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THROUGH POROUS MEDIA

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The following is a treatment of Knudsen flow in a homogeneous, isotropic porous medium. The description of the porous medium is reduced to a statistically significant and measurable function and does not depend on a particular model.

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LOW PRESSURE TRANSPORT THROUGH POROUS MEDIAA B S T R A C T

Knudsen flow in a homogeneous, isotropic porous medium is treated by a technique utilizing an integral equation to calculate the probability that a molecule starting from a solid surface within the medium will ultimately pass out of the medium. The permeability is then calculable from this probability function and the distribution of initial collisions within the medium. The crux of the treatment lies in the kernel of the integral equation, $K(x, \xi)$, which has the physical significance of the probability density that a molecule which starts a free path from a surface somewhere in a slab centered around the coordinate x and normal to the direction of flow terminates its path in a similar slab centered at ξ . This kernel is expressed in terms of a function $p(\rho)$ which is the probability density that a molecule will exhibit a free path ρ inside the medium. This function then characterizes the medium completely. The problem is set up in a general way and detailed results are calculated for some analytically simple functions $p(\rho)$.

The principal merit of the approach is that it reduces the description of the medium required for transport calculations to a statistically significant and measurable function and does not depend on a particular model. The connection between the shape of the function $p(\rho)$ and other properties of the medium such as void fraction and specific surface is not included in the treatment but requires a more specific model. However, a general expression for the average value of ρ is deduced in terms of these quantities. The permeability appears to depend largely on this average value of ρ ; the particular shape of $p(\rho)$ appears to determine only a multiplicative factor of the order of unity.

LOW PRESSURE TRANSPORT THROUGH POROUS MEDIA

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Note added in proof:

Subsequent to the preparation of this report it has been pointed out by W. C. DeMarcus that the evaluation of $\mathcal{V}'_1(x)$ as carried through here is inconsistent with the principle of detailed balance. DeMarcus has suggested a simple and elegant method for obtaining $\mathcal{V}'_1(x)$ and treating a one-dimensional representation of a porous medium in a general fashion. Presumably, the failure of the present approach lies in the use of the same function $p(\rho)$ for a molecule entering the medium as for molecules leaving the wall within the medium. A molecule leaving a wall within the medium is certain of at least a short jump into the void bounded by the wall; this is not the case for a molecule entering into the medium. Only in the case of a strictly homogeneous medium characterized by $p(\rho) = (1/\lambda)\exp(-\rho/\lambda)$ are the arguments for the evaluation of $\mathcal{V}'_1(x)$ strictly valid.

The principal virtue of the technique reported here is the characterization of a porous medium in terms of a free-path distribution function $p(\rho)$ determined by the geometry of the medium alone and the relation of this function to the permeability of the medium. Subject to the limitations described in the text, the relation of $K(x, \xi)$ to $p(\rho)$ and the solutions for the integral equations are believed to be correct, but quantitative results dependent upon the value of $\mathcal{V}'_1(x)$ as calculated here are not reliable.

LOW PRESSURE TRANSPORT THROUGH POROUS MEDIA

INTRODUCTION

The general problem of calculating the molecular transport through a porous medium in the Knudsen regime of very low molecular density has been approached by a variety of techniques. Most of these techniques start from a knowledge of the flow properties of channels of sharply defined geometry and construct a model of the medium in terms of these channels. Unfortunately, photomicrographs of porous media show that such models are unrealistic and a strong need is felt for an approach which places no more detailed requirements on a model than are consistent with measurable characteristics of the medium.

The momentum-loss technique suggested by Knudsen⁽¹⁾ is appealing for this purpose and straight-forward calculations can be made which give dimensionally correct results. However, detailed calculations on systems of known geometry⁽²⁾ make clear that this technique is quite unreliable numerically, and the agreement with more rigorous methods of approach obtained for the very long, circular capillary appears fortuitous. Hence, permeability calculated by this method can be considered reliable only to an arbitrary multiplicative parameter or shape factor which is related in an unpredictable way to the geometry of the medium.

Path tracing techniques analogous to that of Knudsen⁽¹⁾ and Smoluchowski⁽³⁾ have been attempted and lead to expressions for the permeability which also appear dimensionally correct but which involve shape factors related in a very complicated fashion to the nature of the medium.

A rather superficial attempt to approach the problem through a mean-free path calculation was suggested by Derjaguin⁽⁴⁾ which also leads to a dimensionally consistent formula for the permeability but does not adequately reflect the geometry of the medium.

A more rigorous treatment of permeability in the Knudsen regime was first applied by Clausing⁽⁵⁾ and has seen considerable use in other problems of diffusion. In this technique an integral equation is used to express the probability that a molecule leaving the wall at a specified point in the medium will ultimately pass out the back of the medium. Solution of this integral equation for the probability of emission as a function of position in the medium and calculation of the molecular transport by means of this function and the distribution of first collisions within the medium allows a rigorous calculation inclusive of end effects. This treatment was applied by Clausing to calculate the permeability of several systems of sharply defined geometry and its extension to the problem of a porous medium is the purpose of this report.

DERIVATION OF THE INTEGRAL EQUATION AND THE PERMEABILITY

Although the integral equation for diffusion is derived and discussed in references 5 and 6, it seems worthwhile sketching it here for a porous medium. We define a coordinate system (x,y,z) with origin in the face of the medium and such that the direction of gas flow is $+x$. The $(0,y,z)$ plane is then the face of the medium which is assumed to be essentially infinite in extent in order to avoid edge effects. The medium is taken to be of finite thickness L so that $0 \leq x \leq L$ represents the inside of the medium, $x < 0$ is the region occupied by gas at a number density n_1 , $x > L$ represents the low pressure side, considered to be evacuated.

Define $W(x,y,z)$ as the probability density that a molecule leaving a solid surface in the volume element $dx dy dz$ ultimately passes out the back of the medium ($x > L$) without first passing out the front of the medium ($x < 0$). This function may be expressed as

$$W(x,y,z) = W_1(x,y,z) + \int_{\xi=0}^L \int_{\eta} \int_{\zeta} K(x,y,z; \xi, \eta, \zeta) W(\xi, \eta, \zeta) d\xi d\eta d\zeta \quad (1)$$

where $W_1(x,y,z)$ is the probability density that the molecule will pass directly out of the medium ($x > L$) without making another collision with a surface and $K(x,y,z; \xi, \eta, \zeta)$ is the probability density that the molecule will make its next collision in a unit volume at (ξ, η, ζ) . The integral represents the probability that the molecule will make at least one more jump inside the medium before getting out. It is convenient to reduce the equation to one-dimensional form by averaging over all volumes in the (y,z)

slab of thickness dx which actually contain surfaces from which a molecule can start its path. In order to designate such integrals and to distinguish them from integrals including all elements of volume in the (y,z) slab, the symbol prime is attached to the integral sign in this case. Thus,

$$W(x) = \frac{\iint' W(x,y,z) dy dz}{\iint' dy dz}$$

$$= W_1(x) + \int_0^L K(x,\xi) W(\xi) d\xi \quad (2)$$

where it has been assumed that $W(x,y,z) = W(x)$. This assumption is equivalent to excellent connectivity within the medium. Also,

$$K(x,\xi) = \frac{\iiint' K(x,y,z; \xi, \eta, \zeta) dy dz d\eta d\zeta}{\iint' dy dz} \quad (3)$$

In this form, $W(x)dx$ has the physical significance of the probability that a molecule starting from a solid surface somewhere in the (y,z) slab of thickness dx will ultimately escape from the medium on the side $x > L$, $W_1(x)dx$ is the probability that the molecule will escape into $x > L$ on its first jump and $K(x,\xi)d\xi$ is the probability that the molecule will terminate its path on a solid surface somewhere in the (η,ζ) slab of thickness $d\xi$. It is to be noted that $W_1(x)$ may be expressed in terms of $K(x,\xi)$ by the integral

$$W_1(x) = \int_L^\infty K(x,\xi) d\xi \quad (4)$$

In order to calculate the permeability of the medium, a knowledge of the number of molecules suffering their first collision with the medium in a unit volume at (x,y,z) in unit time is required. Designating this quantity as $Z_1(x,y,z)$ and averaging over the face of the medium, a quantity $Z_1(x)$ pertaining to the (y,z) slab at x is obtained. The number $Z_1(x)dx$ then represents the number of molecules suffering their first collision with a

solid wall in the (y,z) slab of thickness dx per unit time and in the steady state, the number of molecules leaving this region per unit time. Hence, the transport of molecules through the medium is given by

$$\bar{V} = \bar{V}_1(>L) + \int_0^L \bar{V}_1(x) W(x) dx \quad (5)$$

where the first term on the right-hand-side represents the contribution to the transport of molecules passing through the medium with no collisions inside the medium and the integral includes collisions anywhere within the medium.

The problem of computing the transport $\bar{V}$ then reduces to (a) choosing a proper kernel, $K(x,\xi)$, (b) solving the integral equation for $W(x)$, and (c) evaluating $\bar{V}_1(x)$.

Choice of the Kernel $K(x,\xi)$ and $\bar{V}_1(x)$

The real crux of the treatment of a porous medium by this technique lies in the choice of a kernel, $K(x,\xi)$, and $\bar{V}_1(x)$ described in terms of a suitable model of the medium. In evaluating these functions it is assumed at the outset that a complete and extremely detailed description of the medium is available. The introduction of simplifying assumptions and the averaging processes necessary to reduce this description to statistically significant, measurable parameters are then evident in each step of the argument.

The calculation of $K(x,\xi)$ proceeds as follows:

Choose a volume element $dx dy dz$ centered around (x,y,z) and a second element $d\xi d\eta d\zeta$ centered around (ξ,η,ζ) . We require $K(x,y,z; \xi,\eta,\zeta) d\xi d\eta d\zeta$, i.e., the probability that a molecule which leaves a surface dS known to exist in $dx dy dz$ will make its next collision on an element of surface $d\Sigma$ in $d\xi d\eta d\zeta$. This quantity may be expressed:

$$K(x,y,z; \xi,\eta,\zeta) d\xi d\eta d\zeta = \left[\frac{\cos\theta d\omega}{\int \cos\theta d\omega} \right] \left[\delta(\vec{p}) \right] \left[\delta(\cos\theta) \right] \left[\delta(\cos\theta') \right] \quad (6)$$

in which the first factor on the right-hand side is the fraction of solid angle subtended at (x,y,z) by the surface $d\Sigma$ weighted by the usual cosine-law term; θ is the angle between the normal to dS and the vector $\vec{p}$ joining (x,y,z) and (ξ,η,ζ) ; $\delta(\vec{p})$ is a function which assumes the value

unity if a surface $d\Sigma$ exists in the volume element $d\xi d\eta d\zeta$ and no other surface cuts $\vec{\rho}$, and is zero otherwise (this function assures the existence of a free path actually starting from dS and terminating at $d\Sigma$); θ' is the angle between the normal to $d\Sigma$ and $\vec{\rho}$; and $\delta(\cos\theta)$ and $\delta(\cos\theta')$ are functions which vanish unless $\cos\theta$ and $\cos\theta'$ are positive, and are equal to unity in this case (these functions insure that only surfaces "visible" to each other will be counted). These coordinates are represented in the accompanying figure in which the vectors $d\vec{S}$ and $d\vec{\Sigma}$ stand for normals to the respective surfaces.

The solid angle $d\omega$ may be expressed as $\frac{d\Sigma \cos\theta' \delta(\cos\theta')}{\rho^2}$ or, in terms of χ and ψ as defined in the figure $d\omega = \sin\chi d\chi d\psi$. Hence according to equation (3)

$$K(x, \xi) = \frac{\int_0^{\pi/2} \sin\chi d\chi \int_0^{2\pi} d\psi \iint' \cos\theta \delta(\cos\theta) \delta(\vec{\rho}) dy dz}{\pi \iint' dy dz} \quad (7)$$

where $\int \cos\theta d\omega$ has been set equal to π and again it must be noted carefully that the integrals over y and z contain contributions from only those volume elements $dx dy dz$ which actually contain surface.

The integration now has the following meaning; choose values of x and ξ with increments dx and $d\xi$. Then choose a vector $\vec{\rho}$ which originates at some point in the (y, z) slab, which terminates in the slab (η, ζ) and which has a range $d\rho$ determined by the increments in ξ, χ and ψ . The integrals over y and z then correspond to a summation of the integrand evaluated with the chosen value of $\vec{\rho}$ over all surfaces that are actually found in the yz and $\eta\zeta$ planes at x and ξ in the increments dx and $d\xi$. The integrals over χ and ψ encompass all choices of $\vec{\rho}$. Consider a particular solid surface

dS in the (y, z) slab. The origin of the vector $\vec{\rho}$ lies in this surface and the end of this vector lies in the slab (η, ξ) . The end of this vector may or may not lie upon a solid surface $d\Sigma$. However, the factor $\delta(\vec{\rho})$ assures us that there is no contribution to the integral in this particular direction of $\vec{\rho}$ from dS unless a surface $d\Sigma$ does exist at the terminus of $\vec{\rho}$ and the path from dS to $d\Sigma$ is free. Because of the isotropic character of the medium the integration over y and z gives a function which is independent of the particular direction of $\vec{\rho}$ but which depends only on the magnitude of $\vec{\rho}$ and the increment $d\xi$. Hence it is convenient to define the function

$$\begin{aligned}
 p(\rho)d\rho &= \frac{4 \iint' \cos\theta \delta(\cos\theta) \delta(\rho) dydz}{\iint' dydz} \\
 &= \frac{\iint' \delta(\rho) dydz}{\iint' dydz} \quad (8)
 \end{aligned}$$

where it has been assumed that $\cos\theta$ and $\delta(\cos\theta)$ within the integral may be given their average values $1/2$ and $1/2$ computed on the basis of the presumed random orientation of all surfaces.

The final expression for $K(x, \xi)$ then becomes

$$\begin{aligned}
 K(x, \xi)d\xi &= 1/2 \int_0^{\pi/2} \sin\chi d\chi p(\rho)d\rho \\
 &= 1/2 d\xi \int_0^{\pi/2} p(\rho) \tan\chi d\chi \\
 &= 1/2 d\xi \int_{|\xi-x|}^{\infty} \frac{p(\rho)d\rho}{\rho} \quad (9)
 \end{aligned}$$

$$\text{since } \rho = \frac{|\xi - x|}{\cos\chi}.$$

The elevation of $\mathcal{N}_1(x)$ proceeds in essentially the same fashion (for convenience of reference to the previous calculations, we use the symbol ξ in place of x in the derivation). Consider an element of volume $d\xi d\eta d\zeta$ located at (ξ, η, ζ) . The number of molecules coming through an open area $dydz$ of the plane $x = 0$ at angles χ and ϕ and colliding on a solid surface in $d\xi d\eta d\zeta$ per unit time is

$$\left[\frac{n_1 \bar{v}}{4} dydz \right] \left[\frac{\cos \chi d\omega}{\int \cos \chi d\omega} \right] \left[\delta(\vec{\rho}) \right] \left[\delta(\cos \theta') \right] \quad (10)$$

in which the first factor is the number of molecules passing the area $dydz$ per unit time, the second factor is the fraction of solid angle at $(0, y, z)$ subtended by "visible" surface $d\Sigma$ in $d\xi d\eta d\zeta$ weighted by the usual cosine factor and the last two factors insure that the path to (ξ, η, ζ) is open and that the surface $d\Sigma$ is correctly oriented. But

$$d\omega = \frac{d\Sigma \cos \theta' \delta(\cos \theta')}{\rho^2} = \sin \chi d\chi d\psi \quad (11)$$

and the total number of molecules colliding between ξ and $\xi + d\xi$ per unit geometrical area per unit time is

$$\begin{aligned} \mathcal{N}_1(\xi) d\xi &= \frac{n_1 \bar{v}}{4A} \iiint \iiint dydz \cos \chi \sin \chi d\chi d\psi \delta(\vec{\rho}) \\ &= \frac{n_1 \bar{v}}{4\pi} \frac{\int_0^{\pi/2} \sin \chi d\chi \int_0^{2\pi} d\psi \iint' \cos \chi \delta(\vec{\rho}) dydz}{\iint dydz} \end{aligned} \quad (12)$$

where the integral over y and z in the numerator is extended over the open areas of the face $x = 0$ only, but the lower integral includes the entire plane, i.e.

$$\iint dydz = A$$

Hence

$$\mathcal{V}_1(\xi) d\xi = \frac{n_1 \bar{v}}{2} \int \sin \chi \cos \chi p(\rho) d\chi \frac{\iint' dy dz}{\iint dy dz} \quad (13)$$

and

$$\mathcal{V}_1(x) = \frac{n_1 \bar{v} \epsilon x}{2} \int_x^\infty \frac{p(\rho)}{\rho^2} d\rho \quad (14)$$

since on the average only a fraction ϵ of the area in the yz plane* is open;

$$\iint' dy dz = \epsilon \iint dy dz = \epsilon A \quad (15)$$

The relation $\rho = \frac{x}{\cos \chi}$ has been used to replace χ in the integral. Hence, both $K(x, \xi)$ and $\mathcal{V}_1(x)$ have now been expressed as integrals involving the function $p(\rho)$ and the problem reduces to that of relating $p(\rho)$ to measurable properties of the medium.

It is interesting to point out that identical expressions are obtained for $K(x, \xi)$ and $\mathcal{V}_1(x)$ if it is assumed that emission from every point in the medium is isotropic and characterized by the function $p(\rho)$. This result is probably a consequence of the statistical uniformity of the medium and the fact that for every surface in one orientation there is another equivalent surface in exactly the opposite direction. A derivation of this result is presented in the appendix.

A physical interpretation of the function $p(\rho)$ can be obtained from the following hypothetical experiment. Suppose the medium can be "surveyed" by scanning along the x -direction with a "beam" of area ΔA which is very small relative to the pore size.

A scan is started in the positive x -direction from a solid surface and continued until it meets another solid surface in the volume elements $\Delta A \Delta \rho$ centered a distance ρ_1 from the start of the scan. This particular scan

*It can readily be shown that the fraction of open area of any plane cutting a homogeneous porous medium is equal to the fraction of void volume, ϵ .

is counted as contributing to the number N_i of free paths of length ρ_i to $\rho_i + \Delta\rho$. Another scan is started from the next surface encountered on going along x and the process continued until sufficiently many scans, N , have been made to characterize adequately the function $p(\rho_i) \Delta\rho = N_i/N$. In the limit $\Delta\rho \rightarrow 0$, this operation then defines $p(\rho)$ as

$$\lim_{\Delta\rho \rightarrow 0} \frac{N_i}{N\Delta\rho}$$

The function previously defined as $p(\rho)d\rho$ is

$$\frac{\iint' \delta(\rho) dydz}{\iint' dydz}$$

where randomness of the angles has already been introduced. In terms of the present scanning technique, $dydz$ is equivalent to ΔA and $\iint' dydz$ becomes $2N\Delta A$. Similarly, for ρ between ρ_i and $\rho_i + \Delta\rho$, $\iint' \delta(\rho) dydz = 2N_i\Delta A$ since the definition of $\delta(\rho_i)$ implies that a surface exists at ρ_i and no other surface cuts ρ_i . Hence

$$p(\rho) = \lim_{\Delta\rho \rightarrow 0} \frac{N_i \Delta A}{\rho N \Delta A}$$

which is identical with the function $p(\rho)$ defined in terms of the scanning operation.

This interpretation of $p(\rho)$ provides at least a qualitative notion of its appearance. Since a scan starts on the surface of a pore and goes into the pore, there are certainly no scans of zero length, but rather a molecule is

assured of at least a small jump into the pore. Thus, $p(\rho) = 0$. Likewise, the chance of a very large jump is small and $p(\infty) = 0$. The function $p(\rho)$ may then be anticipated to resemble the following sketch.

It is to be noted that although the exact shape of this curve cannot be refined further without reference to a specific model of the medium, the mean value of ρ is calculable. Thus,

$$\bar{\rho} = \int_0^{\infty} \rho p(\rho) d\rho \text{ or, in terms of the scanning operation}$$

$$\bar{\rho} = \frac{\sum_i N_i \rho_i}{N}$$

But $\sum_i N_i \rho_i \Delta A$ is just the void volume covered by the scan and is equal to $\epsilon \Delta A L$ where L is the total distance covered by the N scans. Furthermore $N \Delta A$ is just half the total void area covered by the scan projected onto the (y,z) plane. Thus, if ΔS_i is an element of area such that $\Delta A = \Delta S_i \cos \theta_i$, the total area projected onto the (y,z) plane is $\sum_i \Delta S_i \cos \theta_i = 1/2 \sum_i \Delta S_i = 1/2 \sigma (1 - \epsilon) L \Delta A$ where the average value of $\cos \theta = 1/2$ has been used in the summation and σ is the void surface area per unit solid volume. Hence,

$$N \Delta A = 1/4 \sigma (1 - \epsilon) L \Delta A$$

and

$$\bar{\rho} = \frac{\sum N_i \rho_i \Delta A}{N \Delta A} = \frac{\epsilon L \Delta A}{1/4 \sigma (1 - \epsilon) L \Delta A} = \frac{4 \epsilon}{\sigma (1 - \epsilon)} \quad (16)$$

or twice the hydraulic radius, r_h .

For the purpose of calculating the transport an analytic form for $p(\rho)$ is desirable. Several alternatives may be suggested which allow an exact solution of the problem:

1. A simple random-walk type function may be used of the form $K(x, \xi) = 1/2$ for $|x - \xi| = \lambda$ and 0 for all other values. This function is essentially a one-dimensional representation of the entire problem. In terms of this approximation $\mathcal{V}_1(x)$ should be taken as $1/2 n_1 \bar{v} \epsilon$ if $x = \lambda$ and 0 otherwise. For this function $\lambda = \bar{\rho}$.
2. A function of the form $p(\rho) = \frac{1}{\lambda^2} \rho e^{-\rho/\lambda}$ may be used. Here $K(x, \xi)$ is found to be

$$\frac{1}{2\lambda} e^{-\frac{|x - \xi|}{\lambda}}$$

and $\mathcal{V}_1(x)$ becomes $1/2 n_1 \bar{v} \epsilon \frac{x}{\lambda} E_1\left(\frac{x}{\lambda}\right)$

where $E_1\left(\frac{x}{\lambda}\right)$ is the exponential integral $\int_{\frac{x}{\lambda}}^{\infty} \frac{e^{-\mu}}{\mu} d\mu$ and $\lambda = \bar{\rho}/2 = r_h$.

3. A sum of exponentials of the form

$$p(\rho) = \sum_i \frac{f_i \rho}{\lambda_i^2} e^{-\frac{\rho}{\lambda_i}}$$

with $\sum f_i = 1$ may be used. For this function

$$K(x, \xi) = 1/2 \sum_i \frac{f_i}{\lambda_i} e^{-\frac{|x - \xi|}{\lambda_i}}$$

and

$$\mathcal{V}_1(x) = 1/2 n_1 \bar{v} \epsilon \sum_i f_i \frac{x}{\lambda_i^2} E_1\left(\frac{x}{\lambda_i}\right).$$

For this function

$$\bar{\rho} = \sum_i 2 f_i \lambda_i \quad \text{or} \quad \sum_i f_i \lambda_i = r_h.$$

SOLUTIONS AND RESULTS

The integral equation for $W(x)$ can be solved exactly for the three forms of $p(\rho)$ suggested above. For the random-walk and single exponential function the solutions are identical,

$$W(x) = \frac{x + \lambda}{L + 2\lambda} \quad (17)$$

For a sum of just two exponentials characterized by λ_1 and λ_2 the solution is (for a sufficiently thick medium so that $e^{-L/\lambda} \ll 1$)

$$W(x) = \frac{x + \lambda_1 + \lambda_2 - \gamma + \frac{(\gamma - \lambda_1)(\gamma - \lambda_2)}{\gamma} (e^{-x/\gamma} - e^{-(L-x)/\gamma})}{L + 2(\lambda_1 + \lambda_2 - \gamma)} \quad (18)$$

where

$$\gamma = \frac{\lambda_1 \lambda_2}{[f_1 \lambda_1^2 + f_2 \lambda_2^2]^{1/2}}$$

For a sum of more than two exponentials the solution is of the same general form but algebraically more complex.

The molecular transport is calculable from $\mathcal{U}_1(x)$ and $W(x)$ as indicated in equation (5). It is convenient to represent the transport in a form readily comparable with other expressions in the literature and for this purpose the Kozeny-Carmen expression (7) may be used*,

$$\bar{U} = 2/3 \frac{\mu_1 \epsilon r_h}{L} n_1 \bar{v} \quad (19)$$

* In this expression we have used μ_1 as a "shape factor" in place of $1/f_k$ as used by Carman. This expression is such that $\mu_1 = 1$ for a bundle of capillaries of radius r_h .

The expressions obtained for $\bar{\rho}$ and μ_1 are the following:

1. For the simple random-walk approach with $\lambda = \bar{\rho} = 2r_h$

$$\bar{\rho} = \frac{\epsilon r_h}{L + 2r_h} n_1 \bar{v} = \epsilon r_h n_1 \bar{v}/L; \quad \mu_1 = 3/2 \quad (20)$$

2. For the single exponential function with

$$\bar{\rho} = 2\lambda, \quad \lambda = r_h, \quad (e^{-L/\lambda} \ll 1)$$

$$\bar{\rho} = \frac{7}{12} \frac{\epsilon r_h}{L + 4r_h} n_1 \bar{v} = \frac{7}{12} \epsilon r_h n_1 \bar{v}/L; \quad \mu_1 = \frac{7}{8} \quad (21)$$

3. For the sum of two exponential functions, $\bar{\rho} = 2f_1 \lambda_1 + 2f_2 \lambda_2$,

$$f_1 + f_2 = 1, \quad (e^{-L/\lambda} \ll 1)$$

$$\bar{\rho} = \frac{\frac{1}{2} \left[\lambda_1(3 + 4f_1) + \lambda_2(3 + 4f_2) - 3\gamma \right] + \frac{2(\gamma - \lambda_1)(\gamma - \lambda_2)}{\gamma} \left[f_1 G_1 + f_2 G_2 \right]}{4(L + 2\lambda_1 + 2\lambda_2 - 2\gamma)} \epsilon n_1 \bar{v} \quad (22)$$

where

$$G_i = \frac{\gamma^2}{\lambda_i^2} \ln \frac{\gamma + \lambda_i}{\gamma} - \frac{\gamma^2}{\lambda_i(\lambda_i + \gamma)}.$$

The permeability computed for such a $p(\rho)$ is always somewhat larger than that computed for a single exponential with the same value of $\bar{\rho} = 2r_h$ since the presence of longer paths more than compensates for their smaller number as required to maintain $\bar{\rho}$ constant.

SUMMARY

An approach to the problem of transport through a porous medium in the Knudsen regime of very low molecular density is suggested which reduces the requirements on a model of the medium to that of specifying a function $p(\rho)$, the probability density of a free-path of length ρ within the medium. Although this approach may not be completely rigorous due to the manner of introducing certain averaging processes in reducing the integral equation to a tractable form, it offers some improvement over previous methods of calculation of permeability.

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APPENDIX

EVALUATION OF $K(x, \xi)$ AND $\mathcal{U}_1(x)$ FOR AN ISOTROPIC MEDIUM

If the medium is assumed isotropic on a very fine scale, the calculation of $K(x, \xi)$ and $\mathcal{U}_1(x)$ is straight-forward. According to equation (3)

$$K(x, \xi) d\xi = \frac{\iiint \iiint' K(xyz; \xi \eta \zeta) d\xi d\eta d\zeta dy dz}{\iint' dy dz}$$

represents the averaged probability that a molecule leaving a surface somewhere in the (y, z) slab of thickness dx suffers its next collision somewhere in the (y, z) slab of thickness $d\xi$. Because of the fine-grained homogeneity assumed for the medium, this function may be expressed as

$$K(x, \xi) d\xi = \int \int \frac{\cos \chi d\eta d\zeta}{\int d\omega} \frac{p(\rho) d\xi}{\cos \chi} \quad (23)$$

where the first factor on the right-hand-side represents the fraction of solid angle subtended at (x, y, z) by the volume element $d\xi d\eta d\zeta$ and the second factor represents the probability of suffering a collision within the slab $d\xi$ at a distance ρ from (x, y, z) . The coordinates are indicated in the figure

But

$$d\omega = \frac{\cos\chi}{\rho^2} d\eta d\xi = \sin\chi d\chi d\psi, \quad \int d\omega = 4\pi,$$

and

$$\rho = \frac{|\xi - x|}{\cos\chi}$$

so that

$$K(x, \xi) d\xi = \frac{1}{4\pi} \int_0^{\pi/2} \sin\chi d\chi \int_0^{2\pi} d\psi \frac{p(\rho) d\xi}{\cos\chi} \quad (24)$$

and

$$K(x, \xi) = \frac{1}{2} \int_0^{\pi/2} \tan\chi p(\rho) d\chi = \frac{1}{2} \int_{|\xi-x|}^{\infty} \frac{p(\rho) d\rho}{\rho} \quad (25)$$

The same result obtained by the more extended analysis given in the text (equation 9).

The calculation of $\nu_1(x)$ proceeds similarly. For this problem the surface (η, ξ) is chosen at $\xi = 0$, i.e., the face of the medium, and the number of molecules passing through the area $d\eta d\xi$ at an angle χ is $n_1 \bar{v} \epsilon \cos\chi d\eta d\xi$ where n_1 is the gas density outside the medium and ϵ is the void fraction or equivalently the fraction of open area of the plane (η, ξ) . Thus

$$\nu_1(x) dx = \iiint n_1 \bar{v} \epsilon \cos\chi d\eta d\xi \frac{\cos\chi dy dz}{4\pi \rho^2} \frac{p(\rho) dx}{\cos\chi} \quad (26)$$

where the terms have the same significance as before. Making similar substitutions and eliminating χ through the relation $\rho = x/\cos\chi$,

$$\nu_1(x) = \frac{n_1 \bar{v} \epsilon x}{2} \int_x^{\infty} \frac{p(\rho) d\rho}{\rho^2} \quad (27)$$

the same result as given previously (equation 14).

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