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MATHEMATICS/CHEMISTRY

ELECTROKINETIC EFFECTS IN A NETWORK OF CAPILLARIES I

BY

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In a joint paper [1] with WIJGA one of us discussed the phenomenon of the apparent ζ-depression found in electrokinetic experiments with dilute solutions of electrolytes. It was shown that for electro kinetic experiments performed with a set of capillaries in series the apparent ζ-depression could be explained theoretically by taking into account the effect of surface conductance. The question remained open whether in the case of a general network of capillaries the effect of surface conductance would also lead to an apparent ζ-depression. In that case the ζ-depression found in experiments with diaphragms would be explained qualitatively. With the object to answer this question the present mathematical analysis was undertaken. The main result obtained, far from being conclusive, is the following:

A network with cylindrical capillaries of equal diameters will display no change in ζ. If the lengths and diameters of the capillaries are slightly varied the apparent ζ-potential will also vary slightly. The first order change of ζ is always zero, while the second order change of ζ is non-positive. So networks whose capillaries have diameters ϱ which lie in a narrow range about an average value a will display an apparent depression of ζ apart from third and higher order terms in the quantities $\varrho - a$.

There are however also networks with an apparent rise of ζ. A method of constructing such networks was suggested to us by Prof. H. FREUDENTHAL. We shall not carry out this construction here. In our paper [3] simple three-capillary networks with an apparent rise of ζ are discussed. These examples together with experimental evidence seem to suggest that networks with an apparent rise of ζ are rather "rare". However we have not been able to prove this mathematically (under a suitable definition of "rareness").

1. 1. In this section we briefly recall some concepts and theorems of linear algebra needed in the sequel.

Throughout this section R denotes a finite dimensional vectorspace with an inner product. Linear operators to be considered transform R into itself. (x, y) will denote the inner product of x and y.

A linear operator B of R is said to be the *transposed* of a linear operator A if $(Ax, y) = (x, By)$ for every pair of vectors x and y of R. Any linear A has exactly one transposed which will be denoted by A'. $(A')' = A$, $(A_1 A_2 \ldots A_n)' = A_n' \ldots A_2' A_1'$. Transposed operators have with respect to an orthonormal base matrices which are each other's transposed in the usual sense.

A is *symmetric* if $A = A'$.

A symmetric A is *negative definite* (n.d.) (*positive definite* (p.d.)) if $(Ax, x) < 0$ (> 0) for each $x \neq 0$.

A symmetric n.d. operator A has an inverse A^{-1} which is also symmetric n.d.

If A is symmetric, x a vector, and $Ax = \lambda x$ for a suitable scalar λ, then A transforms into itself the space of the vectors perpendicular to x. (y is said to be perpendicular to x if $(x, y) = 0$.)

For a n.d. (p.d.) symmetric A there holds the Cauchy–Schwarz inequality

$$(Ax, x)\ (Ay, y) - (Ax, y)^2 \geqslant 0, \text{ for each pair of vectors } x, y.$$

1. 2. We consider the following linear equations

$$\left\{ \begin{aligned} Lx + Dy &= x' \\ Dx + Fy &= y', \end{aligned} \right. \tag{1}$$

where x, x', y, y' are vectors of R. L, D, F are symmetric operators of R which satisfy the condition

$$(Lx, x) + 2(Dx, y) + (Fy, y) < 0 \text{ if not both } x \text{ and } y \text{ are zero.} \tag{2}$$

First we wish to prove that (1) has a unique solution for arbitrary x' and y' and secondly we wish to obtain this solution explicitly in terms of x', y', L, D, F.

To that end we consider the linear space $[R, R]$ consisting of the pairs $[x, y]$ of vectors x and y of R, with the following law of addition and scalar multiplication

$$\begin{aligned} [x, y] + [x_1, y_1] &= [x + x_1, y + y_1] \\ \lambda[x, y] &= [\lambda x, \lambda y]. \end{aligned}$$

The inner product in $[R, R]$ is defined by

$$([x, y], [x_1, y_1]) = (x, x_1) + (y, y_1).$$

The vector $[x, 0]$ is called the first component of $[x, y]$ and $[0, y]$ is called its second component. R_i denotes the space of the i-th components $(i = 1, 2)$. The operator which transforms each vector into its i-th component $(i = 1, 2)$ will be denoted by P_i. It is easily verified that P_i is linear, symmetric, $P_i P_i = P_i$, $P_1 + P_2 =$ identity operator I, i.e. the operator which transforms each vector into itself.

Let E be an arbitrary linear operator of $[R, R]$. Then according to the aforesaid

$$(3)\quad \begin{cases} E = IEI = (P_1 + P_2)E(P_1 + P_2) = \sum\limits_{\substack{i \\ j} = 1,2} P_i E P_j \\ \qquad = \sum\limits_{i,j} P_i E P_j^2 = \sum\limits_{i,j} E_{ij} P_j, \text{ where } E_{ij} = P_i E P_j. \end{cases}$$

Since $E_{ij}P_j\,[R, R] = E_{ij}R_j$ is contained in R_i we find by means of (3) the following relations between the components of $[x, y]$ and of its image $E[x, y] = [x', y']$:

$$(4)\quad \begin{cases} [x', 0] = E_{11}[x, 0] + E_{12}[0, y] \\ [0, y'] = E_{21}[x, 0] + E_{22}[0, y]. \end{cases}$$

Confusing systematically the vector $[x, 0]$ of R_1 with the vector x of R and the vector $[0, y]$ of R_2 with the vector y of R, and considering the operator E_{ij} of R_j into R_i in an obvious way as an operator of R into itself we may write (4) as follows

$$(4.\ 1)\quad \begin{cases} x' = E_{11}x + E_{12}y \\ y' = E_{21}x + E_{22}y. \end{cases}$$

Conversely if E_{ij} $(i, j = 1, 2)$ are operators of R into itself they determine in a unique way by means of (4. 1) or (4) an operator E of $[R, R]$. $E = I$ if and only if $E_{11} = E_{22} = I$, $E_{12} = E_{21} = 0$. In analogy with matrix notation we write

$$E = \begin{pmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{pmatrix}.$$

Let $K = \begin{pmatrix} K_{11} & K_{12} \\ K_{21} & K_{22} \end{pmatrix}$ be a second operator in $[R, R]$ then

$$(5)\quad KE = \begin{pmatrix} K_{11}E_{11} + K_{12}E_{21} & K_{11}E_{12} + K_{12}E_{22} \\ K_{21}E_{11} + K_{22}E_{21} & K_{21}E_{12} + K_{22}E_{22} \end{pmatrix}.$$

Returning to (4), suppose that E is symmetric, then on account of the symmetry of P_i we have

$$(6)\quad E'_{ij} = (P_i E P_j)' = P_j E P_i = E_{ji}.$$

So E_{11} and E_{22} are symmetric; E_{12} and E_{21} are each other's transposed. Conversely $E'_{11} = E_{11}$, $E'_{12} = E_{21}$, $E'_{22} = E_{22}$ imply the symmetry of E.

For a symmetric E we have

$$(E[x, y],\ [x, y]) = ([E_{11}x + E_{12}y,\ E_{21}x + E_{22}y],\ [x, y]) =$$
$$(E_{11}x, x) + (x, E_{12}y) + (E_{21}x, y) + (E_{22}y, y).$$

Since $E_{12} = E'_{21}$ we find

$$(7)\quad (E[x, y],\ [x, y]) = (E_{11}x, x) + 2(E_{12}x, y) + (E_{22}y, y).$$

So a symmetric E is n.d. if and only if

$$(8)\quad (E_{11}x, x) + 2(E_{12}x, y) + (E_{22}y, y) < 0 \text{ if not both } x \text{ and } y \text{ are zero.}$$

Combining the foregoing with the fact that a n.d. symmetric operator has an inverse, we see that (1) is uniquely solvable for arbitrary x', y' on account of (2).

By putting $y = 0$ in (8) we find that $(E_{11}x, x) < 0$ for $x \neq 0$, and in the same way by putting $x = 0$, $(E_{22}y, y) < 0$ for $y \neq 0$. Hence E_{ii} is necessarily n.d., and so E_{ii} has an inverse E_{ii}^{-1} $(i = 1, 2)$.

Now we shall solve (4. 1) under the assumption that E is n.d. This amounts to the calculation of the inverse $K = \begin{pmatrix} K_{11} & K_{12} \\ K_{21} & K_{22} \end{pmatrix}$ of E. From $KE = I$ we find using (5)

(9. 1) $\quad K_{11}E_{11} + K_{12}E_{21} = I \qquad$ (10. 1) $\quad K_{21}E_{11} + K_{22}E_{21} = 0$

(9. 2) $\quad K_{11}E_{12} + K_{12}E_{22} = 0 \qquad$ (10. 2) $\quad K_{21}E_{12} + K_{22}E_{22} = I.$

Right multiplication of (9. 2) with $E_{22}^{-1}E_{21}$ and subsequent subtraction from (9. 1) yields

$$K_{11}(E_{11} - E_{12}E_{22}^{-1}E_{21}) = I.$$

This shows that

$$E_{11} - E_{12}E_{22}^{-1}E_{21} \tag{11}$$

has an inverse and that

$$K_{11} = (E_{11} - E_{12}E_{22}^{-1}E_{21})^{-1}. \tag{12. 1}$$

In a similar manner we find

$$K_{22} = (E_{22} - E_{21}E_{11}^{-1}E_{12})^{-1}. \tag{12. 2}$$

$$K_{12} = -E_{11}^{-1}E_{12}K_{22} = -E_{11}^{-1}E_{12}(E_{22} - E_{21}E_{11}^{-1}E_{12})^{-1}. \tag{12. 3}$$

$$K_{21} = -E_{22}^{-1}E_{21}K_{11} = -E_{22}^{-1}E_{21}(E_{11} - E_{12}E_{22}^{-1}E_{21})^{-1}. \tag{12. 4}$$

K being the inverse of a symmetric n.d. operator, K itself is symmetric n.d. As a consequence K_{11} and K_{22} are symmetric n.d.; K_{12} and K_{21} are each other's transposed.

In view of subsequent needs we derive a formula which permits us to express K_{11} by means of K_{22} and vice versa.

From $K_{12} = K'_{21}$ we obtain

$$E_{11}^{-1}E_{12}K_{22} = K_{11}E'_{21}E_{22}^{-1} = K_{11}E_{12}E_{22}^{-1}. \tag{13}$$

So we find

$$E_{11}^{-1}E_{12}K_{22}E_{21}E_{11}^{-1} \overset{(13)}{=} K_{11}E_{12}E_{22}^{-1}E_{21}E_{11}^{-1} \overset{(12.1)}{=}$$
$$= K_{11}(E_{11} - K_{11}^{-1})E_{11}^{-1} = K_{11} - E_{11}^{-1}.$$

Hence

$$K_{11} = E_{11}^{-1} + E_{11}^{-1}E_{12}K_{22}E_{21}E_{11}^{-1}, \tag{14}$$

and in a similar way

$$K_{22} = E_{22}^{-1} + E_{22}^{-1}E_{21}K_{11}E_{12}E_{22}^{-1}. \tag{15}$$

2. 1. A network $\mathfrak{N}$ of capillaries is defined as a system of "junction points" or "nodes" interconnected by capillaries in such a way that

(a) any two nodes are joined by *at most* one capillary,
(b) any two nodes may be joined by a "path" consisting of capillaries of $\mathfrak{N}$.

The nodes of $\mathfrak{N}$ will be labelled $1, 2, \ldots, n$ and a capillary joining i and j will be denoted by (i, j).

Suppose that $\mathfrak{N}$ is filled with a liquid. Be L_{ij} the electric conductivity of (i, j), F_{ij} the hydrodynamic conductivity of (i, j), C_{ij} the capacity of conductance of (i, j). The latter quantity is defined as the conductivity of (i, j) divided by the specific conductivity of the liquid if (i, j) is filled with a liquid of high specific conductivity e.g. mercury. Let Z_{ij} be the constant defined by

$$v = Z_{ij} C_{ij} E,$$

where v and E would be the flow of liquid and the potential difference between i and j, if (i, j) were subjected to an electroosmotic experiment. According to [1], [2], [5] Z_{ij} may also be defined by

$$s = Z_{ij} C_{ij} P$$

where s = streaming current, and P = hydrostatic pressure difference between i and j under a streaming potential experiment for (i, j). We set $Z_{ij} C_{ij} = D_{ij}$. Then an electrokinetic process taking place in $\mathfrak{N}$, with

$$\left.\begin{array}{ll} s_i & = \text{electric output current} \\ v_i & = \text{output flow of liquid} \\ e_i & = \text{electric potential} \\ p_i & = \text{hydrostatic pressure} \end{array}\right\} \text{at } i,$$

may be described by the equations (cf. [2])

$$\left\{\begin{array}{c} \sum_{j \neq i} L_{ij}(e_j - e_i) + \sum_{j \neq i} D_{ij}(p_j - p_i) = s_i \\ \sum_{j \neq i} D_{ij}(e_j - e_i) + \sum_{j \neq i} F_{ij}(p_j - p_i) = v_i \\ \sum_i s_i = \sum_i v_i = 0 \end{array}\right\} i = 1, \ldots, n \tag{16}$$

Defining $L_{ii} = -\sum_{j \neq i} L_{ij}$, $D_{ii} = -\sum_{j \neq i} D_{ij}$, $F_{ii} = -\sum_{j \neq i} F_{ij}$, the above equations take the form

$$\left\{\begin{array}{c} \sum_j L_{ij}\, e_j + \sum_j D_{ij}\, p_j = s_i \\ \sum_j D_{ij}\, e_j + \sum_j F_{ij}\, p_j = v_i \\ \sum_i s_i = \sum_i v_i = 0 \end{array}\right\} i = 1, \ldots, n \tag{17}$$

2. 2. We shall write (17) in the abbreviated notations of linear algebra. To that end we define in the cartesian n-space N the following vectors, operators, etc.,

$$\begin{array}{lll} e = (e_1, \ldots, e_n) & s = (s_1, \ldots, s_n) & r = (1, 1, \ldots, 1) \\ p = (p_1, \ldots, p_n) & v = (v_1, \ldots, v_n) & i = (-1, 0, \ldots, 0, 1). \end{array}$$

The inner product of the vector $x = (x_1, \ldots, x_n)$ with the vector $y = (y_1, \ldots, y_n)$ is defined by $(x, y) = \Sigma_i\, x_i y_i$.

$$\left.\begin{array}{ll} L = & \text{operator with matrix } (L_{ij}) \\ D = & \quad ,, \qquad ,, \qquad ,, \quad (D_{ij}) \\ F = & \quad ,, \qquad ,, \qquad ,, \quad (F_{ij}) \end{array}\right\} \text{ symmetric operators.}$$

R = space of vectors perpendicular to r, i.e. the space of the vectors $x = (x_1, \ldots, x_n)$ with $\Sigma_i\, x_i = 0$.

Then we may write (17) in the form

$$\left.\begin{cases} Le + Dp = s \\ De + Fp = v \end{cases}\right\} s \text{ and } v \text{ are vectors of } R. \tag{18}$$

Since L, D, F annihilate r, we may subtract from e and p arbitrary multiples of r without changing the right hand sides of (18). From a physical point of view this subtraction amounts to a change of the zero point on the scales by which we measure the electric potential and the hydrostatic pressure; this clearly does not affect the above equations. By subtracting from e and p suitable multiples of r, e and p become vectors of R, i.e. $\Sigma_i\, e_i = \Sigma_i\, p_i = 0$. Throughout the following sections we suppose e and p to be normalized in this way. Furthermore, since L, D, F annihilate r, they transform R into itself. Therefore we may also consider (18) to be equations in R whenever it is convenient.

2. 3. In order to solve the equation (18) (considered only in R) with respect to e and p we may apply the results of 1. 2., provided that it can be shown that $E = \begin{pmatrix} L & D \\ D & F \end{pmatrix}$ is symmetric n.d.

The symmetry of E is obvious. Therefore we shall only be concerned with the proof that E is n.d., which will be based on the fact that the energy dissipation in $\mathfrak{R}$ is positive.

The dissipated energy in $\mathfrak{R}$ is the sum of the dissipated energies in the separate capillaries. For (i, j) the dissipated energy (per unit of time) equals electric current $\times$ potential difference $+$ flow of liquid $\times$ pressure difference $=$

$$\begin{cases} (L_{ij}(e_j - e_i) + D_{ij}(p_j - p_i))\,(e_j - e_i) + \\ (D_{ij}(e_j - e_i) + F_{ij}(p_j - p_i))\,(p_j - p_i) \geqslant 0. \end{cases} \tag{19}$$

The equality sign holds only if the electric current and the flow of liquid are zero, i.e. if $p_j = p_i$, $e_j = e_i$.

Consequently the energy dissipation in $\mathfrak{R}$ (per unit of time) is

$$\begin{cases} \sum_{\substack{i,j \\ i<j}} (L_{ij}(e_j - e_i) + D_{ij}(p_j - p_i))\,(e_j - e_i) + \\ \sum_{\substack{i,j \\ i<j}} (D_{ij}(e_j - e_i) + F_{ij}(p_j - p_i))\,(p_j - p_i) \geqslant 0. \end{cases} \tag{20}$$

The equality sign in (20) holds only if for each (i, j), $p_i = p_j$, $e_i = e_j$.

Since each node of $\mathfrak{N}$ may be joined by a path of capillaries with node 1 we find that the equality sign in (20) holds only if $e_1 = e_2 = \ldots = e_n$, $p_1 = p_2 = \ldots = p_n$. Since e and p are normalized such that $\Sigma e_i = \Sigma p_i = 0$ this condition means that $e = p = 0$.

Furthermore it is easily verified that the left hand side of (20) may be written as

$$-((Le, e) + 2(De, p) + (Fp, p)),$$

hence (20) implies that

$$E = \begin{pmatrix} L & D \\ D & F \end{pmatrix}$$

is n.d. R.

2. 4. Using the formulas of 1. 2. with $E_{11} = L$, $E_{21} = E_{12} = D$, $E_{22} = F$ we find

$$\left\{\begin{aligned} e &= K_{11}s + K_{12}v \\ p &= K_{21}s + K_{22}v, \end{aligned}\right. \tag{21}$$

where

$$\left\{\begin{array}{l} K_{11} \text{ is symmetric, n.d., } K_{11}^{-1} = L - DF^{-1}D \\ K_{22} \text{ ,, \quad ,, \quad , ,, , } K_{22}^{-1} = F - DL^{-1}D \\ K_{12} = -L^{-1}DK_{22},\ K_{21} = -F^{-1}DK_{11}, \\ K'_{12} = K_{21} \text{ and so } (K_{21}x, x) = (K_{12}x, x) \text{ for every } x \\ K_{11} = L^{-1} + L^{-1}DK_{22}DL^{-1}. \end{array}\right. \tag{22}$$

2. 5. We now assume that a flow of liquid and an electric current can only enter or leave $\mathfrak{N}$ at 1 and n, so

$$s = \lambda i,\ v = \mu i, \quad \text{(cf. 2. 2)}, \tag{23}$$

where $|\lambda|$ and $|\mu|$ are the amounts of electricity and liquid streaming through $\mathfrak{N}$ per unit of time. Putting $E = e_1 - e_n = -(e, i)$, and $P = p_1 + - p_n = -(p, i)$ we find by inserting (23) into (21) and subsequent inner multiplication by i

$$\left\{\begin{aligned} -E &= \lambda(K_{11}i, i) + \mu(K_{12}i, i) \\ -P &= \lambda(K_{21}i, i) + \mu(K_{22}i, i). \end{aligned}\right. \tag{24}$$

In case of electro-osmosis $P = 0$ and we find by an easy computation

$$\mu \left(\frac{(K_{11}i,i)\,(K_{22}i,i)}{(K_{21}i,i)} - (K_{12}i,i)\right) = E \tag{25}$$

$$-\lambda\, \frac{(K_{21}i,i)}{(K_{22}i,i)} \left(\frac{(K_{11}i,i)\,(K_{22}i,i)}{(K_{21}i,i)} - (K_{12}i,i)\right) = E. \tag{26}$$

It may be proved that λ has the same sign as E, a result which is obvious from a physical point of view. Since K_{22} is n.d., we see that $(K_{22}i, i) < 0$. So we find that μ has the same sign as λ if $(K_{12}i, i) > 0$ and opposite sign if $(K_{12}i, i) < 0$. Both cases may occur in practice. Henceforth we shall assume that λ and μ have the same sign, i.e. $(K_{12}i, i) > 0$.

3. 1. We now suppose that $\mathfrak{R}$ is a network whose capillaries are made of the same material. The latter assumption is not strictly needed in the greater part of this section; however it will be convenient. On account of our assumptions Z_{ij} does not depend on (i, j) [1], and so we have $Z_{ij} = Z$.

It has been shown experimentally [5] that for an arbitrary homogeneous network (i.e. a network whose capillaries are made of the same material),

$$\mu = Z'\gamma E, \tag{27}$$

where γ = capacity of conductance of $\mathfrak{R}$, and Z' is a constant depending on $\mathfrak{R}$ and the liquid. It turned out that $Z' < Z$, a phenomenon which bears for various reasons the name of "apparent ζ-depression".

We shall examine what relation between Z' and Z follows from our analysis.

In order to compare the Z' of (27), such as it may be computed from (25), with Z, we must compute the capacity of conductance γ of $\mathfrak{R}$. This calculation will be carried out in 3. 2. We use here only the result that

$$\gamma = -(C^{-1}i, i)^{-1}. \tag{28}$$

C denotes here the operator in the space N whose matrix elements are $C_{ij}(i \neq j)$, $C'_{ii} = -\sum_{j \neq i} C_{ij}$, where for $i \neq j$ C_{ij} denotes the capacity of conductance of (i, j).

The relations $Z' \lesseqgtr Z$ are equivalent to

$$(Z\gamma)^{-1} \lesseqgtr (Z'\gamma)^{-1}. \tag{29}$$

Since $D = ZC$ we find by (28) that $-(D^{-1}i, i) = +(Z\gamma)^{-1}$. Comparing (27) to (25) we find that

$$(Z'\gamma)^{-1} = \left(\frac{(K_{11}i,i)\,(K_{22}i,i)}{(K_{21}i,i)} - (K_{12}i,i)\right).$$

Hence (29) becomes

$$-(D^{-1}i,i) \lesseqgtr \left(\frac{(K_{11}i,i)\,(K_{22}i,i)}{(K_{21}i,i)} - (K_{12}i,i)\right). \tag{30}$$

Since $(K_{21}i, i) > 0$ we find by multiplying (30) by $(K_{21}i, i)$, and replacing $(K_{21}i, i)$ by $(K_{12}i, i)$, that

$$Z' \lesseqgtr Z \text{ if and only if } \Omega \gtreqless 0, \text{ where}$$
$$\Omega = (K_{11}i, i)\,(K_{22}i, i) - (K_{12}i, i)^2 + (K_{12}i, i)\,(D^{-1}i, i).\ ^{1)}$$

Expressing K_{11} by means of K_{22} (cf. (22)), and putting $K_{22} = H^{-1}$, where $H = F - DL^{-1}D$ we find

$$\begin{cases} \Omega = \Omega_1 + \Omega_2, \\ \Omega_1 = (H^{-1}i, i)\,(L^{-1}i, i) - (L^{-1}DH^{-1}i, i)\,(D^{-1}i, i) \\ \Omega_2 = (H^{-1}i, i)\,(L^{-1}DH^{-1}DL^{-1}i, i) - (L^{-1}DH^{-1}i, i)^2. \end{cases} \tag{31}$$

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1) If for the liquid and the network under consideration $(K_{12}\,i, i) < 0$ we find that $Z' \gtreqless Z$ if $\Omega \gtreqless 0$. In this case however Z' and Z are negative, so that the phenomenon of apparent ζ-depression is described by $Z' > Z$ instead of $Z' < Z$, and hence in this case an apparent ζ-depression leads also to $\Omega > 0$.

In absence of surface conductance $L_{ij} = \varkappa C_{ij}$, where $\varkappa$ depends on the liquid only [1], and thus $L = \varkappa C$. Since $D = ZC$, we have $L = aD$ ($a = \varkappa Z^{-1}$). Inserting this result into (31) we find that both Ω_1 and Ω_2 are zero, and hence $\Omega = 0$. So we have

Theorem 1. In absence of surface conductance our analysis leads to the classical results of SMOLUCHOWSKI ([1], [3]), viz. that the constant Z' in (27) depends only on the liquid and the material of the network, but not on the geometrical dimensions of the network.

From 4. it will appear that for a cylindrical capillary with radius r and length l, and endpoints 1, 2, L_{12}, F_{12}, D_{12} may be represented by

(32) $$L_{12} = f_1(r)\, l^{-1},\ \ F_{12} = f_2(r)\, l^{-1},\ \ D_{12} = f_3(r)\, l^{-1},$$

where f_i ($i = 1, 2, 3$) is a suitable function of r.

From (32) it appears that if all capillaries of $\mathfrak{N}$ have the same diameters both L and F are multiples of D, and hence again $\Omega_1 = \Omega_2 = 0$. Hence we find

Theorem 2. If a network consists of cylindrical capillaries of equal diameter, then $Z' = Z$, i.e. there is no apparent rise or depression of ζ.

The fact that an apparent rise or depression of ζ can only be expected for networks with capillaries of different diameters can be made clear in a similar way as in [1] p. 558.

Now we examine Ω for a network whose capillaries have almost equal diameters, i.e. the diameters of whose capillaries lie in a small range about an average value. In that case L and F are "almost" multiples of D, i.e. L and F may be represented by

(33) $$\begin{cases} L = L^0 + \Delta L \\ F = F^0 + \Delta F, \end{cases}$$

where L^0 and F^0 are multiples of D and ΔL and ΔF are "small increases" of L^0 and F^0. Before formulating and proving a theorem on such networks we make some remarks.

From (32) it appears that for a single capillary there exists a relation $\psi(L_{12}, F_{12}, D_{12}) = 0$ between L, F, D (we omit the subscripts for a moment), with a ψ that is homogeneous of the first degree, i.e. $\psi(\lambda L, \lambda F, \lambda D) = \lambda\psi(L, F, D)$. As a consequence $\partial\psi/\partial L$, $\partial\psi/\partial F$, $\partial\psi/\partial D$ are homogeneous of degree zero. Since the operators L^0, F^0 are supposed to be multiples of the operator D, their matrixcoefficients L^0_{ij}, F^0_{ij}, D_{ij} have ratios that are independent of i, j. So

$$\frac{\partial\psi}{\partial L}(L^0_{ij}, F^0_{ij}, D_{ij}),\ \frac{\partial\psi}{\partial F}(L^0_{ij}, F^0_{ij}, D_{ij}),\ \frac{\partial\psi}{\partial D}(L^0_{ij}, F^0_{ij}, D_{ij})$$

are independent of i, j. Furthermore the increases ΔL_{ij}, ΔF_{ij} satisfy

$$\frac{\partial\psi}{\partial L}(L^0_{ij}, F^0_{ij}, D_{ij})\cdot\Delta L_{ij} + \frac{\partial\psi}{\partial F}(L^0_{ij}, F^0_{ij}, D_{ij})\,\Delta F_{ij} = 0$$

except for terms of higher order. Hence we find

$$(34)\qquad \begin{cases} \Delta F_{ij} = \chi \Delta L_{ij} + \text{terms of higher order in } \Delta L_{ij}; \\ \qquad \chi \text{ does not depend on } i, j. \end{cases}$$

Ω may be considered as a function depending on the parameters F_{ij}, L_{ij}, D_{ij}. Taking account of (33) we may expand Ω as follows

$$\begin{aligned} \Omega(L, F, D) &= \Omega(L^0, F^0, D) + \Delta^1\Omega + \Delta^2\Omega + \dots \\ &= \qquad\qquad\qquad\quad \Delta^1\Omega + \Delta^2\Omega + \dots, \end{aligned}$$

where Δ^k denotes the aggregate of terms of order k in ΔL_{ij}, ΔF_{ij}.

We shall next prove theorem 3.