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CONTRIBUTIONS TO THE THEORY OF CHROMATOGRAPHY

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SUMMARY

A general approach to the theory of chromatography, based on the method of moments, is presented. A detailed treatment of packed columns is given, and the steady-state equations for solute transport in such columns are derived. Special consideration is given to the effects that arise from variations in the properties of the packing material. It is shown that non-uniformities in the packing material tend to make the chromatographic peaks more unsymmetrical.

INTRODUCTION

The main obstacle to the development of an universal theory of chromatography is not the lack of knowledge of the basic physical processes involved, but the diversity and inherent complexity of the overall process itself. Thus, the chromatographic process is in general not amenable to an exact theoretical treatment, and one has to resort to simplified models, such as the stochastic theory of Giddings¹ or the diffusion model treatment of the present author². However, for some important variants of chromatography, where the operating conditions and column geometry are sufficiently simple, an exact theoretical treatment is possible. At present this is definitely true only for open-tubular columns with a linear sorption isotherm. A solution to this problem was first given by Golay³, the treatment being later generalized by Aris⁴. The latter approach was based on the method of moments* and thus introduced a new, powerful tool into the theory of chromatography. Unfortunately, the paper by Aris seems to have been overlooked by most workers in the field of chromatography, and the fundamental nature of his work has therefore not been generally recognized. In this paper, the application of the method of moments to chromatography is reconsidered. It is shown that the treatment can be extended in a natural way to packed columns of various geometries. Although the treatment in this instance is necessarily approximate, the model used is sufficiently realistic to make the results applicable to most columns of practical interest.

* In this paper the term "method of moments" refers to the use of statistical moments as a means of transforming differential equations. The author, unaware of the work of Aris⁴, used this method earlier in the treatment based on the diffusion model².

SPECIFICATION OF THE MODEL

For packed columns, an exact treatment of the transport processes in the column is not possible, mainly because the velocity field in the mobile phase is unknown. It is therefore necessary to use a model in which appropriate simplifications have been made. In this treatment we assume the column packing to consist of spherical particles (a similar treatment can be carried out for other particle geometries). We assume that a spherical shell of arbitrary depth is available to the solute, the treatment thus being applicable to both gas-liquid and gel chromatography.

The approximations involved in the model are best understood by following the derivation of the equation for mass balance. Thus, we consider a column of uniform cross-section, filled with a suspension of spherical particles in a fluid. Taking the x -axis parallel to the column axis, we assume that under the influence of a pressure gradient the fluid flows through the column in the direction of the x -axis. The actual velocity field in the interparticle space is too complex for a direct analysis. However, the velocity field contains substantial radial components, which vanish when averaged over a cross-section of the column. To some extent, these radial components of the velocity field cause a convective mixing of the fluid in a cross-section of the column. As a first approximation we therefore replace the actual velocity field by the average velocity, u , in the direction of the x -axis (plug flow), and assume complete convective mixing of the fluid in a cross-section of the column. Deficiencies in the last assumption can be compensated for by adding an extra "eddy diffusion" term to the axial diffusivity in the fluid.

A second approximation is introduced by assuming the particles to be surrounded by fluid of uniform solute concentration. In the spherical particles, therefore, only radial diffusion needs to be considered. The error involved in this approximation decreases when the flow-rate increases, and is probably very small in operative columns. With the above assumptions, the equation for mass balance in a segment of the column can be written. In the fluid phase we obtain the differential equation

$$\frac{\partial c_1}{\partial t} = -u \cdot \frac{\partial c_1}{\partial x} + D_1' \cdot \frac{\partial^2 c_1}{\partial x^2} + \frac{Sn\sigma}{S_1} \cdot j \quad (1)$$

where S is the cross-sectional area of the column, S_1 the average cross-sectional area of the fluid phase, c_1 the concentration in the fluid phase, D_1' the coefficient of axial diffusivity in the fluid phase, n the number of particles per unit volume of the column, σ the surface area of a particle and j the solute diffusion flux at the particle surface (counted as positive in the outward direction).

We assume that the equilibrium distribution of solute between the fluid and a particle is determined by the partition coefficient, K :

$$c_2 = Kc_1 \quad (2)$$

where c_2 is the concentration in the particle.

The solute diffusion flux, j , is then given by

$$j = k(c_2 - Kc_1)_{R_1} \quad (3)$$

where the subscript R_1 refers to the surface of the spherical particle and k is the rate constant for solute transfer across the interface between the phases.

Thus, the differential equation for solute transport in the fluid phase is

$$\frac{\partial c_1}{\partial t} = -u \cdot \frac{\partial c_1}{\partial x} + D_1 \cdot \frac{\partial^2 c_1}{\partial x^2} + \frac{Skn\sigma}{S_1} (c_2 - Kc_1)_{R_1} \quad (4)$$

In the stationary phase, solute transport is governed by the diffusion equation for spheres:

$$\frac{\partial c_2}{\partial t} = D_2 \left(\frac{\partial^2 c_2}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c_2}{\partial r} \right) \quad R_2 < r < R_1 \quad (5)$$

where D_2 is the diffusion coefficient in the stationary phase, r is the radial coordinate in the sphere, R_1 is the radius of the sphere and R_2 is the inner radius of the sorbing shell.

APPLICATION OF THE METHOD OF MOMENTS

It is not necessary to solve eqns. 4 and 5 for the solute distribution functions, but adequate information can be obtained from the moments of the distributions. We thus define the moments ($i \geq 0$)

$$F_i = \int_{-\infty}^{\infty} x^i c_1 dx \quad (6a)$$

and

$$G_i = \int_{-\infty}^{\infty} x^i c_2 dx \quad (6b)$$

where uniform convergence of the integrals is assumed.

The time derivatives of the moments take the form

$$\dot{F}_i = \int_{-\infty}^{\infty} x^i \cdot \frac{\partial c_1}{\partial t} \cdot dx \quad (7a)$$

and

$$\dot{G}_i = \int_{-\infty}^{\infty} x^i \cdot \frac{\partial c_2}{\partial t} \cdot dx \quad (7b)$$

To evaluate these derivatives, eqns. 4 and 5 are substituted into eqn. 7. We then have to consider integrals of the following type:

$$\int_{-\infty}^{\infty} x^i \cdot \frac{\partial c_1}{\partial x} \cdot dx = \int_{-\infty}^{\infty} x^i c_1 - i \int_{-\infty}^{\infty} x^{i-1} c_1 dx = \begin{cases} 0 & \text{for } i = 0 \\ -i F_{i-1} & \text{for } i \geq 1 \end{cases} \quad (8)$$

and

$$\int_{-\infty}^{\infty} x^i \cdot \frac{\partial^2 c_1}{\partial x^2} \cdot dx = \int_{-\infty}^{\infty} x^i \cdot \frac{\partial c_1}{\partial x} - i \int_{-\infty}^{\infty} x^{i-1} \cdot \frac{\partial c_1}{\partial x} \cdot dx = \begin{cases} 0 & \text{for } i = 0, 1 \\ i(i-1) F_{i-2} & \text{for } i \geq 2 \end{cases} \quad (9)$$

Similar equations are valid for the concentration c_2 .

Thus, with the help of eqns. 8 and 9, eqns. 4 and 5 are transformed into the following equations for the moments:

$$\dot{F}_i = i u F_{i-1} + i(i-1) D_1' F_{i-2} + \frac{Skn\sigma}{S_1} (G_i - KF_i)_{R_1} \quad (10)$$

and

$$\dot{G}_i = D_2 \left(\frac{\partial^2 G_i}{\partial r^2} + \frac{2}{r} \frac{\partial G_i}{\partial r} \right) \quad (11)$$

for $i = 0, 1, 2 \dots$ (in eqn. 10 we have to put $F_i = 0$ for $i < 0$).

The general solutions of these differential equations consist of a transient part, which depends on the form of the original concentration distribution in the column, and a steady-state part, which is independent of the original distribution. It can be shown that the transient terms decrease exponentially with time, and the conditions in the column rapidly approach the steady state conditions^{4,5}. With columns of normal length it is sufficient to consider only the steady-state solutions of eqns. 10 and 11.

To make the integration of eqns. 10 and 11 possible, we have to introduce the boundary conditions at the phase boundaries and the condition for conservation of mass. The boundary conditions are

$$\left(\frac{\partial G_i}{\partial r} \right)_{R_2} = 0 \quad (12)$$

and

$$D_2 \left(\frac{\partial G_i}{\partial r} \right)_{R_1} = -k (G_i - KF_i)_{R_1} \quad (13)$$

To obtain the condition for conservation of mass, we have to consider moments for the total solute distribution in the column. Defining first the average moments in the stationary phase, we have

$$\bar{G}_i = \frac{1}{V} \int V G_i dV \quad (14)$$

where the integration is carried out over the volume of the spherical shell. The moments of the total solute distribution now become

$$M_i = S_1 F_i + n SV \bar{G}_i \quad (15)$$

DETERMINATION OF THE ZEROth MOMENT

For the zeroth moment we obtain from eqns. 10 and 11

$$\dot{F}_0 = \frac{Skn\sigma}{S_1} (G_0 - KF_0)_{R_1} \quad (16)$$

and

$$\dot{G}_0 = D_2 \left(\frac{\partial^2 G_0}{\partial r^2} + \frac{2}{r} \frac{\partial G_0}{\partial r} \right) \quad (17)$$

From eqns. 14 and 17 we obtain for the average moment in the stationary phase

$$\dot{\bar{G}}_0 = \frac{4\pi}{V} \int_{R_2}^{R_1} \dot{G}_0 r^2 dr = \frac{\sigma D_2}{V} \left(\frac{\partial G_0}{\partial r} \right)_{R_1} \quad (18)$$

where we have used the boundary condition in eqn. 12, and the relationship $\sigma = 4\pi R_1^2$. From eqns. 16 and 18 and the boundary condition 13 we obtain

$$\dot{M}_0 = S_1 \dot{F}_0 + nSV \dot{\bar{G}}_0 = 0 \quad (19)$$

Thus

$$M_0 = S_1 F_0 + nSV \bar{G}_0 = \text{constant} \quad (20)$$

is the condition for conservation of mass, M_0 being the total amount of solute in the column. Furthermore, from the steady state solutions of eqns. 16 and 17 we obtain

$$G_0 = KF_0 \quad (21)$$

and

$$M_0 = F_0(S_1 + nKSV) \quad (22)$$

In determining the steady-state solutions for the higher moments, we normalize the concentration distribution functions. We then define the moments of the normalized distribution functions as follows:

$$= \frac{F_i}{F_0} \quad (23a)$$

$$g_i = \frac{G_i}{G_0} \quad (23b)$$

$$\bar{g}_i = \frac{\bar{G}_i}{G_0} \quad (24)$$

$$m_i = \frac{M_i}{M_0} = w_1 f_i + w_2 \bar{g}_i \quad (25)$$

where

$$w_1 = \frac{S_1}{S_1 + nKSV} \quad (26a)$$

and

$$w_2 = \frac{nKSV}{S_1 + nKSV} \quad (26b)$$

are the weight fractions of solute in the mobile and stationary phases, respectively.

For the normalized moments the boundary conditions are

$$\left(\frac{\partial g_i}{\partial r}\right)_{R_2} = 0 \quad (27)$$

and

$$D_2 \left(\frac{\partial g_i}{\partial r}\right)_{R_1} = -k(g_i - f_i)_{R_1} \quad (28)$$

DETERMINATION OF THE FIRST MOMENT

The normalized first moment determines the position of the centre of gravity of the solute distribution within the column. For the individual first moments we obtain from eqns. 10 and 11, after normalization

$$\dot{f}_1 = u + \frac{kn\sigma KS}{S_1} (g_1 - f_1)_{R_1} \quad (29)$$

and

$$\dot{g}_1 = D_2 \left(\frac{\partial^2 g_1}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial g_1}{\partial r} \right) \quad (30)$$

The average first moment in the stationary phase is given by

$$\dot{\bar{g}}_1 = \frac{4\pi}{V} \int_{R_2}^{R_1} \dot{g}_1 r^2 dr = \frac{\sigma D_2}{V} \left(\frac{\partial g_1}{\partial r}\right)_{R_1} \quad (31)$$

From eqns. 29, 31 and 25, and the boundary condition 28, we obtain

$$\dot{m}_1 = uw_1 \quad (32)$$

which represents the velocity of the centre of gravity of the peak within the column. After integration we obtain

$$m_1 = uw_1 t + A \quad (33)$$

where A is a constant. It will be found convenient for the subsequent analysis to choose the coordinate system in such a way that

$$A = 0 \quad (34)$$

Eqns. 29 and 30 also have steady-state solutions of the form of eqn. 33. Thus, we can write

$$f_1 = uw_1 t + a_1 \quad (35)$$

and

$$g_1 = uw_1 t + a_2 \quad (36)$$

The parameter α_1 is a constant, since plug flow was assumed in the mobile phase. On the other hand, α_2 is a function of r , satisfying the differential equation

$$\frac{\partial^2 \alpha_2}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial \alpha_2}{\partial r} = \frac{uw_1}{D_2} \quad (37)$$

The general solution of eqn. 37 has the form

$$\alpha_2 = \frac{uw_1}{6D_2} \cdot r^2 + C_1 - \frac{C_2}{r} \quad (38)$$

where the constants C_1 and C_2 have to be determined from eqn. 34 and the boundary conditions 27 and 28.

Introducing the quantity

$$\varrho = \frac{R_2}{R_1} \quad (39)$$

the results of these calculations can be stated in the form

$$\alpha_1 = \frac{uw_1 R_1^2}{6D_2} \left[1 + 2\varrho^3 + \frac{2D_2(1-\varrho^3)}{kR_1} \right] + C_1 \quad (40)$$

and

$$\alpha_2 = \frac{uw_1}{6D_2} \left(r^2 + \frac{2R_2^3}{r} \right) + C_1 \quad (41)$$

where

$$C_1 = -\frac{uw_1 R_1^2}{6D_2} \left[1 + 2\varrho^3 - \frac{2w_2}{5} \cdot \frac{1 + \varrho + \varrho^2 - 4\varrho^3 - 4\varrho^4 + 5\varrho^5}{1 + \varrho + \varrho^2} + \frac{2w_1 D_2 (1 - \varrho^3)}{kR_1} \right] \quad (42)$$

DETERMINATION OF THE SECOND MOMENT

For the second moments we obtain from eqns. 10 and 11, after normalization

$$\dot{f}_2 = 2uf_1 + 2D_1' + \frac{kn\sigma KS}{S_1} (g_2 - f_2)_{R_1} \quad (43)$$

$$\dot{g}_2 = D_2 \left(\frac{\partial^2 g_2}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial g_2}{\partial r} \right) \quad (44)$$

and

$$\ddot{g}_2 = \frac{4\pi}{V} \int_{R_2}^{R_1} \dot{g}_2 r^2 dr = \frac{\sigma D_2}{V} \left(\frac{\partial g_2}{\partial r} \right)_{R_1} \quad (45)$$

From eqns. 43, 45 and 25, and the boundary condition 28, we obtain

$$\dot{m}_2 = 2w_1 (u\dot{f}_1 + D'_1) = 2u^2 w_1^2 t + 2w_1 (D'_1 + u\alpha_1) \quad (46)$$

whence

$$m_2 = u^2 w_1^2 t^2 + 2w_1 (D'_1 + u\alpha_1) t + B \quad (47)$$

where B is the constant of integration and represents the width of the original peak. The variance μ is now obtained as follows:

$$\mu = m_2 - m_1^2 = 2Dt + B \quad (48)$$

where the dispersion coefficient D is found to have the value

$$\begin{aligned} \bar{D} = w_1 (D'_1 + u\alpha_1) = D'_1 w_1 + \frac{u^2 w_1^2 w_2 R_1^2}{15 D_2} \left[\frac{1 + \varrho + \varrho^2 - 4\varrho^3 - 4\varrho^4 + 5\varrho^5}{1 + \varrho + \varrho^2} + \right. \\ \left. + \frac{5D_2 (1 - \varrho^3)}{k R_1} \right] \quad (49) \end{aligned}$$

As stated earlier, D'_1 in eqn. 49 is a composite diffusion coefficient, characterizing axial diffusivity in the fluid phase. It represents the ordinary Brownian diffusion and eddy diffusion. When the two effects are separated we can write

$$D'_1 = D_1 + D_e u^2 \quad (50)$$

where D_1 is the ordinary diffusion coefficient and D_e the eddy diffusion coefficient. Although the nature of the latter effect is still controversial⁶⁻⁸, a quadratic dependence on the average velocity is the most likely. In this respect it is in agreement with the Taylor diffusion in open-tubular columns⁵, and is invariant on flow reversal.

The last term in the square brackets in eqn. 49 requires some comment. This term enters the derivation of the equation in a natural way, being due to the interfacial resistance to solute transfer. It thus represents a real physical quantity, present in all types of columns. However, it is reasonable to assume that in most instances the magnitude of the constant k is such as to make the contribution from this term negligible.

NON-UNIFORM COLUMN PACKING

A very important factor that influences the performance of real columns is the possible non-uniformity of the packing material. Most important are variations in particle size or film thickness although the diffusion coefficient in the particles and the partition coefficient may also vary. These effects will now be considered.

For non-uniform packing materials, eqns. 1, 5 and 3 can be written in the form

$$\frac{\partial c_1}{\partial t} = -u \cdot \frac{\partial c_1}{\partial x} + D_1' \cdot \frac{\partial^2 c_1}{\partial x^2} + \frac{S}{S_1} \sum_{\nu} n_{\nu} \sigma_{\nu} j_{\nu} \quad (51)$$

$$\frac{\partial c_{2\nu}}{\partial t} = D_{2\nu} \left(\frac{\partial^2 c_{2\nu}}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c_{2\nu}}{\partial r} \right) \quad R_{2\nu} < r < R_{1\nu} \quad (52)$$

and

$$j_{\nu} = k_{\nu} (c_{2\nu} - K_{\nu} c_{1\nu})_{R_{1\nu}} \quad (53)$$

where the subscript ν denotes a certain species of the particles, each species being considered as a different phase.

The earlier treatment can now be repeated in a straightforward manner with these new equations. For the zeroth moment we thus obtain

$$M_0 = S_1 F_0 + S \sum_{\nu} n_{\nu} V_{\nu} \bar{G}_{0\nu} = F_0 (S_1 + S \sum_{\nu} n_{\nu} K_{\nu} V_{\nu}) \quad (54)$$

and the weight fractions of solute in the different phases become

$$w_1 = \frac{S_1}{S_1 + S \sum_{\nu} n_{\nu} K_{\nu} V_{\nu}} \quad (55)$$

and

$$w_{2\nu} = \frac{S n_{\nu} K_{\nu} V_{\nu}}{S_1 + S \sum_{\nu} n_{\nu} K_{\nu} V_{\nu}} \quad (56)$$

For the first moment, eqn. 33 is still valid, but the constant A is now given by

$$A = w_1 \alpha_1 + \sum_{\nu} w_{2\nu} \bar{\alpha}_{2\nu} \quad (57)$$

where $\alpha_{2\nu}$ belongs to the first moment of phase ν :

$$g_{1\nu} = u w_1 t + \alpha_{2\nu} \quad (58)$$

the values of $\alpha_{2\nu}$ being determined by equations similar to eqn. 37.

Also the variance is still given by eqn., 48, but the expression for D has to be replaced by the following expression:

$$D = D_1' w_1 + \frac{u^2 w_1^2}{15} \sum_{\nu} \frac{w_{2\nu} R_{1\nu}^2}{D_{2\nu}} \left[\frac{1 + \varrho_{\nu} + \varrho_{\nu}^2 - 4\varrho_{\nu}^3 - 4\varrho_{\nu}^4 + 5\varrho_{\nu}^5}{1 + \varrho_{\nu} + \varrho_{\nu}^2} + \frac{5D_{2\nu} (1 - \varrho_{\nu}^3)}{k_{\nu} R_{1\nu}} \right] \quad (59)$$

Thus, the dispersion coefficient D is the weighted sum (with the weights $w_{2\nu}$) of the contributions from the different phases. If the mode of variation of the different parameters in eqn. 59 is known, the value of D can be obtained directly from eqn. 59.

Alternatively, eqn. 49 may be employed, using the appropriate average values of the parameters. Here we will consider only one important special case, namely gel chromatography, when particle size is the only variable. The average particle radius in eqn. 49 (for $\varrho = 0$, $k = \infty$) is then defined by

$$w_2 \bar{R}_1^2 = \sum_{\nu} w_{2\nu} R_{1\nu}^2 \quad (60)$$

where $w_2 = \sum_{\nu} w_{2\nu}$

Using the expression for $w_{2\nu}$ in eqn. 56 (with $V_{\nu} = \frac{4}{3}\pi R_{1\nu}^3$), we obtain

$$\bar{R}_1^2 = \frac{\sum_{\nu} n_{\nu} R_{1\nu}^5}{\sum_{\nu} n_{\nu} R_{1\nu}^3} \quad (61)$$

This average strongly favours the larger particles. For example, if the packing consists of an equal number of particles with radii R_1 and $2R_1$, the average is $\bar{R}_1 = 1.915 R_1$.

Variation of particle size in the packing material also affects the symmetry of a chromatographic peak, and is at least partly responsible for the occurrence of tailing in gel chromatography. This can be seen from eqn. 57, which indicates how the centre of gravity of the total solute distribution depends on the individual distributions for the different phases. Evaluating $\alpha_{2\nu}$ from eqn. 38 (for $\varrho = 0$, $k = \infty$), we find

$$\alpha_{2\nu} = \frac{uw_1 R_{1\nu}^2}{6D_2} \left[\left(\frac{r}{R_{1\nu}} \right)^2 - 1 \right] + \alpha_1 \quad (62)$$

and

$$\bar{\alpha}_{2\nu} = -\frac{uw_1 R_{1\nu}^2}{15D_2} + \alpha_1 \quad (63)$$

Thus, the distance between α_1 and $\bar{\alpha}_{2\nu}$ is proportional to the square of the particle radius, $R_{1\nu}$. As $\bar{\alpha}_{2\nu}$ represents the centre of gravity of the distribution associated with the ν th phase, eqn. 63 indicates that contributions from large particles accumulate in the tail of the total solute distribution.

HEIGHT EQUIVALENT TO A THEORETICAL PLATE

In practical chromatography, the efficiency of a column is normally expressed in terms of the height equivalent to a theoretical plate, H . This quantity can be defined as follows:

$$H = L \cdot \frac{\mu_{\nu}}{m_{1\nu}^2} \quad (64)$$

where L is the length of the column and m_{1V} and μ_V are the first moment (elution volume) and the variance for the peak in the elution diagram, respectively. Thus, the moments in the foregoing treatment have to be transformed into moments with respect to the efflux volume. This transformation necessarily involves an approximation, as the peak exit process is not amenable to an exact analytical treatment. However, as a first approximation the elution volume m_{1V} is the efflux volume at the time ($t = L/uw_1$) when the first moment of the peak in the column reaches the end point (L) of the column. Thus

$$m_{1V} = \theta \cdot \frac{L}{uw_1} = \frac{LS_1}{w_1} \quad (65)$$

where $\theta = uS_1$ is the rate of volume flow through the column.

Similarly, μ_V is obtained from μ at the time $t = L/uw_1$, by converting to the volume coordinate. As the unit length in the column corresponds to the volume flow θ/uw_1 , we have

$$\mu_V = \frac{\theta^2}{u^2 w_1^2} \cdot \mu\left(\frac{L}{uw_1}\right) = \frac{S_1^2}{w_1^2} \cdot \mu\left(\frac{L}{uw_1}\right) \quad (66)$$

Hence

$$H = \frac{1}{L} \cdot \mu\left(\frac{L}{uw_1}\right) = \frac{2D}{uw_1} + \frac{B}{L} \quad (67)$$

where the last term is the contribution from the initial peak width, and obviously decreases in importance as the length of the column increases. As it does not characterize the performance of a particular column, we have omitted this term in the subsequent treatment.

Concluding the present treatment of packed columns, we can derive expressions for the plate height, H , for conditions normally prevailing in gel and gas-liquid chromatography. To bring the notations into conformity with common chromatographic practice, we introduce the parameter R , denoting the ratio between peak velocity and average mobile phase velocity. From eqns. 32 and 26, we find that

$$w_1 = R \quad (68a)$$

and

$$w_2 = 1 - R \quad (68b)$$

For gel chromatography we thus obtain from eqns. 67 and 49 (with $\varrho = 0$)

$$H = \frac{2D_1}{u} + 2D_e u + \frac{2u R (1 - R) R_1^2}{15D_2} + \frac{2u R (1 - R) R_1}{3k} \quad (69)$$

To obtain the plate height in gas-liquid chromatography we introduce the thickness of the liquid layer, $d = R_1 - R_2$. Then

$$\varrho = 1 - \frac{d}{R_1} \quad (70)$$

and we obtain from eqns. 67 and 49, after series expansion in terms of d/R_1 :

$$H = \frac{2D_1}{u} + 2D_e u + \frac{2u R (1 - R) d^2}{3D_2} \left(1 - \frac{d}{R_1} + \dots\right) + \frac{2u R (1 - R) d}{k} \left(1 - \frac{d}{R_1} + \frac{d^2}{3R_1^2}\right) \quad (71)$$

Comparing these equations with the plate height expressions obtained in earlier theories, we find close agreement with Giddings' treatment in the terms characterizing radial diffusion in the stationary phase⁹, although differences exist in the terms characterizing interfacial resistance to mass transfer¹⁰. This indicates that the approximations involved in the present macroscopic treatment are essentially of the same nature as the approximations used in the stochastic theories.

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