A CONTINUUM MECHANICAL APPROACH TO THE FLOW EQUATIONS FOR MEMBRANE TRANSPORT

I. WATER FLOW

DONALD C. MIKULECKY

From the Division of Biophysics and Neurobiology, Graduate Studies and Research, Meharry Medical College, Nashville, Tennessee 37208

ABSTRACT A concept is presented for modeling flows through membranes using continuum mechanics. Viscous interactions (due to velocity gradients) are explicitly incorporated and position-dependent local water-membrane interactions are taken into account before obtaining slab averages. This is in distinction to other treatments where strictly one-dimensional force balance equations are written using slab average friction coefficients which are really composite functions of local interactions. It is shown that the viscous and other frictional interactions do not simply form linear combinations in the solutions to the equations of motion. Flow profiles for pressure-driven flows ranging from Poiseuille's flow to "diffusion" flow are obtained depending on the strength and extent of the water-membrane interaction. The model is also applied to self-diffusion flows and the measurement of "equivalent pore size." It is shown that for a fixed pore size the ratio of filtration flow to self-diffusion flow for equal driving forces is able to vary over a wide range depending on the water-membrane interaction.

INTRODUCTION

This work is addressed to the modeling of flows through membranes using local equations of motion to describe the local flow of each mobile component. The equations of motion are essentially of the same form as those derived by Bearman and Kirkwood (1) using statistical mechanics. Since the Bearman-Kirkwood equations were derived for simple solutions, we can not claim that those used here are identical with them. One can imagine Bearman-Kirkwood equations of motion being applied directly to the fluid within the interstices of a membrane with interactions with the membrane substance taken into account. (For an example of this approach see Manning [2] where the analysis is made for the case which excludes viscosity.) An alternative, which has been discussed elsewhere (3) is to include the membrane as a component. For the purpose of this work the latter approach is not necessary and would obscure the point being made. In the case of less-than-rigid membranes or liquid membranes this would be the necessary approach. Such equations have been applied by other workers without making a necessary or direct link to their statistical mechanical basis (4, 5). If the reader is more comfortable thinking about the problem in this way it will not detract from the validity of the results obtained here. It should be pointed out that Vaidhyanathan and Perkins (6) used a similar statistical mechanical derivation to that used by Bearman and Kirkwood and, without going through equations of motion, obtained flow equations analogous to those obtained by Kedem and Katchalsky (7) from the nonequilibrium thermodynamic approach. What this work will demonstrate is that if the membrane has the property that velocity gradients resulting in viscous (as opposed to frictional [8]) dissipation occur during the flow process in the membrane, the Kedem-Katchalsky equations are not the general result of solving the equations of motion. This is due to the fact that their approach, like so many others (9–11), introduces a force balance equation which does not take into account viscous interactions in a single component but only those which result from relative motion of various components. Note that the mathematical form in which the viscous forces occur (the laplacian of the velocity field) demands that some notion of the membrane geometry be assumed before solutions of the equations of motion can be obtained, and the approach is thus less general. On the other hand this loss of generality is necessary if a complete description of all the forces involved is to be considered. The procedure used by Kedem and Katchalsky was essentially to perform a force balance by implicitly using average values over a slab of membrane interior, reducing the balance equations to a one-dimensional balance along a direction following a flow path through the membrane. In the case of viscosity such a procedure is not possible simply because the phenomenon itself represents a momentum transport in a direction normal to the flow path, into the membrane matrix.[1] In such cases a three-dimensional balance equation must be written. Such equations usually reduce to two-dimensional equations when radial symmetry or something analogous to long, narrow, rectangular slits can be assumed to represent the membrane geometry. We will use such representations here since the mathematical simplification obtained will help to make the physical significance of the viscosity clear and hence be worth any loss of generality. Note that conformal mapping techniques can be used to carry these solutions into other categories (12).

This paper will be limited to a fairly simple case: the flow of water through a membrane. We will apply the results to the interpretation of equivalent pore size measurements which involve comparison of osmotic or hydraulic permeability to self-diffusion type permeabilities. From the viewpoint expressed above, the essential difference between these equations is the possibility of momentum transfer of the type discussed in footnote 1 (viscosity) in the former experiment and its complete absence in the latter.

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[1] For a very lucid exposition of this point see Chapter 1 of Transport Phenomena by R. B. Bird, W. E. Stewart, and E. N. Lightfoot, 1960, John Wiley and Sons, Inc., New York. The discussion on p. 1–5 is directly pertinent to the point being made above.

In a subsequent paper, solute equations of motion will be introduced and a comparison will be made between the Kedem-Katchalsky frictional coefficients and their analogues obtained by solving equations of motion. Preliminary versions of this work have already been reported (13, 14). It will be demonstrated that the Kedem-Katchalsky slab average coefficients are really composites of the local fractional and viscosity coefficients, even in the simplest special case, as long as velocity gradients do not disappear in the membrane.

The Equation of Motion Applied to Water Flow Through a Membrane

A major question arises when we attempt to interpret the significance of water-membrane interaction in a membrane with a specific geometry. The simplest possible case is the flow of water through a pipe or cylindrical pore. In this case, the steady-state equation of motion reduces to just two contributions: the driving force and the viscous forces which are equal and opposite to them. This is, of course, a fairly straightforward application of Newton's second law of motion when we recognize that accelerations vanish in the steady state for a continuum mechanical course graining. The solution to this equation is well known as Poiseuille's law. To obtain this solution to the second ordinary differential equation of motion, two boundary conditions are applied. The first is the absence of relative motion between the fluid layer adjacent to the pipe or pore wall and the wall itself, and the second is the vanishing of velocity gradients at the center of the pore. It is the first of these boundary conditions that is crucial here. It can be put into perspective by acknowledging that it is equivalent to assuming that the water-membrane interaction is essentially infinite at the pore or pipe wall and negligibly small everywhere else inside the channel. This seems a reasonable approach for large pipes or pores, but leaves out the possibility of specific local water-membrane interactions which depend on the nature of the membrane material. Kedem and Katchalsky simply assumed such specific interactions were possible and introduced them through a slab average water-membrane friction coefficient which multiplies the water velocity (the relative velocity between water and a stationary membrane). When we attempt to introduce these interactions at a local volume element, the first fact we must deal with is that the local friction coefficient is position dependent. This is obvious for the limiting case of Poiseuille's law as described above, where the value of the coefficient increases from some value near zero in the pore to approaching infinity right at the boundary. Without introducing specific models for water-membrane interaction, it is possible to take into account so broad a range of position-dependent water-membrane friction coefficients as to cover the range of possibilities from Poiseuille's law at one limit to a purely "diffusional" flow where velocity gradients disappear at the other.

Let us now model the local water-membrane frictional interaction by the following functional form:

$$F_{wm} = F_{wm}^{*}(r/a)^{n}, \tag{1}$$

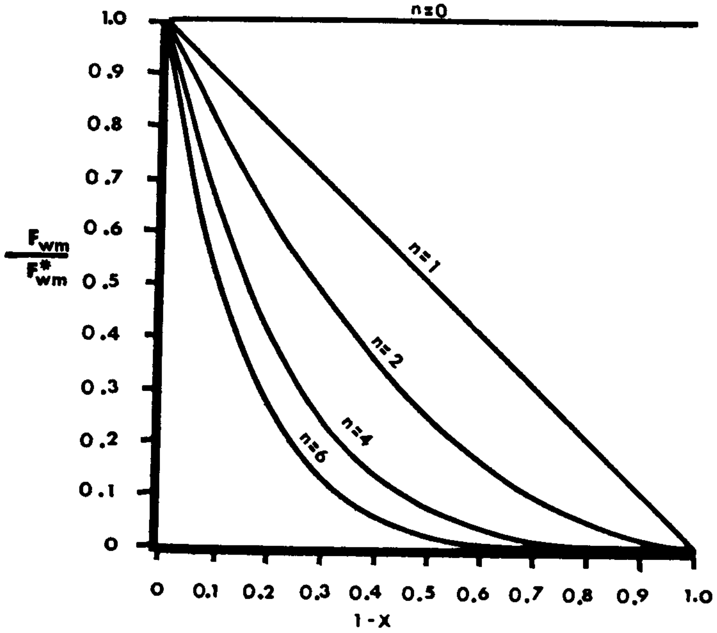

FIGURE 1 The position dependence of the local friction coefficients for various values of the exponent n. The distance from the pore wall is $1 - x$.

Here F^*_{wm} is the value of the interaction at the wall, a is half the distance between walls (the radius in cylindrical geometry), and r is the distance from the channel's midpoint to the point at which the interaction is being evaluated. The exponential parameter n is a measure of how quickly the interaction falls off with distance from the membrane walls (see Fig. 1). Poiseuille's law (vanishing F_{wm}) can be approached as $F^*_{wm} \rightarrow 0$ and/or as $n \rightarrow \infty$. The equation of motion for water as a single mobile species is

$$\eta\nabla^2\bar{v} - F_{wm}\bar{v}_w - c_w\nabla\mu_w = 0, \tag{2}$$

where η is the viscosity of water, $\bar{v}$ is the velocity of the local center of mass, $\bar{v}_w$ is the velocity of water, c_w is the composition variable $c_w = X_w/v$ where X_w is the mole fraction of water and v is the mean molecular volume, ρ_w is the concentration of water in grams per cubic centimeter or its density where $\rho_w = m_w c_w$, m_w is the mass per molecule of water, μ_w is the chemical potential of water. F_{wm} is defined above and related to the type of coefficient derived by Bearman and Kirkwood, ζ_{wm}, by $F_{wm} = c_w\zeta_{wm}c_m$. The center of mass velocity if we consider the membrane as a component is $\bar{v} = (\rho_w\bar{v}_w + \rho_m\bar{v}_m)/\rho$, where $\rho = \rho_m + \rho_w$ is the density of the water membrane system. Since $\bar{v}_m = 0$, $\bar{v} = (\rho_w/\rho)\bar{v}_w$. Since we are considering only the fluid-filled spaces inside the membrane we have also that $\rho_w = \rho$. Equation 2 then becomes

$$\nabla^2\bar{v} - (F_{wm}/\eta)\bar{v} = (c_w/\eta)\nabla\mu_w\,. \tag{3}$$

We will now solve this equation for a cylindrical channel using equation 1 to model the local water membrane interaction. For this case 3 becomes

$$d^2v_y/dr^2 + (1/r)dv_y/dr - \alpha^2(r/a)^n v_y = B, \tag{4}$$

where v_y is the component of the velocity down the pore axis and α^2 and B are defined as

$$\alpha^2 = F_{wm}^*/\eta, \qquad B = \frac{c_w \nabla\mu_w}{\eta}. \tag{5}$$

The boundary conditions are the same as in the case of Poiseuille flow mentioned earlier, namely that

$$v_y = 0 \text{ at } r = a,$$

$$dv_y/dr = 0 \text{ at } r = 0. \tag{6}$$

We make the change of variables $x = (r/a)$ to simplify equation 4 which becomes

$$d^2v_y/dx^2 + (1/x)dv_y/dx - \alpha^2x^n = Ba^2. \tag{7}$$

We look for a solution of the form

$$v_y = [u + x^2 - 1](Ba^2/4), \tag{8}$$

to insure that Poiseuille's law is recovered when $F_{wm}^* \rightarrow 0$ and/or $n \rightarrow \infty$ ($u = 0$ in that case).

Substituting equation 8 into equation 7 using the substitution $A = a\alpha$ we obtain

$$d^2u/dx^2 + (1/x)du/dx - A^2X^n u = A^2(x^2 - 1)x^n. \tag{9}$$

We make one last variable change to put equation 9 in the form of a modified Bessel's equation using

$$\gamma = 2A/(n + 2), \omega = \gamma X^{n/2+1}, \tag{10}$$

in equation 9 we obtain

$$d^2u/d\omega^2 + (1/\omega)du/d\omega - u = [\omega/\gamma]^{4/(n+2)} - 1. \tag{11}$$

This inhomogeneous form of a modified Bessel's equation has the solution

$$u = [f(\gamma) - 1][I_0(\omega)/I_0(\gamma)] + 1 - f(\omega), \tag{12}$$

where

$$f(t) = K_0(t)\int_0^t (\omega/\gamma)^{4/(n+2)}I_0(\omega)\omega d\omega - I_0(t)\int_0^t (\omega/\gamma)^{4/(n+2)}K_0(\omega)\omega d\omega, \tag{13}$$

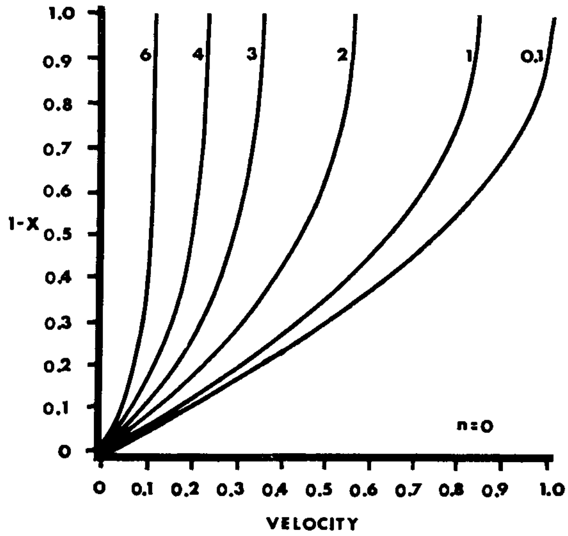

FIGURE 2

FIGURES 2–6 Flow profiles for cylindrical pores. Velocity at each point relative to maximum velocity for Poiseuille flow is plotted in the horizontal direction vs. distance from the pore wall $1 - x$ in the vertical direction. The value of the exponent n in the position-dependent frictional coefficient is given in the lower right-hand corner for each plot. The values of the interaction parameter A appear alongside each curve at the top of each plot.

and I_0 and K_0 are modified zero-order Bessel functions of the first and second kind, respectively. Thus the total local flow along any streamline is given by:

$$v_y = [u + x^2 - 1](Ba^2/4) = \{[f(\gamma) - 1][I_0(\omega)/I_0(\gamma)] - f(\omega) + x^2\}(Ba^2/4). \quad (14)$$

Two parameters are important in determining the shape of the flow profile in the pore: one is the parameter

$$A = a\alpha = a(F_{wm}^{*}/\eta)^{1/2}, \quad (15)$$

which is a dimensionless measure of the strength of the water-membrane interaction at the interface between the membrane matrix and the fluid phase. The other is n, the integral power of the position dependence of the frictional interaction. The larger the value of n, the shorter the range of the interaction. If $n = 0$ the interaction is constant across the pore, if $n = 1$ it falls off linearly, etc. Fig. 1 shows the value of F_{wm} as a function of $1 - x$ for various values of n as a parameter. Figs. 2–6 give the flow profiles, $v_y/v_{\max}$ as a function of $1 - x$ with A as a parameter. Each diagram is for a different value of n.

For small values of A, the curves approach a Poiseuille flow profile. As n increases the water-membrane interaction falls off more steeply with distance from the membrane matrix, and all the curves approximate Poiseuille flow profiles more closely.

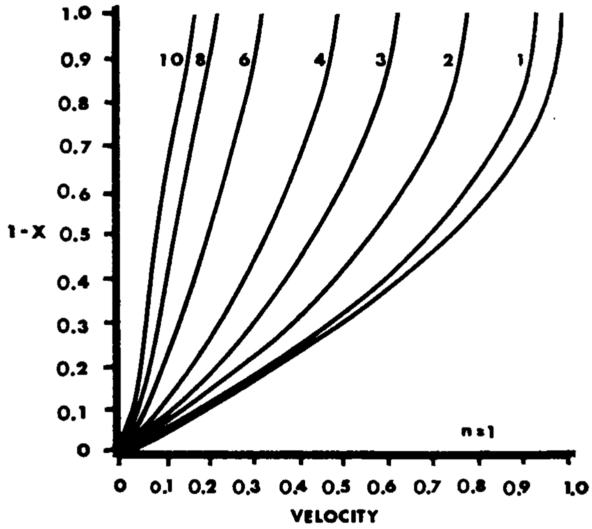

FIGURE 3

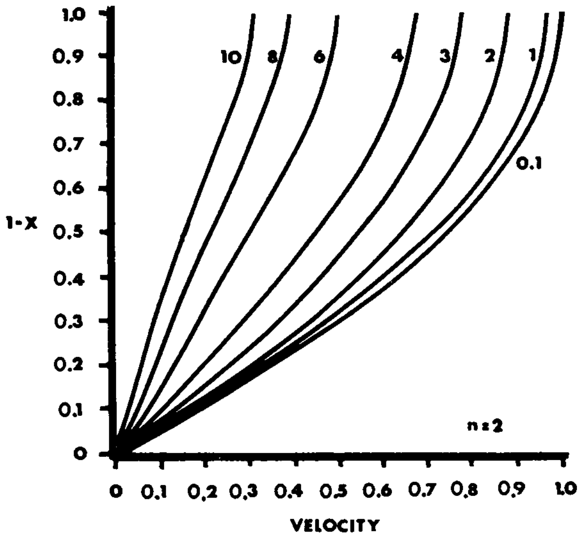

FIGURE 4

The other extreme is when *n* is small and *A* is large (significant water-membrane interaction throughout the membrane interior). The resultant flow profiles are relatively flat and approach the kind of profile usually interpreted as a diffusion-like process. It will be shown below that these results approach the flows obtained in a self-diffusion experiment exactly.

The intermediate values span the range between the two extremes and we have

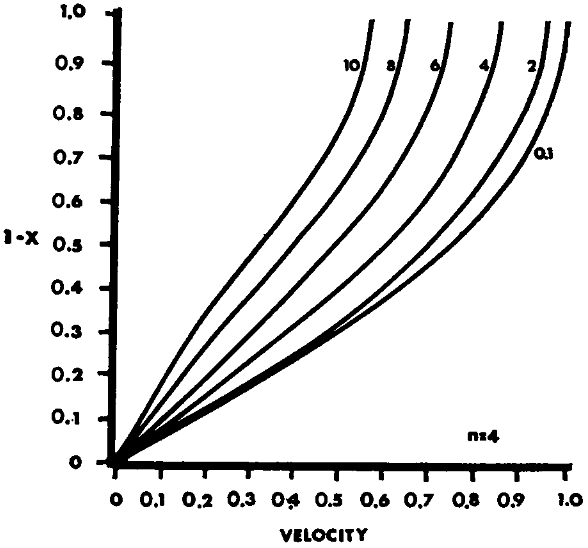

FIGURE 5

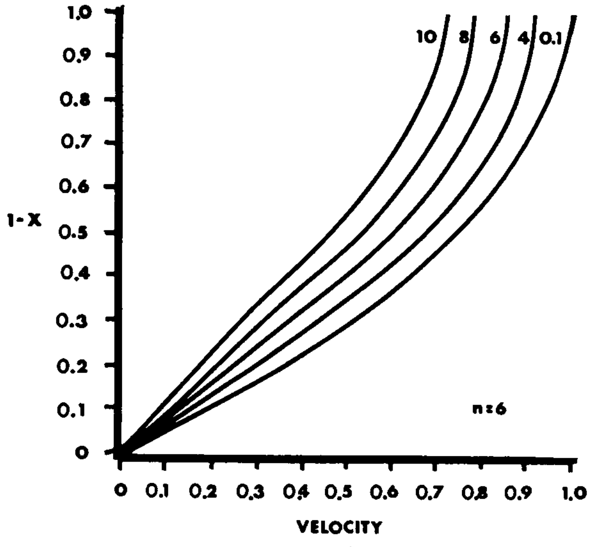

FIGURE 6

generated a continuum theory which should be applicable to all types of water flow through membranes which have a relatively fixed geometry. A more cumbersome problem, but possibly even more relevant to biological systems, can also be approached by using equations of motion, namely, the description of water flow through a membrane with a fluid or semimobile matrix. Additional equations of motion for the membrane itself would have to be incorporated, the restriction that the membrane is strictly stationary removed and some constraint on the motion of membrane molecules imposed. Obviously the latter statement is a physical reality in all cases where pressure gradients can exist in the system without the membrane being torn apart.

These results point to a severe criticism of the use of Poiseuille's law as an approximation for flows in any cases where the membrane is sufficiently "tight" for the approximation $F_{wm}(r) = 0$ to be invalid. This has a direct bearing on the practice of "measuring" pore size in membranes using a combination of Fick's law for diffusion and Poiseuille's law to describe the result of two water flow measurements. In one case, self-diffusion flows are measured; in the second, hydrostatic or osmotic gradient driven flows are measured and the pore size is calculated from their ratio. We will now discuss this problem in detail.

THE MEASUREMENT OF EQUIVALENT PORE SIZE BY COMPARISON OF FILTRATION AND SELF-DIFFUSION

The classical approach was introduced by Pappenheimer et al. (15) and has recently been reviewed by Solomon (16). The approach goes something like this: two sets of measurements are made on the same membrane. One is the self-diffusion of tritiated water across the membrane and the second is the water flow due to a pressure gradient. The flows per unit driving force are compared by taking their ratio.

The theory behind this is as follows: for the self-diffusion flow Fick's first law gives (normalized per unit area)

$$J_{sd} = D(\Delta c/\Delta y), \tag{16}$$

and the pressure driven flow per unit area is given by Poiseuille's law.

$$\langle v_y \rangle = (a^2/8\eta)(\Delta P/\Delta y). \tag{17}$$

(The equations are sometimes corrected for various factors such as the difference in the probabilities that particles will enter the pore in the two different situations and the actual finite size of the water molecules, see Solomon's review for this. A word of caution about using Faxen's equations, they are an approximation which is good only when the size of the permeating molecule is much less than that of the pore. In narrow pores this is a problem [17].)

For our purposes these two equations without the modifications mentioned above will suffice to demonstrate the point. If we put Δc and ΔP in the same units and take the ratio of the volume flows for equivalent driving forces we get

$$\langle v_y \rangle / (J_{sd} \bar{V}_w) = (a^2 RT/8\eta D \bar{V}_w)(\Delta P/\Delta \pi), \tag{18}$$

where $\Delta\pi = RT\Delta c$ so that for ΔP (filtration experiment) $=$ $\Delta\pi$ (self-diffusion experiment),

$$a = [(\langle v_y \rangle / J_{vd})(8\eta D\bar{V}_w/RT)]^{1/2}, \tag{19}$$

where $J_{vd} = J_{sd}\bar{V}_w$ is the volume flow of tritiated water due to self-diffusion in the self-diffusion experiment. Thus with two experiments we get the ratio

$$\langle v_y \rangle / J_{vd} \, ,$$

from which we can calculate a the "equivalent pore radius." For a membrane which consists of cylindrical pores of uniform radius of the pores this is the actual pore dimension. For any other membrane it is an attempt to represent the unknown structure by an equivalent regular structure. We will now carry our three-dimensional analysis further and compare the result with this classical result.

TWO APPROACHES TO THE EQUIVALENT PORE RADIUS EXPERIMENTS

Equations of Motion

We have already seen the changes in the flow pattern due to membrane-water interaction in the pressure driven flows (equation 14 and the flow profiles calculated from it) and we note that Poiseuille flow is one limiting case.

Equations for Self-Diffusion

We now wish to apply the equations of motion to the self-diffusion case. We first note that in a self-diffusion experiment, the center of mass does not move ($\bar{v} = 0$) as the water and tritiated water merely exchange for each other. In this case the equations of motion for water and tritiated water from equation 5 are of the form:

$$-c_w \nabla \mu_w - F_{wt}(\bar{v}_w - \bar{v}_t) - F_{wm}\bar{v}_w = 0, \tag{20}$$

$$-c_t \nabla \mu_t - F_{tw}(\bar{v}_t - \bar{v}_w) - F_{tm}\bar{v}_t = 0, \tag{21}$$

adding equations 20 and 21 and noting that $F_{wm}/\rho_w = F_{tm}/\rho_t$ we get that

$$(F_{tm}/\rho_t)(\rho_w \bar{v}_w + \rho_t \bar{v}_t) = 0, \tag{22}$$

or $J_w = -J_t$ (where we have used the Gibbs-Duhem relation and $\nabla P = 0$) as would be expected for the case where the center of mass is stationary. Thus only one independent equation governs the flow and it can be written in averaged form:

$$J_{sd} = \left[\int_0^1 x \, dx / (F_{wt} + F^*_{wm} x^n \right] (\Delta\pi / \Delta y). \tag{23}$$

The solutions to this equation depend on the value of n and are tabulated in Table I.

TABLE I

AVERAGE SELF-DIFFUSION FLOWS AS A FUNCTION OF THE PARAMETER n

n	$[J_{sd}/(\Delta\pi/\Delta y)] = \int_0^1 (y\,\mathrm{d}y)/(F_{wt} + F_{wm}^* y^n)$
0	$1/(F_{wt} + F_{wm}^*)$
1	$(2/F_{wm}^*)[1 - (F_{wt}/F_{wm}^*) \ln \{(F_{wt} + F_{wm}^*)/F_{wm}^*\}]$
2	$(1/F_{wt}) \ln \{(F_{wt} + F_{wm}^*)/F_{wt}\}$
3	$h^3 = F_{wm}^*/F_{wt}$ $(2/F_{wt})[(1/6h) \ln \{(1 - h + h^2)/(1 + h)^2\} + (1/h\sqrt{3}) \tan^{-1} \{(2 - h)/h\sqrt{3}\} - \tan^{-1} (-1/\sqrt{3})]$
4	$h^2 = F_{wm}^*/F_{wt}\ (1/F_{wm}^* h) \tan^{-1} [1/h]$
6	$h^3 = F_{wm}^*/F_{wt}$ $(1/F_{wm}^*)[(1/6h^2) \ln \{(1 + h)^2/(1 - h + h^2)\} + (1/h^2\sqrt{3}) \tan^{-1} \{(2 - h)/h\sqrt{3}\} - \tan^{-1} \{-1/\sqrt{3}\}]$

We also must calculate the total flow for each case in Table I and for each profile described by equation 14. This is done by performing an integration over the pore cross-section of the following form

$$\langle J \rangle = (2/a^2) \int_0^a J_L\, r\, \mathrm{d}r. \tag{24}$$

Where J_L is the flow along any streamline and $\langle J \rangle$ is the total flow per unit area. To evaluate the diffusional flows in Table I it was necessary to supply some value for the term F_{wt}. The value obtained by Wang (18) for the self-diffusion of water in the absence of a membrane was used for this.

To choose a range of values for the parameter F_{wm}^* aqueous diffusion coefficients for a number of biological substances was used to calculate the corresponding fractional coefficient for their diffusion through water. Although a crude means of estimation, this method should provide an order-of-magnitude estimate and since we allow the value of this parameter to range over three orders of magnitude in our calculations, the range should cover all possible variations in this parameter's value. Fig. 7 shows the variation of total self-diffusion flow, DF, as a function of F_{wm}^* for various values of the parameter n.

In Fig. 8 the ratio Q/Q_p of total filtration flow Q to Poiseuille flow Q_p for the same driving force is given as a function of $A = a(F_{wm}^*/\eta)^{1/2}$, again with n as a parameter.

Using the relation between A and F_{wm}^* we can now calculate the predicted ratio g of total filtration flow to self-diffusion flow for *a given pore size* as a function of the parameters A and n. Using a pore radius a of 10 A leads to the values of the flow ratio g shown in Table II. The important thing to note is that for a given pore radius, $g = \langle v_y \rangle / J_{vd}$ can vary considerably. This would suggest that measurements

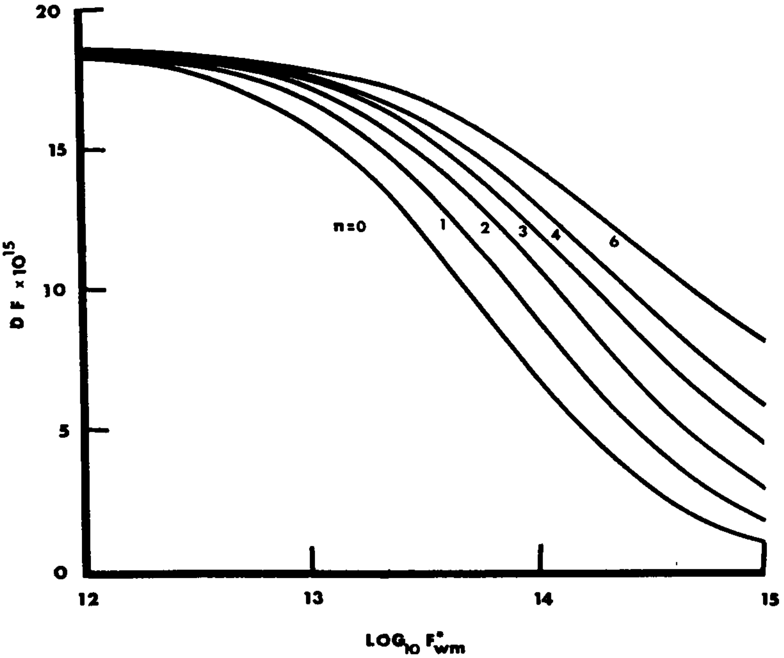

FIGURE 7 Total diffusion flow as a function of log F_{wm} with the exponent n as a parameter.

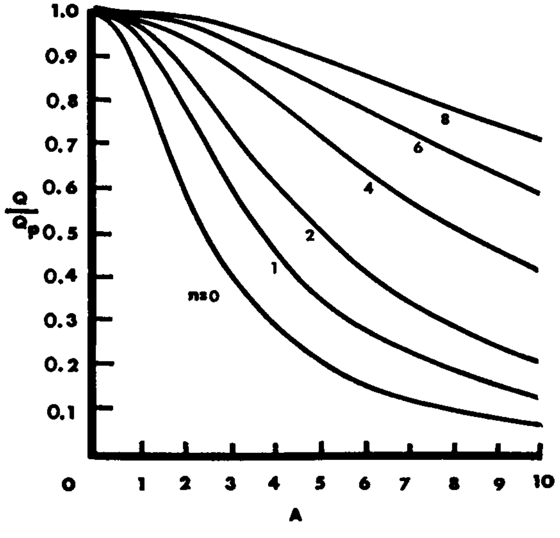

FIGURE 8 The ratio of total filtration flow to Poiseuille flow as a function of the interaction parameter A with the exponent n as a parameter.

of pore size in narrow pores may indeed tell more about the interaction between water and membrane than any physical dimension. Pappenheimer used the one-dimensional approach to deduce the "pore size" in capillaries in the cat's hind foot. He obtained a radius of about 35 A. For such pores, the "wall effect" may be

TABLE II

RATIO OF FILTRATION FLOW TO DIFFUSION FLOW g FOR PORE SIZE a = 10 A AS A FUNCTION OF THE PARAMETERS A AND n

A	n...	0	1	2	4	6
0.1		6.7	6.7	6.7	6.7	6.7
0.5		6.4	6.6	6.6	6.6	6.7
1.0		5.8	6.3	6.5	6.6	6.7
2.0		4.2	5.4	5.9	6.4	6.6
4.0		2.4	3.6	4.6	5.8	6.3
6.0		1.7	2.6	3.6	5.1	5.9
8.0		1.4	2.1	2.9	4.5	5.6
10.0		1.2	1.7	2.5	4.1	5.2

negligible. Solomon and others have used the one-dimensional approach to estimate the size of "equivalent pores" in cell membranes and obtained values less than 10 A! In such cases the wall effect is almost certainly not negligible. The question then becomes: what was actually measured? Without an independent measurement, the contributions of size and water-membrane interaction can not be sorted out. One attempt to find an independent measure of pore size is the use of probe molecules of known radius. The result of these experiments tends to confirm the result of the flow ratio method but this may be fortuitous. The approximations made in the probe method are very gross, for instance the use of Faxen's equation which is only true when the particle is much smaller than the pore (17).

SLITLIKE PORES

We will now repeat the above calculation for pores of a different geometry, namely rectangular slits with a width $2a$ and a length L such that $L \gg 2a$. We also modify the model of the frictional interaction in the following way: instead of an interaction which falls off in some smooth fashion with distance from the membrane matrix, we consider the interaction to be constant over some finite distance δ and then zero else where. It will be shown that varying the parameter δ has roughly the same effect as varying n in the above model. The advantage to this treatment is that the equations obtained are now capable of being solved in matrix form and thus can be extended to include any number of solute species. Each individual solute's local interaction with the membrane can thus be modeled in terms of its value of A and δ. In this paper we will not treat solute flow but continue our analysis of water flow alone. In the next paper, solute flows will be introduced and the influence of local interactions on slab average frictional coefficients and the reflection coefficient σ will be studied.

For the slit geometry the equation of motion (equation 4) takes the form

$$d^2v_y^{I}/dr^2 = B \quad \text{for} \quad \delta \geqq r \geqq 0, \tag{25}$$

$$d^2v_y^{II}/dr^2 - \alpha^2 v_y^{II} = B \quad \text{for} \quad a \geqq r \geqq \delta. \tag{26}$$

Where r is now the coordinate variable perpendicular to both the flow path through the membrane and the long axis of the rectangular pore cross-section.

Boundary conditions take the form

$$\mathrm{d}v_y^{\mathrm{I}}/\mathrm{d}r = 0 \quad \text{at} \quad r = 0, \tag{27}$$

$$\left.\begin{aligned} v_y^{\mathrm{I}} &= v_y^{\mathrm{II}} \\ \mathrm{d}v_y^{\mathrm{I}}/\mathrm{d}r &= \mathrm{d}v_y^{\mathrm{II}}/\mathrm{d}r \end{aligned}\right\}\text{at} \quad r = \delta, \qquad \begin{aligned} &(28) \\ &(29) \end{aligned}$$

$$v_y^{\mathrm{II}} = 0 \quad \text{at} \quad r = a. \tag{30}$$

Using the change of variable

$$x = (r/a) \tag{31}$$

equations 25 and 26 become

$$\mathrm{d}^2v_y^{\mathrm{I}}/\mathrm{d}x^2 = Ba^2, \tag{32}$$

$$\mathrm{d}^2v_y^{\mathrm{II}}/\mathrm{d}x^2 - Av_y^{\mathrm{II}} = Ba^2. \tag{33}$$

The solution has the following form:

$$v_y = v_y^{\mathrm{I}} \quad \text{for} \quad 0 \leqq x \leqq d;\ v_y = v_y^{\mathrm{II}} \quad \text{for} \quad d \leqq x \leqq 1. \qquad (34\,a)$$

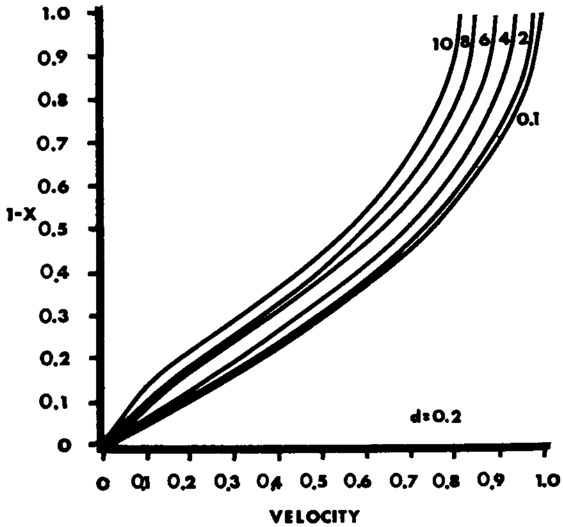

FIGURE 9

FIGURES 9–13 Flow profiles for slitlike pores. Velocity relative to maximum velocity for Poiseuille flow is on the horizontal axis vs. distance from the pore wall $1 - x$ in the vertical direction. The value of the fractional distance the water-membrane interaction extends into the pore, $d = \delta/a$, appears in the lower right-hand corner of each plot. The values of the interaction parameter A appear alongside each curve at the top of each plot.

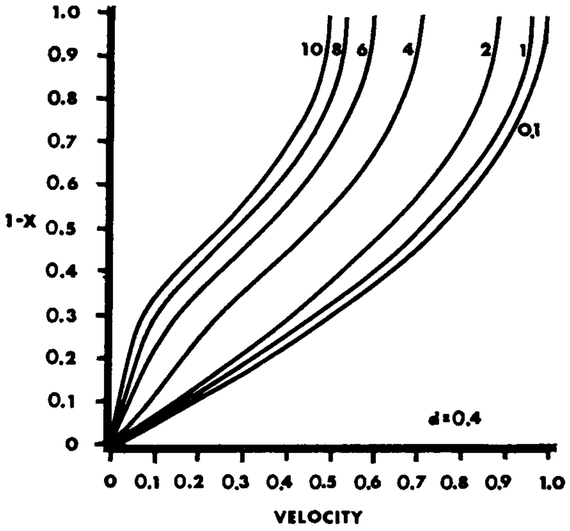

FIGURE 10

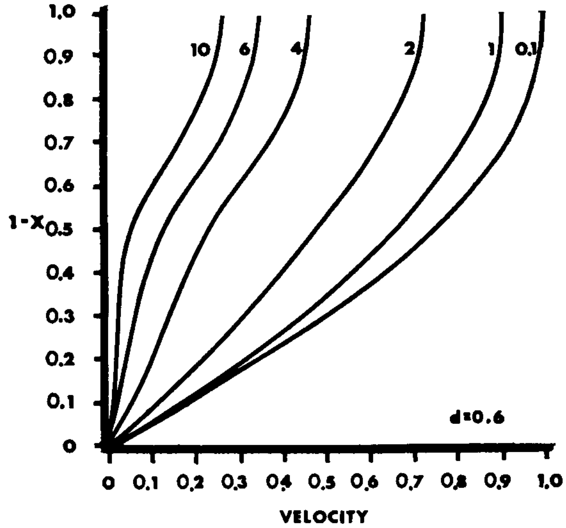

FIGURE 11

Where $d = \delta/a$

$$v_y^{\mathrm{I}} = (Ba^2/2)\{x^2 + (2d/A^2)\tanh(A-d) - (2/A^2)\operatorname{sech}(A-d) + (2/A^2) - (d^2/A^2)\}, \qquad (34\,b)$$

$$v_y^{\mathrm{II}} = (Ba^2/2)\{(2/A^2)[1 + \{d\sinh[A(1-x)] - \cosh(Ax-d)\}/\cosh(A-d)]\}. \qquad (34\,c)$$

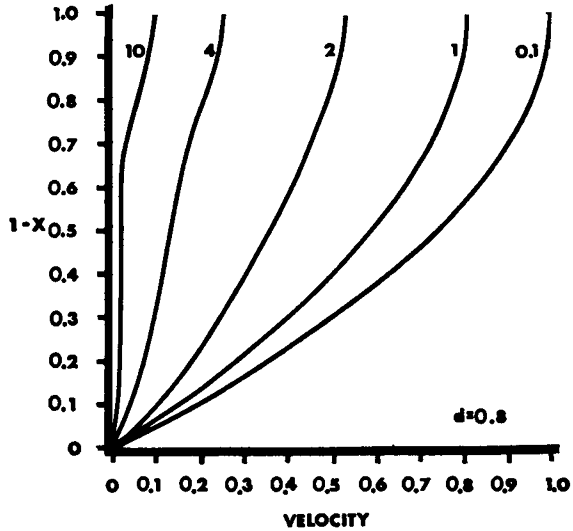

FIGURE 12

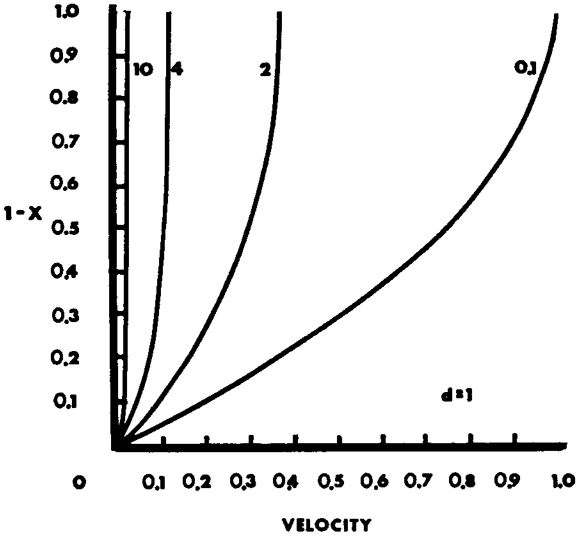

FIGURE 13

The solution for the diffusion flow is very simple:

$$J_{sd} = \{d/F_{wt} + (1 - d)/(F_{wt} + F_{wm}^{*})\}(\Delta\pi/\Delta y).$$

The flow profiles corresponding to equations 34 are plotted in Figs 9–13. Table III gives the values of the flow ratio *g* for a slit with 2*a* of 20 A as a function of *A* and *d*. Each of these results corresponds closely to the results obtained for cylindrical geometry above.

TABLE III

RATIO OF FILTRATION FLOW TO DIFFUSION FLOW g FOR A SLIT OF WIDTH $2a$ (a = 10 A) AS A FUNCTION OF THE PARAMETERS A AND d

A	d... 1.0	0.9	0.8	0.6	0.4	0.2	0
0.1	13.3	13.3	13.3	13.3	13.3	13.4	13.4
0.5	12.1	12.5	12.5	13.0	13.2	13.4	13.4
1.0	9.7	10.3	10.8	12.0	12.9	13.3	13.4
2.0	5.6	6.2	7.1	9.4	11.7	13.2	13.4
4.0	2.4	2.8	3.5	6.2	9.4	12.8	13.4
6.0	1.5	1.8	2.3	4.3	7.9	12.2	13.4
8.0	1.2	1.4	1.7	3.7	7.1	11.7	13.4
10.0	1.1	1.2	1.5	3.4	6.7	11.3	13.4

DISCUSSION

We have presented a concept for modeling flows through membranes using continuum mechanics. The obvious advantage to this approach is the ability to incorporate explicitly viscous interactions (due to velocity gradients) and to model *local* water-membrane interactions with their position dependence *before* obtaining slab averages.

A number of conclusions can be drawn from the results of this calculation. First of all the two "kinds" of dissipative forces, viscous and frictional, do not show up as a simple linear combination in the resultant flow equations. This casts doubt on the procedure of modeling filtration coefficients as linear combinations of Poiseuille flow and a "diffusion term" (16, 19–21). It also casts doubt on the interpretation given to experiments done to estimate the relative diffusion flow vs. hydrodynamic flow making up the total pressure-driven water flow through membranes (22). Since the splitting of the forces into a viscous and frictional term is somewhat arbitrary in the first place (23), it is gratifying to see that this distinction is lost in the macroscopic result of the continuum mechanical model. One is tempted to suggest that the continuum mechanical approach is a handy tool for calculation of macroscopic phenomena, but like the phenomenological theory of nonequilibrium thermodynamics, it leads to no direct interpretation of mechanisms. It brings us a step closer to molecular events, however, in that we incorporate specific information about local geometry and interactions. We also provide a means by which we can proceed from molecular information through statistical mechanics to macroscopic observable phenomena. Although Bearman and Kirkwood's statistical mechanics may not be the exact means by which it will be achieved, there may be a modification of their approach which can incorporate specific information about the presence of a membrane (24, 25).

A second conclusion is that two experiments are not adequate to estimate "pore size" in any membrane where there exists a significant interaction between water and the membrane material. Some independent measurement which can be used in estimating water-membrane local frictional coefficients is necessary. One wonders whether vapor-sorbtion isotherms could yield such information. Information of this sort is not directly available for biological membranes, but can be obtained from models using biological materials (26). Alternatively, if some other means of determining the porosity of a membrane is available, the continuum mechanical theory can provide a means for calculating local water-membrane interactions. Experiments with model membranes of regular pore size coated with biological molecules (27, 28) may be very useful in this respect.

A third conclusion is that the presence of velocity gradients presents a severe limitation to the application of most popular versions of nonequilibrium thermodynamic formalism. Although the network thermodynamic approach (29, 30) seems to have a great deal of promise, it is not clear that viscous flow is within the domain of the connected topologies this approach is applicable to. Oster et al. (30) refer to work by Kron (31) in which the Navier-Stokes equations are modeled by network analogues. The work referred to is a case in which the viscous term has been deliberately omitted. The significance of this fact needs further investigation.

Some recent experimental work on water diffusion in lecithin-water lamellar systems (32–34) provides evidence for the fact that the interaction between water and/or solutes and the lipid lamellae is position dependent as this model assumes. The equations for the slitlike geometry are now being applied to this experimental data in order to calculate local lecithin-water frictional coefficients.

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