ν = stoichiometric coefficient (moles reactant consumed/mole of mineral reacted)
τ = space time, s
ψ = dimensionless reactant concentration
ϕ = porosity

Subscripts

b = breakthrough
h = homogeneous phase reaction
i = reactant species
j = mineral species
n = last of the moving fronts
s = surface reaction

APPENDIX: QUARTZ DISSOLUTION PARAMETERS FROM DATA OF A. D. HILL et al., (1977)

Figure	T (°C)	$Da \cdot Ac$	$\frac{V(1-\phi_0)}{L\phi_0 C_0}$	k_{quartz}(m³/mole/s) × 10^8
7	25	3.226×10^{-3}	0.223	1.21
8	52	4.381×10^{-3}	0.453	3.31

The activation energy between 25° and 52°C is 29.9 kJ/mole.

Figure	T(°C)	Q (cm³/s)	Da_F	Ac_F	Da_Q	Ac_Q
10	25	0.342	0.8633	0.035	0.1139	0.0053
11	52	0.250	1.9495	0.037	0.4269	0.0052

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On the Construction of Dispersion Approximations to the Solution of the Convective Diffusion Equation

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We identify dispersion approximations to the transverse average of the solution of the convective diffusion equation on exacting equality of a finite number of axial Hermite moments. The method unifies the dispersion of chemically active and passive solutes and generalizes dispersion theory to arbitrary transverse averages. We emphasize the importance of the scalar results via their application to the dispersion of a system of chemical isomers.

SCOPE

In the area average and for chemically inactive solute, the dispersion theory of Gill and Sankarasubramanian generates useful approximations to the transverse average of the solution of the convective diffusion equation. Because technical difficulties limit the implied construction in nonarea averages and for chemically active solute, a reformulation of the conditions which define the dispersion coefficients is outlined. The result

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is that the class of systems for which their complete time dependence can be established is substantially enlarged.

Thus we focus on chemically active solute and report the predictions of the second-order approximation in the dispersion of a system of chemical isomers, recording area and flow average results.

CONCLUSIONS AND SIGNIFICANCE

We find that to identify a dispersion approximation, it is necessary and sufficient to deduce the time averages of the corresponding dispersion coefficients. We also find that the time average dispersion coefficients are significantly easier to evaluate than the dispersion coefficients themselves. It follows that the construction of the second-order dispersion approximation $\bar{c}^{(2)}$ is computationally feasible in chemically active systems.

The dependence of the dispersion coefficients on the initial solute distribution suggests the formulation of an asymptotic approximation to $\bar{c}^{(m)}$. We establish an approximation, denoted $\bar{c}_\infty^{(m)}$, which depends only on the constants $X_i|_{t\to\infty}$, where $X_i|_{t\to\infty}$ is independent of the initial solute distribution, and $\int_0^\infty (X_i - X_i|_{t\to\infty})\, dt$. The $X_i|_{t\to\infty}$ become the dispersion coefficients in the constant coefficient approximation, and the $\int_0^\infty (X_i - X_i|_{t\to\infty})\, dt$ establish the correction of the initial condition such that $\bar{c}^{(m)}$ and $\bar{c}_\infty^{(m)}$ coincide as t grows large. We find that $\bar{c}_\infty^{(2)}$ is a substantially better representation of $\bar{c}^{(2)}$ than is the so-called Taylor-Aris approximation which likewise is predicated on the asymptotic dispersion coefficients but takes the prescribed initial condition at face value.

The scalar theory is useful in multisolute dispersion if $\underset{\sim}{D}$ and $\underset{\sim}{K}$ possess a common set of eigenvectors. It is generally useful if $\underset{\sim}{K} = \underset{\sim}{0}$, but not otherwise. For $\underset{\sim}{K} \neq \underset{\sim}{0}$, we report predictions for an isomerization to illustrate certain salient features of multisolute dispersion. Now, in such systems the pseudo species follow the scalar theory, whence the differing chemical activities of the pseudo species imply differing pseudo species velocities. This alone accounts for the splitting of the species waves. We find that the approximation $\underset{\sim}{\bar{c}}_\infty^{(2)}$ estimates $\underset{\sim}{\bar{c}}^{(2)}$ quantitatively throughout the splitting.

INTRODUCTION

We investigate the dispersion of a chemically active solute via the action of a rectilinear flow field in a cylinder of arbitrary cross section. The solute experiences an irreversible first-order decomposition which may be heterogeneous, that is, promoted by a catalyst deposited on the surface of the cylinder, or homogeneous or both.

The plan of the paper is the following. First we define the m^{th} dispersion approximation $\bar{c}^{(m)}$ to the transverse average solute concentration $\bar{c}$ and thereby introduce the dispersion coefficients X_i, which we express via the Hermite moments $\bar{c}_j$ of $\bar{c}$, $j = 0, \ldots, i$. Second we exhibit the m^{th} order dispersion approximation and find that it depends on the dispersion coefficients only through their time integrals which admit exceedingly simple expression via $\bar{c}_i$, $i = 0, \ldots, m$. Third we introduce the constant coefficient dispersion approximation, and we indicate its relation to the so-called Taylor-Aris approximation. The scalar dispersion results can be used in multisolute dispersion for nonreactive solutes, generally, and for reactive solutes under certain conditions. We exhibit the predictions of the theory to illustrate the physics of multisolute dispersion.

THE m^{th} TAYLOR-GILL APPROXIMATION TO THE TRANSVERSE AVERAGE CONCENTRATION FIELD

In the dispersion of a solute cloud under the action of rectilinear flow in a cylinder of arbitrary cross section, the solute concentration c satisfies the convective diffusion equation

$$\frac{\partial c}{\partial t} = D\nabla_A^2 c - v\frac{\partial c}{\partial z} + D\frac{\partial^2 c}{\partial z^2} + K_A c \qquad t > 0,\ (x,y) \in \underset{\sim}{A} \quad z \in (-\infty,\infty) \tag{1}$$

the surface balance condition

$$-D\underset{\sim}{n} \cdot \nabla_A c + Kc = 0 \qquad t > 0,\ (x,y) \in \underset{\sim}{C} \quad z \in (-\infty,\infty)$$

and the initial condition that $c|_{t=0}$ be the prescribed initial solute field. Here $\nabla_A^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2$, and Equation (1) is expressed in scaled variables. Thus, if a prime superscript distinguishes a dimensional from a nondimensional variable, and if L and T denote physically meaningful length and time scales, then we let

$$x = \frac{x'}{L},\quad y = \frac{y'}{L},\quad z = \frac{z'}{L},\quad \nabla_A^2 = \frac{\nabla_A'^2}{L^2},\quad t = \frac{t'}{T}$$

and

$$D = \frac{D'}{L^2T^{-1}},\quad v = \frac{v'}{LT^{-1}},\quad K = \frac{K'}{LT^{-1}},\quad K_A = \frac{K_A'}{T^{-1}}$$

and we write $v(x,y) = N_{pe}\, u(x,y)$.

We introduce the set of Hermite functions $\{\phi_1(z)\}$ such that c can be represented by its Hermite moments c_i; namely

$$c = \sum_{i=0}^{\infty} c_i\phi_i \tag{2}$$

where

$$c_i = (c,\phi_i) = \int_{-\infty}^{\infty} c\phi_i\, e^{z^2}\, dz = \int_{-\infty}^{\infty} ch_i dz$$

where $\phi_i(z) = h_i(z)e^{-z^2}$, and where the set $\{\phi_i\}$ is a complete orthonormal set in the Hilbert space $\mathscr{L}_+^2 \equiv \mathscr{L}^2[(-\infty,\infty), R, (\cdot,\cdot)]$. This follows because the set $\{h_i\}$ is a complete orthonormal set in the Hilbert space $\mathscr{L}_-^2 \equiv \mathscr{L}^2[(-\infty,\infty), R, (\cdot,\cdot)_-]$, where $(\cdot,\cdot)_- = \int_{-\infty}^{\infty} \cdot\cdot\, e^{-z^2}\, dz$, and where $h_i(z)$ is a renormalization of the i^{th} standard Hermite polynomial $H_i(z)$; namely

$$h_i(z) = \frac{H_i(z)}{\sqrt{\sqrt{\pi}2^i i!}}$$

(see Courant and Hilbert, 1966). It follows that

$$\frac{d}{dz} h_i(z) = \sqrt{2i}\, h_{i-1}(z)$$

whence that

$$\frac{d}{dz}\phi_i(z) = -\sqrt{2(i+1)}\,\phi_{i+1}(z)$$

Equation (1) implies that the i^{th} Hermite moment of c must satisfy

$$\frac{\partial c_i}{\partial t} = D\nabla_A^2 c_i + \sqrt{2i}\, N_{pe}\, u\, c_{i-1}$$

$$+ \sqrt{2i}\ \sqrt{2(i-1)}\ D\ c_{i-2} + K_A\ c_i, \qquad (3)$$

$$t > 0,\ (x,y) \in \underset{\sim}{A}$$

$$- D\underset{\sim}{n} \cdot \nabla_A c_i + K c_i = 0 \quad t > 0,\ (x,y) \in \underset{\sim}{C}$$

and

$$c_i\big|_{t=0} = \left(c\big|_{t=0}, \phi_i\right), \qquad t = 0$$

whence the elements of the set $\{c_i\}$ can be evaluated recursively. A formal representation of c_i may be constructed via its ψ_j moments, $<c_i, \psi_j>$, in particular

$$c_i = \sum_{j=1}^{\infty} <c_i, \psi_j> \psi_j \qquad (4)$$

where

$$D\nabla_A^2 \psi_i = -\ \lambda_i^2 \psi_i \qquad (x,y) \in \underset{\sim}{A}$$

$$- D\underset{\sim}{n} \cdot \nabla_A \psi_i + K\ \psi_i = 0 \qquad (x,y) \in \underset{\sim}{C}$$

where $\{-\lambda_i^2\}$ is ordered via $\lambda_i^2 \leq \lambda_{i+1}^2$, and where

$$<c_i, \psi_j> = \int\int_{\underset{\sim}{A}} c_i \psi_j\ dxdy$$

and

$$<\psi_i, \psi_j> = \delta_{ij}$$

It follows from Equation (3) that

$$\frac{d}{dt} <c_i, \psi_j> = -\ \lambda_j^2 <c_i, \psi_j> + \sqrt{2i}\ N_{pe} <uc_{i-1}, \psi_j>$$

$$+ \sqrt{2i}\ \sqrt{2(i-1)}\ D <c_{i-2}, \psi_j> + K_A <c_i, \psi_j>$$

whence, if $K_A = 0$, that

$$<c_i, \psi_j>\big|_{K_A=0} = e^{-\lambda_j^2 t} <c_i\big|_{t=0}, \psi_j>$$

$$+ \int_0^t e^{-\lambda_j^2 (t-\tau)} \Big(\sqrt{2i}\ N_{pe} <uc_{i-1}\big|_\tau, \psi_j>$$

$$+ \sqrt{2i}\ \sqrt{2(i-1)}\ D <c_{i-2}\big|_\tau, \psi_j> \Big) d\tau$$

whereas, if $K_A < 0$, that

$$<c_i, \psi_j> = e^{K_A t} <c_i, \psi_j>\big|_{K_A=0}$$

We conclude that

$$c_i = e^{K_A t}\ c_i\big|_{K_A=0}$$

If we use the notation

$$\sum_j (\ )_i = \sum_{j=1}^{\infty} e^{-\lambda_j^2 t} <c_i\big|_{t=0}, \psi_j> \psi_j$$

$$\sum_j \sum_k (\ )_i = \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \int_0^t e^{-\lambda_j^2 (t-\tau)} e^{-\lambda_k^2 \tau} d\tau <c_i\big|_{t=0},\ \psi_k> <u\psi_k, \psi_j> \psi_j$$

$$\sum_j \sum_k \sum_l (\ )_i = \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \int_0^t e^{-\lambda_j^2 (t-\tau)} \int_0^\tau e^{-\lambda_k^2 (\tau-\tau_0)}\ e^{-\lambda_l^2 \tau_0}\ d\tau_0\ d\tau$$

$$\times <c_i\big|_{t=0}, \psi_l> <u\psi_l, \psi_k> <u\psi_k, \psi_j> \psi_j$$

etc., we find that

$$c_0 = \sum_j (\ )_0$$

$$c_1 = \sum_j (\ )_1 + \sqrt{2}\ N_{pe} \sum_j \sum_k (\ )_0$$

$$c_2 = \sum_j (\ )_2 + \sqrt{2 \cdot 2}\ N_{pe} \Big[\sum_j \sum_k (\ )_1$$

$$+ \sqrt{2}\ N_{pe} \sum_j \sum_k \sum_l (\ )_0 \Big] + \sqrt{2 \cdot 2}\ \sqrt{2}\ D \sum_j \sum_{k=j} (\ )_0$$

$$c_3 = \sum_j (\ )_3 + \sqrt{2 \cdot 3}\ N_{pe} \Big\{ \sum_j \sum_k (\ )_2$$

$$+ \sqrt{2 \cdot 2}\ N_{pe} \Big[\sum_j \sum_k \sum_l (\ )_1 + \sqrt{2}\ N_{pe} \sum_j \sum_k \sum_l \sum_m (\ )_o \Big]$$

$$+ \sqrt{2 \cdot 2}\ \sqrt{2}\ D \sum_j \sum_{k=j} \sum_l (\ )_0 \Big\}$$

$$+ \sqrt{2 \cdot 3}\ \sqrt{2 \cdot 2}\ D \Big[\sum_j \sum_{k=j} (\ )_1 + \sqrt{2}\ N_{pe} \sum_j \sum_{j=k} \sum_l (\ )_0 \Big]$$

etc.

Inasmuch as mean convergence of the series in Equations (2) and (4) is sufficient for the commutativity of the limiting operations of integration and summation, the transverse average solute field, the $\bar{c}$-field, where

$$\bar{c} = <c, w> = \int\int_{\underset{\sim}{A}} cw\ dxdy$$

can be gotten on termwise averaging Equations (2) and (4). Thus

$$\bar{c} = \sum_{i=0}^{\infty} \bar{c}_i \phi_i \qquad (5)$$

where

$$\bar{c}_i = (\bar{c}, \phi_i) = \overline{(c, \phi_i)} = \sum_{j=1}^{\infty} <c_i, \psi_j> \bar{\psi}_j \qquad (6)$$

For $t > 0$, the sums in Equation (6) are readily evaluated for each i. In Equation (5), however, even on placing favorable smoothness conditions on $c|_{t=0}$, the truncation error after summing n terms is $\mathcal{O}(n^{-1/2})$. Thus, Equation (5) is not of practical value in establishing $\bar{c}$.

Gill and co-workers, principally Gill and Sankarasubramanian (1971) and Sankarasubramanian and Gill (1973), produce an infinite-order differential equation for $\bar{c}$ which on truncation generates useful approximations to $\bar{c}$ and ultimately to c. Technical difficulties arise in Sankarasubramanian and Gill (1973) and limit the use of their area average bound theory. In the following we show how to circumvent these difficulties by using the method of moments. In so doing we unify the dispersion theories of chemically active and passive solutes.

We define the m^{th} dispersion approximation to $\bar{c}$, denoted $\bar{c}^{(m)}$, to be the solution of the generalized dispersion equation

$$\frac{\partial \bar{c}^{(m)}}{\partial t} = \sum_{i=0}^{m} (-1)^i\ X_i^{(m)}\ \frac{\partial^i \bar{c}^{(m)}}{\partial z^i} \qquad (7)$$

where $\bar{c}^{(m)}|_{t=0} = \bar{c}|_{t=0}$. Evidently the set $\{X_i^{(m)}\}E$ is transverse average dependent; in what follows we admit arbitrary transverse weighting functions w subject only to the conditions $0 < w(x,y) < \infty$ almost everywhere on $\underset{\sim}{A}$ and $\int_{\underset{\sim}{A}}\int w dxdy = 1$. Equation the dispersion coefficients $\{X_i^{(m)}\}$. For this purpose we construct a formal representation of $\bar{c}^{(m)}$ via its Hermite moments; namely

$$\bar{c}^{(m)} = \sum_{i=0}^{\infty} (\bar{c}^{(m)}, \phi_i) \phi_i$$

It follows from Equation (7) that the i^{th} Hermite moment of $\bar{c}^{(m)}$, $(\bar{c}^{(m)}, \phi_i)$ denoted $\bar{c}_i^{(m)}$, must satisfy
namely, $[\bar{c}^{(m)}, \phi_i]$ denoted $\bar{c}_i^{(m)}$, must satisfy

$$\frac{d}{dt}\ \bar{c}_i^{(m)} = \sum_{j=0}^{MIN(i,m)} \sqrt{\frac{2^j i!}{(i-j)!}}\ X_j^{(m)}\ \bar{c}_{i-j}^{(m)}$$

$$\bar{c}_i^{(m)}\big|_{t=0} = c_i\big|_{t=0} \qquad (8)$$

Inasmuch as

$$\{X_j^{(m)}\}_{j=0}^{m}\ \mathrm{T}\ \{\bar{c}_j^{(m)}\}_{j=0}^{m}\ \mathrm{T}\ \{\bar{c}_j^{(m)}\}_{j=0}^{\infty}$$

we define the m^{th} order dispersion approximation to the transverse average concentration field, on exacting equality of the first $m + 1$ Hermite moments of $\bar{c}^{(m)}$ and $\bar{c}$; namely, on setting

$$\bar{c}_i^{(m)} = \bar{c}_i, \qquad i = 0, \ldots, m$$

TABLE 1. FORMULAS FOR X_0, X_1 AND X_2

$$X_0 = \frac{1}{\bar{c}_0} <c_0, D\nabla_A^2 w> + \frac{1}{\bar{c}_0} \int_{\underset{\sim}{C}} c_0(Kw - D\underset{\sim}{n} \cdot \nabla_A w)ds$$

$$X_1 = \frac{\overline{vc_0}}{\bar{c}_0} + \frac{1}{\sqrt{2}\,\bar{c}_0}\left[<c_1 - c_0\frac{\bar{c}_1}{\bar{c}_0}, D\nabla_A^2 w> + \int_{\underset{\sim}{C}}\left(c_1 - c_0\frac{\bar{c}_1}{\bar{c}_0}\right)(Kw - D\underset{\sim}{n} \cdot \nabla_A w)ds\right]$$

$$X_2 = D + \frac{1}{\sqrt{2}\,\bar{c}_0}\left(\overline{vc_1} - \overline{vc_0}\frac{\bar{c}_1}{\bar{c}_0}\right)$$

$$+ \frac{1}{\sqrt{2^2 2!}\,\bar{c}_0}\left\{<c_2 - c_0\frac{\bar{c}_2}{\bar{c}_0} - \sqrt{2}\left(c_1 - c_0\frac{\bar{c}_1}{\bar{c}_0}\right)\frac{\bar{c}_1}{\bar{c}_0}, D\nabla^2{}_A w> + \int_{\underset{\sim}{C}}\left[c_2 - c_0\frac{\bar{c}_2}{\bar{c}_0} - \sqrt{2}\left(c_1 - c_0\frac{\bar{c}_1}{\bar{c}_0}\right)\frac{\bar{c}_1}{\bar{c}_0}\right](Kw - D\underset{\sim}{n} \cdot \nabla_A w)ds\right\}$$

Therefore, from Equation (8), for $i \leq m$, we deduce the defining relations for the m^{th} order dispersion coefficients:

$$X_0 \equiv X_0^{(m)} = \frac{1}{\bar{c}_o}\frac{d\bar{c}_o}{dt}$$

$$X_i \equiv X_i^{(m)} = \frac{1}{\sqrt{2^i i!}}\frac{1}{\bar{c}_0}\left[\frac{d\bar{c}_i}{dt} - \sum_{j=0}^{i-1}\sqrt{\frac{2^j i!}{(i-j)!}}\,X_j^{(m)}\,\bar{c}_{i-j}\right] \qquad (9)$$

$$i = 1, \ldots, m$$

wherein $\bar{c}_i$ and $d\bar{c}_i/dt$ follow from Equation (6). Evidently, the i^{th} dispersion coefficient evaluated in the m^{th} order dispersion approximation $X_i^{(m)}$, $i \leq m$ is identical to the i^{th} dispersion coefficient in any order equal or exceeding the i^{th}. Thus, we denote $X_i^{(m)}$, by X_i, $i = 0, \ldots, m$ and we rewrite Equation (7) as Equation (7) as

$$\frac{\partial\bar{c}^{(m)}}{\partial t} = \sum_{i=0}^{m}(-1)^i X_i \frac{\partial^i\bar{c}^{(m)}}{\partial z^i} \qquad (10)$$

where

$$\bar{c}^{(m)}|_{t=0} = \bar{c}|_{t=0}$$

It is important to observe that $\bar{c}_i = e^{K_A t}\,\bar{c}_i|_{K_A=0}$ implies that

$$X_0 = X_0|_{K_A=0} + K_A$$

$$X_i = X_i|_{K_A=0}, \qquad i = 1, 2, \ldots$$

It follows that a homogeneous chemical reaction bears solely on the determination of the coefficient X_0 and does so in the obvious way.

Now the X_i's achieve their most general representation via Equation (9). For sufficiently smooth weighting functions, we record in Table 1 the formulas for X_0, X_1 and X_2 which result on use of

$$\frac{d\bar{c}_i}{dt} = D\overline{\nabla_A^2 c_i} + \sqrt{2i}\,\overline{vc}_{i-1} + \sqrt{2i}\,\sqrt{2(i-1)}\,D\,\bar{c}_{i-2}$$

and Green's formula to eliminate $d\bar{c}_i/dt$ and $\overline{\nabla_A^2 c_i}$ from Equation (9). In Table 2, we report the important elements of the formulas in Table 1 for the product class of initial conditions; namely, $c|_{t=0} = \mathscr{g}(x,y)\,\mathscr{h}(z)$.

TABLE 2. IMPORTANT ELEMENTS OF X_0, X_1 AND X_2 IN THE PRODUCT CLASS OF INITIAL CONDITIONS

$$c_1 - c_0\frac{\bar{c}_1}{\bar{c}_0} = \sqrt{2}\,N_{pe}\left[\Sigma\Sigma(\;)_0 - \Sigma(\;)_0\frac{\Sigma\Sigma(\bar{\;})_0}{\Sigma(\bar{\;})_0}\right]$$

$$c_2 - c_0\frac{\bar{c}_2}{\bar{c}_0} - \sqrt{2}\left(c_1 - c_0\frac{\bar{c}_1}{\bar{c}_0}\right)\frac{\bar{c}_1}{\bar{c}_0}$$

$$= \sqrt{2^2 2!}\,N_{pe}^2\left\{\Sigma\Sigma\Sigma(\;)_0 - \Sigma(\;)_0\frac{\Sigma\Sigma\Sigma(\bar{\;})_0}{\Sigma(\bar{\;})_0} - \left[\Sigma\Sigma(\;)_0 - \Sigma(\;)_0\frac{\Sigma\Sigma(\bar{\;})_0}{\Sigma(\bar{\;})_0}\right]\frac{\Sigma\Sigma(\bar{\;})_0}{\Sigma(\bar{\;})_0}\right\}$$

$$\overline{vc_1} - \overline{vc_0}\frac{c_1}{\bar{c}_0} = \sqrt{2}\,N_{pe}^2\left[\overline{u\,\Sigma\Sigma(\;)_0} - \overline{u\,\Sigma(\;)_0}\frac{\Sigma\Sigma(\bar{\;})_0}{\Sigma(\bar{\;})_0}\right]$$

We observe that the dispersion coefficients depend on the initial solute field, the transverse average and the physicochemical parameters of the problem. In general, we find that X_i contains terms proportional to $N_{pe}^j\,j = 0, 1, \ldots, i$ and that the dependence of X_i on the initial solute field is not simple. However, for initial solute distributions of the product class, the terms in X_i proportional to $N_{pe}^j\,j < i$ vanish and X_i is independent of $\mathscr{h}(z)$.* Thus, for this preferred class of initial conditions, we can eliminate the N_{pe} dependence of X_i by scaling X_1 by N_{pe}, $X_2 - D$ by N_{pe}^2 and X_i by N_{pe}^i $i \geq 3$, whence we need only specify $\mathscr{g}(x,y)$, the transverse average and the chemical reactivity to determine X_i.

Graphs of X_0, X_1 and X_2 vs. t for selected initial solute distributions, transverse averages and chemical reactivity can be found in De Gance and Johns (1978*b*). The graphs indicate the features of the average concentration field $\bar{c}$ that are encoded in each of the dispersion coefficients for ready transmission to the dispersion approximation.

EXPRESSION OF $\bar{c}^{(m)}$ VIA $\bar{c}_0, \ldots, \bar{c}_m$

The Fourier transformation can be used to construct a formal solution of Equation (10). Thus, we let $F(u)$ denote the Fourier transformation of u

$$F(u) = \int_{-\infty}^{\infty} e^{i\varpi z}\,u(z)\,dz$$

and observe that

$$F(\bar{c}^{(m)}) = e^{\sum_{i=0}^{m}(-i\varpi)^i(-1)^i\int_0^t X_i(\tau)d\tau}\,F(\bar{c}|_{t=0}) \qquad (11)$$

whence $\bar{c}^{(m)}$ follows via the Fourier inversion theorem.

We conclude that integrals of the first $m + 1$ dispersion coefficients are sufficient to establish the m^{th} dispersion approximation; surprisingly, the expression of the integrals is much simpler than that of the corresponding coefficients. For instance, we find that

$$\int_0^t X_0(\tau)d\tau = \ln\bar{c}_0|_0^t$$

$$\int_0^t X_1(\tau)d\tau = \frac{1}{\sqrt{2}}\frac{\bar{c}_1}{\bar{c}_0}\Big|_0^t$$

$$\int_0^t X_2(\tau)d\tau = \frac{1}{\sqrt{2^2 2!}}\left[\frac{\bar{c}_2}{\bar{c}_0} - \frac{1}{\sqrt{2}}\left(\frac{\bar{c}_1}{\bar{c}_0}\right)^2\right]\Big|_0^t$$

$$\int_0^t X_3(\tau)d\tau = \frac{1}{\sqrt{2^3 3!}}\left[\frac{\bar{c}_3}{\bar{c}_0} - \sqrt{3}\frac{\bar{c}_1}{\bar{c}_0}\frac{\bar{c}_2}{\bar{c}_0} + \frac{1}{\sqrt{3!}}\left(\frac{\bar{c}_1}{\bar{c}_0}\right)^3\right]\Big|_0^t$$

$$\int_0^t X_4(\tau)d\tau = \frac{1}{\sqrt{2^4 4!}}\left[\frac{\bar{c}_4}{\bar{c}_0} - \sqrt{4}\frac{\bar{c}_1}{\bar{c}_0}\frac{\bar{c}_3}{\bar{c}_0} + \sqrt{\frac{4!}{2}}\left(\frac{\bar{c}_1}{0}\right)^2\frac{\bar{c}_2}{\bar{c}_0} - \sqrt{\frac{4!}{2^4}}\left(\frac{\bar{c}_2}{\bar{c}_0}\right)^2 + \sqrt{\frac{1}{4!}}\left(\frac{\bar{c}_1}{\bar{c}_0}\right)^4\right]\Big|_0^t$$

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* The simplification accorded by product class initial conditions is so great that faced with a finite sum of product class functions, we would construct an approximation by summing the dispersion approximations for each product class function even though the result would not be a dispersion approximation of the class being entertained herein.

etc. It follows that $\bar{c}^{(m)}$ can be obtained directly from $\bar{c}_i$, $i = 0, \ldots, m$. In particular, it is neither necessary to establish X_i, see Table 1, nor to perform the quadrature $\int_0^t X_i(\tau)d\tau$.

In certain instances, the inversion of Equation (11) is very simple. In particular, for $m = 2$, if the initial distribution is Gaussian,

$$\bar{c}^{(2)}\big|_{t=0} = \bar{c}\big|_{t=0} = \bar{g}\, e^{-\frac{z^2}{2\sigma^2}}$$

we find that

$$\bar{c}^{(2)} = \bar{g}\sqrt{\frac{\sigma^2}{\sigma^2 + 2\int_0^t X_2(\tau)d\tau}}\; e^{\int_0^t X_0(\tau)d\tau}\; e^{-\frac{(z - \int_0^t X_1(\tau)d\tau)^2}{2(\sigma^2 + 2\int_0^t X_2(\tau)d\tau)}}$$

where in the product class

$$e^{\int_0^t X_0(\tau)d\tau} = \frac{\Sigma\,(\bar{\ })_0}{\bar{c}_0(0)}\bigg|_t$$

$$\int_0^t X_1(\tau)d\tau = N_{pe}\,\frac{\Sigma\Sigma\,(\bar{\ })_0}{\Sigma\,(\bar{\ })_0}\bigg|_t$$

and

$$\int_0^t X_2(\tau)d\tau = Dt + N_{pe}^2\left(\frac{\Sigma\Sigma\Sigma\,(\bar{\ })_0}{\Sigma\,(\bar{\ })_0} - \frac{1}{2}\left[\frac{\Sigma\Sigma\,(\bar{\ })_0}{\Sigma\,(\bar{\ })_0}\right]^2\right)\bigg|_t$$

THE CONSTANT COEFFICIENT APPROXIMATION

The fact that the dispersion coefficients become asymptotically constant for $t \to \infty$ and the fact that all of the coefficients are virtually on their asymptote for $t > 10/(\lambda_2^2 - \lambda_1^2)$, independent of the initial solute configuration, the physicochemical parameters of the system, or the weighting function w, (see De Gance and Johns, 1978*a*,*b*), suggest the introduction of the constant coefficient approximation $\bar{c}_\infty^{(m)}$. This might be called the Taylor-Aris approximation, if $m = 2$, but we do not use that name because of its association with constant coefficient approximations in which the initial distribution is taken to be $\bar{c}|_{t=0}$, thereby precluding $\bar{c}_\infty^{(m)} \to \bar{c}^{(m)}$ for $t \to \infty$.

Thus, we define $\bar{c}_\infty^{(m)}$ via

$$\frac{\partial \bar{c}_\infty^{(m)}}{\partial t} = \sum_{i=0}^{m} (-1)^i X_{i\infty} \frac{\partial^i \bar{c}_\infty^{(m)}}{\partial z^i} \tag{12}$$

and

$$\bar{c}_\infty^{(m)} \to \bar{c}^{(m)} \qquad \text{as } t \to \infty$$

where the coefficients $X_{i\infty}$ denote the long time limiting values of $X_i(t)$, and where we find that

$$X_{0\infty} = -\lambda_1^2$$

$$X_{1\infty} = N_{pe}\langle u\psi_1, \psi_1\rangle$$

$$X_{2\infty} = D + N_{pe}^2 \sum_{j=2}^{\infty} \frac{\langle u\psi_j, \psi_1\rangle^2}{\lambda_j^2 - \lambda_1^2}$$

$$x_{3\infty} = N_{pe}^3 \sum_{m=2}^{\infty} \frac{\langle u\psi_1, \psi_m\rangle^2}{(\lambda_m^2 - \lambda_1^2)^2}(\langle u\psi_m, \psi_m\rangle - \langle u\psi_1, \psi_1\rangle) + N_{pe}^3 \sum_{m=2}^{\infty} \sum_{\substack{n=2 \\ \neq m}}^{\infty} \frac{\langle u\psi_1, \psi_m\rangle\langle u\psi_m, \psi_n\rangle\langle u\psi_n, \psi_1\rangle}{(\lambda_m^2 - \lambda_1^2)(\lambda_n^2 - \lambda_1^2)}$$

etc.

It is worth observing that the asymptotic dispersion coefficients, unlike their finite time antecedents, depend neither on the transverse average used in their construction nor on the solute distribution throughout the cylinder initiating the dispersion process. Such factors can influence $\bar{c}_\infty^{(m)}$ only via the initial condition that must be imposed upon $\bar{c}_\infty^{(m)}$ to certify its faithfulness to $\bar{c}^{(m)}$ for $t \to \infty$.

The Fourier transformation can be used to establish a formal expression for $\bar{c}_\infty^{(m)}$. In particular Equation (12) implies that

$$F(\bar{c}_\infty^{(m)}) = e^{\sum_{i=0}^{m} (-i\varpi)^i (-1)^i X_{i\infty} t}\, F(\bar{c}_\infty^{(m)}|_{t=0}) \tag{13}$$

whence $\bar{c}_\infty^{(m)}|_{t=0}$ follows from the Fourier inversion theorem upon identification of $\bar{c}_\infty^{(m)}|_{t=0}$. We define $\bar{c}_\infty^{(m)}|_{t=0}$ via

$$\lim_{t\to\infty} \frac{F(\bar{c}^{(m)})}{F(\bar{c}_\infty^{(m)})} = 1 \qquad \forall\, \varpi$$

which implies that $\bar{c}_i^{(m)} - \bar{c}_{i\infty}^{(m)} = \mathcal{O}(e^{-\lambda_2^2 t})$, whence $\bar{c}_\infty^{(m)}$ virtually coincides with $\bar{c}^{(m)}$ for $t > 10/(\lambda_2^2 - \lambda_1^2)$.

We introduce Δ_i via

$$\Delta_i \equiv \int_0^t (-1)^i (X_i(\tau) - X_{i\infty})d\tau = (-1)^i\left(\int_0^t X_i(\tau)d\tau - X_{i\infty}t\right)$$

and observe that $\lim_{t\to\infty} \Delta_i \equiv \Delta_{i\infty} < \infty$ inasmuch as $X_i(t) - X_{i\infty} = \mathcal{O}(t^i e^{-(\lambda_2^2 - \lambda_1^2)t})$ (see De Gance and Johns, 1978*a*). It follows that

$$\frac{F(\bar{c}^{(m)})}{F(\bar{c}_\infty^{(m)})} = \left[e^{\sum_{i=0}^{m} (-i\varpi)^i \Delta_i}\right] \frac{F(\bar{c}|_{t=0})}{F(\bar{c}_\infty^{(m)}|_{t=0})}$$

and hence, from Equations (11) and (13), that

$$F(\bar{c}_\infty^{(m)}|_{t=0}) = e^{\sum_{i=0}^{m} (-i\varpi)^i \Delta_{i\infty}}\, F(\bar{c}|_{t=0})$$

Thus we may deduce $\bar{c}_\infty^{(m)}|_{t=0}$ from the Fourier inversion theorem.

In particular, for $m = 2$, if the initial distribution is Gaussian,

$$\bar{c}|_{t=0} = \bar{g}\, e^{-\frac{z^2}{2\sigma^2}}$$

we find that

$$\bar{c}_\infty^{(2)}|_{t=0} = \bar{g}\sqrt{\frac{\sigma^2}{\sigma^2 + 2\Delta_{2\infty}}}\; e^{\Delta_{0\infty}}\; e^{-\frac{(z + \Delta_{1\infty})^2}{2(\sigma^2 + 2\Delta_{2\infty})}}$$

whence

$$\bar{c}_\infty^{(2)} = \bar{g}\sqrt{\frac{\sigma^2}{\sigma^2 + 2\Delta_{2\infty} + 2X_{2\infty}t}}\; e^{\Delta_{0\infty} + X_{0\infty}t}\; e^{-\frac{(z + \Delta_{1\infty} - X_{1\infty}t)^2}{2(\sigma^2 + 2\Delta_{2\infty} + 2X_{2\infty}t)}}$$

and it remains only to establish $\Delta_{i\infty}$, $i = 0,1,2$. We remark that $\Delta_{2\infty}$ is not singly signed, though $\int_0^t X_2 d\tau > 0$, $t > 0$ (see De Gance and Johns 1978*a*), and that in the likely event $\Delta_{2\infty} < 0$, the constant coefficient approximation may be undefined for $t \to 0$.

The line of argument establishing the $\Delta_{i\infty}$ is indicated in the appendix. We list only formulas sufficient for the predictions, namely

$$\Delta_{0\infty} = \ln \langle c_0|_{t=0}, \psi_1\rangle \frac{\bar{\psi}_1}{\bar{c}_0(0)}$$

$$\Delta_{1\infty} = -\sum_{j=2}^{\infty} \frac{1}{\lambda_j^2 - \lambda_1^2}\langle v\psi_j, \psi_1\rangle\left(\frac{\langle c_0|_{t=0}, \psi_j\rangle}{\langle c_0|_{t=0}, \psi_1\rangle} + \frac{\bar{\psi}_j}{\bar{\psi}_1}\right)$$

and

$$\Delta_{2\infty} = -\sum_{j=2}^{\infty} \frac{1}{(\lambda_j^2 - \lambda_1^2)^2}\langle v\psi_j, \psi_1\rangle^2 - \frac{1}{2}\left(\sum_{j=2}^{\infty} \frac{1}{\lambda_j^2 - \lambda_1^2}\langle v\psi_j, \psi_1\rangle \frac{\langle c_0|_{t=0}, \psi_j\rangle}{\langle c_0|_{t=0}, \psi_1\rangle}\right)^2 - \frac{1}{2}\left(\sum_{j=2}^{\infty} \frac{1}{\lambda_j^2 - \lambda_1^2}\langle v\psi_j, \psi_1\rangle \frac{\bar{\psi}_j}{\bar{\psi}_1}\right)^2$$

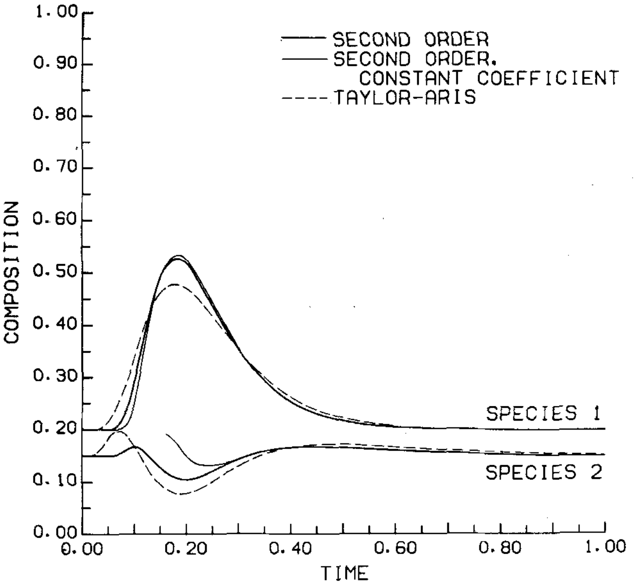

Figure 1. Diffusive dispersion: area average approximations at z = 50.

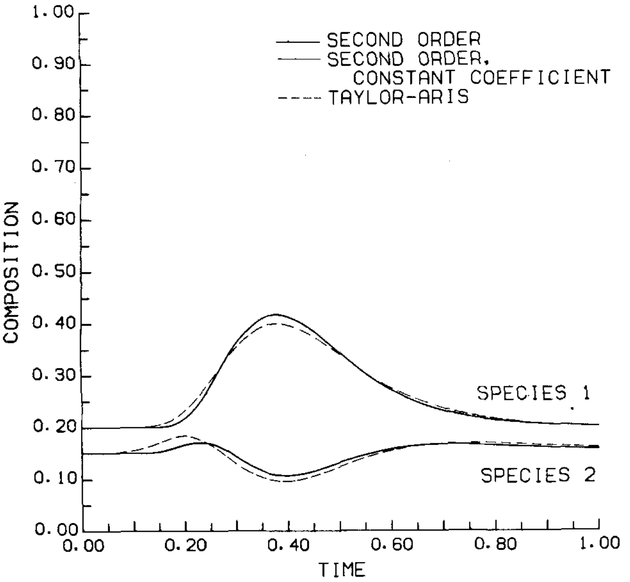

Figure 2. Diffusive dispersion: area average approximations at z = 100.

$$+ \sum_{j=2}^{\infty} \sum_{\substack{k=2\\ \neq j}}^{\infty} \frac{<v\psi_k, \psi_j><v\psi_j, \psi_1>}{(\lambda_k^2 - \lambda_1^2)(\lambda_j{}^2 - \lambda_1^2)} \left(\frac{<c_0|_{t=0}, \psi_k>}{<c_0|_{t=0}, \psi_1>} + \frac{\overline{\psi}_k}{\overline{\psi}_1} \right)$$

$$+ \sum_{j=2}^{\infty} \frac{<v\psi_j, \psi_1>}{(\lambda_j{}^2 - \lambda_1^2)^2} (<v\psi_j, \psi_j> - <v\psi_1, \psi_1>) \times$$

$$\left(\frac{<c_0|_{t=0}, \psi_j>}{<c_0|_{t=0}, \psi_1>} + \frac{\overline{\psi}_j}{\overline{\psi}_1} \right)$$

where $v = N_{pe}u$ and where the expressions for $\Delta_{1\infty}$ and $\Delta_{2\infty}$ are complete only for product class initial conditions. It is important to observe that the $\Delta_{i\infty}$'s depend on the initial solute configuration via $c_0|_{t=0}$ and on the transverse average being entertained via $\bar{\ }$; evidently, that dependence is transmitted to $\bar{c}_\infty^{(m)}|_{t=0}$.

RESULTS

Here, we consider dispersion approximations to the transverse average of the solution of the vector convective diffusion equation, namely, to $\underset{\sim}{c}$, where

$$\frac{\partial \underset{\sim}{c}}{\partial t} = \underset{\sim}{D}\nabla_A^2 \underset{\sim}{c} - N_{pe}u \frac{\partial \underset{\sim}{c}}{\partial z} + \underset{\sim}{D} \frac{\partial^2 \underset{\sim}{c}}{\partial z^2} + \underset{\sim}{K}_A(\underset{\sim}{c} - \underset{\sim}{c}_*)$$

TABLE 3. VALUES OF THE PARAMETERS USED IN FIGURES 1 AND 2

Diffusion coefficients

$D_{11} = 1.0$, $D_{12} = 0.0$

$D_{21} = -0.5$, $D_{22} = 0.5$

Initial state		Rest state
$\underset{\sim}{c}\|_{t=0} - \underset{\sim}{c}_* = \begin{bmatrix} 0.65 \\ 0.0 \end{bmatrix}$	$\|z\| \leq ½Z$	$\underset{\sim}{c}_* = \begin{bmatrix} 0.20 \\ 0.15 \end{bmatrix}$
Pencil length, Z = 25		Peclet number, $N_{pe} = 500$

$$t > 0,\ (x,y) \in \underset{\sim}{A} \qquad (14)$$

$$- \underset{\sim}{D}\underset{\sim}{n} \cdot \nabla_A \underset{\sim}{c} + \underset{\sim}{K}(\underset{\sim}{c} - \underset{\sim}{c}_*) = 0$$

$$t > 0,\ (x,y) \in \underset{\sim}{C}$$

In what follows, we illustrate the scalar theory in the context of vector problems which satisfy conditions sufficient for their reduction to scalar problems. Thus, we consider the purely diffusive dispersion of two solutes in a solvent and the dispersion of a system of chemically active isomers. In each instance, we avoid the fully general coupling implied via fully general $\underset{\sim}{D}$, $\underset{\sim}{K}_A$ and $\underset{\sim}{K}$.

In the case of purely diffusive dispersion, Equation (14) implies the set of scalar equations in the j^{th} pseudo species concentration $(\underset{\sim}{g}_j^+\underset{\sim}{c})$

$$\frac{\partial}{\partial t} (\underset{\sim}{g}_j^+\underset{\sim}{c}) = D_j\nabla_A^2(\underset{\sim}{g}_j^+\underset{\sim}{c}) - N_{pe}u \frac{\partial}{\partial z} (\underset{\sim}{g}_j^+\underset{\sim}{c}) + D_j \frac{\partial^2}{\partial z^2} (\underset{\sim}{g}_j^+\underset{\sim}{c})$$

$$t > 0,\ (x,y) \in \underset{\sim}{A}$$

$$D_j\underset{\sim}{n} \cdot \nabla_A(\underset{\sim}{g}_j^+\underset{\sim}{c}) = 0 \qquad t > 0,\ (x,y) \in \underset{\sim}{C}$$

where $\{D_j\}$, $\{f_j\}$ and $\{g_j\}$ are corresponding eigenvalues and right and left eigenvectors of $\underset{\sim}{D}$, where $\underset{\sim}{c} = \sum_j (\underset{\sim}{g}_j^+\underset{\sim}{c})\underset{\sim}{f}_j$ and where $\underset{\sim}{g}_i^+\underset{\sim}{f}_j = \delta_{ij}$. Evidently, the m^{th} dispersion approximation, $\overline{\underset{\sim}{g}_j^+\underset{\sim}{c}}^{(m)}$, to $\overline{\underset{\sim}{g}_j^+\underset{\sim}{c}}$ can be constructed by scalar means and then assembled via

$$\bar{\underset{\sim}{c}}^{(m)} = \sum_j \overline{\underset{\sim}{g}_j^+\underset{\sim}{c}}^{(m)} \underset{\sim}{f}_j$$

to produce the m^{th} dispersion approximation $\bar{\underset{\sim}{c}}^{(m)}$ to $\bar{\underset{\sim}{c}}$.

The dispersion coefficients X_{ij} corresponding to the j^{th} pseudo species follow from the scalar formulas for X_i on setting $D = D_j$ and $K = 0$, whence $\bar{\underset{\sim}{c}}^{(m)}$ satisfies

$$\frac{\partial \bar{\underset{\sim}{c}}^{(m)}}{\partial t} = \sum_i^m (-1)^i \underset{\sim}{X}_i \frac{\partial^i \bar{\underset{\sim}{c}}^{(m)}}{\partial z^i}$$

where

$$\underset{\sim}{X}_i = \sum_j X_{ij} \underset{\sim}{f}_j\underset{\sim}{g}_j^+$$

In the area average, which is preferred in the dispersion of chemically inactive solute, we find that $\underset{\sim}{X}_0$ vanishes and that for $t \to \infty$, $\underset{\sim}{X}_1$ is spherical. However, $\underset{\sim}{X}_1$ need not be spherical for all time; in particular, we can exercise essentially unlimited control over the pseudo species velocities for short time through the initial solute configuration, the specification of which is our prerogative.

The diffusive coupling is manifested solely in $\underset{\sim}{X}_2$, where for $t \to \infty$

$$\underset{\sim}{X}_{2\infty} - \underset{\sim}{D} \propto N_{pe}^2\, \underset{\sim}{D}^{-1}$$

Evidently, the implications of the diffusive coupling depend strongly on the value of N_{pe}. For instance, if $\underset{\sim}{D}$ is essentially triangular, then

$$\underset{\sim}{X}_{2\infty} = \begin{bmatrix} a_{11} & 0 \\ a_{21} & a_{22} \end{bmatrix}$$

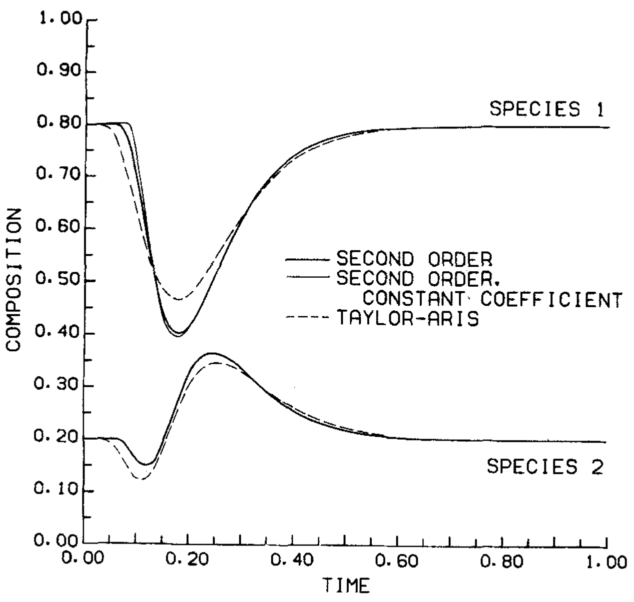

Figure 3. Reactive dispersion: area average approximations at $z = 50$.

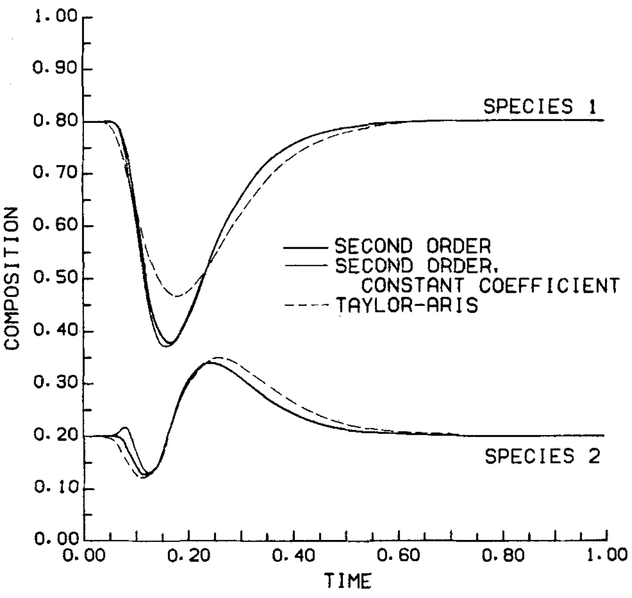

Figure 4. Reactive dispersion: flow average approximations at $z = 50$.

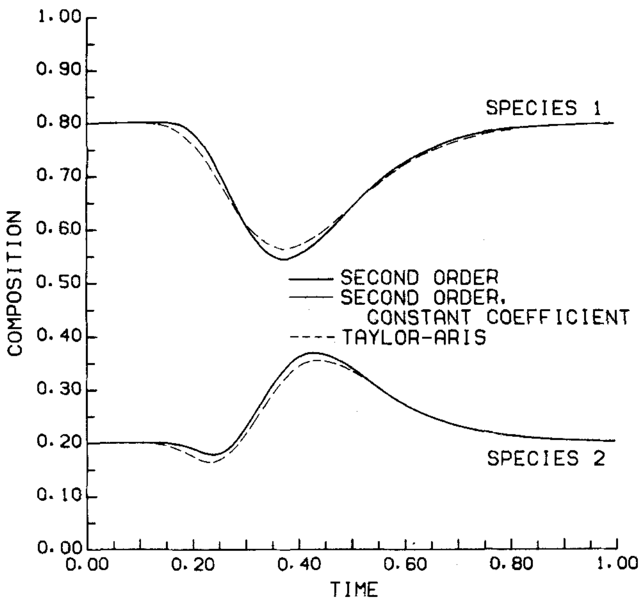

Figure 5. Reactive dispersion: area average approximations at $z = 100$.

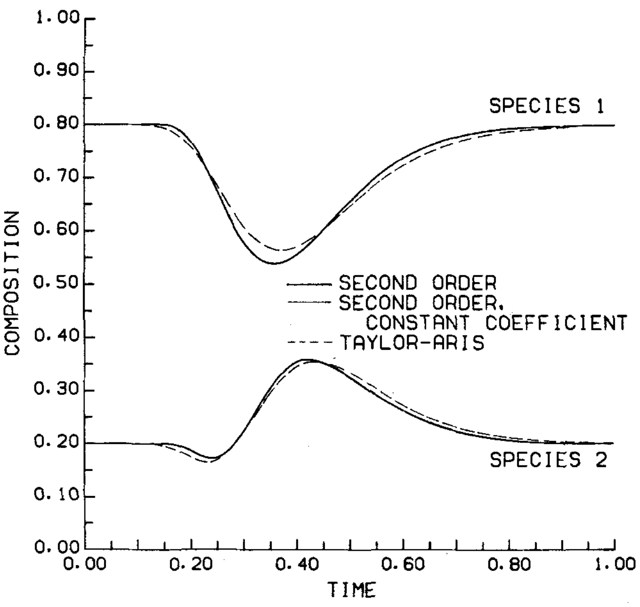

Figure 6. Reactive dispersion: flow average approximations at $z = 100$.

TABLE 4. VALUES OF THE PARAMETERS USED IN FIGURES 3, 4, 5 AND 6

Diffusion coefficients	Rate constants*
$D_{11} = 1.0, \quad D_{12} = 0.0$	$k_{12} = 0.08, \; k_{13} = 0.0, \; k_{21} = 0.02$
$D_{21} = 0.0, \quad D_{22} = 1.0$	$k_{23} = 2.0, \; k_{31} = 0.0, \; k_{32} = 0.0$
Initial state	Equilibrium state
$\underset{\sim}{y}\vert_{t=0} = \underset{\sim}{c}\vert_{t=0} - \underset{\sim}{c}_* = \begin{bmatrix} -0.8 \\ -0.2 \end{bmatrix}$	$\underset{\sim}{c}_* = \begin{bmatrix} 0.8 \\ 0.2 \end{bmatrix}$
$\vert z \vert \leq ½Z$	
Pencil length, $Z = 25$	Peclet number, $N_{pe} = 500$

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* where k_{ij} is the rate constant for the step $j \to i$.

where $a_{11} > 0$, $a_{22} > 0$, but a_{21} is not singly signed; in particular, if $a_{21} > 0$ for $N_{pe} \to 0$, then $a_{21} < 0$ for $N_{pe} \to \infty$. Thus, depending on whether the longitudinal spreading is dictated by axial diffusion ($N_{pe} \to 0$) or convective diffusion ($N_{pe} \to \infty$), the interaction either strengthens or weakens the natural spreading tendency of a solute pulse. In particular, the variance of the distribution of species 1 grows according to $2a_{11}$, whereas that of species 2 grows according to $2a_{21}r + 2a_{22}$, where r is the ratio of the species 1 to species 2 content of the cylinder. Hence, under conditions that are not exception, an initially unimodal species pulse need not remain unimodal.

In Figures 1 and 2, we illustrate the phenomenon of diffusive splitting. The parameters used are recorded in Table 3. The initial solute displacement is uniform on $\underset{\sim}{A}$ and constant for $z \epsilon [-1/2\,Z, 1/2\,Z]$, zero otherwise, whence $\underset{\sim}{X}_1 = \bar{v}\underset{\sim}{I}$. Here, then, the initially unimodal species two pulse splits solely because of the 2-1 diffusive interaction. We observe that in diffusive splitting the species pulse develops a characteristically wigwag shape inasmuch as the pseudo species pulses spread at differing rates.

The use of the scalar theory to make predictions for the dispersion of a set of chemically active isomers does not differ essentially from its use in purely diffusive dispersion outlined above. Here we let $\underset{\sim}{D}$ be spherical, that is, $\underset{\sim}{D} = D\,\underset{\sim}{I}$, which eliminates physical interactions and implies the restriction to chemical isomers, and we let $\underset{\sim}{K}_A = \underset{\sim}{0}$ but let $\underset{\sim}{K}$ remain general, $\underset{\sim}{K}$ being descriptive of a complex unimolecular rearrangement promoted via a catalyst deposited on the inside surface of the cylinder. In particular, we let $\underset{\sim}{y} = \underset{\sim}{c} - \underset{\sim}{c}_*$ be the displacement of the local state from an agreed upon chemical equilibrium state and find that Equation (14) implies the set of the scalar equations in the j^{th} pseudo species displacement $(\underline{g}_j^{+}\underline{y})$:

$$\frac{\partial}{\partial t}(\underline{g}_j^{+}\underline{y}) = D\,\nabla_A^2(\underline{g}_j^{+}\underline{y}) - N_{pe}u\,\frac{\partial}{\partial z}(\underline{g}_j^{+}\underline{y}) + D\,\frac{\partial^2}{\partial z^2}(\underline{g}_j^{+}\underline{y}) \qquad t > 0,\ (x,y) \in \underline{A}$$

and

$$-D\underline{n}\cdot\nabla_A(\underline{g}_j^{+}\underline{y}) + K_j(\underline{g}_j^{+}\underline{y}) = 0, \qquad t > 0,\ (x,y) \in \underline{C}$$

where $\{K_j\}$, $\{\underline{f}_j\}$ and $\{\underline{g}_j\}$ are corresponding eigenvalues and right and left eigenvectors of $\underline{K}$.

Here the dispersion coefficients X_{ij}, corresponding to the j^{th} pseudo species, follow from the scalar formulas on setting $K = K_j$; the corresponding $\underline{X}_i$ follow via

$$\underline{X}_i = \sum_j X_{ij}\,\underline{f}_j\underline{g}_j^{+}$$

Of interest is the fact that the pseudo species translational velocity $X_{1\infty j}$ is dependent on the pseudo species chemical reactivity being higher the higher the reactivity (see DeGance and Johns, (1978*b*), wherein the physical basis of this and other results is explained.) It follows that $\underline{X}_{1\infty}$, and certainly therefore $\underline{X}_1$, is not diagonal; that is, an effective species velocity cannot be identified. Hence, an initially unimodal species pulse need not remain unimodal. In particular, because such a pulse is a linear combination of unimodal pseudo species pulses, which ultimately propagate at different speeds, a lapse of time is sufficient for splitting. Now a large pseudo species chemical reactivity difference favors splitting; yet it implies a rapid disappearance of the highly reactive pseudo species. Nonetheless, the reactive splitting can be seen in the corresponding figures.

In Figures 3 to 6 we illustrate the predictions of our theory for the dispersion of three chemically active isomers in a circular cylinder. Figures 3 and 5 vis-à-vis Figures 4 and 6 afford a comparison of the area and the flow average concentrations. The parameters selected area not exceptional (see Table 4), and the initial distributions have little or no embellishment; namely, each $\underline{g}_j^{+}\underline{y}|_{t=0}$ is uniform on $\underline{A}$ and constant for $z \in [-1/2Z, 1/2Z]$, zero otherwise. Here it is the differing translational speeds of the pseudo species and not their differing dispersion coefficients which cause the splitting of the pulses.

In each figure we also record predictions of the constant coefficient approximation and the Taylor-Aris approximation. The constant coefficient approximation $\underline{\bar{c}}_\infty^{(2)}$, where $\underline{\bar{c}}_\infty^{(2)} \to \underline{\bar{c}}^{(2)}$ as t grows large, is accurate for $t > \epsilon > 0$; in particular, the graphs of $c_\infty^{(2)}$ and $\underline{c}^{(2)}$ in Figures 2, 5, and 6 are indistinguishable and in Figures 1, 3, and 4 only differ at the shortest times. For $\epsilon > t > 0$, the constant coefficient approximation need not be accurate and *in fact can be undefined if some* $\Delta_{2j\infty} < 0$; *we illustrate just* such an instance in Figure 1, wherein the species two concentration is not graphed for $t \to 0$.

The Taylor-Aris approximation differs from $\underline{\bar{c}}_\infty^{(2)}$ only because $\underline{\bar{c}}_\infty^{(2)}|_{t=0} \neq \underline{\bar{c}}|_{t=0}$, that is because $\Delta_{ij\infty} \neq 0$. In the product class of initial conditions, for a fixed pseudo species, the predictions of *the Taylor-Aris approximation in the various transverse averages* are constant multiples of one another. In particular, the multiplicative factor for transforming area average predictions into flow average predictions is the ratio of $<\underline{g},w_f>$ to $<\underline{g},w_a>$, where w_f and w_a are, respectively, the flow and area weighting functions. Thus, insofar as we report predictions only for initial concentrations uniform on $\underline{A}$, the predictions of the Taylor-Aris approximation in the area and flow averages coincide.

COMMENTS

We emphasize that $\bar{c}$ is nowhere in evidence and that we confine what we report to $\bar{c}^{(2)}$, where $\bar{c}^{(2)}|_{t=0} = \bar{c}|_{t=0}$, and approximations thereto. We observe that $\bar{c}^{(2)}$ and $\bar{c}$ agree only through their first three Hermite moments; we speculate that $\bar{c}_i^{(2)}$ is a long time asymptote of $\bar{c}_i$, $i = 3,4,\ldots$, which suggests

$$\bar{c} = \sum_{i=0}^{\infty} \bar{c}_i\phi_i \sim \sum_{i=0}^{\infty} \bar{c}_i^{(2)}\phi_i = \bar{c}^{(2)}$$

It is fair to say that dispersion theory provides a vehicle by which the slowly converging sum can be readily estimated.

Evidently the foregoing extends the material reported in Gill and Sankarasubramanian (1971) to chemically active systems, to non-area averages and to systems in which physical or chemical interactions must be resolved. The incentive for carrying on the work to systems where simplifying conditions on $\underline{D}$ and/or $\underline{K}$ are not in force, but where the dispersion coefficients can be gotten, is dampened by the prospect of constructing the formal solution of

$$\frac{\partial\underline{\bar{c}}^{(m)}}{\partial t} = \sum_{i=0}^{m}(-1)^i\,\underline{X}_i\,\frac{\partial^i\underline{\bar{c}}^{(m)}}{\partial z^i}$$

even if $m = 2$. The prospects are not substantially brightened if $\underline{X}_i$ is replaced by $\underline{X}_{i\infty}$.

NOTATION

$\underline{A}$ = cross section of the cylinder
$\underline{C}$ = boundary of $\underline{A}$
(x,y) = transverse coordinates
z = axial coordinate
$(\cdot,\cdot)$ = $\int^{\infty} \cdot\cdot\, e^{z^2}dz$
$<\cdot,\cdot>$ = $\int\int_{\underline{A}}^{-\infty} \cdot\cdot\, dxdy$
$\bar{\cdot}$ = $\int\int_{\underline{A}} \cdot\, wdxdy$
w = transverse weighting function
$\{\psi_i\}$ = eigenfunctions of $D\nabla_A^2$
$\{-\lambda_i^2\}$ = eigenvalues of $D\nabla_A^2$
N_{pe} = Peclet number, $v_{\max}/LT^{-1}$

APPENDIX: DETERMINATION OF $\Delta_{i\infty}$

We establish expressions for $\Delta_{i\infty} \equiv \lim_{t\to\infty} \Delta_i$, $i = 0,1,2$ where

$$\Delta_i(t) \equiv (-1)^i \int_0^t (X_i(\tau) - X_{i\infty})d\tau$$

$$= (-1)^i\left(\int_0^t X_i(\tau)d\tau - X_{i\infty}t\right)$$

The results provide the basis for the determination of $\bar{c}_\infty^{(2)}|_{t=0}$.

Evidently, Δ_0 can be expressed via

$$\Delta_0(t) = \ln \bar{c}_0(t) - \ln \bar{c}_0(0) + \lambda_1^2 t$$

Thus inasmuch as

$$\ln \bar{c}_0(t) = \ln e^{-\lambda_1^2 t} <c_0|_{t=0},\psi_1>\bar{\psi}_1 \left(1 + \sum_{i=2}^{\infty}(\,)_0 \Big/ \sum_{i=1}^{1}(\,)_0\right)$$

$$= -\lambda_1^2 t + \ln <c_0|_{t=0},\psi_1>\bar{\psi}_1 + \ln\left(1 + \sum_{i=2}^{\infty}(\,)_0 \Big/ \sum_{i=1}^{1}(\,)_0\right)$$

and $\sum_{i=2}^{\infty}(\,)_0/\sum_{i=1}^{1}(\,)_0$ vanishes exponentially as $t \to \infty$, it follows that

$$\lim_{t\to\infty} \Delta_0(t) = \ln <c_0|_{t=0},\psi_1>\bar{\psi}_1 - \ln \bar{c}_0(0)$$

Therefore

$$\Delta_{0\infty} = \ln \frac{<c_0|_{t=0},\psi_1><\psi_1,w>}{<c_0|_{t=0},w>}$$

Now $\bar{c}_1/\bar{c}_0$ can be expressed via

$$\frac{\bar{c}_1}{\bar{c}_0} = \bar{c}_1 \Big/ \sum_{i=1}^{1}(\,)_0 - \frac{\bar{c}_1 \sum_{i=2}^{\infty}(\,)_0 \Big/ \sum_{i=1}^{1}(\,)_0}{1 + \sum_{i=2}^{\infty}(\,)_0 \Big/ \sum_{i=1}^{1}(\,)_0}$$

where the second term on the right-hand side vanishes exponentially as $t \to \infty$. Furthermore

$$\lim_{t\to\infty}\left(\bar{c}_1\Big/\sum_{i=1}^{1}(^-)_0-\sqrt{2}\,X_{1\infty}t\right)=\lim_{t\to\infty}\frac{\sum\limits_{i=1}^{1}(^-)_1+\sqrt{2}\left(\sum\limits_{i=1}^{1}\sum\limits_{j=2}^{\infty}(^-)_0+\sum\limits_{i=2}^{\infty}\sum\limits_{j=1}^{1}(^-)_0\right)}{\sum\limits_{i=0}^{1}(^-)_0}$$

inasmuch as $\sum_{i=2}^{\infty}(^-)_1/\sum_{i=1}^{1}(^-)_0$ and $\sum_{i=2}^{\infty}\sum_{j=2}^{\infty}(^-)_0/\sum_{i=1}^{1}(^-)_0$ vanish exponentially as $t\to\infty$ and $\sum_{i=1}^{1}\sum_{j=1}^{1}(^-)_0/\sum_{i=1}^{1}(^-)_0=X_{1\infty}t$. It follows, therefore, that

$$\Delta_{1\infty}=\sum_{i=2}^{\infty}\frac{1}{\lambda_i^2-\lambda_1^2}\langle v\psi_1,\psi_i\rangle\left(\frac{\langle c_0|_{t=0},\psi_i\rangle}{\langle c_0|_{t=0},\psi_1\rangle}+\frac{\langle w,\psi_i\rangle}{\langle w,\psi_1\rangle}\right)+\frac{1}{\sqrt{2}}\left\{\frac{\langle c_1|_{t=0},\psi_1\rangle}{\langle c_0|_{t=0},\psi_1\rangle}-\frac{\langle c_1|_{t=0},w\rangle}{\langle c_0|_{t=0},w\rangle}\right\}$$

where $v=N_{pe}u$ and where in the product class of initial conditions the bracketed term vanishes.

The analysis for $\Delta_{2\infty}$ follows along established lines but is considerably longer. Hence we report only the result; we find that

$$\begin{aligned}\Delta_{2\infty}=&-\sum_{j=2}^{\infty}\frac{1}{(\lambda_j^2-\lambda_1^2)^2}\langle v\psi_j,\psi_1\rangle^2\\&-\frac{1}{2}\left(\sum_{j=2}^{\infty}\frac{1}{\lambda_j^2-\lambda_1^2}\langle v\psi_j,\psi_1\rangle\frac{\langle c_0|_{t=0},\psi_j\rangle}{\langle c_0|_{t=0},\psi_1\rangle}\right)^2\\&-\frac{1}{2}\left(\sum_{j=2}^{\infty}\frac{1}{\lambda_j^2-\lambda_1^2}\langle v\psi_j,\psi_1\rangle\frac{\langle w,\psi_j\rangle}{\langle w,\psi_1\rangle}\right)^2\\&+\sum_{j=2}^{\infty}\sum_{\substack{k=2\\ \neq j}}^{\infty}\frac{\langle v\psi_k,\psi_j\rangle\langle v\psi_j,\psi_1\rangle}{(\lambda_k^2-\lambda_1^2)(\lambda_j^2-\lambda_1^2)}\left(\frac{\langle c_0|_{t=0},\psi_k\rangle}{\langle c_0|_{t=0},\psi_1\rangle}+\frac{\langle w,\psi_k\rangle}{\langle w,\psi_1\rangle}\right)\\&+\sum_{j=2}^{\infty}\frac{\langle v\psi_j,\psi_1\rangle}{(\lambda_j^2-\lambda_1^2)^2}(\langle v\psi_j,\psi_j\rangle-\langle v\psi_1,\psi_1\rangle)\times\\&\qquad\left(\frac{\langle c_0|_{t=0},\psi_j\rangle}{\langle c_0|_{t=0},\psi_1\rangle}+\frac{\langle w,\psi_j\rangle}{\langle w,\psi_1\rangle}\right)\\&+\left\{\frac{1}{2\sqrt{2}}\left(\left(\frac{\langle c_2|_{t=0},\psi_1\rangle}{\langle c_0|_{t=0},\psi_1\rangle}-\frac{1}{\sqrt{2}}\left(\frac{\langle c_1|_{t=0},\psi_1\rangle}{\langle c_0|_{t=0},\psi_1\rangle}\right)^2\right)\right.\right.\\&\qquad\left.-\left(\frac{\langle c_2|_{t=0},w\rangle}{\langle c_0|_{t=0},w\rangle}-\frac{1}{\sqrt{2}}\left(\frac{\langle c_1|_{t=0},w\rangle}{\langle c_0|_{t=0},w\rangle}\right)^2\right)\right)\\&\qquad+\frac{1}{\sqrt{2}}\sum_{j=2}^{\infty}\frac{1}{\lambda_j^2-\lambda_1^2}\langle v\psi_j,\psi_1\rangle\times\\&\qquad\left.\left(\frac{\langle c_1|_{t=0},\psi_j\rangle}{\langle c_0|_{t=0},\psi_1\rangle}-\frac{\langle c_0|_{t=0},\psi_j\rangle}{\langle c_0|_{t=0},\psi_1\rangle}\frac{\langle c_1|_{t=0},\psi_1\rangle}{\langle c_0|_{t=0},\psi_1\rangle}\right)\right\}\end{aligned}$$

where $v=N_{pe}u$ and where in the product class of initial conditions the bracketed term vanishes.

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Stochastic Simulation of the Motion, Breakup and Stranding of Oil Ganglia in Water-Wet Granular Porous Media During Immiscible Displacement

The problem of immiscible displacement of oil ganglia arises in connection with oil bank formation and attrition during enhanced oil recovery with flooding. A stochastic simulation method is developed here, which enables prediction of the fate of solitary ganglia during immiscible displacement in water-wet unconsolidated granular porous media. This method takes into account the local topology of the porous medium; the initial size, shape and orientation of the oil ganglion and the capillary number. For each ganglion size, hundreds of realizations are performed with random ganglion shapes for a 100 × 200 sandpack. These results are averaged to obtain probabilities of mobilization, breakup and stranding as functions of capillary number and ganglion size. Axial and lateral dispersion coefficients are obtained as functions of the average ganglion velocity. The results from the solitary ganglion analysis can be used with the ganglion population balance equations developed in a companion publication (Payatakes, Ng and Flumerfelt, 1980) to study the dynamics of oil bank formation.

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SCOPE

At the end of secondary oil recovery processes, 40 to 70% of the original amount of oil remains in the reservoir. Usually, this residual oil is dispersed throughout the porous rock in the form of small oil ganglia (nodular blobs) each of which occupies one to, say, fifteen adjoining chambers of the porous medium. The rest of the porous space is taken by brine (formation

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