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DIFFUSIVE AND CONVECTIVE DISPERSION IN CHROMATOGRAPHY

RECENT DEVELOPMENTS

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1. INTRODUCTION

The contributions of diffusion and convection to the dispersion of solutes by fluid flow through packed beds are the most fundamental and generally important. Whereas other contributions to dispersion are limited to some special types or applications of packed beds (*e.g.*, distribution of the solutes over moving and stagnant domains of the fluid is limited to beds of porous particles, and distribution over the moving fluid and the surface of the particles is limited to catalysis and adsorption chromatography), diffusion and convection are important in such diverse fields as hydrology, petroleum engineering, chemical reactor technology and all types of chromatography.

The amount of convective dispersion depends greatly on the packing characteristics of the bed. Therefore, the importance of this phenomenon increased considerably after the introduction of high-performance liquid chromatography. Whereas "good" packings, showing a small amount of longitudinal convective dispersion, can be easily prepared from the relatively large particles that are used in gas chromatography and low-pressure liquid chromatographic techniques (*e.g.*, gel-permeation chromatography and ion-exchange chromatography with soft materials), the preparation of good packings from the very small particles that are used in high-performance

liquid chromatography is difficult. Knowledge of the laws that govern convective dispersion enables one to judge the quality of packings in columns for liquid chromatography, and to compare the merits of different packing techniques. This is one of the aims of the present paper. Another aim is to discuss some new aspects of diffusive and convective dispersion that have been revealed by the painstaking investigations by workers in the fields of chromatography and chemical engineering during the last few years.

2. THEORY

When an amount of solute is injected into a packed bed and transported through it by a moving fluid, the solute is dispersed in both longitudinal and radial directions by diffusion and convection.

For longitudinal dispersion, Giddings¹, in 1959, derived the equation

$$\frac{\sigma^2}{L} \equiv H = \frac{2\gamma D}{u} + \frac{2\lambda d_p}{1 + CD/d_p u} \quad (1)$$

where

- σ = standard deviation of the concentration profile of the solute;
- L = migration distance in the bed;
- H = plate height;
- γ, λ, C = dimensionless coefficients, depending on the geometry of the packing and the dynamics of flow;
- d_p = particle diameter;
- D = diffusion coefficient;
- u = mean fluid velocity*.

An analogous equation had been suggested 2 years earlier by Beran² on a semi-theoretical argument. In the field of chemical engineering, eqn. 1 has been used by Edwards and Richardson³.

The influence of the ratio of the column diameter to particle diameter, ϱ , on the geometry of the packing was realized at a very early stage⁴. As a consequence of this influence, γ, λ and C may be functions of ϱ . Huyten *et al.*⁵ and Sie and Rijnders⁶ introduced the column diameter, d_c , explicitly as a variable:

$$H = \frac{2\gamma D}{u} + \frac{2\kappa d_c^2 u}{\lambda_R d_p u + \gamma D} \quad (2)$$

where κ and λ_R are dimensionless coefficients, depending on the geometry of the packing and the dynamics of flow.

It can be shown easily that eqns. 1 and 2 are equivalent, by introducing the

* u is equal to L/t , where t is the mean time spent by the molecules of an unadsorbed sample in traversing a distance L .

reduced plate height, $h = H/d_p$, and the reduced velocity, $v = ud_p/D$. In terms of these variables, eqns. 1 and 2 are, respectively:

$$h = \frac{2\gamma}{v} + \frac{2\lambda}{1 + C/v} \quad (3)$$

and

$$h = \frac{2\gamma}{v} + \frac{2\kappa\varrho^2/\lambda_R}{1 + \gamma/\lambda_R v} \quad (4)$$

These equations show that λ is equal to $\kappa\varrho^2/\lambda_R$ and C is equal to γ/λ_R .

Eqn. 3 is suitable for use in comparing experimental data obtained for different values of d_p , d_c and D . According to this equation, h depends only on the variable v . However, it must be remembered that the coefficients γ , λ and C may depend on the geometry of the packing (*i.e.*, on ϱ , and on whether the particles are spherical or irregular) and on the dynamics of flow.

Some recent results on the longitudinal and radial dispersion of argon in packed beds of glass spheres⁷ are shown in Fig. 1 as a function of v . The resemblance of the two sets of data points is striking, and suggests that radial dispersion can also be described by an equation of the type of eqn. 3. A unified theory of longitudinal and radial dispersion was given by De Ligny⁸. As this work was published in a journal that is not familiar to most chromatographers, the main points of the derivation are given here for the sake of convenience. The theory resembles Giddings²¹ random walk treatment.

When the molecules of a sample must choose a number of times, n , between two equally probable situations P and Q, in the former of which they make a step p backwards and in the latter of which they make a step q forwards relative to the mean position of the sample, a distribution is generated⁹ with a variance

$$\sigma^2 = npq \quad (5)$$

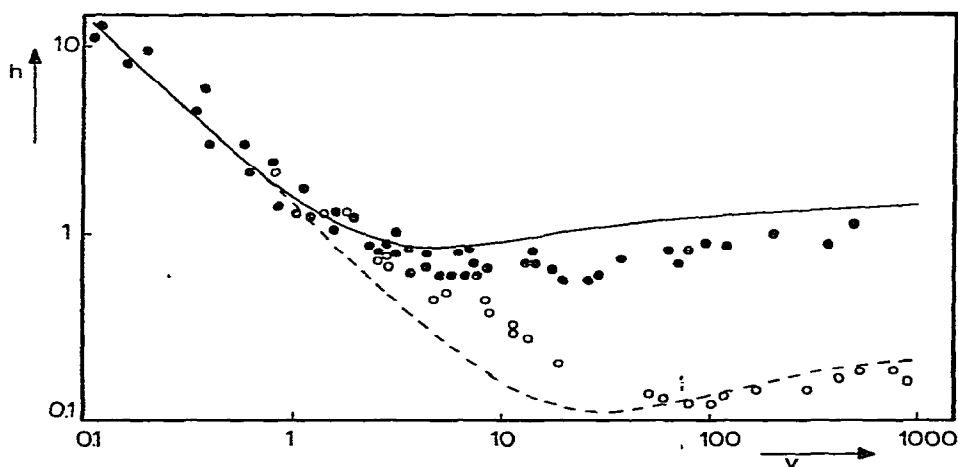


Fig. 1. Data on longitudinal and radial dispersion of argon in packed beds of glass spheres. ●, Experimental data on longitudinal dispersion⁷; ○, experimental data on radial dispersion⁷. Solid line, predicted curve for longitudinal dispersion (eqn. 3, see Table 1); broken line, predicted curve for radial dispersion (eqn. 3, see Table 1).

Suppose that the bed is an arrangement of equal numbers of nearly cylindrical volumes P and Q that are passed by the sample molecules in a random way. The volumes P and Q are characterized by longitudinal velocities $u(1 - C_L)$ and $u(1 + C_L)$, respectively; radial velocities $-uC_R$ and uC_R , respectively; tangential velocities $-uC_T$ and uC_T , respectively; length $C_1(1 - C_L)d_p$ and $C_1(1 + C_L)d_p$, respectively; and a radius C_2d_p (the symbol C denotes a dimensionless coefficient).

The mean longitudinal, radial and tangential velocities are then $u, 0$ and 0 , respectively, and the mean length of a volume is $C_1d_p^*$. Hence the number of volumes that a molecule would pass (in the absence of radial and tangential velocity components and in the absence of diffusion) when it traverses a length L of the bed, *i.e.*, the number of times that the components of its velocity may change, is

$$n_1 = \frac{L}{C_1 d_p} \quad (6)$$

The mean time, τ_f , required to reach a neighbouring volume by radial and tangential flow is

$$\tau_f = \frac{C_3 d_p}{u} \quad (7)$$

The time t spent in traversing the bed length L is equal to L/u . The number of volumes that the molecule passes in this time, *i.e.*, the number of times that its velocity components may change, is

$$n_2 = \frac{t}{\tau_f} = \frac{L}{C_3 d_p} \quad (8)$$

The mean time, τ_d , required to reach a neighbouring volume by radial and tangential diffusion is

$$\tau_d = \frac{C_4 d_p^2}{D} \quad (9)$$

The number of volumes that the diffusing molecule passes in the time t or L/u , *i.e.*, the number of times that its velocity components may change, is

$$n_3 = \frac{t}{\tau_d} = \frac{LD}{C_4 d_p^2 u} \quad (10)$$

Hence the total number of times that the velocity components of a molecule may change is

$$n = n_1 + n_2 + n_3 = L \left(\frac{1}{C_5 d_p} + \frac{D}{C_4 d_p^2 u} \right) \quad (11)$$

* It is immaterial whether or not the longitudinal, radial and tangential velocities are correlated, as assumed here for ease of formulation. The condition that the volumes P and Q be passed by the sample molecules in a random way can be met only if the volumes P and Q are placed in the bed in a nearly random way. This means that the correlation between the velocity profiles in different cross-sections of the bed is thought to be lost after a mean bed length C_1d_p .

The mean residence time in a volume is t/n or L/un . The mean backward and forward steps p and q during this residence time are LC_L/n in the longitudinal direction and LC_R/n in the radial direction. Thus, in both directions the resulting variance is of the form

$$\sigma_{L,R}^2 = n \left(\frac{LC_{L,R}}{n} \right)^2 = LC_{L,R}^2 \cdot \frac{1}{\frac{1}{C_5 d_p} + \frac{D}{C_4 d_p^2 u}} = L \cdot \frac{C'_{L,R} d_p}{1 + C_6 D/d_p u} \quad (12)$$

It follows that the reduced plate height for convective dispersion is

$$h_{L,R(\text{conv})} = \frac{\sigma_{L,R}^2}{Ld_p} = \frac{2\lambda_{L,R}}{1 + C/v} \quad (13)$$

where 2λ is equal to C' and C is equal to C_6 . Addition of the reduced plate height for diffusive dispersion, $2\gamma/v$, yields eqn. 3.

The model is, admittedly, an over-simplification. However, it predicts correctly the shape of graphs of h as a function of v , for both radial and longitudinal dispersion. Identical equations for radial and longitudinal dispersion have been obtained by the application of the spectral theory of the random concentration field of disperse systems¹⁰.

From a large amount of literature data on dispersion in well packed beds, mostly consisting of large particles with a narrow size distribution, the values of the coefficients γ , λ and C have been evaluated^{8,11} as functions of ρ . The values of these coefficients appeared to depend on the shape of the particles and on the physical state of the moving fluid (Table 1). Graphs of λ and C for longitudinal dispersion as a function of ρ are shown in Fig. 2, and graphs of h for longitudinal dispersion as a function of v , calculated by eqn. 3, are shown in Fig. 3. Graphs of this type can be applied to judge the quality of packings and the importance of extra-column and injection effects. This has been done in Fig. 1, where recent experimental data⁷ are

TABLE I
VALUES OF γ , λ AND C AS A FUNCTION OF ρ ^{8,11}

Parameter	Liquid fluid		Gaseous fluid	
	Spherical particles	Irregular particles	Spherical particles	Irregular particles
γ^*	0.73	0.64	0.73	0.64
λ (longitudinal dispersion)	$5\rho/(2\rho + 5)$		0.67	$(8\rho^2 + 155)/(2\rho^2 + 125)$
C (longitudinal dispersion)**	$(8\rho^2 + 155)/\rho^2$			$(16\rho^2 + 310)/3\rho^2$
λ (radial dispersion)***	0.08		0.12	
C (radial dispersion)***	0 (ref. 13)		80	

* γ is about equal for beds consisting of massive particles and for beds consisting of wide-pore porous particles such as Chromosorb¹¹. For beds consisting of narrow-pore, irregularly shaped particles (broken CuO·ZnO catalyst particles, mean pore diameter 350 Å), Suzuki and Smith¹² found $\gamma = 0.58$.

** In the calculation of C for longitudinal dispersion from the data in ref. 11, γ was put equal to 0.67 as an approximation for both spherical and irregular particles.

*** Values holding for $\rho > 10$.

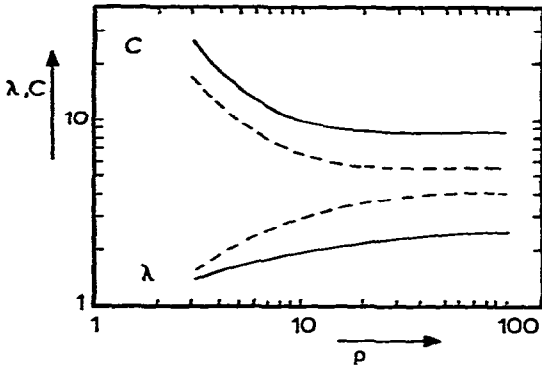


Fig. 2. Coefficients λ and C in eqn. 3 as a function of ρ , for longitudinal dispersion. λ : Solid line, liquid fluid, spherical and irregular particles; broken line, gaseous fluid, irregular particles. C : Solid line, liquid fluid, spherical and irregular particles; broken line, gaseous fluid, spherical and irregular particles.

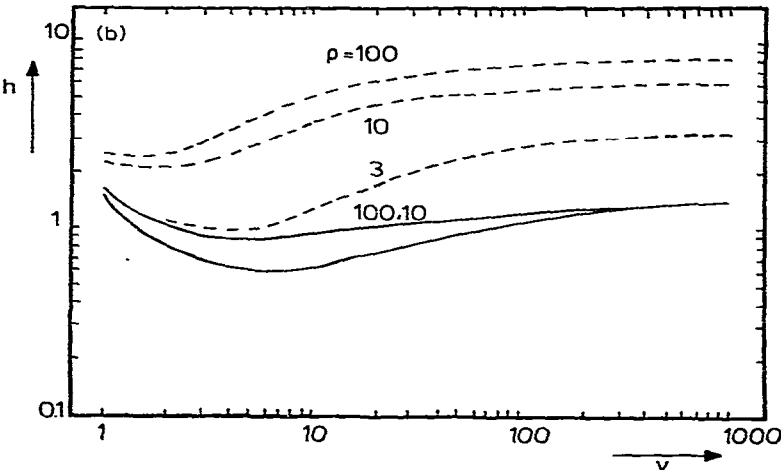
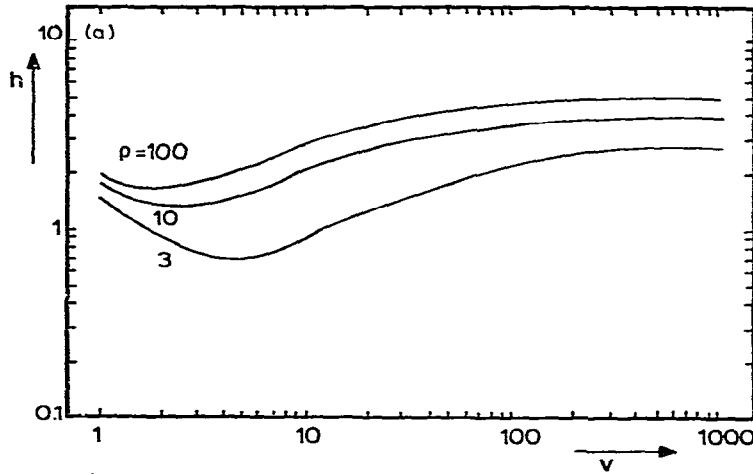


Fig. 3. (a) Reduced plate height, h , as a function of the reduced velocity, v , for longitudinal dispersion and a liquid fluid and for $\rho = 3, 10$ and 100 (for both spherical and irregular particles). (b) Reduced plate height, h , as a function of the reduced velocity, v , for longitudinal dispersion and a gaseous fluid and for $\rho = 3, 10$ and 100 . Solid line, spherical particles; broken line, irregular particles.

compared with the theoretical graphs of h for longitudinal and radial dispersion as a function of v . The experimental data appear to be in good agreement with the theoretical curves.

There are several reasons why experimental data on unadsorbed solutes and massive particles may deviate from the theoretical curves of Fig. 3: microscopic packing irregularities, a wide particle size distribution, and the occurrence of turbulence¹³. In porous media, there are no sharp transitions from laminar to turbulent flow, but rather there is a gradual transition from laminar flow to fully developed turbulence in the range of Reynolds numbers $10 < Re < 10^3$ ($Re = ud_p/\nu$, where ν is the kinematic viscosity of the moving fluid). This transition occurs, for a solute such as benzene, in gaseous fluids in the range of reduced velocities $10 < v < 10^3$, and in liquid fluids in the range $10^3 < v < 10^5$. The theoretical values¹³ of h for fully developed turbulence are $h = 1$ for longitudinal dispersion and $h = 0.18$ for radial dispersion. The limiting value of the right-hand side of eqn. 3 is equal to 2λ . Comparison of the values of λ in Table 1 with the above estimates of h for fully developed turbulence shows that the occurrence of turbulence has only a minor influence on radial dispersion, whereas it decreases h for longitudinal dispersion. As a result, a maximum may occur in graphs of h for longitudinal dispersion as a function of v . According to Perkins and Johnston¹³, in the transition region h should be between the value for laminar flow and the value for fully developed turbulence, as there are probably both types of flow in different pore spaces. They proposed the following equation:

$$1/h = (1-w)/h_{\text{laminar flow}} + w/h_{\text{turbulence}} \quad (14)$$

where w is the turbulence weighing factor. A graph of w as a function of Reynolds number is shown in Fig. 4.

It is obvious that additional contributions to peak dispersion occur if the solute is distributed over the moving inter-particle fluid and either the stagnant intra-

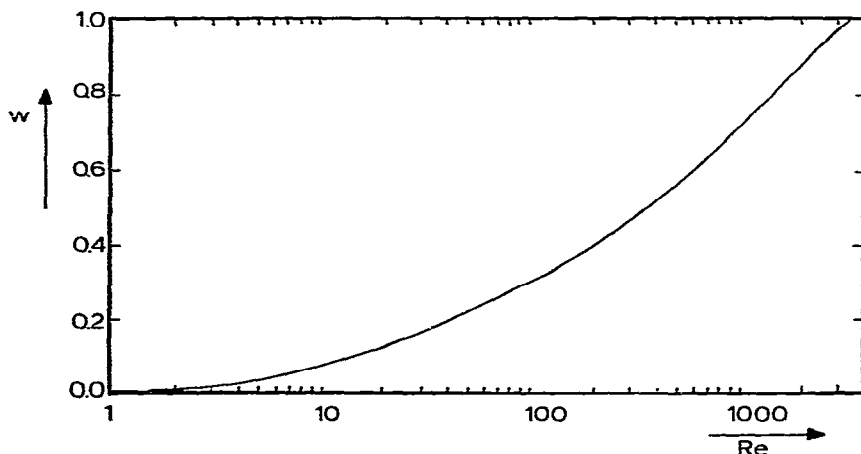


Fig. 4. Turbulence weighing factor, w , as a function of the Reynolds number, $Re = ud_p/\nu$, after ref. 13.

particle fluid in porous particles, or a liquid coating, or the adsorbing surface of the particles. These contributions are beyond the scope of this paper.

It follows from the gradual change of λ and C with ϱ in Fig. 2 that the change of h with ϱ is also gradual; h tends to a limiting value that is attained at $\varrho \approx 100$ (see also Fig. 3). Thus, properly designed and carefully packed preparative columns, for which ϱ is very large, have h values that are comparable to those of analytical columns. Godbille and Devaux¹⁴ reported a minimum value of h equal to 2.5 for a 1.8-cm I.D. column, packed with particles of diameter 10^{-3} cm, for which $\varrho = 1800$, with a liquid eluent. Earlier¹⁵, they had obtained a minimum value of h equal to 4 for an 8-cm I.D. column, packed with particles of diameter $35 \cdot 10^{-4}$ cm ($\varrho = 2300$). The theoretical minimum value of h for massive particles and unadsorbed solutes, from Fig. 3a, is equal to 1.6.

3. DISCUSSION OF SOME RECENT STUDIES

(A) Empirical correlations

Recently, Cluff and Hawkes¹⁶ presented a statistical correlation of 750 literature data on dispersion of non-sorbed solutes in packings of impermeable spheres. The data were fitted to a linear equation involving the variables v , v^2 , v^3 , Re , Re^2 , Re^3 , ε , $1/\varepsilon$, d_c , d_p , d_c/d_p , L , $1/v$, $1/v^2$, $1/Re$, $1/Re^2$, $\log L$, $\log v$, $\log d_c$, $\log d_p$, and $\log Re$ (ε is the porosity of the packing). They were forced to divide the data into two groups, obtained at low and at high reduced velocity. Although eight and four of the above variables, respectively, were retained, the correlation coefficients obtained are not impressive, being 0.855 and 0.955, respectively. A strange result, from the theoretical point of view, is the absence of a diffusion term, proportional to $1/v$, in the low velocity data.

(B) Theory

Gunn¹⁷ applied probability theory to the study of longitudinal dispersion. He returned to a more simple physical model than that underlying eqn. 3, *viz.*, a model wherein the interaction of radial convection with longitudinal dispersion is neglected. As a result, he obtained a complicated equation containing only two parameters: the analogue of the C parameter in eqn. 3 is missing.

One of these parameters (the probability of axial displacement, p) is a function of Reynolds number. In a later paper¹⁸, the effect of variations in the fluid velocity over the cross-section of a packed bed was taken into account by the introduction of a third parameter, σ_v^2 . This parameter is assumed to depend on the quality of the packed bed and on Reynolds number. It follows from the introduction in this paper that the fluid velocity profile, and thus the parameter σ_v^2 , depends also on ϱ , but Gunn has not, as yet, assessed this relationship. Thus, while his equation is suitable for describing experimental data, it is, as yet, less suitable for predicting the amount of dispersion for varying values of ϱ .

Miyauchi and Kikuchi¹⁹, following the classical Van Deemter approach, started from the equations for the material balance in rapidly and slowly moving parts of the streaming fluid. The resulting equation can be formulated as follows, in our symbols:

$$h = \frac{2\gamma}{v} + h_{(\text{conv})} \cdot y \quad (15)$$

The reduced plate height for convective dispersion, $h_{(\text{conv})}$, is a function of Reynolds number. The coefficient y is a function of a special type of Peclet number, Pe_{Mh} , that is equal to $0.67 \varepsilon v p / (1 - p)$. This simple equation, containing only three parameters, gives good correlations with experimental data in both the laminar and turbulent flow regimes. Possibly the correlations will become even better when the dependence of y on ρ and on the physical state of the fluid (as strongly suggested by the data on λ and C in Table 1) is taken into account.

(C) Diffusive dispersion

Although it has been recognized that the value of the "tortuosity factor", γ , depends on the shape of the particles, *i.e.*, on the geometry of the packing (see Table 1), until recently any dependence of γ on the dynamics of flow had not been demonstrated. Hawkes²⁰ was able to show that the value of γ increases from 0.60 at zero flow-rate to a limiting value of 0.75 at a reduced velocity $v \geq 0.1$, in a bed of glass spheres, and with a gaseous fluid. As the limiting value of γ is attained at a low value of the reduced velocity, it is understandable that the value encountered in practice is $\gamma = 0.73$. Hawkes suggested that for radial diffusion the static value $\gamma = 0.60$ should hold. However, experimental data point to a larger value^{13,17,19}.

(D) Turbulence

A careful investigation of turbulence in gas and liquid chromatography was made by Kaizuma *et al.*²¹. Their results are shown in Figs. 5 and 6 as graphs of h as a function of v and as a function of Re , respectively. Details of their columns are given in Table 2. For comparison, data from an analogous investigation by Knox²² have been included in Table 2 and Figs. 5 and 6. It follows from these figures that the amount of dispersion in the column packings prepared by Knox is less than in those prepared by Kaizuma *et al.* This may be the result of one or more of the following differences in experimental conditions: (i) Knox applied a slurry packing technique, Kaizuma *et al.* a dry packing technique; (ii) Knox used columns of length 115 cm, Kaizuma *et al.* of length 300 cm; it is well known that it is easier to prepare good packings in short than in long columns; (iii) the values of d_c/σ_R in the columns investigated by Knox are larger than in those investigated by Kaizuma *et al.*; therefore, the favourable "infinite diameter effect" is also larger (see the next section).

Figs. 5 and 6 clearly show the maximum of h that has been predicted in the introductory section, as a result of the gradual increase of turbulence.

In Table 3 the differences in the experimental values of h , obtained by Kaizuma *et al.*, and the theoretical values for laminar flow, from Fig. 3, are given for various values of v . If the columns were perfectly packed, these differences should be about zero in the laminar flow range, and become negative at the onset of turbulence. Instead, all of the differences are positive, which indicates that the quality of these columns is inferior to that of the packed beds that provided the data on which Fig. 3 is based. The differences are slightly greater for the wider column I, and they are about equal for liquid and gaseous fluids up to $v = 5 \cdot 10^2$. This means that the effect of turbulence on the reduced plate height is of little concern up to this value of the

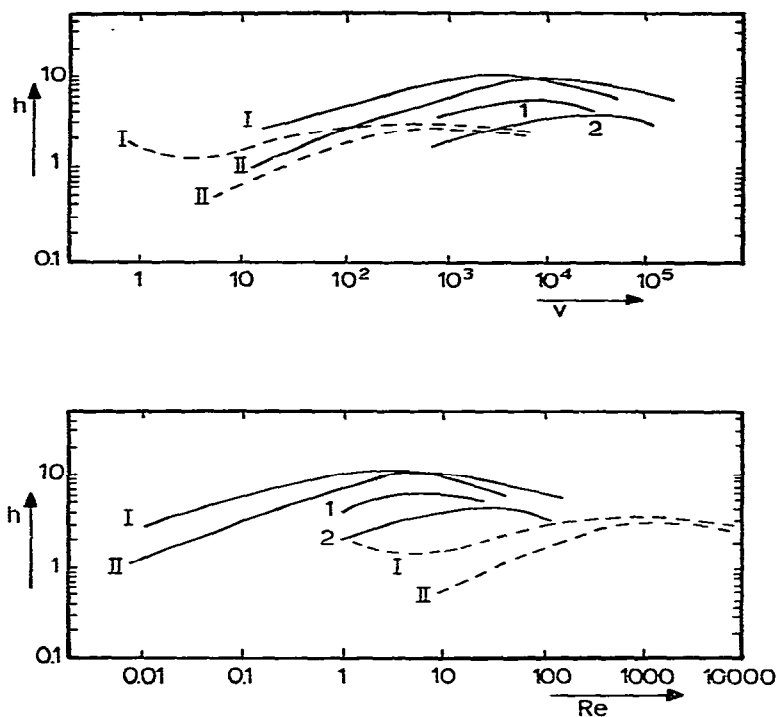


Fig. 5. Turbulence-induced maxima in plots of h as a function of v . Solid line, liquid fluid; broken line, gaseous fluid. I, II: Columns I and II of ref. 21, with $q = 9.91$ and 3.74 , respectively (see Table 2). 1, 2: columns 1 and 2 of ref. 22, with $q = 11.6$ and 3.1 , respectively (see Table 2).

Fig. 6. Turbulence-induced maxima in plots of h as a function of Re . Lines and numbers as in Fig. 5.

TABLE 2

DETAILS OF THE COLUMNS, USED BY KAIZUMA *et al.*²¹ (I, II) AND BY KNOX²² (1, 2)

Parameter	I	II	1	2
Length (cm)	300	300	115	115
Internal diameter (cm)	0.498	0.188	0.57	0.30
Glass bead diameter (cm)	0.050	0.050	0.049	0.097
q	9.91	3.74	11.6	3.1
Packing density ($\text{g}\cdot\text{cm}^{-3}$)	1.552	1.436		
Porosity	0.375	0.423		
d_c/σ_R ($v > 100$, liquid fluid)	0.32	0.12	0.60	0.22

TABLE 3

DIFFERENCES OF EXPERIMENTAL VALUES²¹ OF h AND THEORETICAL VALUES FOR LAMINAR FLOW (FROM FIG. 3) FOR VARIOUS VALUES OF v

v	Liquid fluid		Gaseous fluid	
	Column I	Column II	Column I	Column II
10	0.5	0.1	0.8	0.1
10^2	1.4	0.7	1.7	0.8
$5\cdot 10^2$	2.5	2.1	2.1	1.5
$5\cdot 10^3$	7.0	6.8	1.7	1.3
$5\cdot 10^4$	2.0	5.3		

reduced velocity. At higher values of the latter, h decreases for gaseous fluids owing to the development of strong turbulence. For liquid fluids, the decrease in h does not start until a reduced velocity of $5 \cdot 10^3$ is reached, corresponding to a Reynolds number of 5. Although the only reasonable explanation of the decrease in h seems to be the development of turbulence, it is unexpected that this phenomenon is already manifested at such a low Reynolds number (Knox²² observed the maxima at higher values of Re).

In Fig. 6 the curves for liquid fluids appear to merge into those for gaseous fluids at high Reynolds numbers, as expected, and to lead to the theoretical limit $h = 1$ for fully developed turbulence.

(E) *The "infinite diameter effect"*

Knox and Parcher²³ pointed out that an increase in the column diameter, under otherwise constant experimental conditions, may have a favourable effect on plate height if the solute is introduced in the centre of the cross-section of the column. If the column is very wide, only a small fraction of the solute reaches the wall layer of the packing. Thus, the main fraction of the solute moves through the homogeneously packed central part of the packing, and the appropriate value of λ to be used in eqn. 3 will be smaller than that given in Table 1. The parameter that governs this effect is the ratio of the column diameter, d_c , to the standard deviation for radial dispersion, σ_R . If this ratio is less than 0.12, more than 95% of the solute reaches the wall layer. If it is greater than 4, less than 5% of the solute reaches the wall layer. Hence, the effect of this phenomenon will be manifested in the range $0.12 < d_c/\sigma_R < 4$. According to eqn. 3, this ratio can be calculated from

$$\frac{\sigma_R^2}{d_c^2} = \left(\frac{2\gamma}{v} + \frac{2\lambda_R}{1 + C_R/v} \right) \frac{d_p L}{d_c^2} \quad (16)$$

The term within parentheses is of the same order of magnitude in gas and liquid chromatography, whereas d_p and L are usually much smaller in liquid chromatography. It follows that σ_R/d_c is usually much smaller in liquid chromatography, and consequently the "infinite diameter effect" is more likely to show up in liquid than in gas chromatography. According to Table 1, eqn. 16 can be simplified as follows for liquid chromatography:

$$\frac{\sigma_R^2}{d_c^2} = \left(\frac{1.4}{v} + 0.16 \right) \frac{d_p L}{d_c^2} \quad (17)$$

Knox and Parcher²³ did not verify their predictions experimentally; instead, they demonstrated the favourable effect on plate height of sampling only the central part of the column.

Coq *et al.*²⁴ observed a decrease in plate height in liquid chromatography when the column diameter increased from 0.21, through 0.3, to 0.46 cm. They could not establish whether this effect was due to the "infinite diameter effect" or to extra-column effects.

The favourable effect of a large column diameter in liquid chromatography was also demonstrated by De Stefano and Beachell²⁵, who compared two columns of length 49 cm and I.D. 0.21 and 1.09 cm that were filled with $5 \cdot 10^{-3}$ cm diameter

spherical porous silica (Porasil A). The values of d_c/σ_R were 1.0 and 5.4, respectively.

Beachell and De Stefano²⁶ investigated peak dispersion in liquid chromatography, using spherical $30\text{--}68 \cdot 10^{-4}$ cm diameter particles with controlled surface porosity. They used precision-bore columns of 50 cm length and 0.79 cm I.D. and applied a dry packing technique. All of their columns were of "infinite diameter", d_c/σ_R ranging from 3.5 to 5. Their results on the unadsorbed solute benzene are compared with the theoretical curve in Fig. 7. At low reduced velocity, the experimental data are clearly below the theoretical curve, presumably owing to the "infinite diameter effect". At high reduced velocity, the experimental data are above the theoretical curve, probably because extra-column contributions to peak dispersion occur.

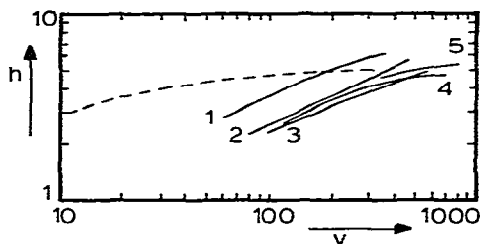


Fig. 7. Comparison of experimental data on longitudinal dispersion in liquid chromatography with theoretical estimates. Solid lines, experimental data. 1, $d_p = 30 \cdot 10^{-4}$ cm; 2, $d_p = 40 \cdot 10^{-4}$ cm; 3, $d_p = 48 \cdot 10^{-4}$ cm; 4, $d_p = 58 \cdot 10^{-4}$ cm; 5, $d_p = 68 \cdot 10^{-4}$ cm. Broken line, theoretical estimates (Fig. 3a).

Recently, Knox *et al.*²⁷ demonstrated convincingly the beneficial influence on plate height in liquid chromatography of a decrease in column length (from 28 to 8.2 cm) and an increase in column diameter (from 0.23 to 0.7 cm), using spherical porous alumina (Spherisorb X). They argued that the region of disturbed packing extends much farther from the wall than was previously thought: at least 15 and more probably 30 particle diameters.

(F) Peak dispersion in gas chromatography

With the aim of achieving high plate numbers with relatively short columns, Huber *et al.*²⁸ filled a column of 150 cm length and 0.1 cm I.D. with $3 \cdot 10^{-3}$ cm spherical porous silica (Spherosil) using a dry packing technique. This column had a maximum plate number of 15,000 for krypton (capacity ratio $k = 0$), pentane ($k = 1$) and hexane ($k = 2.2$). This value of the maximum plate number corresponds with a value of 3 for the minimum reduced plate height. According to Fig. 3b, the minimum reduced plate height for a gaseous fluid, spherical massive particles and $\rho = 30$ is equal to 1.

(G) Peak dispersion in liquid chromatography

Majors²⁹ investigated the influence of the column length for 0.24-cm wide columns, packed with irregularly shaped $13 \cdot 10^{-4}$ cm diameter silica particles (I-Chrosorb SI-60), by the balanced density technique. For column lengths ranging from 15 to 100 cm (the latter column consisting of two individually packed columns con-

nected in series), he could not detect any influence of column length on plate height. This result is unexpected, as it can be estimated that his plate height data (ref. 29, Table III) pertain to a reduced velocity of about 10^3 so that, according to eqn. 17, $0.6 < d_c/\sigma_R < 1.4$. This is just the range of d_c/σ_R in which the "infinite diameter effect" should occur. The explanation may be that the difference in the geometry of the packing of the wall and central parts is less in packings of irregular particles than in packings of spherical particles.

For $23 \cdot 10^{-4}$ cm silica particles the plate height increases with increasing retention of the solutes, as expected. However, for very small particles ($6 \cdot 10^{-4}$ cm), the reverse is observed, probably as a result of the importance of extra-column and injection effects when the capacity ratio k , the particle diameter and the column length are small. Nevertheless, for $6 \cdot 10^{-4}$ cm particles and $k = 20$, the high-velocity limit of h is only 10, which is reasonable compared with the theoretical value of 5. For larger particles ($9 \cdot 10^{-4}$, $13 \cdot 10^{-4}$ and $23 \cdot 10^{-4}$ cm) and $k = 1.2$, the high-velocity limit of h is about 50, and for $45 \cdot 10^{-4}$ cm particles it is as high as *ca.* 100, probably owing to the increasing importance of the mass transfer contribution to plate height.

The mass transfer contribution was separated from the contribution of convection by Endele *et al.*³⁰. They used spherical porous silica particles* and drilled columns (30×0.4 cm) that were re-polished after some use, and applied the balanced density packing technique. They pointed out (in agreement with Table 1 and Fig. 3a) that "if all other parameters are identical, the peak broadening in columns packed with spherical silica is very similar to that obtained with irregular silica. The spherical silica supports, however, have some advantages compared with the "broken" supports:

(1) because of the regular shape, the sieve fractions are narrower if a centrifugal air particle classifier is used;

(2) the reproducibility of the column packing is better".

Endele *et al.*³⁰ applied the equation

$$h = A + Cv \tag{18}$$

where A is the high-velocity limit of the contribution of convective dispersion (and of any extra-column and injection effects) to the plate height and Cv is the mass transfer contribution. For five sieve fractions, with number-averaged particle diameters ranging from $6 \cdot 10^{-4}$ to $33 \cdot 10^{-4}$ cm, they observed A values between 6.1 and 4.7, equal to the theoretical limit. Only for a sixth sieve fraction with $d_p = 16 \cdot 10^{-4}$ cm, an unexplainable high A value of 11.4 was found. The A values were independent of the capacity ratio of the solute, as expected.

In an effort to reach the ultimate limits in liquid chromatography, Halász *et al.*³¹ investigated the performance of columns packed with $4\text{--}5 \cdot 10^{-4}$ cm diameter spherical silica, prepared as described in ref. 30. They used drilled columns of 0.4 cm I.D. A very small A value (about 3) was observed. The value of A was independent of the

* The spherical silica particles were prepared by emulsion polycondensation of poly(ethoxy-siloxane), using a centrifugal air particle classifier. The particle size distributions appeared to be excellent approximations to the normal distribution, with standard deviations of 10% for $d_p = 33 \cdot 10^{-4}$ and $24 \cdot 10^{-4}$ cm, 20% for $d_p = 16 \cdot 10^{-4}$ and $11 \cdot 10^{-4}$ cm and 25% for $d_p = 6 \cdot 10^{-4}$ cm.

column length (between 7.5 and 29 cm) and of the capacity ratio of the solute (between 0 and 15). The observed value of A is below the theoretical value, $A = 5$. This result is probably due to the "infinite diameter effect", as for most of the measurements made by Halász *et al.* it holds that $d_c/\sigma_R > 4$.

4. CONCLUSIONS

Coupling between diffusion and convection occurs both in longitudinal and radial dispersion of matter by fluid flow through packed beds.

The reduced plate heights, h , for longitudinal and radial dispersion increase gradually with increasing values of d_c/d_p , and attain a limiting value at $d_c/d_p \approx 100$. Thus properly designed and carefully packed preparative columns, for which d_c/d_p is very large, have h values that are comparable to those of analytical columns.

For the correlation of dispersion data in both the laminar and the turbulent flow regime, Miyauchi and Kikuchi's approach¹⁹ is promising.

The tortuosity factor, γ , for longitudinal diffusion depends slightly on the flow-rate of the moving fluid.

Turbulence has little effect on plate height at reduced velocities, v , below 500. At higher values of v , turbulence causes a maximum to occur in graphs of h versus v .

The "infinite diameter effect" has been demonstrated clearly, and can be used to obtain small plate heights by employing wide columns (0.4–0.6 cm).

Column packings that give about the theoretical amount of diffusive and convective dispersion can be prepared even with particles as small as $4 \cdot 10^{-4}$ cm, if drilled or polished columns are used and the balanced density slurry packing technique is applied. With larger particles ($3 \cdot 10^{-3}$ cm), good results have also been obtained with the dry packing technique when precision-bore columns of large diameter (0.8 cm) were used.

5. SUMMARY

Recent developments in diffusive and convective dispersion in chromatography are discussed. The topics considered are empirical correlations, theoretical developments, the flow-dependence of the tortuosity factor for diffusion, turbulence, the "infinite diameter effect" and column efficiency in gas and liquid chromatography.

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