \partial\boldsymbol{q}_o \tag{24}$$

with the scalar partial differential operator $\mathcal{L}$ (functionally dependent only upon $\boldsymbol{q}$) given by

$$\mathcal{L} \overset{\text{def.}}{=} -\nabla_q \cdot \boldsymbol{\mathcal{D}} + (\overline{K} - K) \tag{25}$$

Similarly to M_{r0}, the total moment M'_0 does not generally represent a conserved entity. In this connection we intend to choose $\overline{K}$ such that M'_0 will attain a time-independent, nonzero steady-state value as $t \rightarrow \infty$. However, M'_0 chosen in this way will not generally be time-independent at earlier times. We will further choose the as yet unknown function $A(\boldsymbol{q})$ in such a manner that the modified zero-order moment M_0 given by Eq. 19 will be conserved for all times, thus establishing a conserved property for linear reactive systems of the type of Eqs. 1–6. Toward this goal, multiply Eq. 23 by $A(\boldsymbol{q})d\boldsymbol{q}$, integrate both sides of the resulting equation over $\boldsymbol{q}_o$ space, and use the local-space divergence theorem together with the boundary conditions of Eq. 24 to eventually obtain

$$\frac{dM_0}{dt} + \int_{\partial\boldsymbol{q}_o} (kA + \boldsymbol{n} \cdot \mathbf{d}^{\dagger} \cdot \nabla_q A)P_0\, ds - \int_{\boldsymbol{q}_o} P_0\mathcal{L}^*A\, d\boldsymbol{q} = \delta(t) \tag{26}$$

in which $\mathcal{L}^*$ is the partial differential operator

$$\mathcal{L}^*\xi \overset{\text{def.}}{=} \boldsymbol{u} \cdot \nabla_q\xi - e^{E(\boldsymbol{q})}\nabla_q \cdot (e^{-E(\boldsymbol{q})}\,\mathbf{d} \cdot \nabla_q\xi) + (\overline{K} - K)\xi \tag{27}$$

We shall choose the function $A(\boldsymbol{q})$ to be the solution of the problem

$$\mathcal{L}^*A = 0 \quad \text{in } \boldsymbol{q}_o \tag{28}$$

$$\boldsymbol{n} \cdot \mathbf{d}^{\dagger} \cdot \nabla_q A = -kA \quad \text{on } \partial\boldsymbol{q}_o \tag{29}$$

The problem in Eqs. 28 and 29 is a homogeneous one in which the constant $\overline{K}$ is to be determined concurrently with A. Therefore, by their nature, Eqs. 28 and 29 constitute an eigenvalue problem to be solved for the eigenvalues $\{\overline{K}_n\}$ and corresponding eigenfunctions $\{A_n\}$ ($n = 0, 1, 2, \ldots$). Upon supposing that solutions of Eqs. 28 and 29 exist, such solutions generally form an infinite eigenspectrum (Courant and Hilbert, 1966). However, only the eigenfunction $A_0(\boldsymbol{q})$, which corresponds to the eigenvalue $\overline{K}_0$ possessing the smallest real part, enjoys the property of being nonzero within $\boldsymbol{q}_o$. This leading eigenvalue $\overline{K}_0$ is necessarily real in all physical circumstances (Shapiro and Brenner, 1986, 1987), whence $A_0(\boldsymbol{q})$ may be chosen so as to be nonnegative within $\boldsymbol{q}_o$. This eigensolution A_0 and $\overline{K}_0$ will be identified with the respective quantities $A(\boldsymbol{q}')$ and $\overline{K}$ appearing in Eq. 14. As usual, the function $A(\boldsymbol{q})$ is only determined uniquely to within a constant multiplier, which at this stage we do not yet specify. This choice will be made below.

Upon integration of Eq. 26, the above choice of $A(\boldsymbol{q}) \equiv A_0(\boldsymbol{q})$ and $\overline{K} \equiv \overline{K}_0$ immediately yields

$$M_0 = 1 \quad (t \geq 0) \tag{30}$$

so that the modified total moment M_0 represents a conserved attribute of the reactive system.

The conservation property, Eq. 30, suggests that the problem posed by Eqs. 23 and 24 possess a time-independent, asymptotic solution. This solution, $P_0^\infty(\boldsymbol{q})$, say, physically describes the steady-state situation that arises after allowing the solute tracer particle [whose stochastic trajectory is described by $P(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}')$] to sample all accessible positions within $\boldsymbol{q}_o$ space many times. This asymptotic solution obviously satisfies the steady-state version of Eqs. 23 and 24, namely

$$\mathcal{L}P_0^\infty \equiv -\nabla_q \cdot \boldsymbol{j}_0^\infty + (\overline{K} - K)P_0^\infty = 0 \quad \text{in } \boldsymbol{q}_o \tag{31}$$

$$\boldsymbol{n} \cdot \boldsymbol{j}_0^\infty = kP_0^\infty \quad \text{on } \partial\boldsymbol{q}_o \tag{32}$$

where $\boldsymbol{j}_0^\infty = \boldsymbol{\mathcal{D}}P_0^\infty$ represents the steady-state local-space flux vector eventually attained.

As follows from Eq. 23, P_0 attains its asymptotic form in circumstances for which $t \gg l^2/\|\mathbf{d}\|$, where l is a characteristic $\boldsymbol{q}_o$-space linear dimension (length) and $\|\mathbf{d}\|$ is an appropriately chosen norm of $\mathbf{d}(\boldsymbol{q})$.

Equations 31 and 32 also constitute an eigenvalue problem to be solved concurrently for the unknown function $P_0^\infty(\boldsymbol{q})$ and the $\boldsymbol{q}$-independent constant $\overline{K}$. We shall term this the characteristic (local-space) eigenvalue problem, whereas the problem posed by Eqs. 28 and 29 will be termed the adjoint (local-space) eigenvalue problem. Similarly to the adjoint problem of Eqs. 28 and 29, interest exists only in the one physically real, nonnegative solution $P_0^\infty(\boldsymbol{q})$, which is attainable for the minimal (real) eigenvalue $\overline{K}'_0$, say. We will show that $\overline{K}'_0 = \overline{K}_0$. Indeed, upon multiplying Eq. 28 (with $\overline{K} = \overline{K}_0$) by $P_0^\infty(\boldsymbol{q})$, and Eq. 31 (with $\overline{K} = \overline{K}'_0$) by $A(\boldsymbol{q})$, subsequently integrating each of these over $\boldsymbol{q}_o$ space, and subtracting the resulting equations, one eventually obtains

$$(\overline{K}_0 - \overline{K}'_0) \int_{\boldsymbol{q}_o} P_0^\infty(\boldsymbol{q})A(\boldsymbol{q})\, d\boldsymbol{q} = 0 \tag{33}$$

Since each of the pair of functions $P_0^\infty(\boldsymbol{q})$, $A(\boldsymbol{q})$ is nonnegative for all $\boldsymbol{q}$ in $\boldsymbol{q}_o$, the integral appearing on the lefthand side of Eq. 33 is necessarily nonzero, thereby demonstrating the desired equality, $\overline{K}_0 = \overline{K}'_0$.

To complete the determination of $P_0^\infty(\boldsymbol{q})$ and $A(\boldsymbol{q})$, we will further require satisfaction of the pair of normalization conditions

$$\int_{\boldsymbol{q}_o} P_0^\infty(\boldsymbol{q})\, d\boldsymbol{q} = 1 \tag{34}$$

$$\int_{\boldsymbol{q}_o} P_0^\infty(\boldsymbol{q})A(\boldsymbol{q})\, d\boldsymbol{q} = 1 \tag{35}$$

both of which can obviously be satisfied since each of the two functions P_0^∞ and A has only been uniquely defined to within an arbitrary constant multiplier. Equation 34 resembles the usual normalization condition imposed upon the nonreactive probability density (Brenner, 1980a, 1982). Summarizing the above, we observe that Eqs. 34 and 35, along with the imposed nonnegativity requirements, serve to uniquely define the pair of functions $P_0^\infty(\boldsymbol{q})$ and $A(\boldsymbol{q})$.

It will further be assumed that the asymptotic approach of $P_0(\boldsymbol{q}, t|\boldsymbol{q}')$ to its steady-state form $P_0^\infty(\boldsymbol{q})$ is exponentially fast (Shapiro and Brenner, 1986), i.e.,

$$P_0(\boldsymbol{q}, t|\boldsymbol{q}') \simeq f(\boldsymbol{q}')P_0^\infty(\boldsymbol{q}) + \exp \tag{36}$$

in which "exp" generally denotes a time-dependent function that is attenuated exponentially rapidly with time. In Eq. 36, $f(\boldsymbol{q}')$ denotes a function that is dependent upon the tracer's initial local-space position.

Unlike the nonreactive case, the asymptotic long-time state of the reactive tracer is generally dependent upon $\boldsymbol{q}'$, as discussed above. However, due to the normalization of the probability density P_r with $A(\boldsymbol{q}')$ (cf. Eq. 12), $P_0(\boldsymbol{q}, t|\boldsymbol{q}')$ is $\boldsymbol{q}'$-independent for $t \rightarrow \infty$. Indeed, multiplication of both sides of Eq. 36 by $A(\boldsymbol{q})$, integration over $\boldsymbol{q}_o$ space, and subsequent use of Eqs. 30 and 35 eventually yields

$$f(\boldsymbol{q}') = 1 \tag{37}$$

This demonstrates that, analogous to the nonreactive case,

$$P_0(\boldsymbol{q}, t|\boldsymbol{q}') \simeq P_0^\infty(\boldsymbol{q}) + \exp \tag{38}$$

as $t \rightarrow \infty$.

Integration of Eq. 38 over $\boldsymbol{q}_o$ space yields

$$M_0'(t|\boldsymbol{q}') \simeq 1 + \exp \tag{39}$$

as $t \rightarrow \infty$, owing to the normalization condition Eq. 34 imposed upon P_0^∞. Consequently, the tracer's zero-order moment M_0' is conserved for asymptotically long times, although for the nonreactive case such conservation obtains for all times.

Before considering the higher order moments of P, we establish the identity

$$\frac{dM_m}{dt} = \int_{q_o} \Gamma_m A(\boldsymbol{q})\, d\boldsymbol{q} + \delta_{m0}\delta(t) \tag{40}$$

This useful relation is readily obtained upon multiplication of Eq. 20 by $A(\boldsymbol{q})d\boldsymbol{q}$ and subsequent integration over $\boldsymbol{q}_o$ space, followed by application of the local-space divergence theorem, together with use of the boundary condition of Eq. 24 jointly with the properties of $A(\boldsymbol{q})$ defined by the adjoint eigenvalue problem, Eqs. 28 and 29.

First-order moments

Introduce into Eq. 40 (with $m = 1$) the asymptotic form of Γ_1 given by Eq. 22b with P_0 replaced by its long-time expansion, Eq. 38. This yields

$$d\boldsymbol{M}_1/dt \simeq \overline{\boldsymbol{U}} + \exp \tag{41}$$

Here, $\overline{\boldsymbol{U}}$ is the position- and time-independent constant vector

$$\overline{\boldsymbol{U}} = \int_{q_o} \boldsymbol{U}(\boldsymbol{q})P_0^\infty(\boldsymbol{q})A(\boldsymbol{q})\, d\boldsymbol{q} \tag{42}$$

Integration of Eq. 41 gives

$$\boldsymbol{M}_1 = \overline{\boldsymbol{U}}t + \text{const.} + \exp \tag{43}$$

The local first-order moment field $\boldsymbol{P}_1$ is given asymptotically by the solution of the problem posed by the equations

$$\partial \boldsymbol{P}_1/\partial t - \mathcal{L}\boldsymbol{P}_1 = \boldsymbol{U}(\boldsymbol{q})P_0^\infty + \exp \quad \text{in } \boldsymbol{q}_o \tag{44a}$$

$$\boldsymbol{n} \cdot \mathcal{J}\boldsymbol{P}_1 = k\boldsymbol{P}_1 \quad \text{on } \partial\boldsymbol{q}_o \tag{44b}$$

The asymptotic form, Eq. 43, of $\boldsymbol{M}_1$ suggests the following long-time solution for $\boldsymbol{P}_1$:

$$\boldsymbol{P}_1(\boldsymbol{q}, t|\boldsymbol{q}') \simeq P_0^\infty(\boldsymbol{q})[\overline{\boldsymbol{U}}t + \boldsymbol{B}(\boldsymbol{q})] + \exp \tag{45}$$

which form will be verified *a posteriori*. In Eq. 45 $\overline{\boldsymbol{U}}$ is given by Eq. 42 whereas $\boldsymbol{B}(\boldsymbol{q})$ represents a global-space $\boldsymbol{q}$-dependent vector field to be determined.

Substitute Eq. 45 into Eqs. 44a, b to obtain the following problem governing the $\boldsymbol{B}$ field:

$$\boldsymbol{j}_0^\infty \cdot \nabla_q \boldsymbol{B} - \nabla_q \cdot (P_0^\infty \mathbf{d} \cdot \nabla_q \boldsymbol{B}) = (\boldsymbol{U} - \overline{\boldsymbol{U}})P_0^\infty \quad \text{in } \boldsymbol{q}_o \tag{46a}$$

$$P_0^\infty \boldsymbol{n} \cdot \mathbf{d} \cdot \nabla_q \boldsymbol{B} = \boldsymbol{0} \quad \text{on } \partial\boldsymbol{q}_o \tag{46b}$$

It can be shown (Shapiro and Brenner, 1986) that the problem posed by Eqs. 46a, b possesses a solution $\boldsymbol{B}$ that is uniquely determined only to within an arbitrary additive constant vector. This ambiguity will be shown to be without effect upon the three global-scale phenomenological coefficients.

Integration of Eq. 45 over $\boldsymbol{q}_o$ space, together with use of Eq. 34, yields

$$\boldsymbol{M}_1'(t|\boldsymbol{q}') \simeq \overline{\boldsymbol{U}}t + \overline{\boldsymbol{B}} + \exp \tag{47}$$

in which

$$\overline{\boldsymbol{B}} = \int_{q_o} P_0^\infty(\boldsymbol{q})\boldsymbol{B}(\boldsymbol{q})\, d\boldsymbol{q} \tag{48}$$

is a time- and position-independent constant vector. Comparison of Eq. 43 with Eq. 47 shows that the asymptotically long-time total moments $\boldsymbol{M}_1$ and $\boldsymbol{M}_1'$ are identical as regards their leading terms. Each shows the first-order total moment to grow linearly with time.

Second-order moments

Into Eq. 40 (with $m = 2$) introduce Γ_2, given by Eq. 22c, with P_0 and $\boldsymbol{P}_1$ replaced by their respective asymptotic forms, Eqs. 38 and 45, to obtain

$$d\mathbf{M}_2/dt \simeq 2\overline{\boldsymbol{U}}\overline{\boldsymbol{U}}t + 2(\overline{\boldsymbol{B}}'\overline{\boldsymbol{U}})^s + 2(\overline{\mathbf{D}}^M + \overline{\mathbf{D}}^C) + \exp \tag{49}$$

with constants

$$\overline{\boldsymbol{B}}' = \int_{q_o} P_0^\infty(\boldsymbol{q})A(\boldsymbol{q})\boldsymbol{B}(\boldsymbol{q})\, d\boldsymbol{q} \tag{50}$$

$$\overline{\mathbf{D}}^M = \int_{q_o} P_0^\infty(\boldsymbol{q})A(\boldsymbol{q})\mathbf{D}^s(\boldsymbol{q})\, d\boldsymbol{q} \tag{51}$$

$$\overline{\mathbf{D}}^C = \text{sym} \int_{q_o} P_0^\infty(\boldsymbol{q}) A(\boldsymbol{q}) \boldsymbol{B}(\boldsymbol{q}) [\boldsymbol{U}(\boldsymbol{q}) - \overline{\boldsymbol{U}}]\, d\boldsymbol{q} \qquad (52)$$

Integration of Eq. 49 gives

$$\mathbf{M}_2 \simeq \overline{\boldsymbol{U}}\overline{\boldsymbol{U}}t^2 + 2[(\overline{\boldsymbol{B}'}\overline{\boldsymbol{U}})^s + (\overline{\mathbf{D}}^M + \overline{\mathbf{D}}^C)]t + \text{const.} + \exp \qquad (53)$$

The second-order local moment field $\mathbf{P}_2$ is given asymptotically by the solution of the boundary-value problem

$$\partial \mathbf{P}_2/\partial t - \mathcal{L}\mathbf{P}_2 = 2 \text{ sym } [\boldsymbol{U}P_0^\infty(\overline{\boldsymbol{U}}t + \boldsymbol{B}) + \mathbf{D}P_0^\infty] + \exp \quad \text{in } \boldsymbol{q}_o \qquad (54a)$$

$$\boldsymbol{n} \cdot \boldsymbol{\mathscr{J}}\mathbf{P}_2 = k\mathbf{P}_2 \quad \text{on } \partial \boldsymbol{q}_o \qquad (54b)$$

Subject to *a posteriori* verification we assume the asymptotic long-time solution for $\mathbf{P}_2$ to be

$$\mathbf{P}_2(\boldsymbol{q}, t|\boldsymbol{q}') \simeq P_0^\infty(\boldsymbol{q})\{\overline{\boldsymbol{U}}\overline{\boldsymbol{U}}t^2 + 2[\boldsymbol{B}(\boldsymbol{q})\overline{\boldsymbol{U}}]^s t + 2(\overline{\mathbf{D}}^M + \overline{\mathbf{D}}^C)t\} + \mathbf{H}(\boldsymbol{q}) + \exp \qquad (55)$$

This form is suggested by the asymptotic expression, Eq. 53, for the second-order total moment $\mathbf{M}_2$. The global-space dyadic field $\mathbf{H}(\boldsymbol{q})$ remains to be determined. Introduction of Eq. 55 into Eqs. 54a, b yields the following boundary-value problem defining the **H** field:

$$\mathcal{L}\mathbf{H} = 2[\mathbf{D} + (\boldsymbol{U} - \overline{\boldsymbol{U}})\boldsymbol{B}]P_0^\infty - (\overline{\mathbf{D}}^M + \overline{\mathbf{D}}^C)P_0^\infty \quad \text{in } \boldsymbol{q}_o \qquad (56a)$$

$$\boldsymbol{n} \cdot \boldsymbol{\mathscr{J}}\mathbf{H} = k\mathbf{H} \quad \text{on } \partial \boldsymbol{q}_o \qquad (56b)$$

This problem may be shown to possess a solution (Shapiro and Brenner, 1986), thereby demonstrating the validity of the asymptotic trial solution, Eq. 55.

Integration of Eq. 55 over $\boldsymbol{q}_o$ space furnishes the asymptotic form of the second-order total moment $\mathbf{M}_2$ as (cf. Eq. 53)

$$\mathbf{M}_2' \simeq \overline{\boldsymbol{U}}\overline{\boldsymbol{U}}t^2 + 2[(\overline{\boldsymbol{B}}\overline{\boldsymbol{U}})^s + (\overline{\mathbf{D}}^M + \overline{\mathbf{D}}^C)]t + \text{const.} + \exp \qquad (57)$$

In deriving Eq. 57 it was unnecessary to solve Eqs. 56a, b for the dyadic field $\mathbf{H}(\boldsymbol{q})$. Rather, the mere existence of these equations sufficed to obtain the long-time behavior embodied in Eq. 57.

Global-phase Phenomenological Coefficients

The respective asymptotic forms, Eqs. 39, 47, and 57, of the total moments M_0', $\boldsymbol{M}_1'$, $\mathbf{M}_2'$ are identical in appearance to those obtained by Brenner (1982) for the nonreactive case. As regards these total moments, we therefore need not explicitly distinguish between the asymptotic state achieved by a completely nonreactive tracer and that achieved by the hypothetical tracer whose microtransport behavior is that described by the conditional probability density $P(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}')$ defined in Eq. 12. This asymptotic analogy permits us to employ the classical nonreactive definitions (Brenner, 1980a, 1982)

$$\overline{\boldsymbol{U}}^* = \lim_{t\to\infty} \frac{d\boldsymbol{M}_1'}{dt} \qquad (58a)$$

$$\overline{\mathbf{D}}^* = \frac{1}{2} \lim_{t\to\infty} \frac{d}{dt}(\mathbf{M}_2' - \boldsymbol{M}_1'\boldsymbol{M}_1') \qquad (58b)$$

in the reactive case as well.

Introduction of Eqs. 47 and 57 into Eqs. 58a,b immediately yields

$$\overline{\boldsymbol{U}}^* = \overline{\boldsymbol{U}} \qquad (59)$$

$$\overline{\mathbf{D}}^* = \overline{\mathbf{D}}^M + \overline{\mathbf{D}}^C \qquad (60)$$

where $\overline{\boldsymbol{U}}$, $\overline{\mathbf{D}}^M$ and $\overline{\mathbf{D}}^C$ are explicitly given by Eqs. 42, 51, and 52. The dyadics $\overline{\mathbf{D}}^M$ and $\overline{\mathbf{D}}^C$ respectively represent the molecular (Aris) and convective (Taylor) portions of the global-phase dispersivities. An alternative expression for $\overline{\mathbf{D}}^C$, which may be obtained similarly to the derivations of Brenner (1982) and Shapiro and Brenner (1986) for the nonreactive case, is

$$\overline{\mathbf{D}}^C = \int_{q_o} A(\boldsymbol{q}) P_0^\infty(\boldsymbol{q}) (\nabla_q \boldsymbol{B})^\dagger \cdot \mathbf{d}^s \cdot (\nabla_q \boldsymbol{B})\, d\boldsymbol{q} \qquad (61)$$

This form, coupled with the nonnegative natures of P_0^∞ and A, proves both the positive definiteness and symmetry of the dyadic $\overline{\mathbf{D}}^C$. Comparable properties for $\overline{\mathbf{D}}^M$ follow immediately from Eq. 51 as a consequence of the positive definiteness of the molecular diffusivity dyadic $\mathbf{D}(\boldsymbol{q})$.

Eulerian interpretation of the phenomenological coefficients

The Lagrangian global phenomenological coefficients $\overline{\boldsymbol{U}}^*$ and $\overline{\mathbf{D}}^*$ may also be given a Eulerian interpretation as coefficients appearing in the purely global-space equation

$$\partial \overline{P}/\partial t + \overline{\boldsymbol{U}}^* \cdot \nabla_Q \overline{P} - \overline{\mathbf{D}}^* : \nabla_Q \nabla_Q \overline{P} = \delta(\boldsymbol{Q})\delta(t) \qquad (62)$$

governing the temporal and spatial transport of the global conditional probability density

$$\overline{P}(\boldsymbol{Q}, t|\boldsymbol{q}') \overset{\text{def.}}{=} \int_{q_o} P(\boldsymbol{Q}, \boldsymbol{q}, t|\boldsymbol{q}')\, d\boldsymbol{q} \qquad (63)$$

in the limit of long times. This local-space averaged probability density $\overline{P}$ possesses a purely global character as $t \to \infty$; that is, it is asymptotically independent of $\boldsymbol{q}'$ for sufficiently large times. Explicitly, $\overline{P} \simeq \overline{P}(\boldsymbol{Q}, t)$ as $t \to \infty$. This statement follows from the observation (Shapiro and Brenner, 1986) that all of the asymptotic long-time local moments $\boldsymbol{P}_m$ are independent of $\boldsymbol{q}'$.

Although global transport Eq. 62 appears superficially to be that for a nonreactive solute, the transport coefficients $\overline{\boldsymbol{U}}^*$ and $\overline{\mathbf{D}}^*$ in fact differ from those that obtain in the nonreactive case (Brenner, 1982). This difference is a manifestation of the fact that in spite of the global balance existing between the rates of solute diminution [due to the surface and volumetric reactions with respective microscale reactivities $K(\boldsymbol{q})$ and $k(\boldsymbol{s})$] and solute production (due to the superposed uniform volumetric reaction with constant reactivity $\overline{K}$), these tendencies are unbalanced locally within $\boldsymbol{q}_o$ space. This leads to an asymptotically long-time local solute distribution $P_0^\infty(\boldsymbol{q})$ different from that for the nonreactive case. (Compare the reactive case, Eqs. 31, 32, and 34, with the corresponding nonreactive case [Brenner, 1982], obtained by setting $K = k = \overline{K} = 0$ in these equations.) The only obvious exception to this general statement occurs in the case of homogeneous reactions, where $k(\boldsymbol{s}) = 0$ and, simultaneously, $K(\boldsymbol{q}) = \text{const.} \equiv \overline{K}$ (Brenner, 1982; Brenner and Adler, 1982; Shapiro and Brenner, 1986).

As may easily be seen from Eqs. 27–29, in the nonreactive case (as well as in the case of homogeneous reactions discussed above) one obtains $A(\mathbf{q}) = 1$. Therefore, the extent to which $A(\mathbf{q})$ differs from unity measures the local imbalance existing in the reactive case between the rates of solute diminution and production within the local space. In other words, the difference between $A(\mathbf{q})$ and unity is a manifestation of the inhomogeneity of the local-space reactions, which obviously affects the global phenomenological coefficients (cf. Eqs. 42, 51, and 52).

Equation 12 implies the following relationship between the moments M_{rm} and M'_m:

$$M_{rm}(t\,|\,\mathbf{q}') = A(\mathbf{q}')\exp(-\overline{K}t)M'_m(t\,|\,\mathbf{q}') \quad (m = 0, 1, 2, \ldots) \tag{64}$$

One can express in terms of the moments M_{rm} the global transport coefficients as follows (Shapiro and Brenner, 1986):

$$\overline{K}^* = -\lim_{t\to\infty}\frac{d\ln M_{r0}}{dt} \tag{65a}$$

$$\overline{\mathbf{U}}^* = \lim_{t\to\infty}\frac{d}{dt}\left(\frac{\mathbf{M}_{r1}}{M_{r0}}\right) \tag{65b}$$

$$\overline{\overline{\mathbf{D}}}^* = \frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}\left(\frac{\mathbf{M}_{r2}}{M_{r0}} - \frac{\mathbf{M}_{r1}\mathbf{M}_{r1}}{M_{r0}^2}\right) \tag{65c}$$

It is a consequence of Eqs. 63 and 12 that the quantity

$$\overline{P}_r(\mathbf{Q}, t\,|\,\mathbf{q}') \overset{\text{def.}}{=} \int_{q_0} P_r(\mathbf{Q}, \mathbf{q}, t\,|\,\mathbf{q}')\,d\mathbf{q} \tag{66a}$$

is related to $\overline{P}$ by the formula

$$\overline{P}_r(\mathbf{Q}, t\,|\,\mathbf{q}') = A(\mathbf{q}')\exp(-\overline{K}t)\overline{P}(\mathbf{Q}, t\,|\,\mathbf{q}') \tag{66b}$$

wherein the $\mathbf{q}'$ dependence of $\overline{P}_r$ is concentrated entirely in the term $A(\mathbf{q}')$ for asymptotically long times. One deduces from Eq. 62 and the latter equation that for asymptotically long times $\overline{P}_r$ is the solution of the following global-space problem:

$$\partial\overline{P}_r/\partial t + \overline{\mathbf{U}}^*\cdot\nabla_Q\overline{P}_r - \overline{\overline{\mathbf{D}}}^*{:}\nabla_Q\nabla_Q\overline{P}_r + \overline{K}^*\overline{P}_r = A(\mathbf{q}')\delta(\mathbf{Q})\delta(t) \tag{67}$$

wherein $\overline{K}^* = \overline{K}$. Therefore, despite the fact that each of the global phenomenological coefficients $\overline{K}^*$, $\overline{\mathbf{U}}^*$, and $\overline{\overline{\mathbf{D}}}^*$ is independent of the initial tracer location, the conditional global probability density $\overline{P}_r$ depends upon $\mathbf{q}'$, even for asymptotically long times. This $\mathbf{q}'$-dependent terminal behavior does not obtain for the corresponding nonreactive case (which cannot be trivially obtained from Eq. 67 by setting $\overline{K}^* = 0$ since the remaining phenomenological coefficients $\overline{\mathbf{U}}^*$ and $\overline{\overline{\mathbf{D}}}^*$ are not the same in each of the two cases).

The significance of this $\mathbf{q}'$ dependence is best expressed in terms of the solute concentration $c_r(\mathbf{Q}, \mathbf{q}, t)$, which satisfies the same Eqs. 1–6 as does the probability density P_r, except for the lack of a δ-function source term appearing on the righthand side of Eq. 1. In its stead there now appears an arbitrary initial solute concentration distribution, $c_r(\mathbf{Q}, \mathbf{q}, 0)$, say, imposed upon c_r at $t = 0$. It is easily shown (Shapiro and Brenner, 1986) that the long-time global mean solute concentration $\overline{c}_r$, defined as

$$\overline{c}_r(\mathbf{Q}, t) = \int_{q_0} c_r(\mathbf{Q}, \mathbf{q}, t)\,d\mathbf{q} \tag{68}$$

obeys Eq. 9, and is subject to the initial condition

$$\overline{c}_r(\mathbf{Q}, 0) = \int_{q_0} c_r(\mathbf{Q}, \mathbf{q}, 0)A(\mathbf{q})\,d\mathbf{q} \tag{69}$$

The importance of the dependence of $\overline{c}_r$ (governed by Eq. 67 without the righthand source term) upon the initial solute distribution is emphasized, for example, in the reactive chromatographic separation (Shapiro and Brenner, 1987b) of a chemically active solute. The amount of solute separated by this scheme will depend functionally upon the initial local solute distribution within the tube's cross section.

Sedimentation of Reactive Particles from the Flow between Two Parallel Plates

Consider identical reactive pointsize Brownian solute particles present within an arbitrary, incompressible, rectilinear solvent flow $\mathbf{v} = \mathbf{U} = \mathbf{i}_y U(x)$ taking place between two parallel plates spaced b units apart, as in Fig. 1. A net force $\mathbf{F} = \mathbf{i}_x F$ ($F =$ const. > 0), typically gravity, acts transverse to the solvent flow upon each of the particles, causing their sedimentation toward the lower plate $x = b$ with constant velocity $\mathbf{u} = \mathbf{i}_x u$ ($u =$ const. > 0). (Alternatively, the upper and lower plates may be regarded as being permeable to the solvent, but not the solute. In such circumstances the transverse solute velocity u can be created [as in cross-flow filtration; Brenner, 1982] by a uniform solvent flow [at velocity u] from the upper to lower plate, which fluid motion simply carries the neutrally buoyant [$F = 0$] solute particles piggyback fashion toward the lower plate. However, when u arises solely from an external force, we have that $u = MF$, where $M = 1/6\pi\mu_0 a$ is the mobility of the solute particle. Since $D = kTM$ as a consequence of the Stokes-Einstein equation, it follows from Eqs. 72 and 77 that the Peclet number may be written as $Pe = Fb/kT$. Physically, this represents the ratio of the solute particle's potential energy to its thermal energy—a Langevin-type parameter.) On this plate the particles are removed from the bulk fluid at a rate which we assume to be characterized by a first-order irreversible reaction with rate constant k. The upper plate $x = 0$ is taken to be impermeable to the solute (as well as to the solvent too).

Choices of global and local subspaces and corresponding phenomenological-coefficient functions appropriate to the present problem are thus as follows:

$$\mathbf{Q} = y, \quad \mathbf{q} = x \tag{70}$$

$$\mathbf{U} = \mathbf{i}_y U(x), \quad \mathbf{u} = \mathbf{i}_x u, \quad \mathbf{D} = \mathbf{i}_y\mathbf{i}_y D, \quad \mathbf{d} = \mathbf{i}_x\mathbf{i}_x D$$
$$E = 0, \quad K = 0, \quad k = \text{const.} \tag{71}$$

with the constant D the translational diffusivity of a Brownian solute particle, given by the Stokes-Einstein equation

$$D = kT/6\pi\mu_0 a, \tag{72}$$

in which a is the radius of the Brownian particle ($a/b \ll 1$). The flow between the plates is assumed to be fully developed, whence

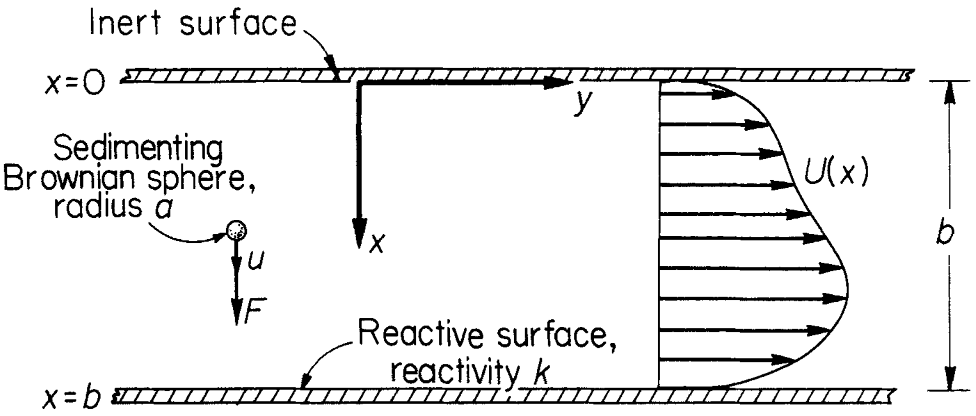

Figure 1. Flow between flat plates.
Solute particles sediment toward the reactive plate, $x = b$

the global-space velocity $U(x)$ is independent of y, as explicitly indicated by its argument.

In terms of the dimensionless coordinate

$$z = x/b \tag{73}$$

and effective (i.e., macroscale) Damkohler number

$$\lambda = \bar{K}b^2/D \tag{74}$$

the pertinent eigenvalue problems (EVP) adopt the following forms. In particular, the adjoint EVP becomes

$$Pe\frac{dA}{dz} + \frac{d^2A}{dz^2} + \lambda A = 0 \tag{75a}$$

$$\frac{dA}{dz} = 0 \quad \text{at } z = 0 \tag{75b}$$

$$-\frac{dA}{dz} = \mu A \quad \text{at } z = 1 \tag{75c}$$

whereas the characteristic EVP takes the form

$$-Pe\frac{dP_0^\infty}{dz} + \frac{d^2P_0^\infty}{dz^2} + \lambda P_0^\infty = 0 \tag{76a}$$

$$PeP_0^\infty - \frac{dP_0^\infty}{dz} = 0 \quad \text{at } z = 0 \tag{76b}$$

$$PeP_0^\infty - \frac{dP_0^\infty}{dz} = \mu P_0^\infty \quad \text{at } z = 1 \tag{76c}$$

Here, Pe and μ are the respective local-space Peclet and surface Damkohler numbers,

$$Pe = ub/D \tag{77a}$$

$$\mu = kb/D \tag{77b}$$

Solutions of the respective eigenvalue problems, Eqs. 75a, b, c and 76a, b, c, may be expressed in the forms

$$A(z) = b^{-1/2}C_o \exp(-\tfrac{1}{2}Pez)\phi(z) \tag{78}$$

$$P_0^\infty(z) = b^{-1/2}E_o \exp(\tfrac{1}{2}Pez)\phi(z) \tag{79}$$

with the function $\phi(z)$ given by

$$\phi(z) = \cosh\beta_0 z + \frac{Pe}{2\beta_0}\sinh\beta_0 z \quad (\mu \le \mu^*) \tag{80a}$$

$$\phi(z) = \cos\beta_0 z + \frac{Pe}{2\beta_0}\sin\beta_0 z \quad (\mu > \mu^*) \tag{80b}$$

in which

$$\mu^* = \frac{Pe^2}{2(2 + Pe)} \tag{81}$$

In the preceding, $\beta_0 \equiv \beta_0(\mu, Pe)$ is the smallest nonzero root of the transcendental equation(s)

$$\tanh\beta - \frac{4\mu\beta}{Pe(Pe - 2\mu) - 4\beta^2} = 0 \quad (\mu < \mu^*) \tag{82a}$$

$$\tan\beta - \frac{4\mu\beta}{Pe(Pe - 2\mu) + 4\beta^2} = 0 \quad (\mu > \mu^*) \tag{82b}$$

Moreover, $\beta_0 = 0$ when $\mu = \mu^*$.

The constants C_o and E_o appearing in Eqs. 78–79 are to be determined from the pair of normalization conditions, Eqs. 34 and 35. It proves necessary only to satisfy Eq. 35, thereby obtaining the product

$$(E_oC_o)^{-1} = \frac{1}{2} + \frac{\sinh 2\beta_0}{4\beta_0} + Pe\frac{(\cosh 2\beta_0 - 1)}{4\beta_0^2} + \frac{Pe^2}{8\beta_0^2}\left(\frac{\sinh 2\beta_0}{2\beta_0} - 1\right) \quad (\mu \le \mu^*) \tag{83a}$$

$$(E_oC_o)^{-1} = \frac{1}{2} + \frac{\sin 2\beta_0}{4\beta_0} + Pe\frac{(1-\cos 2\beta_0)}{4\beta_0^2} + \frac{Pe^2}{8\beta_0^2}\left(1 - \frac{\sin 2\beta_0}{2\beta_0}\right) \quad (\mu > \mu^*) \qquad (83b)$$

In the interests of algebraic simplicity we have abandoned the arbitrary normalization condition, Eq. 34. This choice is without effect upon the global transport coefficients (as follows from the observation that $\bar{U}^*$ and $\bar{\mathbf{D}}^*$, defined by Eqs. 42 and 51, 60, 61, respectively, depend only upon the product of the pair of functions A and P_0^∞).

Phenomenological coefficients

The mean global reaction rate coefficient obtained from the preceding is given by

$$\bar{K}^* = \frac{D}{b^2}\left(\frac{Pe^2}{4} - \beta_0^2\right) \quad (\mu \le \mu^*) \qquad (84a)$$

$$\bar{K}^* = \frac{D}{b^2}\left(\frac{Pe^2}{4} + \beta_0^2\right) \quad (\mu > \mu^*) \qquad (84b)$$

The mean global solute velocity vector $\bar{\mathbf{U}}^* = \mathbf{i}_y\bar{U}^*$ was calculated from Eq. 42 for the case where $U(x)$ is taken to be the two-dimensional Poiseuille flow

$$U(x) = 6\bar{V}\frac{x}{b}\left(1 - \frac{x}{b}\right) \equiv \bar{V}\bar{U}(z) \qquad (85)$$

where $\bar{V}$ is the mean solvent velocity. In particular, substituting Eqs. 78, 79, and 85 into Eq. 42 yields

$$\bar{U}_o \overset{\text{def.}}{=} \frac{\bar{U}^*}{\bar{V}} = 6E_oC_o\left[\frac{1-\zeta^2}{12} + \frac{1+\zeta^2}{2}\left(\frac{\cosh 2\beta_0 + 1}{4\beta_0^2} - \frac{\sinh 2\beta_0}{4\beta_0^3}\right) + \zeta\left(\frac{\sinh 2\beta_0}{4\beta_0^2} - \frac{\cosh 2\beta_0 - 1}{4\beta_0^3}\right)\right] \quad (\mu \le \mu^*) \qquad (86a)$$

$$\bar{U}_o \overset{\text{def.}}{=} \frac{\bar{U}^*}{\bar{V}} = 6E_oC_o\left[\frac{1+\zeta^2}{12} + \frac{1-\zeta^2}{2}\left(\frac{\cos 2\beta_0 + 1}{4\beta_0^2} + \frac{\sin 2\beta_0}{4\beta_0^3}\right) - \zeta\left(\frac{\sin 2\beta_0}{4\beta_0^2} + \frac{\cos 2\beta_0 - 1}{4\beta_0^3}\right)\right] \quad (\mu > \mu^*) \qquad (86b)$$

with $\zeta = Pe/(2\beta_0)$ and with E_oC_o given by Eq. 83.

The problem, Eqs. 46a, b, posed for the $\mathbf{B}$ field adopts the following dimensionless form upon introducing the substitution $\mathbf{B} = \mathbf{i}_yB(z)$:

$$\frac{d^2B}{dz^2} + \frac{dB}{dz}\left(2\frac{d\ln P_0^\infty}{dz} - Pe\right) = -D^{-1}[U(z) - \bar{U}^*]b^2 \qquad (87a)$$

$$P_0^\infty\frac{dB}{dz} = 0 \quad \text{at } z = 0, 1 \qquad (87b)$$

These equations possess the solution

$$B(z) = -\frac{b^2}{D}\int_0^z \frac{d\xi}{\phi^2(\xi)}\int_0^\xi \Delta U(\eta)\,\phi^2(\eta)\,d\eta + \text{const.} \qquad (88)$$

where $\Delta U(\eta) \overset{\text{def.}}{=} U(\eta) - \bar{U}^*$. Calculation of the dispersivity dyadic requires knowledge only of dB/dz, rather than of B itself. For the given velocity profile, Eq. 85, dB/dz is found to be

$$\begin{aligned} -\left(\frac{dB}{dz}\right)\frac{D\phi^2(z)}{6\bar{V}b^2} = \frac{1-\zeta^2}{2}\left(\frac{z^2}{2} - \frac{z^3}{3} - \frac{\bar{U}_oz}{6}\right) &+ \frac{1+\zeta^2}{2}\left[\frac{(z - z^2 - \bar{U}_o/6)\sinh 2\beta_0z}{2\beta_0} - \frac{(1-2z)\cosh 2\beta_0z - 1}{4\beta_0^2} - \frac{\sinh 2\beta_0z}{4\beta_0^3}\right] \\ &+ \zeta\left[\frac{\bar{U}_o/6 + (z - z^2 - \bar{U}_o/6)\cosh 2\beta_0z}{2\beta_0} - \frac{(1-2z)\sinh 2\beta_0z}{4\beta_0^2} - \frac{\cosh 2\beta_0z - 1}{4\beta_0^3}\right] \\ &(\mu < \mu^*) \end{aligned} \qquad (89a)$$

$$\begin{aligned} -\left(\frac{dB}{dz}\right)\frac{D\phi^2(z)}{6\bar{V}b^2} = \frac{1+\zeta^2}{2}\left(\frac{z^2}{2} - \frac{z^3}{3} - \frac{\bar{U}_oz}{6}\right) &+ \frac{1+\zeta^2}{2}\left[\frac{(z - z^2 - \bar{U}_o/6)\sin 2\beta_0z}{2\beta_0} + \frac{(1-2z)\cos 2\beta_0z - 1}{4\beta_0^2} + \frac{\sin 2\beta_0z}{4\beta_0^3}\right] \\ &+ \zeta\left[\frac{\bar{U}_o/6 + (z - z^2 - \bar{U}_o/6)\cos 2\beta_0z}{2\beta_0} + \frac{(1-2z)\sin 2\beta_0z}{4\beta_0^2} + \frac{\cos 2\beta_0z - 1}{4\beta_0^3}\right] \\ &(\mu > \mu^*) \end{aligned} \qquad (89b)$$

Substitution of Eqs. 78, 79, and 88 into Eqs. 51 and 61 yields the following generic expressions for the respective molecular and Taylor contributions to the dispersivity dyadic:

$$\bar{\mathbf{D}}^M = \mathbf{i}_y\mathbf{i}_yD \qquad (90a)$$

$$\bar{\mathbf{D}}^C = \mathbf{i}_y\mathbf{i}_y\bar{D}^C \qquad (90b)$$

with $\bar{D}^C$ given by

$$\frac{\bar{D}^C}{D} = b^{-2}E_oC_o\int_0^1 \phi^2(z)\left(\frac{dB}{dz}\right)^2 dz \qquad (91)$$

The expressions in Eqs. 89a,b for dB/dz permit the calculation of $\bar{D}^C$ upon use of the latter formula.

Numerical Results

Apparent reactivity, $\bar{K}^*$

Figure 2 depicts the dependence of the effective Damkohler number $\bar{K}^*b^2/D$ upon the local-space surface Damkohler number $\mu = kb/D$ for several values of the local-space Peclet number $Pe = ub/D$. All other things being equal, the apparent volumetric reactivity $\bar{K}^*$ increases monotonically with increasing sur-

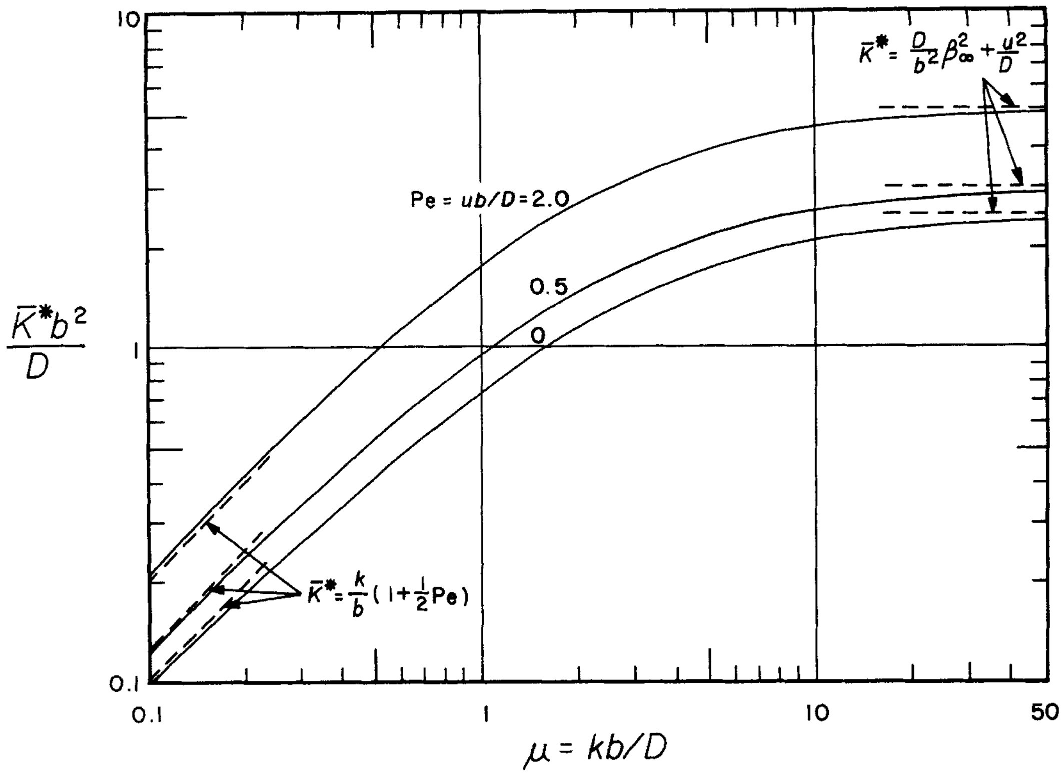

Figure 2. Apparent volumetric macroscale Damkohler number as a function of surface microscale Damkohler number and sedimentary Peclet number.

face reactivity k, although the incremental increase becomes small at the larger values of k, where as Peclet number-dependent asymptotic saturation state is achieved. Consistent with this monotonicity, $\bar{K}^*$ is identically zero in the absence of surface reaction for all Peclet numbers.

In the reactive case the effect of the sedimentation is to facilitate particle transport toward the reactive surface, thereby enhancing the effective volumetric reactivity $\bar{K}^*$.

For small values of μ and Pe an asymptotic solution of Eqs. 82a,b yields

$$\bar{K}^* \simeq \frac{k}{b}\left(1 + \frac{1}{2}Pe\right) \quad (\mu, Pe \ll 1) \tag{92}$$

This limiting behavior is indicated by the dashed lines appearing on the lefthand side of Figure 2. It is evident that the asymptotic formula, Eq. 92, satisfactorily represents the exact solution up to $\mu \simeq 0.5$ and $Pe = 2$.

At very large rates of surface reaction ($\mu \rightarrow \infty$), the surface concentration on the reactive plate $z = 1$ approaches zero. In such circumstances $\bar{K}^*$ attains the limiting value (see the righthand side of Figure 2)

$$\bar{K}^* \simeq \frac{D}{b^2}\beta_\infty^2 + \frac{u^2}{D} \quad (\mu \gg 1) \tag{93}$$

where β_∞ is the smallest positive root of the transcendental equation

$$\tan \beta_\infty + \frac{2\beta_\infty}{Pe} = 0 \tag{94}$$

In particular, for $\mu \gg Pe/2 \gg 1$, Eqs. 93 and 94 combine to yield

$$\bar{K}^* \simeq \frac{D\pi^2}{b^2} + \frac{u^2}{D} \tag{95}$$

The expressions in Eqs. 93 and 95 are independent of the surface reactivity k. Consequently, the rate of the macroscale reaction, as embodied in $\bar{K}^*$, is limited by the diffusional and sedimentary transport rates toward the reactive plate $z = 1$.

Mean solute velocity, $\bar{U}^*$

The mean global solute speed $\bar{U}^*$, nondimensionalized with the mean solvent speed $\bar{V}$, is plotted in Figure 3 as $\bar{U}_o \overset{\text{def.}}{=} \bar{U}^*/\bar{V}$ vs. the surface microscale Damkohler number μ at parameters of Pe.

For $\mu \rightarrow 0$ and $\mu \rightarrow \infty$ the mean velocity attains its (Pe-dependent) limiting values (see the respective dashed lines in Figure 3), which values may be explicitly obtained by the respective substitutions $\beta_0 = Pe/2$ and $\beta_0 = \beta_\infty$ into Eq. 86a (for $\mu = 0$) and Eq. 86b (for $\mu \rightarrow \infty$).

The effect of the surface reaction is to increase the particle flux toward the reactive surface $z = 1$. The concomitant effect of this phenomenon upon the mean solute velocity is obviously different according as the reaction is relatively weak [$\mu \lesssim O(1)$] or strong [$\mu \gtrsim O(1)$]; that is, all other things being equal, for a fixed Pe, $\bar{U}^*$ increases monotonically with increasing k, passes through a maximum at $\mu \approx O(1)$, and subsequently diminishes monotonically with further increases in k.

To illustrate the reason for this behavior, consider the curve for $Pe = 0$, corresponding to the absence of sedimentation.

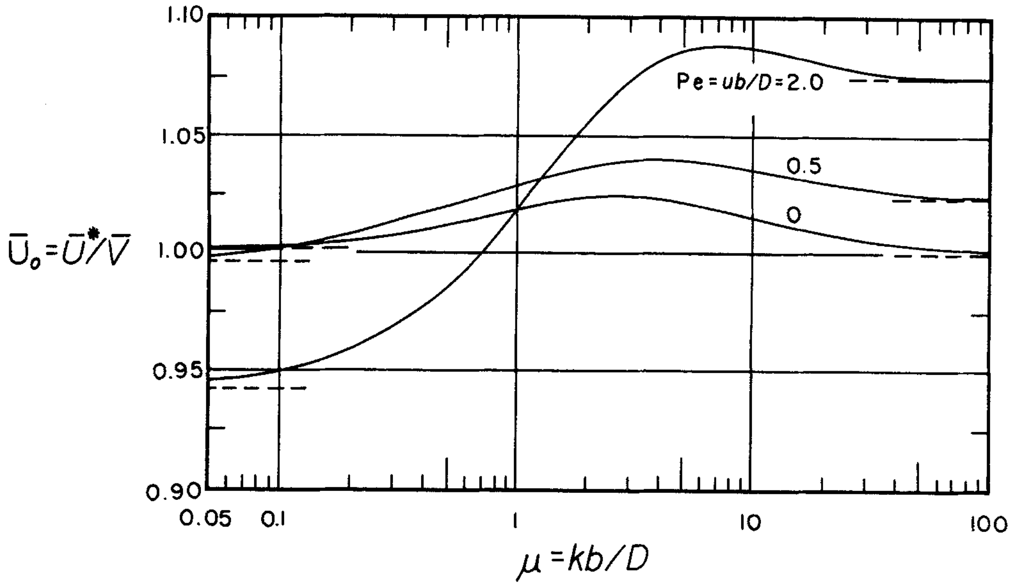

Figure 3. Normalized mean solute velocity as a function of surface microscale Damkohler and sedimentary Peclet numbers.

Values of $\bar{U}^*/\bar{V}$ greater than unity indicate that, on average, the solute moves faster than does the solvent (and conversely for ratios less than unity).

Weak reaction affects the region close to the reactive plate by reducing the solute concentration in its proximity, whereas far from this wall the concentration profile in the cross section y = const. remains virtually unchanged. The mean solute velocity in this case is weighted in favor of the central region, where the solvent streamlines transport the solute particles with higher speeds. This causes the observed monotonic increase of $\bar{U}^*$ with k for $\mu \lesssim 2$. On the other hand, strong surface reaction $[\mu \gtrsim O(1)]$ affects the solute concentration throughout the entire duct cross section $0 \leq z \leq 1$, reducing it particularly in the central region, $z \simeq 0.5$, where the fluid velocity is high. This phenomenon causes a decrease of $\bar{U}^*$ with increasing k for $\mu \geq 2$.

Now consider the effect of sedimentation, i.e., $Pe \neq 0$, upon the mean solute velocity. The sedimentation process transports solute particles toward the reactive plate. Due to this phenomenon a greater proportion of the solute present in the cross section y = const. is concentrated in the region $z \approx 1$ immediately adjacent to the reactive wall, since weak surface reaction is unable to appreciably deplete these particles from the wall's proximity. Hence, in this case, particles are transported in x-direction primarily by the slow moving fluid elements. This explains the decrease of $\bar{U}^*$ with increasing Pe observed in Figure 3. However, for $\mu \gtrsim O(1)$ the effect of sedimentation is different. In this case the intense wall reaction significantly depletes the concentration of solute particles transported to the wall by the external force. The effect of sedimentation is thus to remove solute particles from the neighborhood of the nonreactive plate $z = 0$, and transfer them to the central region $z \approx 0.5$, where the concentration attains its maximum value. Given that the fluid velocity profile also reaches its maximum value in this region, the effect is to cause an increase of $\bar{U}^*$ with increasing Pe (all other things being equal, of course). This phenomenon is observed in Figure 3 for $\mu \gtrsim 5$.

The preceding discussion rationalizes the general shapes of each of the curves Pe = const. appearing in Figure 3, as well as their Pe dependence. Of perhaps equal interest is an explanation of the actual numerical values of the dimensionless solute velocity $\bar{U}_o \equiv \bar{U}^*/\bar{V}$ in relation to the value of unity that would prevail for the nonreactive-nonsedimenting case, $\mu = Pe = 0$. In particular, $\bar{U}_o$ represents the ratio of the mean solute velocity to that of the solvent. Thus, when $\bar{U}_o$ exceeds unity, the solute moves on average faster than the solvent in which it is suspended (and conversely).

In this context we note first that the curve for $Pe = 0$ is such that $\bar{U}_o \geq 1$ for all μ. That the solute here moves on average faster than does the solvent arises from the fact that the solute is depleted in the slow-moving streamlines proximate to the reactive plate. Accordingly, whereas a solvent molecule will, in the long run, sample (by lateral diffusion) all streamlines in the cross section with equal probability, the same will not be true of a solute molecule; rather, of those solute molecules that survive, a greater proportion of them will have sampled the faster moving streamlines than the slower ones.

This argument requires modification for the sedimenting case, $Pe \neq 0$, since the sedimentation can then transport solute particles into the reactive wall region $z = 1$, from which they were previously depleted by the surface reaction. As is evident from Figure 3, the net effect of this at any given Pe is to cause the (surviving) solute molecules to move slower on average than the (inert) solvent molecules in the weak reaction case $\mu \rightarrow 0$, and conversely for the strong reaction case $\mu \rightarrow \infty$. Since this solute-solvent mean velocity difference depends upon the precise values of the parameters Pe and μ, the possibility exists of separating solutes that differ only in their surface reactivities k. In a previous paper (Shapiro and Brenner, 1987) we have coined the term "reaction chromatography" to describe this novel separation scheme.

Dispersivity

Figure 4 shows the convective dispersivity $\bar{D}^C$ (nondimensionalized with its classical, nonreactive, nonsedimenting flat plate

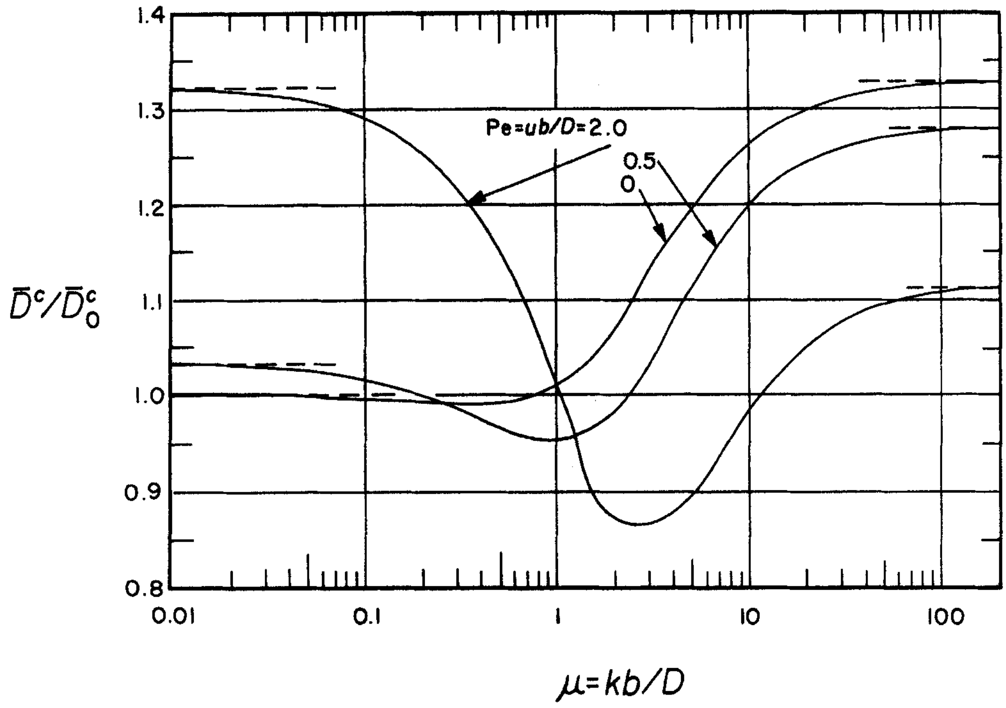

Figure 4. Normalized Taylor (convective) dispersivity as a function of surface microscale Damkohler and sedimentary Peclet numbers.

value $\overline{D}_0^C = (b\overline{V})^2/210D$ [Wooding, 1960] for the case $\mu = Pe = 0$) vs. the microscale surface Damkohler number μ for several parametric values of Pe.

As was observed above, the competing influences of sedimentation and surface reaction result in a nonuniform solute distribution across the gap. When a major proportion of the solute is concentrated in the regions near to the plates, $\overline{D}^C$ increases due to the larger velocity gradients existing there. On the other hand, when the solute is concentrated primarily in the central region, $\overline{D}^C$ decreases owing to the smaller velocity gradients existing there. For the Poiseuille velocity profile considered here, the highest velocity gradients occur where the absolute value of $U(x)$ is least, and conversely. Accordingly, situations for which the mean global solute velocity $\overline{U}^*$ reaches its maximum value, Figure 3, result in a minimum convective dispersivity $\overline{D}^C$, Figure 4, and conversely. This phenomenon manifests itself most strongly for the case $Pe = 2$. In this situation $\overline{D}^C$ is more than 30% greater than $\overline{D}_0^C$ for negligible reaction (i.e., $\mu \rightarrow 0$) due to the influence of sedimentation, which brings solute particles into the high-velocity gradient region adjacent to the wall $z = 1$. However, for this same value ($Pe = 2$), when $\mu \approx 3$ (where $\overline{U}^*$ attains its maximum value) the dispersivity $\overline{D}^C$ diminishes to about 15% less than that of $\overline{D}_0^C$.

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Notation

a = solute particle radius
A = normalizing function, Eq. 12
A_n = eigenfunctions of the adjoint EVP, Eqs. 28, 29
A_0 = leading eigenfunction of the adjoint EVP, Eqs. 28, 29
b = spacing between two parallel plates
$\underline{\boldsymbol{B}}$ = $\boldsymbol{q}$-dependent global-space vector field
$\overline{\boldsymbol{B}}, \overline{\boldsymbol{B}}'$ = vector constants, Eqs. 48, 50
c_r = reactive solute concentration
$\overline{c}_r$ = global ($\boldsymbol{q}_o$-averaged) solute concentration of reactive species
C_o = constant, Eq. 78
$\mathbf{d}$ = local-space molecular diffusivity dyadic
D = solute particle diffusivity constant
$\underline{\mathbf{D}}$ = global-space molecular diffusion dyadic
$\overline{\mathbf{D}}^C$ = convective (Taylor) portion of global dispersivity dyadic
$\overline{\mathbf{D}}^M$ = molecular (Aris) portion of global dispersivity dyadic
$\overline{\mathbf{D}}^*$ = global dispersivity dyadic
$\overline{D}_0^C$ = convective dispersivity in absence of reaction and sedimentation
E = local-space dimensionless potential of external force
E_o = constant, Eq. 79
f = $\boldsymbol{q}'$-dependent function, Eq. 36
$\boldsymbol{F}, F$ = (vector, scalar) external sedimenting force
$\mathbf{H}$ = $\boldsymbol{q}$-dependent global dyadic field
$\boldsymbol{i}_x, \boldsymbol{i}_y$ = unit vectors in x and y directions
$\boldsymbol{j}, \boldsymbol{J}$ = local- and global-space fluxes of modified probability density P
$\boldsymbol{j}_r, \boldsymbol{J}_r$ = local- and global-space fluxes of reactive probability density function P_r
$\boldsymbol{j}_0^\infty$ = steady-state flux of zero-order local moment P_0
$\boldsymbol{\mathcal{J}}$ = local-space flux vector differential operator, Eq. 4
k = local-space surface reactivity function or constant
kT = Boltzmann factor
$\underline{K}$ = local-space volumetric reactivity function
$\overline{K}$ = superposed first-order volumetric production rate constant
$\overline{\underline{K}}_n$ = eigenvalues of EVPs, Eqs. 28, 29 and 31, 32
$\overline{K}_0, \overline{\underline{K}}_0'$ = leading eigenvalues of the spectrum $\{\overline{K}_n\}$
$\overline{K}^*$ = effective reactivity constant
l = characteristic $\boldsymbol{q}_o$-space linear dimension
$\mathcal{L}$ = local-space differential operator, Eq. 25

$\mathcal{L}^*$ = local-space adjoint differential operator, Eq. 27
m = nonnegative integer number
M = total moments of reactive probability density P_r
M_m, M'_m = total moments of modified probability density P
$\boldsymbol{n}$ = unit outer normal vector on local-space boundary $\partial \boldsymbol{q}_o$
P = modified probability density
P_m = local moments of the probability density P
P_r = probability density for reactive solute
$\bar{P}, \bar{P}_r$ = $\boldsymbol{q}_o$-space averaged probability densities
P_0^∞ = asymptotically long-time zero-order local moment
$Pe = ub/D$ = Peclet number
$\boldsymbol{q}, \underline{Q}$ = local- and global-space coordinates
$\boldsymbol{q}'$ = initial local-space tracer location
$\boldsymbol{q}_o, \underline{Q}_\infty$ = local- and global-space domains
$\partial \boldsymbol{q}_o, \partial \underline{Q}_\infty$ = local- and global-space boundaries
s = local-space boundary coordinate on the surface $\partial \boldsymbol{q}_o$
t = time
t_r, t_L = characteristic times for cross-sectional and axial transport
$\boldsymbol{u}, \underline{U}$ = local- and global-space velocity vectors
$\bar{\underline{U}}$ = constant vector, Eq. 42
$\bar{\underline{U}}_o$ = normalized mean global speed of solute particle
$\bar{\underline{U}}^*$ = mean global velocity vector
$\underline{v}$ = fluid velocity
$\bar{V}, \bar{\underline{V}}$ = mean solvent velocity
x, y = Cartesian coordinates
$z = x/b$ = dimensionless axial tube coordinate

Greek letters

β = dimensionless eigenvalue, Eqs. 82a,b
β_0 = smallest nonzero root of Eqs. 82a,b
β_∞ = smallest nonzero root of Eq. 94
$\boldsymbol{\Gamma}_m$ = global-space polyadic functions, Eqs. 22a,b,c
δ = Dirac delta function
δ_{m0} = Kronecker delta
$\zeta = Pe/2\beta_0$ = dimensionless parameter
η = integration variable, Eq. 88
$\lambda = \bar{K}b^2/D$ = effective or apparent macroscale Damkohler number
$\mu = kb/D$ = surface Damkohler number
μ^* = constant, Eq. 81
μ_o = solvent viscosity
ξ = integration variable, Eq. 88
$\boldsymbol{\xi}$ = generic tensor-valued function
ϕ = z-dependent function, Eqs. 80a,b

Subscripts

m = of the order m
0 = corresponding to leading eigensolution
r = corresponding to reactive case

Superscripts

C = convective contribution
M = molecular contribution
s = symmetric portion of a dyadic
∞ = asymptotic long-time limit
$\dagger$ = transpose
$*$ = global phenomenological coefficient, or adjoint operator
$^-$ = (overbar) average over $\boldsymbol{q}_o$ space

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