

UNIVERSITY OF CALGARY

Theory of Electrode Polarization: Application of Variational Methods

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

CALGARY, ALBERTA

AUGUST, 2000

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Abstract

A general theory of electrode polarization for planar electrode systems is developed to account for ionic shielding of the electrodes at low frequency in an electrolyte solution. A general model is derived based on the balancing of forces acting on the ions in solution. A variational theorem, based on the normal modes of the system of differential equations obtained from the model, is used to calculate an optimal approximate solution. These analytic variational solutions are used to account for the ionic shielding of the electrodes for a large variety of planar electrode arrays.

Acknowledgements

I am sincerely grateful to my supervisor, Dr. Reg Paul for all that he has taught me. It has been an inexhaustible source of pleasure working with him.

I would also like to thank Dr. Karan Kaler for many profitable discussions and for providing physical grounding to the analysis.

Finally, I am fortunate to have had the luxury of spending my time with Mike and Paula Cherewko, two very kind and wonderful people, and with Greg Neely, an honest man, and the best scientist I know.

To my parents,
with all my love and gratitude.

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Chapter 1

Introduction

One of the most useful, and least intrusive, methods of investigating the physical characteristics of biological cells and microscopic particles is dielectrophoresis. Dielectrophoresis relies upon the movement of polarized particles in a non-uniform electric field, where the motive force depends on the electric field, the size of the particles and the electrical properties of those particles relative to the surrounding medium. Some dielectrophoretic experiments focus on the electrical properties of the particle, and others focus on the size of the particle, all studies of this type require that the electric field in the vicinity of the particle be known.

Dielectrophoresis experiments are generally carried out in a mildly conductive *electrolyte* solution, so that at low frequencies (<1 kHz) of the applied electrical field, the ions in solution will shield the electrodes producing the field, altering the potential distribution near the particle in some unknown way. The goal of the present analysis is to account for this field shielding in dielectrophoretic data by deriving a general theory of what is called electrode polarization.

1.1 Electrode Polarization

An elementary textbook on electrochemistry (1) generally shows an electrochemical cell consisting of an *ionic* conductor sandwiched between two *electronic* conductors. The term **electrode** is rather loosely applied to the electronic conductor. As has been well stated by Oldham and Mylands (2), however, “it is possible for electricity to cross the interface between an electronic and ionic conductor...by virtue of an **electrochemical reaction** occurring there. The site of this reaction, the interfacial junction, is known as an **electrode**.” For the sake of convenience, the term electrode will be used in its more familiar sense to imply the electrode conductor and the term “electrode surface” will designate its actual physical surface.

For ac systems, the current may be classified as either conductive or capacitive current. Conductive current is the current generated by the movement of charge carriers *through* the circuit. The capacitive current comes about from the *apparent* movement of charge caused by the re-alignment of dipoles (or higher electrical multipoles) in the presence of external fields. Such a phenomenon is observed during the charging of a capacitor (**Figure 1.1**). Though the flow of *conductive* current is of great importance to many branches of physics and chemistry, such as the construction of galvanic and electrolytic cells, there are numerous other applications where it is only of secondary consideration. For example, the methods of electrophoresis and dielectrophoresis involve the generation of electrical fields in chambers containing electrolytes to investigate the

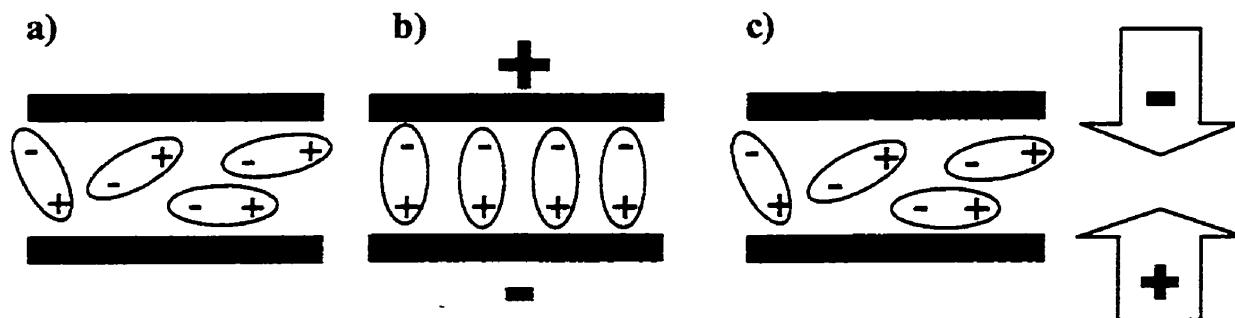


Figure 1.1 - Capacitive current. a) In a capacitor, the dielectric is pictured as an array of randomly oriented dipoles. b) If an external electrical potential is placed across the two plates of the capacitor, the dipoles will align with the field. c) When the potential is removed, the dipoles are redistributed randomly in the dielectric. The reorientation of the dipoles appears as a movement of charge across the capacitor, called the capacitive current (or displacement current), though no charge carriers have actually moved through the capacitor.

response of materials to these fields. These devices are most efficiently operated under conditions of minimum or, preferably, no conductive current flow. The concept of an electrode retains its original meaning, but interest is now focussed on the electrodes in the *absence* of current flow across the surface (i.e. in the absence of electrochemical reactions).

A class of phenomena described under the broad category of **Electrode Polarization** plays an important role in understanding the operation of electrodes. This is a process whereby a charged electrode immersed in an electrolyte solution attracts an oppositely charged ion cloud. Such a counter-ion cloud in contact with the electrode surface, along with the surface itself, is collectively called the “double layer.” From the perspective of an observer within the experimental chamber, containing the electrolyte, the double layer appears as a space charge polarization in the medium (**Figure 1.2a**). In steady state, the charge accumulated in the ion cloud will be of the same magnitude as the charge on the electrode surface, though opposite in sign. Thus, the electrode will appear completely screened to the above observer when located outside the double layer. This full screening is called *complete polarization*, or the electrode is said to be **completely polarizable**, provided no charge is directly conducted from the medium to the electrode.

The restriction that there are no electrochemical reactions at the interface implies that the charge accumulated in the double layer cannot be dissipated through the electrode. This *stable* charge polarization of the ionic medium may be visualised as a rigid “dipole”

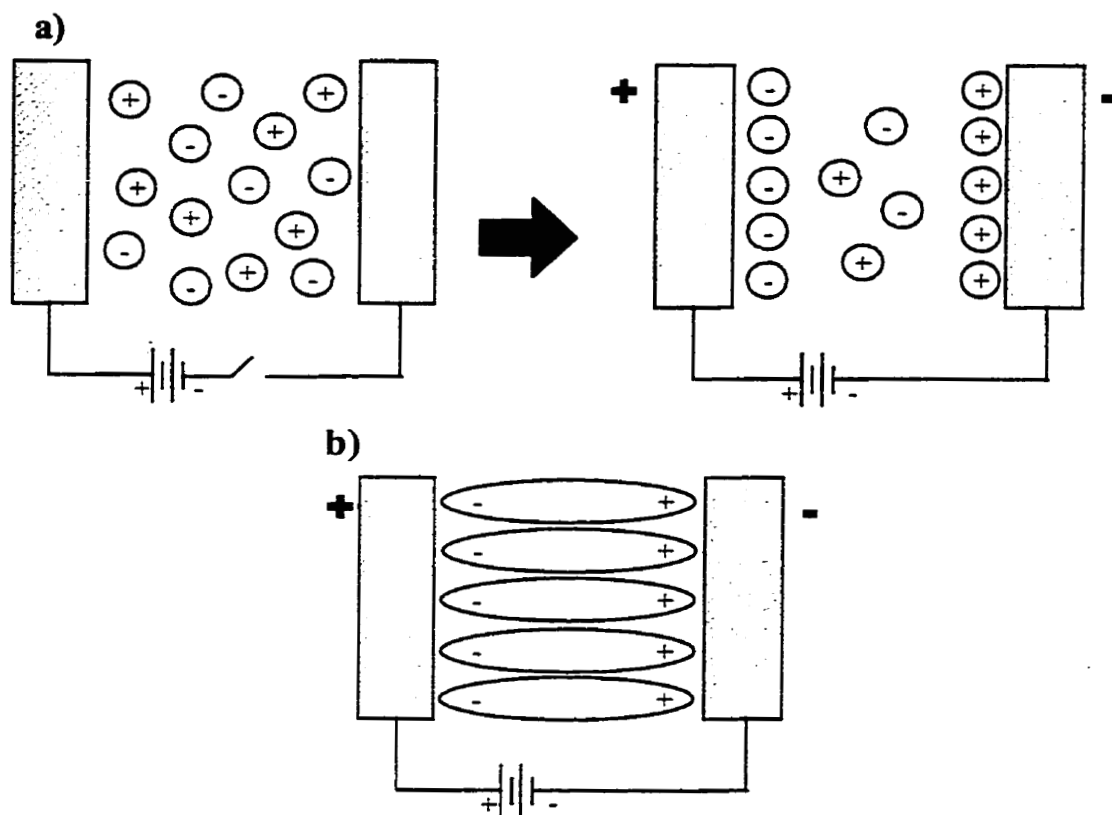


Figure 1.2 -The representation of the space charge polarization in an ionic medium as the alignment of a hypothetical "dipole" with the applied field. a) When an electric field is developed across an electrolytic solution, the ions will neutralise the charge on the electrodes by migrating to the surface. b) The situation can be represented analogously by imagining the local charge accumulations at the surface as the ends of a "dipole" aligned with the field.

aligned with the electric field (Figure 1.2b). This dipole picture has the advantage of being more conducive to electronic circuit modelling than the charge cloud picture. Moreover, an electronic circuit model can clarify the study of electrode polarization considerably.

When an ac potential is applied, current flows even in the absence of electrochemical reactions. This current is due to the “re-orientation” of the “dipoles” as they attempt to follow the alternating polarity of the electrodes (Figure 1.3), and as alluded to above, it is called a capacitive current. A certain amount of time, called the *relaxation time*, is associated with the re-orientation process. At low frequencies, when the period (period = $1/\text{frequency}$) is longer than the relaxation time, the “dipole” will be fully aligned with the alternating field, leading to complete polarization. At frequencies with periods shorter than the relaxation time, the dipoles will be unable to follow the field, and therefore unable to provide complete screening. Thus, *the polarization, P , of the medium, falls to zero when the period T ($T = 1/f$; where $\omega = 2\pi f$) of the applied potential becomes much shorter than the relaxation time* (Figure 1.4). It follows, therefore, that the magnitude of the relaxation time is an important parameter within the context of electrode polarization. Calculation of the relaxation time allows the investigator to predict the frequency ranges over which the ionic screening of the electrode will be present. Such information is of vital importance, since the screening of the electrodes can influence, in an unknown manner, both the magnitude and frequency dependence of the field within the experimental chamber. As a consequence serious errors may result in the computation of dielectrophoretic and electrophoretic forces in the chamber.

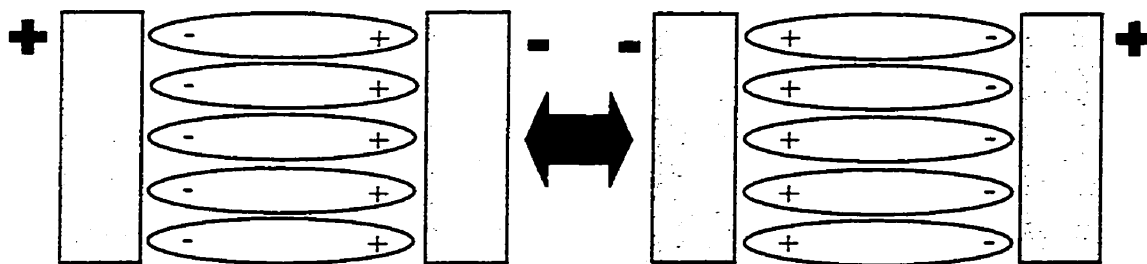


Figure 1.3 - If the field alternates in time, then the dynamic migration of the ions can be imagined as the flipping of a hypothetical "dipole."

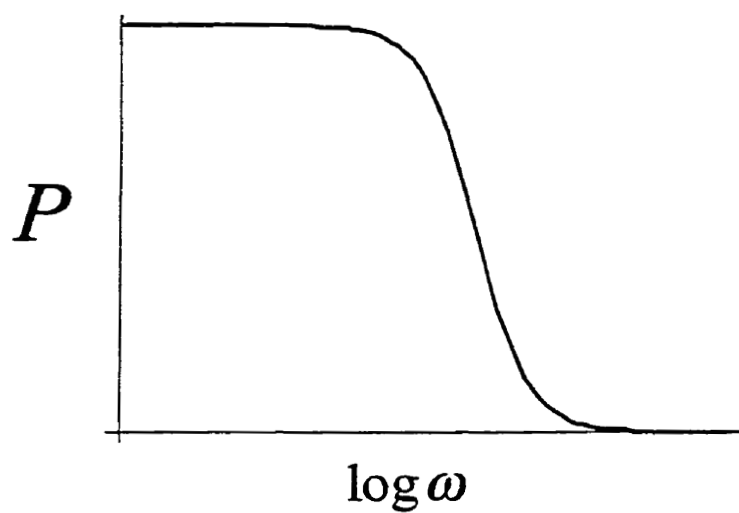


Figure 1.4 - When the field alternates faster than the “dipole” can respond, the ions are unable to completely screen the electrode surface. Consequently, the space charge polarization, P , falls off to zero as the frequency of the applied potential, ω , increases.

Since there is only a single mechanism of polarization in the above description (i.e. the space charge polarization in the ionic medium), there is a single relaxation time associated with the process. An electrical circuit consisting of a resistor in series with a capacitor (**Figure 1.5**) can easily model such a single relaxation process. In this view, the relaxation time of the system is the RC time constant of the resistor-capacitor circuit. Furthermore, the difference between the potential in the bulk (regions outside the double layer) compared to the potential applied to the electrode is generally expressed as a voltage drop across the impedance of the double layer. The advantage of the electrical circuit model is that it allows the vast storehouse of problem solving mechanisms developed in circuit theory to be brought to bear on the study of ionic dielectrics.

In the context of the resistor-capacitor model, the “dipole” picture is re-cast in a manner that allows correspondence with the circuit elements. The resistor in the circuit is the resistance (expressed through the drag coefficients of the ions) the “dipoles” must experience while moving through the medium. While the capacitance is the capacity of the “dipoles” to store charge, a property related to the ability of the “dipoles” to align themselves with the field. The capacitance lends an explicit frequency-dependent character to the circuit.

For pure ac stimulation, during a complete cycle both electrodes (assumed to be identical) experience symmetrical screening from both the positive and negative ends of the “dipoles” (cf. **Figure 1.3**). More realistically, however, there is some dc bias present across the electrodes, generated by either the contact potentials for electrodes of different

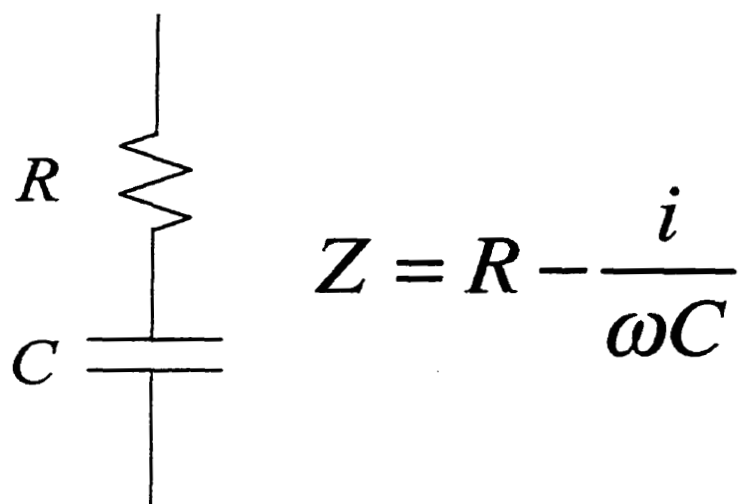


Figure 1.5 - A schematic drawing, and expression for the impedance, of a resistor and a capacitor in series.

materials, or some external battery connected to the circuit. This dc bias breaks the symmetry between the electrodes by creating chemically distinct *static* double layers superposed upon the symmetric *dynamic* double layer formed by the ac field. Chapters 5 and 6 describe the symmetry breaking in detail, extending the physical interpretations of the double layer behaviour from the governing system of equations.

The “rigid dipole”/“electrical circuit” model provides a qualitative description of electrode polarization. From an experimental point of view, what is needed is a quantitative, predictive mathematical model. Gouy (3), Grahame (4), Chapman (5), Stern (6), Debye, Hückel (7) and others developed such a model for dc systems, but new methods are required for the most general case: a dc bias offsetting an ac-applied potential. The next section will be devoted to highlighting some of the recent work done in search of a generalised mathematical description of electrode polarization.

1.2 Mathematical Models

There has been much work done over the past hundred years directed toward explaining electrode polarization. The approaches can be loosely divided into two groups: those using empirical methods to *fit* the data and those building from fundamental principles to generate functions that *predict* the data.

The empirical camp has met with great success in the study of general dielectrics (8), aqueous dielectrics (9), and the dielectric response of biological membranes. The reader

is referred to the reviews by Geddes (10) and Schmukler (11) for a more detailed historical overview of empirical polarization models. A brief highlight of some of the earlier work will be given nonetheless.

In brief, by postulating diffusion driven processes and examining early polarization data, Warburg (12) suggested that the frequency dependence of the resistance and the capacitance of an ionic dielectric are equal. Both decaying as the reciprocal of the square root of the angular frequency, ω ($\omega = 2\pi f$, f is the field frequency), of the applied field, leading to an expression for the complex permittivity of the medium, $\varepsilon^*(\omega)$:

$$\varepsilon^*(\omega) \propto \frac{1}{(i\omega)^{0.5}} \quad [1.1]$$

Later, Fricke (13), using data over a broader frequency range, modified Warburg's formulation to a more general equation, abandoning the exponent 0.5. In Fricke's formulation the capacitance and resistance are not equal, but related to the frequency through a constant m , such that the permittivity is given by the following:

$$\varepsilon^*(\omega) \propto \frac{1}{(i\omega)^m} \quad [1.2]$$

Where,

$$0 < m < 1 \quad [1.3]$$

Schwan (14) and Onaral (15) have extended the work of Warburg and Fricke by suggesting that the parameter m is itself a function of frequency, so that:

$$\varepsilon^*(\omega) \propto \frac{1}{(1 + i\omega\tau)^m} \quad [1.4]$$

$$0 < m(\omega) < 1 \quad [1.5]$$

where τ is the *relaxation time* of the ionic dielectric.

Schwan's permittivity equation was recently derived in a more formal manner by Sun, Charef, Tsao, and Onaral (16) as a cascade of poles and singularities, allowing m and τ to be empirically calculated within some prescribed error. Yet, for all this parameterisation, the fundamental physical processes underlying electrode polarization have eluded both experimentalists and theoreticians. Nevertheless, experimentalists have remained optimistic that the physical processes will be finally elucidated. To quote Sun *et al.* (16), "...succinct mathematical descriptions are...worthwhile in organising and streamlining experimental data even in the absence of physical interpretation. Moreover, they often hold the potential to yield physical insight at a later time and, in this capacity, have predictive value on their own, especially when parameters are reproducibly and strongly linked with experimental variables."

One of the drawbacks of the empirical approach is that the investigator must postulate a function to fit the data. The subsequent conclusions are largely determined by this choice. Classical molecular ionic-dielectric theory predicts a *continuous* distribution of relaxation times arising from stochastic phenomena at the molecular level. Indeed various authors have made a variety of empirical choices for the distribution functions and these choices characterise the tastes of the individual working in the field (17). Typically, these functions result in a distribution of relaxation times about a single mean relaxation time. Although the behaviour of homogeneous *molecular* dielectrics can be modelled as single relaxation processes, there is no guarantee that *ionic* dielectrics can be modelled in this fashion. In fact, from consideration of the chemical potential asymmetry in the system, a single relaxation model seems altogether inappropriate for describing aqueous ionic dielectrics. Theoretical models, based on the balance of forces operating on the ions, have begun to provide clearer insight into the relaxation process itself, suggesting that for a symmetric electrolyte, the data be fit to a dispersion about *two* relaxation times.

In the force balance models, the ionic drift velocity is attributed to a balance of electrical and thermodynamic forces. The electrical force, resulting from both the applied ac field and a dc bias is expressed as the gradient of an electrical potential. The thermodynamic force, resulting from ionic concentration profiles in solution is expressed as the gradient of a chemical potential. The resulting equations, when linearized in the applied field, generate a system of second-order differential equations. These equations can not be solved analytically at the present. Several workers have attempted to approximate the solutions of these equations. To the extent that the system can be solved

numerically, the behaviour can be *simulated*. To the extent that numerical solutions are replaced by analytic functions, the system can be *modelled*. Ideally, it is the modelling approach that allows an understanding of the fundamental physical principles governing electrode polarization.

DeLacey and White (18) developed the first general model. Using a matrix diagonalization technique, they were able to derive an analytic expression for the electrical potential in the double layer under pure ac conditions. However, their analysis required a numerical algorithm to simulate the inclusion of a dc bias.

Gunning, Chan and White (19) used a low-frequency perturbation method (similar to Newman (20) in the pure dc case) to incorporate the effect of the dc bias. The analysis promises a completely analytical solution to the general system of equations, but is restricted to the low frequency domain. Furthermore, the equations are hard to interpret, and difficult to implement.

Scott, Paul, and Kaler (21), building on the analytic results of DeLacey and White, have used a variational theorem to incorporate the effect of the dc bias. The variational approach has the advantage of being completely analytic for typical experimental conditions and, by making a suitable choice for the trial functions, a close contact with the physical processes can be maintained.

The analytic solutions afforded by the variational method suggest that the time-averaged permittivity of the medium will show multiple *discrete* relaxation times, and not a *continuous* dispersion about a single mean relaxation time:

$$\langle \varepsilon^*(\omega) \rangle_t \propto \frac{1}{n} \left[\frac{1}{1+i\omega\tau_1} + \dots + \frac{1}{1+i\omega\tau_n} \right] \quad n=1,2 \quad [1.6]$$

1.3 Summary

In the absence of electrochemical reactions, the interface between electronic and ionic conductors still exhibits complicated behaviour. In particular, electrode polarization, a process describing the potential drop across the double layer, has been the subject of vigorous experimental and theoretical investigation. It is the goal of this investigation to approximately solve the governing system of differential equations (Chapter 2) using a variational theorem (Chapter 4), then apply these results to uncover hitherto obscured aspects of electrode polarization, including a general elucidation of the relaxation behaviour of ionic dielectrics (Chapter 6).

Chapter 2

Basic Model and Governing Equations

In the present analysis considers a general electrode constructed from a planar supporting sheet of an insulating substance on one surface of which has been micro-machined a system of conducting strips. The geometry of the strips is arbitrary, and may comply with several existing forms that have been described in literature (22, 23, 24), which include parallel strips, concentric rings or simply a homogeneous conducting coating (**Figure 2.1**). If the field exists in a region *free of ions*, then it is assumed that the electrical potential distribution $\Psi(x, y, z, t)$ is of the form:

$$\Psi(x, y, z, t) = g(x, y, z) V e^{i\omega t} \quad [2.1]$$

Where x, y and z are spatial co-ordinates (**Figure 2.2**), and t is a time variable. V is the amplitude of the applied potential, alternating with angular frequency ω . The geometry of the potential distribution on the surface of the electrode, and the bulk solution, is represented by the dimensionless differentiable function $g(x, y, z)$.

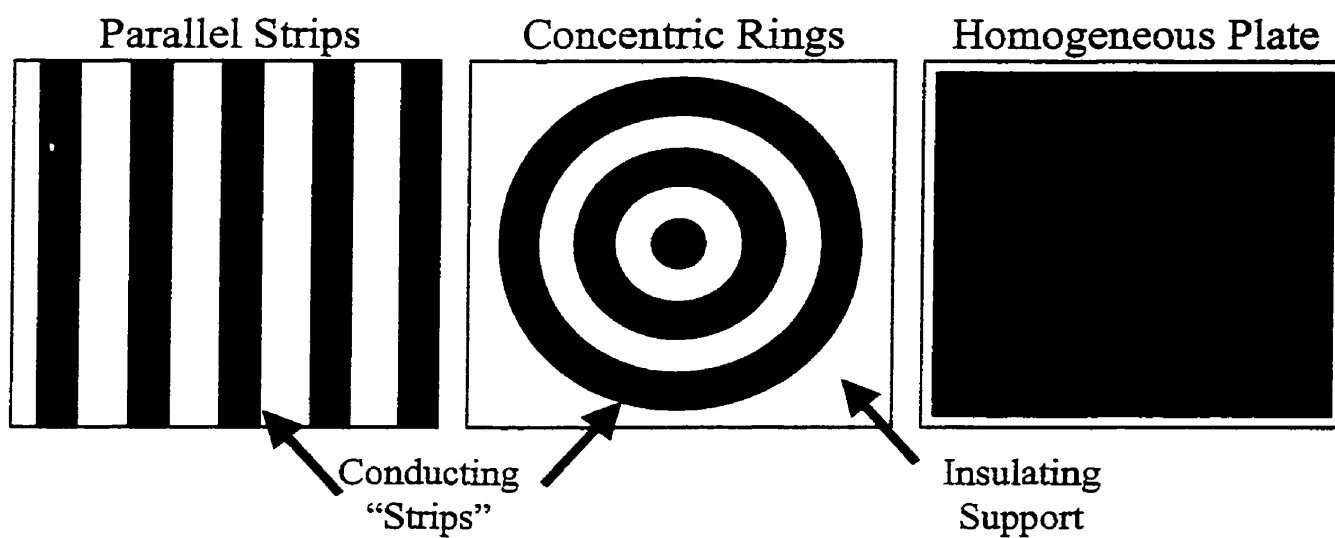


Figure 2.1 - Examples of various planar electrode array geometries.

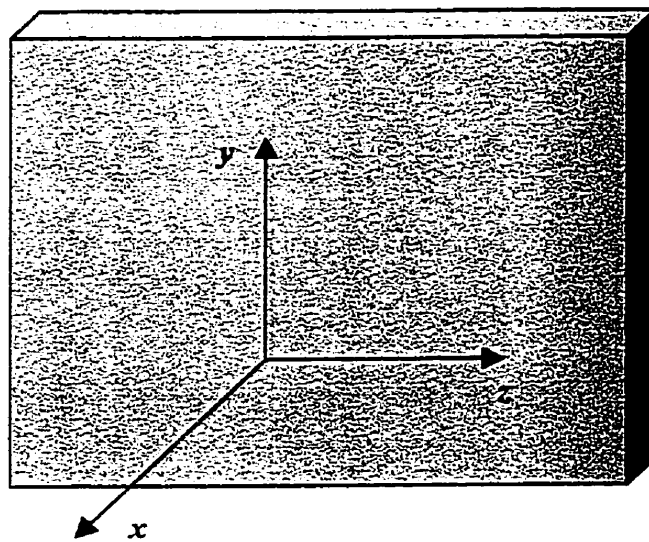


Figure 2.2 - The co-ordinate system.

Most dielectrophoresis, electrorotation, and electrophoresis experiments are performed in an ionic medium. A flux will develop due to the applied field, carrying the ions to the electrode surface. These ions will create a double layer, screening the electrode from the object under experimental study. Thus, the potential will no longer be given by eq. [2.1]. A completely general exposition of the effects of the double layer is difficult; investigation is therefore focused on a simplified model made with the following assumptions:

1. In the presence of ions in the medium, the potential far from the electrode can be expressed by the same mathematical form as eq.[2.1], but with a modified constant, called the *effective potential* V_{eff} , that incorporates the role of the double layer, such that:

$$\frac{V_{eff}}{V} \leq 1 \quad [2.2]$$

V_{eff} is a complex quantity that will describe the amplitude and the phase of the effective potential. The reason for the complex nature of V_{eff} lies in the fact that it is a quantity arising from the response of the ionic medium to an alternating field and such a response will display a phase that lags behind the excitation.

2. During the formation of the double layer, the ionic flux will have components both normal and tangential to the electrode surface. The present model *will only consider*

the normal component, enabling the use of a one-dimensional system of equations. In view of this approximation, and to keep the appearance of the equations as simple as possible, *explicit display of the variables y and z will be suppressed*.

To determine the extent of screening of the electrode by the electrolyte, a dimensionless function $\psi(x)$ is calculated to describe the attenuation of the electrical potential by the double layer. The model is constructed by deriving the Poisson's equation for $\psi(x)$ in terms of the ionic density $n_j(x,t)$, and using the equation of continuity to determine $n_j(x,t)$. The present analysis will be restricted to systems with a small-applied potential V , so that all equations will be linear in V .

Furthermore, when discussing the ionic density, force or velocity, it is important to bear in mind that these are *ensemble-averaged* quantities. For example, the ionic density of the j^{th} species at some point in space and time is the average density calculated if one observes that particular point for a very large ensemble of identical systems.

2.1 The Mathematical Model

In solution, the motion of ions is mediated by forces arising from an unequal distribution of electrochemical potential throughout the system. Formally, the force of motion, F_{m_j} , is the negative gradient of the electrochemical potential, μ_j :

$$F_{m_j} = -\frac{d\mu_j}{dx} \quad [2.3]$$

(Note that although the chemical potential is a general function of x , y , and z , since the tangential ionic flux is neglected, the gradient will be treated as a total derivative in one dimension.) The electrochemical potential of one mole of species j is:

$$\mu_j = \mu_j^\theta + RT \ln \frac{n_j}{N_A} + z_j F \Psi \quad [2.4]$$

Where μ_j^θ is the chemical potential of an ideal reference state, R is the gas constant, T is the absolute temperature, n_j is the ionic density of the j^{th} species, N_A is Avagadro's number, z_j is the valence (including sign) of the j^{th} ionic species, F is Faraday's constant and Ψ is the electrical potential of the system.

The force acting on an average ion of the j^{th} species is:

$$F_{m_j} = -\frac{1}{N_A} \frac{d\mu_j}{dx} = -kT \frac{d \ln n_j}{dx} - z_j e \frac{d\Psi}{dx} \quad [2.5]$$

This motion is opposed by a frictional force, F_{fr_j} , related to the velocity of the ion, v_j , and the ionic mobility in solution, quantified by the viscous drag coefficient λ_j ,

$$F_{fr_j} = v_j \lambda_j \quad [2.6]$$

Under steady state conditions, ignoring transient effects, the forces balance to yield:

$$kT \frac{d \ln n_j}{dx} + z_j e \frac{d\Psi}{dx} + v_j \lambda_j = 0 \quad [2.7]$$

It is useful to redefine the average velocity, in a manner similar to that introduced by DeLacey and White (18), as the gradient of a *velocity potential* $\tilde{\Phi}_j$.

$$v_j = -\frac{z_j e}{\lambda_j} \frac{d\tilde{\Phi}_j}{dx} \quad [2.8]$$

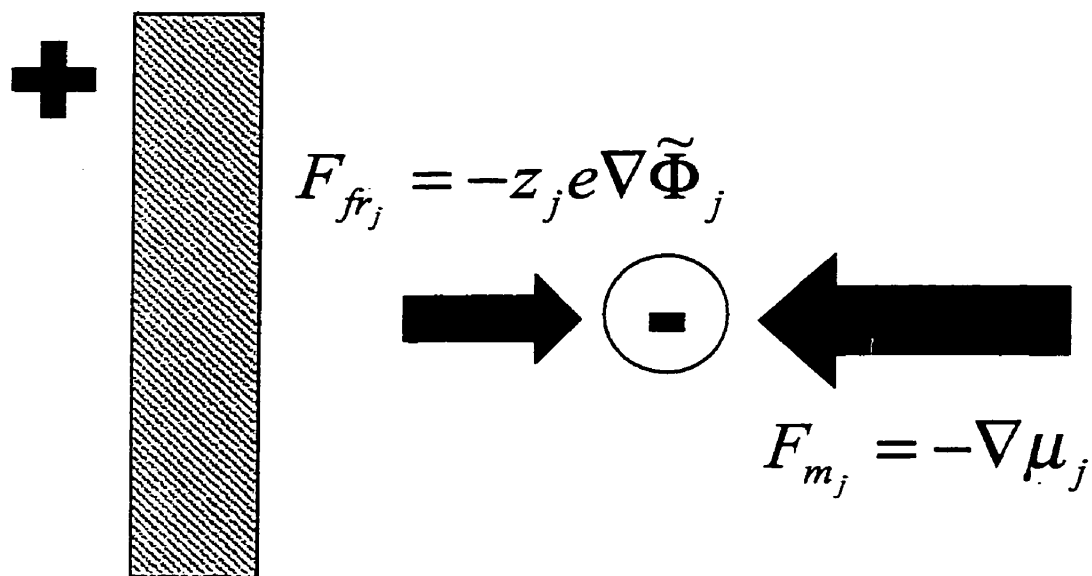


Figure 2.3 - The forces acting on an ion in solution. The ions move due to a motive force, , that is the negative gradient of the electrochemical potential. This motion is resisted by a frictional force, , that is proportional to the negative gradient of the velocity potential.

From eq. [2.6], the velocity potential is related to the force of friction, and can therefore be visualised as the energy lost due to friction when an ion of species j is brought to the point x with velocity v_j (**Figure 2.3**).

With the substitution of the velocity in terms of the velocity potential, eq. [2.7] is formally integrated to determine the ionic density, n_j :

$$n_j(x,t) = n_j^\infty e^{-\frac{z_j e}{kT}(\Psi(x,t) - \tilde{\Phi}_j(x,t))} \quad [2.9]$$

This may be interpreted as a Boltzmann distribution, where the energy of an ion of the j^{th} species at each point in space and time is $z_j e(\Psi(x,t) - \tilde{\Phi}_j(x,t))$.

Far from the electrode, the random thermal forces in the bulk region will supersede the organising influence of the electrostatic forces, and the ionic density will approach the bulk value n_j^∞ . To define precisely what is meant by the *bulk region*, an imaginary grounded plate is placed halfway between the electrode and its mirror image, at a distance L from the surface (**Figure 2.4**). Then,

$$\lim_{x \rightarrow L} n_j(x,t) = n_j^\infty \quad [2.10]$$

$$\lim_{x \rightarrow L} \{\Psi(x,t) - \tilde{\Phi}_j(x,t)\} = 0 \quad [2.11]$$

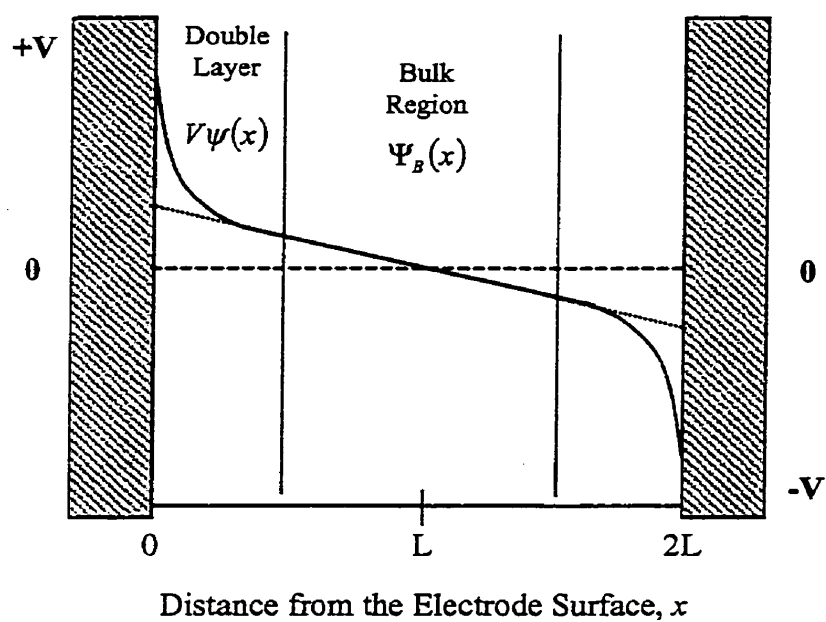


Figure 2.4 - The electrical potential distribution in the solution. Though the bulk electrical potential, Ψ_B , is present throughout, the double layer electrical potential, $V\psi$, falls off very rapidly close to the surface. The area surrounding the imaginary ground plate at L is called the *bulk region*.

As previously mentioned, in an ionic medium the bulk potential $\Psi_B(x)$ for a planar electrode system is given by:

$$\Psi_B(x) = V_{eff} g(x) \quad [2.12]$$

The corresponding field will be:

$$E_{eff}(x) = -V_{eff} \frac{dg(x)}{dx} \quad [2.13]$$

The parameter E_{eff} is called the *effective far field*, and it is the actual field experienced in the bulk region due to the potential applied across the electrodes. The screening of the electrodes by the double layer attenuates the applied field, while the dynamics of the double layer lends distinct frequency dependence to this attenuation. In general, then, the effective far field will also be a complex quantity, and will have magnitude and frequency behaviour different from that of the applied field due to the influence of the double layer.

Owing to the applicability of the principle of superposition, the two potentials, $\Psi(x, t)$ and $\tilde{\Phi}_j(x, t)$, can be further resolved (25). The electrical potential $\Psi(x, t)$ is a linear combination of two parts, called the *equilibrium* and the *steady-state* potentials. The first part, the *equilibrium potential* $\Psi^0(x)$, is a dc potential distribution that exists in the absence of the applied ac potential, and $\Psi^0(x)$ satisfies Poisson's equation:

$$\frac{d^2\Psi^0(x)}{dx^2} = -\frac{4\pi}{\varepsilon_m} \sum_{j=1}^N z_j e n_j^0(x) \quad [2.14]$$

Where ε_m is the permittivity of the medium, and $n_j^0(x)$ is the equilibrium ion density:

$$n_j^0(x) = n_j^\infty e^{-\frac{z_j e}{kT} \Psi^0(x)} \quad [2.15]$$

Furthermore,

$$\Psi^0(0) = \zeta \quad [2.16]$$

where ζ is sometimes called the *zeta potential* by investigators of electrode polarization. The zeta potential represents the dc bias between the electrodes in the absence of the applied ac potential.

The second part of $\Psi(x,t)$ is a time-dependent perturbation $\delta\Psi(x,t)$ that comes about when the system reaches steady state under the influence of the applied ac field. It is composed of the electrical potential attenuation in the double layer $V\psi(x)$, and the bulk electrical potential $\Psi_b(x)$. Thus $\Psi(x,t)$ is written explicitly as a linear superposition of the equilibrium and steady states (**Figure 2.4**):

$$\begin{aligned}\Psi(x,t) &= \Psi^0(x) + \delta\Psi(x,t) \\ &= \Psi^0(x) + (\psi(x) V + \Psi_B(x)) e^{i\omega t}\end{aligned}\tag{2.17}$$

The velocity potential $\tilde{\Phi}_j(x,t)$ is written in a manner analogous to eq. [2.17]:

$$\tilde{\Phi}_j(x,t) = \tilde{\Phi}_j^0(x) + \delta\tilde{\Phi}_j(x,t)\tag{2.18}$$

In the absence of the applied field the *average* velocity must vanish, so the time-independent component of the velocity potential, $\tilde{\Phi}_j^0(x)$, is set to zero. The velocity potential is written as a sum of the velocity potential within the double layer $V\phi_j(x)$, and the bulk electrical potential $\Psi_B(x)$:

$$\tilde{\Phi}_j(x,t) = (V\phi_j(x) + \Psi_B(x)) e^{i\omega t}\tag{2.19}$$

(The introduction of Ψ_B in $\tilde{\Phi}_j$ allows the ionic density $n_j(x,t)$, as defined in eq. [2.9], to become equal to n_j^∞ at L .)

Implicit in the definition of these functions is the assumption that the temporal dependence is completely captured by the oscillating exponential $e^{i\omega t}$, and the potentials Ψ^0 , Ψ_B , ψ , and ϕ_j are functions of position only.

Defining a position-dependent reciprocal Debye screening length function due to the j^{th} ions:

$$b_j(x) = \frac{4\pi e^2}{\epsilon_m kT} z_j^2 n_j^0(x) \quad [2.20]$$

and retaining terms to first order in V , Poisson's equation for $\psi(x)$, for N types of ions, is

$$\frac{d^2\psi}{dx^2} - \sum_{j=1}^N b_j \psi + \sum_{j=1}^N b_j \phi_j = 0 \quad [2.21]$$

At the surface of the electrode, the time-dependent perturbation must be the applied potential. Therefore,

$$\lim_{x \rightarrow 0} \delta\Psi(x, t) = V e^{i\omega t} \quad [2.22]$$

It follows from eqs. [2.17] and [2.22],

$$\lim_{x \rightarrow 0} \psi(x) = 1 - \frac{1}{V} \lim_{x \rightarrow 0} \Psi_B(x) \quad [2.23]$$

Furthermore, from eq. [2.11],

$$\lim_{x \rightarrow L} \psi(x) = 0 \quad [2.24]$$

The differential equation for $\psi(x)$ contains the velocity potential, so an equation describing $\phi_j(x)$ must be derived before $\psi(x)$ is characterised completely. Starting from the continuity equation for each ionic species:

$$\frac{d(n_j v_j)}{dx} = -\frac{dn_j}{dt} \quad [2.25]$$

Linearizing eq. [2.9] in V , the ionic density is given by:

$$n_j(x, t) = n_j^0(x) - \frac{z_j e}{kT} n_j^0(x) \{ \psi(x) - \phi_j(x) \} V e^{i\omega t} \quad [2.26]$$

Substituting eq. [2.26] in eq. [2.25], along with the following definitions:

$$S_j^2 = \frac{\omega \lambda_j}{kT} \quad \hat{\Sigma}_j(x) = -\frac{z_j e}{kT} \frac{d\Psi^0}{dx} \frac{d}{dx} \quad [2.27]$$

a second-order differential equation for $\phi_j(x)$ follows:

$$\mathcal{D}_j \phi_j - i S_j^2 \psi + \hat{\Sigma}_j \frac{\Psi_B}{V} = 0 \quad [2.28]$$

$$\mathcal{D}_j \equiv \frac{d^2}{dx^2} + \hat{\Sigma}_j(x) + i S_j^2 \quad [2.29]$$

The surface boundary condition is determined formally by assuring that ions cannot penetrate the surface of the electrode, leading to a reflective boundary condition:

$$\lim_{x \rightarrow 0} \frac{d}{dx} \tilde{\Phi}_j(x, t) = 0 \quad [2.30]$$

Combining eq. [2.30] with eq. [2.19],

$$\lim_{x \rightarrow 0} \frac{d}{dx} \phi_j(x) = -\frac{1}{V} \lim_{x \rightarrow 0} \frac{d}{dx} \Psi_B(x) \quad [2.31]$$

Furthermore, far from the electrode surface eq. [2.11] requires:

$$\lim_{x \rightarrow L} \phi_j(x) = 0 \quad \lim_{x \rightarrow L} \frac{d}{dx} \phi_j(x) = 0 \quad [2.32]$$

It remains, now, to solve eqs. [2.21] and [2.28] for ψ and ϕ_j , subject to their respective boundary conditions. Unfortunately, there is currently no method for solving this system of equations exactly, so approximate solutions are all that is available. Some of the methods employed to solve these, or related systems, will be examined in Chapter 3, providing motivation for the present inquiry and context for the results presented in Chapter 4.

Chapter 3

Methods of Approximation

We are now in a difficult position: the mathematical model that has been developed gives rise to a system of differential equations that cannot be analytically solved by any known methods. The source of this insolubility is twofold. First, the coefficients in the equations are *non-autonomous*. That is to say, the coefficients are themselves functions of the variable of differentiation (in this case, the position variable x). Typically, the solutions to non-autonomous differential equations are not easily found.

Second, the differential equations are coupled, so that the differential equation characterising one function depends on the solution of a subsequent equation, and vice versa. This interrelation necessitates that the differential equations be solved *simultaneously*, which is often difficult. The two complicating features presented above prohibit the derivation of analytic solutions with currently available techniques. It will turn out, however, that both of these restrictive features are eliminated if the ζ potential is neglected, thereby rendering the system of differential equations autonomous, separable, and exactly solvable. Nevertheless, neglect of the ζ potential is done at the expense of very interesting physical features that are discussed in Chapters 5, 6 and 7.

Given that we cannot expect to find the exact solutions of the system of differential equations, we must seek approximate solutions instead. There are many methods of

approximation available, and the choice of method will often determine the range of applicability of the solutions. Furthermore, not all methods can be used on all differential equations. Indeed, the general form of the differential equation will often suggest the method of approximation to be employed, or, conversely, the form of the differential equation may be transformed to accommodate a particular method of approximation. Table 3.1 outlines some of the more common approximation methods that will be discussed in this Chapter.

Table 3.1 – Comparison of Approximation Methods

	Main Idea	Advantages	Disadvantages
Numerical Methods	Wide range of choices available, but generally the equations are solved point by point along some suitable grid.	Often yields nearly exact solutions without trouble-some simplifying assumptions.	Numerical output provides limited insight into the intrinsic behaviour. May also be time consuming and computationally intensive.
Perturbation Methods	The solution is expressed as a power series in a small parameter.	Sometimes leads to very accurate solutions, with a minimum of computational effort	The series may not converge rapidly enough.

Iterative Methods	The differential equation is recast as an integral. A trial solution of the integral is repeatedly iterated until the trial estimate converges to the exact solution.	Similar to perturbation methods, if the process converges quickly. Iteration can generate accurate solutions.	The iteration may not converge.
Variational Methods	Analogous to geometrical optimisation – a solution is found in function space based on the stationary point of a suitable functional.	Rapidly produces often semi-analytic functions that do not suffer from the convergence problems of alternate techniques.	Quality of the solution depends very intimately upon the choice of trial function used to restrict function space.

3.1 Numerical Method

The most common approach, by far, is the so-called numerical method. In fact, to an extent, all the other methods of approximation generally include some aspects that require numerical evaluation. Numerical methods, insofar as they return tabular or

graphical representations of the solution functions, are difficult to interpret in general. That is, numerical methods can show how a system behaves, but not why it might behave that way. Another way of saying this is that to the extent that a system can be solved numerically, it can be simulated; to the extent that a system can be solved analytically, it can be modelled. Analytic solution functions are often more tangible, allowing much deeper interpretation to be made. The goal, then, of any analysis of a system described by an insoluble set of equations is to generate approximations with a minimum of numerical parameters.

In the pioneering work of DeLacey and White (18) the dc ζ potential is initially set equal to zero, and the governing system of autonomous equations is written in a matrix form, that can be solved via a diagonalization method.

When the dc potential, ζ , is set equal to zero, the equations become autonomous:

$$\frac{d^2\phi_j}{dx^2} + iS_j^2\phi_j - iS_j^2\psi = 0 \quad [3.1]$$

$$\frac{d^2\psi}{dx^2} - \sum_{j=1}^N b_j^\infty \psi + \sum_{j=1}^N b_j^\infty \chi_j = 0 \quad [3.2]$$

Rewriting the solutions as a vector:

$$\bar{y} \equiv \begin{bmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \psi \end{bmatrix} \quad [3.3]$$

The differential equations in matrix form become:

$$\frac{d^2}{dx^2} \bar{y} - \underline{\underline{A}} \cdot \bar{y} = \bar{0} \quad [3.4]$$

Where,

$$\underline{\underline{A}} = \begin{pmatrix} -iS_1^2 & 0 & iS_1^2 \\ 0 & -iS_2^2 & iS_2^2 \\ -b_1^\infty & -b_2^\infty & \kappa^2 \end{pmatrix} \quad [3.5]$$

Further, by defining

$$\bar{y} = \underline{\underline{R}} \cdot \bar{z} \quad [3.6]$$

With, the matrix R chosen such, that the system of differential equations are diagonalized, the set of eigenfunctions $\{z_0, z_1, z_2, \dots, z_N\}$ satisfy the de-coupled equations

$$\frac{d^2 \bar{z}}{dx^2} - \underline{\underline{\alpha}} \cdot \bar{z} = 0 \quad [3.7]$$

Here, $\underline{\underline{\alpha}}$ is a diagonal matrix of eigenvalues. The components of the vector $\bar{z}$ will be called the *normal modes*. Detailed discussion of the normal modes will be reserved for Chapter 4.

The complete solution is a linear combination of the normal modes:

$$\phi_1(x) = C_1 R_{12} e^{-\sqrt{\alpha_1}x} + C_2 R_{13} e^{-\sqrt{\alpha_2}x} \quad [3.8]$$

$$\phi_2(x) = C_1 R_{22} e^{-\sqrt{\alpha_1}x} + C_2 R_{23} e^{-\sqrt{\alpha_2}x} \quad [3.9]$$

$$\psi(x) = C_1 R_{32} e^{-\sqrt{\alpha_1}x} + C_2 R_{33} e^{-\sqrt{\alpha_2}x} \quad [3.10]$$

where C_1 and C_2 are unknown integration constants determined by the boundary conditions. It should be noted that the analysis by DeLacey and Whites as it stands in (18) uses unphysical boundary conditions, marring the results derived therein. Namely, their bulk potential diverges at large x , and x is unbound. Placing the ground plate at L suitably rectifies the boundary conditions.

To incorporate the effect of the dc potential, DeLacey and White resort to a purely numerical scheme, solving the equation set point by point. They argue that outside the double layer, since the equilibrium potential $\Psi^0(x)$, and hence the effects of the ζ

potential, vanish, the solutions as represented by the above normal modes are adequate. Within the double layer, however, they resort to a numerical method of solution.

It may be helpful at this point to suggest why the ζ potential is so important that so much trouble is taken to include its effect in the model. Firstly, from a strictly theoretical point of view, the inclusion of the dc bias brings to the forefront effects that are not seen in either the dc or ac cases alone. As will be discussed in Chapter 5, the dc bias serves to break the symmetry of the oscillating ac double layer via chemical potential barriers at the electrode surface.

Secondly, from a more practical point of view, it may be necessary to model the behaviour of an electrode system operating in the presence of some galvanic process occurring at the electrode surface, generating non-zero dc biases. As electrode systems become smaller and smaller due to micro-machined arrays and lab-on-a-chip type technologies, there will be a corresponding decrease in the applied potentials necessary to generate useful electric fields. For such systems, even small dc biases will be of comparable magnitude to the applied potential, and correspondingly complicate the system.

3.2 Perturbation Method

It would be difficult to overestimate the utility of perturbation methods in approximating solutions for a particular type of differential equations. Perturbation

methods rely on the existence of a small parameter in the differential equation (26, 27). Consider the following second-order differential equation,

$$\begin{aligned}\varepsilon \frac{d^2 y}{dx^2} + y &= f(x) \\ 0 \leq x &\leq 1\end{aligned}\tag{3.11}$$

where ε is a small ($\varepsilon < 1$), positive, unitless parameter. To compute a perturbation solution of eq. [3.11], the function $y(x)$ is assumed to be a power series in ε .

$$y(x) = y_0(x) + \varepsilon y_1(x) + \varepsilon^2 y_2(x) + \dots\tag{3.12}$$

When the power series is substituted into the original differential equation, eq. [3.11], at each power of ε , a far simpler set of differential equations is obtained.

$$\begin{aligned}\text{at } \varepsilon^0: \quad & \frac{dy_0}{dx} = f(x) \\ \text{at } \varepsilon^1: \quad & \frac{dy_1}{dx} = -\frac{d^2 y_0}{dx^2} \\ \text{at } \varepsilon^2: \quad & \frac{dy_2}{dx} = -\frac{d^2 y_1}{dx^2} \\ & \vdots \\ \text{at } \varepsilon^n: \quad & \frac{dy_n}{dx} = -\frac{d^2 y_{n-1}}{dx^2}\end{aligned}\tag{3.13}$$

It is a general feature of perturbation expansions that the solution at some early stage reappears at higher powers of ε , i.e. $y_n(y_{n-1})$. Notice, too, that in this example instead of having to solve a second-order differential equation, by assuming a power series in ε , a family of first-order differential equations is solved up to some arbitrary power of ε . This is a decidedly simpler task, and lends general appeal to the perturbation method.

Nevertheless, at higher powers of ε , the solutions become increasingly more cumbersome, so that perturbation expansions are only practical for rapidly converging series ($\varepsilon \ll 1$). Thus, perturbation solutions are inherently restricted to those conditions that ensure rapid convergence of the expansion.

Gunning, Chan and White (19), in an approach similar to Newman (20), compare the two disparate length parameters that are implicitly present in the governing differential equations: κ , the reciprocal Debye length, and S_d , the typical diffusion length. Taking a quotient of the two, they develop a unitless perturbation parameter, called δ , that is small for large concentrations and low frequency:

$$\delta = \frac{S_d}{\kappa} = \frac{1}{\kappa} \sqrt{\frac{\omega \lambda}{kT}} \quad [3.14]$$

The system of differential equations are recast in terms of the perturbation parameter, then perturbation expansions are developed for regions close to the electrode surface, and for regions far from the surface. The two families of differential equations are solved up

to some unknown integration constants. The constants are then determined by “matching” the solutions in an intermediate region.

Unfortunately, the solutions of the perturbation equations are not trivial. In fact, the analysis contains so many numerical integrals and complicated arguments that the solutions are largely incomprehensible. Moreover, Gunning, Chan and White use the same unphysical boundary conditions discussed in the previous section.

3.3 Iterative Method

If a convenient integral form of the differential equations can be found, then iterative methods can typically be used to find estimations of the exact solutions. As an example, consider the approach used by Yoon (28) to solve the non-linear Poisson-Boltzmann equation.

The non-linear Poisson-Boltzmann equation for the electrical potential Ψ in a spherical-polar co-ordinate frame is:

$$\nabla^2 \Psi = -\frac{e}{\epsilon k T} \sum_{j=1}^N z_j n_j^\infty e^{-z_j e \Psi} \quad [3.15]$$

where ∇^2 is the polar gradient operator, under perfect rotational symmetry, and r is the radial distance from the origin,

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \quad [3.16]$$

extending over the domain $a \leq r < \infty$, with a as the radius of the electrode.

Defining a functional, $H[\Psi]$,

$$-\frac{e}{\varepsilon k T} \sum_{j=1}^N z_j n_j^\infty e^{-z_j e \Psi} - \kappa^2 \Psi \equiv H[\Psi] \quad [3.17]$$

where κ is the reciprocal Debye thickness:

$$\kappa^2 = \frac{e^2}{\varepsilon k T} \sum_{j=1}^N z_j^2 n_j^\infty \quad [3.18]$$

the Poisson-Boltzmann equation can be rewritten in terms of the functional $H[\Psi]$,

$$\frac{d^2 \Psi}{dx^2} - \kappa^2 \Psi = H[\Psi] \quad [3.19]$$

As the potential becomes small, $\Psi \rightarrow 0$, and only the linear term in the exponential is retained, the functional $H[\Psi] \rightarrow 0$, and eq. [3.19] becomes the linear Poisson-Boltzmann equation solved by Debye and Hückel.

When $H[\Psi]$ is not zero, no analytic solution to the Poisson-Boltzmann equation is available. Converting the differential equation into an integral equation, Yoon uses an iterative method to approximate the solution. Green's functions provide an elegant and expedient method for converting a differential equation to the analogous integral equation (Appendix 1).

Using Green's functions, the integral representation of the function Ψ is:

$$\begin{aligned}\Psi(r) = & -\int_V dV(r') H[\Psi] G(|r-r'|) \\ & -\int_S dA(r') \frac{\partial \Psi^s}{\partial n} G(|r-r'|) \\ & +\int_S dA(r') \Psi^s \frac{\partial G(|r-r'|)}{\partial n}\end{aligned}\quad [3.20]$$

Where $G(|r-r'|)$ is the Green's function of eq. [3.19], given by:

$$G(|r-r'|) = \frac{e^{-\kappa|r-r'|}}{4\pi|r-r'|}\quad [3.21]$$

The expression simplifies to:

$$\Psi(r) = \Psi^0 \frac{a}{r} e^{-\kappa(r-a)} + \frac{1}{2\kappa r} \int_a^\infty ds H[\Psi] s \left[e^{-\kappa(s+r-2a)} - e^{-\kappa|r-s|} \right]\quad [3.22]$$

Rewritten as:

$$\Psi(r) = \Psi_{DH}(r) + \int_a^\infty ds K(s, r) H[\Psi(r)] \quad [3.23]$$

Where,

$$\Psi_{DH}(r) = \Psi^0 \frac{a}{r} e^{-\kappa(r-a)} \quad [3.24]$$

$$K(s, r) = \frac{s \left[e^{-\kappa(s+r-2a)} - e^{-\kappa|r-s|} \right]}{2\kappa r} \quad [3.25]$$

Here, Ψ_{DH} is simply the Debye-Hückel solution of the linearized Poisson-Boltzmann equations. The function $K(s, r)$ is called the *kernel of the integral equation*. It is the size of the kernel that ultimately determines the convergence properties of the iterative expansion.

The idea behind iterative expansions is that Ψ_{DH} is known, and yet the potential under the integral sign remains unknown. One could replace the unknown potential by Ψ_{DH} to get a rough estimate of the unknown potential. This rough estimate could be further refined by subsequently replacing the unknown potential by the rough estimate, and so on. If the kernel is *convergent*, then after a finite number of steps, estimations of

this type can be brought arbitrarily close to exact solution of the integral equation. A schematic of this process appears below:

$$\begin{aligned}
\Psi_{DH} + \int_a^\infty ds K(r,s) H[\Psi_{DH}] &= \Psi_1 \\
\Psi_{DH} + \int_a^\infty ds K(r,s) H[\Psi_1] &= \Psi_2 \\
\Psi_{DH} + \int_a^\infty ds K(r,s) H[\Psi_2] &= \Psi_3 \\
&\vdots \\
\Psi_{DH} + \int_a^\infty ds K(r,s) H[\Psi_n] &\approx \Psi
\end{aligned}
\tag{3.26}$$

For our system, there is no guarantee that the kernel of our analogous integral equations would be convergent. More importantly, the integrals generated in this fashion can rarely be solved analytically, so this approach basically amounts to a numerical scheme, and thus falls prey to all the limitations of such methods. Namely, the solutions lack a generalised “feel”; it is very difficult to interpret the results and make any broad conclusions.

3.4 Variational Method

Another alternative that can be used for many differential equations is the variational method. This method has not been used extensively in electrochemistry, although a

general discussion can be found in most advanced books on mathematical methods in physics, such as the well known book by Morse and Feshbach (29).

The heart of variational analysis lies in constructing a functional and relating the stationary points of this functional to the desired solution of a differential equation. A functional $I[v]$ is defined as a quantity that depends upon some function $v(x)$. A functional is simply a function of a function. In our case, we will consider an integral dependence of I on $v(x)$. For example:

$$I[v] = \int_a^b dx F[v(x)] \quad [3.27]$$

Here, a and b are the limits of the variable x and $F[v(x)]$ is a functional of $v(x)$. Like ordinary functions, functionals too, can be differentiated (see Appendix 2). The utility of functionals as a means of solving differential equations comes from the fact that many differential equations can be derived from well-defined functionals through functional differentiation.

Consider a differential equation,

$$\mathcal{L}u(x) = 0 \quad [3.28]$$

where $\mathcal{D}$ is a general differential operator, and $u(x)$ is the unknown function we seek. A functional $I[v]$ is constructed so that when the functional derivative of $I[v]$ is evaluated and set to zero, the resulting equation is the original differential equation:

$$\frac{\delta I[v]}{\delta v} = 0 = \mathcal{D}v(x) \quad [3.29]$$

This implies that $v(x) = u(x)$ is a stationary (minimum or maximum) point of the functional. The problem of finding a solution to the differential equation now becomes one of locating a function $v(x)$ that yields a stationary point of the functional $I[v]$. In practice, it is necessary to limit ones search for a minimizing function by devising a trial function with a certain number of free parameters. The stationary point is then found by differentiating with respect to these parameters, setting the result equal to zero and solving this set of simultaneous equations. The function $v(x)$ thus computed is taken to be the best variational approximation to the solution $u(x)$. The advantage of these variational solutions is that often the form of the trial functions can be made such that the variational parameters can be given physical meaning, even if they must be determined numerically. There are several approaches to a variational solution that are possible for the model described in Chapter 2. The first is the least direct, and relies on calculating a variational approximation of the Green's function for the operator based on Dyson's equation.

3.4.1 Dyson's Equation

Dyson's equation is a method used in particle physics to obtain variational estimates of the Green's function for a given system (see Appendix 1 for more details). For the general differential equation

$$\hat{\mathcal{D}}u(x) = f(x) \quad [3.30]$$

the Green's function $G(x, x')$ is related to the particular solution of $u(x)$ by the integral

$$u(x) = \int_0^{\infty} dx' G(x, x') f(x') \quad [3.31]$$

where $f(x)$ is called the forcing function.

For the differential operator $\hat{\mathcal{D}}$, the Green's function is defined as:

$$\hat{\mathcal{D}}G(x, x') = \delta(x - x') \quad [3.32]$$

If the operator can be separated into two parts, the first related to a known Green's function, and a second part whose contribution to the Green's function is unknown, then

Dyson's equation can be used to estimate the complete Green's function. The operator $\hat{\mathcal{G}}$ is thus partitioned:

$$\hat{\mathcal{G}} = \hat{\mathcal{G}}^0 + \hat{\mathcal{G}}^1 \quad [3.33]$$

where the operator $\hat{\mathcal{G}}^0$ is associated with the known zero-order Green's function $G^0(x, x')$.

Via Dyson's equation, the exact Green's function, $G(x, x')$, that is associated with the full operator $\hat{\mathcal{G}}$, can be related to the zero-order Green's function $G^0(x, x')$ through an integral equation that includes the operator $\hat{\mathcal{G}}^1$:

$$G(x, x') = G^0(x, x') - \int dx'' G^0(x, x'') \hat{\mathcal{G}}^1(x'') G(x'', x') \quad [3.34]$$

Clearly, this integral equation has a kernel $K(x, x'')$ given by:

$$K(x, x'') = G^0(x, x'') \hat{\mathcal{G}}^1(x'') \quad [3.35]$$

So if $K(x, x'')$ is suitably behaved, then the iterative approach presented in the previous section would be appropriate. Nevertheless, the convergence of $K(x, x'')$ cannot be guaranteed in general. It is possible, however, to re-write Dyson's equation as a

functional G^F that obeys a variational theorem describing the optimal estimate of the Green's function corresponding to the exact solution. In the functional, the unknown Green's function is replaced by a trial Green's function. By minimizing the variational functional with respect to the trial function, an optimal estimate of the exact Green's function may be found. That is, at the stationary point of the functional, with respect to the trial function, the trial function is equal to the exact Green's function:

$$\frac{\delta G^F}{\delta G'} = 0 \Rightarrow G'(x, x') = G(x, x') \quad [3.36]$$

The trouble with this method is that it is indirect and cumbersome. We are interested in the solution of the differential equations, so the variational Green's functions must still be integrated to achieve that end. These integrations are not easily done, making the extraction of the solutions from the Green's functions difficult.

Moreover, Green's functions are most convenient if solutions are sought for a large family of forcing functions $f(x)$, so that once the Green's functions for the operator are known, the forcing functions can be integrated along with the Green's functions to obtain the complete solution. In our system, the forcing function is known, so the generality of the Green's function becomes more of a liability than an asset. Fortunately, more direct variational methods are available.

3.4.2 Direct Variational Approach

The Dyson equation is needlessly unwieldy for our particular application, but we can develop a set of coupled functionals directly from our system of differential equations, without having to resort to Green's functions.

In formulating the functional, the first-order derivatives cause serious difficulties and must be eliminated from the operators, which amounts to making the operators on ψ and ϕ_j self-adjoint. To that end, a substitution for ϕ_j is made (see Chapter 4):

$$\phi_j(x) = e^{\frac{\rho_j(x)}{2}} \chi_j(x) \quad [3.37]$$

where χ_j is now the unknown function, and the operator on χ_j is self-adjoint.

The system of functionals, that upon functional differentiation with respect to ψ and χ_j lead back to the differential equations themselves, is:

$$L_0[\psi, \chi_j] = -\int dx' \left[\frac{1}{2} \left(\frac{d\psi}{dx'} \right)^2 - \frac{1}{2} \sum_{j=1}^N b_j(x') \psi^2 + \sum_{j=1}^N b_j(x') e^{\frac{\rho_j(x')}{2}} \chi_j \psi \right] \quad [3.38]$$

$$L_j[\psi, \chi_j] = -\int dx' \left[\frac{1}{2} \left(\frac{d\chi_j}{dx'} \right)^2 - \frac{1}{2} T_j(x') \chi_j^2 - iS_j^2 e^{\frac{\rho_j(x')}{2}} \psi \chi_j + e^{\frac{\rho_j(x')}{2}} \frac{d\rho_j}{dx'} \frac{d\Psi_B}{dx'} \chi_j \right] \quad [3.39]$$

As in the case of the variational functional derived from Dyson's equation, the unknown functions are replaced by trial functions, and the stationary points of the functional found with respect to these trial functions. These integrals cannot be evaluated symbolically, however, so numerical minimization of the functionals with respect to the trial functions is quite a task: the variational trial functions are complex, so it is essentially a numerical optimisation in two dimensions over a grid of unknown size.

Furthermore, to keep the problem tractable, the trial functions must be necessarily vague since nothing is known of the solution to the differential equations in this form. If the differential equations, and therefore the functionals, can be recast in the matrix form suggested by DeLacey and White, discussed in the numerical section of this Chapter, then the known homogeneous solutions can be used as trial functions.

3.4.3 Normal-Mode Variational Approach

DeLacey and White have solved the system of differential equations in the absence of a dc bias. These solutions, although incorrect as far as the full system of equations is concerned, do indeed capture some of the physics and chemistry of the latter. Consequently, it is convenient to adopt the forms of these functions as trial solutions in which the parameters are variationally calculated from the exact system of Lagrangians.

This improved approach seeks the approximate solutions directly, rather than with the Green's function, making use of all the information that is available through the normal modes. Variational correction of the normal modes is the subject of the next Chapter.

Chapter 4

Variational Analysis of the Normal Modes

The system of differential equations presented at the end of Chapter 2:

$$\frac{d^2\psi}{dx^2} - \sum_{j=1}^N b_j \psi + \sum_{j=1}^N b_j \phi_j = 0 \quad [4.1]$$

$$\mathcal{E}_j \phi_j - iS_j^2 \psi + \hat{\Sigma}_j \frac{\Psi_B}{V} = 0 \quad [4.2]$$

$$\hat{\mathcal{E}}_j(x) \equiv \frac{d^2}{dx^2} + \hat{\Sigma}_j(x) + iS_j^2 \quad [4.3]$$

can not be analytically solved. In this Chapter, approximate solutions of eqs. [4.1] and [4.2] are sought via a variational method. To that end, a system of functionals, called *Lagrangians*, are found, such that the stationary points of these Lagrangians are the exact solutions of the original system of differential equations. The details of the development of the Lagrangians, as well as the development of the trial functions used to approximate their stationary points, will be discussed at length throughout this Chapter.

From eq. [4.3], it is evident that the operator $\hat{\mathcal{E}}_j(x)$ contains a first-order derivative, $\hat{\Sigma}_j(x)$. Unfortunately, it is not possible to find a Lagrangian from which such an equation can be derived by the variational method to be discussed. The first-order

derivative is removed from the operator by making the following substitution for $\phi_j(x)$ (Appendix 3):

$$\phi_j(x) = e^{-\rho_j(x)/2} \chi_j(x) \quad [4.4]$$

with

$$\rho_j(x) = -\frac{z_j e}{kT} \Psi^0(x) \quad [4.5]$$

where χ_j is the new unknown function, and the operator on χ_j is self-adjoint (30).

With eq. [4.4], the original system of differential equations becomes

$$\frac{d^2 \chi_j(x)}{dx^2} - T_j(x) \chi_j(x) - iS_j^2 f_{1j}(x) \psi(x) - f_{2j}(x) = 0 \quad j = 1, 2, \dots, N \quad [4.6]$$

$$\frac{d^2 \psi(x)}{dx^2} - \sum_{j=1}^N b_j^\infty e^{\rho_j(x)} \psi(x) + \sum_{j=1}^N b_j^\infty f_{1j}(x) \chi_j(x) = 0 \quad [4.7]$$

Where:

$$T_j(x) = \frac{1}{4} \left(\frac{d\rho_j}{dx} \right)^2 + \frac{1}{2} \frac{d^2 \rho_j}{dx^2} - iS_j^2 \quad [4.8]$$

$$f_{1j}(x) = e^{\rho_j/2} \quad [4.9]$$

$$f_{2j}(x) = \left(\frac{V_{\mathcal{A}}}{V} g'(x) \right) \left(\frac{d\rho_j}{dx} \right) f_{1j} \quad [4.10]$$

$$b_j^{\infty} = \frac{4\pi e^2}{\epsilon_m kT} z_j^2 n_j^{\infty} \quad [4.11]$$

When $\rho_j = 0$, that is, in the absence of the ζ potential (c.f. eq. [4.5]), these equations collapse to a far more simple system that describes the purely dynamic characteristics of the double layer:

$$\frac{d^2 \chi_j}{dx^2} + iS_j^2 \chi_j - iS_j^2 \psi = 0 \quad [4.12]$$

$$\frac{d^2 \psi}{dx^2} - \sum_{j=1}^N b_j^{\infty} \psi + \sum_{j=1}^N b_j^{\infty} \chi_j = 0 \quad [4.13]$$

In fact, as was briefly discussed in the numerical section of Chapter 3, these equations can be decoupled and solved exactly via a matrix diagonalization method proposed by DeLacey and White (18). In the next section, their diagonalization method will be described in more detail, and the results extend, using a variational theorem, to include the effects of an arbitrarily large ζ potential.

4.1 The Normal-Modes

Adopting a matrix-vector formalism, the functions χ_j and ψ are replaced by the vector $\bar{y}$:

$$\bar{y} \equiv \begin{bmatrix} \chi_1 \\ \chi_2 \\ \vdots \\ \psi \end{bmatrix} \quad [4.14]$$

Further, the vector $\bar{z}$ is defined by:

$$\bar{y} = \underline{\underline{R}} \cdot \bar{z} \quad [4.15]$$

Here, the matrix $\underline{\underline{R}}$ diagonalizes the system, and the set of eigenfunctions $\{z_0, z_1, z_2, \dots, z_N\}$ satisfies the decoupled equations

$$\frac{d^2 \bar{z}}{dx^2} - \underline{\underline{\alpha}} \cdot \bar{z} = 0 \quad [4.16]$$

where $\underline{\underline{\alpha}}$ is the diagonal matrix of eigenvalues. The components of the vector $\bar{z}$ are called the *normal modes*.

Rearranging the exact differential equations [4.1] and [4.2] in forms that would explicitly lead to eqs. [4.12] and [4.13] when $\rho_j = 0$, by addition and subtraction of appropriate terms, yields:

$$\frac{d^2 \chi_j}{dx^2} + iS_j^2 \chi_j - iS_j^2 \psi + h_{1j}(x) \psi + h_{2j}(x) \chi_j + h_{3j}(x) = 0 \quad [4.17]$$

$$\frac{d^2 \psi}{dx^2} - \kappa^2 \psi + \sum_{j=1}^N b_j^\infty \chi_j + g_1(x) \psi + \sum_{j=1}^N g_{2j}(x) \chi_j = 0 \quad [4.18]$$

with

$$h_{1j} = -iS_j^2 (e^{\rho_j/2} - 1) \quad [4.19]$$

$$h_{2j} = - \left(T_j + iS_j^2 \right) = - \left(\frac{1}{4} \left(\frac{d\rho_j}{dx} \right)^2 + \frac{1}{2} \frac{d^2 \rho_j}{dx^2} \right) \quad [4.20]$$

$$h_{3j} = \left(\frac{V_{eff}}{V} g'(x) \right) \left(\frac{d\rho_j}{dx} \right) e^{\rho_j/2} \quad [4.21]$$

$$g_1 = - \sum_{j=1}^N b_j^\infty (e^{\rho_j} - 1) \quad [4.22]$$

$$g_{2j} = b_j^\infty (e^{\rho_j/2} - 1) \quad [4.23]$$

$$\sum_{j=1}^N b_j^\infty = \kappa^2 \quad [4.24]$$

where κ is the reciprocal thickness of the Debye double layer.

For a two-ion system ($N = 2$), eqs. [4.17] and [4.18] become a system of three equations:

$$\frac{d^2\chi_1}{dx^2} + iS_1^2\chi_1 - iS_1^2\psi + h_{11}(x)\psi + h_{21}(x)\chi_1 + h_{31}(x) = 0 \quad [4.25]$$

$$\frac{d^2\chi_2}{dx^2} + iS_2^2\chi_2 - iS_2^2\psi + h_{12}(x)\psi + h_{22}(x)\chi_2 + h_{32}(x) = 0 \quad [4.26]$$

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi + b_1^\infty\chi_1 + b_2^\infty\chi_2 + g_1(x)\psi + g_{21}(x)\chi_1 + g_{22}(x)\chi_2 = 0 \quad [4.27]$$

Using a matrix-vector formulation, these three equations can be expressed compactly as:

$$\frac{d^2}{dx^2} \bar{y} - \underline{\underline{A}} \cdot \bar{y} + \underline{\underline{B}}(x) \cdot \bar{y} + \bar{C}(x) = \bar{0} \quad [4.28]$$

Where,

$$\underline{\underline{A}} = \begin{pmatrix} -iS_1^2 & 0 & iS_1^2 \\ 0 & -iS_2^2 & iS_2^2 \\ -b_1^\infty & -b_2^\infty & \kappa^2 \end{pmatrix} \quad [4.29]$$

$$\underline{\underline{B}}(x) = \begin{pmatrix} h_{21}(x) & 0 & h_{11}(x) \\ 0 & h_{22}(x) & h_{12}(x) \\ g_{21}(x) & g_{22}(x) & g_1(x) \end{pmatrix} \quad [4.30]$$

$$\bar{C}(x) = \begin{pmatrix} h_{31}(x) \\ h_{32}(x) \\ 0 \end{pmatrix} \quad [4.31]$$

With the eigenvalues of $\underline{\underline{A}}$:

$$\alpha_0 = 0 \quad [4.32]$$

$$\alpha_1 = \frac{1}{2} \left(\kappa^2 - i(S_1^2 + S_2^2) - \sqrt{(i(S_1^2 + S_2^2) - \kappa^2)^2 + 4(ib_2^\infty S_1^2 + ib_1^\infty S_2^2 + S_1^2 S_2^2)} \right) \quad [4.33]$$

$$\alpha_1 = \frac{1}{2} \left(\kappa^2 - i(S_1^2 + S_2^2) + \sqrt{(i(S_1^2 + S_2^2) - \kappa^2)^2 + 4(ib_2^\infty S_1^2 + ib_1^\infty S_2^2 + S_1^2 S_2^2)} \right) \quad [4.34]$$

and the matrix $\underline{\underline{R}}$:

$$\underline{\underline{R}} = \begin{bmatrix} 1 & \frac{iS_1^2}{iS_1^2 + \alpha_1} & \frac{iS_1^2}{iS_1^2 + \alpha_2} \\ 1 & \frac{iS_2^2}{iS_2^2 + \alpha_1} & \frac{iS_2^2}{iS_2^2 + \alpha_2} \\ 1 & 1 & 1 \end{bmatrix} \quad [4.35]$$

Using eq.[4.15], eq. [4.28] becomes:

$$\underline{\underline{R}} \cdot \frac{d^2}{dx^2} \bar{z} - \underline{\underline{A}} \cdot \underline{\underline{R}} \cdot \bar{z} + \underline{\underline{B}}(x) \cdot \underline{\underline{R}} \cdot \bar{z} + \bar{C}(x) = \bar{0} \quad [4.36]$$

Multiplying from the left by $\underline{\underline{R}}^{-1}$:

$$\frac{d^2}{dx^2} \bar{z} - \underline{\underline{\alpha}} \cdot \bar{z} + \underline{\underline{Q}}(x) \cdot \bar{z} + \bar{D}(x) = \bar{0} \quad [4.37]$$

With

$$\underline{\underline{\alpha}} = \underline{\underline{R}}^{-1} \cdot \underline{\underline{A}} \cdot \underline{\underline{R}} \quad [4.38]$$

$$\underline{\underline{Q}}(x) = \underline{\underline{R}}^{-1} \cdot \underline{\underline{B}}(x) \cdot \underline{\underline{R}} \quad [4.39]$$

$$\bar{D}(x) = \underline{\underline{R}}^{-1} \cdot \bar{C}(x) \quad [4.40]$$

Eq. [4.37] produces three equations:

$$\frac{d^2 z_0}{dx^2} - \alpha_0 z_0 + Q_{00}(x) z_0 + Q_{01}(x) z_1 + Q_{02}(x) z_2 + D_0(x) = 0 \quad [4.41]$$

$$\frac{d^2 z_1}{dx^2} - \alpha_1 z_1 + Q_{10}(x) z_0 + Q_{11}(x) z_1 + Q_{12}(x) z_2 + D_1(x) = 0 \quad [4.42]$$

$$\frac{d^2 z_2}{dx^2} - \alpha_2 z_2 + Q_{20}(x) z_0 + Q_{21}(x) z_1 + Q_{22}(x) z_2 + D_2(x) = 0 \quad [4.43]$$

The off-diagonal elements of the matrix $\underline{Q}$ represent the coupling, under the influence of the ζ potential, of the normal modes (mode-mode coupling), while the diagonal elements are coupling of each mode with itself (self-coupling).

4.2 The Variational Functionals

With the non-constant Q and D coefficients, the differential equations become non-autonomous, ensuring that they cannot be solved analytically, so eqs.[4.41], [4.42], and [4.43] are converted into coupled Lagrangians:

$$L_0 = \int_0^{\infty} dx' \left[-\frac{1}{2} \left(\frac{dz_0}{dx'} \right)^2 - \frac{\alpha_0 z_0^2}{2} + \frac{Q_{00} z_0^2}{2} + Q_{01} z_1 z_0 + Q_{02} z_2 z_0 + D_0 z_0 \right] \quad [4.44]$$

$$L_1 = \int_0^{\infty} dx' \left[-\frac{1}{2} \left(\frac{dz_1}{dx'} \right)^2 - \frac{\alpha_1 z_1^2}{2} + \frac{Q_{11} z_1^2}{2} + Q_{10} z_0 z_1 + Q_{12} z_2 z_1 + D_1 z_1 \right] \quad [4.45]$$

$$L_2 = \int_0^{\infty} dx' \left[-\frac{1}{2} \left(\frac{dz_2}{dx'} \right)^2 - \frac{\alpha_2 z_2^2}{2} + \frac{Q_{22} z_2^2}{2} + Q_{20} z_0 z_2 + Q_{21} z_1 z_2 + D_2 z_2 \right] \quad [4.46]$$

The Lagrangians are constructed so that the stationary points of [4.44], [4.45], and [4.46] are exactly the differential equations [4.41], [4.42], and [4.43] (Appendix 2):

$$\frac{\delta L_0}{\delta z_0} = \frac{d^2 z_0}{dx^2} - \alpha_0 z_0 + Q_{00}(x) z_0 + Q_{01}(x) z_1 + Q_{02}(x) z_2 + D_0(x) = 0 \quad [4.47]$$

$$\frac{\delta L_1}{\delta z_1} = \frac{d^2 z_1}{dx^2} - \alpha_1 z_1 + Q_{10}(x) z_0 + Q_{11}(x) z_1 + Q_{12}(x) z_2 + D_1(x) = 0 \quad [4.48]$$

$$\frac{\delta L_2}{\delta z_2} = \frac{d^2 z_2}{dx^2} - \alpha_2 z_2 + Q_{20}(x) z_0 + Q_{21}(x) z_1 + Q_{22}(x) z_2 + D_2(x) = 0 \quad [4.49]$$

The variational functionals allow the problem to be shifted from that of solving the system of coupled differential equations to that of optimising the coupled Lagrangians (31).

We assume that the electrode is *completely polarizable*, meaning at zero frequency, the potential is completely screened by the double layer, and $E_{\text{eff}} = 0$, where E_{eff} is the bulk field, far from the electrode. That is, we assume the electrode chamber behaves as a loss-less capacitor, with no current conducted across the interface (i.e. no electrochemical reactions). Thus, the constant normal mode z_0 is ignored, as is all of L_0 . This assumption need not necessarily be true, and will not affect the predicted frequency dependence of the relaxation process. If one wishes to include the constant mode z_0 , then an additional set of boundary conditions will be required to characterise ψ and χ_j at zero frequency.

Moreover, the D elements of the Lagrangian contain the effective potential, V_{eff} . The boundary conditions on χ_j and ψ , too, contain V_{eff} . If the solutions are to be kept linear in V_{eff} , then the boundary conditions forbid the inclusion of the D elements in the Lagrangians.

The Lagrangians $\{L_0, L_1, L_2\}$ become:

$$L_1 = \int_0^\infty dx' \left[-\frac{1}{2} \left(\frac{dz_1}{dx'} \right)^2 - \frac{\alpha_1 z_1^2}{2} + \frac{Q_{11} z_1^2}{2} + Q_{12} z_1 z_2 \right] \quad [4.50]$$

$$L_2 = \int_0^\infty dx' \left[-\frac{1}{2} \left(\frac{dz_2}{dx'} \right)^2 - \frac{\alpha_2 z_2^2}{2} + \frac{Q_{22} z_2^2}{2} + Q_{21} z_2 z_1 \right] \quad [4.51]$$

To determine the stationary points of the system of Lagrangians, the final form of the solutions is assumed, and a parameter left undefined. The stationary points of the functionals are then found with respect to this variational parameter. Nevertheless, the solutions are inevitably coloured by the choice of trial function, so it is essential that the choice be as close to the exact solution as one could imagine. For this analysis, the trial function is chosen as the DeLacey and White $\zeta = 0$ solution, with an exponential variational correction, a_j :

$$z_j(x) = e^{-(\sqrt{\alpha_j} + a_j)x} \quad [4.52]$$

In practice, the trial function produces non-linearities in the variational parameter a_j , therefore the Lagrangians must be linearized in a_j to solve for that parameter.

Having chosen the form of the functions to explore, the optimisation is no longer carried out with respect to the functions $\{z_1, z_2\}$, but rather with respect to the variational parameters $\{a_1, a_2\}$, found by solving the simultaneous equations:

$$\frac{\partial L_1}{\partial a_1} = 0 \quad [4.53]$$

$$\frac{\partial L_2}{\partial a_2} = 0 \quad [4.54]$$

By the variational approach, the self and mode-mode coupling between the normal modes are accounted for without making any assumptions about small ζ , or low frequency. In fact, no simplifications have been made in the calculation of the variational parameters, except that all equations are linear in V , and the electrode is completely polarizable.

With eq. [4.15], the general solution for $\bar{y}(x)$ is

$$\bar{y}(x) = \underline{\underline{R}} \cdot \begin{pmatrix} C_0 z_0(x) \\ C_1 z_1(x) \\ C_2 z_2(x) \end{pmatrix} \quad [4.55]$$

where C_0 , C_1 , and C_2 are unknown integration constants determined from the boundary conditions.

Collecting the trial functions, eq. [4.52], together with eq. [4.55], taking $z_0 = 0$,

$$\chi_1(x) = C_1 R_{12} e^{-(\sqrt{\alpha_1} + a_1)x} + C_2 R_{13} e^{-(\sqrt{\alpha_2} + a_2)x} \quad [4.56]$$

$$\chi_2(x) = C_1 R_{22} e^{-(\sqrt{\alpha_1} + a_1)x} + C_2 R_{23} e^{-(\sqrt{\alpha_2} + a_2)x} \quad [4.57]$$

$$\psi(x) = C_1 R_{32} e^{-(\sqrt{\alpha_1} + a_1)x} + C_2 R_{33} e^{-(\sqrt{\alpha_2} + a_2)x} \quad [4.58]$$

From eq. [4.4], then, the complete variational solutions are:

$$\phi_1(x) = e^{-\frac{\rho_1(x)}{2}} \left[C_1 R_{12} e^{-(\sqrt{\alpha_1} + a_1)x} + C_2 R_{13} e^{-(\sqrt{\alpha_2} + a_2)x} \right] \quad [4.59]$$

$$\phi_2(x) = e^{-\frac{\rho_2(x)}{2}} \left[C_1 R_{22} e^{-(\sqrt{\alpha_1} + a_1)x} + C_2 R_{23} e^{-(\sqrt{\alpha_2} + a_2)x} \right] \quad [4.60]$$

$$\psi(x) = C_1 R_{32} e^{-(\sqrt{\alpha_1} + a_1)x} + C_2 R_{33} e^{-(\sqrt{\alpha_2} + a_2)x} \quad [4.61]$$

The eqs. [4.53] and [4.54] are sufficient to calculate the variational parameters over any range of frequency and ζ potential, so that eqs. [4.59], [4.60], and [4.61], constitute optimal approximations of the exact solutions. In the next Chapter, some general physical comments are made about the Lagrangians, the variational parameters and the functions themselves.

Chapter 5

General Physical Comments on the Variational Solutions

5.1 Connection between the Lagrangians and the Free-Energy of the System

In literature (32, 33), it has been shown that the Lagrangian determining ψ , with $\phi_j = 0$, is related to the electrical free energy of the system. The stationary characteristic of the Lagrangian at zero frequency is then related to the minimization of the electrostatic component of the free energy. Our functional representation, however, includes the effect of friction. This is an apparent contradiction, since by definition friction assumes a dissipative system, while the Lagrangians suggest energy conservation.

It seems reasonable to propose that the Lagrangians are related to the electrical free energy *and* the free energy lost to friction. In that way, the dissipative characteristics are contained within the Lagrangian, and the *total* energy is conserved. Thus, the stationary points of the system of Lagrangians physically correspond to the minimization of the total (electrical and frictional) free energy of the system.

5.2 The Variational Parameters

In Chapter 3, it was stated that from a modelling point of view, a closed, analytic solution set is preferred. With a minimum of numerical parameters, the functions themselves can be investigated and physical properties inferred. The variational solutions derived in Chapter 4 still require numerical calculation of the variational parameters a_1 and a_2 . Yet, the advantage of the variational method is that even evaluated numerically, they hold some immediate physical interpretation. From the way the trial function was designed, the variational parameters are corrections to the reciprocal thickness of the double layer manifest through the electrical potential ψ in that region.

For typical dielectrophoretic experiments, the conductivity is kept very low, and no artificial dc bias is applied. Restricting investigation to a physically reasonable range of concentration ($10^{-6}\text{M} - 10\text{M}$), frequency ($>1\text{Hz}$), and ζ potential ($<0.500\text{V}$), the variational solutions become completely analytic. In this range, the fraction containing the variational parameter is always very small (**Table 5.1**):

$$\frac{a_j}{\sqrt{\alpha_j}} < 10^{-17} \quad [5.1]$$

So that,

$$z_j \equiv e^{-\sqrt{\alpha_j}x} \quad [5.2]$$

justifying the linearization in a_j and suggesting there is essentially no coupling between the normal modes due to the ζ potential. The complete solutions to the governing system of equations under these conditions become:

$$\phi_1(x) = e^{-\frac{\sigma_1(x)}{2}} \left[C_1 R_{12} e^{-\sqrt{\alpha_1} x} + C_2 R_{13} e^{-\sqrt{\alpha_2} x} \right] \quad [5.3]$$

$$\phi_2(x) = e^{-\frac{\sigma_2(x)}{2}} \left[C_1 R_{22} e^{-\sqrt{\alpha_1} x} + C_2 R_{23} e^{-\sqrt{\alpha_2} x} \right] \quad [5.4]$$

$$\psi(x) = C_1 R_{32} e^{-\sqrt{\alpha_1} x} + C_2 R_{33} e^{-\sqrt{\alpha_2} x} \quad [5.5]$$

At low frequency, the variational parameter α_1 become comparable in magnitude to α_1 , since that eigenvalue vanishes as $\omega \rightarrow 0$:

$$\lim_{\omega \rightarrow 0} \alpha_1 = 0 \quad [5.6]$$

$$\lim_{\omega \rightarrow 0} \alpha_2 = \kappa^2 \quad [5.7]$$

Although the variational parameter α_1 ceases to be negligible compared to the eigenvalue α_1 , the matrix coefficients R_{j2} and R_{j3} also vanish at low frequency, thus causing ϕ_j to vanish, regardless of the behaviour of the variational parameters.

That is, since

$$\lim_{\omega \rightarrow 0} S_j = 0 \quad [5.8]$$

the matrix coefficients, will vanish:

$$\lim_{\omega \rightarrow 0} R_{j2} = \lim_{\omega \rightarrow 0} R_{j3} = 0 \quad [5.9]$$

so too will ϕ_j :

$$\lim_{\omega \rightarrow 0} \phi_j = 0 \quad [5.10]$$

It is the disappearance of α_1 as $\omega \rightarrow 0$ that necessitates the inclusion of the variational parameter a_1 at low frequency. Table 5.1 shows typical values for the variational correction $\frac{a_1}{\sqrt{\alpha_1}}$ at 1 Hz; for frequencies above 10 Hz, the eigenvalue α_1 is large enough that the correction can be dismissed. Since κ^2 is very large for all practical concentrations of electrolyte, a_2 can be neglected at all frequencies.

Table 5.1 – The absolute values of the variational correction a_1 relative to the frequency dependent eigenvalue $\sqrt{\alpha_1}$ as a function of the concentration of *KCl* and the ζ potential, at a frequency of $\omega=1\text{Hz}$. For $\omega \geq 10\text{Hz}$, the variational correction a_1 vanishes. The correction $\left| \frac{a_2}{\sqrt{\alpha_2}} \right|$ vanishes *at all frequencies*, with *KCl* concentration $>10^{-6}\text{M}$

ζ conc.	0V	0.075V	0.125V	0.500V	0.750V	1.00V
10^{-6}M	0	3.51×10^{-9}	1.40×10^{-8}	1.43×10^{-3}	1.10×10^1	9.8×10^3
10^{-4}M	0	3.52×10^{-11}	1.41×10^{-10}	1.43×10^{-5}	1.10×10^{-1}	1.14×10^3
10^{-2}M	0	3.52×10^{-13}	1.41×10^{-12}	1.43×10^{-7}	1.10×10^{-3}	1.12×10^1
1M	0	3.52×10^{-15}	1.41×10^{-14}	1.43×10^{-9}	1.10×10^{-5}	1.13×10^{-1}
10M	0	3.52×10^{-16}	1.41×10^{-15}	1.43×10^{-10}	1.08×10^{-6}	1.13×10^{-2}

From the table, very high dc biases, along with low concentrations, will require the full calculation of the variational parameters. Nevertheless, for a typical dielectrophoretic experiment without an external dc bias, the ζ potential should be sufficiently low that the eqs. [5.3], [5.4], and [5.5] will suffice without amendment.

The negligibility of the variational parameters occurs *independently* of the boundary conditions and *independently* of the details of the function $g(x, y, z)$ that describes the precise geometry of the field, since C_1 and C_2 are not invoked in the calculation of a_1 and a_2 . Consequently, for the electrical potential ψ , the dc bias is predominantly a

surface effect, having nothing to do with the spatial decay of the function itself. The constants C_1 and C_2 contain implicit ζ dependence from the boundary conditions, but they are completely determined once those boundary conditions are known. The calculation of the precise boundary conditions is not trivial, and a complete discussion is reserved for the following Chapter.

5.3 Concentration Polarization

The exponential pre-factor of ϕ_j contains some important physical implications. Recall from Chapter 2 that the equilibrium ion density is given by:

$$n_j^0(x) = n_j^\infty e^{\frac{z_j e}{kT} \Psi^0(x)} \quad [5.11]$$

so that the pre-factor can be re-written in terms of n_j^0

$$e^{\frac{\rho_j(x)}{1}} = \sqrt{\frac{n_j^\infty}{n_j^0(x)}} \quad [5.12]$$

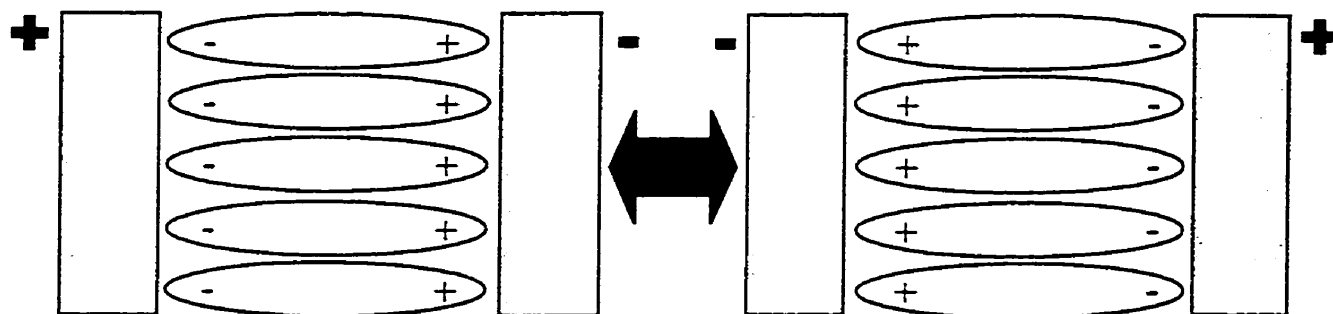
Thus, the exponential that rendered the operator self-adjoint can be equivalently viewed as the ratio between the bulk ionic concentration and the concentration at some arbitrary distance from the electrode. This phenomenon, described by the quotient of ionic densities, is called *concentration polarization* (2).

It is this factor that accounts for the chemical effect of the static double layer. The dc bias will attract a double layer that is superposed upon the double layer produced by the applied ac potential, leading to an asymmetric distribution of chemical potential around the electrode surfaces (**Figure 5.1**).

The origin of the asymmetry produced by the dc bias lies in the distribution of the charges due to the dc component. The ions influenced by it are shown in outlined symbols; the charges due to the ac field and the ions moved by it are shown in bold. If the dc bias is not very large, which is the most common situation encountered, then the dc charges on the electrodes will be completely neutralised by the outlined ions. Part of the assumption that the electrode is completely polarizable, discussed in Chapter 4, implies that there will always be enough ions in solution to fully neutralise the dc potential.

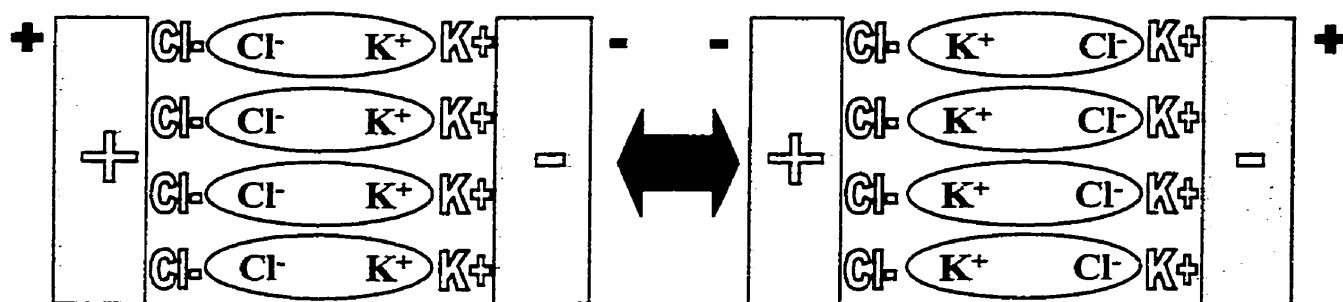
It might appear that with this charge neutralisation at both electrodes, the motion of the bold ions in an ac field would be the same, regardless of the dc field. That is not the case since a purely thermodynamic force will come into play. The electrodes with the K^+ counter-ions will possess a higher chemical potential for K^+ ions and hinder the arrival of the bold K^+ ions. A similar situation arises with respect to the bold Cl^- ions. The free energies of the system will be different during the two half cycles. On the average, the “dipoles” will take a longer time to relax to their steady states during the half cycle with

a)



No dc Bias: One Relaxation Time

b)



Higher Free Energy

Due to the diffusive forces arising from K-K and Cl-Cl interactions, and *not* due to electrostatic effects

Lower Free Energy

dc Bias, Symmetric Salt: Two Relaxation Times

Figure 5.1 – The chemical asymmetry of the electrodes due to the static double layer. a) In the absence of a dc bias, the dynamic double layer responds symmetrically like a charge dipole to the alternating applied field, shown in bold. b) When a dc bias is applied across the electrodes, shown in outline, the electrode surfaces attract static counter-ion clouds, also shown in outline. Now the cycling dynamic double layer will respond differently depending on the direction of the alternating field due asymmetric chemical forces at the surface.

the higher free energy barrier. At a macroscopic level, the time average spectrum will display two relaxation times (see Chapter 7). (Clearly the bold and outlined ions are used as illustrative features, and there is always some dynamic equilibrium between the two types. In reality, the bold and outlined ions are indistinguishable.)

Another way to imagine the situation is that although the alternating electrical force on the dipole is symmetric, through one half of the cycle, the ends must move up a concentration gradient, while through the other half cycle, they must move down. With the field in one direction, the motion of the dipole is hindered, while with the field in the other direction, the motion is aided by the chemical potential gradients at the electrode surface.

5.4 Connection to the Debye-Hückel Potential

It is reassuring to note that when the frequency of the applied potential goes to zero, the Debye-Hückel potential is recovered from the potential equations:

$$\psi(x) = C_1 + C_2 e^{-\alpha} \quad [5.13]$$

$$\phi_j(x) = 0 \quad [5.14]$$

With suitable boundary conditions ($C_1 = 0$, $C_2 = \zeta$), eq. [5.13] is exactly the Debye-Hückel potential.

Chapter 6

The Effective Potential and the Double Layer Impedance

Typically, dielectrophoresis, electrorotation, and electrophoresis experiments involve an examination of particles that are located far from the electrode surface. Consequently, knowledge of the electrical field in the bulk region is of fundamental importance, which, in turn requires a computation of the effective potential, V_{eff} and the potential distribution in the double layer (**Figure 6.1**). Much of the work presented in this Chapter will be applicable to the general electrodes described Chapter 2, while specific calculations to illustrate some important features of electrode polarization will be done in Chapter 7.

Using the variational potential functions derived in Chapter 4, along with an integral transformation of the mass conservation equation derived below, an expression for the effective potential is obtained. Furthermore, from the effective potential, important physical parameters, including the relaxation time and the complex permittivity of the ionic medium, can be calculated.

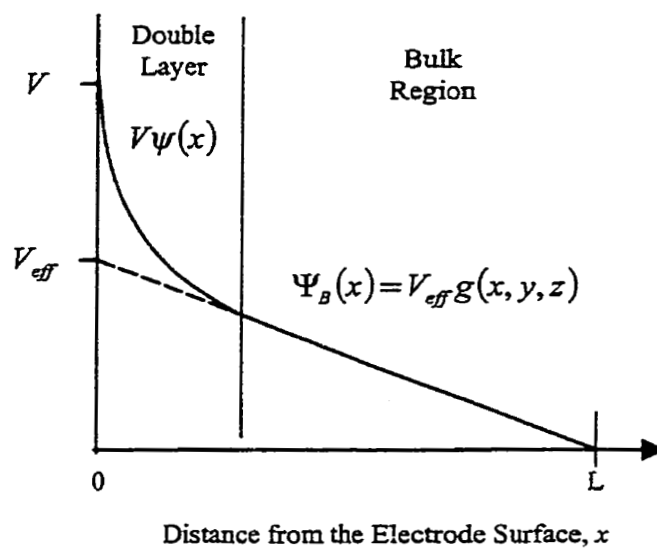


Figure 6.1 - The impedance of the double layer produces a voltage drop between the electrode surface and the bulk region. If we are able to calculate the attenuation of the potential in the double layer, then we can calculate V_{eff} . With V_{eff} the potential far from the double layer is known.

6.1 The Effective Potential, V_{eff}

When considering both the static and dynamic characteristics of the double layer, it is essential to have a description of the ionic density, and the ionic velocity at any point in space and time, for the j species in solution. The variational potential functions derived in Chapter 4 make that description possible explicitly. The reader is reminded that in Chapter 2, the assumption was made that the normal component of the flux is dominant and that the spatial variables y and z will not be explicitly displayed. *This shorthand does not imply that the y and z variables are not present, for they play a very significant role in the boundary conditions of inhomogeneous electrode arrays.*

From Chapter 2, the ionic density, $n_j(x, t)$, and the velocity, $v_j(x, t)$, to first order in the applied potential V , of the j^{th} species are written as:

$$n_j(x, t) = n_j^0(x) - \frac{z_j e}{kT} n_j^0(x) \{ \psi(x) - \phi_j(x) \} V e^{i\omega t} \quad [6.1]$$

$$v_j(x, t) = -\frac{z_j e}{\lambda_j} \frac{d}{dx} (V \phi_j(x) + \Psi_B(x)) e^{i\omega t} \quad [6.2]$$

The equilibrium ionic density $n_j^0(x)$, present in the absence of the applied potential, is:

$$n_j^0(x) = n_j^\infty e^{-\frac{z_j e}{kT} \Psi^0(x)} \quad [6.3]$$

where n_j^∞ is the bulk ionic density and $\Psi^0(x)$ is a dc electrical potential that is present in the absence of the applied ac field. This potential, as pointed out earlier, has its origins in either the naturally present ζ potential or in an applied dc bias.

The system of differential equations derived in Chapter 2 describes the potential and velocity potentials in the double layer.

$$\frac{d^2 \psi}{dx^2} - \sum_{j=1}^N b_j \psi = - \sum_{j=1}^N b_j \phi_j \quad [6.4]$$

$$\frac{d^2 \phi_j}{dx^2} + \hat{\Sigma}_j \phi_j - i S_j^2 (\psi - \phi_j) + \hat{\Sigma}_j \frac{\Psi_B}{V} = 0 \quad j = 0, 1, 2, \dots, N \quad [6.5]$$

The solutions to these equations are subject to the boundary conditions:

$$\lim_{x \rightarrow 0} \psi(x) = 1 - \frac{1}{V} \lim_{x \rightarrow 0} \Psi_B(x) \quad [6.6]$$

$$\lim_{x \rightarrow 0} \frac{d}{dx} \phi_j(x) = -\frac{1}{V} \lim_{x \rightarrow 0} \frac{d}{dx} \Psi_B(x) \quad [6.7]$$

$$\lim_{x \rightarrow L} \psi(x) = 0 \quad [6.8]$$

$$\lim_{x \rightarrow L} \phi_j(x) = 0 \quad \lim_{x \rightarrow L} \frac{d}{dx} \phi_j(x) = 0 \quad [6.9]$$

where L is the distance to an imaginary grounded plate between the electrode and its image, in the bulk region. As discussed in Chapter 2, eq. [6.7] is a mathematical expression of the physical fact that the ions can not penetrate the electrode material.

Chapter 4 described the derivation of approximate solutions to the governing system of differential equations using a variational theorem based on the early work of DeLacey and White. Furthermore, it was demonstrated in Chapter 5 that under typical conditions the parameter $a_j/\sqrt{\alpha_j}$ can be neglected. Using this information, along with the explicit form of matrix $\underline{R}$ from Chapter 4, the variational solutions are:

$$\phi_2(x) = e^{-\frac{\rho_1(x)}{2}} \left(C_1 \left(\frac{iS_1^2}{iS_1^2 + \alpha_1} \right) e^{-\sqrt{\alpha_1}x} + C_2 \left(\frac{iS_1^2}{iS_1^2 + \alpha_2} \right) e^{-\sqrt{\alpha_2}x} \right) \quad [6.10]$$

$$\phi_2(x) = e^{-\frac{\rho_2(x)}{2}} \left(C_1 \left(\frac{iS_2^2}{iS_2^2 + \alpha_1} \right) e^{-\sqrt{\alpha_1}x} + C_2 \left(\frac{iS_2^2}{iS_2^2 + \alpha_2} \right) e^{-\sqrt{\alpha_2}x} \right) \quad [6.11]$$

$$\psi(x) = C_1 e^{-\sqrt{\alpha_1}x} + C_2 e^{-\sqrt{\alpha_2}x} \quad [6.12]$$

Although the above set of equations are analytic expressions, they still contain the two unknown constants C_1 and C_2 that must be evaluated from the boundary conditions at the electrode surface ($x=0$). Eq. [6.6], along with the two equations ($j=1,2$) contained in [6.7] are the appropriate boundary conditions. At first glance, the system appears over determined with three equations defining two unknown constants. However, an examination of the boundary conditions shows that they contain the bulk potential Ψ_B ,

which is still unknown, since it contains V_{eff} . In the following section, the calculation of the three unknowns C_1 , C_2 , and V_{eff} is discussed.

6.1.1 - Calculation of the Integration Constants C_1 and C_2

For a general planar electrode system with an imaginary ground plate at L , the bulk potential at a point x is given by:

$$\Psi_B(x) = V_{eff} g(x) \quad [6.13]$$

DeLacey and White (18) suggest that the boundary conditions on ϕ_1 and ϕ_2 be used to calculate C_1 and C_2 , while V_{eff} be calculated from the boundary conditions on ψ . Eq. [6.7] is re-written in terms of V_{eff} as follows:

$$\lim_{x \rightarrow 0} \frac{d}{dx} \phi_1(x) = \lim_{x \rightarrow 0} \frac{d}{dx} \phi_2(x) = -\frac{V_{eff}}{V} g'(0) \quad [6.14]$$

Implicit in eq. [6.14] is an assumption that the collision process between the ion and the electrode surface be treated as a “hard” collision. That is, a collision occurring only upon contact with the electrode surface. This approximation can be justified only in the absence of the ζ potential. In the presence of a ζ potential, a “softer” collision process must be envisaged, in which the positively and negatively charged ions are stopped at

different distances from the electrode surface. The distance of closest approach being dictated by the concentration profile created by the static double layer.

To account for the difference in the surface collisions between the cations and anions, the function ψ is made j -dependent. In that way, the electrical potential distribution in the double layer is made to depend on whether the dynamic double layer consists of positive or negative ions. The surface boundary conditions become:

$$\psi_j(0) = 1 - \frac{V_{eff,j}}{V} g(0) \quad [6.15]$$

$$\left. \frac{d\phi_j}{dx} \right|_{x=0} = -\frac{V_{eff,j}}{V} g'(0) \quad [6.16]$$

The boundary conditions [6.15] and [6.16] can be used to calculate the unknown constants C_1 and C_2 , while N additional constraining equations will be necessary to define $V_{eff,j}$. Fortunately, an integral representation of the j -dependent effective voltage is available by considering the equation of continuity.

6.1.2 The Integral Representation of V_{eff}

The approach follows that proposed by Dukhin and Shilov (34) in addressing the polarization of colloid particles, and extended by Paul and Kaler (25) to the polarization of hemispherical electrode systems. Integrating both sides of the equation of continuity, given in Chapter 2 (c.f. eq. [2.25]):

$$\int_0^L dx \frac{\partial n_j}{\partial t} = - \int_0^L dx \frac{dJ_j(x)}{dx} \quad [6.17]$$

Using eqs. [6.1] and [6.2], the flux of the j^{th} species is:

$$\bar{J}_j(x, t) = -\frac{z_j e}{\lambda_j} n_j^0(x) \frac{d}{dx} (\phi_j(x) V + \Psi_B(x)) e^{i\omega t} \quad [6.18]$$

Using the boundary conditions, and the general form of Ψ_{B_j} ,

$$\int_0^L dx \frac{dJ_j(x)}{dx} = -\frac{z_j e}{\lambda_j} n_j^\infty V_{\text{eff}_j} g'(L) e^{i\omega t} \quad [6.19]$$

The rate of change in the ionic density when integrated over the “volume” of the electrode chamber yields the difference between the rate of change in the ionic density at the two boundaries.

$$-\int_0^L dx \frac{\partial n_j}{\partial t} = i\omega \frac{z_j e}{kT} V e^{i\omega t} \int_0^L dx n_j^0(x) (\psi_j - \phi_j) \quad [6.20]$$

Equating eqs.[6.19] and [6.20], and solving for V_{eff_j} ,

$$V_{eff_j} = -V \frac{iS_j^2}{g'(L)} \int_0^L dx e^{-\frac{z_j e}{kT} \Psi^0(x)} (\psi_j - \phi_j) \quad [6.21]$$

The voltage V_{eff_j} is j -dependent due to the chemical potential considerations contained in the Boltzmann exponential. The potential actually experienced in the bulk region of the electrode system is assumed to be a time-averaged quantity, $\langle V_{eff} \rangle_t$. In a two-ion system, each ion will dominate the screening for exactly $\frac{1}{2}$ of a cycle, leading to:

$$\langle V_{eff} \rangle_t = \frac{1}{T} \int_0^T dt V_{eff}(t) = \frac{V_{eff_1} + V_{eff_2}}{2} \quad [6.22]$$

6.2 The Total Impedance of the Ionic Solution, Z_{tot}

The boundary conditions, eqs. [6.15] and [6.16], contain the effective potential V_{eff} . It will be convenient to make all the V_{eff} dependence explicit in the functions ψ_j and ϕ_j , so that a complete expression for the effective voltage can be arrived at. To that end, it is useful to introduce two new functions, $\tilde{\psi}_j$ and $\tilde{\phi}_j$, themselves solutions to the system of the differential equations, but with boundary conditions:

$$\tilde{\psi}_j(0) = 1 \quad [6.23]$$

$$\left. \frac{\partial \tilde{\phi}_j}{\partial x} \right|_{x=0} = 1 \quad [6.24]$$

so that,

$$\psi_j(x) = \left(1 - \frac{V_{eff_j}}{V} g(0) \right) \tilde{\psi}_j(x) \quad [6.25]$$

$$\phi_j(x) = \left(-\frac{V_{eff_j}}{V} g'(0) \right) \tilde{\phi}_j(x) \quad [6.26]$$

Using these new functions, eqs. [6.25] and [6.26], along with eq. [6.21], it is possible obtain a formal expression for V_{eff_j}

$$V_{\text{eff}} = C_j(\zeta, \omega) V \quad [6.27]$$

where $C_j(\zeta, \omega)$ is a complex correction term, dependent on the ζ potential and the angular frequency of the alternating field, ω . Written explicitly:

$$C_j(\zeta, \omega) = - \frac{\int_0^L dx e^{\rho_j} \bar{\psi}_j}{\int_0^L dx e^{\rho_j} \{g(0) \bar{\psi}_j - g'(0) \bar{\phi}_j\} + \frac{ig'(L)}{S_j^2}} \quad [6.28]$$

It is evident that $C_j(\zeta, \omega)$ contains the effect of the double layer on the apparent voltage experienced in the bulk region of the chamber. Under steady state conditions, the current per unit area, $Ie^{i\omega t}$, crossing an arbitrary plane parallel to the electrode surface must be the same irrespective of the location of the plane. Consider such a plane outside the double layer, in the bulk region. The complex conductivity, $K(\omega)$, in this region is given by:

$$K(\omega) = \sum_{j=1}^N \frac{e^2 z_j^2 n_j^\infty}{\lambda_j} - \frac{i\omega\epsilon_m}{4\pi} \quad [6.29]$$

It follows that the current flow through the electrolyte is

$$I_j e^{i\omega t} = \frac{K(\omega) V_{\text{eff}}}{L} e^{i\omega t} \quad [6.30]$$

Or,

$$I_j = \frac{K(\omega)V_{eff}}{L} \quad [6.31]$$

From Ohm's law:

$$V = Z_{tot} I_j \quad [6.32]$$

Equivalently, from eq. [6.31],

$$V = Z_{tot} \frac{K(\omega)V_{eff}}{L} \quad [6.33]$$

Solving for the total impedance,

$$Z_{tot} = \frac{VL}{V_{eff}K(\omega)} \quad [6.34]$$

The total impedance is an experimentally accessible parameter. Nevertheless, investigators of electrode polarization often speak of the double layer impedance. Assuming that the total impedance can be represented as sum of the double layer impedance, Z_{DL} , and the impedance of the solution, taken in series:

$$Z_{Tot,j} = Z_{DL,j} + \frac{L}{K(\omega)} \quad [6.35]$$

Combining eqs. [6.33] and [6.35], and solving for $Z_{DL,j}(\zeta, \omega)$

$$Z_{DL,j}(\zeta, \omega) = \frac{L}{K(\omega)} \left[\frac{1}{C_j(\zeta, \omega)} - 1 \right] \quad [6.36]$$

This equation relates the complex correction term to the electrode impedance and the conductivity of the bulk solution.

In the Chapter that follows, explicit calculations of the effective potential and the total impedance will be made for the simple homogeneous planar case and for more exotic non-homogeneous electrode arrays.

Chapter 7

Electrode Polarization for Various Array Geometries

The key result from the previous Chapter was the derivation of an expression for the effective potential, given by:

$$V_{\text{eff}} = V C_j(\zeta, \omega) \quad [7.1]$$

where $C_j(\zeta, \omega)$ is the complex correction term:

$$C_j(\zeta, \omega) = - \frac{\int_0^L dx e^{\rho_j} \psi_j^*}{\int_0^L dx e^{\rho_j} \{g(0) \psi_j^* - g'(0) \phi_j^*\} + \frac{ig'(L)}{S_j^2}} \quad [7.2]$$

that incorporates the effect of the static and dynamic double layers on the field experienced in the bulk region. Much useful information can be drawn from the effective potential, and in particular, from the correction factor. The electrode impedance and the effective potential were outlined in Chapter 6. But more important, perhaps, from an experimental point of view is the relaxation time associated with electrode polarization. Alternately, an investigator may ask themselves: Above what frequency can electrode

polarization effects be neglected? The subject of this Chapter is to calculate the relaxation time for a variety of practical planar electrode arrays.

7.1 The Homogeneous Planar Electrode

As a primary example of a specific application of the methods presented, the case of a strictly planar, homogeneous electrode system is examined. This type of electrode has been studied previously by White *et al* (18, 19), and numerous references to their investigations have already been made. Most of their work has been either of a numerical nature or employing perturbation theory. Now, using the variational results derived in Chapters 4 and 6, it is possible to make theoretical predictions that have thus far not been possible.

For a homogeneous planar electrode, the field in the bulk region is uniform, and the bulk electrical potential given by:

$$\Psi_B(x) = V_{eff} \left(1 - \frac{x}{L} \right) \quad [7.3]$$

For which $g(x)$ is a linear function in x :

$$g(x) = \left(1 - \frac{x}{L} \right) \quad [7.4]$$

Using eq. [7.4] with eq. [7.2], the full form of $C_j(\zeta, \omega)$ in a planar system is:

$$C_j(\zeta, \omega) = \frac{L \int_0^L dx e^{\rho_j} \psi_j^*}{\int_0^L dx e^{\rho_j} \left\{ L \psi_j^* + \phi_j^* \right\} + \frac{i}{S_j^2}} \quad [7.5]$$

The correction factor, $C_j(\zeta, \omega)$, is complete and contains no approximations. In general, the integrals will have to be evaluated numerically, particularly if the equilibrium potential $\Psi^0(x)$ does not have a closed form. Nevertheless, once the values of the integrals are calculated for a given set of parameters, they remain fixed, and can be tabulated and used repeatedly for the same system. In the next section, the correction factor is investigated in the absence of the ζ potential, in which case, the integrals can be done exactly.

7.1.1 Zero ζ Potential in the Planar Case

In the absence of the ζ potential, the homogeneous planar electrode geometry allows considerable simplification of eq. [7.5]. In **Figure 7.1**, the real and imaginary parts of eq. [7.5] are displayed for a solution of $10^{-5}M$ *KCl*, with plates separated by 1 mm. As can be seen from the plot, the imaginary part shows a

single relaxation time A general expression for this relaxation time can be derived in the following manner.

First, the double layer is assumed to be much thinner than the dimension of the chamber, so that:

$$\frac{1}{\kappa} \ll L \quad [7.6]$$

Allowing,

$$\int_0^L dx \approx \int_0^{\infty} dx \quad [7.7]$$

Second, the ionic drag coefficients of the salts in the solution are assumed to be similar enough that they can be replaced by an average drag coefficient, $\bar{\lambda}$, as per Gunning, Chan and White (19). The typical drag coefficient for a general salt $X_{m_1}^1 X_{m_2}^2 \dots X_{m_N}^N$ is:

$$\bar{\lambda} = \frac{\sum_{j=1}^N m_j \lambda_j}{\sum_{j=1}^N m_j} \quad [7.8]$$

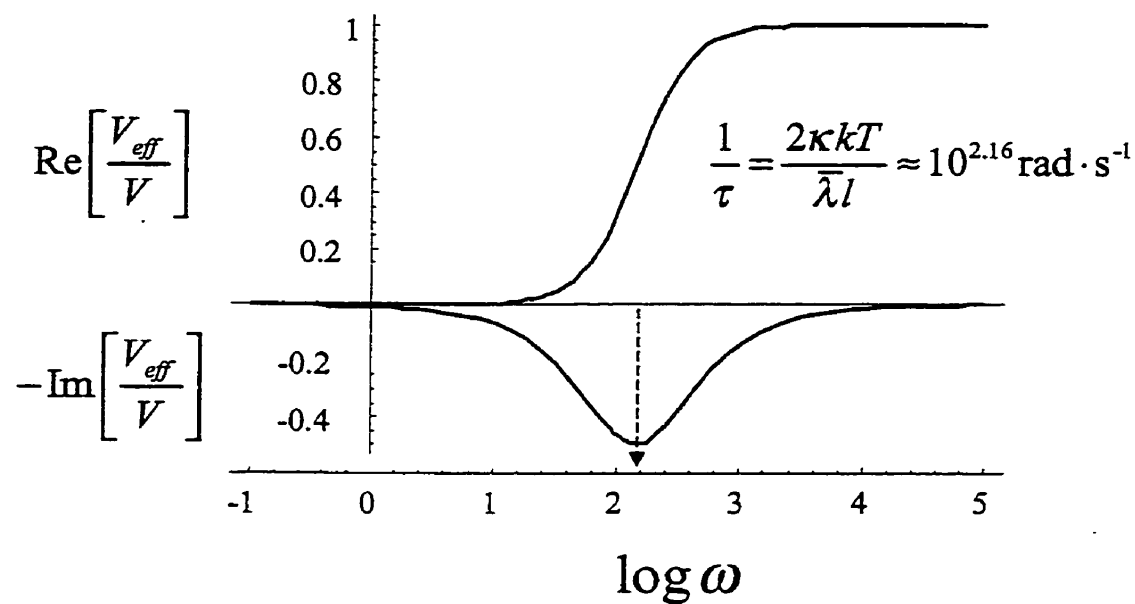


Figure 7.1 – The complex frequency spectra for V_{eff} normalized to unity at high frequency for a homogeneous planar electrode. The relaxation peak in the imaginary part of V_{eff} corresponds to the reciprocal of the relaxation time, $1/\tau$, predicted by eq. [7.9]. Here, the solution is 10^{-3} M KCl between two planar electrodes 1 mm apart.

With these two reasonable simplifications, the relaxation time for an ionic dielectric sandwiched between two planar electrodes separated by a distance l ($l=2L$) is:

$$\tau = \frac{l\bar{\lambda}}{2\kappa kT} \quad [7.9]$$

Therefore, measurements taken at frequencies above $\omega = 1/\tau$, in a homogeneous planar electrode system will be made in the absence of electrode polarization effects.

7.1.2 Non-zero ζ Potential in the Planar Case

To account for a dc bias placed across the electrode chamber, an explicit (though possibly numerical) form of the equilibrium potential $\Psi^0(x)$ must be given to fully define the function $\rho_j(x)$, and its derivative. To that end, we use the Debye-Hückel potential (35):

$$\Psi^0(x) = \zeta e^{-\kappa x} \quad [7.10]$$

Although limited to low ζ potentials, this form of the equilibrium potential represents an initial approximation to more rigorous numerical solutions that one might choose.

The ζ potential appears in the expression for the effective far field, eq. [7.5], via the Boltzmann exponential under the integral sign:

$$\lim_{x \rightarrow 0} e^{-\frac{zF}{RT}\psi^0(x)} = e^{-\frac{zF}{RT}\zeta} \quad [7.11]$$

The j -ionic species dependence of the correction term comes chiefly from the exponential under the integral, related to the ζ potential. When the ζ potential is increased, this exponential corresponds to a sizeable perturbation in the ionic density around the electrode (near $x=0$) in the absence of the applied ac potential, and the ensuing concentration gradients significantly affect the far field. If, for instance, the electrode carries a positive static charge ($\zeta > 0$), then a negative static counter-ion layer will be attracted causing a local increase in the chemical potential of these ions. When an ac field is applied, the charges on the electrode will be perturbed differently during the two halves of the cycle. First, consider that half of the cycle (to be referred to as the *first half* for convenience) during which the electrode carries an additional amount of positive charge. A further quantity of negative ions will be attracted, but these ions must enter a region with higher chemical potential. A similar situation prevails at the counter-electrode, but with opposite charge.

Conversely, during the other half of the cycle (referred to as the *second half* for convenience) all ions are electrostatically attracted to regions of lowered chemical potentials. It follows that during the first half the system must relax into a state of higher free energy than in the second half. The relaxation time of the first half will be longer than that of the second half and two relaxation times will be observed. The origin of these relaxation times is a thermodynamic rather than an electrostatic one. Looked at from

another perspective, note that the dc bias will create different concentration profiles for the differently charged ions which is responsible for the two relaxation times predicted in the time-averaged far field spectrum for a binary electrolyte like *KCl* (Figure 7.2).

For a non-zero ζ potential, the effective potential is no longer constant through the cycling of the applied ac potential, but depends on which half-cycle it is observed. The field in the bulk region, then, will be a time-averaged quantity. An impedance spectrum of the electrolyte solution taken with a frequency response analyser will likely record a weighted average impedance over the whole cycle, favouring the half cycle with the lowest impedance. Since Z_{tot} is proportional to $\frac{1}{V_{eff}}$ (from Chapter 6), the lowest impedance will arise from the low frequency relaxation peak.

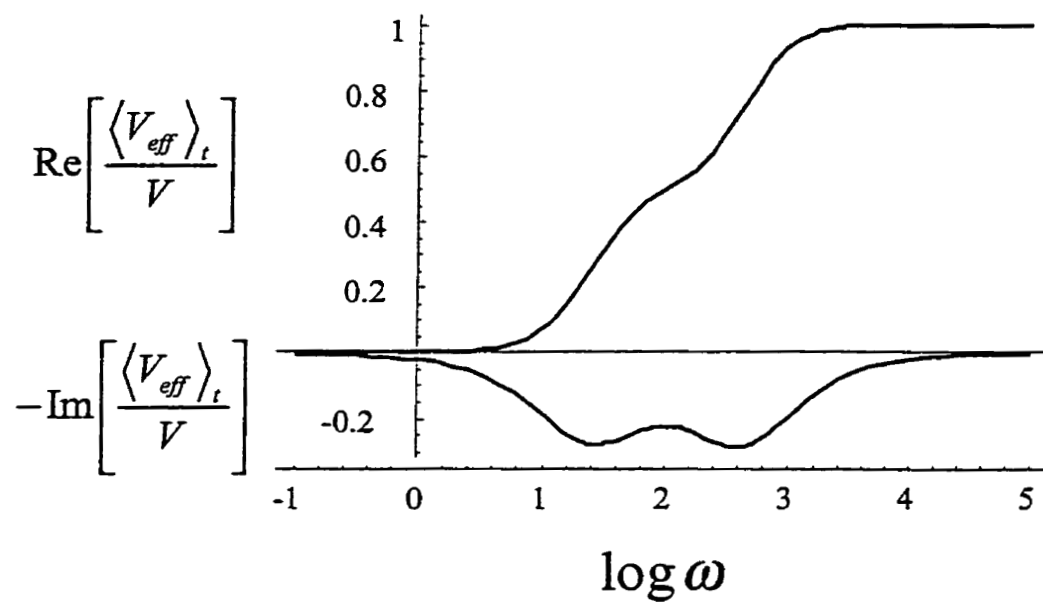


Figure 7.2 - The time-averaged frequency spectrum of V_{eff} normalized to unity at high frequency, with a dc bias of 150 mV between the electrodes. Notice the presence of two relaxation peaks in the imaginary part of V_{eff} . Here again, the solution is 10^{-5} M KCl between two planar electrodes 1 mm apart.

Our calculations have shown that the ζ potential, even though a dc potential, significantly alters the dynamics of the double layer. Comparing **Figure 7.1** with **Figure 7.2** the dynamical alterations are most easily seen.

7.2 Planar Array of Strip Electrodes – Emulating a Pulsating Standing Wave

Often in dielectrophoretic, and electrophoretic experiments, electrodes of complicated geometry are simulated by a planar array of strips (22, 23, 24) that are maintained at different applied potentials. To illustrate the versatility of the present technique, an expression for the effective potential of an array of strip electrodes described by Markx, Pethig, and Rousselet (24) in the absence of a ζ potential is derived, comparing the theoretical results to their experimental data.

Using the same simplifications described above, in section 7.1, the effective potential for a general planar electrode is:

$$V_{eff} = \frac{V}{g(x=0)} \frac{1}{1 + \frac{1}{i\omega\tau}} \quad [7.12]$$

where the relaxation time of the ionic medium, τ , is given by:

$$\tau = \frac{\bar{\lambda} g(x=0)}{\kappa k T \left(-\frac{1}{2} \left(\left. \frac{dg}{dx} \right|_{x=0} + \left. \frac{dg}{dx} \right|_{x=L} \right) \right)} \quad [7.13]$$

For a specific array geometry, the function $g(x, y, z)$ is available, enabling the computation of the effective potential to be carried out. To illustrate, consider a system of parallel electrode strips having width d and separated by a gap of the same distance d (Figure 7.3).

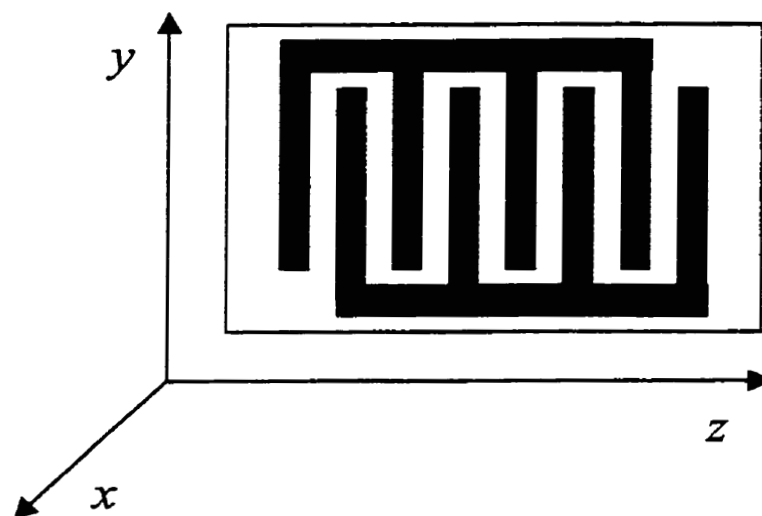
An oscillating voltage $V e^{i\omega t}$ is applied to each alternate strip, while the strip in between is maintained at ground potential. The discrete potential profile along the surface of the array can be roughly approximated by a continuous standing wave of length $4d$. In this continuous approximation, the surface potential along the array lying in the zy -plane, where the electrode strips lie normal to the z -axis (see Figure 7.3), is:

$$\Psi(x=0, y, z, t) = V e^{i\omega t} \cos\left[\frac{z}{2d}\pi\right] \quad [7.14]$$

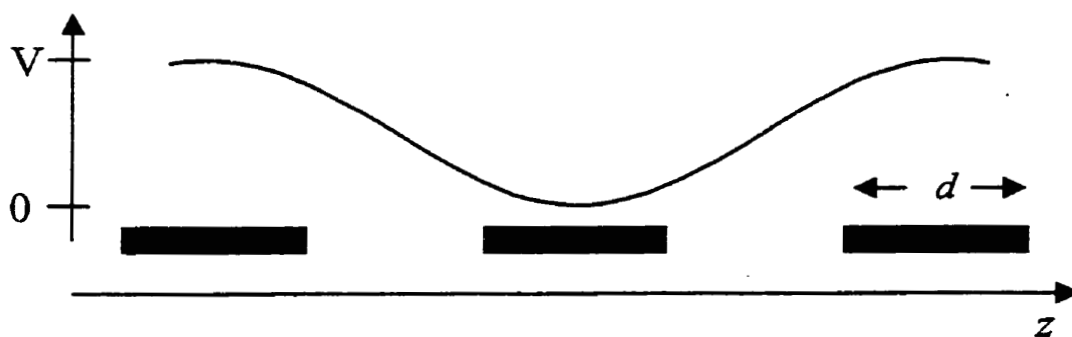
Wang, Wang, Becker and Gascoyne (23) have developed a method using Green's functions to relate the surface potential distribution along an array, eq. [7.14], to some point above the surface. Using their analysis, the general potential distribution above the array is:

$$\Psi(x, y, z) = \frac{1}{4\pi} \int dy' dz' \frac{2x \Psi(x=0)}{\left[(z' - z)^2 + (y' - y)^2 + x^2 \right]^{3/2}} + B_1 + B_2 x \quad [7.15]$$

a)



b)



Pulsating Standing Wave

$$V(x, y, z, t) = V e^{-i\omega t} \cos\left[\frac{z}{2d} \pi\right]$$

Figure 7.3 – a) A schematic diagram of the electrode system used by Markx *et al.* (24) b) Continuous approximation of the potential distribution along the surface of the array.

where B_1 and B_2 are integration constants determined from the boundary conditions. In particular, the constant B_1 satisfies the boundary conditions on the surface,

$$B_1 = \Psi(x=0) \quad [7.16]$$

and the constant B_2 satisfies the boundary conditions at L :

$$B_2 = -\frac{1}{L} \left\{ \frac{1}{4\pi} \int dy' dz' \frac{2L \Psi(x=0)}{\left[(z'-z)^2 + (y'-y)^2 + L^2 \right]^{\frac{1}{2}}} + B_1 \right\} \quad [7.17]$$

From the first equation in Chapter 2, eq. [2.1],

$$\Psi(x, y, z) = Vg(x, y, z) \quad [7.18]$$

so that,

$$\frac{dg}{dx} = \frac{1}{4\pi V} \frac{d}{dx} \int dy' dz' \frac{2x \Psi(x=0)}{\left[(z'-z)^2 + (y'-y)^2 + x^2 \right]^{\frac{1}{2}}} + \frac{B_2}{V} \quad [7.19]$$

Allowing the derivative of g to be evaluated at the end points in a straightforward manner. In practice, there is a singularity in the derivative of g located at the

surface. To avoid this singularity, the surface derivative is evaluated at a distance an ion's radius off the surface.

In the experimental set-up of Markx *et al.*, there is a counter electrode infinitely far from the array. So letting $L \rightarrow \infty$, calculating $g'(x)$ and $g'(L)$ from eq. [7.19], V_{eff} is determined. The imaginary part of the effective potential in an $NaCl$ solution with a medium conductivity of $11 \mu S/cm$ and a characteristic electrode dimension $d = 40 \mu m$, is shown in Figure 7.4. The predicted polarization behaviour of the system is in agreement with the experimental data of Markx, Pethig and Rousselet, as seen in Figure 4 of (24). Our theoretical model predicts a relaxation frequency $f = 1/2\pi\tau$ of about $10^{2.7}$ Hz, while the data of Markx *et al.* suggests a relaxation at about $10^{3.2}$ Hz based on the frequency observed for the onset of levitation.

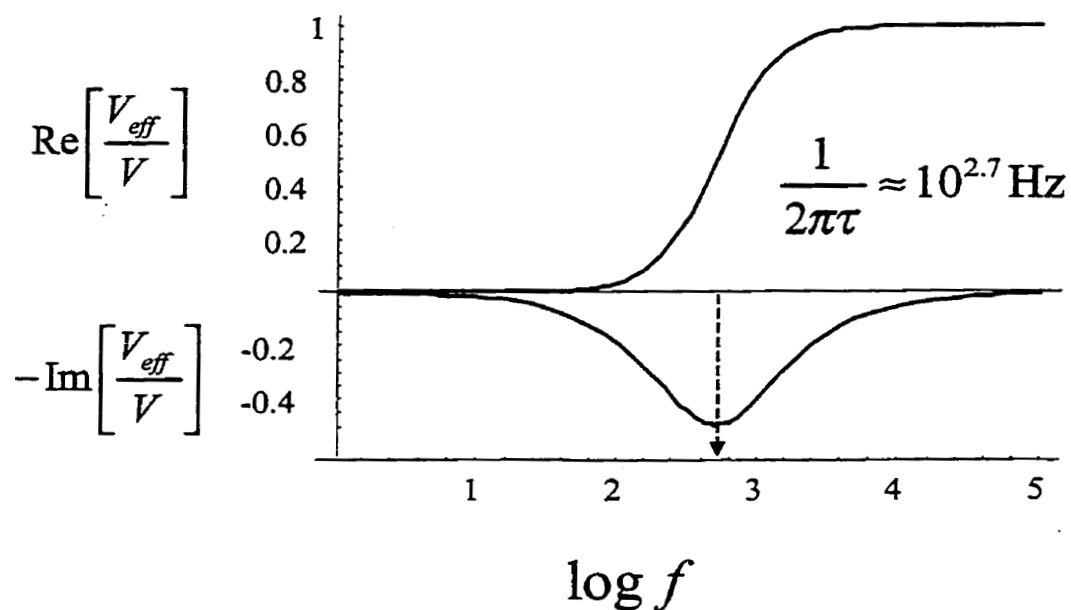


Figure 7.4 - The complex frequency spectra for V_{eff} , normalized to unity at high frequency, for non-homogeneous electrode array used by Markx *et al.* (24), with 40 μm strips spaced 40 μm apart. The relaxation peak occurs at about $10^{2.7}$ Hz. The calculations are for an 11 mS/m solution of NaCl. (Notice that the x-axis is log frequency, not log of the *angular* frequency, to make comparison with Markx *et al.* more amenable.)

7.3 Concentric Array of Ring Electrodes – Emulating a Hemispherical System

To calculate the polarization in a ring array, the procedure is very similar to the one outlined in the previous section dealing with strip electrodes. Due to the rotational symmetry in the concentric rings, it is more convenient to adopt a cylindrical form of eq. [7.15]:

$$\Psi(x, r, \theta) = \frac{1}{4\pi} \int dr' d\theta' \frac{2rx\Psi(x=0)}{[r'^2 + r^2 - 2r'r \cos\theta' + x^2]^{\frac{3}{2}}} + B_1 + B_2x \quad [7.20]$$

Similarly, the derivative of the function $g(x, r, \theta)$ is given by:

$$\frac{dg}{dx} = \frac{1}{4\pi V} \frac{d}{dx} \int dr' d\theta' \frac{2x\Psi(x=0)}{[r'^2 + r^2 - 2r'r \cos\theta' + x^2]^{\frac{3}{2}}} + \frac{B_2}{V} \quad [7.21]$$

where B_2 is:

$$B_2 = -\frac{1}{L} \left\{ \frac{1}{4\pi} \int dr' d\theta' \frac{2L\Psi(x=0)}{[r'^2 + r^2 - 2r'r \cos\theta' + L^2]^{\frac{3}{2}}} + \Psi(x=0) \right\} \quad [7.22]$$

Again, there is a singularity at the surface, $x=0$. To avoid the singularity, the derivative is evaluated either a distance an ion's diameter above the surface, or, if the

electrode array is coated in glass, as they often are, then the derivative is evaluated at the glass surface ($x = 3\mu\text{m}$).

A projection on the plane of a potential distribution arising from a hemispherical electrode of radius a is given roughly by:

$$\Psi(x=0, r) = \frac{aL}{(a+L)\sqrt{a^2 + r^2} - a^2} \quad [7.23]$$

provided $L \gg a$.

Using eqs. [7.12], [7.13], [7.21], and [7.23], the effective potential can be calculated. The real and imaginary parts of the frequency spectrum for V_{eff} in a 10^{-4} M solution of NaCl , with $L=0.5$ mm, emulating a hemispherical electrode of radius $a=75\mu\text{m}$, is shown in Figure 7.5.

In the final Chapter, some general comments are made about the analysis, and suggestions for future work are outlined.

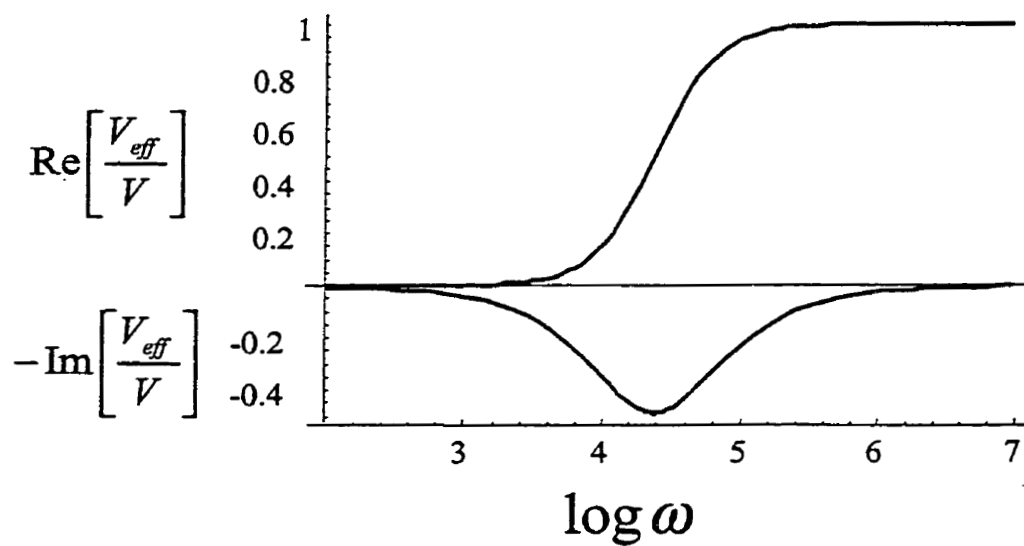


Figure 7.5 – The complex frequency spectra for V_{eff} , normalized to unity at high frequency for a concentric ring array emulating a hemispherical electrode with radius $75 \mu\text{m}$. Here, the solution is 10^{-4} M NaCl between two planar electrodes 1 mm apart.

Chapter 8

Conclusion

8.1 Conclusions Regarding the Variational Analysis

The variational approach has provided an expedient method for solving the mathematical model of electrode polarization developed in Chapter 2. Incorporating the analytic solutions derived in Chapter 4, electrode polarization effects can be predicted in a variety of contexts through the effective potential parameter, V_{eff} , developed in Chapters 6 and 7. To complete the study of electrode polarization, however, there are two main simplifications made in the present model that must be addressed in future work.

8.2 Future Work

There are two areas where future work on electrode polarization should be focussed. First, some account must be taken for the tangential components of the ionic flux. Second, the model must accommodate galvanic electrochemical processes taking place at the electrode surface. Each of these will be addressed in the following sections.

8.2.1 Tangential Ionic Flux

For systems such as the homogeneous planar electrode, or the concentric ring array emulating a hemispherical electrode, the tangential ionic flux, that is the flux parallel to the electrode surface, plays a minimal role. For more complicated array geometries, for example strips emulating a travelling wave, or concentric rings producing a conical field, the tangential ion flux must be incorporated.

The inclusion of the tangential component of the ionic flux requires that equations similar to those derived in Chapter 2 be found in each of the x , y , and z directions. With suitable boundary conditions on this augmented system, the solutions should be open to variational solution.

8.2.2 Electrochemical Reactions at the Surface

Electrochemical reactions at the electrode surface can scarcely be avoided, particularly with high dc bias across the electrodes. To account for the electrochemical evolution and consumption of ions species at the electrodes will require a careful modification of the model.

The equation of continuity invoked in Chapter 2 characterising ϕ_j , will include a source term dependent on the rate of electrochemical ionic production at the surface.

Furthermore, the neglecting electrochemical reactions at the interface allowed for the assumption that the electrode was completely polarizable, i.e. that at zero frequency, the field in the bulk region disappears. It was this behaviour at zero frequency that necessitated the constant normal mode z_0 be set to zero in Chapter 4. Clearly, with reactions going on at the interface, even at zero frequency, the surface will not be completely polarized. So additional boundary conditions must be found to determine the constant normal mode.

On the whole, the present analysis provides a soluble foundation upon which a more inclusive theory of polarization may be built.

Appendix 1 - Green's Functions

For an excellent discussion of Green's functions and their application in physical problem, the reader is directed to the book by Boas (36). This appendix is based in large part on section 11.8 of that book.

The Dirac delta function, $\delta(x)$, is a distribution with the unusual quality that it is zero everywhere, but infinite at the origin. It can be imagined as an impulse at the origin, infinitely large, but infinitely thin, so that

$$\int_{-\infty}^{\infty} dx \delta(x) = 1 \quad [9.1]$$

In fact, since the Dirac delta function is zero everywhere but at the origin,

$$\int_{-\infty}^{\infty} dx f(x) \delta(x) = f(0) \quad [9.2]$$

Alternately, as is more commonly done, the origin may be shifted with respect to a dummy variable,

$$\int_{-\infty}^{\infty} dx' f(x') \delta(x-x') = f(x) \quad [9.3]$$

Consider a non-homogeneous differential equation

$$\mathcal{L}u(x) = f(x) \quad [9.4]$$

where $\mathcal{L}$ is a given operator, and $f(x)$ is a known forcing function. The Green's function $G(x, x')$ is the response of this system to an impulse centred at x' . That is, the Green's function solves the differential equation:

$$\mathcal{L}G(x, x') = \delta(x - x') \quad [9.5]$$

This equation is more tractable than the original differential equation since it is homogeneous everywhere except at $x = x'$. If the Green's function can be determined, then it can easily be related to the full solution of eq. [9.4] via an integral equation:

$$u(x) = \int_{-\infty}^{\infty} dx' G(x, x') f(x') \quad [9.6]$$

If a Green's function can be found for a given operator, then this method provides a convenient way of transforming differential equations to analogous integral equations. Note, too, that no restrictions are placed on $f(x)$, and the forcing function may indeed

be some non-linear function of $u(x)$, as is the case with the system of Yoon, discussed in Chapter 3.

Appendix 2 – Functional Differentiation

Consider a general integral equation,

$$C[A] = \int_0^{\infty} dx' A(x') B(x') \quad [10.1]$$

The functional derivative of C with respect to the function A is:

$$\frac{\delta C[A]}{\delta A(x)} = \int dx' \frac{\delta A(x')}{\delta A(x)} B(x') = \int dx' \delta(x-x') B(x') \quad [10.2]$$

Where $\delta(x-x')$ is the Dirac delta function.

The stationary points of the functional L_1 (from Chapter 4), for instance, can be calculated in the following manner:

$$L_1[z_1] = \int_0^{\infty} dx' \left[-\frac{1}{2} \left(\frac{dz_1}{dx'} \right)^2 - \frac{\alpha_1 z_1^2}{2} + \frac{Q_{11} z_1^2}{2} + Q_{12} z_1 z_2 \right] \quad [10.3]$$

We take the derivative of L_1 with respect to z_1 ,

$$\frac{\delta L_1[z_1]}{\delta z_1(x)} = - \int_0^{\infty} dx' \left[\frac{d}{dx'} \delta(x-x') \frac{d}{dx'} z_1 - \alpha_1 z_1 \delta(x-x') + Q_{11} z_1 \delta(x-x') + Q_{12} z_2 \right] \quad [10.4]$$

Then, setting eq. [10.4] to zero, it is clear that the stationary point corresponds to the solution of the original differential equation,

$$\frac{\delta L_1}{\delta z_1} = \frac{d^2 z_1}{dx^2} - \alpha_1 z_1 + Q_{10}(x) z_0 + Q_{11}(x) z_1 + Q_{12}(x) z_2 = 0 \quad [10.5]$$

Appendix 3 – Transformation of $\mathcal{L}_j$ to a Self-Adjoint Form

A Lagrangian cannot be found for the differential equation of ϕ_j as it stands – the first-order differential operator $\hat{\Sigma}_j$ precludes this type of analysis. The original differential equation:

$$\frac{d^2\phi_j}{dx^2} - \frac{z_j e}{kT} \frac{d}{dx} \Psi^0 \frac{d}{dx} \phi_j - iS_j^2 (\psi - \phi_j) = \frac{z_j e}{kT} \frac{d}{dx} \Psi^0 \frac{d}{dx} \left(\frac{\Psi_B}{V} \right) \quad [11.1]$$

must be altered so that the first-order term, $\frac{\partial}{\partial x} \phi_j$, does not appear. For brevity, we define two functions:

$$\rho_j = -\frac{z_j e}{kT} \Psi^0 \quad F = iS_j^2 \psi + \frac{z_j e}{kT} \frac{d}{dx} \Psi^0 \frac{d}{dx} \left(\frac{\Psi_B}{V} \right) \quad [11.2]$$

Equation [11.1] becomes:

$$\frac{d^2}{dx^2} \phi_j + \frac{d}{dx} \rho_j \frac{d}{dx} \phi_j + iS_j^2 \phi_j = F \quad [11.3]$$

We rewrite ϕ_j as a product of two *unknown* functions:

$$\phi_j(x) = a_j(x) \chi_j(x) \quad [11.4]$$

Equation [11.3] becomes,

$$\frac{d^2}{dx^2}(a_j \chi_j) + \frac{d}{dx} \rho_j \frac{d}{dx}(a_j \chi_j) + i S_j^2 a_j \chi_j = F \quad [11.5]$$

Expanding the left-hand side,

$$a_j \frac{d^2}{dx^2} \chi_j + \chi_j \frac{d^2}{dx^2} a_j + \chi_j \frac{d}{dx} \rho_j \frac{d}{dx} a_j + \left(2 \frac{d}{dx} a_j + a_j \frac{d}{dx} \rho_j \right) \frac{d}{dx} \chi_j + i S_j^2 a_j \chi_j = F \quad [11.6]$$

The unknown function $a_j(x)$ can be chosen so that $\frac{d}{dx} \chi_j(x)$ is eliminated; such that:

$$\left(2 \frac{d}{dx} a_j + a_j \frac{d}{dx} \rho_j \right) = 0 \quad [11.7]$$

Leading to:

$$a_j(x) = e^{-\rho_j/2} \quad [11.8]$$

Substituting in eq. [11.4],

$$\phi_j = e^{-\rho/2} \chi_j \quad [11.9]$$

When $\chi_j(x)$ replaces $\phi_j(x)$ as the unknown function, the differential equation [11.3] becomes:

$$\frac{d^2}{dx^2} \chi_j - T_j \chi_j = e^{\rho/2} F \quad [11.10]$$

Where

$$T_j = \frac{d^2}{dx^2} \frac{\rho_j}{2} + \left(\frac{d}{dx} \frac{\rho_j}{2} \right)^2 - iS_j^2 \quad [11.11]$$

The operator on χ_j is self-adjoint, and a Lagrangian can be readily determined.

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