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The Interference of Eddy Diffusion by Brownian Motion in Randomly Packed Beds

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Abstract

Some processes which are of interest in chromatography are discussed. One process is concerned with the progress of a sample layer of small particles in a fluid which passes very slowly through a vertical tube (column) filled with pebble-shaped beads. The mean and variance of the time for the particles to cover a certain distance are of particular interest as they may be used as a basis for chemical analysis of the sample.

INTRODUCTION

We will be concerned with the flow of a gas or liquid through a bed of regularly or irregularly shaped beads or pebbles which are packed in a random or nonrandom fashion. More specifically, we will study the movement of particles which are in suspension in the moving fluid. We will not address ourselves to the problems which arise when the particles get attached to the beads through adsorption or otherwise and assume that only flow patterns and Brownian motion are relevant to the description of the movement of the particles. Eddy diffusion concerns the former: a particle may temporarily acquire a greater than average downstream velocity by following a relatively open pathway or, in contrast, it may become enmeshed in a restricted channel and lag behind.

It was originally thought that the two causes of deviation from the average progress of particles as mentioned above acted independent of each other so that the total variance due to both would be the sum of the variances attributable to each. This did not check out with experiments. Giddings (*1*), in his coupling theory of Eddy diffusion, however, in attempting a qualitative explanation of the phenomena observed, broke with the classical approach involving independence. In the following section we give a brief account of his theory, which we have stripped from detail, that is rather more relevant to the practical interpretation than to the mathematical description.

From the outset it should be stipulated that we distinguish three effects that Brownian motion may have in the present context.

(1) It interrupts the relatively smooth if irregular flow known as Eddy diffusion by knocking particles about and displacing them from channels with low velocity to relatively open channels and vice versa.

(2) Displacements in the direction of flow or contrary to that direction. These cause random discrepancies from the average progress; this phenomenon will be referred to as longitudinal diffusion. It will be assumed to be independent of effect (1), although this is recognized to be only partially correct since each time a particle is displaced as described in (1) the displacement will have a longitudinal component.

(3) Displacements described under (2) will have the effect that the path to be covered will be either shorter or longer than without them, and as a consequence the particles will be exposed for different periods to the Eddy flow process. This effect is probably only of secondary importance and would require further investigation; we will ignore it here completely.

In the present paper we restrict the discussion to randomly packed beds, although in the second section following the model for a nonrandomly packed bed is indicated. The analysis of the latter would involve a Markov renewal process with four states, which requires rather more advanced tools [cf. Çinlar (*2*)].

GIDDINGS COUPLING THEORY OF EDDY DIFFUSION

Consider the path of a particle in solution as it passes through a cylindrical column of length L which is filled with small pebbles. The projection of the path on the axis of the column is a straight line segment $(0, L)$. Subdivide this line segment in segments of equal length S. Assume that in approximately half these the velocity of the particle is $v + \Delta v$, and $v - \Delta v$ in the other ones. The probability that a particular segment is of a specific kind (i.e., with a flow-velocity of $v + \Delta v$ or $v - \Delta v$) is one half. Due to this random feature, the distance traveled at time $t = L/v$ is a random variable. The variance of its distribution follows easily from the fact that the number **k** of segments traveling at speed $v + \Delta v$ has approximately a binomial distribution with parameters $p = \frac{1}{2}$ and $n = L/S$, so that var $\mathbf{k} = npq = \frac{1}{4}n$. The distance traveled at t is approximately

$$L + \mathbf{k}\frac{\Delta v}{v}S - (n - \mathbf{k})\frac{\Delta v}{v} = L - n\frac{\Delta v}{v}S + 2\mathbf{k}\frac{\Delta v}{v}S$$

The variance of this quantity is therefore

$$\sigma^2 = \frac{1}{4}n\left(2\frac{\Delta v}{v}S\right)^2 = n\left(\frac{\Delta v}{v}\right)^2 S^2 = n\omega^2 S^2 \tag{1}$$

Now consider two distinct such processes with

$$\sigma_1^2 = n_1\omega^2 S_1^2 \qquad \text{and} \qquad \sigma_2^2 = n_2\omega^2 S_2^2 \tag{2}$$

where $n_1 S_1 = n_2 S_2 = L$, and further a third which is a combination of these two:

$$\sigma^2 = n\omega^2 S^2 \tag{3}$$

where $n = n_1 + n_2$ and $nS = L$. The various variances are then related by

$$\sigma^{-2} = \frac{n}{\omega^2 L^2} = \frac{n_1}{\omega^2 L^2} + \frac{n_2}{\omega^2 L^2} = \sigma_1^{-2} + \sigma_2^{-2} \tag{4}$$

Let the index 1 stand for the process due to flow variations (Eddy diffusion) in the absence of Brownian motion and the index 2 stand for the process with speed variations caused exclusively by interruptions due to Brownian motion. It is seen from Eq. (4) that the combined effect of Eddy diffusion and the interference by Brownian motion mentioned under (1) in the Introduction as measured by the variance tends to assume the smaller of the two variances of the individual processes. In particular, if σ_2^2 is extremely small, as will be the case in most practical situations when one deals with small molecular particles in suspension, σ^2 will be nearly as small and the total variance as observed will almost be attributable in full to longitudinal diffusion. A drawback of Giddings's approach is the choice of $p = \frac{1}{2}$, because this limits its generality.

DESCRIPTION OF THE MODEL AND DEFINITIONS

The model for the interference of Eddy diffusion by Brownian motion described in this section and analyzed in the next section with particular reference to the derivation of the resulting mean and variance has been constructed in analogy of Giddings's approach and may be considered as a refinement. Consider a particle traveling along the L-axis. Initially, it is in the point $L = 0$ and has a velocity v in the positive direction. The length the particle will travel at this speed if no interruptions occur is a random variable $\mathbf{v}$ with distribution F. After the elapse of the length $\mathbf{v}$, the speed becomes unity instantaneously and remains so for a length $\mathbf{u}$ with distribution G. Subsequently the speed becomes v again and remains so for a random length, again sampled from the distribution F, and so on. This process is a tentative approximation of the Eddy diffusion process and is described under the name "alternating renewal process" in Cox (*3*). While this process is proceeding, another process is operative independently. This is the Brownian motion interruption process described under (1) in the Introduction (longitudinal diffusion remains divorced from the discussion here altogether). This process interrupts the Eddy diffusion process in a Poisson fashion. To be more specific, interruptions occur at a rate λ per unit *length* in a Poisson process while the speed of the particle is v; at the rate μ while the speed is unity. When an interruption occurs, the speed of the particle may alter: the speed becomes v with probability p and unity with probability $q = 1 - p$, independent of the speed immediately before the interruption. The length $\mathbf{v}$ which is available initially for the particle to move uninterruptedly at speed v will be called the available length. The length actually covered uninterruptedly and at speed v is the minimum of $\mathbf{v}$ and the length up to first interruption (sampled from a negative exponential distribution with parameter λ). The distribution of this minimum is therefore $1 - e^{-\lambda x}[1 - F(x)]$ for $x \geqslant 0$. This distribution also applies following each time the velocity of the particle changes from 1 to v due to expiration of the available length associated with unit speed. After the expiration of an available length associated with speed v, the velocity of the particle becomes unity and the distribution of the available length is G. The distribution of the length actually covered uninterruptedly and at unit speed after the expiration of an available length associated with speed v equals (by the same argument as before) $1 - e^{-\mu x}[1 - G(x)]$ for $x \geqslant 0$.

We now arrive at a moot point in the description of the model, and it will turn out that this is the point where we distinguish between randomly packed beds and beds with regular features. The moot point concerns the distribution F_1 of the available length after an interruption, following which the speed is v. We assume that immediately after an interruption the particle is at an *arbitrary* point in the region where the flow velocity is v; given that it is in this region. (We omit the consideration of up- or downstream displacement; this is taken care of in longitudinal diffusion.) The arbitrary point lies in an interval on the vertical through this point and along which the speed is v throughout. We tacitly assume that "interval" refers to the largest possible one with this property. Intervals along which the speed is v have the distribution F. The fact that an arbitrary point is contained in it, however, implies that we are concerned with an interval which is selected in a very special way. (We will now give an heuristic derivation of the distribution of this specially selected interval and of the distribution of the available length in this case. These distributions are known in renewal theory as those of an interval which covers an arbitrary point on the time axis and of the residual life time.) What is the probability that an arbitrary point in the region with velocity v lies in an interval of length between x an $x + dx$? Obviously, the longer the interval, the more likely it will be chosen. More specifically, if an arbitrary point is to be contained in the interval, then the interval is chosen *with probability proportional to its length*. Intervals of length between x and $x + dx$ occur with relative frequency $dF(x) = F(x + dx) - F(x)$ $[= f(x)\,dx$ if the derivative $f(x)$ of $F(x)$ exists]. Therefore, the probability that an interval of length $\mathbf{x}$ between x and $x + dx$ contains the arbitrary point is proportional to $xdF(x)$. Hence, its distribution is $P\{\mathbf{x} < x\} = a\int_0^x udF(u)$, where a is determined by the fact that the distribution must be proper. This requires $a\int_0^\infty udF(u) = 1$, so that a^{-1} is the mean of F. In order to derive the distribution of the available length, in this case we note that the location of the arbitrary point is selected without preference on the interval and is therefore uniformly distributed over the full length of the interval. Finally then, we have for the distribution F_1 of the available length $\mathbf{y}$, after an interruption which resulted in a displacement of the particle to an arbitrary point in the region with flow velocity v, that

$$\begin{aligned} F_1(y) = P\{\mathbf{y} < y\} &= \int_0^\infty P\{\mathbf{y} < y \mid \mathbf{x} = x\} axdF(x) \\ &= a\int_0^y xdF(x) + a\int_y^\infty \frac{y}{x} xdF(x) \\ &= a\left\{yF(y) - \int_0^y F(x)\,dx + y - yF(y)\right\} \\ &= a\int_0^y \{1 - F(x)\}\,dx \qquad (5) \end{aligned}$$

where $a^{-1} = \int_0^\infty xdF(x)$. A similar argument applied to the available length associated with unit velocity after an interruption yields the fact that its distribution equals $G_1(x) = b\int_0^x \{1 - G(u)\}du$ for $x \geqslant 0$, where $b^{-1} = \int_0^\infty xdG(x)$.

A natural question that comes to mind at this point is whether the distribution of the available length after an interruption can be equal to that of the available length after the expiration of the previous one. In terms of the distributions of available lengths associated with a speed v, this will be the case if $F_1 \equiv F$, so that F must be the solution of the integral equation $F(x) = a\int_0^x \{1 - F(u)\}du$ for $x \geqslant 0$. This happens to be a characterization of the negative exponential distribution with parameter a if one further requires that solution to be a proper distribution of a nonnegative random variable as is easily seen on differentiating both sides of the equation. Analogously for available lengths associated with unit speed, $G_1 \equiv G$, if $G(x) = 1 - e^{-bx}$ for $x \geqslant 0$. Thus the distribution of an available length after the expiration of a previous available length equals the distribution of an available length from an arbitrary point if $F(x) = 1 - e^{-ax}$ for $x \geqslant 0$ and $G(x) = 1 - e^{-bx}$ for $x \geqslant 0$. Accordingly, we define a bed as randomly packed if both F and G are negative exponential distributions.

It would seem appropriate at the conclusion of this section to moderate some of the more categoric assertions made. Obviously, not each and every one of the interruptions of the Eddy diffusion by Brownian motion results in putting the particle in an arbitrary point. More often than not, the particle will not wander far from its immediate neighborhood. This can be taken care of, however, by taking somewhat lower values than the actual average number of displacements per unit length covered for the interruption rates λ and μ. More serious, of course, is the assumption that only two speeds are applicable under the present model and that changes occur instantaneously. The excuse here must be that these assumptions make the present model accessible for analysis and that one can only hope to obtain some feeling for the actual goings on by studying this admittedly crude model. Nevertheless we do have a particular application in mind in electrophoresis where the assumptions may be quite near to reality.

ANALYSIS OF THE MODEL WITH A RANDOMLY PACKED BED

In this section we will analyze the model in which the available lengths have an exponential distribution. We will concentrate on finding the distribution, the mean, and the variance of $\mathbf{x}_L$; the latter is the part of the path $(0, L)$ of the particle which is covered at speed v. That is, $\mathbf{x}_L$ is the sum of the lengths of segments of the path in the interval $(0, L)$ which are traveled at velocity v.

The path of a particle subject to Eddy diffusion with interference by

Brownian motion (but ignoring longitudinal diffusion) may be described by the random lengths $\mathbf{v}_1, \mathbf{u}_1, \mathbf{v}_2, \mathbf{u}_2, \mathbf{v}_3, \ldots$ of the consecutive segments of the path during which the speed is alternatingly v and unity. The families $\mathbf{v}_1, \mathbf{v}_2, \ldots$ and $\mathbf{u}_1, \mathbf{u}_2, \ldots$ form two independent families of independent and identically distributed random variables. The distribution of a length $\mathbf{v}_i$ covered at constant speed v is found from the following argument.

Let the probability of the event that $\mathbf{v}_i$ exceeds y equal $P(y)$. This event happens if one of two mutually exclusive events occurs.

(1) The available length $\mathbf{x}$ exceeds y, $P\{\mathbf{x} > y\} = e^{-ay}$, and no interruptions occur during coverage of the length y; the latter event has probability $e^{-\lambda y}$.

(2) The first interruption occurs at a distance z from the commencement of $\mathbf{v}_i$, $0 < z < y$, and before the available length $\mathbf{x}$ expires, while the interruption does not cause a change of speed, which happens with probability p, and during passage from z to y no speed change occurs. The probability of the latter equals $P(y - z)$, since at z the particle is again in an arbitrary point of the region where the velocity is v. These considerations lead for $y \geqslant 0$ to

$$P\{\mathbf{v}_i > y\} = P(y) = e^{-(a+\lambda)y} + p\lambda \int_0^y P(y - z)e^{-(a+\lambda)z}\, dz$$

which may be rearranged after a change of variable $u = y - z$ to

$$P(y)e^{(a+\lambda)y} = 1 + p\lambda \int_0^y P(u)e^{(a+\lambda)u}\, du$$

Differentiating both sides with respect to y, we obtain a differential equation for $P(y)$, the solution of which, satisfying $P(0) = 1$, equals $P(y) = e^{-(a+q\lambda)y}$ for $y \geqslant 0$. We conclude that the common distribution of the variables $\mathbf{v}_1, \mathbf{v}_2, \ldots$ is a negative exponential with the parameter $r = a + q\lambda$. Similarly it follows that the common distribution of $\mathbf{u}_1, \mathbf{u}_2, \ldots$ is negative exponential with parameter $s = b + p\mu$.

We are now in a position to derive the distribution of $\mathbf{x}_L$, the sum of the lengths of segments $\mathbf{v}_1, \mathbf{v}_2, \ldots$ inside the interval $(0, L)$. It is easily seen that

$$P\{\mathbf{x}_L = L\} = P\{\mathbf{v}_1 > L\} = e^{-rL} \tag{6}$$

For the calculation of the density of $\mathbf{x}_L$ on the interval $(0, L)$, we need the fact that the density of n independent random variables with common exponential distribution with parameter c is the gamma density $c^n x^{n-1}$

$[(n-1)!]^{-1}e^{-cx}$ for $x > 0$ [cf. Feller (*4*)]. For $0 < x < L$, the value of $\mathbf{x}_L$ lies between x and $x + dx$ if, for $n = 1, 2, \ldots$, either

(1) The particle surpasses the distance L in path segment $\mathbf{u}_n$, while

$$x < \sum_{i=1}^{n} \mathbf{v}_i < x + dx, \quad 0 < u < \sum_{i=1}^{n-1} \mathbf{u}_i < u + du < L - x,$$
$$\mathbf{u}_n > L - x - u.$$

(2) The particle surpasses the distance L in path segment $\mathbf{v}_{n+1}$, while

$$L - x - dx < \sum_{i=1}^{n} \mathbf{u}_i < L - x, \quad 0 < u < \sum_{i=1}^{n} \mathbf{v}_i < u + du < x,$$
$$\mathbf{v}_{n+1} > x - u.$$

Thus we obtain the density f of $\mathbf{x}_L$ for $0 < x < L$ as

$$\begin{aligned} f(x) &= \sum_{n=1}^{\infty} \frac{r^n x^{n-1}}{(n-1)!} e^{-rx} \int_{u=0}^{L-x} e^{-s(L-x-u)} \frac{s^{n-1}u^{n-2}}{(n-2)!} e^{-su}\, du \\ &\quad + \sum_{n=1}^{\infty} \frac{s^n(L-x)^{n-1}}{(n-1)!} e^{-s(L-x)} \int_{u=0}^{x} e^{-r(x-u)} \frac{r^n u^{n-1}}{(n-1)!} e^{-ru}\, du \\ &= \sum_{n=1}^{\infty} \frac{r^n x^{n-1}}{(n-1)!} \frac{s^{n-1}(L-x)^{n-1}}{(n-1)!} e^{-rx-s(L-x)} \\ &\quad + \sum_{n=1}^{\infty} \frac{s^n(L-x)^{n-1}}{(n-1)!} \frac{r^n x^n}{n!} e^{-s(L-x)-rx} \end{aligned} \tag{7}$$

which may be expressed in terms of two modified Bessel functions of the first kind. As we are primarily interested in the mean and variance of $\mathbf{x}_L$, we take transforms of Eqs. (6) and (7)

$$\begin{aligned} \int_{L=0}^{\infty} e^{-\alpha L} E\{e^{-\beta \mathbf{x}_L}\} dL &= \int_{L=0}^{\infty} e^{-(\alpha+\beta+r)L}\, dL \\ &\quad + \int_{L=0}^{\infty} e^{-\alpha L}\, dL \int_{x=0}^{\infty} e^{-\beta x} f(x)\, dx \\ &= \frac{1}{\alpha+\beta+r} + \sum_{n=1}^{\infty} \left\{ \frac{r^n}{(\alpha+\beta+r)^n} \frac{s^{n-1}}{(\alpha+s)^n} \right. \\ &\quad \left. + \frac{r^n}{(\alpha+\beta+r)^{n+1}} \frac{s^n}{(\alpha+s)^n} \right\} \\ &= \frac{\alpha+r+s}{(\alpha+\beta+r)(\alpha+s) - rs} \\ &= \frac{\alpha+r+s}{\alpha^2 + (\beta+r+s)\alpha + s} \end{aligned} \tag{8}$$

Using the inversion formula for the Laplace transform and the Dirichlet integral [cf. Widder (5)], we have for $\varepsilon > 0$ that

$$E\{e^{-\beta \mathbf{x}_L}\} = \frac{1}{2\pi i} \lim_{x\to\infty} \int_{\varepsilon - ix}^{\varepsilon + ix} \frac{(\alpha + r + s)e^{\alpha L}}{\alpha^2 + (\beta + r + s)\alpha + s\beta} dx \tag{9}$$

$$= \frac{1}{2\pi i} \lim_{x\to\infty} \int_{\varepsilon - ix}^{\varepsilon + ix} \frac{(\alpha + r + s)e^{\alpha L}}{(\alpha - \alpha_1)(\alpha - \alpha_2)} d\alpha$$

$$= \frac{1}{\alpha_1 - \alpha_2} \{(\alpha_1 + r + s)e^{\alpha_1 L} - (\alpha_2 + r + s)e^{\alpha_2 L}\}$$

where

$$\alpha_1 = \alpha_1(\beta) = -\frac{1}{2}(\beta + r + s) + \frac{1}{2}\sqrt{(\beta + r + s)^2 - 4\beta}$$

and

$$\alpha_2 = \alpha_2(\beta) = -\frac{1}{2}(\beta + r + s) + \frac{1}{2}\sqrt{(\beta + r + s)^2 - 4s\beta}$$

By differentiation of Eq. (9) with respect to β, one may obtain, after some tedious calculations, the first two moments of $\mathbf{x}_L$, from which the mean and vaiance are found as

$$E\{\mathbf{x}_L\} = \frac{sL}{r + s} + \frac{r}{(r + s)^2}(1 - e^{-(r+s)L})$$

$$\mathrm{Var}\{\mathbf{x}_L\} = \frac{r^2 - 4rs}{(r + s)^4} + \frac{2rs}{(r + s)^3} L - \frac{2r(r - s)}{(r + s)^3} - \frac{r^2}{(r + s)^4} e^{-2(r+s)L} + \frac{4rs}{(r + s)^4} e^{-(r+s)L}$$

For large L, relative to a^{-1}, b^{-1}, $(q\lambda)^{-1}$, and $(p\mu)^{-1}$, replacing r and s again, it follows that

$$E\{\mathbf{x}_L\} = \frac{b + p\mu}{a + b + q\lambda + p\mu} L \tag{10}$$

$$\mathrm{Var}\{\mathbf{x}_L\} = \frac{2(a + q\lambda)(b + p\mu)}{(a + b + q\lambda + p\mu)^3} L \tag{11}$$

In conclusion, before we discuss some of the implications of these results, we should emphasize the limitations under which they apply, in particular the restriction to only two possible flow velocities.

Assuming, as we did in the preceding section, that after each Brownian collision (interruption) the particle is left at a random point, the probability p that it is left in a region with flow velocity v equals

$$p = a^{-1}/(a^{-1} + b^{-1}) = b/(a + b)$$

If one further assumes that the interruption process is time homogeneous, that is, if the average number of interruptions per *time* unit is the same in both regions, those with flow velocity v and those with unit velocity, then $v\lambda = \mu$. Under these assumptions one is led to the somewhat unexpected result that the mean total distance covered at speed v is dependent on the interruption rate

$$E\{\mathbf{x}_L\} = \frac{(a + b)b + bv\lambda}{(a + b)^2 + (a + bv)\lambda} \qquad \text{if } \lambda = \mu v^{-1}$$

If, on the other hand, the interruption rates per unit *length* covered are equal, the mean of $\mathbf{x}_L$ is unaffected by Brownian motion and equals $E\{\mathbf{x}_L\} = b/(a + b)$ if $\lambda = \mu$.

Assumptions analogous to those in the section entitled "Giddings Coupling Theory of Eddy Diffusion" are $a = b$, $p = q$, and $\lambda = \mu$. It is seen from Eq. (11) that in this case Eq. (4) holds good. As an indication of the sort of effect that may result from interference, Giddings's approach is most successful. The simplicity of Eq. (4), however, may be misleading in that it could suggest that all relevant information for the explanation of the interference phenomena is contained in the variances of the individual processes.

An interesting situation is one where one of the interruption rates, λ say, predominates. Under these circumstances the mean of $\mathbf{x}_L$ approaches L and once again only the directly observable result of Brownian motion, longitudinal diffusion, will be noticeable in the variance.

Finally, we note that usually the time $\mathbf{t} = \mathbf{x}_L v^{-1} + L - \mathbf{x}_L$ it takes the particle to cover the full length L of the column will be the quantity that can be measured most easily and accurately. Its mean and variance equal

$$E\{\mathbf{t}\} = L + (1 - v)v^{-1}E\{\mathbf{x}_L\}$$

$$\text{Var}\{\mathbf{t}\} = (1 - v)^2 v^{-2}\,\text{Var}\{\mathbf{x}_L\}$$

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