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ON THE ANALYTICAL SOLUTION TO THE
LINEARIZED POISSON-BOLTZMANN EQUATION
IN CYLINDRICAL COORDINATES

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Richard Eugene Rice

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By

Richard Eugene Rice

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ABSTRACT

ON THE ANALYTICAL SOLUTION TO THE LINEARIZED POISSON-BOLTZMANN EQUATION IN CYLINDRICAL COORDINATES

By

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The goal of this work is to obtain a complete analytical solution to the linearized Poisson-Boltzmann equation in cylindrical coordinates: $\partial^2\psi/\partial z^2 + (1/r)\partial(r\partial\psi/\partial r)\partial r = \kappa^2 f^2(z)\psi$, where ψ is the electric potential, κ the inverse Debye length, and $f(z)$ a particular ionic strength distribution. We solve it inside a uniformly charged cylindrical pore in an idealized membrane between two electrolyte solutions at different ionic strengths. The system is assumed to be continuous, isothermal, isotropic, incompressible, free of chemical reactions, and subject only to conservative external forces.

Unable to separate variables with either an additive or multiplicative solution, we turn to the solution $\psi(z,r) = \psi_1(z) + \psi_2(z,r)$, in which z and r are not separable in the final term. This results in two equations: $d^2\psi_1/dz^2 = \kappa^2 f^2(z)\psi_1$ and $\partial^2\psi_2/\partial z^2 + (1/r)\partial(r\partial\psi_2/\partial r)/\partial r = \kappa^2 f^2(z)\psi_2$. the z-derivative, which is small compared to the r-derivative, is neglected, the second of these equations is the modified Bessel equation of order zero. The first of them can also be solved analytically for an explicit f(z).

We choose three expressions for f(z): (1) constant I(z) (ionic strength), (2) I(z) linear in z, and (3) ℓn I(z) linear in z. The first f(z) yields a solution of hyperbolic functions, while the latter two yield modified Bessel functions. The boundary conditions on ψ_1 are determined at each end of the pore in terms of the parameters of the bathing solutions by a mass balance and also by a charge balance.

Next we solve the Poisson-Boltzmann equation for a semi-infinite cylinder by Laplace transforms; the result has the form $\psi(z,r) = f_1(z) + g_1(r) + f_2(z)g_2(r)$. Applying such a solution to the finite cylinder, however, we find it is not possible to separate variables, and again the solution has terms in z and terms in z and r.

In the final chapter we discuss our methods and results in terms of extrascientific considerations involving theory, metaphor, model, paradigm, language, and explanation.

To the Memory of my Grandparents,
Mr. & Mrs. Bertram E. Weston,
who believed in education and in me

But when I consider, how much most of the qualities of bodies, and consequently their operations, depend upon the structure of their minute, and singly invisible particles . . . I cannot but think the doctrine of the small pores of bodies of no small importance to natural philosophy.

--Hon. Robert Boyle
The Porosity of Animal Bodies, 1684

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Each of the members of my doctoral committee has

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CHAPTER 1

THE LINEARIZED POISSON-BOLTZMANN EQUATION

A. Introduction

Much of the theoretical work on steady-state membrane transport rests on some form of the one-dimensional Nernst-Planck flux equations [20,21,62,84,88,89,90,93,94,102,104, 109,110,111,145,146,159,171],

$$J_i = - D_i c_i \left[\frac{d\ell n c_i}{dz} + \frac{z_i F}{RT} \frac{d\psi}{dz} + \frac{\bar{V}_i}{RT} \frac{dp}{dz} \right] + c_i u_0 \ , \qquad (1.1)$$

where J_i is the flux of ion i, D_i its diffusion coefficient, c_i its concentration, z_i its charge, $\bar{V}_i$ its partial molar volume, ψ the electric potential, p the pressure, u_0 the velocity of the solvent, F the faraday, R the gas constant, and T the temperature. In this form the equation applies to each species in the system except the solvent. Despite their neglect of interactions between diffusing species [70], these equations still provide results comparable to experiment.

Usually, the Nernst-Planck equations are solved, either analytically or numerically, in conjunction with other equations. The Navier-Stokes equation [9,11,69], often in curtailed form such as

$$\eta\nabla^2 u = \nabla p + F(\Sigma c_i z_i)\nabla\psi \quad , \tag{1.2}$$

where η is viscosity, provides the barycentric fluid velocity u for the convective term (which is usually, but incorrectly ignored relative to diffusion); Poisson's equation [30,76,117,138],

$$\nabla^2\psi = -\frac{\rho}{\varepsilon} \quad , \tag{1.3}$$

provides the required electric potential term in the case of charged species. Poisson's equation relates the electric potential ψ to the volume charge density ρ, defined as

$$\rho = F\Sigma\, c_i z_i \quad , \tag{1.4}$$

and to the dielectric permitivity ε of a medium, which is surrounded by a surface bearing additional charges. This is exactly the case for the capillary model of a membrane. A pore, frequently idealized as a cylinder for mathematical convenience, contains ions in solution as well as a surface charge, which provides one of the boundary conditions that the potential solution must satisfy.

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Two well-known solutions of the Nernst-Planck and Poisson equations together are those by Planck himself [129] and Goldman [51]. Generalized in various ways by other authors [74,130], Planck's method, which assumes that the thickness of the ionic atmosphere is small relative to that of the diaphragm, gives rise to a potential-difference equation [99] that has been successfully used for calculating liquid-junction potentials, despite the fact that the method's assumption implies electroneutrality when that is not the case. Goldman's approximation of a constant field, which allows immediate integration of the Nernst-Planck equations, leads to an expression that has proven popular in working with potential differences of biological membranes [68,147]. Probably the two most famous applications of Poisson's equation arose in a different context, that by Gouy [52] and Chapman [27] in their independent treatments of the double layer, and that by Debye and Hückel [34] for the case of strong electrolytes. It is instructive to look at both these models, the Debye-Hückel theory in particular since many people have written about its shortcomings and strengths.

B. Gouy-Chapman Model of the Double Layer

Gouy and Chapman succeeded in determining the statistical distribution of ions in a double layer by taking into account both the field from the charged solid surface and the thermal energy of the ions themselves. Although counterions (ions with the charge opposite to that of the solid surface) are attracted towards the surface and co-ions (ions of the same charge) are repulsed, there is no net movement of ions perpendicular to the wall. By setting the Nernst-Planck equation with only terms for diffusion and electromigration equal to zero, Gouy and Chapman obtained a Boltzmann distribution for each ion:

$$c_i(z) = c_i^{\infty} \exp\left[- \frac{z_i F \psi}{RT} \right] . \tag{1.5}$$

The resulting one-dimensional Poisson-Boltzmann equation for a symmetrical electrolyte,

$$\frac{d^2\psi}{dz^2} = \frac{2 z_+ F}{\varepsilon} \sinh \frac{z_+ F \psi}{RT} , \tag{1.6}$$

has a rather complicated solution [167], which, when plotted however, decreases more or less exponentially away from the charged solid wall.

Initially successful in differentiating between thermodynamics and electrokinetic potentials and in systematizing experimentally observed electrokinetic phenomena [41], the Gouy-Chapman model is still important for surface and colloid chemistry, in both its original form and its subsequent modification by Stern [157]. This model is not widely known among chemists, however, largely because it was soon overshadowed by the eminently successful Debye-Hückel theory, which Gouy and Chapman actually anticipated with their work.

C. Debye-Hückel Theory of Strong Electrolytes

Although Michael Faraday [47] distinguished electrolytes from nonelectrolytes on the basis of his electrochemical investigations as early as 1834, the differences in the behavior of these two classes of substances continued to bedevil scientists for many years. The first major breakthrough in understanding electrolytic solutions was Arhennius' concept of dissociation [58], but considerable confusion and disagreement lingered until the work of Debye and Hückel.

Bockris and Reddy [15] point out that even though Gouy and Chapman had already devised the general approach, including the idea of "smooth" charge and the use of the Poisson equation, Debye and Hückel's genius lay in choosing a reference ion whose interactions with the remaining ions in solution are analogous to those treated earlier between an ion and a charged surface.

With Poisson's equation in spherical coordinates,

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{d\psi}{dr} = -\frac{\rho}{\varepsilon} \quad , \tag{1.7}$$

Debye and Hückel wrote a Boltzmann distribution for each ion, as in Equation (1.5), but, unlike Gouy and Chapman, expanded the exponential into a Taylor series and truncated it after the second term. This procedure, which proved fortuitous but also engendered much of the subsequent criticism of the Debye-Hückel theory, results in the so-called linearized Poisson-Boltzmann equation:

$$\frac{1}{r^2}\frac{d}{dr}\, r^2 \frac{d\psi}{dr} = \kappa^2\psi \quad . \tag{1.8}$$

With the boundary conditions that $\psi \rightarrow 0$ as $r \rightarrow \infty$ and $\kappa \rightarrow 0$ as $c_i \rightarrow 0$, the solution to this equation is simply

$$\psi = \frac{z_i F}{\varepsilon}\,\frac{e^{-\kappa r}}{r} \quad , \tag{1.9}$$

which provides the electrostatic potential as a function of distance r from an arbitrary ion with charge z_i.

D. Assessment of the Debye-Hückel Theory

The assumptions underlying the derivation of Equation (1.9) by Debye and Hückel are essentially as follows [15, 48,114]:

(1) the dissolved electrolyte is completely dissociated;

(2) the ions arising from the dissociated electrolyte behave like point charges;

(3) the spherically symmetric atmosphere of excess charge about the reference ion is a time average of all possible ionic configurations;

(4) only coulombic interactions occur between ions, and this allows the potential energy of mean force in the Boltzmann expression to be replaced by the mean electrostatic potential;

(5) the ratio $z_i F\psi/RT << 1$, so that the exponential in Equation (1.5) can be expanded and the terms higher than first order neglected; and

(6) the solvent is a continuum with a constant dielectric constant unchanged by the presence of the electrolyte.

With their model incorporating these sometimes drastic assumptions, Debye and Hückel provided a simple physical picture of an ionic solution and derived Equation (1.9), which led to their famous limiting law for the activity coefficient [114]:

$$\log \gamma_{\pm} = -A|z_+ z_-|I^{1/2} \quad , \qquad (1.10)$$

where A is a temperature-dependent constant. This expression allows comparison with experiment and provides the theory's greatest triumph. As concentration decreases, the Debye-Hückel limiting law more accurately predicts experimental behavior.

Yet despite the theory's simplicity and success, or perhaps because of them, scientists began almost immediately to tinker with it. The first was Onsager [121], who tacked on two electrical effects that tend to decrease the mobility of the reference ion: the asymmetric and electrophoretic effects [114]. Bjerrum [12] and later Fuoss and Krauss [49] suggested the formation of transient ion pairs through electrostatic association to increase the fit between Debye-Hückel theory and experimental data. Lower dielectric constant and smaller ionic radii favor the formation of such pairs, which may still be appreciable in a solvent like water with a high dielectric constant. In 1933 Kirkwood [77] published an extensive discussion of the substitution of the mean potential in place of the potential of the mean force and showed that this approximation, along with some of the others, resulted in "the neglect of an exclusion-volume term and a fluctuation term" [124].

Sixty years after the appearance of Debye-Hückel theory, trying to improve it is still a popular pastime among statistical mechanicians [8,10,92,124,143,156,169]. McQuarrie [101] outlines some of these attempts, but he is forced to concede that statistical mechanics has done little more than confirm the original theory as the exact limit for zero concentration. The strongest praise for modern "improvements" that Levine and Outhwaite can muster is that the Poisson-Boltzmann equation "has been significantly modified in a qualitative manner" [92].

Certainly there are many legitimate objections against Debye-Hückel theory; some of them are [8,131]:

(1) ions are not point charges, and even the extended Debye-Hückel theory, which treats ions as having finite size, has unrealistic boundary conditions;

(2) the dielectric constant is obviously not constant, and the solvent's bulk value does not adequately represent the conditions close to the reference ion;

(3) many ions do not possess spherically symmetric electron distributions, and they are therefore not likely to induce a spherically symmetric ionic atmosphere;

(4) short-range ion-ion and ion-solvent forces, which are ignored, may be significant, especially in more concentrated solutions;

(5) replacing the potential of mean force with the mean potential is apparently essential since there seems to be no better approximation, but the validity of this step is difficult to determine; and

(6) linearization fails at very small distances from the reference ion, and this distance increases with increasing ionic change and decreasing dielectric constant.

Of these objections, the question of linearizing the Poisson-Boltzmann equation is perhaps the most interesting. Since the linearization is an approximation, and apparently a drastic one, it would seem logical that retaining the exponential would improve the result. That is not the case. As Moore, with an uncharacteristic cliché, says, "To discard the linear approximation, and use instead the exact Boltzmann equation, is to jump from the frying pan into the fire" [114].

The reason for this is that one of the assumptions of the Debye-Hückel model is the superposition of potentials; i.e., the potential at a point is the sum of the potentials from the nearby individual charges. This is consistent with the linearized Boltzmann equation, but not with the exact exponential form [15]. Furthermore, the solution of the linearized equation satisfies requirements of self-consistency and exact differentials, while that of the exact equation does not, so that it is the linearization that causes the Debye-Hückel result to be the exact limiting case [101].

Apparently the best advice is that we "keep in mind the fact that not only is the linearization procedure unacceptable except for large ions and low concentrations . . . but also abandonment of the linearization leads to no improvement" [114].

E. Motivation for the Present Work

For whatever reasons, scientists continue trying to solve both the linear and nonlinear forms of the Poisson-Boltzmann equation with both analytical [1,18,30,88,96, 110,126,127,128,151,152,153] and numerical methods [20, 46,55,120,144,168]. In membrane-transport studies that require the electric potential, not only is there no justification for not simply choosing the equation in its linearized form, there are compelling reasons for eschewing any so-called improvements. Indeed, there is some indication that the effects of the various corrections are usually not significant [61,125], and including some corrections while neglecting others may lead to worse results than those obtained from the linearized Poisson-Boltzmann equation, warts and all.

Thus solving the linearized Poisson-Boltzmann equation remains a worthwhile endeavor. The choice between a numerical or analytical solution for our purposes should be equally easy. Although a numerical solution has obvious advantages, its main disadvantage is that it lumps together the results so that relative contributions from different sources may not be obvious. Even in this age of high-speed computers, solving equations analytically is still an important activity.

The next four chapters of this dissertation are devoted to just that: seeking an analytical solution to the linearized Poisson-Boltzmann equation. The resulting $\psi(z,r)$ will then enable us to find $c_1(z,r)$ from Equation (1.5) and u_z from Equation (1.2), both necessary quantities for the further application of the Nernst-Planck equations (1.1) to ion transport across membranes.

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CHAPTER 2

THE FIRST ATTEMPT: SEPARATION OF VARIABLES

A. Introduction

Since the ultimate goal of solving the linearized Poisson-Boltzmann equation is to obtain improved equations for membrane transport, we choose a model system that is both mathematically tractable (at least relatively) and applicable to membranes. We assume an idealized membrane containing uniformly charged cylindrical pores and positioned between two infinitely large reservoirs of electrolyte solutions, which need not be at the same ionic strength (Figure 2.1). We consider this system to be continuous, isothermal, isotropic, incompressible, free of chemical reactions, and subject only to conservative external forces.

For the region inside the pore, i.e., $0 \leq r \leq a$ and $0 \leq z \leq L$, the linearized Poisson-Boltzmann equation is

$$\frac{\partial^2 \psi}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial \psi}{\partial r} = \kappa_0^2 f^2(z)\psi \quad , \qquad (2.1)$$

where ψ is the electric potential at any point z, r; f(z) is some function describing the ionic strength distribution along the length of the pore; and κ_0 is the reciprocal Debye

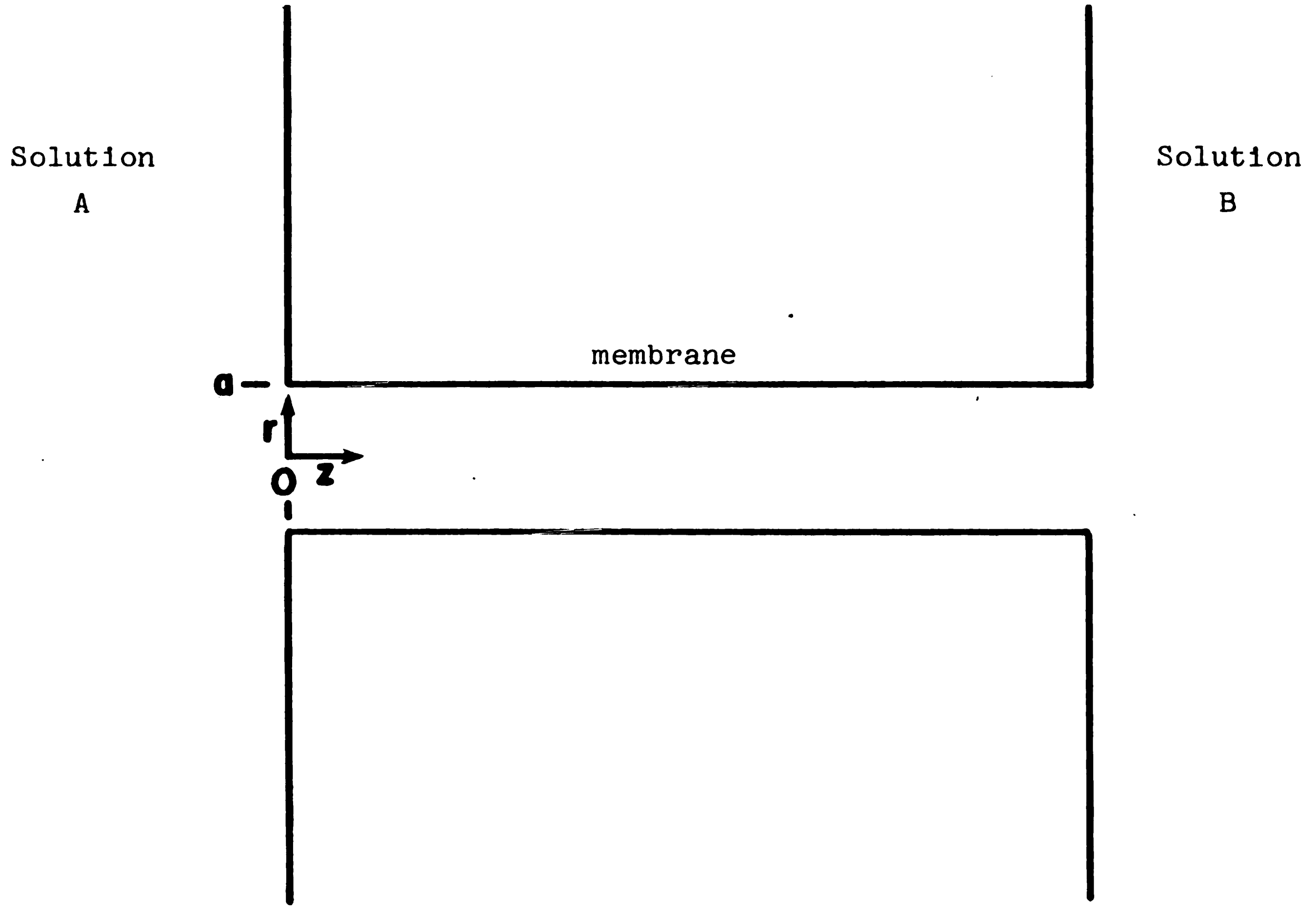

Figure 2.1. Idealized model of a membrane containing a cylindrical pore.

length defined as

$$\kappa_0^2 = \frac{2F^2 I(0)}{\varepsilon RT} \quad , \qquad (2.2)$$

where I(0) is the ionic strength at $z = 0$, and the other symbols have their usual meaning.

It is not possible to solve the Poisson-Boltzmann equation completely without specifying f(z) explicitly. Because neither the individual ion concentrations nor the ionic strength is available at each point within the pore, it is necessary to assume a particular axial gradient of ionic strength. In a recent note [140] we discussed two possible choices: (1) I(z) linear in z and (2) ℓn I(z) linear in z.

For the first case, I(z) linear in z,

$$I(z) = I_A \, [1 + (S^2-1)(z/L)] \quad , \qquad (2.3)$$

where

$$S \equiv \left[\frac{I(L)}{I(0)}\right]^{1/2} \quad . \qquad (2.4)$$

Thus for this case, Equation (2.1) becomes

$$\frac{\partial^2 \psi}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial \psi}{\partial r} = \kappa_0^2 [1 + (S^2-1)(z/L)]^2 \psi \quad . \qquad (2.5)$$

For the second case, $\ln I(z)$ linear in z,

$$I(z) = I(0)S^{2z/L} \quad , \qquad (2.6)$$

and

$$\frac{\partial^2\psi}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial\psi}{\partial r} = \kappa_0^2 S^{2z/L} \psi \; . \qquad (2.7)$$

This form of the linearized Poisson-Boltzmann equation not only appears simpler mathematically (though it is just an appearance), but may also be more reasonable physically. At steady state in the absence of applied pressure and electric potential gradients, $\ln I(z)$ is indeed linear, so that the actual distribution of ionic strength even with applied gradients may not be significantly different.

For this reason we focus upon the second case and expend most of our energy trying to solve Equation (2.7). A third, trivial case, that of $f(z) = 1$, is also of some interest for purposes of comparison.

B. The Method of Separation of Variables

Separation of variables is frequently the first method chosen in any attempt to solve a particular partial differential equation. Although it is simple and straightforward, it seldom works. Nevertheless, Hildebrand claims that despite the method's mathematical restriction "to a comparatively narrow range of differential equations, fortunately this range includes a very large number of those equations which arise in practice" [66]. This seems sufficiently encouraging to try this method for the linearized Poisson-Boltzmann equation.

C. Additive Solution

We assume a solution of the form

$$\psi(z,r) = \psi_1(z) + \psi_2(r) \quad . \tag{2.8}$$

Substituting this into Equation (2.7), we obtain

$$\frac{d^2\psi_1}{dz^2} + \frac{1}{r}\frac{d}{dr}\, r\,\frac{d\psi_2}{dr} = \kappa_0^2 S^{2z/L}(\psi_1+\psi_2) \quad . \tag{2.9}$$

This equation cannot be separated into two ordinary differential equations, one of which depends only on z and the other of which depends only on r.

D. Multiplicative Solution

This time we assume a solution of the form

$$\psi(z,r) = \psi_1(z)\psi_2(r) \quad . \tag{2.10}$$

There is strong precedent for a solution of this type. In analyzing the interaction between two charged cylinders (as models of colloid particles), Sparnaay [155] solved a two-dimensional linearized Poisson-Boltzmann equation with such a solution. Substitution of Equation (2.10) into Equation (2.7) leads to

$$\frac{1}{\psi_1}\frac{d^2\psi_1}{dz^2} + \frac{1}{r\psi_2}\frac{d}{dr}\, r\,\frac{d\psi_2}{dr} = \kappa_0^2 S^{2z/L} \quad , \tag{2.11}$$

in which the functions of z and r can be separated:

$$\frac{1}{\psi_1}\frac{d^2\psi_1}{dz^2} - \kappa_0^2 S^{2z/L} = -\frac{1}{r\psi_2}\frac{d}{dr}\, r\,\frac{d\psi_2}{dr} \quad . \tag{2.12}$$

Since the left-hand side is independent of r and the right-hand side independent of z, in order for them to be equal to each other, they must each be equal to a constant, which we can designate as λ^2. This results in the two ordinary differential equations

$$\frac{d^2\psi_1}{dz^2} - (\kappa_0^2 S^{2z/L} + \lambda^2)\psi_1 = 0 \tag{2.13}$$

and

$$r\frac{d}{dr}\, r\,\frac{d\psi_2}{dr} + \lambda^2 r^2 \psi_2 = 0 \quad . \tag{2.14}$$

The second equation of this pair is immediately recognizable as Bessel's equation, but the first must be transformed because of the term $S^{2z/L}$ before it too can be solved.

With the change of variable

$$x = \frac{\kappa_0 L}{\ell n S} S^{z/L} \quad , \tag{2.15}$$

Equation (2.13) becomes

$$\frac{\ell n^2 S}{L^2} x \frac{d}{dx} x \frac{d\psi_1}{dx} - \left(\frac{\ell n^2 S}{L^2} x^2 + \lambda^2\right)\psi_1 = 0 \quad . \tag{2.16}$$

If we let $\lambda^2 = (n^2 \ell n^2 S)/L^2$, where n need not be an integer, Equation (2.16) simplifies to

$$x \frac{d}{dx} x \frac{d\psi_1}{dx} - (x^2 + n^2)\psi_1 = 0 \quad . \tag{2.17}$$

The solutions to Equations (2.17) and (2.14) are

$$\psi_1(z) = \sum_n a_n I_n(\tau S^{z/L}) + \sum_n b_n K_n(\tau S^{z/L}) \tag{2.18}$$

and

$$\psi_2(r) = \sum_n A_n J_0(n\kappa_0 r/\tau) + \sum_n B_n Y_0(n\kappa_0 r/\tau) \quad , \tag{2.19}$$

where a_n, b_n, A_n, B_n are constants; I_n and K_n are modified Bessel functions of the first and second kind of order n respectively; J_0 and Y_0 are ordinary Bessel functions of the first and second kind of order zero, respectively; and

$$\tau \equiv \frac{\kappa_0 L}{\ell n S} \quad . \tag{2.20}$$

The radial symmetry condition,

$$\frac{\partial\psi(z,0)}{\partial r} = 0 \quad , \tag{2.21}$$

immediately shows that all the B_n must be zero or else the sum for $r = 0$ must be zero since $Y_1(0)$ is undefined. The second radial boundary condition,

$$\frac{\partial\psi(z,a)}{\partial r} = \frac{\sigma}{\varepsilon} \quad , \tag{2.22}$$

where σ is the surface charge density on the wall of the pore, is inconsistent with this solution since it requires that

$$\psi_1(z) = -\frac{\tau\sigma}{\varepsilon\kappa_0}\,\frac{1}{\Sigma n A_n J_1(n\kappa_0 a/\tau)} \tag{2.23}$$

i.e., that $\psi_1(z)$ be constant. This is incompatible with the original separation of $\psi(z,r)$.

One possible way of salvaging this solution is the assumption of a z-dependent surface charge density $\sigma(z)$. Although the derivation of the boundary condition (2.22) from Gauss' law involves an equipotential surface and thus a constant surface charge density [138], Gouy-Chapman theory provides a relationship between surface charge density and surface potential, and thus between charge density and concentration if the surface potential is known [41,123].

Thus for the boundary condition

$$\frac{\partial\psi(z,a)}{\partial r} = \frac{\sigma(z)}{\varepsilon} , \tag{2.24}$$

we have that

$$\psi_1(z) = - \frac{\tau\sigma(z)}{\varepsilon\kappa_0} \frac{1}{\Sigma n A_n J_1(n\kappa_0 a/\tau)} , \tag{2.25}$$

or

$$\psi(z,r) = - \frac{\tau\sigma(z)}{\varepsilon\kappa_0} \frac{\Sigma A_n J_0(n\kappa_0 r/\tau)}{\Sigma n A_n J_1(n\kappa_0 a/\tau)} . \tag{2.26}$$

There are two major difficulties with this solution. First, we have no way to determine the constant A_n. The natural choice, the orthogonality of the Bessel functions, would be useful only if we could relate their argument to

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the zeros of, presumably, J_1. Second, there is no independent method for obtaining the z-dependence of σ, though presumably it would be related to the z-dependence of the ionic strength, and if we simply assume a certain dependence on z, we have thwarted our intent of determining the electric potential ψ as a function of both z and r.

We return to Equation (2.16), and letting $\lambda^2 = -n^2 \ell n^2 S/L^2$, we have the solution,

$$\psi_1(z) = \sum_n a_n I_{in}(\tau S^{z/L}) + \sum_n b_n K_{in}(\tau S^{z/L}) \quad . \qquad (2.27)$$

The solution of Equation (2.14) remains the same. The only change in the form of the solution for $\psi_1(z)$ is that the index of the Bessel functions is imaginary. The choice of $\lambda^2 = \pm n^2$ also results only in a change in the index of the modified Bessel functions of $\psi_1(z)$, in fact a change for the worse since the index becomes $nL/\ell nS$ or $inL/\ell nS$.

None of these choices of λ^2 provides a complete solution of ψ that is consistent with the radial boundary condition at r = a, nor does the assumption of a z-dependent boundary condition save the solution. The conclusion is that the linearized Poisson-Boltzmann equation unfortunately does not fall within the range of partial differential equations for which the separation-of-variables method is useful. Instead, we turn our attention in the next chapter to a different kind of proposed solution.

CHAPTER 3

A NEW VERSION OF AN OLD SOLUTION

A. Introduction

In this chapter we consider an additive solution apparently originated by Osterle and his colleagues [46,55, 116]:

$$\psi(z,r) = \psi_1(z) + \psi_2(z,r) \quad . \tag{3.1}$$

This solution has also been used by others as well [78, 88, 140,144], but the other studies besides our own have always involved numerical, rather than analytical results.

Lee [88], who did obtain an analytical solution, wrote the right-hand side of Equation (2.1) as $\kappa^2\psi$, where κ implicitly contains the z-dependence of the ionic strength:

$$\kappa^2 = \frac{2F^2 I(z)}{\varepsilon RT} \quad , \tag{3.2}$$

and so his final expressions are dependent on z, but not explicitly. Moreover, even though he made the above separation, he ultimately assumed a linear dependence in z for

ψ_1, rather than determining the z-dependence from the resulting equation.

B. Analytical Solutions for $\psi_1(z)$ and $\psi_2(z,r)$

For the moment we consider the more general Equation (2.1), which, with the proposed solution (3.1), becomes

$$\frac{d^2\psi_1}{dz^2} + \frac{\partial^2\psi_2}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial\psi_2}{\partial r} = \kappa_0^2 f^2(z)(\psi_1+\psi_2) \tag{3.3}$$

We now assume that it is legitimate to separate this into two independent equations; i.e., that there is no mixing of the two different functions in the above equations:

$$\frac{d^2\psi_1}{dz^2} = \kappa_0^2 f^2(z)\psi_1 \tag{3.4}$$

and

$$\frac{\partial^2\psi_2}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial\psi_2}{\partial r} = \kappa_0^2 f^2(z)\psi_2 \quad . \tag{3.5}$$

In his solution of Equation (3.5), Lee [88] first assumed and later verified that the z-derivative is small compared to the r-derivative in the case that a/L << 1. The values of pore radius and pore length of "real" systems are of the order of 1 x 10^{-8} m and 1 x 10^{-4} m, respectively, and so this approximation seems like a good one. The omission of the term $\partial^2\psi_2/\partial z^2$ makes the solution of Equation (3.5) considerably easier. It is in fact the modified Bessel equation of order zero and may be solved for any f(z):

$$\psi_2(z,r) = k_1 I_0[\kappa_0 r f(z)] + k_2 K_0[\kappa_0 r f(z)] \quad . \qquad (3.6)$$

The radial condition (2.21) demands that k_2 be zero since $K_0(0)$ is undefined, and the boundary condition (2.22) results in the solution

$$\psi_2(z,r) = \frac{\sigma I_0[\kappa_0 r f(z)]}{\varepsilon\kappa_0 f(z) I_1[\kappa_0 a f(z)]} \quad . \qquad (3.7)$$

This result is well known for the special case of constant ionic strength and is the same as that obtained by Lee [88], except that his solution's axial dependence is hidden in the z-dependent parameter κ.

Lee did not consider Equation (3.4), but simply assumed that ψ_1 varied linearly with z. This is obviously not true since $d^2\psi_1/dz^2 \neq 0$. However, Equation (3.4) cannot be solved for a general f(z) as can Equation (3.5), and so we consider the three possible cases of f(z) mentioned earlier.

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For $f(z) = 1$, the solution is trivial:

$$\psi_1(z) = k_1 \cosh\kappa_0 z + k_2 \sinh\kappa_0 z \quad . \tag{3.8}$$

For the moment we write the boundary conditions on ψ_1 at $z = 0$ and $z = L$ only formally as $\psi_1(0)$ and $\psi_1(L)$. This results in the solution:

$$\psi_1(z) = [\psi_1(0)\sinh\kappa_0(L-z) + \psi_1(L)\sinh\kappa_0 z]\operatorname{csch}\kappa_0 L \quad . \tag{3.9}$$

With $f^2(z) = [1 + (S^2-1)\ (z/L)]$, the solution of Equation (3.4) is no longer trivial. The change of variable

$$\zeta = [1 + (S^2-1)(z/L)]^{1/2} \tag{3.10}$$

gives rise to the equation

$$\zeta^2 \frac{d^2\psi_1}{dz^2} - \zeta\frac{d\psi_1}{dz} - 9\alpha^2\zeta^6\psi_1 = 0 \ , \tag{3.11}$$

where

$$\alpha \equiv \frac{2\kappa_0 L}{3(S^2-1)} \ . \tag{3.12}$$

Even though this equation may not be immediately familiar, it is a special case of a general differential

equation discussed by Hildebrand [66]:

$$x^2 \frac{d^2y}{dx^2} + x(a + 2bx^q) \frac{dy}{dx} + [c + dx^{2s} - b(1-a-q)x^q + b^2x^{2q}]y = 0 \quad , \tag{3.13}$$

where a, b, q, c, d, s are all constants. The solution of this differential equation is

$$y = x^{(1-a)/2} e^{-bx^q/q} Z_p \left[\frac{d^{1/2}}{s} x^2\right] \quad , \tag{3.14}$$

where

$$p \equiv \frac{1}{s} \left[\left(\frac{1-a}{2}\right)^2 - c\right]^{1/2} \quad , \tag{3.15}$$

and

$$Z_p = k_1 J_p + k_2 Y_p \tag{3.16}$$

for $d^{1/2}/s$ real, or

$$Z_p = k_1 I_p + k_2 K_p \tag{3.17}$$

for $d^{1/2}/s$ imaginary. These solutions are required only

for p either zero or an integer, and if p is not zero or an integer, then the two solutions may be written

$$Z_p = k_1 J_p + k_2 J_{-p} \tag{3.18}$$

and

$$Z_p = k_1 I_p + k_2 I_{-p} \tag{3.19}$$

respectively.

To specialize Equation (3.13) to our Equation (3.11), we note that $a = -1$, $b = 0$, $c = 0$, $d = -3\alpha^2$, $s = 3$, $q = 0$, and therefore, since $(-\alpha^2)^{1/2}$ is imaginary,

$$\psi_1(\zeta) = k_1 \zeta I_{1/3}(\alpha\zeta^3) + k_2 \zeta I_{-1/3}(\alpha\zeta^3) \quad , \tag{3.20}$$

or

$$\psi_1(\zeta) = k_1 \zeta I_{1/3}(\alpha\zeta^3) + k_2 \zeta K_{1/3}(\alpha\zeta^3) \quad , \tag{3.21}$$

which are equivalent because of the definition

$$K_p = - \frac{\pi}{2} \frac{I_p - I_{-p}}{\sin p\pi} \tag{3.22}$$

for p not zero or an integer [66].

Applying the same formal boundary conditions as before to Equation (3.20), we obtain

$$\psi_1(\zeta) = \frac{\psi_1(1)\zeta[I_{-1/3}(\alpha S^3)I_{1/3}(\alpha\zeta^3)-I_{1/3}(\alpha S^3)I_{-1/3}(\alpha\zeta^3)]}{I_{1/3}(\alpha)\ I_{-1/3}(\alpha S^3)-I_{1/3}(\alpha S^3)I_{-1/3}(\alpha)}$$

$$-\frac{\psi_1(S)\zeta[I_{-1/3}(\alpha)I_{1/3}(\alpha\zeta^3)-I_{1/3}(\alpha)I_{-1/3}(\alpha\zeta^3)]}{S[I_{1/3}(\alpha)I_{-1/3}(\alpha S^3)-I_{1/3}(\alpha S^3)I_{-1/3}(\alpha)]} \quad , \quad (3.23)$$

where ζ and α are defined in terms of the original variable and constants by Equations (3.10) and (3.12), respectively.

For the third choice of $f^2(z) = S^{2z/L}$, the transformation of Equation (3.4) with the change of variable

$$\xi = \tau S^{z/L} \quad , \qquad (3.24)$$

where

$$\tau \equiv \frac{\kappa_0 L}{\ell n S} \quad , \qquad (3.25)$$

results in the equation

$$\xi^2 \frac{d^2\psi_1}{d\xi^2} + \xi\frac{d\psi_1}{d\xi} - \xi^2\psi_1 = 0 \quad . \qquad (3.26)$$

Not surprisingly, this is again a special case of the differential equation (3.13), this time simply the modified Bessel equation of order zero, and thus the solution is

$$\psi_1(\xi) = k_1 I_0(\xi) + k_2 K_0(\xi) \quad . \tag{3.27}$$

The solution (3.18) is not an option here since p is zero, and in (3.27) K_0 must be retained, since ξ is never zero for $0 \leq z \leq L$.

Application of the same formal boundary conditions results in the solution

$$\psi_1(z) = \frac{\psi_1(0)[K_0(\tau S)I_0(\tau S^{z/L})-I_0(\tau S)K_0(\tau S^{z/L})]}{I_0(\tau)K_0(\tau S)-I_0(\tau S)K_0(\tau)}$$

$$- \frac{\psi_1(L)[K_0(\tau)I_0(\tau S^{z/L})-I_0(\tau)K_0(\tau S^{z/L})]}{I_0(\tau)K_0(\tau S)-I_0(\tau S)K_0(\tau)} \quad . \tag{3.28}$$

Thus beginning with the linearized Poisson-Boltzmann equation, we have obtained a complete analytical solution for different model distributions of ionic strength with only three additional assumptions:

(1) That the form of the solution is given by Equation (3.1);

(2) that Equation (3.3) can be separated into Equations (3.4) and (3.5); and

(3) that in Equation (3.5) the z-derivative is small relative to the r-derivative.

C. An Attempt to Obtain Explicit Boundary Conditions $\psi_1(0)$ and $\psi_1(L)$

The major drawback of the solutions for ψ_1 in Equations (3.9), (3.23), and (3.28) is the boundary conditions, $\psi_1(0)$ and $\psi_1(L)$, which are stated only formally and have no direct connection with the physical system that we are trying to model. In order to try to make this connection, we need to apply boundary conditions that arise from the electrolyte solutions on either side of the membrane. First, however, we need to look at the derivation of the linearized Poisson-Boltzmann equation in more detail, particularly with regard to the definitions of the inverse Debye length κ and the z-dependent ionic strength $I(z)$.

We begin with the equation describing chemical equilibrium for each component i in the radial direction inside the capillary,

$$0 = \overline{V}_i \frac{\partial p}{\partial r} + RT \frac{\partial \ell n f_i}{\partial r} + RT \frac{\partial \ell n x_i}{\partial r} + z_i F \frac{\partial \psi}{\partial r} , \qquad (3.29)$$

where $\overline{V}_i$ is the partial molar volume, f_i the activity coefficient, and x_i the mole fraction, and we assume that (1) the pressure term is negligible [30,71,88], (2) f_i is constant, and thus $\partial \ell n f_i/\partial r = 0$, and (3) the total molar vo

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volume V is constant so that $x_i = c_i$. Ideality is a convenient assumption for simplifying the mathematics and certainly not a bad one for dilute solutions. Equation (3.29) can then be written as

$$\frac{\partial \ell n c_i(z,r)}{\partial r} = \frac{z_i F}{RT} \frac{\partial \psi(z,r)}{\partial r} , \tag{3.30}$$

the solution of which is

$$\ell n c_i(z,r) = - \frac{z_i F}{RT} \psi(z,r) + A(z) . \tag{3.31}$$

The usual derivation of the linearized Boltzmann equation includes the assumptions that at infinity electroneutrality holds and the electric potential diminishes to zero. Although these conditions are certainly met in the bulk solutions outside the capillary, infinity is an unavailable luxury inside the capillary where the radial coordinate varies from 0 to a. Even though in practical terms "infinity" may be only the distance of a few atomic diameters, the conditions of electroneutrality and zero electric potential (relative to the charged wall) do not occur anywhere inside the capillary, not even at r = 0 where ρ and $\psi(z,r)$ may be at a minimum, but they presumably are still not identically zero. Nevertheless, for the time being, we assume that $\overline{c}_i(z)$ represents the concentration of ion i that <u>would</u> occur at z (along r = 0) if $\psi(z,0)$ were zero

at that point, and thus these concentrations, even though they are fictitious, have the advantage of obeying the condition of electroneutrality.

This identifies the integration constant A(z) as ℓn $\bar{c}_i(z)$, and Equation (3.31) becomes

$$\ell n c_i(z,r) = -\frac{z_i F}{RT}\psi(z,r) + \ell n \bar{c}_i(z) \quad , \tag{3.32}$$

or

$$c_i(z,r) = \bar{c}_i(z) e^{-z_i F\psi(z,r)/RT} \quad . \tag{3.33}$$

The linearized form,

$$c_i(z,r) = \bar{c}_i(z)\left[1 - \frac{z_i F\psi(z,r)}{RT}\right] \quad , \tag{3.34}$$

is accurate to within 5% of the nonlinear expression for $\psi(z,r) < 0.287$ V at 300 K. The net volume charge density, defined in Equation (1.4), may now be written as

$$\rho = F\Sigma\bar{c}_i(z)z_i - \frac{F^2\psi(z,r)}{RT}\Sigma\bar{c}_i(z)z_i^2 \quad , \tag{3.35}$$

or

$$\rho = -\frac{2F^2\bar{I}(z)}{RT}\psi(z,r) \quad , \tag{3.36}$$

since the first sum in Equation (3.35) is zero because of electroneutrality, and the ionic strength at zero potential, $\overline{I}(z)$, is defined as

$$\overline{I}(z) = \tfrac{1}{2}\Sigma\overline{c}_i(z)z_i^2 \quad . \tag{3.37}$$

By substituting Equation (3.36) into Equation (1.3), we can write the linearized Poisson-Boltzmann equation in cylindrical coordinates as

$$\nabla^2\psi(z,r) = \frac{2F^2\overline{I}(z)}{\varepsilon RT}\,\psi(z,r) \quad , \tag{3.38}$$

or

$$\nabla^2\psi(z,r) = \overline{\kappa}^2\psi(z,r) \quad , \tag{3.39}$$

where $\overline{\kappa}$, the inverse Debye length at zero potential, is defined by

$$\overline{\kappa}^2 = \frac{2F^2\overline{I}(z)}{RT} \quad . \tag{3.40}$$

If we now assume ψ to be of the form given in Equation (3.1) and separate the resulting equation as before, we obtain

$$\frac{d^2\psi_1(z)}{dz^2} = \bar{\kappa}^2\psi_1(z) \qquad (3.41)$$

and

$$\frac{\partial^2\psi_2(z,r)}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial\psi_2(z,r)}{\partial r} = \bar{\kappa}^2\psi_2(z,r) \quad . \qquad (3.42)$$

These are identical to Equations (3.4) and (3.5) except that $\bar{\kappa}$ and the (hypothetical) reference concentration $\bar{c}_i(z)$ are more clearly defined.

We now return to Equation (3.33) and write it for $r = 0$:

$$c_i(z,0) = \bar{c}_i(z)e^{-z_iF\psi(z,0)/RT} \quad , \qquad (3.43)$$

for which we introduce the less cumbersome notation $c_i^o(z)$ and $\psi^o(z)$ for the quantities $c_i(z,r)$ and $\psi(z,r)$ at $r = 0$:

$$c_i^o(z) = \bar{c}_i(z)e^{-z_iF\psi^o(z)/RT} \quad . \qquad (3.44)$$

Dividing Equation (3.33) by Equation (3.44) yields

$$c_i(z,r) = c_i^o(z)\exp\left\{- \frac{z_iF}{RT}[\psi(z,r)-\psi^o(z)]\right\} \quad , \qquad (3.45)$$

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of ion i anywhere along the midline of the capillary, but the apparent disadvantage that $c_i^\circ(z)$ does not obey the condition of electroneutrality. In fact, this expression may also be derived directly from Equation (3.29) with the same assumptions as before except that the integration constant is identified as

$$A(z) = \frac{z_iF}{RT}\psi^\circ(z) + \ell n c_i^\circ(z) \quad . \tag{3.46}$$

The potential difference $\psi(z,r) - \psi^\circ(z)$ is equivalent to the difference $\psi_2(z,r) - \psi_2^\circ(z)$ since $\psi_1(z)$, being independent of r, simply cancels out in the subtraction. The linearized form of Equation (3.45) is therefore

$$c_i(z,r) = c_i^\circ(z)\left\{1 - \frac{z_iF}{RT}[\psi_2(z,r) - \psi_2^\circ(z)]\right\} \quad , \tag{3.47}$$

from which the net volume charge density is

$$\rho = F\Sigma c_i^\circ(z)z_i - \frac{F^2}{RT}[\psi_2(z,r)-\psi_2^\circ(r)]\Sigma c_i^\circ(z)z_i^2 \quad , \tag{3.48}$$

or

$$\rho = F\Sigma c_i^\circ(z)z_i - \frac{2F^2I^\circ(z)}{RT}[\psi_2(z,r)-\psi_2^\circ(z)] \quad , \tag{3.49}$$

where $I^\circ(z)$, defined in terms of $c_i^\circ(z)$, is the ionic strength along the capillary midline. With the corresponding definition

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of κ°, the net volume charge density yields the following linearized Poisson-Boltzmann equation:

$$\nabla^2\psi(z,r) = -\frac{F}{\varepsilon}\Sigma c_i^\circ(z)z_i + (\kappa^\circ)^2[\psi_2(z,r)-\psi_2^\circ(z)] \quad . \tag{3.50}$$

We again separate this into two equations:

$$\frac{d^2\psi_1(z)}{dz^2} = -\frac{F}{\varepsilon}\Sigma c_i^\circ(z)z_i - (\kappa^\circ)^2\psi_2^\circ(z) \tag{3.51}$$

and

$$\frac{\partial^2\psi_2(z,r)}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}\, r\frac{\partial\psi_2(z,r)}{\partial r} = (\kappa^\circ)^2\psi_2(z,r) \quad . \tag{3.52}$$

Comparing these with Equations (3.41) and (3.42), we see that

$$\bar{\kappa}^2\psi_1(z) = -\frac{F}{\varepsilon}\Sigma c_i^\circ(z)z_i - (\kappa^\circ)^2\psi_2^\circ(z) \tag{3.53}$$

and that $\bar{\kappa} = \kappa^\circ$.

It is not immediately obvious that $\bar{\kappa}$ and κ° should be equal to each other, i.e., that the ionic strength should be the same in both the presence and absence of an electric field. Nevertheless, it seems reasonable if we consider ionic strength as an average over the individual

ions. In the presence of a field, the concentration of cations shifts away from its zero-field value, but, within the limits of the linearization of the Boltzmann equation, the concentration of the anion (for symmetric electrolytes) simultaneously shifts an equal amount in the opposite direction so that their average represented in the ionic strength remains the same as in the absence of a field. This same argument will reoccur later in a more quantitative manner.

Even if we accept the identity of $\overline{I}(z)$ and $I^{\circ}(z)$ (and thus of $\overline{\kappa}$ and κ°), we must still find an expression for the sum $\Sigma c_i^{\circ}(z)z_i$ although $\psi_2^{\circ}(z)$ is already known from the solution for $\psi_2(z,r)$ at $r = 0$. Unfortunately, the form of $\psi_1(z)$ in Equation (3.53) does not satisfy Equation (3.4), but it must still yield the correct value for a particular z, and therefore we hope to obtain the boundary conditions $\psi_1(0)$ and $\psi_1(L)$ from it. However, this is still not an easy task, and we must now consider the bulk solutions at either end of the capillary.

D. The Bulk Solutions As Boundary Conditions

Since each bulk solution is in equilibrium in the z-direction, the appropriate expression, with the same assumptions as those leading up to Equation (3.30), is

$$\frac{d\ell n c_i(z)}{dz} = - \frac{z_i F}{RT} \frac{d\phi(z)}{dz} , \qquad (3.54)$$

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where $c_i(z)$ is the z-dependent concentration and $\phi(z)$ the electric potential in the interphase between the face of the membrane and the bulk solution that bathes it, i.e., in the "<u>region</u> in which there is a continuous transition from the properties of one phase to the properties of the other" [15]. Not surprisingly, the solution to this equation is

$$\ln c_i(z) = -\frac{z_i F}{RT}\phi(z) + A \quad . \tag{3.55}$$

Although it is usually legitimate to assume that the potential is zero at infinity, we will not do that here because we wish to sandwich together the two mathematical solutions for electrolyte solutions A and B, and the assumption of $\phi = 0$ for each would simply result in $\Delta\phi = 0$, hardly an interesting result. Instead, we will assume that for solution A, $\phi_A(z) = \phi_A$ when $c_i^A(z) = c_i^A$, i.e., the value of the potential is the "bulk" potential ϕ_A when the value of the concentration of ion i is the concentration c_i^A. In both cases, the lack of the parenthetical z with each symbol indicates a constant bulk value. And analogously for solution B, $\phi_B(z) = \phi_B$ when $c_i^B(z) = c_i^B$.

It seems valid to consider these bulk potentials ϕ_A and ϕ_B as those obtained from measuring these solutions individually against a reference electrode, such as that of the standard hydrogen or saturated calomel electrode. Presumably either ϕ_A or ϕ_B, or at least their difference, should also be able to include an external potential difference applied across the membrane. This would be important in certain membrane-transport studies, but we will not consider any applied potential differences in our study of the Poisson-Boltzmann equation per se.

Thus for solutions A and B, Equation (3.55) becomes

$$c_i^A(z) = c_i^A \exp\left\{- \frac{z_i F}{RT} [\phi_A(z) - \phi_A]\right\} \tag{3.56}$$

and

$$c_i^B(z) = c_i^B \exp\left\{- \frac{z_i F}{RT} [\phi_B(z) - \phi_B]\right\} \quad , \tag{3.57}$$

or in their linearized form

$$c_i^A(z) = c_i^A \left\{1 - \frac{z_i F}{RT} [\phi_A(z) - \phi_A]\right\} \tag{3.58}$$

and

$$c_i^B(z) = c_i^B \left\{1 - \frac{z_i F}{RT} [\phi_B(z) - \phi_B]\right\} \quad . \tag{3.59}$$

The net volume charge density can now be written for each side of the membrane:

$$\rho_A = F \Sigma c_i^A z_i - \frac{F^2}{RT} [\phi_A(z) - \phi_A] \Sigma c_i^A z_i^2 \tag{3.60}$$

and

$$\rho_B = F\Sigma c_i^B z_i - \frac{F^2}{RT}[\phi_B(z)-\phi_B]\Sigma c_i^B z_i^2 \quad , \qquad (3.61)$$

or

$$\rho_A = -\frac{2F^2 I_A}{RT}[\phi_A(z)-\phi_A] \qquad (3.62)$$

and

$$\rho_B = -\frac{2F^2 I_B}{RT}[\phi_B(z)-\phi_B] \quad , \qquad (3.63)$$

since both c_i^A and c_i^B obey the condition of electroneutrality. The linearized one-dimensional Poisson-Boltzmann equation can now be written for each interphase:

$$\frac{d^2\phi_A(z)}{dz^2} = \frac{2F^2 I_A}{\varepsilon RT}[\phi_A(z)-\phi_A] \qquad (3.64)$$

and

$$\frac{d^2\phi_B(z)}{dz^2} = \frac{2F^2 I_B}{\varepsilon RT}[\phi_B(z)-\phi_B] \quad , \qquad (3.65)$$

or

$$\frac{d^2\phi_A(z)}{dz^2} = \kappa_A^2[\phi_A(z)-\phi_A] \qquad (3.66)$$

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$$\frac{d^2\phi_B(z)}{dz^2} = \kappa_B^2[\phi_B(z)-\phi_B] \quad , \tag{3.67}$$

where κ_A and κ_B are defined as usual.

With the substitutions

$$u_A = \phi_A(z) - \phi_A \tag{3.68}$$

and

$$u_B = \phi_B(z) - \phi_B \quad , \tag{3.69}$$

the solutions to these differential equations can be written down immediately as

$$\phi_A(z) = A_1 e^{\kappa_A z} + A_2 e^{-\kappa_A z} + \phi_A \tag{3.70}$$

and

$$\phi_B(z) = B_1 e^{\kappa_B z} + B_2 e^{-\kappa_B z} + \phi_B \quad , \tag{3.71}$$

but since $\phi_A(z)$ must remain finite at minus infinity and $\phi_B(z)$ at plus infinity, A_2 and B_1 must be zero. The other boundary conditions at the membrane itself, i.e.,

$$\frac{d\phi_A(0)}{dz} = \frac{\sigma_A}{\varepsilon} \tag{3.72}$$

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$$\frac{d\phi_B(L)}{dz} = -\frac{\sigma_B}{\varepsilon} \quad , \tag{3.73}$$

deserve a short digression on the physical meaning -- within the assumed model -- of σ_A and σ_B, the net surface charge densities on the respective faces of the membrane.

As we will subsequently use them, σ_A and σ_B are a quantitative measure of the net charge per unit area on the "solid" part of the membrane, i.e., the total area of each face less the area of the pore openings. Because the latter area is a small fraction of the total surface area (e.g., less than 4% in some of the commercially available Nucleopore polycarbonate membranes [119]), the charge on the "solid" part of the face should be the major contributor to the electric potential and concentration profiles (relative to the bulk) in the interphase. Whatever deviations in potential and concentrations that arise at a pore opening, relative to those at the "solid" surface of the membrane, should be small and more or less washed out by the stronger effects arising from the charge on the rest of the membrane. A better formulation of σ_A (or σ_B) ought to include the relative contributions from both the "solid" surface and the pore openings, i.e., something of the form

$$\sigma_A = A_s\sigma_s + A_p\sigma_p \quad , \tag{3.74}$$

where A_s and A_p are the fractional areas of the "solid" surface and pore openings respectively, and σ_s and σ_p the corresponding charge densities. Presumably, σ_p represents an average charge density at the pore opening since $c_i(0,r)$ (and thus the charge density) varies with r. This seems a relatively minor consideration and need not impede us further.

As originally defined, the surface charge densities σ_A and σ_B are equal to each other if the two membrane faces are identical, although this cannot strictly be true even then, in light of the discussion of the previous paragraph since $c_i(0,r)$ and $c_i(L,r)$ would give rise to different contributions to σ_p at the two faces. However, the important point is that the two faces need not be identical, and this is the real reason for maintaining this distinction between σ_A and σ_B. For example, cellulose acetate membranes, which are important in reverse osmosis and hemodialysis, have structurally different faces with different charge densities.

The boundary conditions presented in Equations (3.72) and (3.73) lead to the complete solutions

$$\phi_A(z) = \frac{\sigma_A}{\varepsilon\kappa_A} e^{\kappa_A z} + \phi_A \tag{3.75}$$

and

$$\phi_B(z) = \frac{\sigma_B}{\varepsilon\kappa_B} e^{\kappa_B(L-z)} + \phi_B \quad . \tag{3.76}$$

The two reciprocal Debye lengths κ_A and κ_B are related to each other through the parameter S, and their definitions, along with that of S, show that

$$\kappa_B = \kappa_A S \quad . \tag{3.77}$$

Therefore, Equation (3.74) may be rewritten as

$$\phi_B(z) = \frac{\sigma_B}{\varepsilon\kappa_A S}\, e^{\kappa_A S(L-z)} + \phi_B \quad . \tag{3.78}$$

With Equations (3.75) and (3.78), Equations (3.56) and (3.57) become

$$c_i^A(z) = c_i^A \exp\left\{- \frac{z_i F}{RT}\left[\frac{\sigma_A}{\varepsilon\kappa_A}\, e^{\kappa_A z} + \phi_A\right]\right\} \tag{3.79}$$

and

$$c_i^B(z) = c_i^B \exp\left\{- \frac{z_i F}{RT}\left[\frac{\sigma_B}{\varepsilon\kappa_A S}\, e^{\kappa_A S(L-z)} + \phi_B\right]\right\} \tag{3.80}$$

The "outside" ion concentrations at the ends of the capillary, $c_i^A(0)$ and $c_i^B(L)$, are readily written down, and a simple mass balance indicates that they should be equal to the "inside" ion concentrations given by Equation (3.45) averaged over the radius. Thus

$$\left\langle c_i(0,r)\right\rangle_r = c_i^A(0) \tag{3.81}$$

and

$$\langle c_i(L,r)\rangle_r = c_i^B(L) \quad , \tag{3.82}$$

where the symbol $< >_r$ indicates the appropriate average over r, i.e.,

$$\langle g(r)\rangle_r = \frac{\int_o^a rg(r)dr}{\int_o^a rdr} \; . \tag{3.83}$$

The average of Equation (3.45) is

$$\langle c_i(z,r)\rangle_r = \left\langle c_i^o(z)\exp\left\{-\frac{z_iF}{RT}[\psi_2(z,r)-\psi_2^o(z)]\right\}\right\rangle_r \; . \tag{3.84}$$

Although the relationship

$$\langle e^{-\beta}\rangle_r = e^{-<\beta>_r} \quad , \tag{3.85}$$

where β is some function of r, is not true in general, the result of applying this relationship is correct as long as we linearize the final exponentials.

Thus, Equation (3.84) may be rewritten as the simpler

$$\langle c_i(z,r)\rangle_r = c_i^o(z)\exp\left\{-\frac{z_iF}{RT}\left[\langle\psi_2(z,r)\rangle_r-\psi_2^o(z)\right]\right\} \; , \tag{3.86}$$

where, from Equation (3.7),

$$\left\langle \psi_2(z,r) \right\rangle_r = \frac{2\sigma}{\varepsilon \kappa_0 a^2 f(z) I_1[\kappa_0 a f(z)]} \int_0^a r I_0[\kappa_0 r f(z)] dr \tag{3.87}$$

and

$$\psi_2^\circ(z) = \frac{\sigma}{\varepsilon \kappa_0 f(z) I_1[\kappa_0 a f(z)]} \ . \tag{3.88}$$

The integral in Equation (3.87) is readily performed [88] with the result

$$\left\langle \psi_2(z,r) \right\rangle_r = \frac{2\sigma}{\varepsilon \kappa_0^2 a f^2(z)} \ , \tag{3.89}$$

and Equation (3.86) becomes

$$\left\langle c_i(z,r) \right\rangle_r = c_i^\circ \exp \left\{ - \frac{z_i F \sigma}{\varepsilon \kappa_0 f(z) RT} \left[\frac{2}{\kappa_0 a f(z)} - \frac{1}{I_1[\kappa_0 a f(z)]} \right] \right\} \ . \tag{3.90}$$

We can now write the matching conditions in Equations (3.81) and (3.82) explicitly. Equating Equations (3.79) and (3.90) for z = 0 and Equations (3.80) and (3.90) for z = L, we obtain

$$c_i^\circ(0) \exp \left\{ - \frac{z_i F \sigma}{\varepsilon \kappa_0 f(0) RT} \left[\frac{2}{\kappa_0 a f(0)} - \frac{1}{I_1[\kappa_0 a f(0)]} \right] \right\}$$

$$= c_i^A \exp \left\{ - \frac{z_i F}{RT} \left[\frac{\sigma_A}{\varepsilon \kappa_A} + \phi_A \right] \right\} \tag{3.91}$$

$$c_i^o(L)\exp\left\{-\frac{z_iF\sigma}{\varepsilon\kappa_0 f(L)RT}\left[\frac{2}{\kappa_0 a f(L)}-\frac{1}{I_1[\kappa_0 a f(L)]}\right]\right\}$$

$$=c_i^B\exp\left\{-\frac{z_iF}{RT}\left[\frac{\sigma_B}{\varepsilon\kappa_A S}+\phi_B\right]\right\}\quad . \tag{3.92}$$

Thus the required linearized expressions for $c_i^o(0)$ and $c_i^o(L)$ are

$$c_i^o(0) = c_i^A\left\{1-\frac{z_iF\sigma}{\varepsilon\kappa_A RT}\left[\frac{\sigma_A}{\sigma}+\frac{\varepsilon\kappa_A\phi_A}{\sigma}-\frac{2\kappa_A}{\kappa_0^2 a f^2(0)}\right.\right.$$

$$\left.\left.+\frac{\kappa_A}{\kappa_0 f(0) I_1[\kappa_0 a f(0)]}\right]\right\} \tag{3.93}$$

and

$$c_i^o(L) = c_i^B\left\{1-\frac{z_iF\sigma}{\varepsilon\kappa_A RT}\left[\frac{\sigma_B}{S\sigma}+\frac{\varepsilon\kappa_A\phi_B}{\sigma}-\frac{2\kappa_A}{\kappa_0^2 a f^2(L)}\right.\right.$$

$$\left.\left.-\frac{\kappa_A}{\kappa_0 f(L) I_1[\kappa_0 a f(L)]}\right]\right\}\quad , \tag{3.94}$$

which relate the concentrations $c_i^o(0)$ and $c_i^o(L)$, needed for the boundary conditions $\psi_1(0)$ and $\psi_1(L)$ from Equation (3.53), to the corresponding bulk concentrations c_i^A and c_i^B.

However, these expressions also each contain both κ_0, defined in terms of I(0), and κ_A, defined in terms of I_A. If we write out the definition for I(0) with Equation (3.93) we have

$$I(0) = \tfrac{1}{2}\Sigma c_i^\circ(0) z_i^2 = \tfrac{1}{2}\Sigma c_i^A z_i^2$$

$$- \frac{F\sigma}{2\varepsilon\kappa_A RT}\left[\frac{\sigma_A}{\sigma} + \frac{\varepsilon\kappa_A\phi_A}{\sigma} - \frac{2\kappa_A}{\kappa_0^2 a f^2(0)}\right.$$

$$\left. + \frac{\kappa_A}{\kappa_0 f(0) I_1[\kappa_0 a f(0)]}\right]\Sigma c_i^A z_i^3 \quad , \qquad (3.95)$$

or

$$I(0) = \frac{1}{2}\ \Sigma c_i^A z_i^2 \qquad (3.96)$$

for all symmetric electrolytes since $\Sigma c_i^A z_i^3 = 0$. I(0) is identically equal to I_A within the linearization scheme of the Boltzmann expression. Thus we also have that κ_0 and κ_A are identically equal to each other, and we can write Equations (3.93) and (3.94) all in terms of κ_A, which is preferable to κ_0 since I_A is an experimentally determined quantity.

$$\begin{aligned} c_i^o(0) = c_i^A \Bigg\{ 1 - \frac{z_i F\sigma}{\varepsilon\kappa_A RT}\Bigg[\frac{\sigma_A}{\sigma} + \frac{\varepsilon\kappa_A\phi_A}{\sigma} - \frac{2}{\kappa_A a f^2(0)} \\ + \frac{1}{f(0)I_1[\kappa_A a f(0)]}\Bigg]\Bigg\} \end{aligned} \tag{3.97}$$

and

$$\begin{aligned} c_i^o(L) = c_i^B \Bigg\{ 1 - \frac{z_i F\sigma}{\varepsilon\kappa_A RT}\Bigg[\frac{\sigma_B}{S\sigma} + \frac{\varepsilon\kappa_A\phi_B}{\sigma} - \frac{2}{\kappa_A a f^2(L)} \\ + \frac{1}{f(L)I_1[\kappa_A a f(L)]}\Bigg]\Bigg\} \quad . \end{aligned} \tag{3.98}$$

From Equation (3.53) we can now write the boundary conditions:

$$\begin{aligned} \psi_1(0) = -\frac{F}{\varepsilon\kappa_A^2}\Sigma c_i^A z_i + \frac{F^2\sigma}{\varepsilon^2\kappa_A^3 RT}\Bigg[\frac{\sigma_A}{\sigma} + \frac{\varepsilon\kappa_A\phi_B}{\sigma} \\ - \frac{2}{\kappa_A a f^2(0)} + \frac{1}{f(0)I_1[\kappa_A a f(0)]}\Bigg] \Sigma c_i^A z_i^2 \\ - \frac{\sigma}{\varepsilon\kappa_A f(0)I_1[\kappa_A a f(0)]} \end{aligned} \tag{3.99}$$

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$$\psi_1(L) = -\frac{F}{\varepsilon\kappa_A^2}\Sigma c_i^B z_i + \frac{F^2\sigma}{\varepsilon^2\kappa_A^3 RT}\left[\frac{\sigma_B}{S\sigma} + \frac{\varepsilon\kappa_A\phi_B}{\sigma} - \frac{2}{\kappa_A a f^2(L)} + \frac{1}{f(L)I_1[\kappa_A a f(L)]}\right]\Sigma c_i^B z_i^2 - \frac{\sigma}{\varepsilon\kappa_A f(L) I_1[\kappa_A a f(L)]}\ , \qquad (3.100)$$

or

$$\psi_1(0) = \frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_A}{\sigma} + \frac{\varepsilon\kappa_A\phi_A}{\sigma} - \frac{2}{\kappa_A a f^2(0)}\right] \qquad (3.101)$$

and

$$\psi_1(L) = \frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_B}{S\sigma} + \frac{\varepsilon\kappa_A\phi_B}{\sigma} - \frac{2}{\kappa_A a f^2(L)}\right]\ . \qquad (3.102)$$

At last, we have obtained explicit expressions for the boundary conditions that are stated only formally in Equations (3.9), (3.23), and (3.28). With the appropriate form of f(z), they can be substituted into each of these three equations for the complete solution of $\psi_1(z)$ for the different ionic strength distribution models.

E. An Alternate Set of Boundary Conditions

The boundary conditions given in Equations (3.101) and (3.102) are not an entirely happy formulation since they contain the bulk potentials ϕ_A and ϕ_B which are not individually accessible. Only their difference can be determined. We now look at an alternate formulation of boundary conditions that do not include these potentials.

Previously, we applied a mass balance in order to obtain boundary conditions; this time we apply a charge balance. In our discussion of the boundary conditions at the membrane faces, we stated that the net surface charges σ_A and σ_B on the "solid" part of the membrane primarily determine the potentials $\phi_A(z)$ and $\phi_B(z)$. If we assume that Equations (3.75) and (3.77) describe these potentials near the pore openings as well as near the "solid" membrane faces, then we can write the following charge balances at the openings:

$$\varepsilon \frac{d\phi_A(0)}{dz} = \varepsilon \left[\frac{d\psi_1(0)}{dz} + \left\langle \frac{\partial\psi_2(0,r)}{\partial z} \right\rangle_r \right] \tag{3.103}$$

and

$$\varepsilon \frac{d\phi_B(L)}{dz} = \varepsilon \left[\frac{d\psi_1(L)}{dz} + \left\langle \frac{\partial\psi_2(L,r)}{\partial z} \right\rangle_r \right] . \tag{3.104}$$

These equations correspond to that given by Levine [91] in his treatment of the potential distribution across an interface of two immiscible liquids. Although the physical nature of our problem is different from his, the two are analogous in that a charge balance is appropriate at each interface. Since in our case $\psi_2(z,r)$ varies radially, it must be averaged over the mouth of the pore.

Thus, taking the z-derivative of $\psi_2(z,r)$ given in Equation (3.7), we have

$$\frac{\partial\psi_2(z,r)}{\partial z} = \frac{\sigma f'(z)}{\varepsilon f(z)}\left\{\frac{rI_1[\kappa_A rf(z)]}{I_1[\kappa_A af(z)]} - \frac{aI_0[\kappa_A af(z)]I_0[\kappa_A rf(z)]}{I_1^2[\kappa_A af(z)]}\right\}. \tag{3.105}$$

The average, defined by Equation (3.83), yields

$$\left\langle\frac{\partial\psi_2(z,r)}{\partial z}\right\rangle_r = -\frac{4\sigma f'(z)}{\varepsilon\kappa_A^2 af^3(z)}\ , \tag{3.106}$$

and therefore

$$\frac{d\psi_1(0)}{dz} = \frac{\sigma}{\varepsilon}\left[\frac{\sigma_A}{\sigma} + \frac{4f'(0)}{\kappa_A^2 af^3(0)}\right] \tag{3.107}$$

and

$$\frac{d\psi_1(L)}{dz} = -\frac{\sigma}{\varepsilon}\left[\frac{\sigma_B}{\sigma} - \frac{4f'(L)}{\kappa_A^2 a f^3(L)}\right] \quad . \qquad (3.108)$$

We return first to Equation (3.8). In order to apply these boundary conditions to this solution, we differentiate with respect to z:

$$\frac{d\psi_1(z)}{dz} = k_1\kappa_A \sinh\kappa_A z + k_2\kappa_A \cosh\kappa_A z \quad . \qquad (3.109)$$

For the case that $f(z) = 1$, $f'(z) = 0$, so that the final result is

$$\psi_1(z) = -\frac{1}{\varepsilon\kappa_A}[\sigma_B \cosh\kappa_A z + \sigma_A \cosh\kappa_A(L-z)]\operatorname{csch}\kappa_A L. \quad . \qquad (3.110)$$

Differentiating Equation (3.20) with respect to ζ, we obtain

$$\frac{d\psi_1(\zeta)}{d\zeta} = 3\alpha\zeta^3[k_1 I_{-2/3}(\alpha\zeta^3) + k_2 I_{2/3}(\alpha\zeta^3)] \quad . \qquad (3.111)$$

Since $\zeta = 1$ at $z = 0$ and $\zeta = S$ at $z = L$, the result of applying the boundary conditions with $f(z) = [1+(S^2 - 1)\ (z/L)]^{1/2}$ is

$$\psi_1(\zeta) = \frac{\frac{d\psi_1(1)}{d\zeta}\zeta[I_{2/3}(\alpha S^3)I_{1/3}(\alpha\zeta^3)-I_{-2/3}(\alpha S^3)I_{-1/3}(\alpha\zeta^3)]}{3\alpha[I_{2/3}(\alpha S^3)I_{-2/3}(\alpha) - I_{2/3}(\alpha)I_{-2/3}(\alpha S^3)}$$

$$- \frac{\frac{d\psi_1(S)}{d\zeta}\zeta[I_{2/3}(\alpha)I_{1/3}(\alpha\zeta^3)-I_{-2/3}(\alpha)I_{-1/3}(\alpha\zeta^3)]}{3\alpha S^3[I_{2/3}(\alpha S^3)I_{-2/3}(\alpha)-I_{2/3}(\alpha)I_{-2/3}(\alpha S^3)]} . \tag{3.112}$$

To obtain the explicit result in terms of the boundary conditions, we need the following relations:

$$\frac{d\psi_1(1)}{d\zeta} = \frac{2L}{S^2-1} \; \frac{d\psi_1(0)}{dz} \tag{3.113}$$

and

$$\frac{d\psi_1(S)}{d\zeta} = \frac{2SL}{S^2-1} \; \frac{d\psi_1(L)}{dz} . \tag{3.114}$$

Thus the complete solution is

$$\psi_1(\zeta) = \frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_A}{\sigma} + \frac{2(S^2-1)}{\kappa_A^2 aL}\right] \times$$

$$- \; \zeta \, \frac{I_{2/3}(\alpha S^3)I_{1/3}(\alpha\zeta^3)-I_{-2/3}(\alpha S^3)I_{-1/3}(\alpha\zeta^3)}{I_{2/3}(\alpha S^3)I_{-2/3}(\alpha)-I_{2/3}(\alpha)I_{-2/3}(\alpha S^3)}$$

$$+ \frac{\sigma}{\varepsilon\kappa_A S^2}\left[\frac{\sigma_B}{\sigma} - \frac{2(S^2-1)}{\kappa_A^2 aLS^4}\right] \times$$

$$\zeta\, \frac{I_{2/3}(\alpha)I_{1/3}(\alpha\zeta^3)-I_{-2/3}(\alpha)I_{-1/3}(\alpha\zeta^3)}{I_{2/3}(\alpha S^3)I_{-2/3}(\alpha)-I_{2/3}(\alpha)I_{-2/3}(\alpha S^3)} \quad . \qquad (3.115)$$

In the final case we have from Equation (3.27) that

$$\frac{d\psi_1(\xi)}{d\xi} = k_1 I_1(\xi) - k_2 K_1(\xi) \quad . \qquad (3.116)$$

Similarly, $\xi = \tau$ at $z = 0$ and $\xi = \tau S$ at $z = L$, and the result with $f(z) = S^{z/L}$ is

$$\psi_1(\xi) = \frac{\frac{d\psi_1(\tau)}{d\xi}[K_1(\tau S)I_0(\xi)+I_1(\tau S)K_0(\xi)]}{I_1(\tau)K_1(\tau S)-I_1(\tau S)K_1(\tau)}$$

$$- \frac{\frac{d\psi_1(\tau S)}{d\xi}[K_1(\tau)I_0(\xi)+I_1(\tau)K_0(\xi)]}{I_1(\tau)K_1(\tau S)-I_1(\tau S)K_1(\tau)}. \qquad (3.117)$$

Again, the relationships between the corresponding boundary conditions are

$$\frac{d\psi_1(\tau)}{d\xi} = \frac{1}{\kappa_A}\frac{d\psi_1(0)}{dz} \tag{3.118}$$

and

$$\frac{d\psi_1(\tau S)}{d\xi} = \frac{1}{\kappa_A S}\frac{d\psi_1(L)}{dz} \quad , \tag{3.119}$$

and the complete solution is

$$\psi_1(z) = \frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_A}{\sigma} + \frac{4\ell nS}{\kappa_A^2 aL}\right]\frac{K_1(\tau S)I_0(\tau S^{z/L})+I_1(\tau S)K_0(\tau S^{z/L})}{I_1(\tau)K_1(\tau S)-I_1(\tau S)K_1(\tau)}$$

$$+\frac{\sigma}{\varepsilon\kappa_A S}\left[\frac{\sigma_B}{\sigma} - \frac{4\ell nS}{\kappa_A^2 aLS^2}\right]\frac{K_1(\tau)I_0(\tau S^{z/L})+I_1(\tau)K_0(\tau S^{z/L})}{I_1(\tau)K_1(\tau S)-I_1(\tau S)K_1(\tau)} \quad . \tag{3.120}$$

F. Final Membrane Potential Formulae

Not only does the charge balance yield $d\psi_1(0)/dz$ and $d\psi_1(L)/dz$, Equations (3.107) and (3.108), with much less effort than was required to obtain $\psi_1(0)$ and $\psi_1(L)$, Equations (3.99) and (3.100), from a mass balance, but the lack of ϕ_A and ϕ_B in the results of this second formulation also enables us to write an equation for the total membrane potential E_M. With our symbols in the expression given by Morf [115], we have

$$E_M = \phi_B - \phi_A = [\phi_A(0) - \phi_A] - [\phi_B(L) - \phi_B]$$

$$+ [\psi_1(L) - \psi_1(0)] + [\langle\psi_2(L,r)\rangle_r - \langle\psi_2(0,r)\rangle_r] \,, \tag{3.121}$$

where the first two differences in brackets represent the total boundary potential difference, and the last two differences in brackets represent the diffusion potential.

We can now write down the total membrane potential for each of the three ionic strength distribution models. Substituting Equations (3.75), (3.76), (3.89), and either (3.110), (3.115), or (3.120) in the above, we obtain for $f(z) = 1$:

$$E_M = \frac{\sigma_A - \sigma_B}{\varepsilon\kappa_A} + \frac{\sigma_A - \sigma_B}{\varepsilon\kappa_A}(\cosh\kappa_A L - 1)\operatorname{csch}\kappa_A L \,, \tag{3.122}$$

which is identically zero for $\sigma_A = \sigma_B$; for $f(z) = [1 + (S^2-1)(z/L)]^{1/2}$:

$$E_M = \frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_A}{\sigma} - \frac{\sigma_B}{S\sigma}\right] - \frac{2\sigma}{\varepsilon\kappa_A^2 a}\left[\frac{S^2-1}{S^2}\right]$$

$$+ \frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_A}{\sigma} + \frac{2(S^2-1)}{\kappa_A^2 aL}\right] \times$$

$$\frac{I_{2/3}(\alpha S^3)[SI_{1/3}(\alpha S^3)-I_{1/3}(\alpha)]-I_{-2/3}(\alpha S^3)[SI_{-1/3}(\alpha S^3)-I_{-1/3}(\alpha)]}{I_{2/3}(\alpha S^3)I_{-2/3}(\alpha)-I_{2/3}(\alpha)I_{-2/3}(\alpha S^3)}$$

$$+\frac{\sigma}{\varepsilon\kappa_A S^2}\left[\frac{\sigma_B}{\sigma}-\frac{2(S^2-1)}{\kappa_A^2 aLS^4}\right]\times$$

$$\frac{I_{2/3}(\alpha)[SI_{1/3}(\alpha S^3)-I_{1/3}(\alpha)]-I_{-2/3}(\alpha)[SI_{-1/3}(\alpha S^3)-I_{-1/3}(\alpha)]}{I_{2/3}(\alpha S^3)I_{-2/3}(\alpha)-I_{2/3}(\alpha)I_{-2/3}(\alpha S^3)} \tag{3.123}$$

and for $f(z) = S^{z/L}$:

$$E_M = \frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_A}{\sigma}-\frac{\sigma_B}{S\sigma}\right]-\frac{2\sigma}{\varepsilon\kappa_A^2 a}\left[\frac{S^2-1}{S^2}\right]$$

$$+\frac{\sigma}{\varepsilon\kappa_A}\left[\frac{\sigma_A}{\sigma}+\frac{4\ell nS}{\kappa_A^2 aL}\right]\times$$

$$\frac{K_1(\tau S)[I_0(\tau S)-I_0(\tau)]+I_1(\tau S)[K_0(\tau S)-K_0(\tau)]}{I_1(\tau)K_1(\tau S)-I_1(\tau S)K_1(\tau)}$$

$$+\frac{\sigma}{\varepsilon\kappa_A S}\left[\frac{\sigma_B}{\sigma}-\frac{4\ell nS}{\kappa_A^2 aLS^2}\right]\times$$

$$\frac{K_1(\tau)[I_0(\tau S)-I_0(\tau)]+I_1(\tau)[K_0(\tau S)-K_0(\tau)]}{I_1(\tau)K_1(\tau S)-I_1(\tau S)K_1(\tau)}\;. \tag{3.124}$$

G. Numerical Calculations

We now calculate values for $\psi_1(z)$, $\langle\psi_2(z,r)\rangle_r$, and E_M with the equations that we have derived. We choose two sets of conditions: (1) $I_A = 0.01$ M with $S^2 = 10$, and (2) $I_A = 0.5$ M with $S^2 = 4$. There are also a number of parameters in these equations for which we must obtain tabulated values or estimates. Probably the most problematic parameter is surface charge density. Since we are ultimately interested in models that simulate biological systems, we choose a value of σ that corresponds to the electrokinetic charge of the red blood cell. Its value was calculated to be in the range from 3.6×10^{-3} C/m^2 to 12.3×10^{-3} C/m^2 [31], and therefore we choose 8.0×10^{-3} C/m^2 as a typical value. For the purpose of these calculations, we assume that σ_A and σ_B are also equal to this same value of σ.

From an analysis of the osmotic data of Grim and Sollner [54], Lee [88] estimated the pore radius of their oxyhemoglobin collodion membranes to be of the order of 10^{-8} m, along with a thickness of 1×10^{-4} m. Lee also used the value of the absolute permittivity of water at 25°C, 7×10^{-10} C/Vm, as an approximate value for electrolyte solutions. We do likewise.

The inverse Debye lengths for the two different concentrations chosen are calculated from Equation (2.2), α from Equation (3.12), and τ from Equation (3.25). The values of these and all other necessary parameters are tabulated in

Table 3.1. Values of Parameters Needed in Calculations.

$\sigma = 8.0 \times 10^{-3}$ C/m^2	$\varepsilon = 7 \times 10^{-10}$ C/V m
$a = 1 \times 10^{-8}$ m	$L = 1 \times 10^{-4}$ m
$R = 8.314$ J/K mole	$F = 96{,}500$ C/mole
$T = 298$ K	
$I_A = 0.01$ M:	$I_A = 0.50$ M:
$S^2 = 10$	$S^2 = 4$
$\kappa_A = 3.277 \times 10^8$ m^{-1}	$\kappa_A = 2.317 \times 10^9$ m^{-1}
$\alpha = 2.427 \times 10^3$	$\alpha = 5.149 \times 10^4$
$\tau = 2.846 \times 10^4$	$\tau = 3.343 \times 10^5$

We look first at the equation derived for $\psi_1(z)$ in the case of no concentration gradient. Replacing the hyperbolic functions of Equation (3.110) with exponentials, we obtain the approximate form

$$\psi_1(z) = -\frac{\sigma}{\varepsilon\kappa_A}\left[e^{-\kappa_A z} + e^{-\kappa_A (L-z)}\right] \quad . \qquad (3.125)$$

The values calculated from this equation for the two different concentrations are tabulated in Table 3.2. For each concentration, $\psi_1(z)$ is tabulated in two ways, both as the

Table 3.2. Calculated Values of $\psi_1(z)$ for Constant Concentration.

		I_A = 0.01 M		I_A = 0.50 M	
		$\psi_1(z)$		$\psi_1(z)$	
z(m)	z/L	$(\sigma/\varepsilon\kappa_A)$	(V x 10^3)	$(\sigma/\varepsilon\kappa_A)$	(V x 10^3)
0	0	-1.0000	-34.88	-1.0000	-4.93
1 x 10^{-11}	0.0000001	-0.9967	-34.76	-0.9771	-4.82
5 x 10^{-11}	0.0000005	-0.9838	-34.31	-0.8906	-4.39
1 x 10^{-10}	0.000001	-0.9678	-33.76	-0.7932	-3.91
5 x 10^{-10}	0.000005	-0.8489	-29.61	-0.3140	-1.55
1 x 10^{-9}	0.00001	-0.7206	-25.13	-0.0986	-0.49
5 x 10^{-9}	0.00005	-0.1943	- 6.78	-9.31 x 10^{-6}	0.00
1 x 10^{-8}	0.0001	-0.0378	- 1.32	-8.67 x 10^{-11}	0.00
5 x 10^{-8}	0.0005	-7.67 x 10^{-8}	0.00	-4.89 x 10^{-51}	0.00
1 x 10^{-7}	0.001	-5.89 x 10^{-15}	0.00	-2.5 x 10^{-101}	0.00

Table 3.2. Continued.

		I_A = 0.01 M		I_A = 0.50 M	
		$\psi_1(z)$		$\psi_1(z)$	
z(m)	z/L	$(\sigma/\epsilon\kappa_A)$	$(V \times 10^3)$	$(\sigma/\epsilon\kappa_A)$	$(V \times 10^3)$
0.999×10^{-4}	0.999	-5.89×10^{-15}	0.00	-2.5×10^{-101}	0.00
0.9995×10^{-4}	0.9995	-7.67×10^{-8}	0.00	-4.89×10^{-51}	0.00
0.9999×10^{-4}	0.9999	-0.0378	-1.32	-8.67×10^{-11}	0.00
0.99995×10^{-4}	0.99995	-0.1943	-6.78	-9.31×10^{-6}	0.00
0.99999×10^{-4}	0.99999	-0.7206	-25.13	-0.0986	-0.49
0.999995×10^{-4}	0.999995	-0.8489	-29.61	-0.3140	-1.55
0.999999×10^{-4}	0.999999	-0.9678	-33.76	-0.7932	-3.91
0.9999995×10^{-4}	0.9999995	-0.9838	-34.31	-0.8906	-4.39
0.9999999×10^{-4}	0.9999999	-0.9967	-34.76	-0.9771	-4.82
1×10^{-4}	1	-1.0000	-34.88	-1.0000	-4.93

fraction of $\sigma/\epsilon\kappa_A$ (which has the units of volts) and as the numerical value in V x 10^3 (i.e., as millivolts). Because $\psi_1(z)$ rapidly decreases inside the cylinder, only the values very close to the ends are tabulated.

For the model with I(z) linear in z, the modified Bessel functions of negative order in Equation (2.115) are rewritten in terms of ones of positive order from Equation (3.22), and these are approximated by the asymptotic expressions for large argument [2]. The resulting equation is

$$\psi_1(\zeta) = -\frac{\sigma}{\epsilon\kappa_A}\left[\frac{1}{\zeta}\, e^{-\alpha(\zeta^3-1)} + \frac{1}{S^{1/2}\zeta^{1/2}}\, e^{-\alpha(S^3-\zeta^3)}\right], \tag{3.126}$$

and the calculations based on it are tabulated in Table 3.3.

Finally for the model with ℓn I(z) linear in z, Equation (3.120) is also simplified with the asymptotic approximations for the Bessel functions, the result being

$$\psi_1(z) = -\frac{\sigma}{\epsilon\kappa_A}\left[\frac{1}{S^{z/2L}}\, e^{-\tau(S^{z/L}-1)} + \frac{1}{S^{1/2}S^{z/2L}}\, e^{-\tau(S-S^{z/L})}\right]. \tag{3.127}$$

Table 3.3. Calculated Values of $\psi_1(z)$ for $I(z)$ Linear in z.

	$I_A = 0.01$ M			$I_A = 0.50$ M		
		$\psi_1(z)$			$\psi_1(z)$	
z/L	ζ	$(\sigma/\varepsilon\kappa_A)$	$(V \times 10^3)$	ζ	$(\sigma/\varepsilon\kappa_A)$	$(V \times 10^3)$
0	1	-1.0000	-34.88	1	-1.0000	-4.93
0.0000001	1.000000450	-0.9967	-34.76	1.000000150	-0.9771	-4.82
0.0000005	1.000002250	-0.9837	-34.31	1.000000750	-0.8906	-4.39
0.000001	1.000004500	-0.9678	-33.76	1.000001500	-0.7932	-3.91
0.000005	1.000022500	-0.8488	-29.61	1.000007500	-0.3139	-1.55
0.00001	1.000044999	-0.7205	-25.13	1.000015000	-0.0985	-0.49
0.00005	1.000224975	-0.1942	- 6.77	1.000074997	-9.29×10^{-6}	0.00
0.0001	1.000449899	-0.0377	- 1.31	1.000149989	-8.62×10^{-11}	0.00
0.0005	1.002247474	-7.50×10^{-8}	0.00	1.000749719	-4.61×10^{-51}	0.00
0.001	1.004489920	-5.42×10^{-15}	0.00	1.001498877	-2.0×10^{-101}	0.00

Table 3.3. Continued.

	I_A = 0.01 M			I_A = 0.50 M		
		$\psi_1(z)$			$\psi_1(z)$	
z/L	ζ	$(\sigma/\varepsilon\kappa_A)$	(V x 10^3)	ζ	$(\sigma/\varepsilon\kappa_A)$	(V x 10^3)
0.999	3.160854315	-3.20×10^{-46}	0.00	1.999249859	-3.2×10^{-202}	0.00
0.9995	3.161566068	-1.00×10^{-23}	0.00	1.999624965	-1.2×10^{-101}	0.00
0.9999	3.162135354	-9.99×10^{-6}	0.00	1.999924999	-3.74×10^{-21}	0.00
0.99995	3.162206508	-1.78×10^{-3}	0.06	1.999962500	-4.32×10^{-11}	0.00
0.99999	3.162263430	-0.1122	-3.91	1.999992500	-4.86×10^{-3}	-0.02
0.999995	3.162270545	-0.1884	-6.57	1.999996250	-0.0493	-0.24
0.999999	3.162276237	-0.2851	-9.94	1.999999250	-0.3146	-1.55
0.9999995	3.162276949	-0.3003	-10.47	1.999999625	-0.3965	-1.96
0.9999999	3.162277518	-0.3130	-10.92	1.999999925	-0.4773	-2.35
1	3.162277660	-0.3162	-11.03	2	-0.5000	-2.47

The calculated values from this equation are presented in Table 3.4.

There are three particularly noteworthy things about these three sets of calculated values for $\psi_1(z)$. That part of $\psi(z,r)$ that depends only on z is essentially zero through 99.99% of the capillary. The precipitous change in $\psi_1(z)$ at each end of the cylinder is obvious in Figure 3.1, which graphically presents the data from Table 3.2 for $I_A = 0.01$, and in Figure 3.2, which presents the analogous data from Tables 3.3 and 3.4. At z/L = 0.0001, i.e., at a distance from the end equal to the radius of the tube, the value of $\psi_1(z)$ diminishes to less than 4% of that at z/L = 0.

Secondly, the change in $\psi_1(z)$ near the end at z = 0 is virtually identical for all three concentration models. Small differences begin to appear at z/L = 0.0005, but by then the value of $\psi_1(z)$ is indistinguishable from zero. In other words, $\psi_1(z)$ diminishes to zero before differences in the concentration models have any effects on it.

And finally, the values for the constant-concentration model are symmetric at the two ends of the capillary, while those for the other two models are not. Although the concentration gradient does not affect $\psi_1(z)$ inside the tube, it shows up in the assymmetry of the values at the two ends (Figure 3.2).

Unlike $\psi_1(z)$, $\psi_2(z,r)$ is nonzero inside the capillary,

Table 3.4. Calculated Values of $\psi_1(z)$ for $\ell n\ I(z)$ Linear in z.

	$I_A = 0.01$ M		$I_A = 0.50$ M	
	$\psi_1(z)$		$\psi_1(z)$	
z/L	$(\sigma/\epsilon\kappa_A)$	(V x 10^3)	$(\sigma/\epsilon\kappa_A)$	(V x 10^3)
0	-1.0000	-34.88	-1.0000	-4.93
0.0000001	-0.9967	-34.76	-0.9772	-4.82
0.0000005	-0.9837	-34.31	-0.8905	-4.39
0.000001	-0.9678	-33.76	-0.7932	-3.91
0.000005	-0.8489	-29.61	-0.3139	-1.55
0.00001	-0.7206	-25.13	-0.986	-0.49
0.00005	-0.1943	- 6.78	-9.29×10^{-6}	0.00
0.0001	-0.0377	- 1.31	-8.63×10^{-11}	0.00
0.0005	-7.62×10^{-8}	0.00	-4.72×10^{-51}	0.00
0.001	-5.75×10^{-15}	0.00	-2.2×10^{-101}	0.00

Table 3.4. Continued.

	I_A = 0.01 M		I_A = 0.50 M	
	$\psi_1(z)$		$\psi_1(z)$	
z/L	$(\sigma/\varepsilon\kappa_A)$	$(V \times 10^3)$	$(\sigma/\varepsilon\kappa_A)$	$(V \times 10^3)$
0.999	-3.32×10^{-46}	0.00	-3.4×10^{-202}	0.00
0.9995	-1.01×10^{-23}	0.00	-1.3×10^{-101}	0.00
0.9999	-9.99×10^{-6}	0.00	-3.74×10^{-21}	0.00
0.99995	-1.78×10^{-3}	-0.06	-4.32×10^{-11}	-0.00
0.99999	-0.1122	-3.91	-4.86×10^{-3}	-0.02
0.999995	-0.1884	-6.57	-0.0493	-0.24
0.999999	-0.2851	-9.994	-0.3146	-1.55
0.9999995	-0.3003	-10.47	-0.3966	-1.96
0.9999999	-0.3130	-10.92	-0.4773	-2.35
1	-0.3162	-11.03	-0.5000	-2.47

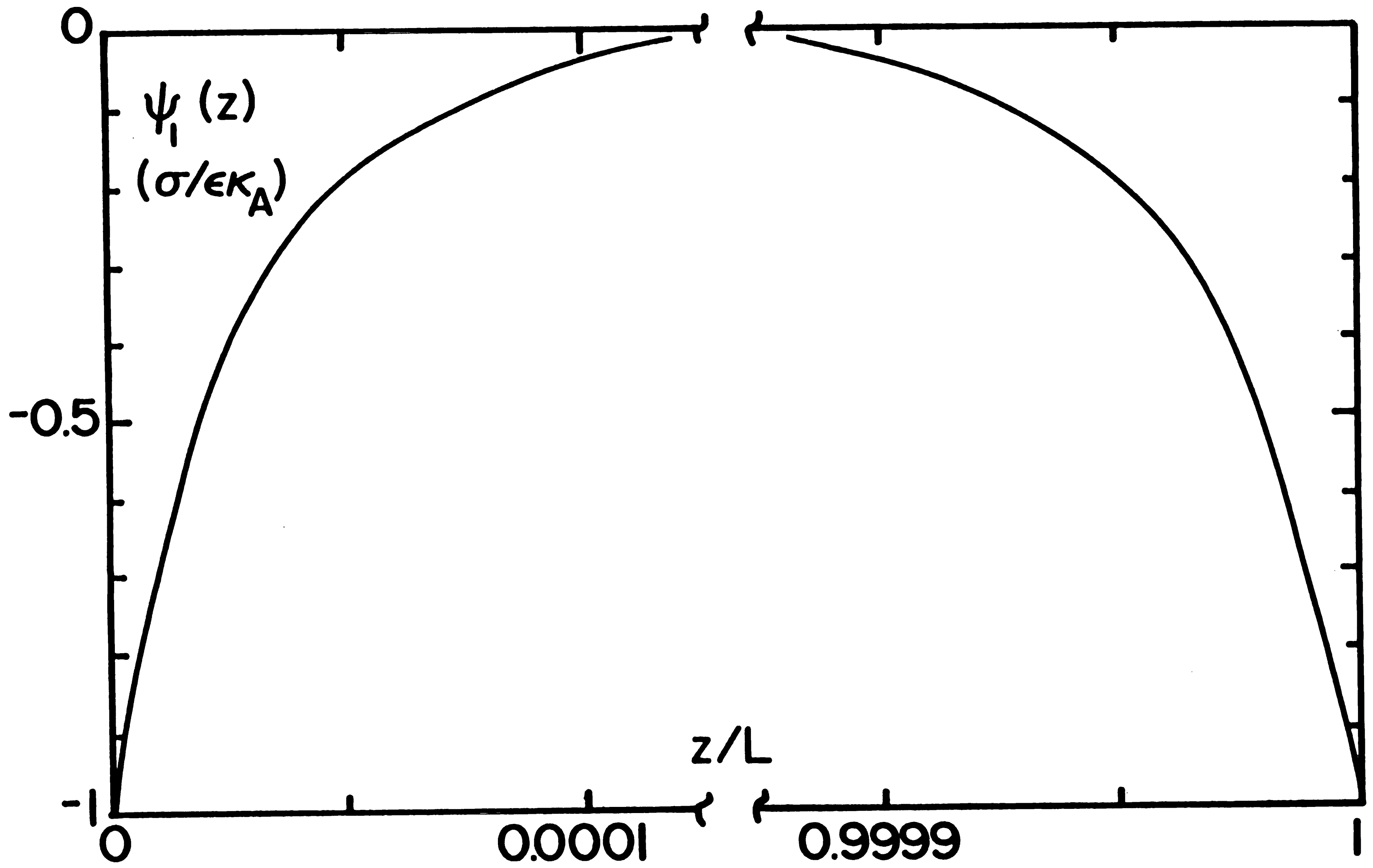

Figure 3.1. $\psi_1(z)$ at each end of the pore for constant ionic strength.

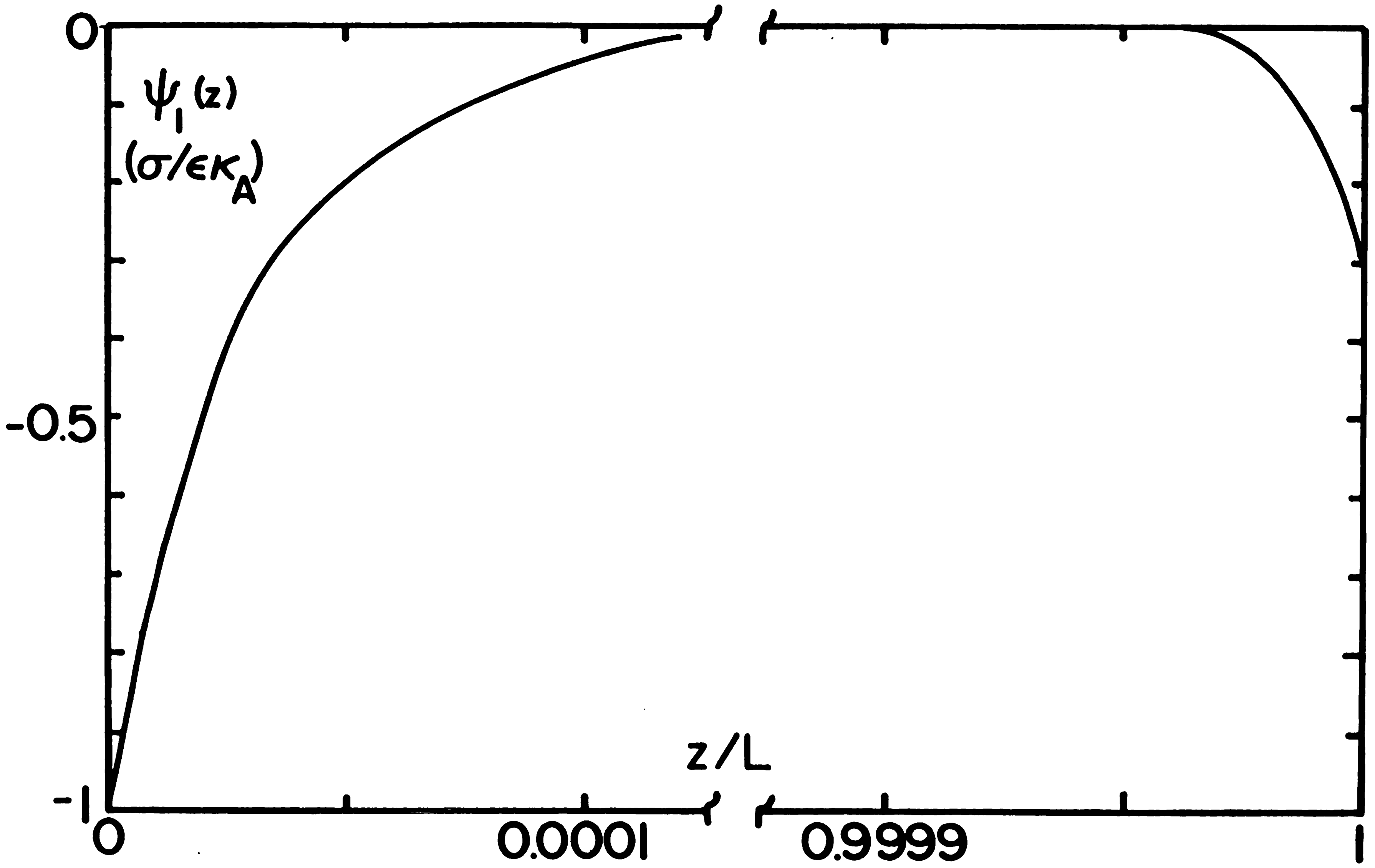

Figure 3.2. $\psi_1(z)$ at each end of the pore for both ionic strength models.

and its profile differs for the two models involving concentration gradients. We calculate $\psi_2(z,r)$ from Equation (3.89), which provides values averaged over r.

For the constant-concentration model,

$$\langle\psi_2(z,r)\rangle_r = \frac{2\sigma}{\varepsilon\kappa_A^2 a} , \tag{3.128}$$

there is obviously no concentration dependence in the z-direction, and the calculated values are 17.4×10^{-3} V for $I_A = 0.01$ M and 2.47×10^{-3} V for $I_A = 0.50$ M.

For the models with I(z) linear in z and ℓn I(z) linear in z, the expressions are

$$\langle\psi_2(z,r)\rangle_r = \frac{2\sigma}{\varepsilon\kappa_A^2[1+(S^2-1)(z/L)]} \tag{3.129}$$

and

$$\langle\psi_2(z,r)\rangle_r = \frac{2\sigma}{\varepsilon\kappa_A^2 S^{2z/L}} \tag{3.130}$$

respectively. The values calculated from Equation (3.129) are presented in Table 3.5; those calculated from Equation (3.130) are presented in Table 3.6. The values for both models are presented graphically in Figure 3.3.

Of course neither $\psi_1(z)$ nor $\psi_2(z,r)$ is experimentally available, and so we look at expressions and values for E_M, the measurable potential difference. Substituting

Table 3.5. Calculated Values of $\langle \psi_2(z,r) \rangle_r$ for I(z) Linear in z.

	I_A = 0.01 M			I_A = 0.50 M		
		$\langle \psi_2(z,r) \rangle_r$			$\langle \psi_2(z,r) \rangle_r$	
z/L	ζ^2	$(\sigma/\varepsilon\kappa_A)$	(V x 10^3)	ζ^2	$(\sigma/\varepsilon\kappa_A)$	(V x 10^3)
0	1	0.6104	21.29	1	0.08632	0.426
0.10	1.90	0.3213	11.21	1.30	0.06640	0.328
0.20	2.80	0.2180	7.60	1.60	0.05395	0.266
0.25	3.25	0.1878	6.55	1.75	0.04933	0.243
0.30	3.70	0.1650	5.75	1.90	0.04543	0.224
0.40	4.60	0.1327	4.63	2.20	0.03924	0.194
0.50	5.50	0.1110	3.87	2.50	0.03453	0.170
0.60	6.40	0.09537	3.33	2.80	0.03083	0.152
0.70	7.30	0.08362	2.92	3.10	0.02785	0.137
0.75	7.75	0.07876	2.75	3.25	0.02656	0.131
0.80	8.20	0.07444	2.60	3.40	0.02539	0.125
0.90	9.10	0.06708	2.34	3.70	0.02333	0.115
1	10.00	0.06104	2.13	4.00	0.02158	0.106

Table 3.6. Calculated Values of $\langle \psi_2(z,r) \rangle_r$ for $\ell n\ I(z)$ Linear in z.

	$I_A = 0.01$ M			$I_A = 0.50$ M		
		$\langle \psi_2(z,r) \rangle_r$			$\langle \psi_2(z,r) \rangle_r$	
z/L	$S^{2z/L}$	$(\sigma/\varepsilon\kappa_A)$	$(V \times 10^3)$	$S^{2z/L}$	$(\sigma/\varepsilon\kappa_A)$	$(V \times 10^3)$
0	1	0.6104	21.29	1	0.08632	0.426
0.1	1.259	0.4849	16.91	1.149	0.07515	0.371
0.2	1.585	0.3851	13.43	1.320	0.06542	0.323
0.25	1.778	0.3432	11.97	1.414	0.06104	0.301
0.3	1.995	0.3059	10.67	1.516	0.05695	0.281
0.4	2.512	0.2430	8.48	1.741	0.04958	0.245
0.5	3.162	0.1930	6.73	2.000	0.04316	0.213
0.6	3.981	0.1533	5.35	2.297	0.03757	0.185
0.7	5.012	0.1218	4.25	2.639	0.03271	0.161
0.75	5.623	0.1085	3.79	2.828	0.03052	0.151
0.8	6.310	0.09674	3.37	3.031	0.02848	0.140
0.9	7.943	0.07684	2.68	3.482	0.02479	0.122
1	10.000	0.06104	2.13	4.000	0.02158	0.106

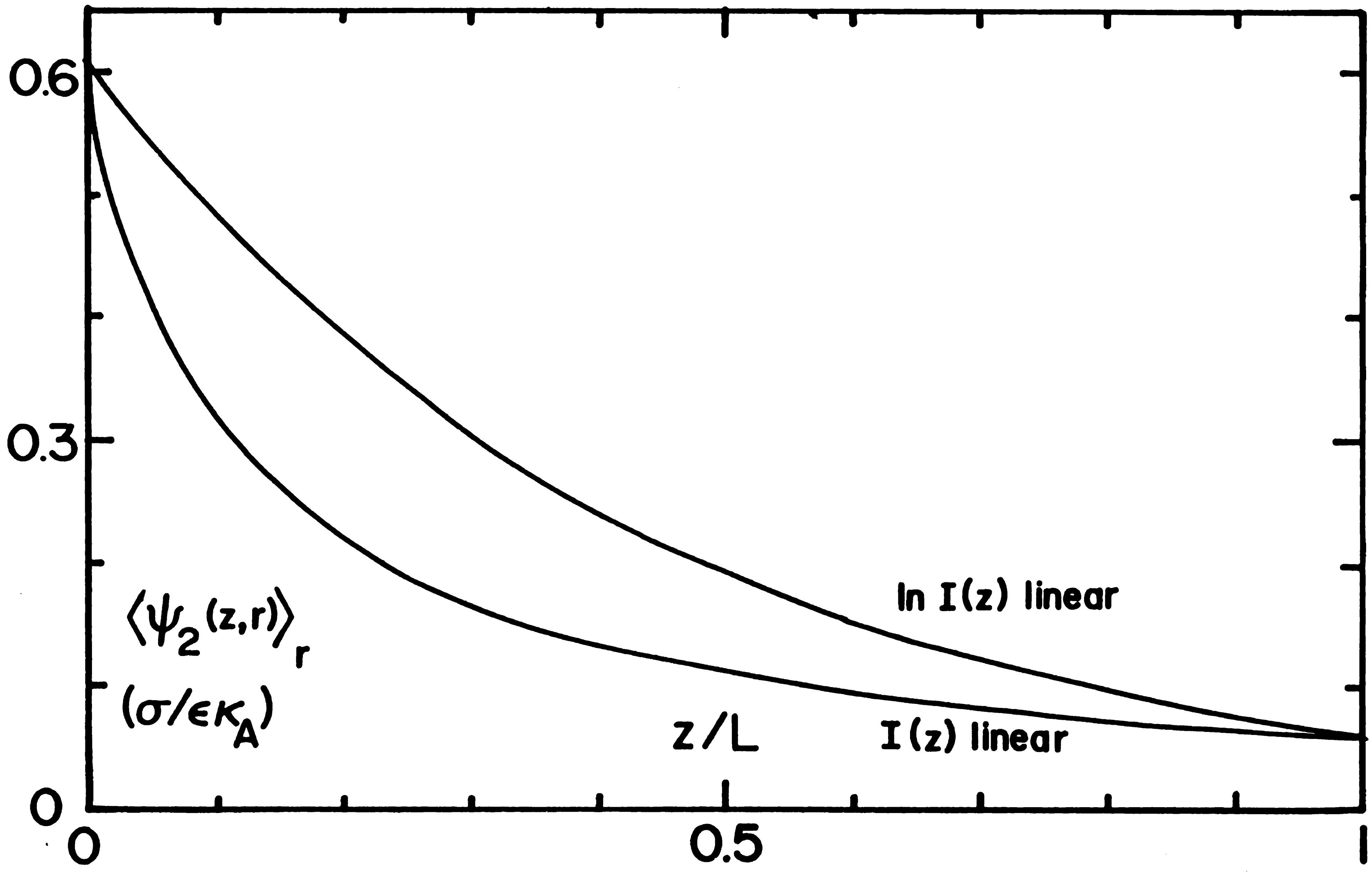

Figure 3.3. $\langle\psi_2(z,r)\rangle_4$ along the pore for the two ionic strength models.

exponentials into Equation (3.122) and retaining only significant terms ($\kappa_A L \sim 10^5$), we obtain

$$E_M = \frac{2(\sigma_A - \sigma_B)}{\varepsilon \kappa_A} \tag{3.131}$$

As we remarked earlier in connection with Equation (3.122), E_M is identically zero when there is no concentration gradient, as long as $\sigma_A = \sigma_B$. However, there can be a potential difference generated across the membrane of a constant-concentration system if $\sigma_A \neq \sigma_B$. Some values of E_M are tabulated in Table 3.7 for several differences in charge density between the two membrane faces.

Applying the asymptotic approximations for the Bessel functions [2] to Equations (3.123) and (3.124), we obtain

$$E_M = \frac{\sigma}{\varepsilon \kappa_A} \left\{ 2\left[1 - \frac{1}{S}\right] - \frac{2(S^2-1)}{\kappa_A a S^2} + \frac{2(S^2-1)}{\kappa_A^2 a L} \left[1 + \frac{1}{S^5}\right] \right\} \tag{3.132}$$

and

$$E_M = \frac{\sigma}{\varepsilon \kappa_A} \left\{ 2\left[1 - \frac{1}{S}\right] - \frac{2(S^2-1)}{\kappa_A a S^2} + \frac{4 \ln S}{\kappa_A^2 a L} \left[1 + \frac{1}{S^3}\right] \right\} , \tag{3.133}$$

where the final term in parentheses in each expression is small, so that the two equations for the membrane potential

Table 3.7. Membrane Potentials of Constant-Concentration Systems.

	$I_A = 0.01$ M	$I_A = 0.50$ M
$\sigma_A - \sigma_B$ ($C/m^2 \times 10^3$)	E_M ($V \times 10^3$)	E_M ($V \times 10^3$)
0.5	4.36	0.617
1.0	8.72	1.23
2.5	21.8	3.08
5.0	43.6	6.17

Table 3.8. Membrane Potentials of Systems with Concentration Gradients, $\sigma_A = \sigma_B = \sigma$.

	$I_A = 0.01$ M	$I_A = 0.50$ M
Ionic Strength Model	E_M ($V \times 10^3$)	E_M ($V \times 10^3$)
I(z) linear	28.5	4.61
ℓn I(z) linear	28.5	4.61

ar

th

v

f

t

are essentially equal to each other. Calculations from these expressions are presented in Table 3.8 (page 76).

In order to determine whether these are reasonable values, we look at some equilibrium potentials calculated for concentration cells. The EMF of such a cell without transference is given by the equation [114]

$$E = \frac{RT}{F} \ell n \frac{a_2}{a_1} , \tag{3.134}$$

where a_1 and a_2 are the ion activities on either side of the cell partition. Replacing the activities with concentrations, which are equal to the ionic strengths, we find the values for $I_A = 0.01$ M and $I_A = 0.50$ M are 59.1×10^{-3} V and 35.6×10^{-3} V respectively.

However, for a concentration cell with transference, which is more similar to the system that we are considering, the EMF is given by

$$E = t_+ \frac{RT}{F} \ell n \frac{a_2}{a_1} , \tag{3.135}$$

where t_+ is the transference number of the cation, in the case that the electrodes are reversible to the anion. Even though such a cell is not reversible, this expression is still a good approximation [87,113,154].

For the salt KCl, for example, t_+ is 0.49 over a wide range of concentrations, and thus the values calculated from Equation (3.135) are 29.0×10^{-3} V and 17.4×10^{-3} V for $I_A = 0.01$ M and $I_A = 0.50$ M, respectively. For the lower ionic strength, this is surprisingly close to the value in Table 3.8, and the larger difference between the values at higher ionic strength is not unexpected since replacing activity by concentration is not as good as for the more dilute system.

H. Summary

In this chapter we have derived expressions for $\psi_1(z)$ and $\psi_2(z,r)$, whose sum gives the total potential $\psi(z,r)$ inside a membrane capillary between two outside solutions. Besides the assumptions implicit in the original linearized Poisson-Boltzmann equation itself, the only other assumptions needed to solve this equation was that the second z-derivative of $\psi_2(z,r)$ is small compared to its second r-derivative. By also solving a one-dimensional Poisson-Boltzmann equation for each interphase region between the face of the membrane and the bulk solution, we were able to obtain boundary conditions on $\psi_1(z)$ both from a mass balance and from a charge balance at each end of the capillary.

Furthermore, the boundary conditions obtained from the charge balance enabled us to derive expressions for the membrane potential, i.e., the potential difference across the entire cell consisting of a membrane separating two electrolyte solutions of different ionic strengths. The values calculated from these expressions are consistent with those from equilibrium thermodynamic theory. Although the agreement is not as good for the values calculated for the higher ionic strength, they are still of the same order of magnitude.

It is now possible to use the expressions that we have derived for $\psi(z,r)$ within the capillary in conjunction with the Navier-Stokes (1.2) and Nernst-Planck (1.1) equations in order to obtain flow equations for steady-state membrane transport. However, since that is another dissertation project in itself, we take a different look at the Poisson-Boltzmann equation in the next chapter.

CHAPTER 4

SOLUTION BY LAPLACE TRANSFORM

A. Introduction

The Laplace transform [66,105,135] of a function f(z), symbolized by $\bar{f}(p)$,

$$L\{f(z)\} = \bar{f}(p) = \int_0^\infty e^{-pz} f(z)\,dz \quad , \qquad (4.1)$$

is sometimes a powerful mathematical tool for solving partial differential equations. Unfortunately, the boundary conditions on the Poisson-Boltzmann equation that we are considering do not lend themselves to a solution by this method. Nevertheless, a purely mathematical treatment devoid of any physical meaning may give us information about the form of the solution.

Thus we consider a semi-infinite cylinder (Figure 4.1) of a radius a, for which we wish to solve the equation

$$\frac{\partial^2\psi}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial\psi}{\partial r} = \kappa_A^2 S^{2z/L} \psi \,. \qquad (4.2)$$

Although we retain the same symbols as in previous chapters,

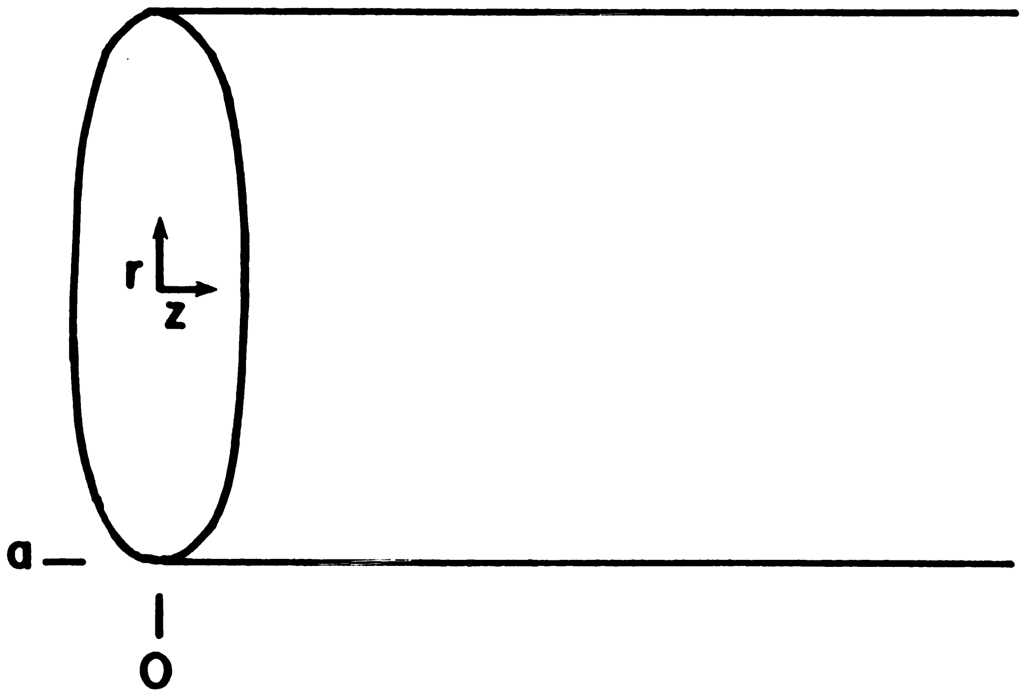

Figure 4.1. Semi-infinite cylinder for the Laplace transform method.

they are intended here to be mathematical quantities without necessarily any physical significance.

The term $S^{2z/L}$, which is equivalent to $\exp[(2z/L)\ell n\ S)]$, introduces additional problems to the Laplace transform method because

$$L\{e^{bz}f(z)\} = \bar{f}(p-b) \quad , \tag{4.3}$$

in which $\bar{f}(p-b)$ represents a linear translation of $\bar{f}(p)$ by b units in the positive p direction. Thus we write the problematic term as a series,

$$S^{2z/L} = 1 + \frac{2z}{L}\ \ell nS + \frac{1}{2!}\left(\frac{2z}{L}\ \ell nS\right)^2 + \frac{1}{3!}\left(\frac{2z}{L}\ \ell nS\right)^3 + \ . \ . \ . \quad , \tag{4.4}$$

and attempt a solution with a perturbation scheme.

B. Perturbation Method

Assuming a solution of the form

$$\psi(z,r) = \psi_0(z,r) + \psi_1(z,r) + \psi_2(z,r) + \ . \ . \ . \ . \ , \tag{4.5}$$

we rewrite Equation (4.2) as

$$\frac{\partial^2}{\partial z^2} (\delta^0\psi_0 + \delta^1\psi_1 + \delta^2\psi_2 + . . .)$$

$$+ \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} (\delta^0\psi_0 + \delta^1\psi_1 + \delta^2\psi_2 + . . .)$$

$$= \kappa_A^2 \left[\delta^0 + \delta^1 \frac{2z}{L} \ell n S + \delta^2 \frac{1}{2!} (\frac{2z}{L} \ell n S)^2 + . . .\right] \times$$

$$(\delta^0\psi_0 + \delta^1\psi_1 + \delta^2\psi_2 + . . .) \quad , \qquad (4.6)$$

where δ is merely a bookkeeping symbol. This can be written as separate equations:

$$\frac{\partial^2\psi_0}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial\psi_0}{\partial r} = \kappa_A^2\psi_0 \quad , \qquad (4.7)$$

$$\frac{\partial^2\psi_1}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial\psi_1}{\partial r} = \kappa_A^2 (\psi_1 + \psi_0 \frac{2z}{L} \ell n S) \quad , \qquad (4.8)$$

$$\frac{\partial^2\psi_2}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial\psi_2}{\partial r} = \kappa_A^2 \left[\psi_2 + \psi_1 \frac{2z}{L} \ell n S\right.$$

$$\left. + \psi_0 \frac{1}{2!} (\frac{2z}{L} \ell n S)^2\right] \quad , \qquad (4.9)$$

etc.

C. Zeroth-Order Solution

The Laplace transform is more easily applied to the z-coordinate than the r-coordinate because of the forms of their respective derivatives. Under this transformation, Equation (4.7) becomes

$$\int_0^\infty e^{-pz} \frac{\partial^2 \psi_0}{\partial z^2} dz + \int_0^\infty e^{-pz} \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \psi_0}{\partial r} dz$$

$$= \int_0^\infty e^{-pz} \kappa_A^2 \psi_0 dz \quad . \qquad (4.10)$$

The parameter p is simply a constant in this integration, as is the coordinate r, and thus the derivative and integral in the second term on the left-hand side can be interchanged:

$$\int_0^\infty e^{-pz} \frac{\partial^2 \psi_0}{\partial z^2} dz + \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \int_0^\infty e^{-pz} \psi_0 dz$$

$$= \kappa_A^2 \int_0^\infty e^{-pz} \psi_0 dz \quad . \qquad (4.11)$$

The first integral on the left-hand side can be done by parts, or the result can simply be found in a table of transforms [66]. With the notation that

$$L\{\psi_0(z,r)\} = \overline{\psi}_0(p,r) \quad , \tag{4.12}$$

Equation (4.11) becomes

$$p^2\,\overline{\psi}_0 - p\psi_0(0,r) - \frac{\partial\psi_0(0,r)}{\partial z} + \frac{1}{r}\frac{d}{dr}\,r\,\frac{d\overline{\psi}_0}{dr} = \kappa_A^2\,\overline{\psi}_0 \ . \tag{4.13}$$

As long as $\psi_0(0,r)$ and $\partial\psi_0(0,r)/\partial z$ are both constants -- it may be necessary to average these functions over the radius of the cylinder or define them at a particular value of r in order to remove their r-dependence -- this equation is now a linear second-order differential equation in only one variable. Rearranging, we get

$$\frac{1}{r}\frac{d}{dr}\,r\,\frac{d\overline{\psi}_0}{dr} + \beta^2\overline{\psi}_0 = p\psi_0(0,r) + \frac{\partial\psi_0(0,r)}{\partial z} \quad , \tag{4.14}$$

where

$$\beta^2 = p^2 - \kappa_A^2 \ . \tag{4.15}$$

If we consider the homogeneous part of this equation, i.e., with the left-hand side set equal to zero,

$$\frac{1}{r}\frac{d}{dr}\,r\,\frac{dy_H}{dr} + \beta^2 y_H = 0 \ , \tag{4.16}$$

we see that this is once again Bessel's equation of order zero, and the homogeneous solution y_H is

$$y_H = k_1 J_0(\beta r) + k_2 Y_0(\beta r) \quad , \tag{4.17}$$

where J_0 and Y_0 are the ordinary Bessel functions of order zero of the first and second kind respectively. By inspection we see that a particular solution of Equation (4.14) is

$$y_P = \frac{p}{\beta^2}\,\psi_0(0,r) + \frac{1}{\beta^2}\,\frac{\partial\psi_0(0,r)}{\partial z} \quad , \tag{4.18}$$

and thus the complete solution is

$$\begin{aligned}\overline{\psi}_0(p,r) = y_H + y_P &= \frac{p}{\beta^2}\,\psi_0(0,r) + \frac{1}{\beta^2}\,\frac{\partial\psi_0(0,r)}{\partial z} \\ &\quad + k_1 J_0(\beta r) + k_2 Y_0(\beta r) \quad .\end{aligned} \tag{4.19}$$

This solution already contains the two boundary conditions in z; the two in r are

$$\frac{\partial\psi(z,0)}{\partial r} = 0 \tag{4.20}$$

and

$$\frac{\partial\psi(z,a)}{\partial r} = \frac{\sigma}{\varepsilon} , \tag{4.21}$$

where σ/ε is merely some constant. Before applying these conditions, we transform them as we did Equation (4.7):

$$\int_0^\infty e^{-pz} \frac{\partial\psi(z,0)}{\partial r} dz = 0 \tag{4.22}$$

and

$$\int_0^\infty e^{-pz} \frac{\partial\psi(z,a)}{\partial r} dz = \int_0^\infty e^{-pz} \frac{\sigma}{\varepsilon} dz , \tag{4.23}$$

or, in the notation of Equation (4.12),

$$\frac{d\bar{\psi}(p,0)}{dr} = 0 \tag{4.24}$$

and

$$\frac{d\bar{\psi}(p,a)}{dr} = \frac{\sigma}{\varepsilon p} . \tag{4.25}$$

We will force $\bar{\psi}_0$ to satisfy these conditions, and thus both of these derivatives will be zero for all other $\bar{\psi}_i$.

Differentiating Equation (4.19) with respect to r, we have

$$\frac{d\bar{\psi}_0}{dr} = -k_1\beta J_1(\beta r) - k_2\beta Y_1(\beta r) \ , \tag{4.26}$$

and it is immediately obvious from the boundary condition in Equation (4.24) that k_2 must be zero since $Y_1(0)$ is undefined. The remaining unknown constant k_2 can be determined from the other boundary condition given in Equation (4.25):

$$k_1 = -\frac{\sigma}{\varepsilon p\beta J_1(\beta a)} \quad . \tag{4.27}$$

Equation (4.19) may now be written as

$$\bar{\psi}_0(p,r) = \frac{p}{\beta^2}\,\psi_0(0,r) + \frac{1}{\beta^2}\,\frac{\partial\psi_0(0,r)}{\partial z} - \frac{\sigma}{\varepsilon}\,\frac{J_0(\beta r)}{p\beta J_1(\beta a)} \ . \tag{4.28}$$

This is the expression that we need to transform back to the original coordinate z in order to obtain the solution $\psi_0(z,r)$ The inverse transforms of the first two terms on the right-hand side may be found in tables [45]:

$$\mathcal{L}^{-1}\left\{\frac{p}{\beta^2}\right\} = \cosh \kappa_A z \tag{4.29}$$

and

$$\mathcal{L}^{-1}\left\{\frac{1}{\beta^2}\right\} = \frac{1}{\kappa_A} \sinh \kappa_A z \quad . \tag{4.30}$$

The inverse of the final term on the right-hand side is not so readily found, and we must turn to the methods of complex integration, since by definition,

$$\mathcal{L}^{-1}\{\overline{f}(p)\} = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} \overline{f}(p)e^{pz}dp \quad . \tag{4.31}$$

This integral can be solved by direct contour integration [105] or indirectly as the sum of residues [66], i.e.,

$$\int \overline{f}(p)e^{pz}dp = 2\pi i \Sigma \mathrm{Res}(p_i) \quad , \tag{4.32}$$

where f(p) has a pole or order m at each point p_i and

$$\mathrm{Res}(p_i) = \frac{1}{(m-1)!}\left\{\frac{d^{m-1}}{dp^{m-1}}\left[(p-p_i)^m \overline{f}(p)e^{pz}\right]\right\}_{p=p_i} \tag{4.33}$$

In our case then,

$$\mathcal{L}^{-1}\left\{\frac{J_0(\beta r)}{p\beta J_1(\beta a)}\right\} = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} \frac{J_0(\beta r)e^{pz}dp}{p\beta J_1(\beta a)} = \sum_i \mathrm{Res}(p_i) \quad . \tag{4.34}$$

It is necessary to find all the singularities of the above function and determine the residue of each. The simple pole at p = 0 is obvious from inspection, and thus

$$\mathrm{Res}(0) = \left\{\frac{J_0(\beta r)e^{pz}}{\beta J_1(\beta a)}\right\}_{p=0} . \tag{4.35}$$

Evaluating this function at p = 0 results in imaginary arguments for the Bessel functions and thus turns them into modified Bessel functions:

$$\mathrm{Res}(0) = \frac{J_0(i\kappa_A r)}{i\kappa_A J_1(i\kappa_A a)} = -\frac{I_0(\kappa_A r)}{\kappa_A I_1(\kappa_A a)} . \tag{4.36}$$

The residues at the other poles at $p = \pm\kappa_A$ are not so easy to evaluate since J_1 also has a singularity at each of these values of p. In fact, because of the oscillatory behavior of the ordinary Bessel functions, J_1 has singularities at each value of p that satisfies the relation

$$(p^2-\kappa_A^2)^{1/2}a = j_{1,s} . \tag{4.37}$$

In order to determine the order of these poles, we first look at the series

$$\frac{J_0(\beta r)}{\beta J_1(\beta a)} = \frac{2}{\beta^2 a}\left[1 - \frac{\beta^2}{2^2 1!2!}(2r^2-a^2) + \ . \ . \ .\right] . \tag{4.38}$$

Thus we see immediately that at $p = \pm\kappa_A$ there are also simple poles. The sum of the residues at these two points is

$$\mathrm{Res}(\kappa_A) + \mathrm{Res}(-\kappa_A) = \frac{2}{\kappa_A^2 a} \cosh \kappa_A z \ . \tag{4.39}$$

Still not obvious, however, is the order of each pole corresponding to a $j_{1,s}$ for $s \geq 1$. For this it is possible to show (with much differentiation) that the functions $[p \pm (j_{1,s}^2 + \kappa_A^2 a^2)^{1/2}(1/a)]/J_1[(p^2 - \kappa_A^2)^{1/2}a]$ are analytic at the points $p = \mp (j_{1,s}^2 + \kappa_A^2 a^2)^{1/2}(1/a)$ respectively; i.e., both the function and its derivative are finite at the particular point. Thus the poles at these points are also simple ones. Applying Equation (4.33) to the complete function in Equation (4.34) and then l'Hospital's rule to determine the limit, we find that the sum of the residues for these two poles is

$$\mathrm{Res}[(j_{1,s}^2 + \kappa_A^2 a^2)^{1/2}(1/a)] + \mathrm{Res}[-(j_{1,s}^2 + \kappa^2{}_A a^2)^{1/2}(1/a)]$$

$$= \frac{2a \cosh[(j_{1,s}^2+\kappa_A^2 a^2)^{1/2}(z/a)]J_0(j_{1,s}r/a)}{(j_{1,s}^2+\kappa_A^2 a^2)J_0(j_{1,s})} \tag{4.40}$$

for $s \geq 1$.

Since the residues at $p = \pm\kappa_A$ can be written as Equation (4.40) for $s = 0$, we combine them all together into one summation. Thus the inverse transform in Equation (4.34) is

$$L^{-1}\left\{\frac{J_0(\beta r)}{p\beta J_1(\beta a)}\right\} = -\frac{I_0(\kappa_A r)}{\kappa_A I_1(\kappa_A a)}$$

$$+ 2a\sum_{s=0}^{\infty}\frac{\cosh[(j_{1,s}^2+\kappa_A^2a^2)^{1/2}(z/a)]}{j_{1,s}^2+\kappa_A^2a^2}\;\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}\;. \tag{4.41}$$

The ultimate goal, the solution $\psi_0(z,r)$ is finally then

$$\psi_0(z,r) = \psi_0(0,r)\cosh\kappa_A z + \frac{\partial\psi_0(0,r)}{\partial z}\frac{1}{\kappa_A}\sinh\kappa_A z$$

$$+ \frac{\sigma}{\epsilon\kappa_A}\left\{\frac{I_0(\kappa_A r)}{I_1(\kappa_A a)}\right.$$

$$\left. -2\kappa_A a\sum_{s=0}^{\infty}\frac{\cosh[(j_{1,s}^2+\kappa_A^2a^2)^{1/2}(z/a)]}{j_{1,s}^2+\kappa_A^2a^2}\;\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}\right\}. \tag{4.42}$$

This is the complete solution of Equation (4.2) for the special case that the right-hand side is equal to $\kappa_A^2\psi$, i.e., without the z-dependent term $S^{2z/L}$. Since we did not assume that the z-derivative is small relative to the r-derivative, this is the exact solution for the equation with no additional assumptions.

D. First-Order Solution

We apply the Laplace transform to Equation (4.8) and obtain

$$\int_0^\infty e^{-pz} \frac{\partial^2 \psi_1}{\partial z^2}\, dz + \int_0^\infty e^{-pz} \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \psi_1}{\partial r}\, dz$$

$$= \kappa_A^2 \int_0^\infty e^{-pz}\, \psi_1 dz + \frac{2\kappa_A^2 \ln S}{L} \int_0^\infty e^{-pz} z\psi_0 dz \ . \qquad (4.43)$$

The only additional transform that we need here is [66]

$$L^{-1}\{zf(z)\} = -\frac{d\bar{f}(p)}{dp} \ , \qquad (4.44)$$

and thus Equation (4.43) becomes

$$p^2\bar{\psi}_1 - p\psi_1(0,r) - \frac{\partial \psi_1(0,r)}{\partial z} + \frac{1}{r}\frac{d}{dr} r \frac{d\bar{\psi}_1}{dr}$$

$$= \kappa_A^2 \bar{\psi}_1 - \frac{2\kappa_A^2 \ln S}{L} \frac{d\bar{\psi}_0}{dp} \ . \qquad (4.45)$$

From Equation (4.28), we find that

$$\frac{d\bar{\psi}_0}{dp} = -\frac{p^2+\kappa_A^2}{\beta^4}\psi_0(0,r) - \frac{2p}{\beta^4}\frac{\partial \psi_0(0,r)}{\partial z}$$

$$+ \frac{\sigma}{\varepsilon}\left[\frac{rJ_1(\beta r)}{\beta^2 J_1(\beta a)} + \frac{J_0(\beta r)}{p^2 \beta J_1(\beta r)} + \frac{aJ_0(\beta a)J_0(\beta r)}{\beta^2 J_1^2(\beta a)}\right] \ . \qquad (4.46)$$

We assume that ψ_0 has satisfied all the boundary conditions so that $\psi_1(0,r) = \partial\psi_1(0,r)/\partial z = 0$, and therefore, Equation (4.45) is

$$\frac{1}{r}\frac{d}{dr}\, r\, \frac{d\bar{\psi}_1}{dr} + \beta^2\bar{\psi}_1 = \frac{2\kappa_A^2 \ell n S}{L}\left[\frac{p^2+\kappa_A^2}{\beta^4}\,\psi_0(0,r)\right.$$

$$+ \frac{2p}{\beta^4}\,\frac{\partial\psi_0(0,r)}{\partial z} - \frac{\sigma}{\varepsilon}\,\frac{rJ_1(\beta r)}{\beta^2 J_1(\beta a)}$$

$$\left. - \frac{\sigma}{\varepsilon}\,\frac{J_0(\beta r)}{p^2\beta J_1(\beta a)} - \frac{\sigma}{\varepsilon}\,\frac{aJ_0(\beta a)J_0(\beta r)}{\beta^2 J_1^2(\beta a)}\right] . \qquad (4.47)$$

Again, the homogeneous solution simply consists of Bessel functions and is identical to the homogeneous solution for ψ_0 in Equation (4.17). It is not so simple as before, however, to find the particular solution, and we resort to a method for reducing the order of an inhomogeneous linear differential equation if one homogeneous solution is known [66].

Writing the solution in the form

$$\bar{\psi}_1 = \omega y_H \qquad (4.48)$$

where ω is also a function only of r, and substituting this into Equation (4.47), we have wh

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or

$$\frac{d}{dr}\,\frac{d\omega}{dr} + \left[\frac{2}{y_H}\,\frac{dy_H}{dr} + \frac{1}{r}\right]\frac{d\omega}{dr}$$

$$+ \left[\frac{d^2y_H}{dr^2} + \frac{1}{r}\,\frac{dy_H}{dr} + \beta^2 y_H\right]\frac{\omega}{y_H} = \frac{h}{y_H}\ , \qquad (4.49)$$

where h represents the entire right-hand side of Equation (4.47). We see that the expression in parentheses is identically zero since it is just the homogeneous equation, and thus we have

$$\frac{d}{dr}\,\frac{d\omega}{dr} + \left[\frac{2}{y_H}\,\frac{dy_H}{dr} + \frac{1}{r}\right]\frac{d\omega}{dr} = \frac{h}{y_H}\quad , \qquad (4.50)$$

which is first order in $d\omega/dr$ with an integrating factor, q,

$$q = \exp\left[\int \frac{1}{r}\,dr\right] = r \quad . \qquad (4.51)$$

Equation (4.50) then becomes

$$\frac{d\omega}{dr} = \frac{1}{ry_H^2}\int r h y_H dr + \frac{k_3}{ry_H^2}\quad , \qquad (4.52)$$

or

$$\frac{d\omega}{dr} = \frac{2\kappa_A^2 \ell n S}{Lry_H^2}\left\{\left[\frac{p^2+\kappa_A^2}{\beta^4}\,\psi_0(0,r)\right.\right.$$

$$+ \frac{2p}{\beta^4} \frac{\partial\psi_0(0,r)}{\partial z}\Bigg] \int r[k_1J_0(\beta r)+k_2Y_0(\beta r)]dr$$

$$- \frac{\sigma}{\varepsilon\beta^2J_1(\beta a)} \int rJ_1(\beta r)[k_1J_0(\beta r)+k_2Y_0(\beta r)]dr$$

$$- \frac{1}{\varepsilon\beta J_1(\beta a)} \left[\frac{1}{p^2} + \frac{aJ_0(\beta a)}{\beta J_1(\beta a)}\right] \int rJ_0(\beta r)[k_1J_0(\beta r)$$

$$+ k_2Y_0(\beta r)]\Bigg\} + \frac{k_3}{ry_H^2} \quad . \qquad (4.53)$$

We look at each of these integrals in turn. The first is simply

$$\int r[k_1J_0(\beta r) + k_2Y_0(\beta r)]dr$$

$$= \frac{1}{\beta} r[k_1J_1(\beta r) + k_2Y_1(\beta r)] \quad , \qquad (4.54)$$

and even though the other two are not trivial, they are still relatively simple and may be performed with known relations among the Bessel functions [165]:

$$\int r^2J_1(\beta r)[k_1J_0(\beta r) + k_2Y_0(\beta r)]dr$$

$$= \frac{k_1}{2\beta} r^2J_1^2(\beta r) + \frac{k_2}{4} r^3[J_1(\beta r)Y_0(\beta r)$$

$$- J_0(\beta r)Y_1(\beta r)] + \frac{k_2}{2\beta} r^2J_1(\beta r)Y_1(\beta r) \quad , \qquad (4.55)$$

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and

$$\begin{aligned}
&\int rJ_0(\beta r)[k_1J_0(\beta r) + k_2Y_0(\beta r)]dr \\
&\quad \doteq \frac{k_1}{2} r^2 \, [J_0^2(\beta r) + J_1^2(\beta r)] \\
&\quad + \frac{k_2}{2} r^2 \, [J_0(\beta r)Y_0(\beta r) + J_1(\beta r)Y_1(\beta r)] \quad . \qquad (4.56)
\end{aligned}$$

The expression for dω/dr is thus

$$\begin{aligned}
\frac{d\omega}{dr} = {} & \frac{2\kappa_A^2 \ell nS}{L} \, \frac{1}{ry_H^2} \Biggl\{ \Biggl[\frac{p^2+\kappa_A^2}{\beta^4} \, \psi_0(0,r) \\
& + \frac{2p}{\beta^4} \, \frac{\partial\psi_0(0,r)}{\partial z} \Biggr] \frac{1}{\beta} \, r \, [k_1J_1(\beta r) + k_2Y_1(\beta r)] \\
& - \frac{\sigma}{\varepsilon} \, \frac{1}{\beta^2 J_1(\beta a)} \Biggl\{ \frac{k_1}{2\beta} \, r^2J_1^2(\beta r) + \frac{k_2}{4} \, r^3[J_1(\beta r)Y_1(\beta r) \\
& - J_0(\beta r)Y_1(\beta r)] + \frac{k_2}{2\beta} \, r^2J_1(\beta r)Y_1(\beta r) \Biggr\} \\
& - \frac{\sigma}{\varepsilon} \, \frac{1}{\beta J_1(\beta r)} \left[\frac{1}{p^2} + \frac{aJ_0(\beta a)}{\beta J_1(\beta a)} \right] \Biggl\{ \frac{k_1}{2} \, r^2[J_0^2(\beta r) + J_1^2(\beta r)] \\
& + \frac{k_2}{2} \, r^2[J_0(\beta r)Y_0(\beta r) + J_1(\beta r)Y_1(\beta r)] \Biggr\} \Biggr\} + \frac{k_3}{ry_H^2}
\end{aligned}$$

(4.57)

To obtain ω, we simply integrate again,

$$\begin{aligned}
\omega = \frac{2\kappa_a^2 \ell nS}{L} \Bigg\{ & \left[\frac{p^2+\kappa_A^2}{\beta^5} \psi_0(0,r) \right. \\
& \left. + \frac{2p}{\beta^5} \frac{\partial \psi_0(0,r)}{\partial z} \right] \int \frac{k_1 J_1(\beta r) + k_2 Y_1(\beta r)}{[k_1 J_0(\beta r) + k_2 Y_0(\beta r)]^2} \, dr \\
& - \frac{\sigma}{\varepsilon} \frac{1}{\beta^2 J_1(\beta a)} \left\{ \frac{1}{2\beta} \int \frac{r J_1(\beta r)[k_1 J_1(\beta r) + k_2 Y_1(\beta r)]}{[k_1 J_0(\beta r) + k_2 Y_0(\beta r)]^2} \, dr \right. \\
& \qquad \left. + \frac{k_2}{4} \int \frac{r^2 [J_1(\beta r) Y_0(\beta r) - J_0(\beta r) Y_1(\beta r)]}{[k_1 J_0(\beta r) + k_2 Y_0(\beta r)]^2} \, dr \right\} \\
& - \frac{\sigma}{\varepsilon} \frac{1}{2\beta J_1(\beta a)} \left[\frac{1}{p^2} + \frac{a J_0(\beta a)}{\beta J_1(\beta a)} \right] \left\{ \int \frac{r J_0(\beta r) dr}{k_1 J_0(\beta r) + k_2 Y_0(\beta r)} \right. \\
& \qquad \left. + \int \frac{r J_1(\beta r)[k_1 J_1(\beta r) + k_2 Y_1(\beta r)]}{[k_1 J_0(\beta r) + k_2 Y_0(\beta r)]^2} \, dr \right\} \Bigg\} \\
& + k_3 \int \frac{dr}{r[k_1 J_0(\beta r) + k_2 Y_0(\beta r)]^2} + k_4 \quad . \qquad (4.58)
\end{aligned}$$

As formidable as these integrals appear, they may be performed individually or in pairs with relative ease. Again, we go through these six integrals, designated I_1 to I_6.

The first may be solved by a simple substitution since

$$dy_H = -\beta[k_1J_1(\beta r) + k_2Y_1(\beta r)]dr; \qquad (4.59)$$

thus

$$I_1 = -\frac{1}{\beta}\int\frac{dy_H}{y_H} = \frac{1}{\beta y_H} \quad . \qquad (4.60)$$

The sixth integral may be performed by combining formulae 6.539.1 and 6.539.2 from Gradshteyn and Ryzhik [53]:

$$I_6 = -\frac{\pi}{2(k_2^2-k_1^2)}\,\frac{k_2J_0(\beta r)+k_1Y_0(\beta r)}{y_H} \qquad (4.61)$$

The second and third integrals and the fourth and fifth integrals may each be solved in pairs. The fourth and fifth are simpler, and their solution is also required for the other pair. It is important to note that I_2 and I_5 are the same integral, but we continue to distinguish them for the time being for convenience. We integrate I_5 by parts:

$$dv = \frac{k_1J_1(\beta r)+k_2Y_1(\beta r)}{y_H^2}\,dr \qquad (4.62)$$

and

$$u = rJ_1(\beta r) \quad . \qquad (4.63)$$

From the result of I_1, we know that

$$v = \frac{1}{\beta y_H} \quad , \tag{4.64}$$

and by direct differentiation, we have

$$du = \beta r J_0(\beta r) dr \quad . \tag{4.65}$$

Thus

$$I_5 = \frac{rJ_1(\beta r)}{\beta y_H} - \int \frac{rJ_0(\beta r)}{y_H} \, dr \quad , \tag{4.66}$$

but the integral on the right-hand side is simply I_4, so that

$$I_4 + I_5 = \frac{rJ_1(\beta r)}{\beta y_H} \quad . \tag{4.67}$$

The integration of I_2 and I_3 is a but more complicated. We first rewrite I_3 with the relationship [66]

$$J_1(\beta r)Y_0(\beta r) - J_0(\beta r)Y_1(\beta r) = \frac{2}{\pi\beta r} \ : \tag{4.68}$$

$$\begin{aligned} \frac{k_2}{4} I_3 &= \frac{k_2}{2\pi\beta} \int \frac{rdr}{y_H^2} \\ &= - \frac{1}{4\beta} \frac{r^2 J_0(\beta r)}{y_H} + \frac{1}{2\beta} \int \frac{rJ_0(\beta r)}{y_H} \, dr \end{aligned} \tag{4.69}$$

We see that the integral on the right-hand side is I_4 again, and thus

$$\frac{1}{2\beta} I_4 - \frac{k_2}{4} I_3 = \frac{1}{4\beta} \frac{r^2 J_0(\beta r)}{y_H} . \tag{4.70}$$

Substituting from Equation (4.68) and I_2 for I_5, we obtain

$$\frac{1}{2\beta} I_2 + \frac{k_2}{4} I_3 = \frac{rJ_1(\beta r)}{2\beta^2 y_H} - \frac{r^2 J_0(\beta r)}{4\beta y_H} , \tag{4.71}$$

which is just the relationship required.

All of these integrals, i.e., Equations (4.60), (4.61), (4.67), and (4.71), may be substituted back into the expression for ω, Equation (4.58), which is simply multiplied by y_H to obtain $\bar{\psi}_1$:

$$\begin{aligned}\bar{\psi}_1 = \frac{2\kappa_A^2 \ell n S}{L} \Bigg\{ & \frac{p^2+\kappa_A^2}{\beta^6} \psi_0(0,r) + \frac{2p}{\beta^6} \frac{\partial \psi_0(0,r)}{\partial z} \\ & - \frac{\sigma}{\varepsilon} \frac{1}{2\beta^3 J_1(\beta a)} \left[\frac{1}{\beta} rJ_1(\beta r) - \frac{1}{2} r^2 J_0(\beta r)\right] \\ & - \frac{\sigma}{\varepsilon} \frac{1}{2\beta^2 J_1(\beta a)} \left[\frac{1}{p^2} + \frac{aJ_0(\beta a)}{\beta J_1(\beta a)}\right] rJ_1(\beta r) \Bigg\} \\ & - \frac{k_3 \pi}{2(k_2^2-k_1^2)} [k_2 J_0(\beta r) + k_1 Y_0(\beta r)] + k_4[k_1 J_0(\beta r) + k_2 Y_0(\beta r)] .\end{aligned} \tag{4.72}$$

Since the radial boundary conditions, Equations (4.20) and (4.21), were applied to ψ_0, here we require that

$$\frac{d\bar{\psi}_1(z,0)}{dr} = 0 \tag{4.73}$$

and

$$\frac{d\bar{\psi}_1(z,a)}{dr} = 0 \quad . \tag{4.74}$$

Differentiation of Equation (4.72) leads to

$$\begin{aligned}\frac{d\bar{\psi}_1}{dr} = \frac{2\kappa_A^2 \ell nS}{L} & \left\{ - \frac{\sigma}{\varepsilon} \frac{r^2 J_1(\beta r)}{4\beta^2 J_1(\beta a)} \right. \\ & \left. - \frac{\sigma}{\varepsilon} \frac{1}{2\beta J_1(\beta a)} \left[\frac{1}{p^2} + \frac{aJ_0(\beta a)}{\beta J_1(\beta a)} \right] rJ_0(\beta r) \right\} \\ & + \frac{k_3 \pi \beta}{2(k_2^2 - k_1^2)} [k_2 J_1(\beta r) + k_1 Y_1(\beta r)] \\ & - k_4 \beta [k_1 J_1(\beta r) + k_2 Y_1(\beta r)] \quad .\end{aligned} \tag{4.75}$$

Even though there are only two boundary conditions for this expression with four unknowns, the last two terms can be combined to yield only two undetermined constants. We can achieve this by setting $k_3 = k_2 = 0$ to remove $Y_1(0)$;

this leaves only one constant, k_1k_4, to find from the remaining condition at $r = a$:

$$k_1k_4 = -\frac{\sigma}{\varepsilon}\frac{a^2}{4\beta^3}\frac{1}{J_1(\beta a)}$$

$$-\frac{\sigma}{\varepsilon}\left[\frac{1}{p^2}+\frac{aJ_0(\beta a)}{\beta J_1(\beta a)}\right]\frac{a}{2\beta^2}\frac{J_0(\beta a)}{J_1^2(\beta a)} \qquad (4.76)$$

Thus the complete solution for $\bar{\psi}_1$ is

$$\bar{\psi}_1(p,r) = \frac{2\kappa_A^2 \ell nS}{L}\left\{\frac{p^2+\kappa_A^2}{\beta^6}\psi_0(0,r) + \frac{2p}{\beta^6}\frac{\partial\psi_0(0,r)}{\partial z}\right.$$

$$+\frac{\sigma}{\varepsilon}\frac{(r^2-a^2)J_0(\beta r)}{4\beta^3 J_1(\beta a)} - \frac{\sigma}{\varepsilon}\frac{rJ_1(\beta r)}{2\beta^4 J_1(\beta a)}$$

$$-\frac{\sigma}{\varepsilon}\frac{rJ_1(\beta r)}{2p^2\beta^2 J_1(\beta a)} - \frac{\sigma}{\varepsilon}\frac{aJ_0(\beta a)J_0(\beta r)}{2p^2\beta^2 J_1^2(\beta a)}$$

$$\left.-\frac{\sigma}{\varepsilon}\frac{aJ_0(\beta a)rJ_1(\beta r)}{2\beta^3 J_1^2(\beta a)} - \frac{\sigma}{\varepsilon}\frac{a^2J_0^2(\beta a)J_0(\beta r)}{2\beta^3 J_1^3(\beta a)}\right\}. \qquad (4.77)$$

Again, this must be transformed back to the original coordinate z in order to obtain the solution $\psi_1(z,r)$.

Each of the first two terms can be expanded by the method of partial fractions and their inverse transforms found in tables [45]:

$$L^{-1}\left\{\frac{p^2+\kappa_A^2}{\beta^6}\right\} = \frac{z^2}{4\kappa_A}\sinh\kappa_A z - \frac{z}{2\kappa_A^2}\cosh\kappa_A z + \frac{1}{4\kappa_A^3}\sinh\kappa_A z \tag{4.78}$$

and

$$2L^{-1}\left\{\frac{p}{\beta^6}\right\} = \frac{z^2}{4\kappa_A^2}\cosh\kappa_A z - \frac{z}{4\kappa_A^3}\sinh\kappa_A z\ . \tag{4.79}$$

The remaining terms must again be transformed through complex integration. The method is the same as in the previous section, although the actual computation of the residues is much more difficult since all the terms to be transformed contain a number of second- and even third-order poles. The results of these inverse transformations, in which we let

$$\gamma_s^2 = j_{1,s}^2 + \kappa_A^2 a^2 \tag{4.80}$$

for convenience, are as follows:

$$L^{-1}\left\{\frac{J_0(\beta r)}{\beta^3 J_1(\beta a)}\right\} = -\frac{2r^2-a^2}{4\kappa_A a}\sinh\kappa_A z + \frac{z}{\kappa_A^2 a}\cosh\kappa_A z - \frac{1}{\kappa_A^3 a}\sinh\kappa_A z + \frac{2a^2\sinh(\gamma_s z/a)}{j_{1,s}^2\gamma_s}\,\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}\ . \tag{4.81}$$

$$\mathcal{L}^{-1}\left\{\frac{J_1(\beta r)}{\beta^4 J_1(\beta a)}\right\} = -\frac{r(r^2-a^2)}{8\kappa_A a}\sinh\kappa_A z$$

$$+\frac{zr}{2\kappa_A^2 a}\cosh\kappa_A z - \frac{r}{2\kappa_A^3 a}\sinh\kappa_A z$$

$$+\frac{2a^3\sinh(\gamma_s z/a)}{j_{1,s}^3\gamma_s}\,\frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})}\ . \tag{4.82}$$

$$\mathcal{L}^{-1}\left\{\frac{J_1(\beta r)}{p^2\beta^2 J_1(\beta a)}\right\} = -\frac{z}{\kappa_A^2}\,\frac{I_1(\kappa_A r)}{I_1(\kappa_A a)}$$

$$+\frac{r}{2\kappa_A^3 a}\sinh\kappa_A z + \frac{2a^3\sinh(\gamma_s z/a)}{j_{1,s}\gamma_5^3}\,\frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$\tag{4.83}$$

$$\mathcal{L}^{-1}\left\{\frac{J_0(\beta a)J_0(\beta r)}{p^2\beta^2 J_1^2(\beta a)}\right\} = \frac{z}{\kappa_A^2}\,\frac{I_0(\kappa_A a)I_0(\kappa_A r)}{I_1^2(\kappa_A a)}$$

$$-\frac{r^2}{2\kappa_A^3 a^2}\sinh\kappa_A z + \frac{2z}{\kappa_A^4 a^2}\cosh\kappa_A z - \frac{6}{\kappa_A^5 a^2}\sinh\kappa_A z$$

$$+\frac{2za^2\cosh(\gamma_s z/a)}{\gamma_s^2}\,\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$- \frac{2a^2 r\sinh(\gamma_s z/a)}{j_{1,s}\gamma_s^3} \frac{J_1(j_{1,s}r/a)}{(J_0(j_{1,s})}$$

$$- \frac{6a^3\sinh(\gamma_s z/a)}{\gamma_s^5} \frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})} \quad . \tag{4.84}$$

$$L^{-1}\left\{\frac{J_0(\beta a)J_1(\beta r)}{\beta^3 J_1(\beta a)}\right\} = - \frac{r^3}{2\kappa_A a^2} \sinh \kappa_A z$$

$$+ \frac{2zr}{\kappa_A^2 a^2} \cosh \kappa_A z - \frac{2r}{\kappa_A^3 a^2} \sinh \kappa_A z$$

$$+ \frac{az\cosh(\gamma_s z/a)}{j_{1,s}\gamma_s^2} \frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$+ \frac{2ar\sinh(\gamma_s z/a)}{j_{1,s}^2\gamma_s} \frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$- \frac{4a^2\sinh(\gamma_s z/a)}{j_{1,s}^3\gamma_s} \frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$- \frac{2a^2\sinh(\gamma_s z/a)}{j_{1,s}\gamma_s^3} \frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})} \quad . \tag{4.85}$$

$$\mathcal{L}^{-1}\left\{\frac{J_0^2(\beta a)J_0(\beta r)}{\beta^3 J_1^3(\beta a)}\right\} = \frac{r^4+2a^2r^2-a^4}{8\kappa_A a^3}\sinh\kappa_A z$$

$$-\frac{z(2r^2+a^2)}{2\kappa_A^2 a^3}\cosh\kappa_A z + \frac{2z^2+2r^2+a^2}{2\kappa_A^3 a^3}\sinh\kappa_A z$$

$$-\frac{z}{\kappa_A^4 a^3}\cosh\kappa_A z + \frac{3}{2\kappa_A^5 a^3}\sinh\kappa_A z$$

$$-\frac{(r^2-a^2)\sinh(\gamma_s z/a)}{j_{1,s}^2\gamma_s}\,\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$+\frac{z^2\sinh(\gamma_s z/a)}{\gamma_s}\,\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$+\frac{2ar\sinh(\gamma_s z/a)}{j_{1,s}\gamma_s^3}\,\frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$+\frac{2ar\sinh(\gamma_s z/a)}{j_{1,s}^3\gamma_s}\,\frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$+\frac{3a^2\sinh(\gamma_s z/a)}{\gamma_s^5}\,\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$- \frac{2zr\cosh(\gamma_s z/a)}{j_{1,s}\gamma_s^2} \frac{J_1(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$- \frac{3za\cosh(\gamma_s z/a)}{\gamma_s^4} \frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})} \quad . \qquad (4.86)$$

Combining these results, we obtain the complete first-order solution $\psi_1(z,r)$, i.e., the inverse transform of Equation (4.77):

$$\psi_1(z,r) = \frac{\kappa_A^2 \ell n S}{L} \left\{ \psi_0(0,r) \left[\frac{z^2}{2\kappa_A} \sinh \kappa_A z \right. \right.$$

$$\left. - \frac{z}{\kappa_A^2} \cosh \kappa_A z + \frac{1}{2\kappa_A^3} \sinh \kappa_A z \right]$$

$$+ \frac{\partial\psi_0(0,r)}{\partial z} \left[\frac{z^2}{2\kappa_A^2} \cosh \kappa_A z - \frac{z}{2\kappa_A^3} \sinh \kappa_A z \right]$$

$$+ \frac{\sigma}{\varepsilon} \left[\frac{r^4}{4\kappa_A a} + \frac{r^2}{\kappa_A^3 a} - \frac{z^2}{\kappa_A^3 a} + \frac{9}{2\kappa_A^5 a} \right] \sinh \kappa_A z$$

$$- \frac{\sigma}{\varepsilon} \left[\frac{zr^2}{\kappa_A^2 a} + \frac{z}{\kappa_A^4 a} \right] \cosh \kappa_A z$$

$$+\frac{\sigma}{\varepsilon}\left[\frac{zr}{\kappa_A^2}\,\frac{I_1(\kappa_A r)}{I_1(\kappa_A a)}-\frac{za}{\kappa_A^2}\,\frac{I_0(\kappa_A a)I_0(\kappa_A r)}{I_1^2(\kappa_A a)}\right]$$

$$-\frac{\sigma}{\varepsilon}\sum_{s=1}^{\infty}\left[\frac{z^2a^2}{(j_{1,s}^2+\kappa_A^2a^2)^{1/2}}+\frac{2a^4}{j_{1,s}^2(j_{1,s}^2+\kappa_A^2a^2)^{1/2}}\right.$$

$$\left.-\frac{3a^4}{(j_{1,s}^2+\kappa_A^2a^2)^{5/2}}\right]\sinh\,[(j_{1,s}^2+\kappa_A^2a^2)^{1/2}(z/a)]\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}$$

$$+\frac{\sigma}{\varepsilon}\sum_{s=1}^{\infty}\frac{za^3}{(j_{1,s}^2+\kappa_A^2a^2)^{1/2}}\cosh\,[(j_{1,s}^2+\kappa_A^2a^2)^{1/2}(z/a)]\times$$

$$\left.\frac{J_0(j_{1,s}r/a)}{J_0(j_{1,s})}\right\}\ . \qquad (4.87)$$

Although the solution for ψ_1 appears more complicated than that for ψ_0, Equation (4.41), its form is similar. It contains functions of z and functions of z multiplied by functions of r, and there is no reason to believe that the higher-order solutions will yield any different result. Since ψ_0 also contains a function of r in addition to the ones mentioned above, the general form of the result for ψ from the Laplace transform method is

$$\psi(z,r) = f_1(z) + g_1(r) + \sum f_2(z)g_2(r)\quad . \qquad (4.88)$$

This differs from the form of the solution that we found in Chapter 3, i.e.,

$$\psi(z,r) = f(z) + g(z,r) \quad , \tag{4.89}$$

in which z and r are not separable in the final term. In the next chapter, therefore, we attempt to find a solution of the form of Equation (4.88) for our model of a cylinder of finite length.

CHAPTER 5

AN ATTEMPTED SOLUTION BASED ON THE LAPLACE TRANSFORM RESULTS

A. Introduction

In this chapter we again consider a cylinder of finite length ($0 \leq z \leq L$). With a proposed solution of the form obtained in the previous chapter, we impose z-dependent boundary conditions at $z = 0$ and $z = L$. The particular model we choose to solve is again for $f(z) = S^{z/L}$, and the complete equation is given in Equation (4.2). Writing $S^{z/L}$ as a series as in Equation (4.4) and (z,r) as a series as in Equation (4.6), we obtain the same differential equations as those given in Equations (4.7) through (4.9).

For each ψ_0, ψ_1, etc., we choose a solution of the form

$$\psi_i(z,r) = f_1(z) + g_1(r) + f_2(z)g_2(r) \quad . \tag{5.1}$$

We apply the boundary conditions in Equations (3.107) and (3.108) and in Equations (2.21) and (2.22) to $f_1(z)$ and $g_1(r)$ of ψ_0 respectively and require that these derivatives be zero for every other function f and g in each ψ_i.

B. Zeroth-Order Solution

Assuming Equation (5.1) for ψ_0 and introducing it into Equation (4.7), we separate the result into three equations:

$$\frac{d^2 f_1}{dz^2} - \kappa_A^2 f_1 = 0 \quad , \tag{5.2}$$

$$\frac{1}{r}\frac{d}{dr}\, r\, \frac{dg_1}{dr} - \kappa_A^2 g_1 = 0 \quad , \tag{5.3}$$

and

$$g_2 \frac{d^2 f_2}{dz^2} + f_2 \frac{1}{r}\frac{d}{dr}\, r\, \frac{dg_2}{dr} - \kappa_A^2 f_2 g_2 = 0 \quad . \tag{5.4}$$

The final equation can be separated into z-dependent and r-dependent parts, and writing the separation constant as λ^2, we obtain

$$\frac{d^2 f_2}{dz^2} - (\lambda^2 + \kappa_A^2) f_2 = 0 \tag{5.5}$$

and

$$\frac{1}{r}\frac{d}{dr}\, r\, \frac{dg_2}{dr} + \lambda^2 g_2 = 0 \quad . \tag{5.6}$$

The solutions to Equations (5.2), (5.3), (5.5), and (5.6) are

$$f_1 = k_1 \cosh \kappa_A z + k_2 \sinh \kappa_A z \quad , \tag{5.7}$$

$$g_1 = k_3 I_0(\kappa_A r) + k_4 K_0(\kappa_A r) \quad , \tag{5.8}$$

$$f_2 = k_5 \cosh(\lambda^2 + \kappa_A^2)^{1/2} z + k_6 \sinh(\lambda^2 + \kappa_A^2)^{1/2} z \; , \tag{5.9}$$

$$g_2 = k_7 J_0(\lambda r) + k_8 Y_0(\lambda r) \quad . \tag{5.10}$$

The z-dependent boundary conditions,

$$\frac{df_1(0)}{dz} = \frac{\sigma_A}{\varepsilon} \tag{5.11}$$

$$\frac{df_1(L)}{dz} = - \frac{\sigma_B}{\varepsilon} \quad , \tag{5.12}$$

result in the solution

$$f_1(z) = - \frac{1}{\varepsilon \kappa_A \sinh \kappa_A L} [\sigma_B \cosh \kappa_A z + \sigma_A \cosh \kappa_A (L-z)] \; , \tag{5.13}$$

which is the same result as Equation (3.110), that obtained for $\psi_1(z)$ in the absence of an ionic strength gradient. The r-dependent boundary conditions applied to $g_1(r)$ yield

$$g_1(r) = \frac{\sigma I_0(\kappa_A r)}{\varepsilon \kappa_A I_1(\kappa_A a)} \quad , \tag{5.14}$$

the same result as $\psi_2(z,r)$ in Equation (3.7) with no ionic strength gradient.

We now apply the conditions

$$f_2 \frac{dg_2(0)}{dr} = f_2 \frac{dg_2(a)}{dr} = 0 \tag{5.15}$$

and

$$g_2 \frac{df_2(0)}{dz} = g_2 \frac{df_2(L)}{dz} = 0 \tag{5.16}$$

to the product $f_2(z)g_2(r)$:

$$f_2 \frac{dg_2}{dr} = -\lambda[k_5\cosh(\lambda^2+\kappa_A^2)^{1/2}a + k_6 \sinh(\lambda^2+\kappa_A^2)^{1/2}z][k_7J_1(\lambda r)+k_8Y_1(\lambda r)] \ . \tag{5.17}$$

The requirement that this expression be zero at $r = 0$ forces $k_8 = 0$ since $Y_1(\lambda r)$ is infinite at this point. At $r = a$, we have

$$-\lambda[k_5\cosh(\lambda^2+\kappa_A^2)^{1/2}z + k_6\sinh(\lambda^2 + \kappa_A^2)^{1/2}z] \times J_1(\lambda a) = 0 \ , \tag{5.18}$$

where k_7 has been subsumed into k_5 and k_6. This condition is satisfied for all

$$\lambda_s = \frac{j_{1,s}}{a} \quad , \tag{5.19}$$

where $j_{1,s}$ is the s-th zero of J_1.

The second set of conditions given by Equation (5.16) applies to the expression

$$g_2 \frac{df_2}{dz} = \frac{1}{a} \sum_{s=0}^{\infty} (j_{1,s}^2+\kappa_A^2 a^2)^{1/2} \left\{k_{5,s} \sinh[(j_{1,s}^2+\kappa_A^2 a^2)^{1/2}(z/a)] + k_{6,s} \cosh[(j_{1,s}^2 + \kappa_A^2 a^2)^{1/2} (z/a)]\right\} J_0(j_{1,s} r/a) \quad ,$$

where the constants $k_{5,s}$ and $k_{6,s}$ may now depend on s. However, the function $J_0(j_{1,s}r/a)$ is orthogonal in the interval $0 \leq r \leq a$ because its derivative vanishes at both $r = 0$ and $r = a$ [66], and thus we can exploit this property to determine these constants.

At $z = 0$,

$$\frac{1}{a} \sum_{s=0}^{\infty} (j_{1,s}^2+\kappa_A^2 a^2)^{1/2} k_{6,s} J_0(j_{1,s}\, r/a) = 0 \quad . \tag{5.21}$$

Multiplying by $rJ_0(j_{1,t}r/a)$, where t is a particular value of s, and integrating over r from 0 to a, we obtain

$$\frac{a}{2}(j_{1,t}^2+\kappa_A^2 a^2)^{1/2} k_{6,t}\, J_0^2(j_{1,t}) = 0 \quad , \tag{5.22}$$

and thus $k_{6,s} = 0$ for every s. Similarly at z = L, applying the condition of orthogonality to the expression

$$\frac{1}{a}\sum_{s=0}^{\infty} (j_{1,s}^2+\kappa_A^2a^2)^{1/2}k_{5,s}\sinh[(j_{1,s}^2+\kappa_A^2a^2)^{1/2}(L/a)] \times$$

$$J_0(j_{1,s}\frac{r}{a}) = 0 \qquad (5.23)$$

results in the requirement that

$$\frac{a}{2}(j_{1,t}^2+\kappa_A^2a^2)^{1/2}k_{5,t}\sinh[(j_{1,t}^2+\kappa_A^2a^2)^{1/2}(L/a)]J_0^2(j_{1,t})=0. \qquad (5.24)$$

This is true only for $k_{5,s} = 0$ for every s.

Thus our complete zeroth-order solution is simply

$$\psi_0(z,r) = -\frac{1}{\varepsilon\kappa_A\sinh\kappa_A L}[\sigma_B\cosh\kappa_A z + \sigma_A\cosh\kappa_A(L-z)] + \frac{\sigma I_0(\kappa_A r)}{\varepsilon\kappa_A I_1(\kappa_A a)} . \qquad (3.25)$$

C. First-Order Solution

We now turn to the first-order solution, for which we must solve the differential equation

$$\frac{\partial^2\psi_1}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial\psi_1}{\partial r} = \kappa_A^2\psi_1 - \frac{2\kappa_A z \ell n S}{\varepsilon L \sinh\kappa_A L}[\sigma_B\cosh\kappa_A z$$

$$+ \sigma_A\cosh\kappa_A(L-z)] + \frac{2\sigma\kappa_A z\ell n S}{\varepsilon L I_1(\kappa_A a)} I_0(\kappa_A r) \quad . \qquad (5.26)$$

Again, we assume a solution of the form given in Equation (5.1). The separation of the resulting expression,

$$\frac{d^2f_1}{dz^2} + g_2\frac{d^2f_2}{dz^2} + \frac{1}{r}\frac{d}{dr} r \frac{dg_1}{dr} + f_2\frac{1}{r}\frac{d}{dr} r \frac{dg_2}{dr}$$

$$= \kappa_A^2 f_1 + \kappa_A^2 g_1 + \kappa_A^2 f_2 g_2 - \frac{2\kappa_A z\ell n S}{\varepsilon L\sinh\kappa_A L}[\sigma_B\cosh\kappa_A z$$

$$+ \sigma_A\cosh\kappa_A(L-z) + \frac{2\sigma\kappa_A z\ell n S}{\varepsilon L I_1(\kappa_A a)} I_0(\kappa_A r) \quad , \qquad (5.27)$$

is problematic. Although we can readily separate out the z-dependent equation,

$$\frac{d^2f_1}{dz^2} - \kappa_A^2 f_1 = - \frac{2\kappa_A z\ell n S}{\varepsilon L\sinh\kappa_A L}[\sigma_B\cosh\kappa_A z + \sigma_A\cosh\kappa_A(L-z)] \ , \qquad (5.28)$$

The remaining z-dependent and r-dependent terms cannot be separated from each other.

We choose to place the remaining inhomogeneous term with g_1 since the homogeneous solution to the equation for g_1 is also modified Bessel functions. Thus we have the two equations

$$\frac{1}{r}\frac{d}{dr} r \frac{dg_1}{dr} - \kappa_A^2 g_1 = \frac{2\sigma\kappa_A z \ell n S}{\varepsilon L I_1(\kappa_A a)} I_0(\kappa_A r) \qquad (5.29)$$

and

$$g_2 \frac{d^2 f_2}{dz^2} + f_2 \frac{1}{r}\frac{d}{dr} r \frac{dg_2}{dr} - \kappa_A^2 f_2 g_2 = 0 \quad . \qquad (5.30)$$

Equation (5.30) is the same as Equation (5.4) in the solution of ψ_0. Since the boundary conditions are the same as before, we see that $f_2 g_2 = 0$, and we need only solve Equations (5.28) and (5.29), treating z as a constant in the latter.

We use the same method here for finding the complete solution when the homogeneous solution is known as we did in the previous chapter. The homogeneous solution of Equation (5.28) is

$$y_H = k_1 \cosh \kappa_A z + k_2 \sinh \kappa_A z \quad . \qquad (5.31)$$

Assuming a complete solution of the form

$$f_1(z) = \omega(z) y_H(z) \quad , \qquad (5.32)$$

we find from Equation (5.28) that

$$\frac{d}{dz}\frac{d\omega}{dz} + \frac{2}{y_H}\frac{dy_H}{dz}\frac{d\omega}{dz} =$$

$$- \frac{2\kappa_A z \ell nS}{\varepsilon L y_H \sinh\kappa_A L}[\sigma_B \cosh\kappa_A z + \sigma_A \cosh\kappa_A (L-z)] . \tag{5.33}$$

The integrating factor is 1 so that

$$\frac{d\omega}{dz} = - \frac{2\kappa_A \ell nS}{\varepsilon L y_H^2 \sinh\kappa_A L}\int(k_1 \cosh\kappa_A z$$

$$+ k_2 \sinh\kappa_A z)[\sigma_B z\cosh\kappa_A z + \sigma_A z\cosh\kappa_A (L-z)]dz + \frac{k_3}{y_H^2} . \tag{5.34}$$

Integration yields

$$\frac{d\omega}{dz} = - \frac{2\kappa_A \ell nS}{\varepsilon L y_H^2 \sinh\kappa_A L}\Bigg\{k_1\sigma_B\Bigg[\frac{1}{4}z^2$$

$$+ \frac{1}{2\kappa_A} z\cosh\kappa_A z\sinh\kappa_A z - \frac{1}{8\kappa_A^2}(\cosh^2\kappa_A z$$

$$+ \sinh^2\kappa_A z)\Bigg] + k_2\sigma_B\Bigg[\frac{1}{4\kappa_A} z\,(\cosh^2\kappa_A z$$

$$+ \sinh^2\kappa_A z) - \frac{1}{4\kappa_A^2}\cosh\kappa_A z\sinh\kappa_A z\Bigg]$$

$$
\begin{aligned}
&+ k_1\sigma_A \Bigg[\frac{1}{4}\, z^2 \cosh\kappa_A L \\
&- \frac{1}{4\kappa_A}\, z[\sinh\kappa_A L(\cosh^2\kappa_A z + \sinh^2\kappa_A z) \\
&- 2\cosh\kappa_A L \cosh\kappa_A z \sinh\kappa_A z] \\
&- \frac{1}{8\kappa_A^2}\, [\cosh\kappa_A L(\cosh^2\kappa_A z + \sinh^2\kappa_A z) \\
&- 2\sinh\kappa_A L \cosh\kappa_A z \sinh\kappa_A z] \Bigg] \\
&+ k_2\sigma_A \Bigg[\frac{1}{4}\, z^2 \sinh\kappa_A L \\
&+ \frac{1}{4\kappa_A}\, z\, [\cosh\kappa_A L(\cosh^2\kappa_A z + \sinh^2\kappa_A z) \\
&- 2\sinh\kappa_A L \cosh\kappa_A z \sinh\kappa_A z] \\
&+ \frac{1}{8\kappa_A^2}\, [\sinh\kappa_A L(\cosh^2\kappa_A z + \mathrm{shin}^2\kappa_A z) \\
&- 2\cosh\kappa_A L \cosh\kappa_A z \sinh\kappa_A z] \Bigg] \Bigg\} + \frac{k_3}{y_H^2} \,. \qquad (5.35)
\end{aligned}
$$

The second integration to obtain ω itself presents a number of integrals that appear difficult. However, by rewriting Equation (5.35), we can obtain the results of several integrals collectively with relative ease, as we did in seeking the general solution for the first-order solution in terms of Bessel functions in the previous chapter. We combine terms in Equation (5.35) and integrate as follows:

$$
\begin{aligned}
\omega = -\frac{2\kappa_A \ell n S}{\varepsilon L \sinh\kappa_A L} \Bigg\{ & \sigma_B \Bigg[\frac{k_1}{4} \int \frac{z^2}{y_H^2}\, dz \\
& + \frac{1}{4\kappa_A} \int \frac{z\cosh\kappa_A z(k_1 \sinh\kappa_A z + k_2 \cosh\kappa_A z)}{y_H^2}\, dz \\
& + \frac{1}{4\kappa_A} \int \frac{z\sinh\kappa_A z}{y_H}\, dz - \frac{1}{8\kappa_A^2} \int \frac{\cosh\kappa_A z}{y_H}\, dz \\
& - \frac{1}{8\kappa_A^2} \int \frac{\sinh\kappa_A z(k_1 \sinh\kappa_A z + k_2 \cosh\kappa_A z)}{y_H^2}\, dz \Bigg] \\
& + \sigma_A \cosh\kappa_A L \Bigg[\frac{k_1}{4} \int \frac{z^2}{y_H^2}\, dz \\
& + \frac{1}{4\kappa_A} \int \frac{z\cosh\kappa_A z(k_1 \sinh\kappa_A z + k_2 \cosh\kappa_A z)}{y_H^2}\, dz \\
& + \frac{1}{4\kappa_A} \int \frac{z\sinh\kappa_A z}{y_H}\, dz - \frac{1}{8\kappa_A^2} \int \frac{\cosh\kappa_A z}{y_H}\, dz \\
& - \frac{1}{8\kappa_A^2} \int \frac{\sinh\kappa_A z(k_1 \sinh\kappa_A z + k_2 \cosh\kappa_A z)}{y_H^2}\, dz \Bigg]
\end{aligned}
$$

$$+ \sigma_A \sinh \kappa_A L \Bigg[\frac{k_2}{4} \int \frac{z^2}{y_H^2}\, dz - \frac{1}{4\kappa_A} \int \frac{z \cosh \kappa_A z}{y_H}\, dz$$

$$- \frac{1}{4\kappa_A} \int \frac{z \sinh \kappa_A z (k_1 \sinh \kappa_A z + k_2 \cosh \kappa_A z)}{y_H^2}\, dz$$

$$+ \frac{1}{8\kappa_A^2} \int \frac{\cosh \kappa_A z (k_1 \sinh \kappa_A z + k_2 \cosh \kappa_A z}{y_H^2}\, dz$$

$$+ \frac{1}{8\kappa_A^2} \int \frac{\sinh \kappa_A z}{y_H}\, dz \Bigg] \Bigg\} + k_3 \int \frac{1}{y_H^2}\, dz + k_4 \,. \qquad (5.36)$$

Each group of integrals within square brackets can be solved as a unit. We demonstrate with the first set, designated I_1 through I_5. The only other integral needed is the final one in Equation (5.36), which can be found with relative ease:

$$\int \frac{1}{y_H^2}\, dz = \frac{\sinh \kappa_A z}{k_1 \kappa_A y_H} = - \frac{\cosh \kappa_A z}{k_2 \kappa_A y_H} \,. \qquad (5.37)$$

Using this result to do the other integrals by parts, we find:

$$I_1 = \frac{z^2 \sinh \kappa_A z}{k_1 \kappa_A y_H} - \frac{2}{k_1 \kappa_A} I_3 \quad , \qquad (5.38)$$

$$I_2 = - \frac{z \cosh \kappa_A z}{\kappa_A y_H} + \frac{1}{\kappa_A} I_4 + I_3 \quad , \qquad (5.39)$$

and

$$I_5 = -\frac{\sinh\kappa_A z}{\kappa_A y_H} + I_4 \quad . \qquad (5.40)$$

Thus, the expression in the first square brackets of Equation (5.36) is

$$\frac{k_1}{4} I_1 + \frac{1}{4\kappa_A} I_2 + \frac{1}{4\kappa_A} I_3 - \frac{1}{8\kappa_A^2} I_4 - \frac{1}{8\kappa_A^2} I_5$$

$$= \frac{1}{4\kappa_A y_H} z^2\sinh\kappa_A z - \frac{1}{2\kappa_A} I_3$$

$$- \frac{1}{4\kappa_A^2 y_H} z\cosh\kappa_A z + \frac{1}{4\kappa_A^2} I_4 + \frac{1}{4\kappa_A} I_3$$

$$+ \frac{1}{4\kappa_A} I_3 - \frac{1}{8\kappa_A^2} I_4 + \frac{1}{8\kappa_A^3 y_H} \sinh\kappa_A z$$

$$- \frac{1}{8\kappa_A^2} I_4$$

$$= \frac{1}{4\kappa_A y_H} z^2\sinh\kappa_A z - \frac{1}{4\kappa_A^2 y_H} z\cosh\kappa_A z$$

$$+ \frac{1}{8\kappa_A^3 y_H} \sinh\kappa_A z \quad . \qquad (5.41)$$

Proceeding similarly for the other groups of integrals, we eventually find that

$$\omega = -\frac{\ln S}{4\varepsilon\kappa_A^2 L y_H \sinh\kappa_A L}\Big\{\sigma_B[2\kappa_A^2 z^2 \sinh\kappa_A z$$

$$- 2\kappa_A z\cosh\kappa_A z + \sinh\kappa_A z] - \sigma_A[2\kappa_A^2 z^2 \sinh\kappa_A(L-z)$$

$$+ 2\kappa_A z\cosh\kappa_A(L-z) + \sinh\kappa_A(L-z)]\Big\} + \frac{k_3}{k_1\kappa_A y_H}\sinh\kappa_A z + k_4 \ , \tag{5.42}$$

and thus that

$$f_1(z) = -\frac{\ln S}{4\varepsilon\kappa_A^2 L\sinh\kappa_A L}\Big\{\sigma_B[2\kappa_A^2 z^2 \sinh\kappa_A z$$

$$- 2\kappa_A z\cosh\kappa_A z + \sinh\kappa_A z] - \sigma_A[2\kappa_A^2 z^2 \sinh\kappa_A(L-z)$$

$$+ 2\kappa_A z\cosh\kappa_A(L-z) + \sinh\kappa_A(L-z)]\Big\}$$

$$+ k_1\cosh\kappa_A z + k_2\sinh\kappa_A z \ , \tag{5.43}$$

where we have lumped the final terms with undetermined coefficients together.

In order to determine k_1 and k_2, we apply the conditions

$$\frac{df_1(0)}{dz} = \frac{df_1(L)}{dz} = 0 \quad . \tag{5.44}$$

The z-derivative of Equation (5.43) is

$$\frac{df_1}{dz} = - \frac{\ell nS}{4\varepsilon\kappa_A^2 L\sinh\kappa_A L}\Big\{\sigma_B[2\kappa_A^3 z^2\cosh\kappa_A z$$

$$+ 2\kappa_A^2 z\sinh\kappa_A z - \kappa_A\cosh\kappa_A z]$$

$$+ \sigma_A[2\kappa_A^3 z^2\cosh\kappa_A(L-z) - 2\kappa_A^2 z\sinh\kappa_A(L-z)$$

$$- \kappa_A\cosh\kappa_A(L-z)]\Big\} + k_1\kappa_A\sinh\kappa_A z + k_2\kappa_A\cosh\kappa_A z \ . \tag{5.45}$$

At z = 0, we find that

$$k_2 = - \frac{\ell nS}{4\varepsilon\kappa_A^2 L\sinh\kappa_A L}(\sigma_B + \sigma_A\cosh\kappa_A L) \quad , \tag{5.46}$$

and at z = L,

$$k_1 = \frac{\ell nS}{4\varepsilon\kappa_A^2 L\sinh^2\kappa_A L}[2\sigma_B(\kappa_A^2 L^2\cosh\kappa_A L$$

$$+ \kappa_A L\sinh\kappa_A L) + \sigma_A(\sinh^2\kappa_A L + 2\kappa_A^2 L^2)] \quad . \tag{5.47}$$

Thus the complete solution for $f_1(z)$ is

$$f_1(z) = -\frac{\ell nS}{4\varepsilon\kappa_A^2 L\sinh\kappa_A L}\Big\{\sigma_B[2\kappa_A^2 z^2\sinh\kappa_A z$$

$$- 2\kappa_A z\cosh\kappa_A z + \sinh\kappa_A z] - \sigma_A[2\kappa_A^2 z^2\sinh\kappa_A(L-z)$$

$$+ 2\kappa_A z\cosh\kappa_A(L-z) + \sinh\kappa_A(L-z)]\Big\}$$

$$+ \frac{\ell nS}{4\varepsilon\kappa_A^2 L\sinh^2\kappa_A L}\Big\{\sigma_B[2\kappa_A^2 L^2\cosh\kappa_A L\cosh\kappa_A z$$

$$+ 2\kappa_A L\sinh\kappa_A L\cosh\kappa_A z - \sinh\kappa_A L\sinh\kappa_A z]$$

$$+ \sigma_A[2\kappa_A^2 L^2\cosh\kappa_A z + \sinh\kappa_A L\sinh\kappa_A(L-z)]\Big\} . \qquad (5.48)$$

We now need to find the solution to Equation (5.29) in the same way. The homogeneous solution is

$$y_H = k_1 I_0(\kappa_A r) + k_2 K_0(\kappa_A r) \quad , \qquad (5.49)$$

and thus we assume a complete solution of

$$g_1(r) = \omega(r) y_H(r) \quad . \qquad (5.50)$$

Substituting this solution into Equation (5.29) yields

$$\frac{d}{dr}\,\frac{d\omega}{dr} + \left[\frac{2}{y_H}\,\frac{dy_H}{dr} + \frac{1}{r}\right]\frac{d\omega}{dr} = \frac{2\sigma\kappa_A z\ell nS}{\varepsilon L y_H I_1(\kappa_A a)}\, I_0(\kappa_A r) \; . \tag{5.51}$$

With an integrating factor of r, this equation yields the solution

$$\frac{d\omega}{dr} = \frac{2\sigma\kappa_A z\ell nS}{\varepsilon L r y_H^2 I_1(\kappa_A a)} \int r I_0(\kappa_A r)[k_1 I_0(\kappa_A r) + k_2 K_0(\kappa_A r)]dr + \frac{k_3}{y_H^2} \; . \tag{5.52}$$

These integrals are straightforward [165], and the result is

$$\frac{d\omega}{dr} = \frac{2\sigma\kappa_A z\ell nS}{\varepsilon L r y_H^2 I_1(\kappa_A a)}\left\{\frac{k_1}{2}\, r^2[I_0^2(\kappa_A r) - I_1^2(\kappa_A r)] + \frac{k_2}{2}\, r^2[I_0(\kappa_A r)K_0(\kappa_A r) + I_1(\kappa_A r)K_1(\kappa_A r)]\right\} + \frac{k_3}{y_H^2} \; . \tag{5.53}$$

The third integral can be performed analogously to that involving ordinary Bessel functions as in Equation (4.61), the result being

$$I_3 = \frac{1}{k_2^2+k_1^2} \frac{k_2 I_0(\kappa_A r) - k_1 K_0(\kappa_A r)}{y_H} \quad . \tag{5.55}$$

The first two integrals are found to be

$$I_1 - I_2 = \frac{r I_1(\kappa_A r)}{y_H} \quad , \tag{5.56}$$

so that the final result is

$$\omega = \frac{\sigma z \ell n S}{\varepsilon L y_H I_1(\kappa_A a)} r I_1(\kappa_A r)$$

$$+ \frac{k_3}{k_2^2+k_1^2} \frac{k_2 I_0(\kappa_A r) - k_1 K_0(\kappa_A r)}{y_H} + k_4 \quad . \tag{5.57}$$

Thus the complete solution to Equation (5.29) is

$$g_1(r) = \frac{\sigma z \ell n S}{\varepsilon L I_1(\kappa_A a)} r I_1(\kappa_A r)$$

$$+ k_1 I_0(\kappa_A r) + k_2 K_0(\kappa_A r) \quad , \tag{5.58}$$

where we have clumped the four constants into a new k_1, k_2. The boundary conditions

$$\frac{dg_2(0)}{dr} = \frac{dg_2(a)}{dr} \tag{5.59}$$

finally result in the solution

$$g_1(r) = \frac{\sigma z \ell n S}{L}\left[\frac{rI_1(\kappa_A r)}{I_1(\kappa_A a)} - \frac{aI_0(\kappa_A a)I_0(\kappa_A r)}{I_1^2(\kappa_A a)}\right] . \qquad (5.60)$$

Thus the complete first-order solution is the sum of Equations (5.48) and (5.60). Higher-order solutions may be found similarly, except for the expenditure of more energy.

D. Critique of the Method

The difficulty with determining $\psi(z,r)$ in this way is the impossibility of separating the z-dependent terms in the equations for ψ_1 (and for higher-order solutions as well). The separation that we have chosen is equivalent to

$$\psi_1(z,r) = f(z) + g(z,r) \quad , \qquad (5.61)$$

where we neglect $\partial^2 g/\partial z^2$ as being small compared to $(1/r)\partial(r\partial g/\partial r)\partial r$.

The method here is also equivalent to our earlier attempt in Chapter 2 with the additive solution of Equation (2.8). There we did not proceed because it was not possible to separate the partial differential equation with this solution into two ordinary differential equations. If we had separated Equation (2.9) as we have here, we would have obtained

$$\frac{d^2 f_1(z)}{dz^2} - \kappa_A^2 S^{2z/L} f_1(z) = 0 \tag{5.62}$$

and

$$\frac{1}{r}\frac{d}{dr}\, r\, \frac{dg_1(r)}{dr} - \kappa_A^2 S^{2z/L} g_2(r) = 0 \quad . \tag{5.63}$$

Treating the variable z as a constant in Equation (5.63) leads to the solution in Equation (3.7), where the ionic strength distribution model f(z) is simply $S^{z/L}$. The perturbation scheme presented in the previous sections thus leads only to an infinite series of hyperbolic functions and modified Bessel functions that are presumably equivalent to the solutions for $\psi_1(z)$ and $\psi_2(z,r)$ with $S^{z/L}$ in Chapter 3.

The form of the solution proposed in Equation (5.1) is apparently due to the imposition of both z-dependent boundary conditions at z = 0. An examination of the zeroth-order solution in Equation (4.43) shows why this is so. For the condition $\psi_0(0,r)$, the hyperbolic cosine is equal to 1, and since it is possible to show that the Fourier-Bessel series for $I_0(\kappa_A r)$ is [165]

$$I_0(\kappa_A r) = 2\kappa_A a I_1(\kappa_A a) \sum_{s=0}^{\infty} \frac{1}{j_{1,s}^2 + \kappa_A^2 a^2} \frac{J_0(j_{1,s} r/a)}{J_0(j_{1,s})} \quad , \tag{5.64}$$

those terms cancel, and $\psi_0(z,r)$ obeys the boundary condition. Similarly, for the boundary condition $\partial\psi_0(0,r)/\partial z$, the term $I_0(\kappa_A r)/I_1(\kappa_A a)$ is zero, as is the hyperbolic sine, and again these two terms vanish so that $\psi_0(z,r)$ obeys the boundary condition.

This relationship between the modified Bessel functions and its Fourier-Bessel series does not work for boundary conditions at values of z other than zero, and thus the term $f_2(z)g_2(r)$ is zero for each solution ψ_1 as we try to impose a solution of the same form on a finite cylinder. Although the method of the Laplace transform has not obtained any new solution for us, it has added further support to the method presented in Chapter 3, i.e., the separation of $\psi(z,r)$ as in (3.1) and the subsequent neglect of the second z-derivative.

CHAPTER 6

MODELS, METAPHORS, AND MATHEMATICS

A. Introduction

On November 10, 1619, the Angel of Truth appeared to Rene Descartes, assuring him that mathematics is indeed the key to unlock the physical universe [22]. Thus Descartes had more tangible evidence for this metaphysical belief than do most of us, who believe in it because others do and because it seems to work. It works in the sense that mathematical predictions about the universe can be tested experimentally; for example, by following the calculated trajectory from earth, Apollo 8 succeeded in orbiting the moon. There can be dramatic corroborations of Newtonian mechanics even in this age of quantum theory.

Mathematical prediction, however, is only one part of the "systematic coherent formulation" that David Hawkins [60] cites, along with empirical verification, as the discipline of science. Science must also provide explanation, distinct from prediction, within this framework, although Erwin Chargaff warns us that explanation is not understanding [29] and chides us that "even the most exact of our exact sciences float above axiomatic abysses that cannot be explored" [28].

No less a scientist than Pierre Duhem states unequivocally that physical theory is not an explanation. The aim of theory "is to summarize and classify logically a group of experimental laws without claiming to explain these laws" [40]. Duhem rejects any explanatory role for theory because such a role, in his view, subordinates physics to metaphysics. How he could avoid such ultimate beliefs is not clear; even his choice to be a physicist rather than a biologist, for example, reflects certain attitudes towards the world. Such beliefs and attitudes are bound up in the research traditions and language of any scientific field, and therefore it seems better to be aware of them than to deny their existence.

For this reason, we use this chapter as an opportunity to step out of the narrow niche of our specialized research topic [139] and take a somewhat broader look at the connections between the object of our study (the distribution of electric potential across a charged membrane) and the tools that we study it with (the Poisson-Boltzmann equation and ancillary mathematics and the membrane model of cylindrical pores). Thomas Kuhn [81] notes that scientists generally have little need for such speculation except during times of crisis that precede scientific revolutions, but we believe occasional reflection on these "extrascientific" questions can save us from the plight of Tolstoy's plasterers

> who are set to plastering one side of a church wall and who, taking advantage of the absence of the work's chief supervisor, in a burst of enthusiasm plaster over the windows, icons, woodwork, and the still unbuttressed wall, and rejoice that from their point of view as plasterers, everything is now smooth and even [162].

Science should never appear smooth and even.

B. Theory

Practicing scientists have had theory bred into their bones, but almost always in an informal or tacit way, so that they are usually uneasy or inept in trying to discuss it as a concept. On the other hand, philosophers of science, whose business it is to define such things, usually lack the scientist's intuitive feel for theory and often portray it as something quite unrecognizable to the scientist. In fact, the current consensus among philosophers of science is that the ideas presented in this section are inadequate for analyzing scientific theory [158], but since philosophers are not able to agree among themselves on a single acceptable alternative and since these ideas provide us with a way of looking at theory and lead us to other topics, we present them anyway, generally as they have been discussed by fluent scientists [23,40,95,118,137].

A theory (T) consists of at least two sets of statements. The first is termed the "calculus" (H)--Campbell calls this the "hypothesis"--and, depending on the scientist doing the defining, is either just made up or deduced from a large number of empirical laws. However it is proposed, the calculus by itself is abstract and may appear quite arbitrary.

The calculus becomes valuable when it is joined with the second set of "correspondence rules" (D), which Campbell refers to as the "dictionary." The correspondence rules relate or connect the ideas of the calculus to concepts (C), ideas that have meaning within the context of physical laws (L) known to be valid empirically.

It must always be possible to deduce additional statements or propositions (P) from the calculus, and if these additional statements, interpreted through the correspondence rules, imply or are consistent with known physical laws, then the proposed theory is deemed valid (Figure 6.1).

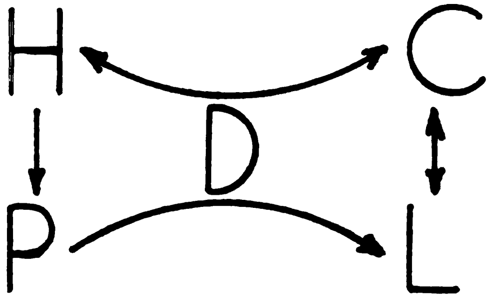

Figure 6.1. Interrelationships involving theory.

If P turns out to be inconsistent with L, then there are usually renewed attempts to find another P that is consistent.

If this is not possible, T itself may be called into question.

In the present study of the Poisson-Boltzmann equation, for example, T is the theory of electrostatics, from which may be deduced P, including Poisson's equation, the particular solutions for $\psi_1(z)$ and $\psi_2(z,r)$ in Equations (3.120) and (3.7) respectively, and finally the expression for E_M in Equation (3.121).

From D we know the correspondences between H and C. For example, $\psi(z,r)$ in H corresponds to electric potential in C, ρ in H, through the definition in Equation (1.4), is related to the Faraday constant, ionic charge, and concentration in C, etc.

We did not perform all the previous mathematical derivations in order to determine whether electrostatics is valid or not; we implicitly believe that it is. Our intent was obviously much more modest. By beginning with a theory that we accept, we are able to test the various (and numerous) assumptions that we made in moving from T to P. Indeed, Equations (3.123) and (3.124) are the main predictive results of our endeavor in that they can be tested against experimental results. If our equations agree with experiment, then we can also feel confident about our results for ψ_1, Equations (3.115) and (3.120), and ψ_2, Equation (3.7), even though these are not experimentally accessible quantities.

If, however, our equations are not in accord with experiment, then our first impulse will be to question the experiment's results and/or suitability. Did the experimenter make any errors in his measurements? Is there a systematic error in the method that could account for the differences? Once we are satisfied that there is no experimental error, we will ask whether the experiments performed actually are a test of our equations. Do the experimental conditions conform to those that we invoked at the beginning of the derivations?

If the experiments seem both correct and applicable, we will set about deriving a new P to test against experiment. Another P incompatible with experimental result will still be unlikely to cast doubt on the theory of electrostatics. Instead, we would probably question the validity of the Poisson-Boltzmann equation, a macroscopic statement, to the system we wish to describe. We may then find a lower limit in size for which the equation is applicable. In this sense the failure of P to agree with experiment may provide us with more definitive information than would agreement, which can tell us nothing about the uniqueness of the derived P.

We assume that we have a T and, we hope, a P consistent with L, but Campbell claims that this is not enough:

> Any fool can invent a logically satisfactory theory to explain any law.. . . If nothing but this were required we should never lack theories to explain our laws; a schoolboy in a day's work could solve the problems at which generations have

> laboured in vain by the most trivial process of trial and error. . . . It is never difficult to find a theory which will explain the laws logically; what is difficult is to find one which will explain them logically and at the same time display the requisite analogy [23].

The key word in this quote is the final one: analogy. Campbell insists that besides being logical, a successful theory must also be analogous to known laws, although Duhem, in acknowledging the heuristic importance of analogy, allows the analogy to exist with other theories.

Modern scientists from Sir Humphrey Davy [33] and James Clerk Maxwell [107] to the present [35,86,182] have recognized the role of analogy in the progress of science, and most writers on this topic equate analogue (the thing analogous to T) with model. In trying to minimize the differences between Duhem and Campbell, who are invariably cited as the starting point for all discussions about scientific models, D. H. Mellor [112] argues that both physicists sharply distinguish between analogues and models, i.e., mechanical models, and more or less agree on their relative importance, although Campbell regards the former as essential to theory, while Duhem does not. Mellor then proceeds to distinguish models as consisting of observable entities--in the sense of being part of a successful theory's observation language--referred to by the set of laws that make up the analogue.

This is very close to the idea of model that we wish to use. In order to make this idea more clear, we back up and approach it from a different perspective, that of the interaction theory of metaphor proposed by Max Black.

C. Metaphors and Models

The modern study of metaphor begins with I. A. Richards, who first named the two parts of metaphor. The terms "tenor" and "vehicle," the "thing-meant" and "thing-said" respectively [44], refer to the "two thoughts of different things active together and supported by a single word, or phrase, whose meaning is a resultant of their interaction" [141].

Max Black, however, is usually credited with the development of the interaction view of metaphor some twenty-five years after the work of Richards [13,14]. He improves Richards' terminology, pointing out that a metaphor consists of some words that function literally, the "frame" or "principal subject," and some that function metaphorically, the "focus" or "subsidiary subject." In the example, "Metaphors are pretty little maidens," the words "pretty little maidens" are the subsidiary subject, which in some nonliteral way describes the principal subject "metaphors."

After commenting on the shortcomings of the substitution and comparative views of metaphor, Black presents the interaction view. Richards says that the mind "connects" the metaphor's two ideas [141]; Black suggests how. A person reading the metaphor mentioned in the previous paragraph understands its intent by transferring his generally held conceptions about pretty little maidens to metaphors. Dictionary or literal meanings of the subsidiary subject are not so important as Black's "system of associated commonplaces." Pretty little maidens are just that: pretty and little, soft and cuddly, pleasant to look at, but insubstantial. So are metaphors. Such commonplaces obviously need not even be true for an effective metaphor; they need only be readily evoked.

While the subsidiary subject bears on the principal subject, the latter turns back on the former--Polanyi [132] likens this to the effect of the thing symbolized on the symbol--and the two "interact" to form a whole. Those traits of the subsidiary subject that make sense in terms of the principal subject are brought to the foreground, while those that do not are relegated to the background. The metaphor acts as a filter; it "suppresses some details, emphasizes others--in short, <u>organizes</u> our view" of metaphors in terms of pretty little maidens [14]. It may even "generate new knowledge and insight by <u>changing</u> relationships between the things designated" [13].

William Empson makes somewhat the same point when he says that

> a metaphor may be a matter of "insight"; it may be used to survey a whole complicated matter as if from a height; it is a device for letting you handle the proportions of the matter intuitively, instead of fiddling about with first one part and then another [44].

The similarity between the functions of metaphor and theory in this respect is apparent from Duhem's comments in speaking of the economy of thought in theories:

> To bring directly before the visual imagination a very large number of objects so that they may be grasped simultaneously in their complex functioning and not taken one by one, arbitrarily separated from the whole to which they are in reality attached--this is for most men an impossible or, at least, a very painful operation [40].

With metaphor well in hand, Black proceeds to models. He distinguishes four types, of which "theoretical models" interest us here. Unlike most other kinds of models, theoretical models cannot be physically constructed; they consist of descriptions and assumptions: "the heart of the method consists in <u>talking</u> a certain way" [14]. Peter Achinstein outlines the characteristics of a theoretical model as follows [4]:

1) a set of assumptions about some object or system;
2) a description of what might be called inner structure, composition, or mechanism;
3) a simplified approximation;

4) a part of a broader framework of some more basic theory or theories; and frequently

5) a formulation on the basis of an analogy.

In our work we applied the machinery of electrostatics, and the Poisson-Boltzmann equation in particular, to the distribution of electric potential across a charged membrane. To attempt this with an actual membrane raises insurmountable mathematical problems: the membrane's geometry is irregular, and necessary physical characteristics, including boundary conditions, are unknown. Instead we chose an idealized membrane with straight, rigid, uniform cylindrical pores in place of the presumably tortuous routes or channels that somehow open and close to allow ions across a real membrane. Our theoretical model provides us with a way of talking and applying the mathematics of electrostatics. In Stephen Toulmin's words, our model puts "flesh on the mathematical skeleton" [164].

Richard Braithwaite states that a theory and an appropriate model share the same calculus [17]. In terms of the idea of model that we wish to develop here, perhaps we should modify this to say that there exists a one-to-one correspondence between the statements of the theory and those of the analogue with which the model is associated. In the view of Carl Hempel, a theoretical model has the character of a theory with a more limited scope of application [63], and in fact in our study, the analogue to the theory is a specific part of the theory, so that this accounts for the two having the same calculus.

Black discusses the problem of scientists' attitudes towards theoretical models. He quotes Maxwell, who initially talks about the ether as "merely a collection of imaginary properties" [106], but later discusses it as something physically real that fills all of space [108]. There is a significant difference between treating a model as a heuristic fiction and as a physical reality, the difference, as Black points out, between thinking of space _as if_ it were filled with an actual medium and as _being_ filled with it.

In connection with this, Romer says

> If the model is no more than an intellectual tool, then there is little point in discussing, for example, wave-particle duality . . . It is only as we believe that light really behaves like waves and like particles that the implied contradiction begins to interest us [142].

Perhaps in our case, there is less chance of identifying our model with the inner structure of a real membrane because the differences are quote obvious, yet there are commercially available artificial membranes with straight, uniform cylindrical pores produced from neutron bombardment [119]. Here at least the geometrical distinctions between our model and a real physical system are not so great, and we may feel, like Maxwell, that the results from our model must say something about the actual situation in such a membrane under the conditions we impose.

However we view the ultimate nature of our model, we must admit that it resembles a metaphor in terms of its "analogical transfer of a vocabulary" [14]. Black talks of the commonplace implications in metaphor, while he admits that specific scientific knowledge is required for model construction. Although Black himself says little about this topic, Thomas Kuhn has a good deal to say.

D. Paradigms and Language

Probably no philosopher of science has created so much furor in recent years as Thomas Kuhn, whose *Structure of Scientific Revolutions* [81] presents a theory of science that emphasizes the sociological and revolutionary, rather than cumulative nature of scientific progress. His critics are legion [26,83,85], and Kuhn has responded to them on numerous occasions [79,80,82]. Regardless of the shortcomings of his theory for the philosophy of science in general, his idea of paradigms fits very nicely with our specific analysis of scientific models.

Basically, Kuhn portrays the development of a science as proceeding from a period of "pre-science," which consists of more or less random fact gathering, to "normal science," which he characterizes as "research firmly based upon one or more past scientific achievements, achievements that some particular scientific community acknowledges for a time as supplying the foundation for its further practice" [81]. The sociological nature of his ideas is already obvious. That these achievements are capable of spawning such normal science, which Kuhn frequently refers to as puzzle solving or even mopping up, arises from two conditions:

> (1) these achievements were sufficiently unprecedented to attract an enduring group of adherents away from competing modes of scientific activity; and
>
> (2) they were sufficiently open-ended to leave all sorts of problems for the redefined group of practitioners to solve [81].

Kuhn terms achievements that fulfill these two conditions "paradigms":

> By choosing it, I mean to suggest that some accepted examples of actual scientific practice--examples which include law, theory, application, and instrumentation together--provide models from which spring particular coherent traditions of scientific research [81].

Much of the criticism directed against Kuhn concerns the imprecise, and in fact multiple meanings of paradigm, and in much of his response he tries to define it more exactly, even renaming it "disciplinary matrix," yet as he responds to each critic, the notion of paradigm becomes less and less clear.

The object of normal science is to work out the implications of the paradigm. Naturally, there are always problems that cannot be solved in terms of the paradigm; although they challenge the foundations of the paradigm, they are usually ignored. It is the build-up of such problems, termed anomalies by Kuhn, to a point that they cannot be ignored that brings on a period of crisis, a time when scientists uncharacteristically question the ultimate basis of their paradigm. The crisis may eventually be solved with the methods of the current paradigm; the anomalies may be set aside; the paradigm may be rejected in favor of a new one, which usually arises in some extra-scientific way. This latter case is termed a scientific revolution, and scientists, at least those who can shift their allegiance, set about working out the "normal-science" implications of the new paradigm.

It is the idea of paradigms as bodies of research tradition that interests us here. Whether science does or does not develop in such a manner, it seems to us that the existence and importance of particular research traditions cannot be denied.

Students are initiated into particular research communities through a long apprenticeship that begins with introductory science courses and frequently culminates in a doctoral dissertation. During that time the student has absorbed the paradigm of his chosen research specialty and has mastered problems that progressively "become more complex and less completely precedented" [81]. Kuhn argues that scientists never learn concepts, laws, theories, etc., in the abstract, but "with and through their applications," which "are not there as embroidery or even as documentation. On the contrary, the process of learning a theory depends upon the study of applications, including practice problem-solving both with a pencil and paper and with instruments in the laboratory" [81].

Thus an undergraduate majoring in chemistry learns to view the world in terms of the paradigm held by the community of scientists who consider themselves chemists. The problems available for study, the theoretical and experimental tools available for attacking those problems, the acceptable forms of answers, these are all determined by the paradigm. As a graduate student who further specializes in physical chemistry, the trainee comes to regard the world in terms of a more specialized paradigm. In equipping a scientist to do research in a particular discipline, a paradigm implicitly imparts to that individual a particular view of the world that he is to study. He expects the world to be a certain way, and as long as it is, the paradigm is successful. It is impossible, in these terms, to imagine how Duhem, trained as a nineteenth-century physicist, could escape having the ultimate beliefs of nineteenth-century physics ingrained in him.

Despite the importance of language for paradigms--since it is the means by which we learn science, disseminate new findings, and ultimately hold our world view--Kuhn spends remarkably little time on it, but what he does say is pertinent. The language used by scientists "embodies a host of expectations about nature and fails to function the moment these expectations are violated." He adds:

> This is not to suggest that pendulums, for example, are the only things a scientist could possibly see when looking at a swinging stone . . . But it is to suggest that the scientist who looks at a swinging stone can have no experience that is in principle more elementary than seeing a pendulum. The alternative is not some hypothetical "fixed" vision, but vision through another paradigm, one which makes the swinging stone something else [81].

E. Fred Carlisle, in his discussion of discourse as it relates to both literature and science [24], points out similar attitudes in the writings of other philosophers of science [59,67,85,133] and makes a beginning at developing some of these ideas. Within the framework of James M. Edie's so-called appresentational view of language [43], Carlisle applies the four levels of reference, or layers of meaning in discourse, to the way that words bear meaning in scientific, as well as literary language.

"Words designate and signify. They point to experienced things and they carry meaning. These two primary functions permit us to organize and communicate experience" [24]. This is the level of the "given," that which is directly and intentionally presented. The three other levels of reference refer to the "given-with," that which is appresented, only implied or expressed indirectly.

Discourse "directs attention toward our experience itself . . . toward the ways we organize and interpret experience and differentiate regions of experience" [24]. According to Carlisle, areas of discourse develop mainly through shared interest, attention ("the *way* one attends to reality"), and intention ("*how* one takes reality").

Discourse, as a form of intersubjective communication, also refers

> to *the expressive-communicative context* out of which it arises . . . through expression and communication, speakers and listeners . . . build up a store of sedimented meanings and functional codes that define regions of discourse and constitute the world view of a linguistic community or the scientific and artistic vision of more specialized communities [24].

Although this level obviously overlaps the previous one, the emphasis here is on the speaker and the listener themselves, the people involved in the discourse, while the previous level emphasizes the experience that provides the basis for the discourse.

Finally, discourse contains "the 'store of sedimented meanings,'" which include "the circumstances, institutions, and traditions within which a discourse occurs and out of which it arises, and it also involves the original, prior meaning of words or a discourse" [24].

The three appresentational levels of reference in particular indicate that the adherents to a particular paradigm speak their own language [149]. In a paper on the philosophy of chemistry, D. W. Theobald [160] suggests that there are many answers to the question "What is an electron?" A solid-state physicist has a different conception of an electron from that of an organic chemist, and indeed their answers may even be incommensurable with each other, yet each is a valid answer within the framework of its appropriate paradigm. This indicates why scientists from different disciplines frequently have difficulty discussing topics of supposedly mutual interest with each other. They may be using the same words, but with different appresentational levels of reference.

Thus we see in paradigms the complex network of implications that can function for models as Black's commonplaces function for metaphors. Just as a layman can evoke from his general background a list of commonly held ideas about pretty little maidens in order to complete the metaphor, a physical chemist can evoke from his paradigmatic background a comparable list of commonly held ideas about charge and ions and electric potential in order to evaluate the model we have chosen to study membranes. If a listener from a culture where there are no pretty little maidens or where ideas about them are vastly different from those of the speaker, the listener may either not understand the metaphor or ascribe to it a different meaning from that intended. Similarly, an adherent to a paradigm in which charge, ion, and electric potential have no meaning or different meanings from those in physical chemistry may construe our model differently than we do.

At last, we have reached a position to consider the final topic of this chapter, the ways that models, paradigms, and language shape scientific explanation.

E. Explanation

Margaret Boden strikes close at least to the dictionary definition of "explain" when she says that it is to make a thing "somehow more intelligible" [16]. Ian T. Ramsey speaks of "insight" that allows us to "articulate" [136]. For W. H. Leatherdale, it is the retention of this insight that is essential to understanding and enables other people as well to understand the discovery [86]. Karl Popper relates this to "testability" [134]. There are as many views of explanation as there are explainers [3,6,19,64, 72,163,170], but the one idea that constantly recurs is that of the analysis of complex phenomena into the "natural" or "familiar" that requires no further explanation.

If the listener can somehow decompose the phenomenon being explained into terms that are familiar to him, he feels that he has grasped its meaning; he can make the phenomenon compatible with his own framework of knowledge. In terms of scientific explanation then, it is the framework of knowledge developed within a paradigm that enables its adherents to "understand," both as students trying to learn the paradigm and as practicing scientists trying to work out its implications.

This agrees with the view of D. W. Theobald, who discusses explanation in terms of emphasis and style:

> Explanations have to be rational . . . Rationality means no more than that explanations have to be commonly reasonable <u>in the circumstances</u>, and this alone guarantees our understanding [160].

Although a paradigm cannot be said to guarantee understanding, it certainly provides the "natural" and "familiar," the language for articulation, the means for insight, the criteria of testability, all the necessities for rationality within the circumstances. Indeed, each paradigm is its own justification for the explanations that it sanctions.

This makes it clear why the solid-state physicist and the organic chemist cannot accept each other's explanations about the electron. Committed to a particular paradigm and the understanding that it affords, a scientist can understand only in terms of that paradigm; he has neither the means nor the inclination to understand in terms of someone else's. He knows what constitutes an explanation--his paradigm tells him--and therefore it is not what the adherent to another paradigm says it is. The unwary scientist may become a victim of his paradigm in the sense that Colin Turbayne refers to as being used by metaphor:

> the victim of a metaphor accepts one way of sorting or bundling or allocating the facts as the

> only way to sort, bundle, or allocate them. The victim not only has a special view of the world but regards it as the only view, or rather, he confuses a special view of the world with the world. He is thus, unknowingly, a metaphysician [166].

So far we have discussed only the circumstances that allow explanation. In order to try to look at explanation itself, we return to theory. As one of the characteristics of theory, Romer lists explanation, which, he says, "implies that we have identified the true cause of it" [142].

We have three objections to this. First, in terms of paradigms, there can be no true causes in the absolute sense, only appropriate or rational ones. Science is not some asymptotic approach to Truth, but a succession of increasingly successful visions of various truths. Secondly, the theory, at least its calculus, can often be applied to quite different kinds of phenomena. For example, even a quick look at chapters on heat flow in cylinders [25] and chemical diffusion in cylinders [32] reveals the mathematical similarities to our equations of potential distribution in a cylinder. There is nothing in the theory itself to explain the particular set or sets of phenomena that it applies to.

Finally, and most compellingly, mathematics, which is the basis of theory, is a descriptive language; it provides no explanations.

> Mathematics can be expected to do no more than draw consequences from the original empirical assumptions. If the functions and equations

> have a familiar form, there may be a background of pure mathematical research readily applicable to the illustration at hand. We may say, if we like, that the pure mathematics provides the *form* of an explanation, by showing what *kinds* of function would approximately fit the *known* data. But *causal* explanations must be sought elsewhere [14].

The continual appearance of Bessel functions, both regular and modified, in our attempts at a solution for $\psi_1(z)$ results from the mathematical analysis of the problem and provides no basis for explaining that particular form of the electric potential.

If theory does not explain, do theoretical models? A number of philosophers of science think so, but how these models provide an explanation is not always clear [5,73, 100,161]. Mary B. Hesse discusses explanation as a metaphoric redescription of the phenomenon to be explained in terms of the model [65]. The model's terminology is transferred to the principal subject, whose own observation language is both altered and extended. Peter Gärdenfors suggests that such redescription must be evaluated within a "knowledge situation" [50], i.e., in our terms, within a particular paradigm.

With our idea of model associated with an analogue A analogous to H, we can diagram a model (Figure 6.2) as we did theory earlier. In this case, however, the concepts C_A and laws L_A are valid for the model rather than any physical system. The replacement of the theory

$$\begin{tikzcd}
A \arrow[rr, leftrightarrow, bend right] \arrow[dd] & & C_A \arrow[dd, leftrightarrow] \\
& D_A & \\
P_A \arrow[rr, bend left] & & L_A
\end{tikzcd}$$

Figure 6.2. Interrelationships involving the analogue associated with a model.

diagrammed in Figure 6.1 by the model diagrammed above constitutes this metaphorical redescription and provides the basis for explaining the phenomenon. Concepts C and L are replaced by concepts C_A and laws L_A respectively, and this tacit correspondence imparts the physical reality to our model that provides it with its explanatory power. As Herbert Butterfield says,

> this modern law of inertia is calculated to present itself more easily to the mind when a transposition has taken place--when we see, not real bodies, moving under the restrictions of the real world and clogged by the atmosphere, but geometrical bodies sailing away in empty Euclidean space [22a].

Michael Scriven charges that all laws of nature are known to be in error [148]. This seems natural if we consider these laws refer directly to a model and only indirectly to a genuine physical system. This is implicit in a scientist's discussion of a particular law and the reasons why it does not describe nature exactly. There are always conditions or restrictions on the physical system that must be met, restrictions that in essence define the model for which the law is exact. Thus models are substitutes for real systems, and this provides them with explanatory power.

F. A Last Look at Electric Potential

As we remarked earlier, there are numerical solutions of the Poisson-Boltzmann equation for a system similar to ours [46,55,144]. We have claimed that they offer numbers with little accompanying explanation. What of our method?

We separate the total potential inside the capillary into $\psi_1(z)$ and $\psi_2(z,r)$, in the latter of which, we claim, z and r cannot be further separated. In the first papers that we can find that make this separation, the authors consider $\psi_1(z)$ to result macroscopically from the imposition of a concentration gradient across the interface separating the two solutions [46,116]. This is essentially the diffusion potential across the interface. Once a capillary structure is assumed for the membrane, $\psi_2(z,r)$ represents the distortion of the original potential; i.e., it is a measure of the effects of the departure from electroneutrality.

The separation of the total potential into these two parts is very closely related to the model explaining capillary osmosis, which is the volume flow in the presence of a concentration difference, but in the absence of applied pressure and electric potential gradients [37]. B. V. Deryagin and his colleagues propose that in the presence of a tangential concentration gradient, the interaction between the ions and a charged solid surface produces microgradients of both pressure and electric potential [36,38,39,41]. These induced gradients then produce a volume flow analogous to that of reverse osmosis and electroosmosis respectively, so that adherents to paradigms in which these two phenomena are familiar have received a satisfactory explanation of anomalous osmosis.

Electroosmosis, for example, may be familiar to certain scientists in terms of ionic rearrangement under the influence of an electric field and the resulting flows of ions along with their associated hydration shells [7]. This might then be viewed in the context of the Kedem-Katchalsky formulation of nonequilibrium thermodynamics [75] or a more rigorous Onsager formulation [57], but in any case, the imposition of a model occurs within a paradigmatic context with which the scientist feels comfortable. Thus if our model and treatment of the electric potential within a charged capillary membrane make sense in terms of the scientific commonplaces that they evoke, then we may feel satisfied that we have explained this particular phenomenon by presenting it in terms that need no further clarification.

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