Some Remarks on Longitudinal Mixing or Diffusion in Fixed Beds

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It has been shown both theoretically and experimentally that the radial Peclet number in a packed bed approaches about 11. If it is assumed that the interstitial volume of the bed forms mixing cells, then a comparison of the solutions obtained from the mixing and turbulent diffusive mechanisms shows that the axial Peclet number for agreement of the two must be about 2, as a limiting case for high Reynolds numbers. This is substantiated by experiment.

The mechanism by which heat or mass is dispersed in a packed bed through which a fluid is flowing has been given a great deal of attention. It is assumed that the dispersion of heat or mass both axially and radially is a diffusional process superimposed upon a convective flow and that the whole is described by the partial differential equation

$$-\text{div}\,(-D\,\text{grad}\,c + \bar{V}c) = \frac{\partial c}{\partial t}$$

This equation is usually simplified further so that for the case of radial symmetry about the axis of mean flow

$$-V\frac{\partial c}{\partial x} + D_r\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) + D_a\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \qquad (1)$$

with a similar equation for heat flow. The substitutions $x = D_p y$, $r = D_p\rho$, $t = (D_p\tau)/V$ reduce Equation (1) to

$$-\frac{\partial c}{\partial y} + \frac{1}{Pe_r}\left(\frac{\partial^2 c}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial c}{\partial \rho}\right) + \frac{1}{Pe_a}\frac{\partial^2 c}{\partial y^2} = \frac{\partial c}{\partial \tau}$$

where $Pe_r = (VD_p)/D_r$ and $Pe_a = (VD_p)/D_a$ which are the radial and axial Peclet numbers, respectively.

Considerable effort has been expended to relate the Peclet numbers to the fluid dynamical character of the problem. In particular, Bernard and Wilhelm (*1*) and Singer and Wilhelm (*7*) have shown that for sufficiently high Reynolds numbers and sufficiently high tube-to-particle-diameter ratio, Pe_r must be about 11. Baron (*2*) from a random-walk analogy in one dimension estimated Pe_r to be between 5 and 13, and Ranz (*6*) in a detailed analysis of the flows in a rhombohedrally packed bed of spheres showed that Pe_r is 11.2. For some time it was thought that packed-bed diffusion should be isotropic; however, recent measurements by Kramers and Alberda (*5*) indicated that the longitudinal Peclet number should be about 1 with a mixing-cell model, and Wilhelm and his coworkers (*10*) showed that Pe_a must be about 2. (Perhaps the difference in the two results may be explained on the basis of by-passing, as different kinds of packing were employed.) Hence the diffusional process is anistropic, the diffusional effect in the axial direction being considerably greater than anticipated.

It is the purpose of this paper to hypothesize a rather simple mechanism and to show on the basis of this mechanism that the Peclet number Pe_a must be about 2 for sufficiently high Reynolds numbers and for spherical packing material.

For the sake of definiteness it will be supposed that the bed is packed with spheres in a rhombohedral blocked-passage arrangement. The spheres are then in layers, each layer having a thickness of γD_p, $\gamma = \sqrt{2/3}$. The void fraction in such a bed is 0.2595, which may be assumed to be the average free area in the bed open to flow. If one examines the free area open to flow from a plane through the centers of a layer of spheres to a plane through the centers in the next layer, it is found that if the layer is divided into thirds, the first third has an average free area of 0.1827, the middle third 0.4132, and the top third 0.1827. The free area in a plane through sphere centers is 0.0933. Thus there are planes in the bed through which the velocity of the fluid is very high followed by regions in which the velocity is considerably less. It will be assumed therefore that the free volume in each layer, that is the layer between planes passing through sphere centers, serves as mixing cells for the fluid, the influent to a cell acting as a jet mixer and thereby increasing the turbulence in the free volume. The effluent from a cell will have the composition of the cell. This situation should certainly be approximated at high Reynolds numbers, and therefore the theory is a limiting one only. Since there is no lag assumed in the fluid flow from one cell to the next, a concentration signal will be instantaneously propagated in attenuated form through the bed just as there is in conventional diffusion theory.

If, following Kramers and Alberda (*5*), one considers a series of well-agitated cells, numbered from 0 to n, initially free of solute, having a volume v, being fed with a stream q, and having introduced into the zeroth cell a solution with a concentration of $c_f(t)$, with $t > 0$, the system is described by

$$qc_{n-1} - qc_n = v\frac{\partial c_n}{\partial t}$$

$$c_n = 0, \quad t = 0$$

$$qc_f - qc_o = v\frac{\partial c_o}{\partial t}, \quad t > 0$$

The Laplace transform $\bar{c}_n$ of the solution c_n is

$$\bar{c}_n = \left(\frac{q}{v}\right)^{n+1}\frac{\bar{c}_f}{\left(\frac{q}{v} + p\right)^{n+1}}$$

and the inverse is

$$c_n = \frac{1}{n!}\left(\frac{q}{v}\right)^{n+1}\cdot\int_0^t c_f(\theta)(t-\theta)^n e^{-(q/v)(t-\theta)}\,d\theta$$

giving the concentration in the nth cell at time t due to a varying input.

If one defines $\tilde{c}_n$ by

$$\tilde{c}_n = \frac{1}{n!}\left(\frac{q}{v}\right)^{n+1}\cdot c_f(\theta)(t-\theta)^n e^{-(q/v)(t-\theta)}\,d\theta$$

then $\tilde{c}_n$ is that part of the concentration in the nth cell at time t which results from $qc_f(\theta)\,d\theta$ molecules having been introduced into the zeroth cell at time θ. Therefore

$$\frac{\tilde{c}_n(\theta)v}{qc_f(\theta)\,d\theta} = \left(\frac{q}{v}\right)^n\frac{1}{n!}(t-\theta)^n e^{-(q/v)(t-\theta)}$$

is the fraction of those molecules introduced at time θ over a time interval $d\theta$

which are in the nth cell at time t or, alternatively, by Bernoulli's theorem

$$P_p = \frac{\left(\frac{q}{v}t\right)^n e^{-(q/v)t}}{n!}$$

is the probability that a molecule introduced into the bed at time $t = 0$ is in the nth layer at time t. One immediately recognizes this as a Poisson probability density function with a mean and dispersion given respectively by (4)

$$\mu_p = \frac{q}{v}t$$

$$d_p = \frac{q}{v}t$$

If one considers the corresponding problem phrased in diffusion language, the required equations are

$$-V\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \qquad (2)$$

$$Vc_f(t) = Vc - D\frac{\partial c}{\partial x},$$

$$x = 0, \quad t > 0 \qquad (3)$$

$$c = 0, \quad t < 0 \qquad (4)$$

where D is used for D_a. It will be shown that probability considerations dictate the use of Equation (3) rather than the condition $c = c_f(t)$ at $x = 0$. This has been discussed in some detail by Kramers and Alberda (5), Danckwerts (3), Wehner and Wilhelm (9), and others. The Laplace transform $\bar{c}$ of the solution c to Equations (2), (3), and (4) is

$$\bar{c} = \bar{c}_f \frac{V \exp\left\{\frac{Vx}{2D}\right\} \exp\left\{-\frac{x}{\sqrt{D}}\sqrt{\frac{V^2}{4D} + p}\right\}}{D\left(\frac{V}{2D} + \frac{1}{\sqrt{D}}\sqrt{\frac{V^2}{4D} + p}\right)}.$$

The inverse transform may be obtained to give

$$c(t) = V\int_0^t c_f(\theta)P_d(x, t - \theta)\,d\theta$$

where

$$P_d(x, \theta) = \frac{1}{\sqrt{\pi D\theta}}\exp\left\{-\frac{(x - V\theta)^2}{4D\theta}\right\} - \frac{V}{2D}\exp\left\{\frac{Vx}{D}\right\}\operatorname{erfc}\left(\frac{x + V\theta}{2\sqrt{D\theta}}\right).$$

$$\frac{\tilde{c}(\theta)\,dx}{Vc_f(\theta)\,d\theta} = P_d(x, t - \theta)\,dx$$

is the fraction of those molecules introduced at time θ over an interval of time $d\theta$ which are in a volume element $1 \cdot dx$ at x at time t. In other words

$$P_d(x, t)\,dx \qquad (5)$$

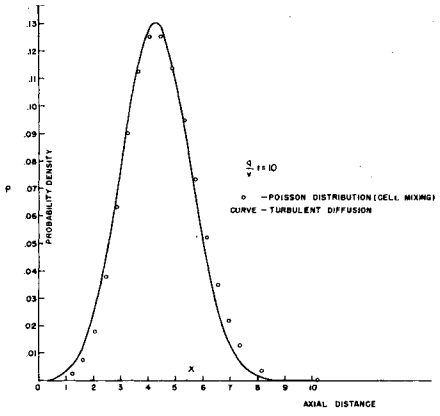

Fig. 1. Comparison of cell mixing and diffusional mechanisms with data as given in the numerical example $(q/v)t = 10$.

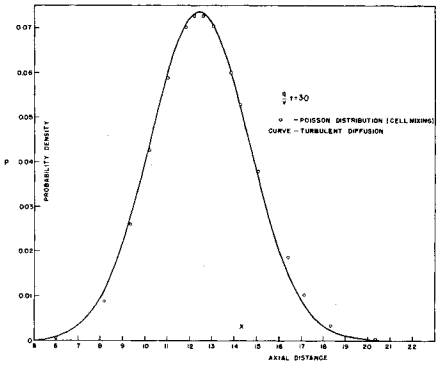

Fig. 2. Comparison of cell mixing and diffusional mechanisms with data as given in the numerical example $(q/v)t = 30$.

is the probability that a molecule introduced into the bed at $x = 0$ at time $t = 0$ is in a volume $1 \cdot dz$ at x at time t. $P_d(x, t)$ is then the probability density function. In order to make this quantity dimensionless it is desirable to let $x = \gamma D_p z$ so that the probability density function becomes

$$\gamma D_p P_d(\gamma D_p z, t) \qquad (6)$$

This analysis could have been carried out by a random walk with a suitable bias on the steps as in reference 8.

In order to show that this is a real probability function it is essential to show that

$$\int_0^\infty P_d(x, t)\,dx = 1$$

This is rather tedious but may be carried out with ease in the p plane to give

$$\int_0^\infty \bar{P}_d(x, p)\,dx = \frac{1}{p}$$

where $\bar{P}_d$ is the Laplace transform of P_d, and since the Laplace transform of 1 is $1/p$ the particle is certainly somewhere in the bed. Thus the use of boundary condition (3) ensures that a molecule once admitted remains in the bed.

Thus the two alternative mechanisms produce two different probability density functions P_p and P_d. It is well known that the Poisson probability density may be approximated by the normal density function

$$P_p \cong \frac{1}{\sqrt{4\pi Dt}}\exp\left\{-\frac{(x - Vt)^2}{4Dt}\right\}$$

The function P_d may be written in the form

$$\frac{1}{\sqrt{\pi Dt}}\exp\left\{-\frac{(x - Vt)^2}{4Dt}\right\} \cdot\left[1 - \frac{Vt}{x + Vt}\left(1 - \frac{2Dt}{(x + Vt)^2} + \frac{12D^2t^2}{(x + Vt)^4}\cdots\right)\right]$$

by making use of the asymptotic expansion for the erfc. For large values of $x + Vt$ and in particular for x in the neighborhood of Vt, this expression reduces to

$$P_n(x, t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left\{-\frac{(x - Vt)^2}{4Dt}\right\}$$

and hence P_d approaches, in the neighborhood of the mean at least, the normal density function. The mean and dispersion of the dimensionless normal density function are (4)

$$\mu_n = Vt/\gamma D_p$$

$$d_n = 2Dt/\gamma^2 D_p^2$$

If these density functions are to give the same distribution of solute in the bed, the means and dispersions must be equal so that

$$\frac{Vt}{\gamma D_p} = \frac{q}{v}t$$

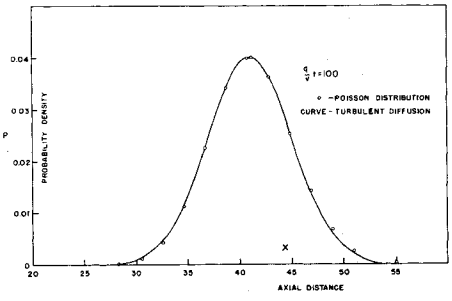

Fig. 3. Comparison of cell mixing and diffusional mechanisms with data as given in the numerical example $(q/v)t = 100$.

$$\frac{2Dt}{(\gamma D_p)^2} = \frac{q}{v}\,t$$

where the dimensionless form of the normal density function is

$$P_n(x,\,t) = \frac{\gamma D_p}{\sqrt{4\pi Dt}} \cdot \exp\left\{-\frac{(\gamma D_p z - Vt)^2}{4Dt}\right\}$$

Hence there results

$$\frac{VD_p}{D} = \frac{2}{\gamma}$$

For rhombohedral close packing

$$\frac{VD_p}{D} = \frac{2}{0.815} = 2.46 \qquad (7)$$

and for random packing γ is about 1 or less, and thus

$$\frac{VD_p}{D} \cong 2$$

as was to be shown.

In this analysis it was shown that the Poisson distribution and diffusional distribution each approached the normal distribution some distance from the bed entrance. It was then suggested that the means and dispersions of the Poisson and normal distributions should be the same. In order to make the analysis complete one should compare all the moments of the Poisson and diffusional distributions. This is tedious, however, and leads to integrals which are difficult to evaluate or estimate. Since the purpose here has been to show the possibility that intracellular mixing obtained in the bed, it is instructive perhaps to exhibit some numerical comparisons of the distribution functions.

A rhombohedrally packed blocked-passage bed with spheres 5 mm. in diameter will be considered. The interstitial average velocity of the fluid is 2 cm./sec. A bed cross section of 1 sq. cm. is taken as a unit.

D_p = 0.5 cm.
α = 0.2595
γ = 0.817
v = 0.106 cc./sq. cm. of bed cross section
V = 2 cm./sec.
$Pe_a = VD_p/D$ = 2.46
D = (2)(0.5)/2.46 = 0.408 sq. cm./sec.

Thus the turbulent diffusivity must be chosen as 0.408 if the two mechanisms are to agree. Also

$q = \alpha V$ = 0.519 (cc./sec.)/sq. cm. of bed cross section
V/D = 4.908 cm.$^{-1}$

It should be noted that q and v are defined for 1 sq. cm. of bed cross section. Thus q is identical with the superficial velocity in the bed and v is the volume of a cell contained in 1 sq. cm. of bed cross section and is γD_p cm. deep.

Figures 1, 2, and 3 were then plotted, (qt/v) being chosen as a parameter. For $(q/V)t = 100$ the two mechanisms give distribution plots which are indistinguishable. In all cases, however, the agreement is satisfactory and convincing.

Earlier in the paper some mention was made of the use of the proper boundary condition. If one assumes the boundary condition to be $c = c_f$ where c_f is a constant for $t > 0$, it is then a simple matter to show that the diffusive mechanism gives as the Laplace transform of the solution

$$\bar{c} = \frac{c_f}{p}\exp\left\{\frac{Vx}{2D}\right\} \cdot \exp\left\{-\frac{x}{\sqrt{D}}\sqrt{\frac{V^2}{4D} + p}\right\}$$

the inverse of which is

$$c = c_f \int_0^t \frac{x}{\sqrt{4\pi D\theta^3}} \cdot \exp\left\{-\frac{(x - V\theta)^2}{4D\theta}\right\} d\theta$$

In order to calculate the total number of molecules in the bed at any time, one may form the quantity

$$\sum = \int_0^\infty c(x,\,t)\,dx$$

It is somewhat easier to integrate the Laplace transform of $c(x, t)$ from zero to infinity and then to invert the transform to give

$$\sum = c_f \int_0^t \left[\frac{\sqrt{D}}{\sqrt{\pi t}}\exp\left\{-\frac{V^2}{4D}\right\} + \frac{V}{2} + \frac{V}{2}\,\mathrm{erf}\left(\frac{V\theta}{2\sqrt{D}}\right)\right] d\theta \qquad (8)$$

The boundary condition $c = c_f$ might be expected to ensure that the number of molecules in the bed would increase linearly with the time. However, Equation (8) does not indicate this, and hence molecules once admitted to the bed have back mixed out of the bed. If one accepts the hypothesis that the packing is responsible for the mixing, this hardly seems possible, and $c = c_f$ at $x = 0$ appears to be an improper boundary condition. This diffusion involves only turbulent, and not molecular, diffusion.

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It should be pointed out that the authors, after the first review of this paper, had the advantage of examining a paper by Wilhelm and McHenry (*10*).

NOTATION

c = concentration in diffusive mechanisn, moles/cc.
c_n = concentration in nth cell, moles/cc.
c_f = influent concentration, moles/cc.
$\bar{c}$ = fractional concentration as defined in text
D = diffusion or mixing coefficient, sq. cm./sec.
D_p = particle packing diameter, cm.
D_a = axial diffusion coefficient, sq. cm./sec.
D_r = radial diffusion coefficient, sq. cm./sec.
d = dispersion of a distribution about the mean
$\mathrm{erf}\,(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-\alpha^2}\,d\alpha$
$\mathrm{erfc}\,(x) = 1 - \mathrm{erf}\,(x)$
P = symbol for a probability density function
Pe_r, Pe_a = Peclet numbers as defined in text
q = flow rate, cc./(sec.)(sq. cm.) of bed cross section
r = radius variable, cm.
ρ = dimensionless radius variable
t = time, sec.
V = interstitial velocity, cm./sec.
V_0 = superficial velocity = αV, cm./sec.
v = volume of a cell = $\alpha\gamma D_p$, cc./sq. cm. of bed cross section
x = axial variable, cm.
y = dimensionless axial variable
bars in general indicate Laplace transform

Subscripts

p = Poisson
d = diffusion
n = normal

Greek Letters

α = fractional void volume
γ = distance between successive layers of spheres
μ = mean of a distribution
τ = time (dimensionless) = $V_0 t/D_p\alpha$
θ = time, sec.

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