Journal of Membrane Science, 19 (1984) 117—136
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

INTERACTION BETWEEN PORES IN DIFFUSION THROUGH MEMBRANES OF ARBITRARY THICKNESS

PETER O. BRUNN

Department of Chemical Engineering and Applied Chemistry, Columbia University, New York, NY 10027 (U.S.A.)

(Received June 22, 1983; accepted in revised form October 21, 1983)

Summary

The model of permeation through membranes used in this paper consists of representing the membrane as an impermeable slab perforated by N circular cylinders (pores), the permeation rate being controlled by the rate at which penetrant diffuses through the membrane. Employing a Green's function approach for the local concentration leads to a simple expression for the flow through each pore. The limit $N \to \infty$ has to be treated carefully, and this is worked out in detail for a membrane with regularly distributed pores. Our results show that the details of the actual pore distribution do enter into the results. For the case of small area fraction of penetration sites, explicit results for the membrane permeability are obtained and serve as an estimate for the error involved in the customary cell method.

1. Introduction

Determination of the relation between the permeability of a membrane and its microscopic structure is an old and important problem [1,2]. For a review of that problem and its relevance to other fields of science, the reader is referred to the paper by Wakeham et al. [3]. The mathematical analysis usually rests upon the idea in which the membrane is modelled as a set of penetration sites (pores) distributed over an impermeable area [1]. To consider the processes occurring within one pore in detail and then to assume that contributions from different pores can simply be summed to get the total flux is characteristic for noninteracting pores (area fraction of pores, σ, tends to zero). Adopting the same technique to the case of nonzero σ is not possible since the disturbance from one pore decays too slowly with increasing distance from the pore. Failure to recognize this leads to divergent (and physically inadmissible) results. The speculation that since the effect of a given pore at some finite distance is only a small fraction of its value close to the pore and thus negligible, may be appealing [4], but it is wrong.

Actually solving the microscopic problem in order to get the macroscopically measurable bulk quantities is complicated. Besides the above mentioned convergence problem, the spatial distribution of pores, C, plays such an important role. Since it does matter whether the neighboring pores are close by or far away, the flux to each pore will in general be different (even for pores of identical size). As far as random distributions are concerned, this fact alone implies that approximations cannot be avoided. Approximating the pores by point sinks seems reasonable if σ is small enough. Utilizing in addition a self-consistency method [5] is another matter, since the objections against this scheme are well known [6]. Additional support from a variational approach [7] was needed to have confidence in the functional relationship between the membrane permeability P and σ for a random distribution [5]:

$$\frac{P-P_0}{P_0} \sim -\sigma \ln \sigma, \quad \text{for} \quad \sigma \ll 1. \tag{1a}$$

For a regular distribution of identical pores, the influence of C is more subtle. In this case, the flux to each pore will be the same, so that it suffices to concentrate on one pore alone. Furthermore, the whole space bounded from below by the membrane will split up into a repeating pattern of cells. The form of these regions will depend upon the details of C and the size of the cells is determined by σ. The customary cell method (CC-method) approximates — for mathematical simplicity — the actual cells by straight circular cylinders [8,9]. In this case, any information about C drops out (for any σ) and the formula equivalent to eqn. (1a) is readily found to be:

$$\frac{P-P_0}{P_0} = g\sqrt{\sigma}, \quad \text{for} \quad \sigma \ll 1, \tag{1b}$$

where g denotes a positive constant. This implies that a regular distribution of pores is — at least for small σ — more efficient in enhancing the permeability than a random distribution.

As said before by approximating the unit cells by straight circular cylinders, any information about the details of C are lost [3]. We do expect that in the correct version of eqn. (1b) the quantity g should actually contain C, i.e., $g = g(C)$. Phrased differently, we expect a different constant g to appear in eqn. (1b) for a hexagonal array than, for example, for a square array of pores.

To prove this and to obtain g for any regular distribution, we utilize a Green's function approach for the local concentration. This will enable us in section 2 to obtain our main formula, eqn. (13). This formula is so general that — besides the assumption of circular pores — it holds, no matter how the pores are spatially distributed (randomly or regularly) and allows for a distribution of pore sizes as well.

Consequences of this equation for any regular distribution of identical pores are obtained in section 3 (eqn. 16). Utilizing three parameters (the actual cell area, A_1, the distance of one pore to its nearest neighbor, ρ_{12}, and b, the radius of the largest inscribed circle of a cell) serves to uniquely classify any unit cell at the membrane surface ($\sigma = \pi a^2/A_1$). For small σ we then calculate g in terms of the three parameters just mentioned. In section 4, the additional influence of a finite membrane thickness is obtained. In section 5, the results are discussed and the error involved in the CC-method is estimated for various regular arrays.

2. Formulation of the problem

Consider a system comprising an infinitely large plane membrane, penetrated by discrete stationary pores and sandwiched between two stagnant fluid layers. If the concentration, c^*, of some solute species X in either layer is held constant (say at c^+ and c^-, respectively), the main concentration drop will occur across the membrane as illustrated in Fig. 1.

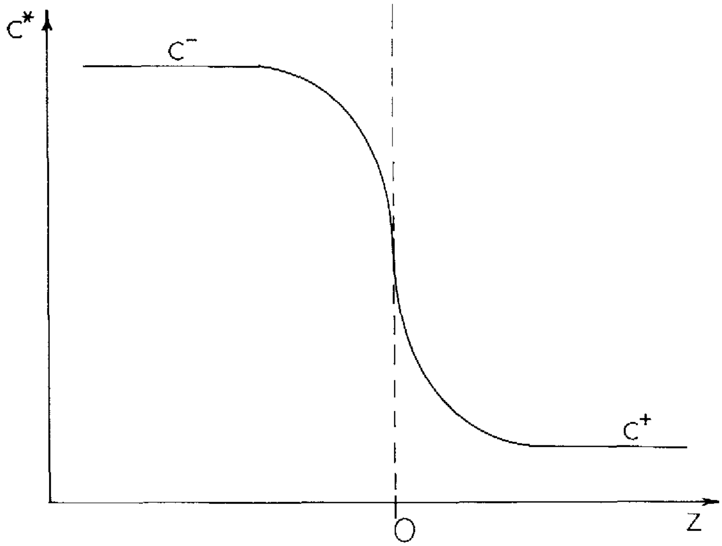

Fig. 1. The concentration distribution for diffusion through the infinitely thin plane membrane, $z = 0$.

The quantity of interest in that problem is the permeability, P, of the membrane. This is defined as:

$$P = \frac{\bar{j}}{\Delta c},$$

where $\bar{j}$ denotes the average flux of species X (average flow per unit of total membrane area) across the membrane, and Δc stands for the applied concentration difference, $\Delta c = |c^- - c^+|$.

In order to obtain P, we model the membrane as an impermeable plane $z = 0$, penetrated by N circular holes (the pores) of radii a_i, $i = 1, \ldots, N$.

Symbolically, we shall denote the total membrane area by S, while $S_i = \pi a_i^2$, $i = 1, \ldots, N$ indicates the pore area. In order to concentrate on interaction effects, we assume that the stagnant layers are essentially infinite (relative to the pore dimensions), i.e., $c^* = c^{\pm}$ for $z \to \pm\infty$. Utilizing the symmetry inherent in this problem and the fact that c^* assumes the value $\frac{1}{2}(c^+ + c^-)$ within each pore, it thus suffices to concentrate on half of the system, i.e., the membrane at $z = 0$ (with c^* prescribed within each pore) with an infinite (stagnant) region above. Choosing the origin of a coordinate system somewhere on the membrane, it proves convenient to write the position vector $\underline{r}$ as $\underline{r} = \underline{\rho} + z\hat{\underline{k}}$, $\underline{\rho} \cdot \hat{\underline{k}} = 0$, where $\hat{\underline{k}}$ stands for the unit vector in the z-direction. Figure 2, a face view of a section of the membrane, shows the various $\underline{\rho}$ vectors we will have to use.

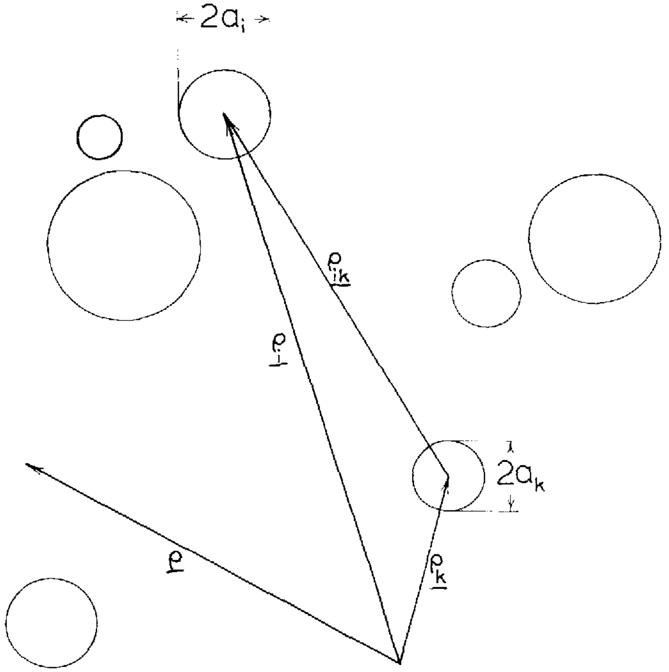

Fig. 2. Face view of membrane showing various position vectors, $\underline{\rho}$.

Introducing $c = c^* - c^+$, the mathematical statement of our model problem reads:

$$\nabla^2 c = 0, \quad z > 0, \tag{2a}$$

subject to the boundary conditions:

$$c \to 0 \quad \text{for } z \to \infty, \tag{2b}$$

$$\left.\begin{array}{ll} c = \dfrac{c^- - c^+}{2} = c_0\,, \quad \underline{\rho} \in S_i\,, \quad i = 1, \dots, N \\[2ex] \dfrac{\partial c}{\partial z} = 0\,, \qquad\qquad \underline{\rho} \notin S_i \end{array}\right\} z = 0\,. \tag{2c}$$

If D denotes the molar diffusivity of species X, the z-component of the flux, j_i, of X from pore i, $i = 1, \dots, N$ is given by:

$$j_i(\underline{\rho}) = -D \left.\frac{\partial c}{\partial z}\right|_{z=0}, \quad \underline{\rho} \in S_i\,. \tag{3}$$

In terms of j_i, the solution to eqns. (2a), (2b) and (2d) has the integral representation:

$$c(\underline{r}) = \frac{1}{2\pi D} \sum_{i=1}^{N} \int_{S_i} \mathrm{d}^2x' \, \frac{j_i(\underline{\rho}')}{|\underline{r} - \underline{\rho}'|}\,. \tag{4}$$

Equation (2c) is satisfied at pore k, provided the following relation holds:

$$c_k(\underline{\rho}) = \frac{1}{2\pi D} \int_{S_k} \mathrm{d}^2x' \, \frac{j_k(\underline{\rho}')}{|\underline{\rho} - \underline{\rho}'|}\,, \quad \underline{\rho} \in S_k\,. \tag{5}$$

Here we have introduced the abbreviation:

$$c_k(\underline{\rho}) \equiv c_0 - \frac{1}{2\pi D} \sum_{\substack{i=1 \\ i \neq k}}^{N} \int_{S_i} \mathrm{d}^2x' \, \frac{j_i(\underline{\rho}')}{|\underline{\rho} - \underline{\rho}'|}\,, \quad \underline{\rho} \in S_k\,. \tag{6}$$

Assuming for the moment that we are employing a cylindrical coordinate system $\underline{\rho} = (\rho, \phi)$ centered at the center of pore k, we multiply eqn. (5) by $2D/\pi(a_k^2 - \rho^2)^{-\frac{1}{2}}$ and integrate over S_k. Making use of the identity:

$$\int_0^{2\pi} \mathrm{d}\phi \int_0^{a_k} \mathrm{d}\rho \, \frac{\rho}{\sqrt{a_k^2 - \rho^2}\sqrt{\rho'^2 + \rho^2 - 2\rho\rho'\cos\phi}} = \begin{cases} \pi^2\,, & \rho' < a_k\,, \\ 2\pi \sin^{-1}\!\left(\dfrac{a_k}{\rho'}\right), & \rho' > a_k\,, \end{cases} \tag{7}$$

yields:

$$J_k = \frac{2D}{\pi} \int_0^{2\pi} \mathrm{d}\phi \int_0^{a_k} \mathrm{d}\rho\rho \, \frac{c_k(\underline{\rho})}{\sqrt{a_k^2 - \rho^2}}\,. \tag{8}$$

Here, J_k denotes the flow of species X from pore k, i.e.:

$$J_k = \int_{S_k} \mathrm{d}^2x \, j_k(\underline{\rho})\,. \tag{9}$$

With c_k defined by eqn. (6), eqn. (8) becomes:

$$J_k = 4Da_k c_0 - \frac{2}{\pi} \sum_{\substack{i=1 \\ i \neq k}}^{N} \int_{S_i} \mathrm{d}^2 x' j_i(\underline{\rho}') \sin^{-1}\left(\frac{a_k}{|\underline{\rho}' - \underline{\rho}_k|}\right), \quad k = 1, \ldots, N. \tag{10}$$

This equation is exact, and has been written relative to our arbitrary coordinate system (ρ_k denotes the position vector of the center of pore k). The first term is the (known) result for pores so far apart that any interaction among them can be neglected. Interaction effects are thus contained entirely within the second term. To evaluate it requires knowledge of the flux j_i. It has been shown that j_i satisfies a Fredholm integral equation [10], but this equation has so far not been solved.

Without knowing j_i, the most we can hope for is information about a first order correction to the noninteracting result, i.e., the result for small but nonzero area fraction σ:

$$\sigma \equiv \lim_{S\to\infty} \lim_{N\to\infty} \frac{\sum_{i=1}^{N} \pi a_i^2}{S}. \tag{11}$$

Intuitively, this seems rather simple. If σ is small enough, the distance between neighboring pores will be large. This suggests the approximation:

$$\sin^{-1}\left(\frac{a_k}{|\underline{\rho}' - \underline{\rho}_k|}\right) \cong \sin^{-1}\left(\frac{a_k}{\rho_{ik}}\right) \tag{12a}$$

in eqn. (10), where $\rho_{ik} = |\underline{\rho}_i - \underline{\rho}_k| = |\underline{\rho}_{ik}|$ denotes the distance between the centers of pores i and k. With this approximation, eqn. (10) becomes:

$$J_k = 4Da_k c_0 - \frac{2}{\pi} \sum_{\substack{i=1 \\ i \neq k}}^{N} J_i \sin^{-1}\left(\frac{a_k}{\rho_{ik}}\right). \tag{12b}$$

Unfortunately, eqn. (12b) does not allow us to take the $N \to \infty$ limit. This is a reflection of the fact that the concentration $c_k(\underline{\rho})$ decays only like $|\underline{\rho} - \underline{\rho}_k|^{-1}$ with increasing distance from that pore. Actually, a decay with any power of the inverse distance would eventually (for higher order interaction effects) be critical, although in our case the dilemma is already present at the lowest level of interaction. We should point out that this feature shows up in all two phase material studies, be they concerned with viscous flow, magnetic and electric susceptibilities, or heat transfer [11].

To overcome that dilemma, we have to realize that the convergence problems associated with eqn. (10) (or eqn. 12b) are of the same nature as that of $c(\underline{\rho})$

as represented by eqn. (4). To take advantage of that fact, we rewrite eqn. (10) as:

$$J_k = 4Da_k(c_0 - c(\underline{\rho})) + \frac{2a_k}{\pi} \int_{S_k} \mathrm{d}^2x' \frac{j_k(\underline{\rho}')}{|\underline{\rho} - \underline{\rho}'|}$$

$$+ \frac{2}{\pi} \sum_{\substack{i=1 \\ i \neq k}}^{N} \int_{S_i} \mathrm{d}^2x' j_i(\underline{\rho}') \left[\frac{a_k}{|\underline{\rho} - \underline{\rho}'|} - \sin^{-1}\left(\frac{a_k}{|\underline{\rho}' - \underline{\rho}_k|} \right) \right], \quad k = 1, \ldots, N. \quad (13)$$

The last term of this equation, which is solely due to interaction among the pores, no longer causes any headache for the $N \to \infty$ limit. It is this fact which makes eqn. (13) useful for our purposes, even though it involves not only the fluxes $j_i(\underline{\rho})$, $i = 1, \ldots, N$, but also $c(\underline{\rho})$.

3. First order interaction effects for regularly spaced pores

To demonstrate the usefulness of eqn. (13) for first order interaction effects, we shall assume that all holes are identical (i.e., $a_1 = \ldots = a_N = a$) and that they are arranged in a perfectly regular fashion. More specifically, we require that the configuration of pores relative to a reference pore is the same no matter what pore is chosen (square array, hexagonal array, etc.). This implies (a) that the flow of species X from a hole will be the same no matter what hole is considered ($J_1 = J_2 = \ldots = J_N = J$) and (b) that the membrane can be divided into a repeating pattern of independent regions (unit cells). The form of these regions will depend upon the details of the actual pore distribution, C, and their size is determined by the total number of pores (the area A_1 of the unit cell is S/N). Utilizing the same numbering system as before and choosing pore k as reference pore, eqn. (13) becomes:

$$J = 4Da(c_0 - c(\underline{\rho})) + \frac{2a}{\pi} \int_{S_k} \mathrm{d}^2x' \frac{j(\underline{\rho}')}{|\underline{\rho} - \underline{\rho}'|}$$

$$+ \frac{2}{\pi} \sum_{\substack{i=1 \\ i \neq k}}^{\infty} \int_{S_i} \mathrm{d}^2x' j(\underline{\rho}') \left[\frac{a}{|\underline{\rho} - \underline{\rho}'|} - \sin^{-1}\left(\frac{a}{|\underline{\rho}' - \underline{\rho}_k|} \right) \right]. \quad (14)$$

This equation is valid for any point $\underline{\rho}$ at the membrane surface, although we shall take a variation into consideration only within the reference cell itself. Let b denote the largest radius of a circular area concentric with pore k which lies entirely within the unit cell. Then clearly:

$$\frac{a}{b} = f\sigma^{1/2}, \quad (15)$$

where f denotes a function dependent upon the actual distribution C of pores*. Examples are:

$$f = \begin{cases} \sqrt{\dfrac{4}{\pi}} = 1.128\,, & \text{square array,} \\ \sqrt{\dfrac{2\sqrt{3}}{\pi}} = 1.050\,, & \text{hexagonal array.} \end{cases} \tag{16}$$

Let S_b denote the area of the inscribed circular domain just introduced ($S_b = \pi b^2$), and let $\tilde{S}_b = S_b - \pi a^2$ denote the impermeable part of S_b (this is the domain outside the pore and bounded by the dashed circle in Figs. 3—5). Integrating eqn. (14) over $\tilde{S}_b$ yields:

$$J\left[1-\left(\frac{a}{b}\right)^2\right] = 4Dac_0\left[1-\frac{a}{b}\,h_1\left(\frac{a}{b}\right)\right] + \frac{8}{\pi^2}\,\frac{a}{b}\int\limits_{S_k} \mathrm{d}^2x'j(\underline{\rho}')\left[\mathcal{E}\left(\frac{\rho'}{b}\right)-\frac{a}{b}\,\mathcal{E}\left(\frac{\rho'}{a}\right)\right] + 4Dac_0\,\frac{a}{b}\,h_2\left(\frac{a}{b}\right) \tag{16}$$

In this equation:

$$h_1\left(\frac{a}{b}\right) = \frac{1}{\pi a^2 c_0}\,\frac{a}{b}\int\limits_{S_b}\mathrm{d}^2x\,c(\underline{\rho})\,, \tag{17a}$$

$$h_2\left(\frac{a}{b}\right) = \frac{1}{2\pi^2 Dc_0a^3}\,\frac{a}{b}\sum_{\substack{i=1\\ i\neq k}}^{\infty}\int\limits_{\tilde{S}_b}\mathrm{d}^2x\int\limits_{S_i}\mathrm{d}^2x'j(\underline{\rho}')\times \times\left[\frac{a}{|\underline{\rho}-\underline{\rho}'|}-\sin^{-1}\left(\frac{a}{|\underline{\rho}'-\underline{\rho}_k|}\right)\right], \tag{17b}$$

and

$$\mathcal{E}(t) = \int_0^1 \mathrm{d}x\sqrt{\frac{1-t^2x^2}{1-x^2}}\,, \tag{17c}$$

is the complete elliptic integral of the second kind. Equation (16) is exact and valid for any $a/b \leqslant 1$.

*If more than one quantity is needed to uniquely specify the unit cell (e.g., rectangular array), then f will depend upon the ratio of these quantities, too (see Fig. 5).

Our main interest concerns the limit of small area fraction σ, i.e., $a/b \ll 1$. With $\rho' \in S_k$ (i.e., $\rho' < a$), we utilize the expansion:

$$\mathcal{E}\left(\frac{\rho'}{b}\right) = \frac{\pi}{2}\left[1 + O\left(\left(\frac{a}{b}\right)^2\right)\right] \tag{18}$$

in the second term on the righthand side of eqn. (16) to obtain:

$$J\left[1 - \frac{4}{\pi}\,\frac{a}{b} + O\left(\left(\frac{a}{b}\right)^2\right)\right] = 4Dac_0\left\{1 + \frac{a}{b}\left[h_2\left(\frac{a}{b}\right) - h_1\left(\frac{a}{b}\right)\right]\right\} \tag{19}$$

Solving for J furnishes:

$$J = \frac{4Dac_0}{\beta}\ , \tag{20}$$

with

$$\beta = 1 - \frac{a}{b}\left[\frac{4}{\pi} + h_2(0) - h_1(0)\right] + o\left(\left(\frac{a}{b}\right)\right)\ . \tag{21}$$

Here, $h_i(0)$ denotes the $a/b = 0$ limit of the functions h_i, $i = 1, 2$. Obtaining it requires the $\sigma = 0$ limit of c and j, i.e., the expressions* [12]

$$\lim_{\sigma\to 0} c(\underline{\rho}) = \begin{cases} c_0\,, & \rho < a \\ \dfrac{2c_0}{\pi}\sin^{-1}\left(\dfrac{a}{\rho}\right), & \rho > a\,, \end{cases} \tag{22a}$$

and

$$\lim_{\sigma\to 0} j(\underline{\rho}) = \begin{cases} \dfrac{2}{\pi}\,\dfrac{c_0 D}{\sqrt{a^2-\rho^2}}\,, & \rho < a\,, \\ 0 & \rho > a\,. \end{cases} \tag{22b}$$

Utilizing eqn. (22a) in eqn. (17a) furnishes:

$$h_1(0) = 4/\pi\ , \tag{23}$$

while the use of eqn. (22b) in eqn. (17b) leads to (see Appendix):

$$h_2(0) = \frac{1}{\pi}\sum_{\substack{i=1\\ i\neq k}}^{\infty}\frac{2b}{\rho_{ik}}\left\{\frac{4}{\pi}\left[\mathcal{K}\left(\frac{b}{\rho_{ik}}\right) - \mathcal{D}\left(\frac{b}{\rho_{ik}}\right)\right] - 1\right\}. \tag{24}$$

---

*In this form, the expressions require that we use cylindrical coordinates measured from the center of the pore in question.

Here:

$$\mathcal{K}(x) = \int_0^1 \frac{dt}{\sqrt{1-t^2}\sqrt{1-x^2t^2}} \tag{25}$$

stands for the complete elliptic integral of the first kind, while $\mathcal{D}(t)$ denotes the combination:

$$\mathcal{D}(t) = \frac{\mathcal{K}(t) - \mathcal{E}(t)}{t^2} = \int_0^1 dx \frac{x^2}{\sqrt{1-x^2}\sqrt{1-t^2x^2}} \tag{26}$$

Note that eqn. (21) now reads:

$$\beta = 1 - \frac{a}{b} h_2(0) + o\left(\frac{a}{b}\right) . \tag{27}$$

To evaluate $h_2(0)$, let us first consider a square array. In a cartesian coordinate system centered at the center of the reference pore and oriented parallel to the principal directions of the membrane, the distance ρ_{ik} is given by:

$$\rho_{ik} = \rho_{12}\sqrt{i_x^2 + i_y^2} , \quad i_x, i_y = 0, \pm 1, \pm 2, \ldots, \quad \text{with } i_x^2 + i_y^2 \geqslant 1 . \tag{28}$$

Here, ρ_{12} denotes the closest distance between two adjacent pores, in our case, $\rho_{12} = 2b$. Introducing the Heaviside function, $H(x)$:

$$H(t) = \begin{cases} 1, & t \geqslant 0 \\ 0, & t < 0, \end{cases} \tag{29}$$

allows us to write eqn. (24) as:

$$h_2(0) = \frac{2b}{\pi\rho_{12}} \sum_{i_x=-\infty}^{\infty} \sum_{i_y=-\infty}^{\infty} \frac{H(i_x^2 + i_y^2 - 1)}{\sqrt{i_x^2 + i_y^2}} \left\{ \frac{4}{\pi}\left[\mathcal{K}\left(\frac{b}{\rho_{12}\sqrt{i_x^2 + i_y^2}}\right) - \mathcal{D}\left(\frac{b}{\rho_{12}\sqrt{i_x^2 + i_y^2}}\right)\right] - 1 \right\} . \tag{30}$$

Quite clearly, the unrestricted double summation can be written as four times a double summation with i_x restricted to positive integers ($i_x = 1, 2, \ldots$) and i_y restricted to nonnegative integers ($i_y = 0, 1, \ldots$). Making use then of Gregory's formula [13]:

$$\sum_{i=0}^{\infty} f(i) = \int_0^{\infty} di f(i) + \tfrac{1}{2} f(0) + \text{error terms} , \tag{31}$$

which implies:

$$\sum_{i_x=1}^{\infty}\sum_{i_y=0}^{\infty} f(i_x^2+i_y^2) = \int_0^{\infty} \mathrm{d}i_x \int_0^{\infty} \mathrm{d}i_y f(i_x^2+i_y^2) - \tfrac{1}{4} f(0) + \text{error terms}$$

$$= \frac{\pi}{2}\int_0^{\infty} \mathrm{d}\tau\, \tau\, f(\tau^2) - \tfrac{1}{4} f(0) + \text{error terms}\,, \tag{32}$$

furnishes:

$$h_2(0) = \frac{4b}{\rho_{12}} \int_1^{\infty} \mathrm{d}\tau \left\{\frac{4}{\pi}\left[\mathcal{K}\left(\frac{b}{\tau\rho_{12}}\right) - \mathcal{D}\left(\frac{b}{\tau\rho_{12}}\right)\right] - 1\right\}$$

$$= 4\frac{b}{\rho_{12}}\left\{1 + \frac{4}{3\pi}\left(\frac{\rho_{12}}{b}\right)^2\left[\left(1-\left(\frac{b}{\rho_{12}}\right)^2\right)\mathcal{K}\left(\frac{b}{\rho_{12}}\right)\right.\right.$$

$$\left.\left. - \left(1+\left(\frac{b}{\rho_{12}}\right)^2\right)\mathcal{E}\left(\frac{b}{\rho_{12}}\right)\right]\right\}. \tag{33}$$

For the square array under consideration, $\rho_{12} = 2b$. Using tabulated values of the complete elliptic integrals, we end up with:

$$h_2(0) = 0.0646\,. \tag{34}$$

For completeness, we note that by using known series-expansions for $\mathcal{K}$ and $\mathcal{D}$, eqn. (24) is equivalent to:

$$h_2(0) = \frac{2}{\pi}\sum_{j=1}^{\infty}\left(\frac{(2j-1)!!}{2^j j!}\right)^2 \frac{1}{(j+1)} \sum_{\substack{i=1\\ i\neq k}}^{\infty}\left(\frac{b}{\rho_{ik}}\right)^{2j+1}. \tag{35}$$

Proceeding as before, the analog to eqn. (33) is:

$$h_2(0) = 4\sum_{j=1}^{\infty}\left(\frac{(2j-1)!!}{2^j j!}\right)^2 \frac{1}{(j+1)(2j-1)}\left(\frac{b}{\rho_{12}}\right)^{2j+1}. \tag{36}$$

Keeping only the first term of eqn. (36) leads to a value of $1/16 = 0.0625$ for $h_2(0)$, i.e., it is in error by only 3.25 percent from the exact value. If the second term is kept also, the result is $(1/16)(1 + 1/32) = 0.0645$, differing by only one-fifth of a percent from eqn. (34). Accepting this small difference implies that eqn. (24) can be approximated by the simple formula:

$$h_2(0) = \frac{1}{4\pi}\sum_{\substack{i=1\\ i\neq k}}^{\infty}\left(\frac{b}{\rho_{ik}}\right)^3\left[1 + \frac{3}{8}\left(\frac{b}{\rho_{ik}}\right)^2\right]. \tag{37}$$

To make progress for arbitrary regular distributions, C, let us scale ρ_{ik} with $\sqrt{A_1}$, where A_1 is the cell-area:

$$\rho_{ik} = \tau_{ik}\sqrt{A_1}\,. \tag{38}$$

The quantity τ_{ik} is thus the dimensionless distance between pore i and the reference pore. Since the pores cover the total membrane area (and not just sections of it), the range of τ_{ik} defines a two-dimensional space. Each unit area of that space is occupied by exactly one pore (or cell), so that the number of pores with distance between τ and $\tau + \mathrm{d}\tau$ from the reference pore is $2\pi\tau\mathrm{d}\tau$, the "area" of that section. Consequently, we can put:

$$\sum_{\substack{i=1\\ i\neq k}}^{\infty}\left(\frac{b}{\rho_{ik}}\right)^{2j+1} = 2\pi\left(\frac{b}{\sqrt{A_1}}\right)^{2j+1}\int_0^\infty \mathrm{d}\tau\,\frac{H(\tau-\tau_{12})}{\tau^{2j}}$$

$$= \frac{2\pi}{2j-1}\,\frac{b^2}{A_1}\,\rho_{12}^{1-2j}\,. \tag{39}$$

Here, $\tau_{12} = \rho_{12}/\sqrt{A_1}$ denotes the dimensionless distance of the reference pore to its nearest neighbors. Utilizing this relation in eqn. (35) furnishes:

$$h_2(0) = \frac{1}{2}\,\frac{b^3}{A_1\rho_{12}}\sum_{j=1}^{\infty}\left(\frac{(2j-1)!!}{2^{j-1}j!}\right)^2\frac{2}{(j+1)(2j-1)}\left(\frac{b}{\rho_{12}}\right)^{2(j-1)} \tag{40}$$

As far as the quantity β is concerned, we thus get:

$$\beta = 1 - g(C)\sigma^{1/2} + O(\sigma)\,. \tag{41}$$

with*:

$$g(C) = \frac{1}{2\sqrt{\pi}}\,\frac{b^2}{\rho_{12}\sqrt{A_1}}\sum_{j=1}\left(\frac{(2j-1)!!}{2^{j-1}j!}\right)^2\frac{2}{(j+1)(2j-1)}\left(\frac{b}{\rho_{12}}\right)^{2(j-1)}$$

$$= \frac{1}{2\sqrt{\pi}}\,\frac{b^2}{\rho_{12}\sqrt{A_1}}\left\{1+\frac{1}{8}\left(\frac{b}{\rho_{12}}\right)^2+\frac{5}{128}\left(\frac{b}{\rho_{12}}\right)^4+\ldots\right\}. \tag{42}$$

The function g contains all the details of the actual distribution, C. For the examples shown in Figs. 3 and 4, respectively, we explicitly have:

$$g = \begin{cases} 0.0729, \text{ square array: } \sqrt{A_1} = \rho_{12} = 2b\,, \\ 0.0783, \text{ hexagonal array: } \sqrt{A_1} = \sqrt{2\sqrt{3}}\,b,\ \rho_{12} = 2b\,. \end{cases} \tag{43}$$

*Alternatively, we could express g in terms of the complete elliptic integrals $\mathcal{E}$ and $\mathcal{K}$ (cf. eqn. 33).

Although for these cases g is simply a number, it is important to realize that for unit cells which require more than one parameter for specification, g will be a function of the ratios of these parameters as well. As an example, consider the parallelogram-like unit cell shown in Fig. 5. Assuming without

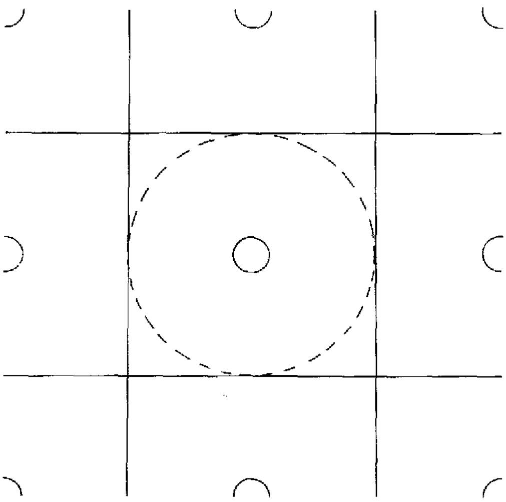

Fig. 3. The unit cell for a square array of pores. For the meaning of the dashed circle (radius b), see text.

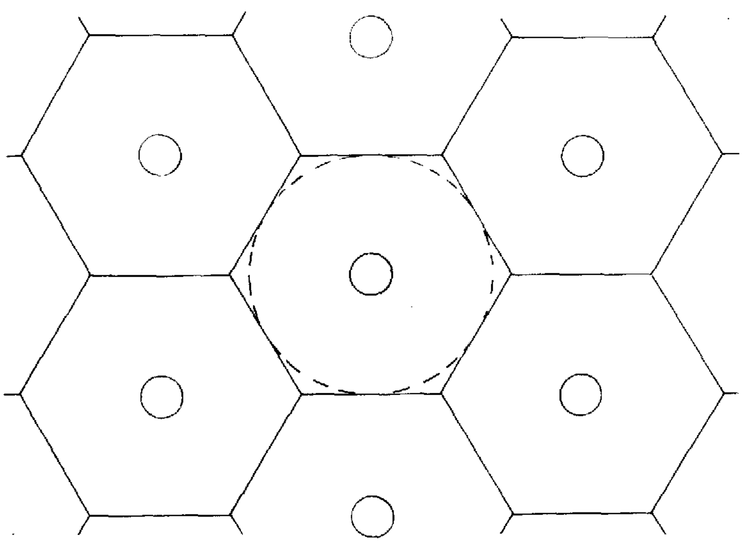

Fig. 4. The unit cell for a hexagonal array of pores. The dashed circle (radius b) has the same meaning as in Fig. 3.

loss of generality $b_1 \leqslant b_2$, we have:

$$A_1 = b_1 b_2 \sin\phi , \quad \rho_{12} = b_1 , \quad b = \frac{b_1}{2} \sin\phi , \tag{44}$$

and consequently,

$$g = \frac{1}{8}\left(\frac{b_1 \sin^3\phi}{\pi b_2}\right)^{1/2} \left\{1 + \frac{1}{32}\sin^2\phi + \frac{5}{2048}\sin^4\phi + \ldots\right\}. \tag{45}$$

Thus, for fixed b_1/b_2, the function g monotonically decreases from its value $0.0729\sqrt{b_1/b_2}$ (rectangular array) with decreasing angle ϕ, $0 < \phi \leqslant \pi/2$.

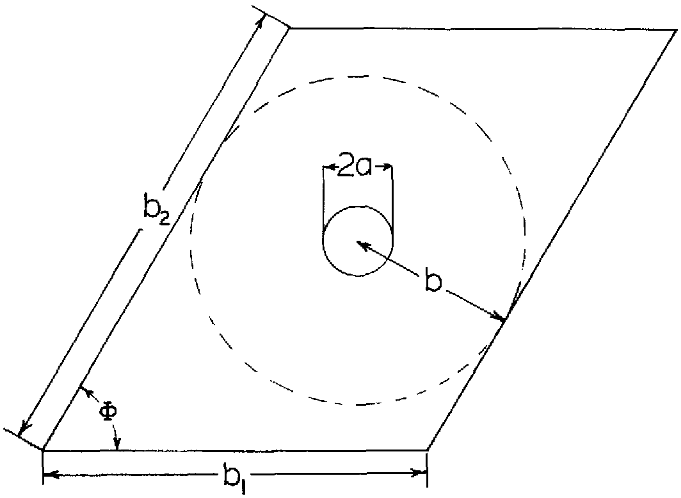

Fig. 5. A parallelogram-like unit cell.

4. First-order interaction effects for membranes of nonzero thickness

Utilizing the same assumptions as laid down in section 1, the concentration distribution $c(\underline{r})$ for a membrane of thickness $2L$ will assume the value c_0 (as defined by eqn. 2c) exactly halfway between pore entrance and pore exit. Measuring z as before, the concentration distribution within the infinite half space $z > 0$ bounded from below by an impenetrable wall at $z = 0$ with circular holes of radius a_i and centers at $\underline{\rho}_i$ ($i = 1, \ldots, N$) — called region I — still allows the representation of eqn. (4). In order to determine the unknown concentration $c_\mathrm{I}(\underline{\rho})$ and flux $j_\mathrm{I}(\underline{\rho})$ within each hole*, the representation (4)

*The subscript I serves to emphasize the fact that these are quantities obtained by taking the $z = 0_+$ limit of eqn. (4).

has to be matched within each hole to a representation of c appropriate for an impermeable circular cylinder (region II), which assumes the known constant c_0 at $z = -L$. Assuming that this has been done (i.e., $c_{\rm I}(\underline{\rho}) = c_{\rm II}(\underline{\rho})$, $j_{i\rm I}(\underline{\rho}) = j_{i\rm II}(\underline{\rho})$ for $\underline{\rho} \in S_i$, $i = 1, \ldots, N$), eqn. (6) merely requires the replacement of c_0 by $c_{\rm I}(\underline{\rho})$ within each hole. This implies that eqn. (10) now reads:

$$J_k = \frac{2D}{\pi} \int_0^{2\pi} \mathrm{d}\phi \int_0^{a_k} \mathrm{d}\rho\, \rho\, \frac{c_{\rm I}(\underline{\rho})}{\sqrt{a_k^2 - \rho^2}}$$

$$- \frac{2}{\pi} \sum_{\substack{i=1 \\ i \neq k}}^{N} \int_{S_i} \mathrm{d}^2 x' j_{i\rm I}(\underline{\rho}') \sin^{-1}\left(\frac{a_k}{|\rho' - \rho_k|}\right), \qquad k = 1, \ldots, N. \tag{46}$$

In contrast to eqn. (10), there is no reason to believe that the first term on the right-hand side of this equation will assume its $\sigma = 0$ value (given by eqn. 50). Thus, in order to make progress we have to resort to some kind of approximation. To this end, we make use of the fact that for noninteracting pores, the assumption of a linear variation in z of $c_{\rm II}$ within each cylinder introduces errors of less than 3 percent as far as the flow J_k is concerned [14] *. This approximation — which is exact for $L/a \to \infty$ — requires that within pore k, $k = 1, \ldots, N$:

$$c_{\rm II} = c_{\rm II}(z) = c_0 - \frac{J_k}{\pi a_k^2 D}(L + z). \tag{47}$$

Since this implies that $c_{\rm I}(\underline{\rho})$ is actually constant within each pore:

$$c_{\rm I}(\underline{\rho}) = c_0 - \frac{J_k L}{\pi a_k^2 D} \equiv c_{{\rm I}k}, \tag{48}$$

we can use all of our previous results provided that c_0 in these formulas is replaced by $c_{{\rm I}k}$. As far as interaction effects are concerned, we thus get in place of eqn. (20):

$$J = \frac{4Dac_{{\rm I}k}}{\beta},$$

i.e.:

$$J = \frac{4Dac_0}{\beta + (4/\pi)L/a}, \tag{49}$$

with β given by eqn. (41). This equation implies that interaction between neighboring pores becomes less and less important the thicker the membrane

*This maximum error occurs around $L/a = 0.5$

is. This is in perfect agreement with a conclusion reached previously [3,14].

If interaction is completely neglected, the correct expression for J is [14]:

$$J = \frac{4Dac_0}{\alpha(L/a) + (4/\pi)L/a} \tag{50}$$

The formula $\alpha(L/a)$ is known numerically: it increases monotonically from its $L/a = 0$ value of one to 1.0461 for $L/a \to \infty$. This small variation indicates that the approximation $\alpha = 1$ is indeed very good (this approximation is equivalent to the linear variation (47) of c_{II}). If greater accuracy is required, the expression:

$$\alpha = 1 + [21.4479 + 0.2564\coth(0.3439\,L/a)]^{-1} \tag{51}$$

not only is exact for $L/a \ll 1$ and $L/a \gg 1$, but differs from the numerical results by less than 0.2 percent [14].

Since eqn. (50) is the correct $\sigma \to 0$ limit for J, we expect that the correct form of J with interaction taken into account should be:

$$J = \frac{4Dac_0}{\alpha(L/a)\beta + (4/\pi)L/a} \;. \tag{52}$$

5. Conclusions

In this study we modelled a membrane as an impermeable slab of thickness $2L$, penetrated by discrete uniform circular cylinders of radius a (the pores). If the pores are distributed in a regular fashion over the membrane, the average flux, $\bar{j}$, per unit of total area is related to the flow, J, via:

$$\bar{j} = \frac{J}{\pi a^2}\,\sigma \;. \tag{53}$$

Since we have treated only half of the problem, the concentration drop appropriate for the permeability, P, is:

$$\Delta c = \frac{c^+ + c^-}{2} - c^+ = \frac{c^- - c^+}{2} = c_0 \;.$$

Making use of eqn. (52), the permeability P thus becomes:

$$P/P_0 = [\alpha(L/a)\beta + (4/\pi)L/a]^{-1} \;, \tag{54}$$

with:

$$P_0 = \frac{4D}{\pi a}\,\sigma \;. \tag{55}$$

the permeability for an infinitely thin membrane with noninteracting pores. The function α is given by eqn. (51), but may very well be approximated by one. For first order interaction effects, β can be written as:

$$\beta = 1 - g(C)\sigma^{1/2} + O(\sigma) . \tag{56}$$

with $g(C)$ given for any regular distribution by eqn. (41). This result implies that interaction among pores enhanced the permeability. This enhancement is larger than linear. Essentially, this reflects the fact that the interaction between pores is "strong" so that contributions from different pores cannot simply be summed (see also the remarks leading to eqn. 13). The function g contains all the information about the actual distribution C and eqns. (43) and (45) list some examples.

Since interaction effects become less important with increasing membrane thickness, the largest error of the CC-method will be encountered for an infinitely thin membrane. Utilizing eqns. (27) and (34) we find for $L = 0$ and $\sigma \ll 1$:

$$P_c/P_0 = 1 + 0.0646\sqrt{\sigma} , \tag{57}$$

where the index c emphasizes the fact that this is the permeability resulting from the CC-method. Consequently:

$$\frac{P - P_c}{P - P_0} = 1 - \frac{0.0646}{g(C)} \tag{58}$$

will be the error associated with the CC-method relative to $P - P_0$. Utilizing eqns. (43) and (45), we explicitly have:

$$\frac{P - P_c}{P - P_0} = \begin{cases} 0.114 , & \text{square array} , \\ 0.178 , & \text{hexagonal array} , \\ 0.114 \sqrt{\dfrac{b_2}{b_1}} , & \text{rectangular array} . \end{cases} \tag{59}$$

Especially for regular arrays of widely different sides, the error can be arbitrarily large. What somehow "saves" the CC-estimate of P is the smallness of σ required for validity of eqn. (57)*. Whether or not the CC-method is not totally off in its estimate for P — at least for some distributions C — for moderate values of σ remains to be seen. Further fundamental study in this direction is clearly called for.

*Note also that $g(C)$ is small for all distributions studied.

List of symbols

a_i	radius of ith pore
a	radius of any pore for pores of identical size
A	area of unit cell, $A_1 = S/N$
b	radius of largest circle inscribed in cell
b_1, b_2	length parameters of the parallelogram-like unit cell (Fig. 5)
c^*	molar concentration of diffusing species
c^+, c^-	concentrations outside the boundary layer
c	$c^* - c^+$, concentration relative to c^+
Δc	$\lvert c^- - c^+ \rvert$, concentration drop across membranes
c_0	$(c^- - c^+)/2$
c_{I}, c_{II}	concentration above and inside the membrane (used only for membranes of nonzero thickness)
C	spatial distribution of pores
D	molar diffusivity
$\mathcal{D}$	the complete elliptic integral of the third kind (eqn. 26)
$\mathcal{E}$	complete elliptic integral of the second kind (eqn. 17c)
$f(C)$	function relating the ratio a/b to $\sigma^{\frac{1}{2}}$ (eqn. 15)
$g(C)$	function describing the $\sigma \ll 1$ influence of C for a regular distribution on the permeability P, eqn. (1b)
h_1, h_2	functions, defined by eqns. (17)
$H(x)$	Heaviside function, eqn. (29)
$j_i = j_i(\underline{\rho})$	local flux from pore i, eqn. (3) (the symbols $j_{i\mathrm{I}}$, $j_{i\mathrm{II}}$ are used if c_{I}, c_{II} are needed)
$j(\underline{\rho})$	local flux from one pore for identical pores
$\bar{j}$	total average flux per unit of total membrane area
J_i, J	flow from pore i, eqn. (9); subscript i omitted for identical pores
$\hat{\underline{k}}$	unit vector in the z-direction
$\mathcal{K}$	complete elliptic integral of the first kind (eqn. 25)
L	thickness of membrane
N	number of pores
P, P_0, P_c	membrane permeability (MP); MP for noninteracting pores; MP resulting from the CC-method
$\underline{r}$	position vector measured from arbitrary origin at membrane surface
S, S_i, S_b, $\tilde{S}_b$	areas: total membrane area; area of ith pore, $S_i = \pi a_i^2$; area of inscribed circle, $S_b = \pi b^2$; $\tilde{S}_b = \pi(b^2 - a^2)$
z	vertical distance from top surface of membrane
$\alpha(L/a)$	function describing the influence of membrane thickness on P, eqn. (50)
$\beta(C, \sigma)$	function describing the influence of C and σ on P, eqn. (20)
ϕ	angle
$\underline{\rho}$	$\underline{r} - z\hat{\underline{k}}$: position vector at membrane surface
$\underline{\rho}_i$, $\underline{\rho}_{ik}$	position vectors defined by Fig. 2

$\rho_{ik} = \lvert\underline{\rho}_{ik}\rvert$	distance between the centers of pore i and k
ρ_{12}	distance of the nearest neighboring pore from the reference pore
τ_{ik}, τ_{12}	dimensionless analogues of ρ_{ik} and ρ_{12}, eqn. (38)
σ	area fraction of pores

References

1 M. Brown and F. Escombe, Static diffusion of gases and liquids in relation to the assimilation of carbon and translocation in plants, Trans. Roy. Soc. London, B193 (1900) 223—260.
2 J. Dainty and C.R. House, Unstirred layers in frog skin, J. Physiol., 182 (1966) 66—69.
3 W.A. Wakeham and E.A. Mason, Diffusion through multiperforate laminae, Ind. Eng. Chem. Fund., 18 (1979) 301—305.
4 L. Nannis and W. Kesselman, Engineering applications of current and potential distributions in disk electrode systems, J. Electrochem. Soc., 118 (1971) 454—461.
5 S. Prager and H.L. Frisch, Interaction between penetration sites in diffusion through thin membranes, J. Chem. Phys., 62 (1975) 89—91.
6 Z. Hashin, Assessment of the self consistent scheme approximation: conductivity of particulate composite, J. Comp. Mat., 2 (1968) 284—300.
7 G.H. Malone, T.E. Hutchinson and S. Prager, Molecular models for permeation through thin membranes: the effect of hydrodynamic interaction on permeability, J. Fluid Mech., 65 (1974) 753—760.
8 K.H. Keller and T.R. Stein, A two dimensional analysis of membrane transport, Math. Biosci., 1 (1967) 421—437.
9 A. Nir and R. Pfeffer, Transport of macromolecules across arterial wall in the presence of local endothial injury, J. Theor. Biol., 81 (1979) 685—711.
10 V.I. Fabrikant, personal communication, 1983.
11 G.K. Batchelor, Transport properties of two phase materials with random structure, Ann. Rev. Fluid Dyn., 6 (1974) 227—255.
12 M.S. Carslaw and J.C. Jaeger, Conduction of Heat in Solids, Oxford University Press, Oxford, 1968.
13 R.W. Hamming, Numerical Methods for Scientists and Engineers, McGraw-Hill, New York, 1954.
14 P.O. Brunn, V.I. Fabrikant and T.S. Sankar, Diffusion through membranes: effect of a nonzero membrane thickness, Q. J. Mech. Appl. Math., in press.

Appendix

Evaluation of $h_2(0)$

Let:

$$h_{2i}\left(\frac{a}{b}\right) = \frac{1}{2\pi^2 D c_0 a^3}\,\frac{a}{b}\int_{\tilde{S}_b} \mathrm{d}^2x \int_{S_i} \mathrm{d}^2x'\,j(\underline{\rho}')\left[\frac{a}{\lvert\underline{\rho}-\underline{\rho}'\rvert} - \sin^{-1}\left(\frac{a}{\lvert\underline{\rho}'-\underline{\rho}_k\rvert}\right)\right], \quad (A.1)$$

then:

$$h_2\left(\frac{a}{b}\right) = \sum_{\substack{i=1\\ i\neq k}}^{\infty} h_{2i}\left(\frac{a}{b}\right). \quad (A.2)$$

Thus, it suffices to concentrate on one term, h_{2i}. In a cylindrical coordinate system centered at hole i, ρ' will be less than a while ρ_k denotes the center of hole k. For $\sigma \to 0$, we thus can utilize the approximation (12a). Inserting eqn. (22b) into eqn. (A.1), and recalling eqn. (7), we thus obtain:

$$h_{2i}\left(\frac{a}{b}\right) = \frac{2}{\pi^2 a^2}\,\frac{a}{b}\int_{\tilde{S}_b} \mathrm{d}^2x\left[\sin^{-1}\left(\frac{a}{\rho}\right) - \sin^{-1}\left(\frac{a}{\rho_{ik}}\right)\right]\ . \tag{A.3}$$

Since ρ is measured from the center of pore i, we explicitly have:

$$\begin{aligned}
h_{2i}\left(\frac{a}{b}\right) = \frac{4}{\pi^2 a^2}\,\frac{a}{b}\Bigg\{ &\int_0^{\sin^{-1}(\frac{b}{\rho_{ik}})} \mathrm{d}\phi \int_{r_{\min}(b,\phi)}^{r_{\max}(b,\phi)} \mathrm{d}\rho\ \rho\ \sin^{-1}\left(\frac{a}{\rho}\right) \\
&- \int_0^{\sin^{-1}(\frac{a}{\rho_{ik}})} \mathrm{d}\phi \int_{r_{\min}(a,\phi)}^{r_{\max}(a,\phi)} \mathrm{d}\rho\ \rho\ \sin^{-1}\left(\frac{a}{\rho}\right)\Bigg\} \\
&- \frac{2}{\pi}\,\frac{b}{a}\left[1 - \left(\frac{a}{b}\right)^2\right]\sin^{-1}\left(\frac{a}{\rho_{ik}}\right),
\end{aligned} \tag{A.4}$$

with:

$$\begin{aligned}
r_{\min}(x,\phi) &= \rho_{ik}\cos\phi - \sqrt{x^2 - \rho_{ik}^2\sin^2\phi}\ , \\
r_{\max}(x,\phi) &= \rho_{ik}\cos\phi + \sqrt{x^2 - \rho_{ik}^2\sin^2\phi}
\end{aligned} \tag{A.5}$$

for $\phi < \sin^{-1}(x/\rho_{ik})$. Taking now the limit $a/b \to 0$, furnishes:

$$\begin{aligned}
h_{2i}(0) &= \frac{8}{\pi^2}\int_0^{\sin^{-1}(\frac{b}{\rho_{ik}})} \mathrm{d}\phi\ \sqrt{1 - \left(\frac{\rho_{ik}}{b}\right)^2 \sin^2\phi} - \frac{2}{\pi}\,\frac{b}{\rho_{ik}} \\
&= \frac{8}{\pi^2}\,\frac{\rho_{ik}}{b}\left\{\mathcal{E}\left(\frac{b}{\rho_{ik}}\right) - \left[1 - \left(\frac{b}{\rho_{ik}}\right)^2\right]\mathcal{K}\left(\frac{b}{\rho_{ik}}\right)\right\} - \frac{2}{\pi}\,\frac{b}{\rho_{ik}}
\end{aligned} \tag{A.6}$$

This is identical to eqn. (24) of the text if the identity (26) is utilized.