

Molecular models for permeation through thin membranes: the effect of hydrodynamic interaction on permeability

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A variational method involving minimization of the energy dissipation rate which was previously developed for transport in polymer systems is applied here to flow of a continuum solvent through a thin membrane. The membrane is represented by an array of spherical particles undergoing Brownian motion, subject to various interactions with one another and with the motion of the solvent. General upper bounds on the solvent permeability of the membrane are obtained in terms of equilibrium distribution functions, and applications of the method are illustrated for the case where membrane elements are confined to a plane. Calculations which treat all beads equivalently give permeability estimates whose dependence on the number n of beads per unit area of membrane has the form, at low n ,

$$\kappa = (6\pi\eta n)^{-1}(1 - \alpha n + \dots),$$

where η is the solvent viscosity and α is a constant. More-elaborate trials which allow the drag on a bead to be influenced by the distribution of other beads in the vicinity give the stronger bounding estimate

$$\kappa = (6\pi\eta n)^{-1}(1 + \alpha'n \ln n + \dots).$$

Comparison with a self-consistent field approach suggests that this logarithmic behaviour is the true first-order correction.

1. Introduction

The permeability of membranes to solvent and solute flows has been extensively studied in the literature, particularly with regard to biological systems and desalination processes. Theoretical treatments are still for the most part of a macroscopic nature, the most common approaches resulting in linear phenomenological relations with transport coefficients to be determined by experiment (Kedem & Katchalsky 1958; Blank 1962). More-detailed models sometimes postulate a static porestructure (Solomon 1960; Luzatti *et al.* 1966); an alternative has been suggested by Blank (1964), who considers fluctuations in membrane

structure as creating sites for solute permeation. This approach is promising, but it neglects solvent flow and does not really treat the dynamic character of the fluctuations.

The reason for such simplifications is obvious: more-realistic membrane models are exceedingly difficult to treat. A complete model would have to include explicitly forces between membrane and solute particles, as well as perturbations in solvent flow caused by the membrane. Membrane transport at this level of detail must be represented by a Liouville equation, or at least by a many-particle Brownian motion in which different particles move subject to complex mutual interactions.

An approach is suggested by the work of polymer physical chemists (Kirkwood & Risemann 1948; Rouse 1953; Zimm 1956), who have had considerable success treating the related problem of the motion of a polymer chain in solution. The idea we wish to advance here is that a membrane may be considered as a giant macromolecule moving relative to the solvent, and may thus be discussed along lines similar to those developed by Kirkwood & Risemann (1948) and their successors. In particular, we shall adapt a variational method used by Rotne & Prager (1969) for the calculation of polymer diffusion coefficients to the permeation of solvent through a thin membrane.

2. The model

The membrane is considered to be a random array of spherical beads, each with radius a , representing segments of polymer chains. This bead radius is the only free parameter in our calculations; for a series of membranes prepared from the same material but differing, for example, in solvent content, the same value of a must of course apply to all members. The instantaneous location of the i th bead is given by the vector $\mathbf{r}_i \equiv (x_i, y_i, z_i)$, and interactions (primary bonds, van der Waals forces, etc.) between beads are characterized by a potential function $U(\mathbf{r}_1, \mathbf{r}_2, \dots)$; if the membrane is a thin film centred about the plane $z = 0$, then U should increase fairly rapidly with increasing $|z_i|$, since otherwise individual beads would simply be carried away by convection and diffusion processes.

The solvent which is passing through the membrane is represented as a continuous incompressible Newtonian fluid (of viscosity η) in creeping flow occupying all space exterior to the membrane beads. This neglect of the molecular nature of the solvent probably limits the applicability of the model to membranes having pores large compared with the solvent molecules, such as those investigated by Yasuda, Lamaze & Peterlin (1971). If solute molecules are present they can be represented as beads whose interactions with one another and with membrane particles must be included in the potential function U ; in this paper we consider only solvent transport.

In addition to the approximations inherent in the model, we shall also assume that the driving forces responsible for transport through the membrane are small, so that the various configurational distribution functions for the membrane particles will deviate only slightly from their equilibrium forms. This is not in

practice a severe restriction, since it merely limits the discussion to the usual linear phenomenological relationships between forces and fluxes.

The specific problem to be treated in this paper is the calculation of the mean volume flux \bar{u} of solvent through a membrane of infinite extent in the x, y plane induced by a pressure drop from a value $P_0 + \Delta P$ at $z = -\infty$ to P at $z = +\infty$.† The ratio $\kappa \equiv \bar{u}/\Delta P$ is the solvent permeability of the membrane, and we shall obtain rigorous upper bounds on κ for the model described in this section.

3. Problem and variational method

The direct treatment of the problem just formulated would proceed through a many-particle diffusion equation for the joint configurational distribution function $\Psi(t, \mathbf{r}_1, \mathbf{r}_2 \dots)$ of the membrane beads. If \mathbf{v}_i is the velocity of the i th bead at time t , then one can write down a continuity equation which under steady-state conditions becomes

$$\frac{\partial \Psi}{\partial t} = - \sum_i \frac{\partial}{\partial \mathbf{r}_i} (\mathbf{v}_i \Psi). \tag{1}$$

To obtain the required diffusion equation, this must be supplemented by a relationship between the \mathbf{v}_i and the forces $\mathbf{f}_1, \mathbf{f}_2, \dots$, acting on individual beads, as well as by a further relation between \mathbf{f}_i and Ψ .‡ The latter is a straightforward generalization of the familiar thermodynamic relation between forces and potential gradients:

$$\mathbf{f}_i = -kT \frac{\partial \ln \Psi}{\partial \mathbf{r}_i} - \frac{\partial U}{\partial \mathbf{r}_i} = -kT \frac{\partial \ln (\Psi/\Psi_e)}{\partial \mathbf{r}_i}, \tag{2}$$

where k is the Boltzmann constant, T is the temperature and

$$\Psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots) \equiv e^{-U/kT} / \left(\int e^{-U/kT} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots \right)$$

is the equilibrium distribution function when ΔP is zero.

The relation between the \mathbf{v}_i and \mathbf{f}_i is a much more difficult matter. For an isolated spherical bead, the creeping-flow assumption we have made would lead to the simple Stokes relation

$$\mathbf{v}_i = \bar{u} \hat{\mathbf{z}} + \mathbf{f}_i / 6\pi a \eta$$

($\hat{\mathbf{z}}$ is a unit vector in the z direction). In the actual membrane, hydrodynamic interaction between beads produces the more complex result

$$\mathbf{v}_i = \bar{u} \hat{\mathbf{z}} + \frac{1}{kT} \sum_j \mathbf{D}_{ij}(\mathbf{r}_1, \mathbf{r}_2, \dots) \cdot \mathbf{f}_j, \tag{3}$$

where the second-order tensor coefficients \mathbf{D}_{ij} are still to be determined. They can be thought of as generalized diffusion coefficients with each \mathbf{D}_{ij} having a

† The specification of pressure far from the membrane rather than at the membrane surfaces is necessary here, since in our model the membrane surfaces are not sharply defined, and may indeed be quite irregular.

‡ These forces must of course be exactly balanced by the hydrodynamic drag force on each particle.

3×3 matrix realization. To obtain them is a problem in hydrodynamics, requiring the solution of the creeping-flow Navier–Stokes equations for the velocity field $\mathbf{u}(\mathbf{r})$, pressure $P(\mathbf{r})$ and viscous stress $\boldsymbol{\tau}(\mathbf{r})$ at every point \mathbf{r} in the region V occupied by solvent:

$$\nabla \cdot (\boldsymbol{\tau} - P\mathbf{I}) = 0, \quad (4)$$

$$\boldsymbol{\tau} = \eta[\nabla\mathbf{u} + (\nabla\mathbf{u})^T], \quad (5)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (6)$$

with boundary conditions

$$\mathbf{u}(\mathbf{r}) = \mathbf{v}_i \quad \text{for } \mathbf{r} \text{ on } S_i \quad (\text{for all } i), \quad (7)\dagger$$

where S_i is the surface of the i th bead,

$$P(\mathbf{r}) = \begin{cases} P_0 + \Delta P & \text{as } z \rightarrow -\infty, \\ P_0 & \text{as } z \rightarrow \infty. \end{cases} \quad (8)$$

Once the system (4)–(8) has been solved for a given set of bead positions and velocities, the forces \mathbf{f}_i may be calculated by integration of the normal component of the stress over the surface of each bead:

$$\int_{S_i} (\boldsymbol{\tau} - P\mathbf{I}) \cdot \hat{\mathbf{v}}_i d^2\mathbf{r} = \mathbf{f}_i \quad (9)$$

($\hat{\mathbf{v}}_i$ is the inward unit normal at a point \mathbf{r} on S_i). The mean volume flux \bar{u} and the \mathbf{D}_{ij} coefficients in (3) for that particular configuration may then be determined.

Of course, complete execution of the scheme just outlined is not feasible for the many-particle system with which we are concerned. However, it is possible to formulate a fully equivalent variational problem which permits us to use approximate solutions to obtain upper-bound estimates for the membrane permeability. The procedure is essentially that of Rotne & Prager (1969), and we give here only an outline of the method. It involves the minimization of the energy dissipation rate with respect to a set of trial forces $\mathbf{f}_i^*(\mathbf{r}_1, \mathbf{r}_2, \dots)$, a trial pressure distribution $P^*(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{f}_1^*, \mathbf{f}_2^*, \dots)$ and a viscous stress distribution $\boldsymbol{\tau}^*(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{f}_1^*, \mathbf{f}_2^*, \dots)$. Conditions for acceptability as trial functions are that (i) the \mathbf{f}_i^* be derivable from some trial distribution function $\Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots)$ according to (2); (ii) $\boldsymbol{\tau}^*$ be a symmetric traceless tensor, compatible (a) with the \mathbf{f}_i^* according to (9) and (b) with P^* according to (4); and (iii) P^* be consistent with the applied pressure differences as required by (8).

The choice of trial functions is similar to that used by Rotne & Prager, but in order to avoid edge effects we shall minimize the energy dissipation rate per unit area of membrane, and introduce a limiting process which allows the membrane area to become infinite. First consider the surface S' enclosing a cylinder

† Condition (7) ignores the possibility of bead rotation. This feature can be included by adding a torque balance condition for each bead, and a rotational term $\boldsymbol{\omega}_i \times (\mathbf{r} - \mathbf{r}_i)$ to each \mathbf{v}_i , where $\boldsymbol{\omega}_i$ is the angular velocity of bead i . Allowing the possibility of rotation will naturally increase the rate of energy dissipation produced by a given ΔP and therefore increase the permeability. However, the trial functions to be chosen later [equation (13)] for use in a variational approach to the problem also satisfy the new conditions, so the final upper bound on the permeability is valid whether or not the membrane beads are allowed to rotate.

with axis in the z direction, extending from $z = -L$ to $z = L$, and having a circular cross-section of area A ; such a surface will cut $N \equiv nA$ beads (numbered 1 to N) out of an infinite membrane containing n beads per unit area and centred on the plane $z = 0$. We designate by V' the interior of this cylinder and by V the region consisting of all points lying in V' but not inside one of the membrane beads. At any point \mathbf{r} in V , the local energy dissipation rate per unit volume corresponding to a trial stress $\boldsymbol{\tau}^*$ is $\boldsymbol{\tau}^* : \boldsymbol{\tau}^* / 2\eta$. The rate ϵ^* of energy dissipation per unit area of the infinite membrane is then taken as the limit

$$\epsilon^* \equiv \frac{1}{2\eta} \lim_{L \rightarrow \infty} \lim_{A \rightarrow \infty} \left[\frac{1}{A} \int_{V'} \dots \int_{V'} \Psi_N \left(\int_V \boldsymbol{\tau}_N^* : \boldsymbol{\tau}_N^* d^3\mathbf{r} \right) d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \right], \quad (10)$$

where $\Psi_N(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the true N -bead distribution function and $\boldsymbol{\tau}_N^*$ is the trial stress when there are N beads in V' .

If, as we have assumed, ΔP (and therefore \bar{u}) is small, then Ψ_N in (10) can be approximated by the equilibrium N -bead distribution function $\Psi_{N,e}$ (i.e. the distribution function for $\Delta P = 0$) and we can write

$$\epsilon^* = \frac{1}{2\eta} \lim_{L \rightarrow \infty} \lim_{A \rightarrow \infty} \left[\frac{1}{A} \int_{V'} \dots \int_{V'} \Psi_{N,e} \left(\int_V \boldsymbol{\tau}_N^* : \boldsymbol{\tau}_N^* d^3\mathbf{r} \right) d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \right]. \quad (11)$$

If the $\Psi_{N,e}$ approximation is valid, then it can be shown (Woodbury & Prager 1964; Keller, Rubinfeld & Molyneux 1967) that the minimization of ϵ^* subject to conditions (i)–(iii) is completely equivalent to solving the diffusion problem (1)–(9). Furthermore, any approximate set of functions $\boldsymbol{\tau}^*$, P^* , \mathbf{f}_i^* and Ψ^* satisfying (i)–(iii) will give an estimate ϵ^* for the energy dissipation rate which is greater than the true rate ϵ . Since, in terms of macroscopic variables,

$$\epsilon = \bar{u}\Delta P = \kappa(\Delta P)^2,$$

it follows that any such set of trial functions can also be used to obtain an upper bound on the solvent permeability of the membrane:

$$\kappa < \epsilon^* / (\Delta P)^2. \quad (12)$$

This is the fundamental inequality upon which our calculations will be based.

4. Choice of trial functions

Our formulation of suitable trial functions proceeds in two stages: first, the selection of a stress distribution $\{\boldsymbol{\tau}^*, P^*\}$ compatible with a given set of forces \mathbf{f}_i^* , and second, the selection of the \mathbf{f}_i^* themselves. For $\boldsymbol{\tau}^*$ we shall follow Rotne & Prager (1969), who write

$$\boldsymbol{\tau}_N^*(\mathbf{r}) = \sum_{i=1}^N \boldsymbol{\tau}_i^*(\mathbf{r} - \mathbf{r}_i), \quad (13)$$

where $\boldsymbol{\tau}_i^*(\mathbf{r} - \mathbf{r}_i)$ is the viscous stress field which would surround bead i if the force acting on it were \mathbf{f}_i^* and there were no other particles present:

$$\boldsymbol{\tau}_i(\boldsymbol{\rho}) = \frac{1}{2}\eta (\partial \mathbf{w}_i^* / \partial \boldsymbol{\rho} + (\partial \mathbf{w}_i^* / \partial \boldsymbol{\rho})^T), \quad (14)$$

$$\mathbf{w}_{ij}^*(\boldsymbol{\rho}) \equiv (kT)^{-1} (\mathbf{D}^{(0)}(\boldsymbol{\rho}) + \mathbf{D}^{(1)}(\boldsymbol{\rho})) \cdot \mathbf{f}_i^*, \quad (15)$$

$$\mathbf{D}^{(0)}(\boldsymbol{\rho}) \equiv \frac{kT}{8\pi\eta\rho} \left(\mathbf{1} + \frac{\boldsymbol{\rho}\boldsymbol{\rho}}{\rho^2} \right), \quad \mathbf{D}^{(1)}(\boldsymbol{\rho}) \equiv \frac{kT a^2}{8\pi\eta\rho^3} \left(\frac{\mathbf{1}}{3} - \frac{\boldsymbol{\rho}\boldsymbol{\rho}}{\rho^2} \right). \quad (16)$$

\mathbf{w}_i^* is just the Stokes–Oseen velocity distribution around the i th bead. For later convenience we have split the tensor coefficient in (15) into a far contribution $\mathbf{D}^{(0)}$, dominant at large distances ρ , and a near part $\mathbf{D}^{(1)}$, which becomes important as $\rho \rightarrow a$. The trial stress (13) and the associated pressure distribution P_N^* determined by it according to (4) will satisfy conditions (ii) and (iii) provided that

$$\frac{1}{A} \sum_{i=1}^N \mathbf{f}_i^* = \Delta P \hat{\mathbf{z}}. \quad (17)$$

In order to obtain reasonably simple results, we replace the integration over the region V (consisting of all points lying exterior to the membrane beads) by an integration over all space, thereby making ϵ^* larger still and reinforcing the inequality (12). With this modification, substitution of (13) into (11) gives, after some manipulation as described in Rotne & Prager,†

$$\kappa(\Delta P)^2 < \epsilon^* < \lim_{L \rightarrow \infty} \lim_{A \rightarrow \infty} \left\{ \frac{1}{A} \left[A \bar{u}_N^* \Delta P + \frac{1}{kT} \int_{V'} \dots \int_{V'} \Psi_{N,e}(\mathbf{r}_1, \dots, \mathbf{r}_N) \right. \right. \\ \left. \left. \times \sum_{i=1}^N \sum_{j=1}^N (\mathbf{D}_{ij}^*(\mathbf{r}_i - \mathbf{r}_j) : \mathbf{f}_i^* \mathbf{f}_j^*) d^3 \mathbf{r}_1 \dots d^3 \mathbf{r}_N \right] \right\}, \quad (18)$$

where

$$\mathbf{D}_{ij}^*(\boldsymbol{\rho}) = \begin{cases} (kT/6\pi a \eta) \mathbf{I} & (i = j) \\ \mathbf{D}^{(0)}(\boldsymbol{\rho}) + 2\mathbf{D}^{(1)}(\boldsymbol{\rho}) & (i \neq j) \end{cases} \quad (19)$$

and \bar{u}_N^* is the mean solvent flux corresponding to the stress $\boldsymbol{\tau}_N^*$:

$$\bar{u}_N^* = \frac{1}{A \Delta P} \int_{V'} \dots \int_{V'} \Psi_{N,e} \left[\sum_{i=1}^N \int_{S'} \mathbf{w}_i^*(\mathbf{r} - \mathbf{r}_i) \cdot (\boldsymbol{\tau}_N^*(\mathbf{r}) - P^*(\mathbf{r}) \mathbf{I}) \right. \\ \left. \times \hat{\mathbf{v}}(\mathbf{r}) d^2 \mathbf{r} \right] d^3 \mathbf{r}_1, \dots, d^3 \mathbf{r}_N \quad (20)$$

(S' is the outer boundary of the system).

The limit $A \rightarrow \infty$ in (18) must be taken with care; in particular, it is not permissible to invert the limit and summation processes, since both $A \bar{u}_N^* \Delta P$ and the multiple-integral terms in (18) increase faster than A as A becomes large, although their sum becomes proportional to A . The difficulty arises from the slow decay of \mathbf{w}_i^* and \mathbf{D}_{ij}^* with increasing $|\mathbf{r} - \mathbf{r}_i|$: both vanish only as $|\mathbf{r} - \mathbf{r}_i|^{-1}$.

This is essentially the same difficulty as is faced in all calculations of sedimentation velocity, viscosity and particle forces in suspensions. One way to resolve the divergence is to subtract off a quantity which has the same long-range behaviour as the terms comprising the sum, yet whose mean value is known exactly. This technique was used successfully by Batchelor (1972) and Batchelor & Green (1972) in treating the sedimentation and bulk stress of a suspension of spheres.

In our case the problem may be cured by a rearrangement of (18). Physically, the rearrangement is motivated by the realization that when A and L are large, so that most points on S' are far from the membrane, \bar{u}_N^* will become insensitive to the detailed membrane structure and to the forces \mathbf{f}_i^* acting on individual beads, and depend only on the total force per unit area. The argument is similar

† A derivation of (19) by more physical arguments has been given by Yamakawa (1970).

to that used by Hasimoto (1959) for flow past a periodic array of spheres and later by Childress (1972) for fixed random arrays; these authors recognized that it is essential to take account of the mean pressure gradient in order that the sum of velocities and forces due to an infinite number of elements will converge. The term \bar{u}_N^* is this mean force contribution, and it must be modified and combined with the double sum in (18) so that convergence is assured.

We begin by noting that in the limit of large A and L only the contribution $\mathbf{D}^{(0)}$ in the expression (15) for \mathbf{w}_i^* need be retained in calculating \bar{u}_N^* , since $\mathbf{D}^{(1)}(\rho)$ vanishes as ρ^{-3} as $\rho \rightarrow \infty$. Thus, if we are only interested in the limit $A \rightarrow \infty$, $L \rightarrow \infty$, equation (20) may be replaced by

$$A\Delta P\bar{u}_N^* = -\frac{1}{A} \int_{V'} \int_{V''} \left(\int_{S'} \mathbf{D}^{(0)}(\mathbf{r}-\mathbf{r}'') d^2\mathbf{r} \right) : \mathbf{q}^*(z') \mathbf{q}^*(z'') d^3\mathbf{r}' d^3\mathbf{r}'', \quad (21)$$

where $\mathbf{q}^*(z') d^3\mathbf{r}'$ is the average force exerted on the membrane beads lying in a volume element $d^3\mathbf{r}'$ centred on the plane $z = z'$:

$$\left. \begin{aligned} \mathbf{q}^*(z') \equiv \int_{V'} \dots \int_{V'} \Psi_{N,e}(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_{i=1}^N \delta(\mathbf{r}' - \mathbf{r}_i) \mathbf{f}_i^*(\mathbf{r}_1, \dots, \mathbf{r}_N) d^3\mathbf{r} \dots d^3\mathbf{r}_N \\ \left(\int_V \mathbf{q}^*(z') d^3\mathbf{r}' = \hat{\mathbf{z}} A \Delta P \right). \end{aligned} \right\} \quad (22)$$

It is also convenient to define here a two-point force density distribution

$$\left. \begin{aligned} \mathbf{S}^*(\mathbf{r}', \mathbf{r}'') \equiv \int_{V'} \dots \int_{V''} \Psi_{N,e}(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_{\substack{i,j=1 \\ i \neq j}}^N \delta(\mathbf{r}' - \mathbf{r}_i) \delta(\mathbf{r}'' - \mathbf{r}_j) \mathbf{f}_i^* \mathbf{f}_j^* d^3\mathbf{r} \dots d^3\mathbf{r}_N \\ (\mathbf{S}^*(\mathbf{r}', \mathbf{r}'') \rightarrow \mathbf{q}^*(z') \mathbf{q}^*(z'') \quad \text{as } |\mathbf{r}' - \mathbf{r}''| \rightarrow \infty). \end{aligned} \right\} \quad (23)$$

The rearrangement now consists of writing the right-hand side of (18) in terms of the force density correlation $(\mathbf{S}^*(\mathbf{r}', \mathbf{r}'') - \mathbf{q}^*(z') \mathbf{q}^*(z''))$, which, since it goes to zero as $|\mathbf{r}' - \mathbf{r}''|$ becomes large, allows us to take the limit $A, L \rightarrow \infty$ in (18) on a term-by-term basis. In this way we arrive at the inequality

$$\left. \begin{aligned} \kappa < \left(\int_{-\infty}^{\infty} q^*(z') dz' \right)^{-2} \left[\frac{n \langle f^{*2} \rangle}{6\pi\eta a} + \frac{1}{kT} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int \mathbf{D}^{(0)}(\mathbf{r}' - \mathbf{r}'') : \right. \\ & \left. (\mathbf{S}^*(\boldsymbol{\xi}, z', z'') - \mathbf{q}^*(z') \mathbf{q}^*(z'')) d^2\boldsymbol{\xi} dz' dz'' + \frac{2}{kT} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int \mathbf{D}^{(1)}(\mathbf{r}' - \mathbf{r}'') : \right. \\ & \left. \mathbf{S}^*(\boldsymbol{\xi}, z', z'') d^2\boldsymbol{\xi} dz' dz'' \right], \end{aligned} \right\} \quad (24)$$

in which $\boldsymbol{\xi} \equiv (\mathbf{r}' - \mathbf{r}'') \cdot (\mathbf{I} - \hat{\mathbf{z}}\hat{\mathbf{z}})$ is the component of $\mathbf{r}' - \mathbf{r}''$ normal to the z direction,

$$\langle f^{*2} \rangle = \lim_{N \rightarrow \infty} \left\langle \left(\frac{1}{N} \sum_{i=1}^N f_i^{*2} \right) \right\rangle, \quad \text{where } \langle () \rangle \equiv \int_{V'} \dots \int_{V'} \Psi_{N,e}(\dots) d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N,$$

and the integration over $\boldsymbol{\xi}$ extends over the entire x, y plane. The inequality (24) is our basic result; it remains valid for our general model provided that \mathbf{q}^* , \mathbf{S}^* , and $\langle f^{*2} \rangle$ are derived from a set of \mathbf{f}_i^* satisfying condition (i).

5. An example

To illustrate how (24) is applied, we shall in this and the following section determine upper bounds on the permeability for a simplified membrane model in which the bead centres are constrained to lie in the plane $z = 0$, although they may still move in the x and y direction. The two-point force correlation then has the form

$$\mathbf{S}^*(\boldsymbol{\xi}, z', z'') = \delta(z') \delta(z'') \mathbf{s}^*(\boldsymbol{\xi}).$$

For the \mathbf{f}_i^* we shall first make the simplest possible choice (to be refined in § 6) by setting them all equal to the mean force per bead $\bar{f}\hat{\mathbf{z}}$, which clearly satisfies condition (i).

With these simplifications it is easy to see from (22) and (23) that $\mathbf{q}^*(z) = n\bar{f}\delta(z)\hat{\mathbf{z}}$ and $\mathbf{s}^*(\boldsymbol{\xi}) = n^2\bar{f}^2g(\boldsymbol{\xi})\hat{\mathbf{z}}\hat{\mathbf{z}}$, where $g(\boldsymbol{\xi})$ is the equilibrium pair distribution function for the membrane beads, normalized to unity as $\xi \rightarrow \infty$. Thus only the zz component of the integrals in (24) is needed and the bound on the permeability becomes

$$\kappa < (6\pi\eta na)^{-1} \left\{ 1 + \frac{3}{4}na \int (g(\boldsymbol{\xi}) - 1)\xi^{-1}d^2\boldsymbol{\xi} + \frac{1}{2}na^3 \int g(\boldsymbol{\xi})\xi^{-3}d^2\boldsymbol{\xi} \right\}. \quad (25)$$

For an explicit result, we still need the pair distribution $g(\boldsymbol{\xi})$. If the beads are assumed to interact in pairwise additive fashion, so that

$$U = \sum_{i < j} \phi(\boldsymbol{\xi}_i - \boldsymbol{\xi}_j),$$

then, as shown in Hill (1956, p. 202), $g(\boldsymbol{\xi})$ can be expanded as a power series in the bead density n :

$$g(\boldsymbol{\xi}) = \exp(-\phi(\boldsymbol{\xi})/kT) \left\{ 1 + n \iint [\exp(-\phi(\boldsymbol{\xi}')/kT) - 1] \times [\exp(-\phi(|\boldsymbol{\xi} - \boldsymbol{\xi}'|)/kT) - 1] d^2\boldsymbol{\xi} d^2\boldsymbol{\xi}' + \dots \right\}. \quad (26)$$

If we use the hard-sphere potential, the integral in (26) can be evaluated, and we find that

$$g(\boldsymbol{\xi}) = \left. \begin{cases} 0 & (\xi \leq 2a), \\ 1 & (\xi > 4a), \\ 1 + \frac{1}{2}n[-4a^2 \sin^{-1}(\xi/4a) - 2a\xi(4 - \xi^2/4a^2)^{\frac{1}{2}} + \frac{1}{8}\pi\xi^2] & (2a < \xi \leq 4a). \end{cases} \right\} \quad (27)$$

Finally, substitution into (24) gives

$$\kappa < (6\pi\eta an)^{-1} [1 - \frac{5}{2}\sigma - 3\sigma^2 \dots], \quad (28)$$

where σ is the area fraction of the membrane which is occupied by beads:

$$\sigma = n\pi a^2.$$

The inequality (28) is, of course, applicable only when σ is small, but it should be remembered that this limitation was introduced by the expansion (26) of the distribution function; the parent inequality (25) is valid at *all* values of σ , right up to the dense-packing maximum ($\sigma = \pi/2\sqrt{3} = 0.91$). Whether the

upper bound given by (25) is also a good estimate for the permeability is another matter, to be settled by investigating the improvements obtainable from more elaborate trial functions; such an investigation is the subject of §6. But even with this simple treatment, we have shown so far that, for the many-particle Brownian motion model which we have used, rigorous upper bounds on the permeability can be obtained in terms of equilibrium distribution functions. Improved results will inevitably require distribution functions of higher order than the simple pair distribution used in (25), but at any level the calculation of the permeability bound is reduced to a problem in equilibrium statistical mechanics.

6. More-general trial functions

We shall now refine the permeability estimates of §5, again with particular attention to the case where the number n of beads per unit area is small. Why this emphasis on a situation which is unlikely to occur in practice? Because the highly porous membrane raises fundamental questions concerning membrane – permeant interaction which will be encountered in models where the membrane elements are more closely packed. These problems have their origin in the long-range nature of hydrodynamic interactions between membrane beads: the perturbation of solvent flow caused by a bead moving through the solvent falls off only as the reciprocal of the first power of the distance from the bead, behaving in this respect rather like the Coulomb potential around a charge.

Just as the Coulomb interaction between ions produces unexpectedly early departure from ideal behaviour in electrolyte solutions, so too does hydrodynamic interaction between the particles of a dilute array of spheres result in significant corrections to simple Stokes-law behaviour at remarkably low values of the bead concentration. Some time ago, Brinkman (1948) showed that the three-dimensional permeability coefficient κ' of a bed of spheres containing c particles per unit volume is given by

$$\kappa' = (6\pi a \eta c)^{-1} (1 - \frac{3}{2} 2^{\frac{1}{2}} (\frac{4}{3} \pi a^3 c)^{\frac{1}{2}} + \dots), \quad (29)$$

a result which has recently been placed on a more rigorous footing by Childress (1972). The appearance of non-integer powers of c in (29) means that any attempt to correct for hydrodynamic interaction by examining the flow around isolated pairs, triplets, etc., of beads will fail, because the resulting permeability correction will always be expressible as a Taylor series in c ; even the dilute bed of spheres must be considered as a many-particle problem.

It seems likely that similar care is needed in treating flow through a highly porous membrane, and that the permeability estimate (28) can be significantly improved through the use of better trial functions. We shall show that this is indeed the case, at least at low n , although the improvement is less drastic than for the three-dimensional bed of spheres.

6.1. Trial functions

We again begin with the inequality (24), which, if we assume that the beads are isotropically distributed in the plane of the membrane and restrict ourselves to trial forces having no components parallel to the membrane plane, can be written as

$$\kappa < \frac{1}{6\pi a\eta n^2 \bar{f}^2} \left[n\bar{f}^2 + \frac{3}{2}\pi a \int_0^\infty (s(\rho) - n^2 \bar{f}^2) d\rho + \pi a^3 \int_0^\infty \frac{s(\rho)}{\rho^2} d\rho \right], \quad (30)$$

where the two-point pressure distribution s is given by

$$s(\rho) = \sum_{\substack{i,j=1 \\ i \neq j}}^N \int_A \dots \int_A f_i f_j \delta(\boldsymbol{\xi}_i) \delta(\boldsymbol{\xi}_j - \boldsymbol{\rho}) \Psi_{N,e} d^2 \boldsymbol{\xi}_1 \dots d^2 \boldsymbol{\xi}_N \quad (31)$$

and the averages \bar{f} and \bar{f}^2 are defined as

$$\bar{f} \equiv \frac{1}{N} \sum_{i=1}^N f_i, \quad \bar{f}^2 \equiv \frac{1}{N} \sum_{i=1}^N (f_i)^2.$$

We derived the inequality (28) by choosing $f_i = \bar{f}$ for all i . To get a better result we must take into account the fact that f_i should really depend on the distribution of other membrane particles in the vicinity of particle i . Since the simplified model we are using restricts the centres of the membrane beads to lie on a plane, the requirement that admissible trial forces be derivable from some potential function (condition (i)) applies only to components parallel to that plane, and is trivially satisfied by our having taken these to be zero. Thus any choice of the f_i will lead to a valid bound on the permeability; in order to introduce interactions between beads, we write

$$f_i = f_0 \prod_{j(\neq i)} [1 + h(|\boldsymbol{\xi}_i - \boldsymbol{\xi}_j|)], \quad (32)$$

where f_0 is a constant and h is an as yet undetermined function of the distance between beads i and j , the only restriction on which is that it be integrable over the membrane plane. We expect, of course, to choose h so as to minimize the right-hand side of (30), but first we must deal with the calculation of \bar{f} , \bar{f}^2 and s , which are no longer, as in §5, obtainable from one- and two-particle distributions alone.

6.2. Calculation of \bar{f} , \bar{f}^2 and s

Since our concern here is primarily with highly porous membranes, we shall seek to develop a series expansion around the limit $n \rightarrow 0$. In doing so it is important to remember that there are two expansion parameters: the bead density n and the unknown function h ; we expect the optimum h itself to depend on n , and in fact we shall see that there is a singularity at $n = 0$. The proper strategy is therefore to expand in powers of n , but to evaluate each coefficient of the expansion to *all* powers of h .

We illustrate the procedure with the calculation of \bar{f} . From (31) and (32) we have

$$\bar{f} = f_0 \int_A \dots \int_A \left[\prod_{\substack{j=1 \\ j \neq i}}^N (1 + h(|\boldsymbol{\xi}_i - \boldsymbol{\xi}_j|)) \right] \Psi_{N,e}(\boldsymbol{\xi}_1, \dots, \boldsymbol{\xi}_N) d^2 \boldsymbol{\xi}_1 \dots d^2 \boldsymbol{\xi}_N, \quad (33)$$

where, for hard-core interactions, the equilibrium N -bead distribution is

$$\Psi_{N,e} = \frac{\prod_{\substack{l,m=1 \\ l < m}}^N [1 + \omega(|\xi_l - \xi_m|)]}{\int_A \dots \int_A \prod_{\substack{l',m'=1 \\ l' < m'}}^N [1 + \omega(|\xi_{l'} - \xi_{m'}|)] d^2\xi_1 \dots d^2\xi_N}, \quad (34)$$

$$\omega(\rho) \equiv \begin{cases} -1 & (\rho < 2a), \\ 0 & (\rho > 2a). \end{cases}$$

We now carry out a Mayer cluster expansion in ω , the zeroth term of which is just the value of \bar{f} in the limit $a \rightarrow 0$, n finite:

$$(\bar{f})_0 = f_0 \left(1 + \frac{1}{A^2} \int_A \int_A h(|\xi - \xi'|) d^2\xi d^2\xi' \right)^N \rightarrow f_0 \exp \left(2\pi n \int_0^\infty h(\rho) \rho d\rho \right) \quad \text{as } N = nA \rightarrow \infty.$$

Higher-order terms may also be obtained:

$$\bar{f}/f_0 = \exp \left(2\pi n \int_0^\infty \tilde{h}(\rho) \rho d\rho \right) \left(1 + \frac{1}{2}n^2 \int H(\rho, \rho') \omega(|\rho - \rho'|) d^2\rho d^2\rho' + \dots \right), \quad (35)$$

$$H(\rho, \rho') \equiv \tilde{h}(\rho) + \tilde{h}(\rho') + \tilde{h}(\rho) \tilde{h}(\rho'),$$

$$\tilde{h}(\rho) \equiv (1 + h(\rho))(1 + \omega(\rho)) - 1 = \begin{cases} -1 & (\rho < 2a), \\ h(\rho) & (\rho > 2a). \end{cases}$$

By similar arguments,

$$\bar{f}^2 = \bar{f}^2 \exp \left(2\pi n \int_0^\infty \tilde{h}^2(\rho) d\rho \right) \left(1 + \frac{1}{2}n^2 \iint H^2(\rho, \rho') \omega(|\rho - \rho'|) d^2\rho d^2\rho' + \dots \right), \quad (36)$$

$$s(\rho) = n^2 \bar{f}^2 (1 + \tilde{h}(\rho))^2 \exp \left(n \int \tilde{h}(\xi) \tilde{h}(|\xi + \rho|) d^2\xi \right) \times \left(1 + \frac{1}{2}n^2 \iint G(\xi, \xi', \rho) \omega(|\xi - \xi'|) d^2\xi d^2\xi' + \dots \right), \quad (37)$$

$$G(\xi, \xi', \rho) \equiv H(|\xi + \rho|, |\xi' + \rho|) H(\xi, \xi') + H(|\xi + \rho|, |\xi' + \rho|) - H(\xi, \xi').$$

6.3. Optimization

For any given h function, (35), (36) and (37) are perfectly straightforward series in ascending powers of n . However, we intend to optimize with respect to h , and this, as we have already remarked, leads to an optimum h which may vary with n . It is therefore uncertain at this point whether the higher-order terms in (35)–(37) become negligible as $n \rightarrow 0$. We shall tentatively assume that they do, and also that the exponentials appearing in (35)–(37) may be replaced by their linear approximations. These assumptions (and others to be made below) will be justified *a posteriori*, that is we shall use them in carrying out the optimization and then show that the terms omitted are indeed small compared with those retained in calculating the permeability bound (30).

With the approximations just described, the inequality (30) becomes, after substitution of (35)–(37) and rearrangement,

$$\begin{aligned} \kappa < \frac{1}{6\pi a \eta n} \left[1 - \frac{5}{2} \pi a^2 n + 2\pi n \int_{2a}^{\infty} \tilde{h}^2(\rho) \left(1 + \frac{3a}{4\rho} + \frac{a^3}{2\rho^3} \right) \rho d\rho \right. \\ \left. + 3\pi a n \int_{2a}^{\infty} \tilde{h}(\rho) \left(1 + \frac{2}{3} \frac{a^2}{\rho^2} \right) d\rho + \frac{3n^2}{4} \iint_{\rho > 2a} \tilde{h}(\xi) \tilde{h}(|\xi + \rho|) \left(\frac{a}{\rho} + \frac{2a^3}{3\rho^3} \right) d^2\xi d^2\rho + \dots \right]. \end{aligned} \tag{38}$$

Even in this reduced form, the right-hand side of (38) is not trivial to minimize. However, further simplification is possible if we recall that the main purpose of introducing the trial function (32) was to allow for long-range hydrodynamic interaction between beads. The most important feature of the \tilde{h} function as $n \rightarrow 0$ is therefore its behaviour at $\rho \gg a$, and for sufficiently small n we may accordingly omit all but the leading term in a/ρ in each of the integrals in (38); in addition, we shall overlook the excluded region $\rho < 2a$ and extend the integrals over the entire membrane plane.

The result of all this is the bound

$$\begin{aligned} \kappa < \frac{1}{6\pi a \eta n} \left[1 + 2\pi n \int_0^{\infty} \tilde{h}^2(\rho) \rho d\rho + 3\pi a n \int_0^{\infty} \tilde{h}(\rho) d\rho \right. \\ \left. + \frac{3}{4} n^2 a \iint \frac{\tilde{h}(\xi) \tilde{h}(|\xi + \rho|)}{\rho} d^2\xi d^2\rho + O(\sigma) \right], \end{aligned} \tag{39}$$

to be minimized with respect to $\tilde{h}(\rho)$, subject to the restriction [see (35)]

$$\tilde{h}(\rho) = -1 \quad \text{for } \rho < 2a. \tag{40}$$

The resulting integral equation for the optimum \tilde{h} is

$$\tilde{h}(\rho) = -\lambda(\rho) - \frac{3a}{4} \frac{1}{\rho} - \frac{3an}{4} \int \frac{\tilde{h}(\xi')}{|\xi' - \rho|} d^2\xi', \tag{41}$$

where $\lambda(\rho)$ is a Lagrangian multiplier function which vanishes for $\rho > 2a$, and must for $\rho < 2a$ be determined so that \tilde{h} satisfies (40).

Actually, we shall solve (41) with λ set equal to zero everywhere, and then simply replace the solution by $\tilde{h} = -1$ in the interval $0 < \rho < 2a$. On this basis $\tilde{h}(\rho)$ for $\rho > 2a$ is readily found by Fourier transforms:

$$\tilde{h}(\rho) = -(3a/4\rho) [1 - \frac{1}{2} \pi b \rho (H_0(b\rho) - Y_0(b\rho))] \quad (b \equiv \frac{3}{2} \pi n a), \tag{42}$$

where H_0 and Y_0 are the zeroth-order Struve and Neumann functions, respectively.

Equation (42) may be considered to represent the behaviour of \tilde{h} in the limit of ρ/a becoming large at fixed $b\rho$; when $b\rho$ is small, $\tilde{h} \rightarrow -3a/4\rho$ and when $b\rho$ is large, $\tilde{h} \rightarrow -3a/4b^2\rho^3$. Evidently there are two distance scales, a and $1/b$, and our main interest is in the range $a \ll \rho \ll 1/b$. As $\sigma = \pi n a^2 \rightarrow 0$ this range becomes extensive, and for all ρ within it \tilde{h} will be dominated by the first term in (42). For purposes of examining the permeability of highly porous membranes, we may therefore replace (42) with the simpler function

$$\tilde{h}(\rho) = \begin{cases} -1 & (\rho < \alpha a), \\ -3a/4\rho & (\alpha a < \rho < \beta/b), \\ 0 & (\rho > \beta/b), \end{cases} \tag{43}$$

the constants α and β being of order unity.

The arguments of this section are far from rigorous. However, it is perfectly admissible to suggest (43), whatever the methods by which it was obtained, as a trial function to be inserted into (30). When this trial function is used to calculate \bar{f}, \bar{f}^2 and s from (35)–(37) and the results are inserted in (30), one obtains for small σ

$$\kappa < \kappa_0(1 + \frac{9}{8}\sigma \ln \sigma + O(\sigma)) \quad (\kappa_0 = 1/6\pi a\eta n \equiv a/6\eta\sigma). \tag{44}$$

The constants α and β , which were introduced into (43) to reflect our uncertainty about the range over which \bar{h} may be satisfactorily replaced by $-3a/4\rho$, do not appear in (44) until the $O(\rho)$ term; even using (42) in place of (43) leaves the first two terms in (44) unchanged. Equation (43) is to be compared with the bound (28)

$$\kappa < \kappa_0(1 - \frac{5}{2}\sigma + O(\sigma^2)) \tag{45}$$

obtained for $\bar{h} = 0$. For sufficiently small σ , (44) will always lie below (45), or for that matter below *any* expansion for κ/κ_0 in terms of non-negative integer powers of σ . Since (44) is an upper bound on κ , we have shown therefore that κ cannot be expanded as a Taylor series in σ , and that the fractional deviation $(\kappa_0 - \kappa)/\kappa_0$ of the permeability from κ_0 must, as σ increases from zero, go up *at least* as fast as $-\frac{9}{8}\sigma \ln \sigma$.

Actually, although we do not have a rigorous proof, there is reason to believe that the first deviation of κ from κ_0 given by (44) is in fact correct. In the following section, we advance a physical argument in support of this suggestion.

7. A self-consistent field approach to permeability

The arguments given here are patterned on Brinkman's (1948) calculation of the permeability of a three-dimensional bed of spheres. Brinkman looked in detail at the flow around a 'test' sphere, treating the rest of the bed as a uniform continuum. In the same spirit, we shall consider the flow around a single membrane particle imbedded in an infinite plane sheet of permeability κ , and being held stationary against a mean flux \bar{u} of fluid passing through the membrane by the application of a force f normal to the membrane. We then obtain κ from the self-consistency condition that

$$-nf = \bar{u}/\kappa. \tag{46}$$

Let the test bead be centred at the origin, and consider the fluid velocity $u(\xi)$ normal to the membrane at a point ξ in the membrane plane. To keep the membrane in the vicinity of ξ from being swept away by the flow this requires application of a force $f = -u(\xi)/\kappa$ per unit area, which in turn generates a velocity perturbation $-f/8\pi\eta|\xi' - \xi|$ at points ξ' in the membrane plane. The total velocity perturbation $u(\xi) - \bar{u}$ must then include both a contribution from the test bead and also a sum of such terms from the remaining membrane elements, so that the total perturbation is, using (46),

$$u(\xi) - \bar{u} = \frac{f}{8\pi\eta\xi} - \frac{1}{8\pi\eta\kappa} \int \frac{(u(\xi') - \bar{u})}{|\xi - \xi'|} d^2\xi'. \tag{47}$$

In writing (47) the test bead has been treated as a point particle, although strictly speaking the force f should have been distributed over the interior of the bead in

such a way as to make u vanish at all points on the bead surface. This is permissible if σ is small.

Equation (47) is identical in form to (41) for the trial function \tilde{h} , and must then also have the same solution:

$$\begin{aligned} u(\xi) - \bar{u} &= (f/8\pi\eta\xi) (1 - \frac{1}{2}\pi b'\xi(H_0(b'\xi) - Y_0(b'\xi))) \\ &\rightarrow (f/8\pi\eta\xi) (1 + b'\xi \ln b'\xi + O(b'\xi)) \quad \text{as } b'\xi \rightarrow 0 \quad (b' \equiv 1/4\eta\kappa). \end{aligned} \quad (48)$$

In analogy with (42), we expect (48) to hold in the interval $a \ll \rho \ll 1/b'$.

We now introduce the boundary condition at the surface of the test bead by requiring that $u(\alpha a) = 0$, where α is once again a constant of order unity. That α does not equal unity arises from the fact that (48) is not an accurate approximation to $u(\xi)$ when ξ is comparable with a ; the actual value of α will be determined so as to make $\kappa \rightarrow \kappa_0$ as $\sigma \rightarrow 0$.

Inserting the boundary condition at αa into (48) gives, in conjunction with (46),

$$\kappa = (8\pi\eta\alpha a n)^{-1} (1 + b'\alpha a \ln b'\alpha a + O(b'\alpha a)) \rightarrow 1/8\pi\eta\alpha a n \quad \text{as } \sigma \rightarrow 0. \quad (49)$$

Since $\kappa_0 = 1/6\pi\eta a n$, we must have $\alpha = \frac{3}{4}$. At low n , we can replace b' with $1/4\eta\kappa_0$, to obtain once again the expression (44) for κ .

8. Summary and conclusion

We have used a variational method to examine the effect of long-range hydrodynamic interaction between membrane particles on the permeability of highly porous membranes. For a membrane consisting of spherical beads randomly distributed over a plane, hydrodynamic interactions introduce logarithmic terms into the expansion (44) of the permeability in powers of the fraction σ of membrane area occupied by beads, terms which become important when σ is low.

It appears then that, to obtain bounds which can also serve as estimates of the permeability, it is necessary to use trial functions \mathbf{f}_i involving relative positions of the membrane particles. Although this does complicate the evaluation of averages such as $s(\rho)$, the main obstacle comes from the forces the particles exert on one another; for example, all terms beyond the first in (35)–(37) are due to hard-core repulsions between beads. Calculating f, \bar{f}^2 and s is a problem in statistical mechanics, not very different from the determination of equilibrium partition and distribution functions in other systems: difficult but amenable to a variety of approximate or computer methods.

In seeking stronger permeability bounds, we must not forget that the stress distribution also need not be restricted to a simple superposition of contributions from individual beads [equation (13)], and that extending the energy dissipation integral to include points lying in the interior of membrane beads [equation (18)] will significantly weaken the results obtainable at higher values of σ .

Finally, although the bounds we have derived so far are valid when the membrane particles undergo lateral Brownian motion, the trial functions used do not explicitly contain contributions from this source. Future refinements should introduce trial forces with components normal to the direction of flow, to reflect more accurately the dynamic nature of fluctuations in membrane structure.

REFERENCES

- BATCHELOR, G. K. 1972 Sedimentation in a dilute dispersion of spheres. *J. Fluid Mech.* **52**, 245.
- BATCHELOR, G. K. & GREEN, J. T. 1972 The determination of the bulk stress in a suspension of spherical particles to order c^2 . *J. Fluid Mech.* **56**, 401.
- BLANK, M. 1962 Monolayer permeability and the properties of natural membranes. *J. Phys. Chem.* **66**, 1911.
- BLANK, M. 1964 An approach to a theory of monolayer permeation by gases. *J. Phys. Chem.* **68**, 2793.
- BRINKMAN, H. C. 1948 On the permeability of media consisting of closely packed porous particles. *Appl. Sci. Res., Hague*, **A1**, 81.
- CHILDRESS, S. 1972 Viscous flow past a random array of spheres. *J. Chem. Phys.* **56**, 2527.
- HASIMOTO, H. 1959 On the periodic fundamental solutions of the Stokes equations and their application to viscous flow past a cubic array of spheres. *J. Fluid Mech.* **5**, 317.
- HILL, T. 1956 *Statistical Mechanics*. McGraw-Hill.
- KEDEM, O. & KATCHALSKY, A. 1958 Thermodynamic analysis of the permeability of biological membranes to non-electrolytes. *Biochim. Biophys. Acta*, **27**, 229.
- KELLER, J. B., RUBENFELD, L. A. & MOLYNEUX, J. E. 1967 Extremum principles for slow viscous flows with applications to suspensions. *J. Fluid Mech.* **30**, 97.
- KIRKWOOD, J. G. & RISEMAN, J. 1948 The intrinsic viscosities and diffusion constants of flexible macromolecules in solution. *J. Chem. Phys.* **16**, 565.
- LUZATTI, V., REISS-HUSSON, F., RIVAS, E. & GULIK KRZYWICKI, T. 1966 Structure and polymorphism in lipid-water systems, and their possible biological implications. *Ann. N.Y. Acad. Sci.* **137**, 409.
- ROTNE, J. & PRAGER, S. 1969 Variational treatment of hydrodynamic interaction in polymers. *J. Chem. Phys.* **50**, 4831.
- ROUSE, P. E. 1953 A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys.* **21**, 1272.
- SOLOMON, A. K. 1960 Red cell membrane structure and ion transport. *J. Gen. Physiol.* **43** (suppl. 1), 1.
- WOODBURY, G. W. & PRAGER, S. 1964 Brownian motion in many-particle systems. I. Forced interdiffusion of two species. *J. Am. Chem. Soc.* **86**, 3417.
- YAMAKAWA, H. 1970 Transport of polymer chains in dilute solution: hydrodynamic interaction. *J. Chem. Phys.* **53**, 436.
- YASUDA, H., LAMAZE, G. E. & PETERLIN, A. 1971 Diffusive and hydraulic permeabilities of water in water-swollen polymer membranes. *J. Polymer Sci.* **A2**, 1117.
- ZIMM, B. H. 1956 Dynamics of polymer molecules in dilute solution: viscoelasticity, flow birefringence and dielectric loss. *J. Chem. Phys.* **24**, 269.