

GENERAL CONTINUUM ANALYSIS OF TRANSPORT THROUGH PORES

I. PROOF OF ONSAGER'S RECIPROCIDY

POSTULATE FOR UNIFORM PORE

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ABSTRACT The nonelectrolyte (J_s) and volume (J_v) flux across a membrane is usually described in terms of two equations derived from the theory of irreversible thermodynamics:

$$J_s = \omega RT\Delta c + (1 - \sigma_s)\bar{c}J_v$$

$$J_v = L_p(\Delta P - \sigma_v RT\Delta c)$$

where Δc and ΔP are the concentration and pressure difference; ω and L_p are the diffusive and hydraulic permeability; and σ_s and σ_v are the reflection coefficients. If Onsager's reciprocity postulate is assumed, it can be shown that σ_s and σ_v are equal. This is an important assumption because it allows one to apply the continuum theory relationship between σ_s and the pore radius to experimental measurements of σ_v . In this paper, general continuum expressions for both the J_v (a new result) and J_s equation will be derived and the equality of σ_s and σ_v proved. The proof uses only general hydrodynamic results and does not require explicit solutions for the drag coefficients or, for example, the assumption that the solute is in the center of the pore. The proof applies to arbitrarily shaped solutes and any pore whose shape is independent of axial position (uniform). In addition, new expressions for the functional dependence of ω and σ on the pore radius are derived (including the effect of the particle lying off the pore axis). These expressions differ slightly from earlier results and are probably more accurate.

INTRODUCTION

The nonelectrolyte (J_s) and volume (J_v) flux that results from an applied concentration (Δc) and pressure (ΔP) difference across a membrane can be described by the following two equations (Katchalsky and Curran, 1965):

$$J_s = \omega RT\Delta c + (1 - \sigma_s)\bar{c}J_v \tag{1}$$

$$J_v = L_p(\Delta P - \sigma_v RT \Delta c) \quad (2)$$

where ω is the diffusive permeability, L_p is the hydraulic permeability, \bar{c} is some average of the concentration on the two sides of the membrane (see below), and σ_s and σ_v are the reflection coefficients for the two equations. These equations follow directly from the assumption that the two fluxes are linearly dependent on the two driving forces (ΔP and Δc). If the theory of irreversible thermodynamics is applied to this problem and Onsager's reciprocity postulate is assumed, then it can be shown that σ_s and σ_v are equal.

In order to interpret the parameters in Eqs. 1 and 2 in terms of membrane properties (i.e. pore radius) a mechanistic model must be assumed. The continuum model is the best available for the relatively large pores that are found in most artificial membranes and in the intercellular spaces of many biological membranes (capillary endothelium, intestinal epithelium, etc.). The pores in cell membranes are probably too small to allow the use of the continuum theory and can be described more accurately by a different model (Levitt, 1974; Levitt and Subramanian, 1974). The theoretical dependence of ω and σ_s on the pore radius for the continuum model was derived by comparing a continuum expression for J_s with Eq. 1 (Bean, 1972). Since a continuum expression for J_v had not been previously derived, it was necessary to assume that Onsager's postulate was correct and that σ_s was equal to σ_v in order to relate the experimental σ_s to the pore radius. This assumption is especially important because in many experimental studies σ_s can be measured much more accurately than σ_v . In most cases it is not possible to test the equivalence of σ_s and σ_v because of experimental difficulties. It is well recognized that Onsager's postulate is only a postulate and that, if possible, it should be verified for the particular case by an exact kinetic derivation (Fitts, 1962; Duda and Vrentas, 1964). In this paper a general continuum proof of the equivalence of σ_s and σ_v will be presented.

In the first section of this paper a brief continuum derivation of the J_s equation will be described. Recently, Bean (1972) and, independently, Verniory et al. (1973) have shown that there was a serious error in the earlier continuum derivation for σ_s . The derivation of the J_s equation in this paper is based on the approach of these authors and is similar to the recent detailed analysis of Anderson and Quinn (1974). In the second section, a continuum derivation of the J_v equation will be obtained and it will be shown that σ_s equals σ_v . This equality follows from a general continuum analysis and does not require explicit solutions to the hydrodynamical equations. This is essential since a rigorous series solution is only available for the case where the solute is located on the pore axis. The derivation will be given for the special case of a cylindrical pore and spherical solute particle. It will be shown that the derivation can be easily generalized to the case of a solute of arbitrary shape and to any pore that is uniform in the axial direction. Pores whose cross section vary as a function of axial position (non-uniform) will be considered in a second paper (Levitt, 1975). In the third section, the best available explicit solutions will be applied to the general results and expressions for ω and σ in terms of the pore radius will be obtained.

LIST OF SYMBOLS

R, T, N_A	Gas constant, absolute temperature, Avogadro's number.
a, R_p, L	Solute radius; pore radius and length.
x, b	Axial position and distance from pore axis of particle center.
$\lambda, \beta, \gamma, \kappa$	Dimensionless parameters: $a/R_p, b/a, b/R_p, -(1 - \sigma)J_v/\omega RT$.
E_1, E_2, S_i	Pore ends and part of surface of particle i that is within the pore.
η	Viscosity of water.
U, \bar{V}	Linear velocity of solute and average velocity of solvent.
$\Delta\mu_w, \Delta\mu_s$	Chemical potential difference of water and solute.
\bar{V}_w, \bar{V}_s	Molar volume of water and solute.
$c, \Delta c$	Concentration and concentration difference ($c_1 - c_2$).
$\omega, \sigma_s, \sigma_v$	Diffusive permeability; reflection coefficient for solute and volume equations.
D	Total drag of water on solute.
$H_\lambda(\beta), G_\lambda(\beta), J_\lambda(\beta)$	Drag functions.
ϕ, Φ^0, Φ	Local frictional dissipation; total pore dissipation in absence and presence of solute.
L_p^0, L_p	Hydraulic permeability in absence and presence of solute.
$\Delta P^0, \Delta P$	Pressure difference in absence and presence of solute.
V^0, V, Π^0, Π	Velocity vector and pressure tensor in absence and presence of solute.

I. DERIVATION OF THE J_s EQUATION

It is shown in the appendix that the drag (D) on a particle in a pore can be written in the form:

$$D = \eta a H_\lambda [U - G_\lambda \bar{V}], \quad (3)$$

where U is the velocity of the particle, \bar{V} is the average velocity of the water, η is the viscosity, and a is the radius of the solute particle. The drag coefficients $H_\lambda(\beta)$ and $G_\lambda(\beta)$ depend on the dimensionless parameters $\lambda (= a/R_p$; where R_p is the pore radius) and $\beta (= b/a$; where b is the displacement of the particle from the pore axis). Although the drag is usually expressed in a form similar to Eq. 3, it has not been previously recognized that this is a very general result that follows directly from the "creep flow" hydrodynamic equations (see Appendix).

The J_s equation is derived by setting the drag of the water on the solute (Eq. 3) equal to the thermodynamic force on the solute:

$$-N_A^{-1}(d\mu/dx) = -N_A^{-1}[RTc^{-1}(dc/dx) + \bar{V}_s(dp/dx)] = \eta a H_\lambda [U - G_\lambda \bar{V}]. \quad (4)$$

It is assumed that the solution is ideal and that the concentration profile is given by the following relation:

$$c(x, \beta) = \begin{cases} 0 & \lambda^{-1} - 1 < \beta < \lambda^{-1} \\ c(x) & 0 \leq \beta \leq \lambda^{-1} - 1. \end{cases} \quad (5)$$

Although Eq. 5 is usually considered as an additional assumption, it is the only condition that is compatible with the continuum model. That is, in the derivation of Eq. 3 it is assumed that there is no solute-solute interaction and that the only effect of the wall is through the boundary condition that the velocity of the water is zero at the wall. Thus, at equilibrium, the solute moves in a uniform potential bounded by the wall and must have the concentration profile of Eq. 5. This equilibrium will not be disturbed by the flows that occur because radial diffusion will be very rapid in pores of the size that are found in membranes, and because the well known tendency of particles to accumulate in the center of a flowing stream is the result of the inertial terms which are not included in Eq. 3 and are negligible in these small pores.

Substituting Eq. 5 into Eq. 4 and rearranging:

$$c(x)U(x, \beta) = -(N_A \eta a H_\lambda)^{-1} [RT(dc/dx) + \bar{V}_s c(dp/dx)] + G_\lambda \bar{V} c. \quad (6)$$

The solute flux is then equal to:

$$\begin{aligned} J_s &= \int_0^{R_p} c U(2\pi b) db = 2\pi a^2 \int_0^{\lambda^{-1}-1} c(x) U(x, \beta) \beta d\beta \\ &= -2\pi a (\eta N_A)^{-1} [RT(dc/dx) + \bar{V}_s c(dp/dx)] \int_0^{\lambda^{-1}-1} H_\lambda^{-1} \beta d\beta \\ &\quad + 2\pi a^2 \bar{V} c \int_0^{\lambda^{-1}-1} G_\lambda \beta d\beta. \end{aligned} \quad (7)$$

Finally, integrating Eq. 7 across the length of the pore (in the steady state J_s is independent of x):

$$J_s = \omega [RT\Delta c + \bar{V}_s \overline{c\Delta P}] + (1 - \sigma_s) \bar{V}_w J_w \bar{c}, \quad (8)$$

where the following definitions have been used:

$$\begin{aligned} \omega &= (2\pi a / N_A \eta L) \int_0^{\lambda^{-1}-1} H_\lambda^{-1} \beta d\beta; & \sigma_s &= 1 - 2\lambda^2 \int_0^{\lambda^{-1}-1} G_\lambda \beta d\beta; \\ \bar{c} &= (1/L) \int_0^L c(x) dx; & \overline{c\Delta P} &= (1/L) \int_0^L c dP; \end{aligned} \quad (9)$$

and where $\pi R_p^2 \bar{V}$ has been set equal to the volume flux of the water ($\bar{V}_w J_w$). Substituting the relation:

$$\bar{V}_w J_w = J_v - \bar{V}_s J_s \quad (10)$$

into Eq. 8:

$$J_s [1 + (1 - \sigma_s) \bar{c} \bar{V}_s] = \omega [RT\Delta c + \bar{V}_s \overline{c\Delta P}] + (1 - \sigma_s) \bar{c} J_v. \quad (11)$$

Since the integral $\overline{c\Delta P}$ is of the order $\bar{c}\Delta P$ and for a dilute solution $\bar{c}\bar{V}_s \ll 1$, the terms involving \bar{V}_s in Eq. 11 can be dropped and Eq. 1 is derived:

$$J_s = \omega RT\Delta c + (1 - \sigma_s)\bar{c}J_v. \quad (1)$$

Eq. 9 relates the parameters ω and σ_s of Eq. 1 to the pore radius and it provides a precise definition of \bar{c} (which is left rather ambiguous in the thermodynamic derivations). Actually, Eq. 1 is not really a solution since \bar{c} is not known and is a function of J_v and Δc . For an exact solution, Eq. 7 should be considered as a differential equation for c (neglecting the pressure term) which can be solved to yield:

$$\begin{aligned} J_s &= (1 - \sigma_s)J_v(c_2e^{\kappa} - c_1)/(e^{\kappa} - 1) \\ \kappa &= -(1 - \sigma_s)J_v/\omega RT. \end{aligned} \quad (12)$$

Although Eq. 12 is a more complete solution, it does not allow a separation of J_s into a convective and diffusive term. A more useful expression can be obtained by solving the differential Eq. 7 for $c(x)$:

$$c(x) = (c_2 - c_1e^{-\kappa})(1 - e^{-\kappa x/L})/(1 - e^{-\kappa}) + c_1e^{-\kappa x/L}. \quad (13)$$

Substituting this equation for $c(x)$ into the definition of \bar{c} (Eq. 9):

$$\bar{c} = (c_2 - c_1e^{-\kappa})/(1 - e^{-\kappa}) + (c_1 - c_2)/\kappa. \quad (14)$$

If the exponentials in Eq. 14 are expanded (to third order) a useful approximation to \bar{c} is obtained:

$$\bar{c} = \frac{1}{2}(c_1 + c_2) + (\kappa/12)(c_2 - c_1). \quad (15)$$

This is a remarkably accurate approximation. For a κ of ± 1.5 , \bar{c} (Eq. 15) differs from the exact \bar{c} (Eq. 14) by only 1%. For a κ of ± 2.5 , the error is less than 6%. Since in most membrane studies κ is less than 1.5, no significant error is introduced if Eq. 1 with \bar{c} (Eq. 15) substituted for \bar{c} is used in place of the exact expression for J_s .

II. DERIVATION OF J_s EQUATION

As in the case of the J_v equation, the derivation is based on a combination of continuum hydrodynamics and thermodynamics. Consider the situation where a membrane separates two homogeneous compartments with concentrations and pressures of c_1, P_1 and c_2, P_2 . First consider the case in which the transfer of water (J_w , mol/s) and solute (J_s) between the reservoirs is carried out reversibly by going through some apparatus W . (A set of pistons and semipermeable membranes can be set up to carry out this reversible transfer.) If the system is isothermal then the rate of reversible work (\dot{W}) associated with the transfer is:

$$\dot{W} = \Delta\mu_w J_w + \Delta\mu_s J_s, \quad (16)$$

where $\Delta\mu_w$ and $\Delta\mu_s$ are the chemical potential differences on the two sides of the membrane for the water and solute. During the spontaneous irreversible process, all this work must be dissipated through frictional loss in the pore. In this section, an exact expression for the frictional dissipation (Φ) in the continuum model will be derived. It will be shown that if this expression is set equal to Eq. 16, the J_s equation can be derived.

The basic ideas of this derivation can be simply illustrated by first considering the special case where the membrane is perfectly semipermeable (impermeable to the solute, $J_s = 0$). It will be assumed throughout this section that the solution is dilute and ideal so that:

$$\Delta\mu_w = (\Delta P - RT\Delta c)\bar{V}_w. \quad (17)$$

Since $J_s = 0$, $J_v = \bar{V}_w J_w$, and Eq. 16 becomes:

$$\dot{W} = \Phi = (\Delta P - RT\Delta c)J_v. \quad (18)$$

The derivation is based on comparing this expression with the energy that would be dissipated (Φ^0) for the situation where exactly the same flow of water (J_v) occurred, but there was no solute present in the bulk solution:

$$\Phi^0 = \Delta P^0 J_v, \quad (19)$$

where ΔP^0 is the pressure difference that would be needed to produce this volume flow. If the membrane is semipermeable and the pores are uniform, the solute must be completely excluded from the membrane and the flows occurring in the pore must be the same in the two cases and Φ must equal Φ^0 . Then, defining L_p^0 by the relation:

$$J_v = L_p^0 \Delta P^0$$

and setting Eq. 18 equal to Eq. 19:

$$J_v = L_p^0 (\Delta P - RT\Delta c) \quad (20)$$

Eq. 20 is a special case of Eq. 2 ($\sigma = 1$). It is a completely general derivation and does not depend on any continuum assumptions. If it is assumed that the pore water is a continuum (and one neglects entrance effects, etc.) then L_p^0 is given by the Poiseuille relation:

$$L_p^0 = \pi R_p^4 / 8\eta L \quad (21)$$

where η is the viscosity of water.

The derivation for the general case follows the same procedure. The energy dissipated in the pore (Φ) is obtained from Eqs. 16 and 17:

$$\Phi = (\Delta P - RT\Delta c) \bar{V}_w J_w + \Delta\mu_s J_s. \quad (22)$$

Again, Φ is compared with the energy that would be dissipated if the same water flow (J_w) occurred and there were no solutes in the bulk solutions (ΔP^0 is the pressure necessary to produce the flow $\bar{V}_w J_w$):

$$\Phi^0 = \Delta P^0 \bar{V}_w J_w \quad \text{and} \quad \bar{V}_w J_w = L_p^0 \Delta P^0. \quad (23)$$

Defining Φ^+ as the difference between these two terms:

$$\Phi^+ = \Phi - \Phi^0 = [\Delta P - \Delta P^0 - RT\Delta C_s] \bar{V}_w J_w + \Delta\mu_s J_s. \quad (24)$$

For the creeping or low Reynolds number flow approximation which is applicable for these pores the local energy dissipation (ϕ) is given by (Happel and Brenner, 1965):

$$\phi = \nabla \cdot (V \cdot \Pi), \quad (25)$$

where V is the velocity vector of the water and Π is the pressure tensor. The total energy dissipated in the pore is given by the integral of ϕ over all the water in the pore:

$$\Phi = \int_v \phi \, dv, \quad (26)$$

where v is the water volume and does not include the volume occupied by the solute. Applying Green's theorem to Eq. 26, the volume integral can be converted to a surface integral:

$$\Phi = \int_s V \cdot \Pi \cdot ds, \quad (27)$$

where the surface of the water (S) is made up of the pore walls and ends and the surface of the solute particles contained in the pores. The integral over the pore wall surface is zero because of the boundary condition that $V = 0$ at the pore walls. Thus Eq. 27 can be written as:

$$\Phi = \int_{E_1 + E_2 + \sum_j S_j} V \cdot \Pi \cdot ds, \quad (28)$$

where E_1 and E_2 are the surfaces at the pore ends and are assumed to lie just outside the pore in the bulk solutions (see Fig. 1) and S_j is the surface of the j th solute par-

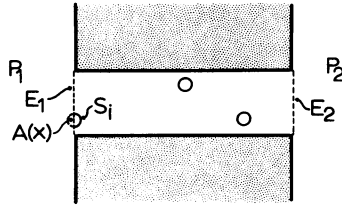


FIGURE 1 Diagram of pore used in text. The ends of the pore (E_1, E_2) lie just outside the pore in the bulk solutions which have bulk pressures P_1 and P_2 . Three particles are shown. The surface S includes only that part of the particle surface that lies within the pore (see S_i). The surface $A(x)$ is the intersection of E_1 and particle i .

ticle in the pore. Similarly:

$$\Phi^0 = \int_{E_1+E_2} V^0 \cdot \Pi^0 \cdot ds, \quad (29)$$

where the superscript 0 refers to the condition when no solute is present. Subtracting Eq. 29 from Eq. 28:

$$\Phi^+ = \Phi - \Phi^0 = \int_{E_1+E_2+\sum S_j} V \cdot \Pi \cdot ds - \int_{E_1+E_2} V^0 \cdot \Pi^0 \cdot ds. \quad (30)$$

Eq. 30 can be rearranged so that it is the sum of six terms

$$\begin{aligned} \Phi^+ = & \int_{E_1+E_2} (V - V^0) \cdot \Pi \cdot ds - \int_{E_1+E_2} (V^0 - V) \cdot \Pi^0 \cdot ds \\ & + \sum_j \int_{S_j} V \cdot \Pi \cdot ds + \left[\int_{E_1+E_2+\sum S_j} V^0 \cdot \Pi \cdot ds - \int_{E_1+E_2+\sum S_j} V \cdot \Pi^0 \cdot ds \right] \\ & + \sum_j \int_{S_j} V \cdot \Pi^0 \cdot ds - \sum_j \int_{S_j} V^0 \cdot \Pi \cdot ds. \end{aligned} \quad (31)$$

These six terms will be separately evaluated in the following paragraphs.

(1,2) Since the surfaces E_1 and E_2 are just outside the pore in the bulk solutions (see Fig. 1), the pressure tensor on these surfaces is just the bulk pressures (P_1 and P_2). Thus, integral 1 can be written as:

$$\int_{E_1+E_2} (V - V^0) \cdot \Pi \cdot ds = P_1 \int_{E_1} (V - V^0) \cdot ds + P_2 \int_{E_2} (V - V^0) \cdot ds. \quad (32)$$

Both of the integrals on the right side of Eq. 32 are zero since the velocity field V^0 was chosen so that it had the same net water flow as in the case when solute was present, that is:

$$\int_{S'} V \cdot ds = \int_{S'} V^0 \cdot ds, \quad (33)$$

where S' is any cross-sectional surface in the pore. The second term in Eq. 31 is zero for the same reason.

(3) On the surface of the solute particle one has the boundary condition that $V = U_j$ (plus a rotational term that is perpendicular to ds) where U_j is the velocity of the j th particle. Thus the third term can be written as:

$$\sum_j \int_{S_j} V \cdot \Pi \cdot ds = \sum_j U_j \int_{S_j} \Pi \cdot ds = \sum U_j D_j \quad (34)$$

where D_j is the drag exerted on the j th particle by the water (see Eq. 74). The average value of this sum is equal to the following integral:

$$\sum U_j D_j = \int_v U D \rho dV, \quad (35)$$

where $\rho(x, b)$ is the probability per unit volume of finding a particle at a given position in the pore and is proportional to the concentration. This average can be regarded either as the value of the sum averaged over a large number of pores or for a single pore averaged over a period of time. As in the derivation of the J_s equation, it will be assumed that the drag is equal to the thermodynamic force. Substituting $N_A c$ for ρ and $-N_A^{-1}(d\mu_j/dx)$ for D_j , the third term in Eq. 31 becomes:

$$\sum_j \int_{S_j} V \cdot \Pi \cdot ds = \sum U_j D_j = - \int_0^L dx \frac{d\mu}{dx} \int_0^{R_p} c U 2\pi b db = \Delta\mu_s J_s. \quad (36)$$

(4) The fourth term in Eq. 31 (brackets) is zero due to a general theorem which is valid for "creep" flow. This theorem, which is derived and discussed in detail by Happel and Brenner (1965) states that:

$$\int_S ds \cdot \Pi' \cdot V'' = \int_S ds \cdot \Pi'' \cdot V', \quad (37)$$

where S is a closed surface bounding any fluid and (V', Π') and (V'', Π'') are the velocity and stress fields corresponding to any two motions of the same fluid.

(5) Applying the boundary condition that $V = U_i$ on the surface of the sphere, the fifth term in Eq. 31 can be written as:

$$\sum_j \int V \cdot \Pi^0 \cdot ds = \sum_j U_j \int_{S_j} \Pi^0 \cdot ds. \quad (38)$$

Now for solute particles that are contained entirely within the pore the surface integral can be converted into a volume integral by Green's theorem:

$$\int_{S_j} \Pi^0 \cdot ds = \int_{V_j} \nabla \cdot \Pi^0 dV = 0. \quad (39)$$

The volume integral equals zero because $\nabla \cdot \Pi$ is zero for any creeping flow. Only particles that are not completely contained in the pore contribute to the sum. Fig. 1 shows an example of such a particle which intersects the surface E_1 . Consider the volume that is bounded by S_j (the part of the sphere surface that lies within the pore) and $A(x)$ where A is the intersection of the sphere and E_1 . Since, as in Eq. 39, the integral over any closed surface is zero, the surface integral over S_j must be equal to minus the integral over $A(x)$ and since Π^0 on the surface A is equal to the bulk pressure (P_1^0) the integral in Eq. 38 can be written in the form:

$$\int_{S_j} \Pi^0 \cdot ds = P_1^0 \int_{A(x)} ds = P_1^0 A(x). \quad (40)$$

The summation in Eq. 38 is now over only the particles which intersect the ends. As in Eq. 35 this summation can be replaced by the following integral:

$$\sum_j U_j \int_{S_j} \Pi^0 \cdot ds = P_1^0 \int_{-a}^a dx A(x) \int_0^{R_p} (N_A c) U(2\pi b) db = J_s \bar{V}_s P_1^0. \quad (41)$$

The integral over the particles which intersect E_2 gives rise to a similar expression ($-J_s \bar{V}_s P_2$) so that the fifth term becomes:

$$\sum_j \int_{S_j} V \cdot \Pi^0 \cdot ds = \Delta P^0 \bar{V}_s J_s. \quad (42)$$

(6) Only the last term in Eq. 31 remains to be evaluated:

$$\sum_j \int_{S_j} V^0 \cdot \Pi \cdot ds. \quad (43)$$

This term contains all the physics of the problem and an exact expression for it requires a solution of the continuum hydrodynamics. Fortunately, an exact solution is not needed in order to show that the J_v equation has the form of Eq. 2 and to identify σ_v . It will again be assumed that the solution is dilute so that solute-solute interactions can be neglected and the integral in Eq. 43 can be evaluated for the case where no other solute particles are present. Three different conditions of the solute velocity (U), average water velocity (\bar{V}), and pressure tensor (Π) will be considered: condition I, $U_1 = U$, $\bar{V}_1 = 0$, Π_1 ; condition II, $U_{II} = 0$, $\bar{V}_{II} = \bar{V}$, Π_{II} ; and condition III, no sol-

utes present, $\Pi_{III} = \Pi^0$, and $V = V^0$ where V^0 is given by Poiseuille's law:

$$V^0 = 2\bar{V}(1 - b^2/R_p^2), \quad (44)$$

and where the total water flow is equal to $\bar{V}_w J_w$. Since the "creep flow" hydrodynamic equations are linear (see Appendix), the pressure tensor (Π) is just equal to the sum of the pressure tensors for the two special boundary conditions ($\Pi_1 + \Pi_2$). Thus, the integral in Eq. 43 can be reduced to the sum of the integrals for Π_1 and Π_2 . The reciprocity theorem, Eq. 37, for the case where the surface consists of the one solute particle (S), the pore walls, and the ends (E_1, E_2) in the bulk solution can be written as:

$$\int_{E_1+E_2+S} V' \cdot \Pi'' \cdot ds = \int_{E_1+E_2+S} V'' \cdot \Pi' \cdot ds. \quad (45)$$

Since the velocity is zero on the pore walls, this surface has not been included in Eq. 45. Applying this theorem to the flow conditions I and III defined above:

$$\Delta P_1 \bar{V}_w J_w + \int_S V^0 \cdot \Pi_1 \cdot ds = U \int_S \Pi^0 \cdot ds. \quad (46)$$

As in Eq. 39, the integral on the right side is zero and:

$$\int_S V^0 \cdot \Pi_1 \cdot ds = -\Delta P_1 \bar{V}_w J_w. \quad (47)$$

Applying the theorem (Eq. 45) again to the flow conditions I and II:

$$\Delta P_1 \bar{V}_w J_w = U \int_S ds \cdot \Pi_{II} = U D_{II} = -\eta a H_\lambda G_\lambda U \bar{V}, \quad (48)$$

where Eq. 3 with $U = 0$ has been substituted for D_{II} . From Eqs. 47 and 48:

$$\int_S V^0 \cdot \Pi_1 \cdot ds = +\eta a H_\lambda G_\lambda U \bar{V}. \quad (49)$$

Unfortunately, the integral involving Π_{II} cannot be evaluated this easily. However, this integral can be approximated by substituting Π'_I for Π_{II} where Π'_I is chosen so that the drag D'_I is equal to D_{II} . That is, the integral can be written in the form:

$$\int_S V^0 \cdot \Pi_{II} \cdot ds = \int_S V_0 \cdot \Pi'_I \cdot ds + \eta a \bar{V}^2 J_\lambda(\beta), \quad (50)$$

where

$$D_{II} = \int_S \Pi_{II} \cdot ds = \int_S \Pi'_I \cdot ds = D'_I. \quad (51)$$

The second term on the right in Eq. 50 is the correction to the approximation. The dependence of this term on \bar{V}^2 follows from a dimensional analysis similar to that carried out in the Appendix. An estimate of J_λ for the case where $\lambda \ll 1$ is given below. Substituting Eq. 3 for D_{II} and D'_I into Eq. 51:

$$-\eta a G_\lambda H_\lambda \bar{V} = \eta a H_\lambda U'. \quad (52)$$

Solving this equation for U' and substituting into Eqs. 49 and 50:

$$\int_S V^0 \cdot \Pi_{II} \cdot ds = -\eta a H_\lambda G_\lambda^2 \bar{V}^2 + \eta a \bar{V}^2 J_\lambda. \quad (53)$$

The integral in Eq. 43 is then:

$$\begin{aligned} \int_S V^0 \cdot \Pi \cdot ds &= \int_S V^0 \cdot (\Pi_I + \Pi_{II}) \cdot ds = -\eta a G_\lambda \bar{V} (H_\lambda U - H_\lambda G_\lambda \bar{V}) + \eta a \bar{V}^2 J_\lambda \\ &= G_\lambda \bar{V} D + \eta a \bar{V}^2 J_\lambda, \end{aligned} \quad (54)$$

where D is the total drag (Eq. 3). Substituting the gradient of the chemical potential for the drag (see Eq. 4) and replacing the summation in Eq. 43 by an integral over the pore volume weighted by the concentration (see Eqs. 35 and 36), the sixth term in Eq. 31 becomes (substituting $\bar{V}_w J_w / \pi R_p^2$ for \bar{V}):

$$\begin{aligned} \sum_j \int_{S_j} V^0 \cdot \Pi \cdot ds &= 2 \bar{V}_w J_w \lambda^2 \bar{G}_\lambda R T \Delta c + 2 \eta L N_A \lambda^4 (\bar{V}_w J_w)^2 \bar{c} \bar{J}_\lambda / \pi a \\ \bar{G}_\lambda &= \int_0^{\lambda^{-1}-1} G_\lambda \beta d\beta; \quad \bar{J}_\lambda = \int_0^{\lambda^{-1}-1} J_\lambda \beta d\beta, \end{aligned} \quad (55)$$

and where the pressure term has been dropped as in Eq. 18 because the solution is dilute.

Substituting Eqs. 36, 42, and 55 into Eq. 31, equating Eq. 31 to Eq. 24, and rearranging terms:

$$\Delta P^0 J_v - 2 \eta L N_A \lambda^4 (\pi a)^{-1} (\bar{V}_w J_w)^2 \bar{J}_\lambda \bar{c} = [\Delta P - R T \Delta c (1 - 2 \lambda^2 \bar{G}_\lambda)] \bar{V}_w J_w. \quad (56)$$

Substituting $\bar{V}_w J_w / L_p^0$ for ΔP^0 (Eq. 23):

$$J_v - 2 \eta L N_A \lambda^4 (\pi a)^{-1} \bar{J}_\lambda \bar{c} \bar{V}_w J_w L_p^0 = L_p^0 [\Delta P - R T \Delta c (1 - 2 \bar{G}_\lambda \lambda^2)]. \quad (57)$$

Since the second term on the left is second order to begin with, $\bar{V}_w J_w$ can be approximated by J_v and the final form of the equation is obtained:

$$\begin{aligned} J_v &= L_p[\Delta P - (1 - 2\lambda^2 \bar{G}_\lambda)RT\Delta c] \\ L_p &= L_p^0/(1 + K\bar{c}) \\ K &= -2\eta L N_A \lambda^4 \bar{J}_\lambda L_p^0/\pi a = -\frac{1}{4}N_A a^3 \bar{J}_\lambda, \end{aligned} \quad (58)$$

where in the second quality for K , Eq. 21 has been substituted for L_p^0 . It can be seen that Eq. 58 is of the same form as Eq. 2 and that σ_v is:

$$\sigma_v = 1 - 2\lambda^2 \bar{G}_\lambda = 1 - 2\lambda^2 \int_0^{\lambda^{-1}-1} G_\lambda \beta d\beta = \sigma_s. \quad (59)$$

This completes the general proof of the equality of σ_s (Eq. 9) and σ_v .

This result is in apparent disagreement with the recent results of Anderson and Malone (1974). These authors derived an expression for σ_v which differs slightly from the value of σ_s obtained by Bean (1972). On the basis of this disagreement, Anderson and Malone concluded that, in general, $\sigma_v \neq \sigma_s$. However, their derivation of σ_v is based on a set of assumptions and approximations that are significantly different from the continuum assumptions used by Bean in the derivation of σ_s . In fact, considering the differences in the two approaches, the agreement between the two values of σ is rather surprising. In contrast, I have shown in this paper that within the framework of the continuum theory and its assumptions, σ_s and σ_v are identical.

The function K in Eq. 59 can be easily determined for the case where the pore is much larger than the particle ($\lambda \ll 1$). Using Eq. 21, L_p can be written in the form:

$$L_p = \pi R_p^4/8\eta' L; \quad \eta' = \eta(1 + K\bar{c}), \quad (60)$$

where η' is the "equivalent viscosity" of the pore fluid. For the case where the particles in the suspension are small compared to the dimensions of the container, η' can be obtained from the solution (first due to Einstein, see Happel and Brenner, 1965):

$$\eta' = \eta(1 + (5/2)\alpha), \quad (61)$$

where α is the fractional volume occupied by the particles:

$$\alpha = \bar{V}_s \bar{c}. \quad (62)$$

Thus, comparing Eqs. 60 and 61, the first order approximation for K can be determined:

$$K = (5/2)\bar{V}_s.$$

And, for spherical particles of radius a (see Eq. 58):

$$\bar{J}_\lambda \approx 40\pi/3. \quad (63)$$

The proof of the equality of σ_s and σ_v can be easily generalized to the case of a non-spherical particle in a noncylindrical pore that is uniform in the x (axial) direction. For this general case the drag coefficients H and G would be characterized by some shape function instead of just the parameter λ . The drag coefficients would also become functions of two center of mass and three orientation variables and the integrals in Eqs. 9 and 59 would be over all these five variables. It will be shown in a second paper that for the case where the shape of the pore is a function of x (nonuniform) then only in certain special limits can σ_s and σ_v be defined and shown to be equal.

III. RELATIONSHIP BETWEEN DRAG COEFFICIENTS AND PORE RADIUS

The results in sections I and II have only required the knowledge that the drag could be written in the form of Eq. 3. In order to relate ω and σ to the pore radius, the hydrodynamic equations must be solved and explicit expressions for $H_\lambda(\beta)$ and $G_\lambda(\beta)$ obtained. A rigorous series solution to these equations is only available for the special case where the particle is on the pore axis ($\beta = 0$) and the problem becomes two-dimensional. The results of Haberman and Sayre (H-S) (1958) will be used here. Expressing the results of H-S in the form of Eq. 3, the functions $H_\lambda(0)$ and $G_\lambda(0)$ can be identified:

$$H_\lambda(0) = 6\pi K_1,$$

$$G_\lambda(0) = 2(1 - 2/3 \lambda^2 - 0.20217 \lambda^5)/(1 - 0.75857 \lambda^5),$$

$$K_1 = h(\lambda)(1 - 0.75857 \lambda^5),$$

$$1/h(\lambda) = 1 - 2.1054 \lambda + 2.0805 \lambda^3 - 1.7068 \lambda^5 + 0.72603 \lambda^6. \quad (64)$$

In order to determine ω and σ , H_λ and G_λ must be known for all values of β . Anderson and Quinn (1974) approximated $H_\lambda(\beta)$ by empirically connecting the known solution for a particle near a plane wall with the known solution for the particle on the axis ($\beta = 0$). For the lack of a better solution, it has usually been assumed that G does not depend on β .

In this section the solution of Greenstein and Happel (G-H) (1968) will be used to derive expressions for $H_\lambda(\beta)$ and $G_\lambda(\beta)$ which should be more accurate than previous estimates. This solution is based on a series of reflections and is supposed to provide a solution accurate to order λ^2 . The G-S solution for the drag is:

$$D = 6\pi\eta a \{ [U - 2\bar{V}(1 - \gamma^2)][1 + f(\gamma)\lambda + f^2(\gamma)\lambda^2] + 4/3 \bar{V}\lambda^2 \} + 0(\lambda^3)$$

$$\gamma = b/R_p = \beta\lambda^{-1} \quad (65)$$

where $f(\gamma)$ is tabulated by G-H for γ varying from 0 to 1. Since $f(0) = 2.105$, the following relation is correct to order λ^2 :

$$1 + f(0)\lambda + f^2(0)\lambda^2 = 1/(1 - f(0)\lambda) + O(\lambda^3) = h(\lambda) + O(\lambda^3).$$

Using this result, expressions for the drag coefficients can be obtained which are identical to those of H-S (Eq. 64) for $\beta = 0$, and, to order λ^2 , are equivalent to the solution of G-H when $\beta \neq 0$:

$$\begin{aligned} H_\lambda(\beta) &= H_\lambda(0)[g(\gamma)/g(0)], \\ G_\lambda(\beta) &= 2(1 - 2/3\lambda^2 - 0.20217\lambda^5 - \gamma^2)/(1 - 0.75857\lambda^5), \\ g(\gamma) &= 1 + f(\gamma)\lambda + f^2(\gamma)\lambda^2. \end{aligned} \quad (66)$$

These expressions for H and G are very accurate for $\beta = 0$ and should at least provide a good approximation when $\beta \neq 0$. Substituting this result for H_λ into Eq. 9:

$$\omega = 2\pi a(\eta LN_A)^{-1} \int_0^{\lambda^{-1}-1} H_\lambda^{-1} \beta d\beta = a(6\eta LN_A K_1)^{-1} \lambda^{-2} (1 - \lambda)^2 g(0)/\bar{g},$$

where \bar{g} is defined by:

$$1/\bar{g} = \int_0^{\lambda^{-1}-1} g^{-1} \beta d\beta / \int_0^{\lambda^{-1}-1} \beta d\beta = 2(1 - \lambda)^{-2} \lambda^2 \int_0^{\lambda^{-1}-1} g^{-1} \beta d\beta. \quad (67)$$

The unrestricted permeability (ω_0) is defined by:

$$\omega_0 RT \Delta c = \pi R_p^2 D_0 \Delta c / L \quad \text{or} \quad \omega_0 = a / (6\eta LN_A \lambda^2), \quad (68)$$

where $D_0 (= \kappa T / 6\pi \eta a)$ is the unrestricted (free) diffusion coefficient. The restricted permeability is then:

$$\omega/\omega_0 = [(1 - \lambda)^2 / K_1] [g(0)/\bar{g}] = [\omega/\omega_0]_a [g(0)/\bar{g}], \quad (69)$$

where the subscript a indicates the expression for ω/ω_0 , that would be found if it was assumed that H_λ was equal to $H_\lambda(0)$ for all values of β . The ratio $g(0)/\bar{g}$ should provide at least a first order correction to this "axial" approximation. This ratio can be evaluated by numerically integrating Eq. 67 using the tabulated values of G-H. These are shown in Table I. It can be seen that this ratio is very close to 1 for all values of λ which indicates that the "axial" approximation is satisfactory. This conclusion is supported by the observation that experimental measurements of ω/ω_0 in nearly uniform pores are accurately described by the "axial" approximation (Bean, 1972).

TABLE I
CORRECTION TO AXIAL APPROXIMATION AS A FUNCTION OF λ (SEE EQ. 69)

λ	$g(0)/\bar{g}$	λ	$g(0)/\bar{g}$
0.0	1.0	0.33	0.996
0.03	0.968	0.36	1.003
0.06	0.947	0.39	1.009
0.09	0.940	0.42	1.013
0.12	0.940	0.45	1.015
0.15	0.947	0.48	1.019
0.18	0.953	0.51	1.022
0.21	0.962	0.54	1.022
0.24	0.971	0.57	1.022
0.27	0.980	0.6	1.022
0.30	0.990		

The expression for σ can be obtained by substituting the expression for G_λ (Eq. 66) in Eq. 9 (or 59) (neglecting the terms of order λ^5):

$$\begin{aligned} \sigma &= 1 - 2\lambda^2 \int_0^{\lambda^{-1}-1} G_\lambda \beta d\beta = 1 - 4 \int_0^{1-\lambda} \left(1 - \frac{2}{3}\lambda^2 - \gamma^2\right) \gamma d\gamma \quad (70) \\ &= \frac{16}{3}\lambda^2 - \frac{20}{3}\lambda^3. \end{aligned}$$

This result differs slightly from that of Bean (1972) (σ_B) who defined G in terms of the local velocity $V(\beta)$ rather than \bar{V} and assumed that it did not depend on β :

$$\sigma_B = 1 - 4\left(1 - \frac{2}{3}\lambda^2\right) \int_0^{1-\lambda} (1 - \gamma^2) \gamma d\gamma = \frac{14}{3}\lambda^2 - 4\lambda^3. \quad (71)$$

Although Eq. 70 should be more accurate than Eq. 71 since it is based on a better estimate of the dependence of G on β , the differences between the two results are so small that it would be difficult to distinguish between them experimentally.

APPENDIX

All the general results in the text require only the knowledge that the drag can be written in the form:

$$D = \eta a H_\lambda (U - G_\lambda \bar{V}). \quad (72)$$

For spherical particles in a cylindrical pore the drag functions H and G depend only on the two parameters λ, β . If the particles are nonspherical and the pore is not cylindrical (but uniform in the axial direction) then the functions will depend on additional shape and position variables. In order to demonstrate the generality of Eq. 72 (which has not been previously recognized) it is necessary to first provide a brief introduction to the hydrodynamics.

The inertial terms in the general Navier-Stokes equations can be neglected for the flows that occur in membranes so that the velocity components of the water (V_1, V_2, V_3) satisfy the differential equations for "creep" flow:

$$\partial P / \partial X_i = \eta[(\partial^2 V_i / \partial X_1^2) + (\partial^2 V_i / \partial X_2^2) + (\partial^2 V_i / \partial X_3^2)]; \quad i = 1, 2, 3 \quad (73)$$

where P is the hydrostatic pressure and η is the viscosity. The development and solution of these equations for a large number of problems is well described in the monograph of Happel and Brenner (1965). For the calculation of the drag on a solute particle it is usually assumed that the solution is so dilute that one can neglect interactions between particles. That is Eq. 73 is solved for the boundary conditions that (1) the velocity on the pore wall is zero, (2) the velocity at the surface of the sphere is equal to the sphere velocity, and (3) at positions far upstream and downstream of the particle the velocity profile is described by Poiseuille's law (Eq. 44). The drag (D) on the particle is then given by the integral of the pressure tensor (Π) over the surface (S) of the particle:

$$D = \int_S \Pi \cdot ds \quad (74)$$

where

$$\Pi_{ij} = -P \delta_{ij} + \eta[(\partial V_i / \partial X_j) + (\partial V_j / \partial X_i)]; \quad i, j = 1, 2, 3 \quad (75)$$

These equations are difficult to solve. The only rigorous solutions available are for the special case where the solute is in the center of the pore and the problem can be reduced to a two-dimensional form. The derivation of Eq. 72, however, requires only the following simple dimensional analysis.

In general, one wants to solve the set of differential equations (Eq. 73) for the following boundary conditions:

(1) On pore wall ($X_2^2 + X_3^2 = R_p^2$): $V_i = 0$; $i = 1, 2, 3$;

(2) On sphere surface [$X_1^2 + (X_2 - b)^2 + X_3^2 = a^2$]:

$$V_1 = U + a\omega g_1(\theta, \phi); \quad V_2 = a\omega g_2(\theta, \phi); \quad V_3 = 0;$$

(3) As $X_1 \rightarrow \pm \infty$: $V_1 = 2\bar{V}[1 - (X_2^2 + X_3^2)/R_p^2]$; $V_2 = V_3 = 0$. (76)

The sphere is centered at $X_1 = 0$, $X_2 = b$, and $X_3 = 0$ where b is the distance from the sphere center to the pore axis. If the sphere is off the axis ($b \neq 0$) it will spin with some velocity ω about the X_3 axis and g_1 and g_2 are combinations of sin and cos functions of the orientational variables θ and ϕ . The drag (D) and torque (T) on the sphere are given by:

$$D = \int_S \Pi \cdot R ds; \quad T = \int_S R \times \Pi ds \quad (77)$$

where Π is the pressure tensor and R is the radial vector of the sphere and the integral is over the sphere surface (θ, ϕ). Since Eq. 73 is linear, the solution can be written as a superposition of the solutions for the following three simplified boundary conditions: (i) $\bar{V} = 0$,

$U = 0, \omega \neq 0$; (ii) $\bar{V} = 0, U \neq 0, \omega = 0$; and (iii) $\bar{V} \neq 0, U = 0, \omega = 0$. First, consider case (i) and define the dimensionless variables:

$$\begin{aligned} v_i &= V_i/a\omega; & x_i &= X_i/a; & p &= P/\eta\omega; \\ r &= R/R_p; & \lambda &= a/R_p; & \beta &= b/a. \end{aligned} \quad (78)$$

In terms of these variables, Eq. 73 and the boundary conditions (Eq. 76) for case (i) can be written as:

$$\partial p / \partial x_i = [(\partial^2 v_i / \partial x_1^2) + (\partial^2 v_i / \partial x_2^2) + (\partial^2 v_i / \partial x_3^2)] \quad (79)$$

- (1) On $x_2^2 + x_3^2 = \lambda^{-2}$: $v_i = 0$;
- (2) On $x_1^2 + (x_2 - \beta)^2 + x_3^2 = 1$: $v_1 = g_1(\theta, \phi)$, $v_2 = g_2(\theta, \phi)$, $v_3 = 0$;
- (3) $x_1 \rightarrow \pm \infty$; $v_i = 0$.

The solution to the set of Eqs. 79 is in terms of a dimensionless pressure ($p_\lambda(\beta)$) and velocity ($v_\lambda(\beta)$) which are functions of λ and β . The pressure tensor (Eq. 75) can then be written in terms of a dimensionless tensor (π):

$$\Pi^i = \eta\omega\pi_\lambda^i(\beta). \quad (80)$$

Substituting Eq. 80 into Eq. 77, the drag and torque for case (i) can be written in the form:

$$\begin{aligned} D_i &= \eta K_\lambda^i(\beta) a^2 \omega; & T_i &= \eta E_\lambda^i(\beta) a^2 \omega \\ K_\lambda^i(\beta) &= \int_{s_\lambda(\beta)} \pi^i \cdot r ds; & E_\lambda^i(\beta) &= \int_{s_\lambda(\beta)} r x \pi_\lambda^i ds. \end{aligned} \quad (81)$$

The same procedure can be carried out for cases (ii) and (iii) with the dimensionless variable U/a and \bar{V}/a substituted respectively for ω in Eq. 78 to yield:

$$\begin{aligned} D_{ii} &= \eta a K_\lambda^{ii}(\beta) U; & T_{ii} &= \eta a E_\lambda^{ii}(\beta) U \\ D_{iii} &= \eta a K_\lambda^{iii}(\beta) \bar{V}; & T_{iii} &= \eta a E_\lambda^{iii}(\beta) \bar{V}. \end{aligned} \quad (82)$$

Since the general solution is just a linear superposition of these three solutions:

$$\begin{aligned} D &= \eta a (K_\lambda^i a \omega + K_\lambda^{ii} U + K_\lambda^{iii} \bar{V}) \\ T &= \eta a (E_\lambda^i a \omega + E_\lambda^{ii} U + E_\lambda^{iii} \bar{V}). \end{aligned} \quad (83)$$

For the solute in the pore, the torque (T) is zero and the drag (D) will be equated with the gradient of the chemical potential. Setting T equal to zero and solving for ω :

$$\omega = -UE_\lambda^{ii}/E_\lambda^i - \bar{V}E_\lambda^{iii}/E_\lambda^i. \quad (84)$$

If this expression for ω is substituted into D (Eq. 83), the drag can be written in the form:

$$D = \eta a(H_\lambda U + K_\lambda \bar{V}).$$

Finally, defining the function $G_\lambda = -K/H$, Eq. 72 is obtained.

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