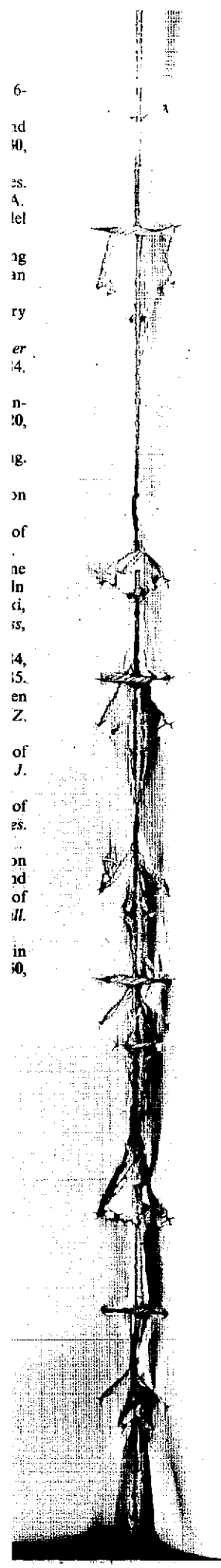

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AXIAL AND RADIAL DISPERSION IN FIXED BEDS

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Abstract—Several different methods of describing dispersion in fixed beds are defined and compared with experiment by means of a number of criteria for model validity. The principal criteria are statistical adequacy of the model when compared with experiments, consistency of bed-independent parameters when estimated from bed response, and consistency of parameters of dispersion with respect to variations in the Schmidt group and Reynolds number. The characteristics of axial and radial dispersion for fixed beds of impermeable spheres, hollow and solid cylinders, are shown to be consistent with dispersion characteristics measured for permeable particles. The dependence of axial and radial Péclet groups for dispersion of mass upon the Schmidt and Reynolds groups is correlated throughout the range of Reynolds number by fundamentally-based equations for beds of spherical and cylindrical particles.

INTRODUCTION

The characterization of mixing in fixed beds by dispersion models has been supported by a substantial number of experimental investigators using a variety of experimental techniques (Gunn, 1968). Most of the experiments on mass dispersion were performed on beds in which the particles were impermeable to the penetration of diffusant, so that the response of the bed to the stimulus of a concentration change is affected only by such known properties as porosity and flow rate, and the single unknown parameter, the dispersion coefficient. However, particles in practical reactors are often permeable to the penetration of diffusant; and although experiments on the characterization of fixed beds of permeable particles were first performed some time ago, the interpretation of the experiments was at first hampered by the lack of sufficient theory, and then by the lack of effective methods of parameter estimation because the minimum number of unknown parameters is now three.

The early experimental investigators into fixed beds of permeable particles employed the Fourier transform or methods of frequency response in beds of spheres. Subsequently pulse response methods have been used with theoretical analysis of the experiments based upon theories of dispersion in chromatographic columns due to Kubin (1965) and Kucera (1965), and also for beds of spheres; parameters in the experiments on pulse response were estimated by the method of moments. The analysis of the response of fixed beds of permeable particles was extended by Gunn (1970) who solved equations for the Fourier transform of the response, and for the Laplace transform of the response to a general input pulse for beds containing particles of different shape including hollow, cored and solid cylinders, parallelpipeds, spheres and cored spheres; he suggested that parameters could be estimated by comparing experimental and theoretical Laplace transforms of the response, or by comparing theoretical and experimental Fourier transforms.

Another difficulty to be resolved was the description of dispersion when the solid phase was permeable, because there are several possibilities. Thus separate dispersive fluxes could be postulated in the fluid and the solid phase with interphase transfer at the surface of the particles (model 1); or, dispersion in the fluid phase only may be considered together with interphase transfer (model 2); or the dispersive flux may be considered to occur in both phases under the driving force of the concentration gradient in the fluid phase with simultaneous transfer between fluid and particles (model 3). In the latter models the unknown parameters are dispersion coefficient, the fluid–particle mass transfer coefficient and the intraparticle diffusivity, but the first model requires two independent dispersion coefficients to give a total of four unknown parameters in all. The differences between the models have very important consequences for the analogous process of dispersion of heat, but the differences for dispersion of mass are often small because of the low effective permeability for mass dispersion in the solid phase.

The first model is the more complicated in that when examining a dynamic response the eigenvalues of a quartic equation must be found and therefore the model has not been investigated at all fully because of the attendant difficulties in analysing experiments—an important disadvantage. The second model is not consistent with the large differences between the Péclet groups for the dispersion of heat and for the dispersion of mass found in experiment. But the experimental results for both heat and mass dispersion are consistent with the third and this model has been examined in a number of different experiments.

There are three principal criteria for a satisfactory model. The first is that the form of the experimental response should be satisfactorily represented by the theoretical response according to statistical tests designed to examine the validity of models such as the variance ratio test and the χ^2 test. Many investigators have not used statistical tests, but have estimated dispersion coefficients, for example, without examining the validity of the model. However, when

examined, the third model has been found to represent the experimental response very closely. Not all models satisfy the form of the experimental results and it has been shown, for example, that a model for heat transfer in packed beds in which axial thermal dispersion is neglected does not describe the thermal response of a packed bed at low Reynolds number, whereas the third model does (Gunn and de Souza, 1974).

The second requirement is that the parameters of a model found from a set of different experiments should be physically consistent from one experiment to another. For example, the replacement of impermeable particles by porous particles of low permeability in mass dispersion experiments should not have a significant effect upon the dispersion coefficient, and therefore dispersion coefficients for beds of impermeable particles should show the same dependence upon Reynolds number as beds of catalyst particles. There is now sufficient experimental information available to examine the consistency of parameter estimates provided by the third model.

The third criterion is that the parameters or coefficients of the model should depend upon the physical properties of the fluid and solid in a manner that is consistent with the established laws of fluid mechanics, heat and mass transfer. Although not always possible it is desirable that the analysis of fluid flow, heat and mass transfer in the system should lead to a theoretical form for the dependence of the process coefficients upon the physical properties of the system. If the physical description is comprehensive the dependence of the process coefficients upon such properties as molecular diffusivity or thermal conductivity may be tested in experiment and compared with the dependence expected from theory to give further evidence of the validity of the model.

The objects of this paper are to present evidence on the third model that contributes to the second and third criteria and to summarize experimental and theoretical results in forms suitable for process design.

STATISTICAL TESTS OF MODEL VALIDITY

There have been several statistical tests of model accuracy both for heat transfer and for mass transfer in fixed beds. The tests have been mainly based upon variance analysis but there are also some applications of the χ^2 tests; the analysis of variance is particularly powerful when replicate experiments have been included in the experimental design.

Statistical tests have been employed on both random and regular arrays of spheres; neither the dispersion model nor the mixing cell model described axial spreading in regular arrays of spheres, but the dynamic response of beds packed with impermeable particles was well described by the dispersion model (Gunn and Pryce, 1969). The frequency response of fixed beds of porous catalyst particles to concentration waves has been examined (Gunn and England, 1971), and the intraparticle diffusivity and axial dispersion coefficient has been estimated from the attenuation of the waves. Gunn and de Souza (1974) examined the frequency response to heat of several beds of glass and of metallic particles, and found the axial thermal dispersion coefficient, the particle to fluid heat transfer coefficient, and the intraparticle thermal conductivities from the dependence of wave attenuation upon frequency. Bashi and Gunn (1977) studied the response of fixed beds of catalyst particles to a concentration pulse and calculated intraparticle diffusivities and axial Péclet groups. Gunn *et al.* (1984) examined the response of fixed beds to a temperature pulse and estimated the thermal dispersion coefficients, intraparticle thermal conductivity and fluid to particle heat transfer coefficients. Replicate experiments were included in the experimental schemes, so that the applicability of the dispersion model could be found from variance analysis. It was found in all cases that the variance of the experimental points about the theoretical equations was most probably due to experimental error so confirming the validity of the model. Thus the first criterion is satisfied.

The set of experimental results included some experiments on the dynamic response of fixed beds of metallic particles, but in other cases the intraparticle gradients due to heat or mass flow were significant. Such gradients may be described by the fluid dispersion model, but the mathematical complexities of models that include a solid phase temperature gradient in particles during dispersion have not yet been resolved.

AXIAL DISPERSION

The consistency of the model is most easily examined in the light of a stochastic model for dispersion in fixed beds that satisfies the dimensional analysis of dispersion, and the observed experimental dependence of the dispersion coefficient upon the Schmidt group and other properties of the system (Gunn, 1969). The convective motion in the fixed bed is represented by the probability of a tracer particle either remaining at rest, or travelling a distance downstream in the space of a characteristic time interval d/U. The probability p of motion downstream may be identified with the relative proportions of the moving region of fluid in a cell of particles to the slow moving or static regions of fluid.

A molecule in either the fast or static regions of fluid is subject to random motion that can move the particle between streams by molecular diffusion, so that the total displacement of the molecule with time is a result of both convective and diffusive motions. The analysis of the particle motion leads to an expression for the coefficient of axial dispersion:

$$\frac{D}{Ud} = \frac{Re\,Sc}{4\alpha_1^2(1-\varepsilon)}(1-p)^2 + \frac{Re^2\,Sc^2}{16\alpha_1^4(1-\varepsilon)^2}p(1-p)^3 \times \left[\exp\left(\frac{-4(1-\varepsilon)\alpha_1^2}{p(1-p)Re\,Sc}\right) - 1\right] + \frac{\varepsilon}{\tau Re\,Sc} \qquad (1)$$

where α_1 is the first root of $J_0(u) = 0$, ε is the porosity of the bed, τ is a tortuosity and other symbols have the

usual connotations. This expression was found to agree with experiment when the particles were well-packed; values of the probability p were estimated from dispersion experiments in which the effect of molecular diffusion was very small and given as a table showing the change with Reynolds number.

When particles in a fixed bed are not well-packed, dispersion is increased. This effect may be included in the theory leading to eq. (1) by considering the effect of variation in velocity over the cross-section of the bed and introducing σ_v^2, the dimensionless variance of the distribution of the ratio of velocity to average velocity over the cross-section. By including the variation of velocity in the theory leading to eq. (1), eq. (2) was obtained (Gunn, 1971):

$$\frac{D}{Ud} = \left\{ \frac{ReSc}{4\alpha_1^2(1-\varepsilon)}(1-p)^2 + \frac{Re^2Sc^2}{16\alpha_1^4(1-\varepsilon)}p(1-p)^3 \times \left[\exp\left(\frac{-4\alpha_1^2(1-\varepsilon)}{p(1-p)ReSc} \right) - 1 \right] \right\}(1+\sigma_v^2) + \frac{\sigma_v^2}{2} + \frac{\varepsilon}{\tau ReSc}. \quad (2)$$

Equation (2) was required to describe some conditions of fluid phase dispersion, particularly when conditions in the bed were close to incipient fluidization, but when the quality of packing in the bed is not poor or subject to strong fluid disturbance eq. (1) is adequate. Although eq. (2) will also describe well-packed beds, for this particular case the slightly simpler form of eq. (1) may be preferred, and therefore the discussion of axial dispersion in this paper is directed to eq. (1).

Although the probability p is known to be a function of Reynolds number only, it is a disadvantage that values of p should be available only in the form of a table showing the variation with Reynolds number. A study of the experimental results for dispersion in beds of spheres, and in beds of cylinders shows that the dependence of p upon Reynolds number may be expressed by the following equations,

$$p = 0.17 + 0.33\exp(-24/Re), \quad \text{spheres, } \tau = 1.4 \quad (3)$$

$$p = 0.17 + 0.29\exp(-24/Re), \quad \text{solid cylinders, } \tau = 1.93 \quad (4)$$

$$p = 0.17 + 0.20\exp(-24/Re), \quad \text{hollow cylinders, } \tau = 1.8. \quad (5)$$

The three equations give constant values for p below $Re = 1$ and above 1000 with the major change in p taking place from $Re = 1$ to 200. The lower limit of Reynolds number is the upper limit of the regions of creeping flow in fixed beds, and $Re = 200$ is about the onset of turbulence. Thus the range of Reynolds number includes the growth of fluid inertia in laminar motion and the transition that is reflected by the changes in the probability of axial displacement p.

A comparison of experimental results for fixed beds of permeable and impermeable solids gives information on the consistency of the model. In some cases the comparison has been based upon eq. (2), but the comparison here is based upon eq. (1) when the dependence of probability p upon Reynolds number is based upon eqs (3), (4) or (5) as appropriate.

The form of eq. (1) is illustrated in Fig. 1 where it is compared with the experimental results of Gunn and Pryce (1969) for the dispersion of argon in beds of impermeable particles at a value for the Schmidt group of 0.77, and with the experimental results of Vermeulen and Jacques (1957) and of Miller and King (1966) who each employed an ionic salt solution as tracer injected into water for which the Schmidt groups were approximately 800.

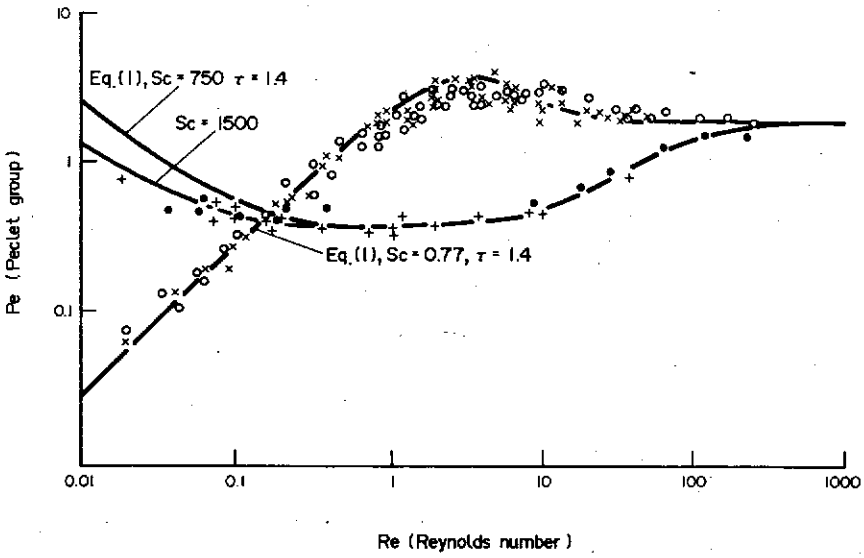

Fig. 1. Comparison of experimental measurements for axial dispersion in beds of spheres. Gas phase: ○ Gunn and Pryce (1969); × Edwards and Richardson (1968); Liquid phase: ● Jacques and Vermeulen (1957); + Miller and King (1966). The full lines correspond to eq. (1) with $\tau = 1.4$ and p defined by eq. (3).

It is evident that the dependence of the axial Péclet groups upon both Reynolds and Schmidt groups is well described by eq. (1), a severe test since there is a 1000-fold difference in Schmidt groups between the gas and liquid phase values. Indeed the values of Péclet groups are quite different although the high Reynolds number asymptote is common to both for Reynolds numbers > 300 where Pe approaches the widely quoted value of 2 at Reynolds numbers approaching 1000. The liquid phase molecular diffusivity is much smaller, but the axial dispersion coefficient within the range of $0.2 < Re < 300$ is greater for the liquid phase reaching a maximum difference of a factor of 10 at $Re \sim 3$.

There are considerable experimental difficulties in the measurement of dispersion in the liquid phase at small Reynolds number. The usual method of achieving low Reynolds number is to reduce the particle size, and beds of small particles are prone to disturbance by the flow of liquid. This, in itself, will tend to increase the axial coefficient, and therefore there is uncertain agreement between experiment and theory at low Reynolds number.

The experimental results of McHenry and Wilhelm (1957), for the dispersion of ethylene in nitrogen in beds of impermeable spheres, and of hydrogen in nitrogen, and the experimental estimates of Edwards and Richardson for (1968) the dispersion of argon in air are well supported by eq. (1). The experimental results of Ebach and White (1957) for liquid phase dispersion in fixed beds of spheres are also in agreement with eq. (1), a set of experimental results that show an increasing trend as Re is reduced (Gunn, 1969) in accordance with the predictions of eq. (1). Indeed this equation is generally in satisfactory accord with experiment, although for some measurements of liquid phase dispersion in beds of spheres, particularly near the condition of incipient fluidisation, σ_v^2 and eq. (2) instead of eq. (1) are necessary for a close description (Gunn, 1971).

Equations (1) and (2) hold for beds of solid and hollow cylinders when the probability p is defined by eqs (4) and (5), respectively. Equations (4) and (5) are based upon the experimental results of England and Gunn (1970), for the dispersion of argon in beds of solid and hollow cylinders. The experimental results are shown in Fig. 2 with eqs (1) and (4), or (1) and (5) shown on the figures. At higher Reynolds number the fit is acceptably within the range of variation found for experiments of this type. Within the range of Re from 1 to 10 the fit is not so good with eq. (1) skirting above the experimental points. A better fit at lower Reynolds number is given by eq. (2) and this equation is shown for the solid cylinders; packing of solid cylinders was noticeably poor (England and Gunn, 1970) and the quality of packing appears to be the most likely reason that eq. (2) is required at low Reynolds number.

The comparison between eqs (1) and (5) and experiments for liquid phase axial dispersion is shown in Fig. 3 where the experimental results for hollow cylinders are those of Carberry and Bretton (1958), Ebach and White (1958) including some measurements of dispersion in beds of Intalox saddles and Berl saddles, and of Hiby (1962) for axial dispersion in beds of 3-, 6- and 12-mm rings. Agreement is clearly satisfactory for the majority of the estimates although there is evidence of excessive mixing, possibly due to poor packing, in the results for the 2-mm rings of Carberry and Bretton. The experimental results of Hiby were determined for the full cross-section of the bed, in contrast to the experimental method he used for beds of spheres where dispersion was measured over a small cross-section at the onset of flow. Hiby's results for spheres give much lower values for the dispersion coefficient than other experimental techniques (Gunn, 1968), but the experimental measurements for beds of hollow cylinders agree with eq. (1) with p given by eq. (5). It is of interest that the experimental estimates of Ansari quoted in Abbi and Gunn (1976) lie significantly above eq. (1) on this figure, due to the measurement of axial

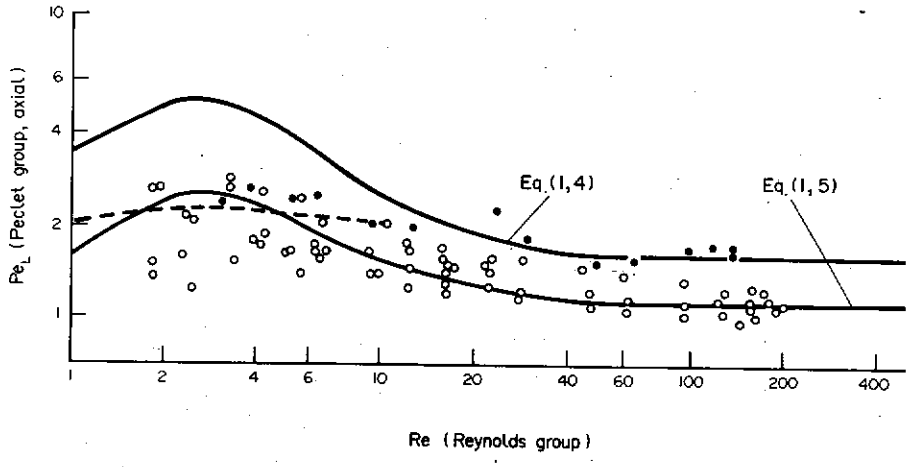

Fig. 2. Comparison of experimental measurements for gas-phase axial dispersion in beds of cylinders. The full lines correspond to eq. (1) with p given by eqs (4) and (5). The dotted line corresponds to eq. (2) with p given by eq. (4) (solid cylinders): ● England and Gunn (1970), solid cylinders; O England and Gunn (1970), hollow cylinders.

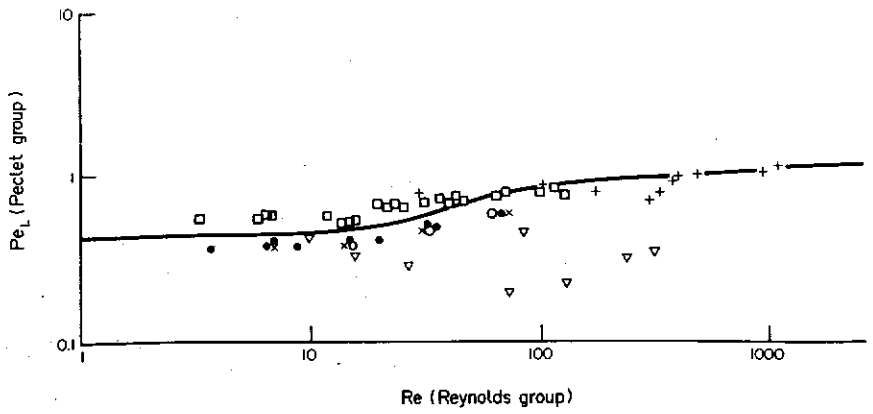

Fig. 3. Experimental results for liquid-phase axial dispersion in beds of hollow cylinders. The full line is eq. (1) with p given by eq. (5): □ Hiby (1962), rings; + Carberry and Bretton (1958), 6-mm rings; ▽ Carberry and Bretton (1958), 2-mm rings; ● Ebach and White (1957), rings; ○ Ebach and White (1957), Berl saddles; × Ebach and White (1957), Intalox saddles.

dispersion over a small central region of the fixed bed, rather than a representative region, the same deficiency as found in Hiby's measurements of axial dispersion in beds of spheres.

A contribution towards meeting the second criterion is provided by experiments on permeable particles. Figure 4 shows the experimental estimates of axial dispersion for impermeable spheres compared with estimates for the dispersion coefficient in fixed beds of porous spheres by Gunn and England (1971) and Bashi and Gunn (1977) compared with eqs (1) and (3). The experimental results of Gunn and England for LA-type particles have not been included because of the dusty and fragile condition of the particles, and the consequent poor quality of packing in their experiments. However, in spite of this reservation, it is clear that eqs (1) and (3) describe dispersion coefficients estimated for beds of impermeable particles shown in Fig. 1, and dispersion coefficients estimated for beds of permeable particles.

The consistency of the experimental results for porous particles may also be illustrated by comparing the experimental estimates of the intraparticle diffusivity for several grades of permeable particles given by Gunn and England (1971), Bashi and Gunn (1977), and calculated by Bashi (1976) from experimental measurements of the isobaric diffusive flux across a flat particle. The comparison is given in Table 1 where the

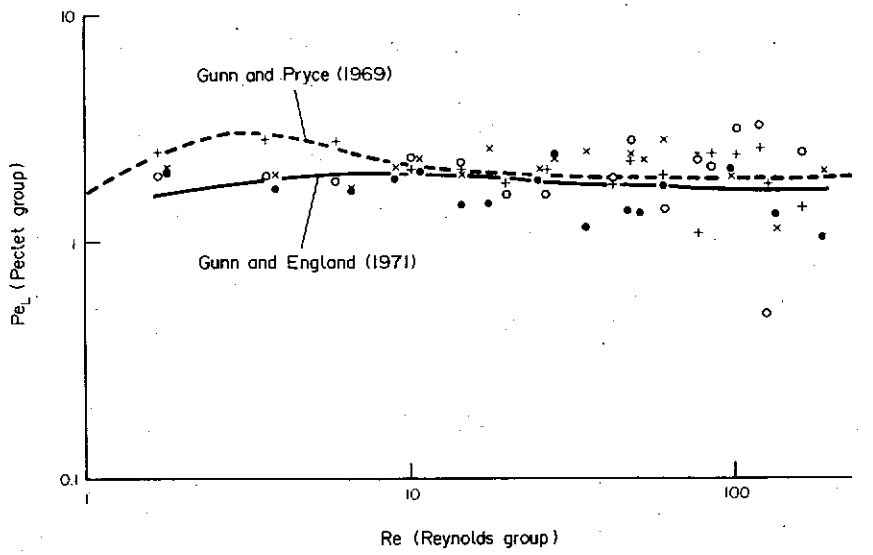

Fig. 4. Comparison of Péclet groups for axial dispersion in beds of impermeable spheres represented by eq. (1) when p is given by eq. (3), with estimates of Péclet group for beds of permeable spheres: – – – Gunn and Pryce (1969), impermeable spheres; —— Gunn and England (1971) permeable spheres SA201, SA203; ● Bashi and Gunn (1977), Fourier transform SA201 spheres; × Bashi and Gunn (1977), Laplace transform SA201 spheres; ○ Bashi and Gunn (1977), Fourier transform LA622 spheres; + Bashi and Gunn (1977), Laplace transform LA622 spheres.

Table 1. Comparison of three estimates of intraparticle diffusivity

Particle type	D/D_{AB} Estimated from frequency response	Estimated from pulse response	Measured from isobaric counter-diffusion
SA201	0.083	0.075	0.087
SA203	0.095	—	0.101
LA622	0.087	0.087	0.093
LA623	0.123	—	0.139

diffusivity is shown as the ratio of the effective to the molecular diffusivity.

It is evident that the experiments and supporting theory fully satisfy the second and third criteria, as they have satisfied the first. The predictions of the stochastic theory concerning the effect of the Reynolds and Schmidt groups and porosity agree with experiment, and the theory itself is founded upon a fluid-mechanical description of flow that although simple, yet transcribes the important features of the interaction between convection and molecular diffusion.

THE EFFECT OF TUBE TO PARTICLE DIAMETER RATIO UPON AXIAL DISPERSION

It is common lore that experiments on dispersion or pressure loss in fixed beds are sensibly independent of the tube to particle diameter ratio, provided that the ratio is greater than about 10. The reason is suggested to be a high porosity, high velocity region near the wall of the tube that extends about 0.5 diameters from the wall for particles of normal imperfection of size and shape. The first investigators to measure the extent of the high velocity region were Schwartz and Smith (1953) who found that a region of enhanced velocity extended 1–3 particle diameters from the wall. However, it has been shown by Vortmeyer and Schuster (1983) that velocity profiles develop very sharply from the end of the bed if the space beyond the bed is empty without constraints to radial flow. If the profiles are measured when flow is not allowed to develop, as in the method of Price (1968), it is found that the region of high velocity is restricted to the region of high porosity that extends no more than $0.5d_p$ from the wall (Roblee *et al.*, 1958; Schuster and Vortmeyer, 1980). If the profiles are measured some distance from the end of the bed without constraints to radial flow, profiles such as those measured by Schwartz and Smith are obtained. The measurements of Schuster and Vortmeyer by laser–doppler anemometry confirmed the experimental results of Price.

However, a criterion based upon the analysis of the quantitative interaction between wall and bulk flows has not yet been advanced for single phase flow, although the same problem is of importance in the analysis of dispersion in packed columns, and a treatment of that problem may be adapted for this application (Gunn, 1980).

The fixed bed is divided into a bulk region of radius R_b and the region from the edge of the bulk to the wall. The flow is developed so that there are no radial components although the velocities in the wall and bulk regions are supposed different. If the motion of a tracer particle is considered that may be placed with probability θ in the bulk and $(1-\theta)$ in the wall region, molecular diffusion of the particle may be analysed to give the probability of transfer between the bulk and the wall regions. The probabilities may then be analysed to consider both axial and transverse motion. Although the resulting equations are complex, when the solutions are expressed in terms of the two-sided Laplace transform in space, limiting processes on the transform variable may be applied to find the coefficient of dispersion expressed for the entire region of the bed.

The result is (Gunn, 1980)

$$\frac{D}{D_b} = 1 + \left(\frac{U_w}{U_b} - 1\right)^2 \frac{\theta(1-\theta)^2}{4\alpha_1^2} PePe_R \left(\frac{d_t}{d} - 2\right)^2 \times \left\{1 + Pe_R \frac{(1-\theta)}{4\alpha_1^2}\left(\frac{d_t - 2d}{x}\right)\left(\frac{d_t - 2}{d}\right) \times \left[\exp\left(\frac{4\alpha_1^2}{1-\theta}\cdot\frac{x}{d_t - 2d}\cdot\frac{d}{d_t - 2d} Pe_R\right) - 1\right]\right\} \quad (6)$$

where θ and $(1-\theta)$ are the relative proportions of the bulk and wall region. The factor of concern in eq. (6) is the ratio of U_w/U_b *within* the bed. If we consider the experimental results of Price (1968), he found that the ratio of velocity in the wall region to velocity in the bulk measured outside the bed u_w/u_b was (1.65). By continuity

$$u_w = U_w \bar{e}_w; \quad U_b e = u_b \quad (7)$$

so that

$$\frac{u_w}{u_b} = 1.65 = \frac{U_w \bar{e}_w}{U_b e}. \quad (8)$$

The voidage in the bulk of a fixed bed of spheres is about 0.37 and the mean porosity in the wall region $\bar{e}_w$ lies within the range $0.37 < \bar{e}_w < 1.0$, with $\bar{e}_w$ less than the mean of 0.37 and 1.0 in the wall region of extent $0.5d$, say 0.6. On substituting these values in eq. (8) we find that U_w/U_b is 1.02, suggesting that there may be no significant differences between interstitial velocities in the bulk and wall regions. Equation (6) then shows that the dispersion coefficient in a fixed bed is independent of diameter, always provided that the quality of packing is comparable.

Although this conclusion is clearly subject to the results of more detailed investigations of interstitial velocities, it is not at variance with measurements of axial dispersion when the ratio of tube to particle diameter has been varied. It has been found (Gunn and Pryce, 1969) that experimental results for dispersion in beds of spheres are independent of the ratio of tube to particle diameter within the limits of experimental precision for this type of experiment and for ratios of $d_t/d > 10$.

RADIAL DISPERSION

The form of eq. (1) owes much to diffusion–convection interaction in sustained axial flow. In a packed bed there is no sustained radial flow and therefore radial molecular diffusion and convective dispersion may be considered to be independent stochastic motions. The Péclet group for radial dispersion is therefore given by the equation:

$$\frac{1}{Pe} = \frac{1}{Pe_f} + \frac{\varepsilon}{\tau ReSc} \tag{9}$$

where Pe_f is the fluid-mechanical Péclet number for radial dispersion and τ is the tortuosity. There is some evidence that the tortuosities measured in the axial direction, and in the radial direction, differ by small amounts. The Péclet group Pe_f is a function of Reynolds number, and a study of the experimental results for radial dispersion in beds of impermeable and porous particles shows that the functions may be expressed by the following equations:

$$Pe_f = 40 - 29\exp(-7/Re) \text{ spheres, } \tau = 1.2 \tag{10}$$

$$Pe_f = 11 - 4\exp(-7/Re) \text{ solid cylinders, } \tau = 1.93 \tag{11}$$

$$Pe_f = 9 - 3.3\exp(-7/Re) \text{ hollow cylinders, } \tau = 1.8. \tag{12}$$

The effect of the Reynolds and Schmidt groups may be compared in experiment with the experimental results of Gunn and Pryce (1969) for the radial dispersion of argon, and Hiby (1962) for the radial dispersion of carbon dioxide, both measured in beds of spheres, and the comparison is shown in Fig. 5. The agreement is good in that the theory correctly predicts the change due to Reynolds number and the change due to the difference in the Schmidt groups for argon and carbon dioxide. (The legend for the data points in the comparison shown in the earlier paper was unfortunately reversed).

Experimental estimates of radial dispersion for gases in fixed beds by Roemer *et al.* (1962), Bernard and Wilhelm (1950), Sinclair and Potter (1965) and Fahien and Smith (1955) were analysed according to different analytical expressions. The analyses did not correct for the effect of axial dispersion, but given the difference the results agree with eq. (9); this is true for the results of Fahien and Smith reported in the bulk of the bed but not near the wall region where the velocity profile of Schwartz and Smith was used in the analysis of their results.

The much larger change due to an increase in Schmidt group from 0.8 to 540 is shown in Fig. 5, in which eqs (9) and (10) are compared with the experimental results of Hiby (1962) for liquid phase dispersion in beds of spheres. The agreement is clearly satisfactory.

The effect of particle shape has been considered by England and Gunn (1970) who measured the dispersion of argon in beds of solid cylinders and in beds of hollow cylinders. They found good agreement with eq. (9) and values of Pe_f according to eqs (11) and (12), and the comparison with their experimental results is given in Fig. 6.

The application of eqs (9) and (12) found for gas phase radial dispersion in beds of cylinders to liquid

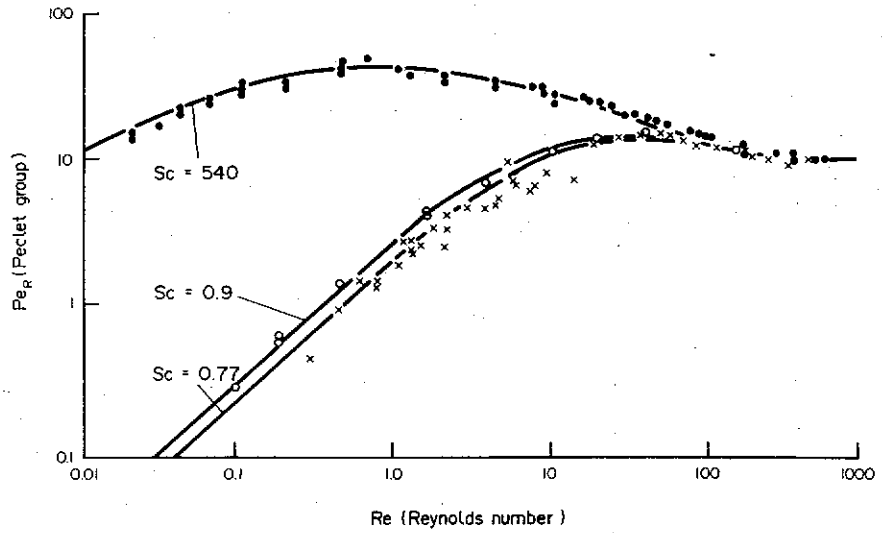

Fig. 5. Comparison of radial dispersion in fixed beds of impermeable spheres with eq. (4) shown as solid lines for stated values of Schmidt group. The value of Pe_f is given by eq. (10): × Gunn and Pryce (1969), $Sc = 0.77$; ○ Hiby (1962), $Sc = 0.90$; ● Hiby (1962), $Sc = 540$.

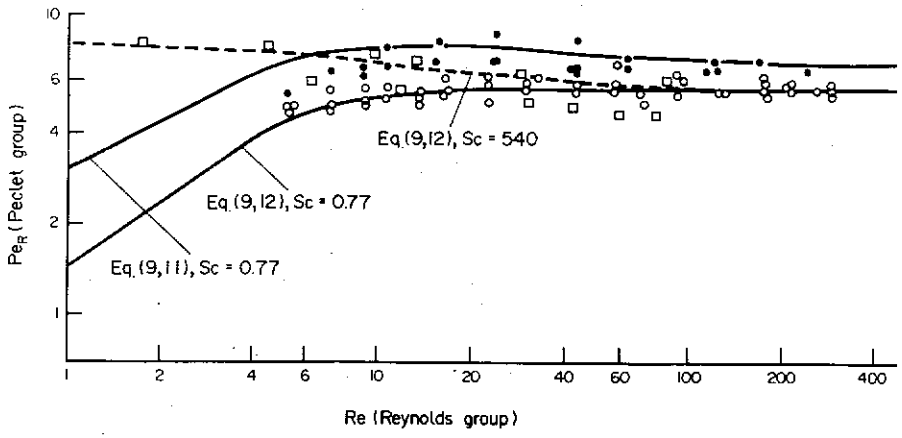

Fig. 6. Comparison of radial dispersion in fixed beds of impermeable cylinders, both hollow and solid, with eq. (9), when Pe_f is given by eqs (11) or (12) as appropriate. The full line is eq. (9) ○ England and Gunn (1971), hollow cylinders $Sc = 0.77$; ● England and Gunn (1971), solid cylinders $Sc = 0.77$; □ Hiby (1962) rings, $Sc = 540$.

phase dispersion is shown in Fig. 6 for the experimental measurements of Hiby for radial dispersion in hollow cylinders. Here Pe_f for hollow cylinders is given by eq. (12). Pe_f for spheres is given by eq. (10); the difference between the two is considerable, particularly at low Reynolds number but both sets of results support eq. (9).

Some measurements of radial dispersion have been interpreted by means of the velocity profiles of Schwartz and Smith (Fahien and Smith, 1955). Their results near the wall of a fixed bed have not been considered here because the Schwartz and Smith profiles appear not to be representative of conditions within the bed (Vortmeyer and Schuster, 1983).

A comparison of the theory with the available experimental measurements of radial dispersion in beds of porous spheres is shown in Fig. 7 in which the points represent the experimental estimates of Gunn and England (1971) for LA and SA particles. As the porous particles showed a low permeability to the penetration of diffusant the experimental results should be similar to those found for beds of impermeable particles, and a comparison of Figs 5 and 7 confirms that this is so. Evidently, the theory leading to eqs (2) and (9) is in satisfactory accord with the experimental results for axial and radial dispersion in beds of spheres and cylinders, and also is beds of porous spheres.

The similarity of the experimental estimates for the coefficient of mass dispersion for porous and impermeable particles is due to the low permeability of porous particles for mass dispersion. The relative contribution for dispersion of the solid phase is much greater for heat dispersion (Gunn and Vortmeyer, 1984) and as yet a satisfactory relationship between dispersion coefficients in beds of impermeable particles, and coefficients in beds of particles of high thermal conductivitiy has not been established. But for mass dispersion both experiment and theory are consistent when the fluid-phase dispersion model 3 is used.

FLUID TO PARTICLE MASS TRANSFER COEFFICIENTS

When experiments are carried out on the transient response to mass of beds of porous particles, the response in theory is affected by the particle to fluid mass transfer coefficient. However, as the intraparticle

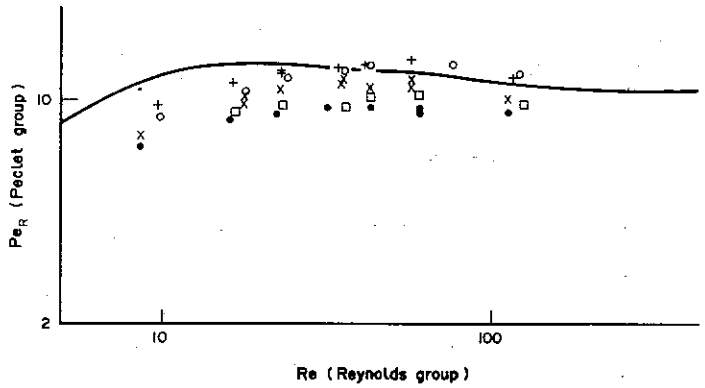

Fig. 7. Comparison of eq. (9) with experimental results for radial dispersion in beds of permeable spheres (Gunn and England, 1970): × SA201 spheres; ○ SA203; □ LA617; + LA622; ● LA623.

diffusivity of porous particles is about 10% of molecular (Table 1) the dominant resistance is that due to intraparticle diffusion, and therefore the sensitivity of the experimental response to the mass transfer coefficient is too small for accurate estimates.

The sensitivity of the transient response to heat of the particle to fluid heat transfer coefficients is much greater. Hence better estimates of the mass transfer coefficient may be obtained by applying the analogy between heat and mass transfer to particle transfer processes. This approach has been followed by Gunn (1978) who showed that for particle fluid mass transfer, the dependence of the Sherwood group upon the Reynolds and Schmidt groups may be expressed as:

$$Sh = (7-10\varepsilon+5\varepsilon^2)\,(1+0.7Re^{0.2}Sc^{1/3}) + (1.33-2.4\varepsilon+1.2\varepsilon^2)Re^{0.7}Sc^{1/3}. \quad (13)$$

CHOICE OF BOUNDARY CONDITIONS FOR TRANSIENT PROCESSES AND FIXED BED REACTORS

The differential equations for fixed beds in applications of process separation and chemical reaction require boundary conditions at the inflow and outflow faces. The difficulty in the choice of boundary conditions arises from the mixed hyperbolic–parabolic nature of the equations, since at low velocities the influence of velocity on the boundary conditions is not important while at high velocities the influence of velocity is dominant.

If the fixed bed is regarded as a sequence of stirred tanks only initial conditions at the entrance of the bed are required and this condition was studied by Kramers and Alberda (1953). However, Gunn and Pryce (1969), by studying mixing in regular rhombohedral and cubic arrays of spheres, showed that mixing in the interstices of regular arrays was not complete, and therefore the mixing cell model owed its utility more to the Central Limit Theorem than to the analogy of mixing between stirred tanks and fixed beds.

In the same year Danckwerts (1953) proposed the following set of boundary conditions for a tubular reactor of length L

$$Uc_0 = Uc - D\frac{\partial c}{\partial x} \quad \text{at} \quad x = 0$$
$$\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = L. \quad (14)$$

A related set of boundary conditions for transient operation was presented by Wehner and Wilhelm (1956).

It was pointed out (Gunn, 1968, 1969) that evidence from mixing studies in fixed beds as portrayed in Fig. 1 for example, showed that dispersion was dominated by molecular diffusion when $ReSc < 1$. For $ReSc > 1$ dispersion was dominated by convection, and for convection-dominated dispersion there was no diffusion of material against the direction of flow. Convection-dominated dispersion was well illustrated in a photograph by Hiby (1962) of tracer injection into a fixed bed when $ReSc \gg 1$ in which all tracer material was contained in a parabolic envelope downstream from the point of injection. For diffusion-dominated dispersion when the equations are parabolic in nature, the conditions of Danckwerts are appropriate at the steady state. But when $ReSc > 1$ under conditions of convection dominated dispersion the boundary conditons are:

$$Uc_0 = Uc - D\frac{\partial c}{\partial x} \quad \text{at} \quad x = 0$$
$$c \to c_{eq} \quad \text{as} \quad x \to \infty \quad (15)$$

where c_{eq} is the condition that would be attained if the conditions at the end of the reactor were brought to equilibrium.

When the solution to the differential equations is analytical eq. (15) gives the constants of integration, but when the solution is numerical conditions (15) are not easy to implement except where the reactor or separation unit is long. However, if the equations at the end of the reactor are replaced by a form that does have an analytical solution, the solution may be used to obtain conditions at the end of the reactor that extend to the same equilibrium condition.

Consider a chemical reactor that is described by the differential equation at the steady state,

$$D\frac{\partial^2 c}{\partial x^2} - U\frac{\partial c}{\partial x} - r(c, c_{eq}) = 0 \quad (16)$$

where r is the rate of reaction. If the rate $r(c, c_{eq})$ is first-order irreversible the analytical solution to (16) is

$$c = \frac{Uc_0}{(U+D\lambda)}\exp\left\{\left[\frac{U}{2D} - \sqrt{\left(\frac{U^2}{4D^2}+\frac{k}{D}\right)}\right]x\right\} \quad (17)$$

for which the condition at some point $x = l$ is

$$\lambda = \sqrt{\left(\frac{U^2}{4D^2}+\frac{k}{D}\right)} - \frac{U}{2D}$$
$$\frac{\partial c}{\partial x} = \left[\frac{U}{2D} - \sqrt{\left(\frac{U^2}{4D^2}+\frac{k}{D}\right)}\right]c \quad (18)$$

and if c is interpreted as $(c - c_{eq})$ and k is interpreted as $r(c, c_{eq})/(c - c_{eq})$ then eq. (18) is a downstream boundary condition that when applied to eq. (16) ensures that $c \to c_{eq}$ as $x \to \infty$. Thus the first equation of (15) and eq. (18) are an equivalent form of the convection-dominated boundary condition that may be used in a numerical scheme.

For a pulse-type transient operation in a fixed bed described by the convection-dominated boundary conditions the change with (x, t) of an injected pulse is given by

$$c = \frac{1}{2\sqrt{(\pi Dt)}}\exp\left[-\frac{(x-Ut)^2}{4Dt}\right] \quad (19)$$

for which

$$\frac{\partial c}{\partial x} = \frac{1}{2D}\left(U - \frac{l}{t}\right)c \quad (20)$$

to give a condition at $x = l$ that is equivalent to the convection-dominated set (15) but may be used in a numerical scheme.

For a step-change type transient operation for which the analytical solution may be expressed by $\text{erf}[(x-Ut)/2\sqrt{(Dt)}]$, the appropriate condition is

$$\frac{\partial c^2}{\partial x^2} = \frac{1}{2D}\left(U - \frac{l}{t}\right)\frac{\partial c}{\partial x}. \quad (21)$$

Boundary conditions equivalent to (15) may be found by similar methods for other examples of processing units including units where radial concentration or temperature gradients are significant.

CONCLUSIONS

The fluid-phase dispersion model satisfies the three principal criteria that have been set out for a satisfactory model of mixing processes in fixed beds. The nature of the model has now been brought to a state of refinement in which the transport coefficients are found to be the same when measured under different conditions of experimentation, and are the recognizable results of interactions between transport processes in fixed beds. There are still points of experimental uncertainty, particularly when concerned with conditions near the retaining walls, but for conditions within the bulk regions the transport equations and coefficients may be closely defined for industrial applications.

NOTATION

d	particle diameter
D	coefficient of axial dispersion
D_{AB}, D_m	molecular diffusivity
D_b	coefficient of axial dispersion in bulk region
D_R	coefficient of radial dispersion
h_m	mass transfer coefficient
$J_0(u)$	zero-order Bessel function, first kind
p	probability of axial displacement
Pe	Péclet group, Ud/D or Ud/D_R
Pe_f	fluid mechanical Péclet group for radial dispersion
Re	Reynolds number, $dU_0\rho/\mu$
Sc	Schmidt group, $\mu/(\rho D_m)$
Sh	Sherwood Group, $h_m d/D_m$
u	velocity outside bed
U	interstitial velocity within bed
U_0	superficial velocity

Greek leters

α_1	first root of $J_0(u) = 0$
ε	bed porosity
σ_v^2	variance of dimensionless interstitial velocity over cross-section of bed
τ	bed tortuosity
ρ	fluid density
μ	fluid viscosity

REFERENCES

Abbi, Y. P. and Gunn, D. J., 1976, Dispersion characteristics from pulse response. *Trans. Inst. Chem. Engrs* **54**, 225.

Bashi, H. Y., 1976, Studies in chemical reactor engineering: intraparticle diffusion in fixed and fluidised bed processes. Ph.D. thesis, University of Wales.

Bashi, H. Y. and Gunn, D. J., 1977, The characterization of fixed beds of porous solids from pulse response. *A.I.Ch.E. J.* **23**, 40.

Bernard, R. A. and Wilhelm, R. H., 1950, Turbulent diffusion in fixed beds of packed solids. *Chem. Engng Prog.* **46**, 233.

Carberry, J. J. and Bretton, R. H., 1958, Axial dispersion of mass in flow through fixed beds. *A.I.Ch.E. J.* **4**, 367.

Danckwerts, P. V., 1953, Continuous flow systems, distribution of residence times. *Chem. Engng Sci.* **2**, 1.

Ebach, E. R. and White, R. R., 1958, Mixing of fluids flowing through beds of packed solids. *A.I.Ch.E. J.* **4**, 161.

Edwards, M. F. and Richardson, J. F., 1968, Gas dispersion in packed beds. *Chem. Engng Sci.* **23**, 109.

England, R. and Gunn, D. J., 1970, Dispersion, pressure drop, and chemical reaction in packed beds of cylindrical particles. *Trans. Inst. Chem. Engrs* **48**, 265.

Fahien, R. and J. M. Smith, 1955, Mass Transfer in packed beds. *A.I.Ch.E. J.* **1**, 128.

Gunn, D. J., 1968, Mixing in packed and fluidised beds. *Chem. Engr* 1968, 153.

Gunn, D. J., 1969, Theory of axial and radial dispersion in packed beds. *Trans. Inst. Chem. Engrs* **47**, 351.

Gunn, D. J., 1970, The transient and frequency response of particles and beds of particles. *Chem. Engng Sci.* **25**, 53.

Gunn, D. J., 1971, Axial dispersion in packed beds: the effect of the quality of packing. *Trans. Inst. Chem. Engrs* **49**, 109.

Gunn, D. J., 1978, Transfer of heat or mass to particles in fixed and fluidised beds. *Int. J. Heat Mass Transfer* **21**, 467.

Gunn, D. J., 1980, Theory of liquid phase dispersion in packed columns. *Chem. Engng Sci.* **35**, 2405.

Gunn, D. J. and Pryce, C., 1969, Dispersion in packed beds. *Trans. Inst. Chem. Engrs* **47**, 341.

Gunn, D. J. and England, R., 1971, Dispersion and diffusion in beds of porous particles. *Chem. Engng Sci.* **26**, 1413.

Gunn, D. J. and de Souza, J. F. C., 1974, Heat transfer and axial dispersion in packed beds. *Chem. Engng Sci.* **29**, 1363.

Gunn, D. J. and Vortmeyer, D., 1982, Heat transfer in fixed bed chemical reactors. *Proc. 7th Int. Heat Transfer Conference*, Munich, Vol. 6, CP3, 13.

Gunn, D. J. and Vortmeyer, D., 1984, The experimental estimation of axial thermal dispersion in fixed beds. *8th Int. Chem. Reaction Engineering Conference*, Edinburgh, *Inst. Chem. Engrs Symp. Ser.* **87**, 583.

Gunn, D. J., Dhingra, S. C. and Narayanan, P. V., 1984, The analysis of heat transfer in fixed beds of particles at low and intermediate Reynolds numbers. *Int. J. Heat Mass Transfer* **27**, 2377.

Hiby, J. W., 1962, Longitudinal and transverse mixing during single phase flow through granular beds. *Proc. Symp. The Interaction between Fluids and Particles*, p. 312. Institute of Chemical Engineers, London.

Kubin, M., 1965, *Coll. Czech. Chem. Commun.* **30**, 1104.

Kucera, E., 1965, *J. Chromat.* **19**, 237.

Kramers, H. and Alberda, G., 1953, Frequency response analysis of continuous flow systems. *Chem. Engng Sci.* **2**, 173.

McHenry, K. W. and Wilhelm, R. H., 1957, Axial mixing of binary gas mixtures flowing in a random bed of spheres. *A.I.Ch.E. J.* **3**, 83.

Miller, S. F. and King, C. J., 1966, Axial dispersion in liquid flow through packed beds. *A.I.Ch.E. J.* **12**, 767.

Price, J., 1968, The distribution of fluid velocities for randomly packed beds of spheres. *Mech. Chem. Engng Trans.* May, 7.

Roblee, L. H. S., Baird, R. M. and Tierney, J. W., 1958, Radial porosity variations in packed beds. *A.I.Ch.E. J.* **4**, 460.

Roemer, G., Dranoff, J. S. and Smith, J. M., 1962, Diffusion in packed beds at low flow rates. *Ind. Engng Chem. Fundam.* **1**, 284.

Schwartz, C. E. and Smith, J. M., 1953, Flow distributions in packed beds. *Ind. Engng Chem.* **45**, 1209.

Schuster, J. and Vortmeyer, D., 1980, *Chem. Engng Techn.* **52**, 848.
Sinclair, R. J. and Potter, O. E., 1965, The dispersion of gas in flow through a bed of packed solids. *Trans. Inst. Chem. Engrs* **43**, 3.
Vermeulen, T. and Jacques, G. L., 1951, University of California Radiation Laboratory, Report No. 8029, U.S. Atomic Energy Commission.
Vortmeyer, D. and Schuster, J., 1983, Evaluation of steady flow profiles in rectangular and circular packed beds by a variational method. *Chem. Engng Sci.* **38**, 1691.
Wehner, J. F. and Wilhelm, R. H., 1956, Boundary conditions of flow reactor. *Chem. Engng Sci.* **6**, 89.