Calculation of Dispersion Coefficients by Means of Moments

F. J. M. HORN
Rice University, Houston, Texas

The problem of evaluating the coefficient of dispersion in a general linear two-component chromatographic system is equivalent to a steady state source problem in multidimensional Euclidean space. The equivalence of the two physical problems provides an intuitive insight into the contributions of different transport processes to dispersion. For a wide class of systems the dispersion coefficient can be expressed as the maximum of a functional. This can be utilized in the numerical evaluation of dispersion coefficients and in the application of perturbation techniques.

REPRESENTATION OF CHROMATOGRAPHIC SYSTEMS

Consider the infinitely long tube which is generated by translating the region X in the x_1, x_2 plane (see Figure 1) along the z axis. Suppose that this tube is filled with one or more phases which are in motion. The components of the fluid velocity will be denoted by v_1, v_2, and v_z. It will be assumed that the shapes and positions of the subregions of the cross section X occupied by different phases are independent of the position of the cross section. Similarly, it will be assumed that the velocity vector does not depend on z, although it may depend on the position in X, that is, on the coordinates x_1 and x_2. The velocity field will be assumed to describe the time-independent motion of an incompressible fluid.

The propagation of a tracer which is introduced into the system at time $t = 0$ will be studied. Thus the thermodynamic properties of the different phases with respect to the tracer will be of importance. It will be assumed that all equilibrium relationships are linear in the concentration of c of the tracer. In this case each phase can be characterized by a constant K denoting the concentration of the tracer in the respective phase which is in equilibrium with unit tracer concentration in a (fictitious or real) reference phase. Since the column may contain several phases, K, in general, is a function of position in X. If the column is in equilibrium

$$\frac{c(x_1, x_2)}{K(x_1, x_2)}$$

is independent of the position.

Obviously K is defined only up to an arbitrary position independent factor. This ambiguity will, however, not cause any difficulty in what follows.

It will be assumed that the tracer is transported not only by convection but also by mechanisms which can be described mathematically by diffusion. The components of the diffusional flux vector will be denoted by q_1, q_2, and q_z. The two-dimensional vector with components q_1 and q_2 will be denoted by q. The symbol ∇ will denote the two-dimensional gradient in X. It will be assumed that the diffusional flux is given by

$$\mathbf{q} = -\mathbf{D} \cdot \nabla c \tag{1}$$

$$q_z = -D_z \frac{\partial c}{\partial z} \tag{2}$$

D is a positive definite symmetrix matrix and D_z is a scalar. Both D and D_z may depend on x_1 and x_2 but are supposed to be independent of z.

Consider now the flux across an interface between phases. If there is no accumulation of tracer at the interface, the normal component will be continuous across the interface. The following relationship between flux and driving force will be assumed to be satisfied:

$$\mathbf{n} \cdot \mathbf{q} = -k\left(\frac{c_2}{K_2} - \frac{c_1}{K_1}\right) \tag{3}$$

Here n denotes the unit vector orthogonal to the interface and pointing from phase 1 to phase 2. c_1 and c_2 denote tracer concentrations at opposite points of the interface in phases 1 and 2, respectively.

K_1 and K_2 are the values of the equilibrium constants in the two phases and k is the mass transfer coefficient. The case of zero mass transfer resistance will not be excluded ($k = \infty$). In this case the equilibrium relation

$$\frac{c_1}{K_1} = \frac{c_2}{K_2} \tag{4}$$

is satisfied at the interface.

In general k is a function of the position on the interface. k and K are determined only up to a position-independent factor, although the ratio of k and K is defined uniquely for a particular problem.

Some physical problems require models in which X is an n-dimensional space where n may be larger than 2. Such models correspond to chromatography in an $n + 1$ dimensional space. The reason for considering this general situation will become clear later when some examples will be discussed. The definitions given previously for two-dimensional X space can easily be extended to an n-dimensional cross section: a phase occupies an n-dimensional subregion of X and an interface is an $(n - 1)$-

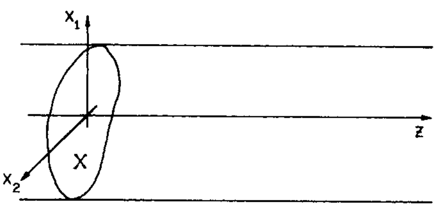


Fig. 1. Chromatographic column. The axes x_1, x_2, and z are orthogonal. X is a subregion of the x_1, x_2-plane.

F. J. M. Horn is at the University of Rochester, Rochester, New York.

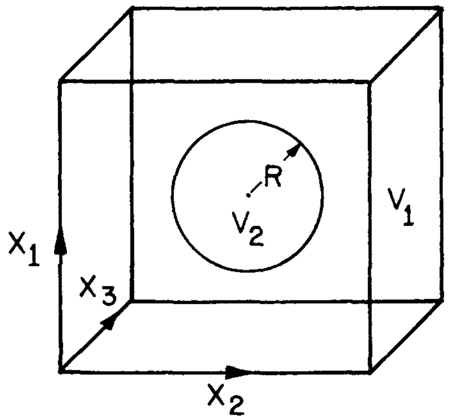


Fig. 2. X space for a packed column: sphere of radius R enclosed by box. Volume of sphere $= V_1$, volume of box $= V_1 + V_2$. Phases 1 and 2 occupy volumes 1 and 2, respectively.

dimensional hypersurface in X. A mass balance over an element of the $(n + 1)$-dimensional space spanned by $x_1, x_2, \ldots, x_n, z$ yields the following partial differential equation:

$$\frac{\partial c}{\partial t} = - v_z \frac{\partial c}{\partial z} - \mathbf{v} \cdot \nabla c + D_z \frac{\partial^2 c}{\partial z^2} + \nabla \cdot \mathbf{D} \cdot \nabla c \quad (5)$$

$\mathbf{v}$ is an n-dimensional velocity vector with components $v_1, v_2, \ldots, v_n$, that is, entirely in the space orthogonal to the z axis.

$\mathbf{D}$ is an n-dimensional, positive definite, symmetric square matrix. ∇ denotes the vector with components $\partial/\partial x_i$. The quantities v_z and D_z are scalars, the latter of which is non-negative. All magnitudes may depend on x_i but are supposed to be independent of z with the exception of c. The vector $\mathbf{v}$ describes the motion of an incompressible n-dimensional flow. Thus

$$\nabla \cdot \mathbf{v} = 0 \quad (6)$$

Since v_z is independent of z Equation (6) is equivalent to the incompressibility of the $(n + 1)$-dimensional flow represented by the vector with components $v_1, v_2, \ldots, v_n, v_z$.

The boundary conditions for c are given by

$$\mathbf{n} \cdot \mathbf{D} \cdot \nabla c = k \Delta \, (c/K) \text{ at } B \quad (7)$$

where the operator Δ and the vector $\mathbf{n}$ are defined such that Equation (7) becomes equivalent to Equation (3). B stands for interface and for the boundary of X. It will be assumed that the latter is impermeable for the tracer. That is, $k = 0$ at the boundary of X. Similarly, the velocity field will be assumed to satisfy

$$\mathbf{n} \cdot \mathbf{v} = 0 \text{ at } B \quad (8)$$

Cases will be considered where there is no diffusional resistance against transport within X and in certain subregions of X or where there is no resistance along certain directions within X, That is, the elements of $\mathbf{D}$ may become infinite. In these cases c will be position independent in certain subregions or will be constant along certain lines. Then in addition to Equation (5) overall mass balances have to be considered. For instance, if c is position independent within a phase in X, the rate of change of c will equal the total influx of tracer into the subregion occupied by the phase in question divided by the volume of this subregion. (See example 2, next section.) For brevity the general equations will be written always for nonzero diffusional resistance; however, the extension of the mathematical discussion leading to an expression for the dispersion coefficient to the general case will be obvious. The final result will be stated such that it applies to both zero and nonzero resistance in X.

EXAMPLES FOR CHROMATOGRAPHIC SYSTEMS

1. Taylor's Problem: Laminar Flow in a Cylindrical Tube (See reference 1)

In this case the X space is two dimensional $(n = 2)$. If D is the coefficient of the molecular diffusion $\mathbf{D}$ and D_z are given by

$$\mathbf{D} = D\mathbf{I} \qquad D_z = D \quad (9a)$$

K is position independent in X and can be set equal to unity (say). The velocity has no component in X

$$\mathbf{v} = 0 \quad (9b)$$

and v_z is given by

$$v_z = v_0 \left(1 - \frac{r^2}{R^2}\right) \quad (9c)$$

where v_0 is the velocity at the center of the tube, r is the distance from the center, and R is the radius of the tube.

2. Chromatography in a Packed Column

Consider a column packed with spherical particles of equal size into which the tracer can diffuse. The radius R of the particles is assumed to be so small that the change of tracer concentration in the fluid phase surrounding the particles can be neglected along a distance equal to $2R$. The longitudinal mixing due to the flow around the spheres will be described by a dispersion coefficient D_{z1}, values for which are available in the literature. The coefficient of diffusion for the tracer in the spheres will be denoted by D_2 and the mass transfer from the bulk of the fluid to the sphere will be described by a relation equivalent to Equation (3). The transport of the tracer in the column is then governed by the following relations:

$$\epsilon \frac{\partial c_1}{\partial t} = - \epsilon v_{z1} \frac{\partial c_1}{\partial z} + \epsilon D_{z1} \frac{\partial^2 c_1}{\partial z^2} - 4\pi N R^2 k \left(c_1 - \frac{c_2}{K_2} \right) \quad (10a)$$

$$\frac{\partial c_2}{\partial t} = D_2 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_2}{\partial r} \right) \quad (10b)$$

$$D_2 \frac{\partial c_2}{\partial r} = k \left(c_1 - \frac{c_2}{K_2} \right) \text{ at } r = R \quad (10c)$$

N is the number of spheres per unit volume of the column. ϵ is the void fraction which is related to N and R by

$$\epsilon = 1 - N \frac{4\pi}{3} R^3 \quad (10d)$$

c_1 is the bulk concentration of the tracer in the fluid phase, which depends on z and t. c_2, the concentration of the tracer in the particles, depends on the position of the particle in the column, z, on the position within the particle, r, and on the time t. v_{z1} is the average velocity of the fluid in the void space. k is the mass transfer coefficient for the transport of tracer from the bulk of the fluid phase to boundary of the sphere. K_2 is the equilibrium constant. That is, in the case of equilibrium between particles and fluid the relation

$$c_2 = K_2 c_1 \quad (11)$$

is satisfied. The value of K_1 has been set equal to unity in this example.

It will now be shown that this model of a packed column is a special case of the general representation of a chro-

Table 1. Distribution of the Characteristic Parameters Over X for the Packed-Column Problem

	Phase 1	Phase 2
K	1	K_2
v_z	v_{z1}	0
v	0	0
D_z	D_{z1}	0
D	∞	D_2I

matographic system as discussed in the previous section. Consider a three-dimensional X space as shown in Figure 2. This space is filled with two phases: phase 2 occupies the sphere of radius R and phase 1 occupies the rest of X. The values of the parameters in the subregions of X occupied by the two different phases are listed in Table 1.

The assumption of zero diffusional resistance within phase 1 is made because the mass transfer resistance from the bulk of the fluid to the sphere has been incorporated already into the phenomenological transfer coefficient k. In this example X is the three-dimensional cross section of a four-dimensional chromatographic column. The transport Equation (5) has to be modified in order to take into account the zero transport resistance in phase 1. A mass balance over an element dz of the column yields

$$V_1 \frac{\partial c_1}{\partial t} = - V_1 v_{z1} \frac{\partial c_1}{\partial z} + D_z V_1 \frac{\partial^2 c_1}{\partial z^2} - 4\pi R^2 k \left(c_1 - \frac{c_2}{K_2} \right) \quad (12)$$

There are two more equations which are identical to Equations (10*b*) and (10*c*), respectively. It can be seen easily that Equation (12) becomes identical to Equation (10*a*) if in X the volume V_1 of the fluid phase is chosen so that the ratio of the fluid phase volume to the volume of the sphere is identical to the corresponding volume ratio of the phases in the real column.

The advantage of representing the real column in some standard way, that is, by the geometry of X and by the distribution of certain magnitudes (as given in Table 1) over X, will become clear in the following sections.

3. A Simple Model for Chromatography

In the simplest model of chromatography the X space is represented by two adjoining rectangles as shown in Figure 3. One rectangle (area a_1) represents the part of the cross section occupied by the moving phase, the other one (area a_2) the part occupied by the stationary phase. The length l of the side common to both rectangles is equal to the area of interface per unit length of column. Other parameters can be found in Table 1 which apply also to this example.

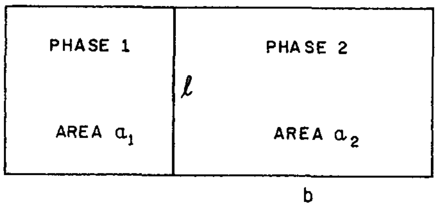


Fig. 3. *X* **space for a simple model of chromatography.** *b* **equals diffusion length.**

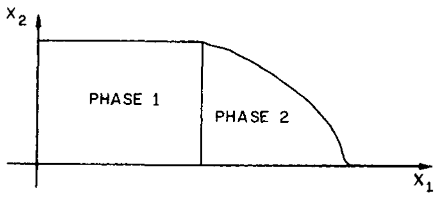


Fig. 4. X space for the case of pore length distribution.

Table 2. Distribution of the Characteristic Parameters Over X for the Model with Diffusion into Pores

	Phase 1	Phase 2
K	1	K_2
v_z	v_{z1}	0
v	0	0
D_z	D_{z1}	0
D_{11}	∞	D
D_{22}	∞	0
$D_{12} = D_{21}$	0	0

4. Diffusion into Pores of Different Length

Suppose that the tracer diffuses into pores of the stationary phase of a given length distribution. The previous representation can be easily adapted to this case (see Figure 4). The shape of the curved boundary of phase 2 is given by the pore length distribution. The parameters of the representation are listed in Table 2. This example shows that it is important to consider a diffusional tensor in the general model. If the distribution is on length and diameter, we need a third coordinate x_3, and D will depend on x_3, in general.

5. Representation of a Complex Pore System

Suppose that the diffusion of the tracer in the stationary phase takes place in a system of pores as shown schematically in Figure 5*a*. There is a small pore system which is connected via big pores with the moving phase. The X space of the general representation is shown in Figure 5*b* for this case and the parameters are listed in Table 3.

The five examples show that the representation of a chromatographic system given in the previous section is quite general. In some cases the X space represents directly the cross section of the column. Examples are Taylor dif-

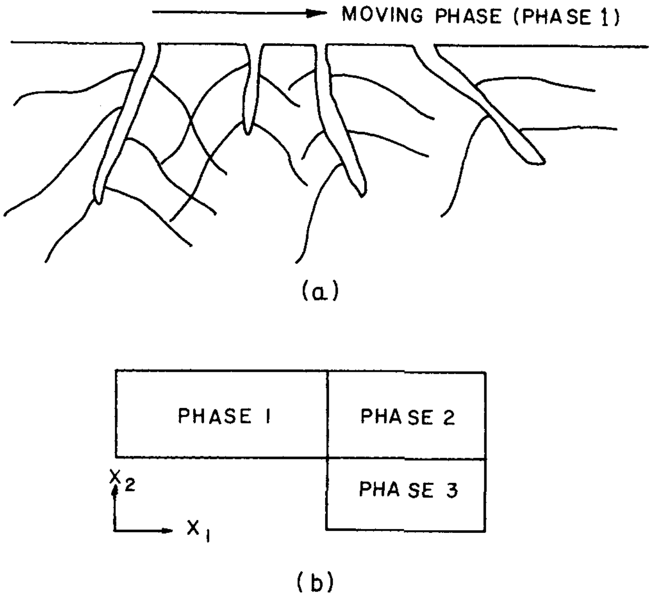


Fig. 5*a*. Schematic representation of a complex pore system. Phases 2 and 3 represent macro- and micropore systems, respectively. Fig. 5*b*. *X* space representation for a complex pore system.

fusion (example 1), Taylor diffusion in the presence of secondary flow ($\mathbf{v} \neq 0$), and a coated tube chromatographic column. In other cases the X space is an artificial construction (examples 2, 3, 4, and 5) and then it may be necessary to use a more than two-dimensional X (example 2). A four-dimensional X space will be needed, for example, if a packed column with spherical particles of given size distribution is considered.

The first step in the calculation of the dispersion coefficient is the construction of X and the determination of the magnitudes K, v_z, $\mathbf{v}$, D_z, $\mathbf{D}$, and k which are, in general, position dependent on X.

DEFINITION OF THE DISPERSION COEFFICIENT AND APPLICATION OF THE MOMENT TRANSFORMATION

Suppose that for $t < 0$ no tracer is present in the system and that at $t = 0$ a finite amount of tracer is introduced into a finite part of the column. The time-dependent distribution of the tracer belonging to such an initial condition will be called a peak. Certain parameters of the peak are independent of the way in which the tracer is distributed initially over the finite part of the column and they can also be determined easily experimentally. The calculation of such parameters from the parameters of the X space will be discussed in this and in the next section.

It is possible to characterize the peak by its moments $\mu^{(n)}(\mathbf{x}, t)$ which are defined by (see reference 2)

$$\mu^{(n)}(\mathbf{x}, t) = \int_{-\infty}^{+\infty} z^n \, c(\mathbf{x}, z, t) dz \tag{13}$$

The operation on the right-hand side of Equation (14) will be called a moment transformation and will be abbreviated by $\boldsymbol{\mu}$ in what follows. $\boldsymbol{\mu}$ transforms a function of the variable z into a function of the non-negative integers (denoted n in reference 13). Equation (14) can be written in the form

$$\mu = \boldsymbol{\mu} c \tag{14}$$

The integration over the X space will be denoted by the symbol $\boldsymbol{\alpha}$. Thus

$$\boldsymbol{\alpha} c(\mathbf{x}, z, t) = \int_X c(\mathbf{x}, z, t) dV \tag{15}$$

where dV denotes a volume element of X. The operations $\boldsymbol{\alpha}$ and $\boldsymbol{\mu}$ obviously commute:

$$\begin{aligned} M^{(n)}(t) &= \int_X \int_{z=-\infty}^{+\infty} z^n \, c(\mathbf{x}, z, t) dz \; dV \\ &= \int_{z=-\infty}^{+\infty} \int_X z^n \, c(\mathbf{x}, z, t) dV \; dz \end{aligned} \tag{16}$$

The center z^* of the peak is defined by

$$z^*(t) = \frac{M^{(1)}(t)}{M^{(0)}(t)} \tag{17}$$

and the width σ of the peak is defined by

$$\sigma^2(t) = \frac{M^{(2)}(t)}{M^{(0)}(t)} - z^{*2}(t) \tag{18a}$$

or by

$$\sigma^2(t) = \frac{M^{*(2)}(t)}{M^{(0)}(t)} \tag{18b}$$

where $M^{*(2)}$ denotes the second moment about the center of the peak.

If v_z, K, and D_z are position independent in X, if $\mathbf{v}$ and $\mathbf{D}$ are zero, and if at $t = 0$ the tracer is concentrated in a small interval about $z = 0$, then the differential Equation (5) can be integrated easily. The peak becomes a Gaussian distribution, the center and width of which are given by

TABLE 3. DISTRIBUTION OF THE CHARACTERISTIC PARAMETERS OVER X FOR A COMPLEX PORE SYSTEM. PHASE 2 REPRESENTS THE MACROPORE SYSTEM AND PHASE 3 THE MICROPORE SYSTEM

	Phase 1	Phase 2	Phase 3
K	1	K_2	K_3
v_z	v_{z1}	0	0
$\mathbf{v}$	0	0	0
D_z	D_{z1}	0	0
D_{11}	∞	D_2	0
D_{22}	∞	∞	D_3
$D_{12} = D_{21}$	0	0	0

$$z^*(t) = v_z t \tag{19a}$$

$$\sigma^2(t) = 2D_z t \tag{19b}$$

It will be shown later that in the general case z^* and σ are given by

$$z^*(t) = v^* t + C_1 + \exp \tag{20a}$$

$$\sigma^2(t) = 2D^* t + C_2 + \exp \tag{20b}$$

Here exp stands for terms which decrease exponentially with time. These terms and the constants C_1 and C_2 depend on the initial conditions, that is, on the way in which the tracer has been distributed initially over the column. The constants v^* and D^* are independent of the initial conditions; they depend only on the distribution of the characteristic parameters over the cross section. v^* and D^* will be called asymptotic center velocity and dispersion coefficient, respectively.

In order to calculate v^* and D^* in the general case, the moment transformation will be applied to Equation (5). $\boldsymbol{\mu}$ commutes with all differential operators except with $\partial/\partial z$. However, it can be shown easily by integration by parts (see reference 2) that

$$\boldsymbol{\mu} \; \partial/\partial z = - \mathfrak{S} \; \boldsymbol{\mu} \tag{21}$$

where the operator $\mathfrak{S}$ is defined by

$$\begin{aligned} \mathfrak{S}\mu^{(n)} &= n\mu^{(n-1)}, \quad n \geq 1 \\ \mathfrak{S}\mu^{(0)} &= 0 \end{aligned} \tag{22}$$

Application of $\boldsymbol{\mu}$ to Equation (5) transforms this equation into a set of relations for $n = 0, 1, 2, \ldots\ldots$ Only the first three of these relations will be needed:

$$\frac{\partial \mu^{(0)}}{\partial t} = - \mathbf{v} \cdot \nabla \mu^{(0)} + \nabla \cdot \mathbf{D} \cdot \nabla \mu^{(0)} \tag{23a}$$

$$\frac{\partial \mu^{(1)}}{\partial t} = v_z \mu^{(0)} - \mathbf{v} \cdot \nabla \mu^{(1)} + \nabla \cdot \mathbf{D} \cdot \nabla \mu^{(1)} \tag{23b}$$

$$\begin{aligned} \frac{\partial \mu^{(2)}}{\partial t} = 2v_z \mu^{(1)} + 2D_z \mu^{(0)} - \mathbf{v} \cdot \nabla \cdot \mu^{(2)} \\ + \nabla \cdot \mathbf{D} \cdot \nabla \mu^{(2)} \end{aligned} \tag{23c}$$

The boundary conditions in Equation (7) transform into

$$\mathbf{n} \cdot \mathbf{D} \cdot \nabla \mu^{(n)} = k \Delta \frac{\mu^{(n)}}{K} \quad \text{at } B \tag{24}$$

INTEGRATION OF THE MOMENT EQUATIONS

The homogeneous and linear partial differential Equation (23a) can be interpreted as an equation describing the transport of a substance within the X space. The concentration of this substance is denoted by $\mu^{(0)}$. The equilibrium concentration is given by

$$\mu^{(0)} = \text{const. } K \tag{25}$$

Obviously this satisfies the differential Equation (23*a*) and the boundary conditions in Equation (24), and therefore Equation (25) is a particular solution of Equation (24). For physical reasons this concentration distribution should be approached from any initial condition in such a way that for large times the difference between Equation (25) and the actual concentration decreases exponentially with time. Mathematically this result can be obtained by an eigenfunction expansion. Putting the trial function

$$\mu^{(0)}\,(\mathbf{x}, t) = y(\mathbf{x})e^{\lambda t} \tag{26}$$

into Equation (23*a*) yields

$$\lambda y = -\,\mathbf{v}\cdot\nabla\, y + \nabla\cdot\mathbf{D}\cdot\nabla\, y \tag{27}$$

Because of the positive definiteness of $\mathbf{D}$, the eigenvalues of this equation are nonpositive real numbers. This follows from multiplying Equation (27) by y/K, integrating the result over each subspace occupied by one phase, applying the divergence theorem, and summing up over all the phases under consideration of the boundary conditions:

$$\mathbf{n}\cdot\mathbf{D}\cdot\nabla y = k\,\Delta(y/K) \quad \text{at} \quad B \tag{28}$$

The result thus obtained is

$$\lambda \int_X \frac{1}{K}\, y^2\, dV = -\frac{1}{K}\int_X (\nabla y)\cdot D\cdot(\nabla y)\, dV - \int_B k(\Delta\; y/K)^2\, dS \tag{29}$$

where dS denotes the $n-1$ dimensional surface element of an interface B. Since D is positive definite and k and K are positive, it follows that

$$\lambda \leqq 0 \tag{30}$$

Therefore the general solution of Equation (23*a*) is given by

$$\mu^{(0)} = \text{const}\cdot K + \exp \tag{31}$$

It is easily seen that the exp terms will generate again exponentially decreasing terms in the solutions of Equations (23*b*) and (23*c*) if Equation (31) is put into Equation (23*b*). Since only the asymptotic behavior of the solutions will be studied in this paper, the exponential terms can be omitted. Furthermore, the constant in Equation (31) can be set equal to unity without loss of generality since only ratios of the moments will appear in the final result. Thus the solution of Equation (23*a*) used in the following is given by

$$\mu^{(0)} = K \tag{32}$$

Putting Equation (32) into the partial differential Equation (23*b*) yields

$$\frac{\partial\mu^{(1)}}{\partial t} = Kv_z - \mathbf{v}\cdot\nabla\,\mu^{(1)} + \nabla\;\cdot D\cdot\nabla\,\mu^{(1)} \tag{33}$$

This relation can be interpreted physically as an equation describing the transport of a substance, the concentration of which is denoted by $\mu^{(1)}$, in the X space in the presence of sources. The local source intensity is given by Kv_z. Since no material can pass the boundary of X and since the integral source intensity $\alpha\; K\, v_z$ does not vanish necessarily, the differential Equation (34) will not admit time-independent solution in general. Mathematically this is obtained in the following way. From the divergence theorem it follows that for the boundary conditions given by Equation (25)

$$\alpha\cdot\mathbf{v}\cdot\nabla\,\mu^{(n)} = \alpha\nabla\cdot\mathbf{D}\cdot\nabla\,\mu^{(n)} = 0 \tag{34}$$

Thus, if α is applied to Equation (33) it follows that

$$\frac{d}{dt}\,\alpha\,\mu^{(1)} = \alpha\; Kv_z \tag{35}$$

Hence, for a stationary solution the total source strength must be zero.

In order to find a particular solution of Equation (34), the following trial function can be used:

$$\mu^{(1)}(\mathbf{x}, t) = KHt + \psi(\mathbf{x}) \tag{36}$$

where H is a time- and position-independent constant and ψ is a function depending on position alone. Putting Equation (36) into Equation (33) yields

$$KH = Kv_z - \mathbf{v}\cdot\nabla\,\psi + \nabla\cdot\mathbf{D}\cdot\nabla\,\psi \tag{37}$$

This equation describes the steady state distribution of a fictitious substance in X (concentration ψ) which is created in X by sources of intensity

$$Kv_z - KH \tag{38}$$

and is transported by the velocity field described by v and by a diffusional mechanism described by $\mathbf{D}$. It can be seen that $\mu^{(1)}$ given by Equation (36) will satisfy the boundary conditions in Equation (24) if ψ satisfies

$$\mathbf{n}\cdot\mathbf{D}\cdot\nabla\psi = k\,\Delta(\psi/K) \quad \text{at} \quad B \tag{39}$$

In the case of zero mass resistance at an interface ($k = \infty$), ψ/K is continuous across that interface.

For reasons discussed previously solution of Equation (37) under the condition of Equation (33) exists only if

$$\alpha(Kv_z - KH) = 0 \tag{40}$$

It follows that

$$H = \frac{\alpha\; Kv_z}{\alpha K} \tag{41}$$

The operation on the right-hand side of Equation (41) corresponds to averaging v_z over X with K as weight. This operation will be denoted by a bar. Thus

$$H = \bar{v}_z \tag{42}$$

The particular solution of Equation (33) becomes

$$\mu^{(1)} = K\bar{v}_z t + \psi \tag{43}$$

It should be noted that ψ/K is only determined up to a position-independent constant. This fact, as well as the general form of Equation (43), agrees with what one would expect intuitively if one considers the source problems associated with Equations (33) and (24). If the undetermined additive constant in ψ/K is taken into account, the general solution of Equation (33) differs from Equation (43) only by terms which decrease exponentially with t. These terms will be omitted in the following discussion for reasons explained previously.

Application of α to Equation (32) yields

$$M^{(0)} = \alpha\; K \tag{44}$$

Application of α to Equation (43) yields

$$M^{(1)} = \bar{v}_z\; \alpha\; Kt + \alpha\;\psi \tag{45}$$

Hence

$$\frac{M^{(1)}}{M^{(0)}} = \bar{v}_z t + \overline{\psi/K} \tag{46}$$

Applying α to Equation (23*c*) under consideration of

Equation (34) yields

$$\frac{dM^{(2)}}{dt} = 2\,\alpha\, v_z\, \mu^{(1)} + 2\,\alpha\, D_z\, \mu^{(0)} \qquad (47)$$

Substituting for $\mu^{(1)}$ and $\mu^{(0)}$ the expressions from Equations (32) and (43), respectively, and dividing by $M^{(0)}$ yields

$$\frac{1}{M^{(0)}}\frac{dM^{(2)}}{dt} = 2\,\bar{v}_z^2 t + 2(\overline{v_z\,\psi/K} + \bar{D}_z) \qquad (48)$$

By integration the following result can be obtained:

$$\frac{M^{(2)}}{M^{(0)}} = \bar{v}_z^2 t^2 + 2(\overline{v_z\,\psi/K} + \bar{D}_z)t + \text{const.} \qquad (49)$$

From this and Equations (17), (18*a*), and (46) it follows that

$$\sigma^2 = 2(\overline{v_z\,\psi/K} - \bar{v}_z \cdot \overline{\psi/K} + \bar{D}_z)t + \text{const.} \qquad (50)$$

Thus according to Equation (20*b*)

$$D^* = \overline{v_z\,\psi/K} - \bar{v}_z \cdot \overline{\psi/K} + \bar{D}_z \qquad (51)$$

or

$$D^* = \overline{(v_z - \bar{v}_z)\,\psi/K} + \bar{D}_z \qquad (52)$$

SUMMARY OF THE CALCULATION PROCEDURE

The asymptotic center velocity and the dispersion coefficient can be calculated in four steps.

Step I: The chromatographic system has to be represented by a cross-sectional space X (if necessary more than two-dimensional) and by the distribution of certain parameters over it.

Step II: The asymptotic center velocity v^* is given by [see Equations (17), (20*a*), and (46)]

$$v^* = \bar{v}_z \qquad (53)$$

where the bar denotes a K-weighted average over X.

Step III: A source problem in X has to be solved. This source problem is defined as follows. Consider a fictitious substance (concentration ψ) which is transported convectively by the velocity field v and in addition by a diffusion mechanism described by the tensor field **D**. There may be interfaces with a mass transfer resistance. The diffusional flux across such an interface equals $k\,\Delta\,\psi/K$ [see Equation (39)]. The boundaries of X are impermeable for the fictitious substance. The substance is created in X by sources of intensity [see Equations (38) and (42)].

$$Kv_{zr} \qquad (54)$$

where v_{zr}, the relative velocity, is given by

$$v_{zr} = v_z - \bar{v}_z \qquad (55)$$

The integral source intensity is then zero in X. The steady state concentration ψ of the substance is determined only up to a constant multiple of K, that is, ψ can be assumed arbitrarily at one point of X.

Step IV: If the source problem is solved, that is, if ψ is known, the dispersion coefficient can be calculated in the following way [see Equations (51), (52), and (55)]:

$$D^* = D_T^* + \bar{D}_z \qquad (56)$$

D_T^*, the Taylor contribution to the dispersion, is given by

$$D_T^* = \overline{v_{zr}\,\psi/K} \qquad (57)$$

Because of

$$\overline{v_{zr}} = 0 \qquad (58)$$

the undetermined constant in ψ/K has no influence on the result. It can be shown (see next section) that D_T^* is always non-negative as would be expected intuitively.

THE DISPERSION COEFFICIENT AS MAXIMUM OF A FUNCTIONAL

In order to simplify the following equations, it will be assumed that

$$\alpha\, K = \int_X K dV = 1 \qquad (59)$$

Since K is determined only up to a position-independent factor, it is always possible to define K such that Equation (59) is valid. Equation (57) then becomes

$$D_T^* = \alpha\, v_{zr}\, \psi \qquad (60)$$

ψ satisfies the relation [see Equations (37), (42), and (55)]

$$K\, v_{rz} - \mathbf{v} \cdot \nabla\, \psi + \nabla \cdot \mathbf{D} \cdot \nabla\, \psi = 0 \qquad (61)$$

From this and Equation (60) it follows that

$$D_T^* = \alpha(\psi\, \mathbf{v} \cdot \nabla\psi - \psi\nabla \cdot \mathbf{D} \cdot \nabla\psi)/K \qquad (62)$$

This can be transformed by the divergence theorem using boundary conditions for ψ similarly as discussed previously in connection with Equations (28) and (29). The result is given by

$$D_T^* = \int_X (\nabla\psi) \cdot \mathbf{D} \cdot (\nabla\psi)/K\, dV + \int_B k(\Delta\psi/K)^2\, dS \qquad (63)$$

Since **D** is positive definite and k is positive, it follows that

$$D_T^* \geqq 0 \qquad (64)$$

a result which is obvious intuitively.

For the following discussion it will be assumed that the velocity has no component in the X space:

$$\mathbf{v} = 0 \qquad (65)$$

From Equations (60) and (63) it follows that D_T^* is given by

$$D_T^* = F[\psi] \qquad (66)$$

where F is the functional acting on ψ defined by

$$F[\psi] = \int_X [2\psi v_{zr} - (\nabla\psi) \cdot \mathbf{D} \cdot (\nabla\psi)/K]dV - \int_B k(\Delta\psi/K)^2\, dS \qquad (67)$$

This functional will be shown to assume its maximum value for the function ψ defined by the source problem by proving that for any function ψ^*

$$F[\psi + \psi^*] \leqq F[\psi] \qquad (68)$$

where ψ is defined by the source problem. Inserting $\psi + \psi^*$ into F yields

$$F[\psi + \psi^*] = F[\psi] - \int_X (\nabla\psi^*) \cdot \mathbf{D} \cdot (\nabla\psi^*)/K\, dV - \int_B k(\psi^*/K)^2\, dS + 2P \qquad (69)$$

where P is given by

$$P = \int_X [\psi^* v_{zr} - (\nabla\psi^*) \cdot \mathbf{D} \cdot (\nabla\psi)/K]dV - \int_D k(\Delta\psi^*/K)(\Delta\psi/K)dS \qquad (70)$$

By using the identity

$$(\nabla\psi^*)\cdot\mathbf{D}\cdot(\nabla\psi) = \nabla\cdot(\psi^*\,\mathbf{D}\cdot\nabla\psi) - \psi^*\,\nabla\cdot\mathbf{D}\cdot\nabla\psi \qquad (71)$$

and by applying the divergence theorem to each subregion occupied by a phase followed by summing over all phases, this can be transformed into

$$P = \int_X \psi^*\,[Kv_{zr} + \nabla\cdot\mathbf{D}\cdot\nabla\psi]/K\,dV \qquad (72)$$

(The integral over B cancels out when the boundary conditions for ψ are considered.) The integral in Equation (72) vanishes for any ψ^* because the term in the brackets is identically zero [see Equations (61) and (65)]. Since P is zero, $\mathbf{D}$ is positive definite, and K and k are positive, the inequality (68) follows from (69). Thus $D_T{}^*$ can be expressed as the maximum of a functional

$$D_T{}^* = \max_{\varphi} \int_X [2\varphi v_{zr} - (\nabla\varphi)\cdot\mathbf{D}\cdot(\nabla\varphi)/K]\,dV - \int_B k(\Delta\varphi/K)^2\,dS \qquad (73)$$

The maximization is to be carried out over all functions φ which are differentiable in the interior of the regions occupied by the different phases (in subregions of volume zero differentiability is not required if φ is continuous everywhere except possibly at B). Any such arbitrary function inserted into the functional will produce a lower bound for the dispersion coefficient.

Slight modifications are necessary if mass transfer resistance is negligible. One obtains the following result without difficulty.

If $k = \infty$ at a given interface then one has to set

$$k(\Delta\varphi/K)^2 = 0 \qquad (74)$$

in Equation (75) and the function φ/K must be continuous across that particular interface. Similarly, if $D = \infty$ in a subregion one has to set

$$(\nabla\varphi)\cdot\mathbf{D}\cdot(\nabla\varphi) = 0 \qquad (75)$$

in this subregion and φ must be chosen constant ($\nabla\varphi = 0$) in that region.

It is well known that good estimates for the extreme of a functional can be obtained by applying the functional to a function containing several parameters and then extremizing the function of the parameters thus obtained. An example will be given in the next section. This method does not give good approximations for the extremizing function itself, but in the problem in question this function, that is, ψ, is of no physical significance.

Another advantage of the representation (73) is the possibility of obtaining directly the first-order perturbation of D^* with respect to the variation of parameters of a problem. Suppose that p is some parameter, for example, a parameter on which the velocity profile depends. The functional F then will depend on p explicitly and also implicitly through the dependence of ψ on p. Denote, for the moment, with p_1 the parameter occurring explicitly in F and with p_2 the parameter occurring in ψ then

$$D_T{}^* = F_{p_1}[\psi_{p_2}] \qquad (76)$$

and

$$\frac{dD_T{}^*}{dp} = \frac{\partial F}{\partial p_1} + \frac{\partial F}{\partial p_2} \qquad (77)$$

The second derivative on the right-hand side of this equation is zero because of the maximum property so that

$$\frac{dD_T{}^*}{dp} = \frac{\partial F}{\partial p} \qquad (78)$$

where now the differentiation of F is to be carried out for fixed ψ [corresponding to the differentiation with respect to p_1 in (77)].

As an example assume that v_z depends on a parameter p. Then

$$\frac{dD_T{}^*}{dp} = 2\int_X \psi\,\frac{\partial v_{zr}}{\partial p}\,dV \qquad (79)$$

Thus in order to obtain the perturbation of $D_T{}^*$ only an integration has to be carried out. It is not necessary to solve the more difficult problem of finding the perturbation of ψ.

EXAMPLES

1. Taylor Diffusion

The dispersion coefficient for laminar flow in a circular tube has been calculated by Taylor (*1*) and by Aris (*2*). It is given by

$$D_T{}^* = \frac{R^2 v_0{}^2}{192D} \qquad (80)$$

In this case an analytical solution of the source problem is easily obtained. The variational method of the previous section will be tested with Taylor's probelm.

The function

$$\varphi = \alpha r^2 + \beta r^4 \qquad (81)$$

is an obvious trial function. It yields, after maximization of the functional in Equation (73) (set $K = 1/\pi R^2$ and omit integral over B) with respect to α and β, the correct result (80). The parameters α and β obtained are given by

$$\alpha = -\frac{v_0}{8D} \qquad \beta = \frac{v_0}{16DR^2} \qquad (82)$$

If these parameters are put into Equation (81), the exact ψ as defined by the source problem is obtained.

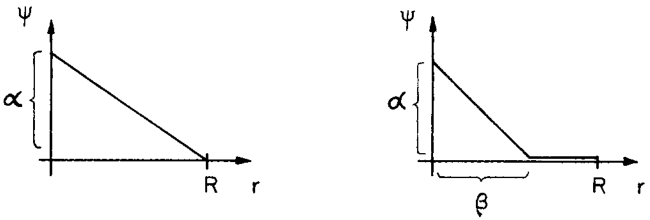
In Figure 6 two trial functions are shown which are obviously not good approximations of the correct ψ (corners and violation of the natural boundary condition in one case). Trial function (*a*) yields

$$D_T{}^* = \frac{R^2 v_0{}^2}{225D} \qquad (83)$$

In this function only one parameter α is available for maximization. The two-parameter trial function (*b*) which contains function (*a*) as a special case yields

$$D_T{}^* = \frac{R^2 v_0{}^2}{207.4D} \qquad (84)$$

These results appear to be quite food if one considers the simplicity of the trial functions chosen.



(a) (b)

Fig. 6. Trial functions for Taylor's problem.

2. Chromatography in a Packed Column

The necessary information about the X space is given by Figure 2 and Table 1. The K-weighted average of the velocity is given by

$$\bar{v}_z = \frac{V_1}{V_1 + K_2V_2}\, v_{z1} \tag{85}$$

From this

$$Kv_{zr} = \begin{cases} \dfrac{K_2V_2}{V_1 + K_2V_2}\, v_{z1} & \text{in phase 1} \\ \dfrac{K_2V_1}{V_1 + K_2V_2}\, v_{z1} & \text{in phase 2} \end{cases} \tag{86}$$

The steady state distribution in a sphere of a substance, the local rate of disappearance of which is given by

$$K_2V_1v_{z1}/(V_1 + K_2V_2)$$

is easily found to

$$\psi = \frac{K_2V_1}{V_1 + K_2V_2}\, \frac{v_{z1}}{6D}\, r^2 + \text{const.} \tag{87}$$

Since ψ can be assumed arbitrarily at one point of X, the constant in Equation (87) can be set equal to zero. The value of ψ in phase 1 is constant since $D = \infty$ in this phase. This constant value can be determined from the boundary condition

$$4\pi R^2k\Delta \frac{\psi}{K} = \frac{K_2V_1V_2}{V_1 + K_2V_2}\, v_{z1} \tag{88}$$

Thus the following result is obtained:

$$\psi = \begin{cases} \dfrac{K_1V_1v_{z1}}{V_1 + K_2V_2} \left(\dfrac{R^2}{6D} + \dfrac{K_2V_2}{4\pi R^2k} \right) & \text{in phase 1} \\ \dfrac{K_2V_1v_{z1}}{V_1 + K_2V_2}\ \dfrac{r^2}{6D} & \text{in phase 2} \end{cases} \tag{89}$$

After the averaging procedure of Equation (57) is carried out, it is found that

$$D_T{}^* = \frac{K_2{}^2V_1{}^2V_2}{(V_1 + K_2V_2)^3} \left[\frac{v_{z1}{}^2R^2}{15K_2D} + \frac{v_{z1}{}^2R}{3k} \right] \tag{90}$$

3. Simple Model of Chromatography

The problem defined by Figure 3 and Table 1 will be solved by the variational method for negligible diffusional resistance in both phases. In this case ψ/K is position independent within each phase. If ψ and φ are set zero in phase 2 and if the normalization procedure of Equation (59) is carried out, Equation (73) becomes

$$D_T{}^* = \frac{1}{a_1 + K_2a_2} \max_{\varphi} \left\{ \frac{2K_2a_1a_2v_{z1}}{a_1 + K_2a_2}\, \varphi_1 - kl\varphi_1{}^2 \right\} \tag{91}$$

where φ_1 is now position independent. From this

$$D_T{}^* = \frac{1}{a_1 + K_2a_2} \left(\frac{K_2a_1a_2}{a_1 + K_2a_2} \right)^2 \frac{v_{z1}{}^2}{kl} \tag{92}$$

It will be shown that this agrees with the result obtained for a packed column in example 2. If the simple model of chromatography is applied to the packed column, one has

$$\frac{a_1}{a_2} = \frac{V_1}{V_2}, \quad \frac{l}{a_2} = \frac{4\pi R^2}{\dfrac{1}{3}\, 4\pi R^3} = \frac{3}{R} \tag{93}$$

Thus from Equation (92)

$$D_T{}^* = \frac{K_2{}^2V_1{}^2V_2}{(V_1 + K_2V_2)^3}\, \frac{v_{z1}{}^2R}{3k} \tag{94}$$

This agrees with Equation (90) if $D = \infty$, which corresponds to no resistance to mass transfer within the packing.

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NOTATION

a = area
B = boundary of cross-sectional space or interfacial boundary
c = tracer concentration
$\mathbf{D}$ = *diffusivity tensor in cross-sectional space*
D_z = axial diffusivity
D^* = dispersion coefficient as defined by Equation (20*b*)
$D_T{}^*$ = Taylor contribution as defined by Equation (56)
F = functional as defined by Equation (67)
H = constant as defined by Equation (36)
I = unit tensor
k = mass transfer coefficient
K = equilibrium constant
$M^{(n)}$ = integral n^{th} moment as defined by Equation (16)
$\mathbf{n}$ = vector of unit length normal to boundary
n = dimension of cross-sectional space
N = number of particles per unit volume of column
p = parameter in perturbation problem, Equation (76)
$\mathbf{q}$ = flux of tracer
r = radial coordinate in circle or sphere
R = radius of circle or sphere
dS = boundary element
t = time
$\mathbf{v}$ = fluid velocity vector in cross-sectional space
v_z = axial velocity
v_{zr} = axial relative velocity as defined by Equation (55)
v_0 = center velocity in Poiseuille flow
v^* = asymptotic peak velocity as defined by Equation (20*a*)
$\mathbf{x}$ = vector (coordinates $x_1, x_2, \ldots$) defining point in cross-sectional space
X = cross-sectional space, see Figure 1
z = axial coordinate, see Figure 1
z^* = center of peak as defined by Equation (17)

Greek Letters

α = parameter, Equation (81)
$\boldsymbol{\alpha}$ = operator as defined by Equation (15)
β = parameter, Equation (81)
$\boldsymbol{\beta}$ = operator as defined by Equation (22)
ϵ = void fraction in packed column
λ = eigenvalue
$\mu^{(n)}$ = *n^{th} moment as defined by Equation* (13)
$\boldsymbol{\mu}$ = operator, defined by Equation (13)
σ = variance or peak-width as defined by Equation (18)
φ = function as defined by Equation (73)
ψ = concentration of a fictitious substance in the source problem, see Equation (36)

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