

# Mass Transport and Chemical Reaction in Taylor-Vortex Flows with Entrained Catalytic Particles: Applications to a Novel Class of Immobilized Enzyme Biochemical Reactors

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# Mass transport and chemical reaction in Taylor-vortex flows with entrained catalytic particles: applications to a novel class of immobilized enzyme biochemical reactors

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The general problem of mass transport and chemical reaction in spatially periodic annular flows with entrained catalytic particles is investigated using generalized Taylor–Aris dispersion theory arguments. Generic formulas are derived for the effective solute reaction rate, mean axial velocity and dispersivity in terms of the numerous geometric, kinematic, kinetic and material physicochemical parameters

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defining the complex three-dimensional transport and reaction problem. The theoretical analysis constitutes a prelude to rationalizing the behaviour (and optimizing the design) of a class of immobilized enzyme biochemical reactors, in which the 'catalytic' enzyme is distributed over the surfaces of small entrained particles.

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## 1. Introduction

The following exposition addresses the general problem of mass transport and chemical reaction in ordered vortical flows, with direct applications to a class of immobilized enzyme biochemical reactors whose purpose it is to remove a solute (e.g. protein) from a solvent (e.g. blood) by means of a catalytic chemical reaction. These reactors are composed of a stationary outer cylinder and a concentric inner cylinder rotating about its axis, with a net axial flow occurring in the annular gap between them, as in figure 1. The catalyst (e.g. an enzyme) is distributed either over the surface of the inner cylinder, or on the surfaces of small, non-neutrally buoyant particles (or beads), each of which sediments under the influence of gravity relative to the net (vertical) axial flow.

Given that the outer cylinder is stationary, toroidal vortices will exist in the annular fluid at sufficiently large rates of rotation of the inner cylinder (Taylor 1923; Chandrasekhar 1981). This vortex phenomenon (on which is superposed an axial flow) represents a type of *Taylor instability*, with the resulting fluid-mechanical flow pattern formed composed of *Taylor vortices*. Numerous experiments (see, for example, Cohen & Maron 1983; Koenig *et al.* 1954; Coeuert & Legrand 1981) have demonstrated a significant improvement in the effectiveness of both catalytic bead and wall reactors at rotation rates exceeding the Taylor instability threshold. This enhancement is primarily manifested by an increased overall reaction rate, although several peripheral benefits also ensue (e.g. the reactor does not clog with the crushed cells that are invariably present in the blood; moreover, the gentle mixing action provided by the Taylor vortices often proves to be sufficiently mild so as not to mechanically damage living blood cells). Accordingly, both types of reactors (when operated at rotation rates above the Taylor instability threshold) have recently achieved a growing popularity.

The aim of the research reported here is to quantify the effects of Taylor vortices upon the performance of the bead-containing reactors. (Comparable catalytic wall reactors will be addressed separately.) Towards this goal we will theoretically investigate the (non-conservative) diffusive and convective transport of reactive solute molecules in a spatially periodic vortical flow. The term 'non-conservative' as used here connotes the fact that the solute molecules may disappear permanently from the system as a result of a catalytic chemical reaction occurring on the surfaces of the beads. Solute molecules and beads will be modelled as brownian entities, each undergoing both molecular diffusion and convection. The solute molecules will be assumed to be of infinitesimal size, whereas the beads will be assumed to be of a finite size, at least insofar as each bead possesses a non-zero surface area, allowing for both solute mass transfer between the solvent and beads, as well as solute reaction on the bead surfaces. The bead radii will be supposed much smaller than the annular gap between the cylinders, so that hydrodynamic wall effects upon the bead's motion resulting from their non-zero size may be ignored.

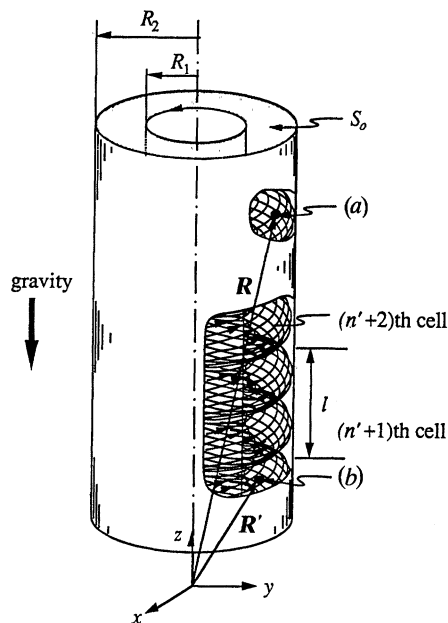


Figure 1. The annular vortex reactor. The reactor is composed of two concentric cylinders, a stationary outer cylinder and a rotating inner cylinder. Solvent flows upward (along  $z$ -axis) through the annular gap between the cylinders. The non-neutrally buoyant beads (not shown) sediment downward under the influence of gravity relative to this upward flow. A single toroidal vortex-pair represents a unit cell, with  $l$  the length of the cell in the axial direction. Cells are numbered sequentially as  $n = 0, \pm 1, \pm 2, \dots$ , with  $n$  increasing along the positive  $z$ -axis. The solute tracer molecule was initially introduced into cell  $n'$  at time  $t = 0$ , and is currently (i.e. at time  $t$ ) located in cell  $n$ . Current (a) tracer position vector is  $\mathbf{R} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z$ ; initial (b) tracer position vector is  $\mathbf{R}' = x'\mathbf{e}_x + y'\mathbf{e}_y + z'\mathbf{e}_z$ .

Given that a single solute molecule is initially introduced into the reactor at some annular point (whose position vector is)  $\mathbf{R}'$  at time  $t = 0$ , the conditional probability density  $P(\mathbf{R}, t | \mathbf{R}')$  of subsequently finding that molecule at a point  $\mathbf{R}$  at a later time  $t$  is assumed to be governed by an appropriate system of 'convective-diffusive-reactive' equations (Brenner 1980). In general, these equations (incorporating an appropriate set of (linear) boundary conditions) may be solved numerically for  $P$  at each point  $\mathbf{R}$  and each instant  $t$ ; however, such an exhaustively detailed (i.e. *microscale*) solution often proves unnecessary in applications (Brenner 1980). In practice, having initially introduced a known distribution of solute into the reactor, one generally measures only the total amount (i.e. the cross-sectionally area-averaged concentration) of solute exiting from the reactor as a function of time, without actually investigating the detailed concentration distribution existing at each point  $\mathbf{R}$  of the reactor at each instant of time. It can be shown (Shapiro & Brenner 1988) that this area-averaged solute concentration,  $\bar{P}$ , say, may be uniquely characterized (cf. (10.4) and (10.6)) by three *macroscale* phenomenological parameters, namely: (i) an effective solute reaction rate coefficient  $\bar{K}^*$  (appearing as the multiplier of  $\bar{P}$  in a first-order irreversible reaction); (ii) the average axial velocity  $\bar{U}^*$  of the solute (which, due to the chemical reaction, is not necessarily the same as the average velocity  $\bar{V}$  of the inert solvent carrier); and (iii) the axial dispersivity  $\bar{D}^*$  of the solute (which differs in a major way from molecular diffusivity of the solute through the solvent, and often exceeds the latter by many orders of magnitude;

moreover, owing to the chemical reaction,  $\bar{D}^*$  will generally differ (Shapiro & Brenner 1988) from the axial dispersivity  $\bar{D}_0^*$  that would prevail in the absence of reaction, all things being equal).

The ultimate aim of this research is to parametrically establish the functional dependence of  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$  upon the geometrical and operating characteristics of the reactor (e.g. the radii of the cylinders, the rate of rotation of the inner cylinder, the annular axial volumetric flow rate, etc.) as well as the physicochemical material properties of the solute, solvent and catalytic surface(s). To this end, we shall theoretically investigate the dependence of  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$  upon the spectral characteristics of the detailed solvent velocity and vorticity fields, as well as upon the other fixed parameters of the problem. This task may be conveniently executed within the framework of *generalized Taylor–Aris dispersion theory* owing to the spatially periodic nature (Brenner 1980) of the vortical flow field.

## 2. Taylor dispersion formulation of the two-phase system

Consider a system composed of a flowing inert solvent containing an entrained monodisperse suspension of non-neutrally buoyant beads. This two-phase system will be envisioned as composed of two interpenetrating continua (cf. Haber & Brenner 1993). In particular, the spatial distribution of beads will be regarded as a continuum-mechanical field variable, with  $c \equiv c(\mathbf{R}, t)$  the instantaneous microscale number density or ‘concentration’ of the continuous bead ‘phase’ at a point  $\mathbf{R}$  of the reactor at time  $t$  (although we will ultimately simplify the analysis by confining attention to the case where the beads are homogeneously distributed, so that  $c = \text{const.}$ , independent of position and time). The solute itself may exist either in a dissolved state within the solvent phase, or in an adsorbed state on the bead surfaces; an irreversible first-order chemical reaction, serving to deplete the solute, is assumed to occur on these bead surfaces. No reaction is assumed to occur within the solvent itself (or on the bounding reactor walls, from which catalyst is here supposed absent).

In the spirit of Taylor dispersion theory (Brenner 1980), a solute molecule will be represented as a material brownian ‘tracer’. As such, local transport of this solute tracer may be regarded as occurring by four distinct mechanisms: (i) convective transport by the flowing solvent; (ii) molecular diffusion within this solvent; (iii) ‘piggy-back’ convection; and (iv) ‘piggy-back’ diffusion, occurring by virtue of the bead phase’s respective convective and diffusive motions. (Each carrier bead itself undergoes ‘passive’ convection by virtue of being entrained within the flowing solvent; ‘active’ convection by virtue of the bead’s non-neutral buoyancy; and brownian diffusion by virtue of the colloidal beads’ random motion relative to the local solvent flow.) Overall transport of the solute tracer is necessarily non-conservative owing to the fact that the tracer may disappear by virtue of chemical reaction on the bead surfaces.

We will assume that inner cylinder rotation rate exceeds the Taylor instability threshold, so that the annular flow field is dominated by Taylor vortices, albeit with a superposed axial flow (e.g. Gu & Fahidy 1985). As these vortices (including the superposed axial flow) form a well-defined *stationary* spatially periodic flow pattern (with spatial periodicity existing parallel to the reactor axis), we may use the well-known extension (Brenner 1980; Shapiro & Brenner 1988) of Taylor dispersion theory to spatially periodic systems as the basis for our analysis of the reactor. As the relevant spatially periodic paradigm embodying this extension is rather abstract,

we have chosen in the following development to emphasize clarity over generality; accordingly, all subsequent derivations will be specific to the two types of the reactors being considered, with a single toroidal Taylor vortex pair comprising the repetitive basic unit cell. In this context of simplicity, scalar (rather than tensor) probabilistic moments will be employed, consistent with the axial unidirectional spatial periodicity (along, say,  $z$ -axis). In all other respects, the subsequent notation and the assumptions will closely follow those used in the general theory for reactive systems (Shapiro & Brenner 1988).

Let  $\mathbf{u}_v \equiv \mathbf{u}_v(\mathbf{R})$  and  $\mathbf{u}_b \equiv \mathbf{u}_b(\mathbf{R})$  be the respective (spatially periodic) time-independent microscale vector velocity fields of the interpenetrating solvent ( $v$ ) and bead ( $b$ ) continua; similarly, denote by  $D_v$  and  $D_b$  the respective (time- and position-independent) molecular and brownian diffusion coefficients of the solute and bead phases through the solvent. Both of the preceding velocity fields will be assumed to satisfy continuity equations of the respective forms

$$\nabla \cdot \mathbf{u}_v = 0, \quad \nabla \cdot \mathbf{u}_b = 0, \quad (2.1 a, b)$$

with 
$$\mathbf{n} \cdot \mathbf{u}_v = 0, \quad \mathbf{n} \cdot \mathbf{u}_b = 0 \quad \text{on the reactor walls,} \quad (2.2 a, b)$$

wherein  $\mathbf{n}$  denotes a unit normal vector on the appropriate surface. Note, that equations (2.1) imply time- and position-independent solvent density, as well as time- and position-independent bead-phase number density.

The brownian bead diffusivity  $D_b$  plays a minor, inherently nonsingular role in the subsequent theory. As such no mathematical or other difficulty arises in setting  $D_b = 0$  for the case of large, non-brownian beads, or whenever such an assumption is warranted. In contrast, in the case of the solvent phase, it is essential that  $D_v > 0$ ; otherwise, it would not prove possible to attain the asymptotic quasi-steady solute distribution within a unit cell, necessary for the validity of the subsequent theory.

Let  $P_v \equiv P_v(\mathbf{R}, t | \mathbf{R}'; \zeta)$  and  $P_b \equiv P_b(\mathbf{R}, t | \mathbf{R}'; \zeta)$  denote the respective conditional probability densities that the solute tracer is situated at point  $\mathbf{R}$  at time  $t$  (either dissolved in the solvent or adsorbed on the surface of the beads), given that the tracer was located at point  $\mathbf{R}'$  at time  $t = 0$  in an initially dissolved or adsorbed state: one quantified by a single real-valued 'partition' coefficient,  $0 \leq \zeta \leq 1$ . Explicitly, at time  $t = 0$ ,

$$P_v(\mathbf{R}, 0 | \mathbf{R}'; \zeta) = \zeta \delta(\mathbf{R} - \mathbf{R}'), \quad P_b(\mathbf{R}, 0 | \mathbf{R}'; \zeta) = (1 - \zeta) \delta(\mathbf{R} - \mathbf{R}'). \quad (2.3 a, b)$$

Thus, for example, the choice  $\zeta = 0$  connotes the tracer was initially (at time  $t = 0$ ) wholly adsorbed on the beads, whereas with  $\zeta = 1$  the tracer was initially wholly dissolved in the solvent.

The probability densities  $P_v$  and  $P_b$  will be supposed governed by convective-diffusive-reactive equations of the respective forms

$$\frac{\partial P_v}{\partial t} + \nabla \cdot \mathbf{J}_v + S = \zeta \delta(\mathbf{R} - \mathbf{R}') \delta(t), \quad (2.4 a)$$

$$\frac{\partial P_b}{\partial t} + \nabla \cdot \mathbf{J}_b - S + \gamma P_b = (1 - \zeta) \delta(\mathbf{R} - \mathbf{R}') \delta(t), \quad (2.4 b)$$

in which the conditional probability flux density vectors appearing therein are given by the fickian constitutive equations

$$\mathbf{J}_v = \mathbf{u}_v P_v - D_v \nabla P_v, \quad \mathbf{J}_b = \mathbf{u}_b P_b - D_b \nabla P_b. \quad (2.5 a, b)$$

In (2.4), the position- and time-independent phenomenological constant  $\gamma \geq 0$  represents the specific reaction-rate constant governing the local rate of disappearance of solute from the bead surfaces via a first-order irreversible reaction. Moreover, the algebraically-signed scalar (Haber & Brenner 1991)

$$S = k_1(k_2 ac P_v - P_b) \equiv k_4 P_v - k_1 P_b \quad (2.6)$$

represents the rate of solute transfer from the (dissolved state in the) solvent to the (adsorbed state on the) beads, per unit of superficial volume.† Here,  $k_1 \geq 0$  and  $k_2 \geq 0$  are non-negative constants,  $a$  is the surface area of a single bead, and the constant  $k_4 \geq 0$  is defined as

$$k_4 \stackrel{\text{def}}{=} k_1 k_2 ac. \quad (2.7)$$

Note, that when  $k_1 = 0$  no transfer of solute between the solvent and beads is possible; consequently, in such special circumstances, respective solute transport by the solvent and beads may be regarded as two independent uncorrelated processes occurring in parallel. This case will be discussed at length at the end of this presentation. In the interim, we shall proceed on the assumption that  $k_1 \neq 0$ . Subsequently, in §11, the phenomenological coefficients  $\gamma, k_1, k_2, a$  and  $c$  appearing above are interpreted in terms of their respective geometric, physicochemical and velocity-field functional dependencies.

The corresponding boundary conditions (Brenner 1980) to be imposed upon the above system of equations are: (i) solute may neither be added to nor removed from the reactor through its walls; this condition may be formally written as

$$\mathbf{n} \cdot \mathbf{J}_\alpha = 0 \quad \text{on the reactor walls}; \quad (2.8a)$$

(ii) solute is absent from the reactor before its initial introduction into the system at time  $t = 0$ ; this requires that

$$P_\alpha = 0 \quad \text{for all } t < 0. \quad (2.8b)$$

In these, as well as in all subsequent equations, the index  $\alpha$  implicitly represents both the indices b and v; that is

$$\alpha \equiv (\text{b}, \text{v}). \quad (2.9)$$

For example, in (2.8a) the boundary condition  $\mathbf{n} \cdot \mathbf{J}_\alpha = 0$  represents the pair of boundary conditions

$$\mathbf{n} \cdot \mathbf{J}_b = 0, \quad \mathbf{n} \cdot \mathbf{J}_v = 0 \quad \text{on the reactor walls.}$$

Integrating the respective probability densities at time  $t = 0$  (2.3) over the reactor's infinitely extended annular domain  $V_\infty$ , one finds that

$$\int_{V_\infty} d^3 \mathbf{R} P_v = \zeta, \quad \int_{V_\infty} d^3 \mathbf{R} P_b = 1 - \zeta \quad \text{at } t = 0, \quad (2.10a, b)$$

† With  $s \stackrel{\text{def}}{=} ac$  the 'specific surface', namely the bead surface area per unit of superficial volume, the quantity  $p_b \stackrel{\text{def}}{=} P_b/s$  represents the areal density (i.e. surface 'concentration') of solute adsorbed on the beads. In turn, the respective constants  $k_1$  and  $k_2$  are readily identified (Bird *et al.* 1960) as the solute mass-transfer coefficient and Henry's law adsorption coefficient in the equilibrium linear constitutive relation  $p_b = k_2 P_v$  (see the further discussion in §11).

with  $\mathbf{R} \in V_\infty$ , and  $d^3\mathbf{R} = dx dy dz$ . The integral

$$\Pi(t|\mathbf{R}'; \zeta) \stackrel{\text{def}}{=} \int_{V_\infty} d^3\mathbf{R} [P_v(\mathbf{R}, t|\mathbf{R}'; \zeta) + P_b(\mathbf{R}, t|\mathbf{R}'; \zeta)] \quad (2.11)$$

represents the *total* probability that the tracer is situated *somewhere* within the reactor's annular (effectively axially unbounded) spaced domain at time  $t$ , either dissolved in the solvent or adsorbed on the beads. This probability is conserved in the absence of chemical reaction (in which case  $\Pi = 1$  for all  $t \geq 0$ ); otherwise, it diminishes monotonically with time. Thus,

$$0 < \Pi \leq 1 \quad (t \geq 0), \quad (2.12)$$

where the equality sign applies only at  $t = 0$  (or in the absence of chemical reaction).

### 3. Local and total moments

Upon utilizing the axial spatial periodicity of the annual vortex flow field, define (Brenner 1980) the  $m$ th-order ( $m = 0, 1, 2, \dots$ ) local and total moments of the respective pair of conditional probability densities  $P_v$  and  $P_b$  as

$$P_\alpha^{(m)}(\mathbf{r}, t|\mathbf{r}'; \zeta) \stackrel{\text{def}}{=} l^m \sum_{n=-\infty}^{\infty} (n - n')^m P_\alpha(\mathbf{r} + n\mathbf{e}_z, t|\mathbf{r}' + n'\mathbf{e}_z; \zeta) \quad (3.1)$$

and

$$M_\alpha^{(m)}(t|\mathbf{r}'; \zeta) \stackrel{\text{def}}{=} \int_{\tau_0} d^3\mathbf{r} P_\alpha^{(m)}(\mathbf{r}, t|\mathbf{r}'; \zeta), \quad (3.2)$$

with  $\mathbf{r} \in \tau_0$ . In these expressions, the integer  $n = 0, \pm 1, \pm 2, \dots$  is the current cell number;  $n'$  denotes the number of the initial cell into which the tracer was originally introduced into the system at  $t = 0$ ;  $l$  is the length of a unit cell in the axial direction;  $\mathbf{e}_z$  is a unit vector parallel to the axis of the reactor (see figure 1);  $d^3\mathbf{r} \equiv dx dy dz$  is a volume element within a unit cell; and the domain  $\tau_0$  denotes the superficial region occupied by a unit cell (as well as the actual magnitude of the unit cell volume). With the cells numbered sequentially,  $\mathbf{r} = \mathbf{R} - n\mathbf{e}_z \equiv \mathbf{e}_x x + \mathbf{e}_y y + \mathbf{e}_z z$  denotes the (local) position vector of a point within a unit cell, whereas  $\mathbf{r}' = \mathbf{R}' - n'\mathbf{e}_z \equiv \mathbf{e}_x x' + \mathbf{e}_y y' + \mathbf{e}_z z'$  denotes the initial local position vector of the solute tracer molecule (within the unit cell  $n'$  into which the tracer was originally introduced at time). Note that in generalized Taylor dispersion theory (Brenner 1982),  $\mathbf{r}$  and  $n\mathbf{e}_z$  may be respectively identified with the continuous *local* ( $\mathbf{q}$ ) and the discrete *global* ( $\mathbf{Q}$ ) coordinates.

In subsequent derivations it will prove convenient to represent the respective local and total moments of the pair of probability densities as column vectors of order two; explicitly

$$\mathbf{P}^{(m)} \stackrel{\text{def}}{=} \begin{pmatrix} P_v^{(m)} \\ P_b^{(m)} \end{pmatrix}, \quad \mathbf{M}^{(m)} \stackrel{\text{def}}{=} \begin{pmatrix} M_v^{(m)} \\ M_b^{(m)} \end{pmatrix}. \quad (3.3a, b)$$

The velocity fields  $\mathbf{u}_\alpha$  are assumed to be spatially periodic functions, and thus functionally dependent only upon  $\mathbf{r}$ , but not  $n$ ; moreover, the diffusivity coefficients  $D_\alpha$  appearing in (2.5) are assumed to be everywhere constant. Accordingly, substitution of (3.1) into (2.4) leads to the expression

$$\frac{\partial \mathbf{P}^{(m)}}{\partial t} + [\mathcal{L}] \mathbf{P}^{(m)} + [A] \mathbf{P}^{(m)} = \delta_{m0} \delta(\mathbf{r} - \mathbf{r}') \delta(t) \begin{pmatrix} \zeta \\ 1 - \zeta \end{pmatrix}, \quad (3.4)$$



( $m = 0, 1, 2, \dots$ ), for the temporal evolution of the local moments; (compare with Brenner (1980)). Here,

$$[A] \stackrel{\text{def}}{=} \begin{pmatrix} k_a & -k_1 \\ -k_a & k_1 + \gamma \end{pmatrix} \quad (3.5)$$

is a  $2 \times 2$  matrix of constant phenomenological coefficients jointly quantifying both the rate of (conservative) solute transfer (between the dissolved and adsorbed states), and the (non-conservative) rate of solute depletion by chemical reaction from the adsorbed state. Additionally,

$$[\mathcal{L}] \stackrel{\text{def}}{=} \begin{pmatrix} \mathcal{L}_v & 0 \\ 0 & \mathcal{L}_b \end{pmatrix}, \quad (3.6a)$$

in which, with  $F$  a generic (scalar) field,

$$\mathcal{L}_\alpha F \stackrel{\text{def}}{=} \nabla \cdot (\mathbf{u}_\alpha F - D_\alpha \nabla F); \quad (3.6b)$$

that is, the matrix  $[\mathcal{L}]$  is a linear second-order differential operator that pertains to the collective convective-diffusive transport of the solute tracer by both the solvent and beads.

The boundary conditions to be satisfied by the local moments may be evaluated (Brenner 1980) directly from (2.8) and (3.1); thus, the condition (2.8a) of no solute flux at the cylinder walls requires that

$$\mathbf{n} \cdot [\mathbf{u}_\alpha P_\alpha^{(m)} - D_\alpha \nabla P_\alpha^{(m)}] = 0 \quad \text{on the reactor walls} \quad (3.7a)$$

for each  $m = 0, 1, 2, \dots$  for each  $\alpha = v, b$ . Moreover, the lack of dependence of the local moments upon the particular choice of unit cell in the sequence  $n - n' = 0, \pm 1, \pm 2, \dots$  requires that (Brenner 1980)

$$\|P_\alpha^{(0)}\| = 0, \quad \|P_\alpha^{(1)}\| = -\|zP_\alpha^{(0)}\|, \quad \|P_\alpha^{(2)}\| = \|P_\alpha^{(1)^2}/P_\alpha^{(0)}\|, \dots, \quad \|P_\alpha^{(m)}\| = \dots \quad (3.7b)$$

Here, the 'jump' function operator, defined by the double modulus bars, namely

$$\|F\| \stackrel{\text{def}}{=} F(\mathbf{R} + l\mathbf{e}_z) - F(\mathbf{R}), \quad (3.8)$$

with  $F$  a generic scalar function, denotes the increase in the value of  $F$  between equivalent points of adjacent cells. Note that for  $F$  any analytic function, the jump function operator commutes with the gradient operator  $\nabla \equiv \partial/\partial \mathbf{R} = \partial/\partial \mathbf{r}$ ; explicitly

$$\nabla \|F\| = \|\nabla F\|. \quad (3.9)$$

As such, one need not impose any first-derivative boundary conditions on the functions  $\|\partial P_\alpha^{(m)}/\partial z\|$  ( $m = 0, 1, 2, \dots$ ), of the type suggested in earlier papers (Brenner 1980; Shapiro & Brenner 1988) addressed to spatially periodic systems. In particular, because of the generic identity (3.9), all first-derivative boundary conditions that might otherwise have appeared are automatically satisfied by satisfaction of (3.7b).

In conjunction with use of the properties of the jump operator, integration of (3.4) leads to the following equation for the temporal evolution of the total moments:

$$\frac{d\mathbf{M}^{(m)}}{dt} + [A]\mathbf{M}^{(m)} = \int_{S_0} d^2\mathbf{r} \begin{pmatrix} -u_v \|P_v^{(m)}\| + D_v \|\partial P_v^{(m)}/\partial z\| \\ -u_b \|P_b^{(m)}\| + D_b \|\partial P_b^{(m)}/\partial z\| \end{pmatrix} + \delta_{m0} \delta(t) \begin{pmatrix} \zeta \\ 1 - \zeta \end{pmatrix} \quad (3.10)$$

( $m = 0, 1, 2, \dots$ ), in which  $S_0$  denotes the annular cross-sectional domain of the reactor;  $d^2\mathbf{r} \equiv dx dy$  is a corresponding cross-sectional areal element of that annular domain; and  $u_\alpha \equiv \mathbf{e}_z \cdot \mathbf{u}_\alpha$ , with  $\alpha$  given by (2.9), are the axial velocity components of the respective solvent and bead phases.

#### 4. Macroscale phenomenological coefficients $\bar{K}^*$ , $\bar{U}^*$ and $\bar{D}^*$

Derivation of the basic Taylor dispersion paradigms relating the macroscale phenomenological coefficients  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$  to the prescribed microscale phenomenological data is addressed in subsequent sections. Prerequisite to the derivation of such formulas are the formal definitions of these three coefficients, discussed below.

##### (a) Definition of $\bar{K}^*$

In view of the axial spatial periodicity of the Taylor vortex flow field, the (infinite) annular domain  $V_\infty$  of the reactor may be conveniently decomposed into an infinite number of geometrically congruent (and kinematically identical) unit cells, each of volume  $\tau_0$ . Thus, the obvious identity

$$\int_{V_\infty} d^3\mathbf{R} F(\mathbf{R}) \equiv \sum_{n=-\infty}^{\infty} \int_{\tau_0} d^3\mathbf{r} F(\mathbf{r} + n\mathbf{l}e_z), \quad (4.1)$$

holds for any (generic) function  $F \equiv F(\mathbf{R})$ . Hence, by definition (cf. (3.2)), the zero-order total moments,  $M_v^{(0)}$  and  $M_b^{(0)}$ , constitute the *individual probabilities* of observing the solute tracer somewhere within the reactor in the respective dissolved and adsorbed states at time  $t$ , given that the tracer was originally introduced at the point  $\mathbf{R}'$  within the reactor at time  $t = 0$  in a certain initial state, quantified by the phase-partitioning parameter  $\zeta$ . Equivalently, these moments may also be envisioned as the respective amounts of solute remaining within the reactor at time  $t$  in the corresponding states, given that the amounts  $\zeta$  and  $1 - \zeta$  of solute were introduced at the point  $\mathbf{R}'$  (at  $t = 0$ ) into the solvent and onto the beads, respectively. Thus, the sum

$$\Pi \equiv M_v^{(0)} + M_b^{(0)}, \quad (4.2)$$

constitutes the total amount of unreacted solute in the reactor at time  $t$ . (The above identity immediately follows from (2.11), (3.2) and (4.1).)

By using moment-matching methods, it may be demonstrated (Shapiro & Brenner 1988) that in the long-time limit, the relative rate of disappearance of solute from the *system* (namely, the reactor) as a whole asymptotically obeys the first-order irreversible reaction rate law,

$$d\Pi/dt \sim -\bar{K}^* \Pi,$$

with  $\Pi$  defined in (2.11), and  $\bar{K}^*$  the reaction-velocity constant. The concomitant exponential solute decay rate implicit in the above expression, eventually leads to the following calculational 'definition' of the specific reaction-rate coefficient:

$$\bar{K}^* \stackrel{\text{def}}{=} -\lim_{t \rightarrow \infty} \frac{d}{dt} [\ln (M_b^{(0)} + M_v^{(0)})]. \quad (4.3)$$

(b) Definition of  $\bar{U}^*$ 

The mean global axial displacement  $\overline{z-z'} \equiv \bar{\Delta z}$  of the tracer at time  $t$  from its initial axial position  $z'$  at time  $t = 0$ , is given by the expression

$$\bar{\Delta z} \stackrel{\text{def}}{=} \frac{\int_{V_\infty} d^3 \mathbf{R} (z-z') [P_v(\mathbf{R}, t | \mathbf{R}'; \zeta) + P_b(\mathbf{R}, t | \mathbf{R}'; \zeta)]}{\int_{V_\infty} d^3 \mathbf{R} [P_v(\mathbf{R}, t | \mathbf{R}'; \zeta) + P_b(\mathbf{R}, t | \mathbf{R}'; \zeta)]}. \quad (4.4)$$

The integral appearing in the denominator may be readily identified (cf. (3.1) and (3.2)) with the sum  $M_v^{(0)} + M_b^{(0)}$  of zero-order total moments or, equivalently, the 'survival' probability  $\Pi$  (cf. (4.2)). On the other hand, after a sufficiently long time following introduction of the tracer into the system, the probabilities  $P_v$  and  $P_b$  become almost constant over a given unit cell, in which case the integral in the numerator may be closely approximated by the sum  $M_v^{(1)} + M_b^{(1)}$  of first-order total moments. In fact, one may demonstrate (Shapiro & Brenner 1988) that, asymptotically,

$$\bar{\Delta z} \sim (M_v^{(1)} + M_b^{(1)}) / (M_v^{(0)} + M_b^{(0)}). \quad (4.5)$$

Thus, in terms of the zero- and first-order total moments, the average tracer velocity may be defined as

$$\bar{U}^* \stackrel{\text{def}}{=} \lim_{t \rightarrow \infty} \frac{d\bar{\Delta z}}{dt} \equiv \lim_{t \rightarrow \infty} \frac{d(M_v^{(1)} + M_b^{(1)})}{d(M_v^{(0)} + M_b^{(0)})}. \quad (4.6)$$

(c) Definition of  $\bar{D}^*$ 

Following the same steps that lead to (4.5), one can demonstrate (Shapiro & Brenner 1988) that the mean square displacement  $(\Delta z - \bar{\Delta z})^2$  of the tracer from its initial position at time  $t = 0$ , may be expressed asymptotically by the following combination

$$\overline{(\Delta z - \bar{\Delta z})^2} \equiv \overline{\Delta z^2} - \bar{\Delta z}^2 \sim \frac{M_v^{(2)} + M_b^{(2)}}{M_v^{(0)} + M_b^{(0)}} - \left( \frac{M_v^{(1)} + M_b^{(1)}}{M_v^{(0)} + M_b^{(0)}} \right)^2 \quad (4.7)$$

of zero-, first- and second-order total moments. Accordingly, the effective dispersivity of the solute may be formally defined (Shapiro & Brenner 1988) as a limit

$$\bar{D}^* \stackrel{\text{def}}{=} \frac{1}{2} \lim_{t \rightarrow \infty} \frac{d \overline{(\Delta z - \bar{\Delta z})^2}}{dt} \equiv \frac{1}{2} \lim_{t \rightarrow \infty} \frac{d}{dt} \left[ \frac{M_v^{(2)} + M_b^{(2)}}{M_v^{(0)} + M_b^{(0)}} - \left( \frac{M_v^{(1)} + M_b^{(1)}}{M_v^{(0)} + M_b^{(0)}} \right)^2 \right]. \quad (4.8)$$

(d) Alternative interpretations of  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$ 

In lieu of the phenomenological coefficients describing the total solute transport (in both the solvent and bead phases), one may also define comparable transport coefficients for the respective individual phases, namely

$$\bar{K}_\alpha^* \stackrel{\text{def}}{=} - \lim_{t \rightarrow \infty} \frac{d}{dt} [\ln M_\alpha^{(0)}], \quad (4.9)$$

$$\bar{U}_\alpha^* \stackrel{\text{def}}{=} \lim_{t \rightarrow \infty} \frac{d}{dt} \left( \frac{M_\alpha^{(1)}}{M_\alpha^{(0)}} \right) \quad (4.10)$$

and

$$\bar{D}_\alpha^* \stackrel{\text{def}}{=} \lim_{t \rightarrow \infty} \frac{d}{dt} \left[ \frac{M_\alpha^{(2)}}{M_\alpha^{(0)}} - \left( \frac{M_\alpha^{(1)}}{M_\alpha^{(0)}} \right)^2 \right], \quad (4.11)$$

as each of these limits can be shown to exist.

A sufficiently long time after introducing the solute into the reactor, a quasi-steady partitioning of the solute between the solvent and beads is obtained (cf. (5.10), (6.3) and (7.5)), in which the ratio of solute present in both phases attains a *time-independent* value (although the actual amounts of solute present in each phase diminish exponentially in time). In this quasi-steady case, the definitions (4.3), (4.6) and (4.8) should be formally equivalent with definitions (4.9)–(4.11). And equivalent they are, as may easily be verified by repeating the subsequent computations (based upon definitions (4.3), (4.6) and (4.8)) using these latter definitions. Thus,

$$\bar{K}_\alpha^* \equiv \bar{K}^*, \quad \bar{U}_\alpha^* \equiv \bar{U}, \quad \bar{D}_\alpha^* \equiv \bar{D}^*. \quad (4.12a-c)$$

## 5. Effective solute reaction rate coefficient $\bar{K}^*$

### (a) Zero-order total moments

Following (3.10) (with  $m = 0$ ), the temporal evolution of the zero-order total moments is governed by the equation

$$\frac{d\mathbf{M}^{(0)}}{dt} + [A]\mathbf{M}^{(0)} = \delta(t) \begin{pmatrix} \zeta \\ 1 - \zeta \end{pmatrix}. \quad (5.1)$$

As  $[A]$  is a matrix composed of constant elements, the most general solution of (5.1) may be sought in the form

$$\mathbf{M}^{(0)} = \hat{M}_+^{(0)} \exp(-\lambda_+ t) \mathbf{E}_+ + \hat{M}_-^{(0)} \exp(-\lambda_- t) \mathbf{E}_-, \quad (5.2)$$

wherein  $\hat{M}_\pm^{(0)}$  are constant scalar coefficients to be determined; moreover,

$$\lambda_\pm = \frac{1}{2}\{k_1 + k_4 + \gamma \pm [(k_1 + k_4 + \gamma)^2 - 4k_4\gamma]^{\frac{1}{2}}\} \quad (5.3)$$

are the eigenvalues of  $[A]$ , and

$$\mathbf{E}_\pm \equiv \begin{pmatrix} E_\alpha^\pm \\ E_\beta^\pm \end{pmatrix} = \begin{pmatrix} 1 \\ k_\pm \end{pmatrix}, \quad k_\pm \stackrel{\text{def}}{=} \frac{k_4}{k_1 + \gamma - \lambda_\pm} \equiv \frac{k_4 - \lambda_\pm}{k_1}, \quad (5.4a, b)$$

are the corresponding eigenvectors; that is

$$[A]\mathbf{E}_\pm = \lambda_\pm \mathbf{E}_\pm. \quad (5.5)$$

Our prior assumption that  $k_1 > 0$  assures the existence of two different eigenvalues,  $\lambda_+ > \lambda_-$ , for the system in question. Thus, even in the absence of a chemical reaction (when  $\lambda_- = \gamma = 0$ ), the system necessarily manifests exponentially attenuated temporal behaviour. This fact is related to the eventual establishment of a local quasi-steady solute partitioning between the solvent and bead phases.

The coefficients  $\hat{M}_+^{(0)}$  and  $\hat{M}_-^{(0)}$  are determined by the initial conditions prevailing at  $t = 0$ , namely by the physical ‘state’  $\zeta$  in which the solute tracer molecule existed when it was originally introduced into the system; either initially dissolved in the solvent, affixed to a bead, or fractionally partitioned between these two states. From (2.10) (or, equivalently, upon integration of (5.1) with respect to time between  $t = 0^-$  and  $t = 0^+$ ), one finds that

$$\hat{M}_+^{(0)} \mathbf{E}_+ + \hat{M}_-^{(0)} \mathbf{E}_- = \begin{pmatrix} \zeta \\ 1 - \zeta \end{pmatrix}. \quad (5.6)$$

Consequently, we obtain the explicit values

$$\hat{M}_{\pm}^{(0)} = \pm \frac{(k_{\mp} + 1)\zeta - 1}{k_- - k_+} \quad (5.7)$$

in terms of the parameters of the problem. It will be assumed henceforth that  $\hat{M}_{\pm}^{(0)} \neq 0$ .

The sum

$$\Pi = (1 + k_+) \hat{M}_+^{(0)} \exp(-\lambda_+ t) + (1 + k_-) \hat{M}_-^{(0)} \exp(-\lambda_- t) \quad (5.8)$$

of the zero-order moments, constitutes (cf. (2.11), (4.2) and (5.2)) the probability of the tracer existing within the reactor at time  $t$  (and, hence, not partially destroyed by chemical reaction on the bead surfaces). In the complete absence of chemical reaction, namely when  $\gamma = 0$ , one has that

$$\begin{aligned} \lambda_- &= 0, \quad \lambda_+ = k_1 + k_4, \quad k_- = k_4/k_1, \quad k_+ = -1, \\ \hat{M}_-^{(0)} &= k_1/(k_1 + k_4), \quad \hat{M}_+^{(0)} = ((k_1 + k_4)\zeta - k_1)/(k_1 + k_4), \end{aligned}$$

in which case,  $\Pi \equiv 1$  for all  $t \geq 0$ , independently of the initial conditions embodied in  $\mathbf{r}'$  and  $\zeta$ . This accords with (2.12).

It is clear, that after a sufficiently long interval of time has elapsed following the initial introduction of the tracer into the system (cf. (5.20) for a quantification of the phrase 'long-time'), the behaviour of the system will be dominated by the algebraically smallest eigenvalue, namely  $\lambda_-$ . Hence, by virtue of the definition (4.3) of the macroscale reaction-velocity constant, we obtain

$$\bar{K}^* = \lambda_- \equiv \frac{1}{2} \{k_1 + k_4 + \gamma - [(k_1 + k_4 + \gamma)^2 - 4k_4\gamma]^{\frac{1}{2}}\}. \quad (5.9)$$

Thus, for  $t \rightarrow \infty$ ,

$$\mathbf{M}^{(0)} \sim \hat{M}_-^{(0)} \exp(-\lambda_- t) \mathbf{E}_-. \quad (5.10)$$

In the kinetically controlled limit, where  $\gamma \ll k_1 + k_4$ , one finds from (5.9) that

$$\bar{K}^* \approx k_4 \gamma / (k_1 + k_4), \quad (5.11)$$

whence  $\bar{K}^* \rightarrow 0$  as  $\gamma \rightarrow 0$ , as already observed. In the opposite extreme, wherein the reaction rate on the surface of the beads is extremely large, so that  $\gamma \gg k_1 + k_4$ , the effective rate of disappearance of the solute from the system via reaction is controlled solely by the surface-access coefficient  $k_4$ ; explicitly, we find in this 'surface access controlled' limit that

$$\bar{K}^* \approx k_4. \quad (5.12)$$

### (b) Zero-order local moments

The temporal evolution of the zero-order local moments is governed by the equation

$$\frac{\partial \mathbf{P}^{(0)}}{\partial y} + [\mathcal{L}] \mathbf{P}^{(0)} + [A] \mathbf{P}^{(0)} = \delta(\mathbf{r} - \mathbf{r}') \delta(t) \begin{pmatrix} \zeta \\ 1 - \zeta \end{pmatrix}, \quad (5.13)$$

easily obtained by setting  $m = 0$  in (3.4). Following a known scheme for the single-phase flow of a chemically reactive solute (Shapiro & Brenner 1988), the most general solution of (5.13) may be sought in the form

$$\mathbf{P}^{(0)} = \frac{1}{\tau_0} \mathbf{M}^{(0)} + \sum_{n=1}^{\infty} \exp(-\lambda_n t) \begin{pmatrix} K_v^{(n)} \\ K_b^{(n)} \end{pmatrix}, \quad (5.14)$$

with  $\lambda_n$  the eigenvalues, and  $K_\alpha^{(n)} \equiv K_\alpha^{(n)}(\mathbf{r}|\mathbf{r}'; \zeta)$  the respective eigenfunctions ( $n = 1, 2, \dots$ ) of the operator  $[\mathcal{L} + A]$  (with boundary conditions (3.7)). Here, it is implicitly assumed that  $\lambda_n \neq \lambda_-$ ,  $\lambda_n \neq \lambda_+$  ( $n = 1, 2, \dots$ ). By following the same steps (Brenner 1980, Appendix C) as those leading to the comparable result in classical Taylor dispersion theory, it may be demonstrated (cf. Appendix A) that  $\lambda_n > \lambda_-$  ( $n = 1, 2, \dots$ ). Consequently, in the asymptotic long-time limit, the zero-order local moments adopt the respective forms

$$\mathbf{P}^{(0)} \sim (1/\tau_0) \hat{M}^{(0)} \exp(-\lambda_- t) (\mathbf{E}_- + \mathbf{O}_{\text{exp}}), \quad (5.15)$$

where  $\mathbf{O}_{\text{exp}}$  denotes (generic) terms involving the time  $t$  that decay exponentially to zero as  $t \rightarrow \infty$ .

The transition from the general solution (5.14) to the asymptotic solution (5.15) of (5.13) is clearly characterized by two distinctive timescales,

$$T_1 = (\lambda_{\min} - \lambda_-)^{-1} \quad (5.16)$$

(where  $\lambda_{\min}$  denotes the algebraically smallest eigenvalue among  $\lambda_1, \lambda_2, \dots$ ), and

$$T_2 = (\lambda_+ - \lambda_-)^{-1} \equiv (k_4 - \lambda_-)/(k_1 k_4 + (k_4 - \lambda_-)^2), \quad (5.17)$$

corresponding to two different physical processes. In fact, for times  $t$  satisfying the inequality  $t \gg T_1$ , a quasi-steady, position-independent, spatially uniform solute distribution

$$\mathbf{P}^{(0)} \sim (1/\tau_0) \mathbf{M}^{(0)} \quad (5.18)$$

is established within a unit cell, owing to molecular diffusion of the solute (Brenner 1980). On the other hand, for times  $t \gg T_2$ , a local quasi-steady solute *partitioning* (compare (5.10))

$$P_b^{(0)}/P_v^{(0)} \sim k_- \quad (5.19)$$

is established between the solvent and bead phases, owing to interphase solute transport.

In the sequel we shall not distinguish between these two different timescales; rather, it will be supposed that the pair of inequalities

$$t \gg T_1, \quad t \gg T_2, \quad (5.20a, b)$$

are both implicitly satisfied in all subsequent asymptotic expressions.

## 6. Average solute velocity $\bar{U}^*$

### (a) First-order total moments

Following (3.10) (with  $m = 1$ ), the temporal evolution of the first-order total moments is governed by the equation

$$\frac{d\mathbf{M}^{(1)}}{dt} + [A] \mathbf{M}^{(1)} = \int_{S_0} d^2\mathbf{r} \begin{pmatrix} -u_v \|P_v^{(1)}\| + D_v \|\partial P_v^{(1)}/\partial z\| \\ -u_b \|P_b^{(1)}\| + D_b \|\partial P_b^{(1)}/\partial z\| \end{pmatrix}.$$

We seek an asymptotic solution of this equation for  $t \rightarrow \infty$ . With the aid of (3.7b) and (3.9), together with the fact that in the long-time asymptotic limit the zero-order local moments are position-independent [cf. (5.13)], one finds that diffusional terms on the right-hand side of this equation vanish, whereas the remaining expression may be written in the form

$$\frac{d\mathbf{M}^{(1)}}{dt} + [A] \mathbf{M}^{(1)} \sim \hat{M}^{(0)} \exp(-\lambda_- t) \begin{pmatrix} \bar{u}_v & 0 \\ 0 & \bar{u}_b \end{pmatrix} (\mathbf{E}_- + \mathbf{O}_{\text{exp}}), \quad (6.1)$$

wherein

$$\bar{u}_\alpha \stackrel{\text{def}}{=} \frac{l}{S_0} \int_{S_0} d^2 r u_\alpha \quad (6.2)$$

are the average axial velocities of the solvent and bead continua.

As  $\lambda_-$  is, by definition, the eigenvalue of  $[A]$ , we seek (subject to a *posteriori* verification) a solution of (6.1) in the form

$$\mathbf{M}^{(1)} \sim \exp(-\lambda_- t) [\hat{M}_-^{(1)} t \mathbf{E}_- + \hat{M}_-^{(0)} \mathbf{W} + \mathbf{O}_{\text{exp}}], \quad (6.3)$$

where the time- and position-independent scalar coefficient  $\hat{M}_-^{(1)}$ , as well as the time- and position-independent column vector  $\mathbf{W}$  (of order two) remain to be determined. With the use of the identity (5.5) for the negative index, substitution of (6.3) into (6.1) leads to the exact (since all terms appearing therein are time-dependent) expression

$$\hat{M}_-^{(1)} \mathbf{E}_- + \hat{M}_-^{(0)} \{[A] - \lambda_- [I]\} \mathbf{W} = \hat{M}_-^{(0)} \begin{pmatrix} \bar{u}_v & 0 \\ 0 & \bar{u}_b \end{pmatrix} \mathbf{E}_-, \quad (6.4)$$

with

$$[I] \stackrel{\text{def}}{=} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

the second-order unit matrix. Observe, that the matrix

$$\{[A] - \lambda_- [I]\} \equiv \begin{pmatrix} k_4 - \lambda_- & -k_1 \\ -k_4 & k_1 + \gamma - \lambda_- \end{pmatrix}$$

appearing on the left-hand side of (6.4) is singular by definition. Hence, upon multiplying the upper and the lower of the pair of equations (6.4) by  $k_4$  and  $k_4 - \lambda_-$ , respectively, and subsequently adding the resulting two expressions, one obtains the simple algebraic equation

$$\hat{M}_-^{(1)} [k_4 + k_- (k_4 - \lambda_-)] = \hat{M}_-^{(0)} [k_4 \bar{u}_v + k_- (k_4 - \lambda_-) \bar{u}_b]$$

for the unknown coefficient  $\hat{M}_-^{(1)}$ . With the use of (5.4*b*) it thus follows that

$$\hat{M}_-^{(1)} = \hat{M}_-^{(0)} [(k_4 - \lambda_-)^2 \bar{u}_b + k_1 k_4 \bar{u}_v] / [(k_4 - \lambda_-)^2 + k_1 k_4], \quad (6.5)$$

in which  $\hat{M}_-^{(0)}$  is given by (5.7).

At this point, the existing data already suffice to evaluate the average axial solute velocity  $\bar{U}^*$ . In particular, substitution of (5.2), (6.3) and (6.5) into (4.6), and subsequent use of (5.4*b*), eventually yields

$$\bar{U}^* = \hat{M}_-^{(1)} / \hat{M}_-^{(0)} \equiv [(k_4 - \lambda_-)^2 \bar{u}_b + k_1 k_4 \bar{u}_v] / [(k_4 - \lambda_-)^2 + k_1 k_4]. \quad (6.6)$$

In particular, when the effective reaction rate is zero, namely when  $\bar{K}^* \equiv \lambda_- = 0$ , one finds that

$$\bar{U}^* = (k_1 \bar{u}_v + k_4 \bar{u}_b) / (k_1 + k_4), \quad (6.7a)$$

consistent with Henry's law equilibrium solute partitioning (cf. footnote to (2.6) and (11.2)) between the adsorbed and dissolved states. In the opposite extreme, when either  $k_4 = 0$  or  $\gamma \rightarrow \infty$ ,

$$\bar{U}^* = \bar{u}_v, \quad (6.7b)$$

consistent with fact that under these circumstances no solute is adsorbed on the beads.

To complete the determination of the first-order total moments, it remains to find the vector  $\mathbf{W}$ . Toward this end, multiply the upper of equations (6.4) (i.e. the 'v' equation) by  $k_-$ , and then subtract the resulting expression from the lower of equations (6.4) (i.e. the 'b' equation). This leads to the expression

$$[k_-(k_4 - \lambda_-) + k_4] W_v - (k_- k_1 + k_1 + \gamma - \lambda_-) W_b = k_-(\bar{u}_v - \bar{u}_b),$$

wherein  $W_v$  and  $W_b$  are the respective components of  $\mathbf{W}$ . Subsequent simplification may be achieved by use of (5.4b), which, after some algebra, yields

$$W_v - \frac{k_1}{k_4 - \lambda_-} W_b = \frac{k_4 - \lambda_-}{(k_4 - \lambda_-)^2 + k_4 k_1} (\bar{u}_v - \bar{u}_b). \quad (6.8)$$

Since only one such equation exists serving to relate the components  $W_v$  and  $W_b$ , the latter pair is not uniquely defined. A comparable non-uniqueness exists (Brenner 1980; Shapiro & Brenner 1988) in classical Taylor dispersion theory. However, similar to the latter case, this lack of uniqueness proves physically inconsequential, insofar as the phenomenological coefficients  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$  are concerned.

(b) *First-order local moments*

First-order local moments are governed by the equation

$$\frac{d\mathbf{P}^{(1)}}{dt} + [\mathcal{L}] \mathbf{P}^{(1)} + [A] \mathbf{P}^{(1)} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \quad (6.9)$$

obtained by setting  $m = 1$  in (3.4). Following a known scheme for the single-phase flow of a chemically reactive solute (Shapiro & Brenner 1988), and employing the preceding results for the first-order total moments, assume (subject to *a posteriori* verification) that the asymptotic solution of (6.9) is of the form

$$\mathbf{P}^{(1)} \sim \frac{1}{\tau_0} \hat{M}_-^{(0)} \exp(-\lambda_- t) \begin{pmatrix} \bar{U}^* t + B_v + O_{\text{exp}} & 0 \\ 0 & \bar{U}^* t + B_b + O_{\text{exp}} \end{pmatrix} \mathbf{E}_-, \quad (6.10)$$

wherein  $B_v \equiv B_v(\mathbf{r})$  and  $B_b \equiv B_b(\mathbf{r})$  are time-independent scalar fields to be determined, and in which the constant  $\hat{M}_-^{(0)}$  is given by (5.7). The average values of these fields over a unit cell, namely

$$\bar{B}_\alpha \stackrel{\text{def}}{=} \frac{1}{\tau_0} \int_{\tau_0} d^3\mathbf{r} B_\alpha, \quad (6.11)$$

are closely related to the respective components  $W_v$  and  $W_b$ . In fact, by comparing (6.10) with (6.3), one has that

$$W_v = \bar{B}_v, \quad W_b = k_- \bar{B}_b. \quad (6.12)$$

Hence, with use of (6.8),

$$\bar{B}_v - \bar{B}_b = \frac{k_4 - \lambda_-}{(k_4 - \lambda_-)^2 + k_4 k_1} (\bar{u}_v - \bar{u}_b). \quad (6.13)$$

Substitution of (6.10) into (6.9) yields the pair of (exact) equations

$$\begin{pmatrix} \mathcal{L}_v + k_4 - \lambda_- & -k_1 k_- \\ -k_4/k_- & \mathcal{L}_b + k_1 + \gamma - \lambda_- \end{pmatrix} \begin{pmatrix} B_v \\ B_b \end{pmatrix} = -\bar{U}^* \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \quad (6.14)$$



These may be further simplified with the use of (5.4*b*). In fact, it follows from the latter that

$$k_- k_1 = k_4 - \lambda_- \quad \text{and} \quad k_4/k_- = k_1 + \gamma - \lambda_-.$$

Thus, (6.14) becomes finally

$$\begin{pmatrix} \mathcal{L}_v + k_4 - \lambda_- & -(k_4 - \lambda_-) \\ -(k_1 + \gamma - \lambda_-) & \mathcal{L}_b + k_1 + \gamma - \lambda_- \end{pmatrix} \begin{pmatrix} B_v \\ B_b \end{pmatrix} = -\bar{U}^* \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \quad (6.15)$$

The corresponding boundary conditions to be satisfied by the fields  $B_v$  and  $B_b$  are easily derived (cf. Brenner 1980) from (3.7), and (6.1); explicitly, it is required that

$$\|B_\alpha\| = -l \quad (6.16a)$$

and

$$\mathbf{n} \cdot (\mathbf{u}_\alpha B_\alpha - D_\alpha \nabla B_\alpha) = 0 \quad \text{on the reactor walls.} \quad (6.16b)$$

(Again, because of the generic identity (3.9), it is unnecessary to impose the first-derivative boundary condition  $\|\partial B_\alpha/\partial z\| = 0$  (Shapiro & Brenner 1988), as this will automatically be satisfied in consequence of (6.16*a*).

## 7. Effective solute dispersivity $\bar{D}^*$

Consider now the second-order total moments. Upon setting  $m = 2$  in (3.10), one obtains

$$\frac{d\mathbf{M}^{(2)}}{dt} + [A]\mathbf{M}^{(2)} = \int_{S_0} d^2\mathbf{r} \begin{pmatrix} -u_v \|P_v^{(1)^2}/P_v^{(0)}\| + D_v \left\| \frac{\partial}{\partial z} [P_v^{(1)^2}/P_v^{(0)}] \right\| \\ -u_b \|P_b^{(1)^2}/P_b^{(0)}\| + D_b \left\| \frac{\partial}{\partial z} [P_b^{(1)^2}/P_b^{(0)}] \right\| \end{pmatrix}, \quad (7.1)$$

wherein the pertinent local moments  $P_\alpha^{(0)}$  and  $P_\alpha^{(1)}$  are given asymptotically by (5.13) and (6.10) respectively.

In accord with the asymptotic definition (4.8) of the axial solute dispersivity  $\bar{D}^*$ , we seek an *asymptotic* solution of (7.1) for  $t \rightarrow \infty$ . To this end, consider first the asymptotic behaviour of the right-hand side of (7.1); explicitly,

$$\begin{aligned} & \int_{S_0} d^2\mathbf{r} \left\{ -u_\alpha \|P_\alpha^{(1)^2}/P_\alpha^{(0)}\| + D_\alpha \left\| \frac{\partial}{\partial z} [P_\alpha^{(1)^2}/P_\alpha^{(0)}] \right\| \right\} \\ & \sim \frac{1}{\tau_0} \hat{M}_-^{(0)} E_\alpha^- \int_{S_0} d^2\mathbf{r} \left\{ -u_\alpha \|(\bar{U}^*t + B_\alpha)^2\| + D_\alpha \left\| \frac{\partial}{\partial z} [(\bar{U}^*t + B_\alpha)^2] \right\| + O_{\text{exp}} \right\} \exp(-\lambda_- t) \\ & = \hat{M}_-^{(0)} E_\alpha^- \left\{ 2\bar{U}^* \bar{u}_\alpha t - \frac{1}{\tau_0} \int_{S_0} d^2\mathbf{r} u_\alpha \|B_\alpha^2\| + \frac{D_\alpha}{\tau_0} \int_{S_0} d^2\mathbf{r} \left\| \frac{\partial}{\partial z} B_\alpha^2 \right\| + O_{\text{exp}} \right\} \exp(-\lambda_- t) \\ & \equiv \hat{M}_-^{(0)} E_\alpha^- (2\bar{U}^* \bar{u}_\alpha t + G_\alpha + O_{\text{exp}}) \exp(-\lambda_- t), \quad (7.2a) \end{aligned}$$

$$\text{wherein} \quad G_\alpha \stackrel{\text{def}}{=} -\frac{1}{\tau_0} \int_{S_0} d^2\mathbf{r} u_\alpha \|B_\alpha^2\| + \frac{D_\alpha}{\tau_0} \int_{S_0} d^2\mathbf{r} \left\| \frac{\partial}{\partial z} B_\alpha^2 \right\|. \quad (7.2b)$$

More explicitly, upon transforming the surface integrals into corresponding volume integrals via use of the boundary conditions (6.16*b*) together with the identity (3.9),

and after applying the continuity equations (2.1) for the pair of velocity fields, one finds that

$$\begin{aligned} G_\alpha &= \frac{1}{\tau_0} \int_{\tau_0} d^3\mathbf{r} [-\nabla \cdot (\mathbf{u}_\alpha B_\alpha^2) + D_\alpha \nabla^2 B_\alpha^2] \\ &= \frac{2}{\tau_0} \int_{\tau_0} d^3\mathbf{r} \{-B_\alpha \nabla \cdot (\mathbf{u}_\alpha B_\alpha) + D_\alpha [\nabla B_\alpha \cdot \nabla B_\alpha + B_\alpha \nabla^2 B_\alpha]\} \\ &\equiv \frac{2}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (-B_\alpha \mathcal{L}_\alpha B_\alpha + D_\alpha \nabla B_\alpha \cdot \nabla B_\alpha). \end{aligned} \quad (7.3)$$

Upon using (7.2a), equation (7.1) adopts the asymptotic form

$$\frac{d\mathbf{M}^{(2)}}{dt} + [A]\mathbf{M}^{(2)} \sim \hat{M}_-^{(0)} \exp(-\lambda_- t) \begin{pmatrix} 2\bar{U}^* \bar{u}_v t + G_v + O_{\text{exp}} & 0 \\ 0 & 2\bar{U}^* \bar{u}_b t + G_b + O_{\text{exp}} \end{pmatrix} \mathbf{E}_-. \quad (7.4)$$

As  $\lambda_-$  is, from (5.5), an eigenvalue of  $[A]$ , we seek (subject to *a posteriori* verification) an asymptotic solution of (7.4) in the form

$$\mathbf{M}^{(2)} \sim [\hat{M}_-^{(2)} \mathbf{E}_- t^2 + \hat{M}_-^{(0)} \mathbf{V} t + \hat{M}_-^{(0)} \mathbf{T} + \mathbf{O}_{\text{exp}}] \exp(-\lambda_- t), \quad (7.5)$$

wherein  $\hat{M}_-^{(2)}$  is a time- and position-independent coefficient;  $\mathbf{V}$  and  $\mathbf{T}$  are time- and position-independent column vectors (of order two). The vector  $\mathbf{T}$  will prove to be immaterial in the subsequent discussion, whereas the computation of  $\hat{M}_-^{(2)}$  and  $\mathbf{V}$  will be addressed in the same manner as were  $\hat{M}_-^{(1)}$  and  $\mathbf{W}$  in the previous section.

Substitute (7.5) into (7.4) and collect together all similar terms, thereby obtaining, exactly (compare with (6.4)),

$$2\hat{M}_-^{(2)} \mathbf{E}_- + \hat{M}_-^{(0)} \{[A] - \lambda_- [I]\} \mathbf{V} = 2\bar{U}^* \hat{M}_-^{(0)} \begin{pmatrix} \bar{u}_v & 0 \\ 0 & \bar{u}_b \end{pmatrix} \mathbf{E}_- \quad (7.6)$$

and 
$$\mathbf{V} + \{[A] - \lambda_- [I]\} \mathbf{T} = \begin{pmatrix} G_v & 0 \\ 0 & G_b \end{pmatrix} \mathbf{E}_-. \quad (7.7)$$

We shall now follow the very same steps that led to (6.5) and (6.8). In fact, respectively multiply by  $k_4$  and  $k_4 - \lambda_-$  the upper and the lower equations of (7.6), and add together the resulting two expressions to obtain the following expressions for  $\hat{M}_-^{(2)}$ :

$$\hat{M}_-^{(2)} [k_4 + k_-(k_4 - \lambda_-)] = \bar{U}^* \hat{M}_-^{(0)} [k_4 \bar{u}_v + k_-(k_4 - \lambda_-) \bar{u}_b].$$

Hence, upon utilizing (5.4b) and (6.6), one finds that

$$\hat{M}_-^{(2)} = \hat{M}_-^{(0)} \bar{U}^{*2}. \quad (7.8)$$

Multiply the former of equations (7.6) by  $k_-$ , and subtract from that result the second of equations (7.6), so as to obtain the expression

$$[k_-(k_4 - \lambda_-) + k_4] V_v - (k_- k_1 + k_1 + \gamma - \lambda_-) V_b = 2\bar{U}^* k_- (\bar{u}_v - \bar{u}_b), \quad (7.9a)$$

relating the components  $V_v$  and  $V_b$  of  $\mathbf{V}$ . The additional equation required to determine each of these components separately may conveniently be obtained from (7.7) upon multiplying the upper and the lower of these equations respectively by  $k_4$  and  $k_4 - \lambda_-$ , and subsequently adding one to another. This yields

$$k_4 V_v + (k_4 - \lambda_-) V_b = k_4 G_v + k_-(k_4 - \lambda_-) G_b. \quad (7.9b)$$

Thus, with the aid of (5.4b), one obtains

$$V_v = 2\bar{U}^* \frac{(k_4 - \lambda_-)^3}{[(k_4 - \lambda_-)^2 + k_1 k_4]^2} (\bar{u}_v - \bar{u}_b) + \frac{k_4 k_1 G_v + (k_4 - \lambda_-)^2 G_b}{(k_4 - \lambda_-)^2 + k_1 k_4}, \quad (7.10a)$$

$$V_b = \frac{k_4 - \lambda_-}{k_1} \left\{ -2\bar{U}^* \frac{k_1 k_4 (k_4 - \lambda_-)}{[(k_4 - \lambda_-)^2 + k_1 k_4]^2} (\bar{u}_v - \bar{u}_b) + \frac{k_4 k_1 G_v + (k_4 - \lambda_-)^2 G_b}{(k_4 - \lambda_-)^2 + k_1 k_4} \right\} \quad (7.10b)$$

for the components of  $V$ .

The solute dispersivity may now be derived from the formal definition (4.8) by substitution of the pertinent expressions (cf. (5.2), (6.3) and (7.5)) for the total probability moments. This gives

$$\bar{D}^* = \frac{1}{2} \frac{V_v + V_b}{1 + k_-} - \bar{U}^* \frac{W_v^- + W_b^-}{1 + k_-} \equiv \frac{1}{2} \frac{V_v + V_b}{1 + k_-} - \bar{U}^* \frac{\bar{B}_v + k_- \bar{B}_b}{1 + k_-}.$$

Introduce (5.4b) and (7.10) into this equation, so as to obtain

$$\bar{D}^* = \frac{k_4 k_1 G_v + (k_4 - \lambda_-)^2 G_b}{2[(k_4 - \lambda_-)^2 + k_1 k_4]} - \frac{k_1 \bar{U}^*}{k_1 + k_4 - \lambda_-} \left\{ \frac{\lambda_- (k_4 - \lambda_-)^2 (\bar{u}_v - \bar{u}_b)}{[(k_4 - \lambda_-)^2 + k_1 k_4]^2} + \bar{B}_v + \left( \frac{k_4 - \lambda_-}{k_1} \right) \bar{B}_b \right\}.$$

On the other hand, it follows from (6.15) and (7.3) that

$$\begin{aligned} \frac{k_1 k_4 G_v + (k_4 - \lambda_-)^2 G_b}{2[(k_4 - \lambda_-)^2 + k_1 k_4]} &= \frac{\bar{U}^*}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} \frac{(k_4 - \lambda_-)^2 B_b + k_1 k_4 B_v}{(k_4 - \lambda_-)^2 + k_1 k_4} \\ &+ \frac{1}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} \frac{k_1 k_4 (k_4 - \lambda_-) (B_v - B_b)^2}{(k_4 - \lambda_-)^2 + k_1 k_4} \\ &+ \frac{1}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} \frac{(k_4 - \lambda_-)^2 D_b \nabla B_b \cdot \nabla B_b + k_1 k_4 D_v \nabla B_v \cdot \nabla B_v}{(k_4 - \lambda_-)^2 + k_1 k_4}. \end{aligned}$$

Consequently,

$$\begin{aligned} \bar{D}^* &= \bar{U}^* H + \frac{k_1 k_4 (k_4 - \lambda_-)}{(k_4 - \lambda_-)^2 + k_1 k_4} \frac{1}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (B_v - B_b)^2 \\ &+ \frac{(k_4 - \lambda_-)^2}{(k_4 - \lambda_-)^2 + k_1 k_4} \frac{D_b}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (\nabla B_b)^2 + \frac{k_1 k_4}{(k_4 - \lambda_-)^2 + k_1 k_4} \frac{D_v}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (\nabla B_v)^2, \end{aligned}$$

wherein

$$H \stackrel{\text{def}}{=} \frac{(k_4 - \lambda_-)^2 \bar{B}_b + k_1 k_4 \bar{B}_v}{(k_4 - \lambda_-)^2 + k_1 k_4} - \frac{k_1}{k_1 + k_4 - \lambda_-} \left\{ \frac{\lambda_- (k_4 - \lambda_-)^2 (\bar{u}_v - \bar{u}_b)}{[(k_4 - \lambda_-)^2 + k_1 k_4]^2} + \bar{B}_v + \frac{k_4 - \lambda_-}{k_1} \bar{B}_b \right\}.$$

Substitution of (6.13) into the above reveals that  $H \equiv 0$  identically. Thus, the solute dispersivity may be written as

$$\begin{aligned} \bar{D}^* &= \frac{k_1 k_4 (k_4 - \lambda_-)}{(k_4 - \lambda_-)^2 + k_1 k_4} \frac{1}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (B_v - B_b)^2 \\ &+ \frac{(k_4 - \lambda_-)^2}{(k_4 - \lambda_-)^2 + k_1 k_4} \frac{D_b}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (\nabla B_b)^2 + \frac{k_1 k_4}{(k_4 - \lambda_-)^2 + k_1 k_4} \frac{D_v}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (\nabla B_v)^2, \quad (7.11) \end{aligned}$$

consisting of a sum of three terms, each involving squared integrands.

It is easily demonstrated that  $\bar{D}^*$  is strictly positive. To do so, note firstly that the possible solutions  $B_\alpha = \text{constant}$  are incompatible (Brenner 1980) with the system of equations (6.15) and (6.16) defining  $B_\alpha$ . Secondly, observe (cf. (5.3)) that with the strictly positive choice  $k_1 > 0$ , the following inequality prevails:

$$k_4 - \lambda_- \equiv \frac{1}{2}\{k_4 - k_1 - \gamma + [(k_4 - k_1 - \gamma)^2 + 4k_4 k_1]^{\frac{1}{2}}\} \geq 0; \quad (7.12a)$$

moreover, 
$$\lim_{k_4 \rightarrow 0} \left[ \frac{k_1 k_4}{(k_4 - \lambda_-)^2 + k_1 k_4} \right] = 1. \quad (7.12b)$$

Consequently, since  $D_v$  is (assumed) strictly positive and  $D_b$  non-negative, and since, of the three integrals appearing in (7.11), the final two are each strictly positive, whereas the remaining one is non-negative, it follows that  $\bar{D}^*$  is itself strictly positive. Q.E.D.

When the effective reaction rate is zero, namely when  $\bar{K}^* \equiv \lambda_- = 0$ , the preceding expression for  $\bar{D}^*$  reduces to the form

$$\bar{D}^* = \frac{k_1 k_4}{k_1 + k_4} \frac{1}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (B_v - B_b)^2 + \frac{k_4}{k_1 + k_4} \frac{D_b}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (\nabla B_b)^2 + \frac{k_1}{k_1 + k_4} \frac{D_v}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (\nabla B_v)^2, \quad (7.13)$$

in agreement with a previously known result (Haber & Brenner 1993) for non-reactive systems. Furthermore, when there is no adsorption of solute onto the beads, namely when  $k_4 = 0$ , one finds that

$$\bar{D}^* = \frac{D_v}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (\nabla B_v)^2, \quad (7.14)$$

again in agreement with a known result (Brenner 1980) from classical Taylor dispersion theory for a non-reactive single-phase system.

This latter expression (7.14) is also applicable in the case when the reaction rate on the surface of the beads is extremely large, so that  $\gamma \gg k_1 + k_4$ , as may easily be verified by direct substitution of (5.12) into (7.12). In fact, under these circumstances, all the solute that 'arrives' at the beads' surface is 'immediately' destroyed by the chemical reaction, leaving the macroscale transport of the solute to be controlled solely by the solvent.

## 8. The case $k_1 = 0$

It has been supposed in the preceding analysis that  $k_1 > 0$ , corresponding to a non-zero rate of solute transfer between the solvent and beads. Consider now the limiting case for which this interphase transfer rate vanishes (i.e. when  $k_1 = 0$ ). In doing so, one may conveniently distinguish four subcases.

(i) The solute is initially introduced into the solvent (i.e.  $\zeta = 1$ ) rather than onto the surface(s) of the bead(s). This initial partitioning implies that no solute can henceforth be transported by the beads, since no interphase solute transfer can subsequently occur. Consequently, one may use a known result (Brenner 1980) from classical Taylor dispersion theory for the purely single-phase (solvent) continuum transport case, namely

$$\bar{K}^* = 0, \quad \bar{U}^* = \bar{u}_v, \quad \bar{D}^* = \frac{D_v}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (\nabla B_v)^2. \quad (8.1a-c)$$

(ii) The solute is initially introduced onto the surface(s) of the bead(s) (i.e.  $\zeta = 0$ ) rather than into the solvent. Similarly, as with the previous case, no mechanism exists for interphase solute transfer, whence the solute cannot dissolve in (and hence be transported by) the solvent. In such circumstances, one may use a known result (Shapiro & Brenner 1988) from classical Taylor dispersion theory for the purely single-phase reactive (bead) continuum transport case, namely

$$\bar{K}^* = \gamma, \quad \bar{U}^* = \bar{u}_b, \quad \bar{D}^* = \frac{D_b}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (\nabla B_b)^2. \quad (8.2a-c)$$

(iii) The solute is initially introduced simultaneously into both phases by partitioning (i.e.  $0 < \zeta < 1$ ), and a chemical reaction occurs on the surfaces of the beads (i.e.  $\gamma > 0$ ). In this case, although  $k_1 = 0$ , the system still possesses two separate eigenvalues, namely 0 and  $\gamma$ . Consequently, the expressions obtained in preceding sections for the macroscale parameters remain applicable, albeit with  $k_1 \rightarrow 0$  and  $k_4 \rightarrow 0$ . In particular, upon carefully evaluating the pertinent limits in (5.9), (6.6) and (7.11) (bearing in mind that with  $\gamma \gg k_4 + k_1$ , the lowest eigenvalue is given by  $\lambda_- \approx k_4$  (cf. (5.12)), one finds that

$$\bar{K}^* = 0, \quad \bar{U}^* = \bar{u}_v, \quad \bar{D}^* = \frac{D_v}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (\nabla B_v)^2. \quad (8.3a-c)$$

This result is consistent with asymptotic behaviour of the system, since (with  $\gamma > 0$ ) that portion  $1 - \zeta$  of the solute that was initially introduced into the bead phase will have been completely depleted after a sufficiently long period of time has elapsed. The remaining portion  $\zeta$  of the solute that was initially dissolved in the solvent does not undergo any chemical reaction, and hence is axially transported undiminished by the solvent at a rate governed by the classical single-phase (Brenner 1980) non-reactive values cited in (8.3).

(iv) The solute is initially introduced into both phases by partitioning (i.e.  $0 < \zeta < 1$ ), and no chemical reaction occurs on the surfaces of the beads (i.e.  $\gamma = 0$ ). The absence of reaction requires that

$$\bar{K}^* = 0. \quad (8.4a)$$

To find the pertinent total moments of the probability density, one may either repeat the preceding derivations with  $[\mathbf{A}] = [\mathbf{0}]$ , or use known results from classical Taylor dispersion theory (Brenner, 1980); both lead to the same result, namely

$$\begin{aligned} M_v^{(0)} &= \zeta, \quad M_b^{(0)} = 1 - \zeta, \\ M_\alpha^{(1)} &\sim M_\alpha^{(0)}(\bar{u}_\alpha t + \bar{B}_\alpha + O_{\text{exp}}), \\ M_\alpha^{(2)} &\sim M_\alpha^{(0)}(\bar{u}_\alpha^2 t^2 + G_\alpha + T_\alpha + O_{\text{exp}}). \end{aligned}$$

In the preceding, the  $T_\alpha$  are physically immaterial constants, whereas the constants  $G_\alpha$  are explicitly given by the expressions

$$G_\alpha = 2\bar{u}_\alpha \bar{B}_\alpha + 2D_\alpha \frac{1}{\tau_0} \int_{\tau_0} d^3\mathbf{r} (\nabla B_\alpha)^2.$$

Moreover, the  $B$ -fields satisfy the pair of equations

$$\mathcal{L}_\alpha B_\alpha = -\bar{u}_\alpha,$$

subject to the boundary conditions (6.16*a, b*). Consequently, using the respective definitions of the average velocity (4.6) and dispersivity (4.8), one finds that

$$\bar{U}^* = \zeta \bar{u}_v + (1 - \zeta) \bar{u}_b \quad (8.4b)$$

and

$$\begin{aligned} \bar{D}^* = \zeta(1 - \zeta) \lim_{t \rightarrow \infty} [(\bar{u}_v - \bar{u}_b)^2 t + (\bar{u}_v - \bar{u}_b)(\bar{B}_v - \bar{B}_b)] \\ + D_v \frac{\zeta}{\tau_0} \int_{\tau_0} d^3 r (\nabla B_v)^2 + D_b \frac{1 - \zeta}{\tau_0} \int_{\tau_0} d^3 r (\nabla B_b)^2. \end{aligned}$$

The latter reduces to the respective alternative forms

$$\bar{D}^* = \begin{cases} D_v \frac{\zeta}{\tau_0} \int_{\tau_0} d^3 r (\nabla B_v)^2 + D_b \frac{1 - \zeta}{\tau_0} \int_{\tau_0} d^3 r (\nabla B_b)^2 & (\bar{u}_v = \bar{u}_b), \\ \infty & (\bar{u}_v \neq \bar{u}_b), \end{cases} \quad (8.4c)$$

$$(8.4d)$$

according as the mean solvent- and bead-phase velocities are the same or different. The singular result  $\bar{D}^* = \infty$  for circumstances in which the average axial velocities of the solvent and beads differ, indicates that in this case one cannot simply describe the overall macroscale solute distribution (both in the dissolved and adsorbed states) by a single macroscale velocity  $\bar{U}^*$  and single macroscale dispersivity  $\bar{D}^*$  (cf. (10.6)). Rather, separate macrotransport equations, each involving its own phenomenological coefficients  $\bar{U}_\alpha^*$  and  $\bar{D}_\alpha^*$  (cf. (4.10), (4.11) and (10.4)), would be required for the separate solvent and bead phases.

## 9. Examples

The derivations thus far have been quite general, the only major assumption being that the system under consideration possesses unidirectional spatial periodicity. It is apparent, however, that the  $B$ -field equations (6.15) and (6.16) are not generally amenable to closed-form analytical solution in this general case. Moreover, as the number of particular cases in which such solutions may be attained is actually quite limited, a comprehensive parametric study of dispersivity phenomena in the bead reactor has to be executed numerically. With the latter study to be published elsewhere, the theory just developed may nevertheless be elucidated here by considering a particular case wherein the brownian diffusivity  $D_b$  of the colloidal beads through the solvent is negligible. As the size of the beads normally used in the reactor is in excess of 100  $\mu\text{m}$ , this assumption is quite realistic.

Introduce the (spatially periodic) fields

$$\check{B}_\alpha \stackrel{\text{def}}{=} B_\alpha - z \quad (9.1)$$

into (6.15) and (6.16) so as to establish the pair of equations,

$$\nabla \cdot (\mathbf{u}_v \check{B}_v - D_v \nabla \check{B}_v) + (k_4 - \lambda_-) (\check{B}_v - \check{B}_b) = u_v - \bar{U}^*, \quad (9.2a)$$

$$\nabla \cdot (\mathbf{u}_b \check{B}_b) - \frac{k_1 k_4}{k_4 - \lambda_-} (\check{B}_v - \check{B}_b) = u_b - \bar{U}^*, \quad (9.2b)$$

governing these fields, together with the respective (homogeneous) boundary conditions

$$\|\check{B}_v\| = \|\check{B}_b\| = 0 \quad (9.3a)$$

and  $\mathbf{n} \cdot \nabla \check{B}_v = 0$  on the reactor walls. (9.3b)

In deriving (9.2b) we have conveniently used (5.4b) to eliminate  $\gamma$ , whereas in deriving (9.3b) we have used the boundary conditions (2.2) imposed upon the velocity fields, together with the fact that  $\mathbf{n} \cdot \mathbf{e}_z \equiv 0$  on reactor walls.

In view of (2.1), (9.3) and (6.6), substitution into (7.11) of (9.1) and (9.2b), together with the supposition that  $D_b = 0$ , yields

$$\begin{aligned} \bar{D}^* = KD_v + K^3 T (\bar{u}_b - \bar{u}_v)^2 + \frac{KT}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (u_b - \bar{u}_b)^2 \\ + \frac{K}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} [(\nabla \check{B}_b)^\dagger \cdot \check{D}_b \cdot (\nabla \check{B}_b) + (\nabla \check{B}_v)^\dagger \cdot \mathbf{D}_v \cdot (\nabla \check{B}_v)], \end{aligned} \quad (9.5)$$

in which

$$T \equiv (k_4 - \lambda_-)^3 / (k_1 k_4)^2 \quad (9.6a)$$

is the timescale for interphase solute transport (compare with  $T_2$ , (5.17)), and

$$K \equiv k_1 k_4 / (k_1 k_4 + (k_4 - \lambda_-)^2). \quad (9.6b)$$

Moreover, with  $\mathbf{I}$  the dyadic idemfactor,

$$\mathbf{D}_v \equiv D_v \mathbf{I} \quad (9.6c)$$

and

$$\check{D}_b \equiv T \mathbf{u}_b \mathbf{u}_b. \quad (9.6d)$$

The latter may be envisioned as the ‘effective diffusivity dyadic’ of the *adsorbed* solute. Note that in contrast with diffusivity dyadic (9.6c) of the dissolved solute, which is position-independent, the value of  $\check{D}_b$  varies locally within the unit cell. Moreover, it is a well-known fact, that diffusivity is necessarily independent to the choice of the frame of reference. In this context, the velocity field  $\mathbf{u}_b$  appearing in (9.6d), should be understood as a *relative* velocity; the latter being measured with respect to the reference frame in which the velocity field is *time-independent*.

Consider the above expression for the dispersivity. With usual Taylor–Aris-type dispersion contributions for the *dissolved* solute embodied in the first and last of the five terms appearing on the right-hand side of (9.5), the remaining terms represent the contribution of the ‘piggy-back’ convection of solute by the beads. In fact, in complete analogy with classical Taylor-type convective dispersion contributions, characterized by the ability of a solute molecule to cross stream lines (and hence to sample different velocities), the new contribution is characterized by the ability of a solute molecule to change its physical *state*, namely from being dissolved in the solute to being adsorbed on the surfaces of the beads and vice versa. (As the solute molecules move at different velocities in each of these two states, this difference provides the Taylor dispersion mechanism manifested in the non-traditional dispersion contributions appearing in (9.5).) In this sense, the characteristic timescale (9.6a) of the latter process is completely analogous to the diffusive time scale  $d^2/D_v$  underlying the classical convective contribution to Taylor dispersion (here,  $d$  is the gap between the cylinders).

Within the context of the prior assumption that  $D_b = 0$ , consider the following two cases.

(i) The reactor operates at rotation rates below the Taylor instability threshold. In such circumstances, Taylor vortices are absent from the flow field, whence the respective solvent and bead velocity fields are strictly helical, as well as being independent of the axial coordinate  $z$ .

Select a right-handed cylindrical polar coordinate system  $(\varpi, \phi, z)$ , with  $(\mathbf{e}_\varpi, \mathbf{e}_\phi, \mathbf{e}_z)$  the respective basis unit vectors. In view of the assumptions imposed upon the velocity fields, we assume subject to *a posteriori* verification that the modified  $B$ -fields are independent of  $\phi$  and  $z$ . Thus, with

$$\mathbf{u}_\alpha \equiv u_\alpha(\varpi) \mathbf{e}_z + v_\alpha(\varpi) \mathbf{e}_\phi$$

the respective velocity fields,  $R_1$  and  $R_2$  the radii of the inner and the outer cylinders respectively (see figure 1), (9.2) and (9.3) become

$$-\frac{D_v}{\varpi} \frac{d}{d\varpi} \left( \varpi \frac{d\check{B}_v}{d\varpi} \right) + (k_4 - \lambda_-) (\check{B}_v - \check{B}_b) = u_v - \bar{U}^*, \quad (9.7a)$$

$$-\frac{k_1 k_4}{k_4 - \lambda_-} (\check{B}_v - \check{B}_b) = u_b - \bar{U}^* \quad (9.7b)$$

and 
$$\|\check{B}_v\| = \|\check{B}_b\| = 0, \quad \left. \frac{d\check{B}_v}{d\varpi} \right|_{\varpi=R_1, \varpi=R_2} = 0. \quad (9.7c, d)$$

A closed-form solution for the dispersivity now immediately follows. In fact, substitution of (9.7b) into (9.7a), and integration of the resulting equation with respect to  $\varpi$  subject to the boundary conditions (9.7d), yields

$$\frac{d\check{B}_v}{d\varpi} = -\frac{1}{KD_v \varpi} \int_{R_1}^{\varpi} d\varpi \varpi (U^* - \bar{U}^*), \quad (9.8)$$

wherein 
$$U^* \stackrel{\text{def}}{=} \frac{(k_4 - \lambda_-)^2 u_b + k_1 k_4 u_v}{(k_4 - \lambda_-)^2 + k_1 k_4} \quad (9.9)$$

is the 'effective' solute velocity. (Note that in the case considered,  $U^* \equiv U^*(\varpi)$ .) Thus, by introducing (9.8) into (9.5), one eventually finds

$$\begin{aligned} \bar{D}^* = & KD_v + K^3 T (\bar{u}_b - \bar{u}_v)^2 + \frac{2KT}{R_2^2 - R_1^2} \int_{R_1}^{R_2} d\varpi \varpi (u_b - \bar{u}_b)^2 \\ & + \frac{2}{KD_v (R_2^2 - R_1^2)} \int_{R_1}^{R_2} \frac{d\varpi'}{\varpi'} \left[ \int_{R_1}^{\varpi'} d\varpi \varpi (U^* - \bar{U}^*) \right]^2. \end{aligned} \quad (9.10)$$

The  $D_v$  and  $D_v^{-1}$  contributions embodied in the first and the last terms of the latter equation are similar to those appearing in conventional Taylor-Aris dispersion expressions. However, the additional dispersion contribution, embodied in the second and the third terms, is independent of the solute diffusivity  $D_v$ . This contribution possesses no counterpart in classical Taylor dispersion theory, a fact which is clearly illustrated by considering the example of the homogeneous plug-type flow,  $u_\alpha \equiv \bar{u}_\alpha$ , for both the solvent and beads. In such circumstances, (9.10) yields

$$\bar{D}^* = K[D_v + K^2 T (\bar{u}_b - \bar{u}_v)^2]. \quad (9.11)$$

Owing to the homogeneity of the flow, the convective contribution to the dispersion arises solely from the bead/solvent velocity difference. When this difference is zero, namely when  $\bar{u}_b \equiv \bar{u}_v$ , one obtains  $\bar{D}^* = KD_v$ . In particular, in the non-reactive case,  $\gamma = 0$ , this reduces to

$$\bar{D}^* = k_1 / (k_1 + k_4) D_v.$$



Thus,  $\bar{D}^* \leq D_v$ . The fact that the solute dispersivity is less than the molecular diffusivity through the solvent arises from the fact that some of the solute is adsorbed on the surface of the beads, and we have assumed that the beads themselves do not diffuse.

Appearances to the contrary notwithstanding, it cannot be concluded from (9.11) that dispersion phenomena of this type exist when the solute diffusivity  $D_v \rightarrow 0$ . This restriction arises from the singular nature of the *dual* limit  $D_b = D_v = 0$ , implicit in (2.4) and inequality (5.20a). In fact, consider the case wherein the gap between cylinders is relatively small, namely  $d \ll R_1$ , and for which the velocity fields  $\mathbf{u}_\alpha \equiv \bar{u}_\alpha \mathbf{e}_z + \bar{v}_\alpha \mathbf{e}_\phi$  are uniform. It is easily verified by direct substitution that under these circumstances,

$$\lambda_{\min} = \lambda_- + \pi^2 \frac{D_v + D_b}{2d^2} + \frac{k_1 k_4}{2K(k_4 - \lambda_-)} - \left\{ \left[ \pi^2 \frac{D_v + D_b}{2d^2} + \frac{k_1 k_4}{2K(k_4 - \lambda_-)} \right]^2 - \left( \pi^2 \frac{D_v}{d^2} + k_4 - \lambda_- \right) \left( \pi^2 \frac{D_b}{d^2} + \frac{k_1 k_4}{k_4 - \lambda_-} \right) + k_1 k_4 \right\}^{\frac{1}{2}}$$

is the second algebraically smallest eigenvalue of the operator  $[\mathcal{L} + A]$  (cf. (5.13)–(5.16)), whereas

$$K_\alpha^{(\min)} = q_\alpha^{(\min)}(\mathbf{r}', \zeta) \sin [\pi(2\varpi - R_1 - R_2)/2d]$$

is the respective eigenvector. When both diffusivities become vanishingly small, i.e. when

$$\left( D_v + D_b \ll \frac{d^2 k_1 k_4}{k_4 - \lambda_-} \right),$$

the difference

$$\lambda_{\min} - \lambda_- \equiv \frac{1}{T_1} \approx \frac{\pi^2 D_v k_1 k_4 + D_b (k_4 - \lambda_-)^2}{d^2 k_1 k_4 + (k_4 - \lambda_-)^2}$$

becomes vanishingly small as well, whereas the respective timescale  $T_1$  (cf. (5.16)) become infinitely large. Thus, the inequality (5.20a), underlining the above theory, cannot be satisfied for any *finite*  $t$ , however large.

In the absence of the beads (corresponding to  $k_4 = 0$ ), and when the gap between the cylinders is sufficiently small to satisfy the inequality  $d \ll R_1$ , the preceding problem reduces to the well-known Taylor–Aris problem of flow and dispersion between parallel planes (Wooding 1960). From (5.3) it follows that  $\lambda_- = 0$  when  $k_4 = 0$ , whence, the dispersivity (9.10) adopts the form

$$\bar{D}^* = D_v + \frac{1}{D_v d} \int_{R_1}^{R_2} d\varpi' \left\{ \int_{R_1}^{\varpi'} d\varpi (u_v - \bar{u}_v) \right\}^2.$$

For Poiseuille flow between parallel planes

$$u_v = \frac{3}{2} \bar{u}_v \left[ 1 - \frac{(2\varpi - R_2 - R_1)^2}{d^2} \right],$$

whereupon integration yields the expression

$$\bar{D}^* = D_v + \bar{u}_v^2 d^2 / 210 D_v,$$

in accord with Taylor–Aris result for this case (Wooding 1960).

(ii) The Peclet number  $|\mathbf{u}_\alpha \times \mathbf{e}_\phi|d/D_v$  is small as compared with unity and, simultaneously the annular gap is relatively small, so that  $d \ll R_1$ . Under the former of these assumptions, the modified (spatially periodic)  $B$ -fields are governed, to leading order, by the equations

$$-D_v \nabla^2 \check{B}_v + (k_4 - \lambda_-)(\check{B}_v - \check{B}_b) \approx u_v - \bar{U}^*, \quad (9.12a)$$

$$-\frac{k_1 k_4}{k_4 - \lambda_-}(\check{B}_v - \check{B}_b) \approx u_b - \bar{U}^*, \quad (9.12b)$$

with boundary conditions still given by (9.3). Upon substitution of the first of (9.12) into the second, we obtain

$$\nabla^2 \check{B}_v \approx -(U^* - \bar{U}^*)/KD_v, \quad (9.13)$$

in which  $U^*$  is given by (9.9). When  $d \ll R_1$ , the above equation may be conveniently solved using Fourier series. In fact, suppose that the coefficients  $U_m^n$  appearing in the complex Fourier expansion

$$U^* - \bar{U}^* = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} U_m^n \exp\left(i2\pi m \frac{z}{l} + i\pi n \frac{\varpi}{d}\right) \quad (9.14)$$

are known. Upon substitution into (9.13) one obtains the solution

$$\check{B}_v = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} B_m^n \exp\left(i2\pi m \frac{z}{l} + i\pi n \frac{\varpi}{d}\right), \quad (9.15a)$$

$$\text{in which } B_m^n \approx \frac{1}{\pi^2 KD_v} \left(\frac{4m^2}{l^2} + \frac{n^2}{d^2}\right)^{-1} U_m^n \quad (|m| + |n| \neq 0). \quad (9.15b)$$

Thus, with  $\check{B}_v$  approximated by (9.15), and since

$$(\nabla \check{B}_b)^\dagger \cdot \check{\mathbf{D}}_b \cdot (\nabla \check{B}_b) \ll (\nabla \check{B}_v)^\dagger \cdot \check{\mathbf{D}}_v \cdot (\nabla \check{B}_v) \quad \text{when } |\mathbf{u}_\alpha \times \mathbf{e}_\phi|d/D_v \ll 1, \quad (9.16)$$

the information already available suffices to evaluate  $\bar{D}^*$ . Toward this end, substitute explicit expressions (9.15) and (9.16) into (9.5) to obtain

$$\begin{aligned} \bar{D}^* \approx K \left[ D_v + K^2 T (\bar{u}_b - \bar{u}_v)^2 + \frac{T}{ld} \int_0^l dz \int_{R_1}^{R_2} d\varpi (u_b - \bar{u}_b)^2 \right] \\ + \frac{1}{\pi^2 KD_v} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \left(\frac{4m^2}{l^2} + \frac{n^2}{d^2}\right)^{-1} U_m^n U_{-m}^{-n}. \end{aligned}$$

On the other hand, with  $F_m^n$  denoting a respective coefficient in a complex Fourier expansion of a (generic) real-valued function  $F(\varpi, z)$ , the identity

$$F_m^n F_{-m}^{-n} = |F_m^n|^2 \quad (9.17)$$

holds for any  $m$  and  $n$ . As the velocity  $U^* - \bar{U}^*$  is indeed a real-valued function, one eventually finds that

$$\begin{aligned} \bar{D}^* \approx K \left[ D_v + K^2 T (\bar{u}_b - \bar{u}_v)^2 + \frac{T}{ld} \int_0^l dz \int_{R_1}^{R_2} d\varpi (u_b - \bar{u}_b)^2 \right] \\ + \frac{1}{\pi^2 KD_v} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \left(\frac{4m^2}{l^2} + \frac{n^2}{d^2}\right)^{-1} |U_m^n|^2. \quad (9.18) \end{aligned}$$

Finally, introduction of the complex Fourier expansion

$$u_b - \bar{u}_b = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} u_m^n \exp\left(i2\pi m \frac{z}{l} + i\pi n \frac{w}{d}\right), \quad (9.19)$$

into the penultimate term of the preceding expression, permits (9.18) to be rewritten in the symmetrical form

$$\bar{D}^* \approx KD_v + K^3 T (\bar{u}_b - \bar{u}_v)^2 + \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \left\{ KT |u_m^n|^2 + \frac{1}{\pi^2 KD_v} \left( \frac{4m^2}{l^2} + \frac{n^2}{d^2} \right)^{-1} |U_m^n|^2 \right\}. \quad (9.20)$$

Assume for the sake of argument that the Taylor vortices are simply superimposed upon an otherwise uniform (Poiseuille) flow. With the expansion coefficients  $u_0^n$  and  $U_0^n$  ( $n \neq 0$ ) pertaining only to the uniform flow, and the remaining ( $n \neq 0, m \neq 0$ ) coefficients pertaining only to the circulatory flow, the resulting increase in solute dispersivity arising from the presence of the vortices is apparent.

## 10. Asymptotic formulation of the macroscale transport process

Within the framework of Taylor dispersion theory for spatially periodic systems (Brenner 1980), the terms ‘macroscale’ and ‘long-time’ respectively connote that: (i) the behaviour of the system is being contemplated on a length scale,  $L$ , say, that is large compared with the characteristic linear dimension  $l$  of a unit cell (whence  $L \gg l$ ); and (ii) that a sufficient time has elapsed for locally quasi-steady solute distribution state to prevail within a generic unit cell (cf. (5.16)–(5.20)).

Since, in the present circumstances, the spatial periodicity is posited to be unidirectional with respect to the reactor axis, the macroscale problem acquires a one-dimensional character. In this context, with  $Z = nl$  (and  $Z' = n'l$ ), let

$$\bar{P}_\alpha(Z, t | Z', \mathbf{r}'; \zeta) \stackrel{\text{def}}{=} \int_{\tau_0} d^3 \mathbf{r} P_\alpha(\mathbf{r} + \mathbf{e}_z nl, t | \mathbf{r}' + \mathbf{e}_z n'l; \zeta), \quad (10.1)$$

be the conditional probability density that the solute tracer is situated somewhere within phase  $\alpha$  in a given cell  $n$  at time  $t$ . For  $Z = O(L)$ , (or, equivalently,  $|n - n'| \gg 1$ ), the macroscale variable  $Z$  will henceforth be regarded as a continuous (rather than discrete) global-space coordinate. On physical grounds,  $\bar{P}_\alpha$  is necessarily dependent only upon the difference  $Z - Z'$ , rather than upon  $Z$  and  $Z'$  separately. Moreover, in the long-time limit,  $\bar{P}_\alpha$  necessarily ‘forgets’ the precise local position  $\mathbf{r}'$  within the unit cell at which the tracer was originally introduced into cell  $n'$  (Shapiro & Brenner 1988). However, as subsequently discussed,  $\bar{P}_\alpha$  necessarily retains memory of the solvent/bead initial partition distribution parameter  $\zeta$ . Thus, after sufficiently long time following the introduction of the solute tracer into the system, one can expect the asymptotic functional dependence

$$\bar{P}_\alpha \sim \bar{P}_\alpha(Z - Z', t | \zeta) \quad (10.2)$$

explicitly displayed in the latter argument of  $\bar{P}_\alpha$ .

Asymptotic matching of the total microscale moments  $M_\alpha^{(m)}$  (cf. (3.2)) with the comparable total macroscale moments,

$$\bar{M}_\alpha^{(m)}(t | \zeta) \stackrel{\text{def}}{=} \int_{-\infty}^{\infty} dz z^m \bar{P}_\alpha(z, t | \zeta) \quad (10.3)$$

( $m = 0, 1, 2, \dots$ ), allows one to establish (Shapiro & Brenner 1988) the equation

$$\frac{\partial \bar{\mathbf{P}}}{\partial t} + \bar{U}^* \frac{\partial \bar{\mathbf{P}}}{\partial Z} - \bar{D}^* \frac{\partial^2 \bar{\mathbf{P}}}{\partial Z^2} + \bar{K}^* \bar{\mathbf{P}} = \hat{M}_{-}^{(0)}(\zeta) \mathbf{E}_{-} \delta(Z-Z') \delta(t) \quad (\lambda_{+} \neq \lambda_{-}), \quad (10.4)$$

governing macroscale transport of the solute in the long-time limit. Here,

$$\bar{\mathbf{P}} \stackrel{\text{def}}{=} \begin{pmatrix} \bar{P}_v \\ \bar{P}_b \end{pmatrix}, \quad (10.5)$$

consistent with previously adopted notation (3.3*a, b*); moreover, using (5.7) and (5.4*a, b*), we have explicitly that

$$\hat{M}_{-}^{(0)}(\zeta) \mathbf{E}_{-} = \frac{1 - (k_{+} + 1)\zeta}{k_{-} - k_{+}} \begin{pmatrix} 1 \\ k_{-} \end{pmatrix} \equiv \frac{k_1(1 - \zeta) - (k_4 - \lambda_{+})\zeta}{k_1(\lambda_{+} - \lambda_{-})} \begin{pmatrix} k_1 \\ k_4 - \lambda_{-} \end{pmatrix}, \quad (10.6)$$

as the initial-condition coefficient appearing on the right-hand side of (10.4).

Note that the phenomenological coefficients  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$  obtained by the moment-matching scheme are the same for both phases (as long as the interphase transport is non-zero) in accord with our previous results (4.12). Moreover, these coefficients are independent of the initial tracer data; explicitly of the microscale position  $r'$  and  $n'$ , as well as of the initial partition parameter  $\zeta$ .

The solution of (10.4) satisfying the boundary condition that  $\bar{P}_{\alpha} \rightarrow 0$  as  $|Z - Z'| \rightarrow \infty$  is (e.g. Chandrasekhar 1943):

$$\bar{\mathbf{P}}(Z - Z', t | \zeta) = \hat{M}_{-}^{(0)}(\zeta) G(Z - Z', t) \mathbf{E}_{-}, \quad (10.7)$$

where

$$G(z, t) = \frac{1}{2(\pi \bar{D}^* t)^{\frac{1}{2}}} \exp \left[ -\frac{1}{4\bar{D}^* t} (z - \bar{U}^* t)^2 - \bar{K}^* t \right], \quad (10.8)$$

is the (normalized) Green's function of equation (10.4). The pair of macroscale conditional probability densities  $\bar{P}_v$  and  $\bar{P}_b$ , as well as the total conditional probability density,

$$\bar{P}(Z - Z', t | \zeta) \stackrel{\text{def}}{=} \bar{P}_v + \bar{P}_b \equiv \frac{k_1 - (k_1 + k_4 - \lambda_{+})\zeta}{k_1(\lambda_{+} - \lambda_{-})} (k_1 + k_4 - \lambda_{-}) G(Z - Z', t), \quad (10.9)$$

are functions of the initial partition parameter  $\zeta$ . In other words, the amount of the solute remaining in the system after a sufficiently long time will depend, in general, upon what portion  $\zeta$  of the tracer was initially introduced onto the bead surfaces. This residual dependence of  $\bar{\mathbf{P}}$  (but not of the macroscale phenomenological coefficients  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$ ) upon the initial partition data is similar to a comparable result in classical (i.e. 'single-phase') Taylor dispersion theory (Shapiro & Brenner 1988), where the solute may undergo (a first-order irreversible) catalytic chemical reaction on the walls of the vessel. In that case, the amount of the solute left in the system after a sufficiently long time will depend upon the initial distance between the tracer and the catalytic wall.

The dependence of  $\bar{\mathbf{P}}$  upon the initial partition data  $\zeta$ , as embodied in the appearance of the fictitious initial condition appearing on the right-hand side of (10.4) in place of the true initial condition, namely

$$\bar{\mathbf{P}}(Z - Z', 0 | \zeta) = \delta(Z - Z') \begin{pmatrix} \zeta \\ 1 - \zeta \end{pmatrix} \quad (10.10)$$

(derived from (2.3)), seems to be a direct consequence of the fact that (5.1) governing the temporal evolution of zero-order total moments possess two eigenvalues. As only the *algebraically smallest* eigenvalue represents the reaction rate coefficient  $\bar{K}^*$ , macroscale equations such as the left-hand side of (10.4), namely

$$\frac{\partial \bar{\mathbf{P}}}{\partial t} + \bar{U}^* \frac{\partial \bar{\mathbf{P}}}{\partial Z} - \bar{D}^* \frac{\partial^2 \bar{\mathbf{P}}}{\partial Z^2} + \bar{K}^* \bar{\mathbf{P}} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad (t > 0), \quad (10.11)$$

do not accurately represent the temporal evolution of the system at those ‘short’ times, i.e.  $0 \leq t < O(T_1, T_2)$ , for which inequalities (5.20) fail to be satisfied. Thus, if a disproportionate amount of solute was initially present on the reactive bead surfaces (compared with that initially present in the inert solvent), then a ‘disproportionate amount of solute’ will have been destroyed via reaction during the interval preceding the time (cf. (5.20)) at which (10.11) does become applicable. Subjecting the latter equation to the fictitious initial condition,

$$\bar{\mathbf{P}}(Z - Z', 0 | \zeta) = \hat{M}_{-}^{(0)}(\zeta) \delta(Z - Z') \mathbf{E}_{-}, \quad (10.12)$$

nullifies this initial imbalance, and effectively restores the proper asymptotic solvent/bead proportions

$$\bar{P}_b / \bar{P}_v \sim k_{-} \quad (10.13)$$

(cf. (5.19)). The simplicity of the form adopted by this fictitious initial condition, in contrast with that for the classical reactive (Shapiro & Brenner 1988) case, arises because of the fact that only two eigenvalues characterize the temporal evolution of the zero-order total moments, as opposed to a comparably infinite discrete spectrum of eigenvalues pertaining to the *inhomogeneous* single-phase system.

In this context of fictitious initial conditions, note that if no reaction occurs on the beads surfaces (i.e.  $\gamma = 0$ ), then  $\lambda_{-} = 0$ ,  $\lambda_{+} = k_1 + k_4$  (cf. (5.3)) and, consequently,

$$\hat{M}_{-}^{(0)} \mathbf{E}_{-} = \frac{1}{k_1 + k_4} \begin{pmatrix} k_1 \\ k_4 \end{pmatrix}.$$

As such, the long-time asymptotic distribution of the solute is independent of the initial state  $\zeta$  of the tracer, a fact consistent with the previous discussion. Similarly, if the initial partitioning  $\zeta$  is chosen such that it already corresponds to the quasi-steady asymptotic partitioning (10.13), namely

$$\zeta = 1/(1 + k_{-}),$$

then the true and fictitious initial conditions become identical, since then (following (10.6)),

$$\hat{M}_{-}^{(0)} \mathbf{E}_{-} = \frac{(1 + k_{-}) - (1 + k_{+})}{(k_{-} - k_{+})(1 + k_{-})} \begin{pmatrix} 1 \\ k_{-} \end{pmatrix} = \frac{1}{1 + k_{-}} \begin{pmatrix} 1 \\ k_{-} \end{pmatrix} \equiv \begin{pmatrix} \zeta \\ 1 - \zeta \end{pmatrix}.$$

## 11. Discussion. Functional dependence of the macroscale phenomenological coefficients upon the microscale parameters defining the system

The principal results of this paper are embodied in the respective generic expressions (5.9), (6.6) and (7.11) for the three macroscale coefficients  $\bar{K}^*$ ,  $\bar{U}^*$  and  $\bar{D}^*$ . The first two coefficients are expressed more-or-less directly in terms of the given microscale phenomenological data, or elementary algebraic variations thereof. As

such, calculations of  $\bar{K}^*$  and  $\bar{U}^*$  are immediate; these are described below. However, computation of  $\bar{D}^*$  via (7.11) necessitates that the  $B$ -fields, defined by (6.15) and (6.16), first be solved for as an intermediate step in the calculation. Although we have derived analytical results in §9 for several special cases, solution of these coupled second-order partial differential equations is, in general, a daunting task, one which can only be accomplished numerically. This is especially true given the complex structure of the Taylor-vortex velocity fields appearing therein. Such calculations are reserved for a companion paper, which will also include a comparison with experimental data in the parametric range of interest in applications.

(a) *Effective reaction rate  $\bar{K}^*$*

In discussing the functional dependence of  $\bar{K}^*$  upon the microscale parameters characterizing the problem, it is convenient to recast (5.9) into a form that clearly distinguishes between intrinsic or material physicochemical parameters, and externally-imposed parameters, the latter being those under the control of experimentalist, and hence independently manipulable. In this context, it is convenient to introduce three dimensionless quantities: (i) a Damkohler number,

$$\delta \stackrel{\text{def}}{=} \frac{\gamma}{k_1 + k_4} \equiv \frac{\gamma}{k_1(1 + sk_2)}; \quad (11.1)$$

(ii) the product  $sk_2$  of the Henry's law adsorption coefficient  $k_2$  (which has the dimensions of length) and specific surface  $s$  of the beads (which has the dimensions of a reciprocal length);† and (iii) the combination,

$$\kappa \stackrel{\text{def}}{=} \frac{sk_2}{1 + sk_2} \frac{\delta}{(1 + \delta)^2}. \quad (11.2)$$

In terms of these alternative parameters, (5.9) may be reformulated as

$$\bar{K}^* = sk_1 k_2 \frac{\delta}{1 + \delta} F(\kappa), \quad (11.3)$$

wherein

$$F(\kappa) = \frac{1}{2\kappa} [1 - (1 - 4\kappa)^{\frac{1}{2}}]. \quad (11.4)$$

Since  $\kappa$ , defined in (11.2), spans the range  $0 \leq \kappa \leq \frac{1}{4}$ , it is readily established that  $F(\kappa)$  is monotonic, and varies only over the bounded interval  $1 \leq F(\kappa) \leq 2$ . This latter property permits a complete and elementary delineation of the qualitative properties of  $\bar{K}^*$  over the complete parametric range of interest. In particular, upon noting that

$$\kappa \rightarrow 0 \quad \text{as either} \quad \delta \rightarrow 0 \quad \text{or} \quad \delta \rightarrow \infty \quad \text{or} \quad sk_2 \rightarrow 0, \quad (11.5)$$

one obtains the limiting value

$$\bar{K}^* = sk_1 k_2 \frac{\delta}{1 + \delta} \quad (\kappa \rightarrow 0).$$

This constitutes a generalization of (5.11) and (5.12), previously derived.

Note that although the effective reaction-rate coefficient  $\bar{K}^*$  is *explicitly*

† Following the Henry's law constitutive relation outlined in connection with the footnote to (2.6), the product  $sk_2$  actually represents the equilibrium ratio of the respective amounts of adsorbed and dissolved solute at each point  $\mathbf{R}$  of a non-reactive system.

independent of the velocity field, there nevertheless exists an *implicit* dependence, arising from the generic dependence of the mass transfer coefficient  $k_1$  upon the microscale velocity field.

(b) *Average axial solute velocity  $\bar{U}^*$*

Using the notation adopted in the preceding subsection (6.6) for average axial solute velocity  $\bar{U}^*$  adopts the form

$$\bar{U}^* = \left\{ \bar{u}_v + sk_2 \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^2 \bar{u}_b \right\} \left\{ 1 + sk_2 \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^2 \right\}^{-1}. \quad (11.6)$$

This velocity is clearly independent of the mass transfer coefficient  $k_1$  for a given Damkohler number  $\delta$ . As the Henry's law adsorption coefficient  $k_2$  is, by definition, independent of the velocity field, it thus follows that  $\bar{U}^*$  is both *explicitly* and *implicitly* independent of the circulatory nature of the velocity field. It does depend, however, upon the respective average axial velocities of the solvent and bead continua, namely  $\bar{u}_v$  and  $\bar{u}_b$ . (Insofar as its lack of dependence upon the 'strength' of the circulation is concerned, the present result is reminiscent of the comparable vortex-strength-independent result of Dungan & Brenner (1988) for the sedimentation velocity of a brownian particle through a spatially periodic vortex flow.)

Following (5.4) and (11.3), the dimensionless quantity

$$k_- \equiv sk_2 \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right] \quad (11.7)$$

represents the ratio of the respective amounts of solute existing in the dissolved and adsorbed states at each point  $\mathbf{R}$  of the system, at least for sufficiently long times. On physical grounds this ratio should be small when either the Henry's law adsorption coefficient is small (in which case no solute 'arrives' at the bead surfaces), or when the Damkohler number is large (in which case all solute arriving at the bead surfaces is immediately depleted by the chemical reaction). Indeed, from (11.7), one finds that  $k_- \rightarrow 0$  as  $sk_2 \rightarrow 0$  or  $\delta \rightarrow \infty$ . Moreover, as no solute is present on the beads in this limit, the average solute velocity  $\bar{U}^*$  should coincide with the average solvent velocity  $\bar{u}_v$ . Evaluation of the pertinent limits in (11.6) confirms this assertion (cf. (6.7b)).

When the Damkohler number is small, all adsorbed solute destroyed via the chemical reaction is immediately replenished via mass transfer, whence the ratio of the respective amounts of solute existing in the dissolved and adsorbed states should correspond to the Henry's law equilibrium solute partitioning. In fact, with  $\delta \ll 1$ , one finds from (11.7) that  $k_- \approx sk_2$ . Under these circumstances, the general expression (11.6) for  $\bar{U}^*$  adopts the form

$$\bar{U}^* \approx \frac{\bar{u}_v + sk_2 \bar{u}_v}{1 + sk_2} \quad (\delta \ll 1),$$

in accord with (6.7a), as well as with companion result of Haber & Brenner (1993).

(c) *Axial solute dispersivity  $\bar{D}^*$*

Again, using the notation adopted in §11a, and upon further defining

$$N \stackrel{\text{def}}{=} k_1 d^2 / D_v \quad (11.8)$$

as the respective Nusselt number (with  $d$  the annual gap thickness), the general expression for the dispersivity (7.11) may be rewritten as

$$\begin{aligned} \bar{D}^* = D_v \left\{ 1 + sk_2 \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^2 \right\}^{-1} & \left\{ sk_2 N \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right] \frac{1}{d^2 \tau_0} \int_{\tau_0} d^3 \mathbf{r} (B_v - B_b)^2 \right. \\ & \left. + sk_2 \frac{D_b}{D_v} \left[ 1 - \frac{\delta}{1-\delta} F(\kappa) \right]^2 \frac{1}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (\nabla B_b)^2 + \frac{1}{\tau_0} \int_{\tau_0} d^3 \mathbf{r} (\nabla B_v)^2 \right\}. \end{aligned} \quad (11.9)$$

Moreover, with  $\hat{u}_\alpha$  the characteristic circulatory velocity  $|\mathbf{u}_\alpha - \bar{u}_\alpha \mathbf{e}_z|$  of the respective continua, and with

$$\hat{\pi}_\alpha \stackrel{\text{def}}{=} \hat{u}_\alpha d / D_v, \quad \bar{\pi}_\alpha \stackrel{\text{def}}{=} \bar{u}_\alpha d / D_v \quad (11.10a, b)$$

the respective *circulatory* and *axial* Peclet numbers, (6.15) governing the  $B$ -fields become

$$\hat{\pi}_v \frac{\mathbf{u}_v - \bar{u}_v \mathbf{e}_z}{\hat{u}_v} \cdot \nabla' B'_v + \bar{\pi}_v \mathbf{e}_z \cdot \nabla' B'_v - \nabla'^2 B'_v + sk_2 N \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right] (B'_v - B'_b) = -\bar{\pi}^*, \quad (11.11a)$$

$$\hat{\pi}_b \frac{\mathbf{u}_b - \bar{u}_b \mathbf{e}_z}{\hat{u}_b} \cdot \nabla' B'_b + \bar{\pi}_b \mathbf{e}_z \cdot \nabla' B'_b - \frac{D_b}{D_v} \nabla'^2 B'_b - N \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^{-1} (B'_v - B'_b) = -\bar{\pi}^*. \quad (11.11b)$$

Here,  $\nabla' \equiv d\nabla$  is the dimensionless gradient operator;  $B'_\alpha \equiv d^{-1} B_\alpha$  is the respective dimensionless  $B$ -field; whereas (in view of (11.6))

$$\bar{\pi}^* \stackrel{\text{def}}{=} \frac{\bar{U}^* d}{D_v} \equiv \left\{ \bar{\pi}_v + sk_2 \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^2 \bar{\pi}_b \right\} \left\{ 1 + sk_2 \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^2 \right\}^{-1}.$$

Thus, the ratio  $\bar{D}^*/D_v$  depends upon all the dimensionless parameters previously introduced, namely  $sk_2$ ,  $\delta$ ,  $N$ ,  $D_b/D_v$ ,  $\hat{\pi}_v$ ,  $\hat{\pi}_b$ ,  $\bar{\pi}_v$  and  $\bar{\pi}_b$ , as well as upon the particular patterns  $(\mathbf{u}_\alpha - \bar{u}_\alpha \mathbf{e}_z)/\hat{u}_\alpha$  of the respective velocity fields. With a detailed numerical study of this extremely complex functional dependence to be published in a companion paper, we cite here several preliminary conclusions.

(i) When either  $sk_2 \rightarrow 0$  or  $\delta \rightarrow \infty$ , the axial dispersivity  $\bar{D}^*$  of the solute in a bead reactor is the same as if the beads were absent. From a mathematical standpoint, this result is an immediate consequence of (11.7). In fact, under these circumstances  $k_- \rightarrow 0$  (cf. the paragraph immediately following (11.7)), whereas, in view of (11.6) and (11.11), one readily finds that  $\bar{U}^* = \bar{u}_v$ , and that the  $B$ -fields are uncoupled. In view of (7.14), the above result is apparent. From a physical standpoint, the explanation of this phenomenon presents no difficulties; for in such circumstances all the solute that arrives at the beads' surface is either insignificant in amount (when  $sk_2 \rightarrow 0$ ) or is immediately destroyed by the chemical reaction (when  $\delta \rightarrow \infty$ ), leaving the macroscale transport of the solute controlled exclusively by the solvent.

(ii) When  $\gamma \rightarrow 0$  and the difference between velocity fields of the solvent and beads is small, the macroscale (axial) dispersivity  $\bar{D}^*$  of the solute in a bead reactor may actually be less than the comparable dispersivity in the absence of the beads. In fact, upon assuming that the beads are carried along the streamlines of the solvent, and that the diffusivity of the beads is negligible, that portion of the solute that is



adsorbed onto the beads does not diffuse at all (cf. (9.11)), and hence does not contribute to the dispersion process.

(iii) With increasing difference in velocity fields between the beads and solvent,  $\bar{D}^*$  increases (cf. (9.5) and (9.10)). The reason again lies in 'piggy-back' convection of the solute by the beads. This latter process is clearly characterized by the time scale

$$T \equiv \frac{sk_2}{k_1} \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^3,$$

introduced in (9.6a). With  $T$  supposed large compared with the characteristic time scale of the molecular diffusion process, the piggy-back convection of solute by the beads may become the principal mechanism contributing to  $\bar{D}^*$ . With the characteristic time scale of the diffusion process being roughly  $d^2/D_v$  (cf. the paragraph following (9.11)), these circumstances may be described by the inequality

$$\frac{sk_2}{N} \left[ 1 - \frac{\delta}{1+\delta} F(\kappa) \right]^3 \gg 1.$$

In particular, when  $\kappa \rightarrow 0$  (cf. (11.5)), this inequality adopts the form

$$sk_2 \gg N(1+\delta)^3,$$

consistent with the fact that when no solute is present on the beads – namely when either  $\delta \rightarrow \infty$  or  $sk_2 \rightarrow 0$  (cf. paragraph (i) above) – piggy-back diffusion cannot possibly be dominant.

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### Appendix A. Derivation of (5.15)

Subject to *a posteriori* verification, assume the following eigenfunction expansion of the zero-order local moments:

$$\mathbf{P}^{(0)} = \frac{1}{\tau_0} \mathbf{M}^{(0)} + \sum_{n=1}^{\infty} \exp(-\lambda_n t) \begin{pmatrix} K_v^{(n)} \\ K_b^{(n)} \end{pmatrix}, \quad (\text{A } 1)$$

with  $\lambda_n$  the eigenvalues, and  $K_\alpha^{(n)} \equiv K_\alpha^{(n)}(\mathbf{r} | \mathbf{r}'; \zeta)$  the respective eigenfunctions ( $n = 1, 2, \dots$ ) of the operator  $[\mathcal{L} + A]$  appearing in (5.13) (with boundary conditions (3.7)). Here, and in all subsequent formulas,  $\alpha$  is given by (2.9). Substitute (A 1) into (3.4) and (3.5) (with  $m = 0$ ), and subsequently utilize (5.1) and (5.2), thereby establishing that these eigenquantities are governed by the system of equations

$$(\lambda_n - \lambda_-) \begin{pmatrix} K_v^{(n)} \\ K_b^{(n)} \end{pmatrix} = \begin{pmatrix} \mathcal{L}_v K_v^{(n)} \\ \mathcal{L}_b K_b^{(n)} \end{pmatrix} + \{[A] - \lambda_- [I]\} \begin{pmatrix} K_v^{(n)} \\ K_b^{(n)} \end{pmatrix}, \quad (\text{A } 2)$$

$$\mathbf{n} \cdot [\mathbf{u}_\alpha K_\alpha^{(n)} - D_\alpha \nabla K_\alpha^{(n)}] = 0 \quad \text{on the reactor walls}, \quad (\text{A } 3)$$

$$\|K_\alpha^{(n)}\| = 0, \quad (\text{A } 4)$$

( $n = 1, 2, \dots$ ). In addition, it is required that

$$\sum_{n=1}^{\infty} K_v^{(n)} = \zeta \left[ \delta(\mathbf{r} - \mathbf{r}') - \frac{1}{\tau_0} \right], \quad \sum_{n=1}^{\infty} K_b^{(n)} = (1 - \zeta) \left[ \delta(\mathbf{r} - \mathbf{r}') - \frac{1}{\tau_0} \right] \quad (\text{A } 5a, b)$$

so as to satisfy the initial conditions at  $t = 0$ .

In order to derive (5.15) from the general expansion (A 1) it suffices to prove that the residuals  $\lambda_1 - \lambda_-, \lambda_2 - \lambda_-, \dots$  are strictly positive. To this end, multiply the upper of equations of (A 2) by  $K_v^{(n)}$  and integrate over the domain  $\tau_0$  of a unit cell to obtain, with use of some obvious identities,

$$\begin{aligned} (\lambda_n - \lambda_-) \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)}]^2 &= \int_{\tau_0} d^3\mathbf{r} \nabla \cdot \left\{ \frac{1}{2} \mathbf{u}_v [K_v^{(n)}]^2 - D_v K_v^{(n)} \nabla K_v^{(n)} \right\} + D_v \int_{\tau_0} d^3\mathbf{r} [\nabla K_v^{(n)}]^2 \\ &\quad + (k_4 - \lambda_-) \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)}]^2 - k_1 \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)} K_b^{(n)}]. \end{aligned}$$

The left-most integral on the right-hand side of this equation vanishes identically in view of boundary conditions (2.2a), (A 3) and (A 4); thus,

$$\begin{aligned} (\lambda_n - \lambda_-) \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)}]^2 &= D_v \int_{\tau_0} d^3\mathbf{r} [\nabla K_v^{(n)}]^2 \\ &\quad + (k_4 - \lambda_-) \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)}]^2 - k_1 \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)} K_b^{(n)}]. \quad (\text{A } 6a) \end{aligned}$$

Similarly, upon multiplying the lower of equations (A 2) by  $K_b^{(n)}$  and subsequently integrating over the volume of a unit cell, one finds (with use of (5.4b)) that

$$(\lambda_n - \lambda_-) \int_{\tau_0} d^3\mathbf{r} [K_b^{(n)}]^2 = D_b \int_{\tau_0} d^3\mathbf{r} [\nabla K_b^{(n)}]^2 + \frac{k_1 k_4}{k_4 - \lambda_-} \int_{\tau_0} d^3\mathbf{r} [K_b^{(n)}]^2 - k_4 \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)} K_b^{(n)}]. \quad (\text{A } 6b)$$

Multiply (A 6a, b) by  $k_4$  and  $k_1$ , respectively, and add together the resulting pair of expressions to obtain,

$$\begin{aligned} &(\lambda_n - \lambda_-) \left\{ k_4 \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)}]^2 + k_1 \int_{\tau_0} d^3\mathbf{r} [K_b^{(n)}]^2 \right\} \\ &= k_4 D_v \int_{\tau_0} d^3\mathbf{r} [\nabla K_v^{(n)}]^2 + k_1 D_b \int_{\tau_0} d^3\mathbf{r} [\nabla K_b^{(n)}]^2 \\ &\quad + k_4 (k_4 - \lambda_-) \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)}]^2 - 2k_1 k_4 \int_{\tau_0} d^3\mathbf{r} [K_v^{(n)} K_b^{(n)}] + \frac{k_1^2 k_4}{k_4 - \lambda_-} \int_{\tau_0} d^3\mathbf{r} [K_b^{(n)}]^2 \\ &\equiv k_4 D_v \int_{\tau_0} d^3\mathbf{r} [\nabla K_v^{(n)}]^2 + k_1 D_b \int_{\tau_0} d^3\mathbf{r} [\nabla K_b^{(n)}]^2 + \frac{k_4}{k_4 - \lambda_-} \int_{\tau_0} d^3\mathbf{r} [(k_4 - \lambda_-) K_v^{(n)} - k_1 K_b^{(n)}]^2. \end{aligned}$$

The coefficients  $D_v$  and  $D_b$  are both strictly positive, whereas  $k_1$  and  $k_4$  are non-negative by definition; moreover,  $k_4 - \lambda_-$  is non-negative in view of (7.12). Thus (except possibly for the trivial case where

$$K_v^{(n)} = \text{const.}, \quad K_b^{(n)} = k_- K_v^{(n)},$$

for which  $\lambda_n \equiv \lambda_-$ ), the non-negative nature of the above integrands shows that  $\lambda_n > \lambda_-$ . Q.E.D.

## Appendix B. Nomenclature

$a$	surface area of a bead
$[A]$	matrix defined in (3.5)
$B_v, B_b$	scalar fields representing the solution of (6.15)
$\bar{B}_v, \bar{B}_b$	average values of the respective $B$ -fields over a unit cell
$\tilde{B}_v, \tilde{B}_b$	spatially periodic fields defined in (9.1)
$B_m^n$	coefficient in complex-form Fourier expansion of $\tilde{B}_v$
$d$	annular gap between the cylinders
$D_v$	molecular diffusivity of the solute in the solvent
$D_b$	brownian diffusivity of the beads in the solvent
$\bar{D}^*$	effective axial dispersivity
$\tilde{D}_b$	effective diffusivity dyadic of the adsorbed solute defined in (9.6 <i>d</i> )
$c$	number density of the beads
$e_x, e_y, e_z$	unit basis vectors
$E_-, E_+$	eigenvectors (of length 2) of $[A]$
$E_\alpha^-, E_\alpha^+$	respective components of $E_-, E_+$
$F(\kappa)$	auxiliary function defined in (11.4)
$G$	Green's function of (10.4)
$G_v, G_b$	scalar quantities in (7.2)
$H$	constant arising during the derivation of (7.11)
$I$	dyadic idemfactor
$[I]$	unit $2 \times 2$ matrix
$J_v, J_b$	respective probability flux density vectors
$k_1$	mass transfer coefficient in (2.6)
$k_2$	Henry's law constant in (2.6)
$k_4$	coefficient in (2.6)
$k_-, k_+$	coefficients in (5.4)
$K$	constant defined in (9.6 <i>b</i> )
$\bar{K}^*$	effective reaction rate
$l$	linear dimension of a unit cell in axial direction
$[\mathcal{L}]$	matrix-form operator defined in (3.6 <i>a</i> )
$\mathcal{L}_v, \mathcal{L}_b$	linear second-order differential operators defined in (3.6 <i>b</i> )
$M^{(m)}$	column vector (of length 2) of $m$ th-order total moments
$M_v^{(m)}, M_b^{(m)}$	respective components of $M^{(m)}$
$\hat{M}_+^{(0)}, \hat{M}_-^{(0)}$	coefficients in (5.2)
$\hat{M}_+^{(1)}, \hat{M}_-^{(2)}$	coefficient in (6.3) and (7.5), respectively
$n$	unit cell position index
$\mathbf{n}$	unit normal vector to reactor vessel wall
$N$	Nusset number (cf. (11.8))
$O_{\text{exp}}$	generic quantity that vanishes exponentially as $t \rightarrow \infty$
$P_v, P_b$	conditional probability densities for the instantaneous position of solute molecule in the respective phases (states)
$\bar{P}$	sum, $\bar{P}_v + \bar{P}_b$
$\bar{P}$	column vector (of length 2) with respective components $\bar{P}_v$ and $\bar{P}_b$ , defined in (10.5)
$\bar{P}_v, \bar{P}_b$	conditional probability densities for the instantaneous axial position of solute molecule in the respective phases (states)
$P^{(m)}$	column vector (of length 2) of $m$ th-order local moments

$P_v^{(m)}, P_b^{(m)}$	respective components of $P^{(m)}$
$r$	position vector of a point within a unit cell
$R$	position vector of a point in reactor's annular domain
$R_1, R_2$	respective radii of the inner and outer cylinders
$s$	specific surface (cf. footnote to (2.6))
$S$	source term in (2.4)
$S_0$	cross-sectional domain of the reactor
$t$	time
$T$	timescale underlining interphase solute transport (cf. (9.6a))
$T$	column vector (of length 2) in (7.5)
$T_1$	time scale for establishing a uniform solute distribution within a unit cell
$T_2$	time scale for establishing constant solute partitioning between solvent and beads
$u_v, u_b$	respective solvent and beads (vector) velocity fields
$u_v, u_b$	respective solvent and bead (scalar) axial velocities
$\bar{u}_v, \bar{u}_b$	respective average solvent and bead axial velocities
$u_m^n$	coefficient in complex-form Fourier expansion of $u_b - \bar{u}_b$
$U^*$	effective solute velocity defined in (9.9)
$\bar{U}^*$	macroscale average axial solute velocity
$U_m^n$	coefficient in complex-form Fourier expansion of $U^* - \bar{U}^*$
$V$	column vector (of length 2) in (7.5)
$V_v, V_b$	components of $V$
$V_\infty$	annular domain
$W$	column vector (of length 2) in (6.4)
$W_v, W_b$	components of $W$
$x, y, z$	cartesian coordinates
$Z$	axial (macroscale) coordinate
$\alpha$	state of solute tracer molecule
$\gamma$	rate of solute depletion on bead's surface (cf. (2.4))
$\delta$	Damkohler number (cf. (11.1))
$\delta(r-r')$	Dirac delta function
$\delta_{mn}$	Kronecker delta
$\zeta$	initial phase-partition parameter
$\kappa$	dimensionless parameter defined in (11.2)
$\lambda_-, \lambda_+$	eigenvalues of $[A]$
$\lambda_n$	( $n = 1, 2, \dots$ ), eigenvalues of the operator $[\mathcal{L}] + [A]$
$\varpi$	radial coordinate
$\hat{\pi}_v, \hat{\pi}_b$	circulatory Peclet numbers defined in (11.10a)
$\bar{\pi}_v, \bar{\pi}_b$	axial Peclet numbers defined in (11.10b)
$\Pi$	total conditional probability density for instantaneous position of solute molecule
$\tau_0$	unit cell volume
<i>indices</i>	
$\alpha$	$\alpha$ th-phase
v	solvent
b	beads
—	algebraically smallest eigenvalue of $[A]$

- + algebraically largest eigenvalue of  $[A]$   
 ( $m$ )  $m$ th-order moment ( $m = 0, 1, 2, \dots$ )  
 ' initial position of solute tracer molecule

*marks over symbols*

- average over a unit cell, or a macroscale quantity  
 ^ coefficient in an eigenvector expansion  
 ~ spatially periodic quantity

*standard operators*

- $\nabla$  gradient operator  
 || || 'jump' operator denoting an increase in value of the argument between equivalent points in adjacent cells

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