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Note on the Capillary Model of Transport through Charged Membranes

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The capillary model of transport through charged membranes has been reformulated by transport equations of non-equilibrium thermodynamics. Two geometries of pores has been considered – a capillary and a slit. It has been assumed that the distribution of mobile components is governed by the zero components of forces in the plane perpendicular to the direction of transport. It has been shown that the part of transport coefficients, describing the motion of the center of mass, depends on the distribution of species inside the capillary and on the viscosity of the solution. The transport coefficients, averaged over the cross-section, are symmetrical.

Key words: capillary model, charged membrane, non-equilibrium thermodynamics

The capillary model of transport of electrolyte solutions through charged membranes has been discussed and applied by many authors, *e.g.* [1–13] and references therein. Usually, for the description of transport the Nernst-Planck equation has been used. The convective contribution has been calculated from the Navier-Stokes equation. Trying to find the analytical solutions of Poisson-Boltzmann equation, governing the distribution of ions, many simplifying assumptions have been introduced, which make the final expressions of limited applicability. The Nernst-Planck equation, neglecting the couplings between ions, has also been used in papers correlating the parameters of the capillary model with the coefficients of transport equations of non-equilibrium thermodynamics, which from the formal point of view is not correct.

Thus, the aim of this paper is to derive the general transport equations of the capillary model basing on the non-equilibrium thermodynamics. Prior to the derivation one comment on the distribution of particles inside a capillary should be made. In most cases (exceptions are [10,12]) the distribution of ions has been described by the Boltzmann equation:

$$c_i = c_i(\psi = 0)\exp(-z_i F\psi/RT) \tag{1}$$

where c_i is the concentration of ion i in the place of a potential ψ. This equation is consistent with the Nernst-Planck equation:

$$\boldsymbol{j}_i = -D_i\left(z_i c_i \frac{F}{RT}\nabla\psi + \nabla c_i\right) \tag{2}$$

in that sense, that after differentiating (1) is the same as the condition for $\boldsymbol{j}_i$ to be zero:

$$\nabla c_i = -z_i c_i \frac{F}{RT}\nabla\psi \tag{2a}$$

To be in agreement with applied transport equations (4) and (7) it is assumed here that the distribution of mobile species is given by the assumption of the zero radial flows, *i.e.* by the equation (17). Two geometries of pores in a membrane are considered (Fig. 1) – a capillary and a slit. The membrane is assumed to be rigid.

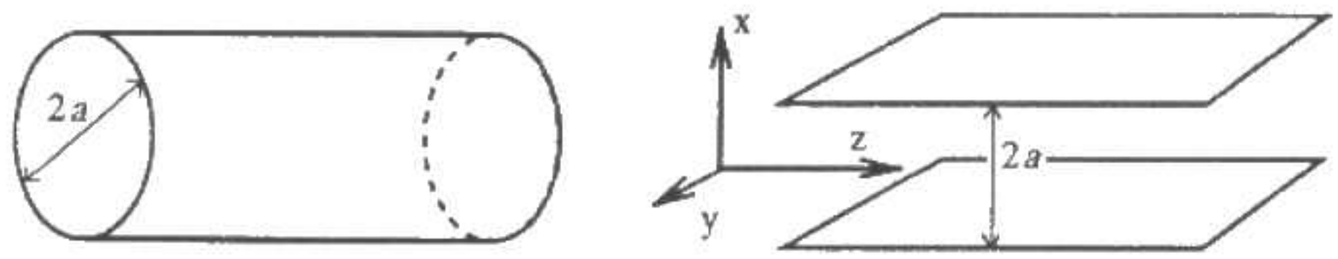

Figure 1. Two pore geometries: capillary of radius a and slit – the distance of walls is $2a$.

DISSIPATION FUNCTION

The system considered is isothermal, no chemical reaction takes place, the rotation energy is not included. For such conditions the dissipation function at the given point of the cross-section of a capillary is [14,(7.30)]:

$$\Phi = \sum_{i=0}^{n-1} \boldsymbol{J}_i \cdot \boldsymbol{X}_i - \underline{\Pi}:\mathrm{Grad}\mathbf{v} \tag{3}$$

The indices denote 0 – solvent, 1,.., n-1 – other mobile species (ions, *etc.*), n – membrane.

In the solution, filling a capillary, the density of the membrane is zero, $\rho_n = 0$, *i.e.* the membrane is considered only as a wall of capillary. Because of a simpler form of equations, the densities are used instead of molar concentrations. The symbols have their usual meaning. $\boldsymbol{J}_i$ is the flow of i relative to the local center of mass, $\boldsymbol{X}_i$ – thermodynamic force coupled with $\boldsymbol{J}_i$, $\boldsymbol{F}_i$ – external force, $\underline{\Pi}$ – viscosity tensor, $\mathbf{v}$ – velocity of local center of mass:

$$\boldsymbol{J}_i = \rho_i(\mathbf{v}_i - \mathbf{v}) = \sum_{k=0}^{n-1} l_{ik}\, \boldsymbol{X}_k \qquad \boldsymbol{X}_i = -(\nabla\mu_i)_{T,p} - \bar{v}_i \nabla p + \boldsymbol{F}_i \qquad \boldsymbol{F}_i = -z_i F \nabla\psi \tag{4,5,5a}$$

$$\mathbf{v} = \sum_{i=0}^{n-1} \rho_i \mathbf{v}_i / \rho \qquad \rho = \sum_{i=0}^{n-1} \rho_i \tag{6,6a}$$

Introducing the flows relative to the capillary:

$$\boldsymbol{J}_i^n = \rho_i(\mathbf{v}_i - \mathbf{v}_n) = \boldsymbol{J}_i + \rho_i(\mathbf{v} - \mathbf{v}_n) = \sum_{k=0}^{n-1} l_{ik}^n\, \boldsymbol{X}_k \tag{7}$$

(3) is rewritten to:

$$\Phi = \sum_{i=0}^{n-1} \boldsymbol{J}_i^n \cdot \boldsymbol{X}_i - (\mathbf{v} - \mathbf{v}_n) \cdot \sum_{k=0}^{n-1} \rho_k \boldsymbol{X}_k - \underline{\Pi}:\mathrm{Grad}\mathbf{v} \tag{8}$$

Scalar multiplying of the motion equation [14,(4.18)]:

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla p - \nabla \cdot \underline{\Pi} + \rho \boldsymbol{F} \qquad \text{where} \qquad \rho \boldsymbol{F} = \sum_{k=0}^{n-1} \rho_k \boldsymbol{F}_k \tag{9,9a}$$

by $(\mathbf{v} - \mathbf{v}_n)$ and combining with the tensor identity:

$$\underline{\Pi}:\mathrm{Grad}(\mathbf{v} - \mathbf{v}_n) = \nabla \cdot (\underline{\Pi} \cdot (\mathbf{v} - \mathbf{v}_n)) - (\mathbf{v} - \mathbf{v}_n) \cdot (\nabla \cdot \underline{\Pi}) \tag{10}$$

give:

$$\underline{\Pi}:\mathrm{Grad}(\mathbf{v} - \mathbf{v}_n) = \nabla \cdot (\underline{\Pi} \cdot (\mathbf{v} - \mathbf{v}_n) + (\mathbf{v} - \mathbf{v}_n) \cdot (\nabla p - \rho \boldsymbol{F}) + \rho (\mathbf{v} - \mathbf{v}_n) \cdot \frac{d\mathbf{v}}{dt} \tag{11}$$

For a rigid membrane and its constant velocity the following equations are valid (there is no need to assume $\mathbf{v}_n = 0$):

$$\frac{d\mathbf{v}}{dt} = \frac{d(\mathbf{v} - \mathbf{v}_n)}{dt}, \qquad \mathrm{Grad}(\mathbf{v} - \mathbf{v}_n) = \mathrm{Grad}\mathbf{v} \tag{12a,b}$$

Thus, with (11), (12) and:

$$\sum_{k=0}^{n-1} \rho_k \boldsymbol{X}_k = -\nabla p + \rho \boldsymbol{F} \tag{13}$$

resulting from the Gibbs-Duhem equation and:

$$\sum_{k=0}^{n-1} \rho_k \bar{\mathrm{v}}_k = 1 \tag{14}$$

where $\bar{\mathrm{v}}_k$ is the partial specific volume of species k, the dissipation function (8) is transformed to:

$$\Phi = \sum_{i=0}^{n-1} \boldsymbol{J}_i^n \cdot \boldsymbol{X}_i - \rho (\mathbf{v} - \mathbf{v}_n) \cdot \frac{d(\mathbf{v} - \mathbf{v}_n)}{dt} - \nabla \cdot (\underline{\Pi} \cdot (\mathbf{v} - \mathbf{v}_n)) = \sum_{i=0}^{n-1} \boldsymbol{J}_i^n \cdot (\boldsymbol{X}_i - d(\mathbf{v} - \mathbf{v}_n)/dt) - \\ -\nabla \cdot (\underline{\Pi} \cdot (\mathbf{v} - \mathbf{v}_n)) \tag{15}$$

In the mechanical equilibrium, defined as $d\mathbf{v}/dt = 0$, the term $d(\mathbf{v} - \mathbf{v}_n)/dt$ obviously disappears (see (12a)). This condition is frequently postulated, however, it would be interesting to compare $d(\mathbf{v} - \mathbf{v}_n)/dt$ with $\boldsymbol{X}_i$. For a rather small gradient of electrical potential 10 mV/1 mm and a molecular weight M = 50 g/mol the electrical part of $\boldsymbol{X}_i$ is $F\nabla\varphi/M = 2 \times 10^7$ m/s^2. The concentration part of $\boldsymbol{X}_i$ for the activity ratio of an

electrolyte $a_s''/a_s' = 2$ is $(RT/M)\nabla \ln a_s = 3.4 \times 10^7$ m/s^2. It is rather doubtful that such accelerations could exist in the membranes filled with electrolyte solutions. Thus, the term $d(\mathbf{v} - \mathbf{v}_n)/dt$ is negligible comparing with X_i.

(15) expresses the dissipation function at a given point of a cross-section of capillary. Because these points are not equivalent, one should integrate (15) to obtain a representative quantity for the capillary. It will be assumed here that:

1) $\nabla \cdot \mathbf{v} = 0$ (16)

2) in the cross-section perpendicular to the z axis the components of X_i are zero:

$(X_i)_{\xi \neq z} = 0 \quad i = 0,1,..., n\text{-}1$ and, consequently $(J_i)_{\alpha \neq z}, (\mathbf{v})_{\alpha \neq z} = 0$ (17,17a).

From here the z components of these quantities will be denoted simply by X_i, J_i, ν.

After integrating the term $\nabla \cdot (\underline{\Pi} \cdot \mathbf{v})$ disappears [15]. With (16) the viscosity tensor is expressed as [14, p.149]:

$$\underline{\Pi} = -2\eta(\mathring{\mathrm{Grad}}\mathbf{v})^s \tag{18}$$

With (18) and (17) $\nabla \cdot (\underline{\Pi} \cdot \mathbf{v})$ reduces to:

capillary [15]: $\nabla \cdot (\underline{\Pi} \cdot \mathbf{v}) = \frac{1}{r}\frac{\partial}{\partial r}\left(r\eta\nu\frac{\partial \nu}{\partial r}\right)$ slit: $\nabla \cdot (\underline{\Pi} \cdot \mathbf{v}) = \frac{\partial}{\partial x}\left(\eta\nu\frac{\partial \nu}{\partial x}\right)$ (19a,b)

Setting the boundary condition $\nu(a) = 0$, and for the slit additionally $\partial\nu/\partial x(0) = 0$, the integrals of (19) are zero. Thus, neglecting $d(\mathbf{v} - \mathbf{v}_n)/dt$ the integrated, averaged over the cross-section form of (15) is [3,15]:

$$\langle \Phi \rangle = \sum_{i=0}^{n-1} \langle J_i \rangle X_i - \langle \underline{\Pi} : \mathrm{Grad}\mathbf{v} \rangle = \sum_{i=0}^{n-1} \langle J_i^n \rangle X_i \tag{20}$$

It is seen that the averaged flows $\langle J_i^n \rangle$ and coupled forces X_i absorbed the viscosity part of the dissipation function. This would not be that case, if the coupled forces with J_i^n were X_i^n, defined by (A4).

THE COEFFICIENTS OF TRANSPORT EQUATIONS

The coefficients l_{ik} in (4) are dependent, because of the dependence of J_i, defined relative to the local center of mass. From the definition (6) and (4) we obtain:

$$\sum_{i=0}^{n-1} l_{ik} = 0 \quad k = 0, 1,..., n\text{-}1 \tag{21}$$

It is assumed that they are symmetrical $l_{ik} = l_{ki}$. Contrary to l_{ik}, l_{ik}^n from (7) are independent, because they connect independent flows and forces. However, they are not symmetrical. From (4), (6) and (7) we get:

$$l_{ik}^{n} = l_{ik} + \frac{\rho_i}{\rho} \sum_{j=0}^{n-1} l_{jk}^{n} \tag{22}$$

The erroneous symmetry assumption would lead to $n(n\text{-}1)/2$ equations relating independent coefficients l_{ik}^{n} [15, (35)]

$$\rho_i \sum_{j=0}^{n-1} l_{jk}^{n} = \rho_k \sum_{j=0}^{n-1} l_{ji}^{n} \qquad (i \neq k = 0, 1,.., \text{n-1}).$$

The asymmetry of l_{ik}^{n} can be also demonstrated on the base of general transformation rules of fluxes and forces (Appendix A). As it will be shown below, the averaged l_{ik}^{n} are symmetrical. The symmetry of averaged transport coeffcients under various assumptions was proved in [3,4]. In [16] a proof can be found for two cases 1) without any external forces and 2) with the constant concentration. Here it is shown for the case limited by (16), (17) and $d\nu/dt = 0$. In these conditions (9) is expressed as:

$$\text{capillary: } -\frac{\partial p}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\eta\frac{\partial \nu}{\partial r}\right) + \rho F = 0 \qquad \text{slit: } -\frac{\partial p}{\partial z} + \frac{\partial}{\partial x}\left(\eta\frac{\partial \nu}{\partial x}\right) + \rho F = 0 \tag{23}$$

Integrating (23) two times, with $\nu(a) = 0$ as a boundary condition and additionally for a slit $\partial\nu/\partial x(0) = 0$, we get:

$$\text{capillary: } \nu(r) = a^2 \int_r^1 \frac{1}{r\eta} \int_0^r \left(\rho F - \frac{\partial p}{\partial z}\right) r dr dr \quad \text{slit: } \nu(x) = a^2 \int_x^1 \frac{1}{\eta} \int_0^x \left(\rho F - \frac{\partial p}{\partial z}\right) dx dx \tag{24}$$

In the integrals r, x are dimensionless – $r = r/a$, $x = x/a$. The meaning of a is explained in Fig. 1. It is not assumed that the viscosity, η, is constant, because it depends not only on the concentration but also on the electric field [17], strong in the charged capillary. Substituting (13) into (24) we get for ν:

$$\nu(\xi) = \sum_{k=0}^{n-1} B_k(\xi) X_k \qquad \xi = r, x \tag{25}$$

$$\text{where capillary: } B_k(r) = a^2 \int_r^1 \frac{1}{\eta r} \int_0^r \rho_k \, r dr^2 \quad \text{slit: } B_k(x) = a^2 \int_x^1 \frac{1}{\eta} \int_0^x \rho_k \, dx^2 \quad k = 0, 1, n\text{-}1 \tag{26}$$

Here a comment concerning the boundary condition $\nu(a) = 0$ should be given. If it was non-zero, then ν in (25) would be also non-zero, even if all $X_k = 0$, explicable only when the friction is zero. Thus, $\nu(a) = 0$ is the only reasonable assumption. The flows related to the membrane, according to (4), (7), and (25), are expressed as:

$$J_i^n = \rho_i \nu + J_i = \rho_i \nu + \sum_{k=0}^{n-1} l_{ik} X_k = \sum_{k=0}^{n-1} l_{ik}^{n} X_k \qquad i = 0, 1, n\text{-}1 \qquad l_{ik}^{n} = \rho_i B_k + l_{ik} \tag{27,27a}$$

(27a) confirms the previous statement that l_{ik}^n are not symmetrical, because of the inequality: $\rho_i B_k \neq \rho_k B_i$. Only in the case of independent distributions of densities would these coefficients be symmetrical. After averaging the flows over cross-section:

$$\text{capillary: } \langle J_i^n \rangle = \frac{1}{\pi a^2} 2\pi a^2 \int_0^1 J_i^n r dr = 2\int_0^1 J_i^n r dr \quad \text{slit: } \langle J_i^n \rangle = \frac{1}{2a} 2a \int_0^1 J_i^n dx = \int_0^1 J_i^n dx \tag{28}$$

$$\text{we get: } \langle J_i^n \rangle = \sum_{k=0}^{n-1} \langle l_{ik}^n \rangle X_k \qquad i = 0, 1, 2 \tag{29}$$

$$\text{where: capillary: } \langle l_{ik}^n \rangle = 2\left(B_{ik} + \int_0^1 l_{ik} r dr\right) \qquad \text{slit: } \langle l_{ik}^n \rangle = B_{ik} + \int_0^1 l_{ik} dx \tag{30}$$

$$B_{ik}(r) = a^2 \int_0^1 \rho_i r \int_1^r \frac{1}{\eta r} \int_0^r \rho_k r dr^3 \qquad B_{ik}(x) = a^2 \int_0^1 \rho_i \int_x^1 \frac{1}{\eta} \int_0^x \rho_k dx^3 \tag{31}$$

$\langle l_{ik}^n \rangle = \langle l_{ki}^n \rangle$ under the conditions that:

$$\int_0^1 l_{ik}\, r dr = \int_0^1 l_{ki} r dr \quad \text{and} \quad B_{ik} = B_{ki} \tag{32a,b}$$

The first equality is fulfilled, if $l_{ik} = l_{ki}$. The second one can be easily proved expanding ρ_i, ρ_k, $1/\eta$ into a power series of r or x (Appendix B). The averaged ν is:

$$\langle \nu \rangle = \sum_{k=0}^{n-1} \langle B_k \rangle X_k \tag{33}$$

$$\text{where capillary: } \langle B_k \rangle = \frac{1}{\pi a^2} 2\pi a^2 \int_0^1 B_k(r) r dr = 2a^2 \int_0^1 r \int_r^1 \frac{1}{\eta r} \int_0^r \rho_k r dr^3 \tag{34a}$$

$$\text{slit: } \langle B_k \rangle = \frac{1}{2a} 2a \int_0^1 B_k(x) dx = a^2 \int_0^1 \int_x^1 \frac{1}{\eta} \int_0^x \rho_k dx^3 \tag{34b}$$

(33) differs significantly from (45) in [15].

It should be noticed, that even if there is no coupling between the flows relative to the local center of mass ($l_{ik} = 0$), $\langle l_{ik}^n \rangle$ is still non-zero because B_{ik} does not disappear. Whereas l_{ik} can be related with the frictional interactions and the Spiegler model of transport [18], the meaning of B_{ik} is different. This coefficient depends on two factors: 1) the distribution of ions and other particles, influenced by the charged wall of a capillary, and 2) viscosity, which is a common factor for all B_{ik}. Thus, the

interpretation of interactions in a system with a membrane of ordered pore structure on the base of the Spiegler model should be treated very carefully.

The number of independent $<l_{ik}^{n}>$ is $n(n+1)/2$. This number includes $n(n-1)/2$ independent $<l_{ik}>$ (the symmetry of $<l_{ik}>$ and (21) have been taken into account), one viscosity coefficient, and n-1 independent distributions of concentration of ions. The distribution of solvent concentration can be calculated using (14). The general formula for the distribution of components is given by (17). Introducing (5) and $(\nabla\mu_i)_{T,p} = RT\nabla\ln a_i$, it can be expressed in detail as:

$$(RT\nabla\ln a_i + \bar{v}_i\nabla_p + z_iF\nabla\psi)_{\xi\neq z} = 0 \tag{35}$$

If the Boltzmann equation is assumed, then the concentration profiles of ions are dependent on the profile of electric potential only. In that case the number of independent parameters of the capillary model decreases from $n(n+1)/2$ to $n(n-1)/2+2$. The definition of a capillary model is finished by introducing the assumption of equality of (electro)chemical potentials on the boundary: membranelexternal solution. The assumption enables to relate the driving forces X_i with the parameters of external solutions surrounding the membrane.

CONCLUSIONS

The equations describing transport of ions and solvent in a charged pore of two geometries (capillary, slit) have been derived. In contrast to the previous derivations, the present one includes all coupling effects between mobile species and is not based on any simplifying assumption, like the ideality of electrolyte solutions, *etc.* The transport coefficients are constituted of two parts – one relative to the local center of mass and the second one – describing the contribution of the movement of the center of mass. The last one depends on the distribution of mobile ions inside the pore and on the viscosity of a solution filling the pore. The derived equations make possible to simulate the transport of electrolyte solutions in the charged capillaries, which is interesting from the practical point of view.

Appendix

A. Transformation of fluxes and symmetry of transport coefficients

Let us assume that the matrix of coefficients, $\underline{L}$, relating $\boldsymbol{J}$ and $\boldsymbol{X}$ is symmetrical. In order to keep the symmetry of the coeffcients and the invariance of entropy production:

$$\Phi_{JX} = \boldsymbol{J}^T\boldsymbol{X} = \boldsymbol{J}^{aT}\boldsymbol{X}^a \tag{A1}$$

when the reference system is changed:

$$\boldsymbol{J}^a = \underline{\boldsymbol{A}}\boldsymbol{J} \tag{A2}$$

the forces $\boldsymbol{X}$ have to be transformed according to [19]:

$$\boldsymbol{X}^a = \underline{\boldsymbol{A}}^{-1T}\boldsymbol{X} \tag{A3}$$

In this paper the forces in (4) and (7) are the same. Thus, assuming the symmetry of l_{ik} in (4), l^n_{ik} in (7) cannot be symmetrical. From (4), (6) and (7) the following relation results:

$$J_i = J^n_i - \frac{\rho_i}{\rho}\sum_{k=0}^{n-1} J^n_k, \quad i.e. \qquad a^{-1}_{ik} = \delta_{ik} - \rho_i/\rho \tag{A4}$$

From (A3) and (A4) we get the forces X^n_i coupled with J^n_i :

$$X^n_i = X_i - \frac{1}{\rho}\sum_{k=0}^{n-1} \rho_k X_k \tag{A5}$$

X^n_i , contrary to J^n_i , are dependent:

$$\sum_{i=0}^{n-1}\rho_i X^n_i = \sum_{i=0}^{n-1}\rho_i X_i - \sum_{i=0}^{n-1}\rho_i \sum_{k=0}^{n-1}\rho_k X_k/\rho = 0 \tag{A6}$$

(A5) and (A6) are the same as (18) and (4) in [20]. Introducing (13) into (A4) we get the form cited in [21,15]. It should be added, that because of the dependence of J_i (and/or X^n_i), the matrix $[a^{-1}_{ik}]$, defined by (A4) is singular and cannot be the inverse of $[a_{ik}]$, "−1" has only a symbolic meaning. The problem of inverting the linear relations between fluxes and forces in the case when the matrix of conductance coefficients is singular is solved in [22].

It should be stated here that the form of thermodynamic forces given by (5) is based on the global relations for the kinetic energy and the linear momentum [14,16]. However, using the individual balance equations the form of thermodynamic forces is different ((14) in [23], (108) in [24]. The feature of these forces is that, contrary to the forces given by (5), they are linear dependent. Consequently, they can be applied to any flow of the arbitrary frame of reference without violation of the invariance of entropy production. In the case when both fluxes and forces are dependent, the phenomenological coefficients are not uniquely defined and can be chosen in such a manner that the Onsager reciprocity holds [16].

B. Proof of the symmetry of B_{ik}

Expanding ρ_i, ρ_k, $1/\eta$:

$$\rho_i = \sum_{\alpha=0}^{\infty} a_{i,\alpha} r^{\alpha}, \; \rho_k = \sum_{\beta=0}^{\infty} a_{k,\beta} r^{\beta}, \; 1/\eta = \sum_{\gamma=0}^{\infty} b_{\gamma} r^{\gamma} \tag{B1}$$

and substituting into (31) yield:

$$\text{capillary: } B_{ik} = a^2 \sum_{\alpha=0}^{\infty}\sum_{\gamma=0}^{\infty}\sum_{\beta=0}^{\infty} \int_0^1 a_{i,\alpha}\, r^{\alpha+1} \int_r^1 b_{\gamma}\, r^{\gamma-1} \int_0^r a_{k,\beta} r^{\beta+1} dr^3 \tag{B2a}$$

slit: $$B_{ik} = a^2 \sum_{\alpha=0}^{\infty} \sum_{\gamma=0}^{\infty} \sum_{\beta=0}^{\infty} \int_0^1 a_{i,\alpha} x^{\alpha} \int_x^1 b_{\gamma} x^{\gamma} \int_0^x a_{k,\beta} x^{\beta} dx^3 \tag{B2b}$$

Integrating (B2) the following expressions are obtained:

capillary: $$B_{ik} = a^2 \sum_{\alpha=0}^{\infty} \sum_{\gamma=0}^{\infty} \sum_{\beta=0}^{\infty} \frac{a_{i,\alpha} b_{\gamma} a_{k,\beta}}{(\alpha+\gamma+\beta+4)(\alpha+2)(\beta+2)} = B_{ki} \tag{B3a}$$

slit: $$B_{ik} = a^2 \sum_{\alpha=0}^{\infty} \sum_{\gamma=0}^{\infty} \sum_{\beta=0}^{\infty} \frac{a_{i,\alpha} b_{\gamma} a_{k,\beta}}{(\alpha+\gamma+\beta+3)(\alpha+1)(\beta+1)} = B_{ki} \tag{B3b}$$

The B_{ik} given by (B3) are symmetrical regarding the exchange of indices i and k.

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