# Chapter 4
# Transport Phenomena in Porous Structures

## 4.1 Introduction

The problem of solute dispersion during underground water movement has attracted interest from the early days of the last century [127], but it was only since the 1950s that the general topic of hydrodynamic dispersion, or miscible displacement, became the subject of more systematic study. This topic has interested hydrologists, geophysicists, petroleum and chemical engineers, among others, and for some time now it is treated at length in books on flow through porous media (e.g. [9, 116]). Some books on chemical reaction engineering (ex: [24, 55, 141]) treat the topic of dispersion (axial and lateral) in detail and it is generally observed that data for liquids and gases do not overlap, even in the "appropriate" dimensionless representation.

Since the early experiments of Slichter [127] and particularly since the analysis of dispersion during solute transport in capillary tubes, developed by Taylor [133] and Aris [5, 6], much work has been done on the description of the principles of solute transport in porous media of inert particles (ex: soils) and in packed bed reactors (see [9, 44]).

Gray [59], Bear [9] and Whitaker [143] derived the proper form of the transport equation for the average concentration of solute in a porous medium, by using the method of volume or spatial averaging, developed by Slattery [126].

Brenner [20] developed a general theory for determining the transport properties in spatially periodic porous media in the presence of convection, and showed that dispersion models are valid asymptotically in time for the case of dispersion in spatially periodic porous media, while Carbonell and Whitaker [26] demonstrated that this should be the case for any porous medium. These authors presented a volume–average approach for calculating the dispersion coefficient and carried out specific calculations for a two-dimensional spatially periodic porous medium. Eidsath et al. [48] have computed axial and lateral dispersion coefficients in packed beds based on these spatially periodic models, and have compared the

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results to available experimental data. The axial dispersion coefficient calculated by Eidsath et al. [48] shows a Peclet number dependence that is too strong, while their radial dispersion. However, in soils or underground reservoirs, large scale non-uniformities lead to values of dispersion coefficients that differ much from those measured in packed beds, and for these cases spatially periodic models cannot be expected to provide excellent results without modifications.

There have been other attempts at correlating and predicting dispersion coefficients based on a probabilistic approach [38, 60, 70, 114] where the network of pores in the porous medium is regarded as an array of cylindrical capillaries with parameters governed by probability distribution functions.

Dispersion in porous media has been studied by a significant number of investigators; using various experimental techniques. However, measurements of axial and lateral dispersion are normally carried out separately, and it is generally recognised that ‘experiments on lateral dispersion are much more difficult to perform than those on axial dispersion’ [116].

When a fluid is flowing through a bed of inert particles, one observes the dispersion of the fluid in consequence of the combined effects of molecular diffusion and convection in the spaces between particles. Generally, the dispersion coefficient in axial direction is superior to the dispersion coefficient in radial direction by a factor of 5, for values of Reynolds number larger than 10. For low values of the Reynolds number (say, $\mathrm{Re} < 1$), the two dispersion coefficients are approximately the same and e qual to molecular diffusion coefficient.

The detailed structure of a porous medium is greatly irregular and just some statistical properties are known. An exact solution to characterize flowing fluid through one of these structures is basically impossible. However, by the method of volume or spatial averaging it is possible to obtain the transport equation for the average concentration of solute in a porous medium [9, 143].

At a “macroscopic” level, the quantitative treatment of dispersion is currently based on Fick’s law, with the appropriate dispersion coefficients; cross stream dispersion is related to the radial dispersion coefficient, $D_\mathrm{T}$, whereas stream-wise dispersion is related to the axial dispersion coefficient, $D_\mathrm{L}$.

If a small control volume is considered, a mass balance on the solute, without chemical reaction, leads to

$$D_\mathrm{L}\frac{\partial^2 C}{\partial z^2}+\frac{1}{r}\frac{\partial}{\partial r}\left(D_\mathrm{T} r\frac{\partial C}{\partial r}\right)-u\frac{\partial C}{\partial z}=\frac{\partial C}{\partial t} \tag{4.1}$$

where $C$ is the mean solute concentration, $u\,(=U/\varepsilon$, where $U$ is the superficial velocity and $\varepsilon$ the porosity of the porous media of inert particles with diameter $d$) the mean interstitial velocity of fluid and $t$ the time.

A large number of theories, namely the theories based on a probabilistic approach, have been proposed to explain dispersion in porous media; however, the theory of Saffman [114], who modelled the microstructure of a porous media as a network of capillary tubes of random orientation, and Koch and Brady [83] were the most referred.

## 4.2 Diffusion

Diffusion in porous media is a general subject that involves many fields of research, such as chemistry (e.g. porous catalytic pallets), biology (e.g. porous cellular organelles), and materials science (e.g. porous polymer matrixes for controlled-release and gas-storage materials).

Diffusivity or diffusion coefficient is a proportionality constant between the molar flux due to molecular diffusion and the gradient in the concentration of the species (or the driving force for diffusion). Diffusivity is encountered in Fick's law and numerous other equations of physical chemistry.

The effective diffusion coefficient, $D_\mathrm{e}$, describes diffusion through the pore space of porous media. It is macroscopic in nature, because it is not individual pores but the entire pore space that needs to be considered. Under steady state conditions the mass flux, $F$, depends on the concentration gradient and is expressed by Fick's first law:

$$F = -D_e \frac{dC}{dx} \tag{4.2}$$

The effective diffusion coefficient for transport through the pores is estimated as follows:

$$D_e = \frac{D_\mathrm{m} \varepsilon \delta}{\tau} \tag{4.3}$$

where $\tau$ and $\delta$ are dimensionless factors accounting for tortuosity ($> 1$) and constrictivity ($\leq 1$) of the pores, respectively, and $\varepsilon$ is the effective porosity which accounts for the reduced cross-sectional area available for diffusion when diffusion occurs only in the pore space. The constrictivity describes the slowing down of diffusion by increasing the viscosity in narrow pores as a result of greater proximity to the average pore wall. It is a function of pore diameter and the size of the diffusing particles.

### 4.2.1 Constrictivity Factor

The constrictivity factor $\delta$ depends on the ratio of the solute diameter to the pore diameter ($\lambda_\mathrm{p}$):

$$\lambda_p = \frac{\text{molecule diameter}}{\text{pore diameter}} \tag{4.4}$$

may be quantified by empirical equations, as developed by Beck and Schultz [11] and Chantong and Massoth [28], respectively:

$$\delta = \left(1 - \lambda_p\right)^4 \tag{4.5}$$

$$\delta = 1.03 \exp\left(-4.05\lambda_p\right) \tag{4.6}$$

### 4.2.2 Tortuosity Factor

The tortuosity factor, $\tau$, in Eq. 4.3 accounts for the pore geometry and is defined as the square of the ratio of the effective path length, *le*, in the pore to the shortest distance, *l*, in a porous medium:

$$\tau = \left(\frac{le}{l}\right)^2 \tag{4.7}$$

Tortuosity is not a physical constant and depends first of all on other porous media characteristics, like porosity, pore diameter, channel shape, etc. In general, in granular packings or beds the value of tortuosity lies in the region 1.1–1.7 (see [9] and Dullien [43]), and our experimental results obtained with packed beds of narrow size particles are in this range.

Several empirical correlations, suggesting a relationship between tortuosity and porosity, have been found in the literature since the end of the nineteen century:

$$\tau = 1.5 - 0.5\varepsilon \quad \text{Ref. [113]} \tag{4.8}$$

$$\tau = \varepsilon^{-n} \quad \text{Ref. [4]} \tag{4.9}$$

$$\tau = 1 - 0.5 \times \ln(\varepsilon) \quad \text{Ref. [168]} \tag{4.10}$$

$$\tau = \sqrt{1 - \ln(\varepsilon^2)} \quad \text{Ref. [22]} \tag{4.11}$$

$$\tau = 1 - 0.41 \times \ln(\varepsilon) \quad \text{Ref. [42]} \tag{4.12}$$

$$\tau = 1/\sqrt{\varepsilon} \quad \text{Refs. [27], [113]} \tag{4.13}$$

Recently, Yun et al. [148] presented a theoretical geometry model for tortuosity of tortuous streamtubes in a porous media with spherical particles. The authors suggested an average value of tortuosity given by

$$\tau = \frac{\tau_1 + \tau_2}{2} \tag{4.14}$$

with

$$\tau_1 = \frac{\left[1 + \frac{\sqrt{3}(\pi - 2)}{6 + 3P}\right] + \left[\frac{\sqrt{2 + 3P^2/4 + 3P} + \arcsin\left(\sqrt{3}(2 + P)/2\right)^{-1}}{\sqrt{3}(2 + P)/2}\right]}{4} + \frac{\frac{1}{\sqrt{1 - \left[\frac{1}{\sqrt{3}(2 + P)/2}\right]^2}} + \frac{1}{\sqrt{1 - \left[\frac{1}{\sqrt{3}(2 + P)/2 - 1}\right]^2}}}{4} \tag{4.15}$$

$$\tau_2 = \left(1 - \frac{P_1}{P_1 + 1}\right)\left(1 + \frac{\pi - 2}{P_1 + 2}\right) + \frac{P_1}{P_1 + 1} \tag{4.16}$$

where $P = \sqrt{2\pi/\left(\sqrt{3}(1 - \varepsilon)\right)} - 2$ and $P_1 = \sqrt{\pi/(1 - \varepsilon)} - 2$.

Equations 4.8–4.14 all satisfy the condition $\tau = 1$ for $\varepsilon = 1$, and this is consistent with the physical situation observed. Yun et al. [148] and Sen et al. [120] showed that for an isotropic medium with spherical particles the tortuosity of porous and granular media decreases with increasing bed voidage and increase for non-spherical particles.

### 4.2.3 Porosity Factor

The overall porosity, $\varepsilon$, of porous media can be determined (pore size distribution and tortuosities are unknown). Therefore the relative diffusivity $(D^* = D_e/D_m)$ is often defined as an empirical function of $\varepsilon$ alone $(\delta = 1)$:

$$D_e = D_m \varepsilon^m \tag{4.17}$$

where $m$ is an empirical exponent.

Archie [4] found that the exponent m varied between 1.8 and 2.0 in consolidated materials. In unconsolidated sand he found a value of 1.3. For an isotropic packing of spherical particles a theoretical value of m = 3/2 was derived [21]. Adler et al. [1] reported a value of m = 1.64 for Fontainebleau sandstone. Probst and Wohlfahrt [107] found that m equals 1.43 for loose packings of catalyst particles and Millington and Quirk [96] reported a value of 4/3 for diffusive flow of gases at normal pressures or diffusion of ions in solution in soils. In experiments on the diffusion of gases through compacted sands a value of m = 1.5 was determined [122].

### 4.2.4 Diffusion in Semi-Infinite Porous Media

In the limit of very low fluid velocity, where $u \to 0$, dispersion is determined solely by molecular diffusion, with $D_T = D_L = D_m/\tau = D_e$. Diffusion may be the dominant mass transfer mechanism (compared to advection) in zones of low hydraulic conductivity. The geometry of these layers may be considered as plane sheets and analytical solutions of Fick's second law are available for a variety of initial and boundary conditions [36].

Thick confining layers and bedrock formations of low permeability may represent a sink for contaminants which are spread out in an aquifer or a landfill. On the other hand, once such low-permeability domains are contaminated, they may become a long-term source during remediation of the aquifer (e.g. pump-and-treat). These formations can be considered as semi-infinite media for diffusion. If the low conductivity zone is free of the contaminant initially and then exposed to a constant concentration at the surface for a given period of time, the initial and boundary conditions are:

$$t = 0 \quad x > 0 \quad C = C_1 \tag{4.18a}$$

$$t > 0 \quad x = 0 \quad C = C_0 \tag{4.18b}$$

$$t > 0 \quad x \to \infty \quad C = C_1 \tag{4.18c}$$

The concentration profile at a given time is:

$$\frac{C - C_1}{C_0 - C_1} = 1 - erf\left(\frac{x}{2\sqrt{D_e t}}\right) \tag{4.19}$$

The quantity $2\sqrt{D_e t} = d_p$ can be considered as "penetration depth" which represents the time dependent distance within which 87% of the mass of the diffusing substance occurs. Accordingly, the "penetration time" then represents the time after which 87% of the diffusing molecules have not yet moved beyond a given distance.

The special case of zero surface concentration is obvious. The rate of loss diffusing substance from the semi-infinite medium when the surface concentration is zero, is

$$D_e\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{D_e C_0}{\sqrt{D_e t}} \tag{4.20}$$

and the total amount $M_t$ of diffusing substance which has left the medium at time $t$ is given by integrating Eq. 4.19 and is

$$M_t = 2C_0\sqrt{\frac{D_e t}{\pi}} \tag{4.21}$$

### 4.2.5 Diffusion in a Plane Sheet

In this case we consider one-dimensional diffusion through a plane sheet of thickness $2d$, initially at a uniform concentration $C_0$ and with the surface at constant concentration $C_1$.

The boundary conditions are:

$$t = 0 \quad -d < x < d \quad C = C_1 \tag{4.22a}$$

$$t > 0 \quad x = 0 \quad C = C_0 \tag{4.22b}$$

$$t > 0 \quad x \to \infty \quad C = C_1 \tag{4.22c}$$

The mass of solute per unit area which has diffused after a certain time is:

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\left(\frac{(2n+1)\pi x}{2d}\right)\exp\left(\frac{(2n+1)^2\pi^2 D_e t}{4d^2}\right) \tag{4.23}$$

and the total amount $M_t$ of diffusing substance which has entered the plane sheet at time $t$ is given by

$$\frac{M_t}{M\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(\frac{(2n+1)^2\pi^2 D_e t}{4d^2}\right) \tag{4.24}$$

where $M_\infty$ is the corresponding quantity after infinite time. The corresponding solutions for small times are:

$$\frac{C - C_1}{C_0 - C_1} = \sum_{n=0}^{\infty}(-1)^n erfc\frac{(2n+1)d - x}{2\sqrt{D_e t}} + \sum_{n=0}^{\infty}(-1)^n erfc\frac{(2n+1)d + x}{2\sqrt{D_e t}} \tag{4.25}$$

and

$$\frac{M_t}{M\infty} = \frac{2}{d}\sqrt{D_e t}\left[\pi^{-1/2} + 2\sum_{n=1}^{\infty}(-1)^n ierfc\frac{nd}{\sqrt{D_e t}}\right] \tag{4.26}$$

### 4.2.6 *Diffusion in a Cylinder*

If we consider a circular cylinder in which the diffusion is radial, concentration is then a function of radius and time, and the diffusion equation is obtained:

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_e\frac{\partial C}{\partial r}\right) \tag{4.27}$$

Considering the following boundary conditions:

$$t = 0 \quad 0 < r < a \quad C = C_1 \tag{4.28a}$$

$$t > 0 \quad r = a \quad C = C_0 \tag{4.28b}$$

$$t > 0 \quad r \to \infty \quad C = C_1 \tag{4.28c}$$

the solution obtained is:

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{1}{\alpha_n J_1(a\alpha_n)} \exp(-D_e \alpha_n^2 t) J_0(r\alpha_n) \tag{4.29}$$

where $\alpha_n$ is the positive roots of $J_0(a\alpha_n) = 0$, $J_0(x)$ is the Bessel function of the first kind of order zero, and $J_1(x)$ is the Bessel function of the first order.

The total amount $M_t$ of diffusing substance which has entered or left the cylinder at time $t$ is given by

$$\frac{M_t}{M\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp(-D_e \alpha_n^2 t) \tag{4.30}$$

where $M_\infty$ is the corresponding quantity after infinite time. The corresponding solutions for small times are:

$$\begin{aligned} \frac{C - C_1}{C_0 - C_1} = {} & \sqrt{\frac{a}{r}}\, erfc \frac{a - r}{2\sqrt{D_e t}} + \frac{(a - r)\sqrt{D_e a t}}{4ar^{3/2}}\, ierfc \frac{a - r}{2\sqrt{D_e t}} \\ & + \frac{(9a^2 - 7r^2 - 2ar)D_e t}{32a^{3/2} r^{5/2}}\, i^2 erfc \frac{a - r}{2\sqrt{D_e t}} + \ldots \end{aligned} \tag{4.31}$$

and

$$\frac{M_t}{M\infty} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{D_e}{a^2} t} - \frac{D_e}{a^2} t - \frac{1}{3\sqrt{\pi}} \left( \frac{D_e}{a^2} t \right)^{3/2} + \ldots \tag{4.32}$$

### 4.2.7 Diffusion in a Sphere

If we consider a sphere in which the diffusion is radial, concentration is then a function of radius and time, and the diffusion equation is obtained:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} D_e \frac{\partial C}{\partial r} \tag{4.33}$$

Considering the following boundary conditions:

$$t = 0 \quad 0 < r < a \quad C = C_1 \tag{4.34a}$$

$$t > 0 \quad r = a \quad C = C_0 \tag{4.34b}$$

$$t > 0 \quad r \to \infty \quad C = C_1 \tag{4.34c}$$

the solution obtained is:

$$\frac{C - C_1}{C_0 - C_1} = 1 + \frac{2a}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi r}{a}\exp\left(-\frac{D_e n^2\pi^2}{a^2}t\right) \tag{4.35}$$

And the concentration at the centre of the sphere, $r \to 0$, is given by

$$\frac{C - C_1}{C_0 - C_1} = 1 + 2\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{D_e n^2\pi^2}{a^2}t\right) \tag{4.36}$$

The total amount $M_t$ of diffusing substance which has entered or left the sphere at time $t$ is given by

$$\frac{M_t}{M\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{D_e n^2\pi^2}{a^2}t\right) \tag{4.37}$$

where $M_\infty$ is the corresponding quantity after infinite time. The corresponding solutions for small times are:

$$\frac{C - C_1}{C_0 - C_1} = \frac{a}{r}\sum_{n=0}^{\infty}\left[\mathit{erfc}\frac{(2n+1)a - r}{2\sqrt{D_e t}} - \mathit{erfc}\frac{(2n+1)a + r}{2\sqrt{D_e t}}\right] \tag{4.38}$$

and

$$\frac{M_t}{M\infty} = 6\sqrt{\frac{D_e}{a^2}t}\left[\pi^{-1/2} + 2\sum_{n=0}^{\infty}\mathit{ierfc}\frac{na}{\sqrt{D_e t}}\right] - 3\frac{D_e}{a^2}t \tag{4.39}$$

## 4.3 Axial Dispersion

Over the past 5 decades, axial dispersion in porous media has been measured and correlated extensively for gaseous and liquid systems. Many publications are available for a variety of applications, including: packed bed reactors [29, 47, 65, 89, 135] and soil column systems [9, 99, 102, 103].

One of the first results published about axial dispersion in packed beds of inertial particles was in the 1950s by Danckwerts [37], who published his celebrated paper on residence time distribution in continuous contacting vessels, including chemical reactors, and thus provided methods for measuring axial dispersion rates. The author studied dispersion along the direction of flow for a step input in solute concentration ($C_S$) in a bed of Raschig rings (with length $L$), crossed by water ($C_0$) with a value of $\mathrm{Re}(= \rho U d/\mu)$ approximately equal to 25 and obtained a $\mathrm{Pe_L}(= ud/D_L)$ value of 0.52.

Kramers and Alberda [85] followed Danckwerts's study with a theoretical and experimental investigation by the response to a sinusoidal input signal. These authors proposed that packed beds could be represented as consecutive regions of well-mixing rather than a sequence of stirred tanks (mixing-cell model) and suggested a $\mathrm{Pe_L} \cong 1$, for $\mathrm{Re} \to \infty$. McHenry and Wilhelm [94] assumed the axial distance between the mixing-cells in a packing to be equal to particle diameter and showed that $\mathrm{Pe_L}$ must be about two for high Reynolds number. The difference in the two results may be explained on the basis of experimental results of Kramers and Alberda [85] while are obtained with $L/D \approx 4.6$, a value significantly less than $L/D > 20$ [66]. Klinkenberg et al. [81] and Bruinzeel et al. [22] show that radial dispersion can be neglected for a small ratio of column diameter to length and large fluid velocity.

Brenner [19] presented the solution of a mathematical model of dispersion for a bed with finite length, $L$, and the most relevant conclusion of his work was that for $\mathrm{Pe_a}(= uL/D_\mathrm{L}) \geq 10$, the equations obtained by Danckwerts [37] for an input step in solute concentration and Levenspiel and Smith [89] for a pulse in solute concentration, that assumed an infinite bed, are corrected.

Hiby [75] proposed a better empirical correlation to cover the range of Reynolds numbers to 100. The author reported experimental results with the aid of photographs to compare the two dispersion mechanisms presented above: diffusional model in turbulent flow and the mixing-cell model.

Sinclair and Potter [124] used a frequency response technique applied to the flow of air through beds of glass ballotini in a Reynolds number range between 0.1 and 20. A further investigation in the intermediate Reynolds number region has been carried out by Evans and Kenney [50] who used a pulse response technique in beds of glass spheres and Raschig rings.

Experiments reported by Gunn and Pryce [68] showed that axial dispersion coefficients given by the theoretical equation for the diffusional model and the theoretical equation for the mixing-cell model are very similar. The authors also showed that neither the mixing-cell model nor the axially dispersed plug flow model could describe axial dispersion phenomena.

The description of solute transport in packed beds by dispersion models has been studied since the 1950s and has long attracted the attention of engineers and scientists.

Typically, the boundary conditions adopted, by the vast majority of the investigators reported above, have corresponded to the semi-infinite bed, i.e., $L$ is sufficiently large $(L/D > 20)$. Dispersion of the given tracer was measured at two points in the outlet and the distortion of a tracer forced by a pulse input (ex: [13, 25, 128]), frequency response (ex: [39, 45, 85, 94, 130]) and step input (ex: [37, 75, 95, 100]). Figure 4.1 illustrates some experimental data points for axial dispersion in liquid and gaseous systems. The experimental dispersion data are most frequently presented in logarithmic plots of $\mathrm{Pe_L}$ (or $D_\mathrm{L}/D_\mathrm{m}$) *vs*. $\mathrm{Pe_m}(= ud/D_\mathrm{m})$, spanning six or more orders of magnitude.

### *4.3.1 Parameters Influencing Axial Dispersion: Porous Medium*

Perkins and Johnston [102] in their article review showed some of the variables that influence axial and radial dispersion. However, before attempting in the

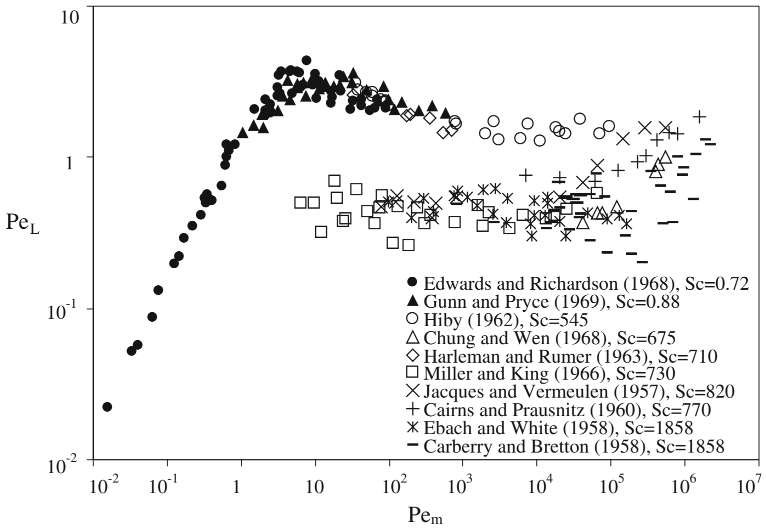


**Fig. 4.1** Some experimental data points for axial dispersion in liquid systems and gaseous systems

parameters influencing dispersion, it is important to consider the effect of the packing of the bed on dispersion coefficients. Gunn and Pryce [68] and Roemer et al. [111] showed that when particles in packed beds are not well packed the dispersion coefficient is increased. Experimental results of Gunn and Pryce [68] showed that different re-packing of the bed gave deviations of 15% in radial Peclet values. These experiments confirm that fluid mechanical characteristics are not only defined by the values of the porosity and tortuosity (easy to reproduce), but depend of the quality of packing in the bed.

The effect of radial variations of porosity and velocity on axial and radial transport of mass in packed beds was analytically quantified by Choudhary et al. [30], Lerou and Froment [88], Vortmeyer and Winter [138] and Delmas and Froment [41].

A rigorous measurement of the porosity in a packed bed is fundamental to minimize the errors in the experimental measurements, because the porosity between the inert particles of the bed helps the diffusion of a tracer and gradually increases dispersion.

A more coherent interpretation of the experimental data may be obtained through the use of dimensional analysis. As a starting point it is reasonable to accept the functional dependence

$$D_L = \phi(L, D, u, d, \rho, \mu, D_m) \tag{4.40}$$

for randomly packed beds of mono sized particles with diameter $d$, where $\rho$ and $\mu$ are the density and viscosity of the liquid, respectively, and $D_m$ is the coefficient of molecular diffusion of the solute. Making use of Buckingham's $\pi$ theorem, Eq. 4.40 may be rearranged to give

$$\frac{D_\mathrm{L}}{D_\mathrm{m}} \text{ or } \mathrm{Pe}_\mathrm{L} = \Phi\left(\frac{L}{D}, \frac{D}{d}, \frac{ud}{D_\mathrm{m}}, \frac{\mu}{\rho D_\mathrm{m}}\right) \tag{4.41}$$

and it is useful to define $\mathrm{Pe}_\mathrm{m} = ud/D_\mathrm{m}$ and $\mathrm{Sc} = \mu/\rho D_\mathrm{m}$. This result suggests that experimental data be plotted as $(D_\mathrm{L}/D_\mathrm{m})$ *vs.* $\mathrm{Pe}_\mathrm{m}$.

#### 4.3.1.1 Effect of Column Length

One first aspect to be considered, as a check on the experimental method (infinite medium), is the influence of the length of the bed ($L$) on the measured value of axial dispersion. In reality, if an experimental method is valid, values of the dispersion coefficient measured with different column lengths, under otherwise similar conditions, should be equal, within the reproducibility limits.

The dependence of the axial dispersion coefficient on the position in packed beds was first examined by Taylor [133]. The author showed that, in laminar flow, dispersion approximation would be valid if the following equation is satisfied,

$$\theta = \frac{D_\mathrm{m} t}{R^2} \gg 0.14 \tag{4.42}$$

where $R$ is the tube radius. Carbonell and Whitaker [26] concluded that the axial dispersion coefficient becomes constant if the following expression is satisfied

$$\theta = \left(\frac{1-\varepsilon}{\varepsilon}\right)^2 \frac{D_\mathrm{m} t}{d^2} \gg 1 \tag{4.43}$$

Han et al. [69], see Fig. 4.2, showed that values of the axial dispersion coefficient, for uniform size packed beds, measured at different positions in the bed are function of bed location unless the approximate criterion

$$\frac{L}{d}\frac{1}{\mathrm{Pe}_\mathrm{m}}\left(\frac{1-\varepsilon}{\varepsilon}\right)^2 \geq 0.3 \quad \text{or} \quad \theta = \frac{D_\mathrm{m} t}{d^2} \geq 0.15 \tag{4.44}$$

is satisfied. The authors showed that for $\mathrm{Pe}_\mathrm{m} < 700$, axial dispersion coefficients were nearly identical for all values of $x = L$, and for $\mathrm{Pe}_\mathrm{m} > 700$ observed an increase in the value of dispersion coefficients with increasing distance down the column.

#### 4.3.1.2 Ratio of Column Diameter to Particle Diameter

It is well known (e.g. [137]) that the voidage of a packed bed (and therefore the fluid velocity) is higher near a containing flat wall. The effects of radial variations

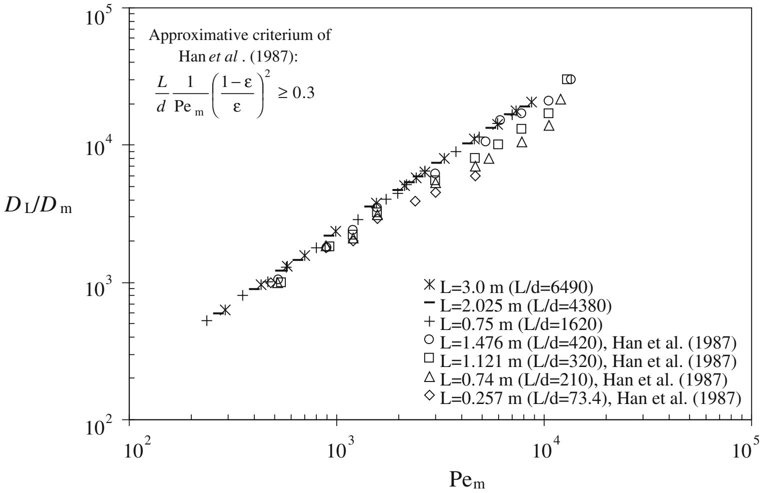


**Fig. 4.2** Effect of bed length on axial dispersion

of porosity and velocity on axial and radial transport of mass in packed beds were analytically quantified by several investigators like Choudhary et al. [30], Lerou and Froment [88], Vortmeyer and Winter [138] and Delmas and Froment [41].

Schwartz and Smith [118] were the first to present experimental data showing zones of high porosity extending two or three particle diameters from the containing flat wall. The results indicated that unless $D/d > 30$ important velocity variations exist across the packed bed. Other studies showed that packed bed velocity profiles significantly differ from flows with large diameter particles in small diameter tubes ([23, 34]).

Hiby [75] showed that the effect of $D/d$ is not significant in the measured of axial dispersion coefficient when the ratio is greater than 12.

Stephenson and Stewart [129] showed that the area of high fluid velocities limits to the area of high porosities, and this area does not extend more than a particle diameter of the wall and the assumption of a flat velocity profile is reasonable. This work confirms the earlier experiments reported by Roblee et al. [110], Schuster and Vortmeyer [117] and Vortmeyer and Schuster [137].

A similar effect was observed in measuring pressure drops across packings, so an empirical rule can be considered that the variations, in radial position, of the fluid velocity, porosity and dispersion coefficient can be negligible, if $D/d > 15$ [3, 66].

#### 4.3.1.3 Ratio of Column Length to Particle Diameter

Strang and Geankoplis [130] and Liles and Geankoplis [90] make much of the effect of $L/d$ but the evidence from fluid mechanical studies [67] was that the effect is confined to a dozen layers of particles and is not very important.

Experimental results of Guedes de Carvalho and Delgado [61], presented in Fig. 4.3, with two different spherical particles diameter and the same length of the packed bed showed that axial dispersion coefficient does not increased with particle diameter, as long as the condition $D/d > 15$ is satisfied (see Vortmeyer and Schuster [137] and Ahn et al. [2], for wall effects).

#### 4.3.1.4 Particle Size Distribution

Another aspect of dispersion in packed beds that needs to receive attention is the effect of porous medium structure. In a packed bed of different particle sizes, the small particles accumulate in the interstices between large particles, and porosity tends to decrease.

Raimondi et al. [108] and Niemann [98] studied the effect of particle size distribution on axial dispersion and concluded that $D_{\mathrm{L}}$ increases with a wide particle size distribution. Eidsath et al. [48] indicated a strong effect of particle size distribution on dispersion. As the ratio of particle diameters went from a value of 2 to 5, the axial dispersion increased by a factor of 1.5, and radial dispersion decreased by about the same factor.

Han et al. [69] showed that for a size distribution with a ratio of maximum to minimum particle diameter equal to 7.3, axial dispersion coefficient are 2–3 times larger than the uniform size particles (see Fig. 4.3).

Wronski and Molga [146] studied the effect of particle size non-uniformities on axial dispersion coefficients during laminar liquid flow through packed beds (with a ratio of maximum to minimum particle diameter equal to 2.13) and proposed a generalized function to determine the increase of the axial dispersion coefficients in non-uniform beds relative to those obtained in uniform beds.

Guedes de Carvalho and Delgado [61] obtained the same conclusion in their experiments, with ballotini and a ratio of maximum to minimum particle diameter equal to 3.5 in comparison with glass ballotini that have the same size.

#### 4.3.1.5 Particle Shape

The effect of particle shape on axial dispersion has been studied by several investigators, such as Bernard and Wilhelm [14], Ebach and White [45], Carberry and Bretton [25], Strang and Geankopolis [130], Hiby [75], Klotz [82] and more recently Guedes de Carvalho and Delgado [61]. The authors have used beds of spheres, cubes, Raschig rings, sand, saddles and other granular material, and have concluded that generally axial dispersion coefficient tend to be greater with packs of nonspherical particles than with packs of spherical particles, with the same size.

Figure 4.4 shows that particle shape is a significant parameter, with higher values of $D_{\mathrm{L}}$ (i.e., lower $\mathrm{Pe}_{\mathrm{L}}$) being observed in packed beds of sand and Raschig rings comparatively with the results obtained with spherical beds.

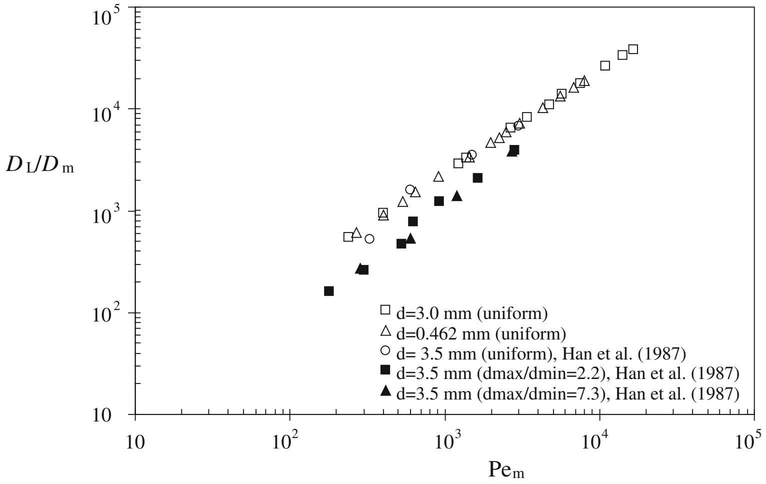


**Fig. 4.3** Effect of particle size distribution on axial dispersion

Therefore, increased particle sphericity correlates with decreased dispersion, with a sphericity defined as the surface area of a particle divided by the surface area of a sphere of volume equal to the particle.

## *4.3.2 Parameters Influencing Axial Dispersion: Fluid Properties*

### 4.3.2.1 Viscosity and Density of the Fluid

Some investigators, like Hennico et al. [74], used glycerol and obtained significant effect of viscosity, at large Reynolds number, on axial dispersion coefficient. In vertical miscible displacements, if a less viscous fluid displaced another fluid viscous fingers will be formed [102]. However, if a more viscous fluid displaced a different fluid the dispersion mechanisms are unaffected, but the situation will tend to reduce convective dispersion. This leads to increased dispersion relative to the more viscous fluid displacing a less viscous one.

The importance of density gradients was recently investigated by Benneker et al. [12] and their experiments showed that axial dispersion coefficient is considerably affected by fluids with different densities due the action of gravity forces. Fluid density creates similar effects to fluid viscosity. In a displacement with a denser fluid above the less-dense fluid, gravity forces cause redistribution of the fluids. However, if a denser fluid is on the bottom, usually, a stable displacement occurs.

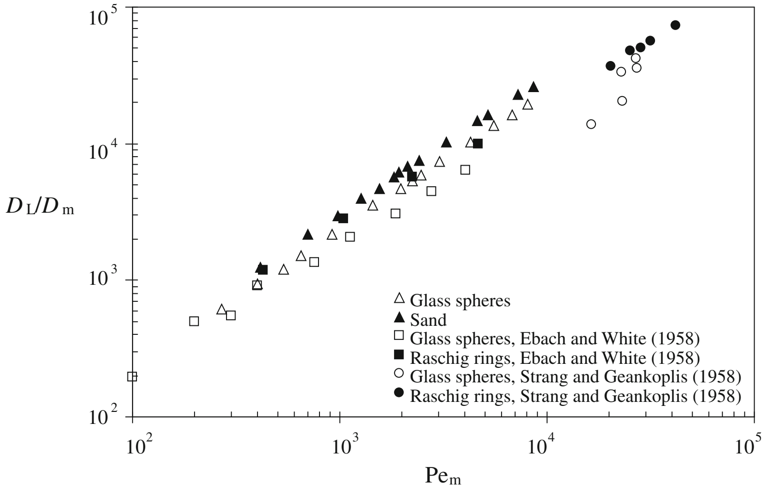


**Fig. 4.4** Effect of particle shape on axial dispersion

#### 4.3.2.2 Fluid Velocity

The first two groups of Eq. 4.8 have importance only when $D/d$ is less than 15 and $L/D$ is so small that the characteristics of dispersion are affected by changing velocity distributions. So, for packed beds we will usually have $D_L/D_m = \Phi(Pe_m,\ Sc)$.

In order to understand the influence of fluid velocity on the dispersion coefficient, it is important to consider the limiting case where $u \to 0$. If $D_L$ was defined based on the area open to diffusion (see Eq. 2), in the limit $u \to 0$, solute dispersion is determined by molecular diffusion, with $D_L = D'_m = D_m/\tau$ ($\tau$ being the tortuosity factor for diffusion and it is equal to $\sqrt{2}$ as suggested by Sherwood et al. [121]).

As the velocity of the fluid is increased, the contribution of convective dispersion becomes dominant over that of molecular diffusion (see [144]) and $D_L = ud/Pe_L(\infty)$, where $u$ is the interstitial fluid velocity and $Pe_L(\infty) \cong 2$ for gas or liquid flow through beds of (approximately) isometric particles, with diameter $d$ [23, 79].

Assuming that the diffusive and convective components of dispersion are additive, the same authors suggest that $D_L = D'_m + ud/Pe_L(\infty)$, which may be written in dimensionless form [66] as

$$\frac{D_L}{D_m} = \frac{1}{\tau} + \frac{1}{2}\frac{ud}{D_m} \quad \text{or} \quad \frac{1}{Pe_L} = \frac{1}{\tau}\frac{\varepsilon}{ReSc} + \frac{1}{2} \tag{4.45}$$

This equation is expected to give the correct asymptotic behaviour in gas and liquid flow through packed beds, at high and low values of $Pe_m(=ud/D_m)$. For gases this is confirmed in Fig. 4.5, but for liquids (Fig. 4.6) the data do not cover the extreme conditions.

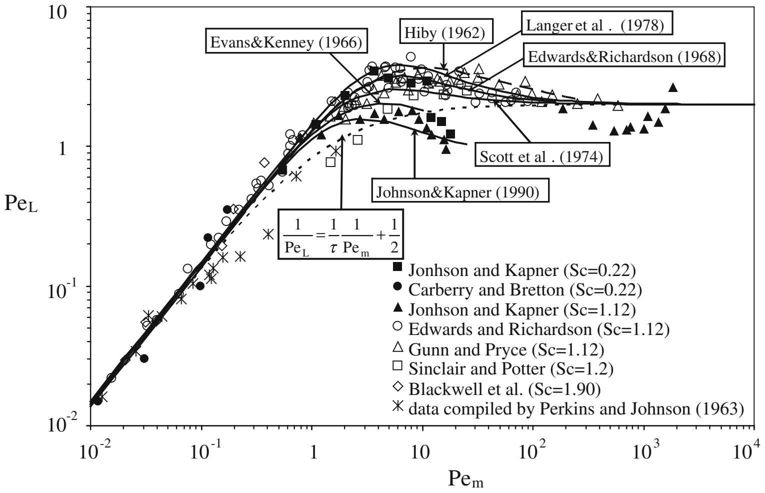


**Fig. 4.5** Axial dispersion in gases

But these figures show that Eq. 4.45 is inaccurate over part of the intermediate range of $Pe_m$. In the case of gas flow, shown Fig. 4.5, significant deviations are observed only in the range $0.6 < Pe_m < 60$, as pointed out by several of the authors [47, 66, 75, 136]. The experimental values of $Pe_L (= ud/D_L)$ are generally higher than predicted by Eq. 4.12. Several equations have been proposed to represent the data in this intermediate range and the equations of Hiby [75], Edwards and Richardson [47], Evans and Kenney [50], Scott et al. [119], Langer et al. [80] and Johnson and Kapner [80] are shown to fit the data points reasonably well (see Fig. 4.5).

With liquids, deviations from Eq. 4.45 occur over the much wider range $2 < Pe_m < 10^6$, the experimental values of $Pe_L$ being significantly lower than predicted by that equation. The difference in behaviour between gases and liquids has to be ascribed to the dependence of $Pe_L$ on Sc $(= \mu/\rho D_m)$.

#### 4.3.2.3 Fluid Temperature (or Schmidt Number)

The coefficient of axial dispersion for gas flow $(Sc \cong 1)$ is predicted with good accuracy by Eq. 4.45, except in the approximate range $0.5 < Pe_m < 100$, where experimental values may be more than twice those given by the equation, as confirmed by Fig. 4.5.

For liquid flow, a large number of data are available, that were obtained with different solutes in water at near ambient temperature, corresponding to values of Sc in the range $500 < Sc < 2000$. Most of the data reported in the literature, for this range of Sc, are shown in Fig. 4.6, and they form a “thick cloud” running parallel

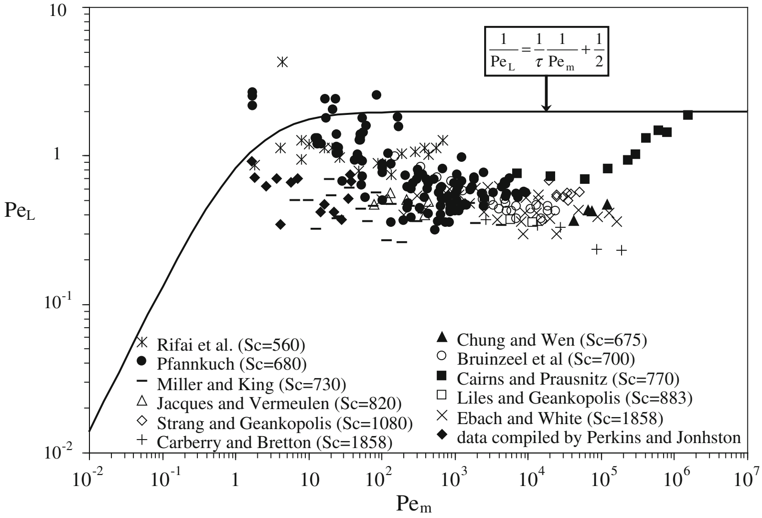


**Fig. 4.6** Axial dispersion in liquids

to the line defined by Eq. 4.45, though somewhat below it (at approximately, $0.3 < Pe_L < 2$).

In recent years, data on axial dispersion have been made available for values of Sc between the two extremes of near ideal gas ($Sc \cong 1$) and cold water ($Sc > 550$). Such data were obtained either supercritical carbon dioxide ($1.5 < Sc < 20$) or heated water ($55 < Sc < 550$) and are presented in Fig. 4.7.

Figure 4.7 show a consistent increase in $Pe_L$ with a decrease in Sc and it may be seen that the dependence is slight for the higher values of Sc (say for Sc of order 750 and above). At the lower end of the range of $Pe_m$ investigated there seems to be a tendency for $Pe_L$ to become independent of Sc, even if the values of $D_L$ are still significantly above $D_m$. In the intermediate range, $100 < Pe_m < 5000$, values of $Pe_L$ are very nearly constant, for each value of Sc. The convergence of the different series of points at about $Pe_m \cong 20$ seems to suggest that $Pe_L$ is insensitive to Sc below this value of $Pe_m$, for the range of Sc presented.

A good additional test of the consistency of the data of Guedes de Carvalho and Delgado [61] is supplied by the plot in Fig. 4.8, where it may be seen that all the series of points converge at high Re, as would be expected for turbulent flow. The agreement with the data of Jacques and Vermeulen [79] and Miller and King [95], for cold water, is worth stressing.

Recently, some workers have measured axial dispersion for the flow of supercritical carbon dioxide through fixed beds and this provides important new data in the range $1.5 < Sc < 20$. However, the various authors fail to recognize the direct dependence of $Pe_L$ on Sc. Catchpole et al. [27] represent their data and those of Tan and Liou [132] in a single plot (their Fig. 4.3) of $Pe_L$ *vs*. Re. The majority of points are in the range of $1 < Re < 30$ and the data of both groups, together,

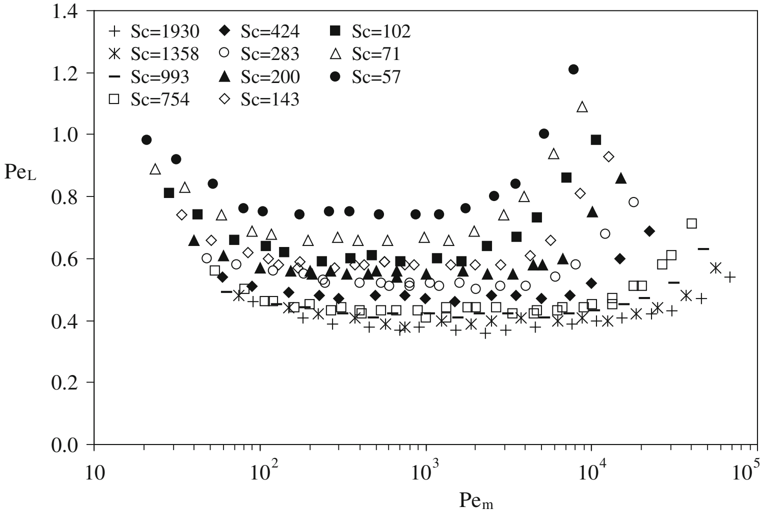


**Fig. 4.7** Dependence of $Pe_L$ on $Pe_m$ for different values of Sc

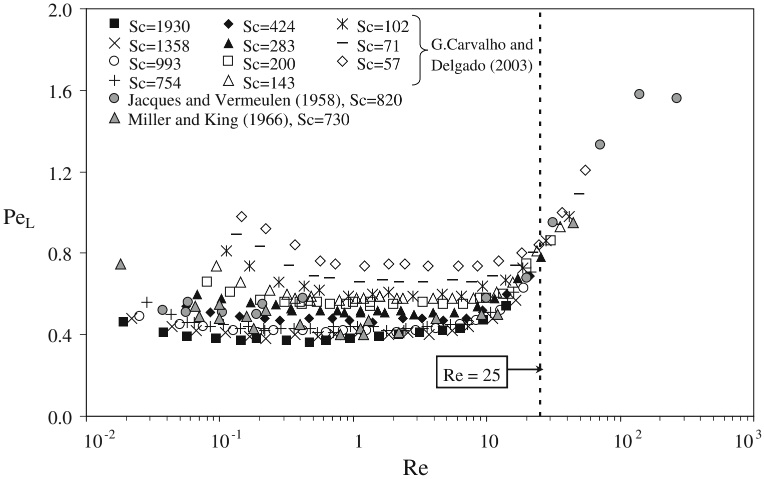


**Fig. 4.8** Dependence of $Pe_L$ on Re for different values of Sc

define a horizontal cloud with mid line at about $Pe_L \cong 0.8$, spreading over the approximate range $0.3 < Pe_L < 1.1$.

The data of Yu et al. [147] are for $0.01 < Re < 2$ and $2 < Sc < 9$. It is worth referring here that the modelling work of Coelho et al. [32] gives theoretical support to experimental findings for low Re, both for spherical and non-spherical particles. No influence of Sc on $Pe_L$ is detected, but unfortunately the results are not very consistent, particularly in the range $1 < Pe_m < 20$, where the scatter is high and the values of $Pe_L$ are much too low.

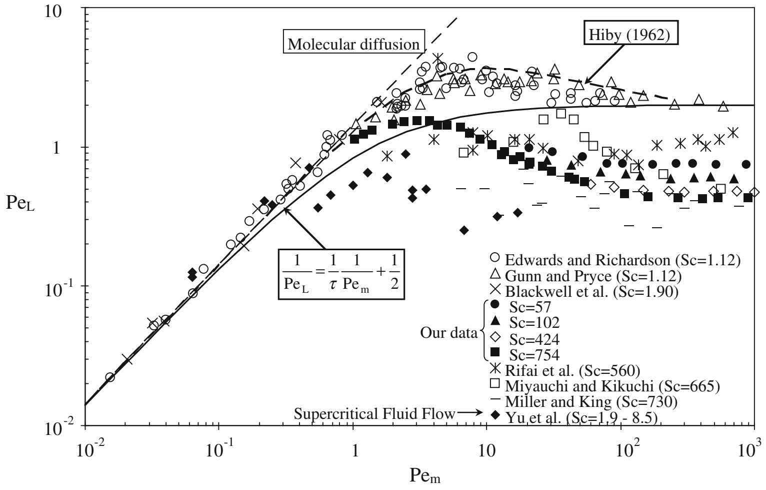


**Fig. 4.9** Dependence of $Pe_L$ on $Pe_m$ for Stokes flow regime

Figure 4.9 shows that for low values of $Pe_m$ (Stokes flow regime) there seems to be a tendency for $Pe_L$ to become independent of Sc. The values of $Pe_L$ reported by Miller and King [95], for $6 < Pe_m < 100$, are much too low; this may be because the particles used in most experiments are too small (particle sizes of 55 and 99 μm) and this is known to yield enhanced dispersion coefficients, possibly due to particle agglomeration (see [64, 75]). The data reported by Miyauchi and Kikuchi [97] and plotted in Fig. 4.9, for $6 < Pe_m < 300$, are higher than our experimental data.

There are considerable experimental difficulties in the measurement of axial dispersion in the liquid phase at small Reynolds number, because the usual method of obtaining low Reynolds number is to reduce particle size and this is known to yield enhanced dispersion coefficients.

## 4.4 Radial Dispersion

Generally, radial dispersion coefficients are measured in non-reactive conditions, because the rate of mass transfer, observed experimentally, is directly related to the coefficient of radial dispersion in the bed.

The most popular technique for the measurement of radial dispersion consists in feeding a continuous stream of tracer from a “point” source somewhere in the bed (usually along the axis, if there is one) and measuring the radial variation of tracer concentration at one or more downstream locations.

The first study of mass transfer by radial dispersion in gaseous systems was carried out by Towle and Sherwood [134]. The results presented were very important for packed bed dispersion because they showed that dispersion was not influenced by the tracer molecular weight.

Bernard and Wilhelm [14] reported the first measurements, in liquid systems, of experimental values of radial dispersion coefficients in packed beds of inerts by a Fickian model. The authors took into account the wall effect condition and their experiments suggested that for high values of Reynolds number the value of $\mathrm{Pe_T}$ is constant and between 11 and 13.

Baron [7] proposed a new model of radial dispersion in which a particle of tracer executes a simple random-walk displacement of ±½ particle diameter to give a transversal Peclet number between 5 and 13, when $\mathrm{Re} \to \infty$. The basis for this prediction is the random-walk theory, in which a statistical approach is employed. This method does not take into account effects of radial variations in velocity and void space. Latinen [87] extended the random-walk concept to three dimensions and predicted a value of 11.3, for $\mathrm{Pe_T}(\infty)$.

Klinkenberg et al. [81] solved Eq. 4.1 for anisotropic dispersion, but considered that dispersion occurs in an infinite medium. In the same work were considered the particulate cases of isotropic dispersion and axial dispersion neglected.

Plautz and Johnstone [105] used the equation derived by Wilson [145], for heat transfer, and suggested a $\mathrm{Pe_T}$ between 11 and 13, for $\mathrm{Re} \to \infty$. Fahien and Smith [51] assumed that for Reynolds numbers in the range between 40 and 100, the Peclet number is independent of fluid velocity and equal to 8. The authors were the first to consider that the tracer pipe can be of significant diameter compared to the diameter of the bed.

Dorweiler and Fahien [42] used the equation derived by Fahien and Smith [51] to study mass transfer in laminar and transient flows. The results showed that for $\mathrm{Re} < 200$, the Peclet number based on the radial dispersion coefficient is a linear function of the fluid velocity and for $\mathrm{Re} > 200$, at room temperature, the Peclet number is constant as also shown by Bernard and Wilhelm [14], Plautz and Johnstone [105] and Fahien and Smith [51]. The authors have demonstrated a difference in the Peclet number with radial position. The transversal Peclet number is constant from the axis to 0.8 times the radius and then rises near the wall.

Hiby and Schummer [76], and later Roemer et al. [111], presented the solution of the mass balance equation (Eq. 4.1), considering the tracer pipe to be of significant diameter compared to the diameter of the packed bed.

Saffman [114] considered the packed bed as a network of capillary tubes randomly orientated with respect to the main flow. At high Peclet number and at very long time, Saffman found that the dispersion never becomes truly mechanical, with zero velocity of the fluid at the capillary walls, the time required for a tracer particle to leave a capillary would become infinite as its distance from the walls goes to zero. The author proposed that $D_\mathrm{T} = (3/16)ud$ when $\mathrm{Re} \to \infty$, but this prevision of radial dispersion coefficient is higher than observed experimentally.

Hiby [75] and Blackwell [16] presented an experimental technique in which they divided the sampling region into two annular regions and calculated the transversal dispersion coefficient from the averaged concentrations of each of the two samples.

The experimental data points of Wilhelm [144] suggested that $\mathrm{Pe_T}(\infty) = 12$, for beds of closely sized particles, and this value is accepted for the majority of the investigators (ex: [15, 33, 66, 75, 144]).

Roemer et al. [111] studied radial mass transfer in packed beds at low flow rates, Re $<100$. The authors considered the tracer pipe to be of significant diameter compared to the diameter of the bed ("finite source" model) and axial and radial dispersion are equal. In this work the authors compared the values of $\mathrm{Pe}_{\mathrm{T}}$ obtained with two methods ("instantaneous finite source" and "point source") and concluded that the values of $\mathrm{Pe}_{\mathrm{T}}$ obtained with the "point source" method were 10% less that the values obtained with the "instantaneous finite source" method. The authors estimated that the neglecting the axial dispersion in calculations of $D_{\mathrm{T}}$, for low values of Reynolds numbers, can cause errors of 10%.

Coelho and Guedes de Carvalho [33] developed a new experimental technique, based on the measurement of the rate of dissolution of planar or cylindrical surfaces, buried in the bed of inert particles and aligned with the flow direction. This alternative technique is simple to use, allows the determination of the coefficient of radial dispersion in packed beds over a wide range of flow rates, and it is easily adaptable to work over a range of temperatures above ambient, as shown by Guedes de Carvalho and Delgado [63] and Delgado and Guedes de Carvalho [40].

In recent years, nuclear magnetic resonance has been used to determine both diffusion and dispersion coefficients (e.g. [8, 57]), with significant advantages, but this technique were limited to low fluid velocities.

It is important to remember that, at high Reynolds numbers, the main mechanism of radial dispersion is the fluid deflection caused by deviations in the flow path caused by the particles in the bed (axial dispersion is caused by differences in fluid velocity in the flow), i.e., dispersion is caused by hydrodynamic mechanisms (macroscopic scale) and not by molecular diffusion (Brownian motion).

The result is a poor mixture at the "microscopic scale". In fact, there are detected different values of solute concentration over a distance of the order of a particle diameter or less, what explains the convenience of use of an efficient averaging procedure [66]. This is probably one of the reasons that explain the difference observed in some experimental results of dispersion (see Fig. 4.10). Gunn and Pryce [68] showed that the standard deviation without repacking in the measurement of $\mathrm{Pe}_{\mathrm{T}}$ was 5%, while when the bed was repacked each time of measurement, the standard deviation found was 15%.

## *4.4.1 Parameters Influencing Radial Dispersion: Porous Medium*

### 4.4.1.1 Length of the Packed Column

Han et al. [69] showed that values of the radial dispersion coefficient, for uniform size packed beds, measured at different positions in the bed are not a function of bed location, *i.e.*, they observed no time dependent behaviour for radial dispersion, because radial dispersion is caused by mechanical mechanism alone.

An important aspect to be considered, as a check on the experimental method of Coelho and Guedes de Carvalho [33], is the influence of the length of the test

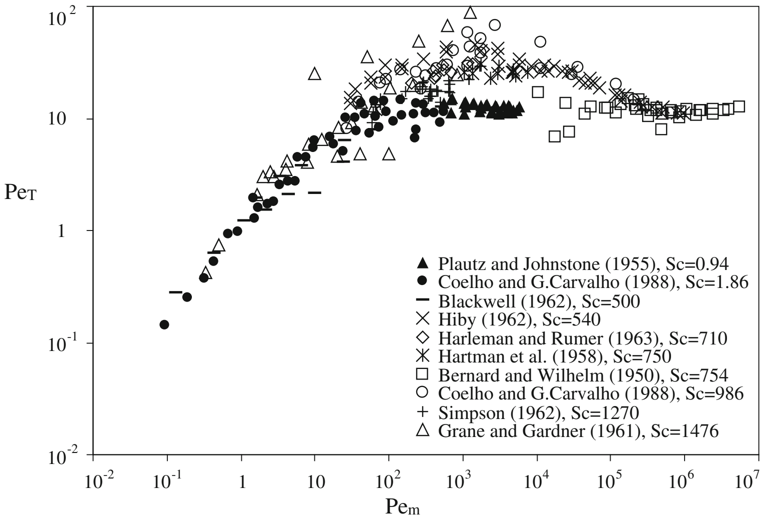


**Fig. 4.10** Some experimental data points for radial dispersion in liquid systems and gaseous systems

cylinder on the measured value of $D_T$. In reality, the two variables are independent, provided that the criterion given by Eq. 4.46 is satisfied (see Fig. 4.11 )

$$\frac{L}{d} \geq 0.62 \left(\frac{ud}{D_m}\right) \tag{4.46}$$

#### 4.4.1.2 Ratio of Column Diameter to Particle Diameter

Several investigators, like Fahien and Smith [51], Latinen [87] and Singer and Wilhelm [125], have studied the wall effect on radial dispersion coefficient. The experiments suggested that in a packing structure characterized by significant variations of void fraction in radial direction, up to distance of about two particle diameters from the wall, a non-uniform radial velocity profile is induced, with a maximum just near the wall. As result, wall effects occur due large voidage fluctuations near the wall. The above investigators also showed that the increase in radial dispersion in the laminar region would be the same order of magnitude as in the turbulent region.

#### 4.4.1.3 Particle Size Distribution

Eidsath et al. [48] studied the effect of particle size distribution on dispersion. As the ratio of particle diameter went from a value of 2 to 5, the radial dispersion decreased by a factor of 3, but perhaps the results were a cause of the simple

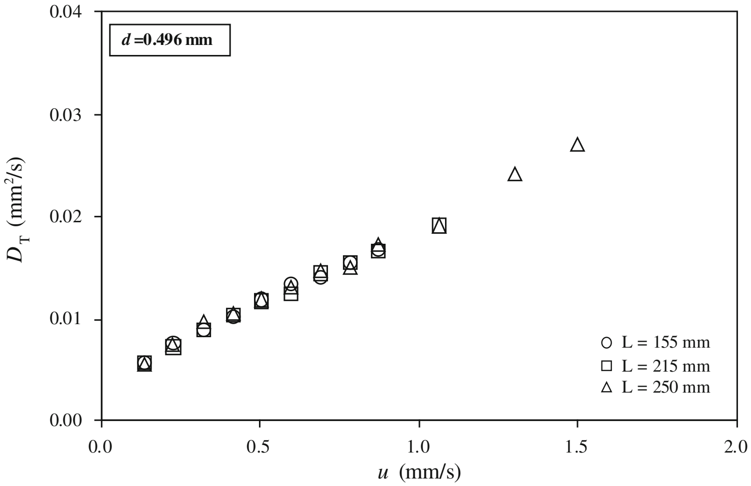


**Fig. 4.11** Effect of length of soluble cylinder on the measurement of radial dispersion

geometry employed in these computations (packed bed of cylinders). Steady-state measurements of radial dispersion reported by Han et al. [69], with the same void fraction and mean particle diameter, but different particle size range (ratio of maximum to minimum particle diameter equal to 2.2 and 7.3), showed that there was no evidence to indicate a change in radial dispersion with particle size distribution (see Fig. 4.12a).

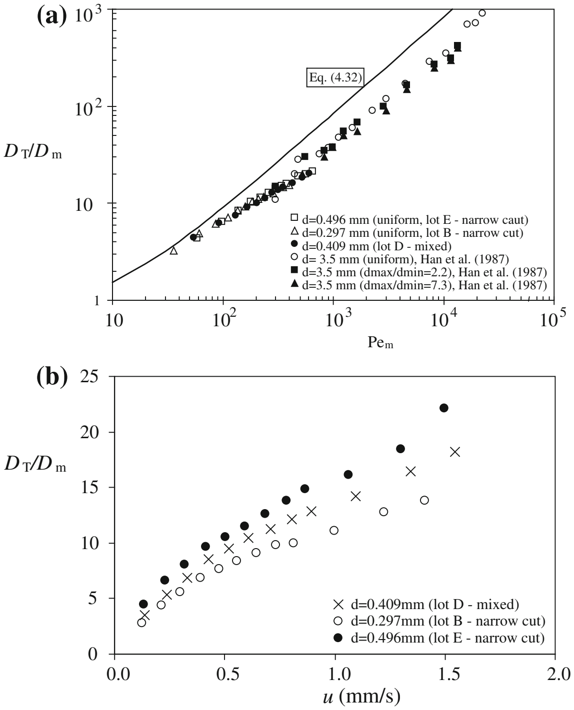
The effect of a distribution of particle sizes within the bed, on the radial dispersion coefficient, may be assessed from Guedes de Carvalho and Delgado [63]. In particular, lot D was prepared by carefully blending lots B and E in a proportion of 1:1 (by weight). In Fig. 4.12b, dispersion data obtained with the mixed lot are seen to fall in between the data for the original separate lots, as might be expected. Figure 4.12a shows that in a plot of $D_T/D_m$ *vs.* $\mathrm{Pe}_m$, the data for the three lots fall along the same line, when *d* (in $\mathrm{Pe}_m$) is taken to represent the average particle size in the bed.

#### 4.4.1.4 Particle Shape

The effect of particle shape on the radial dispersion coefficient has been given attention by several investigators both for gaseous and liquid systems. England and Gunn [49] measured the dispersion of argon in beds of solid cylinders and beds of hollow cylinders and have concluded that $D_T$ tend to be greater with packs of hollow cylinders than with packs of solid cylinders, and these results were greater than obtained with packs of spherical particles (see Fig. 4.13).

The same conclusion, in liquid systems, was been obtained by Hiby [75], who used packed beds of glass spheres and Rachig rings, and Bernard and Wilhem [14],

**Fig. 4.12** Effect of particle size distribution on radial dispersion. **a** $D_T/D_m$ *vs.* $Pe_m$; **b** $D_T/D_m$ *vs.* *u*.



who used packed beds of cubes, cylinders and glass spheres. Figure 4.13 shows that the radial dispersion coefficient tends to be greater in packed beds of non-spherical particles.

However, Blackwell [16], List [91], Guedes de Carvalho and Delgado [63] and others reported experiments with packed beds of sand and showed that $D_T$ obtained with glass ballotini are very close to those for sand (not pebble or gravel) and the conclusion seems to be that particle shape has only a small influence on lateral dispersion, for random packings of "isometric" particles.

## 4.4.2 Parameters Influencing Radial Dispersion: Fluid Properties

### 4.4.2.1 Viscosity and Density of the Fluid

The effect of fluid densities and viscous forces on radial dispersion has been studied by Grane and Garner [58] and Pozzi and Blackwell [106]. They concluded that when a fluid is displaced from a packed bed by a less viscous fluid, the viscous forces create an unstable pressure distribution and the less viscous fluid will penetrate the medium in the form of fingers, unless the density has an opposing effect.

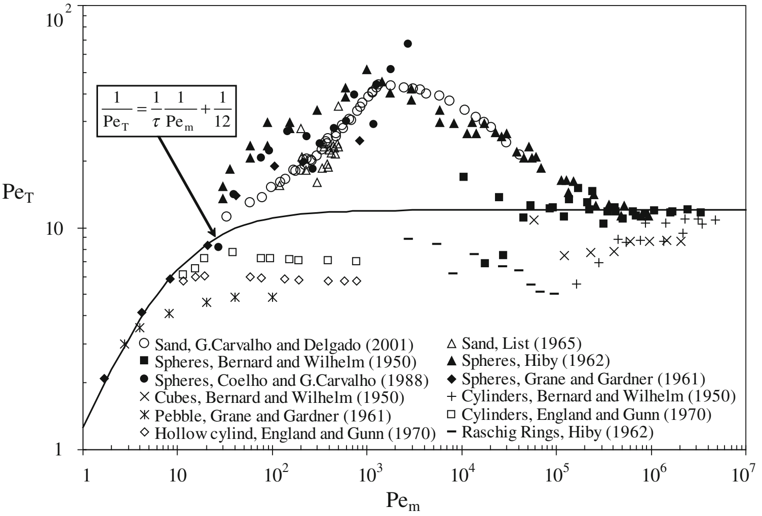


**Fig. 4.13** Effect of particle shape on radial dispersion

#### 4.4.2.2 Fluid Velocity

For very low fluid velocities, $u$, dispersion is the direct result of molecular diffusion, with $D_T = D'_m$. As the velocity of the fluid is increased, the contribution of convective dispersion becomes dominant over that of molecular diffusion and $D_T$ becomes less sensitive to temperature. According to several authors (see [15, 33, 66, 75, 144]) $D_T \to ud/\mathrm{Pe}_T(\infty)$, for high enough values of $u$, where $d$ is particle size and $\mathrm{Pe}_T(\infty) \cong 12$ for beds of closely sized particles. Assuming that the diffusive and convective components of dispersion are additive, the same authors suggest that $D_T = D'_m + ud/K$, which may be written in dimensionless form as

$$\frac{D_T}{D_m} = \frac{1}{\tau} + \frac{1}{12}\frac{ud}{D_m} \quad \text{or} \quad \frac{1}{\mathrm{Pe}_T} = \frac{1}{\tau}\frac{\varepsilon}{\mathrm{ReSc}} + \frac{1}{12} \tag{4.47}$$

This equation has been shown (see [33]) to give a fairly accurate description of radial dispersion in gas flow through packed beds, but it is not appropriate for the description of dispersion in liquids, over an intermediate range of values of $ud/D_m$, as pointed out by several of the authors mentioned above.

Figure 4.14a–b shows that the value of the radial dispersion coefficient is seen to increase with fluid velocity and comparison between the two plots shows that $D_T$ also increases with particle size.

Data on dispersion in randomly packed beds of closely sized, near spherical particles, lend themselves to simple correlation by means of dimensional analysis. Making use of Buckingham's theorem it may therefore be concluded that

$$\frac{D_{\mathrm{T}}}{D_{\mathrm{m}}} = \Phi\left(\frac{ud}{D_m}, \frac{\mu}{\rho D_m}\right) \quad \text{or} \quad \mathrm{Pe_L} = \Phi(\mathrm{Re, Sc}) \tag{4.48}$$

and it is useful to make $\mathrm{Pe_m} = ud/D_{\mathrm{m}}$ and $\mathrm{Sc} = \mu/\rho D_{\mathrm{m}}$.

#### 4.4.2.3 Fluid Temperature (or Schmidt Number)

The dependence of $D_{\mathrm{T}}$ on liquid properties and velocity is best given in plots of $\mathrm{Pe_T}$ *vs.* $\mathrm{Pe_m}$, for different values of Sc. Not surprisingly, Fig. 4.15 shows that the variation of $\mathrm{Pe_T}$ with $\mathrm{Pe_m}$ gets closer to that for gas flow as the value of Sc is decreased. For the lowest Sc tested ($\mathrm{Sc} = 54$; $T = 373$ K), $\mathrm{Pe_T}$ does not differ by more than 30% from the value given by Eq. 4.47, with $\mathrm{Pe_T}(\infty) = 12$, over the entire range of $\mathrm{Pe_m}$. However, for the higher values of Sc, the experimental values of $\mathrm{Pe_T}$ may be up to four times the values given by Eq. 4.47.

Delgado and Guedes de Carvalho [40] had studied the dependence of $D_{\mathrm{T}}/D_{\mathrm{m}}$ on Sc, up to $\mathrm{Pe_m} \cong 1350$, and they reported a smooth increase in $D_{\mathrm{T}}/D_{\mathrm{m}}$ with $\mathrm{Pe_m}$, for all values of Sc. But the data in Fig. 4.15 show that there is a sudden change in the trend of variation of $\mathrm{Pe_T}$ with $\mathrm{Pe_m}$, somewhere above $\mathrm{Pe_m} \cong 1,350$, a maximum being reached in the approximate range $1,400 < \mathrm{Pe_m} < 1,800$ (depending on Sc). The fact that the change in trend corresponds to a much enhanced increase in $D_{\mathrm{T}}$ (*i.e.* a decrease in $\mathrm{Pe_T}$), in response to a small increase in $u$ (*i.e.* in $\mathrm{Pe_m}$), strongly suggests a connection with the transition from laminar to turbulent flow in the interstices of the packing. The plot of $\mathrm{Pe_T}$ *vs.* Re, shown in Fig. 4.16, seems to support this view, since the maxima in $\mathrm{Pe_T}$ are reached for $0.3 < \mathrm{Re} < 10$ (depending on Sc) and this is the approximate range of values of Re for the transition from laminar to turbulent flow. The range $1 < \mathrm{Re} < 10$ is often indicated for that transition (see for example [9]), but Scheidegger [116] as giving $\mathrm{Re} = 0.1$ for the lower limit of that transition.

The plot in Fig. 4.16 also suggests that "purely mechanical" fluid dispersion will be observed above about $\mathrm{Re} = 100$; this value is estimated as the convergence of the data points for liquids with the line representing Eq. 4.47. Figure 4.17 shows the data reported by most other authors (all for $\mathrm{Sc} \geq 540$) in a plot of $\mathrm{Pe_T}$ *vs.* $\mathrm{Pe_m}$. With the exception of the data of Hoopes and Harleman [78] and some of the points of Grane and Gardner [58] and Bernard and Wilhelm [14], general agreement is observed with Guedes de Carvalho and Delgado [62] data for high Sc.

## 4.5 Dispersion in Packed Beds Flowing by Non-Newtonian Fluids

Hilal et al. [77], Edwards and Helail [46], Payne and Paker [101] and Wen and Yin [142] reported results of axial dispersion coefficients for the flow of two polymer solutions through a packed bed and their results were similar to the corresponding

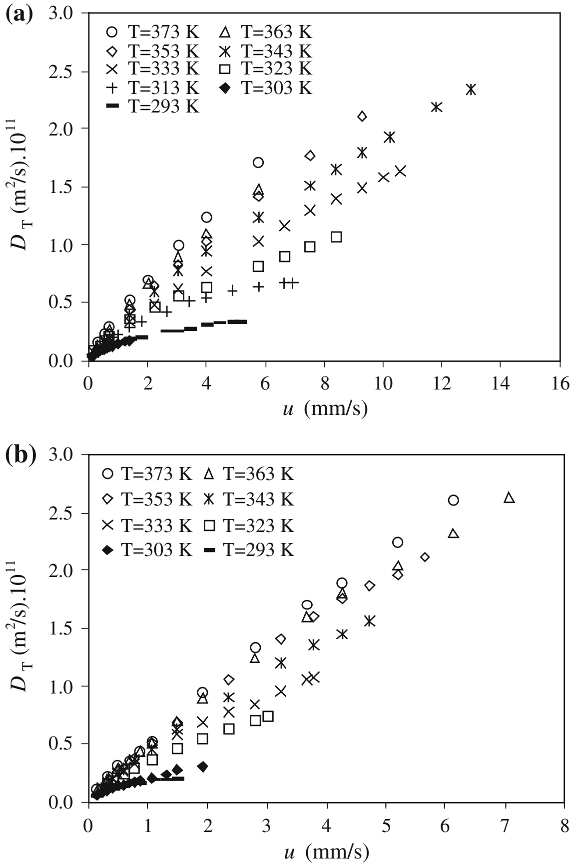


**Fig. 4.14** Variation of radial dispersion coefficient with fluid velocity. **a** sand size $d = 0.297$ mm; **b** sand size $d = 0.496$ mm

Newtonian results (see Table 4.1). Wen and Fan [140] correlate the previous results for packed beds with the following expression:

$$\mathrm{Pe}\left(=\frac{Ud}{D_{\mathrm{L}}}\right) = 0.2 + 0.011\mathrm{Re}_n^{0.48}\ \text{with}\ \mathrm{Re}_n = \frac{\rho d^n U^{2-n}}{m} \tag{4.49}$$

where $m$ is the power law consistency coefficient. Note that Eq. 4.49 for $n = 1$ (Newtonian fluids) reduces to the correlation obtained by Chung and Wen [31], for Newtonian fluid through packed beds.

The only study on the influence of Non-Newtonian fluid in radial dispersion coefficients is reported by Hassell and Bondi [73]. who showed that the quality of mixing deteriorate with increasing viscosity.

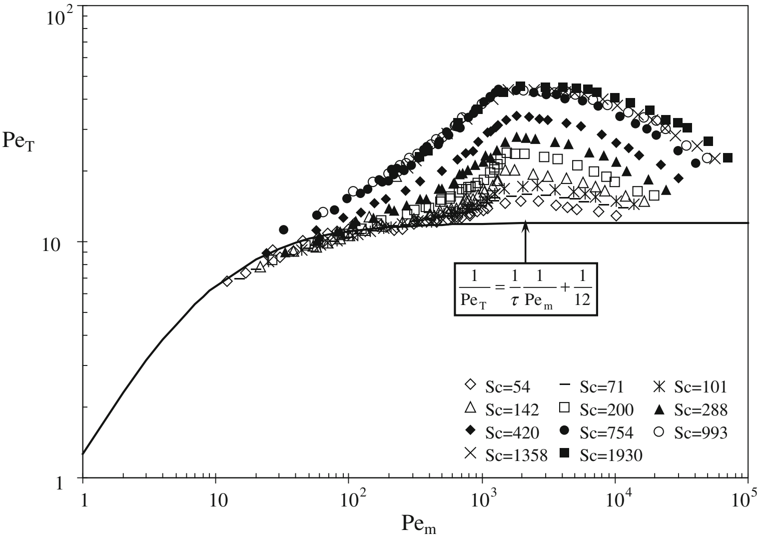


**Fig. 4.15** Dependence of $Pe_T$ on $Pe_m$ for different values of Sc

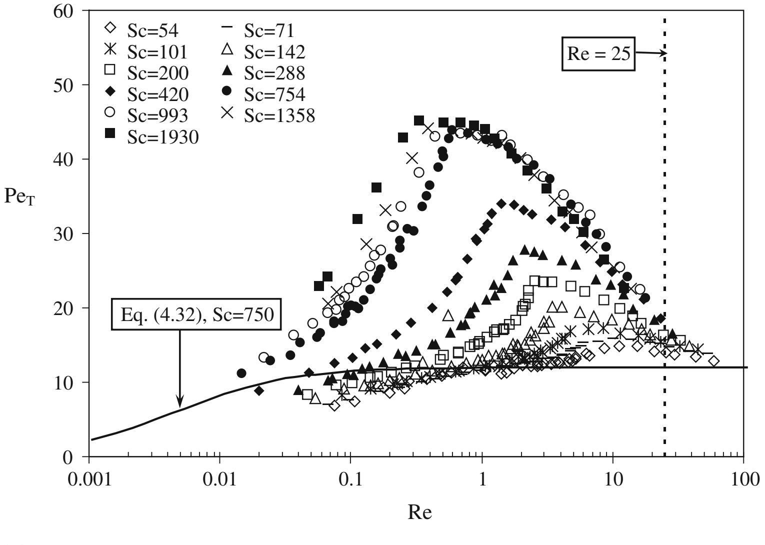


**Fig. 4.16** Dependence of $Pe_T$ on Re for different values of Sc

## 4.6 Correlations

Many equations have been proposed to correlate dispersion experimental data in porous media, and the most used are the equations proposed by Bear and Verruijt [10] in groundwater works and the equations proposed by Koch and Brady [83].

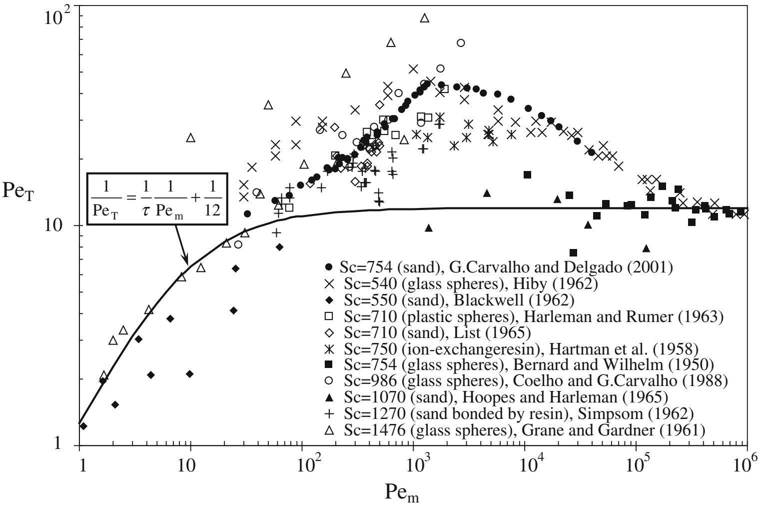


**Fig. 4.17** Comparison between our data points and the results of other authors for $\mathrm{Sc} \geq 540$

The coefficients of radial and longitudinal dispersion are not linear function of velocity and expressions with the form $D_\mathrm{L} = D'_\mathrm{m} + \alpha_\mathrm{L} u^n$ or $D_\mathrm{T} = D'_\mathrm{m} + \alpha_\mathrm{T} u^n$ are suggested. The coefficients $\alpha_\mathrm{T}$ and $\alpha_\mathrm{L}$ are the radial and longitudinal dispersivities, respectively, of the porous medium in the direction of transport and $n$ is an empirically constant, $n = 1 - 2$ [53]. In most applications, the exponent, $n$, is assumed to be unity, i.e., dispersion coefficient is assumed to be a linear function of fluid velocity. However, $n$ may be greater than unity in many situations [10]. Also, the dispersivity, $\alpha_\mathrm{L}$, is probably scale dependent with larger values for $\alpha_\mathrm{L}$ being associated with greater transport distances [104]. For example, values of $\alpha_\mathrm{L}$ reported from the results of field studies may be as much as four or six orders of magnitude greater than the corresponding laboratory measured values which commonly are found to range between 0.1 and 10 mm [53]. Ratios of $\alpha_\mathrm{L}/\alpha_\mathrm{T}$ of 5:1–100:1 have been reported in the literature [10].

Some of most referred works were developed by Fried and Combarnous [54] and Bear and Verruijt [10, p. 166]; the authors showed the existence of five dispersion regimes, in unconsolidated porous media. Sahimi [115] and Marsily [92] analyze the data compiled by Fried and Combarnous [54] to characterize longitudinal dispersion in five dispersion regimes and radial dispersion in four dispersion regimes and a hold-up dispersion. The (1) pure molecular diffusion regime, for very low fluid velocity, is represented by Koplik et al. [84]

$$\frac{D_\mathrm{L}}{D_\mathrm{m}} = \frac{D_\mathrm{T}}{D_\mathrm{m}} = \frac{1}{\tau} \tag{4.50}$$

The (2) superposition regime $(0.3 < \mathrm{Pe_m} < 5)$ not quantify by an equation. In this zone the effect of molecular diffusion and dispersion are of the same order of magnitude. The (3) predominant mechanical dispersion $(5 < \mathrm{Pe_m} < 300)$:

**Table 4.1** Summary of the previous work with experimental data on axial and radial dispersion of non-newtonian fluids in packed beds

| Reference | Experimental method | Packed bed | $\varepsilon$ | $d$ (mm) | $L$ (mm) | $D$ (mm) | $\mathrm{Re}_\gamma$ | Sc |
|---|---|---|---|---|---|---|---|---|
| Wen and Yin [142] | Pulse response ($H_2O$+Polyox 301)—$Na_2C_{20}H_{10}O_5$ ($n = 0.90$ and 0.81) | Glass spheres | 0.40<br>0.50 | 4.76<br>14.3 | 1066.8 | 50.8 | 7–800 | $\cong 10^6$ |
| Payne and Parker [101] | Step function ($H_2O$+Polyox 301)—blue dye ($n = 0.95$ and 0.52) | Glass spheres | 0.365 | 0.374 | 595 | 38.1 | $9 \times 10^{-6}$–$1.5 \times 10^{-3}$ | $8 \times 10^6$–$10^9$ |
| Edwards and Helail [46] | | Glass spheres | | | | | | |
| Hilal et al. [77] | Frequency response (Potassium ferricyanide and ferrocyanid +CMC sodium salt+$Na_2CO_3$) | Glass spheres parallelepiped particles | 0.39 | 2–51.05 × 5.0 ($d = 0.42$) | | | | |
| Hassel and Bondi [73] | | Glass spheres | | 5.0 | | | | |

$$\frac{D_{\mathrm{L}}}{D_{\mathrm{m}}} = \frac{1}{\tau} + 0.5\mathrm{Pe}_{\mathrm{m}}^{1.2} \tag{4.51a}$$

$$\frac{D_{\mathrm{T}}}{D_{\mathrm{m}}} = \frac{1}{\tau} + 0.025\mathrm{Pe}_{\mathrm{m}}^{1.1} \tag{4.51b}$$

The (4) pure mechanical dispersion $\left(300 < \mathrm{Pe}_{\mathrm{m}} < 10^5\right)$ represented by

$$\frac{D_{\mathrm{L}}}{D_{\mathrm{m}}} = \frac{1}{\tau} + (1.8 \pm 0.4)\mathrm{Pe}_{\mathrm{m}} \tag{4.52a}$$

$$\frac{D_{\mathrm{T}}}{D_{\mathrm{m}}} = \frac{1}{\tau} + 0.025\mathrm{Pe}_{\mathrm{m}} \tag{4.52b}$$

In this zone (yet in the range of validity of Darcy's law) the effect of molecular diffusion is negligible. The (5) dispersion out of Darcy domain $\left(\mathrm{Pe}_{\mathrm{m}} > 10^5\right)$ not quantify by an equation. This is the region in which the effects of inertia and turbulence cannot be neglected.

The (6) holdup dispersion [83]:

$$\frac{D_{\mathrm{L}}}{D_{\mathrm{m}}} = \frac{D_{\mathrm{T}}}{D_{\mathrm{m}}} \approx \mathrm{Pe}_{\mathrm{m}}^2 \tag{4.53}$$

Probably one of the most important studies in dispersion topic was presented by Saffman [113, 114]. These works are the most detailed analysis of dispersion in porous media, but the correlation proposed for axial and radial dispersion diverge slightly from the existing experimental data, in the literature (see Fig. 4.18). The author proposed the following equation, for longitudinal dispersion:

$$\frac{D_{\mathrm{L}}}{D'_{\mathrm{m}}} = \frac{\mathrm{Pe}'_{\mathrm{m}}}{6}\left[\ln\left(\frac{3}{2}\tau\mathrm{Pe}'_{\mathrm{m}}\right) - \frac{1}{4}\right] \quad \text{valid for} \quad \mathrm{Pe}'_{\mathrm{m}} \gg 1 \tag{4.54}$$

Another important study was presented by Koch and Brady [83] who showed that the ratio of the dispersion coefficient to the molecular diffusivity is only a function of the product ReSc. However, experimental measurements show that the dispersion Peclet group is a function of both Reynolds and Schmidt groups as $\mathrm{Pe} = f(\mathrm{Re},\ \mathrm{Sc})$ and not $\mathrm{Pe} = f(\mathrm{ReSc})$. For Stokes flow through a random packed bed of spheres, Koch and Brady [83] derived analytical expressions for the longitudinal and radial dispersion coefficients. Since the solid phase is not permeable to the tracer, for $\mathrm{Pe}'_{\mathrm{m}} > 1$, $D_{\mathrm{L}}/D'_{\mathrm{m}}$ and $D_{\mathrm{T}}/D'_{\mathrm{m}}$ are given by:

$$\frac{D_{\mathrm{L}}}{D'_{\mathrm{m}}} = 1 + \frac{3}{4}\frac{\mathrm{Pe}'_{\mathrm{m}}}{2} + \frac{\pi^2}{6}(1-\varepsilon)\frac{\mathrm{Pe}'_{\mathrm{m}}}{2}\ln\left(\frac{\mathrm{Pe}'_{\mathrm{m}}}{2}\right) \tag{4.55}$$

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = 1 + \frac{63\sqrt{2}}{320}\sqrt{1-\varepsilon}\,\frac{\mathrm{Pe}'_{\mathrm{m}}}{2} \tag{4.56}$$

The works of Saffman [113, 114] and Koch and Brady [83] have shown that $D_{\mathrm{L}}/D'_{\mathrm{m}} \sim \mathrm{Pe}'_{\mathrm{m}} \ln(\mathrm{Pe}'_{\mathrm{m}})$ and $D_{\mathrm{T}}/D'_{\mathrm{m}} \sim \mathrm{Pe}'_{\mathrm{m}}$. The logarithmic dependence results from the fact that velocity of fluid at the walls is zero. Different Peclet number contributions to dispersion were identified: hold-up in a closed circulation region $\left(\mathrm{Pe}'_{\mathrm{m}}2\right)$, particle boundary layer $\left(\mathrm{Pe}'_{\mathrm{m}} \ln(\mathrm{Pe}'_{\mathrm{m}})\right)$ and random velocity field contribution $\left(\mathrm{Pe}'_{\mathrm{m}}\right)$. The agreement with the experimental results of Fried and Combarnous [54] was very good for both longitudinal and radial dispersivities. Saffman [113] modelled random porous media with randomly oriented capillary tubes and found Fickian dispersion at long times with dispersivity approaching a $\mathrm{Pe}'_{\mathrm{m}}\ln(\mathrm{Pe}'_{\mathrm{m}})$ behaviour.

It's important to enhance the fact that in literature, it was possible to find a large number of empirical correlations. For example, Fetter [52] used the experimental data obtained by Carberry and Bretton [25], Raimondi et al. [108], Blackwell et al. [17] and Rosenberg [112] to conclude that longitudinal dispersion coefficient is well represented by the fitted curve:

$$\frac{D_{\mathrm{L}}}{D'_{\mathrm{m}}} = 1 + 1.75\mathrm{Pe}'_{\mathrm{m}} \quad \text{valid for } \mathrm{Pe}'_{\mathrm{m}} < 50\tau \tag{4.57}$$

and the data of Blackwell [16] and Grane and Gardner [58], to suggest the following equation for radial dispersion:

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = 1 + 0.055\mathrm{Pe}'_{\mathrm{m}} \tag{4.58}$$

Gunn [65] admitted the existence of two regions in the packing, one of fast flowing and the other of nearly stagnant fluid, to deduce the following expression for the axial dispersion coefficient in terms of probability theory

$$\begin{aligned} \frac{1}{\mathrm{Pe}_{\mathrm{L}}} = {} & \frac{\varepsilon \mathrm{Pe}_{\mathrm{m}}}{4\alpha_1^2(1-\varepsilon)}(1-p)^2 + \left[\frac{\varepsilon \mathrm{Pe}_{\mathrm{m}}}{4\alpha_1^2(1-\varepsilon)}\right]^2 p(1-p)^3 \\ & \times \left\{ \exp\left[-\frac{4(1-\varepsilon)\alpha_1^2}{p(1-p)\varepsilon\, \mathrm{Pe}_{\mathrm{m}}}\right] - 1 \right\} + \frac{1}{\tau\, \mathrm{Pe}_{\mathrm{m}}} \end{aligned} \tag{4.59}$$

where $\alpha_1$ is the first zero of equation $J_0(U) = 0$ and $p$ is defined, for a packing of spherical particles, by

$$\mathrm{p} = 0.17 + 0.20 \times \exp\left(-\frac{24}{\mathrm{Re}}\right) \quad \text{for spheres, } \tau = \sqrt{2} \tag{4.60a}$$

$$\mathrm{p} = 0.17 + 0.20 \times \exp\left(-\frac{24}{\mathrm{Re}}\right) \quad \text{for solid cylinders, } \tau = 1.93 \tag{4.60b}$$

$$\mathrm{p} = 0.17 + 0.20 \times \exp\left(-\frac{24}{\mathrm{Re}}\right) \quad \text{for hollow cylinders, } \tau = 1.8 \tag{4.60c}$$

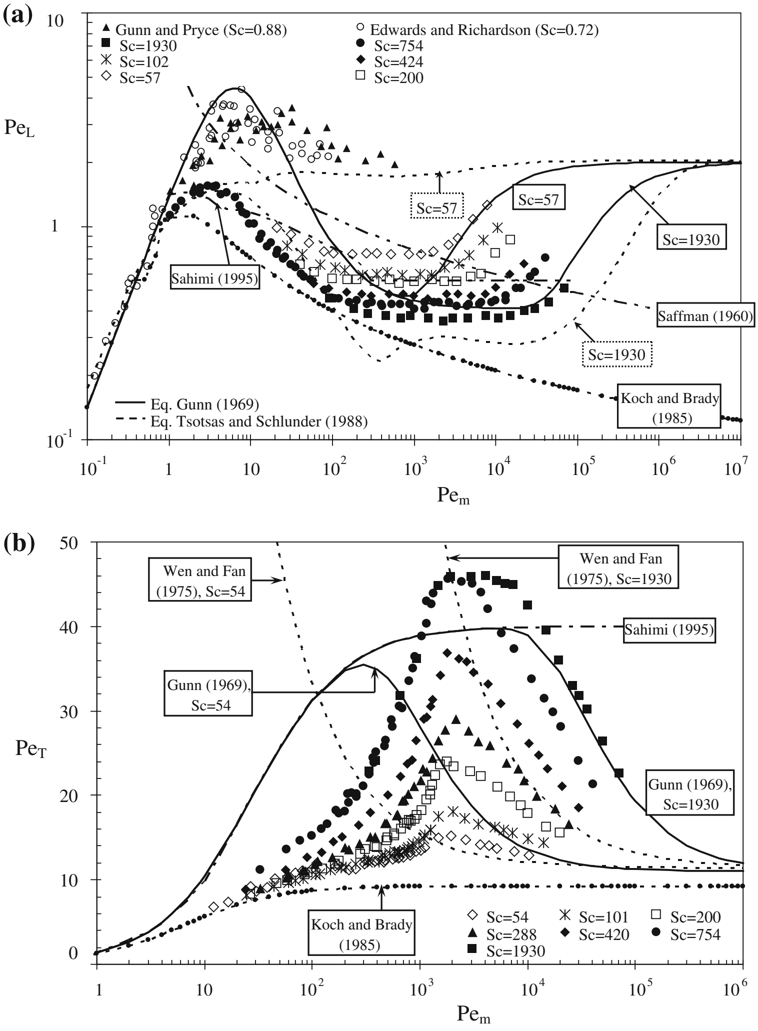


**Fig. 4.18** Comparison between experimental data and correlations presented in the literature

Tsotsas and Schlunder [135] deduced an alternative correlation for the prediction of $\mathrm{Pe_L}$. The authors defining two zones in a simple flow model consisting of a fast stream (central zone in the model capillary) and a stagnant fluid, but the mathematical expressions associated with it are a little cumbersome,

$$\frac{1}{\mathrm{Pe_L}} = \frac{1}{\tau}\left[\frac{1}{\mathrm{Pe_{z,1}}} + \frac{1}{\mathrm{Pe'_m}}\left(1-\xi_c^2\right)\right] + \frac{1}{32}\left(\frac{D_c}{d}\right)^2\left[\mathrm{Pe_{r,1}}\xi_c^2 f_1(\xi_c) + \mathrm{Pe'_m} f_2(\xi_c)\right] \tag{4.61}$$

where the axial and radial Peclet number of the fast stream is

$$\frac{1}{\mathrm{Pe}_{z,1}} = \frac{1}{\mathrm{Pe}'_1} + \frac{1}{1.14(1 + 10/\mathrm{Pe}'_1)} \tag{4.62a}$$

$$\frac{1}{\mathrm{Pe}_{r,1}} = \frac{1}{\mathrm{Pe}'_1} + \frac{1}{8} \tag{4.62b}$$

$$\mathrm{Pe}'_1 = \frac{u_1 d}{D'_\mathrm{m}} \tag{4.62c}$$

and $u_1 = u/\xi_c^2$ is the interstitial velocity of the fast stream, with $\xi_c$ (the dimensionless position of the velocity jump, *i.e*. the ratio between the radius of the zone of high velocities and the radius of packed bed) equal to

$$\mathrm{Re} \le 0.1 \rightarrow \xi_c = 0.2 + 0.21\exp(2.81y) \tag{4.62d}$$

$$\mathrm{Re} \ge 0.1 \rightarrow \xi_c = 1 - 0.59\exp[-\mathrm{f}(y)] \tag{4.62e}$$

with

$$y = \log(\mathrm{Re}) + 1 \tag{4.62f}$$

$$\mathrm{f}(y) = y\left(1 - 0.274y + 0.086y^2\right) \tag{4.62g}$$

Finally, the distributions functions $f_1(\xi_c)$ and $f_2(\xi_c)$ are defined by:

$$f_1(\xi_c) = \left(1 - \xi_c^2\right)^2 \tag{4.62h}$$

$$f_2(\xi_c) = 4\xi_c^2 - 3 - 4\ln(\xi_c) - \xi_c^4 \tag{4.62i}$$

In Fig. 4.18a, the lines corresponding to the correlations of Gunn [65] and of Tsotsas and Schlunder [135] are represented, for the higher and lower values of Sc in our experiments (Sc = 57 and 1,930), as well as for gas flow (Sc = 1). It may be seen that the correlation of Gunn [65] is not sensitive to changes in Sc, for $\mathrm{Pe_m} < 10^3$, and the correlation of Tsotsas and Schlunder [135] is much too sensitive to variations in Sc; however, this correlation describes dispersion in gas flow with good accuracy.

In this context it is interesting to consider, for radial dispersion, the predicting accuracy of some alternative empirical correlations that have been proposed to represent the experimental data in liquid flow, as the equation of Gunn [65]:

$$\frac{1}{\mathrm{Pe_T}} = \frac{1}{\mathrm{Pe_f}} + \frac{1}{\tau}\frac{\varepsilon}{\mathrm{ReSc}} \tag{4.63}$$

where the fluid-mechanical Peclet number, $\mathrm{Pe_f}$, is defined by,

$$\mathrm{Pe_f} = 40 - 29\mathrm{e}^{-7/\mathrm{Re}} \quad \text{for spheres, } \tau = \sqrt{2} \tag{4.64a}$$

$$\mathrm{Pe_f} = 11 - 4\mathrm{e}^{-7/\mathrm{Re}} \quad \text{for solid cylinders, } \tau = 1.93 \tag{4.64b}$$

$$\mathrm{Pe_f} = 9 - 3.3\mathrm{e}^{-7/\mathrm{Re}} \quad \text{for hollow cylinders, } \tau = 1.8 \tag{4.64c}$$

And the empirical equation proposed by Wen and Fan [141],

$$\mathrm{Pe_T} = \frac{17.5}{\mathrm{Re}^{0.75}} + 11.4 \quad (\text{for high values of } \mathrm{Pe_m}) \tag{4.65}$$

In Fig. 4.18b, the lines corresponding Gunn [65] and Wen and Fan [141] correlations are represented for the two extreme values of Schmidt observed in our experiments (Sc = 54 and 1,930); comparison with the experimental points shows that the correlations are very inadequate over significant ranges of $\mathrm{Pe_m}$.

In conclusion, we can say that it was possible to find a large number of equations in the literature that have been proposed to correlate dispersion experimental data in porous media. However, the vast amount of data available is obtained mostly for air and water at room temperature (the influence of Schmidt number is not taking into account).

### 4.6.1 New Correlations: Axial Dispersion

In the limit of very low fluid velocity, dispersion is determined solely by molecular diffusion, with $D_\mathrm{L} = D_\mathrm{m}/\tau$ ($\tau$ being the tortuosity factor for diffusion). At high fluid velocities, dispersion is purely "fluid mechanical" (see [144]), with $D_\mathrm{L} = ud/\mathrm{Pe_L}(\infty)$, where $u$ is the interstitial fluid velocity and $\mathrm{Pe_L}(\infty) \cong 2$ for gas or liquid flow through beds of (approximately) isometric particles, with diameter $d$. A common approximation for the intermediate range of fluid velocities is to assume that the effects of molecular diffusion and fluid mechanical dispersion are additive and the resulting expression is given by

$$D_\mathrm{L} = D'_\mathrm{m} + ud/\mathrm{Pe_L}(\infty) \tag{4.66}$$

where $D'_\mathrm{m} = D_\mathrm{m}/\tau$. This equation is expected to give the correct asymptotic behaviour at high and low values of $\mathrm{Pe_m}$. In the case of gas flow, see Fig. 4.19, significant deviations are observed in the range $0.6 < \mathrm{Pe_m} < 60$; the experimental values of $\mathrm{Pe_L}$ are generally higher than predicted by Eq. 4.66, with $\mathrm{Pe_L}(\infty) \cong 2$. Several equations have been proposed to represent the data in this intermediate range and the equation presented by Hiby [75],

$$\frac{D_\mathrm{L}}{D'_\mathrm{m}} = 1 + \frac{0.65\mathrm{Pe'_m}}{1 + 7\sqrt{\tau/\mathrm{Pe'_m}}} \quad (\text{valid for } \mathrm{Re} < 100) \tag{4.67}$$

is shown to fit the data points reasonably well.

For most gaseous mixtures, far from the critical point, the value of Sc is close to unity, whereas for most solutes in cold water, it is $550 < \mathrm{Sc} < 2,000$. In recent years, data on longitudinal dispersion have been made available for values of Sc between these ranges, such data were obtained with either supercritical carbon dioxide $(1.5 < \mathrm{Sc} < 20)$ or heated water $(55 < \mathrm{Sc} < 550)$.

Some workers have measured axial dispersion for the flow of supercritical carbon dioxide through fixed beds and this provides important new data in the range $1.5 < \mathrm{Sc} < 20$ (see Fig. 4.19). The experiments of Catchpole et al. [27] were performed in the range $8 < \mathrm{Sc} < 20$, but the individual values of Sc, for the data points represented, are not given by the authors. One would expect that the data of Catchpole et al. [27] would lie somewhere between the series of points for $\mathrm{Sc} = 57$ and the line corresponding to Eq. 4.67. It turns out that values of $\mathrm{Pe_L}$ are a little lower than expected, possibly as a result of low accuracy; the scatter is certainly very pronounced. The data of Tan and Liou [132] represents some 90 data points by those authors, for $0.3 < \mathrm{Re} < 135$ and $1.5 < \mathrm{Sc} < 3$; the points are more or less evenly distributed, meaning that scatter is very significant.

The data of Yu et al. [147] are for $0.01 < \mathrm{Re} < 2$ and $2.0 < \mathrm{Sc} < 9.1$. Unfortunately they are not very consistent, particularly in the range $1 < \mathrm{Pe_m} < 20$, where the scatter is high and the values of $\mathrm{Pe_L}$ are much too low. The experiments of Ghoreishi and Akgermanb [56], again for the flow of supercritical carbon dioxide, are for $0.1 < \mathrm{Re} < 0.3$ and $3.3 < \mathrm{Sc} < 5.8$. No influence of Sc on $\mathrm{Pe_L}$ is detected, but this is what might be expected, considering that the values of Re are generally very low, with the consequence that the points are partly in the range where dispersion is totally determined by molecular diffusion.

For the case of liquid flow in a porous media, our group used the division in five dispersion regimes to obtain the expressions presented below.

(1) Diffusion regime (valid for $\mathrm{Pe_m} < 0.1$):

$$\frac{D_\mathrm{L}}{D'_\mathrm{m}} = 1 \tag{4.68}$$

(2) Predominant diffusional regime (valid for $0.1 < \mathrm{Pe_m} < 4$) :

$$\frac{D_\mathrm{L}}{D'_\mathrm{m}} = \frac{\mathrm{Pe'_m}}{0.8/\mathrm{Pe'_m} + 0.4} \tag{4.69}$$

with a an average relative deviation lesser than 14%.

(3) Predominant mechanical dispersion (valid for $4 < \mathrm{Pe_m}$ and $\mathrm{Re} < 10$) :

$$\frac{D_\mathrm{L}}{D'_\mathrm{m}} = \frac{\mathrm{Pe'_m}}{\sqrt{18\,\mathrm{Pe_m^{-1.2}} + 2.35\,\mathrm{Sc}^{-0.38}}} \tag{4.70}$$

with a deviation lesser than 11%, over the entire range of $\mathrm{Pe'_m}$ and Sc.

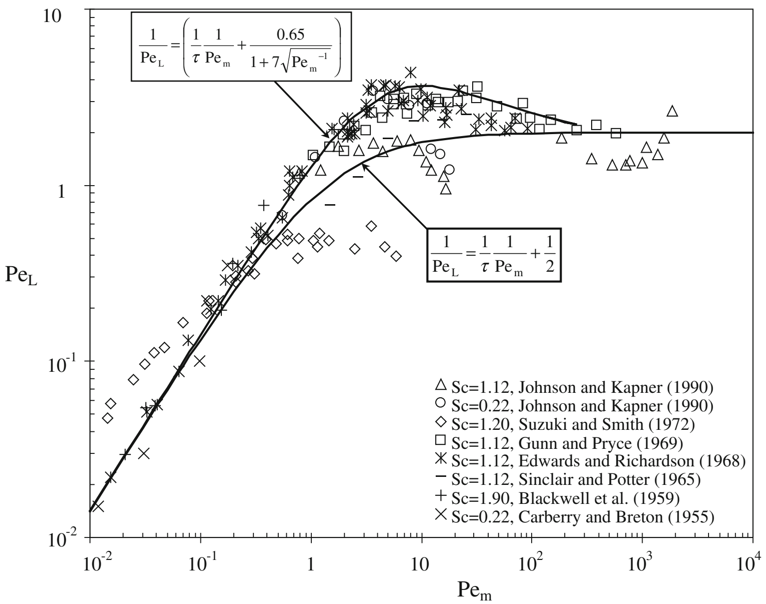


**Fig. 4.19** Axial dispersion in gas flow

(4) Pure mechanical dispersion (valid for $10 < \mathrm{Re}$ and $\mathrm{Pe_m} < 10^6$) :

$$\frac{D_\mathrm{L}}{D'_\mathrm{m}} = \frac{\mathrm{Pe}'_\mathrm{m}}{25\mathrm{Sc}^{1.14}/\mathrm{Pe}'_\mathrm{m} + 0.5} \tag{4.71}$$

with a an average relative deviation lesser than 16%, over the entire range of $\mathrm{Pe}'_\mathrm{m}$ and Sc.

(5) Dispersion out of Darcy domain (valid for $\mathrm{Pe_m} > 10^6$) :

$$\frac{D_\mathrm{L}}{D'_\mathrm{m}} = \frac{\mathrm{Pe}'_\mathrm{m}}{2} \tag{4.72}$$

The correlations proposed are shown (see Fig. 4.20) to be significantly more accurate than previous correlations (see Fig. 4.18) and they cover the entire spectrum of values of $\mathrm{Pe_m}$ and Sc expected to be useful. It is important to have in mind that Eqs. 4.68–4.72 are recommended only for random packings of approximately "isometric" particles.

## *4.6.2 New Correlations: Radial Dispersion*

For gas flow, by simply adding the contributions of molecular diffusion and turbulent dispersion, we suggested the well-known equation (in dimensionless form)

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = 1 + \frac{\mathrm{Pe}'_{\mathrm{m}}}{12} \tag{4.73}$$

with a an average relative deviation lesser than 12%. Equation 4.73 give the correct asymptotic behaviour (both for very high and very low $\mathrm{Pe_m}$) for both gases and liquids, as reported by several workers (see [65, 144]).

In the intermediate range of $\mathrm{Pe_m}$ they are still a reasonable approximation for gases, the wider deviation being observed in the intervals $3 < \mathrm{Pe_m} < 300$, as shown in Fig. 4.21.

For the case of liquid flow in a porous media, our group used the division in four dispersion regimes to obtain the expressions presented below.

(1) Diffusion regime (valid for $\mathrm{Pe_m} < 1$) :

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = 1 \tag{4.74}$$

(2) Predominant mechanical dispersion (valid for $1 < \mathrm{Pe_m} < 1600$) :

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = 1 + \frac{1}{2.7 \times 10^{-5}\mathrm{Sc} + 12/\mathrm{Pe}'_{\mathrm{m}}} \quad \text{for Sc} < 550 \tag{4.75a}$$

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = 1 + \frac{1}{0.017 + 14/\mathrm{Pe}'_{\mathrm{m}}} \quad \text{for Sc} \geq 550 \tag{4.75b}$$

with a deviation lesser than 8 and 5%, respectively, over the entire range of $\mathrm{Pe}'_{\mathrm{m}}$ and Sc.

(3) Pure mechanical dispersion (valid for $1{,}600 < \mathrm{Pe_m} < 10^6$):

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = \frac{\mathrm{Pe}'_{\mathrm{m}}}{(0.058\mathrm{Sc} + 14) - (0.058\mathrm{Sc} + 2)\exp\left(-\frac{500\mathrm{Sc}^{0.5}}{\mathrm{Pe}'_{\mathrm{m}}}\right)} \quad \text{for Sc} < 550 \tag{4.76a}$$

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = \frac{\mathrm{Pe}'_{\mathrm{m}}}{45.9 - 33.9 \times \exp\left(-\frac{21\mathrm{Sc}}{\mathrm{Pe}'_{\mathrm{m}}}\right)} \quad \text{for Sc} \geq 550 \tag{4.76b}$$

and the experimental data do not deviate by more than 6 and 4% from the values given by Eqs. 4.76a and 4.76b, respectively.

(4) Dispersion out of Darcy domain (valid for $\mathrm{Pe_m} > 10^6$):

$$\frac{D_{\mathrm{T}}}{D'_{\mathrm{m}}} = \frac{\mathrm{Pe}'_{\mathrm{m}}}{12} \tag{4.77}$$

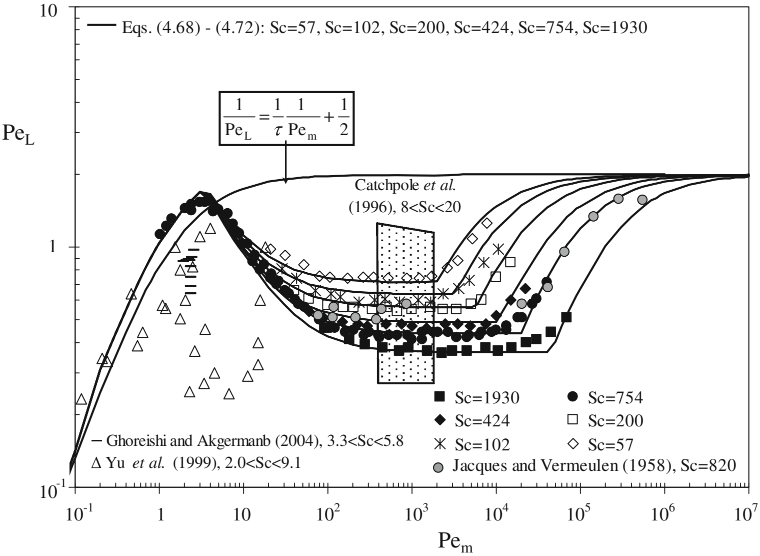


**Fig. 4.20** Comparison between experimental data and correlations given by Eqs. 4.68–4.72

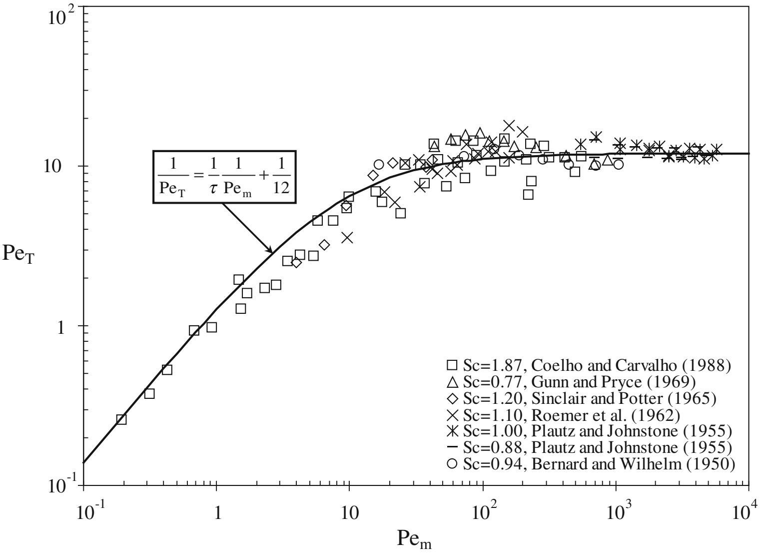


**Fig. 4.21** Radial dispersion in gas flow

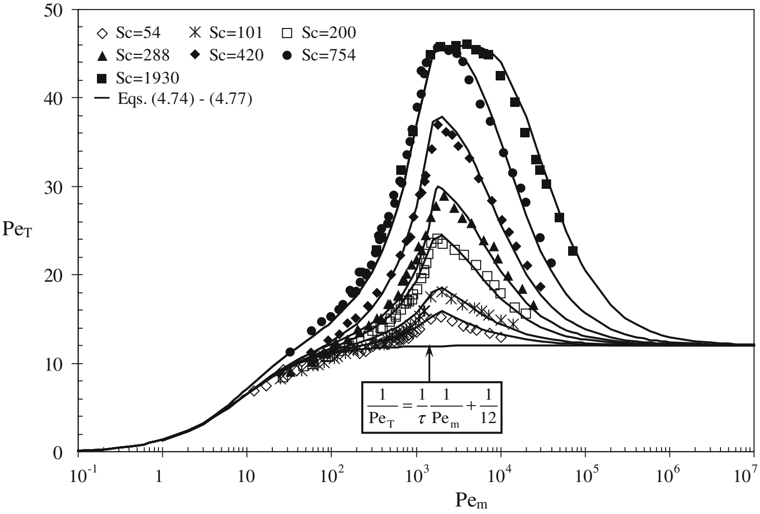


**Fig. 4.22** Comparison between experimental data and our correlations, for radial dispersion

The experimental data are shown in Fig. 4.22, alongside the solid lines corresponding to Eqs. 4.74–4.77, for the values of Sc indicated in the figure. The agreement is seen to be generally very good, even when the values of $Pe_T$ are represented on a linear scale. For Sc > 550 (see experiments with values of Sc of 754 and 1,930), the above equations representing the data must take into account that $Pe_T$ is only dependent on $Pe_m$, in the ascending part of the curve $Pe_T$ *vs.* $Pe_m$ and that $Pe_T$ only depends on $Re(= \varepsilon\, Pe_m/Sc)$, in the descending part of the same curve.

In conclusion, the present chapter increases our knowledge about diffusion and dispersion in packed beds by providing a critical analysis on the effect of fluid properties and porous medium on the values of axial and radial dispersion coefficients.

Different experimental techniques are presented in full detail and the data obtained from these techniques are very similar. An improved technique for the determination of the coefficient of radial dispersion in fluid flow through packed beds is described more detailed, which is based on the measurement of the rate of dissolution of buried flat or cylindrical surfaces.

A large number of experimental data on dispersion available in literature for packed beds were examined to pave the way for the formulation of new correlations for the prediction of $Pe_T$ and $Pe_L$. The correlations proposed are shown to be more accurate than previous correlations and they cover the entire range of values of $Pe_m$ and Sc. The axial dispersion coefficient can be calculated by Eqs. 4.68–4.72 and the radial dispersion coefficient by Eqs. 4.73–4.77.

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