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J. F. G. Reis[a]; E. N. Lightfoot[a]; P. T. Noble[a]; A. S. Chiang[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

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Chromatography in a Bed of Spheres

J. F. G. REIS, E. N. LIGHTFOOT, P. T. NOBLE,
and A. S. CHIANG

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN 53706

Abstract

A computationally efficient method is presented for calculating the combined effects of intraparticle diffusion, interphase mass-transfer resistance, and fluid-phase axial dispersion for chromatography in a column of uniform regularly packed spheres. The method uses an extension of the generalized Sturm-Liouville theory of Ramkrishna and Amundson to adapt the Taylor-Gill-Subramanian dispersion analysis to two-phase systems. The primary utility of the analysis is to determine the importance of diffusional transients and to obtain asymptotic limiting behavior for very long columns. Simple closed-form solutions are given for this limiting condition. Our analysis suggests that the transients neglected in presently used lumped-parameter analyses are in fact often small, especially for small packing diameter and low flow rates. In addition, the Glueckauf and Coates approximation for internal diffusional resistance is found to be a valid asymptotic limit. However, conditions do arise in practice where transients should be considered.

INTRODUCTION

It is the objective of this development to estimate the combined effects of intraparticle diffusion, fluid-phase boundary-layer mass-transfer resistance, and axial dispersion in a chromatographic column. To do this we idealize the column as a regular array of uniform homogeneous spheres and assume the mass transfer to be described by

$$\varepsilon\left(\frac{\partial c_f}{\partial t} + v_0\frac{\partial c_f}{\partial z} - \mathscr{E}\frac{\partial^2 c_f}{\partial z^2}\right) = (k_c a)(\alpha c_{SR} - c_f) \tag{1}$$

$$(1 - \varepsilon)\left(\frac{\partial c_{S_m}}{\partial t}\right) = -(k_c a)(\alpha c_{SR} - c_f) \tag{2}$$

$$\partial c_S/\partial t = \frac{\mathscr{D}_S}{r^2}\frac{\partial}{\partial r}r^2\,\partial c_S/\partial r \tag{3}$$

with

$$-\mathscr{D}_S\frac{\partial c_S}{\partial r}\bigg|_{r=R} = k_c(\alpha c_{SR} - c_f) \tag{4}$$

where z = distance of any sphere center from column entrance
r = distance from center of any sphere
R = sphere radius
t = time
$c_f = c_f(z, t)$ = bulk fluid-phase composition
$c_S = c_S(r, z, t)$ = local solid-phase composition
$c_{SR} = c_S(R, z, t)$ = surface composition of the solid phase
c_{S_m} = volume-average composition of the solid phase
v_0 = interstitial mean fluid velocity in the z-direction
ε = fractional fluid volume in column
$\mathscr{E}$ = effective fluid-phase dispersion coefficient, assumed known
$\mathscr{D}_S$ = effective binary solute diffusivity in the solid phase
k_c = fluid-phase (boundary-layer) mass transfer coefficient, assumed known
a = interfacial area per unit volume of column $= 3(1 - \varepsilon)/R$
α = the equilibrium ratio of fluid to solid-phase concentration, normally a function of c_f or c_S

Integration of Eqs. (1) through (4) has proven to be a formidable task, even for constant values of all parameters, and, so far as we are aware, no serious attempt to use more complex models has yet been made.

A formal analytical solution to these equations has been provided by Amundson (*1*, *2*), but its complexity appears to have prevented its widespread use. Instead it has been the practice to use one of a number of available approximations in which at least one of the terms in the above description has been substantially modified.

Most frequently [see, however, Rosen (*3*, *4*)] the internal diffusional resistance of the solid is represented by a lumped-parameter approximation of the form

$$-\mathscr{D}_S \frac{\partial c_S}{\partial r}\bigg|_{r=R} \doteq k_s(c_{Sm} - c_{SR}) \tag{5}$$

It is furthermore the custom to assume

$$k_s = 5\mathscr{D}_S/R \tag{6}$$

Equation (6), which appears first to have been suggested by Glueckauf and Coates (*5*) [See also Helfferich (*6*, p. 286)], is the correct asymptotic expression for constant solute flux at the sphere surface. We shall have more to say about this equation later.

In addition to the simplification represented by Eq. (5), it is a common practice either to assume $\mathscr{E}$ to be zero or k_c and k_s to be infinite. However, it may be shown that for sufficiently long columns the effects of axial dispersion and mass-transfer resistance are additive (*7*). The higher-order coupling of eddy dispersion and diffusion described by Giddings (*11*) cannot be treated quantitatively by any model using a uniform packing. Either a dispersion or mass-transfer limited model may be used:

$$\mathscr{E} \rightarrow \mathscr{E}_{\text{tot}} \equiv \mathscr{E} + \mathscr{E}_{\text{diff}} \tag{7}$$

$$k_c \rightarrow k_{c,\text{tot}} \equiv \left(\frac{1}{k_c} + \frac{1}{(k_c)_{\text{disp}}}\right)^{-1} \tag{8}$$

We shall also have more to say about these approximations.

An alternate approach has been to use the method of moments to obtain approximations to integral concentration profiles. This appears to have been done first by Smith and colleagues (see, for example, Ref. *8*) for short feed pulses and has since been used by many others (*9*). It has been shown by Knight (*10*) that Eqs. (7) and (8) are equivalent to a second-moment analysis, which is the highest order normally attempted.

For linear systems (concentration-independent α) a large number of useful asymptotic expressions is available for approximating the integral profiles (*11*). These are particularly useful for investigating the effects of approximations made at the microscopic level of Eqs. (*1*)–(*8*) at low computational cost.

Below we suggest an alternate approach based on the Gill-Subramanian expansion (*12*) and the generalized Sturm-Liouville theory of Ramkrishna and Amundson (*13*) which permits very high-order approximations at low computational cost. It is a natural extension of a previous analysis of transient transport in cylindrically symmetric systems by our group (*14*).

We begin by expressing concentration anywhere in the system by

$$c = \sum_{n=0}^{\infty} f_n(r, t)\frac{\partial^n \bar{c}(z, t)}{\partial z^n} \tag{9}$$

where

$$\bar{c} \equiv \varepsilon c_f + (1 - \varepsilon)c_{S_m} \tag{10}$$

Our immediate purpose then is to obtain expressions for the f_n, and to do this it will prove convenient to use scaled variables.

We thus rewrite our description in the form

$$\frac{\partial \theta_f}{\partial \tau} + \frac{\partial \theta_f}{\partial \zeta} - \frac{1}{P^2}\frac{\partial^2 \theta_f}{\partial \zeta^2} = N(\alpha\theta_{SR} - \theta_f) \tag{11}$$

$$\frac{\partial \theta_S}{\partial \tau} - Q\frac{1}{\eta^2}\frac{\partial}{\partial \eta}\eta^2\frac{\partial \theta_S}{\partial \eta} = 0 \tag{12}$$

$$\left.\frac{\partial \theta_S}{\partial \eta}\right|_{\eta=1} = -M(\alpha\theta_{SR} - \theta_f) \tag{13}$$

where $\theta_f, \theta_S = c_f/c_0, c_S/c_0$
$\tau = t\mathscr{E}/R^2$
$\zeta = (z/R)(\mathscr{E}/v_0R) = z/RP$
$\eta = r/R$
$N = k_c a R^2/\varepsilon\mathscr{E}$
$M = k_c R/\mathscr{D}_S$
$P = v_0 R/\mathscr{E}$ = fluid-phase Péclet number
$Q = \mathscr{D}_S/\mathscr{E}$

and c_0 is a reference concentration to be chosen. We see then that the behavior of this system is governed by the five dimensionless parameters N, M, P, Q, and α.

Equation (9) may now be replaced by the two relations

$$\theta_f = \sum_{n=0}^{\infty} h_n(\tau)\frac{\partial^n \bar{\theta}(\zeta, \tau)}{\partial \zeta^n} \qquad \text{(fluid region)} \tag{14}$$

$$\theta_S = \sum_{n=0}^{\infty} g_n(\eta, \tau)\frac{\partial^n \bar{\theta}(\zeta, \tau)}{\partial \zeta^n} \qquad \text{(solid region)} \tag{15}$$

where $\bar{\theta}$ is $\bar{c}/c_0$ and

$$h_n(\tau) = (RP)^{-n} f_n \qquad \text{(fluid region)} \tag{16}$$

$$g_n(\eta, \tau) = (RP)^{-n} f_n \qquad \text{(solid region)} \tag{17}$$

Note that for our model the f_n are functions only of time in the fluid region.

We next note that Eqs. (1) and (2) may be added to obtain

$$\frac{\partial\bar{\theta}}{\partial\tau} + \varepsilon\frac{\partial\theta_f}{\partial\zeta} - \frac{\varepsilon}{P^2}\frac{\partial^2\theta_f}{\partial\zeta^2} = 0 \tag{18}$$

in terms of our scaled variables. The fluid-phase concentration may be eliminated from Eq. (18) to obtain

$$\frac{\partial\bar{\theta}}{\partial\tau} + \varepsilon h_0\frac{\partial\bar{\theta}}{\partial\zeta} - \varepsilon\left(\frac{h_0}{P^2} - h_1\right)\frac{\partial^2\bar{\theta}}{\partial\zeta^2} = \varepsilon\sum_{n=3}^{\infty}\left(\frac{h_{n-2}}{P^2} - h_{n-1}\right)\frac{\partial^n\bar{\theta}}{\partial\zeta^n} \tag{19}$$

which completes our restatement of the problem.

The strategy we shall follow to obtain concentration profiles is as follows: (a) Determine sufficient h_n and g_n for desired accuracy in determining θ_f and θ_S from Eqs. (14) and (15), and to permit integration of Eq. (19). A systematic procedure for doing this is developed in the next section. (b) Integrate Eq. (19) to obtain $\bar{\theta}(z, t)$ to the desired accuracy and for boundary conditions of physical interest. This is done in the section entitled "Macroscopic Description of Column Performance."

Finally, in the section entitled "Quantitative Aspects: The Importance of Transients" we discuss the significance of our results.

DETERMINATION OF THE RADIAL DISTRIBUTION FUNCTIONS

We begin by putting Eq. (15) into (12) to obtain

$$\sum_{n=0}^{\infty}\left(\left(\frac{\partial g_n}{\partial\tau}\right)\frac{\partial^n\bar{\theta}}{\partial\zeta^n} + g_n\frac{\partial^n}{\partial\zeta^n}\frac{\partial\bar{\theta}}{\partial\tau}\right) = Q\sum_{n=0}^{\infty}\left(\frac{1}{\eta^2}\frac{\partial}{\partial\eta}\eta^2\frac{\partial g_n}{\partial\eta}\right)\frac{\partial^n\bar{\theta}}{\partial\zeta^n} \tag{20}$$

We next eliminate the time derivative from this expression with the aid of Eq. (19). We thus obtain

$$\begin{aligned}\sum_{n=0}^{\infty}\frac{\partial g_n}{\partial\tau}\frac{\partial^n\bar{\theta}}{\partial\zeta^n} + \sum_{n=0}^{\infty} g_n\frac{\partial^n}{\partial\zeta^n}\Bigg[-\varepsilon h_0\frac{\partial\bar{\theta}}{\partial\zeta} + \varepsilon\left(\frac{h_0}{P^2} - h_1\right)\frac{\partial^2\bar{\theta}}{\partial\zeta^2} \\ + \varepsilon\sum_{m=3}^{\infty}\left(\frac{h_{m-2}}{P^2} - h_{m-1}\right)\frac{\partial^m\bar{\theta}}{\partial\zeta^m}\Bigg] = Q\sum_{n=0}^{\infty}\left(\frac{1}{\eta^2}\frac{\partial}{\partial\eta}\eta^2\frac{\partial g_n}{\partial\zeta}\right)\frac{\partial^n\bar{\theta}}{\partial\zeta^n}\end{aligned} \tag{21}$$

Equating coefficients of like spatial derivatives yields

$$\sum_{n=0}^{\infty}\left(\frac{\partial g_n}{\partial\tau} + Lg_n - r_n\right)\frac{\partial^n\bar{\theta}}{\partial\zeta^n} = 0 \tag{22}$$

where

$$L = -\frac{Q}{\eta^2}\frac{\partial}{\partial\eta}\eta^2\frac{\partial}{\partial\eta} \tag{23}$$

$$r_0 = 0 \tag{24}$$

$$r_1 = \varepsilon h_0 g_0 \tag{25}$$

$$r_2 = \varepsilon h_0 g_1 - \varepsilon g_0\left(\frac{h_0}{P^2} - h_1\right) \tag{26}$$

and so forth. Experience with this approach (*12*) shows that only g_0 and g_1 are normally significant, and that terms of higher order than g_2 should be truly negligible under conditions of probable interest in chromatographic operations.

Equation (22) is satisfied by

$$\frac{\partial g_n}{\partial\tau} + Lg_n = r_n \tag{27}$$

and it is clear from Eqs. (24)–(26) that the r_n contain only terms in g of lower order. We may thus solve the individual equations represented by (27) by proceeding in sequence. In general, however, the r_n contain contributions from the h_n, and we therefore must obtain descriptions of these.

These may be obtained by putting Eq. (14) into (11) and again eliminating the resulting time derivative via Eq. (19). Once again collecting like spatial derivatives, we obtain

$$\sum_{n=0}^{\infty}\left(\frac{dh_n}{d\tau} - S_n(\tau)\right)\frac{\partial^n\theta}{\partial\zeta^n} = 0 \tag{28}$$

which is again satisfied by

$$dh_n/d\tau = S_n(\tau) \tag{29}$$

where

$$S_0 = N[\alpha g_0(1,\tau) - h_0] \tag{30}$$

$$S_1 = \varepsilon h_0{}^2 - h_0 + N[\alpha g_1(1,\tau) - h_1] \tag{31}$$

and so forth.

It remains to write initial and boundary conditions for the distribution functions, including matching conditions for the g_n and h_n. We begin with those conditions fixed by the nature of the system. At $\eta = 0$,

$$\partial g_n/\partial\eta = 0 \tag{32}$$

At $\eta = 1$,

$$\partial g_n / \partial \eta = -M(\alpha g_n - h_n) \tag{33}$$

Equation (32) is a requirement of system symmetry, and Eq. (33) follows directly from Eq. (13).

As an initial condition we shall assume all solute to be in the mobile phase and normalized so that $\langle f_0 \rangle$ is unity:

$$g_n(\eta, 0) = 0 \tag{34}$$

$$h_n(0) = \delta_{0n}/\varepsilon \tag{35}$$

where

$$\begin{aligned} \delta_{0n} &= 1, \qquad n = 0 \\ &= 0, \qquad n \neq 0 \end{aligned}$$

This choice specializes our development, but it offers the advantage of yielding specific results. Extension of results below to other initial conditions is straightforward.

The Zero-Order Functions g_0 and h_0

For these the above description reduces to

$$\partial g_0 / \partial \tau = \frac{Q}{\eta^2} \frac{\partial}{\partial \eta} \eta^2 \frac{\partial g_0}{\partial \eta} \tag{36}$$

$$dh_0/d\tau = N(\alpha g_0|_1 - h_0) \tag{37}$$

with

$$g_0(\eta, 0) = 0 \tag{38}$$

$$\partial g_0 / \partial \eta |_0 = 0 \tag{39}$$

$$h_0(0) = 1/\varepsilon \tag{40}$$

$$\partial g_0 / \partial \eta |_1 = -M[\alpha g_0(1, \tau) - h_0] \tag{41}$$

We shall begin our solution by noting that g_0 and h_0 approach asymptotic values at large time, which we shall denote as g_∞ and h_∞, respectively. These may be simply determined by suppressing the time derivatives in Eqs. (36) and (37); they are

$$g_\infty = [(1 - \varepsilon) + \alpha\varepsilon]^{-1} \tag{42}$$

$$h_\infty = \alpha/[(1 - \varepsilon) + \alpha\varepsilon] \tag{43}$$

We may now define transient contributions

$$g_t = g_0 - g_\infty \tag{44}$$

$$h_t = h_0 - h_\infty \tag{45}$$

and put these definitions into Eqs. (37)–(41). All except Eqs. (38)–(40) take the same form, with the subscripts zero replaced by t; the latter become

$$g_t(0, \eta) = -[(1 - \varepsilon) + \alpha\varepsilon]^{-1} \tag{46}$$

$$h_t(0) = \left(\frac{1 - \varepsilon}{\varepsilon}\right)\frac{1}{[(1 - \varepsilon) + \alpha\varepsilon]} \tag{47}$$

The forms of Eqs. (36) and (37) now suggest that we write both g_t and h_t in the general form

$$f_t = \sum c_n F_n(\eta) T_n(\tau) \tag{48}$$

with

$$f_t = g_t(\eta, \tau) \quad \text{(solid phase)} \tag{49}$$

$$= h_t(\tau) \quad \text{(fluid phase)} \tag{50}$$

$$F_n = H_n(\eta) \quad \text{(solid phase)} \tag{51}$$

$$= E_n \quad \text{(fluid phase)}$$

where the c_n and E_n are constants to be determined. It is now easily shown that

$$T_n = e^{-Q\beta_n^2\tau} \tag{52}$$

$$H_n = \frac{1}{\eta}\sin \beta_n\eta \tag{53}$$

where the β_n are real constants.

If we now put these results into Eq. (41), we find

$$E_n = [\beta_n \cos \beta_n + (\alpha M - 1)\sin \beta_n]/M \tag{54}$$

which completes definition of the F_n in terms of the β_n.

We next put our expressions for the F_n and T_n into Eq. (37) and rearrange the result to obtain

$$\tan \beta_n/\beta_n = \left(\frac{N}{Q} - \beta_n^2\right)\Bigg/\left[\beta_n^2(\alpha M - 1) + \frac{N}{Q}\right] \tag{55}$$

This is the characteristic equation needed to determine the β_n.

As we will see below, c_n is an odd function of β_n; the terms to be summed in Eq. (48) are then even functions of β_n and therefore only nonnegative zeroes of Eq. (55) need be considered. Furthermore, $\beta_0 = 0$ (corresponding to the asymptotic solution already obtained), so we need determine only the positive roots of Eq. (55).

It remains only to find an orthogonality relation for determining the coefficients c_n.

The form of Eq. (53) suggests that we start our development of an orthogonality condition by writing

$$\begin{aligned} -\beta_n^2 \int_0^1 \eta^2 H_n H_m \, d\eta &= \int_0^1 H_m \frac{d}{d\eta} \eta^2 \frac{dH_n}{d\eta} \, d\eta \\ &= H_m \eta^2 \frac{dH_n}{d\eta}\bigg|_0^1 - \int_0^1 \eta^2 \frac{dH_n}{d\eta} \frac{dH_m}{d\eta} \, d\eta \end{aligned} \tag{56}$$

and similarly

$$-\beta_m^2 \int_0^1 \eta^2 H_n H_m \, d\eta = H_n \eta^2 \frac{dH_m}{d\eta}\bigg|_0^1 - \int_0^1 \eta^2 \frac{dH_m}{d\eta} \frac{dH_n}{d\eta} \, d\eta \tag{57}$$

Subtracting Eq. (56) from (57) gives

$$(\beta_n^2 - \beta_m^2) \int_0^1 \eta^2 H_n H_m \, d\eta = H_n \frac{dH_m}{d\eta}\bigg|_1 - H_m \frac{dH_n}{d\eta}\bigg|_1 \equiv I_{nm} \tag{58}$$

as

$$\eta^2 H_m \frac{dH_n}{d\eta}\bigg|_0 = \eta^2 H_n \frac{dH_m}{d\eta}\bigg|_0 = 0$$

Since the right side of Eq. (58) is not identically zero for our boundary conditions, we must examine it further.

From Eq. (41) we may write

$$\frac{dH_n}{d\eta}\bigg|_1 = -M[\alpha H_n(1) - E_n] \tag{59}$$

and therefore that

$$\begin{aligned} I_{nm} &= H_n \frac{dH_m}{d\eta}\bigg|_1 - H_m \frac{dH_n}{d\eta}\bigg|_1 \\ &= H_n[-M\alpha H_m + ME_m] - H_m[-M\alpha H_n + ME_n] \\ &= M(H_n E_m - H_m E_n)|_1 \end{aligned} \tag{60}$$

Now, from Eq. (37)

$$-E_n Q \beta_n^2 = N[\alpha H_n(1) - E_n] \tag{61}$$

and

$$H_n(1) = E_n\left(1 - Q\frac{\beta_n^2}{N}\right)\Big/\alpha \tag{62}$$

Putting Eq. (62) into (60) yields

$$I_{nm} = \frac{MQ}{N\alpha} E_m E_n (\beta_m^2 - \beta_n^2) \tag{63}$$

We may now combine this result with Eq. (58) to obtain

$$(\beta_n^2 - \beta_m^2)\left[\int_0^1 \eta^2 H_n H_m \, d\eta + \left(\frac{MQ}{N\alpha}\right) E_m E_n\right] = 0 \tag{64}$$

and therefore that

$$\int_0^1 \eta^2 H_n H_m \, d\eta + \frac{MQ}{N\alpha}\left(\frac{D_n D_m}{c_n c_m}\right) = 0 \qquad (n \neq m) \tag{65}$$

or

$$\int_0^1 \eta^2 H_n H_m \, d\eta + \frac{Q}{MN\alpha}[\beta_m \cos \beta_m + (\alpha M - 1) \sin \beta_m] \times [\beta_n \cos \beta_n + (\alpha M - 1) \sin \beta_n] = 0 \tag{66}$$

which is our desired orthogonality relation. It may be written more conveniently by recognizing that

$$MQ/N\alpha = \varepsilon/[3(1 - \varepsilon)\alpha] \tag{67}$$

so that

$$\alpha(1 - \varepsilon)\langle H_m H_n\rangle + \varepsilon E_n E_m = 0 \tag{68}$$

where

$$\langle H_m(\eta) H_n(\eta)\rangle = \frac{\int_0^1 \eta^2 H_m(\eta) H_n(\eta)\, d\eta}{\int_0^1 \eta^2 \, d\eta} = 3\int_0^1 \eta^2 H_m(\eta) H_n(\eta)\, d\eta \tag{69}$$

This is of the form

$$\langle W F_m F_n\rangle = 0 \tag{70}$$

where the weighting function

$$W = \alpha \qquad \text{(solid phase)} \tag{71}$$

$$= 1 \qquad \text{(fluid phase)} \tag{72}$$

Equation (70) is consistent with the corresponding result of Tepper et al. (*14*).

We are now in a position to determine the c_n and D_n via Eq. (68). We use the initial concentration profiles:

$$g_t(\eta, 0) = \sum_{n=1}^{\infty} c_n H_n(\eta) = -[(1 - \varepsilon) + \alpha\varepsilon]^{-1} \tag{73}$$

$$h_t(0) = \left(\frac{1 - \varepsilon}{\varepsilon}\right)[(1 - \varepsilon) + \alpha\varepsilon]^{-1} = \sum_{n=1}^{\infty} c_n E_n \tag{74}$$

in Eq. (69) to show that

$$\begin{aligned} &3\alpha(1 - \varepsilon)c_n^2 \int_0^1 \eta^2 H_n^2 \, d\eta + \varepsilon(c_n E_n)^2 \\ &\quad = -\frac{3\alpha(1 - \varepsilon)}{(1 - \varepsilon) + \alpha\varepsilon} c_n \int_0^1 \eta^2 H_n \, d\eta + \frac{(1 - \varepsilon)}{[(1 - \varepsilon) + \alpha\varepsilon]} c_n E_n \end{aligned} \tag{75}$$

It follows after some manipulation that

$$c_n = \left\{\left(\frac{\alpha\varepsilon}{2}\right)\left[\frac{\beta_n - \sin\beta_n \cos\beta_n}{\cos\beta_n - \dfrac{1}{\beta_n}\sin\beta_n}\right] + 3(1 - \varepsilon)\left[\frac{\beta_n \cos\beta_n - \sin\beta_n}{\beta_n^2}\right]\right\}^{-1} \tag{76}$$

This completes determination of the zero-order functions.

The First-Order Functions g_1 and h_1

These functions are described by the equations

$$\frac{\partial g_1}{\partial \tau} - \frac{Q}{\eta^2}\frac{\partial}{\partial \eta}\eta^2 \frac{\partial g_1}{\partial \eta} = \varepsilon h_0 g_0 \tag{77}$$

$$\frac{dh_1}{d\tau} = \varepsilon h_0^2 - h_0 + N[\alpha g_1(1, \tau) - h_1] \tag{78}$$

with

$$g_1(\eta, 0) = 0 \tag{79}$$

$$\partial g_1/\partial\eta|_0 = 0 \tag{80}$$

$$h_1(0) = 0 \tag{81}$$

$$\partial g_1/\partial\eta|_1 = -M[\alpha g_1 - h_1] \tag{82}$$

as boundary conditions.

It is clear from the form of this description that the two first-order expressions can be put in the form

$$f_1 = \sum_{n=0}^{\infty} F_n(\eta) T_{1n}(\tau) \tag{83}$$

where

$$f_1 = g_1(\eta, \tau)RP \qquad \text{(solid phase)} \tag{84}$$

$$= h_1(\tau)RP \qquad \text{(fluid phase)} \tag{85}$$

and the F_n are the functions defined above for the zero-order functions.

Putting this form of solution into Eq. (77) yields the equation

$$\sum_{n=0}^{\infty} \left[F_n \frac{dT_{1n}}{d\tau} + F_n Q\beta_n^2 T_{1n} \right] = \varepsilon h_0 g_0 \qquad \text{(solid phase)} \tag{86}$$

A similar expression can be obtained from Eq. (78) if it is recognized from the zero-order development that

$$-E_n Q\beta_n^2 = N[\alpha H_n(1) - E_n] \tag{87}$$

The result is

$$\sum_{n=0}^{\infty} \left[F_n \frac{dT_{1n}}{d\tau} + F_n Q\beta_n^2 T_{1n} \right] = \varepsilon h_0^2 - h_0 \qquad \text{(fluid phase)} \tag{88}$$

Equations (86) and (88) thus differ both in the expressions used for the F_n and in their inhomogeneous parts.

They can be used in connection with the orthogonality relation already devised,

$$\langle WF_n F_m \rangle = \delta_{nm} \langle WF_n^2 \rangle$$

to obtain a differential equation for the T_{1n}:

$$\frac{dT_{1n}}{d\tau} \langle WF_n^2 \rangle + Q\beta_n^2 T_{1n} \langle WF_n^2 \rangle = \langle WF_n S \rangle \tag{89}$$

where

$$S = \varepsilon h_0 g_0 \qquad \text{(solid phase)} \tag{90}$$

$$= \varepsilon h_0^2 - h_0 \qquad \text{(fluid phase)} \tag{91}$$

Then

$$T_{1n} = e^{-Q\beta_n^2 \tau} \int_0^{\tau} G_n(\tau) e^{Q\beta_n^2 \tau}\, d\tau \tag{92}$$

where

$$G_n(\tau) = \langle WF_nS\rangle / \langle WF_n^2\rangle \tag{93}$$

This completes our solution in a formal sense.

Now, from Eqs. (90) and (91):

$$\begin{aligned} G_n(\tau) &= \frac{\varepsilon h_0}{\langle WF_n^2\rangle}\left\{3\alpha(1-\varepsilon)\int_0^1 \eta^2 H_n g_0 \,\mathrm{d}\eta + \varepsilon E_n h_0 - E_n\right\} \\ &= \varepsilon h_0\left\{c_n e^{-Q\beta_n^2\tau} - \frac{E_n}{\langle WF_n^2\rangle}\right\} \end{aligned} \tag{94}$$

Then

$$T_{1n} = e^{-Q\beta_n^2\tau}\int_0^\tau \varepsilon h_0\left\{c_n - \frac{E_n e^{Q\beta_m^2\tau}}{\langle WF_n^2\rangle}\right\} d\tau \tag{95}$$

Noting that

$$h_0 = \sum_{n=0}^{\infty} c_n E_n e^{-Q\beta_n^2\tau} \tag{96}$$

we find

$$\begin{aligned} T_{1n} = \varepsilon e^{-Q\beta_n^2\tau}\Bigg[& c_n D_0 \tau + \sum_{m\neq 0}^{\infty} c_n D_m \frac{(1 - e^{-Q\beta_m^2\tau})}{Q\beta_m^2} - \frac{D_n^2}{c_n\langle WF_n^2\rangle}\tau \\ & - \frac{D_n}{c_n\langle WF_n^2\rangle}\sum_{\substack{m\neq n\\ m=0}}^{\infty}\frac{D_n(e^{Q(\beta_n^2-\beta_m^2)\tau} - 1)}{Q(\beta_n^2 - \beta_m^2)}\Bigg] \end{aligned} \tag{97}$$

This result is clearly well behaved for finite β_m, but it must be further examined for $\beta_m = 0$ (or $n = 0$). Now for this case

$$\left[c_n D_0 - \frac{D_n^2}{c_n\langle WF_n^2\rangle}\right] = c_0 D_0 - \frac{D_0^2}{c_0\langle WF_0^2\rangle} = 0 \tag{98}$$

This result follows from the relation

$$\langle WF_0^2\rangle = 3\int_0^1 \eta^2 \alpha H_0^2 \, d\eta \,(1-\varepsilon) + \frac{D_0^2}{c_0^2}\varepsilon \tag{99}$$

Here H_0 is constant, and from our initial condition

$$c_0 H_0 = D_0/\alpha \tag{100}$$

Therefore

$$\begin{aligned} \langle WF_0^2\rangle &= \alpha(1-\varepsilon)\frac{D_0^2}{c_0^2\alpha^2} + \frac{D_0^2}{c_0^2}\varepsilon \\ &= \frac{D_0^2}{\alpha c_0^2}[(1-\varepsilon) + \alpha\varepsilon] \end{aligned} \tag{101}$$

and

$$c_0 D_0 - \frac{D_0{}^2}{c_0 \langle WF_0{}^2 \rangle} = c_0 \left[D_0 - \frac{\alpha}{(1-\varepsilon) + \alpha\varepsilon} \right] \tag{102}$$

Now

$$D_0 = h_\infty = \alpha/[(1-\varepsilon) + \alpha\varepsilon] \tag{103}$$

so

$$c_0 D_0 - D_0{}^2/(c_0 \langle WF_0{}^2 \rangle) = 0 \tag{104}$$

as it should: no term in the series for g_1 or h_1 should blow up at large time. The solution is therefore complete and well-behaved in the form given.

It is instructive to examine the asymptotic behavior of the solution. At large time, only one term in Eq. (97) remains, and

$$f_{1\infty} = -\frac{\varepsilon RP}{Q} \sum_{n=1}^{\infty} F_n(n) \frac{E_n D_0}{\langle WF_n{}^2 \rangle \beta_n{}^2} \tag{105}$$

However, it is more convenient to determine the asymptotic behavior separately, which also serves to check the above solution. To do this, one only need suppress the time derivatives in Eq. (77) and Eq. (78) to obtain

$$-\frac{Q}{\eta^2} \frac{d}{d\eta} \eta^2 \frac{dg_{1\infty}}{d\eta} = \varepsilon h_\infty g_\infty \tag{106}$$

$$\varepsilon h_\infty{}^2 - h_\infty + N[\alpha g_{1\infty}(1) - h_{1\infty}] = 0 \tag{107}$$

Equation (106) may be readily integrated with the aid of Eq. (80) to give

$$g_{1\infty} = -\frac{\varepsilon g_\infty h_\infty}{Q} \frac{\eta^2}{6} + K \tag{108}$$

where K is the integration constant. Substituting this expression into

$$0 = \varepsilon h_1 + (1-\varepsilon)\langle g_1 \rangle \tag{109}$$

which is derived from Eq. (10), we find

$$K = \left(\frac{\varepsilon g_\infty{}^2 h_\infty}{Q} \right) \left[\frac{1-\varepsilon}{10} + \frac{\varepsilon}{3} \left(\frac{1}{M} + \frac{\alpha}{2} \right) \right] \tag{110}$$

and

$$h_{1\infty} = -\left(\frac{\varepsilon g_\infty h_\infty}{3Q} \right) \left(\frac{1}{M} + \frac{\alpha}{2} \right) + \alpha K \tag{111}$$

Equations (107), (109), and (110) are simple to calculate and have been found to agree with the convergent series in Eq. (105). Further use of these equations will be made in the next section.

MACROSCOPIC DESCRIPTION OF COLUMN PERFORMANCE

For most practical purposes it is sufficient to describe the volume-average solute concentration $\bar{\theta}$, as expressed by Eq. (19), and to neglect the entire right side of this equation. We may then concentrate our attention on the relation

$$\frac{\partial\bar{\theta}}{\partial\tau} + u(\tau)\frac{\partial\bar{\theta}}{\partial\zeta} - E(\tau)\frac{\partial^2\bar{\theta}}{\partial\zeta^2} \doteq 0 \tag{112}$$

where

$$u(\tau) = \varepsilon h_0$$

$$E(\tau) = \varepsilon\left(\frac{h_0}{P^2} - h_1\right)$$

Equation (112) is a dimensionless example of the one-dimensional convective heat transfer equation with time-dependent velocity u and dispersion coefficient E. Once it is integrated for a suitable set of boundary conditions, fluid- and solid-phase concentration distributions may be obtained from Eqs. (14) and (15), respectively. It only remains to integrate this equation, to relate it to presently used chromatographic models, and to consider the importance of the time dependence of u and E.

Explicit Descriptions of Mean Solute Concentration

We shall consider in detail only the long-column limit for which appropriate boundary conditions on ζ are

$$\bar{\theta},\ \partial\bar{\theta}/\partial\zeta = 0 \quad \text{as} \quad \zeta \rightarrow \pm\infty \tag{113}$$

and use the convenient initial condition

$$\bar{\theta}(\zeta, 0) = \delta(\zeta) \tag{114}$$

It then follows (see, for example, Ref. *15*) that

$$\bar{\theta} = \frac{1}{4\sqrt{\pi\xi}}\exp\left[-Z^2/4\xi\right] \tag{115}$$

where

$$Z = \zeta - \int_0^\tau u(\tau)\, d\tau \tag{116}$$

$$\xi = \varepsilon \int_0^\tau \left(\frac{h_0}{P^2} - h_1\right) d\tau' \tag{117}$$

Solutions for other initial distributions can be readily produced from Eq. (117) by superposition.

Normally the long-column approximation used here will be acceptable. Where this is not the case, it is the usual practice to use Danckwerts boundary conditions (*16*), and this will normally require numerical procedures. This approach has already been used by Tepper et al. for a closely related problem with cylindrical symmetry (*14*). If the time dependence of u and E may be neglected, one may obtain a compact solution using the transformation of Bastian and Lapidus (*17*), apparently developed independently by Brenner (*18*).

Asymptotic Behavior and Comparison with Other Approaches

In a sufficiently long column, u and E in Eq. (112) will approach the asymptotic values given by Eqs. (42), (43), (108), (110), and (111):

$$\lim_{\tau \to \infty} \{u(\tau)\} = \alpha\varepsilon/[(1 - \varepsilon) + \alpha\varepsilon] \equiv u_\infty \tag{118}$$

and

$$\begin{aligned}\lim_{\tau \to \infty} \{E(\tau)\} &= \frac{\alpha\varepsilon}{[(1 - \varepsilon) + \alpha\varepsilon]}\left\{\left(\frac{\mathscr{E}}{R_0 v_0}\right)^2 \right.\\ &\qquad \left. + \left(\frac{\mathscr{E}}{\mathscr{D}_S}\right)\frac{\varepsilon(1 - \varepsilon)}{[(1 - \varepsilon) + \alpha\varepsilon]^2}\,\frac{1}{3}\left(\frac{1}{M} + \frac{\alpha}{5}\right)\right\}\\ &\equiv E_\infty \end{aligned} \tag{119}$$

These results will perhaps be more meaningful if Eq. (11) is rewritten in terms of z and t:

$$\frac{\partial\theta}{\partial t} + uv_0\frac{\partial\theta}{\partial z} - E\left(\frac{R^2 v_0{}^2}{\mathscr{E}}\right)\frac{\partial^2\theta}{\partial z^2} = 0 \tag{120}$$

Then at large time

$$\begin{aligned}&\frac{\partial\theta}{\partial t} + \frac{\alpha\varepsilon}{[(1 - \varepsilon) + \alpha\varepsilon]}v_0\frac{\partial\theta}{\partial z} - \frac{\alpha\varepsilon}{[(1 - \varepsilon) + \alpha\varepsilon]}\\ &\quad \times \left\{\mathscr{E} + \frac{(Rv_0)^2}{\mathscr{D}_S}\,\frac{\varepsilon(1 - \varepsilon)}{[(1 - \varepsilon) + \alpha\varepsilon]^2}\,\frac{1}{3}\left(\frac{\mathscr{D}_S}{Rk_c} + \frac{\alpha}{5}\right)\right\}\frac{\partial^2\theta}{\partial z^2} = 0\end{aligned} \tag{121}$$

The coefficient of the second derivative may be written as $\mathscr{E}' + \mathscr{D}_T$ where

$$\mathscr{D}_T = \frac{(Rv_0)^2}{\mathscr{D}_S} \frac{\alpha\varepsilon^2(1-\varepsilon)}{[(1-\varepsilon)+\alpha\varepsilon]^3} \frac{1}{3}\left(\frac{\mathscr{D}_S}{Rk_c} + \frac{\alpha}{5}\right) \tag{122}$$

may be defined as a *generalized Taylor dispersion coefficient.* We shall defend this definition shortly.

First we note that Eq. (121) is just the one-dimensional convective diffusion equation with constant coefficients. More specifically, it is a special form of this well-known equation describing dispersion dominated chromatography with local equilibrium in which the axial dispersion coefficient $\mathscr{E}$ has been replaced by $(\mathscr{E}' + \mathscr{D}_T)$. If one assumes local equilibrium, defined by $c_f = \alpha c_{Sm}$, then the local fraction $\mathscr{R}$ of solute in the fluid phase is

$$\mathscr{R} = \alpha\varepsilon/[(1-\varepsilon)+\alpha\varepsilon] \tag{123a}$$

where this is just the retention ratio of the chromatographic literature. It is only this fraction which is free to move by convection or to be dispersed axially by nonuniformities in fluid-phase motion. As a result, the average convective velocity is $\mathscr{R}v_0$ as stated in Eq. (121), and the effective average dispersion coefficient is $\mathscr{R}(\mathscr{E}' + \mathscr{D}_T)$.

Now if there truly is local equilibrium between phases, it would be necessary that $\mathscr{D}_S$ and k_c both be infinitely large, and under these circumstances $\mathscr{D}_T$ would be zero. The term $\mathscr{D}_T$ thus describes the effect of mass-transfer resistance and is the $\mathscr{E}_{\text{diff}}$ of Eq. (7). We thus find that Eq. (7) is consistent with our analysis for sufficiently long time.

It may further be shown that $\mathscr{D}_T$ is the two-phase equivalent of Taylor dispersion by paralleling Taylor's original development (*19*) for our conditions. This is done in the Appendix. This is to be expected since our analysis is in effect a generalization of Taylor's approach.

Finally we may note that the term $\alpha/5$ in Eq. (121) is equivalent to a lumped-parameter mass-transfer coefficient for the solid phase of the form

$$k_{cs} = 5\mathscr{D}_S/R \tag{123b}$$

so that the overall mass-transfer coefficient is

$$\frac{1}{K_c} = \frac{1}{k_c} + \frac{\alpha}{k_{cs}} \tag{124}$$

in accordance with the classic two-film theory of mass transfer. Furthermore, Eq. (123b) is just the Glueckauf expression given in the Introduction as Eq. (6).

We find then that for sufficiently long times our analysis is consistent with the most widely used approximations. It remains to determine the rate of approach to these asymptotic conditions.

QUANTITATIVE ASPECTS: THE IMPORTANCE OF TRANSIENTS

The primary utility of the above analysis is in providing a means for estimating the importance of diffusional transients, necessarily neglected in the more convenient lumped-parameter models, and for describing their effects if necessary. The large number of parameters in the above description makes a comprehensive study of this type a formidable problem, however, and we therefore content ourselves here with a small number of examples.

We chose for these examples conditions representative of current liquid-phase chromatographic separations:

$$\mathscr{D}_S = 10^{-6}\ \text{cm}^2/\text{sec}$$

$$R = 10^{-3}\ \text{to}\ 10^{-1}\ \text{cm}$$

$$v_0 = 0.07\ \text{to}\ 0.7\ \text{cm/sec}$$

$$\varepsilon = 0.38$$

Dispersion coefficients were calculated from the correlation of Edwards and Richardson (*20*) for packed beds of nonporous beads:

$$\mathscr{E} = 2v_0R\left[\frac{0.365\,\mathscr{D}_f}{Rv_0} + \frac{0.5}{1 + \dfrac{7.05\,\mathscr{D}_f}{Rv_0}}\right] \tag{125}$$

This equation is an empiricism tested for gases. Mass-transfer coefficients are taken from the correlation of Pfeffer (*21*):

$$k_c = A(\mathscr{D}_f/2R)^{2/3}{v_0}^{1/3} \tag{126}$$

with $\mathscr{D}_f$ taken as 10^{-5} cm^2/sec. The coefficient

$$A = 1.26(1 - \gamma^5)/(2 - 3\gamma + 3\gamma^5 - 2\gamma^6) \tag{127a}$$

where

$$\gamma = (1 - \varepsilon)^{1/3} \tag{127b}$$

Numerical evaluations of g_0, at various points within the spheres, and h_0 are obtained from the following equations:

$$g_0 = \sum_{n=1}^{\infty} C_n \frac{\sin \beta_n e^{-Q\beta_n^2\tau}}{\beta_n} + \frac{1}{1 - \varepsilon + \alpha\varepsilon} \tag{128}$$

$$h_0 = \sum_{n=1}^{\infty} \frac{C_n(\beta_n \cos \beta_n + (\alpha M - 1) \sin \beta_n)e^{-Q\beta_n^2\tau}}{M} + \frac{\alpha}{1 - \varepsilon + \alpha\varepsilon} \tag{129}$$

$$C_n = \left\{\left(\frac{\alpha\varepsilon}{2}\right)\left[\frac{\beta_n - \sin \beta_n \cos \beta_n}{\cos \beta_n - \dfrac{\sin \beta_n}{\beta_n}}\right] + 3(1 - \varepsilon)\left[\frac{\beta_n \cos \beta_n - \sin \beta_n}{\beta_n^2}\right]\right\}^{-1} \tag{130}$$

Eigenvalues, β_n, were determined from Eq. (55), using Newton's method. Calculations of g_1 and h_1 were made from

$$g_1 = \sum_{n=1}^{\infty} \frac{\sin \beta_n}{\beta_n} T_{1n} \tag{131}$$

$$h_1 = \sum_{n=1}^{\infty} \frac{(\beta_n \cos \beta_n + (\alpha M - 1) \sin \beta_n)T_{1n}}{M} \tag{132}$$

$$\begin{aligned} T_{1n} = \varepsilon e^{-Q\beta_n^2\tau}\Bigg[& \frac{C_n\alpha\tau}{1 - \varepsilon + \alpha\varepsilon} + \sum_{m=1}^{\infty} \frac{C_n D_m(1 - e^{-Q\beta_n^2\tau})}{Q\beta_n^{\,n}} \\ & - \frac{D_n^{\,2}\tau}{C_n\langle WF_n^{\,2}\rangle} - \frac{D_n}{C_n\langle WF_n^{\,2}\rangle} \sum_{\substack{m=0 \\ m \neq n}}^{\infty} \frac{D_m(e^{-Q(\beta_n^2 - \beta_m^2)\tau} - 1)}{Q(\beta_n^{\,2} - \beta_m^{\,2})}\Bigg] \end{aligned} \tag{133}$$

$$D_m = C_m(\beta_m \cos \beta_m + (\alpha M - 1) \sin \beta_m)/M \tag{134}$$

$$\begin{aligned} \langle WF_n^{\,2}\rangle = \Bigg[& \frac{3(1 - \varepsilon)\alpha}{2} + \frac{\varepsilon}{M^2}\beta_n^{\,2} \cos^2 \beta_n \\ & + \left(\frac{2\varepsilon(\alpha M - 1)\beta_n^{\,2}}{M^2} - \frac{3(1 - \varepsilon)\alpha}{2\beta_n}\right) \cos \beta_n \sin \beta_n \\ & + \frac{\varepsilon(\alpha M - 1)^2 \sin^2 \beta_n}{M^2}\Bigg] \end{aligned} \tag{135}$$

Calculations were performed on the University Univac 1110 2X2 computer. The series contained in the above expressions were terminated when increments became smaller than one part in 100,000 or at 750 terms. All 750 terms were used only at very short times, where convergence is slow, due to small values of Q in the exponential terms, $e^{-Q\beta_n^2\tau}$.

In Figs. 1 to 6 the functions h_0 and h_1 are plotted as functions of time. They are seen to approach the expected initial values and asymptotic limits. For larger spheres, transients may be important, as evidenced for

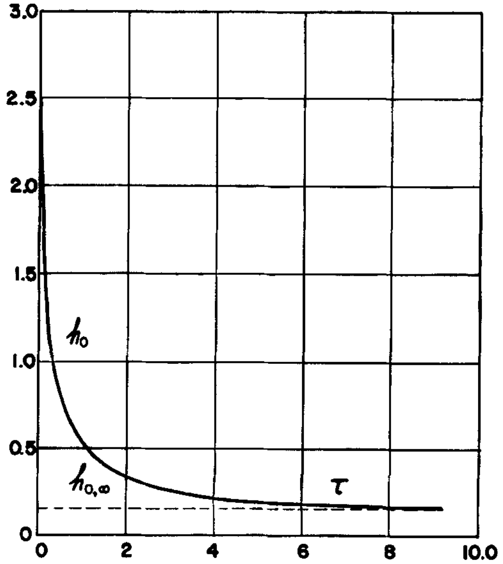

FIG. 1. Decay of the transients of h_0. $\alpha = 0.1$. $R = 0.01$ cm.

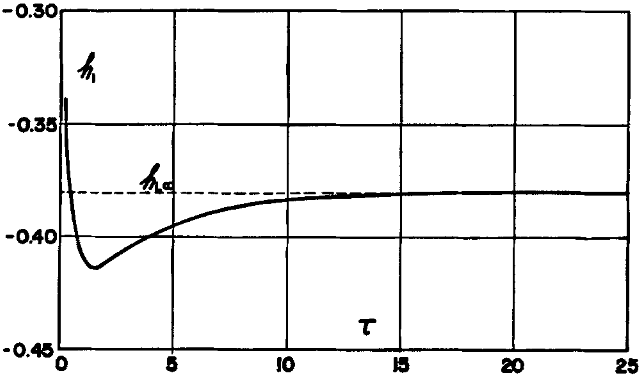

FIG. 2. Decay of the transients of h_1. $\alpha = 0.1$. $R = 0.01$ cm.

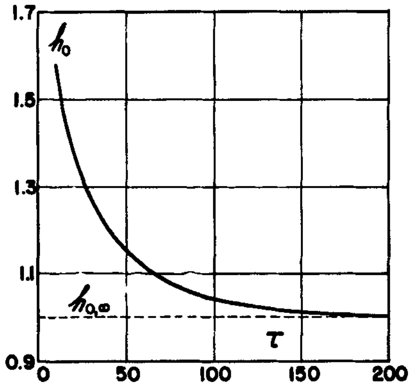

FIG. 3. Decay of the transients of h_0. $\alpha = 1.0$. $R = 0.01$ cm.

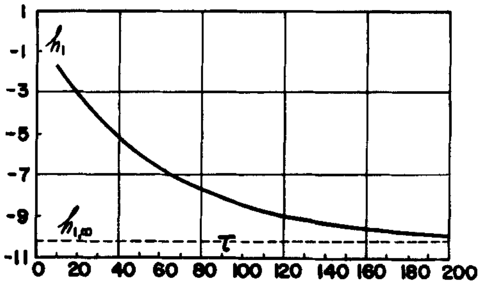

FIG. 4. Decay of the transients of h_1. $\alpha = 1.0$. $R = 0.01$ cm.

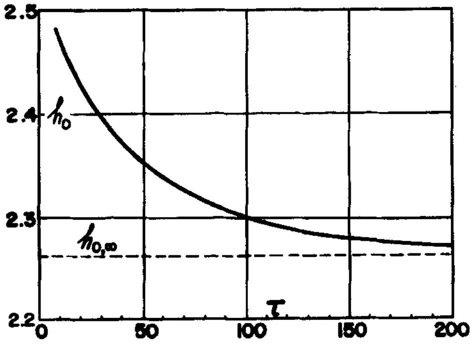

FIG. 5. Decay of the transients of h_0. $\alpha = 10.0$. $R = 0.01$ cm.

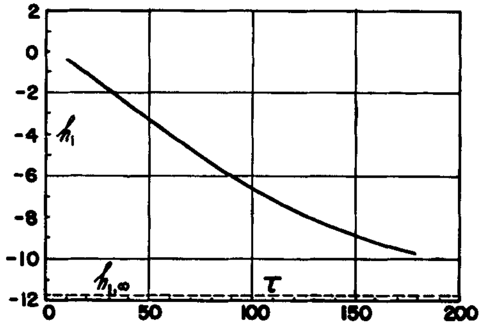

FIG. 6. Decay of the transients of h_1. $\alpha = 10.0$. $R = 0.01$ cm.

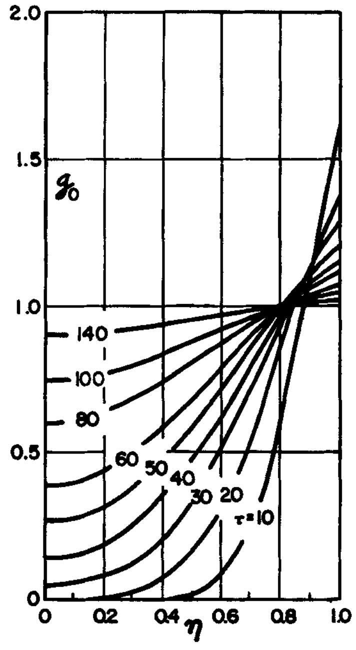

FIG. 7. Time-dependent radial profiles g_0. $\alpha = 1.0$. $R = 0.01$ cm.

the response with $R = 0.1$ cm. In many practical cases, however, the asymptotic expressions for h_0 and h_1, as expressed in Eqs. (43), (110), and (111), should be sufficient to describe column performance.

In Figs. 7 and 8 the time-dependent radial profiles g_0 and g_1 are plotted for a column with $\alpha = 1.0$ and $R = 0.01$ cm. Again, the functions approach the correct initial values, and rapidly reach their respective asymptotic limits. The time duration of the transient behavior appears to be the same for the fluid and solid phases.

Integration of the general differential equation for the column allows breakthrough curves (i.e., exit concentrations as a function of time) to

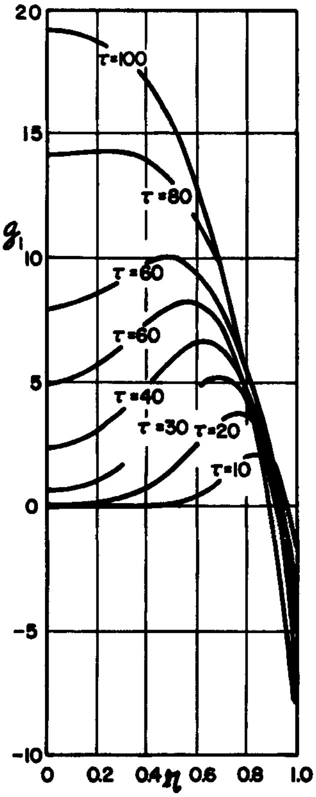

FIG. 8. Time-dependent radial profiles g_1. $\alpha = 1.0$. $R = 0.01$ cm.

be calculated. The explicit expression for long columns is

$$c_f = \left[h_0 - \frac{Zh_1}{2\xi}\right]\frac{1}{4\sqrt{\pi\xi}}\exp\left(-Z^2/4\xi\right) \tag{136}$$

where Z and ξ are defined by Eqs. (116) and (117). If we assume that h_0 and h_1 can be approximated by the constant asymptotic values, this expression reduces to

$$c_f = \left[h_\infty - \frac{\zeta h_{1\infty}}{2E_\infty\tau} + \frac{\varepsilon h_\infty h_{1\infty}}{2E_\infty}\right]\frac{1}{4\sqrt{\pi E_\infty\tau}}\exp\left[\frac{-(\zeta - \varepsilon h_\infty\tau)^2}{4E_\infty\tau}\right] \tag{137}$$

where

$$E_\infty = \varepsilon\left[\frac{h_\infty}{P^2} - h_{1\infty}\right]$$

A summary of key results for all choices of parameters used is given in Table 1. The steady-state combined dispersion coefficient *for the fluid* phase is given by

$$E_f \equiv E\Big/\left\{\frac{\alpha}{1-\varepsilon+\alpha\varepsilon}\right\} = \varepsilon\mathscr{E} + \frac{(Rv_0)^2}{\mathscr{D}_S}\frac{\varepsilon^2(1-\varepsilon)}{[(1-\varepsilon)+\alpha\varepsilon]^2}\frac{1}{3}\left[\frac{\mathscr{D}_S}{Rk_c} + \frac{\alpha}{5}\right] \tag{138}$$

This expression is also given more simply in terms of h_∞ and $h_{1\infty}$ as

$$E_f = \varepsilon Rv_0\left[\frac{1}{P} - \frac{h_{1\infty}}{h_\infty}P\right] \tag{139}$$

Using this coefficient, we can arrive at a simple parameter expressing the extent of peak spreading in a column of a typical length, 50 cm:

$$\sigma = \sqrt{100E_f/\mathscr{R}v_0} \tag{140}$$

where $\mathscr{R}$ is expressed in Eq. (123a). We can see that smaller spheres contribute less to peak spreading, as expected. The contribution of mass transfer to dispersion is also clearly seen in σ as α becomes smaller.

SUMMARY

The utility of the Gill-Subramanian expansion for analysis of chromatographic columns has been demonstrated. High order approximation of column behavior is possible at low computational cost. Moreover, the technique can accommodate even higher order approximations for the

TABLE 1
Calculated Asymptotic Behavior

R (cm)	v_0 (cm/sec)	α	h_∞	$h_{1\infty}$	$g_\infty(R)$	$g_{1\infty}(R)$	σ (cm)	E_f (cm^2/sec)
0.001	0.07	10.0	2.262	−0.7709	0.2262	−0.07625	0.1578	3.107×10^{-5}
0.001	0.07	1.0	1.00	−0.6729	1.00	−0.6565	0.2272	4.574×10^{-5}
0.001	0.07	0.1	0.15198	−0.02682	1.5198	−0.2304	0.5892	2.382×10^{-5}
0.01	0.07	10.0	2.262	−11.78	0.2262	−1.178	1.705	1.75×10^{-3}
0.01	0.07	1.0	1.00	−10.21	1.00	−10.09	3.468	3.20×10^{-3}
0.01	0.07	0.1	0.15198	−0.3809	1.5198	−3.541	4.901	9.71×10^{-4}
0.1	0.7	10.0	2.262	−1275.9	0.2262	−127.4	49.97	15.03
0.1	0.7	10.0	1.00	−1100.0	1.00	−1097.3	104.9	29.29
0.1	0.7	10.0	0.15198	−39.14	1.5198	−385.2	130.4	6.877

behavior of fast responding columns by including more terms in the series for the f_n as well as calculating additional f_n. This is at the expense of additional computational effort.

For many columns of practical interest, however, the transient behavior is short lived, and simple asymptotic expressions, as presented in this paper, are all that are needed to predict column performance.

APPENDIX: TAYLOR DISPERSION IN A PACKED COLUMN

The convective diffusion analog for chromatographic columns is

$$\varepsilon\left[\frac{\partial c_f}{\partial t} + v_0\frac{\partial c_f}{\partial z} - \mathscr{E}\frac{\partial^2 c_f}{\partial z^2}\right] = k_c a(\alpha c_{SR} - c_f) \tag{141}$$

$$(1-\varepsilon)\frac{\partial c_S}{\partial t} = (1-\varepsilon)\frac{\mathscr{D}_S}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c_S}{\partial r} \tag{142}$$

$$-\mathscr{D}_S\frac{\partial c_S}{\partial r_r}\bigg|_{r=R} = k_c(\alpha c_{SR} - c_f) \tag{143}$$

which is the same as Eqs. (1), (3), and (4).

Now, in the near-equilibrium situation the average convection velocity of solute is

$$\langle v\rangle = v_0\frac{\mathscr{E}c_f}{\varepsilon c_f + (1-\varepsilon)c_S} \tag{144}$$

with

$$c_{Sm} \doteq \frac{1}{\alpha}c_f \tag{145}$$

so that

$$\langle v\rangle = v_0\frac{\alpha\varepsilon}{\alpha\varepsilon + (1-\varepsilon)} \equiv \mathscr{R}v_0 \tag{146}$$

Now define

$$x = z - \langle v\rangle t \tag{147}$$

Then Eqs. (141) and (142) become

$$\varepsilon\left[\left(\frac{\partial c_f}{\partial t}\right)_x + (v_0 - \langle v\rangle)\left(\frac{\partial c_f}{\partial x}\right)_t\right] = \varepsilon\mathscr{E}\frac{\partial^2 c_f}{\partial x^2} + k_c a(\alpha c_S - c_f) \tag{148}$$

$$(1-\varepsilon)\left[\left(\frac{\partial c_S}{\partial t}\right)_x - \langle v\rangle\left(\frac{\partial c_S}{\partial x}\right)_t\right] = (1-\varepsilon)\frac{\mathscr{D}_S}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c_S}{\partial r} \tag{149}$$

Next assume with Taylor that transients in this modified coordinate system and fractional variations in $\partial c/\partial x$ are small relative to the effect of radial gradients. Equation (149) then takes the simplified form

$$-\langle v\rangle\left(\frac{\partial \bar{c}_S}{\partial x}\right)_t \doteq \frac{\mathscr{D}_S}{r^2}\frac{d}{dr}r^2\frac{dc'_S}{dr} \tag{150}$$

where

$$c_S = \bar{c}_S + c'_S \tag{151}$$

with $\bar{c}_S$ = mean stationary phase concentration
c'_S = deviation from this mean, presumed independent of time and axial position

Integrating Eq. (150) gives

$$c'_S(r) - c'_S(R) = \frac{\langle v\rangle R^2}{6\mathscr{D}_S}\left[1 - \left(\frac{r}{R}\right)^2\right]\frac{\partial \bar{c}_S}{\partial x} \tag{152}$$

The volumetric mean concentration within the sphere is

$$c_{Sm} = \frac{3}{4\pi R^3}\int_0^R\int_0^\pi\int_0^{2\pi} c_S r^2 \sin\theta \, dr\, d\theta\, d\phi \tag{153}$$

$$= \bar{c}_S + c'_S(R) + \frac{1}{15}\frac{R^2\langle v\rangle}{\mathscr{D}_S}\frac{\partial \bar{c}_S}{\partial x} \tag{154}$$

From Eq. (151),

$$c_S(R) = \bar{c}_S + c'_S(R) \tag{155}$$

hence

$$c_{Sm} = c_S(R) + \frac{1}{15}\frac{R^2\langle v\rangle}{\mathscr{D}_S}\frac{\partial \bar{c}_S}{\partial x} \tag{156}$$

From Eqs. (150) and (143), we get

$$\left(\frac{\langle v\rangle R}{3}\right)\left(\frac{\partial \bar{c}_S}{\partial x}\right)_t = k_c(\alpha c_S|_R - c_f) \tag{157}$$

Then

$$c_f = \alpha c_S(R) - \frac{\langle v\rangle R}{3k_c}\left(\frac{\partial \bar{c}_S}{\partial x}\right)_t \tag{158}$$

Combine Eqs. (156) and (158),

$$c_f = \alpha c_{Sm} - \frac{\alpha}{15}\left(\frac{vR^2}{\mathscr{D}_S}\right)\frac{\partial \bar{c}_S}{\partial x} - \frac{1}{3}\left(\frac{\langle v\rangle R}{k_c}\right)\frac{\partial \bar{c}_S}{\partial x} \tag{159}$$

The total convective transport of solute relative to x is

$$W^* = \varepsilon c_f(v_0 - \langle v \rangle) - (1 - \varepsilon)c_{S_m}\langle v \rangle \tag{160}$$

Plug Eqs. (146), (156), and (158) into Eq. (160) to obtain

$$\begin{aligned} W^* &= -\left(\frac{\partial \bar{c}_S}{\partial x}\right)\frac{Rv_0^{\,2}}{\mathscr{D}_S}\left[\frac{1}{15}\frac{\alpha^2\varepsilon^2(1-\varepsilon)}{(\alpha\varepsilon + (1-\varepsilon))^2} + \frac{1}{3}\left(\frac{\mathscr{D}_S}{Rk_c}\right)\frac{\alpha\varepsilon^2(1-\varepsilon)}{(\alpha\varepsilon + (1-\varepsilon))^2}\right] \\ &\equiv -\mathscr{D}_T\frac{\partial \bar{c}}{\partial x} \end{aligned} \tag{161}$$

where

$$\bar{c} = [\alpha\varepsilon + (1-\varepsilon)]\bar{c}_S \tag{162}$$

Therefore

$$\mathscr{D}_T = \frac{(Rv_0)^2}{\mathscr{D}_S}\frac{\alpha\varepsilon^2(1-\varepsilon)}{[(1-\varepsilon) + \alpha\varepsilon]^3}\frac{1}{3}\left[\frac{\mathscr{D}_S}{Rk_c} + \frac{\alpha}{5}\right] \tag{163}$$

which is the same as Eq. (122).

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