Monte Carlo Analysis of Knudsen Flow*

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ABSTRACT

As part of a general study of Knudsen flow in porous media, three special cases have been analyzed using Monte Carlo simulation. Steady flow through cylindrical tubes has been studied, the results indicating the range of validity of the analytic short and long tube formulas. Transient flow in tubes with adsorption on the walls has been analyzed. The results indicate that the diffusion equation adequately describes the flow, provided $(L/r_0) \geqslant 50$. The response of short tubes, $(L/r_0) \sim 1$, to a point source pulse illustrates special characteristics which might be useful for an experimental determination of wall adsorption times. Lastly, the flow in a converging-diverging tube has been studied, and the results indicate that significant reductions in the flow rate can occur for channels having the same average diameter but varying degrees of curvature in the direction of flow.

INTRODUCTION

When the mean free path, or the average distance traveled by molecules between collisions, becomes large compared to the characteristic dimension of a system, the molecule–molecule collisions become unimportant, and the molecule-wall collisions dominate the transport processes. This situation can occur when the density is very low, as in high altitude flight or in cryogenic pumping, or when the characteristic dimension of the system is very small, as in a catalyst pellet. In the Knudsen, or free-molecule flow regime the flight path of a molecule is a straight line,[2] and one

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[2] Gravitational, electrostatic, and electromagnetic effects are considered negligible here.

need only know the wall collision characteristics in order to completely determine the molecular motion for any given system. The molecule-wall interaction is obviously enormously complex; however, the extreme conditions in gas-solid collision phenomena are conceptually quite simple, i.e., elastic scattering at one extreme and diffuse scattering at the other. In the former case the scattering angle (i.e., the angle between the normal to the surface and the direction of the scattered molecule) is equal to the angle of incidence, while in the latter case the scattering angle is distributed as the cosine. On clean, crystal planes experiments indicate that neither of these simplifications nor a simple combination of them is justified ([1], pages 346-540); however, for contaminated surfaces or microscopically rough surfaces diffuse scattering is a satisfactory description of the gas-solid collision process. Under these circumstances the molecular motion is completely and simply determined, at least in a statistical sense.

Free molecular flows occurring under these conditions can be analyzed in terms of classical kinetic theory ([2], ([3], page 292)) leading to integral equations for wall and exit plane flux distributions [4, 5, 6]. These integral equations are identical to those found in the treatment of radiant energy transfer [7], and in general they are not amenable to analytic solution. Since numerical solution of the integral equations is the usual route to a satisfactory answer, the use of direct Monte Carlo simulation of the molecular process offers considerable appeal. It should be noted that we can consider ourselves to be dealing with a two dimensional integral when asking for only the transit probability. If the wall flux distribution can be specified a priori (as it can for the "long tube") the integration is straightforward. In general the wall flux must be determined from an integral equation for which there is no explicit solution, and iterative techniques must be used. Thus the solution is more complex than solving a simple two dimensional integral. Furthermore, the complexity of the problem is increased if: (a) the geometry is irregular, (b) energy transfer is considered during wall collisions, and (c) finite wall adsorption times are incorporated into the analysis. In general Monte Carlo methods are superior for analyzing integral problems of greater than three dimensions, and while the iterated integral solution cannot be directly interpreted as a higher order integral, it is clear that at some point in the analysis of an increasingly complicated system Monte Carlo becomes the method of choice. For simpler systems it is not preferred, but it must be done if only to check the simulation against the deterministic integral solution.

This type of approach appears to have first been used by Davis [8] for the calculation of free-molecule flow rates in a number of different piping systems, one of which was the straight cylindrical tube analyzed in this work. Other investigators [9, 10] have used this method for the analysis of flow in geometrically complex systems, and Ballance [11] extended the technique to include molecule–molecule collisions and thus obtain values for the flow rate in the slip-flow region.

Monte Carlo simulation has a distinct advantage over the numerical solution of the integral equations in that the problem is conceptually easy to formulate, especially if one is concerned with modifying the wall-collision process to include adsorption, nondiffuse scattering, distributed adsorption lifetimes, chemical reaction, surface diffusion, etc. Since processes occurring at solid-gas interfaces are often of prime importance to the chemical engineer interested in catalytic reactions, adsorption, and surface mass transport, the method appears to be especially suitable as an analytic tool to be used in conjunction with experimental catalytic reaction rate studies.

DISCUSSION

The work described in this paper is concerned with calculating transmission factors (often called Clausing factors) for steady flow in a tube, for transient flow in a tube with and without adsorption on the tube walls, and for steady flow in a converging-diverging channel. Calculation of transmission factors for steady flow in a straight tube provides a test of our calculations with previous solutions obtained by both Monte Carlo simulation [8] and by numerical integration of the integral equations [5]. The analysis of transient flow in a tube has allowed us to confirm the assumption of Clausing [12], later verified by the theoretical analysis of Gordon and Ponomarev [13], that nonstationary, free-molecule flows in straight channels are described by the diffusion equation. Gordon and Ponomarev further showed that the diffusion equation also described the flow when the molecules were adsorbed for finite times upon collision with the walls of the channel. The calculations presented in this paper indicate that the diffusion equation, in both the form postulated by Clausing and with the modified diffusion coefficient given by Gordon and Ponomarev for finite adsorption times, is only valid for $L/r_0 > 50$. Further, we find that for values of $L/r_0 < 10$ and $\tau \approx L/\bar{v}$ (where $\bar{v}$ is the average molecular speed and τ the average adsorption time) the transient flow rate through a tube fed from a point source is peaked around times given approximately by τ, 2τ, 3τ, etc. Such phenomena would appear to be ideally suited to the experimental study of adsorption times provided a satisfactory method of accurately measuring the flow rates can be devised.

The analysis of steady flow in a converging-diverging channel provides us with some idea of the reduction in flow rate that can occur because of curvature in the direction of flow. Since the pores in catalyst pellets are likely to be of a converging-diverging nature ([14], [15], ([16], page 14)) these results give some indication of the validity of the cylindrical pore model ([17], [18], ([19], page 51)) for the analysis of Knudsen flow in porous media.

Steady Flow in a Straight Tube

The system to be studied is illustrated in Fig. 1. We assume that the tube is connected to a low density reservoir at $z = 0$ containing molecules in an equilibrium state, i.e., the velocity distribution is Maxwellian. At $z = L$ we assume the tube is connected to a perfect vacuum so that no molecules enter the tube at $z = L$.
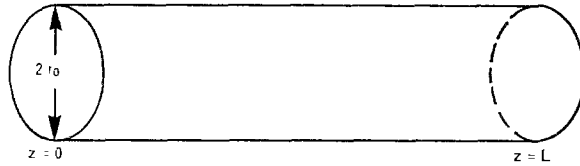

Fig. 1.   The straight tube.

The transmission factor η is defined as

$$\eta = \left(\frac{\text{number of molecules leaving the tube at } z = L}{\text{number of molecules entering the tube at } z = 0} \right) \tag{1}$$

Knowledge of the transmission factor allows one to quickly calculate the flow rate provided we assume that the flow through the tube does not disturb the equilibrium nature of the molecules in the reservoir at $z = 0$. Under these circumstances the number of molecules entering the tube is given by

$$\Gamma = \frac{\pi n \bar{v} r_0^2}{4} \tag{2}$$

where $\bar{v}$ is the mean molecular speed, and n is the number density.

Although the velocity distribution of the gas molecules has no influence on the transmission factor, it is important for studies of energy and momentum transfer as well as in the analysis of time dependent transmission. We assume that the equilibrium distribution at the entrance to the tube is given by

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \tag{3}$$

Here $f(v)$ is defined such that $f(v) \, dv$ is the fraction of molecules having a velocity in the range v to $v + dv$. As we are interested in the flux of molecules passing through the entrance plane, we wish to randomly select molecules of velocity v from the distribution $vf(v)$; i.e., we shall select a random number ξ (distributed uniformly from 0 to 1) and associate it with a velocity v by the expression

$$\xi = \int_{\zeta=0}^{\zeta=U} \zeta f^*(\zeta) \, d\zeta \tag{4}$$

Here $U = c/\bar{v}$ where $\bar{v}$ is the average velocity and $f^*(\zeta)$ is the dimensionless form of the distribution function given by Eq. (3). Given U, there is no problem in finding ξ; the relation is unique, and a table could be constructed so that one would select a ξ and find (perhaps interpolate to) the corresponding U. Shreider ([20], page 151) gives an alternative procedure: generate ξ, then solve by iteration

$$a_{i+1} = \ln(1 + a_i) - \ln \xi, \qquad a_0 = 1 \tag{5}$$

and set

$$U = (a)^{1/2} \tag{6}$$

where a is the converged solution of the iteration suggested by Eq. (5).

The point of entry is distributed uniformly across the face of the tube provided the flow does not influence the distribution of velocities in the reservoir, i.e., we assume the flow into the tube to be a negligible sink in the reservoir. For computational speed, we use a rejection technique in which two random numbers ξ_1 and ξ_2 are generated, and the entry coordinates are calculated as

$$x = (2\xi_1 - 1)r_0 \tag{7a}$$

$$y = (2\xi_2 - 1)r_0 \tag{7b}$$

If $x^2 + y^2 > r_0^2$, the values of ξ_1 and ξ_2 are rejected, and a new pair is introduced. Since about 78 % of the pairs are accepted, the routine is faster than computing x and y by the expression

$$x = r_0 \cos(2\pi\xi_1) \tag{8a}$$

$$y = r_0 \sin(2\pi\xi_2). \tag{8b}$$

The angle of entry is given in terms of the three direction cosines α, β, γ with respect to the x, y, z axes where the first γ, i.e., γ_0, must be positive. If we note that $\alpha = \sin \phi \cos \theta$, $\beta = \sin \phi \sin \theta$, and $\gamma = \cos \phi$, we can generate three random numbers ξ_1, ξ_2, ξ_3 and form $\nu_1 = \xi_1$, $\nu_2 = \xi_2$, $\nu_3 = 2\xi_3 - 1$. If $\nu_2^2 + \nu_3^2 > 1$, we must pick another pair of ξ_2 and ξ_3. If $\nu_2^2 + \nu_3^2 \leqslant 1$, then

$$\gamma_0 = \nu_1^{1/2} \tag{9a}$$

$$\alpha_0 = (1 - \nu_1)^{1/2} \left[\frac{\nu_2^2 - \nu_3^2}{\nu_2^2 + \nu_3^2} \right] \tag{9b}$$

$$\beta_0 = (1 - \nu_1)^{1/2} \left[\frac{2\nu_2\nu_3}{\nu_2^2 + \nu_3^2} \right] \tag{9c}$$

The molecule begins its flight from the position x_0, y_0, 0 in a direction specified in terms of α_0, β_0, γ_0.

After the first flight of length l, it moves to

$$x_1 = x_0 + \alpha_0 l \tag{10a}$$

$$y_1 = y_0 + \beta_0 l \tag{10b}$$

$$z_1 = \gamma_0 l \tag{10c}$$

For free-molecule flow, the flight either terminates at the wall ($x^2 + y^2 = r_0^2$), or the molecule passes out the end of the tube ($z_1 = \gamma_0 l = L$). We determine which occurs by setting $z_1 = L$ to find l by Eq. (10c) and then calculating x_1 and y_1 by Eqs. (10a, b). If $x_1^2 + y_1^2 > r_0^2$, we know a wall-collision occurred, and we can set $x_1^2 + y_1^2 = r_0^2$ in order to solve for l. The axial position z_1 can then be determined, and the molecule is thereby located on the wall of the tube.

Although it was not done in this work, molecule–molecule collisions can be introduced at this point; however, their introduction does lead to the necessity of performing successive iterations to determine the transmission factor. If we *assume* a molecular density and a collision cross-section σ, the mean free path for molecule–molecule interaction can be estimated from simple kinetic theory considerations as

$$\lambda = (n\sigma)^{-1} \tag{11}$$

It should be remembered that this result is applicable to a low-density gas at equilibrium conditions. On the basis of the assumed density n and the calculated value of λ we can generate a random number ξ and compute

$$l' = -\lambda \ln \xi \tag{12}$$

It is known ([3], page 102) that l' is distributed as the distance between collisions. If $l' > l$, the flight path terminates in either a wall-collision or an exit from the tube, and the calculation of the flight is determined by Eqs. (10). If $l' < l$, a molecular collision takes place at the location

$$x_1 = x_0 + \alpha_0 l' \tag{13a}$$

$$y_1 = y_0 + \beta_0 l' \tag{13b}$$

$$z_1 = \gamma_0 l' \tag{13c}$$

A scattering angle is then computed, and the flight path calculation is repeated to determine whether the next event is an exit from the tube, a wall-collision, or a molecule–molecule collision. In calculations of this type we must keep account of the flight times so that information about the density distribution in the tube can be acquired and the original assumed density distribution corrected if necessary. This point was apparently overlooked in the initial attempt at this type of analysis by Ballance [9].

The results presented in this paper deal only with the limiting condition of free-molecule flow, thus a given flight results in either a wall-collision or an exit from the tube. Upon striking the wall, the molecule is reflected. Even if there is no adsorption, one can convincingly argue that for microscopically rough surfaces the reflection is diffuse rather than specular. Present ([21], page 57) suggests that the impact point be considered a "window" into a reservoir of gas such that as the original molecule disappears another appears having a flight direction selected in the same manner as we use to produce α_0 . β_0 , γ_0 . (Note that we may simulate heat transfer by giving these "wall reservoirs" a different temperature than that of the entrance reservoir at $z = 0$.) This process is repeated until the molecule either passes out the exit of the tube at $z = L$ or returns to the reservoir at $z = 0$.

Our results for the transmission factor, plotted in Fig. 2, are in good agreement with the analytic forms for long tubes [6] and for direct transmission for very short
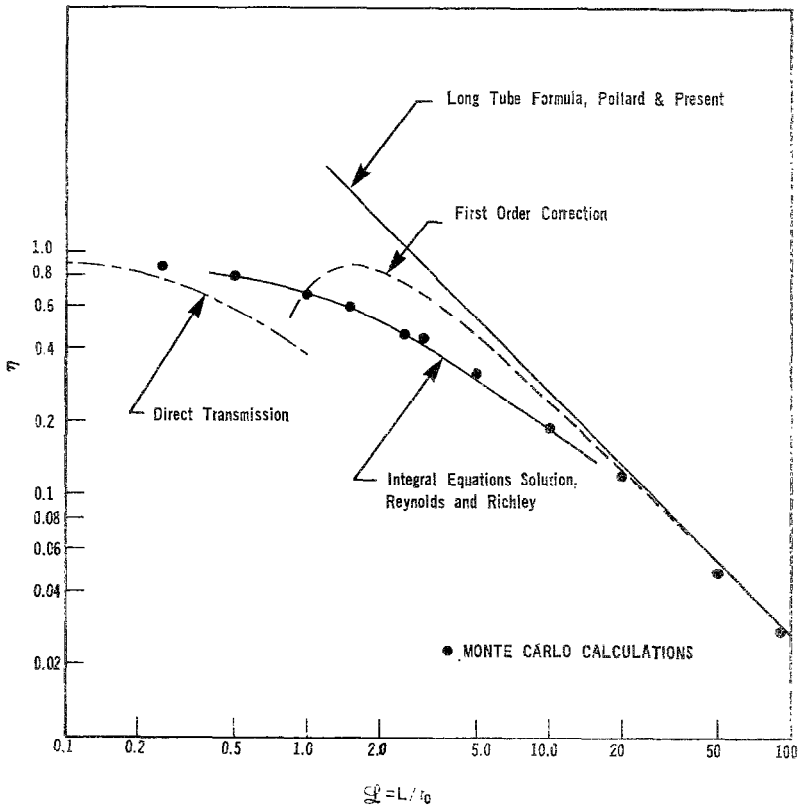

FIG. 2. Transmission factor versus dimensionless tube length.

tubes [5]. The calculated points also fall very close to the integral solution [5] for tubes of intermediate length, and are essentially identical with the original values calculated by Davis [8] which covered the range $1 \leqslant \mathscr{L} \leqslant 8$ where $(\mathscr{L} = L/r_0)$.

The error associated with the values of η shown in Fig. 2 can be estimated ([22], page 21) by the expression

$$\sigma_\eta = \left(\frac{\eta(1 - \eta)}{N} \right)^{1/2} \tag{14}$$

where N is the total number of molecules striking the entrance of the tube. If the transmission factor is 0.5, and we wish to determine this number to within 1 %, Eq. (14) indicates that we need to examine the history of 10^4 molecules. This situation occurs when $\mathscr{L}$ is on the order of 2. On the other hand, if $\mathscr{L}$ is on the order of 20, and η is on the order of 0.1, we must examine the history of approximately 10^5 molecules. Obviously the accurate determination of transmission factors for $\mathscr{L}$ greater than 100 becomes a time consuming computational problem, not only because of the large number of molecules that must be observed, but also because the average number of flights per molecule increases.

The inverse dependence of the flux on the tube length for long tubes suggests that the molecular flux J_z can be expressed in terms of the density gradient and a Knudsen diffusion coefficient $\mathscr{D}_K$.

$$J_z = -\mathscr{D}_K \left(\frac{dn}{dz} \right) \tag{15}$$

Here J_z is the flux of molecules in the z-direction (molecules per unit volume), and n is the molecular density (molecules per unit volume). For long tubes[3] the Knudsen diffusion coefficient is given by

$$\mathscr{D}_K = 2\bar{v}r_0/3 \tag{16}$$

This form for Knudsen flow has served as the basis for many studies [23, 24, 25] of mass transport in catalyst pellets in the Knudsen flow regimes.

TRANSIENT TRANSMISSION

Having verified our computational method, we turn to situations where the Monte Carlo technique offers unique advantages. One such case is an exploration of the situation examined by Gordon and Ponomarev [26] who were concerned with transient Knudsen flow in a tube. In essence they have noted the relaxation

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[3] From Fig. 2 we see that a long tube is one where $(\mathscr{L} = L/r_0) > 100$.

of the molecular random walk problem into the time dependent diffusion equation. The molecular density n must therefore satisfy

$$\frac{\partial n}{\partial t} = \mathscr{D}_K \left(\frac{\partial^2 n}{\partial z^2} \right) \tag{17}$$

$$\mathscr{D}_K = \frac{4r_0^2/3}{2r_0/\bar{v} + \tau} \tag{18}$$

where τ is the mean adsorption lifetime. That this is true for a large number of collisions is well known (Chandrasekar [27] suggests that 10 collisions are satisfactory), but we have found for tubes of $L \sim 20$, where there is still a significant difference between the diffusion theory and the Monte Carlo calculation, that most particles make on the order of 100–1000 collisions. One may then pose the question of agreement of diffusion theory with computational experiments.

Another interesting point to be explored is the approximate extrapolation length of tube to be used in formulating the boundary value problem associated with the use of the diffusion equation. The true governing equation is, of course, the linear, integro-differential Boltzman Transport Equation. The diffusion equation may be derived from the BTE and is valid far from sources and sinks, among other conditions. To apply the diffusion equation near a boundary[4], one procedure is to require the flux of molecules to be zero at an extrapolated distance beyond the boundary. For Knudsen flow through tubes, this correction is on the order of (r_0/L) and is trivial for long tubes. Just what constitutes a long tube may be determined by examination of Fig. 2 which indicates that the diffusion theory begins to break down for $(L/r_0) \sim 20$.

As a test of the diffusion theory we consider the following situation: A tube is sealed at one end ($z = 0$) and connected to a perfect vacuum at the other ($z = L$). At time $t = 0$ the sealed end is exposed to a low density reservoir for a negligibly short time (i.e., the pulse time is small compared to the characteristic process time), and then sealed off to prevent any flow out of the tube at $z = 0$. This type of process can be approximated in the laboratory by simply opening and closing a valve between the tube and a low density reservoir; this is exactly the process proposed by Gordon and Ponomarev [26] for the experimental study of adsorption lifetimes. This process was realized in our computer program by not allowing flights into the region $z < 0$. When such a flight occurred, the flight was terminated at $z = 0$, and values of α, β, γ for a diffuse wall collision were chosen subject to the restriction that $\gamma > 0$. As each molecule travelled down the tube, its accumulated time of flight was incremented by a quantity τ at each collision.

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[4] Other than a solid boundary.

Gordon and Ponomarev [26] solved Eq. 17 subject to the following boundary conditions:

B.C. 1 $n = 0$, $t = 0$, $z \geqslant 0$ (19)

B.C. 2 $n = n_0$, $t > 0$, $z = 0$ (20)

B.C. 3 $n = 0$, $t \geqslant 0$, $z = L$ (21)

B.C. 4 $\dfrac{\partial n}{\partial x} = 0$, $t \geqslant t_1$, $z = 0$ (22)

One of the results of their solution was that as the duration of the pulse became small, i.e.,

$$\frac{t_1 \pi^2 \mathscr{D}_K}{L^2} < 10^{-2}$$

the time, $t_{\max}$, at which the maximum concentration occurs at the outlet is independent of t_1 and is given by

$$t_{\max} = L^2/2\mathscr{D}_K \tag{23}$$

Defining a dimensionless time, $\mathscr{T}$, as

$$\mathscr{T} = t\bar{v}/r_0 \tag{24}$$

we may express the result given by Eq. (23) as

$$\mathscr{T}_{\max} = (\tfrac{3}{8}) \, \mathscr{L}^2 (2 + T) \tag{25}$$

where Y is the dimensionless adsorption time. In Fig. 3 we show the comparison between Eq. (25) and our calculated results for dimensionless adsorption times of zero and ten. The latter case would be roughly equivalent to a nitrogen molecule residing (on the average) on the wall for 10^{-5} seconds if we were considering flow in a 0.10 cm diameter tube at room temperature. For $T = 0$ the Monte Carlo calculations are in good agreement with the diffusion equation for $\mathscr{L} \geqslant 20$. This is similar to the agreement found for transmission factors shown in Fig. 2. However, for finite adsorption times one must go to progressively longer lengths before agreement is obtained. Although it is not clearly shown in Fig. 3, the agreement with the diffusion equation is excellent for values of $\mathscr{L}$ greater than or equal to 50. The times shown in Fig. 3 are obtained by collecting the output times for groups of molecules and plotting the histogram of fraction of molecules versus time. Two such plots are shown in Figs. 4 and 5.

The delay time owing to finite adsorption times is proportional to the square of the length,

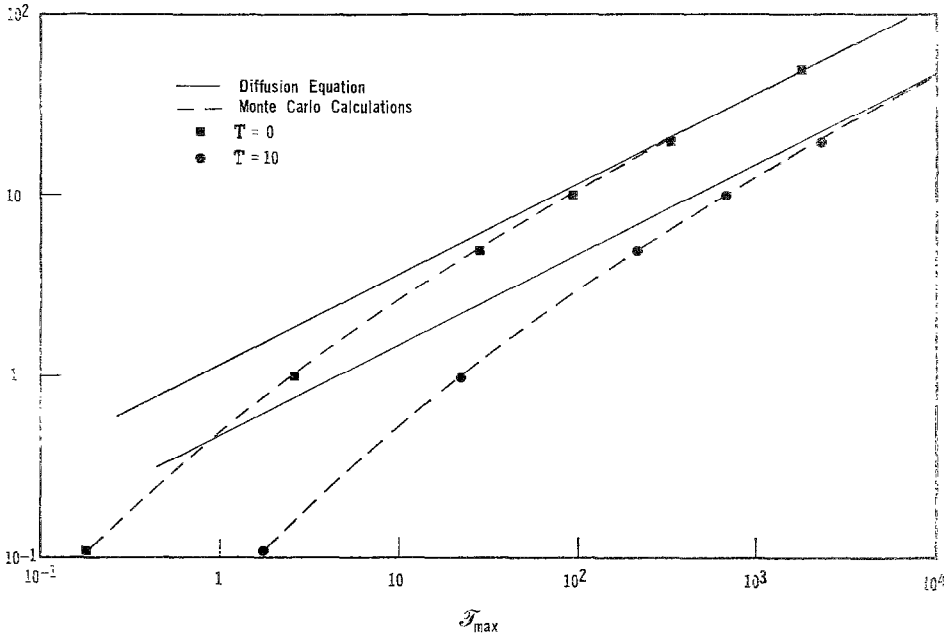$$\text{delay time} = (\tfrac{3}{8}) \, \mathscr{L}^2 T \tag{26}$$

FIG. 3. Time at which maximum concentration occurs as a function of distance.

thus it would appear that long tubes are preferred from the experimentalist's point of view since measurement of the peak time is difficult, while the measurement of the length of the tube is trivial. However, the range of times during which the function f (and therefore the concentration) will be within 10% (for instance) is also proportional to $\mathscr{L}^2$, thus the error in determining the delay time will be proportional to $\mathscr{L}^2$, and the long tube, in reality, has no experimental advantage over the short tube, except that one is able to minimize end effects by use of a long tube. In fact, it is not at all clear how one could perform an experiment which satisfied the restrictions of the analysis for a tube having a length equal to the diameter, i.e., $\mathscr{L} = 2.0$.

In considering this problem we were led to consider the use of a "pinhole" at $z = 0$ as a means of introducing a pulse in a short tube without introducing undesirable end effects. The mechanics of such an experiment would seem to be feasible, and the Monte Carlo code is easily altered to analyze such a process. One need only restrict the entrance of molecules into the tube to the location $x = y = 0$. For comparison with experiments the entry region in the calculation could be increased to exactly reproduce the experimental conditions. The results of this type of computation are shown in Fig. 6. Here we see three peaks in f occurring near $\mathscr{T} = 1$, $\mathscr{T} = 2$, and $\mathscr{T} = 5$. This phenomenon can readily be explained as follows: A
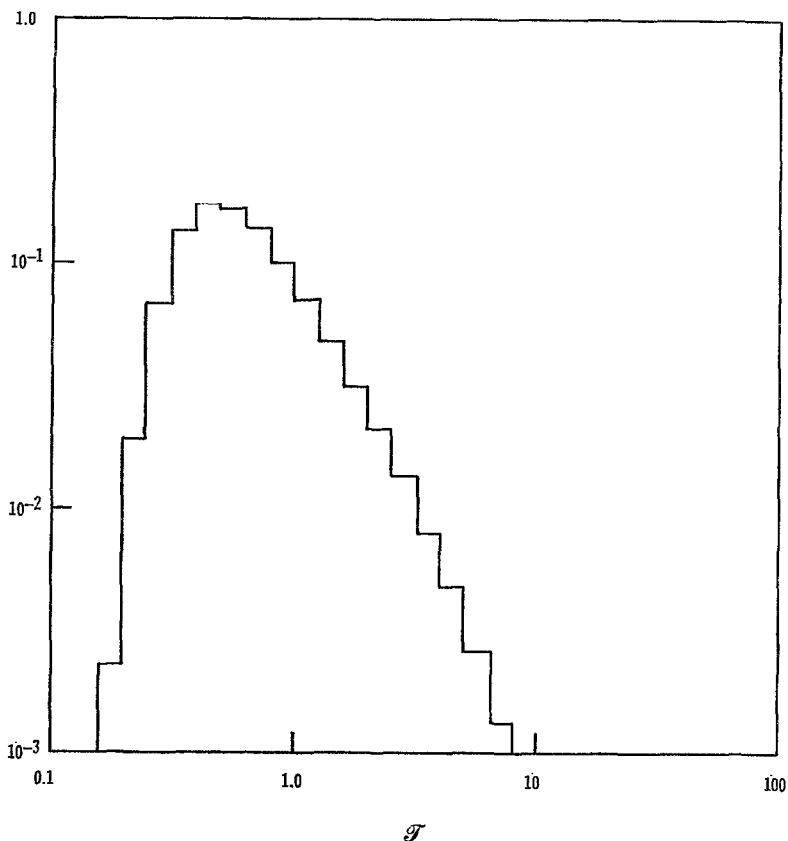
FIG. 4.   Emergence times for $\mathscr{L} = 0.25$ and $T = 0.0$.

certain fraction of the molecules pass through the tube without colliding with the walls; these molecules give rise to a peak in f around $\mathscr{T} = 1$. The peak is "smeared" owing to the Maxwellian velocity distribution and the distribution of flight paths which range from L to $(L^2 + (r_0)^2)^{1/2}$. The second peak results from those molecules which have suffered one wall collision, and thus have a total flight time of approximately 2; half of this time being spent adsorbed on the wall. The third peak results from those molecules which suffer two wall collisions. The peak occurs at a time greater than 3.0 because the length of the flight path is increased considerably over the minimum distance, L.

The spacing between the peaks is always larger than T, approaching it as a limit as the ratio of mean transit time to T approaches zero. As we tend to that limit, however, the second and all subsequent peaks become less prominent.
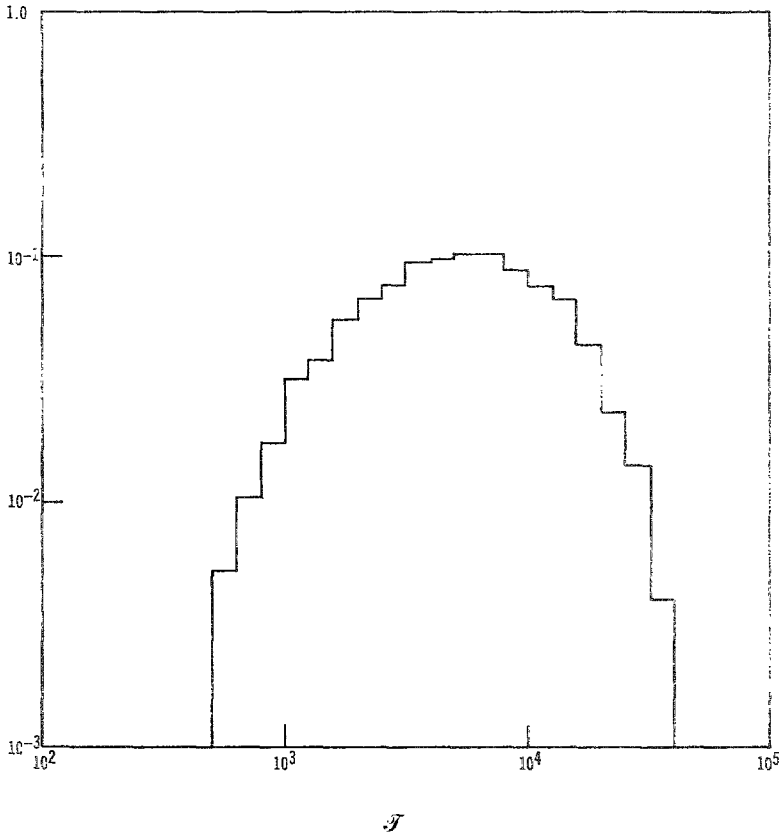
FIG. 5. Emergence times for $\mathscr{L} = 100.0$ and $T = 0.0$.

(Analytical expressions for the collision probabilities also can be derived. By this we mean that we can compute the fraction of particles that suffer no, one, two...., collisions. We can then find the relative heights of the peaks. Unfortunately, to do this, one must make the assumption that the mean free path for wall collisions is independent of position—an assumption suitable only for long tubes where the ratio of mean transit time to T is large.)

One of the suggestions made by Gordon and Ponomarev [26] was that the distribution of adsorption lifetimes could be determined by the spread of the concentration peak. In order to explore this possibility the value of τ was chosen in three ways: (1) τ had but a single value; (2) τ was drawn from a normal distribution with standard deviation equal to 10% of the mean; and (3) τ was drawn from a quasi-normal distribution with a standard deviation of 50% of the mean. In the
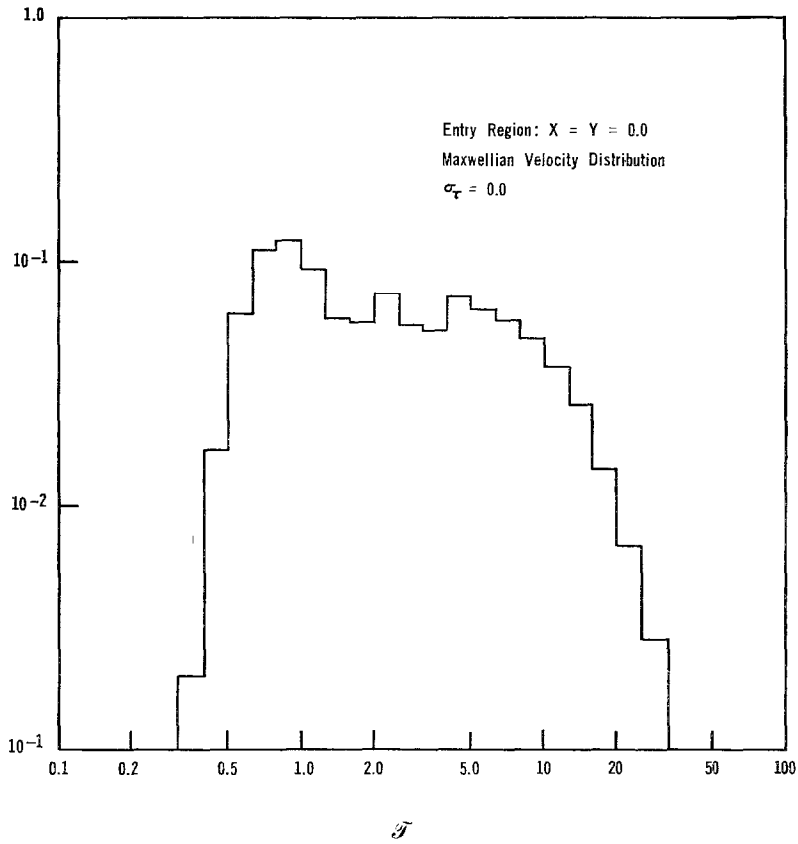
$$\mathcal{T}$$

FIG. 6.   Emergence times for $\mathcal{L} = 1.0$ and $T = 1.0$.

latter case, when τ was less than zero, it was replaced with $\tau = 0$, thus giving the quasi-normal distribution. In an effort to enhance the effect of the distribution of adsorption times, the input was taken to be a mono-energetic source. This eliminates the smearing of the peaks due to the distribution of velocities. From Figs. 7, 8, and 9 there is no significant difference between the three outputs. We conclude that the distribution of adsorption residence times cannot be detected by experiments of this type; however, the mean adsorption time should be relatively easy to measure experimentally.

STEADY FLOW IN A CONVERGING-DIVERGING CHANNEL

The importance of diffusion in porous catalyst pellets has been discussed by a number of authors [14–19], and a number of attempts have been made to develop
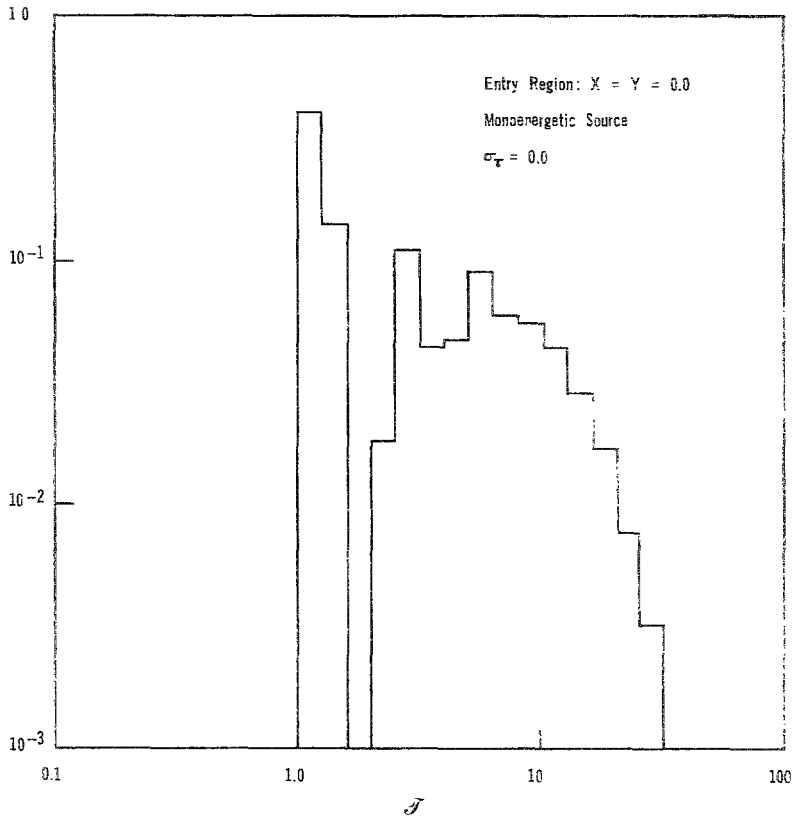
FIG. 7.   Emergence times for $\mathscr{L} = 1.0$ and $T = 1.0$.

acceptable models of this complex flow phenomenon. In one way or another all these models are based on the elementary process of flow in a straight channel. The exception to this statement is the work of Evans, Watson, and Mason [28] in which the porous media and gas are represented as a "dusty gas". Although this approach explains certain characteristics of flow in porous media, a tortuosity coefficient or an effective diffusivity must be inserted into the theory in order to obtain agreement with experiment.

There are two quite obvious statements that one can make about porous media: (1) The pores or channels are not likely to be right circular cylinders, but are very likely to be converging-diverging channels; and (2) the use of flow equations for right circular cylinders is a very attractive course of action, and it is expected that any workable model of flow in porous media will probably include this simplifica-
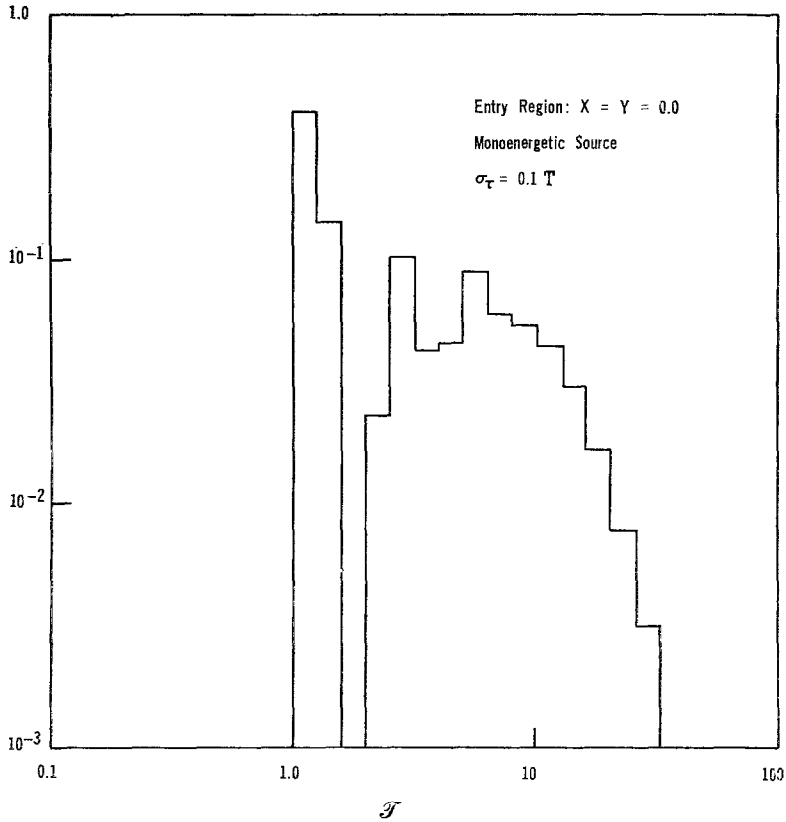
FIG. 8.   Emergence times for $\mathscr{L} = 1.0$ and $T = 1.0$.

tion. Because of this it seems wise to investigate the flow phenomena in a converging-diverging channel and compare the results with those for a straight cylindrical channel. In this way we can determine the effect of curvature (in the longitudinal direction) on the flow, and perhaps gain some insight as to how the straight tube model might be improved.

The geometrical configuration used in this study is shown in Fig. 10. The radius of the channel is given by

$$r(z) = RC + r_0 - \left(RC^2 - \left(z - \frac{L}{2}\right)^2\right)^{1/2} \tag{27}$$

Clearly there are three parameters describing the geometry: RC, r_0, and L.

Entry Region: X = Y = 0.0
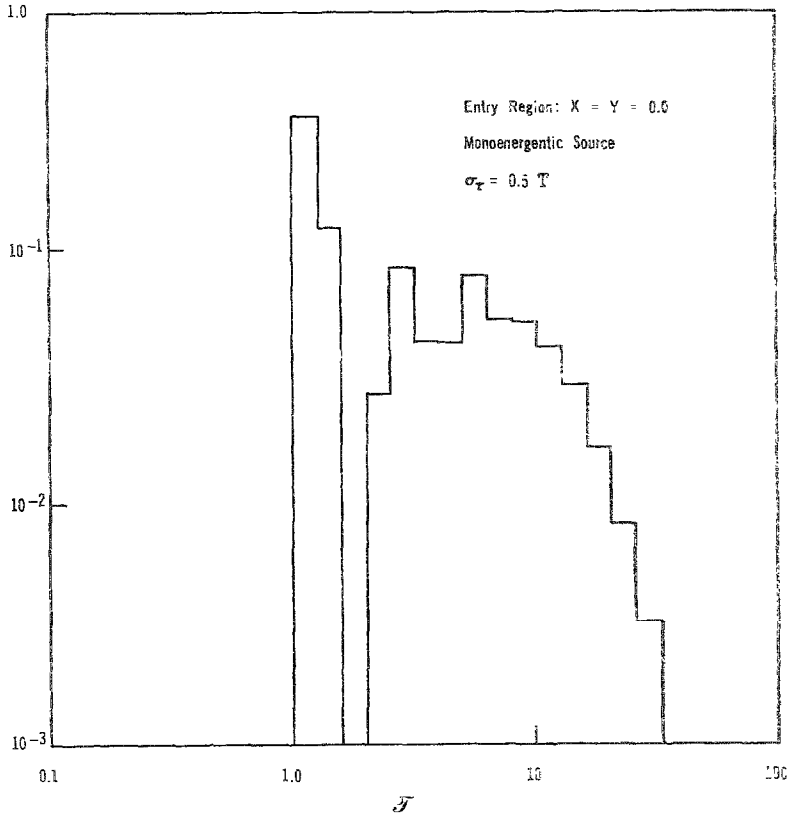Monoenergentic Source
$\sigma_{\tau} = 0.5\ T$

FIG. 9.   Emergence times for $\mathscr{L} = 1.0$ and $T = 1.0$.

However, in order to compare the results with those for straight channels it seems best to use $\bar{r}$, the average radius, as a parameter. Forming the dimensionless distances

$$R(Z) = r(z)/\bar{r}$$

$$\mathscr{RC} = RC/\bar{r}$$

$$Z = z/\bar{r}$$

$$\mathscr{L} = L/\bar{r}$$

gives

$$R(Z) = \mathscr{RC} + (r_0/\bar{r}) - \left(\mathscr{RC}^2 - \left(Z - \frac{\mathscr{L}}{2}\right)^2\right)^{1/2} \tag{28}$$
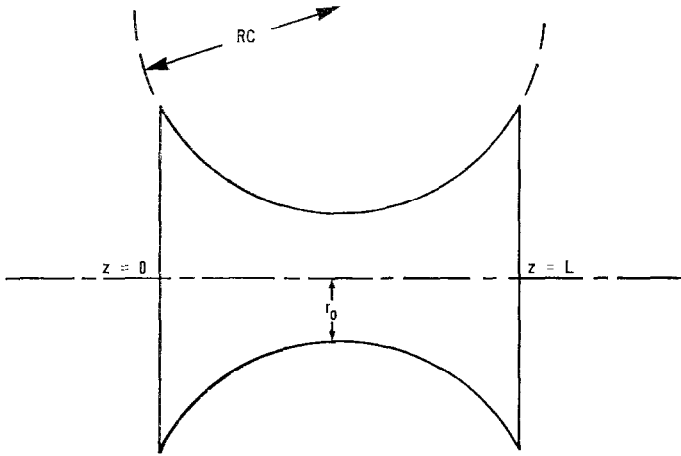
FIG. 10.   Converging-diverging channel.

The ratio $r_0/\bar{r}$ is determined by noting that

$$\frac{1}{\mathscr{L}} \int_0^1 R(Z)\, dZ = 1 \tag{29}$$

allowing us to express $r_0/\bar{r}$ as

$$\left(\frac{r_0}{\bar{r}}\right) = 1 - \mathscr{RC} + \frac{\mathscr{RC}}{2}\left[\sqrt{1 - \left(\frac{\mathscr{L}}{2\mathscr{RC}}\right)^2} + \frac{1}{\mathscr{L}}\sin^{-1}(\mathscr{L})\right] \tag{30}$$

From Fig. 10 we see that the length of the channel is restricted by the condition

$$L \leqslant 2RC \qquad \text{or} \qquad \mathscr{L} \leqslant 2\mathscr{RC}$$

A second restriction is that $(r_0/\bar{r}) \geqslant 0$. Using Eq. (30) we obtain values of $\mathscr{L}$ in terms of $\mathscr{RC}$ if the channel is to remain open. This restriction is shown graphically in Fig. 11. For values of $\mathscr{RC}$ less than 4.66 the upper bound on $\mathscr{L}$ is $2\mathscr{RC}$, while values of $\mathscr{RC}$ greater than 4.66 give rise to an upper bound determined by Eq. (30).

The determination of the transmission coefficient for this geometry is similar to that described for the straight channel. In this case the flight path is determined by marching along the line of flight until either the wall or an exit is reached. Emission from the wall is assumed to be diffuse relative to a plane tangent to the channel wall.

The results of the calculations are shown in Fig. 12 for $\mathscr{RC} = 1, 2, 5, 10$, and infinity. It is clear that the transmission factor for a converging-diverging channel
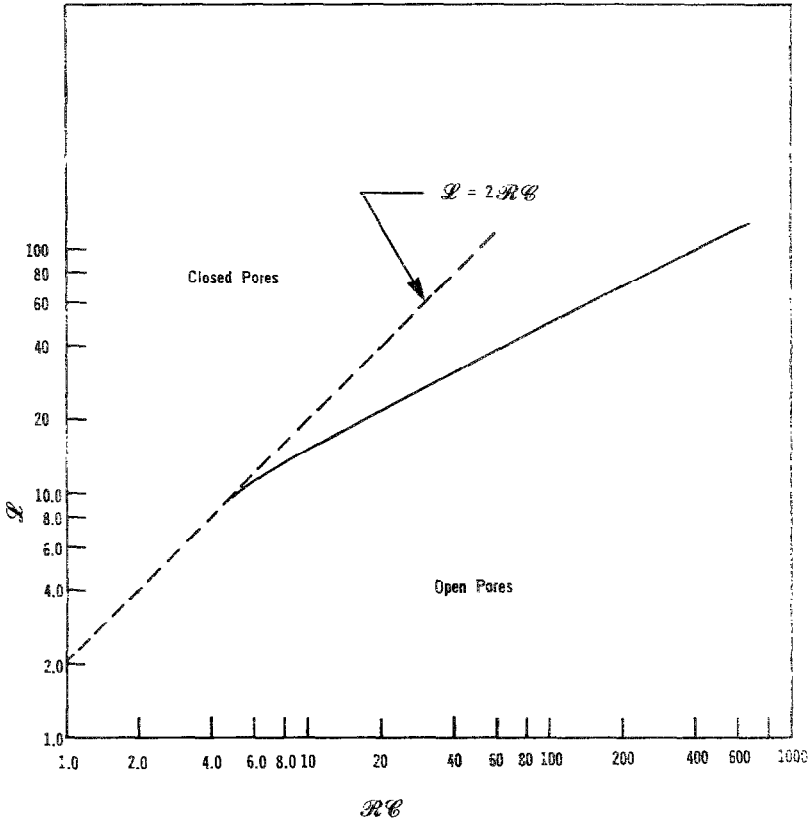
FIG. 11. Length versus radius of curvature for a closed pore.

can be greatly reduced over that for a straight channel, especially in the region near the upper bound on $\mathscr{L}$ illustrated in Fig. 11. To illustrate the importance of this effect, let us consider a porous media made up of impermeable spheres of radius r^*, thus

$$RC = O(r^*)$$

$$L = O(2r^*)$$

If the packing of the spheres is face-center cubic, the porosity and the Wheeler mean pore radius [29] are,

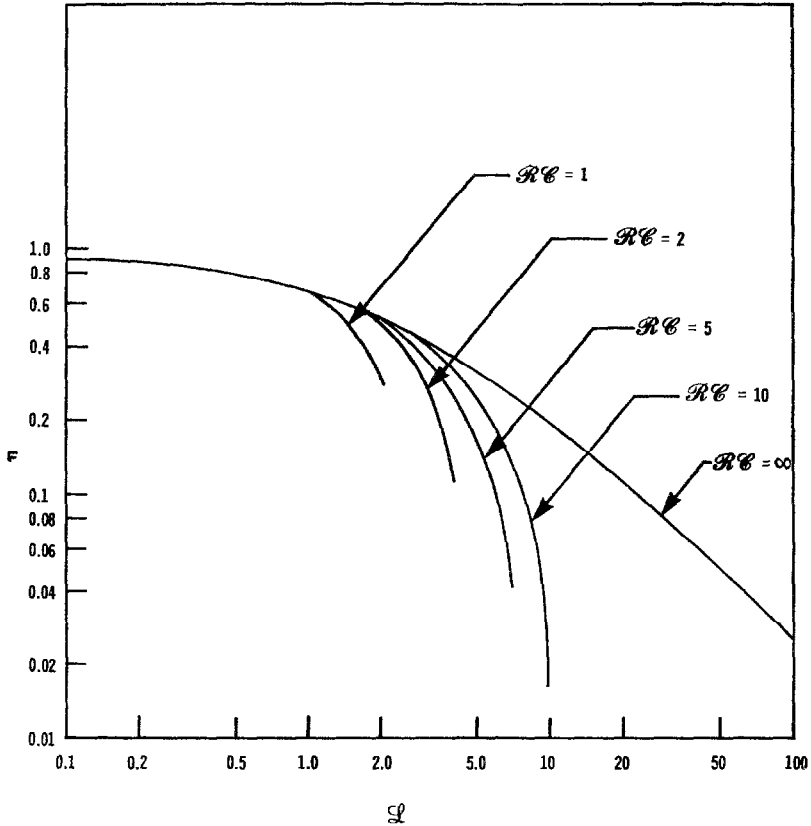$$\epsilon = 0.26, \qquad \bar{r} = 0.234\, r^*$$

FIG. 12.   Effect of curvature on the transmission factor.

and for body-centered cubic packing the quantities are

$$\epsilon = 0.32, \qquad \bar{r} = 0.313\, r^*$$

Using these quantities we can estimate that the dimensionless length and radius of curvature are of the order of magnitude

$$\mathscr{RC} = O(3)$$

$$\mathscr{L} = O(6)$$

From Fig. 12 we can see that these estimates would lead us to conclude that a reduction in the flow rate of anywhere from a factor of two to a factor of ten could result from the converging-diverging nature of the channel.

CONCLUSIONS

The Monte Carlo calculations presented in this paper have established the range of validity of the diffusion equation in predicting Knudsen flow rates for both steady and transient flow in straight channels with and without adsorption on the walls of the channel. In addition the results for both types of flow in short tubes are given. Results for converging-diverging channels indicate a significant reduction in the flow over that for comparable straight channels.

REFERENCES

1. H. SALTSBURG, J. N. SMITH, JR., AND M. ROGERS, eds., "Fundamentals of Gas-Solid Interactions," Academic Press, New York, 1967.
2. W. C. DEMARCUS, "The Problem of Knudsen Flow. Pt I. General Theory." AEC Rep. No. K-1302 (1956).
3. E. H. KENNARD, "Kinetic Theory of Gases." McGraw-Hill Book Co., Inc., 1938.
4. W. C. DEMARCUS, "The Problem of Knudsen Flow. Pt II. Solution of Integral Equations with Probability Kernels." AEC Rep. No. K-1302 (1956).
5. T. W. REYNOLDS AND E. A. RICHLEY, "Free-Molecule Flow and Surface Diffusion through Slots and Tubes—A Summary." NASA Tech. Rep. 255 (1967).
6. W. G. POLLARD AND R. D. PRESENT, On gaseous self-diffusion in long capillary tubes. *Phys. Rev.* **73**, 762 (1948).
7. W. C. DEMARCUS, "The Problem of Knudsen Flow. Pt V. Application of the Theory of Radiative Transfer." AEC Rep. No. K-1302 (1957).
8. D. H. DAVIS, Monte Carlo calculation of molecular flow rates through a cylindrical elbow and pipes of other shapes. *J. Appl. Phys.* **31**, 1169 (1960).
9. J. O. BALLANCE, W. K. ROBERTS, AND D. W. TARBELL, A study of cryopump configurations in free-molecular-flow regions. *In* "Advances in Cryogenic Engineering," Vol. 8, edited by K. D. Timmerhaus, page 46. Plenum Press, New York, 1963.
10. J. W. WARD, R. N. R. MULFORD, AND R. L. BIVINS, Study of some of the parameters affecting Knudsen effusion. II. A Monte Carlo computer analysis of parameters deduced from experiments. *J. Chem. Phys.* **47**, 1718 (1967).
11. J. O. BALLANCE, Monte Carlo solutions of Knudsen and near-Knudsen flow through infinitely wide, parallel and skewed, flat plates. NASA Tech. Memo. X-53112 (1964).
12. P. CLAUSING, *Ann. Physik* **7**, 521 (1930).
13. E. B. GORDON AND A. N. PONOMAREV, Molecular flow in long tubes. *Soviet Physics-Technical Physics* **12**, 685 (1967).
14. R. J. ARROWSMITH AND J. M. SMITH, Diffusion and reaction in solids. *I. & E. C. Fund. Quart.* **5**, 327 (1966).

15. E. E. Petersen, Diffusion in a pore of varying cross section. *AIChE J.* 4, 343 (1958).
16. C. N. Satterfield and T. K. Sherwood, "The Role of Diffusion in Catalysis." Addison-Wesley Publishing Co., Reading, Mass.
17. N. Wakao and J. M. Smith, Diffusion and reaction in porous catalysts. *I. & E. C. Fund. Quart.* 3, 123 (1964).
18. R. N. Foster and J. B. Butt, A computational model for the structure of porous materials employed in catalysis. *AIChE J.* 12, 180 (1966).
19. E. E. Petersen, "Chemical Reaction Analysis." Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1965.
20. Yu. A. Shreider, editor, "The Monte Carlo Method." Pergamon Press, Oxford. 1966.
21. R. D. Present, "Kinetic Theory of Gases." McGraw-Hill, New York, 1958.
22. J. M. Hammersley and D. C. Handscomb, "Monte Carlo Methods." Methuen & Co., Ltd., London, 1964.
23. D. S. Scott and F. A. L. Dullien, The flow of rarified gases. *AIChE J.* 8, 293 (1962).
24. N. Wakao and J. M. Smith, Diffusion in catalyst pellets. *Chem. Engr. Sci.* 17, 825 (1962).
25. N. Wakao, S. Otani, and J. M. Smith, Significance of pressure gradients in porous materials. Pt I. Diffusion and flow in fine capillaries, Pt II. Diffusion and flow in porous catalysts. *AIChE J.* 11, 435 (1965).
26. E. B. Gordon and A. N. Ponomarev, Determination of the lifetimes of molecules and atoms adsorbed on solid surfaces. *Kinetics and Catalysis* 8, 565 (1967).
27. S. Chandrasekhar, Stochastic problems in physics and astronomy. *Rev. Mod. Physics* (1945).

29. A. Wheeler, Reaction rates and selectivity in catalyst pores. *In* "Catalysis," Vol. II, edited by P. H. Emmett. Reinhold Publishing Corp., New York, 1955.