Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Fluendy, M. A. D. and Horne, D. S.(1968) 'Investigation of Diffusion through Packed Beds by a Monte Carlo Method', Separation Science and Technology, 3: 2, 203 — 208
To link to this Article: DOI: 10.1080/01496396808053471
URL: http://dx.doi.org/10.1080/01496396808053471

SEPARATION SCIENCE, 3(2), pp. 203–208, April, 1968

Investigation of Diffusion through Packed Beds by a Monte Carlo Method

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Summary

A Monte Carlo method is used to study diffusion through packed beds. It is found that the distribution remains approximately Gaussian and can be well represented by a multiplicative factor γ on the free-space diffusion coefficient. For cubically packed beds, γ is given to good approximation by the Giddings theory.

INTRODUCTION

Diffusion through packed beds is of practical importance in reactor vessels where diffusion is rate controlling and in gas chromatography where the resolution is in part determined by this process.

Fickian diffusion (*1*) of this type is well represented by a relation of the form

$$\frac{\partial C}{\partial T} = D\left(\partial^2 C/\partial x^2 + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) \tag{1}$$

where C is the concentration at x, y, and z and D is the diffusion constant (a property of the molecular species involved). In many cases this equation can be solved exactly or tackled by conventional numerical means. The boundary conditions appropriate to a packed bed are, however, prohibitive of such methods. In this situation an obstructive factor γ, defined as

$$\gamma = D \text{ apparent through bed}/D \text{ free space} \quad (2)$$

has been used to describe the influence of the packing.

An approximate theory developed by Giddings (2) calculates γ in terms of the porosity and geometry of the packing. This theory is consistent with experiment, e.g., Knox (3), although only a small range of porosities is accessible experimentally and uncertainties in the geometry limit the precision with which comparisons can be made. A more accurate test for Gidding's theory can be provided by a Monte Carlo type of calculation (4). This paper reports the results of such a computation.

The diffusion equation (1) can be related to the random-flight process in the limit of sufficiently small steps, as shown by Chandrashekar (5). For a particle in random flight the probability of finding the particle in a region between r and $r + dr$ at time t, $W(r, t)\, dr$, when it is executing n steps of length l per second in random directions is

$$W(r, t)\, dr = Nr^2 \exp\,(-|r|^2/4Dt)/2\pi^{1/2}D^{3/2}t^{3/2}\, dr \quad (3)$$

where $D = nl^2/6$ and $r = 0$ at $t = 0$. By making the step length l small enough, $W(r, t)$ can be made to mimic the concentration distribution obtained by solution of Eq. (1) as closely as desired. The Monte Carlo realization of a diffusion process is thus a random flight through a suitably bounded space.

In this article attention is directed particularly at the relative rates of diffusion through packed beds as compared to unhindered situations, i.e., with γ. The number of steps executed per second may therefore take the arbitary value of unity. The diffusion constant is most readily calculated from the variance, σ^2, of the distance diffused r.

Since

$$\sigma^2 = \overline{r^2} - (\bar{r})^2 = \overline{r^2} \qquad (\bar{r} = 0)$$

$$\sigma^2 = \int_{-\infty}^{\infty} r^4 C \exp(-r^2/4Dt)\, dr \Big/ \int_{-\infty}^{\infty} r^2 C \exp(-r^2/4Dt)\, dr$$

where $C = 4\pi n/(4\pi Dt)^{3/2}$

$$\sigma^2 = 6Dt$$

i.e., $\gamma = \sigma^2$ for obstructed flight/σ^2 for free-space random flight.

THE MODEL

In this application the model resembles the physical situation rather directly. A series of particles are allowed to execute random flights from a point source by making a sequence of steps on a cubic lattice. Thus the coordinates of the particle may change by $\pm\Delta x$, $\pm\Delta y$, and $\pm\Delta z$ with equal probability; only one coordinate is allowed to change at each step. The packing is represented by regions of space which are excluded to the flight. A particle attempting to step into such a region on the ith step is returned to its position at the end of the $(i-1)$th step, and the step is counteradvanced by 1 to i. In the present work the regions of excluded space were represented by spheres arranged on a regular cubic lattice and were not randomly packed, although this is not a necessary restriction of the method. After each step has been made, the distance of the particle from the origin of diffusion (R_i) is calculated and running estimates of $|\overline{R_i}|$ and $\overline{R_i^2}$ are maintained. At the end of each computation $\overline{R_i^2}$ was plotted against i to yield a straight line with a gradient of $6\gamma D$.

RESULTS

The plots of $\overline{R_i^2}$ vs. the number of steps from which γ was calculated were found to be accurately linear and yielded values for the obstructive factor in good agreement with those calculated from plots of $|R|$ vs. i. Satisfactory convergence in γ was obtained after approximately 1500 random flights had been executed, and calculations with different random-number sequences then agreed to the precision suggested by the sample standard deviations. The circles in Fig. 1 represent 95% confidence levels calculated from sample standard deviations. Another source of error arises from the finite size of the steps taken in the flight. To check this point, a number of calculations were repeated using a step of half the usual size. These gave essentially identical results except in the region of 0.5 and 0.8 porosity, where they showed rather better agreement with the Giddings theory. The relatively large error in the longer step-length calculations at these porosities is due to sharp changes in the number of lattice paths through the most constricted region between the packing spheres. This is purely a feature of the lattice idealization and has no counterpart in the physical diffusion process being modeled.

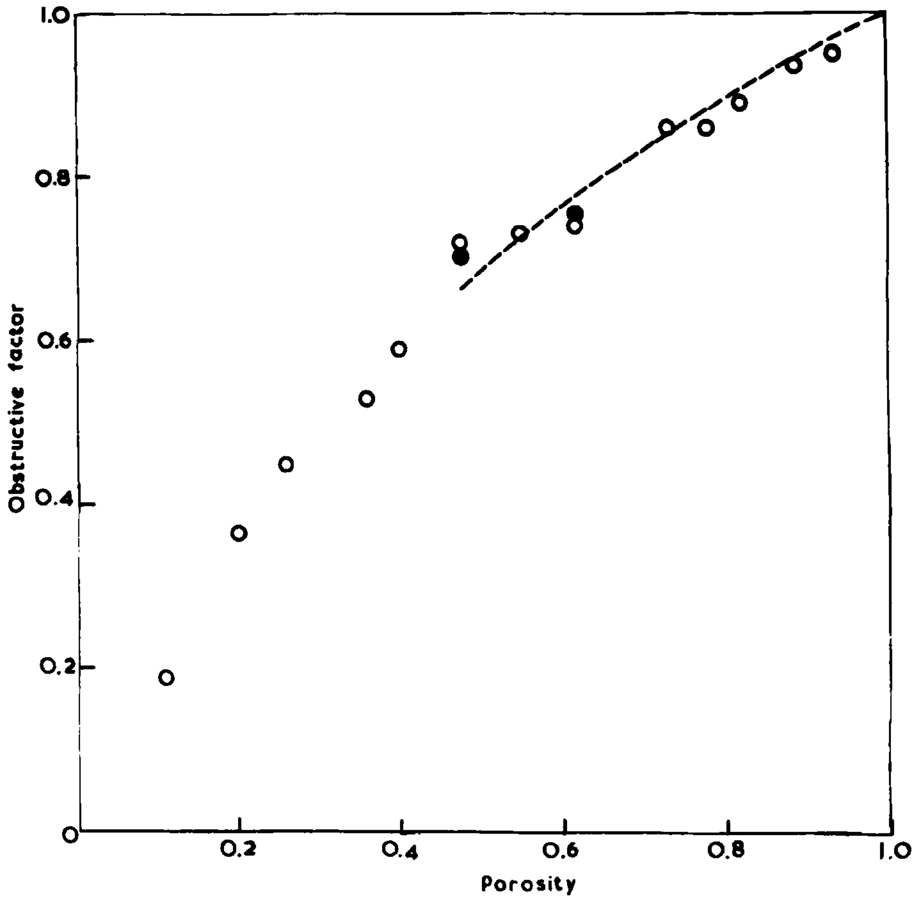

FIG. 1. Plot of obstructive factor vs. porosity for diffusion through a cubic lattice of packing beads. Open circles, 10 steps per lattice cell; closed circles, 20 steps per lattice cell. Dashed curve calculated from Giddings' theory.

From Fig. 1 it is seen that the Giddings theory is in good agreement with these calculations. Indeed it appears that a simple extrapolation would yield equally good results in the low-porosity region where the overlapping spheres produce a honeycomb-like void space.

In Fig. 2 a typical histogram shows the distribution of particles in shells of radius r to $r + 1$ after diffusing for a specified time. In Fig. 2(c) the number of particles in each shell is normalized by the

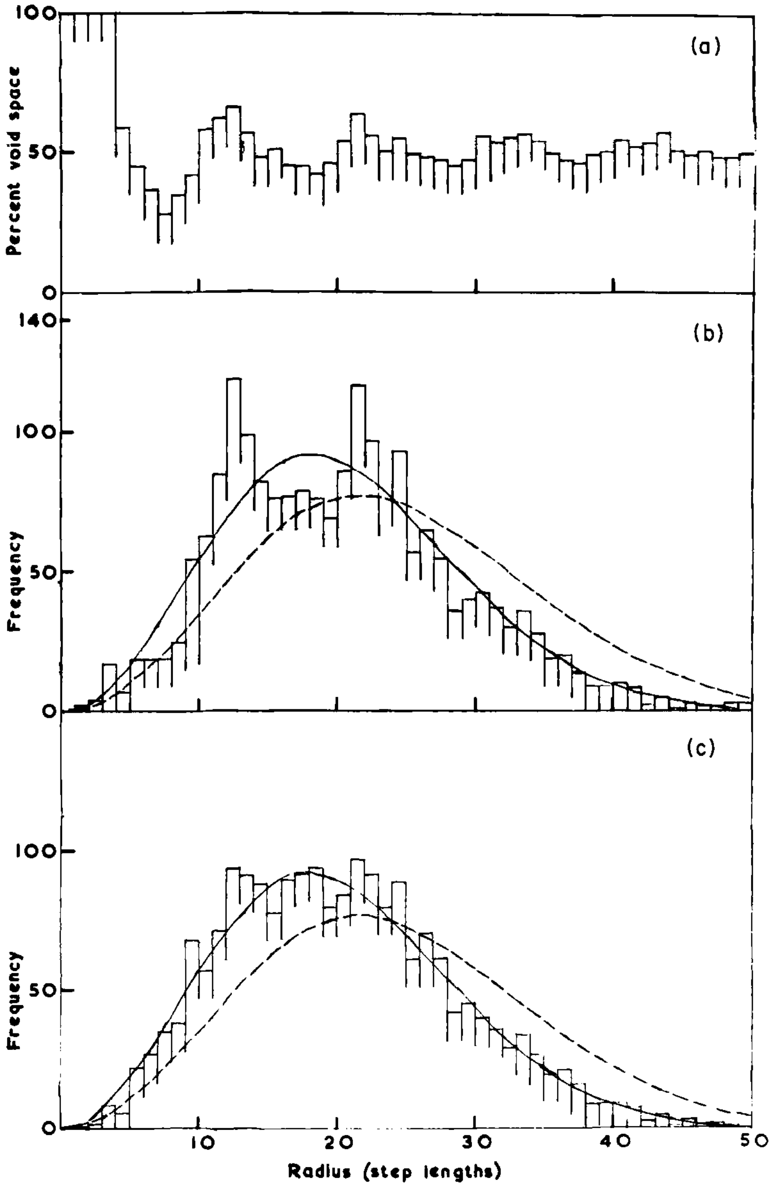

FIG. 2. Particle distribution after diffusion through packing of 0.47 porosity for 700 steps. (a) Percent occupiable space; (b) shell distribution, i.e., number in each shell; (c) number in each shell normalized to the available space. Solid curve calculated using γD; dashed curve using D.

space available for occupation in that shell [Fig. 2(a)]. The bimodal behavior in the uncorrected distribution is thus very largely due to simple exclusion effects. In terms of concentration in "solvent" space, the observed distribution is quite closely represented by a modified Gaussian using γD rather than D as the diffusion constant in Eq. (3). The assumption that the effect of packing on diffusion can be represented in this fashion by a multiplicative factor is therefore supported.

Acknowledgment

The authors are glad to acknowledge stimulating discussions with Dr. J. H. Knox of this department.

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Received by editor February 28, 1968
Submitted for publication March 8, 1968