Applications of Interdigital Dielectrometry to Moisture and Double Layer Measurements in Transformer Insulation

by

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Chairman, Departmental Committee on Graduate Students
To the late
Professor James R. Melcher,
a mentor and a friend
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Abstract

The objectives of this thesis are to develop sensors for the continuous on-line measurement of the moisture content of transformer oil and paper, and to provide a theoretical understanding of the relationships involved in these measurements.

A commercially-available sensor, designed and manufactured by Leeds & Northrup to measure the relative humidity of air, is adapted to measure the moisture content of transformer oil. This capacitive sensor relies on the moisture-induced change in the permittivity of polyimide to measure the moisture content of the surrounding fluid. By correlating the output of the sensor to the moisture content of two oils with different solubility characteristics, the sensor is shown to respond to the relative saturation of moisture in the oils. For mixtures in which at least one constituent exhibits ideal behavior, such as the oil in a single-phase mixture of water and oil, relative saturation is defined as the ratio of the mole fraction of the trace constituent to the mole fraction of the same constituent under saturated conditions.

The permittivity of the polyimide is found to be linear with the relative saturation of water in the oils. This linear relationship is identical to that observed for the permittivity of polyimide as a function of the relative humidity of air, supporting the idea that the relative saturation of water in the oils is equal to the relative humidity of the air in contact with the oils. This equality, derived from fundamental thermodynamic principles for ideal, semi-ideal, and polymeric mixtures in mutual stable equilibrium, is used to relate the moisture content of the oil to that of the polyimide and provides an understanding of the mechanism by which the moisture sensor works.

Parylene-coated flexible interdigital-electrode structures are designed and manufactured to measure the moisture content of transformer paper by exploiting the sensitivity of the dielectric properties of paper to moisture. The estimation of the dielectric properties of materials from measurements made with these sensors requires an additional component of the coupling admittance to account for the finite thickness of the electrodes. A semi-empirical first-order estimate of this unmodeled component is provided.

Measurements of the dielectric properties of transformer oil and paper are made over a frequency range of 5 mHz to 10 kHz using a single-wavelength interdigital-electrode structure. Dispersion in the dielectric properties of transformer oil is associated with space-charge polarization resulting in a double layer at the Parylene/oil interface. The dependence of the dielectric properties of paper on the moisture content shows that a change of one order of magnitude in the moisture content results in a frequency shift of seven orders of magnitude in the complex permittivity or an increase of four orders of
magnitude in the loss factor at a given frequency. Thus, the dielectric properties provide a sensitive method to monitor the moisture content of paper.

Because the electric field associated with these sensors is quasistatic, the electrode structures are most sensitive to the properties of the medium out to about one-third of the spatial wavelength. By monitoring the absorption of moisture into dry pressboard at 10 mHz using an electrode structure with spatial wavelengths of 1 mm, 2.5 mm, and 5 mm, the diffusion coefficient of water in oil-free 1 mm-thick EHV-Weidmann HI-VAL transformer pressboard at room temperature is estimated to be $2.7 \times 10^{-11}$ m$^2$/s.

A mass-transfer model is formulated to relate the moisture content of the oil to that of the paper under transient conditions. The paper/oil system is driven out of equilibrium by a thermal transient whose time constant is short compared with the characteristic mass-transfer times. The model involves the numerical solution of a non-self-adjoint problem that couples the diffusion of moisture in the paper to the transport of moisture in the oil at high Reynolds numbers. Representative results reveal that, as the concentration of water in the oil reaches its equilibrium value, the concentration of water in the paper remains highly nonuniform. For typical values of the parameters of the system, the time scale over which the concentration of water in the oil reaches the apparent equilibrium is found to be at least one order of magnitude smaller than the time scale over which the system reaches equilibrium. The error associated with the estimation of the equilibrium moisture content of the paper from apparent equilibrium measurements of the moisture content of the oil is examined. Estimates obtained from measurements of the moisture content of the oil during cooling transients yield a value of $2.6 \times 10^{-13}$ m$^2$/s for the diffusion coefficient of water in oil-impregnated 1 mm-thick EHV-Weidmann HI-VAL pressboard at 15°C and a value of $6.0 \times 10^{-10}$ m$^2$/s for the diffusion coefficient of water in Shell Diala A transformer oil at 15°C.

The increased polarization observed in the low-frequency measurement of the dielectric properties of transformer oil is modeled using a linearized bipolar model for a diffuse double layer. The frequency spectrum associated with the effective dielectric properties of the double layer is shown to exhibit characteristics associated with space-charge polarization. Because such a spectrum is indistinguishable from the polarization spectrum associated with simple dipole orientation, it is described by the Debye dispersion relation. For large values of the normalized zeta potential, the response of electrode structures with spatial wavelengths large compared with the Debye length is shown to reduce to a response associated with a surface conductivity at the interface between the dielectric layer covering the electrode structure and an ohmic infinite half-space with the permittivity and bulk conductivity of the fluid. The heterogeneity of the double layer is verified experimentally through a measurement of the dielectric properties of transformer oil by means of interdigital-electrode structures with spatial wavelengths ranging from 50 μm to 5 mm. Because the double layer is heterogeneous, its representation in terms of a single set of dielectric properties leads to estimated values that depend on the spatial wavelength of the electrode structure.

Thesis Supervisor: Markus Zahn
Title: Professor of Electrical Engineering
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developed the data acquisition system for the flexible sensors (Chapter 6). Mr. Tony Calloggero assisted in the manufacturing and assembly of these units. His help is also appreciated in the fabrication of the Couette Facility (Chapter 5) and various experimental prototypes. Most of the machining was done with the assistance of Mr. Rocco Albano. I would like to thank him for his excellent workmanship. In his shop, I always knew I was working with a real professional.

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Chapter 1

Introduction

The purpose of this chapter is to present the objectives of the thesis, the approach taken to address these objectives, and a brief outline of the thesis.

1.1 Scope of Thesis

The objectives of this thesis are twofold: to develop sensors for the continuous on-line measurement of the moisture content of transformer oil and paper, and to provide a theoretical understanding of the relationships involved in these measurements.

Excessive amounts of moisture in the insulation of a transformer lead to detrimental effects on the electrical and mechanical properties of the insulation. Prior to the developments made in this thesis, available technology allowed only periodic off-line measurements of the moisture content of transformer oil. As the reliability of large power transformers became more critical to the operation of the electrical network, the need developed for a device that provides continuous on-line measurements of the moisture in the oil. Such a measurement, together with other key parameters, provides the critical information necessary for the assessment of the condition of the transformer and the detection of incipient hazardous conditions.

1.2 Research Approach

With regards to the first objective, two types of sensors were developed. First, a commercially-available sensor, designed to measure the relative humidity of air, was adapted to measure the moisture content of transformer oil. This capacitive sensor relies on the moisture-induced change in the permittivity of polyimide to measure the moisture content of the surrounding fluid. By correlating the output of the sensor to the moisture content of two oils with different solubility characteristics, the sensor is shown
to respond to the relative saturation of moisture in the oils.

Thermodynamic principles are used to show the usefulness of relative saturation in describing the equilibrium between two systems in partial mutual stable equilibrium. For mixtures in which at least one constituent exhibits ideal behavior, such as the oil in a single-phase mixture of water and oil, relative saturation is defined as the ratio of the mole fraction of the trace constituent to the mole fraction of the same constituent under saturated conditions. Equilibrium relationships such as Henry's law, which relate the amount of the trace constituent in each system, are expressed as an equality of relative saturation. This equality is then used to relate the moisture content of the oil to that of the polyimide and provide an understanding of the mechanism by which the moisture sensor works.

The second type of sensor consists of flexible interdigital-electrode structures with one and three spatial wavelengths. These sensors were designed and manufactured to measure the moisture content of transformer paper. They rely on the sensitivity of the dielectric properties of paper to moisture, which is demonstrated using an electrode structure with a spatial wavelength comparable to the thickness of the paper. Because the electric field is quasistatic, the electrode structure is most sensitive to the properties of the medium out to about one-third of the spatial wavelength. Exploiting this feature of interdigital-electrode structures, an estimate for the diffusion coefficient of water in oil-free paper is obtained by monitoring the absorption of moisture into dry pressboard using an electrode structure with three spatial wavelengths.

To complete the goals set forth in the second objective, a mass-transfer model is formulated to relate the moisture content of the oil to that of the paper under transient conditions. In the model, the paper/oil system is driven out of equilibrium by a thermal transient whose time constant is short compared with the characteristic mass-transfer times. Representative results show that the concentration of water in the paper assumes a highly nonuniform distribution as the concentration of water in the oil reaches its equilibrium value. Thus, the estimation of the equilibrium moisture content of the paper from apparent equilibrium measurements of the moisture content of the oil would be in error. Measurements of the moisture content of the oil during thermal transients are used to obtain estimates of the diffusion coefficient of water in oil and oil-impregnated paper.
1.3 Outline of Thesis

Following a brief discussion in Chapter 2 of the background and motivation for the measurement of moisture in transformer insulation, Chapters 3 and 4 deal with the theoretical and experimental description of an immersible moisture sensor for fluids. In Chapter 3 the equilibrium conditions resulting from the first and second laws of thermodynamics are used to derive the equality of relative saturation for a trace constituent common to two systems in partial mutual stable equilibrium. The concept of relative saturation is extended to nonideal polymeric mixtures, such as the polyimide/water mixture that comprises the moisture sensor. The experimental results in Chapter 4 demonstrate the usefulness of relative saturation in describing the partitioning of moisture between the moisture sensor and the fluid.

The relationship between the moisture content of the oil and that of the paper is explored in Chapter 5 through a mass-transfer model that couples the diffusion of moisture in the paper to the transport of moisture in the oil at high Reynolds numbers. Representative results reveal the disparity between the time constants that characterize the temporal evolution of moisture in the oil and the paper.

Equilibrium and transient measurements of the moisture content of paper are described in Chapter 6. Flexible interdigital-electrode structures are used to measure the moisture content of paper by taking advantage of the sensitivity of the dielectric properties of paper to moisture. Use of a multiple-wavelength electrode structure is demonstrated in monitoring the absorption of moisture into dry pressboard.

The increased polarization observed in the low-frequency measurement of the dielectric properties of transformer oil is modeled in Chapter 7 using a linearized bipolar model for a diffuse double layer. Once the sensitivity of the electrode structure to the parameters describing the double layer is established, the heterogeneity of the double layer is verified experimentally through a measurement of the dielectric properties of transformer oil with multiple interdigital-electrode structures.

The thesis is concluded with Chapter 8, wherein implications and suggestions for future work are discussed. A series of appendices serves to complement the ideas developed in the thesis.

Section 1.3: Outline of Thesis
Chapter 2

Background and Motivation

The purpose of this chapter is to provide the background and motivation for the measurement of moisture in transformer insulation. This is accomplished through a discussion of the economics of transformer reliability, the effects of moisture on transformer insulation, and techniques for the on-line measurement of moisture in paper.

2.1 Economics of Transformer Reliability

With the growing demand for more power and higher quality service, the reliability of large power transformers is becoming more critical. The economics associated with ensuring this reliability are in direct competition with those associated with minimizing the capital investment costs. The more redundancies that are implemented in the design of transformers, the higher the capital investment costs. The economic tradeoff lies in the lower operational costs, including loss of sales of electricity, that are incurred as a result of more reliable operation.

Economic constraints lead to transformers designed to withstand higher energy densities. As a result, increased stresses are placed on the insulation of the transformer. Furthermore, stricter requirements are placed on the cooling specifications in order to dissipate the increased electrical losses. This, in turn, leads to increased oil flow rates in the transformer which give rise to flow electrification problems.

The increased stresses in the transformer lead to increased failure rates. Statistics collected over recent years reveal the magnitude of the problem. For example, Fig. 2.1 shows the number and replacement costs associated with the failure of EHV transformers (345 kV and higher) of the American Electric Power Service Corporation over twelve years [1]. This data indicates an average failure rate of four transformers per year. Associated with the failure of each transformer is a replacement cost of three million dollars and a loss of sales of electricity ranging up to two million dollars depending on
Figure 2.1: Statistics on the failure rate of EHV transformers (345 kV and higher) from the American Electric Power Service Corporation over twelve recent years indicating an average failure rate of four transformers per year. Associated with the failure of each transformer is a replacement cost of three million dollars and a loss of sales of electricity ranging up to two million dollars depending on the load conditions of the transformer.

As a result of these failures, efforts have been made to develop an on-line monitoring system to perform trend analysis. This system involves the detection of anomalous changes, the diagnosis of internal conditions, and the prognosis of future behavior in the transformer [2]. Critical to every aspect of the analysis is the measurement of parameters that reflect the condition of the transformer. One such parameter is the moisture content of the insulation. As illustrated in Fig. 2.2, a schematic of a three-phase core-type power transformer [3], the insulation in a transformer consists of pressboard and oil. The pressboard is used to insulate the winding structure while the oil is used both as an insulator and as a coolant. Chemical analysis of the oil, such as its moisture content,
provides information about the state of the insulation in the transformer just as blood analysis provides information about the health of the body.

2.2 Effects of Moisture on Transformer Insulation

Moisture affects the electrical properties of the insulation in a transformer to varying degrees. Whereas the conductivity of transformer oil is not significantly affected, its dielectric breakdown strength is reduced by small amounts of water dissolved in the oil [4]. Impurities play an important role in determining the degree to which moisture affects the breakdown strength of the oil [5]. The electrical properties of pressboard, such as the loss factor and the dielectric breakdown strength, are strongly dependent on its moisture content [6, 7, 8, 9, 10]. The sensitivity of these properties to moisture is greatly enhanced at elevated temperatures. In addition, the thermal degradation of the mechanical and physicochemical properties of paper is enhanced by the presence of water in the insulation [11, 12, 13].

Pressboard naturally contains approximately 5% of water by weight at atmospheric conditions [14, 15, 16]. In the commissioning of transformers, most of this water is removed through the use of vacuum pumps. This process is aided by using a hot-oil spray or saturated kerosene vapor to heat the solid insulation prior to evacuation [17, 18, 19, 20]. Once the pressboard is sufficiently dry, transformer oil is introduced into the transformer under vacuum. The remaining moisture in the insulation then distributes itself between the pressboard, a hydrophilic solid, and the oil, a hydrophobic liquid.

Optimum conditions in a transformer involve a finite amount of water in the insulation. If the pressboard is too dry, charge can accumulate on its surface as a result of flow electrification and lead to a surface flashover or breakdown across the bulk of the insulation. The accumulating charge is associated with the ubiquitous double layer present at the oil/pressboard interface. If the pressboard is too wet, the reduction in the insulation strength can lead to breakdown between the windings.

2.3 On-Line Measurement of Moisture in Paper

Accessibility to the pressboard during operation of the transformer is prohibited because the potentials associated with the devices used to measure moisture in the pressboard undermine the dielectric strength of the insulation. As a result, the moisture content of the pressboard must be inferred from measurements of the moisture content of the oil. In this way, the oil acts as a carrier of information for the pressboard, much like human

Section 2.2: Effects of Moisture on Transformer Insulation
Figure 2.2: Schematic view of a three-phase core-type power transformer. While pressboard is used primarily to insulate the winding structure, transformer oil is used both as an insulator and as a coolant. Chemical analysis of the oil, such as its moisture content, provides information about the state of the insulation in a transformer just as blood analysis provides information about the health of the body. (From Reference [3].)
blood carries information about the condition of the organs.

The use of paper probes, located near the tank of the transformer, has been suggested as a means to determine the moisture content of the pressboard in the core of the transformer [9, 21]. Under equilibrium conditions, the moisture content of the paper should be the same as the moisture content of the pressboard. The measurement of the moisture in the paper relies on an empirical relationship between the dielectric properties of the paper and its moisture content.

The assumption that the paper and the pressboard have the same moisture content is valid only when the transformer is in equilibrium. Unfortunately, analysis of the mass-transfer time constants, in view of the load cycles of a typical power transformer, indicates that the transformer is never in moisture equilibrium. The task of relating the measured moisture content, whether in the paper probe or directly in the oil, to the moisture content of the pressboard involves a detailed knowledge of the geometry of the structure and an understanding of the mass-transfer impedances at the paper/oil interface along the oil flow paths in a transformer.
Chapter 3

Equilibrium Relations for Trace Constituents in Simple Systems

The purpose of this chapter is to develop equilibrium relations that determine the partitioning of a trace constituent between simple systems. Once the chemical potential of the trace constituent in a mixture is described, equilibrium relations are derived based on the conditions for equilibrium between two simple systems.

3.1 Introduction

Thermodynamic principles provide the foundation for deriving equilibrium relations that determine the partitioning of matter between simple systems in partial mutual stable equilibrium. In this context, the systems are thought of as being separated from one another by a movable partition permeable to energy, entropy, and one common constituent, but no other constituents. Thus, because the systems are in partial mutual stable equilibrium, the values of the temperature, pressure, and chemical potential of the exchangeable constituent are common to all systems [22: Section 11.5].

In order to determine the equilibrium relations, a description of the chemical potential of the exchangeable constituent in each system is required. The chemical potential of a constituent can be interpreted as the potential that governs the tendency of the constituent to pass from one system to another in the course of an interaction between the two systems [22: Section 10.3]. Because the chemical potential is a property of a system in a stable equilibrium state, it depends on the temperature and pressure of the system, and the amounts of the constituents in the system. Thus, the chemical potential of the ith constituent in a mixture can be expressed as
\[ \mu_i = \mu_i(T, p, \mathbf{y}) \]  
\[ \text{(3.1)} \]

where \( \mathbf{y} = \{y_1, y_2, \ldots, y_r\} \) denotes the mole fractions of the \( r \) constituents in the system which are subject to the constraint
\[ \sum_{i=1}^{r} y_i = 1 \]  
\[ \text{(3.2)} \]

The assumption of a simple system implies that volume is the only parameter describing the influence of external forces on the constituents [22: Section 17.1]. As a result, external forces due to gravitational, electric, and magnetic fields are excluded in the description of the system. The effect of an external force on the properties of a system remains a topic of further research. Consider, for example, a system of electrically neutral constituents subject to an electric field. The presence of the electric field results in polarization forces on the constituents of the system. The escaping tendency of a constituent in such a system is described by what is commonly referred to as the electrochemical potential. This property is defined as the partial of the energy \( E \) with respect to the amount of the \( i \)th constituent \( n_i \) while holding constant the entropy \( S \), the amounts of the other constituents \( n \), the volume \( V \), and the parameter describing the influence of the electric field on the constituents \( \beta_e \).

\[ \mu_{ie} = \left( \frac{\partial E}{\partial n_i} \right)_{S,n,V,\beta_e} \]  
\[ \text{(3.3)} \]

Because there is energy storage associated with the electric field, and the dielectric constant in general depends on the temperature, pressure, and amounts of constituents in the system, the electrochemical potential will depend on the electric field. The manner in which the electric field is self-consistently described as a parameter of the system remains unresolved.\(^1\) Many of the formulations in the literature are in disagreement regarding this topic [23, 24, 25, 26].

Except for ideal-gas mixtures, the equilibrium relations are derived for binary systems. Even for a multicomponent system, the assumption of a binary system is often a valid one. Moist transformer oil, for example, can be treated as a binary mixture of dry transformer oil and water even though the composition of transformer oil is quite complex [27]. Because its composition is fixed, dry transformer oil can be thought of as a pure substance consisting of a single constituent with an average molecular weight.

\(^1\)For those who consider thermodynamics a closed subject this is only one of the many topics of frontier research.
3.2 Chemical Potentials

3.2.1 Pure Constituents

In general, the chemical potential of a pure constituent depends only on the temperature and pressure of the system.

\[ \mu = \mu(T, p) \] (3.4)

For a single-constituent simple system the Gibbs-Duhem relation relates the specific volume to the partial of the chemical potential with respect to the pressure [22: Section 17.5]

\[ v(T, p) = \left( \frac{\partial \mu}{\partial p} \right)_T \] (3.5)

so that the chemical potential of the pure constituent can be expressed in terms of the specific volume as

\[ \mu = \mu(T, p^*) + \int_{p^*}^{p} v(T, p') \, dp' \] (3.6)

where \( p^* \) is a reference pressure.

If the constituent exhibits ideal-gas behavior [22: Section 20.1] in a temperature range about \( T \) and a pressure range that includes the pressure \( p \) and the reference pressure \( p^* \), then the equation of state

\[ v(T, p) = \frac{RT}{p} \] (3.7)

can be used to express the chemical potential of the pure constituent as

\[ \mu = \mu(T, p^*) + RT \ln \frac{p}{p^*} \] (3.8)

If the constituent, in a liquid or solid form of aggregation, exhibits ideal incompressible behavior [22: Section 20.4] in a temperature range about \( T \) and a pressure range that includes the reference pressure \( p^* \), then the specific volume can be taken to be independent of temperature and pressure,

\[ v(T, p) \approx \text{constant} \] (3.9)

and the chemical potential of the pure constituent can be expressed from Eq. 3.6 in the following form.

Section 3.2: Chemical Potentials
\[ \mu = \mu(T, p^*) + v[p - p^*] \]  

(3.10)

### 3.2.2 Constituents in Mixtures

The chemical potential of the \( i \)th constituent in a mixture \( \mu_i \) can always be expressed in terms of the chemical potential of the pure constituent \( \mu_{ii} \) as

\[ \mu_i = \mu_{ii}(T, p_{ii}(T, p, y)) \]  

(3.11)

where \( p_{ii} \) is the partial pressure of the \( i \)th constituent and corresponds to the pressure to which an auxiliary system \( ii \) must be brought in order to inhibit any flow of constituent \( i \) across a rigid semipermeable membrane that separates system \( ii \) from the mixture [22: Section 26.3]. System \( ii \) consists of substance \( i \) and is in partial mutual stable equilibrium with the mixture [22: Section 11.5].

#### Ideal-Gas Mixtures

Using Eqs. 3.6 and 3.11, the chemical potential of the \( i \)th constituent in a mixture can be expressed as

\[ \mu_i = \mu_{ii}(T, p^*) + \int_{p^*}^{p_{ii}} v_{ii}(T, p') dp' \]  

(3.12)

If the \( i \)th constituent exhibits ideal-gas behavior in a temperature range about \( T \) and a pressure range that includes the partial pressure \( p_{ii} \) and the reference pressure \( p^* \), then the chemical potential of the constituent can be written with the help of Eq. 3.7 as

\[ \mu_i = \mu_{ii}(T, p^*) + RT \ln \frac{p_{ii}}{p^*} \]  

(3.13)

If, in addition, the system behaves as an ideal-gas mixture [22: Section 27.2], the partial pressure of the \( i \)th constituent \( p_{ii} \) is related to the mole fraction of the constituent \( y_i \) and the pressure of the mixture \( p \) by the relation

\[ p_{ii} = y_i p \]  

(3.14)

so that the chemical potential of the \( i \)th constituent can be written in the form

\[ \mu_i = \mu_{ii}(T, p^*) + RT \ln \frac{y_i p}{p^*} \]  

(3.15)

Note that in deriving this expression we did not assume that the \( i \)th constituent exhibits ideal-gas behavior at the temperature \( T \) and pressure \( p \) of the mixture. Such an

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*Chapter 3: Equilibrium Relations*
Figure 3.1: Plot of the compressibility factor $Z = pv/RT$ of saturated water vapor as a function of the reduced temperature $T_R = T/T_c$, where $T_c = 374.14^\circ$C is the critical temperature of water. This figure indicates that ideal-gas behavior at saturated conditions is exhibited for temperatures below $100^\circ$C.

assumption would be valid only at relatively low pressures and high temperatures.

Except for a limited temperature range, the choice of the saturation pressure $p_{sat,n}(T)$ as the reference pressure $p^*$ is not valid because at such temperature and pressure the constituent does not exhibit ideal-gas behavior. This is illustrated in Fig. 3.1, a plot of the compressibility factor $Z = pv/RT$ of saturated water vapor as a function of the reduced temperature $T_R = T/T_c$, where $T_c = 374.14^\circ$C is the critical temperature of water. This figure indicates that ideal-gas behavior at saturated conditions is exhibited for temperatures below $100^\circ$C. It is important to note that, even though the choice of the reference pressure is somewhat arbitrary, its value does not affect the value of the chemical potential. This is evident from the initial expression for the chemical potential given by Eq. 3.11.
Semi-Ideal Mixtures

Consider a binary mixture in a liquid or solid form of aggregation in which constituent 2 is present in trace amounts. In this system only constituent 1 is assumed to exhibit ideal-solution behavior. As such, the mixture is referred to as a *semi-ideal* mixture. For molecules of comparable size, this assumption is accurate as long as the mole fraction of constituent 1 approaches unity so that the nearest neighbors of the constituent’s molecules are almost always the same molecules [22: Section 27.5]. Under such conditions, the chemical potential of constituent 1 is given by an expression of the form

\[
\mu_1 = \mu_{11}(T, p) + RT \ln y_1 \tag{3.16}
\]

where \( \mu_{11}(T, p) \) is the chemical potential of pure constituent 1 at the temperature \( T \) and pressure \( p \) of the mixture.

The ideal-solution behavior of constituent 1 in the binary mixture has important implications on the behavior of the trace constituent. The Gibbs-Duhem relation for the mixture can be expressed as [22: Section 17.3]

\[
s \, dT - v \, dp + y_1 \, d\mu_1 + y_2 \, d\mu_2 = 0 \tag{3.17}
\]

where \( s \) and \( v \) are the specific entropy and volume of the system respectively.

Differentiation of Eq. 3.16 under isothermobaric conditions (constant temperature and pressure) yields

\[
y_1 \, d\mu_1 = RT \, dy_1 \tag{3.18}
\]

so that, under the same conditions, the Gibbs-Duhem relation reduces to

\[
RT \, dy_1 + y_2 \, d\mu_2 = 0 \tag{3.19}
\]

Because the sum of the mole fractions is unity, the dependence of the chemical potential of the trace constituent on the mole fraction of constituent 1 can be eliminated.

\[
\mu_2 = \mu_2(T, p, y_2) \tag{3.20}
\]

Thus, under isothermobaric conditions the differential form of the chemical potential becomes

\[
d\mu_2 = \left( \frac{\partial \mu_2}{\partial y_2} \right)_{T, p} \, dy_2 \tag{3.21}
\]

Using this relation and the fact that \( dy_1 + dy_2 = 0 \), Eq. 3.19 can be expressed as
\[
\left( \frac{\partial \mu_2}{\partial \ln y_2} \right)_{T,p} = RT 
\]

Integration yields the desired relation for the chemical potential of the trace constituent in the mixture

\[
\mu_2 = \lambda_2(T,p) + RT \ln y_2
\]

where the constant of integration \( \lambda_2(T,p) \) is a function of temperature and pressure only. This relation demonstrates that, even if the behavior of the trace constituent is not ideal, the ideal-solution behavior of the constituent 1 implies a definite dependence of the chemical potential \( \mu_2 \) on the mole fraction \( y_2 \). Note also that if, in addition to constituent 1, the trace constituent exhibited ideal-solution behavior, the constant of integration \( \lambda_2(T,p) \) would be equal to the chemical potential of the pure constituent \( \mu_{22}(T,p) \).

**Polymeric Mixtures**

If the molecular weights of the constituents in a binary mixture differ by several orders of magnitude, then both constituents exhibit large deviations from ideality, even for relatively small concentrations of either of the constituents. This is the case for mixtures involving polymers, whose molecular weight is a thousand times larger than the molecular weight of typical molecules. For these mixtures the chemical potential of the constituents is often expressed in terms of volume fractions rather than mole fractions.

Consider a binary mixture in a solid form of aggregation in which constituent 1 is a polymer whose volume fraction is much larger than that of constituent 2. At concentrations for which the randomly coiled polymer molecules overlap one another extensively, the chemical potential of the polymeric constituent can be expressed as [28]

\[
\mu_1 = \mu_{11}(T,p) + RT \left[ \ln v_1 - (x - 1)(1 - v_1) + x \chi_{12}(1 - v_1)^2 \right] 
\]

where \( \mu_{11}(T,p) \) is the chemical potential of pure constituent 1 at the temperature \( T \) and pressure \( p \) of the mixture.

The dimensionless parameter \( x \) corresponds to the ratio of the volume occupied by a polymer molecule to the volume occupied by a nonpolymeric molecule. It can be expressed in terms of the number of chain segments in the polymer molecule \( x_n \) as

\[
x = \left( \frac{M_{1u}}{M_2} \right) \left( \frac{\rho_2}{\rho_1} \right) x_n
\]

*Section 3.2: Chemical Potentials*
where $M_1$ and $M_2$ represent the molecular weight of the polymer unit and nonpolymeric constituent respectively, and $\rho_1$ and $\rho_2$ are the mass densities of the two constituents. For heterogeneous polymers, the parameter $z$ is replaced by an equivalent number-average quantity.

The dimensionless parameter $\chi_{12}$ is the polymer-solvent interaction parameter. It represents the interaction of the two constituents in the mixture and is assumed to be independent of the amounts of the constituents. The quantity $RT\chi_{12}$ represents the difference in energies of a nonpolymeric molecule surrounded by polymer molecules compared with one surrounded by molecules of its own kind. As such, the parameter can assume positive or negative values.

The volume fractions $v_i$ are related to the number of moles $n_i$ of the constituents by the following relations,

$$v_1 = \frac{x n_1}{x n_1 + n_2}$$  

$$v_2 = \frac{n_2}{x n_1 + n_2}$$  

so that $v_1 + v_2 = 1$. In the limit in which the two constituents have the same molecular size ($z \to 1$), the volume fractions reduce to the mole fractions.

Just as for a trace constituent in a semi-ideal nongaseous mixture, the form of the chemical potential of constituent 1 has important consequences on the behavior of constituent 2. The Gibbs-Duhem relation for the mixture can be stated as [22: Section 17.3]

$$S \, dT - V \, dp + n_1 \, d\mu_1 + n_2 \, d\mu_2 = 0$$  

where $S$ and $V$ are the entropy and volume of the system respectively. Under isothermalobaric conditions, this relation can be expressed in terms of the volume fractions of the constituents.

$$v_1 \, d\mu_1 + z v_2 \, d\mu_2 = 0$$  

Upon differentiation of Eq. 3.24, this condition reduces to

$$RT \left[1 + (z - 1)v_1 - 2x\chi_{12}v_1(1 - v_1)\right]dv_1 + z v_2 \, d\mu_2 = 0$$  

Because the sum of the volume fractions is unity, the dependence of the chemical potential of constituent 2 on the volume fraction of constituent 1 can be eliminated.

$$\mu_2 = \mu_2(T, p, v_2)$$  

Chapter 3: Equilibrium Relations
Thus, under isothermobaric conditions the differential form of the chemical potential can be expressed as

\[
d\mu_2 = \left( \frac{\partial \mu_2}{\partial v_2} \right)_{T,p} dv_2
\]  

(3.31)

Using this relation and the fact that \(dv_1 + dv_2 = 0\), we can rewrite Eq. 3.29 as

\[
\left( \frac{\partial \mu_2}{\partial v_2} \right)_{T,p} = RT \left[ \frac{1}{v_2} - (1 - 1/x) - 2\chi_{12}(1 - v_2) \right]
\]  

(3.32)

Integration yields the desired relation for the chemical potential of constituent 2 in the mixture

\[
\mu_2 = \lambda_2(T,p) + RT \left[ \ln v_2 + (1 - 1/x)(1 - v_2) + \chi_{12}(1 - v_2)^2 \right]
\]  

(3.33)

where the constant of integration was chosen to be \(\lambda_2(T,p) + RT [(1 - 1/x) + \chi_{12}]\). Note that, if the mixture were in a liquid form of aggregation, the constant \(\lambda_2(T,p)\) would be equal to the chemical potential of the pure constituent \(\mu_{22}(T,p)\) [28]. Furthermore, in the limit in which the two constituents have the same molecular size (\(x \rightarrow 1\)) and they don't interact (\(\chi_{12} \rightarrow 0\)), this expression reduces to the chemical potential of a trace constituent in a semi-ideal mixture, Eq. 3.23.

### 3.3 Equilibrium Relations

Equipped with expressions for the chemical potential of constituents in mixtures, equilibrium relations can be derived for constituents common to the systems. This is accomplished by deriving an equilibrium relation directly from the condition of chemical potential equality, developing an expression for the solubility of the constituent in the interacting systems, and using this result to express the equilibrium condition in terms of an equality of relative saturation. The solubility of a constituent in a mixture is defined as the maximum amount of the constituent that can be stored in the single-phase mixture at the temperature and pressure of the system.

#### 3.3.1 Ideal-Gas Mixtures

**Equality of Mole Fraction**

Consider two simple systems, system \(A\) and system \(B\), in partial mutual stable equilibrium. Both systems are ideal-gas mixtures in which the \(i\)th constituent is the common constituent. Because the two systems are in partial mutual stable equilibrium, the val-
ues of the temperature $T$, pressure $p$, and chemical potential of the $i$th constituent $\mu_i$ in both systems are equal.

The condition of chemical potential equality for the $i$th constituent can be expressed as

$$\mu_i^A = \mu_i^B$$

(3.34)

where the subscript $g$ denotes a vapor phase. Using Eq. 3.15 to express the chemical potential of the $i$th constituent in each system,

$$\mu_i = \mu_{ig}(T, p^*) + RT \ln \frac{y_{ig} p}{p^*}$$

(3.35)

the condition of chemical potential equality yields the relation,

$$y_i^A = y_i^B$$

(3.36)

where a common reference pressure was selected for each system. Thus, the condition of partial mutual stable equilibrium results in the requirement that the mole fraction of the common constituent be equal in the two systems. This result can be extended to include any other constituent common to both systems.

**Solubility in an Ideal-Gas Mixture**

To determine the solubility of a constituent in an ideal-gas mixture, consider the partial mutual stable equilibrium of an ideal-gas mixture and a pure constituent in the liquid or solid form of aggregation. The $i$th constituent of the ideal-gas mixture is also the pure constituent. In this condition the mixture is saturated with the $i$th constituent and is assumed to behave as an ideal-gas mixture. Because the systems are in partial mutual stable equilibrium, the values of the temperature $T$, pressure $p$, and chemical potential of the common constituent $\mu_i$ in both systems are equal.

The chemical potential of the $i$th constituent in the ideal-gas mixture is described by Eq. 3.15

$$\mu_i = \mu_{ig}(T, p^*) + RT \ln \frac{y_{ig} p}{p^*}$$

(3.37)

where $y_{ig}$ is the mole fraction of the common constituent in the saturated mixture. The equality of chemical potential

$$\mu_i = \mu_{ig}$$

(3.38)
yields an expression for the solubility of the common constituent in the ideal-gas mixture,

$$y_{ig}^*(T, p) = \frac{p^*}{p} \exp \left[ \frac{\mu_{ii}(T, p) - \mu_{ii}(T, p^*)}{RT} \right]$$  \hspace{1cm} (3.39)

where the subscript $f$ denotes a liquid or solid phase.

If the pure constituent exhibits ideal-gas behavior along the dew-point curve as well as ideal incompressible behavior along the bubble-point curve, then the saturation pressure $p_{sat, ii}(T)$ can be chosen as the reference pressure and, with the help of Eq. 3.10 and the condition of chemical potential equality between the vapor phase and the liquid or solid phase of the $i$th pure constituent,

$$\mu_{ii}(T, p_{sat, ii}(T)) = \mu_{ii}(T, p_{sat, ii}(T))$$  \hspace{1cm} (3.40)

the solubility can be expressed as

$$y_{ig}^*(T, p) = \frac{p_{sat, ii}(T)}{p} \exp \left\{ \frac{v_{ii}}{RT} [p - p_{sat, ii}(T)] \right\}$$  \hspace{1cm} (3.41)

where $v_{ii}$ is the specific volume of the $i$th pure constituent in the liquid or solid form of aggregation. If the pure constituent is in the liquid form of aggregation, the saturation pressure $p_{sat, ii}(T)$ is the vaporization pressure, which is defined for temperatures above the triple-point temperature $T_\text{tp}$ and below the critical temperature $T_c$. If the pure constituent is in the solid form of aggregation, the saturation pressure $p_{sat, ii}(T)$ is the sublimation pressure, which is defined for temperatures below the triple-point temperature $T_\text{tp}$. The exponential term in Eq. 3.41 is usually referred to as the Poynting correction and, for ordinary substances, is approximately equal to unity [22: Section 20.6].

$$y_{ig}^*(T, p) \approx \frac{p_{sat, ii}(T)}{p}$$  \hspace{1cm} (3.42)

In this form, the expression for the solubility is a special case of Raoult's law [22: Section 27.7]. Note that, for a gaseous mixture, the solubility of a constituent is defined only for temperatures and pressures at which the pure constituent is in a liquid or solid form of aggregation.

Equality of Relative Saturation

The equilibrium relation for a constituent common to ideal-gas mixtures is given by Eq. 3.36. If we divide both sides of this equation by the solubility of the constituent in each mixture we find

Section 3.3: Equilibrium Relations

39
\[
\left( \begin{array}{c}
\frac{y^A_{ig}}{y^A_{ig}} \\
\frac{y^B_{ig}}{y^B_{ig}}
\end{array} \right) = \left( \begin{array}{c}
\frac{y^B_{ig}}{y^B_{ig}}
\end{array} \right) \left[ \frac{y^{B_s}}{y^{A_s}} \right]
\]  

(3.43)

Because the solubility of the \(i\)th constituent depends only on the temperature and pressure of the system, the term in the square brackets is unity and the equilibrium relation can be expressed as

\[
\phi^A_{ig} = \phi^B_{ig}
\]

(3.44)

where \(\phi\) is the relative saturation of the \(i\)th constituent in the mixture and is defined as the ratio of the mole fraction of the \(i\)th constituent to the mole fraction under saturated conditions.

\[
\phi = \frac{y_i}{y_i^s}
\]

(3.45)

Note that for gaseous mixtures in which water is the common constituent relative saturation is commonly referred to as relative humidity. The equality of relative saturation holds if the vapor-phase mixtures exhibit ideal-gas behavior up to saturated conditions and the \(i\)th pure constituent is in a liquid or solid form of aggregation at the temperature \(T\) and pressure \(p\) of the mixture.

### 3.3.2 Ideal-Gas and Semi-Ideal Mixtures

**Henry's Law**

Consider two simple systems in partial mutual stable equilibrium. One system consists of an ideal-gas mixture; the other consists of a binary semi-ideal mixture in a liquid or solid form of aggregation. Constituent 2 in the binary mixture is present in trace amounts and is common to both systems. Because the systems are in partial mutual stable equilibrium, the values of the temperature \(T\), pressure \(p\), and chemical potential of the common constituent \(\mu_2\) in both systems are equal.

The chemical potential of constituent 2 in the ideal-gas mixture is described by Eq. 3.15.

\[
\mu_{2g} = \mu_{2g}(T, p^*) + RT \ln \frac{y_{2g}p}{p^*}
\]

(3.46)

Because constituent 2 is present in trace amounts, Eq. 3.23 provides a description of the chemical potential of constituent 2 in the binary mixture.

\[
\mu_{2f} = \lambda_2(T, p) + RT \ln y_{2f}
\]

(3.47)
Equating these two expressions yields *Henry's law* which relates the partial pressure of the common constituent in the vapor phase $p_{2g}$ to the mole fraction of the constituent in the liquid or solid phase $y_{2f}$,

$$p_{2g} = y_{2g}p = y_{2f}H_{2fg}(T, p) \tag{3.48}$$

where

$$H_{2fg}(T, p) = p^* \exp \left[ \frac{\lambda_{2f}(T, p) - \mu_{2g}(T, p^*)}{RT} \right] \tag{3.49}$$

is known as *Henry's constant* for trace constituent 2 and is a function of temperature and pressure only.

If the common constituent exhibits ideal-gas behavior at the saturation pressure $p_{sat,22}(T)$, the choice of the saturation pressure as the reference pressure is valid and, together with the condition of chemical potential equality between the vapor phase and the liquid or solid phase of pure constituent 2,

$$\mu_{2g}(T, p_{sat,22}(T)) = \mu_{2fg}(T, p_{sat,22}(T)) \tag{3.50}$$

Henry’s constant can be expressed as a property of the liquid- or solid-phase mixture.

$$H_{2fg}(T, p) = H_{2f}(T, p) = p_{sat,22}(T) \exp \left[ \frac{\lambda_{2f}(T, p) - \mu_{2fg}(T, p_{sat,22}(T))}{RT} \right] \tag{3.51}$$

Even though the choice of the reference pressure $p^*$ is somewhat arbitrary, its value does not affect the value of Henry’s constant. To prove this it is sufficient to show that the values of Henry’s constant for two different choices of the reference pressure are equal.

$$H_{2fg}(T, p; p_1^*) = H_{2fg}(T, p; p_2^*) \tag{3.52}$$

Using the definition of Henry’s constant, Eq. 3.49, this equality can be expressed as

$$\frac{p_1^*}{p_2^*} = \exp \left[ \frac{\mu_{2fg}(T, p_1^*) - \mu_{2fg}(T, p_2^*)}{RT} \right] \tag{3.53}$$

Because constituent 2 is assumed to exhibit ideal-gas behavior in a temperature range about $T$ and a pressure range that includes the reference pressures $p_1^*$ and $p_2^*$, the chemical potential of the pure constituent at the pressure $p_1^*$ can be expressed in the following form.

Section 3.3: Equilibrium Relations
\[ \mu_{22g}(T, p^*_1) = \mu_{22g}(T, p^*_2) + RT \ln \frac{p^*_1}{p^*_2} \]  

(3.54)

With this expression, the right-hand side of Eq. 3.53 reduces to \( p^*_1/p^*_2 \), proof that the value of Henry's constant is independent of the choice of the reference pressure.

**Solubility in a Semi-Ideal Mixture**

To determine the solubility of a constituent in a semi-ideal nongaseous mixture, consider the partial mutual stable equilibrium of a binary semi-ideal mixture and a pure constituent in the liquid or solid form of aggregation. Constituent 2 of the mixture is also the pure constituent. In this condition the binary mixture is saturated with constituent 2 while constituent 1 is assumed to exhibit ideal-solution behavior. This implies that, even under saturated conditions, constituent 2 is present in trace amounts. Because the systems are in partial mutual stable equilibrium, the values of the temperature \( T \), pressure \( p \), and chemical potential of the common constituent \( \mu_2 \) in both systems are equal.

The chemical potential of constituent 2 in the binary mixture is described by Eq. 3.23,

\[ \mu_{2f} = \lambda_{2f}(T, p) + RT \ln y_{2f}^* \]  

(3.55)

where \( y_{2f}^* \) is the mole fraction of the common constituent in the saturated mixture. The equality of chemical potential

\[ \mu_{2f} = \mu_{22f} \]  

(3.56)

yields an expression for the solubility of the common constituent in the binary mixture.

\[ y_{2f}^*(T, p) = \exp \left[ \frac{\mu_{22f}(T, p) - \lambda_{2f}(T, p)}{RT} \right] \]  

(3.57)

Using this expression, the constant of integration \( \lambda_{2f}(T, p) \) can be eliminated from Eq. 3.49. Thus, Henry's constant can be expressed as

\[ \mathcal{H}_{2f}(T, p) = \frac{p^*}{y_{2f}^*(T, p)} \exp \left[ \frac{\mu_{22f}(T, p) - \mu_{22g}(T, p^*)}{RT} \right] \]  

(3.58)

If the pure constituent exhibits ideal-gas behavior along the dew-point curve as well as ideal incompressible behavior along the bubble-point curve, then the saturation pressure \( p_{sat,22}(T) \) can be chosen as the reference pressure and, with the help of Eqs. 3.10 and 3.50, Henry's constant can be expressed in terms of the properties of the pure constituent and the solubility.

Chapter 3: Equilibrium Relations
\[ \mathcal{H}_{2f}(T, p) = \frac{p_{\text{sat.}22}(T)}{y_{2f}^*(T, p)} \exp \left\{ \frac{v_{22f}}{RT} [p - p_{\text{sat.}22}(T)] \right\} \]  

(3.59)

For ordinary substances the exponential term is approximately unity and this expression reduces to

\[ \mathcal{H}_{2f}(T, p) \approx \frac{p_{\text{sat.}22}(T)}{y_{2f}^*(T, p)} \]  

(3.60)

Equality of Relative Saturation

The equilibrium relation for a constituent common to an ideal-gas mixture and a semi-ideal nongaseous mixture is given by Henry's law. This relation can be expressed in a form that doesn't involve Henry's constant. In particular, if we divide both sides of Eq. 3.48 by the solubility of the constituent in each mixture we find

\[ \left( \frac{y_{2g}}{y_{2g}^*} \right) = \left( \frac{y_{2f}}{y_{2f}^*} \right) \left[ \left( \frac{y_{2f}}{y_{2g}} \right) \left( \frac{\mathcal{H}_{2fg}}{p} \right) \right] \]  

(3.61)

Using Eqs. 3.39, 3.49, and 3.57 the term in the square brackets reduces to unity and Henry's law can be expressed as a condition of relative saturation equality similar to Eq. 3.44,

\[ \phi_{2g} = \phi_{2f} \]  

(3.62)

where \( \phi_2 \) is defined by Eq. 3.45.

The equality of relative saturation holds if the vapor-phase mixture acts as an ideal-gas mixture up to saturated conditions and constituent 1 in the binary mixture always exhibits ideal-solution behavior. This latter condition requires that constituent 2 in the semi-ideal mixture be present only in trace amounts, even under saturated conditions. Furthermore, this relation holds only for temperatures and pressures at which the pure common constituent is in a liquid or solid form of aggregation.

3.3.3 Ideal-Gas and Polymeric Mixtures

Equilibrium Relation

Consider two simple systems in partial mutual stable equilibrium. One system consists of an ideal-gas mixture; the other consists of a binary polymeric mixture in a solid form of aggregation. Constituent 2 in the binary mixture is present in trace amounts and is common to both systems. Because the systems are in partial mutual stable equilibrium,
the values of the temperature $T$, pressure $p$, and chemical potential of the common constituent $\mu_2$ in both systems are equal.

The chemical potential of constituent 2 in the polymeric mixture is described by Eq. 3.33 in the form,

$$\mu_{2p} = \lambda_{2p}(T,p) + RT\ln \nu_{2p}$$  \hspace{1cm} (3.63)

where the subscript $p$ denotes a polymeric phase and

$$\nu_{2p} = \nu_{2p} \exp \left[ (1 - 1/x)(1 - \nu_{2p}) + \chi_{12}(1 - \nu_{2p})^2 \right]$$  \hspace{1cm} (3.64)

is the volume fraction of the common constituent in the polymeric mixture corrected by the interaction of the constituent with the polymer molecules and the fact that the sizes of the two molecules are highly disparate. Equating this expression to that for the chemical potential of constituent 2 in the ideal-gas mixture, Eq. 3.46, yields a relation between the partial pressure of the common constituent in the vapor phase $p_{22g}$ and the corrected volume fraction of the constituent in the polymeric phase $\nu_{2p}$,

$$p_{22g} = y_{2g}p = \nu_{2p} G_{2pg}(T,p)$$  \hspace{1cm} (3.65)

where the constant

$$G_{2pg}(T,p) = p^* \exp \left[ \frac{\lambda_{2p}(T,p) - \mu_{2g}(T,p^*)}{RT} \right]$$  \hspace{1cm} (3.66)

is a function of temperature and pressure only and, like Henry's constant, its value is independent of the choice of the reference pressure.

**Solubility in a Polymeric Mixture**

To determine the solubility of a constituent in a polymeric mixture, consider the partial mutual stable equilibrium of a binary polymeric mixture and a pure constituent in the liquid or solid form of aggregation. Constituent 2 of the mixture is also the pure constituent. In this condition the binary mixture is saturated with the common constituent while the volume fraction of constituent 1 is assumed to remain much larger than that of constituent 2. Because the systems are in partial mutual stable equilibrium, the values of the temperature $T$, pressure $p$, and chemical potential of the common constituent $\mu_2$ in both systems are equal.

The chemical potential of constituent 2 in the binary mixture is described by Eq. 3.63,

$$\mu_{2p} = \lambda_{2p}(T,p) + RT\ln \nu_{2p}^*$$  \hspace{1cm} (3.67)
where \( \nu^*_{2p} \) is the corrected volume fraction of the common constituent in the saturated binary mixture and is defined by Eq. 3.34. The condition of chemical potential equality

\[
\mu_{2p} = \mu_{22f}
\]  

(3.68)
yields an expression for the solubility of the common constituent in the binary mixture,

\[
\nu^*_{2p} = \exp \left[ \frac{\mu_{22f}(T, p) - \lambda_{2p}(T, p)}{RT} \right]
\]  

(3.69)
which can be solved to give the saturated volume fraction using Eq. 3.64.

**Equality of Relative Saturation**

The equilibrium relation given by Eq. 3.65 can be expressed in a form that doesn't involve the constant \( G_{2pg} \). In particular, if we divide both sides of the equation by the solubility of the constituent in each mixture we find

\[
\left( \frac{y_{2g}}{y^*_{2g}} \right) = \left( \frac{\nu^*_{2p}}{\nu^*_{2p}} \right) \left[ \left( \frac{\nu^*_{2p}}{y^*_{2g}} \right) \left( \frac{G_{2pg}}{p} \right) \right]
\]  

(3.70)

Using Eqs. 3.39, 3.66, and 3.69 the term in the square brackets reduces to unity and the equilibrium relation can be expressed as a condition of relative saturation equality similar to Eq. 3.44,

\[
\phi_{2g} = \phi^*_{2p}
\]  

(3.71)
where \( \phi_{2g} \) is defined by Eq. 3.45 and \( \phi^*_{2p} \) is the relative saturation of constituent 2 in the polymeric mixture expressed in terms of the corrected volume fractions.

\[
\phi^*_{2p} \equiv \frac{\nu_{2p}}{\nu^*_{2p}}
\]  

(3.72)
This relation holds if the volume fraction of constituent 2 in the polymeric mixture remains much smaller than that of the polymeric constituent, even under saturated conditions, and the pure common constituent is in a liquid or solid form of aggregation at the temperature \( T \) and pressure \( p \) of the mixture.

### 3.3.4 Semi-Ideal Mixtures

**Equilibrium Relation**

Consider two simple systems, system \( A \) and system \( B \), in partial mutual stable equilibrium. Each system consists of a binary semi-ideal mixture in the liquid or solid form of
aggregation. Constituent 2 is common to both systems and is present in trace amounts. Because the systems are in partial mutual stable equilibrium, the values of the temperature \( T \), pressure \( p \), and chemical potential of the common constituent \( \mu_2 \) in both systems are equal.

Using Eq. 3.47 to express the chemical potential of constituent 2 in each system, the condition of chemical potential equality

\[
\mu^A_{2f} = \mu^B_{2f} \tag{3.73}
\]

yields a relation between the mole fractions of the common constituent in both systems,

\[
y^A_{2f} = y^B_{2f} \mathcal{F}_{2f}(T, p) \tag{3.74}
\]

where the constant

\[
\mathcal{F}_{2f}(T, p) = \exp \left[ \frac{\lambda^B_{2f}(T, p) - \lambda^A_{2f}(T, p)}{RT} \right] \tag{3.75}
\]

is a function of temperature and pressure only. Note that, using Eq. 3.49, the constant \( \mathcal{F}_{2f}(T, p) \) can be expressed in terms of Henry's constant for the common constituent in each system.

\[
\mathcal{F}_{2f}(T, p) = \frac{\mathcal{H}^B_{2f}(T, p)}{\mathcal{H}^A_{2f}(T, p)} \tag{3.76}
\]

**Equality of Relative Saturation**

The equilibrium relation given by Eq. 3.74 can be expressed in a form that doesn't involve the constant \( \mathcal{F}_{2f} \). In particular, if we divide both sides of Eq. 3.74 by the solubility of the constituent in each mixture we find

\[
\left( \frac{y^A_{2f}}{y^A_{2f}} \right) = \left( \frac{y^B_{2f}}{y^B_{2f}} \right) \left[ \left( \frac{y^B_{2f}}{y^A_{2f}} \right) \mathcal{F}_{2f} \right] \tag{3.77}
\]

Using Eqs. 3.57 and 3.75 the term in the square brackets reduces to unity and the equilibrium relation can be expressed as a condition of relative saturation equality similar to Eq. 3.44,

\[
\phi^A_{2f} = \phi^B_{2f} \tag{3.78}
\]

where \( \phi_{2f} \) is defined by Eq. 3.45. This relation holds if the constituent in each semi-ideal mixture is present in trace amounts, even under saturated conditions.
3.3.5 Semi-Ideal and Polymeric Mixtures

Equilibrium Relation

Consider two simple systems in partial mutual stable equilibrium. One system consists of a binary semi-ideal mixture in the liquid or solid form of aggregation; the other consists of a binary polymeric mixture in a solid form of aggregation. Constituent 2 is common to both systems and is present in trace amounts. Because the systems are in partial mutual stable equilibrium, the values of the temperature $T$, pressure $p$, and chemical potential of the common constituent $\mu_2$ in both systems are equal.

Using Eqs. 3.47 and 3.63 to express the chemical potential of the common constituent in the two systems, the condition of chemical potential equality

$$\mu_{2f} = \mu_{2p}$$

(3.79)

yields a relation between the mole fraction of the common constituent in the semi-ideal mixture $y_{2f}$ and the corrected volume fraction of the constituent in the polymeric mixture $\nu_{2p}$,

$$y_{2f} = \nu_{2p} \mathcal{P}_{2pf}(T, p)$$

(3.80)

where the constant

$$\mathcal{P}_{2pf}(T, p) = \exp \left[ \frac{\lambda_{2p}(T, p) - \lambda_{2f}(T, p)}{RT} \right]$$

(3.81)

is a function of temperature and pressure only. Note that, using Eqs. 3.49 and 3.66, the constant $\mathcal{P}_{2pf}(T, p)$ can also be expressed as

$$\mathcal{P}_{2pf}(T, p) = \frac{\zeta_{2pf}(T, p)}{\mathcal{H}_{2f}(T, p)}$$

(3.82)

Equality of Relative Saturation

The equilibrium relation given by Eq. 3.80 can be expressed in a form that doesn’t involve the constant $\mathcal{P}_{2pf}$. In particular, if we divide both sides of the equation by the solubility of the constituent in each mixture we find

$$\left( \frac{y_{2f}}{y'_{2f}} \right) = \left( \frac{\nu_{2p}}{\nu'_{2p}} \right) \left[ \frac{\nu_{2p}^e}{y'_{2f}} \right] \mathcal{P}_{2pf}$$

(3.83)

Using Eqs. 3.57, 3.69, and 3.81 the term in the square brackets reduces to unity and the equilibrium relation can be expressed as a condition of relative saturation equality
similar to Eq. 3.71,

\[ \phi_{2f} = \phi_{2p}^* \]  \hspace{1cm} (3.84)

where \( \phi_{2f} \) is defined by Eq. 3.45 and \( \phi_{2p}^* \) is defined by Eq. 3.72. This relation holds if constituent 2 in the semi-ideal mixture is present in trace amounts and the volume fraction of constituent 2 in the polymeric mixture is much smaller than that of the polymeric constituent, even under saturated conditions.

3.4 Summary

Equipped with expressions for the chemical potential of constituents in mixtures, several equilibrium relations were derived for constituents common to ideal-gas mixtures, semi-ideal nongaseous mixtures, and polymeric mixtures. All of the equilibrium relations were further expressed as an equality of the relative saturation of the common constituent in the interacting systems. This quantity relates the amount of the constituent in the system to the solubility of the constituent, the largest amount that the system can hold under the specified conditions. Relative saturation is expressed as a ratio of mole fractions for systems in which at least one of the constituents exhibits ideal behavior or as a ratio of corrected volume fractions for polymeric mixtures.
Chapter 4

A Relative Saturation Moisture Sensor

The purpose of this chapter is to describe a sensor that measures the moisture content of fluids. Just as the sensor responds to the relative humidity of air, the sensor is shown to respond to the relative saturation of water in the fluid. Equilibrium relations between the fluid and the sensing material reveal the mechanism by which the sensor responds in this fashion.

4.1 Introduction

4.1.1 Motivation

The reliability of power transformers depends on the accurate measurement of critical parameters that describe the state of the insulation. One important parameter is the moisture content of the circulating oil and the solid insulation. The migration of a minute amount of moisture has been associated with flow electrification at pressboard/oil interfaces [29, 30, 31] as well as the formation of gas bubbles in the oil [32, 33]. Although equilibrium data [11, 34, 35] is used to predict the moisture content of the solid insulation from measurements of the moisture content of the oil, analysis of the mass-transfer time constants, in view of the load cycles of a typical power transformer, indicates that the transformer is never in moisture equilibrium. Nonetheless, comparison of the measured moisture content with that predicted from dynamic or quasi-stationary adaptive models can provide information about the incipience of anomalous behavior in the transformer [2]. The ability to continuously measure the moisture content of the circulating oil in a transformer can thus prevent catastrophic failures that may not be avoided using present industry practices.
4.1.2 Preliminary Work

The difficulty and expense encountered in mounting monitoring equipment in a transformer requires that the sensors be stable and reliable over the lifetime of a transformer or at least over the period between scheduled maintenances. In addition, the sensors need to withstand the harsh operating conditions of a transformer which include a maximum top oil temperature of 100°C with a corresponding maximum hot-spot temperature of 140°C [36].

Recent attempts to develop immersible moisture sensors made use of thin-film plasma-deposited bromobenzene whose dielectric properties were found to be sensitive to the moisture content of the oil. Experimental evidence showed that these films acted as semipermeable membranes, acting as barriers to transformer oil but absorbing moisture in proportion to the absolute moisture content of the oil [37]. Unfortunately, the long-term loss of sensitivity, particularly at elevated temperatures, rendered the sensors unreliable over periods of weeks without periodic recalibration.

4.1.3 Properties of Polyimide

Polyimide films form the basis of numerous versions of capacitive humidity sensors [38, 39, 40, 41]. Polyimide has been found to absorb moisture up to 3% of its dry weight. Because of the high polarizability of the water molecule, the absorbed moisture results in changes in the dielectric constant of up to 30% [42, 43]. The permittivity was found to be a linear function of the ambient relative humidity. This moisture-induced change in permittivity indicated that the absorbed moisture has a dipole moment nearly equal to that of free water, suggesting that microvoids in the polymeric network dominate the observed absorption phenomena [42, 44].

The use of thin films in the micron range enables sensors to respond with a time constant on the order of minutes. This time constant is dominated by the diffusion of moisture into the polyimide. The diffusion coefficient of moisture in polyimide was measured to be $4 \times 10^{-13}$ m$^2$/s at room temperature with an activation energy of 0.33 eV [45]. Along with these characteristics, the stability, high temperature capability, and chemical inertness of polyimide films render them good candidates for use in a transformer environment.
4.2 Apparatus

4.2.1 Sensor Description

A polyimide-based sensor, designed and manufactured by Leeds & Northrup [39, 40] to measure the relative humidity of air, is shown schematically in Fig. 4.1. The 4 mm × 4 mm structure consists of a pair of gold-plated nickel electrodes deposited in a planar interdigitated arrangement on an insulating substrate of high purity aluminum oxide. The electrodes are covered with a lower polyimide film, a thin platinum mesh, and an upper polyimide film.

As moisture diffuses into the structure, the dielectric constant of the polyimide increases. As a result, the capacitance of the structure also increases. Measured at a frequency of 100 kHz, the capacitance nominally ranges between 80 and 105 pF as the polyimide goes from dry to saturated conditions. Because the platinum mesh is sufficiently conducting to act as an equipotential, the electric field above the electrodes is enhanced within the lower polyimide layer. This reduces the sensitivity of the sensor to changes in the permittivity of the substrate. The electric field below the electrodes is mostly contained within the substrate because its thickness is large compared with the spacing between interdigitated electrodes. As the mesh is left floating, the electric field extends into the upper layer through the openings in the mesh. In order to minimize the coupling to the exterior, the upper layer is thick enough to capture most of the field fringing from the mesh. This is achieved by making the thickness of the upper layer on the order of the diameter of the openings. This arrangement reduces the sensitivity of the sensor to fouling and contamination while allowing the thickness of the lower polyimide layer to be minimized.

The presence of the conducting mesh affects the diffusion of moisture into the lower film. This effect is minimized by making the mesh porous such that the size of the openings is large enough not to significantly inhibit the mass-transfer process. In addition, the openings are spaced close enough such that the lateral diffusion under the mesh is not rate-limiting. This is achieved by making the distance between the holes small compared to the thickness of the lower film, thus providing a uniform distribution of moisture in the polyimide during moisture transients. Because the response time is dominated by the diffusion of moisture through the polyimide layers, the use of thin films enable the sensor to respond with a time constant that is short compared with the characteristic mass-transfer times of the system.
Figure 4.1: Cutaway view of the Leeds & Northrup sensor. The $4 \text{ mm} \times 4 \text{ mm}$ structure consists of a pair of gold-plated nickel (Au on Ni) electrodes deposited in a planar interdigitated arrangement on an insulating substrate of high purity aluminum oxide ($\text{Al}_2\text{O}_3$). The electrodes are covered with a lower polyimide (PI) film, a thin platinum (Pt) mesh, and an upper polyimide (PI) film. As the lower polyimide film absorbs moisture, its dielectric constant increases resulting in an increase in the high-frequency capacitance of the structure. The porous conducting mesh and the upper film reduce the sensitivity of the sensor to fouling and contamination while allowing the film thicknesses to be minimized. (Adapted from Reference [46].)
4.2.2 Calibration Setup

Two units, each consisting of a Leeds & Northrup sensor and the associated transmitter [47, 48], were mounted in a facility for calibration as well as comparison purposes. The sensors were mounted in a Pyrex reaction kettle. The calibration kettle contained approximately one liter of oil which was continuously stirred with a magnetic stirrer. The sensors were mounted without their protective shields to avoid trapped gas bubbles and remained completely immersed during the calibration. The oil was heated by means of heating coils wrapped around the kettle and driven by a temperature controller. The temperature of the oil was independently measured using a partial-immersion, mercury-filled glass thermometer accurate to 0.2°C.

To control the moisture content of the oil, a mixture of dry and wet nitrogen was bubbled through the oil as it was being stirred. The wet nitrogen was produced by bubbling dry nitrogen through a wetting flask. The nitrogen mixture was then dispersed into the oil with the help of a porous distributor plate. The moisture content of the oil was measured using a Mitsubishi Moisture Meter (Model CA-05) which uses microprocessor-controlled coulometric Karl-Fischer titrimetry. For transformer oil the anode and cathode solutions were Aquamicron A and C respectively. Because the titration current is a function of the number of moles of water present in the solution, the instrument measures the weight of the water in the sample. The moisture content of the oil is then calculated as the ratio of the weight of the water to the weight of the oil sample. The oil was sampled with a 10 ml glass syringe. The sample size was chosen to insure a maximum uncertainty of 1 ppm based on the precision of the instrument (±3 μg). Each measurement was made with the sensors and the oil in moisture equilibrium. Typical equilibration times were 4, 3, and 2 hours at 35, 50, and 70°C. These times reflect the wetting process of the oil, not the response time of the sensors. The steady state was verified by observing that the output signal from the two sensors did not change over a period of 30 minutes. The transmitters provide a 4 to 20 mA output current which was measured as a voltage across a 249 Ω ± 1% load resistor with an accuracy of 1 mV, corresponding to a 0.025% change over the 1 to 5 V output range.

4.3 Sensor Calibration

4.3.1 Transient Response

To determine the rate-limiting process in the measurement of moisture dynamics it is important to know the time constant associated with the sensor. With this goal in mind,
the sensors were subjected to a step change in the moisture content of the surrounding fluid. This was accomplished by transferring the sensors from ambient air into a bath of well-stirred transformer oil. The air was at 22.5°C with a relative humidity of 18%; the oil was at 35.0°C with a moisture content of 15.0 ppm corresponding to a relative saturation of 15%. Typical transient responses for each sensor are shown in Fig. 4.2. In this figure the output voltage and the corresponding increase in capacitance over the dry capacitance of the sensors are plotted as a function of time. To compute the increase in capacitance, a sensitivity of 160 mV/pF was assumed for both sensors. In both plots time zero corresponds to the time when the sensor was immersed in the oil.

Prior to immersion, the output signal provides a measure of the relative humidity of the ambient air. As the sensors make contact with the oil, the output voltage at first increases sharply and then decreases exponentially. The exponential decay is associated with the transfer of moisture out of the sensors. As water leaves the polyimide, the capacitance of the sensor decreases. The time constant of the exponential decay was estimated to be 33.1 ± 0.3 s for sensor #1 and 33.9 ± 0.3 s for sensor #2. These values were calculated using the expressions derived in Appendix A which are encoded in the program leastexp.for listed in Appendix M. In the calculations, we assumed equal uncertainty in the measurement of the output voltage and virtually no uncertainty in the measurement of time. These estimates imply that the time required for these sensors to equilibrate with the surrounding fluid is on the order of a few minutes.

The initial increase in output voltage is due to the sudden change in the dielectric constant of the surrounding fluid. This was verified by immersing sensor #2 in transformer oil at various temperatures and in three fluids at room temperature with relative dielectric constants ranging from 2.2 to 26.6. The fluids and the corresponding relative dielectric constants are given in Table 4.1. The overvoltage was found to be linear with the dielectric constant of the fluid and independent of the temperature of the oil. A plot of the overvoltage and corresponding increase in capacitance as a function of the relative dielectric constant of the fluid is shown in Fig. 4.3. A least-squares fit of the data to the line $y = Bx$ yielded a slope of 10.8 ± 0.3 mV per unit change in the relative dielectric constant. The slope and its uncertainty were calculated using the program leastbx.for listed in Appendix M and assuming equal uncertainty in the measurement of the overvoltage and virtually no uncertainty in the measurement of the relative dielectric constant [49: Problem 8.3].

The correlation coefficient for this fit was calculated to be 0.99998. A more quantitative measure of the linear fit is provided by a probability for the calculated correlation coefficient. For any observed correlation coefficient $r_o$, the number $P_N(|r| \geq |r_o|)$ is the
Figure 4.2: Typical transient response of the Leeds & Northrup sensors plotted in the form of the output voltage and the corresponding increase in capacitance over the dry capacitance of the sensors as a function of time. Time zero corresponds to the time when the sensors were immersed in the oil. In this case the sensors were transferred from ambient air at 22.5°C and 18% relative humidity into a bath of well-stirred transformer oil at 35.0°C and 15.0 ppm moisture content, which corresponds to a relative saturation of 15%. The responses indicate that the time required for the sensor to equilibrate with the surrounding fluid is on the order of a few minutes.

Section 4.3: Sensor Calibration
Table 4.1: Values of the relative dielectric constant of fluids used to measure the dependence of the capacitance of the Leeds & Northrup sensor on the permittivity of the surrounding fluid.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\epsilon_f/\epsilon_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transformer oil</td>
<td>2.2</td>
</tr>
<tr>
<td>Castor oil</td>
<td>4.67</td>
</tr>
<tr>
<td>Acetone</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Figure 4.3: Plot of the initial increase in the output voltage and capacitance of sensor #2 during a moisture transient as a function of the permittivity of the surrounding fluid at room temperature. The solid line drawn represents a least-squares fit of the data to the line $y = Bx$ with a slope of $10.8 \pm 0.3$ mV per unit change in the relative dielectric constant. The two solid lines bounding this curve represent limiting cases in which the platinum mesh is solid and in which the platinum mesh is not present.
probability that \( N \) measurements of two uncorrelated variables would give a correlation coefficient \( r \) as large as \( r_0 \). Thus if we obtain a coefficient \( r_0 \) for which \( P_N(\mid r \mid \geq \mid r_0 \mid) \) is small, then it is correspondingly unlikely that the variables are uncorrelated; that is a correlation is indicated. In particular, if \( P_N(\mid r \mid \geq \mid r_0 \mid) \leq 5\% \), the correlation is called significant; if it is less than 1\%, the correlation is called highly significant [49: Section 9.4]. In this case the probability \( P_3(\mid r \mid \geq 0.99998) \) was calculated to be 0.4\% indicating a highly significant correlation.

Neglecting the dependence of the sensor capacitance on the permittivity of the aluminum oxide substrate and the polyimide films, we can express the dependence of the sensor capacitance \( C \) on the permittivity of the surrounding fluid \( \epsilon_f \) as a Taylor series expansion about the permittivity of free space \( \epsilon_o \):

\[
C(\epsilon_f) = C|_{\epsilon_f=\epsilon_o} + \frac{\partial C}{\partial \epsilon_f}|_{\epsilon_f=\epsilon_o} (\epsilon_f - \epsilon_o) + \cdots
\] (4.1)

The fact that the sensor capacitance is linear with the permittivity of the surrounding fluid suggests that, over the range of interest, the higher-order terms in the above expression can be neglected. This result is consistent with Fig. 4.3 which indicates a change of less than 2\% in the capacitance of the sensor over the entire range. Nonlinear effects are expected to become significant when the energy associated with the electric field in the fluid becomes comparable to the electrical energy stored in the polyimide layers.

Because the increase in capacitance is associated with the penetration of the electric field beyond the platinum mesh, its magnitude depends on the size of the pores in the mesh. If there were no pores in the conducting mesh, the electric field would not penetrate beyond this barrier and there would be no increase in the sensor capacitance with a change in the permittivity of the surrounding fluid. On the other hand, if the pore sizes were so large that the mesh was essentially not present the increase in sensor capacitance resulting from a change in the permittivity of the surrounding fluid would be maximum. The capacitance of this latter structure was computed using the program \texttt{mz2.for} [50: Appendix F] and assuming the configuration illustrated in Fig. 4.4 with values of the parameters given in Table 4.2. The two limiting cases are plotted in Fig. 4.3 along side with the data. The fact that the measured response lies between the two limiting cases gives validity to the proposed mechanism.

\textit{Section 4.3: Sensor Calibration}
Figure 4.4: Cross-sectional view of the Leeds & Northrup sensor. The interdigitated electrode structure lies above an aluminum oxide substrate of thickness $h$ and permittivity $\varepsilon_{ox}$ and is covered by two polyimide films of thickness $d$ and permittivity $\varepsilon$. Between the polyimide layers there is a platinum mesh with a surface conductivity $\sigma_s$. A fluid of permittivity $\varepsilon_f$ surrounds the entire structure.

Table 4.2: Values of parameters used in the computation of the capacitance of the Leeds & Northrup sensor with no platinum mesh.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spatial wavelength</td>
<td>$\lambda$</td>
<td>305 $\mu$m</td>
</tr>
<tr>
<td>Interelectrode spacing</td>
<td>$a$</td>
<td>0.1 $\lambda$</td>
</tr>
<tr>
<td>Electrode meander length</td>
<td>$M_{el}$</td>
<td>37.7 mm</td>
</tr>
<tr>
<td>Oxide layer thickness</td>
<td>$h$</td>
<td>635 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of aluminum oxide</td>
<td>$\varepsilon_{ox}$</td>
<td>9.63 $\varepsilon_o$</td>
</tr>
<tr>
<td>Thickness of polyimide layer</td>
<td>$d$</td>
<td>1 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of polyimide</td>
<td>$\varepsilon$</td>
<td>3.5 $\varepsilon_o$</td>
</tr>
<tr>
<td>Surface conductivity of platinum mesh</td>
<td>$\sigma_s$</td>
<td>0 S $\mu$m</td>
</tr>
<tr>
<td>Frequency</td>
<td>$f$</td>
<td>100 kHz</td>
</tr>
</tbody>
</table>
4.3.2 Calibration in Transformer Oil

Using the apparatus described in Sect. 4.2.2, the Leeds & Northrup sensors were calibrated in transformer oil. Shell Diala A was chosen as an oil representative of insulating fluids used in power transformers. The sensors were calibrated at 35, 50, and 70°C. During the calibration, the temperature was kept constant as the moisture content of the oil was varied.

The results of the calibrations are shown in Fig. 4.5. Here, the output voltage is plotted as a function of the moisture content of the oil together with the corresponding increase in capacitance over the dry capacitance of the sensors. In each plot, the moisture content is expressed as a mass fraction \( x_w \) on the lower axis and as a mole fraction \( y_w \) on the upper axis. These two quantities are related by the expression

\[
\frac{1}{y_w} = 1 + \left( \frac{M_w}{M_o} \right) \left( \frac{1}{x_w} - 1 \right)
\]

(4.2)

where \( M_w \) and \( M_o \) are the molecular weights of water (18.015 kg/kmol) and transformer oil [51] (261 kg/kmol) respectively. In the following discussions, the term moisture content will continue to refer to the measured mass fraction of water in the oil.

The plots indicate that the output voltage, together with the corresponding increase in capacitance over the dry capacitance of the sensors, is a linear function of the moisture content. The decrease in slope implies a reduction in the sensitivity of the sensors to changes in the moisture content of the oil at elevated temperatures.

This sensitivity and its corresponding uncertainty was calculated at each temperature using the program leastsq.for listed in Appendix M and assuming equal uncertainty in the measurement of the moisture content at each temperature and virtually no uncertainty in the measurement of the output voltage [49: Chapter 8]. The results, tabulated in Table 4.3, indicate that the sensitivity of the sensors is reduced at temperatures typical of operating transformers. In addition the sensitivities associated with the two sensors are equal within the calculated uncertainties.

Possibly of more practical importance is the sensitivity of the estimated moisture content of the oils to changes in the output voltage of the Leeds & Northrup sensors. This sensitivity is simply the inverse of the sensitivity of the sensors to changes in the moisture content of the oil and is tabulated together with the corresponding uncertainty in Table 4.4. These values quantify the increase with temperature of the uncertainty in the estimation of the moisture content from a measurement of the output voltage.

Section 4.3: Sensor Calibration
Figure 4.5: Calibration of the Leeds & Northrup sensors in Shell Diala A transformer oil indicating that the output voltage, together with the corresponding increase in capacitance over the dry capacitance of the sensors, is a linear function of the moisture content. The decrease in slope implies a reduction in the sensitivity of the sensors to changes in the moisture content of the oil at elevated temperatures.
Table 4.3: Temperature dependence of the sensitivity of the output voltage of the Leeds & Northrup sensors to changes in the moisture content of Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sensitivity (mV/ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Transformer oil</td>
</tr>
<tr>
<td></td>
<td>Sensor #1</td>
</tr>
<tr>
<td>35</td>
<td>34.7 ± 0.4</td>
</tr>
<tr>
<td>50</td>
<td>17.3 ± 0.3</td>
</tr>
<tr>
<td>70</td>
<td>8.8 ± 0.5</td>
</tr>
</tbody>
</table>

4.3.3 Calibration in Silicone Oil

To discriminate whether the Leeds & Northrup sensor responds to the absolute moisture content or the relative saturation of water in the oil, the calibration was repeated with Dow Corning 200 fluid (10 cSt) silicone oil, which is known to have a higher solubility than transformer oil [35]. Early in the process of measuring the moisture content of silicone oil using the Mitsubishi Moisture Meter together with the reagents used for transformer oil, we found that trace amounts of ketones normally present in silicone oils clouded the titration of water in the cell. A new set of anode and cathode solutions (Aquamicron AU and CK) was identified to eliminate this problem.

The results of the calibrations are shown in Fig. 4.6, where the mass fraction of water in the oil is related to the mole fraction of water in the oil by Eq. 4.2 with the average molecular weight of silicone oil equal to 1000 kg/kmol [52]. Although the calibration was not as extensive as in transformer oil, here too we found that the output voltage is a linear function of the moisture content and that the slope of the line decreases with the temperature of the oil.

Table 4.4: Temperature dependence of the sensitivity of the estimated moisture content of the oils to changes in the output voltage of the Leeds & Northrup sensors.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sensitivity (ppm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Transformer oil</td>
</tr>
<tr>
<td></td>
<td>Sensor #1</td>
</tr>
<tr>
<td>35</td>
<td>28.8 ± 0.3</td>
</tr>
<tr>
<td>50</td>
<td>58 ± 1</td>
</tr>
<tr>
<td>70</td>
<td>114 ± 7</td>
</tr>
</tbody>
</table>

Section 4.3: Sensor Calibration
Figure 4.6: Calibration of the Leeds & Northrup sensors in Dow Corning 200 fluid (10 cSt) silicone oil. Just as for transformer oil, the output voltage is a linear function of the output voltage and the slope of the line decreases with the temperature of the oil. Comparison of these curves with those for transformer oil reveals that for the same moisture content the output voltage generated in transformer oil is greater than that generated in silicone oil at the same temperature. This observation eliminates the possibility that the sensors respond to the absolute moisture content of the oil. If they did, the output voltages in the two cases would have been the same.
Just as for the calibration in transformer oil, the sensitivity of the sensors was calculated at each temperature. The results, tabulated in Tables 4.3 and 4.4 along with those for transformer oil, indicate that, in addition to the reduction in sensitivity associated with the increase in temperature, the sensitivity of the sensors to changes in the moisture content of the oil is reduced for oils with higher solubilities.

4.4 Sensor Characterization

4.4.1 Absolute Moisture Content vs Relative Saturation

The calibration of the Leeds & Northrup sensors in transformer oil and silicone oil was motivated not only by the need to correlate the output signal to the moisture content of the oil, but also by an interest in the thermodynamic nature of the sensors. The results of these calibrations help to discriminate whether the sensors respond to the absolute moisture content or the relative saturation of water in the oils. Relative saturation is defined by Eq. 3.45 as the ratio of the mole fraction of water in the oil to the mole fraction under saturated conditions.

Comparison of the calibration curves for transformer oil and silicone oil shows that, for the same temperature and moisture content, the output voltage generated in transformer oil is greater than that generated in silicone oil. This observation eliminates the possibility that the sensors respond to the absolute moisture content of the oils. If they did, the output voltages in the two cases would have been the same.

4.4.2 Solubility of Moisture in Oil

To compute the relative saturation, an independent measurement of the solubility of water in transformer oil and silicone oil was made as a function of temperature. In order to provide an ‘infinite’ reservoir of moisture for the oils, a 2 cm × 5 cm piece of 1 mm-thick EHV-Weidmann HI-VAL pressboard was impregnated under vacuum with deionized water and its surface was padded dry. The piece of pressboard was then attached to the bottom part of the stem of a thermometer which was immersed in a 500 ml Erlenmeyer flask full of oil. To insure that the moisture remained dissolved in the oil, all the air was removed and the flask was sealed at the desired temperature. The experiment was allowed to equilibrate for 24 hours during which a magnetic stirrer was used to enhance the mass-transfer process. The oil was then sampled through a sampling port and its moisture content was measured with the moisture meter. The flask was then opened to the atmosphere and the Leeds & Northrup sensors were quickly immersed in
Table 4.5: Comparison of estimated parameters describing the Arrhenius form of the solubility of water in Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Transformer oil</th>
<th>Silicone oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
<td>$B$ (K)</td>
</tr>
<tr>
<td>Oommen [34]</td>
<td>7.4</td>
<td>1670</td>
</tr>
<tr>
<td>Griffin [35]</td>
<td>7.1 ± 0.2</td>
<td>1570 ± 80</td>
</tr>
<tr>
<td>Shell [51]</td>
<td>7.3 ± 0.1</td>
<td>1630 ± 30</td>
</tr>
<tr>
<td>von Guggenberg</td>
<td>7.3 ± 0.3</td>
<td>1600 ± 100</td>
</tr>
</tbody>
</table>

the saturated oil. As the oil was exposed to ambient conditions, the output voltage of the sensors rapidly decreased from the saturation value indicating that the moisture in the oil was reaching a new equilibrium with the ambient air. Evidence of free water was observed only after the oil had cooled to ambient conditions.

The temperature dependence of the solubility of water in Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil is shown in the form of Arrhenius plots in Fig. 4.7. The solid lines drawn represent least-squares fits of the data to the expression

$$\log x_w^* = A - \frac{B}{T}$$

(4.3)

with the saturated mass fraction $x_w^*$ measured in ppm, and the temperature $T$ in kelvin. The estimated values of the parameters $A$ and $B$, together with their corresponding uncertainty, are listed in Table 4.5 along with values reported in the literature. Whenever sufficient information was given, the values of the parameters and their uncertainty were calculated using the program leastsq for listed in Appendix M and assuming that the uncertainty in the measurement of the temperature is insignificant compared with the uncertainty in the measurement of the solubility [49: Chapter 8]. Furthermore, because the estimation was performed using the logarithm of the solubility, we assumed equal fractional uncertainty rather than equal absolute uncertainty in the measurement of the solubility [49: Section 2.7]. This assumption is justified considering the wide range of values measured. From the table it is clear that, within the calculated uncertainties, our measurements agree well with those reported in the literature. This validates the measurement procedures followed during the experiment.

The measurement of the solubility of water in oil can be used to estimate Henry's constant. This constant can then be used together with Henry's law, Eq. 3.48, to predict...
Figure 4.7: Arrhenius plot of the solubility of water in Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil. The solid lines drawn represent least-squares fits of the data to the expression $\log x_w^* = A - B/T$ with the saturated mass fraction $x_w^*$ measured in ppm, and the temperature $T$ in kelvin. The estimated values of the parameters $A$ and $B$ agree, within the calculated uncertainties, with values reported in the literature. This validates the measurement procedures followed during the experiment.
Table 4.6: Estimated parameters describing the Arrhenius form of Henry's constant for water in Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil at atmospheric pressure.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Transformer oil</th>
<th>Silicone oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathcal{H}_0 ) (GPa)</td>
<td>0.4 ± 0.2</td>
<td>1.4 ± 0.6</td>
</tr>
<tr>
<td>( E_a ) (eV)</td>
<td>0.12 ± 0.02</td>
<td>0.22 ± 0.01</td>
</tr>
</tbody>
</table>

the moisture content of the oil for conditions other than saturation. Using Eq. 3.60 and tabulated values of the saturated pressure and specific volume of water [22: Appendix B, Table B.14], Henry's constant for water in each oil at atmospheric pressure was calculated and plotted in Arrhenius form in Fig. 4.8. These values differ by less than 1% from those calculated using Eq. 3.58 with the triple point pressure of water (0.61133 kPa) as the reference pressure. The higher value of Henry's constant for water in transformer oil reflects the fact that the solubility of water in transformer oil is lower than that in silicone oil.

The solid lines drawn in the figure represent least-squares fits of the data to the Arrhenius expression for Henry's constant,

\[
\mathcal{H}_{wo}(T, p_{atm}) = \mathcal{H}_0 e^{-E_a/kT} \tag{4.4}
\]

where the constant \( k \) is Boltzmann's constant (8.6173 × 10^{-5} eV/K). The estimated values of the parameter \( \mathcal{H}_0 \) and the activation energy \( E_a \), together with their corresponding uncertainty, are tabulated in Table 4.6 for Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil. These values were estimated in the same way as the parameters \( A \) and \( B \) in Eq. 4.3 with the help of Eqs. A.17 and A.18.

4.4.3 Universal Response

Using the measured values of the solubilities, the calibration data shown in Figs. 4.5 and 4.6 can be expressed in terms of the relative saturation of water in the oils \( \phi_w \). This quantity is defined as

\[
\phi_w = \frac{y_w}{y_{w0}} = \frac{1 + \left( \frac{M_w}{M_o} \right) \left( \frac{1}{x_{w0}} - 1 \right)}{1 + \left( \frac{M_w}{M_o} \right) \left( \frac{1}{x_w} - 1 \right)} \tag{4.5}
\]

where the mass fractions \( x_w \) and \( x_{w0} \) represent the moisture content and solubility of water in the oils, and \( M_w \) and \( M_o \) are the molecular weights of water and oil respectively.
Figure 4.8: Arrhenius plot of Henry's constant for water in Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil at atmospheric pressure. The solid lines drawn represent least-squares fits of the data to an Arrhenius expression for Henry's constant. This constant can be used together with Henry's law, Eq. 3.48, to predict the moisture content of the oil for conditions other than saturation. The higher value of Henry's constant for water in transformer oil reflects the fact that the solubility of water in transformer oil is lower than that in silicone oil.
Table 4.7: Estimated parameters describing the dependence of the output voltage of the Leeds & Northrup sensors on the relative saturation of water in Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sensor #1</th>
<th>Sensor #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$1.114 \pm 0.007$</td>
<td>$1.016 \pm 0.007$</td>
</tr>
<tr>
<td>$b \ (V^{-1})$</td>
<td>$3.36 \pm 0.04$</td>
<td>$3.28 \pm 0.04$</td>
</tr>
</tbody>
</table>

Figure 4.9 shows the results of this normalization. The fact that the data for all three temperatures and both oils falls on one line demonstrates that the sensors respond to the relative saturation of water in the oils. In addition, these plots show that the output voltage, together with the corresponding increase in capacitance over the dry capacitance of the sensors, is a linear function of the relative saturation of water in the oils.

The solid lines drawn represent least-squares fits of the normalized calibration data to the expression

$$V = a + b\phi_w$$  \hspace{1cm} (4.6)

The correlation coefficient for both fits was calculated to be 0.998 with a probability $P_{41}(|r| \geq 0.998)$ less than 0.05% indicating a highly significant correlation. The estimated values of the parameters $a$ and $b$, together with their corresponding uncertainty, are tabulated in Table 4.7. The values of the parameters and their uncertainty were calculated using the program leastsq.for listed in Appendix M and assuming equal uncertainty in the measurement of the relative saturation and virtually no uncertainty in the measurement of the output voltage [49: Chapter 8]. Comparison of these values indicates that, while the slopes agree within the calculated uncertainties, the units have slightly different offsets. This difference can be accounted for by variations in the electronics of the transmitter.

The solid lines drawn in Figs. 4.5 and 4.6 were generated using Eqs. 4.5 and 4.6, together with the values of the estimated parameters $a$ and $b$, and the solubilities of water at each temperature. The resulting equation indicates that, in general, the output voltage is not a linear function of the moisture content. Nevertheless, for dilute solutions such as these oils, where the conditions
Figure 4.9: Demonstration that the Leeds & Northrup sensors respond to the relative saturation of water in oil. The calibration data for Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil is replotted in the form of the output voltage, together with the corresponding increase in the capacitance over the dry capacitance of the sensors, as a function of relative saturation. The fact that the data for all three temperatures and both oils falls on one line demonstrates that the sensors respond to relative saturation.

Section 4.4: Sensor Characterization
Table 4.8: Values of parameters used in the computation of the capacitance of the Leeds & Northrup sensor with the platinum mesh.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spatial wavelength</td>
<td>( \lambda )</td>
<td>305 ( \mu \text{m} )</td>
</tr>
<tr>
<td>Interelectrode spacing</td>
<td>( a )</td>
<td>0.1 ( \lambda )</td>
</tr>
<tr>
<td>Electrode meander length</td>
<td>( M_{el} )</td>
<td>37.7 mm</td>
</tr>
<tr>
<td>Oxide layer thickness</td>
<td>( h )</td>
<td>635 ( \mu \text{m} )</td>
</tr>
<tr>
<td>Permittivity of aluminum oxide</td>
<td>( \epsilon_{ox} )</td>
<td>9.63 ( \epsilon_0 )</td>
</tr>
<tr>
<td>Thickness of polyimide layer</td>
<td>( d )</td>
<td>1 ( \mu \text{m} )</td>
</tr>
<tr>
<td>Permittivity of fluid</td>
<td>( \epsilon_f )</td>
<td>2.2 ( \epsilon_0 )</td>
</tr>
<tr>
<td>Surface conductivity of platinum mesh</td>
<td>( \sigma_s )</td>
<td>1 mS</td>
</tr>
<tr>
<td>Frequency</td>
<td>( f )</td>
<td>100 kHz</td>
</tr>
</tbody>
</table>

\[
x_w \ll 1
\]

(4.7)

hold, the output voltage is essentially linear with the moisture content.

Figure 4.9 shows the relationship between the capacitance of the sensors and the relative saturation of water in the oils. The capacitance of the sensors depends on the permittivity of the polyimide. This dependence, shown in Fig. 4.10, was calculated using the program mz2.for [50: Appendix F] and assuming the configuration illustrated in Fig. 4.4 with values of the parameters given in Table 4.8. Furthermore, the conducting mesh was assumed to be solid. This assumption is justified because the diameter of the pores is small compared to the spatial wavelength of the electrode structure [39, 40]. Because the thickness of the polyimide is small compared to the spatial wavelength, the capacitance is a linear function of the permittivity of the polyimide. In effect, the electric field in the lower polyimide layer distributes itself as in two parallel-plate capacitors in series.

Using the relationship between the capacitance of the sensor and the permittivity of the polyimide, the data shown in Fig. 4.9 can be replotted in the form of the normalized permittivity of the polyimide as a function of the relative saturation of water in the oils. The result of this mapping is shown in Fig. 4.11, where the solid line drawn is a line of unity slope. A least-squares fit of the data to the line \( y = Bx \) yielded a slope of 1.018 \( \pm 0.008 \). The slope and its uncertainty were calculated using the program.

Chapter 4: Moisture Sensor
Figure 4.10: Plot of the capacitance of the Leeds & Northrup sensor as a function of the permittivity of the polyimide layers. Because the thickness of the polyimide is small compared to the spatial wavelength, the capacitance is a linear function of the permittivity of the polyimide. In effect, the electric field in the lower polyimide layer distributes itself as in two parallel plate capacitors in series.

1eastbx.for listed in Appendix M and assuming equal uncertainty in the measurement of the relative saturation and virtually no uncertainty in the measurement of the normalized permittivity [49: Problem 8.3].

This figure shows that the permittivity of the polyimide is a linear function of the relative saturation of water in the oils. This linear relationship is identical to that observed for the permittivity of polyimide as a function of the relative humidity of air [42], supporting the idea that the relative saturation of water in the oils is equal to the relative humidity of the air in contact with the oils. Furthermore, this is consistent with the fact that, over the temperature range examined, the permittivity of the polyimide at a fixed relative saturation is essentially constant [45].

Section 4.4: Sensor Characterization
Figure 4.11: Plot of the normalized permittivity of polyimide as a function of the relative saturation of water in Shell Diala A transformer oil and Dow Corning 200 fluid (10 cSt) silicone oil. Whereas the solid line drawn is a line of unity slope, a least-squares fit of the data to the line $y = Bx$ yielded a slope of $1.018 \pm 0.008$. This figure shows that the permittivity of the polyimide is a linear function of the relative saturation of water in the oils. This linear relationship is identical to that observed for the permittivity of polyimide as a function of the relative humidity of air, supporting the idea that the relative saturation of water in the oils is equal to the relative humidity of the air in contact with the oils. Furthermore, this is consistent with the fact that, over the temperature range examined, the permittivity of the polyimide at a fixed relative saturation is essentially constant.

Chapter 4: Moisture Sensor
4.4.4 Polarization Characteristics of Polyimide

Constitutive relations describe the interdependence of two or more properties of a system. Figure 4.11 shows the relationship between the properties of two systems: the permittivity of the polyimide and the relative saturation of water in the oil in contact with the polyimide. The equilibrium relations derived in Chapter 3 allow us to relate the relative saturation of water in the oil to that in the polyimide. This step provides a description of the constitutive relation for the permittivity of the polyimide in terms of properties of the polyimide-water mixture.

According to Eq. 3.84, the relative saturation of water in the oil is equal to the relative saturation of water in the polyimide. In deriving this relation we assumed that water is present in trace amounts in the oil and the polyimide under all conditions, including saturation. As demonstrated in Fig. 4.7, a plot of the temperature dependence of the solubility of water, this requirement is met by both oils. At the highest temperature of 70°C, the mole fraction of water in transformer oil is 0.005 whereas the mole fraction of water in silicone oil is 0.04. Polyimide has been found to absorb moisture up to 3% of its dry weight [42, 43]. Using a value of 1.42 for the specific gravity of polyimide [43], this solubility corresponds to a value of 0.04 for the volume fraction of water in the polyimide. Thus, because the assumptions are valid, the results shown in Fig. 4.11 can be reinterpreted to describe the dependence of the permittivity on the relative saturation of water in the polyimide-water mixture.

Having characterized the dielectric behavior of polyimide, it is possible to relate the permittivity, a macroscopic property, to the polarizability of the water molecule in the polyimide, a microscopic property. The simplest relation between the dielectric permittivity and the polarizability is obtained by assuming that the field acting locally on the molecular sites is the same as the applied field. This is valid only in dilute phases, such as in gases or in dilute solutions of non-polar material, where the dipoles are distant from one another. The Clausius-Mossotti relation provides a fair approximation for condensed non-polar material or a dilute solution of polar molecules in a non-polar solvent [53, 54]. This relation can be expressed in the form [55: Part II, Section 2]

\[
\frac{\kappa - 1}{\kappa + 2} = \Pi_w + \Pi_d
\]

(4.8)

where \( \kappa = \epsilon / \epsilon_0 \) is the relative dielectric constant of the polyimide-water mixture, and \( \Pi_w \) and \( \Pi_d \) are the normalized polarizability per unit volume of the water and the polyimide molecules respectively. The normalized polarizability per unit volume is defined as
\[ \Pi = \frac{N\alpha}{3\varepsilon_o} \]  

(4.9)

where \( N \) is the number of dipoles per unit volume and \( \alpha \) is the electronic and ionic polarizability of the molecule. In the absence of any water molecules the Clausius-Mossotti relation becomes

\[ \Pi_d = \frac{\kappa_d - 1}{\kappa_d + 2} \]  

(4.10)

where \( \kappa_d \) is the relative dielectric constant of dry polyimide. Using this expression in Eq. 4.8, the normalized polarizability per unit volume of the water molecule can be expressed in terms of the permittivity of the polyimide-water mixture and the permittivity of dry polyimide.

\[ \Pi_w = \frac{\kappa - 1}{\kappa + 2} - \frac{\kappa_d - 1}{\kappa_d + 2} \]  

(4.11)

Solving for the increase in the relative dielectric constant of the polyimide-water mixture due to the water molecules, we obtain the expression

\[ \kappa - \kappa_d = \frac{(\kappa_d + 2)^2 \Pi_w}{3 - (\kappa_d + 2) \Pi_w} \]  

(4.12)

which reflects the Clausius-Mossotti catastrophe for a critical concentration of water molecules [54][55: Part II, Section 23].

\[ \Pi_w = \frac{N_w \alpha_w}{3\varepsilon_o} = \frac{3}{\kappa_d + 2} \]  

(4.13)

According to Fig. 4.11, the increase in the relative dielectric constant of the polyimide-water mixture is proportional to the relative saturation of water in the polyimide.

\[ \kappa - \kappa_d = \beta \phi_w^* \]  

(4.14)

Equating these last two equations leads to a relationship between the normalized polarizability per unit volume of the water molecule and the relative saturation of water in the polyimide.

\[ \Pi_w = \frac{3\beta \phi_w^*}{(\kappa_d + 2)[(\kappa_d + 2) + \beta \phi_w^*]} \]  

(4.15)

This relationship is plotted in Fig. 4.12 using the estimated value of the proportionality constant \( \beta \) and a value of 3.37 for the relative dielectric constant of dry polyimide [42].

Chapter 4: Moisture Sensor
Figure 4.12: Plot of the normalized polarizability per unit volume of the water molecule in polyimide as a function of the relative saturation of water in polyimide. This figure was generated using the estimated value of the proportionality constant $\beta$ and a value of 3.37 for the relative dielectric constant of dry polyimide. To highlight the nonlinearity of the resulting curve, a straight line with a slope equal to the slope of the curve at the origin is drawn in the figure.

To highlight the nonlinearity of the resulting curve, a straight line with a slope equal to the slope of the curve at the origin is drawn in the figure. This curve is consistent with that generated by Denton et al. for the polarizability of the water molecule as a function of the concentration of water absorbed in the polyimide [42].

### 4.5 Sensor Dynamics

Present industry practice in transformer monitoring involves the periodic measurement of the absolute moisture content of the oil. Unless this value is reported with the temperature of the oil, it provides only limited information about the state of the insulation.
For example, while an equilibrium moisture content of 50 ppm at 100°C is an indication of a ‘dry’ transformer, the same moisture content measured at 50°C is an indication of a ‘wet’ transformer. It appears therefore that the measurement of interest is the relative saturation rather than the absolute moisture content of the oil.

Operation of a transformer following a temperature transient can lead to the formation of free water and consequently failure of the insulation. This condition is illustrated in Fig. 4.13, a possible scenario for a transformer during a cooling cycle. The moisture content of the paper is taken to be 1% and the time constant associated with the moisture dynamics is taken to be five times longer than that associated with the temperature of the system. As a result, the temperature of the oil decreases sufficiently fast that during a period of time the solubility of moisture in the oil lies below the absolute moisture content of the oil. In this case the excess water may remain dissolved in the oil under supersaturated conditions or nucleate in the form of water droplets. Monitoring of the absolute moisture content of the oil during the transient would not indicate the incipience of a hazardous condition. The direct measurement of the relative saturation of water in the oil therefore provides dynamic information about the integrity of the insulation in the transformer.

To demonstrate this behavior, experiments were performed using the output of a Leeds & Northrup sensor as a direct measure of the relative saturation of water in oil during cooling transients. The Leeds & Northrup sensor was mounted in a 500 ml Erlenmeyer flask together with a thermocouple probe whose tip was located next to the sensor. The flask was filled with Shell Diala A transformer oil, which was continuously stirred with a magnetic stirrer, and sealed from the environment with a rubber stopper equipped with holes for the Leeds & Northrup sensor probe and the thermocouple. The feedthrough for the thermocouple probe allowed some passage of air into the flask. The Erlenmeyer flask was placed inside a 1500 ml beaker partially filled with water which was heated using a heating tape controlled by a temperature controller and a second thermocouple probe immersed in the water bath. No condensation of water was observed on the rubber stopper during the experiments. An ice-water bath mounted on a second magnetic stirrer provided means to rapidly cool the oil. After the moisture in the oil had reached a steady-state value, the Erlenmeyer flask was removed from the hot water beaker and quickly immersed in the ice-water bath. The magnetic stirrer was then turned on to provide mixing of the oil.

During the experiments, the output voltage of the transmitter and the temperature of the oil were recorded every 12 seconds. The relative saturation of water in the oil was calculated from the output voltage according to the expression
Figure 4.13: Possible scenario for a transformer during a cooling cycle leading to the formation of free water and failure of the insulation. The moisture content of the paper is taken to be 1% and the time constant associated with the moisture dynamics is taken to be five times longer than that associated with the temperature of the system. As a result, the temperature of the oil decreases sufficiently fast that during a period of time the solubility of moisture in the oil lies below the absolute moisture content of the oil. In this case the excess water may remain dissolved in the oil under supersaturated conditions or nucleate in the form of water droplets.

Section 4.5: Sensor Dynamics
\[ \phi_w = 0.25(V - 1.) \] (4.16)

with the voltage measured in Volts. The moisture content of the oil was then computed using Eq. 4.5 in the form

\[ x_w = \frac{\phi_w x^*_w}{1 + \left[ 1 - \frac{M_o}{M_w} \right] (\phi_w - 1) x^*_w} \] (4.17)

where the solubility \( x^*_w \) is given by Eq. 4.3.

Prior to the first experiment, three 4 cm \( \times \) 0.5 cm pieces of 1 mm-thick EHV-Weidmann HI-VAL pressboard, previously oil-impregnated, were attached to the bottom part of the sensor probe in such a way as not to obstruct the flow of oil near the surface of the sensor. The moisture content of the pressboard was measured to be approximately 4.6%. The results of this experiment are shown in Fig. 4.14 where time zero represents the time when the flask was removed from the hot water beaker and placed in the ice-water bath. Prior to the transient, the moisture content of the oil was 60 ppm at a temperature of 66°C. This moisture content corresponds to the equilibrium value associated with the measured moisture content of the pressboard [11]. The relative saturation at this temperature was 0.2 indicating a relatively dry oil.

As soon as the flask was placed in the ice-water bath, the temperature of the oil quickly dropped toward 0°C while the relative saturation rose to a steady-state value of 0.9. The calculated moisture content seems to indicate that water was being removed from the oil at a rate sufficiently fast to prevent the oil from reaching saturation. On the other hand, visual inspection revealed that the oil was cloudy. This condition indicates the presence of free water in the oil. To insure that the pressboard was not having a significant effect on the moisture dynamics, the experiment was repeated without pressboard. The results of this experiment are shown in Fig. 4.15. Even though the initial moisture content was more than twice that of the first experiment and the time constant associated with the thermal transient was 25% smaller, the relative saturation of water in the oil did not reach unity. Cloudiness of the oil was also observed at the end of this experiment.

To support the notion that free water was present in the oil, moisture measurements were made using the Mitsubishi Moisture Meter. The measured values were at least twice the value of the moisture content calculated from the output voltage of the transmitter, indicating that the output of the Leeds & Northrup sensor did not reflect the condition of the oil. From these observations we can conclude that during the temperature transient a
Figure 4.14: Cooling transient during which an oil-filled flask with pressboard is removed from a hot water beaker and placed in an ice-water bath. Prior to the transient, the moisture content of the oil is 60 ppm at a temperature of 66°C. The relative saturation at this temperature is 0.2 indicating a relatively dry oil. As soon as the flask is placed in the ice-water bath, the temperature of the oil quickly drops toward 0°C while the relative saturation rises to a steady-state value of 0.9. The calculated moisture content seems to indicate that water is being removed from the oil at a rate sufficiently fast to prevent the oil from reaching saturation.

Section 4.5: Sensor Dynamics
Figure 4.15: To insure that the pressboard was not having a significant effect on the moisture dynamics, the cooling transient depicted in Fig. 4.14 was repeated without pressboard. Even though the initial moisture content is more than twice that of the first experiment and the time constant associated with the thermal transient is 25% smaller, the relative saturation of water in the oil does not reach unity.
fraction of the water dissolved in the oil came out of solution creating an emulsion of free water droplets in the oil. The remaining water dissolved in the oil was not sufficient to saturate the oil during the temperature transient. Even though free water was present in the oil, the output of the Leeds & Northrup sensor did not saturate because the sensor was responding to the moisture dissolved in the oil adjacent to the sensor. To demonstrate this characteristic, the sensor was immersed in a beaker of oil at room temperature. As the oil was being stirred, water was added with a pipette. Even with large amounts of free water in the oil, the sensor did not record a value corresponding to a relative saturation of unity. Only 12 hours later did the sensor indicate saturated conditions.

These observations have important implications on the interpretation of measured values of the relative saturation of water in oil during cooling cycles in a transformer. Because the Leeds & Northrup sensor responds to moisture dissolved in the oil, its output may indicate near-saturation conditions while free water is present in the oil.

4.6 Summary

A commercially-available sensor, designed to measure the relative humidity of air, was adapted to measure the moisture content of transformer oil. This capacitive sensor relies on the moisture-induced change in the permittivity of polyimide to measure the moisture content of the surrounding fluid.

The transient response of the sensor was characterized by subjecting the sensor to a step change in the moisture content of the surrounding fluid. The response of the sensor showed an initial increase in the output voltage followed by an exponential decay associated with the transfer of moisture out of the sensor. The initial increase was shown to be associated with the sudden change in the dielectric constant of the surrounding fluid. This was verified by immersing the sensor in fluids with different relative dielectric constants. The overvoltage was found to be linear with the dielectric constant of the fluid and independent of the temperature of the system.

The output of the sensor was correlated to the moisture content of two oils with different solubility characteristics: transformer oil and silicone oil. The output voltage was found to be linear with the moisture content of the oils and the slope of the line decreased with increasing temperature. The decrease in the slope of the line implies a reduction in the sensitivity of the sensor to changes in the moisture content of the oils at elevated temperatures. Furthermore, this sensitivity was found to be smaller for silicone oil, which has a higher solubility. Comparison of the calibration curves for
the two oils revealed that, for the same temperature and moisture content, the output voltage generated in transformer oil was greater than that generated in silicone oil. This observation excluded the possibility that the sensor responds to the absolute moisture content of the oil. If it did, the output voltages in the two cases would have been the same.

To compute the relative saturation of water in the oils, an independent measurement of the solubility of water in the two oils was made as a function of temperature. The measured values were found to be in agreement with published values, thereby validating the measurement procedures followed during the experiment. The values of the solubility were then used to estimate Henry's constant for water in the oils. The temperature dependence of Henry's constant was found to fit an Arrhenius form.

Using the measured values of the solubility and the relationship between the capacitance of the sensor and the permittivity of the polyimide, the calibration data for the two oils was expressed in terms of the permittivity of the polyimide as a function of the relative saturation of water in the oils. The fact that the data for all three temperatures and both oils fell on one line demonstrated that the sensor responds to the relative saturation of water in the oils. The linear relationship between the permittivity of the polyimide and the relative saturation of water in the oils was shown to be identical to that observed for the permittivity of polyimide as a function of the relative humidity of air, supporting the idea that the relative saturation of water in the oils is equal to the relative humidity of the air in contact with the oils. Furthermore, these results were shown to be consistent with the fact that, over the temperature range examined, the permittivity of the polyimide at a fixed relative saturation is essentially constant.

With the aim of providing a description of the constitutive relation for the permittivity of the polyimide in terms of properties of the polyimide-water mixture, the equilibrium relations derived in Chapter 3 were used to relate the relative saturation of water in the oils to that in the polyimide. In addition, the permittivity of the polyimide-water mixture was related to the polarizability of the water molecule in the polyimide using the Clausius-Mossotti relation. The resulting expression for the polarizability of the water molecule as a function of the relative saturation of water in the polyimide was found to be consistent with reported values for the polarizability of the water molecule as a function of the concentration of water absorbed in the polyimide.

The response of the sensor to highly saturated oil was examined during cooling transients. These experiments demonstrated that the output of the sensor does not necessarily saturate when free water is present in the oil in the form of an emulsion. This occurs because, under these dynamic conditions, the sensor responds to the moisture
dissolved in the adjacent oil. These results have important implications on the interpretation of measured values of the relative saturation of water in oil during cooling cycles in a transformer.
Chapter 5

Moisture Dynamics
in Paper/Oil Systems

The purpose of this chapter is to develop a model that predicts the spatial and temporal evolution of moisture in a system comprising of transformer pressboard and oil subject to a thermal transient. The model involves the numerical solution of a non-self-adjoint problem which couples the diffusion of moisture in the pressboard to the fluid dynamics in the oil. Representative results show that the concentration of water in the paper assumes a highly nonuniform distribution as the concentration in the oil reaches its equilibrium value. The implications of these results on the estimation of the equilibrium moisture content of the paper from measurements of the moisture content of the oil are examined. Comparison with experimental results yields estimates of the diffusion coefficients of water in oil and oil-impregnated paper.

5.1 Introduction

Under a project sponsored by the Electric Power Research Institute (EPRI), a Couette Facility has been developed to study charge transfer processes at paper/oil interfaces [29, 30, 31]. This facility, illustrated in Fig. 5.1, consists of coaxial metal cylinders covered with pressboard. The annulus formed by the concentric cylinders is filled with oil, whose residence time can be controlled independently from the fluid mechanics in the charge transfer region. Rotation of the inner cylinder controls the Reynolds number in the oil and the thickness of diffusion boundary layers at the inner and outer walls. The outer cylinder is equipped with heating tape and cooling coils, thereby permitting accurate control of the temperature in the system. This facility is thus well suited to study the mass transfer of moisture between oil and paper under conditions of controlled heat transfer.
Figure 5.1: Schematic diagram of the Couette Facility showing the characteristic lengths and moisture contents of the system. This facility consists of coaxial metal cylinders covered with pressboard. The annulus formed by the concentric cylinders is filled with oil, whose residence time can be controlled independently from the fluid mechanics in the mass-transfer region. Rotation of the inner cylinder controls the Reynolds number in the oil and the thickness of diffusion boundary layers at the inner and outer walls. The outer cylinder is equipped with heating tape and cooling coils, thereby permitting accurate control of the temperature in the system.
The coupling between charge and mass transfer processes is of particular relevance to the flow electrification problem in transformers. Moisture contributes to the leakage process because the dielectric properties of pressboard are strongly dependent on the amount of water present in the insulation [6, 7, 8, 9, 10]. As moisture is driven out of the paper by the drier oil the leakage rate decreases and more charge is allowed to accumulate on the surface of the pressboard. This condition can lead to the dielectric failure of the insulation.

Moisture has been implicated in the measurement of flow electrification parameters that describe the generation of charge at the paper/oil interface. Migration of a minute amount of moisture, and perhaps trace impurities as well, is thought to be the cause of observed charge polarity reversals following temperature excursions [29, 30]. These long time scale variations in the charge density have been associated with the moisture in the oil and the pressboard coming to equilibrium [31]. In addition, there appears to be a correlation between absolute moisture levels and measured charge densities in the oil.

These results point to the coupling between the interfacial moisture and the electrochemical nature of the paper/oil interface. The apparent relationship between these phenomena and electrical breakdown in transformers is a compelling reason for examining moisture dynamics in these systems. Thus, the mass-transfer model presented provides the foundation for understanding of the role of moisture dynamics on static electrification through analysis of experimental results from the Couette Facility.

Such a model, combined with the bubble prediction models developed under EPRI programs [32, 33], could also identify safe temperature limits and duration times for dynamic transformer loading beyond nameplate rating. The moisture content of oil-impregnated paper immediately adjacent to the winding hot-spot is the dominant parameter determining the temperature at which drastic reduction in dielectric strength can result from bubble formation. Models used to predict the moisture content in the paper from measurements in the oil rely on the paper being in equilibrium with the oil. Knowledge of the dominant time constant associated with the mass-transfer process can be used to supplement the equilibrium data that has been developed over the years to improve the accuracy of predictions on the state of the insulation.

5.2 Characteristic Lengths and Time Constants

To gain insight into the dominant processes that govern the dynamics of moisture in paper/oil systems it is useful to examine the characteristic lengths and time constants of the system. For high Schmidt-number flows the thickness of the diffusion sublayer is
given by the empirical relation [56, 57]

\[ \delta_d = \frac{11.7 \nu_o}{S^{1/3} v_s} \]  \hspace{1cm} (5.1)

where \( \nu_o \) is the kinematic viscosity of the oil. The Schmidt number \( S \) and the friction velocity \( v_s \) are defined as

\[ S = \frac{\nu_o}{D_o} \]  \hspace{1cm} (5.2)

\[ v_s^2 = \frac{\tau_w}{\rho_o} \]

where \( D_o \) is the diffusion coefficient of water in oil and \( \rho_o \) is the mass density of the oil. The outer-wall shear stress \( \tau_w \) for smooth concentric cylinders is given by the empirical relation [58]

\[ \frac{\tau_w}{\rho_o (\Omega R_2)^2} \approx 0.1 R^{1/2} \quad 300 \leq R_{\nu} \leq 10,000 \]  \hspace{1cm} (5.3)

in terms of the angular velocity of the inner cylinder \( \Omega \), the radius of the outer cylinder \( R_2 \), and the fluid Reynolds number, \( R_{\nu} \),

\[ R_{\nu} = \frac{\Omega R_2 d}{\nu_o} \]  \hspace{1cm} (5.4)

where \( d = R_2 - R_1 \) is the gap spacing between inner and outer cylinders.

For lack of any available data, the diffusion coefficient of water in oil is assumed to be of the same order as that of the positive ions in the oil, whose diffusion coefficient is related to a mobility through Einstein's relation,

\[ D_o = b \frac{kT}{q} \]  \hspace{1cm} (5.5)

where \( k \) is Boltzmann's constant \((1.38066 \times 10^{23} \text{ J/K})\), \( q \) is the charge of the assumed monovalent ions \((1.6022 \times 10^{-19} \text{ C})\), and \( T \) is the temperature of the oil in degrees kelvin. The mobility of ions in highly insulating liquids is given by Walden's rule [59]

\[ b = \frac{\lambda}{\rho_o \nu_o} \]  \hspace{1cm} (5.6)

where \( \lambda \approx 1.5 \times 10^{-11} \text{ C/m} \) for positive ions in viscous liquids [60]. The temperature dependence of the density of the oil is related to the coefficient of thermal expansion \( \beta \) by the expression
\[ \rho_o = \frac{\rho_{oo}}{[1 + \beta(T - T_{oo})]} \]  
(5.7)

where typical values of the parameters for transformer oil are [51]

\[ \rho_{oo} = 0.885 \times 10^3 \text{ kg/m}^3 \]
\[ \beta = 0.75 \times 10^{-3} \text{ K}^{-1} \]
\[ T_{oo} = 288 \text{ K} \]

The temperature dependence of the kinematic viscosity takes the Arrhenius form

\[ \nu_o = \nu_{oo} \exp \left( W_o \left( \frac{1}{T} - \frac{1}{T_{\nu o}} \right) \right) \]  
(5.9)

where typical values of the parameters for transformer oil are [51]

\[ \nu_{oo} = 20.9 \times 10^{-6} \text{ m}^2/\text{s} \]
\[ W_o = 3394 \text{ K} \]
\[ T_{\nu o} = 298 \text{ K} \]

The effective density of oil-impregnated paper is related to the apparent density of paper \( \rho_{pa} \) and the mass ratio of oil absorbed in dry paper [61] \( r_o \) by the relation

\[ \rho_p = \rho_{pa}(1 + r_o) \]  
(5.11)

where typical values of the parameters for transformer pressboard are [62]

\[ \rho_{pa} = 1.00 \times 10^3 \text{ kg/m}^3 \]
\[ r_o = 0.24 \]

The temperature dependence of the diffusion coefficient of water in oil-impregnated paper has been found to have the Arrhenius form

\[ D_p = D_{p0} \exp \left( W_p \left( \frac{1}{T_{p0}} - \frac{1}{T} \right) \right) \]  
(5.13)

where the values of the parameters for a concentration of water in the paper of 0.5% are [63]

\[ D_{p0} = 1.71 \times 10^{-13} \text{ m}^2/\text{s} \]
\[ W_p = 8074 \text{ K} \]
\[ T_{p0} = 298 \text{ K} \]

The thickness of the diffusion sublayer associated with a rotational speed of 400 rpm at 15°C and 70°C is given in Table 5.1 along with the dimensions of the Couette

\textit{Section 5.2: Characteristic Lengths and Time Constants}
Table 5.1: Dimensions of the Couette Facility and thickness of the diffusion sublayer associated with a rotational speed of 400 rpm at 15°C and 70°C.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of Couette Facility</td>
<td>( \ell )</td>
<td>40.6 cm</td>
</tr>
<tr>
<td>Radius of outer cylinder</td>
<td>( R_2 )</td>
<td>10.2 cm</td>
</tr>
<tr>
<td>Radius of inner cylinder</td>
<td>( R_1 )</td>
<td>7.6 cm</td>
</tr>
<tr>
<td>Thickness of pressboard</td>
<td>( \Delta )</td>
<td>1.0 mm</td>
</tr>
<tr>
<td>Thickness of sublayer at 15°C</td>
<td>( \delta_d )</td>
<td>15.7 ( \mu )m</td>
</tr>
<tr>
<td>Thickness of sublayer at 70°C</td>
<td>( \delta_d )</td>
<td>14.4 ( \mu )m</td>
</tr>
</tbody>
</table>

Facility. The fluid Reynolds number is 3,483 at 15°C and 23,046 at 70°C. Values of the molecular diffusion coefficient of water in oil and paper at 15°C and 70°C are given in Table 5.2 together with values of the thermal diffusivity in oil [64] and paper [62]. Using these tabulated values, the characteristic thermal and molecular diffusion times are computed in Table 5.3. The thermal diffusion times in the oil are overestimates because the thickness of the thermal diffusion sublayer is much smaller than the thickness of the molecular diffusion sublayer for values of the Prandtl number \( (Pr = \nu_o/\alpha_o) \) much greater than unity [57, 65, 66]. In fact, the Prandtl number is 419 at 15°C and 98 at 70°C.

Comparison of the thermal and molecular diffusion times indicates that the system reaches thermal equilibrium on a time scale that is short compared with the mass-transfer times. It is reasonable therefore to assume that the system is in quasi-stationary thermal equilibrium during the thermal transient. In addition, comparison of the molecular diffusion time across the diffusion sublayer with the remaining molecular times indicates that this region remains fully developed during the mass-transfer process. Note also that the molecular diffusion time across the paper is orders of magnitude greater than any other characteristic time. We expect therefore that the diffusion of moisture in the

Table 5.2: Thermal and molecular diffusion coefficients of water in oil and paper at 15°C and 70°C.

<table>
<thead>
<tr>
<th>Diffusion coefficient</th>
<th>Symbol</th>
<th>Value @ 15°C</th>
<th>Value @ 70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal diffusivity in oil</td>
<td>( K_o )</td>
<td>( 7.4 \times 10^{-8} ) m²/s</td>
<td>( 4.8 \times 10^{-8} ) m²/s</td>
</tr>
<tr>
<td>Thermal diffusivity in paper</td>
<td>( K_p )</td>
<td>( 1.3 \times 10^{-7} ) m²/s</td>
<td>( 0.8 \times 10^{-7} ) m²/s</td>
</tr>
<tr>
<td>Molecular diffusivity in oil</td>
<td>( D_o )</td>
<td>( 1.4 \times 10^{-11} ) m²/s</td>
<td>( 1.1 \times 10^{-10} ) m²/s</td>
</tr>
<tr>
<td>Molecular diffusivity in paper</td>
<td>( D_p )</td>
<td>( 6.7 \times 10^{-14} ) m²/s</td>
<td>( 6.0 \times 10^{-12} ) m²/s</td>
</tr>
</tbody>
</table>

Chapter 5: Moisture Dynamics
Table 5.3: Characteristic thermal and molecular time constants associated with the diffusion of water in the Couette Facility at 15°C and 70°C.

<table>
<thead>
<tr>
<th>Diffusion time</th>
<th>Definition</th>
<th>Value @ 15°C</th>
<th>Value @ 70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal diffusion across sublayer</td>
<td>( \tau_{T_d} = \delta_d^2/K_o )</td>
<td>3.3 ms</td>
<td>4.3 ms</td>
</tr>
<tr>
<td>Thermal diffusion into the oil</td>
<td>( \tau_{T_o} = d\delta_d/2K_o )</td>
<td>2.8 s</td>
<td>3.9 s</td>
</tr>
<tr>
<td>Thermal diffusion across paper</td>
<td>( \tau_{T_p} = \Delta^2/K_p )</td>
<td>7.7 s</td>
<td>12.5 s</td>
</tr>
<tr>
<td>Molecular diffusion across sublayer</td>
<td>( \tau_d = \delta_d^2/D_o )</td>
<td>18.2 s</td>
<td>1.9 s</td>
</tr>
<tr>
<td>Molecular diffusion into the oil</td>
<td>( \tau_o = d\delta_d/2D_o )</td>
<td>4.1 hr</td>
<td>0.5 hr</td>
</tr>
<tr>
<td>Molecular diffusion across paper</td>
<td>( \tau_p = \Delta^2/D_p )</td>
<td>0.5 yr</td>
<td>2.0 dy</td>
</tr>
</tbody>
</table>

paper will dominate the dynamics of the system.

5.3 Basic Laws

Assuming that moisture does not appreciably contribute to the weight of oil-impregnated paper, which is justified if the mass fraction is less than one percent, the mass transport equation for moisture in oil-impregnated paper can be described by the diffusion equation derived in Appendix B:

\[
\frac{\partial c_p}{\partial t} = D_p \frac{\partial^2 c_p}{\partial x^2}
\]  

(5.15)

where \( c_p \) is the mass fraction of moisture in oil-impregnated paper. As shown in Fig. 5.1, the spatial coordinate is measured from the paper/oil interface into the bulk of the paper. The one-dimensional approximation implied by the diffusion equation is consistent with the fact that the thickness of the pressboard is small compared with the radii of the concentric cylinders. In the presence of thermal gradients across the paper, the diffusion equation would be modified to include the Soret effect as discussed in Appendix C.

The initial and final conditions reflect uniform concentrations of water in the paper.

\[
c_p = c_{pi} \quad t = 0
\]

\[
c_p \rightarrow c_{pf} \quad t \rightarrow \infty
\]  

(5.16)

The boundary adjacent to the cylinder is modeled as impermeable to moisture. Assuming that there is no local accumulation of moisture at the paper/oil interface, the fluxes are continuous across this interface. Furthermore, consistent with the fact that the moisture profile in the diffusion sublayer becomes fully developed on a time scale that is short compared with the dominant time constant for the moisture dynamics,
the concentration of water in the sublayer is taken to vary linearly from an interfacial concentration, \( c_w \), to the concentration of water in the turbulent core, \( c_o \). The use of a linear approximation for the concentration gradient is sometimes referred to as the Nernst layer approximation [67]. The boundary conditions can thus be expressed with the help of Eq. B.3 as

\[
\left. \frac{\partial c_p}{\partial x} \right|_{z=\Delta} = 0
\]

\[
\rho_p D_p \left. \frac{\partial c_p}{\partial x} \right|_{z=0} = \rho_o D_o \frac{c_w - c_o}{\delta_d}
\]

Note that in writing the boundary condition at the paper/oil interface we tacitly assumed that the diffusion-sublayer thickness is the same at the inner and outer walls. This assumption is consistent with the one-dimensional approximation made in the description of the spatial development of moisture in the paper on the inner and outer cylinders.

Prior to the transient, the paper is in equilibrium with the oil and the flux of moisture at the interface is zero. This moisture equilibrium can be represented by a temperature-dependent distribution coefficient [68] \( K(T) \), which is equal to the ratio of the concentration of water in the oil to that in the paper. This linear relationship between the moisture concentrations holds for values of the moisture content of the pressboard less than one percent. This is illustrated in Fig. 5.2, a plot of the equilibrium relationship between the moisture content of transformer oil and paper for temperatures ranging from 20°C to 100°C [11, 34, 35]. The concentration of water in the oil is thus related to the concentration of water in the paper through the initial distribution coefficient \( K_i \).

\[
c_o = c_w = K_i c_{pi} \quad t < 0
\]

Following the temperature transient, regions extending a few molecular mean free paths on either side of the paper/oil interface are assumed to reach steady-state on a time scale that is short compared with any other mass-transfer time constant of the system. Assuming that the interfacial regions remain in a near-equilibrium state throughout the moisture transient, the time-dependent concentrations of water on either side of the paper/oil interface can be related by a final distribution coefficient \( K_f \). Thus, the distribution coefficient is assumed to undergo a step change from its initial value \( K_i \) to its final value \( K_f \). The interfacial concentration \( c_w \) can then be expressed as
Figure 5.2: Equilibrium relationship between the moisture content of transformer oil and paper for temperatures ranging from 20°C to 100°C. For values of the moisture content of the pressboard less than one percent, this moisture equilibrium can be represented by a temperature-dependent distribution coefficient, which is equal to the ratio of the concentration of water in the oil to that in the paper.

\[ c_w(t) = K(t) c_p(x = 0, t) \]
\[ K(t) = K_i + (K_f - K_i)u(t) \]  \hspace{1cm} (5.19)

where \( u(t) \) represents the unit step function described by

\[ u(t) = \begin{cases} 
0, & \text{if } t < 0 \\
1, & \text{if } t \geq 0 
\end{cases} \]  \hspace{1cm} (5.20)

It is this sudden change of conditions at the interface that drives the system out of equilibrium.

For tests in which there is no net flux of moisture out of the system, the concentration of water in the oil can be related to that in the paper by a statement of conservation of

Section 5.3: Basic Laws
Table 5.4: Normalization of variables used to describe the moisture dynamics in the Couette Facility.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Normalization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>( t = \ell \tau_p )</td>
</tr>
<tr>
<td>Length</td>
<td>( x = x \Delta )</td>
</tr>
<tr>
<td>Concentration of water in the paper ( \ldots ) ( c_p = c_p(c_{pf} - c_{pi}) + c_{pi} )</td>
<td></td>
</tr>
<tr>
<td>Concentration of water at the wall ( \ldots ) ( c_w = c_w(K_f c_{pf} - K_i c_{pi}) + K_i c_{pi} )</td>
<td></td>
</tr>
<tr>
<td>Concentration of water in the oil ( \ldots ) ( c_o = c_o(K_f c_{pf} - K_i c_{pi}) + K_i c_{pi} )</td>
<td></td>
</tr>
</tbody>
</table>

Mass in the system,

\[
c_o = K_i c_{pi} - \frac{r_m}{\Delta} \int_0^\Delta (c_p - c_{pi}) \, dx
\tag{5.21}
\]

where \( r_m \) is the ratio of the weight of the oil-impregnated paper on the two cylinders to the weight of the oil in the annulus.

\[
r_m = \left( \frac{\rho_p}{\rho_o} \right) \left[ \frac{2\pi(R_1 + R_2)\Delta \ell}{\pi(R_2^2 - R_1^2)\ell} \right] = \left( \frac{\rho_p}{\rho_o} \right) \left[ \frac{2\Delta}{d} \right]
\tag{5.22}
\]

In the mass conservation equation we neglected the moisture stored in the diffusion sublayer in excess to that due to the concentration of water in the turbulent core. This approximation is valid because the diffusion-sublayer thickness at each wall is much smaller than the corresponding radius. Using the conservation of mass equation, the initial and final concentrations of water in the paper can be related by the following expression.

\[
\frac{c_{pf}}{c_{pi}} = \frac{r_m + K_i}{r_m + K_f}
\tag{5.23}
\]

Note that this problem could also have been formulated in terms of a partial differential equation describing the diffusion of moisture in the paper, Eq. 5.15, coupled to an ordinary differential equation describing the time rate of change of the water in the oil in terms of the flux of moisture through the diffusion sublayers. This alternative formulation is described in Appendix D.

### 5.4 Solution of a Non-Self-Adjoint Problem

With an underscored equation number indicating that all variables have been normalized according to Table 5.4, the diffusion equation becomes
\[
\frac{\partial c_p}{\partial t} = \frac{\partial^2 c_p}{\partial x^2}
\]  \hspace{1cm} (5.24)

subject to the initial and final conditions

\[
c_p = 0 \quad t = 0
\]
\[
c_p \rightarrow 1 \quad t \rightarrow \infty
\]  \hspace{1cm} (5.25)

and the boundary conditions

\[
\frac{\partial c_p}{\partial x} \bigg|_{z=1} = 0
\]  \hspace{1cm} (5.26)
\[
-\tau r \frac{\partial c_p}{\partial x} \bigg|_{z=0} = c_w - c_o
\]

where \(\tau r\) is the ratio of the time constant associated with the diffusion of water into the oil \(\tau_o\) to the time constant associated with the diffusion of water across the paper \(\tau_p\).

The concentration of water at the wall is related to the concentration of water in the paper by an equilibrium relation.

\[
c_w = \left[1 - \frac{K_f}{\tau_m} \left(c_p|_{z=0} - 1\right)\right] u(t)
\]  \hspace{1cm} (5.27)

Conservation of mass relates the moisture content of the oil to that of the paper.

\[
c_o = \int_0^1 c_p \, dx
\]  \hspace{1cm} (5.28)

If we substitute the last two expressions in the boundary condition at the paper/oil interface, Eq. 5.26b, we obtain a nonclassical [69] lateral condition [70].

\[
\int_0^1 c_p \, dx + \frac{K_f}{\tau_m} c_p|_{z=0} - \tau r \frac{\partial c_p}{\partial x} \bigg|_{z=0} = 1 + \frac{K_f}{\tau_m}
\]  \hspace{1cm} (5.29)

The diffusion equation can be solved using the method of separation of variables. The solution is written as an eigenfunction expansion satisfying the equilibrium solution and the boundary condition at \(z = 1\),

\[
c_p(x, t) = 1 - \sum_{n=1}^{\infty} B_n \cos \gamma_n(1 - x)e^{-t/\tau_n}
\]  \hspace{1cm} (5.30)

where \(\tau_n\) is the time constant associated with the eigenvalue \(\gamma_n\).

\[
\gamma_n^2 = \frac{1}{\tau_n}
\]  \hspace{1cm} (5.31)

Section 5.4: Solution of a Non-Self-Adjoint Problem
Figure 5.3: Graphical representation of the normalized transcendental equation describing the eigenvalues associated with the moisture dynamics in the paper and the oil. Lines (a) and (b) represent the left and right side of Eq. 5.32 respectively. The values of the parameters used in this figure are: $r_m = 0.12$, $r_r = 9.5 \times 10^{-3}$, and $K_f = 1.0 \times 10^{-3}$.

The lateral condition, Eq. 5.29, gives rise to the transcendental equation

$$
\frac{r_m}{K_f} \left[ r_r \gamma_n^2 - 1 \right] = \gamma_n \cot \gamma_n \tag{5.32}
$$

shown graphically in Fig. 5.3 for typical values of the parameters of the system.

To satisfy the initial condition we require

$$
1 = \sum_{n=1}^{\infty} B_n \cos \gamma_n (1 - x) \tag{5.33}
$$

If we multiply both sides of the equation by $\cos \gamma_m (1 - x)$ and integrate over the thickness of the paper using the variable substitution $u = 1 - x$ we obtain
\[
\int_0^1 \cos \gamma_m u \, du = \sum_{n=1}^{\infty} B_n \int_0^1 \cos \gamma_n u \cos \gamma_m u \, du \quad (5.34)
\]

If the eigenfunctions were orthogonal to each other the integral on the right-hand side would be equal to zero for all \( m \neq n \), and the coefficients \( B_n \) would be determined analytically. In this non-self-adjoint problem [69] the eigenfunctions are not orthogonal (see Appendix E) and we resort to a numerical technique [71]. If we write the above equation for \( m = 1, \ldots, N \) and take only \( N \) terms in the summation we obtain a system of equations that can be solved for the vector \( B \).

\[
AB = C \quad (5.35)
\]

where the matrix \( A \) is symmetric and its elements are given, together with those of the vector \( C \), by the expressions

\[
A_{ij} = \int_0^1 \cos \gamma_i u \cos \gamma_j u \, du = \frac{1}{2} \left[ \frac{\sin(\gamma_i - \gamma_j)}{\gamma_i - \gamma_j} + \frac{\sin(\gamma_i + \gamma_j)}{\gamma_i + \gamma_j} \right]
\]

\[
A_{ii} = \int_0^1 \cos^2 \gamma_i u \, du = \frac{1}{2} \left[ 1 + \frac{\sin 2\gamma_i}{2\gamma_i} \right] \quad (5.36)
\]

\[
C_i = \int_0^1 \cos \gamma_i u \, du = \frac{\sin \gamma_i}{\gamma_i}
\]

Eigenfunction expansions do not converge for times short compared with the dominant time constant. Otherwise, convergence is assured with at most 10 terms. To insure accuracy we require that the value of these coefficients not change if we take one more term in the eigenvalue expansion. In practice 100 terms are sufficient for convergence of the coefficients as illustrated in Fig. 5.4 for typical values of the parameters of the system. This figure was generated using the program bn.f or listed in Appendix M. Finally, even if the infinite set of eigenfunctions is not complete [72: Section 9.4], the set obtained has been observed to represent the initial conditions of interest.

Once the system of equations has been solved for the coefficients \( B_n \), the concentrations can be obtained by summing all terms.

---

Section 5.4: Solution of a Non-Self-Adjoint Problem
Figure 5.4: Values of the first four normalized eigenfunction coefficients as a function of the number of terms in the infinite sum. This plot indicates that 50 terms are sufficient for convergence of the values of the first four eigenfunction coefficients. The values of the parameters used in this figure are: $r_m = 0.12, r_r = 9.5 \times 10^{-3}$, and $K_f = 1.0 \times 10^{-3}$.

\[ c_p(x,t) = 1 - \sum_{n=1}^{N} B_n \cos \gamma_n (1 - x) e^{-t/\tau_n} \]
\[ c_w(t) = \left[ 1 + \left( \frac{K_f}{r_m} \right) \sum_{n=1}^{N} B_n \cos \gamma_n e^{-t/\tau_n} \right] u(t) \]
\[ c_o(t) = 1 - \sum_{n=1}^{N} B_n \frac{\sin \gamma_n}{\gamma_n} e^{-t/\tau_n} \]

These normalized concentrations are plotted in Fig. 5.5 using the same values of the parameters as in Fig. 5.3. Specifically, the conditions are such that the system is heated from $15^\circ C$ to $70^\circ C$. As a result, the concentration of water in the oil rises from 1.0 ppm ($c_o = 0$) to 5.0 ppm ($c_o = 1$). The initial moisture content of the paper is $0.5\%$ ($c_p = 0$).
Because the increase in the total moisture in the oil is a small fraction of the total moisture in the paper, the moisture content of the paper only changes by 0.7% of its initial value. This figure was generated using the program cpo.f or listed in Appendix M.

The figure reveals that the concentration of water in the oil reaches an apparent equilibrium on a time scale that is one order of magnitude smaller than that of the paper. In addition, the concentration of water in the paper at this apparent equilibrium time is highly nonuniform. This occurs because the diffusion process in the paper is much slower than that across the diffusion sublayer thickness. In essence, the paper releases moisture from a thin subregion in order to satisfy the new condition at the paper/oil interface. Diffusion then slowly distributes the moisture in the paper as equilibrium is established.

This effect is even more dramatic at lower temperatures. This is illustrated in Fig. 5.6 where the system is returned to its original conditions at 15°C. In this case, when the concentration of water in the oil appears to have reached its final value, the concentration of water in the paper is still far from its equilibrium distribution. This figure was also generated using the program cpo.f or listed in Appendix M.

Note that, even though Figs. 5.5 and 5.6 appear to be identical, the time scales for the concentration of water in the oil differ by one order of magnitude. Because of the disparity in the values of the time constant associated with the diffusion of water across the paper at the two temperatures, a normalized time of 0.1 in Fig. 5.5 corresponds to a time of 5 hours whereas a normalized time of 0.01 in Fig. 5.6 corresponds to a time of 40 hours.

5.5 Solution for Short Times

The results of the previous section suggest that the critical moisture dynamics occur in a short period of time following the temperature transient. To ease the evaluation and improve the accuracy of the solution during this period we develop analytical expressions valid for times that are short compared with the diffusion time across the paper. This assumption is implemented by taking the limit in which the thickness of the paper goes to infinity.

The partial differential equation describing the diffusion of moisture in the paper can be transformed into an ordinary differential equation using the unilateral Laplace transform [73: Part 2, Lesson 13]. Thus, denoting the transformed variables by uppercase letters, the diffusion equation becomes

Section 5.5: Solution for Short Times
Figure 5.5: Normalized spatial distribution of the concentration of water in the paper as a function of time and temporal evolution of the concentrations of water in the oil for a temperature increase in the Couette Facility. The conditions are such that the system is heated from 15°C to 70°C. As a result, the concentration of water in the oil rises from 1.0 ppm ($c_o = 0$) to 5.0 ppm ($c_o = 1$). The initial moisture content of the paper is 0.5% ($c_p = 0$). Because the increase in the total moisture in the oil is a small fraction of the total moisture in the paper, the moisture content of the paper only changes by 0.7% of its initial value.
Figure 5.6: Normalized spatial distribution of the concentration of water in the paper as a function of time and temporal evolution of the concentrations of water in the oil for a temperature decrease in the Couette Facility. The system is returned to its original conditions at 15°C. In this case, when the concentration of water in the oil appears to have reached its final value, the concentration of water in the paper is still far from its final equilibrium distribution.

Section 5.5: Solution for Short Times
\[
\frac{d^2 C_p}{dx^2} = sC_p
\]  
(5.38)

subject to the boundary conditions

\[
\left. \frac{dC_p}{dx} \right|_{x \to \infty} = 0
\]  
(5.39)

\[
-\left. r_r \frac{dC_p}{dx} \right|_{x=0} = C_w - C_o
\]

The equilibrium relation describing the concentration of water at the wall transforms to

\[
C_w = \left[ 1 + \frac{K_f}{r_m} \right] \left( \frac{1}{s} - \frac{K_f}{r_m} C_p \right)_{x=0}
\]  
(5.40)

while the statement of conservation of mass remains

\[
C_o = \int_0^\infty C_p \, dx
\]  
(5.41)

The solution to this ordinary differential equation can be expressed in the form

\[
C_p(x, s) = \frac{1}{r_r} \left[ 1 + \frac{K_f}{r_m} \right] \left[ \frac{e^{-\sqrt{s}x}}{\sqrt{s}(\sqrt{s} + \eta_+)(\sqrt{s} + \eta_-)} \right]
\]

\[
C_w(s) = \left[ 1 + \frac{K_f}{r_m} \right] \left[ \frac{1}{s} - \left( \frac{K_f}{r_m r_r} \right) \frac{1}{\sqrt{s}(\sqrt{s} + \eta_+)(\sqrt{s} + \eta_-)} \right]
\]  
(5.42)

\[
C_o(s) = \frac{1}{r_r} \left[ 1 + \frac{K_f}{r_m} \right] \left[ \frac{1}{s(\sqrt{s} + \eta_+)(\sqrt{s} + \eta_-)} \right]
\]

where

\[
\eta_\pm = \frac{K_f}{2r_m r_r} \pm \sqrt{\left( \frac{K_f}{2r_m r_r} \right)^2 - \frac{1}{r_r}}
\]  
(5.43)

Using a partial fraction expansion of each expression, the inverse Laplace transform of the concentrations can be shown to depend on the nature of the parameters \( \eta_\pm \) [74][75: Section 29.3]. Thus, the solution is given for three cases:
Case I: \(\eta\)'s are real and distinct.

\[
c_p(x, t) = -\left[1 + \frac{K_f}{r_m}\right] \left[\frac{\eta_+\eta_-}{\eta_+ - \eta_-}\right].
\]

\[
\left\{e^{\eta_+(x + \eta t)} \text{erfc} \left[\frac{x}{2\sqrt{t}} + \eta_+\sqrt{t}\right] - e^{\eta_-(x + \eta t)} \text{erfc} \left[\frac{x}{2\sqrt{t}} + \eta_-\sqrt{t}\right]\right\} u(t)
\]

\[
c_w(t) = \left[1 + \frac{K_f}{r_m}\right].
\]

\[
\left\{1 + \frac{K_f}{r_m} \left[\frac{\eta_+\eta_-}{\eta_+ - \eta_-}\right]\right\} \left\{e^{\eta_+ t} \text{erfc} \left[\eta_+\sqrt{t}\right] - e^{\eta_- t} \text{erfc} \left[\eta_-\sqrt{t}\right]\right\} u(t)
\]

\[
c_o(t) = \left[1 + \frac{K_f}{r_m}\right].
\]

\[
\left\{1 + \left[\frac{\eta_+\eta_-}{\eta_+ - \eta_-}\right]\right\} \left\{\frac{e^{\eta_+ t}}{\eta_+} \text{erfc} \left[\eta_+\sqrt{t}\right] - \frac{e^{\eta_- t}}{\eta_-} \text{erfc} \left[\eta_-\sqrt{t}\right]\right\}
\]

Case II: \(\eta\)'s are real and equal.

\[
c_p(x, t) = \frac{1}{r_r} \left[1 + \frac{K_f}{r_m}\right] \left\{2\frac{\sqrt{t}}{\sqrt{\pi}} e^{-x^2/4t} - (x + 2\eta t)e^{\eta(x + \eta t)} \text{erfc} \left[\frac{x}{2\sqrt{t}} + \eta\sqrt{t}\right]\right\}
\]

\[
c_w(t) = \left[1 + \frac{K_f}{r_m}\right] \left\{1 - \left(\frac{2}{r_r}\right) \left(\frac{K_f}{r_m}\right) \frac{\sqrt{t}}{\sqrt{\pi}} - \eta t e^{\eta t} \text{erfc} \left[\eta\sqrt{t}\right]\right\} u(t)
\]

\[
c_o(t) = \left[1 + \frac{K_f}{r_m}\right] \left\{1 - 2\eta \frac{\sqrt{t}}{\sqrt{\pi}} - (1 - 2\eta^2 t)e^{\eta t} \text{erfc} \left[\eta\sqrt{t}\right]\right\}
\]

Case III: \(\eta\)'s are complex conjugates.

\[
c_p(x, t) = -\frac{2}{r_r} \left[1 + \frac{K_f}{r_m}\right] \Re \left\{\frac{e^{\eta_+(x + \eta t)}}{\eta_+ - \eta_-} \text{erfc} \left[\frac{x}{2\sqrt{t}} + \eta_+\sqrt{t}\right]\right\}
\]

\[
c_w(t) = \left[1 + \frac{K_f}{r_m}\right] \left\{1 + \left(\frac{2}{r_r}\right) \left(\frac{K_f}{r_m}\right) \Re \left\{\frac{e^{\eta_+ t}}{\eta_+ - \eta_-} \text{erfc} \left[\eta_+\sqrt{t}\right]\right\}\right\} u(t)
\]

\[
c_o(t) = \left[1 + \frac{K_f}{r_m}\right] \left\{1 + \left(\frac{2}{r_r}\right) \Re \left\{\frac{e^{\eta_+ t}}{\eta_+(\eta_+ - \eta_-)} \text{erfc} \left[\eta_+\sqrt{t}\right]\right\}\right\}
\]

Section 5.5: Solution for Short Times
This last set of equations was expressed using the identity [75: Section 7.1]

\[ \text{erfc}(\xi) = \overline{\text{erfc}(z)} \] (5.47)

Using system parameters identical to those used for Fig. 5.6 these expressions are plotted in Fig. 5.7. This figure was generated using the program ci.for listed in Appendix M. In this case the \( \eta \)'s are complex conjugates. Comparison of the resulting curves to those in Fig. 5.6 yields an error less than 1\% for the temporal evolutions of the concentrations of water in the oil and the spatial distributions in the paper for times less than 0.02 of the diffusion time across the paper.

5.6 Apparent Equilibrium Time

As noted earlier, the concentration of water in the oil reaches an apparent equilibrium on a time scale that is at least one order of magnitude smaller than that of the paper. To quantify this effect, the apparent equilibrium time, \( t_* \), is arbitrarily chosen to be the time when the concentration of water in the oil has reached 5\% of its final value. This can be expressed in terms of the final concentrations of water in the paper and the distribution coefficients as

\[ \frac{c_o(t_*) - K_f c_{pf}}{K_i c_{pi} - K_f c_{pf}} = 0.05 \] (5.48)

or in normalized terms as

\[ 1 - c_o(t_*) = 0.05 \] (5.49)

To understand the effect of the parameters of the system on this characteristic time and extend the results to similar paper/oil systems, a mapping of the normalized apparent equilibrium time was made as a function of the ratio of the weight of oil-impregnated paper to the weight of the oil, \( r_m \), and the ratio of the time constant associated with the diffusion of water into the oil to the time constant associated with the diffusion of water across the paper, \( r_\tau \). Two mappings are shown in Fig. 5.8 for values of the final distribution coefficient corresponding to the heating \( (K_f = 1.0 \times 10^{-3}) \) and cooling \( (K_f = 2.0 \times 10^{-4}) \) transients depicted in Figs. 5.5 and 5.6. These mappings were generated using the programs tstar.for and isot.for listed in Appendix M. The stars identify the assumed parameters for the Couette Facility.

In these mappings we can identify two limiting regimes for the apparent equilibrium time. The regimes are best understood by expressing the product of the ratios in terms
Figure 5.7: Normalized spatial distribution of the concentration of water in the paper as a function of time and temporal evolution of the concentrations of water in the oil for a temperature decrease in the Couette Facility with special emphasis on short times. The conditions are identical to those for Fig. 5.6. Comparison of the resulting curves yields an error less than 1% for the temporal evolutions of the concentrations of water in the oil and the spatial distributions in the paper for times less than 0.02 of the diffusion time across the paper.

Section 5.6: Apparent Equilibrium Time
Figure 5.8: Lines of constant normalized apparent equilibrium time, $t_e/\tau_p$, as a function of the ratio of the weight of oil-impregnated paper to the weight of the oil, $r_m$, and the ratio of the time constant associated with the diffusion of water into the oil to the time constant associated with the diffusion of water across the paper, $r_r$. The values of the final distribution coefficient correspond to the heating ($K_f = 1.0 \times 10^{-3}$) and cooling ($K_f = 2.0 \times 10^{-4}$) transients depicted in Figs. 5.5 and 5.6. The stars identify the assumed parameters for the Couette Facility.
of the ratio of the diffusion velocity of water in the paper $D_p/\Delta$ to the diffusion velocity of water across the diffusion sublayer $D_o/\delta_d$.

$$r_m r_r = \left( \frac{\rho_p}{\rho_o} \right) \left[ \frac{D_p/\Delta}{D_o/\delta_d} \right]$$

(5.50)

For the case in which the product of the ratios is much less than unity, this relation requires that the diffusion velocity of water in the paper be much smaller than that across the diffusion sublayer. This implies that the diffusion of water in the paper is the rate limiting factor in reaching equilibrium. This observation is supported by the fact that, in this regime, the normalized apparent equilibrium time is essentially independent of the ratio of the time constants. Thus, the apparent equilibrium time depends only on the diffusion time across the paper and the ratio of the weights. As such, the apparent equilibrium time is equal to a heterogeneous time involving both the thickness of the paper and the gap spacing between the inner and outer cylinders, much the same way that the diffusion time into the oil involves the product of two different length scales: the diffusion sublayer thickness and the gap spacing. This region of the parameter space is characterized by systems in which the paper represents a small fraction of the total weight and the diffusion time across the paper is much smaller than that into the oil.

For the case in which the product of the ratios is greater than unity, Eq. 5.50 implies that the diffusion of water across the diffusion sublayer is the rate limiting factor in reaching equilibrium. This is supported by the fact that, in this regime, the value of the normalized apparent equilibrium time is essentially independent of the ratio of the weights and it approaches the ratio of the time constants as the ratio of the weights increases. Thus, in this limit the apparent equilibrium time is equal to the diffusion time into the oil. This region of the parameter space is characterized by systems in which the paper represents a significant fraction of the total weight and the diffusion time across the paper is comparable with the diffusion time into the oil.

During the transient the oil is not in equilibrium with the paper. Even when it appears to have reached equilibrium, the oil is not in equilibrium with the bulk of the paper. Instead, it is in equilibrium with a subregion at the interface. As a result, estimates of the average moisture content of the paper from apparent equilibrium measurements of the moisture content of the oil would clearly be in error. The estimate of the moisture content of the paper is determined by the concentration of water in the oil at the apparent equilibrium time and the final distribution coefficient $K_f$. The deviation of this estimate from the true equilibrium value defines the error.

Section 5.6: Apparent Equilibrium Time

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Error = \frac{c_o(t_*)/K_f - c_p}{c_p} \quad (5.51)

Using the definition of the apparent equilibrium time, Eq. 5.48, and the relationship between the final and initial concentrations of water in the paper, Eq. 5.23, the error can be expressed in terms of the distribution coefficients and the ratio of the weights.

\[
\text{Error} = 0.05 \left[ \frac{K_i/K_f - 1}{K_i/r_m + 1} \right] \quad (5.52)
\]

The value of this error for the heating and cooling transients in the Couette facility is -4% and 20% respectively. These values indicate the error associated with the estimate of the moisture content of the paper from apparent equilibrium measurements of the moisture content in the oil. Estimates made from earlier measurements yield larger errors.

5.7 Comparison with Experimental Results

Heating and cooling transient experiments were performed on the Couette Facility. The moisture content of the oil was monitored continuously using a Leeds & Northrup sensor. While pressboard covered the inner cylinder, the outer cylinder was left bare. The rotational speed of the inner cylinder was 400 rpm. Shell Diala A transformer oil and 1 mm thick EHV-Weidmann HI-VAL pressboard were used in these experiments.

The results of these experiments are shown in Figs. 5.9 and 5.11. The time constant associated with the thermal transients is limited by the heating and cooling power available and is not a reflection of the thermal diffusion times across the system. During the heating experiment the moisture content of the oil follows the temperature. This indicates that the time constant associated with the moisture dynamics is short compared with the time constant associated with the thermal transient. Thus, the oil remains in quasi-stationary equilibrium during the thermal transient.

During the cooling experiment, on the other hand, the moisture content of the oil lags the temperature after the first hour. Assuming that the thermal transient can be modeled as a step, the data following the first hour was used to estimate the time constants associated with the diffusion of water into the oil and across the paper at 15°C. The estimation was performed using the program est.for listed in Appendix M.

The estimated values of these time constants were found to differ from those calculated in Table 5.3. The time constant associated with the diffusion of water across the paper was estimated to be 3.9 times smaller. This implies that the diffusion coef-
cient of water in the paper is 3.9 times larger than that given in Table 5.2, namely $2.6 \times 10^{-13}$ m$^2$/s. Considering the large uncertainty in the reported values and possible variations associated with differences in the density of the paper, this discrepancy is within bounds.

The time constant associated with the diffusion of water into the oil was estimated to be 12.5 times smaller than the value given in Table 5.3. This latter value was corrected by the factor $1 + R_1/R_2$ to account for the fact that paper is present only on the inner cylinder and that the diffusion sublayer at the inner cylinder is smaller than the one at the outer cylinder by the factor $R_1/R_2$ [30]. It is difficult to ascertain what proportion of the difference in the values of the time constant is attributable to uncertainty in the shear stress at the wall versus uncertainty in the diffusion coefficient of water in the oil. To see this, it is useful to express the time constant associated with the diffusion of water into the oil with the help of Eqs. 5.1 and 5.2.

$$
\tau_o = \frac{d\delta_d}{2D_o}
$$

$$
= 11.7 \left( \frac{d}{v_*} \right) S^{2/3}
$$

$$
= 11.7d \left( \frac{\nu_o}{D_o} \right)^{2/3} \left( \frac{\tau_w}{\rho_o} \right)^{1/2}
$$

(5.53)

From this expression it can be seen that a higher value of the shear stress, resulting perhaps from the increased surface roughness of the pressboard, will result in a smaller value of the time constant. Furthermore, the diffusion coefficient of water in oil is expected to be larger than that given in Table 5.2 because the fluctuations in the turbulent core penetrate the diffusion sublayer [57]. This effect will also result in a smaller value of the time constant associated with the diffusion of water into the oil.

To account for the factor of 12.5 in the estimated value of the time constant, either the diffusion coefficient would have to be 44 times larger than that given in Table 5.2 or the shear stress would have to be 156 times larger than that calculated from Eq. 5.3. If the uncertainty in the stress stress were insignificant, the discrepancy would yield a value of $6.0 \times 10^{-10}$ m$^2$/s for the diffusion coefficient of water in oil. This estimate is consistent with values of the diffusion coefficient of positively charged ions in transformer oil estimated from flow electrification measurements in the Couette Facility [30].

Using the estimated values of the time constants, the concentration of water in the oil was calculated and plotted in Fig. 5.11 along with the experimental data. The theoretical curve agrees well with the experimental data for times longer than those
during which the moisture content of the oil followed the temperature. Assuming that the ratio of the estimated and the calculated values remains invariant with temperature, the concentration of water in the oil was calculated for the heating transient experiment and plotted in Fig. 5.9 along with the experimental data. The theoretical curve supports the notion that the time constant associated with the moisture dynamics is short compared with the time constant associated with the thermal transient. The theoretical curves in Figs. 5.9 and 5.11 were generated using the programs cpx.for and cix.for respectively. These programs are listed in Appendix M.

To gain insight into the moisture dynamics in the paper, the concentrations of water in the oil and the paper are plotted in Figs. 5.10 and 5.12 for both experiments. Whereas the moisture content of the paper reaches its final distribution quickly after the heating transient, the distribution of moisture in the paper remains highly nonuniform long after the cooling transient.

5.8 Summary

A mass-transfer model was developed to describe the spatial and temporal evolution of moisture in the Couette Facility. The model couples the diffusion of moisture in the paper to the transport of moisture in the oil at high Reynolds numbers. The system is assumed to be driven out of equilibrium by a thermal transient whose time constant is short compared with the characteristic mass-transfer times. The model involved the numerical solution of a non-self-adjoint problem. For times short compared with the time constant associated with the diffusion of water across the paper, Laplace transform techniques were used to obtain analytical expressions for the concentrations of water in the system.

Representative results revealed that, as the concentration in the oil reaches its equilibrium value, the concentration of water in the paper remains highly nonuniform. For typical values of the parameters of the system, the time scale over which the concentration of water in the oil reaches the apparent equilibrium was found to be at least one order of magnitude smaller than the time scale over which the system reaches equilibrium. As a result, the estimation of the equilibrium moisture content of the paper from measurements of the moisture content of the oil at this apparent equilibrium time was found to be in error, particularly at the lower temperatures where the disparity between the time constants is greater.

Measurements of the moisture content of the oil during cooling transients were used to obtain estimates of the diffusion coefficient of water in oil and oil-impregnated paper.
Figure 5.9: Temporal evolution of the temperature and the moisture content of the oil during a heating experiment in the Couette Facility. The time constant associated with the thermal transient is limited by the heating power available and is not a reflection of the thermal diffusion times across the system. The fact that the moisture content of the oil follows the temperature indicates that the time constant associated with the moisture dynamics is short compared with the time constant associated with the thermal transient. This is supported by the temporal evolution of the concentration of water in the oil calculated assuming a step change in the temperature.
Figure 5.10: Spatial distribution of the concentration of water in the paper as a function of time and temporal evolution of the concentrations of water in the oil for the heating experiment in the Couette Facility. The conditions are such that the system is heated from 15°C to 69°C. As a result, the concentration of water in the oil increases from 1.1 ppm to 5.1 ppm. The moisture content of the paper, initially at 0.540%, reaches its final value of 0.532% quickly after the heating transient.
Figure 5.11: Temporal evolution of the temperature and the moisture content of the oil during a cooling experiment in the Couette Facility. The time constant associated with the thermal transient is limited by the cooling power available and is not a reflection of the thermal diffusion times across the system. The theoretical curve, calculated assuming a step change in the temperature, agrees well with the experimental data for times longer than those during which the moisture content of the oil followed the temperature.

Section 5.8: Summary
Figure 5.12: Spatial distribution of the concentration of water in the paper as a function of time and temporal evolution of the concentrations of water in the oil for the cooling experiment in the Couette Facility. The conditions are such that the system is cooled from 69°C to 15°C. As a result, the concentration of water in the oil decreases from 5.6 ppm to 1.2 ppm. The moisture content of the paper, initially at 0.59%, remains highly nonuniform long after the cooling transient.
Estimates could not be obtained during heating transients due to the fact that the time constant associated with the moisture dynamics in the oil was short compared with the time constant associated with the thermal transient. The estimated values were found to be in reasonable agreement with values available in the literature for the diffusion coefficient of water in paper and the diffusion coefficient of positively charged ions in transformer oil.
Chapter 6
Flexible Interdigital-Electrode Structures

The purpose of this chapter is to describe the development of flexible sensors to measure the dielectric properties of materials used in transformer insulation. Because the dielectric properties of transformer paper are strongly dependent on the moisture content, these sensors can be used to monitor the moisture content of the paper. Equilibrium measurements are demonstrated using a flexible sensor with a single spatial wavelength. Dynamic measurements using a sensor with three spatial wavelengths lead to estimates of the diffusion coefficient of water in pressboard.

6.1 Introduction

Interdigital dielectrometry is used to measure the dielectric properties of a material by imposing a spatial wavelength $\lambda = 2\pi/k$ by means of an array of interdigitated electrodes driven with a temporal frequency $f = \omega/2\pi$. This technique, illustrated in Fig. 6.1, represents the 'imposed $\omega$-$k$' approach to dielectrometry [76].

Because signals are attenuated to a degree dependent upon the imposed wavelength, the spatial frequency response of multiple-wavelength interdigital-electrode structures permits the derivation of a composite dielectric profile in the direction normal to the plane of the electrodes [77]. The deduction of inhomogeneities in the material properties is sometimes attempted from the temporal frequency response information alone, but this process cannot be implemented without assuming that the frequency dispersion of the material is known, as illustrated in Appendix F.

In contrast with remote sensing, where electromagnetic fields are used to resolve the properties of materials at distances large compared with the wavelength of the electromagnetic wave, the quasistatic fields associated with interdigital dielectrometry tend to
Figure 6.1: Schematic illustration of the imposed $\omega$-$k$ approach to dielectrometry. Using this approach the temporal frequency, $f = \omega/2\pi$, can be controlled independently from the spatial wavelength, $\lambda = 2\pi/k$, which is determined by the periodicity of the electrode structure. While one electrode is driven with a variable-frequency AC voltage, a high-impedance measurement of the induced voltage on the other electrode is made. Whereas the frequency of excitation determines the coupling regime of the sensor and the dispersive nature of the electrical properties, the spatial wavelength determines the penetration depth of the electric field. As such, the interdigitated electrode structure is most sensitive to the properties of the medium out to about one-third of the wavelength. This feature can be exploited to measure the heterogeneous properties of the medium by using multiple wavelengths. (Adapted from Reference [76].)
be confined to the immediate neighborhood of the interdigital-electrode structure. As a result, it is advantageous to minimize the distance between the electrode structure and the material under test. For nonplanar surfaces, such intimate sensing can be achieved with flexible electrode structures.

Mass-transfer processes that affect the electrical properties of a material can be studied using interdigital dielectrometry. The electrical properties of transformer paper are known to depend on the amount of moisture present in the insulation [6, 7, 8, 9, 10]. It is therefore possible to follow the absorption of moisture by measuring the dielectric properties of the paper using multiple-wavelength interdigital-electrode structures. Note that, because the dielectric loss of paper increases with the moisture content, the desorption of water out of the insulation cannot be monitored as the region adjacent to the electrodes in effect shorts out the more insulating regions above.

6.2 A Single-Wavelength Sensor

6.2.1 Description of the Sensor

A single-wavelength flexible sensor was designed and manufactured to measure the dielectric properties of insulating materials used in transformer insulation structures. The layout of this flex sensor is shown in Fig. 6.2. The 2 in × 2 in electrode structure is composed of a set of interdigitated electrodes with a spatial wavelength of 1 mm. As a result, the penetration depth of the electric field is approximately 300 μm. The number of spatial wavelengths in the electrode structure is 50.

The electrode structure is surrounded by the driven electrode to shield the sensing electrode from external sources. The sensing electrode is brought out to the terminals through two traces at the center of the strip. On either side of these leads there are two shield electrodes driven at the potential of the sensing electrode. These leads minimize the coupling of the sensing electrode to the remaining traces on the strip. Adjacent to the shield electrodes is a pair of electrodes at signal ground. These electrodes are connected to a ground plane below the electrode structure through openings in the substrate. The two leads on the outer edge of the terminal strip are connected to the driven electrode. In summary, the following is a description of the leads of the sensor from left to right in Fig. 6.2:

1. Driven electrode

2. Ground electrode
Figure 6.2: Layout of the flex sensor. The 2 in × 2 in electrode structure is composed of a set of interdigitated electrodes with a spatial wavelength of 1 mm. As a result, the penetration depth of the electric field is approximately 300 μm. The number of spatial wavelengths in the electrode structure is 50. The driven electrode is excited with a 1 V peak AC signal in the frequency range of 5 mHz to 10 kHz. The measured signal at the sensing electrode is a function of the dielectric properties of the substrate and the material above the electrode structure.
3. Shield electrode
4. Sensing electrode
5. Sensing electrode
6. Shield electrode
7. Ground electrode
8. Driven electrode

The terminal strip plugs into an interface box that is connected to a controller. The interface box provides the capacitive load for the sensing electrode and the signal for the shield electrodes through a high-impedance unity-gain buffer. The controller provides the excitation signal, a 1 V peak AC signal in the frequency range of 5 mHz to 10 kHz, measures the buffered sensing signal, and computes the corresponding gain and phase. The controller is linked to a computer which allows the user to initiate a measurement in the form of a frequency scan or a time scan. The frequency scan involves a single measurement at each frequency over a specified frequency range in intervals of 0.1 on a logarithmic frequency scale; the time scan involves multiple measurements at a single frequency over a period of time. Below 1 Hz, only three periods are allowed for sinusoidal steady-state. The measurement is performed during the last period. Before each measurement the sensing electrode is shorted to ground through a 1 MΩ resistor by means of a high-impedance relay in the interface box. This eliminates any DC offset that has accumulated as a result of the leakage current into the high-impedance amplifier.

6.2.2 Manufacturing and Cleaning of the Sensor

The manufacturing of the flex sensor involves several steps that require specific protocols to insure that the fabricated sensor will be operational. The term ‘operational’ in this context means that the electrical properties of the material used in the manufacturing process are sufficiently insulating that the frequency response of the sensor in air does not show any phase shift. Conduction in the sensor will result in a nonzero phase shift in the measured signal. The background response in air insures that the dielectric properties of highly insulating materials such as transformer oil can be measured without any ambiguity.

The first step in the manufacture of the sensor is the definition of the electrode structure. This was accomplished by selectively etching copper from a copper/Kapton
composite. Kapton, a commercially-available polyimide film developed by Du Pont, was selected as a suitable substrate material because of its relatively low dielectric constant and highly insulating characteristics [43, 78, 79]. The raw material consists of an adhesiveless clad of 0.7 mil thick (1/2 oz.) copper on one side of a 2 mil thick Kapton film [80]. The Kapton film was selected so that its thickness would be minimized while allowing the load capacitance to remain much larger than the input capacitance of the high-impedance amplifier and achieve a high-frequency gain of \(-40\) dB. The minimization of the permittivity and the thickness of the substrate provides increased sensitivity to the dielectric properties of the medium above the electrodes [81]. The etching of the copper was performed using standard photolithographic techniques used in the manufacturing of flexible printed circuits [82]. Two holes were etched in the Kapton to provide contacts for a ground plane.

To prevent the formation of an oxide, the electrodes were gold-plated using an electrodeposition process involving a nickel flash coating and a gold plating. The resulting thickness of the gold cladding was typically 2 \(\mu\)m. Techniques involving antioxidants were not used to prevent contamination of the system with surface active agents. One such chemical, 1,2,3-benzotriazole (BTA), has been used to reduce flow electrification in large power transformers [83].

The second step in the manufacturing process is the deposition of the ground plane on the underside of the sensor. To accomplish this the sensor was mounted in a physical mask with the ground plane area and the contact points to the leads exposed. This surface was cleaned with acetone and methanol to remove any surface contaminants. The mask, capable of processing five sensors at once, was then mounted in an electron-beam vapor deposition chamber where 1 \(\mu\)m of copper was deposited on the back plane of the electrodes. This copper layer forms the ground plane for the sensor. Upon removal from the mask, the top surface of the sensor was cleaned with acetone and methanol to remove any gross contaminants from the sensing area. From this point onward in the manufacturing process, the sensor was handled in such a way as to avoid any contact with the upper plane of the sensor.

The third and final step in the manufacturing process is the deposition of a hydrophobic polymer film that covers the entire sensor [84]. This final step is necessary to protect the ground plane and prevent moisture from being absorbed by the substrate. The dielectric constant of polyimide increases by up to 30% as it absorbs water [42, 43]. The polymer used was Parylene C, a commercially-available polymer developed by Union Carbide. The vapor deposition of this polymer, illustrated in Fig. 6.3, is performed at room temperature under a partial vacuum and provides a pinhole-free conformal coating
Figure 6.3: Schematic illustration of the Parylene deposition process indicating approximate operating conditions. The vapor deposition of this polymer is performed at room temperature under a partial vacuum and provides a pinhole-free conformal coating that has a very low permeability to moisture and is highly insulating. The deposition rate is typically 0.2 μm/min, thereby permitting accurate control of the thickness of the Parylene layer. (From Reference [86].)

that has a very low permeability to moisture and is highly insulating [85]. The deposition rate is typically 0.2 μm/min, thereby permitting accurate control of the thickness of the Parylene layer.

Prior to the Parylene coating process, the sensor was exposed to an oxygen plasma at 300 W for two minutes. This etching process converts the polyimide to a volatile phase by chemical reaction with ions, electrons, and free radicals produced in the gas discharge [87]. Contaminants present at the surface are removed in the process.

The etching rate of the plasma was characterized by exposing one side of a 25 μm thick film of polyimide to the same conditions for 10 minutes. The polyimide layer was spin-coated onto a silicon wafer. The thickness of the etched polyimide film was then measured using a Sloan Dektak II profilometer. A typical output of the profilometer is

Section 6.2: A Single-Wavelength Sensor

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Figure 6.4: Characteristic output of the Sloan Dektak II profilometer used to measure the thickness of a polyimide layer after exposure to an oxygen plasma for 10 minutes. This figure shows the vertical height versus the horizontal displacement of the stylus as it traverses a groove scored in the polyimide. The average thickness of the polyimide is 23 µm, yielding an etching rate of 0.2 µm/min. Prior to the plasma etch, the thickness of the polyimide film was 25 µm.

shown in Fig. 6.4, which shows the vertical height versus the horizontal displacement of the stylus as it traverses a groove scored in the polyimide. The average thickness was calculated to be 23 µm, yielding an etching rate of 0.2 µm/min. Thus, less than 1% of the 50 µm thick substrate is removed when the sensor is exposed to the oxygen plasma.

As part of the characterization, the surface of the etched polyimide was analyzed using X-ray photoelectron spectroscopy (XPS). A characteristic output is shown in Fig. 6.5, where the number of emitted electrons is plotted as a function of their binding energy. This spectrum indicates that the surface of the polyimide does not contain metal atoms which can be emitted as a result of energetic collisions of the plasma with the walls of the chamber.

Following the plasma treatment, the sensor was transferred to the Parylene deposition
Figure 6.5: Analysis of the etched polyimide surface using X-ray photoelectron spectroscopy (XPS). In this figure the number of emitted electrons is plotted as a function of their binding energy. The spectrum indicates that the surface of the polyimide does not contain metal atoms which can be emitted as a result of energetic collisions of the plasma with the walls of the chamber.

chamber where it was subjected to vacuum at room temperature for more than 12 hours. The overnight process removes moisture and other volatile substances from the bulk of the Kapton substrate. Without exposure to ambient conditions, the sensor was then coated with Parylene. The nominal coating thickness was 5 μm. Typically, five sensors were coated at the same time. Along with the flex sensors, a microchip sensor was included in the Parylene deposition chamber. This commercially-available sensor [88] does not require any cleaning and is used to measure the thickness of the Parylene layer after the deposition. Because the spatial wavelength of the microchip sensor is 50 μm, it is well suited for measuring thicknesses of thin films in the micron range.

By measuring the high-frequency gain of three sensors in air before and after the Parylene coating, the average thickness of the Parylene layer was calculated to be 5.5 μm[50: Section 4.2.1][89]. The estimates of the Parylene layer thickness were performed using the values of the gain at 10 kHz and a value of 3.05 ε₀ for the permittivity of Parylene. Using a Sloan Dektak II profilometer, the thickness of the Parylene coating on a wit-

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<td>Disc: 8018-1</td>
</tr>
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<td>Spot: 600 u</td>
<td># of Scans: 1</td>
</tr>
<tr>
<td>Flood Gun: 6.0 eV</td>
<td>Resolution: 4</td>
</tr>
<tr>
<td>Description: OFF-SITE PLASMA ETCHED PI SAMPLE</td>
<td>Operator: UV</td>
</tr>
</tbody>
</table>

\[
\text{Counts vs. Binding Energy (eV)}
\]

Section 6.2: A Single-Wavelength Sensor
ness strip was independently measured to be 5.7 μm. The frequency response of one microchip sensor with and without the Parylene coating is shown in Fig. 6.6, where the measured gain and phase are plotted as a function of the logarithm of the frequency. The slight negative slope in the gain of the Parylene-coated sensor reflects some dispersion in the dielectric properties of the Parylene layer. In addition, because no appreciable phase shift was measured over the entire frequency range, the conductivity of the Parylene can be estimated to be less than 0.02 μS/m. This value was computed based on a phase shift of less than one degree at 5 mHz.

The frequency response of two Parylene-coated flex sensors is shown in Fig. 6.7. Whereas one of the sensors was exposed to the oxygen plasma, the other one was cleaned only with a chemical rinse. Occasionally, the chemical rinse would be sufficient to clean the surface of the sensor. This figure indicates that the chemical rinse is not a reliable method to clean the surface of the sensor and that the plasma etch is necessary to insure a successful manufacturing process. The frequency response of the sensor cleaned only with the chemical rinse is associated with a surface conduction on the plane of the electrodes. The fact that no appreciable phase shift was measured over the entire frequency range of the sensor cleaned with the oxygen plasma indicates that the conductivity of the Kapton substrate is less than 0.03 pS/m. This value was computed based on a phase shift of less than one degree at 5 mHz.

6.2.3 Unmodeled Parasitic Structures

Using the values of the parameters for the flex sensor given in Table 6.1, the calculated high-frequency gain in air differs from the measured value by 4 dB. This discrepancy cannot be accounted for by uncertainties in the parameters describing the sensor. As shown in Table 6.2, significant deviations from the nominal or measured values of the parameters are necessary to account for this difference. As a result, it appears that the continuum model [76] used to calculate the response of the sensor does not appropriately take into account certain structures of the sensor. In particular, the model neglects end effects associated with the electrodes and assumes that the electrodes are infinitely thin.

To understand the effect of the finite thickness of the electrodes, it is useful to examine the physical structure of the sensor near the plane of the electrodes. This structure is illustrated schematically in Fig. 6.8. Because the electrodes are not thin compared with the thickness of the Parylene layer, the planarity assumed in the continuum model is inaccurate. In particular, there is an additional coupling between the driven and the sensing electrodes due to the finite thickness of the electrodes. This coupling can be represented by the lumped-parameter model shown in Fig. 6.9.
Figure 6.6: Frequency response of a microchip sensor in air with and without the Parylene coating. In this figure the measured gain and phase are plotted as a function of the logarithm of the temporal frequency. The frequency response reflects some dispersion in the dielectric properties of the Parylene layer. In addition, because no appreciable phase shift was measured over the entire frequency range, the conductivity of the Parylene can be estimated to be less than 0.02 pS/m. This value was computed based on a phase shift of less than one degree at 5 mHz. By measuring the high-frequency gain of three sensors in air before and after the Parylene coating, the average thickness of the Parylene layer was calculated to be 5.5 μm.

Section 6.2: A Single-Wavelength Sensor
Figure 6.7: Frequency response of two Parylene-coated flex sensors. Whereas one of the sensors was exposed to the oxygen plasma, the other one was cleaned only with a chemical rinse. This figure indicates that the chemical rinse is not a reliable method to clean the surface of the sensor and that the plasma etch is necessary to insure a successful manufacturing process. The fact that no appreciable phase shift was measured over the entire frequency range of the sensor cleaned with the oxygen plasma indicates that the conductivity of the Kapton substrate is less than 0.03 pS/m. This value was computed based on a phase shift of less than one degree at 5 mHz.
Figure 6.8: Schematic diagram of the structure of the flex sensor near the plane of the electrodes. Because the electrodes are not thin compared with the thickness of the Parylene layer, the planarity assumed in the continuum model is inaccurate. In particular, there is an additional coupling between the driven and the sensing electrodes due to the finite thickness of the electrodes.

Figure 6.9: Lumped-parameter model describing the additional coupling between the driven and the sensing electrodes due to the finite thickness of the electrodes. At high frequencies, the coupling is dominated by the capacitance of the fluid $C_f$ and the capacitance of the Parylene along the Kapton surface $C_{px}$.

Section 6.2: A Single-Wavelength Sensor
Table 6.1: Values of parameters describing the flex sensor.

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<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
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<tr>
<td>Spatial wavelength</td>
<td>$\lambda$</td>
<td>1.02 mm</td>
</tr>
<tr>
<td>Interelectrode spacing</td>
<td>$a$</td>
<td>0.24 $\lambda$</td>
</tr>
<tr>
<td>Electrode meander length</td>
<td>$M_{el}$</td>
<td>2.6 m</td>
</tr>
<tr>
<td>Thickness of polyimide layer</td>
<td>$h$</td>
<td>50.8 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of polyimide</td>
<td>$\epsilon_{Pi}$</td>
<td>3.0 $\epsilon_0$</td>
</tr>
<tr>
<td>Thickness of parylene layer</td>
<td>$d_{pX}$</td>
<td>5.5 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of parylene</td>
<td>$\epsilon_{pX}$</td>
<td>3.05 $\epsilon_0$</td>
</tr>
<tr>
<td>Load capacitance</td>
<td>$C_l$</td>
<td>857 pF</td>
</tr>
</tbody>
</table>

At high frequencies, the admittance of this network can be expressed as

$$Y_p = \frac{j\omega (C_l + C_{pX})}{1 + \frac{\omega^2 (C_l + C_{pX})}{C_w}}$$  \hspace{1cm} (6.1)

where the capacitances can be approximated using the expression for a parallel-plate structure.

Table 6.2: Sensitivity of the high-frequency gain in air to the parameters describing the flex sensor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Function</th>
<th>Value</th>
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</thead>
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<td>$[\partial G/\partial \lambda]_{a/\lambda}$</td>
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<tr>
<td>Interelectrode spacing</td>
<td>$[\partial G/\partial (a/\lambda)]_{\lambda}$</td>
<td>$-60$ dB</td>
</tr>
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<td>Electrode meander length</td>
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<td>$+2$ dB/m</td>
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<tr>
<td>Thickness of polyimide layer</td>
<td>$[\partial G/\partial h]$</td>
<td>$+0.2$ dB/\mu m</td>
</tr>
<tr>
<td>Permittivity of polyimide</td>
<td>$[\partial G/\partial (\epsilon_{Pi}/\epsilon_0)]$</td>
<td>$-1$ dB</td>
</tr>
<tr>
<td>Thickness of parylene layer</td>
<td>$[\partial G/\partial d_{pX}]$</td>
<td>$+0.1$ dB/\mu m</td>
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<tr>
<td>Permittivity of parylene</td>
<td>$[\partial G/\partial (\epsilon_{pX}/\epsilon_0)]$</td>
<td>$+0.2$ dB</td>
</tr>
<tr>
<td>Load capacitance</td>
<td>$[\partial G/\partial C_l]$</td>
<td>$-6$ dB/nF</td>
</tr>
</tbody>
</table>
\[
C_w = 2 \frac{\varepsilon_{px} d_{el} M_{el}}{d_{px}} \\
C_f = 2 \frac{\varepsilon_f (d_{el} - d_{px}) M_{el}}{a - 2 d_{px}} \\
C_{px} = 2 \frac{\varepsilon_{px} d_{px} M_{el}}{a - 2 d_{px}}
\]

(6.2)

The factor of two arises from the fact that the coupling occurs on either side of each electrode. Using the values of the parameters describing the sensor we find that

\[
\frac{C_f + C_{px}}{C_w} \ll 1
\]

(6.3)

so that Eq. 6.1 reduces to

\[
Y_p \approx j \omega (C_f + C_{px})
\]

(6.4)

At frequencies for which the dielectric relaxation time is comparable with the period of excitation \((\omega \tau_e \sim 1)\), conduction phenomena in the fluid become significant and the admittance of the network becomes

\[
Y_p \approx j \omega (C_f + C_{px}) + \frac{1}{R_f}
\]

(6.5)

where the resistance \(R_f\) and capacitance \(C_f\) are related by the dielectric relaxation time in the fluid.

\[
R_f C_f = \frac{\varepsilon_f}{\sigma_f}
\]

(6.6)

The parasitic admittance associated with the finite thickness of the electrodes can be incorporated into the pi network representation of the sensor shown in Fig. 6.10. The complex gain is then expressed as

\[
\hat{G} = \frac{\hat{V}_G}{\hat{V}_D} = \frac{Y_{12} + Y_p}{Y_{11} + Y_{12} + Y_p + Y_f}
\]

(6.7)

To understand the nature of the coupling associated with this structure, the high-frequency gain of the flex sensor was measured in three fluids of known dielectric constant: air \((1.0\varepsilon_0)\), Exxon Univolt 60 transformer oil \((2.2\varepsilon_0)\), and Dow Corning 561 silicone transformer oil \((2.7\varepsilon_0)\). Using the measured values of the gain, together with the calculated values of the capacitances \(C_{11}\) and \(C_{12}\) given in Table 6.3, the parasitic capacitance was calculated by means of Eq. 6.7. Figure 6.11 shows the results of this calculation.

Section 6.2: A Single-Wavelength Sensor
Figure 6.10: Pi network representation of the flex sensor. The parasitic admittance $Y_p$ represents the unmodeled coupling between the driven and the sensing electrodes due to the finite thickness of the electrodes.

as well as the parasitic capacitance calculated using Eq. 6.4. A least-squares fit of the data to a straight line yielded a slope of $5.4 \pm 0.1 \text{ pF}$ and an intercept of $6.2 \pm 0.1 \text{ pF}$. The values of the parameters and their uncertainty were calculated using the program leastsq.f for listed in Appendix M and assuming equal uncertainty in the measurement of the capacitance and virtually no uncertainty in the measurement of the relative dielectric constant [49: Chapter 8]. The correlation coefficient for the fit was calculated to be 0.99975 with a probability of $P_5(|r| \geq 0.99975)$ of 1.4% indicating a significant correlation.

The fact that the parasitic capacitance is linear with the permittivity of the fluid supports the notion that the unmodeled structure is associated with the finite thickness of the electrodes. The discrepancy between the two lines in the figure is a result of the fact that the parasitic capacitance cannot be simply modeled by a parallel-plate structure. These semi-empirical results were incorporated in the parameter estimation of the dielectric properties of materials from measurements performed with interdigital-electrode structures such as the flex sensor. The estimation was performed using a version of the
Table 6.3: Calculated values of the sensor capacitances as a function of the relative dielectric constant of the surrounding fluid.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\epsilon_f/\epsilon_0$</th>
<th>$C_{11}$ (pF)</th>
<th>$C_{12}$ (pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.0</td>
<td>451.2</td>
<td>10.4</td>
</tr>
<tr>
<td>Transformer oil</td>
<td>2.2</td>
<td>474.6</td>
<td>25.3</td>
</tr>
<tr>
<td>Silicone oil</td>
<td>2.7</td>
<td>482.7</td>
<td>32.1</td>
</tr>
</tbody>
</table>

Figure 6.11: Plot of the parasitic capacitance in the flex sensor as a function of the relative dielectric constant of the fluid surrounding the sensor. Using the measured values of the high-frequency gain, together with the calculated values of the capacitances $C_{11}$ and $C_{12}$ given in Table 6.3, the parasitic capacitance was calculated by means of Eq. 6.7. A least-squares fit of the data to a straight line yields a slope of $5.4 \pm 0.1$ pF and an intercept of $6.2 \pm 0.1$ pF. The solid line below this curve represents the parasitic capacitance calculated using Eq. 6.4. The discrepancy between the two lines is a result of the fact that the coupling associated with the finite width of the electrodes cannot be simply modeled by a parallel-plate structure.

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program parest for [50: Appendix F] modified to incorporate the parasitic admittance in the calculation of the complex gain of the sensor.

6.2.4 Dielectric Properties of Transformer Insulation

Transformer Oil

The insulating nature of the materials used in the manufacturing of the flex sensor provides the opportunity to measure the dielectric properties of highly insulating liquids, such as transformer oil. The frequency response of the sensor in Exxon Univolt 60 transformer oil at room temperature is shown in Fig. 6.12. At high frequencies, the sensor operates in a purely capacitive regime and, as a result, the measured signal is in phase with the driven signal. In this regime, the gain is determined by the dielectric constant of the oil, the properties of the substrate, and the load capacitance. As the frequency approaches the point where the relaxation time of the oil is comparable with the period of excitation ($\omega \tau_e \sim 1$), the phase decreases toward $-90^\circ$ and the gain increases toward 0 dB.

Using the values of the parasitic admittance and the parameters describing the sensor, the dielectric properties of the oil were estimated at each measurement frequency. The results of this estimation are shown in Fig. 6.13. In this plot, the normalized real and imaginary parts of the complex permittivity

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

(6.8)

are plotted as a function of the logarithm of the frequency. While the dielectric constant of the oil was estimated throughout the entire frequency range, lack of sufficient phase information prevented the reliable estimation of the loss factor above 1 Hz.

The solid line drawn in the plot of the dielectric constant represents the estimated high-frequency value of $2.19\varepsilon_0$. As shown in Sect. 7.6, the deviation from this value at low frequencies is associated with space-charge polarization resulting in a double layer at the Parylene/oil interface. The solid line drawn in the plot of the loss factor represents a least-squares fit of the data to a straight line. The correlation coefficient for this fit was calculated to be 0.99997 with a probability $P_{20}(|r| \geq 0.99997)$ less than 0.05% indicating a highly significant correlation. The slope of the line was calculated to be $-0.975 \pm 0.002$ indicating that the oil exhibits nearly ohmic behavior. An ohmic medium would yield a slope of $-1$. From the intercept of the line the conductivity of the oil was calculated to be $0.937 \pm 0.005$ pS/m. Using this value of the conductivity and the high-frequency value of the dielectric constant, the gain and phase were calculated and plotted along
Figure 6.12: Frequency response of the flex sensor in Exxon Univolt 60 transformer oil at room temperature. At high frequencies, the sensor operates in a purely capacitive regime and, as a result, the measured signal is in phase with the driven signal. In this regime, the gain is determined by the dielectric constant of the oil, the properties of the substrate, and the load capacitance. As the frequency approaches the point where the relaxation time of the oil is comparable with the period of excitation ($\omega \tau_e \sim 1$), the phase decreases toward $-90^\circ$ and the gain increases toward 0 dB. The solid line drawn represents the predicted response of an ohmic medium. The deviation of the line from the data is a reflection of how accurately an ohmic model fits the experimental results.
Figure 6.13: Frequency dependence of the dielectric properties of Exxon Univolt 60 transformer oil at room temperature. The solid line drawn in the plot of the dielectric constant represents the estimated high-frequency value of $2.19\epsilon_0$. The solid line drawn in the plot of the loss factor represents a least-squares fit of the data to a straight line. The slope of the line was calculated to be $-0.975 \pm 0.002$ indicating that the oil exhibits nearly ohmic behavior. An ohmic medium would yield a slope of $-1$. From the intercept of the line the conductivity of the oil was calculated to be $0.937 \pm 0.005$ pS/m.
with the data in Fig. 6.12 in the form of a solid line. The deviation of the line from the data is a reflection of how accurately an ohmic model fits the experimental results.

The values of the parameters and the uncertainties associated with the loss factor were calculated using the program leastsq.for listed in Appendix M with the help of Eq. A.18a. The uncertainty in the measurement of the frequency was assumed to be insignificant compared with the uncertainty in the measurement of the dielectric loss. Furthermore, because the estimation was performed using the logarithm of the normalized dielectric loss, we assumed equal fractional uncertainty rather than equal absolute uncertainty in the measurement of the dielectric loss. This assumption is valid considering the wide range of values measured.

**Transformer Paper**

To investigate the dependence of the dielectric properties of transformer paper on the moisture content, the flex sensor was used to measure dielectric properties of a 5 mil thick piece of Crocker Kraft paper at room temperature before, during, and after evacuation. The paper was not oil-impregnated. To insure intimate contact with the sensor, the paper was wrapped over the sensor against a plastic bobbin. The edges of the paper were glued to two metal strips which were held together by means of three springs. The leads of the sensor were extended to the interface box through the rubber seals on the door and the outside wall of a vacuum chamber.

Over the course of the experiment, three measurements of the electrical properties were made. The first measurement was made with the bobbin in the vacuum chamber at atmospheric pressure. In this state, the paper was in equilibrium with the ambient air at 50% relative humidity. As a result, the moisture content of the paper was approximately 7% [14]. The second measurement was made with the paper under vacuum. The moisture content of the paper in this state was estimated to be less than 0.5% based on prior experience with vacuum impregnation. The last measurement was made soon after the sensor was removed from the vacuum chamber.

The results of these measurements are shown in Fig. 6.14. From this figure it can be seen that the frequency response maintains a characteristic shape as the moisture content in the paper changes. The response shifts down in frequency as the moisture in the paper decreases. Except for the measurement of dry paper, the low-frequency gain levels off to a nonzero value. This occurs because the paper is not in intimate contact with the electrode surface of the sensor due to the presence of the Parylene layer and any additional air gap between the Parylene and the paper. At such frequencies the paper becomes a 'perfect conductor' so that the phase between the driven and the sensing

*Section 6.2: A Single-Wavelength Sensor*
signal is zero.

Using the low-frequency gain of the first two measurements, the thickness of the air layer between the Parylene and the paper was calculated to be $3.0 \pm 0.3$ $\mu$m, which is comparable to the surface roughness of the paper. The uncertainty reflects the variation of the thickness between the two measurements. Using this information, the dielectric properties of the paper were estimated at each frequency for all three measurements. The results of these estimations are shown in Fig. 6.15 where the real and the imaginary parts of the complex permittivity are plotted as a function of the logarithm of the frequency. Because the value of the dielectric constant is frequency-dependent and the slope of the loss factor is not $-1$, this figure implies that the paper is not ohmic and exhibits dispersion in the frequency domain.

Over the frequency range examined, the dielectric constant of the paper increases by one order of magnitude while the loss factor increases by three orders of magnitude. These two quantities are related by the Kramers-Krönig relations [90, 91], a Hilbert transform pair [72: Section 7.3] of the form

$$
\varepsilon'(\omega) = \varepsilon_{\infty} + \frac{2}{\pi} P \int_0^\infty \frac{\omega \varepsilon''(\alpha)}{\alpha^2 - \omega^2} d\alpha
$$

$$
\varepsilon''(\omega) = \frac{\sigma}{\omega} - \frac{2}{\pi} P \int_0^\infty \frac{\omega \varepsilon'(\alpha)}{\alpha^2 - \omega^2} d\alpha
$$

(6.9)

where $\varepsilon_{\infty}$ is the high-frequency dielectric constant, $\sigma$ is the ohmic conductivity, and $P$ denotes the Cauchy principal value, which is simply the result of the integration over all frequencies except $\omega$. These relations are a direct consequence of the principle of causality. In the limit of zero frequency the first relation requires that the difference between the static and the high-frequency dielectric constant be proportional to the integral of the loss factor over the entire frequency domain.

$$
\varepsilon'(0) - \varepsilon_{\infty} = \frac{2}{\pi} \int_0^\infty \varepsilon''(\alpha) d(\ln \alpha)
$$

(6.10)

Because the dielectric constant reaches a plateau at low frequencies, this equation requires that the dispersive component of the dielectric loss reach a peak and decrease toward zero with decreasing frequency. This transition was not observed experimentally. As a result, the consistency of the data in Fig. 6.15 cannot be verified using the Kramers-Krönig relations.

Nonetheless, Fig. 6.15 shows the effect of water on the dielectric properties of the paper. A change of one order of magnitude in the moisture content results in a frequency shift of seven orders of magnitude in the complex permittivity or an increase of four
Figure 6.14: Frequency response of the flex sensor to Crocker Kraft transformer paper at room temperature before, during, and after evacuation. From this figure it can be seen that the frequency response maintains a characteristic shape as the moisture content in the paper changes. The response shifts down in frequency as the moisture in the paper decreases. Except for the measurement of dry paper, the low-frequency gain levels off to a nonzero value. This occurs because the paper is not in intimate contact with the electrode surface of the sensor due to the presence of the Parylene layer and any additional air gap between the Parylene and the paper. At such frequencies the paper becomes a ‘perfect conductor’ so that the phase goes to zero.
Dielectric Properties of Crocker Kraft Paper

Figure 6.15: Frequency dependence of the dielectric properties of Crocker Kraft transformer paper at room temperature before, during, and after evacuation. A change of one order of magnitude in the moisture content results in a frequency shift of seven orders of magnitude in the complex permittivity or an increase of four orders of magnitude in the loss factor at a given frequency. Thus, the dielectric properties provide a sensitive method to monitor the moisture content of paper.
orders of magnitude in the loss factor at a given frequency. Thus, the dielectric properties provide a sensitive method to monitor the moisture content of paper.

6.3 A Three-Wavelength Sensor

6.3.1 Description of the Sensor

A three-wavelength flexible sensor was designed and manufactured to measure the heterogeneous properties of materials whose thickness is on the order of one millimeter. The layout of the three-wavelength sensor is shown in Fig. 6.16. The 2 in × 2 in electrode structure is composed of three sets of interdigitated electrodes with spatial wavelengths of 1 mm, 2.5 mm, and 5 mm. The number of spatial wavelengths in each section is 10.

Whereas the driven electrode is shared, the sensing electrodes for the three wavelengths are isolated from each other by a pair of shield electrodes and a pair of ground electrodes. Each pair of shield electrodes is driven at the potential of the corresponding sensing electrode. Two of the four ground electrodes lead to triangular pads which are connected to a ground plane below the electrode structure through openings in the substrate. The following is a description of the leads of the sensor from left to right in Fig. 6.16:

1. Driven electrode
2. Ground electrode
3. Shield electrode for 1 mm wavelength
4. Sensing electrode for 1 mm wavelength
5. Shield electrode for 1 mm wavelength
6. Ground electrode
7. Shield electrode for 5 mm wavelength
8. Sensing electrode for 5 mm wavelength
9. Shield electrode for 5 mm wavelength
10. Ground electrode
11. Shield electrode for 2.5 mm wavelength

Section 6.3: A Three-Wavelength Sensor
Figure 6.16: Layout of the three-wavelength sensor. The 2 in. × 2 in electrode structure is composed of three sets of interdigitated electrodes with spatial wavelengths of 1 mm, 2.5 mm, and 5 mm. The number of spatial wavelengths in each section is 10. The measured signal at each sensing electrode is related to the dielectric properties of the substrate and the material above the electrode structure up to a depth proportional to the wavelength. Thus it is possible to monitor mass-transfer processes that affect the dielectric properties of materials.
Table 6.4: Values of parameters describing the three-wavelength sensor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spatial wavelength</td>
<td>$\lambda$</td>
<td>1.0 mm 2.5 mm 5.0 mm</td>
</tr>
<tr>
<td>Interelectrode spacing</td>
<td>$a$</td>
<td>0.24 $\lambda$ 0.24 $\lambda$ 0.24 $\lambda$</td>
</tr>
<tr>
<td>Electrode meander length</td>
<td>$M_{el}$</td>
<td>0.15 m 0.15 m 0.30 m</td>
</tr>
<tr>
<td>Thickness of polyimide layer</td>
<td>$h$</td>
<td>127 $\mu$m 127 $\mu$m 127 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of polyimide</td>
<td>$\epsilon_{PI}$</td>
<td>3.0 $\epsilon_0$ 3.0 $\epsilon_0$ 3.0 $\epsilon_0$</td>
</tr>
<tr>
<td>Thickness of parylene layer</td>
<td>$d_{PX}$</td>
<td>5.0 $\mu$m 5.0 $\mu$m 5.0 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of parylene</td>
<td>$\epsilon_{PX}$</td>
<td>3.05 $\epsilon_0$ 3.05 $\epsilon_0$ 3.05 $\epsilon_0$</td>
</tr>
<tr>
<td>Load capacitance</td>
<td>$C_l$</td>
<td>226 pF 38 pF 6 pF</td>
</tr>
</tbody>
</table>

12. Sensing electrode for 2.5 mm wavelength

13. Shield electrode for 2.5 mm wavelength

14. Ground electrode

15. Driven electrode

The terminal strip plugs into an interface box with three high-impedance amplifiers, one for each sensing electrode. Each amplifier is equipped with a load capacitor and a high-impedance relay, much like in the interface box used for the flex sensor. The protocols used for the manufacturing of this sensor were similar to those followed for the flex sensor [92]. Only chemicals were used in cleaning the surface of the sensor. The values of the parameters describing the three wavelengths on the sensor are given in Table 6.4.

6.3.2 Moisture Tracking in Transformer Pressboard

To monitor the moisture content of pressboard in the Couette Facility, the three-wavelength sensor was mounted in a side port of the facility that provided access to the pressboard on the outer cylinder. The 1 mm-thick pressboard was EHV-Weidmann HI-VAL transformer pressboard and was not oil-impregnated for these tests. The sensor was glued onto a 1 in-thick piece of Neoprene sponge allowing the flexible sensor to conform to the pressboard surface. The sponge was in turn glued to a piece of Lexan machined such that its front side had a curvature equal to that of the outer cylinder. The piece of Lexan was mounted on the shaft of a linear-motion vacuum feedthrough.
The leads of the sensor were brought out of the side port through a separate Lexan feedthrough.

With the assembly in place, the sensor was brought against the surface of the pressboard by means of a number adjustments of the linear-motion feedthrough. Because the dielectric constant of pressboard is higher than the permittivity of free space, the point of intimate contact could be determined by monitoring the high-frequency gain of the three wavelengths on the sensor. This process is illustrated in Fig. 6.17, where the gain at 10 kHz is plotted as a function of the number of adjustments. Note that the gain of the smallest wavelength does not level off as rapidly as the gain of the two larger wavelengths. This is due to the fact that the smallest wavelength is more sensitive to any air gap between the sensor and the pressboard surface.

With the sensor in contact with the pressboard, a measurement of the dielectric properties of the pressboard was taken with all three wavelengths. The frequency response is shown in Fig. 6.18. During the measurement, the pressboard was in equilibrium with the ambient air. As a result, the moisture content of the pressboard was approximately 4%. The fact that the phase peak for all three wavelengths occurs at the same frequency indicates that the moisture in the pressboard was uniformly distributed. The positive phase at frequencies below 10 mHz is probably a result of the influence of the triangular ground pads on the coupling between the driven and the sensing electrodes.

Using the low-frequency gain, the thickness of the air gap between the Parylene and the pressboard surface was estimated for each wavelength. The resulting thickness was calculated to be $15.0 \pm 0.3 \, \mu m$, which is comparable to the surface roughness of the pressboard. The uncertainty in the value reflects the variation of the thickness over the three wavelengths. Using this information, the dielectric properties of the pressboard were estimated at each frequency for all three wavelengths. The results of these estimations are shown in Fig. 6.19 where the real and the imaginary parts of the complex permittivity are plotted as a function of the logarithm of the frequency. The fact that the dielectric properties estimated from the three wavelengths agree with each other, supports the notion that the moisture was uniformly distributed in the pressboard.

Following the frequency scan, the Couette Facility was evacuated. After several days of vacuum processing, a second frequency scan was taken to determine the condition of the pressboard. The measurement was performed with the facility still under vacuum. The results of this measurement are shown in Fig. 6.20. The fact that there are no significant changes in the gain and phase of all three wavelengths over the entire frequency range indicates that the pressboard was dry. When the pressboard was eventually oil-impregnated, the moisture content was measured to be less than 0.2%. This
Figure 6.17: Monitoring of the position of the three-wavelength sensor relative to a pressboard surface using the measured high-frequency gain. Because the dielectric constant of pressboard is higher than the permittivity of free space, the point of intimate contact can be determined by monitoring the high-frequency (10 kHz) gain of the three wavelengths on the sensor. Note that the gain of the smallest wavelength does not level off as rapidly as the gain of the two larger wavelengths. This is due to the fact that the smallest wavelength is more sensitive to any air gap between the sensor and the pressboard surface.

Section 6.3: A Three-Wavelength Sensor
Figure 6.18: Frequency response of the three-wavelength sensor to EHV-Weidmann HIVAL transformer pressboard at room temperature with 4% moisture content. During the measurement, the pressboard was in equilibrium with the ambient air. As a result, the moisture content of the pressboard was approximately 4.0%. The fact that the phase peak for all three wavelengths occurs at the same frequency indicates that the moisture in the pressboard is uniformly distributed. The positive phase at frequencies below 10 mHz is probably a result of the influence of the triangular ground pads on the coupling between the driven and the sensing electrodes.
Figure 6.19: Frequency dependence of the dielectric properties of EHV-Weidmann HIVAL transformer pressboard at room temperature with 4% moisture content. The fact that the dielectric properties of the pressboard estimated from the three wavelengths agree with each other, supports the notion that the moisture is uniformly distributed in the pressboard.
measurement was made using a Mitsubishi Water Vaporizer (Model VA-05) connected to a Mitsubishi Moisture Meter (Model CA-05).

To test the reversibility of the process, the Couette Facility was filled with ambient air. After 14 hours of exposure a third frequency scan was taken. The results of this measurement are identical to those shown in Fig. 6.20. This indicates that, even after 14 hours of exposure to ambient air, the bulk of the pressboard had not acquired sufficient moisture from the air in the Couette Facility to bring it back to its initial condition. With the volume of the Couette Facility approximately 6 liters, the amount of moisture in the air at 50% relative humidity and 20°C is roughly 54 mg [22: Section 27.4]. Assuming the worst case in which all of the water in the air were to be absorbed into the bulk of the pressboard, the moisture content of the pressboard would increase by only 0.01%. The mass of the pressboard in the Couette Facility is 454 g. Because there was no flow of air in the Couette Facility, the amount of water absorbed into the pressboard was limited by the amount of water in the air contained in the Couette Facility.

To enhance the mass transfer of moisture into the pressboard, wet nitrogen was bubbled through the Couette Facility. The wet nitrogen was produced by bubbling dry nitrogen through a wetting flask full of water. The flow rate of the nitrogen was approximately 4 ml/sec, corresponding to a residence time in the Couette Facility of 25 minutes. During this process the output of each of the three wavelengths was monitored as a function of time at a frequency of 10 mHz. This frequency was selected to insure that a significant change in the gain and phase would be observed as moisture was absorbed into the pressboard and the phase peak moved toward higher frequencies. The results of the experiment are shown in Fig. 6.21 where the measured gain and phase are plotted as a function of time for the three wavelengths of the sensor. The flow of wet nitrogen was started at time zero. Sometime between hours 14 and 18 the source of nitrogen ran out. In addition, because of the limitations in the data storage of the controller, no data was collected between the hours 18 and 24. The experiment was restarted at hour 24 by retrieving the stored data, clearing the memory of the controller, and restoring the supply of nitrogen.

From the figure it can be seen that, as moisture diffuses into the pressboard, the gain and phase of the largest wavelength begin to change while the output of the smallest wavelength is hardly affected due to its limited penetration depth of 300 μm. As the moisture further penetrates into the pressboard, the gain and phase of the smallest wavelength start to show appreciable changes. The delay between the response of the smallest wavelength and the largest wavelength can be estimated to be 5 ± 1 hours. Based on this delay and a thickness of 0.7 mm, the difference between the thickness
Figure 6.20: Frequency response of the three-wavelength sensor to EHV-Weidmann HI-VAL transformer pressboard at room temperature with less than 0.2% moisture content. The fact that there are no significant changes in the gain and phase of all three wavelengths over the entire frequency range indicates that the pressboard is dry.
Figure 6.21: Time scan reflecting the absorption of moisture into EHV-Weidmann HIVAL pressboard at room temperature. During this process the output of each of the three wavelengths was monitored as a function of time at a frequency of 10 mHz. The delay between the response of the smallest wavelength and the largest wavelength can be estimated to be $5 \pm 1$ hours. Based on this delay and a thickness of 0.7 mm, the difference between the thickness of the pressboard and the penetration depth of the smallest wavelength, the diffusion coefficient of water in pressboard can be estimated to be $(2.7 \pm 0.5) \times 10^{-11}$ m$^2$/s.
of the pressboard and the penetration depth of the electric field associated with the smallest wavelength, the diffusion coefficient of water in pressboard can be estimated to be \((2.7 \pm 0.5) \times 10^{-11} \text{ m}^2/\text{s}\). This estimate agrees well with the value of \(2.1 \times 10^{-11} \text{ m}^2/\text{s}\) for the diffusion coefficient of water in oil-free Kraft paper at room temperature \([63]\). After the initial delay, the gain of each wavelength increases with time. Meanwhile, the phase initially decreases, reaches a minimum, and then begins to rise toward zero. The minimum in the phase is achieved when the minimum phase of the frequency response occurs at 10 mHz, the frequency at which the measurement is being made. These trends are consistent with the frequency response shifting toward higher frequencies as moisture is absorbed into the pressboard.

### 6.4 Summary

Using the protocols developed, flexible electrode structures with polyimide as a substrate were manufactured and cleaned to such a degree that the dielectric properties of highly insulating materials could be measured without any ambiguity. The estimation of the dielectric properties of materials from measurements of the gain and phase of the sensor required an additional component of the coupling admittance to account for the finite thickness of the electrodes. A semi-empirical first-order estimate of this unmodeled component was used to estimate the dielectric properties of transformer oil and paper.

Equilibrium measurements were made of the dielectric properties of transformer oil and paper using a single-wavelength interdigital-electrode structure. Estimation of the dielectric properties of transformer oil over the frequency range examined revealed the presence of a double layer at the Parylene/oil interface. The dependence of the dielectric properties of paper on the moisture content showed that a change of one order of magnitude in the moisture content results in a frequency shift of seven orders of magnitude in the complex permittivity or an increase of four orders of magnitude in the loss factor at a given frequency. Thus, the dielectric properties provide a sensitive method to monitor the moisture content of paper.

The use of a three-wavelength interdigital-electrode structure was demonstrated for monitoring the evacuation and reabsorption of moisture in transformer pressboard. The experimental results indicated that the frequency response of the sensor provides information about the moisture content of the pressboard above a undetermined value greater than 0.2%. Below this value, the pressboard is sufficiently insulating that no information about the moisture content can be obtained over the frequency range examined.

Because the penetration depth of the electric field is proportional to the spatial wave-
length of the electrode structure, the sensor provided a way to monitor the absorption of moisture into pressboard. During the absorption process the heterogeneous distribution of moisture could be observed in the measurement of the gain and phase of the three wavelengths on the sensor. This information provided an order of magnitude estimate of the diffusion coefficient of water in oil-free pressboard. Even though the measurements were made on oil-free pressboard, the concept can easily be extended to oil-impregnated pressboard. The time constant describing the diffusion of moisture in oil-impregnated pressboard is expected to be at least two orders of magnitude greater than that for oil-free pressboard [63].
Chapter 7
An Electrically-Perturbed Diffuse Double Layer

The purpose of this chapter is to develop a model that describes the response of an interdigital-electrode structure to a diffuse double layer. The response of the electrode structure to the double layer is examined in terms of the effective dielectric properties of the bipolar medium. Once the sensitivity of the electrode structure to the parameters describing the double layer is established, the dependence of the effective dielectric properties of the medium on the spatial wavelength is verified experimentally.

7.1 Motivation

The frequency spectrum of the dielectric properties of fluids often contains dispersion characteristics that can be attributed to the formation of a space-charge layer near one of the interfaces in the system. The assembly of the space-charge layer and its image, located either on the surface or in the volume, is referred to as a double layer. The dynamics of the charged species in the fluid determine the frequency range in which the effects of space-charge polarization manifest themselves. At high frequencies, the charges don't have sufficient time to respond to the alternating applied electric field. At low frequencies, the polarization of the charges results in the measurement of an effective dielectric constant that is much higher than its high-frequency value.

In the study of electrochemistry, which includes the double layer, the modeling of bulk phenomena often highlights the role of the interface in understanding the physics of the system. The fact that many of the critical assumptions are made in the description of the interface reflects the lack of knowledge available about the physicochemical nature of interfaces. Thus, modeling the charge transport in the bulk of a bipolar fluid allows the focus of experimental investigations to be placed on the charge transfer characteristics
at the interface of the double layer. This information is of paramount importance in
the study of flow electrification, in which charge is stripped from the double layer and
carried downstream where it can accumulate and lead to failure of the insulation.

7.2 Bipolar Medium

As a charged species is adsorbed on the interface between a solid and a fluid, a double
layer of charge develops in the fluid. The length scale that characterizes the spatial
distribution of the charge in the double layer is the Debye length. Whereas in aqueous
solutions this length is on the order of the molecular size of the ions, in highly insu-
lating fluids it can be as much as 10 \( \mu \)m. Thus, using interdigital-electrode structures
with submillimeter spatial wavelengths, such as those obtained through microfabrication
techniques [93], it is possible to probe the structure of this diffuse double layer.

A cross-sectional view of the electrodes and the adjacent media is shown in Fig. 7.1.
The electrodes are covered by a thin layer of dielectric material with a uniform permitt-
itivity \( \varepsilon_a \). Beyond this layer is an infinite half-space filled with a stationary fluid with an
ionizable neutral species of density \( n \) and two bipolar species with charge densities \( \rho_\pm \).
In this medium, recombination is proportional to the product of the charge densities
while generation is proportional to the \( \gamma \)'th power of the neutral number density. The
recombination \( \alpha \) and generation \( \beta \) coefficients, the mobilities \( b_\pm \) and diffusivities \( k_\pm \) of
the ions, the diffusivity of the neutrals \( k_n \), and the permittivity of the fluid \( \epsilon \) are assumed
to be uniform.

In equilibrium, the interface between the dielectric layer and the fluid is described
by a zeta potential \( \zeta \), and the fluxes of the neutral and ionized species are zero ev-
erywhere. As the double layer is perturbed by an applied AC field, the fluxes at this
interface are assumed to remain zero. For this condition to hold, the frequency of the
excitation signal is required to be sufficiently high so that the time constant associated
with physicochemical reactions at the interface is long compared with the period of the
applied signal. The formulation of the problem allows for alternative descriptions of the
fluxes at the interface to include finite reaction rates [56, 94, 95, 96].

The applied AC signal results in a time-varying electric field at the interface between
the dielectric layer and the bipolar medium. If the magnitude of this field is small
compared with the electric field associated with the double layer, the space-charge layer
is only slightly perturbed about its stationary equilibrium. As a result, the electrical
variables can be linearized about their equilibrium values.
Figure 7.1: Schematic cross-section of an interdigitated-electrode structure and the adjacent media. The electrodes are covered by a thin layer of dielectric material with a uniform permittivity $\varepsilon_a$. Beyond this layer is an infinite half-space filled with a stationary fluid with an ionizable neutral species of density $n$ and two bipolar species with charge densities $\rho_{\pm}$. In equilibrium, the interface between the dielectric layer and the fluid is described by a zeta potential $\zeta$.

### 7.3 Electrical laws

With generation and recombination described by Eqs. G.7 in Appendix G, the conservation laws for the charged species take the form [97]

\[
\frac{\partial \rho_{\pm}}{\partial t} \pm \nabla \cdot \vec{J}_{\pm} = \beta n \gamma - \frac{\alpha}{q} \rho_+ \rho_-
\]  

(7.1)

where $\rho_{\pm} \geq 0$. Because the motion of the ionized species in the neutral medium is collision dominated, the current densities can be expressed as a sum of diffusion and migration terms.

\[
\vec{J}_{\pm} = \mp \kappa_\pm \nabla \rho_{\pm} + b_\pm \rho_{\pm} \vec{E}
\]  

(7.2)

Note that the form of the diffusion term implies that the mole fraction of the ionized species is much less than unity (see Appendix H).

Conservation of the neutral species is written recognizing that the net addition to the charged species from generation and recombination is a loss of neutrals,

\[
\frac{\partial n}{\partial t} + \nabla \cdot \vec{J} = -\gamma \frac{\beta}{q} n \gamma + \gamma \frac{\alpha}{q^2} \rho_+ \rho_-
\]  

(7.3)

Section 7.3: Electrical laws
where the neutral particle flux density is described simply by a diffusion term.

$$\vec{\Gamma} = -\kappa_n \nabla n$$  \hspace{1cm} (7.4)

Just as for the ionized species, the form of the flux implies that the mole fraction of the ionizable neutrals is much less than unity. This is consistent with the fact that, in addition to the ionizable neutrals, there exists a background of neutral molecules that do not participate in the generation and recombination processes.

Gauss' law requires that the divergence of the displacement vector be equal to the net charge density in the fluid.

$$\nabla \cdot \vec{D} = \rho_+ - \rho_-$$  \hspace{1cm} (7.5)

If we assume that the fluid can be modeled as a linearly-polarizable isotropic medium, the displacement flux density is related to the electric field intensity by the permittivity.

$$\vec{D} = \varepsilon \vec{E}$$  \hspace{1cm} (7.6)

Because the length scales of the system are small compared with the wavelength of the electromagnetic wave associated with the excitation, the fields are assumed to be electroquasistatic [98]. Thus, the electric field is made irrotational by its representation in terms of a scalar potential.

$$\vec{E} = -\nabla \Phi$$  \hspace{1cm} (7.7)

### 7.3.1 Stationary Equilibrium

In the absence of a signal applied to the electrodes, an equilibrium double layer forms adjacent to the dielectric layer. Assuming that the electrical variables vary only in the direction perpendicular to the interface, the conservation laws for the charged and neutral species reduce to

$$\pm \frac{dJ \pm}{dx} = \beta n \gamma - \frac{\alpha}{q} \rho_+ \rho_-$$  \hspace{1cm} (7.8)

$$\frac{d\Gamma_+}{dx} = -\frac{\beta}{q} n \gamma + \frac{\alpha}{q^2} \rho_+ \rho_-$$

where the fluxes are given by
\[ J_{\pm} = \mp \kappa_\pm \frac{d\rho_{\pm}}{dx} + b_\pm \rho_{\pm} E_s \]  
(7.9)

\[ \Gamma_s = -\kappa_n \frac{dn_s}{dx} \]

Gauss’ law becomes

\[ \frac{dD_s}{dx} = \rho_{s+} - \rho_{s-} \]  
(7.10)

where the displacement flux density is related to the electric potential by

\[ D_s = -\epsilon \frac{d\Phi_s}{dx} \]  
(7.11)

In equilibrium there is no motion in the fluid. Thus, the flux of charged and neutral species is zero and generation balances recombination everywhere in the system.

\[ J_{\pm} = \mp \kappa_\pm \frac{d\rho_{\pm}}{dx} + b_\pm \rho_{\pm} E_s = 0 \]  
(7.12)

If the diffusivities are related to the mobilities by the Einstein relation,

\[ \frac{\kappa_\pm}{b_\pm} = \frac{kT}{q} = V_T \]  
(7.13)

the electric field intensity can be expressed as

\[ E_s = -\frac{d\Phi_s}{dx} = \pm \frac{kT}{q} \frac{d}{dx} \ln(\rho_{\pm}) \]  
(7.14)

Integration from an arbitrary position to infinity, where the potential is zero and the charge densities are \( \rho_0 \), yields an expression for the charge densities in terms of the potential distribution.

\[ \rho_{\pm} = \rho_0 \exp \left[ \mp \frac{\Phi_s}{V_T} \right] \]  
(7.15)

Note that this result is identical to that obtained in Appendix I, where the system is assumed to be in a stable equilibrium state. The generation coefficient can then be expressed in terms of the recombination coefficient through the equality of generation and recombination rates.

\[ \beta = \frac{\alpha_0^2}{q n_0^2} \]  
(7.16)

Using the expression for the charge densities, Eqs. 7.10 and 7.11 can be combined to

Section 7.3: Electrical laws
Table 7.1: Normalization of variables used to describe the diffuse double layer.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Normalization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lengths ( (x, y, z) = (z, y, z)\ell_D )</td>
<td></td>
</tr>
<tr>
<td>Frequency ( \omega = \omega \rho_o (b_+ + b_-)/\epsilon )</td>
<td></td>
</tr>
<tr>
<td>Wavenumber ( k = k/\ell_D )</td>
<td></td>
</tr>
<tr>
<td>Charge densities ( \rho_\pm = \rho_\pm \rho_o )</td>
<td></td>
</tr>
<tr>
<td>Neutral density ( n = n \rho_o )</td>
<td></td>
</tr>
<tr>
<td>Electric potential ( \Phi = \Phi V_T )</td>
<td></td>
</tr>
<tr>
<td>Electric field intensity ( \vec{E} = \vec{E}(V_T/\ell_D) )</td>
<td></td>
</tr>
<tr>
<td>Electric displacement flux density ( \vec{D} = \vec{D}(\rho_o \ell_D) )</td>
<td></td>
</tr>
<tr>
<td>Current density ( \vec{j}<em>\pm = \vec{j}</em>\pm \rho_o^2 \ell_D (b_+ + b_-)/\epsilon )</td>
<td></td>
</tr>
<tr>
<td>Neutral flux density ( \vec{n} = \vec{n}(\rho_o \ell_D (b_+ + b_-)/\epsilon )</td>
<td></td>
</tr>
<tr>
<td>Surface capacitance density ( C = C(\rho_o \ell_D/V_T) )</td>
<td></td>
</tr>
</tbody>
</table>

give the Poisson-Boltzmann equation,

\[
\frac{d^2 \Phi_s}{dx^2} = \sinh \Phi_s \tag{7.17}
\]

where an underscored equation number indicates that all variables have been normalized according to Table 7.1. If we multiply both sides by \( d\Phi_s/dx \) we can integrate this equation from an arbitrary position to infinity, where \( \Phi_s \) and \( d\Phi_s/dx \) go to zero.

\[
E_s = -\frac{d\Phi_s}{dx} = 2 \sinh \frac{\Phi_s}{2} \tag{7.18}
\]

Further integration from \( x = 0 \), where \( \Phi_s = \zeta \), the zeta potential, to an arbitrary position yields an expression for the potential distribution

\[
\frac{\tanh(\Phi_s/4)}{\tanh(\zeta/4)} = e^{-x} \tag{7.19}
\]

A closed-form solution can be obtained using the identity

\[
\tanh^{-1} x = \frac{1}{2} \ln \left[ \frac{1 + x}{1 - x} \right] \quad x^2 < 1 \tag{7.20}
\]

so that the potential distribution can be expressed as

\[
\Phi_s(x) = 2 \ln \left[ \frac{1 + \tanh(\zeta/4)e^{-x}}{1 - \tanh(\zeta/4)e^{-x}} \right] \tag{7.21}
\]

For a weak double layer, the linear Debye-Hückel approximation (\( \zeta \ll V_T \)) yields
\[ \Phi_s = E_s = \zeta e^{-z} \quad (7.22) \]

The potential and associated charge density distributions are plotted in normalized form in Fig. 7.2 for several values of the zeta potential.

### 7.3.2 Perturbation Dynamics

The excitation at the electrodes perturbs the double layer. Assuming that the perturbation is small enough that the laws governing the dynamics can be linearized, the electrical variables take the following form:

\[
\begin{align*}
\Phi &= \Phi_s + \Phi' \\
D &= D_s + D' \\
\rho_\pm &= \rho_{s\pm} + \rho'_{\pm} \\
J_\pm &= J'_{\pm} \\
n &= n_s + n' \\
\Gamma &= \Gamma'
\end{align*} \quad (7.23)
\]

With the stationary terms canceled out, the linearized conservation laws for the charged and neutral species can be written as

\[
\begin{align*}
\frac{\partial \rho'_\pm}{\partial t} + \nabla \cdot J'_\pm &= \gamma \beta \gamma_n^{-1} n' - \frac{\alpha}{q}[\rho_{s+} \rho'_- + \rho_{s-} \rho'_+] \\
\frac{\partial n'}{\partial t} + \nabla \cdot \Gamma' &= -\gamma \beta \gamma_n^{-1} n' + \gamma \frac{\alpha}{q^2}[\rho_{s+} \rho'_- + \rho_{s-} \rho'_+] \quad (7.24)
\end{align*}
\]

where the fluxes are given by

\[
\begin{align*}
J'_\pm &= \mp \kappa_\pm \nabla \rho'_\pm + b_\pm \rho'_\pm E_s i_s - b_\pm \rho_{s\pm} \nabla \Phi' \\
\Gamma' &= -\kappa_n \nabla n'
\end{align*} \quad (7.25)
\]

Gauss' law becomes

\[
\nabla \cdot \vec{D}' = \rho'_+ - \rho'_- \quad (7.26)
\]

where the perturbed electric potential and displacement flux density are related by

\[
\vec{D}' = -\epsilon \nabla \Phi' \quad (7.27)
\]

With the objective of determining the response of the system to a single Fourier component, each perturbation variable can be represented in terms of a complex amplitude as

\[
A' = \Re \{ \hat{A}(x) e^{i(\omega t - kv)} \} \quad (7.28)
\]

*Section 7.3: Electrical laws*
Figure 7.2: Normalized spatial distributions of the potential and charge densities in the double layer at equilibrium. The potential is plotted for values of the normalized zeta potential of 1, 3, and 10; the charge densities are plotted for a value of the normalized zeta potential of 1.
Table 7.2: Definition of parameters used to describe the diffuse double layer.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order of generation kinetics</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>Generation coefficient</td>
<td>$\beta = \alpha \rho_0^2 / q n_s^\gamma$</td>
</tr>
<tr>
<td>Normalized recombination coefficient</td>
<td>$\alpha = \alpha e / q (b_+ + b_-)$</td>
</tr>
<tr>
<td>Normalized zeta potential</td>
<td>$\zeta = \zeta / V_T$</td>
</tr>
<tr>
<td>Ionization factor</td>
<td>$p = \rho_0 / q n_s$</td>
</tr>
<tr>
<td>Mobility factor</td>
<td>$r_\pm = 2 b_\pm / (b_+ + b_-)$</td>
</tr>
<tr>
<td>Diffusion factor</td>
<td>$r_n = 2 \kappa_n / (\kappa_+ + \kappa_-)$</td>
</tr>
<tr>
<td>Debye length</td>
<td>$\ell_D = \sqrt{\varepsilon V_T / 2 \rho_o}$</td>
</tr>
</tbody>
</table>

where the wavenumber $k$ associated with the fundamental mode is related to the spatial wavelength by

$$k = \frac{2\pi}{\lambda} \quad (7.29)$$

Using the normalizations given in Table 7.1 and the parameters defined in Table 7.2, Eqs. 7.24–7.27 can be expressed in terms of the complex amplitudes as

$$\frac{d}{dx} \begin{bmatrix} \hat{D} \\ \hat{\rho}_\pm \\ \hat{n} \\ \hat{\phi} \\ \hat{J}_\pm \\ \hat{\Gamma} \end{bmatrix} = \begin{bmatrix} (\hat{\rho}_+ - \hat{\rho}_-) - 2k^2 \hat{\phi} \\ \pm \frac{i}{2} \rho_{s\pm} \hat{D} \mp E_s \hat{\rho}_\pm \mp \frac{1}{r_\pm} \hat{J}_\pm \\ -\frac{1}{r_n} \hat{\Gamma} \\ -\frac{1}{2} \hat{D} \\ \mp (i \omega + r_\pm k^2) \hat{\rho}_\pm \mp \alpha (\rho_{s-} \hat{\rho}_+ + \rho_{s+} \hat{\rho}_- - \gamma \hat{n}) - r_\pm k^2 \rho_{s\pm} \hat{\phi} \\ -(i \omega + r_n k^2) \hat{n} + p \alpha \gamma (\rho_{s-} \hat{\rho}_+ + \rho_{s+} \hat{\rho}_- - \gamma \hat{n}) \end{bmatrix} \quad (7.30)$$

where the current densities $\hat{J}_\pm$ and the neutral flux density $\hat{\Gamma}$ are the complex amplitudes of the respective $x$-directed components.

Note that the normalized recombination coefficient is defined to be unity if recombination is described by Langevin's relation, which is derived in Appendix J. If the mobilities are equal, the mobility factors $r_+$ and $r_-$ are unity. If the neutral diffusion coefficient is equal to the average of that of the ion species, the diffusion factor $r_n$ is unity. Thus, all of the coefficients in Eqs. 7.30 are of order unity except the ionization factor $p$ which is related to the ionization fraction $\nu$ by the following relation.

Section 7.3: Electrical laws
\[ p = \frac{\nu}{1 - \nu} \quad (7.31) \]

The limiting values of the ionization fraction \( \nu \) are unity for complete dissociation and zero for no dissociation.

### 7.4 Surface Capacitance Density

The heterogeneous medium above the electrodes can be described in terms of a surface capacitance density. This quantity represents the response of the medium to one Fourier component of the potential applied at the electrodes. It is defined as the ratio of the complex amplitudes of the normal displacement flux density to the electric potential,

\[ \hat{C}^a = \frac{\hat{D}^a}{\hat{\Phi}^a} \quad (7.32) \]

where the superscript identifies the side of the interface where this quantity is to be evaluated. The regions above the electrodes and the corresponding interfaces are shown schematically in Fig. 7.3.

The interface between the dielectric layer and the bipolar medium is modeled as a passive boundary, where the fluxes of the charged and neutral species are zero. Consequently, there is no accumulation of perturbation surface charge and the Fourier component of the dielectric flux density is continuous at this interface. Because the potential is also continuous, the surface capacitance density across this surface is continuous. Thus, the surface capacitance density at the surface of the electrodes \( \hat{C}^a \) can be expressed in terms of the surface capacitance density at the surface below the double layer \( \hat{C}^b = \hat{C}^c \) through the transfer relations for the dielectric layer [76].

\[ \hat{C}^a = \epsilon_\alpha k \text{coth}(kd) - \frac{(\epsilon_\alpha k)^2}{\sinh^2(kd)\left[\epsilon_\alpha k \text{coth}(kd) + \hat{C}^b\right]} \quad (7.33) \]

To facilitate the computation of the surface capacitance density at the interface between the dielectric layer and the bipolar medium, the region above this interface is divided into a layer of thickness \( h \), over which the coefficients in Eqs. 7.30 vary, and an infinite half-space where these coefficients are essentially constant. With the thickness \( h \) large compared to a Debye length \( \ell_D \), the electrical variables are continuous across the interface between these two regions.

In the infinite half-space, the space-varying coefficients in Eqs. 7.30 become
Figure 7.3: Schematic illustration of the regions above the electrodes consisting of a dielectric layer of thickness $d$ and a bipolar medium of semi-infinite extent. To facilitate the computation of the surface capacitance density at the interface between the dielectric layer and the bipolar medium, the region above this interface is subdivided into a layer of thickness $h$, over which the coefficients in Eqs. 7.30 vary, and an infinite half-space where these coefficients are essentially constant. With the thickness $h$ large compared to a Debye length $\ell_D$, the electrical variables are continuous across the interface between these two regions.

\[ E_s \rightarrow 0 \]
\[ \rho_{s\pm} \rightarrow 1 \]  \hfill (7.34)

The resulting system of constant-coefficient equations has solutions of the form

\[
\begin{bmatrix} F \\ G \end{bmatrix} = \lambda e^{\beta x} \]
\hfill (7.35)

where the vectors $F$ and $G$ represent the perturbation variables

\[
F = \begin{bmatrix} \dot{D} \\ \hat{\rho}_+ \\ \hat{\rho}_- \\ \hat{n} \end{bmatrix} \quad G = \begin{bmatrix} \dot{\phi} \\ \hat{j}_+ \\ \hat{j}_- \\ \hat{\Gamma} \end{bmatrix} \]
\hfill (7.36)

and $\beta$ satisfies the eigenvalue equation obtained by substituting Eq. 7.35 into Eqs. 7.30
$$M \begin{bmatrix} F \\ G \end{bmatrix} = \beta \begin{bmatrix} F \\ G \end{bmatrix}$$  \hspace{1cm} (7.37)

with the matrix $M$ defined as

$$M = \begin{bmatrix}
0 & 1 & -1 & 0 & -2k^2 & 0 & 0 & 0 \\
+\frac{1}{2} & 0 & 0 & 0 & 0 & -\frac{1}{r_+} & 0 & 0 \\
-\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & \frac{1}{r_-} & 0 \\
-\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{r_n} \\
0 & -S_+ & -\alpha & +\alpha \gamma & -r_+ k^2 & 0 & 0 & 0 \\
0 & \alpha & S_- & -\alpha \gamma & -r_- k^2 & 0 & 0 & 0 \\
0 & p\alpha \gamma & p\alpha \gamma & -S_n & 0 & 0 & 0 & 0
\end{bmatrix}$$  \hspace{1cm} (7.38)

and where

$$S_+ = j\omega + r_+ k^2 + \alpha$$
$$S_- = j\omega + r_- k^2 + \alpha$$
$$S_n = j\omega + r_n k^2 + \alpha \gamma^2 p$$  \hspace{1cm} (7.39)

In general, the solutions for the perturbation variables consist of a superposition of eight terms,

$$\begin{bmatrix} F \\ G \end{bmatrix} = \sum_{j=1}^{8} A_j \begin{bmatrix} F_j \\ G_j \end{bmatrix} e^{\beta_j z}$$  \hspace{1cm} (7.40)

where $F_j$ and $G_j$ constitute the eigenvector corresponding to the $j$th eigenvalue. Because the equilibrium electric field is absent in this region, it is expected that four of the solutions will decay in the $z$ direction, while the other four will grow with eigenvalues that are the negatives of those for the decaying modes. Thus, the values of the four coefficients associated with the growing solutions are set to zero to insure that the perturbation variables remain bounded. With the remaining four coefficients $A_j$ specified by the boundary conditions, the eight perturbation variables at the $(d)$ surface in Fig. 7.3 are known.

$$\begin{bmatrix} F^d \\ G^d \end{bmatrix} = \sum_{j=1}^{4} A_j \begin{bmatrix} F_j \\ G_j \end{bmatrix}$$  \hspace{1cm} (7.41)

These variables can then be determined at the interface between the dielectric layer and the bipolar medium by integrating Eqs. 7.30 from the $(d)$ surface to the $(c)$ surface. This process can be summarized by the following relations,
\[
F^c = PA \\
G^c = QA
\]  

(7.42)

where the \(j\)th column in the \(P\) and \(Q\) matrices corresponds to the perturbation variables computed at the \((c)\) surface by setting \(A_j = 1\) and the remaining three coefficients equal to zero.

Finally, the combination of the coefficients \(A_j\) that gives the desired conditions at the \((c)\) surface is determined. This is accomplished by inverting Eq. 7.42b and solving for the coefficients with the vector \(G^c\) having the prescribed values of the fluxes.

\[
A = Q^{-1}G^c = Q^{-1}
\begin{bmatrix}
1 \\
0 \\
0 \\
0
\end{bmatrix}
\]  

(7.43)

Note that the perturbation component of the potential was arbitrarily chosen to be unity. The desired surface capacitance density follows then from Eq. 7.42a.

\[
\hat{C}^b_{\phi} = \hat{C}^c = \frac{\hat{D}^c}{\hat{\phi}^c} = \sum_{j=1}^{4} P_{1j}A_j
\]  

(7.44)

An equivalent expression for the surface capacitance density of a double layer with a reactive boundary is derived in Appendix K.

### 7.5 Limit of Equal Ion Mobilities

With the goal of providing a means of verification for the numerical procedure proposed in the previous section, and to gain further insight into the physics of the double layer, an analytical expression for the surface capacitance density is derived in the limit of zero zeta potential and equal ion mobilities.

In this limit we find that

\[
E_s \to 0 \\
\rho_{s\pm} \to 1 \\
r_{s\pm} \to 1
\]  

(7.45)

so that the system of equations describing the perturbation variables, Eqs. 7.30, reduces to
\[
\frac{d}{dx} \begin{bmatrix}
\hat{D} \\
\hat{\rho}_\pm \\
\hat{n} \\
\hat{\Phi} \\
\hat{J}_\pm \\
\hat{\gamma}_n
\end{bmatrix} = \begin{bmatrix}
(\hat{\rho}_+ - \hat{\rho}_-) - 2k^2\hat{\Phi} \\
\pm \frac{1}{2} \hat{D} + \hat{J}_\pm \\
-\frac{1}{r_n}\hat{\gamma}_n \\
-\frac{1}{2} \hat{D} \\
\mp (j\omega + k^2)\hat{\rho}_\pm + \alpha(\hat{\rho}_+ + \hat{\rho}_- - \gamma\hat{n}) - k^2\hat{\Phi} \\
-(j\omega + r_n k^2)\hat{n} + p\alpha\gamma(\hat{\rho}_+ + \hat{\rho}_- - \gamma\hat{n})
\end{bmatrix} \quad (7.46)
\]

By differentiating the second through the fifth equation, this system of equations can be expressed as

\[
\frac{d^2}{dx^2} \begin{bmatrix}
\hat{\Phi} \\
\hat{\rho}_\pm \\
\hat{n} \\
\hat{\gamma}_n
\end{bmatrix} = \begin{bmatrix}
k^2\hat{\Phi} - \frac{1}{2}(\hat{\rho}_+ - \hat{\rho}_-) \\
(S + \frac{1}{2})\hat{\rho}_\pm + (\alpha - \frac{1}{2})\hat{\rho}_\mp - \alpha\gamma\hat{n} \\
\frac{1}{r_n}\hat{S}_n\hat{n} - \frac{1}{r_n}p\alpha\gamma(\hat{\rho}_+ + \hat{\rho}_-) \\
\end{bmatrix} \quad (7.47)
\]

where the parameters \( S = S_\pm \) and \( S_n \) are defined in Eq. 7.39. Assuming a solution of the form of Eq. 7.35, the eigenvalue equation becomes

\[
\text{det} \begin{bmatrix}
\beta^2 - k^2 & \frac{1}{2} & -\frac{1}{2} & 0 \\
0 & \beta^2 - (S + \frac{1}{2}) & \frac{1}{2} - \alpha & \alpha\gamma \\
0 & \frac{1}{2} - \alpha & \beta^2 - (S + \frac{1}{2}) & \alpha\gamma \\
0 & \frac{1}{r_n}p\alpha\gamma & \frac{1}{r_n}p\alpha\gamma & \beta^2 - \frac{1}{r_n}S_n
\end{bmatrix} = 0 \quad (7.48)
\]

The first two eigenvalues are associated with a Laplacian field distribution.

\[
\beta_1^2 = k^2 \quad (7.49)
\]

A second pair of eigenvalues can be identified as

\[
\beta_2^2 = (S + \frac{1}{2}) + (\frac{1}{2} - \alpha) = j\omega + k^2 + 1 \quad (7.50)
\]

The remaining four eigenvalues can be obtained from the biquadratic equation

\[
[\beta^2 - (S + \alpha)][\beta^2 - \frac{1}{r_n}S_n] - \frac{2}{r_n}p\alpha^2\gamma^2 = 0 \quad (7.51)
\]

whose solutions can be expressed in the limit of \( r_n = 1 \) as

\[
\beta_3^2 = j\omega + k^2 \\
\beta_4^2 = j\omega + k^2 + 2\alpha + p\alpha\gamma^2 \quad (7.52)
\]

The eigenvectors associated with the eigenvalues with negative roots are obtained

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from the matrix equation, Eq. 7.37, with \( r_\pm = 1 \). The results can be summarized in terms of the matrices \( P \) and \( Q \) of Eq. 7.42.

\[
P = \begin{bmatrix}
-2\beta_1 & -2\beta_2 & 0 & 0 \\
0 & -(1 + j\omega) & \rho(\beta_3) & \rho(\beta_4) \\
0 & +(1 + j\omega) & \rho(\beta_3) & \rho(\beta_4) \\
0 & 0 & 1 & 1 \\
\end{bmatrix}
\]  

\[
(7.53)
\]

\[
Q = \begin{bmatrix}
1 & 1 & 0 & 0 \\
-\beta_1 & j\omega\beta_2 & -\beta_3\rho(\beta_3) & -\beta_4\rho(\beta_4) \\
-\beta_1 & j\omega\beta_2 & +\beta_3\rho(\beta_3) & +\beta_4\rho(\beta_4) \\
0 & 0 & -r_n\beta_3 & -r_n\beta_4 \\
\end{bmatrix}
\]  

\[
(7.54)
\]

where

\[
\rho(\beta) = -\frac{r_n\beta^2 - S_n}{2p\alpha\gamma}
\]  

\[
(7.55)
\]

The coefficients \( A_j \) are obtained by imposing the boundary conditions as in Eq. 7.43.

\[
A_3 = \frac{1}{1 + \left[\frac{\beta_1}{j\omega\beta_2}\right]^{\pm 1}}
\]  

\[
(7.56)
\]

\[
A_4 = 0
\]

The desired surface capacitance density follows then from Eq. 7.44.

\[
\hat{C}_\nu = 2k \left[ 1 - \frac{k - \sqrt{j\omega + k^2} + 1}{k + j\omega\sqrt{j\omega + k^2} + 1} \right]
\]  

\[
(7.57)
\]

Note that the boundary conditions chosen to represent the interface between the dielectric layer and the bipolar medium lead to an expression for the surface capacitance density that is independent of the order of generation kinetics \( \gamma \), the recombination coefficient \( \alpha \), and the ionization \( p \) and diffusion \( r_n \) factors.

In the high-frequency limit of

\[
\omega \gg k \quad \text{for} \; k \ll 1
\]

\[
\sqrt{\omega} \gg k \quad \text{for} \; k \ll 1
\]  

\[
(7.58)
\]

the expression for the surface capacitance density reduces to

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\[ \dot{C}^b = 2k \left[ 1 - \frac{j}{\omega} \right] \quad (7.59) \]

which is the normalized form of the surface capacitance density for an ohmic medium:

\[ \dot{C}^b = \varepsilon^* k \quad \varepsilon^* = \varepsilon - j \frac{2\rho_o b}{\omega} \quad (7.60) \]

The low-frequency value of the effective dielectric constant of the medium \( \varepsilon^* \) can be expressed as

\[ \frac{\varepsilon^*}{\varepsilon} = \lim_{\omega \to 0} \frac{\dot{C}^b}{\varepsilon k} = \sqrt{1 + \frac{1}{(k\ell_D)^2}} \quad (7.61) \]

Thus, the effective dielectric constant increases for spatial wavelengths large compared with the Debye length. This effect is due to the polarization of the ionic species in the bipolar medium. At low frequencies, the ions have sufficient time to migrate and form two space-charge layers separated by a distance equal to the Debye length. The charge stored in these space-charge layers can be much larger than the polarization charge associated with dipole orientation leading, as a result, to an increased apparent dielectric constant.

For spatial wavelengths large compared with the Debye length \( k\ell_D \ll 1 \) the effective dielectric constant is associated with a parallel-plate capacitor whose electrode width is \( \lambda/2\pi \) and whose gap spacing is the Debye length \( \ell_D \). As the spatial wavelength becomes small compared with the Debye length \( k\ell_D \gg 1 \) the effect of space-charge polarization is reduced and the effective dielectric constant is equal to the permittivity of the fluid.

### 7.6 Characteristic Responses

With the surface capacitance density at the surface of the electrodes given by Eqs. 7.32 and 7.44, the continuum model developed by Zaretsky et al. [76] can be used to calculate the gain and phase associated with the response of an interdigital-electrode structure to a double layer. This was accomplished using the program dd1. for listed in Appendix M. Once the gain and phase are calculated, the effective dielectric properties of the bipolar medium are estimated assuming that the heterogeneous medium above the dielectric layer has uniform properties. The results of this estimation provide a description of the medium as seen from the interface between the dielectric layer and the bipolar medium. This step was accomplished using a version of the program parstat. for [50: Appendix F] modified to allow multiple data points.

The nominal values of the input parameters describing the electrode structure and
Table 7.3: Nominal values of the input parameters describing a microchip sensor and the bipolar medium above the dielectric layer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Fourier modes</td>
<td>$N$</td>
<td>100</td>
</tr>
<tr>
<td>Number of collocation points</td>
<td>$k$</td>
<td>25</td>
</tr>
<tr>
<td>Normalized double layer thickness</td>
<td>$h_D / \ell_D$</td>
<td>3.0</td>
</tr>
<tr>
<td>Error tolerance for double layer</td>
<td>$\delta$</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Spatial wavelength</td>
<td>$\lambda$</td>
<td>50 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of substrate</td>
<td>$\epsilon_b$</td>
<td>34.5 pF/m</td>
</tr>
<tr>
<td>Normalized substrate thickness</td>
<td>$\lambda / 4h_b$</td>
<td>7.5</td>
</tr>
<tr>
<td>Normalized interelectrode spacing</td>
<td>$a / \lambda$</td>
<td>0.25</td>
</tr>
<tr>
<td>Normalized load capacitance</td>
<td>$C_L / \epsilon_b M_{el}$</td>
<td>1.5</td>
</tr>
<tr>
<td>Thickness of dielectric layer</td>
<td>$d$</td>
<td>5 $\mu$m</td>
</tr>
<tr>
<td>Permittivity of dielectric layer</td>
<td>$\epsilon_a$</td>
<td>3.05 $\epsilon_o$</td>
</tr>
<tr>
<td>Permittivity of fluid</td>
<td>$\epsilon$</td>
<td>2.2 $\epsilon_o$</td>
</tr>
<tr>
<td>Bulk conductivity of fluid</td>
<td>$\sigma_o$</td>
<td>100.0 pS/m</td>
</tr>
<tr>
<td>Normalized zeta potential</td>
<td>$\zeta / V_T$</td>
<td>0.0</td>
</tr>
<tr>
<td>Thermal voltage</td>
<td>$V_T$</td>
<td>25.0 mV</td>
</tr>
<tr>
<td>Ionization fraction</td>
<td>$\nu$</td>
<td>0.1</td>
</tr>
<tr>
<td>Mobility ratio</td>
<td>$b_-/b_+$</td>
<td>2.0</td>
</tr>
<tr>
<td>Positive ion mobility</td>
<td>$b_+$</td>
<td>$1.0 \times 10^{-9}$ m$^2$/Vs</td>
</tr>
<tr>
<td>Diffusion factor</td>
<td>$r_n$</td>
<td>1.0</td>
</tr>
<tr>
<td>Normalized recombination coefficient</td>
<td>$\alpha \epsilon / q(b_+ + b_-)$</td>
<td>1.0</td>
</tr>
<tr>
<td>Order of generation kinetics</td>
<td>$\gamma$</td>
<td>2</td>
</tr>
</tbody>
</table>

The bipolar medium are given in Table 7.3. The values describing the sensor are representative of a microchip sensor, whose penetration depth is comparable to the Debye length. The Debye length for these input parameters is 2.7 $\mu$m. The value of the normalized load capacitance was selected to yield a typical value of $-42$ dB for the high-frequency gain of the bare sensor in air.

The nominal value of the zeta potential was chosen to be zero. This does not imply that the fluid is ohmic. Rather, this value indicates that there is no adsorbed charge at the interface. Thus, the effect of the parameters on the dielectric properties of the bipolar medium can be examined without any ambiguity associated with the surface effects introduced by a nonzero value of the zeta potential.

Section 7.6: Characteristic Responses
The value of the bulk conductivity was selected to insure a significant change in the gain and phase over the frequency range of interest. This value is used to specify the bulk charge density of the fluid $\rho_o$ through the relation

$$\sigma_o = \rho_o (b_+ + b_-)$$  \hspace{1cm} (7.62)

The remaining values of the parameters describing the bipolar medium are representative of liquid hydrocarbons. Because the electrical laws have been linearized, the insights developed from this set of parameters is not limited to a narrow range in the parameter space.

For cases in which the value of the zeta potential is nonzero, the thickness of the region with space-varying coefficients was scaled in proportion to the distance over which different Fourier components of the electrical variables vary according to the expression

$$h_n = \frac{h_1}{n}$$  \hspace{1cm} (7.63)

The values of the thickness of the region with space-varying coefficients and the error tolerance for the numerical integration across the double layer are used only for cases of nonzero zeta potential.

### 7.6.1 Ionic Mobility

To examine the effect of the mobilities on the effective dielectric properties of the bipolar medium, the value of the positive ion mobility was varied over three orders of magnitude while keeping the ratio of the mobilities constant. The bulk conductivity of the medium changed in proportion to the value of the mobilities according to Eq. 7.62. The bulk charge density and all other parameters remained constant at their nominal value.

The calculated gain and phase as well as the estimated values of the real and imaginary parts of the complex permittivity are plotted as a function of the temporal frequency in Fig. 7.4. Lines (a), (b), and (c) correspond to values for the positive ion mobility of $1.0 \times 10^{-10}$ m$^2$/Vs, $1.0 \times 10^{-9}$ m$^2$/Vs, and $1.0 \times 10^{-8}$ m$^2$/Vs. This figure shows that the characteristic shape of the frequency response remains invariant as it shifts toward higher frequencies in proportion to the bulk conductivity.

The frequency spectrum of the complex dielectric constant is characteristic of space-charge polarization and is indistinguishable from the polarization spectrum associated with dipole orientation [55: Part II, Section 31]. These spectra are described by the Debye dispersion relation [55: Part II, Section 22],
Figure 7.4: Effect of the mobility of the ions in a bipolar medium on the frequency response of a microchip sensor and the estimated values of the effective dielectric properties of the medium. Lines (a), (b), and (c) correspond to values for the positive ion mobility of $1.0 \times 10^{-10}$ m$^2$/Vs, $1.0 \times 10^{-6}$ m$^2$/Vs, and $1.0 \times 10^{-8}$ m$^2$/Vs. This figure shows that the characteristic shape of the frequency response remains invariant as it shifts toward higher frequencies in proportion to the bulk conductivity.

Section 7.6: Characteristic Responses
\[
\varepsilon'(\omega) = \frac{\varepsilon_s - \varepsilon}{1 + (\omega \tau)^2} + \varepsilon
\]

\[
\varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon}{1 + (\omega \tau)^2} \omega \tau
\]

where \( \tau \) is the space-charge relaxation time. The peak in the loss factor \( \varepsilon'' \) occurs when \( \omega \tau = 1 \). Note that these expressions satisfy the Kramers-Kröning relations described by Eqs. 6.9 with \( \varepsilon_{\infty} = \varepsilon \) and \( \sigma = 0 \). The DC conductivity associated with this spectrum is zero because the boundary conditions at the interface between the dielectric and the bipolar medium require that the current densities be zero.

Even though the dielectric properties of the bipolar medium are dispersive there is a regime in the frequency domain over which the medium exhibits ohmic behavior. In particular, for \( \omega \tau \gg 1 \), the dielectric constant is equal to the permittivity of the fluid and the loss factor has a slope of \( -1 \). At lower frequencies, the effects of space-charge polarization become significant and the dielectric properties of the medium deviate from the ohmic response.

As the mobility of the ions is varied over three orders of magnitude the low-frequency value of the dielectric constant remains fixed at \( 7.5 \varepsilon_o \). The frequency at which the peak in the loss factor occurs, on the other hand, increases proportionally with the value of the mobility. This is illustrated in Fig. 7.5, a plot of the space-charge relaxation time as a function of the electrical relaxation time

\[
\tau_e = \frac{\varepsilon}{\sigma_o}
\]

The fact that the slope of the line is unity indicates that the space-charge relaxation time is proportional to the electrical relaxation time, and is consequently associated with the migration of the ions in the bipolar medium.

With the sum of the mobilities constant, the ratio of the ionic mobilities was varied from 0.125 to 8.0. Over this range no significant change in the calculated gain and phase was observed. In particular, the responses associated with a value of the mobility ratio and its inverse were identical. This latter observation is consistent with the fact that, in the absence of preferential adsorption at the interface, the positive and negative ions are indistinguishable from each other.
Figure 7.5: Plot of the space-charge relaxation time associated with variations in the mobility of the ions in a bipolar medium as a function of the electrical relaxation time. The fact that the slope of the line is unity indicates that the space-charge relaxation time is proportional to the electrical relaxation time, and is consequently associated with the migration of the ions in the bipolar medium.

7.6.2 Bulk Charge Density

The total number density of neutrals in the medium, including those that can be formed by recombination of the charged species, is

\[ n_o = n_s + \frac{\rho_o}{q} \]  \hspace{1cm} (7.66)

As this number density increases, perhaps as a result of the addition of ionizable species, the value of the bulk charge density increases. If the ionization fraction remains constant, the increase in the bulk charge density is proportional to the increase in the total number density. This is evident by rewriting the expression for the total number density with
the help of Eq. 7.31 and the definition of the ionization factor in Table 7.2.

\[ n_o = \frac{\rho_o}{q\nu} \quad (7.67) \]

By varying the bulk conductivity of the bipolar medium and keeping all other parameters constant, the value of the bulk charge density was varied over three orders of magnitude. The calculated gain and phase as well as the estimated values of the real and imaginary parts of the complex permittivity are plotted as a function of the temporal frequency in Fig. 7.6. Lines (a), (b), and (c) correspond to values for the bulk conductivity of 10.0 pS/m, 100.0 pS/m, and 1000.0 pS/m.

Just as in the frequency spectrum associated with mobility variations, the dielectric properties of the bipolar medium exhibit ohmic behavior over the regime in the frequency domain for which \( \omega \tau \gg 1 \). However, in this case, the low-frequency value of the dielectric constant increases with the bulk conductivity and the frequency at which the peak in the loss occurs does not scale in proportion to the bulk conductivity.

The low-frequency value of the dielectric constant normalized to the corresponding high-frequency value is plotted as a function of the Debye length normalized to the spatial wavelength in Fig. 7.7. The Debye length is used here to represent the bulk charge density according to the definition in Table 7.2. This figure shows that, for small values of the normalized Debye length, the normalized dielectric constant is inversely proportional to the Debye length. This is consistent with Eq. 7.61, which describes the dependence of the low-frequency value of the dielectric constant on the normalized wavenumber.

The space-charge relaxation time is plotted as a function of the electrical relaxation time in Fig. 7.8. This figure clearly shows that the space-charge relaxation time is not linear with the electrical relaxation time. The intersection of this curve with the line along which the space-charge relaxation time is equal to the electrical relaxation time delineates two regimes. For relatively conducting fluids, the space-charge relaxation time is longer than the relaxation time. In this regime self-field effects in the medium impede the migration of the ions while the increased bulk charge density enhances the conduction process. For relatively insulating fluids, on the other hand, the reduced bulk charge density limits the conduction process and the electrical relaxation time is longer than the space-charge relaxation time.
Figure 7.6: Effect of the bulk charge density in a bipolar medium on the frequency response of a microchip sensor and estimated values of the effective dielectric properties of the medium. The bulk charge density is varied by changing the value of the bulk conductivity while keeping all other parameters constant. Lines (a), (b), and (c) correspond to values for the bulk conductivity of 10.0 pS/m, 100.0 pS/m, and 1000.0 pS/m.

Section 7.6: Characteristic Responses
Figure 7.7: Plot of the normalized low-frequency value of the dielectric constant associated with variations in the bulk charge density of a bipolar medium as a function of the normalized Debye length. The Debye length is used to represent the bulk charge density. This figure shows that, for small values of the normalized Debye length, the dielectric constant is inversely proportional to the Debye length.

7.6.3 Spatial Wavelength

The spatial wavelength of an interdigital-electrode structure determines the length scale over which the structure is sensitive to the dielectric properties of the medium. Because the bipolar medium is heterogeneous, its representation in terms of a single set of dielectric properties will lead to estimated values that depend on the spatial wavelength of the electrode structure. To examine this effect, the spatial wavelength was varied over three orders of magnitude while keeping all other parameters constant at their nominal value. The normalized substrate thickness and the normalized interelectrode spacing were kept constant.

The calculated gain and phase as well as the estimated values of the real and imagi-
Figure 7.8: Plot of the space-charge relaxation time associated with variations in the bulk charge density of a bipolar medium as a function of the electrical relaxation time. This figure clearly shows that the space-charge relaxation time is not linear with the electrical relaxation time. The intersection of this curve with the line along which the space-charge relaxation time is equal to the electrical relaxation time delineates two regimes in which self-field effects determine the relative magnitudes of the two time constants.

The imaginary parts of the complex permittivity are plotted as a function of the temporal frequency in Fig. 7.9. Lines (a), (b), and (c) correspond to values for the spatial wavelength of 50 μm, 500 μm, and 5000 μm. This figure shows that the frequency range over which the bipolar medium exhibits ohmic behavior increases with the spatial wavelength.

The dependence of the low-frequency value of the effective dielectric constant on the spatial wavelength is identical to that shown in Fig. 7.7, a plot of the normalized low-frequency dielectric constant as a function of the normalized Debye length. The space-charge relaxation time is plotted as a function of the normalized wavelength in Fig. 7.10. This figure shows that, because the spatial wavelength determines the length scale over
Figure 7.9: Heterogeneity of the double layer examined from the point of view of the frequency response of an interdigital-electrode structure to a bipolar medium and estimated values of the effective dielectric properties of the medium. Lines (a), (b), and (c) correspond to values for the spatial wavelength of 50 μm, 500 μm, and 5000 μm. This figure shows that, because the bipolar medium is heterogeneous, its representation in terms of a single set of dielectric properties leads to estimated values that depend on the spatial wavelength of the electrode structure.
Figure 7.10: Plot of the space-charge relaxation time associated with variations in the spatial wavelength of an interdigital-electrode structure as a function of the electrical relaxation time. This figure shows that, because the spatial wavelength determines the length scale over which the electrode structure is sensitive, the frequency at which the effects of space-charge polarization become significant is reduced for larger wavelengths.

which the electrode structure is sensitive, the frequency at which the effects of space-charge polarization become significant is reduced for larger wavelengths. In other words, the frequency at which this transition is observed depends on the spatial wavelength of the electrode structure used in the measurement. At a given frequency, the electrode structure with the smaller wavelength will be sensitive to smaller displacements of the charged species from their equilibrium position. This is consistent with Eq. 7.58a which describes the frequency range over which the bipolar medium exhibits ohmic behavior in the limit of zero zeta potential and equal ion mobilities.

Section 7.6: Characteristic Responses
7.6.4 Zeta Potential

To examine the effect of a finite zeta potential on the effective dielectric properties of the bipolar medium, the value of the normalized zeta potential was varied from $-10$ to $+10$. All other parameters remained constant at their nominal value. The calculated gain and phase as well as the estimated values of the real and imaginary parts of the complex permittivity are plotted as a function of the temporal frequency in Fig. 7.11 for positive values of the zeta potential. Figure 7.12 shows the equivalent plots for negative values of the zeta potential. Lines (a), (b), and (c) correspond to values for the normalized zeta potential of $\pm 2$, $\pm 5$, and $\pm 10$. Instabilities in the numerical integration limited the frequency range over which the response could be computed.

The low-frequency value of the dielectric constant and the ohmic conductivity of the medium, calculated over the frequency range for which $\omega \tau \gg 1$, are plotted as a function of the zeta potential in Fig. 7.13. This figure shows that the low-frequency value of the dielectric constant increases exponentially for large values of the normalized zeta potential. This is consistent with the fact that, according to Eq. 7.15, the charge density at the interface between the dielectric layer and the bipolar medium increases exponentially with the zeta potential. This charge density leads to an increase in effective dielectric constant due to space-charge polarization at the interface.

The ratio of the effective conductivity to the bulk conductivity of the medium also increases exponentially for large values of the normalized zeta potential. Just as for the low-frequency value of the dielectric constant, this effect is due to the increased charge density in the double layer resulting from the adsorption of charge at the interface. Note that the shape of the curve is skewed toward negative values of the zeta potential. This is due to the fact that the mobility of the negative ions is greater than that of the positive ions. For equal magnitudes of the zeta potential, the effective conductivity is greater for positive values of the zeta potential because, in this case, the majority charge carriers in the double layer are the negative ions.

Over a small range of negative values for the normalized zeta potential, the effective conductivity of the medium is smaller than the bulk conductivity. To explain this phenomenon it is useful to consider the spatial distribution of the conductivity in the double layer.

\[
\sigma = \rho_+ b_+ + \rho_- b_-
\]

(7.68)

This is illustrated in Fig. 7.14, a plot of the product of the density and mobility of each charged species and the corresponding difference between the conductivity in the
Figure 7.11: Effect of positive values of the zeta potential on the frequency response of a microchip sensor and the estimated values of the effective dielectric properties of the medium. Lines (a), (b), and (c) correspond to values for the normalized zeta potential of 2, 5, and 10. This figure shows how the conduction in the bipolar medium is enhanced by the adsorption of ionized species on the interface.

Section 7.6: Characteristic Responses
Figure 7.12: Effect of negative values of the zeta potential on the frequency response of a microchip sensor and the estimated values of the effective dielectric properties of the medium. Lines (a), (b), and (c) correspond to values for the normalized zeta potential of $-2$, $-5$, and $-10$. This figure also shows how the conduction in the bipolar medium is enhanced by the adsorption of ionized species on the interface.
Figure 7.13: Plot of the low-frequency value of the dielectric constant and the ohmic conductivity of the medium as a function of the zeta potential. This figure shows that the normalized low-frequency value of the dielectric constant and the ratio of the effective conductivity to the bulk conductivity of the medium increases exponentially for large values of the normalized zeta potential. This effect is due to the increased charge density in the double layer resulting from the adsorption of charge at the interface.
double layer and the bulk conductivity of the medium as a function of the distance from the interface normalized to the Debye length. For small values of the normalized zeta potential, this figure shows that the conductivity in the double layer is everywhere smaller than the bulk conductivity. The selected value of —0.5 for the normalized zeta potential yields a difference as high as 6%. If the ratio of the mobilities were less than unity, the range of values for the zeta potential over which this phenomenon occurs would be positive. Finally, if the mobilities of the ionic species were equal, the conductivity in the double layer would everywhere be greater than the bulk conductivity of the medium.

As the spatial wavelength of the interdigital-electrode structure becomes much larger than the Debye length, the enhanced conduction associated with large values of the normalized zeta potential reduces to a surface conduction at the interface between the dielectric layer and the bipolar medium. This is clearly illustrated in Fig. 7.15, a plot of the calculated gain and phase for two structures with spatial wavelengths of 500 μm and 5000 μm as a function of the temporal frequency. The normalized wavenumber associated with these spatial wavelengths is 0.034 and 0.0034 respectively. Lines (a), (b), and (c) correspond to values for the normalized zeta potential of 5, 10, and 15. The surface conductivity associated with a value for the normalized zeta potential of 15 is 0.65 pS.

For large values of the normalized zeta potential, the response of each interdigital-electrode structure assumes a shape that is characteristic of a surface conductivity at the interface between the dielectric layer and the bipolar medium. This response is clearly distinguishable from the bulk response of the double layer. The slope of the gain is steeper and the gain has an overshoot. The phase curve is asymmetric and the phase peaks at a larger angle than the bulk response. All these are characteristics of a surface charge diffusion process [76].

Even though the incipience of the overshoot in the gain occurs at higher values of the zeta potential, the response associated with the larger wavelength converges to a surface response faster than the response associated with the smaller wavelength. This is consistent with the fact that the structure with the larger wavelength is less sensitive to the dispersive characteristics of the double layer. Furthermore, for the surface conduction to dominate the bulk conduction in the medium, the values of the surface conductivity and the wavenumber must be such that [76]

\[ \sigma_o \ll \sigma_s k \]  \hspace{1cm} (7.69)

For a given value of the bulk conductivity, the structure with the smaller wavelength will satisfy this condition for smaller values of the surface conductivity.
Figure 7.14: Plot of the product of the density and mobility of each charged species and the corresponding difference between the conductivity in the double layer and the bulk conductivity of the medium as a function of the distance from the interface normalized to the Debye length. For a value of $\zeta = -0.5$ for the normalized zeta potential, this figure shows that the conductivity in the double layer is smaller than the bulk conductivity by as much as 6%.
Figure 7.15: Effect of positive values of the zeta potential on the frequency response of interdigital-electrode structures with spatial wavelengths much larger than the Debye length. The values of the spatial wavelength are 500 μm and 5000 μm. The normalized wavenumber associated with these spatial wavelengths is 0.034 and 0.0034 respectively. Lines (a), (b), and (c) correspond to values for the normalized zeta potential of 5, 10, and 15. This figure shows how large values of the normalized zeta potential give rise to a response that is characteristic of a surface conduction at the interface between the dielectric layer and the bipolar medium. The surface conductivity associated with a value for the normalized zeta potential of 15 is 0.65 pS.
7.6.5 Parameters Associated with Neutrals

With all remaining parameters maintained at their nominal values, each of the double layer parameters associated with the neutral density was varied individually to examine their effect on the dielectric properties of the bipolar medium. In particular, the ionization fraction was varied from 1% to 90%, the diffusion factor was varied from 0.01 to 100, the normalized recombination coefficient was varied from 0.01 to 100, and the order of generation kinetics was varied from 0 to 4. All of these variations yielded insignificant changes in the calculated gain and phase, even with nonzero values of the normalized zeta potential.

These results suggest that the neutrals do not participate in the dynamics of the double layer. This is consistent with the expression for the surface capacitance density of the double layer derived in the limit of zero zeta potential and equal ion mobilities, Eq. 7.60. Because the magnitude of the applied electric field is small compared with that associated with the double layer and the interface between the dielectric layer and the bipolar medium is passive, the applied electric field only perturbs the equilibrium charge distribution. As a result, generation and recombination effectively balance everywhere in the system and the neutrals appear to be stationary. The effect of the parameters associated with the neutrals is expected to become significant as the magnitude of the applied electric field becomes comparable to the magnitude of the self-field in the double layer and higher-order terms are included in the series expansion of the electrical variables.

7.7 Experimental Results

The heterogeneity of the double layer was verified experimentally by measuring the effective dielectric properties of transformer oil with the microchip, flex, and three-wavelength sensors. The electrodes of each sensor were coated with a thin Parylene layer which is assumed to provide a passive boundary between the dielectric and the medium. This experiment was motivated by the results shown in Fig. 6.13, a plot of the frequency dependence of the dielectric properties of transformer oil showing space-charge polarization associated with a double layer at the Parylene/oil interface.

The frequency response of the sensors in used Shell Diala A transformer oil at room temperature is shown in Fig. 7.16. The responses are associated with spatial wavelengths of 50 μm (microchip), 1 mm (flex), and 5 mm (three-wavelength). Only the response of the largest wavelength (5 mm) of the three-wavelength sensor is shown. From this figure it can be seen that the high-frequency gain of the microchip sensor is affected by

Section 7.7: Experimental Results
the slight dispersive nature of the Parylene. The high-frequency gain of the other two sensors is not significantly affected because these structures have spatial wavelengths that are much larger than the thickness of the Parylene layer and therefore are relatively insensitive to variations in the dielectric properties of the Parylene.

In order to account for the dispersive nature of Parylene in the estimation of the effective dielectric properties of transformer oil as seen by the microchip sensor, the experimental data shown in Fig. 6.6 was used to estimate the dielectric properties of Parylene at each measurement frequency. The results of this calculation are shown in Fig. 7.17. This figure shows that the relaxation frequency associated with the spectrum of the dielectric properties of Parylene is greater than 10 kHz.

Using these calculated values, the dielectric properties of transformer oil were estimated at each measurement frequency for the microchip sensor. For the larger wavelengths, the Parylene was assumed to be a perfect insulator with a value for the permittivity of 3.05ε₀. In these estimations we tacitly assumed that the estimated dielectric properties of Parylene are not affected by the oil. The results of these calculations are shown in Fig. 7.18.

The solid line drawn in the plot of the dielectric constant represents the estimated high-frequency value of 2.19 ε₀; that drawn in the plot of the loss factor represents a least-squares fit of the data for the flex sensor to a straight line. The correlation coefficient for this fit was calculated to be 0.99995 with a probability $P_{33}(|r| \geq 0.99995)$ less than 0.05% indicating a highly significant correlation. The slope of the line was calculated to be $-0.974 \pm 0.002$ indicating that the oil exhibits nearly ohmic behavior. An ohmic medium would yield a slope of $-1$. From the intercept of the line the conductivity of the oil was calculated to be 10.94 ± 0.05 pS/m. Using this value, together with the nominal values for the parameters describing the bipolar medium given in Table 7.3, the thickness of the double layer was calculated to be 8.2 μm.

The values of the parameters and the uncertainties associated with the loss factor were calculated using the program leastsq.f90 listed in Appendix M with the help of Eq. A.18a. The uncertainty in the measurement of the frequency was assumed to be insignificant compared with the uncertainty in the measurement of the dielectric loss. Furthermore, because the estimation was performed using the logarithm of the normalized dielectric loss, we assumed equal fractional uncertainty rather than equal absolute uncertainty in the measurement of the dielectric loss. This assumption is valid considering the wide range of values measured.

The effect of the spatial wavelength on the frequency response of the dielectric properties of transformer oil is similar to that shown in Fig. 7.9. The effects of space-charge
Figure 7.16: Frequency response of interdigital-electrode structures in used Shell Di-
ala A transformer oil at room temperature. The responses are associated with spatial
wavelengths of 50 μm (microchip), 1 mm (flex), and 5 mm (three-wavelength). Only
the response of the largest wavelength (5 mm) of the three-wavelength sensor is shown.
From this figure it can be seen that the high-frequency gain of the microchip sensor
is affected by the slight dispersive nature of the Parylene. The high-frequency gain of
the other two sensors is not significantly affected because these structures have spatial
wavelengths that are much larger than the thickness of the Parylene layer and therefore
are relatively insensitive to variations in the dielectric properties of Parylene.

Section 7.7: Experimental Results
Figure 7.17: Frequency dependence of the dielectric properties of Parylene estimated from the experimental data shown in Fig. 6.6. This figure shows that the relaxation frequency associated with the spectrum of the dielectric properties of Parylene is greater than 10 kHz.
Figure 7.18: Verification of the heterogeneity of the double layer in used Shell Diala A transformer oil at room temperature. The solid line drawn in the plot of the dielectric constant represents the estimated high-frequency value of 2.19 $\varepsilon_0$; that drawn in the plot of the loss factor represents a least-squares fit of the data for the flex sensor to a straight line. From the intercept of the line the conductivity of the oil was calculated to be 10.94 ± 0.05 pS/m, which corresponds to a double-layer thickness of 8.2 $\mu$m.
polarization are clearly evident in the real part of the complex permittivity and the frequency at which the polarization effects become significant decreases with increasing wavelength. Over the frequency range examined, the imaginary part of the complex permittivity measured by the two larger wavelengths does not appear to be affected by space-charge polarization. Only the electrode structure with the smallest wavelength shows significant deviations from the ohmic response. This is consistent with the observation that the frequency range over which the bipolar medium exhibits ohmic behavior increases with the spatial wavelength.

The model used to describe the response of the electrode structure to a double layer assumes that the bipolar medium is perturbed by an applied electric field whose magnitude is small compared with the self-field of the double layer. This criterion is not met in the experiments. The magnitude of the self-field can be estimated to be

\[ E_{dl} \approx \frac{V_T}{l_D} = 3.1 \text{ kV/m} \]  

where the thickness of the double layer obtained from the measurement of the bulk conductivity and the value of the thermal voltage at room temperature were used in the calculation.

The magnitude of the electric field at the Parylene/oil interface can be estimated by assuming that the medium above the electrodes is homogeneous and the electric field in the medium is described by the fundamental mode associated with the spatial distribution of the imposed potential. Thus, the electric field at a distance \( d \) from the surface of the electrodes can be expressed as

\[ E_{ac} \approx V_0 e^{-kd} \]  

where \( V_0 \) is the peak magnitude of the applied voltage and \( k \) is the wavenumber of the fundamental mode which is related to the spatial wavelength by Eq. 7.29.

The value of the electric field at the Parylene/oil interface is tabulated in Table 7.4 for the three spatial wavelengths associated with the microchip, flex, and three-wavelength sensors. In these calculations, a nominal value of 5 \( \mu \text{m} \) was used for the thickness of the Parylene layer and a value of 1 V was used for the peak magnitude of the applied voltage. Comparison of these values with that associated with the double layer shows that the criterion is not met by the two sensors with the smaller wavelengths and is marginally satisfied by the sensor with the largest wavelength. As a result, the model cannot be used to extract double layer parameters from the experimental data. Note that the value of the applied electric field associated with the microchip sensor is large
Table 7.4: Magnitude of the applied electric field at the Parylene/oil interface for the microchip, flex, and three-wavelength sensors.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>λ (µm)</th>
<th>$E_{ac}$ (kV/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microchip</td>
<td>50</td>
<td>67.0</td>
</tr>
<tr>
<td>Flex</td>
<td>1000</td>
<td>6.1</td>
</tr>
<tr>
<td>Three-wavelength</td>
<td>5000</td>
<td>1.2</td>
</tr>
</tbody>
</table>

enough to significantly affect the structure of the double layer.

Because the magnitude of the applied electric field at the Parylene/oil interface is larger than the self-field associated with the double layer, the distribution of charge in the double layer is significantly disrupted from its equilibrium condition. At a given frequency, the effects due to space-charge polarization are reduced by the increased migration of the ions. As a result, the effective dielectric properties of the medium lead to underestimates of the mobilities of the ions. In fact, the ionic mobilities estimated from the data shown in Fig. 7.18 are one order of magnitude smaller than those reported in the literature [60, 99].

### 7.8 Summary

A self-consistent model was developed to describe the response of an interdigital-electrode structure to a diffuse double layer. The magnitude of the applied AC field was assumed to be sufficiently small that the double layer was only slightly perturbed from its stationary equilibrium. As a result, the electrical variables were linearized about their equilibrium values. The sensitivity of the response to the parameters describing the double layer was examined by calculating the gain and phase and estimating from these values the effective dielectric properties of the bipolar medium.

The frequency spectrum associated with the effective dielectric properties of the double layer was shown to exhibit characteristics associated with space-charge polarization. Because such a spectrum is indistinguishable from the polarization spectrum associated with simple dipole orientation, it is described by the Debye dispersion relation. One characteristic of this spectrum is that, at high frequencies ($\omega \tau \gg 1$), the dielectric properties of the bipolar medium follow those of an ohmic medium with the permittivity and bulk conductivity of the fluid.

The increase in the low-frequency value of the dielectric constant was shown to be consistent with the formation of two space-charge layers separated a distance equal to

Section 7.8: Summary
the Debye length. In addition, the space-charge time constant used to describe the Debye dispersion relation was shown to be associated with the migration of the ions in the bipolar medium. This time constant also reflects the relative length scales in the system associated with the spatial wavelength of the electrode structure.

The effect of a finite zeta potential on the effective dielectric properties of the medium revealed that the low-frequency value of the dielectric constant and the ohmic conductivity of the medium were enhanced by the increased space charge in the double layer. The difference in the values of the ionic mobilities yielded an asymmetry in the response of the electrode structure to positive and negative values of the zeta potential. The asymmetry was found to be consistent with the mobility of the majority carrier in the double layer. For small values of the normalized zeta potential, a narrow regime was identified in which the conductivity of the double layer is smaller than the bulk conductivity of the medium. For large values of the normalized zeta potential, the response of electrode structures with spatial wavelengths large compared with the Debye length was shown to reduce to a response associated with a surface conductivity at the interface between the dielectric layer and an ohmic infinite half-space with the permittivity and bulk conductivity of the fluid. This feature is explored in Appendix L as a means to measure the mobility of the ionic species.

The lack of sensitivity of the calculated response to the parameters associated with the neutrals indicated that, for the choice of parameters used to describe the bipolar medium, the neutrals do not participate in the dynamics of the double layer. The assumptions made in the model about the magnitude of the applied electric field and the boundary conditions used to describe the interface between the dielectric layer and the bipolar medium were implicated in these results. Under such conditions the applied electric field only perturbs the equilibrium charge distribution such that the neutrals appear to be stationary.

Because the bipolar medium is heterogeneous, its representation in terms of a single set of dielectric properties led to estimated values that depend on the spatial wavelength of the electrode structure. In particular, because the spatial wavelength determines the length scale over which the electrode structure is sensitive, the frequency at which the effects of space-charge polarization become significant was reduced for larger wavelengths. This was shown to be consistent with the expression describing the frequency range over which the bipolar medium exhibits ohmic behavior derived in the limit of zero zeta potential and equal ion mobilities.

The heterogeneity of the double layer was verified experimentally through a measurement of the dielectric properties of transformer oil by means of electrode structures with
spatial wavelengths ranging from 50 μm to 5 mm. The experimental results were shown to be consistent with the observation that the frequency range over which the bipolar medium exhibits ohmic behavior increases with the spatial wavelength. Quantitative estimates of the parameters of the double layer were not performed due to the fact that the magnitude of the applied field at the interface between the dielectric layer and the bipolar medium was not small compared with the self-field of the double layer.
Chapter 8

Conclusions and Future Work

The purpose of this chapter is to discuss the implications of the results of the thesis and provide suggestions for future research. The chapter is subdivided into a number of sections corresponding to each of the main topics in the thesis.

8.1 Equilibrium Relations

Thermodynamic principles were used to show the usefulness of relative saturation in describing the equilibrium between two systems in partial mutual stable equilibrium. For mixtures in which at least one constituent exhibits ideal behavior, such as the oil in a single-phase mixture of water and oil, relative saturation is defined as the ratio of the mole fraction of the trace constituent to the mole fraction of the same constituent under saturated conditions. Thus, relative saturation is defined only for temperatures and pressures at which the pure constituent exhibits saturation in the mixture. For example, relative humidity, the relative saturation of water in air, is defined only for temperatures below the boiling point of water.

The equality of relative saturation is a direct consequence of the condition of chemical potential equality derived from the first and second laws of thermodynamics. For two-phase mixtures this equality represents an alternative form of Henry's law. In fact, according to Eq. 3.60, Henry's constant is inversely proportional to the solubility of the constituent in the fluid. Expressed in terms of the relative saturation of the constituent, this form of the equilibrium relation provides a more intuitive way to understand the relationship between the concentration of the constituent in the two systems.

A practical application of the equality of relative saturation involves the calibration of sensors that measure the concentration of trace constituents in liquid or solid mixtures by means of an auxiliary system. For example, the Leeds & Northrup sensor measures the concentration of water in oil through the moisture-induced change in permittivity of
a polyimide layer. If the property being measured in the auxiliary system depends on the relative saturation of the constituent and not on any other constituent in the mixture, the sensor can be calibrated in the gas phase rather than the liquid or solid phase. In the case of the Leeds & Northrup sensor, the measurement of relative humidity is easier than the measurement of the moisture content of the oil.

The expression for the chemical potential of a constituent is the key to deriving the equilibrium relation that describes the partitioning of the constituent between two interacting systems. The chemical potential of constituents in ideal and semi-ideal mixtures is well known. The chemical potential of constituents in nonideal mixtures, mixtures where none of the constituents exhibit ideal behavior, remains a topic of further research. The tools of quantum thermodynamics could provide the basis for the development of the chemical potential of constituents in nonideal mixtures [100, 101, 102, 103]. Just as for polymeric mixtures, it is expected that these expressions would contain a parameter similar to the polymer-solvent interaction parameter.

### 8.2 Moisture Sensor

If any of the electromagnetic properties of a mixture depend on the concentration of a constituent in the mixture, the amount of the constituent can be determined by measuring the electromagnetic properties of the system. The moisture content of transformer pressboard, for example, can be determined by measuring dielectric properties of the pressboard because of the strong dependence of the dielectric properties on the amount of moisture present in the pressboard. If the electromagnetic properties of the mixture are not affected by the presence of the constituent, the concentration may be determined by allowing the mixture to interact with an auxiliary system whose electromagnetic properties are affected by the constituent. In the application of the Leeds & Northrup sensor to the measurement of the moisture content of transformer oil, water is the constituent of interest and the polyimide-water mixture is the auxiliary system. The electromagnetic property being measured is the permittivity of the polyimide-water mixture. The Leeds & Northrup sensor is just one example of a class of sensors that relies on an auxiliary system to measure the properties of a system.

The constitutive relation for the electromagnetic properties of the auxiliary system together with the equilibrium relation describing the relationship between the concentration of the constituent in the two systems allows the concentration of the constituent in the mixture to be determined through a measurement of the electromagnetic properties of the auxiliary system. In practice, the electromagnetic properties of the auxiliary sys-
tem are directly correlated to the concentration of the constituent in the mixture. This information can be used to determine either the constitutive relation or the equilibrium relation if one of them is known or can be empirically determined. In the case of the Leeds & Northrup sensor, the constitutive relation was obtained using an equilibrium relation derived from fundamental thermodynamic principles.

The expression for the chemical potential of water in polyimide accounts for the interaction between the water and the polyimide molecules through the polymer-solvent interaction parameter. An estimate of this parameter can be obtained by measuring the amount of water absorbed in polyimide as a function of the relative humidity of the air in contact with the polyimide. The dipole moment of the water molecule in polyimide has been found to be nearly equal to that of a free water molecule [42, 44]. As such, the polymer-solvent interaction parameter for water in polyimide is expected to be negative.

The Leeds & Northrup sensor can be used to measure the diffusion coefficient of water in materials that can be applied on the surface of the sensor. By subjecting the sensor to a step change in the relative humidity of the air, the diffusion coefficient can be estimated from the step response of the sensor. Because the constitutive relation for the permittivity of the polyimide assumes that the moisture in the sensor is uniformly distributed, the thickness of the material should be such that the time constant associated with the diffusion of water across the material is long compared with the time constant associated with the diffusion of water across the two polyimide layers. Assuming a value of $1.0 \times 10^{-13}$ m$^2$/s for the diffusion coefficient of water in the material and a value of 10 s for the time constant associated with the diffusion of water across the polyimide, this constraint requires the thickness of the material to be much larger than 1 $\mu$m.

The insights obtained from the dynamic measurements of relative saturation highlight the difficulty in interpreting moisture data taken on a transformer during a cooling cycle. As demonstrated in Section 4.5, the Leeds & Northrup sensor responds to the moisture dissolved in the oil adjacent to the sensor. As such, it cannot be used to obtain information about the heterogeneity of the moisture in the system under dynamic conditions. Thus, a measurement indicating nearly saturated conditions may, in fact, be associated with the presence of free water in the bulk of the oil.

### 8.3 Moisture Dynamics

The description of the spatial and temporal evolution of moisture in the Couette Facility required the solution of a non-self-adjoint problem. This example is part of a class of problems involving diffusion subject to an integral constraint [104]. Such problems
describe, for example, the diffusion of heat in a rod subject to a constraint on the energy of the system [69, 105]. In the formulation of the moisture dynamics in the Couette Facility, mass conservation represented the integral constraint. Because of the similarities associated with these types of problems, the numerical technique developed can be applied to solve other parabolic partial differential equations subject to integral constraints.

Comparison of the thermal and molecular time constants in the Couette Facility indicated that the temperature of the system could be assumed to remain uniform throughout the transient. Under conditions in which the pressboard supports a temperature gradient, the Soret effect augments the flux of water due concentration gradients in the paper and the diffusion sublayer. Even though the Soret coefficient in paper is not known, the procedure outlined in Appendix C provides a way to estimate its value by measuring the equilibrium distribution of moisture resulting from an imposed thermal gradient.

As formulated, the model assumes that the initial conditions in the pressboard are described by a uniform distribution. This assumption is valid only when the system is in equilibrium. This is not the case for power transformers where the period associated with variations in the load is typically smaller than the time constant associated with the diffusion of water in the pressboard. Load variations in a transformer result in changes in the temperature of the windings and the electrical insulation. To understand the implications of this ordering of time constants, future efforts should focus on the moisture dynamics of paper/oil systems under conditions in which the temperature is periodically cycled between two values. The understanding developed from such an analysis would provide a starting point for the estimation of the average moisture content of the pressboard in a transformer from measurements of the temperature and moisture content of the oil.

For lack of any available models that describe the moisture dynamics in a transformer, the average moisture content of the pressboard is commonly estimated using equilibrium isotherms such as those depicted in Fig. 5.2. The error associated with such an estimate decreases as the transformer approaches equilibrium. An underestimate of this equilibration time is given by the apparent equilibrium time defined by Eq. 5.48. This time was shown to be at least one order of magnitude smaller than the time constant for equilibrium. Furthermore, because the Reynolds number of the oil in the ducts of a transformer is typically smaller than that of the oil in the Couette Facility, the equilibration time in a transformer will be even longer. Even though the precise value of this time constant cannot be easily determined, the apparent equilibrium time provides
a lower bound for the time required to insure accuracy in the estimate of the average moisture content of the pressboard in a transformer using equilibrium relations.

Experimental results derived from transient experiments in the Couette Facility were used to estimate the molecular diffusion coefficient of water in oil and oil-imregnated pressboard. Because the fluctuations in the turbulent core penetrate the diffusion sublayer, the estimated value of the diffusion coefficient of water in oil is an overestimate. Furthermore, lack of knowledge about the effect of the surface roughness of the pressboard on the shear stress at the wall resulted in uncertainties in the estimated value of the diffusion coefficient. Future efforts should be directed at examining the fluid dynamics in this sublayer region in order to correlate the rotational rate of the inner cylinder to the diffusion sublayer thickness at the paper/oil interface.

The Couette Facility was originally developed to study the charge transfer process at paper/oil interfaces. The understanding of the moisture dynamics in this facility provides the opportunity to explore the coupling between the interfacial moisture and the electrochemical nature of the interface. In addition, because the dielectric properties of pressboard are strongly dependent on the moisture content, the distribution of moisture in the pressboard will affect the leakage process. It is the competition between this process and that associated with charge accumulation that determines the maximum amount of charge that can be stored at the interface.

8.4 Flexible Sensors

The development of flexible sensors to measure the dielectric properties of insulating materials led to the identification of parasitic structures that were not accounted for by the continuum model developed by Zaretsky et al. [76]. The identification came about as a result of the discrepancy between the measured value of the high-frequency gain in air and the value estimated from the nominal values of the parameters describing the sensor. Uncertainties in the values of the parameters were not sufficient to account for the difference. The discrepancy was shown to be due to the capacitance associated with the finite thickness of the electrodes. This parasitic capacitance was estimated to be a significant fraction of the modeled capacitance between the driven and sensing electrodes. To account for the finite thickness of the electrodes, it is necessary to modify the way in which the model deals with the interface between the medium above the electrodes and the substrate. What is required is a collocation of the potential along the upper plane of the electrodes in addition to the collocation of the potential along the lower plane of the electrodes.
The substrate of the flexible sensors is composed of polyimide, whose dielectric constant depends on the amount of water absorbed from the environment. A variation in the permittivity of the polyimide corresponding to a change from dry to wet conditions would result in a change of 1 dB in the measured gain of the sensor. To prevent such variations, the sensors were coated with Parylene, a hydrophobic polymer. Because Parylene is not completely impermeable to water [85], the presence of this layer only slows down the absorption of moisture into the sensor. The sensitivity and response time of the Leeds & Northrup sensor could be used to determine the rate of water absorption into the substrate of the flexible sensors. In the proposed experiment, the diffusion coefficient of water in Parylene could be measured by monitoring the absorption of moisture into a Parylene-coated Leeds & Northrup sensor exposed to a humid environment.

The estimation of the dielectric properties of solids such as pressboard is limited by the uncertainty in the thickness of the ubiquitous gap between the surface of the electrodes and the material under test. If the sensor is Parylene-coated, the gap lies between the top surface of the Parylene layer and the bottom surface of the solid. In order to estimate the dielectric properties of the solid, the thickness and dielectric properties of the material in this gap have to be known a priori. If the material in the gap is more insulating than the solid and its dielectric constant is known, the thickness of the gap can be estimated from measurements of the low-frequency gain. This process requires that the material under test be sufficiently conducting that the low-frequency gain reaches a plateau as the phase approaches zero. In this regime, the solid acts as a 'perfect conductor'. For such a plateau to exist at 5 mHz, the conductivity of the material under test must be greater than 10 pS/m. To avoid the problem associated with the uncertainty in the thickness of the gap, it may be possible to position the material under test at a known distance from the surface of the sensor. Because the penetration depth of the electric field associated with an interdigital-electrode structure is at most a third of the wavelength, this approach requires that the spatial wavelength of the sensor be much larger than the thickness of the gap.

A three-wavelength interdigital-electrode structure was used to examine the heterogeneity of the dielectric properties of transformer pressboard during moisture absorption. Even though the experimental results yielded an estimate of the diffusion coefficient of water in oil-free pressboard at room temperature, the data could not be used to estimate the dielectric properties of the pressboard during the transient. Parameter estimation techniques are available which yield a stair-step distribution of the dielectric properties in a medium from measurements performed with multiple-wavelength interdigital-electrode structures [77]. Unfortunately, design and fabrication issues resulted in anomalous pos-
itive phase shifts that cannot be explained using the continuum model developed for the sensor [76]. This effect can be seen in Fig. 6.18 at frequencies below 10 mHz. Future efforts should address these issues by measuring the cross talk between the three wavelengths on the sensor and examining the effect of the triangular ground pads on the plane of the electrodes (see Fig. 6.16).

The use of multiple-wavelength interdigital-electrode structures can provide useful information about the electrical characteristics of the insulation used to study flow electrification in the Couette Facility. For example, the leakage process and field distribution in the pressboard can be better understood by monitoring the spatial distribution of the loss factor in the pressboard. In addition, the measurement of the effective dielectric properties of the double layer at the paper/oil interface can be used to obtain estimates of the electrokinetic parameters describing the charge generation process. Given typical values of the zeta potential [29, 106], it appears difficult to perform this latter measurement with an interdigital-electrode structure located behind the pressboard. The frequency at which the effects of space-charge polarization become significant is reduced for electrode structures with spatial wavelengths large compared with the Debye length. The only way to achieve such a measurement would be to imbed a sensor in the pressboard a fraction of a Debye length away from the paper/oil interface. Unfortunately, this technique would prevent the diffusion of moisture at the interface thereby precluding the opportunity to study the correlation between the interfacial moisture content and the electrochemical nature of the interface.

8.5 Double Layer

The results derived from the double-layer model indicate that fluids in which the conduction is dominated by ionic species are dispersive in nature. In the high-frequency range, where the effects of space-charge polarization are not significant, the dielectric properties of the fluid exhibit ohmic behavior. Below this frequency range, the effects of space-charge polarization dominate the response of the bipolar medium and the dielectric properties of the fluid no longer exhibit ohmic behavior. This description contributed to the understanding of the increased low-frequency polarization observed in the measurement of the dielectric properties of transformer oil with interdigital-electrode structures. The qualitative agreement between the predictions of the model and the experimental results suggests that conduction in transformer oil is dominated by ionizable species.

The dispersive nature of the double layer has important implications on the measurement of the dielectric properties of oil-impregnated paper. Because the paper is typically
not in intimate contact with the electrodes of the interdigital-electrode structure, the
gap between the paper and the electrodes is filled with oil. The low-frequency dispersion
associated with the double layer in the oil layer can mask the dispersive properties of the
paper and lead to erroneous measurements. The magnitude of the error is determined
by the relative location of the measurement frequency and the frequency at which the
effects of space-charge polarization become significant. Because the frequency at which
this transition is observed depends on the spatial wavelength of the interdigital-electrode
structure, the magnitude of the error will be reduced for electrode structures with wave-
lengths large compared with the Debye length. If the values of the parameters describing
the bipolar medium are known, the expression derived for the surface capacitance den-
sity of the double layer allows these effects to be taken into account in the parameter
estimation algorithm.

In the description of the double layer, the assumed boundary conditions model the
interface between the dielectric layer and the bipolar medium as a passive boundary,
where the fluxes of the charged and neutral species are zero. These conditions imply
that the frequency of the excitation signal is sufficiently high so that the time constant
associated with physicochemical reactions at the interface is long compared with the
period of the applied signal. If this is not the case, the boundary conditions proposed
in Appendix K provide an alternative description of the fluxes in terms of reaction rate
constants. For systems in which the dynamics at the boundary affect the concentration
of the ionic species in the volume, the reaction rates would play a role in determining
the distribution of the charged species in the medium.

The experimental results described in Section 7.7 provided only a qualitative veri-
fication of the double-layer model. In the formulation of the model, the magnitude of
the applied electric field at the interface between the dielectric layer and the bipolar
medium was assumed to be small compared with the self-field of the double layer. This
assumption was not satisfied in the experiments. Future efforts should insure that this
assumption is met by decreasing the magnitude of the driven signal while maintaining a
reasonable signal-to-noise ratio. The results of these experiments could lead to accurate
estimates of the mobility of the ions in the medium. The concept of a voltage-controlled
double layer, introduced in Appendix L, should also be explored further as a technique
to measure the mobility of ions in fluids. Because the charge density in the double layer
can be augmented by applying a bias field across the adjacent dielectric, this technique
could be used to enhance the electrohydrodynamic pumping of semi-insulating fluids.
Appendix A

Least-Squares Fitting of Exponential Functions

One of the most important functions in physics and engineering is the exponential function

\[ y = Ae^{Bx} \]  \hspace{1cm} \text{(A.1)}

where \(A\) and \(B\) are constants. Given a set of measured points \((x_1, y_1), \ldots, (x_N, y_N)\) we wish to obtain values of the coefficients \(A\) and \(B\) that best fit the data. To simplify the solution to this problem, we can transform this nonlinear relation between the two variables \(x\) and \(y\) into a linear relation by taking the logarithm of both sides of the equation. This operation results in the following linear relation between the same variable \(x\) and a new variable \(z\).

\[ z = C + Dx \]  \hspace{1cm} \text{(A.2)}

where

\[ z = \log_a y \]
\[ C = \log_a A \]
\[ D = B \log_a e \]  \hspace{1cm} \text{(A.3)}

Thus, given a set of measured points \((x_1, y_1), \ldots, (x_N, y_N)\), we can compute the set of points \((x_1, z_1), \ldots, (x_N, z_N)\) and use the method of least-squares to obtain values of the coefficients \(C\) and \(D\) and consequently values for the coefficients of interest \(A\) and \(B\).

In the calculation of the coefficients \(A\) and \(B\) we assume that, while the measurements of \(y\) suffer some uncertainty, the uncertainty in the measurements of \(x\) is insignificant. In addition, we assume that the uncertainties in \(y\) all have the same magnitude and that

\[ \text{This derivation is parallel to that given by Taylor in Reference [49: Chapter 8].} \]
the measurements of each \( y_i \) are described by a Gaussian distribution with the same standard deviation. Even though the uncertainties in \( y \) are equal, the uncertainties in \( z \) will not be. In fact, simple error propagation gives the following relation between the uncertainties of the two variables \([49: \text{Section 3.9}]\).

\[
\sigma_z = \left| \frac{dz}{dy} \right| \sigma_y = (\log_e e) \frac{\sigma_y}{|y|} \tag{A.4}
\]

Because we assumed that each value \( z_i \) has no uncertainty, the true value of \( z_i \) can be computed using the expression

\[
\tilde{z}_i = \tilde{C} + \tilde{D}x_i \tag{A.5}
\]

where a tilde denotes the value of the parameter obtained from an infinite number of measurements. The value of each \( z_i \) is governed by a normal distribution centered on its true value \( \tilde{z}_i \) with a standard deviation \( \tilde{\sigma}_{z_i} \). Thus, the probability of obtaining the value \( z_i \) can be expressed as

\[
P(z_i) \propto \frac{1}{\tilde{\sigma}_{z_i}} e^{-\left(\frac{z_i - \tilde{z}_i}{\tilde{\sigma}_{z_i}}\right)^2} \tag{A.6}
\]

Because the measurements of \( y \) are independent, the probability of obtaining the complete set of values \( z_1, \ldots, z_N \) is equal to the product of each of the probabilities

\[
P(z_1, \ldots, z_N) = P(z_1) \cdots P(z_N) \propto \frac{1}{\prod_{i=1}^{N} \tilde{\sigma}_{z_i}} e^{-\chi^2 / 2} \tag{A.7}
\]

where the exponent is given by

\[
\chi^2 = \sum_{i=1}^{N} \frac{(z_i - \tilde{C} - \tilde{D}x_i)^2}{\tilde{\sigma}_{z_i}^2} \tag{A.8}
\]

According to the principle of maximum likelihood, the best estimates for the unknown coefficients \( \tilde{C} \) and \( \tilde{D} \) are those values for which the probability \( P(z_1, \ldots, z_N) \) is maximum or the sum of squares \( \chi^2 \) is minimum. This can be expressed using the rules of calculus by the equations

\[
\frac{\partial \chi^2}{\partial \tilde{C}} = -2 \sum_{i=1}^{N} \tilde{w}_i (z_i - \tilde{C} - \tilde{D}x_i) = 0 \tag{A.9}
\]

\[
\frac{\partial \chi^2}{\partial \tilde{D}} = -2 \sum_{i=1}^{N} \tilde{w}_i x_i (z_i - \tilde{C} - \tilde{D}x_i) = 0
\]
where \( \bar{w}_i = 1/\hat{\sigma}_i^2 \), which can be rewritten in the following convenient form.

\[
C \sum w_i + D \sum w_i x_i = \sum w_i z_i \\
C \sum w_i x_i + D \sum w_i x_i^2 = \sum w_i x_i z_i
\]  
(A.10)

This set of equations can be solved to give the least-squares estimates for the coefficients \( \hat{C} \) and \( \hat{D} \).

\[
C = \frac{(\sum w_i x_i^2)(\sum w_i z_i) - (\sum w_i x_i)(\sum w_i x_i z_i)}{(\sum w_i)(\sum w_i x_i^2) - (\sum w_i x_i)^2} \\
D = \frac{(\sum w_i)(\sum w_i x_i z_i) - (\sum w_i x_i)(\sum w_i z_i)}{(\sum w_i)(\sum w_i x_i^2) - (\sum w_i x_i)^2}
\]  
(A.11)

Note that these two equations represent the solution of a linear least-squares problem with unequal uncertainties in one of the variables. In this case, Eq. A.4 gives

\[
w_i = \frac{1}{\sigma_i^2} = \frac{y_i^2}{(\sigma_y \log a e)^2}
\]  
(A.12)

and, because the uncertainties in \( y \) are assumed equal, the least-squares estimates for the coefficients \( \hat{C} \) and \( \hat{D} \) reduce to

\[
C = \frac{(\sum x_i^2 y_i^2)(\sum y_i^2 z_i) - (\sum x_i y_i^2)(\sum x_i y_i^2 z_i)}{(\sum y_i^2)(\sum x_i^2 y_i^2) - (\sum x_i y_i^2)^2} \\
D = \frac{(\sum y_i^2)(\sum x_i y_i^2 z_i) - (\sum x_i y_i^2)(\sum y_i^2 z_i)}{(\sum y_i^2)(\sum x_i y_i^2) - (\sum x_i y_i^2)^2}
\]  
(A.13)

Because the estimates of the coefficients are well-defined functions of the measured values \( y_1, \ldots, y_N \) and the uncertainty \( \sigma_y \) is the same for all measured values of \( y \), we can use the error propagation formulas [49: Section 3.9]

\[
\sigma_C^2 = \sigma_y^2 \sum_{i=1}^N \left( \frac{\partial C}{\partial y_i} \right)^2 \\
\sigma_B^2 = \sigma_y^2 \sum_{i=1}^N \left( \frac{\partial D}{\partial y_i} \right)^2
\]  
(A.14)

to compute the squares of the uncertainties in the coefficients \( C \) and \( D \). Due to the complexity of Eqs. A.13, evaluation of these uncertainties is best done numerically.

Even though in the course of measuring the values \( y_1, \ldots, y_N \) we have formed some idea of their uncertainty, it is possible to estimate the uncertainty \( \hat{\sigma}_y \) using the principle of maximum likelihood. The best estimate of this uncertainty is the value for which

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the probability of obtaining the measured values \( y_1, \ldots, y_N \) is maximum. Differentiating Eq. A.7 with respect to \( \sigma_y^2 \) and setting the resulting expression to zero, we obtain the best estimate for the square of the uncertainty in the measurement of \( y \).

\[
\sigma_y^2 = \frac{1}{N} \sum_{i=1}^{N} \left[ \frac{y_i(z_i - \tilde{C} - \tilde{D}x_i)}{\log_a e} \right]^2 \quad (A.15)
\]

Because the result is expressed in terms of the true values of the coefficients, this estimate of the uncertainty is not useful. If, in place of these values, we use the best estimates for the values of the coefficients, the factor \( N \) in the denominator must be replaced by the number of degrees of freedom, the number of independent measurements minus the number of parameters calculated from these measurements. In this case, the computation of the best estimates for the two coefficients reduces the number of degrees of freedom by two so that the best estimate of the uncertainty becomes

\[
\sigma_y^2 = \frac{1}{N - 2} \sum_{i=1}^{N} \left[ \frac{y_i(z_i - C - Dx_i)}{\log_a e} \right]^2 \quad (A.16)
\]

In summary, the best estimates for the unknown coefficients \( \tilde{A} \) and \( \tilde{B} \) are obtained from Eqs. A.3,

\[
\begin{align*}
A &= a^C \\
B &= \frac{D}{\log_a e}
\end{align*}
\quad (A.17)
\]

together with Eqs. A.13. In addition, the uncertainties in the coefficients \( A \) and \( B \) can be expressed using principles of error propagation as \[49: \text{Section 3.9}\]

\[
\begin{align*}
\sigma_A &= \left( \frac{|A|}{\log_a e} \right) \sigma_C \\
\sigma_B &= \left( \frac{1}{\log_a e} \right) \sigma_D
\end{align*}
\quad (A.18)
\]

where the uncertainties in the coefficients \( C \) and \( D \) are given by Eqs. A.14.
Appendix B

Transport of Moisture in Oil-Impregnated Paper

The equation of continuity for moisture in oil-impregnated paper may be written as [107: Section 18.1]

\[
\frac{\partial \rho_w}{\partial t} + \nabla \cdot \bar{\Gamma}_w = G_w - R_w
\]  

(B.1)

where the mass concentration \( \rho_w \) is the mass of water per unit volume of solution. The word 'solution' in this case represents a single-phase mixture of water, oil, and paper. The terms on the right-hand side of the equation represent the rate of production and depletion of water by chemical reaction.

In the absence of temperature gradients (Soret effect), pressure gradients, and external forces, an equivalent form of Fick's first law can be used to express the mass flux of water relative to a stationary reference frame [107: Sections 16.2 and 18.4] as

\[
\bar{\Gamma}_w = c_w(\bar{\Gamma}_w + \bar{\Gamma}_o + \bar{\Gamma}_p) - \rho D_w \nabla c_w
\]  

(B.2)

where the term \( c_w(\bar{\Gamma}_w + \bar{\Gamma}_o + \bar{\Gamma}_p) \) represents the mass flux of water resulting from the bulk motion of the system, and \( D_w \) is the effective diffusion coefficient of water in the solution. In this expression the mass fraction of water, \( c_w = \rho_w / \rho \), is defined as the mass concentration of water divided by the total mass density of the solution [107: Section 16.1]. Note that the use of a single diffusion coefficient assumes that the spectrum of mobilities of the water molecules is such that it can be represented by a single coefficient. The mass fraction of water in oil-impregnated paper is typically less than one percent [11, 34, 35]. In this limit, Eq. B.2 reduces to

\[
\bar{\Gamma}_w \approx -\rho D_w \nabla c_w
\]  

(B.3)
Because water is a trace constituent, the total mass density of the solution can be assumed to be a constant. In the absence of chemical reactions responsible for the generation or loss of water molecules in the paper, the equation of continuity can be expressed in terms of the mass fraction of water in the solution.

\[
\frac{\partial c_w}{\partial t} = \nabla \cdot [D_w \nabla c_w]
\]  \hspace{1cm} (B.4)

In the special case in which the diffusion coefficient is uniform throughout the solution, the one-dimensional form of the equation of continuity becomes

\[
\frac{\partial c_w}{\partial t} = D_w \frac{\partial^2 c_w}{\partial x^2}
\]  \hspace{1cm} (B.5)

which is called Fick's second law of diffusion or simply the diffusion equation [107: Section 18.1].
Appendix C

The Soret Effect

There are many situations in the power apparatus industry where there are temperature gradients across the insulation. This is the case in the cooling ducts of a transformer where convection is used to hold down adjacent hot-spots.

The Soret effect describes the flux of moisture due to thermal gradients [107: Section 18.4]. This flux augments the flux due to concentration gradients of moisture in the paper,

$$\frac{\partial c_p}{\partial t} = \frac{\partial}{\partial x} \left[ D_p(T(x)) \frac{\partial c_p}{\partial x} + D_t(T(x)) \frac{d}{dx}(\ln T(x)) \right]$$  \hspace{1cm} (C.1)

where $T$ is the local temperature in degrees kelvin and $D_t$ is the thermodiffusion coefficient. With $D_t$ positive, the term involving the gradient in temperature describes the flux of moisture from hot to cold regions.

The value of the thermodiffusion coefficient in oil-impregnated paper is not known, but can be estimated from mass-transfer experiments involving thermal gradients. The ratio of the thermodiffusion coefficient to the molecular diffusion coefficient can be obtained from measurements of the equilibrium distribution of moisture in the insulation. In equilibrium, the net flux of moisture at the boundaries is zero and the diffusion equation can be integrated to yield the desired information.

$$\frac{D_t(T(x))}{D_p(T(x))} = -\frac{\partial c_p}{\partial x} \frac{T(x)}{dT/dx}$$  \hspace{1cm} (C.2)

The temperature dependence of the thermodiffusion coefficient can then be estimated from the molecular diffusion coefficient, whose temperature dependence is given by Eq. 5.13.
Appendix D

Alternative Formulation to Moisture Dynamics

In Chapter 5, the model used to describe the spatial and temporal evolution of moisture in the Couette Facility was formulated in terms of a partial differential equation describing the diffusion of moisture in the paper, Eq. 5.15, coupled to an expression accounting for conservation of moisture in the system, Eq. 5.21. This conservation statement can be alternatively formulated in terms of an ordinary differential equation describing the time rate of change of the moisture content of the oil in terms of the flux of moisture through the diffusion sublayer at the inner and outer walls.

In general, the conservation of moisture in the system can be expressed as a continuity condition

\[
\frac{d}{dt} \int_V \rho_o c_o \, dV = - \int_S (\vec{\tau} \cdot \vec{n}) \, da \tag{D.1}
\]

where \( \rho_o \) is the density of the oil, \( c_o \) is the concentration of water in the oil expressed as a mass fraction, \( V \) is the volume of the oil, and \( \vec{\tau} \) is the flux of water leaving the oil at the boundaries of the volume.

If we neglect the moisture stored in the diffusion sublayer in excess to that due to the concentration of moisture in the turbulent core, the integrals give

\[
\frac{d}{dt} \left[ \rho_o c_o \pi (R_2^2 - R_1^2)\ell \right] = \rho_o D_o \frac{c_w - c_o}{\delta_d} 2\pi (R_1 + R_2)\ell \tag{D.2}
\]

where the left-hand side of Eq. 5.17b was used to express the flux of moisture into the oil. Upon simplification, this equation can be expressed as

\[
\tau_o \frac{dc_o}{dt} = c_w - c_o \tag{D.3}
\]

where \( \tau_o \) is the time constant associated with the diffusion of moisture into the oil defined
in Table 5.3. Together with the initial condition for the concentration of water in the oil given by Eq. 5.18, this differential equation provides an alternative description of the mass conservation equation that relates the concentration of water in the paper to that in the oil.
Appendix E

Self-Adjointness and Orthogonality

Consider the eigenvalue problem

\[ Lu + \lambda ru = 0 \quad (E.1) \]

defined over the interval \( a \leq x \leq b \), where \( L \) is an \( n \)th order linear ordinary differential operator of the form

\[ L = a_n(x) \frac{d^n}{dx^n} + a_{n-1}(x) \frac{d^{n-1}}{dx^{n-1}} + \cdots + a_0(x) \quad (E.2) \]

Since the operator \( L \) is of \( n \)th order, there will be \( n \) homogeneous boundary conditions of the general form

\[ B_j(u) = 0 \quad j = 1, 2, \ldots, n \quad (E.3) \]

where the \( B_j \)'s are prescribed functionals\(^1\) limited to linear combinations of \( u \) and its derivatives, through order \( n-1 \), at the two endpoints \( a \) and \( b \). Specifically, each boundary condition may be expressed as

\[ B_j(u) = a_{j,n-1} u^{n-1}(a) + \cdots + a_{j,1} u(a) + b_{j,n-1} u^{n-1}(b) + \cdots + b_{j,1} u(b) \quad (E.4) \]

where \( u^n \) represents the \( n \)th derivative of \( u \) with respect to \( x \).

The differential operator \( L \) and the boundary conditions \( B_j \) completely specify the operator \( L \). For each operator \( L \) there is an adjoint operator \( L^* \) defined by the relation

\[ (Lu, v) = (u, L^*v) \quad (E.5) \]

\(^1\)A functional is a ‘function of a function’ whose domain is a set of functions and whose range is a set of numbers.
where the inner product \((f, g)\) is defined by

\[
(f, g) = \int_a^b f(x)g(x) \, dx
\]  \hspace{1cm} (E.6)

Thus, the adjoint operator \(L^*\) consists of the differential operator \(L^*\) and the adjoint boundary conditions \(B_j^*(v)\) which force the boundary terms, arising through the integration by parts of Eq. E.5, to vanish. In the event that \(L^* = L\) and \(B_j^* = B_j\) for \(j = 1, 2, \ldots, n\) we say that the operator \(L\) is self-adjoint [108].

If we denote by \(\lambda_m\) and \(\lambda_n\) any two different eigenvalues of the problem and by \(\phi_m\) and \(\phi_n\) their corresponding eigenfunctions, then we can write according to Eq. E.1

\[
L\phi_m + \lambda_m r\phi_m = 0
\]
\[
L\phi_n + \lambda_n r\phi_n = 0
\]  \hspace{1cm} (E.7)

If we multiply the first and second of these equations by \(\phi_n\) and \(\phi_m\) respectively, subtract them, and integrate the result over the domain we obtain

\[
(\lambda_m - \lambda_n)(\sqrt{r}\phi_m, \sqrt{r}\phi_n) = (L\phi_n, \phi_m) - (\phi_n, L\phi_m)
\]  \hspace{1cm} (E.8)

By definition, if the operator \(L\) is self-adjoint, the right side of this equation vanishes giving the orthogonality condition

\[
(\sqrt{r}\phi_m, \sqrt{r}\phi_n) = 0
\]  \hspace{1cm} (E.9)

Thus, the orthogonality of the eigenfunctions in an eigenvalue problem is assured if the operator describing the differential operator and its associated boundary conditions is self-adjoint.

Note that the requirement of homogeneity in the boundary conditions does not limit the scope of this discussion because techniques used to ‘homogenize’ boundary conditions are available [73: Part 2, Lesson 6].
Appendix F

Measurement of Heterogeneous Dielectric Properties†

In the nondestructive evaluation of composite materials, the information obtained from the measurement of the heterogeneity in the structure is used to detect the presence of defects and adjust parameters in the manufacturing process. When the heterogeneity is reflected in a spatial variation of the dielectric properties, the use of multiple-wavelength interdigital-electrode structures provides a means to perform such a measurement. The deduction of the inhomogeneity in the material properties is sometimes attempted from the temporal frequency response of parallel-plate structures or single-wavelength interdigital-electrode structures, but this process does not give a unique distribution and cannot be implemented without assuming that the frequency dispersion of the material is known.

Using the electroquasistatic form of Maxwell's equations in the sinusoidal steady-state, what follows is an attempt to show that the use of a parallel-plate structure provides at most a spatial average of the dielectric properties in a material. Furthermore, the feasibility of determining the heterogeneity in the dielectric properties is demonstrated when the measurement is performed using multiple-wavelength interdigital-electrode structures. The distribution thus obtained is shown to be unique when the heterogeneity can be assumed to be a small perturbation about a uniform distribution in the dielectric properties.

†Some parts of this appendix are taken from Reference [50: Section 4.3.1].
F.1 Maxwell’s Equations in the Sinusoidal Steady-State

In the electroquasistatic regime, Maxwell’s equations can be written in the following form.

\[ \nabla \cdot D = \rho_u \]
\[ \nabla \times E = 0 \]
\[ \nabla \cdot J + \frac{\partial \rho_u}{\partial t} = 0 \]  \hspace{1cm} (F.1)

Furthermore, if the system is in the sinusoidal steady-state, each quantity can be expressed as the real part of a complex variable

\[ A = \Re \{ \hat{A}(r, \omega) e^{jwt} \} \]  \hspace{1cm} (F.2)

so that the electroquasistatic laws can be written in the frequency domain as

\[ \nabla \cdot \hat{D} = \hat{\rho}_u \]
\[ \nabla \times \hat{E} = 0 \]
\[ \nabla \cdot \hat{J} + j\omega \hat{\rho}_u = 0 \]  \hspace{1cm} (F.3)

For linearly-polarizable isotropic media the displacement flux density is related to the electric field by the dielectric constant \( \varepsilon' \).

\[ \hat{D} = \varepsilon' \hat{E} \]  \hspace{1cm} (F.4)

If, in addition, we assume that the current density and the electric field are linearly related through the loss factor \( \varepsilon'' \),

\[ \hat{J} = \omega \varepsilon'' \hat{E} \]  \hspace{1cm} (F.5)

then Gauss’ law can be written in a form that includes the effects of charge conservation

\[ \nabla \cdot \varepsilon' \hat{E} = 0 \]  \hspace{1cm} (F.6)

where the complex permittivity is defined as

\[ \varepsilon^* = \varepsilon'(r, \omega) - j\varepsilon''(r, \omega) \]  \hspace{1cm} (F.7)

with the real and imaginary parts related by the Kramers-Krönig relations [90, 91].

The electroquasistatic laws for the sinusoidal steady-state can thus be summarized
Figure F.1: Schematic illustration of a parallel-plate structure in which the plate separation is much smaller than the dimensions of the plates and the complex permittivity varies only in the direction normal to the plane of the electrodes. At the terminals of the electrode structure the applied potential difference \( v(t) = \mathbb{R}\{\hat{V}e^{j\omega t}\} \) results in the flow of a current \( i(t) = \mathbb{R}\{\hat{I}e^{j\omega t}\} \)
as follows:

\[
\nabla \cdot \varepsilon^* \hat{E} = 0 \tag{F.8} \\
\nabla \times \hat{E} = 0
\]

Note that because the electric field is irrotational it can be expressed as the gradient of a potential.

\[
\hat{E} = -\nabla \hat{\Phi} \tag{F.9}
\]

### F.2 Parallel-Plate Structure

Consider the parallel-plate structure shown in Fig. F.1 in which the applied potential

\[
v(t) = \mathbb{R}\{\hat{V}e^{j\omega t}\} \tag{F.10}
\]

results in a flow of current at the terminals.

\[
i(t) = \mathbb{R}\{\hat{I}e^{j\omega t}\} \tag{F.11}
\]

If the plate separation is much smaller than the dimensions of the plates and the complex permittivity varies only in the direction normal to the plane of the electrodes, the electric field can be modeled as being one-dimensional and Gauss' law, Eq. F.8a, reduces to
\[
\frac{d}{dx} \left[ \varepsilon^*(x) \hat{E}_x \right] = 0 
\] (F.12)

Integration of this differential equation from \( x = 0 \) to an arbitrary position in the medium yields

\[
\varepsilon^*(x) \hat{E}_x = \hat{o}_{su} 
\] (F.13)

where \( \sigma_{su} \) is the free surface charge density on the upper electrode. According to Eq. F.9, the electric field can be expressed in terms of the electric potential as

\[
\hat{E}_x = -\frac{d\hat{\Phi}}{dx} 
\] (F.14)

Integrating this expression across the medium gives

\[
\hat{V} = \int_0^d \hat{E}_x \, dx = \hat{o}_{su} \int_0^d \frac{1}{\varepsilon^*(x)} \, dx 
\] (F.15)

where we used Eq. F.13 to express the electric field in terms of the complex permittivity of the medium.

The complex impedance of the structure is defined as

\[
\hat{Z} = \frac{\hat{V}}{\hat{I}} = \frac{\hat{V}}{j\omega A \hat{o}_{su}} 
\] (F.16)

where \( A \) is the surface area of the electrodes. Using the expression for the complex amplitude of the applied potential, Eq. F.15, we obtain an expression for the impedance of the structure in terms of the complex permittivity of the medium

\[
\hat{Z}(\omega) = \frac{1}{j\omega A} \int_0^d \frac{1}{\varepsilon^*(x,\omega)} \, dx 
\] (F.17)

From this expression it is clear that the measurement of the complex impedance of a parallel-plate structure provides at most a spatial average of the complex permittivity distribution. Thus, the spatial distribution of the complex permittivity cannot be extracted from measurements in the temporal frequency domain. Only the dispersive nature of the spatially-averaged complex permittivity can be obtained from the frequency response of the complex impedance.
F.3 Multiple-Wavelength Interdigital-Electrode Structure

Consider an interdigitated set of electrodes whose length is much greater than the spatial wavelength as illustrated in Fig. 6.1. One electrode is driven with a variable AC voltage while a high impedance measurement of the induced voltage on the other electrode is made. In this two-dimensional problem the potential can be described as

\[ \Phi(x, y, t) = \Re \{ \hat{\Phi}(x, y)e^{j\omega t} \} \]  

where variations in the y direction are assumed to be periodic,

\[ \hat{\Phi}(x, y) = \sum_{-\infty}^{+\infty} \hat{\Phi}_n(x)e^{-j\kappa_n y} \]  

and the wavenumber is defined as

\[ k_n = \frac{2\pi n}{\lambda} \]  

Assuming that the complex permittivity varies only in the direction normal to the plane of the electrodes, Gauss’ law, Eq. F.8a, becomes

\[ \frac{\partial}{\partial x} \left( \epsilon^* \hat{E}_x \right) + \epsilon^* \frac{\partial \hat{E}_y}{\partial y} = 0 \]  

Because the electric field is irrotational the y component of the electric field can be evaluated using Eq. F.19.

\[ \hat{E}_y = -\frac{\partial \hat{\Phi}}{\partial y} = j \sum_{-\infty}^{+\infty} k_n \hat{\Phi}_n e^{-j\kappa_n y} \]  

Using this result Gauss’ law can be written in the form

\[ \frac{\partial}{\partial x} \left( \epsilon^* \hat{E}_x \right) + \epsilon^* \sum_{-\infty}^{+\infty} k_n^2 \hat{\Phi}_n e^{-j\kappa_n y} = 0 \]  

Integrating this equation from \( x = 0 \), where \( \epsilon^* \hat{E}_x = \epsilon_n^* \hat{E}_x^a \), to infinity, where the electric field goes to zero and the complex permittivity is finite, we find an expression for the normal electric displacement flux density at the plane of the electrodes.

\[ \epsilon_n^* \hat{E}_x^a = \sum_{-\infty}^{+\infty} \epsilon_n^* \hat{E}_x^a = \int_0^\infty \epsilon^*(x, \omega) \sum_{-\infty}^{+\infty} k_n^2 \hat{\Phi}_n(x)e^{-j\kappa_n y} dx \]  

The medium above the electrodes can be described in terms of a surface capacitance
density. This quantity represents the response of the medium to one Fourier component of the potential applied at the electrodes. It is defined as the ratio of the complex amplitudes of the normal displacement flux density to the electric potential [76]

$$\hat{C}^a_n = \frac{\epsilon_n^a \hat{E}_n^a}{\hat{\Phi}_n^a} \quad (F.25)$$

Using the expression for the normal electric displacement flux density, the surface capacitance density can be written as

$$\hat{C}^a_n(\omega, k_n) = \frac{k_n}{\hat{\Phi}_n^a} \int_0^\infty \epsilon^* (x, \omega) \hat{\Phi}_n(x) k_n dx \quad (F.26)$$

In contrast with the result obtained in Eq. F.17, the spatial distribution of the complex permittivity acts as a weighing function to the potential distribution. For a given wavenumber, the potential will decay with a characteristic length scale inversely proportional to the imposed spatial wavelength. Thus, it seems possible to extract the spatial distribution of the complex permittivity from measurements of the surface capacitance density at different wavenumbers.

For the sake of evaluating the above integral, assume that the spatial variation in the complex permittivity is a perturbation about a uniform value $\epsilon_0^*$.

$$\epsilon^* (x, \omega) = \epsilon_0^*(\omega) + \tilde{\epsilon}(x, \omega) \quad (F.27)$$

As a result of this perturbation in the complex permittivity the potential will suffer a perturbation about the distribution associated with a uniform value of the complex permittivity.

$$\hat{\Phi}_n(x) = \hat{\Phi}_n^0 e^{-k_n x} + \hat{\Phi}_n(x) \quad (F.28)$$

With the complex permittivity and the potential linearized, the surface capacitance density above the electrodes can be expressed to first order as

$$\frac{\hat{C}_n^a(\omega, k_n)}{\epsilon_0^*(\omega)k_n} = 1 + \int_0^\infty \frac{\tilde{\epsilon}(x, \omega)}{\epsilon_0^*(\omega)} e^{-k_n x} k_n dx + \int_0^\infty \frac{\hat{\Phi}_n(x)}{\hat{\Phi}_n^0} k_n dx \quad (F.29)$$

If we model the medium as piece-wise uniform, perhaps as an approximation of a continuous distribution, the evaluation of this expression using perturbation techniques is tantamount to linearizing the surface capacitance density. Consider, for example, a piece-wise uniform medium composed of $M$ homogeneous layers, as shown in Fig. F.2. The top layer ($j = 1$) is the semi-infinite region. The $j$th layer has a complex permittivity $\epsilon_j^*$, a thickness $d_j$, and an upper surface designated by $(j)$. The surface capacitance
Figure F.2: Schematic illustration of a piece-wise uniform medium composed of $M$ homogeneous layers. The top layer ($j = 1$) is the semi-infinite region. The $j$th layer has a complex permittivity $\varepsilon_j^*$, a thickness $d_j$, and an upper surface designated by $(j)$. The surface capacitance density of the $j$th interface is defined in terms of the properties of the layers above that interface.

Density of the $j$th interface is defined in terms of the properties of the layers above that interface through the following recursive relation [76]

$$C_n^{(j+1)} = \varepsilon_j^* k_n \coth(k_n d_j) - \frac{(\varepsilon_j^* k_n)^2}{\sinh(k_n d_j) [\varepsilon_j^* k_n \coth(k_n d_j) + C_n^{(j)}]} \quad (F.30)$$

The surface capacitance density at the plane of the electrodes is then given by

Section F.3: Interdigital-Electrode Structure
\( \hat{\mathbf{C}}_n^a = \hat{\mathbf{C}}_n^{(M+1)} \)  

(F.31)

If we assume that the complex permittivity of each layer differs from a common uniform value by a small perturbation, the surface capacitance density can be expressed as a linear superposition of the complex permittivities of the layers in the medium. In particular, for a medium composed of one, two, or three layers, the surface capacitance density at the plane of the electrodes can be written as

\[
\begin{align*}
M &= 1 \quad & \hat{C}_n^a &= \varepsilon_1^* k_n \\
M &= 2 \quad & \hat{C}_n^a &= \varepsilon_2^* k_n - (\varepsilon_2^* - \varepsilon_1^*) k_n e^{-2k_n d_2} \\
M &= 3 \quad & \hat{C}_n^a &= \varepsilon_3^* k_n - (\varepsilon_3^* - \varepsilon_2^*) k_n e^{-2k_n d_3} - (\varepsilon_2^* - \varepsilon_1^*) k_n e^{-2k_n (d_2 + d_3)}
\end{align*}
\]  

(F.32)

The form of these expressions suggest the following expression for the linearized surface capacitance density of a medium with \( M \) layers,

\[
\hat{C}_n^a = \varepsilon_M^* k_n + \sum_{j=1}^{M-1} (\varepsilon_j^* - \varepsilon_{j+1}^*) k_n e^{-2k_n h_j}
\]  

(F.33)

where the height of each layer above the plane of the electrodes is given by

\[
h_j = \sum_{i=j+1}^{M} d_i
\]  

(F.34)

Thus, the surface capacitance density can be expressed as a linear combination of the complex permittivities of the layers.

\[
\hat{\mathbf{C}}_{inl}(\omega_i, k_{nl}) = \sum_{j=1}^{M} B_{jnl}(d_j, h_j, k_{nl}) \varepsilon_j^* (\omega_i)
\]  

(F.35)

where \( k_{nl} \) is the wavenumber associated with the \( n \)th mode and the \( l \)th wavelength.

\[
k_{nl} = \frac{2\pi n}{\lambda_l}
\]  

(F.36)

If we perform \( M \) measurements of the surface capacitance density at a single frequency using \( M \) distinct wavelengths, the set of complex surface capacitance densities can be linearly related to the complex permittivities of each layer.

\[
\begin{bmatrix}
\hat{C}_{in1}^a \\
\vdots \\
\hat{C}_{inM}^a
\end{bmatrix} =
\begin{bmatrix}
B_{1n1} & \cdots & B_{Mn1} \\
\vdots & \ddots & \vdots \\
B_{1nM} & \cdots & B_{MnM}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_1^* (\omega_i) \\
\vdots \\
\varepsilon_M^* (\omega_i)
\end{bmatrix}
\]  

(F.37)
Thus, because the rows of the matrix are linearly independent, the complex permittivities of the layers can be uniquely determined from a multiple-wavelength measurement of the complex surface capacitance density.

If, on the other hand, we perform $M$ measurements of the surface capacitance density at $M$ distinct temporal frequencies using a single wavelength, the set of complex surface capacitance densities can be written as

$$
\begin{bmatrix}
\hat{C}_{1\text{nl}}^a \\
\vdots \\
\hat{C}_{M\text{nl}}^a
\end{bmatrix} =
\begin{bmatrix}
\epsilon_1^*(\omega_1) & \cdots & \epsilon_M^*(\omega_1) \\
\vdots & \ddots & \vdots \\
\epsilon_1^*(\omega_M) & \cdots & \epsilon_M^*(\omega_M)
\end{bmatrix}
\begin{bmatrix}
B_{1\text{nl}} \\
\vdots \\
B_{M\text{nl}}
\end{bmatrix} \quad (F.38)
$$

With the goal of solving for the complex permittivity of the layers at a common frequency $\omega_0$, we assume, without loss of generality, that the frequency dispersion characteristics of each layer can be expressed as

$$
\epsilon_j^*(\omega) = \epsilon_j'(\omega_0)f_j'(\omega, \omega_0) - j\epsilon_j''(\omega_0)f_j''(\omega, \omega_0) \quad (F.39)
$$

The real and the imaginary parts of the surface capacitance density can then be linearly related to the real and imaginary parts of the complex permittivity.

$$
\Re \begin{bmatrix}
\hat{C}_{1\text{nl}}^a \\
\vdots \\
\hat{C}_{M\text{nl}}^a
\end{bmatrix} =
\begin{bmatrix}
B_{1\text{nl}}f_1'(\omega_1, \omega_0) & \cdots & B_{M\text{nl}}f_M'(\omega_1, \omega_0) \\
\vdots & \ddots & \vdots \\
B_{1\text{nl}}f_1'(\omega_M, \omega_0) & \cdots & B_{M\text{nl}}f_M'(\omega_M, \omega_0)
\end{bmatrix}
\begin{bmatrix}
\epsilon_1'(\omega_0) \\
\vdots \\
\epsilon_M'(\omega_0)
\end{bmatrix} \\
\Im \begin{bmatrix}
\hat{C}_{1\text{nl}}^a \\
\vdots \\
\hat{C}_{M\text{nl}}^a
\end{bmatrix} =
\begin{bmatrix}
B_{1\text{nl}}f_1''(\omega_1, \omega_0) & \cdots & B_{M\text{nl}}f_M''(\omega_1, \omega_0) \\
\vdots & \ddots & \vdots \\
B_{1\text{nl}}f_1''(\omega_M, \omega_0) & \cdots & B_{M\text{nl}}f_M''(\omega_M, \omega_0)
\end{bmatrix}
\begin{bmatrix}
\epsilon_1''(\omega_0) \\
\vdots \\
\epsilon_M''(\omega_0)
\end{bmatrix} \quad (F.40)
$$

In general these matrices can be inverted to give the complex permittivities of the layer. If the layers exhibit ohmic conduction, the complex permittivity of each layer can be expressed in terms of the dielectric constant $\epsilon_j$ and the conductivity $\sigma_j$ as

$$
\epsilon_j^* = \epsilon_j' - j\frac{\sigma_j}{\omega} \quad (F.41)
$$

so that the dispersion functions reduce to

$$
f_j'(\omega, \omega_0) = 1 \\
f_j''(\omega, \omega_0) = \frac{\omega_0}{\omega} \quad (F.42)
$$

Section F.3: Interdigital-Electrode Structure
Under these conditions the matrices in Eqs. F.40 become singular and the complex permittivities of the layers cannot be uniquely determined from the temporal frequency response.

The complex admittance describing the coupling between the driven and the sensing electrodes is not linearly related to the surface capacitance density. Yet there is evidence that, given a measurement of the complex admittance, there exists only one physical value of the complex permittivity, and therefore one physical value of the surface capacitance density that describes the response [76].

In summary, the spatial profile of a material's complex permittivity can be uniquely deduced using the spatial frequency response of multiple-wavelength interdigital-electrode structures. The deduction of inhomogeneities in the material properties can be achieved from temporal frequency response information alone, but this process cannot be implemented without assuming that the frequency dispersion of the material is known. Furthermore, if the material properties are not dispersive the temporal frequency response information does not give a unique distribution. These results assume that the spatial variation in the complex permittivity is only a perturbation about a uniform value. If this is not the case, the inversion of the spatial profile of the complex permittivity of an ohmic material using the temporal frequency response is possible if the relaxation times of the layers are distinct [50: Section 3.2.2].
Appendix G

Chemical and Electrical Laws in an Ionized Fluid

If only three reactive species are involved, the $\gamma$-molecular ionization reaction of a neutral species $C$ into ionized species $A$ and $B$ is described by the ionic equation [109]

$$\gamma C \overset{k_d}{\underset{k_r}{\rightleftharpoons}} A^{+q} + B^{-q} \quad (G.1)$$

where $k_d$ and $k_r$ are the dissociation and recombination rate constants related by the equilibrium constant $K_{eq}$ through the following relation.

$$K_{eq} = \frac{k_d}{k_r} \quad (G.2)$$

With the square brackets indicating the molar concentration of the species, the rate equation for a homogeneous system can be written in the following form [110].

$$\frac{d}{dt}[A^{+q}] = \frac{d}{dt}[B^{-q}] = -\left(\frac{1}{\gamma}\right) \frac{d}{dt}[C] = k_d[C]^\gamma - k_r[A^{+q}][B^{-q}] \quad (G.3)$$

The equivalent electrical law relates the increase in the densities of the species to the generation $G$ and recombination $R$ rates,

$$\frac{d\rho_+}{dt} = \frac{d\rho_-}{dt} = -\left(\frac{q}{\gamma}\right) \frac{dn}{dt} = G - R \quad (G.4)$$

where $\rho_\pm$ are the charge densities of the ionized species, $q$ is the charge per ion, and $n$ is the number density of the neutral species.

Comparison of these last two expressions allows us to relate the concentrations of the electrical constituents to their chemical equivalent.
\[ \rho_+ = qN_A[A^{+q}] \]
\[ \rho_- = qN_A[B^{-q}] \]
\[ n = N_A[C] \] (G.5)

as well as the generation and recombination rates

\[ G = qN_Ak_d[C]^\gamma \]
\[ R = qN_Ak_r[A^{+q}][B^{-q}] \] (G.6)

where \( N_A \) is Avogadro's number \((6.022 \times 10^{23} \text{ molecules/mole})\). The generation and recombination terms can then be written in terms of the electrical variables.

\[ G = \beta n^\gamma \quad \beta = \frac{qk_d}{N_A^{\gamma-1}} \] (G.7)
\[ R = \alpha \frac{\rho_+ \rho_-}{q} \quad \alpha = \frac{k_r}{N_A} \]

These expressions justify the assumed form of the generation and recombination terms in the electrical laws of Sect. 7.3 and provide a basis for understanding the coupling between the chemical and the electrical variables.
Appendix H

Diffusion Fluxes in an Ionized Fluid

Consider a system composed of four types of constituents. Two of the constituents are oppositely charged ions. The remaining two are neutral species, only one of which participates in the generation and recombination of the ionized species. The fourth constituent is inert. In the absence of temperature gradients (Soret effect), pressure gradients, and external forces, an equivalent form of Fick's first law can be used to express the molar flux of each of the constituents relative to a stationary reference frame [107: Section 18.4] as

\[ \dot{N}_i = y_i \sum_{j=1}^{4} \dot{N}_j - cD_{im} \nabla y_i \quad \text{for } i = 1, 2, 3, 4 \]  

(H.1)

where the term \( y_i \sum_{j=1}^{4} \dot{N}_j \) represents the molar flux of the ith constituent resulting from the bulk motion of the system, and \( D_{im} \) is the diffusion coefficient of the constituent in the mixture. The mole fraction of the ith constituent \( y_i \) is related to the molar concentration of the constituent \( c_i \) by the relation

\[ y_i = \frac{c_i}{c} \]  

(H.2)

where \( c = \sum_{i=1}^{4} c_i \) is the molar density of the solution.

If we assume that the inert neutral species is present in such concentrations that its mole fraction is essentially unity, the molar density of the solution can be assumed to be a constant. In this limit, the expression for the molar fluxes of the active species reduces to

\[ \dot{N}_i \approx -D_{im} \nabla c_i \quad \text{for } i = 1, 2, 3 \]  

(H.3)
The number-based flux of the active species is then obtained by multiplying this expression by Avogadro's number ($6.022 \times 10^{23}$ molecules/mole),

$$\vec{\Gamma}_i \approx -D_{im} \nabla n_i$$

for $i = 1, 2, 3$ \hfill (H.4)

where $n_i$ is the number density of the $i$th species.
Appendix I

Equilibrium Relations for an Ionized Fluid

Consider a system in which two of the constituents are oppositely charged ions, present perhaps as a result of the ionization of a neutral species. The preferential adsorption of one of the charged species onto a surface results in a double layer. Such a heterogeneous system can be represented by a large number of homogeneous subsystems. For each subsystem the electrochemical potential of the ionized species can be written as [111]

\[ \mu_\pm = \mu_\pm^c \pm qN_A \Phi \]  

(I.1)

where \( \mu_\pm^c \) is the chemical potential of the ionized species, \( q \) is the charge per ion, \( N_A \) is Avogadro's number \( (6.022 \times 10^{23} \text{ molecules/mole}) \), and \( \Phi \) is the electric potential.

In general, the chemical potential of each constituent depends on the temperature and pressure of the system, and on the mole fractions of all the constituents in the system. If we assume that the ionized constituents exhibit ideal-solution behavior, the chemical potentials can be expressed in terms of their mole fraction alone [22: Section 27.5],

\[ \mu_\pm = \mu_\pm^0(T,p) + RT \ln y_\pm \]  

(I.2)

where \( \mu_\pm^0 \) is the chemical potential of the pure constituent at the temperature \( T \) and pressure \( p \) of the system, \( R \) is the universal gas constant \( (8.3145 \text{ J/mol K}) \), and \( y_\pm \) is the mole fraction of the ionized species in the solution.

For the system to be in a stable equilibrium state, the temperature, pressure, and electrochemical potential of the constituents must be equal in all the subsystems. In fact, because each subsystem can be very small—almost infinitesimal—we can think of the temperature, the pressure, and the electrochemical potential as being defined locally and having uniform values throughout the spatial extension of the composite system [22:
Section 18.1]. The condition of uniformity for the electrochemical potential of the ionized species can thus be expressed as

$$\nabla \mu_\pm = 0 \quad (I.3)$$

Using Eqs. I.1 and I.2, this condition reduces to

$$kT \nabla \ln y_\pm + q \nabla \Phi = 0 \quad (I.4)$$

where $k = R / N_A$ is Boltzmann's constant ($1.38066 \times 10^{-23}$ J/K molecule).

Because the electric field is irrotational, it can be expressed as the gradient of the electric potential.

$$\vec{E} = -\nabla \Phi \quad (I.5)$$

Using this relation, and the fact that the mole fraction of each ionized species is related to the charge density through the number-specific volume of the system, $v = V/n$,

$$y_\pm = \left( \frac{v}{q} \right) \rho_\pm \quad (I.6)$$

Eq. I.4 can be written as

$$\vec{E} = \pm \frac{kT}{q} \nabla \ln \rho_\pm \quad (I.7)$$

Upon integration, this equation yields an expression for the charge densities in terms of the potential distribution,

$$\rho_\pm = \rho_o \exp \left[ \mp \frac{\Phi}{V_T} \right] \quad (I.8)$$

where $\rho_o$ is the charge density at the location of zero potential, and $V_T = kT/q$ is the thermal voltage. Note that this result is identical to that obtained in Sect. 7.3.1, where the current density of each ionized species is assumed to be zero, and is consistent with equilibrium relations derived on the basis of the Boltzmann distribution law of classical statistical mechanics [112].

Appendix I: Equilibrium in an Ionized Fluid
Appendix J

Langevin's Recombination Coefficient†

Consider an isotropic distribution of ions in a weakly ionized fluid where the ionic separation is much larger than the intermolecular distance and the mean-free-path. Because the motion of the ions is collision dominated, the probability of three or more ions interacting is very small and the recombination process is assumed to involve only two oppositely-charged ions. Furthermore, the probability that a neutral molecule will result from the mutual approach of these two ions is assumed to be unity.

In a process where the oppositely-charged ions are attracted to each other with a Coulombic force that is reduced by the collisions between the ions and the neutral molecules, the velocity of each ion is related to the local electric field by a mobility. Thus, the velocities of the ions measured in a stationary reference frame can be expressed as

\[ \vec{v}_\pm = \pm b_\pm \left( \vec{E}_\pm + \vec{E}_c \right) \]  \hspace{1cm} (J.1)

where \( b_\pm \) is the mobility of each ion, \( \vec{E}_\pm \) is the electric field due to ions in the bulk or on the surface of adjacent conductors, and \( \vec{E}_c \) is the Coulombic field due to the two oppositely-charged ions separated by a distance \( r \) and possessing a charge of magnitude \( q \).

\[ \vec{E}_c = \frac{q}{4\pi \varepsilon r^2} \vec{i}_r \]  \hspace{1cm} (J.2)

To determine the number of collisions occurring in a differential volume element \( dV \) in a time period \( dt \), we compute the number of positive ions \( N_+ \) that during this period traverse an ensemble of surfaces \( S_i \), each connected to a negative ion. The velocity flux through each surface \( S_i \) can be expressed as

\[ \text{flux through } S_i = \vec{v}_+ \cdot \vec{d}S_i \]

---

†This derivation is similar to that given by Langevin in Reference [113].
\[ \Gamma_i = \oint_{S_i} (\vec{v}_r \cdot \vec{n})_i \, da \]  

(J.3)

where \( \vec{v}_r \) is the relative velocity of a positive ion with respect to the negative ion.

\[ \vec{v}_r = \vec{v}_+ - \vec{v}_- = b_+ \vec{E}_+ + b_- \vec{E}_- + (b_+ + b_-) \vec{E}_c \]  

(J.4)

With \( n_{\pm} \) denoting the density of the ions in the fluid, the number of positive ions traversing the \( n_- dV \) surfaces \( S_i \) is proportional to the sum of the fluxes through each surface.

\[ N_+ = n_+ dt \sum_{i=1}^{n_- dV} \Gamma_i \]

\[ = n_+ dt \sum_{i=1}^{n_- dV} \oint_{S_i} (\vec{v}_r \cdot \vec{n})_i \, da \]  

(J.5)

\[ = n_+ dt \sum_{i=1}^{n_- dV} \left[ b_+ \oint_{S_i} (\vec{E}_+ \cdot \vec{n})_i \, da + b_- \oint_{S_i} (\vec{E}_- \cdot \vec{n})_i \, da \right. \]

\[ \left. + (b_+ + b_-) \oint_{S_i} (\vec{E}_c \cdot \vec{n})_i \, da \right] \]

Gauss' law requires that the two integrals involving the electric fields associated with charges in the bulk be identically zero because the fields \( \vec{E}_\pm \) are those generated by charges outside the volume enclosed by the surface \( S_i \). By the same token, the last integral yields a value of \( q/\epsilon \), and the sum reduces to

\[ N_+ = \frac{q(b_+ + b_-)}{\epsilon} n_+ n_- dt \, dV \]  

(J.6)

If each positive ion that traverses a surface \( S_i \) collides and thus recombines with a negative ion, the number of positive ions entering the ensemble of surfaces is equal to the decrease in the number of ions present in the differential volume element \( dV \),

\[ dn_\pm = -\frac{N_+}{dV} = -\frac{q}{\epsilon} (b_+ + b_-) n_+ n_- dt \]  

(J.7)

so that from the definition

\[ dn_\pm = -\alpha n_+ n_- dt \]  

(J.8)

Langevin's recombination coefficient can be identified as

\[ \alpha = \frac{q}{\epsilon} (b_+ + b_-) \]  

(J.9)
Consistent with the description of an isotropic distribution, this result does not take into account the effects of diffusion on the flux of the ions. In a double layer, where diffusion competes with migration in establishing the concentration profile of the ionic species, such effects are significant and need to be accounted for [114]. Furthermore, because the ions are assumed to be point charges, Brownian motion does not contribute to the recombination rate. The classical theory of Von Smoluchowski [115] and Debye [114] includes the effects of diffusion and finite molecular size in the description of ionic recombination rates. For dilute solutions, this theory predicts the same value for the recombination coefficient as that given by Langevin for gases at high pressure [116].
Appendix K

A Double Layer with a Reactive Boundary

For systems which support physicochemical processes such as adsorption, desorption, and charge transfer at the boundaries, the normal components of the fluxes at an interface can be expressed in terms of the reaction rate constants of the ions $k_\pm$ and the neutrals $k_n$ as \[56, 94, 95, 96]\n
\[
    J_\pm = \pm k_\pm (\rho_\pm - \rho_{*\pm})
    \Gamma = k_n (n - n_*)
\] (K.1)

These constitutive relations express the fact that, when the density of a species at the boundary is higher than its equilibrium value, there will be a flux of the species into the system. As such, the flux relations are consistent with the fact that in equilibrium there is no motion in the fluid.

Assuming that these relations describe the fluxes of the charged and neutral species at the interface between the dielectric layer and the bipolar medium described in Chapter 7, the complex amplitudes of the fluxes at the (c) surface in Fig. 7.3 can be expressed as

\[
    \hat{J}_\pm^c = \pm k_\pm \hat{\rho}_\pm^c
    \hat{\Gamma}^c = k_n \hat{n}^c
\] (K.2)

where the variables are normalized according to Table 7.1 and the reaction rate constants are normalized as follows.

\[
    k = \frac{k_e}{\rho\ell_D (b_+ + b_-)}
\] (K.3)

The normalized surface capacitance density at this surface is given by Eq. 7.44
\[
\hat{C}^c = \frac{\hat{D}^c}{\hat{\Phi}^c} = \sum_{j=1}^{4} P_{1j} A_j \tag{K.4}
\]

where the coefficients \(A_j\) are given by the solution of the matrix equation

\[
QA = G^c = \begin{bmatrix}
1 \\
+ k_+ \hat{\rho}_+ \\
- k_- \hat{\rho}_- \\
k_n \hat{n}
\end{bmatrix} \tag{K.5}
\]

Note that the perturbation component of the potential was arbitrarily chosen to be unity. Because the fluxes of the species are expressed in terms of the electrical variables, the vector \(G^c\) can be written in terms of the vector \(A\) as

\[
QA = G^c = \begin{bmatrix}
1 \\
0 \\
0 \\
0
\end{bmatrix} + KPA \tag{K.6}
\]

where the matrix \(K\) is defined by the reaction rate constants as

\[
K = \begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & +k_+ & 0 & 0 \\
0 & 0 & -k_- & 0 \\
0 & 0 & 0 & k_n
\end{bmatrix} \tag{K.7}
\]

The coefficients \(A_j\) can then be obtained by inverting the resulting equation.

\[
A = [Q - KPA]^{-1} \begin{bmatrix}
1 \\
0 \\
0 \\
0
\end{bmatrix} \tag{K.8}
\]

The surface capacitance densities above and below the interface between the dielectric layer and the bipolar medium are not continuous. Even though the potential is continuous across this interface, the displacement flux density is discontinuous by the surface charge \(\hat{\sigma}_{su}\).

\[
\hat{D}^c - \hat{D}^b = \hat{\sigma}_{su} \tag{K.9}
\]

Because the dielectric layer does not support any conduction, the continuity condition representing charge conservation relates the current density above the interface to the time rate of change of the surface charge.

\[
\hat{J}^c = -j\omega \hat{\sigma}_{su} \tag{K.10}
\]

Appendix K: Reactive Boundary
The current density at this interface is given by the superposition of the current densities associated with the two charged species.

$$\dot{J}^c = \dot{J}_+^c + \dot{J}_-^c = k_+ \dot{\rho}_+ - k_- \dot{\rho}_- \quad (K.11)$$

Combining these last three equations yields an expression that relates the normalized surface capacitance density below the interface to that above the interface.

$$\dot{C}^b = \dot{C}^c + \frac{1}{j\omega}[k_+ \dot{\rho}_+ - k_- \dot{\rho}_-] \quad (K.12)$$

In summary, the surface capacitance density of a double layer with a reactive boundary is given by this expression together with Eqs. 7.42, K.4, K.7, and K.8.
Appendix L

A Voltage-Controlled Double Layer

In a MOS device, the application of a bias field across the oxide layer controls the concentration of electrons or holes in the channel and leads to enhanced conduction between the source and the drain. The concentration of ionic species in a double layer can be controlled in a similar way by applying a bias field across a dielectric layer adjacent to the bipolar medium. The electric field is applied through an electrode, located behind the dielectric layer, which can be biased to an arbitrary potential with respect to ground. The ground electrode is located many Debye lengths away from the interface such that the potential is assumed to be zero at infinity.

The effect of the bias field on the double layer is reflected in the potential at the interface between the dielectric layer and the bipolar medium. Thus, the interfacial potential is equal to the superposition of a potential that depends on the bias voltage and a potential associated with the adsorbed charge at the interface, the zeta potential. A schematic view of the media and the associated potential distribution is shown in Fig. L.1.

The interface between the dielectric layer and the bipolar medium is modeled as a passive boundary where the fluxes of the charged and neutral species are zero. As the bias field is applied, the fluxes at this interface are assumed to remain zero. This condition assumes that the duration of the bias field is short compared with the time constant associated with physicochemical reactions at the interface. Thus, because the Debye length is large compared with molecular distances, the interface only supports polarization charge and the adsorbed charge associated with the zeta potential.

L.1 Interfacial Potential

The adsorbed charge at the interface between the dielectric layer and the bipolar medium is given by the jump in the displacement flux density with no applied field.
Figure L.1: Schematic view of a voltage-controlled double layer and associated potential distribution. Just as in MOS devices, the concentration of the ionic species in a double layer can be controlled by applying a bias field across a dielectric layer adjacent to the bipolar medium. The effect of the bias field on the double layer is reflected in the potential at the interface between the dielectric layer and the bipolar medium. Thus, the interfacial potential is composed of a potential that depends on the bias voltage and a potential associated with the adsorption of charge at the interface.

\[
\sigma_d = [\varepsilon_w F_w + \varepsilon E_w(0)]_{v=0} \tag{L.1}
\]

Due to the nature of the interface, the surface charge is not affected by the presence of a bias field. Thus, the electric fields in the two media are related by the expression

\[
\varepsilon_w E_w + \varepsilon E_w(0) = \sigma_d \tag{L.2}
\]

where the uniform electric field in the dielectric layer is determined by the potentials at the two boundaries.

\[
E_w = [\zeta - \xi(v) + v]/d \tag{L.3}
\]

Using Eq. 7.18 to express the electric field in the bipolar medium, the bias voltage can be related to the interfacial potential by
Figure L.2: Plot of the normalized interfacial potential in a voltage-controlled double layer as a function of the normalized bias voltage for several values of the normalized thickness of the dielectric layer. The value of the zeta potential is set to zero.

\[ v = \xi + 2d \left[ \sinh \left( \frac{\xi}{2} \right) - \sinh \left( \frac{\xi - \xi}{2} \right) \right] \]  \hspace{1cm} (L.4)

where the potentials have been normalized to the thermal voltage, \( kT/q \), and the thickness of the dielectric layer is normalized as

\[ d = \left( \frac{d}{\ell_D} \right) \left( \frac{\epsilon}{\epsilon_0} \right) \]  \hspace{1cm} (L.5)

with the Debye length \( \ell_D \) defined in Table 7.2. The interfacial potential is plotted in Fig. L.2 as a function of the bias voltage for several values of the normalized thickness of the dielectric layer. In this plot the value of the zeta potential was set to zero.

Two limiting cases can be identified from the expression relating the bias voltage to the interfacial potential. For large values of the normalized bias voltage and thick-
nesses of the dielectric layer larger than the Debye length, Eq. L.4 yields a closed-form expression for the interfacial potential,

\[ \xi \approx \pm 2 \ln |v/d| \]  
(\text{L.6})

where the minus sign is associated with negative values of the bias voltage.

When the interfacial potential is zero, the net charge in the double layer is zero and the surface charge at the interface between the dielectric layer and the bipolar medium is imaged by the surface charge on the bias electrode. This condition occurs when

\[ \xi(v) = \zeta \]  
(\text{L.7})

so that the applied voltage is related to the zeta potential by the following expression.

\[ v = \zeta + 2d \sinh(\zeta/2) \]  
(\text{L.8})

### L.2 Surface Conductivity

Access to the potential at the interface between the dielectric layer and the bipolar medium allows the concentration of the ionic species in the double layer to be controlled with the bias field. This induced mobile charge can then be used to measure the mobility of the ions in the bipolar medium by applying an electric field with a component tangential to the interface and measuring the resulting surface current.

If the bias voltage is large compared with the thermal voltage and the spatial periodicity of the applied field is large compared with the Debye length, the conduction in the double layer gives rise to a response that is characteristic of a surface conductivity at the interface between the dielectric layer and the bipolar medium and a bulk ohmic conductivity in the region above. This result is described in Section 7.6.4, where the effect of the zeta potential on the response of an interdigital-electrode structure is examined. For large values of the normalized zeta potential, the response of electrode structures with spatial wavelengths much larger than the Debye length takes on the singular characteristics of a surface response. Even though typical values of the zeta potential for systems involving liquid hydrocarbons are on the order of the thermal voltage [29, 106], the interfacial potential can be augmented by applying a bias field across the dielectric layer.

Under these conditions, the surface conductivity associated with the mobile charges in the double layer can be expressed in terms of the difference between the conductivity in the double layer and that in the bulk.
\[ \sigma_s = \int_0^\infty (\rho_+ b_+ + \rho_- b_-) \, dx - \int_0^\infty (\rho_0 b_+ + \rho_0 b_-) \, dx \]  
(L.9)

Note that, for the case where the value of the interfacial potential is zero, this expression gives a value of zero for the surface conductivity at the interface between the dielectric layer and the ohmic medium.

Using Eq. 7.15 for the charge densities of the ionic species, the surface conductivity can be expressed as

\[ \sigma_s = \frac{1}{2} \int_0^\infty \left[ r_+(e^-^{\Phi} - 1) + r_-(e^+^{\Phi} - 1) \right] \, dx \]  
(L.10)

where the parameters \( r_{\pm} \) are defined in Table 7.2 and an underscored equation number indicates that all variables have been normalized according to Table 7.1. The surface conductivity has been normalized as follows.

\[ \sigma_s = \frac{\sigma_s}{\ell D \rho_0 (b_+ + b_-)} \]  
(L.11)

Using Eq. 7.18, the integral can be expressed in terms of the normalized potential through a change of variables.

\[ \sigma_s = \frac{1}{4} \int_0^{\frac{\zeta - \ell}{2}} \frac{r_+(e^-^{\Phi} - 1) + r_-(e^+^{\Phi} - 1)}{\sinh(\Phi/2)} \, d\Phi \]  
(L.12)

The identities

\[ e^{\pm z} - 1 = e^{\pm z/2}(e^{\pm z/2} - e^{\mp z/2}) = \pm 2e^{\pm z/2} \sinh(z/2) \]  
(L.13)

allow the integral to be further expressed as

\[ \sigma_s = \frac{1}{2} \int_0^{\zeta - \ell} \left[ -r_+ e^{-\Phi/2} + r_- e^{\Phi/2} \right] \, d\Phi \]  
(L.14)

which can be evaluated to give

\[ \sigma_s = r_+ [e^{-(\zeta - \ell)/2} - 1] + r_- [e^{(\zeta - \ell)/2} - 1] \]  
(L.15)

For large positive and negative values of the normalized interfacial potential, the surface conductivity reduces to

\[ \sigma_s \approx r_\pm e^{\left|\zeta - \ell\right|/2} \]  
(L.16)

Note that this expression predicts the same value for the surface conductivity as that estimated from the response associated with a normalized zeta potential of 15 in Fig. 7.15.

For large positive and negative values of the normalized bias voltage, the surface conductivity...
conductivity associated with the mobile charges in the double layer reduces to

$$\sigma_s \approx r_\pm |v/d|$$  \hspace{1cm} (L.17)

where Eq. L.6 was used to relate the interfacial potential to the applied bias voltage. Because the surface conductivity is proportional to the mobility of the majority carrier in the double layer, this expression shows how the value of the ionic mobilities can be obtained from a measurement of the surface conductivity at the interface between the dielectric layer and the bipolar medium.

L.3 Experimental Results

In order to examine the effects of a bias field on the properties of the double layer, a Parylene-coated microchip sensor was used to simulate the structure shown in Fig. L.1. Whereas Exxon Univolt 60 transformer oil was used as the bipolar fluid, the dielectric layer was represented by a combination of the substrate and the Parylene layer. The bias field was imposed by applying a voltage between ground plane of the sensor and a grounded electrode in the oil. The ground plane of the sensor was driven at the potential of the bias voltage. Even though the interdigitated electrodes shunted part of the bias field, they provided a means to apply a time-varying field with a component tangential to the Parylene/oil interface.

The results of the experiments are shown in Fig. L.3. In the absence of a bias field, the frequency response of the sensor has the characteristics of a double layer with a relatively small value of the normalized zeta potential. With a positive bias voltage of 5 V, which corresponds to a value of 200 times the thermal voltage at room temperature, the conduction in the double layer is enhanced by the increased density of positive ions. With a negative bias voltage of the same magnitude, the conduction in the double layer increases due to the larger mobility of the negative ions. The ratio of the peak frequencies associated with the response of the sensor to a negative and positive bias voltage is five. Assuming that the bias voltage is sufficiently high to insure that Eq. L.17 holds, this ratio implies that the mobility of the negative ions is five times larger than the mobility of the positive ions. Estimates of the ratio of the mobilities obtained from Kerr electro-optic measurements of the electric field distribution in an oil gap yielded a value of four [99] whereas direct measurements of the mobilities of ions in dielectric liquids yielded a value of two [60]. Differences between these values may be associated with the ionizable species that are responsible for conduction in the liquid.
Figure L.3: Effect of a bias field on the frequency response of the microchip sensor in Exxon Univolt 60 transformer oil at room temperature. In the absence of a bias field, the frequency response of the sensor has the characteristics of a double layer with a small value of the normalized zeta potential. With a positive bias voltage of 5 V, which corresponds to a value of 200 times the thermal voltage, the conduction in the double layer is enhanced by the increased density of positive ions. With a negative bias voltage of the same magnitude, the conduction in the double layer increases due to the larger mobility of the negative ions. The ratio of the peak frequencies indicates that the ratio of the mobilities is 5.
Appendix M

Program Listings

The following table lists, in alphabetical order, all the programs in the thesis. The program name is followed by a list of the dependent subroutines, if any, that are necessary for the compilation and execution of the program. The source code of the programs and subroutines is listed in alphabetical order following the table.

<table>
<thead>
<tr>
<th>Program</th>
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<sup>1</sup>LINPACK subroutine [117, 118].
<sup>2</sup>EISPACK subroutine [117, 119, 120].
<sup>3</sup>MINPACK subroutine [117].
<sup>4</sup>Subroutine by Zaretzky [50: Appendix F].

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This program computes the value of the eigenfunction coefficients, B_n, as a function of the number of terms in the series that describes the moisture concentrations in the Couette Facility.

Output files:

outfile: this file contains the input parameters, computed coefficients and time constants.
outfile.bn: this is a plot file describing the evolution of the eigenfunction coefficients as a function of the number of terms in the series.

Parameters:

xacc: accuracy of root
MAX: maximum number of terms in sum

program bn

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (xacc=PI/1.D9)
parameter (MAX=250)

character outfile*10
double precision Kf
dimension gam(MAX),bm(MAX,MAX)
dimension am(MAX,MAX),cm(MAX)
dimension a(MAX,MAX),c(MAX)
dimension kpvt(MAX),z(MAX)
dimension Nb(4)
external trans
common /out/outfile,na
common /param/Kf,rm,rt

Enter input parameters.

call input
print *, 'Enter 4 eigenmodes to be plotted: '
read *, (Nb(i),i=1,4)
print *, 'Enter maximum number of terms in sum: '
read *, N
if (N.gt. MAX) STOP 'Number of terms exceeds maximum (250)'

determine eigenvalues using Newton-Raphson method.
write (3,*) 'Computed time constants:'
x1 = 0.
do 10 i = 1, N
   x1 = x1 + xacc
   x2 = x1 + PI
   x1 = rtsafe(trans,x1,x2,xacc)
gam(i) = x1
   write (3,*) 'tau(i)/tau_p = ', 1./(gam(i)*gam(i))
10 continue

Setup matrix to determine eigenfunction coefficients.
Only upper triangular is needed because of symmetry.

am(1,1) = (1.+dsin(2.*gam(1))/(2.*gam(1)))/2.
cm(1) = dsin(gam(1))/gam(1)
bm(1,1) = cm(1)/am(1,1)
do 60 j = 2, N
   do 20 i = 1, j-1
      am(i,j) = dsin(gam(i)-gam(j))/(gam(i)-gam(j))
      am(i,j) = (am(i,j) + dsin(gam(i)+gam(j))/(gam(i)+gam(j)))/2.
20 continue
am(j,j) = (1.+dsin(2.*gam(j))/(2.*gam(j)))/2.
cm(j) = dsin(gam(j))/gam(j)
do 40 k = 1, j
   do 30 i = 1, k
      a(i,k) = am(i,k)
30 continue
   c(k) = cm(k)
40 continue
call dsico(a,MAX,j,kpvt,rcond,z)
rcond = 1.0 + rcond
if (rcond .eq. 1.0) goto 70
call dsisl(a,MAX,j,kpvt,c)
do 50 i = 1, j
   bm(i,j) = c(i)
50 continue
60 continue

Display eigenfunction coefficients.

70 open (unit=4,file=outfile(:na)//'.bn')
print *, 'Writing ', outfile(:na)//'.bn', ' ...'
write (4,*)
   * 'title top "Eigenfunction Coefficients vs Number of Terms"
   * write (4,*) 'label left "B_{n}"
   * write (4,*) 'label bottom "n"
   do 90 i = 1, 4

Appendix M: bn.for
if (Nb(i) .ge. M) goto 90
write (4,*) '# B(,,Nb(i),')'
write (4,*) 'plot spline'
do 80 k = Nb(i), j-1
   write (4,*) k, bm(Nb(i),k)
80    continue
90    continue
print *, '... done'
end
This function computes product of cexp(z2) and the complex complementary error function erfc(z1) using an infinite series approximation with fractional error everywhere less than 10^{-16}.

The infinite series approximation for the complex complementary error function corresponds to entry 7.1.29 in the Handbook of Mathematical Functions by M. Abramowitz and I.A. Stegun.

complex*16 function cerfc(z1,z2)

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (acc=1.D-16,arg=709.,MAX=50)
complex*16 z1,z2,w1,w2,fgn

x1 = dreal(z1)
y1 = dimag(z1)
x2 = dreal(z2)
y2 = dimag(z2)
w2 = dcmplx(dcos(y2),dsin(y2))
xx = x1*x1
if (dabs(xx-x2) .gt. arg) then
   cerfc = erfcc(x1,x2)*w2
   return
endif

 cerfc = (0.,0.)
do 10 n = 1, MAX
   w1 = dexp(-n*n/4.D0)/(n*n+4.*xx)*fgn(n,x1,y1)
   if (cabs(w1) .lt. acc) goto 20
   cerfc = cerfc + w1
10 continue

STOP 'CERFC - Problems with convergence'
20 cerfc = cerfc*2./PI*dexp(x2-xx)
if (x1 .eq. 0.) then
   w1 = dcmplx(0.D0,2.*y1)
else
   w1 = dcmplx(1.-dcos(2.*x1*y1),dsin(2.*x1*y1))/x1
endif

 cerfc = erfcc(x1,x2)-dexp(x2-xx)/(2.*PI)*w1-cerfc
 cerfc = cerfc*w2
return
end

complex*16 function fgn(n,x,y)

implicit double precision (a-h,o-z)
parameter (arg=709.)

if (dabs(n*y) .gt. arg) STOP 'FGH - Argument out of bounds'
fn=2.*x*(1.-dcosh(n*y)*dcos(2.*x*y))+n*dsinh(n*y)*dsin(2.*x*y)
gn=2.*x*dcosh(n*y)*dsin(2.*x*y)+n*dsinh(n*y)*dcos(2.*x*y)
fgn=dcmplx(fn,gn)
return
end
This subroutine read information about the sensor from standard input.

subroutine chipinfo()

real LAM, eox, h, g, YLOAD
complex Lmin, y11, y12, yl

common /float/h, g, eox, LAM, YLOAD
common /comp1/Lmin, y11, y12, yl

print *, 'SENSOR INPUTS:'
print *, 'Input spatial wavelength: '
read 10, LAM
print *, 'lambda =', LAM
print *, 'Input substrate permittivity: '
read 10, eox
print *, 'e_o =', eox
print *, 'Input normalized width (w/h): '
read 10, rw
print *, 'w/h =', rw
h=1.0/(4.0*rw)
print *, 'h/lambda =', h
print *, 'Input normalized interelectrode spacing (a/lambda): '
read 10, g
print *, 'a/lambda =', g
print *, 'Input normalized load capacitance: '
read 10, YLOAD
print *, 'Y_load =', YLOAD
yl = cmplx(YLOAD, 0.0)
format (E9.0)

Echo inputs to output file.

write (3,20)
format ('SENSOR INPUTS:')
write (3,30) LAM
format ('Spatial wavelength = ',1PE9.3)
write (3,40) eox
format ('Insulating layer permittivity = ',1PE9.3)
write (3,50) rw
format ('Electrode width (w/h) = ',F5.2)
write (3,60) g
format ('Interelectrode spacing (a/lambda) = ',F5.4)
write (3,70) YLOAD
format ('Normalized load capacitance = ',F5.2)
write (3,80)
format ('***************')
return
end
This program computes the spatial and temporal dependence of
the moisture concentrations in the Couette Facility for times
short compared with the diffusion time in the paper. All variables
are dimensionless.

Output files:

outfile: this file contains the input parameters, computed
coefficients and time constants.
outfile.ci: this is a plot file describing the evolution of
moisture in the paper and the oil.

Parameters:

tol: tolerance for apparent equilibrium time
kx: number of evaluation points

program ci

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (tol=0.05)
parameter (kx=100)

c
character outfile*10
double precision Kf
complex*16 ecp,ecm,cerfc
dimension tk(3)
common /out/outfile,na
common /param/Kf,rm,rt

Enter input parameters.

call input
print *, 'Enter max time for concentration in the oil (t/tp): '
read *, tmax
print *, 'Enter 3 times for concentration in the paper (t/tp): '
read *, (tk(i),i=1,3)

c
Determine nature and value of etas.

fac = 1.+Kf/rm
eta = Kf/(2.*rm*rt)
sq = eta*eta-1./rt
if (sq) 10,20,30
print *, 'etas are complex conjugate'

Appendix M: ci.for
ecp = dcmplx(eta,dsqrt(-sq))
ecm = dcmplx(eta,-dsqrt(-sq))
goto 40
20
print *, 'etas are real and equal'
PI2 = dsqrt(PI)
goto 40
30
print *, 'etas are real and distinct'
erp = eta+dsqrt(sq)
erm = eta-dsqrt(sq)

Compute spatial distribution in the paper.

open (unit=4,file=outfile(:na)//'.ci')
print *, 'Writing ', outfile(:na)//'.ci', ' ...'
write (4,*) 'window'
write (4,*) 'frame suppress'
write (4,*)
* 'title top "Moisture Concentrations in Paper and Oil"
write (4,*) 'window top'
write (4,*) 'label left "i - c_{p}"'
write (4,*) 'label bottom "x"'
write (4,*) 'plot line'
write (4,*) 0.00, 0.00
write (4,*) 1.00, 0.00
delx = PI/(2.*kk)
do 100 i = 1, 3
write (4,*) '# t/tau_p = ', tk(i)
write (4,*) 'plot spline'
t = tk(i)
t2 = dsqrt(t)
do 90 j = 0, kk
x = 1.-dcos(j*delx)
if (sq) 50,60,70
50
   cp = -2.*dreal(cerfc((x/(2.*t2)+ecp*t2)),
   *(ecp*(x+ecp*t)))/(ecp-ecm))
goto 80
60
   cp = erfcc((x/(2.*t2)+eta*t2),(eta*(x+eta*t)))
   cp = -(x+2.*eta*t)*cp+2*t2/PI2*dexp(-x*x/(4.*t))
goto 80
70
   cp = erfcc((x/(2.*t2)+erp*t2),(erp*(x+erp*t)))
   cp = cp-erfcc((x/(2.*t2)+erm*t2),(erm*(x+erm*t)))
   cp = -cp/(erp-erm)
80
   cp = 1.-fac*cp/rt
if (dabs(cp) .le. 1.) write (4,*) x, cp
90
continue
100
continue

Compute temporal distribution at the wall.
c
write (4,*) 'window bottom'
write (4,*) 'label left "i - c"'
write (4,*) 'label bottom "t"'
write (4,*) '# c_w'
write (4,*) 'plot spline'
do 150 i = 0, kx
   t = tmax*(1.-dcos(i*delx))
   t2 = dsqrt(t)
   if (sq) 110,120,130
110   cw = dreal(cerfc((ecp*t2),(ecp*ecp*t))/(ecp-ecm))
go to 140
120   cw = -t2/PI2+eta*t*erfcc((eta*t2),(eta*eta*t))
go to 140
130   cw = erfcc((er*t2),(er*er*t))
   cw = (cw-erfcc((erm*t2),(erm*erm*t)))/(2.*(er-erm))
140   cw = 1.-fac*(1.+eta*cw)
write (4,*) t, cw
continue

c
Compute temporal distribution in the oil.
c
write (4,*) '# c_o'
write (4,*) 'plot spline'
iflag = 0
do 200 i = 0, kx
   t = tmax*(1.-dcos(i*delx))
   t2 = dsqrt(t)
   if (sq) 160,170,180
160   co = dreal(cerfc((ecp*t2),(ecp*ecp*t))/(ecp*(ecp-ecm)))
   co = co*2./rt
   goto 190
170   co = (2.*eta*eta*t-1.)*erfcc((eta*t2),(eta*eta*t))
   co = co-2.*eta*t2/PI2
   goto 190
180   co = erfcc((er*t2),(er*er*t))/er
   co = (co-erfcc((erm*t2),(erm*erm*t))/erm)/(rt*(er-erm))
190   co = 1.-fac*(1.+co)
write (4,*) t, co
if (((co < e. tol) .and. (iflag < eq. 0)) then
   write (3,*) 't_3/tau_p =', t
   iflag = 1
end if
continue
end
This program computes the spatial and temporal dependence of
the moisture concentrations in the Couette Facility for times
short compared with the diffusion time in the paper.

Output files:

outfile: this file contains the input parameters, computed
coefficients and time constants.
outfile.cix: this is a plot file describing the evolution of
moisture in the paper and the oil.

Parameters:

tol: tolerance for apparent equilibrium time
kx: number of evaluation points

program cix

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (tol=0.05)
parameter (kx=100)

character outfile*10
complex*16 ecp,ecm,cerfc
double precision Ki,Kf
dimension tk(3)
common /out/outfile,na
common /param/Kf,rm,rt
common /norm/Ki,cfi,cpi,tp

Enter input parameters.

call inexp
print *, 'Enter max time for concentration in the oil (hr): '
read *, tmax
print *, 'Enter 3 times for concentration in the paper (hr): '
read *, (tk(i),i=1,3)

Determine nature and value of etas.

fac = 1.+Kf/rm
eta = Kf/(2.*rm*rt)

sq = eta*eta-1./rt
if (sq) 10,20,30
10 print *, 'etas are complex conjugate'
Appendix M: cix.for
write (4,*) 'window bottom'
write (4,*) 'label left "c (ppm)"
write (4,*) 'label bottom "t (hr)"
write (4,*) '# c_w'
write (4,*) 'plot spline'
cpi = cpi*1.D4
cpf = cpf*1.D4
cb = Ki*cpi-Kf*cpf
do 150 i = 0, kx
t = tmax*(1.-dcos(i*delx))/tp
t2 = dsqrt(t)
   if (sq) 110,120,130
110   cw = dreal(cerfc((ecp*t2),(ecp*ecp*t))/((ecp-*ecm))
goto 140
120   cw = -t2/PI2+eta*t*erfcc((eta*t2),(eta*eta*t))
goto 140
130   co = erfcc((erp*t2),(erp*erp*t))
cw = (cw-erfcc((erm*t2),(erm*erm*t)))/(2.*(erp-erm))
140   write (4,*) t*tp, (1.-fac*(1.+eta*cw))*cb+Kf*cpf
   continue
   c
   Compute temporal distribution in the oil.
   c
write (4,*) '# c_o'
write (4,*) 'plot spline'
iflag = 0
do 200 i = 0, kx
t = tmax*(1.-dcos(i*delx))/tp
t2 = dsqrt(t)
   if (sq) 160,170,180
160   co = dreal(cerfc((ecp*t2),(ecp*ecp*t))/((ecp*ecp-ecm)))
   co = co*2./rt
   goto 190
170   co = (2.*eta*eta+t-1.)*erfcc((eta*t2),(eta*eta*t))
   co = co-2.*eta*eta2/PI2
   goto 190
180   co = erfcc((erp*t2),(erp*erp*t))/erp
   co = (co-erfcc((erm*t2),(erm*erm*t))/erm)/(rt*(erp-erm))
190   co = 1.-fac*(1.+co)
   write (4,*) t*tp, co*cb+Kf*cpf
   if ((co <.le. tol) .and. (iflag .eq. 0)) then
      write (3,*) 't_*(hr) =', t*tp
         iflag = 1
   endif
200   continue
   end

262   Appendix M: cix.for
This subroutine computes the concentration of moisture in the oil and its derivative as a function of time.

subroutine coil(t,co,dco)

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (tol=0.05)

complex*16 ecp,ecm,cerfc,z
double precision Kf
common /param/Kf,rm,rt

Determine nature and value of etas.

fac = 1.*Kf/rm
eta = Kf/(2.*rm*rt)
 sq = eta*eta-1./rt
if (sq) 10,30,20
ecp = dcmplx(eta,dsqrt(-sq))
ecm = dcmplx(eta,-dsqrt(-sq))
goto 30

ERP = eta+dsqrt(sq)
ERM = eta-dsqrt(sq)

Evaluate concentration and its slope.

30
PI2 = dsqrt(PI)
t2 = dsqrt(t)
if (sq) 40,50,60
z = cerfc((ecp*t2),(ecp*ecp*t))/(ecp-ecm)
co = 1.-fac*(1.+2./rt)*dreal(z/ecp)-tol
dco = -fac*(2./rt)*dreal(z*ecp-2./(PI2*ecp*(ecp-ecm)))
return

50
C = erfcc((eta*eta2),(eta*eta)*t)
co = 1.-fac*(1.-2.*eta*eta2/PI2-(1.-2.*eta*eta)*c)-tol
dco = eta*eta*eta*(1.+2.*eta*eta)*c
dco = -fac*(2./PI2-eta/(PI2*t2)-4.*eta*eta*t/PI2+dco)
return

60
CP = erfcc((erp*t2),(erp*erp)*t)
CM = erfcc((erm*t2),(erm*erm)*t)
co = 1.-fac*(1.+(cp/erp-cm/erm)/(rt*(erp-erm)))-tol
dco = -fac*(2./PI2+(cp*erp-cm*erm)/(rt*(erp-erm)))
return
end
This program computes the spatial and temporal dependence of the moisture concentrations in the Couette Facility. All variables are dimensionless.

Output files:

outfile: this file contains the input parameters, computed coefficients and time constants.
outfile.cpo: this is a plot file describing the evolution of moisture in the paper and the oil.

Parameters:

sacc: accuracy of sum
xacc: accuracy of root
tol: tolerance for apparent equilibrium time
kx: number of evaluation points
MAX: maximum number of terms in sum

program cpo

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (sacc=1.D-9,xacc=PI/1.D9)
parameter (tol=0.05)
parameter (kx=100,MAX=250)

character outfile=10
double precision Kf
dimension gam(MAX)
dimension am(MAX,MAX),bm(MAX)
dimension kpvt(MAX),z(MAX)
dimension tk(3)
external trans
common /out/outfile,na
common /param/Kf,rm,rt

Enter input parameters.

call input
print *, 'Enter max time for concentration in the oil (t/tp): '
read *, tmax
print *, 'Enter 3 times for concentration in the paper (t/tp): '
read *, (tk(i),i=1,3)
print *, 'Enter number of terms in sum: '
read *, N
if (N .gt. MAX) STOP 'Number of terms exceeds maximum (250)

Determine eigenvalues using Newton-Raphson method.

write (3,*) 'Computed time constants:'
x1 = 0.
do 10 i = 1, N
   x1 = x1 + xacc
   x2 = x1 + PI
   x1 = rtsafe(trans,x1,x2,xacc)
   gam(i) = x1
   write (3,*) 'tau(’,i,’)/tau_p =’, 1./(gam(i)*gam(i))
10 continue

Setup matrix to determine eigenfunction coefficients.
Only upper triangular is needed because of symmetry.
do 30 j = 1, N
   do 20 i = 1, j-1
      am(i,j) = dsin(gam(i)-gam(j))/(gam(i)-gam(j))
      am(i,j) = (am(i,j) + dsin(gam(i)+gam(j))/(gam(i)+gam(j)))/2.
20 continue
   am(j,j) = (1.+dsin(2.*gam(j))/(2.*gam(j)))/2.
   bm(j) = dsin(gam(j))/gam(j)
30 continue

Solve for eigenfunction coefficients: bm(N).
call dscopy(am,MAX,N,kpvt,rcond,z)
rcond = 1.0 + rcond
if (rcond .eq. 1.0)
   STOP 'LINPACK - Matrix is singular to working precision'
call dsysl(am,MAX,N,kpvt,bm)

Compute spatial distribution in the paper.
open (unit=4,file=outfile(:na)//'.cpo')
print *, 'Writing ', outfile(:na)//'.cpo', ' ...'
write (4,*), 'window'
write (4,*), 'frame suppress'
write (4,*)
* 'title top "Moisture Concentrations in Paper and Oil"'
write (4,*), 'window top'
write (4,*), 'label left "1 - c_{p}"'
write (4,*), 'label bottom "x"'
write (4,*), 'plot line'
write (4,*), 0.0, 0.0
write (4,*), 1.0, 0.0

Appendix M: cpo.for
\[
delx = \pi/(2.*kx)
\]
do 70 i = 1, 3
  write (4,*), '# t/tau_p =', tk(i)
  write (4,*), 'plot spline'
do 60 j = 0, kx
  cp = 0.0
  x = 1.-dcos(j*delx)
do 40 k = 1, M
  cpm = bm(k)*dcos(gam(k)*1.D0-x)*dexp(-tk(i)*gam(k)*gam(k))
  if (dabs(cpm) .lt. sacc) goto 50
  cp = cp + cpm
  continue
40
50  if (dabs(cp) .le. 1.) write (4,*) x, cp
60  continue
70 continue

c Compute temporal distribution at the wall.
c
write (4,*), 'window bottom'
write (4,*), 'label left "1 - c"'
write (4,*), 'label bottom "t"'
write (4,*), '# c_w'
write (4,*), 'plot spline'
write (4,*), 0.D0, -Kf/rm
do 100 i = 1, kx
  t = tmax*(1.-dcos(i*delx))
  cw = 0.
do 80 k = 1, M
  cwm = bm(k)*dcos(gam(k))*dexp(-t*gam(k)*gam(k))
  if (dabs(cwm) .lt. sacc) goto 90
  cw = cw + cwm
80 continue
90 write (4,*) t, -cw*Kf/rm
100 continue
c c Compute temporal distribution in the oil.
c
write (4,*), '# c_o'
write (4,*), 'plot spline'
write (4,*), 0.D0, 1.D0
iflag = 0
do 130 i = 1, kx
  t = tmax*(1.-dcos(i*delx))
  co = 0.0
do 110 k = 1, M
    com = bm(k)*dsin(gam(k))/gam(k)*dexp(-t*gam(k)*gam(k))
    if (dabs(com) .lt. sacc) goto 120
    co = co + com
 110 continue
130 continue
110      continue
120      write (4,*) t, co
       if ((co .le. tol) .and. (iflag .eq. 0)) then
220      write (3,*) 't_*/tau_p =', t
        iflag = 1
       endif
130      continue
      print *, '... done'
      end
This program computes the spatial and temporal dependence of the moisture concentrations in the Couette Facility.

Output files:

outfile: this file contains the input parameters, computed coefficients and time constants.
outfile.cpx: this is a plot file describing the evolution of moisture in the paper and the oil.

Parameters:

sacc: accuracy of sum
xacc: accuracy of root
tol: tolerance for apparent equilibrium time
kx: number of evaluation points
MAX: maximum number of terms in sum

program cpx

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (sacc=1.D-9,xacc=PI/1.D9)
parameter (tol=0.05)
parameter (kx=100,MAX=250)

c
c
c
character outfile*10
double precision KI,Kf
dimension gam(MAX)
dimension am(MAX,MAX),bm(MAX)
dimension kpvt(MAX),z(MAX)
dimension tk(3)
external trans
common /out/outfile,na
common /param/Kf,rm,rt
common /norm/Ki,cfi,cpi,tp

c
c
Enter input parameters.

c
call inexp
print *, 'Enter max time for concentration in the oil (hr): '
read *, tmax
print *, 'Enter 3 times for concentration in the paper (hr): '
read *, (tk(i),i=1,3)
print *, 'Enter number of terms in sum: '
read *, N
if (N .gt. MAX) STOP 'Number of terms exceeds maximum (250)'

c
Determine eigenvalues using Newton-Raphson method.

c
write (3,*) 'Computed time constants:'
x1 = 0.
do 10 i = 1, N
   x1 = x1 + xacc
   x2 = x1 + PI
   x1 = rtsafe(trans,x1,x2,xacc)
gam(i) = x1
   write (3,*) 'tau(',i,') (hr) =', tp/(gam(i)*gam(i))
10 continue

c
Setup matrix to determine eigenfunction coefficients.
Only upper triangular is needed because of symmetry.

c
do 30 j = 1, N
   do 20 i = 1, j-1
      am(i,j) = dsin(gam(i)-gam(j))/(gam(i)-gam(j))
      am(i,j) = (am(i,j) + dsin(gam(i)+gam(j))/(gam(i)+gam(j)))/2.
20 continue
   am(j,j) = (1.+dsin(2.*gam(j))/(2.*gam(j)))/2.
bm(j) = dsin(gam(j))/gam(j)
30 continue

c
Solve for eigenfunction coefficients: bm(N).

c
call dsico(am,MAX,N,kpvt,rcond,z)
rcond = 1.0 + rcond
if (rcond .eq. 1.0)
   STOP 'LINPACK - Matrix is singular to working precision'
call dsisl(am,MAX,N,kpvt,bm)

c
Compute spatial distribution in the paper.

c
open (unit=4,file=outfile(:na)//'.cpx')
print *, 'Writing ', outfile(:na)//'.cpx', ' ...
write (4,*) 'window'
write (4,*) 'frame suppress'
write (4,*)
   * 'title top "Moisture Concentrations in Paper and Oil"
write (4,*) 'window top'
write (4,*) 'label left "c_p (%)"
write (4,*) 'label bottom "x / \Delta t"
  cpi = cpi*100.
cpf = cfi*cpi
write (4,*) 'y axis scale', cpi, cpi

Appendix M: cpx.for

delx = PI/(2.*kx)
do 70 i = 1, 3
   write (4,*), '# t (hr) =', tk(i)
   write (4,*), 'plot spline'
   tk(i) = tk(i)/tp
do 60 j = 0, kx
   cp = 0.0
   x = 1.-dcos(j*delx)
do 40 k = 1, n
   cpm=bn(k)*dcos(gam(k) *(1.D0-x))*dexp(-tk(i) * gam(k) * gam(k))
   if (dabs(cpm) .lt. sacc) goto 50
   cp = cp + cpm
   continue
40
50   write (4,*), x, cp*(cpi-cpf)+cpf
60   continue
70   continue

Compute temporal distribution at the wall.

c
write (4,*), 'window bottom'
write (4,*), 'label left "c (ppm)"'
write (4,*), 'label bottom "t (hr)"
write (4,*), '# c_w'
write (4,*), 'plot spline'
cpi = cpi*1.04
cpf = cpf*1.04
cb = Kr*cpf
write (4,*), 0.0, -(Kf/rm)*cb+Kf*cpf

100 do i = 1, kx
   t = tmax*(1.-dcos(i*delx))/tp
cw = 0.
do 80 k = 1, n
   cwm = bm(k)*dcos(gam(k)) * dexp(-t * gam(k) * gam(k))
   if (dabs(cwm) .lt. sacc) goto 90
   cw = cw + cwm
80   continue
90   write (4,*), t*tp, -cw*(Kf/rm)*cb+Kf*cpf
100 continue

Compute temporal distribution in the oil.

c
write (4,*), '# c_o'
write (4,*), 'plot spline'
write (4,*), 0.0, cb+Kf*cpf
iflag = 0
do 130 i = 1, kx
   t = tmax*(1.-dcos(i*delx))/tp
cr = 0.
do 110 k = 1, N
    com = bm(k)*dasin(gam(k))/gam(k)*dexp(-t*gam(k)*gam(k))
    if (dabs(com) .lt. sacc) goto 120
    co = co + com
110   continue
120   write (4,*) t*tp, co*cb+Kf*cpf
    if ((co .le. tol) .and. (iflag .eq. 0)) then
        write (3,*) 't_*(hr) =', t*tp
        iflag = 1
    endif
130   continue
   print *, '... done'
   end
crkf45.for

fehlberg fourth-fifth order runge-kutta method

written by h.a.watts and l.f.shampine
  sandia laboratories
  albuquerque,new mexico

modified by p.a.von guggenber
  to allow integration of complex variables and
  monitoring of good and bad steps

crkf45 is primarily designed to solve non-stiff and mildly stiff
differential equations when derivative evaluations are inexpensive.
crkf45 should generally not be used when the user is demanding
high accuracy.

abstract

subroutine crkf45 integrates a system of neqn first order
ordinary differential equations of the form
  dy(i)/dt = f(t,y(1),y(2),...,y(neqn))
  where the y(i) are given at t.
typically the subroutine is used to integrate from t to tout but it
can be used as a one-step integrator to advance the solution a
single step in the direction of tout. on return the parameters in
the call list are set for continuing the integration. the user has
only to call crkf45 again (and perhaps define a new value for tout).
actually, crkf45 is an interfacing routine which calls subroutine
rkfs for the solution. rkfs in turn calls subroutine fehl which
computes an approximate solution over one step.

crkf45 uses the runge-kutta-fehlberg (4,5) method described
in the reference
  e.fehlberg, low-order classical runge-kutta formulas with stepsize
  control , nasa tr r-315

the performance of crkf45 is illustrated in the reference
l.f.shampine,h.a.watts,s.davenport, solving non-stiff ordinary
differential equations—the state of the art,
sandia laboratories report sand75-0182 ,
to appear in siam review.

the parameters represent—
f — subroutine f(t,y,yp) to evaluate derivatives yp(i)=dy(i)/dt
neqn -- number of equations to be integrated
y(*) -- solution vector at t
t -- independent variable
tout -- output point at which solution is desired
relerr, abserr -- relative and absolute error tolerances for local
  error test. at each step the code requires that
  abs(local error) .le. relerr*abs(y) + abserr
  for each component of the local error and solution vectors
iflag -- indicator for status of integration
work(*) -- array to hold information internal to crkf45 which is
  necessary for subsequent calls. must be dimensioned 3
  cwork(*) -- complex array to hold information internal to crkf45
  necessary for subsequent calls. must be dimensioned 6*neqn
iwork(*) -- integer array used to hold information internal to
  crkf45 which is necessary for subsequent calls. must be
dimensioned 7

first call to crkf45

the user must provide storage in his calling program for the arrays
in the call list - y(neqn), work(3), cwork(6*neqn), iwork(7),
declare f in an external statement, supply subroutine f(t,y,yp) and
initialize the following parameters-

neqn -- number of equations to be integrated. (neqn .ge. 1)
y(*) -- vector of initial conditions
t -- starting point of integration, must be a variable
tout -- output point at which solution is desired.
t=tout is allowed on the first call only, in which case
  crkf45 returns with iflag=2 if continuation is possible.
relerr, abserr -- relative and absolute local error tolerances
  which must be non-negative. relerr must be a variable while
  abserr may be a constant. the code should normally not be
  used with relative error control smaller than about 1.e-8.
  to avoid limiting precision difficulties the code requires
  relerr to be larger than an internally computed relative
  error parameter which is machine dependent. in particular,
  pure absolute error is not permitted. if a smaller than
  allowable value of relerr is attempted, crkf45 increases
  relerr appropriately and returns control to the user before
  continuing the integration.
iflag -- +1,-1 indicator to initialize the code for each new
  problem. normal input is +1. the user should set iflag=-1
  only when one-step integrator control is essential. in this
  case, crkf45 attempts to advance the solution a single step
  in the direction of tout each time it is called. since this
  mode of operation results in extra computing overhead, it
  should be avoided unless needed.
output from crkf45

y(*) -- solution at t

t -- last point reached in integration.

iflag = 2 -- integration reached tout. indicates successful return
and is the normal mode for continuing integration.

 = -2 -- a single successful step in the direction of tout has been taken. normal mode for continuing integration one step at a time.

 = 3 -- integration was not completed because relative error tolerance was too small. relerr has been increased appropriately for continuing.

 = 4 -- integration was not completed because more than 3000 derivative evaluations were needed. this is approximately 500 steps.

 = 5 -- integration was not completed because solution vanished making a pure relative error test impossible. must use non-zero abserr to continue. using the one-step integration mode for one step is a good way to proceed.

 = 6 -- integration was not completed because requested accuracy could not be achieved using smallest allowable stepsize. user must increase the error tolerance before continued integration can be attempted.

 = 7 -- it is likely that crkf45 is inefficient for solving this problem. too much output is restricting the natural stepsize choice. use the one-step integrator mode.

 = 8 -- invalid input parameters

 this indicator occurs if any of the following is satisfied - neqn .le. 0

t ..tout and iflag .ne. +1 or -1

 relerr or abserr .lt. 0.

 iflag .eq. 0 or .lt. -2 or .gt. 8

work(*), cwork(*), iwork(*) -- information which is usually of no interest to the user but necessary for subsequent calls. cwork(1),...,cwork(neqn) contain the first derivatives of the solution vector y at t. work(1) contains the stepsize h to be attempted on the next step. iwork(1) contains the derivative evaluation counter. iwork(6) contains the number of good steps taken. iwork(7) contains the number of bad steps taken but retried and fixed.

subsequent calls to crkf45
subroutine crkf45 returns with all information needed to continue
the integration. if the integration reached tout, the user need only
define a new tout and call crkf45 again. in the one-step integrator
mode (iflag=-2) the user must keep in mind that each step taken is
in the direction of the current tout. upon reaching tout (indicated
by changing iflag to 2), the user must then define a new tout and
reset iflag to -2 to continue in the one-step integrator mode.

if the integration was not completed but the user still wants to
continue (iflag=3,4 cases), he just calls crkf45 again. with iflag=3
the relerr parameter has been adjusted appropriately for continuing
the integration. in the case of iflag=4 the function counter will
be reset to 0 and another 3000 function evaluations are allowed.

however, in the case iflag=5, the user must first alter the error
criterion to use a positive value of abserr before integration can
proceed. if he does not, execution is terminated.

also, in the case iflag=6, it is necessary for the user to reset
iflag to 2 (or -2 when the one-step integration mode is being used)
as well as increasing either abserr, relerr or both before the
integration can be continued. if this is not done, execution will
be terminated. the occurrence of iflag=6 indicates a trouble spot
(solution is changing rapidly, singularity may be present) and it
often is inadvisable to continue.

if iflag=7 is encountered, the user should use the one-step
integration mode with the stepsize determined by the code or
consider switching to the adams codes de/step, intrp. if the user
insists upon continuing the integration with crkf45, he must reset
iflag to 2 before calling crkf45 again. otherwise, execution will be
terminated.

if iflag=8 is obtained, integration can not be continued unless
the invalid input parameters are corrected.

it should be noted that the arrays work, cwork, iwork contain information
required for subsequent integration. accordingly, work, cwork and iwork
should not be altered.

subroutine crkf45(f, neqn, y, t, tout, relerr, abserr, iflag,
  1   work, cwork, iwork)

integer neqn, iflag, iwork(7)
double precision t, tout, relerr, abserr, work(3)
complex*16 y(neqn), cwork(6*neqn)
external f

integer k1,k2,k3,k4,k5

compute indices for the splitting of the cwork array

k1=neqn+1
k2=k1+neqn
k3=k2+neqn
k4=k3+neqn
k5=k4+neqn

calling list via the splitting apart of two working storage
arrays. If this is not compatible with the users compiler,
he must use rkfs directly.

call rkfs(f,neqn,y,t,tout,relerr,abserr,iflag,cwork(1),work(1),
1 cwork(k1),cwork(k2),cwork(k3),cwork(k4),cwork(k5),
2 work(2),work(3),iwork(1),iwork(2),iwork(3),iwork(4),
3 iwork(5),iwork(6),iwork(7))

c return
end

subroutine rkfs(f,neqn,y,t,tout,relerr,abserr,iflag,yp,h,f1,f2,f3,
1 f4,f5,savre,savae,nfe,kop,init,jflag,kflag,
2 nok,nbad)

fehlberg fourth-fifth order runge-kutta method

rkfs integrates a system of first order ordinary differential
equations as described in the comments for crkf45.
The arrays yp,f1,f2,f3,f4, and f5 (of dimension at least neqn) and
the variables h,savre,savae,nfe,kop,init,jflag, and kflag are used
internally by the code and appear in the call list to eliminate
local retention of variables between calls. Accordingly, they
should not be altered. Items of possible interest are

yp - derivative of solution vector at t
h - an appropriate stepsize to be used for the next step
nfe - counter on the number of derivative function evaluations

logical hfaild,output

integer neqn,iflag,nfe,kop,init,jflag,kflag,nok,nbad
double precision  t,tout,relerr,abserr,h,savre,savae
complex*16  y(neqn),yp(neqn),
1  f1(neqn),f2(neqn),f3(neqn),f4(neqn),f5(neqn)
c
exernal f
c
double precision  a,as,dt,ee,eest,esttol,et,hmin,remin,rer,s,
1  scale,tol,toln,twoeps,u26,ypk
c
integer  k,maxnfe,mflag
c
double precision  dabs,cdabs,dmax1,dmin1,dsign,dimach
c
remin is the minimum acceptable value of relerr. attempts
to obtain higher accuracy with this subroutine are usually
cvery expensive and often unsuccessful.
c
data remin/1.d-12/
c
cethe expense is controlled by restricting the number

do function evaluations to be approximately maxnfe.
as set, this corresponds to about 500 steps.
c
data maxnfe/3000/
c
c here two constants embodying the machine epsilon is present
twoeps is set to twice the machine epsilon while u26 is set
to 26 times the machine epsilon
c
data twoeps, u26/4.4d-16, 5.72d-15/   ***
c
twoeps = 2.*dimach(4)   ***
c
u26 = 13.*twoeps   ***
c
ccheck input parameters
c
cif (neqn .lt. 1) go to 10
if ((relerr .lt. 0.0d0) .or. (abserr .lt. 0.0d0)) go to 10
mflag=abs(iflag)
if ((mflag .ge. 1) .and. (mflag .le. 8)) go to 20
c
invalid input
10 iflag=8
return
is this the first call
20 if (mflag .eq. 1) go to 50

check continuation possibilities

if ((t .eq. tout) .and. (kflag .ne. 3)) go to 10
if (mflag .ne. 2) go to 25

iflag = +2 or -2
if (kflag .eq. 3) go to 45
if (init .eq. 0) go to 45
if (kflag .eq. 4) go to 40
if (((kflag .eq. 5) .and. (abserr .eq. 0.0d0)) go to 30
if (((kflag .eq. 6) .and. (relerr .le. savre) .and.
    (abserr .le. savae)) go to 30
    go to 50

iflag = 3,4,5,6,7 or 8
25 if (iflag .eq. 3) go to 45
if (iflag .eq. 4) go to 40
if (((iflag .eq. 5) .and. (abserr .gt. 0.0d0)) go to 45

integration cannot be continued since user did not respond to
the instructions pertaining to iflag=5,6,7 or 8
30 stop

reset function evaluation counter
40 nfe=0
    if (mflag .eq. 2) go to 50

reset flag value from previous call
45 iflag=jflag
    if (kflag .eq. 3) mflag=iabs(iflag)

save input iflag and set continuation flag value for subsequent
input checking
50 jflag=iflag
kflag=0

save relerr and abserr for checking input on subsequent calls
savre=relerr
savae=abserr

restrict relative error tolerance to be at least as large as
2*eps+remin to avoid limiting precision difficulties arising
from impossible accuracy requests
rer=2*eps+remin
if (relerr .ge. rer) go to 55

relative error tolerance too small
relerr=rer
iflag=3
kflag=3
return

55 dt=tout-t

if (mflag .eq. 1) go to 60
if (init .eq. 0) go to 65
go to 80

initialization --
set initialization completion indicator,init
set indicator for too many output points,kcp
evaluate initial derivatives
set counter for function evaluations,nfe
evaluate initial derivatives
set counter for function evaluations,nfe
estimate starting stepsize

60 init=0
kcp=0
nok=0
nbad=0

a=t
call f(a,y,yp)
nfe=1
if (t .ne. tout) go to 65
iflag=2
return

65 init=1
h=dabs(dt)
toln=0.
do 70 k=1,neqn
   toln=relerr*cfabs(y(k))+abserr
   if (tol .le. 0.) go to 70
   toln=tol
   ypk=cfabs(yp(k))
   if (ypk*h**5 .gt. toln) h=(tol/ypk)**0.2d0
70 continue
if (toln .le. 0.0d0) h=0.0d0
h=dmax1(h,u26*dmax1(dabs(t),dabs(dt)))
jflag=isign(2,iflag)

set stepsize for integration in the direction from t to tout

80 h=dsign(h,dt)

test to see if crkf45 is being severely impacted by too many
output points

if (dabs(h) .ge. 2.0d0*dabs(dt)) kop=kop+1
if (kop .ne. 100) go to 85

unnecessary frequency of output
kop=0
iflag=7
return

85 if (dabs(dt) .gt. u26*dabs(t)) go to 95

if too close to output point, extrapolate and return

do 90 k=1,neqn
90   y(k)=y(k)+dt*yp(k)
a=tout
call f(a,y,yp)
nfe=nfe+1
go to 300

initialize output point indicator

95 out= .false.

to avoid premature underflow in the error tolerance function,
scale the error tolerances

scale=2.0d0/relerr
as=scale=abserr

step by step integration

100 hfaild= .false.

set smallest allowable stepsize
hmin=u26*dabs(t)
adjust stepsize if necessary to hit the output point.
look ahead two steps to avoid drastic changes in the stepsize and
thus lessen the impact of output points on the code.

dt=tout-t
if (dabs(dt) .ge. 2.0d0*dabs(h)) go to 200
if (dabs(dt) .gt. dabs(h)) go to 150

the next successful step will complete the integration to the
output point

output= .true.
h=dt
go to 200

150 h=0.5d0*dt

core integrator for taking a single step

the tolerances have been scaled to avoid premature underflow in
computing the error tolerance function et.
to avoid problems with zero crossings, relative error is measured
using the average of the magnitudes of the solution at the
beginning and end of a step.
the error estimate formula has been grouped to control loss of
significance.
to distinguish the various arguments, h is not permitted
to become smaller than 26 units of roundoff in t.
practical limits on the change in the stepsize are enforced to
smooth the stepsize selection process and to avoid excessive
chattering on problems having discontinuities.
to prevent unnecessary failures, the code uses 9/10 the stepsize
it estimates will succeed.
after a step failure, the stepsize is not allowed to increase for
the next attempted step. this makes the code more efficient on
problems having discontinuities and more effective in general
since local extrapolation is being used and extra caution seems
warranted.

test number of derivative function evaluations.
if okay, try to advance the integration from t to t+h

200 if (nfe .le. maxnfe) go to 220
too much work
iflag=4
kflag=4
return

advance an approximate solution over one step of length h

220 call feh1(f, neqn, y, t, h, yp, f1, f2, f3, f4, f5, f1)
nfe=nfe+5

c compute and test allowable tolerances versus local error estimates
and remove scaling of tolerances. note that relative error is
measured with respect to the average of the magnitudes of the
solution at the beginning and end of the step.

esoct=0.0d0
d0 250 k=1, neqn
   et=cdaabs(y(k))+cdaabs(f1(k))+ae
   if (et .gt. 0.0d0) go to 240

inappropriate error tolerance
iflag=5
return

240  es=cdabs((-2090.0d0*yp(k)+(21970.0d0*f3(k)-15048.0d0*f4(k)))+
           (22528.0d0*f2(k)-27360.0d0*f5(k)))
250  esoct=dmax1(esoct, es/et)

esttol=dabs(h)*esoct*scale/752400.0d0

if (esttol .le. 1.0d0) go to 260

unsuccessful step
reduce the stepsize, try again
the decrease is limited to a factor of 1/10

nbad=nbad+1
hfail= .true.
output= .false.
s=0.1d0
if (esttol .lt. 59049.0d0) s=0.9d0/esttol**0.2d0
h=s*h
if (dabs(h) .gt. hmin) go to 200

requested error unattainable at smallest allowable stepsize
iflag=6
kflag=6
return

successful step

store solution at \( t+h \)
and evaluate derivatives there

260  noc=noc+1
    t=t+h
    do 270  k=1,neqn
270  \ y(k)=f1(k) \n    a=t
    call f(a,y,yp)
    nfe=nfe+1

choose next stepsize
the increase is limited to a factor of 5
if step failure has just occurred, next
stepsize is not allowed to increase

s=5.0d0
if (esttol .gt. 1.889568d-4) s=0.9d0/esttol**0.2d0
if (hfail) s=dmin1(s,1.0d0)
h=dsign(dmax1(s*dabs(h),hmin),h)

end of core integrator

should we take another step

if (output) go to 300
if (iflag .gt. 0) go to 100

integration successfully completed

one-step mode
iflag=-2
return

interval mode
300  t=tout
    iflag=2
    return

end

subroutine fehl(f,neqn,y,t,h,yp,f1,f2,f3,f4,f5,s)
fehl integrates a system of neqn first order ordinary differential equations of the form
dy(i)/dt=f(t,y(1),---,y(neqn))
where the initial values y(i) and the initial derivatives yp(i) are specified at the starting point t. fehl advances
the solution over the fixed step h and returns
the fifth order (sixth order accurate locally) solution approximation at t+h in array s(i).
f1,---,f5 are arrays of dimension neqn which are needed for internal storage.
the formulas have been grouped to control loss of significance.
fehl should be called with an h not smaller than 13 units of roundoff in t so that the various independent arguments can be distinguished.

```
integer neqn
double precision t,h
complex*16 y(neqn),yp(neqn),f1(neqn),f2(neqn),
1 f3(neqn),f4(neqn),f5(neqn),s(neqn)

double precision ch
integer k

ch=h/4.0d0
do 221 k=1,neqn
221    f5(k)=y(k)+ch*yp(k)
call f(t+ch,f5,f1)

ch=3.0d0*h/32.0d0
do 222 k=1,neqn
222    f5(k)=y(k)+ch*(yp(k)+3.0d0*f1(k))
call f(t+3.0d0*h/8.0d0,f5,f2)

ch=h/2197.0d0
do 223 k=1,neqn
223    f5(k)=y(k)+ch*((1932.0d0*yp(k)+(7296.0d0*f2(k)-7200.0d0*f1(k))))
call f(t+12.0d0*h/13.0d0,f5,f3)

ch=h/4104.0d0
do 224 k=1,neqn
224    f5(k)=y(k)+ch*((8341.0d0*yp(k)-845.0d0*f3(k))+
1 (29440.0d0*f2(k)-32832.0d0*f1(k)))
call f(t+h,f5,f4)
```
\begin{verbatim}
ch=h/20520.0d0
do 225 k=1,neqn
225   f1(k)=y(k)+ch*((-6080.0d0*yp(k)+(9295.0d0*f3(k)-
     1      5643.0d0*f4(k)))+(41040.0d0*f1(k)-28352.0d0*f2(k)))
call f(t+h/2.0d0,f1,f5)

compute approximate solution at t+h

ch=h/7618050.0d0
do 230 k=1,neqn
230   s(k)=y(k)+ch*(((902880.0d0*yp(k)+(3855735.0d0*f3(k)-
     1      1371249.0d0*f4(k)))+(3953664.0d0*f2(k)+
     2      277020.0d0*f5(k)))

return
end
\end{verbatim}
This program computes the gain-phase response over a specified frequency range given a set of complex permittivities, layer thicknesses, and sensor dimensions.

This program has been adapted to run the diffuse double layer model. The frequencies used are evenly spaced on a logarithmic scale.

program ddl

parameter (PI=3.141592654)
character cfile=10
integer f
real freq(100)
complex A(50,50),I(50),V(50),L(1000),C(1000),gp

Need for sensor specification.

integer k,N,nmax
integer M1,M2
real h,g,eox,LAM,YLOAD
real e,d,En0,w1
complex rea,rsea,Lmin,y11,y12,yl
common /comp/rea,rsea
common /com1/Lmin,y11,y12,yl
common /com2/e,d
common /flog/h,g,eox,LAM,YLOAD
common /flot/En0
common /flot2/w1
common /tin/k,N,nmax
common /tin1/M1,M2

Need for diffuse double layer region.

integer gam
double precision zet,alp,p,rp,rm,sn
double precision eps,1D
double precision ar(8,8),ai(8,8)
double precision wb,kb
double precision he,err
complex*16 sp,sm,sn,Gd(4)
common /par/zet,alp,gam,p,rp,rm,sn
common /nor/eps,1D
common /eig/ar,ai,Gd
common /wk/wb,kb
common /sfr/sp,sm,sn
common /herr/he, err

En0=0.0

Get output file name.

print *, 'Input output filename: '
read 10, ofile
format(10a)
print *, 'Output file: ', ofile
open(unit=3, file=ofile)

Get information about numerical aspect.

call num

call chipinfo

Get information about chip.

call scapinfo
call ddiinfo

Set up appropriate scan sequence.

call setfreq(f, freq)

Compute gain at requested frequencies.

write (3, 20)
format (' log(freq)', TR12, 'gain', TR14, 'phase')
write (3, 30)
format('$$')
print *, 'OUTPUTS:'

Normalize the complex permittivity.

rea = cmplx(e/orx, 0.0)
rsea = (0.0, 0.0)
do 50 i = 1, f
   print *, 'freq =', freq(i)
   wi = 2*PI*freq(i)

Compute the surface capacitance density: Cn.
call update
call scap(C)

C Compute gain.

call gain1(C,A,X,V,L,gp)
write (3,40) alog10(freq(i)), real(gp), aimag(gp)
format (F10.4,TR9,F8.3,TR10,F8.3)
continue
write (3,30)
end
ddlcn.for

This subroutine computes the surface capacitance
density of a semi-infinite diffuse double layer region.
The input variable is the fourier mode \( m \); the output variable
is the complex value for the surface capacitance density \( C_n \).
All other variables are obtained from memory through the common
statements.

subroutine ddlcn (n,Cn)

external derivs
integer i,j,m,n,gam
integer ierr,ipvt(4),iwork(7)
double precision zet,alp,p,rp,rm,rn
double precision eps,1D
double precision wb,kb,kn,ksq
double precision x,he,err,rcond
double precision work(3)
double precision ar(8,8),ai(8,8),eigr(8,8),eigi(8,8)
double precision fvi(8),fv2(8),fv3(8),wr(8),wi(8)
double precision zr(8,8),zi(8,8)
complex Cn
complex*16 sp,sm,sn
complex*16 Cb,Gd(4),Gc(4),y(8)
complex*16 zwork(4),cwork(6*8)
complex*16 zv(8,4),Pm(4,4),Qm(4,4)

Get variables from memory.

common /par/zet,alp,gam,p,rp,rm,sn
common /nor/eps,1D
common /eig/ar,ai,Gd
common /wk/wb,kb
common /sjr/sp,sm,sn
common /herr/he,err

Setup eigenvalue matrix elements that depend
on fourier mode. Only \( ar(1,5) \), \( ar(6,5) \), \( ar(6,2) \)
\( ar(7,5) \), \( ar(7,3) \), \( ar(8,4) \) are affected.

\[
\begin{align*}
kn &= kb * n \\
ksq &= kn * kn \\
ar(1,5) &= -2.0D0 * ksq \\
ar(6,5) &= -rp * ksq \\
ar(6,2) &= ar(6,5) - alp \\
ar(7,5) &= -rm * ksq \\
\end{align*}
\]
ar(7,3) = -ar(7,5) + alp
ar(8,4) = -rn * ksq - ar(8,2) * gam
sp = dcmplx(ar(8,5),dimag(sp))
sm = dcmplx(-ar(7,5),dimag(sm))
sn = dcmplx(-rn*ksq,dimag(sn))

c
Copy eigenvalue matrix.
c
EISPACK routines destroy contents of eigenvalue matrix.
c
do 20 j = 1, 8
do 10 i = 1, 8
   eigr(i,j) = ar(i,j)
eigi(i,j) = ai(i,j)
10
   continue
20
   continue

c
Solve for eigenvalues and eigenvectors.
c
Results are in (wr,wi) and (zr,zi).
c
cg is a driver routine for complex general matrices.
c
call cg(8,8,eigr,eigi,wr,wi,1,zr,zi,fv1,fv2,fv3,ierr)
if (ierr .ne. 0) then
   print *, '*********** EISPACK ERROR ***********'
   print *, 'The calculation of the',ierr,'th'
   print *, 'eigenvalue failed to converge.'
   print *, '*********** EISPACK ERROR ***********'
   write (3,30)
30
   format ('$')
   STOP
endif

c
Collect the four eigenvectors
c
whose eigenvalues have a negative real part.
c
m = 0
do 50 j = 1, 8
   if (wr(j) .lt. 0.0D0) then
      m = m + 1
      do 40 i = 1, 8
         zv(i,m) = dcmplx(zr(i,j),zi(i,j))
40
      continue
50
   endif

c
Start integration loop
c
to determine transfer relation matrices.
c
do 90 j = 1, 4
Setup boundary conditions at $x = h$.

do 60 i = 1, 8
   $y(i) = zv(i,j)$
   continue
60

Integrate variables to dielectric surface: $x = 0$.

$crkf45$ is a driver routine for the Fehlberg fourth-fifth order Runge-Kutta method with monitoring of local truncation errors to ensure accuracy and adaptive stepsize control.

if (zet .eq. 0.0D0) goto 70
   $x = he/n$
   ierr = 1
   call $crkf45$ (derivs,8,y,x,0.0D0,err,err,ierr,
      work,cwork,iwork)
      *
      if (ierr .gt. 2) then
         print *, '************ CRKF45 ERROR ************'
         print *, 'Error flag =', ierr
         print *, 'consult documentation.'
         print *, '************ CRKF45 ERROR ************'
         write (3,30)
      STOP
   endif
70

Assign results of integration to transfer relation matrices and copy boundary conditions (LINPACK destroys contents).

do 80 i = 1, 4
   $Pm(i,j) = y(i)$
   $Qm(i,j) = y(i+4)$
80
   continue
   $Gc(j) = Gd(j)$
90
   continue

Compute coefficients $A_{-j}$: QA=G'd.

ASSUMPTIONS: current and neutral particle flux density are zero at the lower boundary of the diffuse double layer.

call zgseco (Qm,4,4,ipvt,rcond,zwork)
   rcond = 1.0D0 + rcond
   if (rcond .eq. 1.0D0) then
      print *, '************ LINPACK ERROR ************'
      print *, 'Transfer relation matrix Q'
      print *, 'is singular to working precision'
      print *, '************ LINPACK ERROR ************'
      write (3,30)
STOP
endif

call zgesl (Qm,4,4,ipvt,Gc,0)

c
Compute normalized surface capacitance density.

c
Cb = (0.0D0,0.0D0)
do 100 i = 1, 4
     Cb = Cb + Pm(1,i)*Gc(i)
100 continue

c
Unnormalize surface capacitance density.

c
Cn = Cb*eps/(2.0D0*1D)

c
return
end
This subroutine gets the necessary parameters for a diffuse double layer. In addition, it sets up the eigenvalue matrix elements that are independent of fourier mode or temporal frequency.

subroutine ddlinfo()

integer i,j,gam
real h,g,eox,LAM,YLOAD
double precision zet,alp,p,rp,rm,rn
double precision eps,sig,ld,Vt,nu
double precision wb,kb
double precision br,bp,bm,PI
double precision ar(8,8),ai(8,8)
complex*16 Gd(4)
parameter(PI=3.14159265358979323846D0)

Get variables from memory.

common /f10t/h,g,eox,LAM,YLOAD
common /par/zet,alp,gam,p,rp,rm,rn
common /nor/eps,ld
common /eig/ar,ai,Gd
common /wk/wb,kb

print *, 'DDL INPUTS:'
print *, 'Input permittivity: '
read 10, eps
print *, 'eps =', eps
print *, 'Input conductivity: '
read 10, sig
print *, 'sig =', sig
print *, 'Input normalized zeta potential: '
read 10, zet
print *, 'zet =', zet
print *, 'Input thermal voltage: '
read 10, Vt
print *, 'Vt =', Vt
print *, 'Input ionization fraction: '
read 10, nu
print *, 'nu =', nu
print *, 'Input ratio of negative to positive ion mobility: '
read 10, br
print *, 'br =', br
print *, 'Input positive ion mobility: '
read 10, bp
print *, 'bp =', bp
print *, 'Input diffusion factor: '
read 10, rn
print *, 'rn =', rn
print *, 'Input normalized recombination coefficient: '
read 10, alp
print *, 'alp =', alp
print *, 'Input order of generation kinetics: '
read 20, gam
print *, 'gam =', gam
10 format (E9.0)
20 format (I2)
c
c Echo double layer inputs.
c
c write (3,30)
30 format ('DDL INPUTS:')
write (3,40) eps
40 format ('Permittivity = ', 1PE10.3)
write (3,50) sig
50 format ('Conductivity = ', 1PE10.3)
write (3,60) zet
60 format ('Normalized zeta potential = ', 1PE10.3)
write (3,70) Vt
70 format ('Thermal voltage = ', 1PE10.3)
write (3,80) nu
80 format ('Ionization fraction = ', 1PE10.3)
write (3,90) br
90 format ('Ratio of negative to positive ion mobility = ', 1PE10.3)
write (3,100) bp
100 format ('Positive ion mobility = ', 1PE10.3)
write (3,110) rn
110 format ('Diffusion factor = ', 1PE10.3)
write (3,120) alp
120 format ('Normalized recombination coefficient = ', 1PE10.3)
write (3,130) gam
130 format ('Order of generation kinetics = ', I2)
write (3,140)
140 format ('******************************')
c
c Compute parameters.
c
p = nu/(1.D0-nu)
 rp = 2.D0/(1.D0+br)
 rm = 2.D0-rp
1D = dsqrt(eps*Vt*bp*(1.D0+br)/(2.D0*sig))
 kb = 2.D0*PI*1D/LAM
 wb = eps/sig

Appendix M: ddinfo.for
bm = br*bp

c
Echo double layer parameters.
c
write (3,150)
format ('TIME CONSTANTS: ')
write (3,160) w1/(alpha*p)
format ('Generation time = ', 1PE10.3)
write (3,170) wb
format ('Electrical time = ', 1PE10.3)
write (3,180) wb/(2.0D0*kb)
format ('Migration time = ', 1PE10.3)
write (3,190) wb/(kb*kb*rp*rm)
format ('Ionic diffusion time = ', 1PE10.3)
write (3,200) wb/(kb*kb*rn)
format ('Molecular diffusion time = ', 1PE10.3)
write (3,210)
write (3,220)
format ('CHARACTERISTIC LENGTHS: ')
write (3,230) LAM
format ('Wavelength = ', 1PE10.3 )
write (3,240) 1D
format ('Debye length = ', 1PE10.3)
write (3,250) 1D*sqrt(rn)
format ('Molecular diffusion length = ', 1PE10.3)
write (3,260) kb
format ('Normalized wave number = ', 1PE10.3)
write (3,270) Vt
format ('CHARACTERISTIC POTENTIALS: ')
write (3,280) zeta*Vt
format ('Zeta potential = ', 1PE10.3)
write (3,290) zeta
format ('Normalized zeta potential = ', 1PE10.3)
write (3,300)
write (3,310) bp
format ('Mobility of positive ions = ', 1PE10.3)
write (3,320) bm
format ('Mobility of negative ions = ', 1PE10.3)
write (3,330) rp
format ('Mobility factor of positive ions = ', 1PE10.3)
write (3,340) rm
format ('Mobility factor of negative ions = ', 1PE10.3)
write (3,140)
write (3,350)
format ('DIFFUSION COEFFICIENTS:')
write (3,360) Vt*bp
write (3,370) Vt*bm
write (3,380) rn*Vt*(bp+bm)/2.D0
write (3,390) rn
write (3,410) nu
write (3,420) p
write (3,430) alp
write (3,440) gam
write (3,450) I2

Setup eigenvalue matrix elements.

do 460 j = 1, 8
   do 450 i = 1, 8
      ar(i,j) = 0.0D0
      ai(i,j) = 0.0D0
   continue
450 continue
460 continue
ar(1,2) = 1.0D0
ar(1,3) = -1.0D0
ar(2,1) = 0.5D0
ar(2,6) = -1./xp
ar(3,1) = -0.5D0
ar(3,7) = 1./rm
ar(4,8) = -1./rn
ar(5,1) = -0.5D0
ar(6,3) = -alp
ar(6,4) = gam * alp
ar(7,2) = alp
ar(7,4) = - ar(6,4)
ar(8,2) = p * alp * gam
ar(8,3) = ar(8,2)

Setup boundary conditions.

Appendix M: ddlinfo.for
Gd(1) = (1.0D0, 0.0D0)
Gd(2) = (0.0D0, 0.0D0)
Gd(3) = (0.0D0, 0.0D0)
Gd(4) = (0.0D0, 0.0D0)

return
end
This subroutine computes the derivatives of the normalized double layer variables.

subroutine derivs(x,y,dydx)

integer gam
double precision zet,alp,p,rp,rm,rn
double precision x,Phis,Es,rhosp,rhosm
double precision ar(8,8),ai(8,8)
complex*16 sp,sm,sn,temp1,temp2
complex*16 Gd(4),y(8),dydx(8)

Get variables from memory.

common /par/zet,alp,gam,p,rp,rm,rn
common /eig/ar,ai,Gd
common /sjr/sp,sm,sn

Compute static variables.

Phis = dexp(-x) * cth(zet/4.D0)
Phis = 2.D0*dlog((1.D0+Phis)/(1.D0-Phis))
Es = -2.D0*dasin(Phis/2.D0)
rhosp = dexp(-Phis)
rhosm = dexp(+Phis)
temp1 = y(1) / 2.D0
temp2 = alp * (rhosp*y(3) + rhosm*y(2) - gam*y(4))

Compute dynamic slopes.

dydx(1) = ar(1,5)*y(5) + y(2)-y(3)
dydx(2) = -y(6)/rp + rhosp*temp1 + Es*y(2)
dydx(3) = y(7)/rm - rhosm*temp1 - Es*y(3)
dydx(4) = -y(8)/rn
dydx(5) = -temp1
dydx(6) = sp*y(2)-temp2+ar(6,5)*rhosp*y(5)
dydx(7) = sm*y(3)+temp2+ar(7,5)*rhosm*y(5)
dydx(8) = sn*y(4)+p*gam*temp2

return
end
erfcc.for

This subroutine returns the product of \( \exp(y) \) and the complementary error function \( \text{erfc}(x) \) with fractional error everywhere less than \( 1.2 \times 10^{-7} \).

The approximation of the complementary error function is based on the routine erfcc.for in Section 6.2 of Numerical Recipes by W.H. Press et al.

double precision function erfcc(x,y)

implicit double precision (a-h,o-z)
parameter (arg=709.)

erfcc=0.
z=dabs(x)
if (dabs(y) .gt. arg) STOP 'ERFCC - Argument out of bounds'
if (z.gt.26.) goto 10
w=1./(1.+0.5*z)
t = y-z*z-1.26551223+w*(1.00002368+w*(-.37409196+
* .09678418+w*(-.18628806+w*(-.27886807+w*(-1.13520398+
* .148851587+w*(-.82215223+w*.17087277))))))
if (dabs(t) .gt. arg) STOP 'ERFCC - Argument out of bounds'
erfcc=w*dexp(t)
10 if (x.lt.0.) erfcc=2.*dexp(y)-erfcc
return
end
This program estimates the diffusion time constants for water into the oil and across the paper given a set of transient data for the moisture content of the oil in the Couette Facility.

Input file:

outfile.exp: this file contains a collection of data describing the measurement time and the moisture content of the oil.

Output file:

outfile: this file contains the input parameters and computed coefficients.

program est

implicit double precision (a-h,o-z)
parameter (n=2)
parameter (max=250)
parameter (lwa=max*n+5*n+n+max)

character datafile*14,outfile*10
dimension x(n),iwa(n)
dimension fvec(max),wa(lwa)
dimension t(max),co(max)

common /out/outfile,na
common /param/rm,Kf,cof,cb
common /data/t,co
external fcn

Read data.

call inest
open (unit=4,file=outfile(:na)//'.exp')
print *, 'Reading ', outfile(:na)//'.exp', ' ...'
do 10 i = 1, max
   read (4,*,err=20,end=20) t(i),co(i)
10   continue
m = i-1

Enter initial guesses and tolerance.

print *, 'Enter initial guess for tau_o (hr): ' read *, x(1)
print *, 'Enter initial guess for tau_p (hr): '

Appendix M: est.for
read *, x(2)
print *, 'Enter tolerance: '
read *, tol

Estimate parameters.

call lmdif1(fcn,m,n,x,fvec,tol,info,iwa,wa,wa)

Output diagnostic information on estimation.

c
if (info.eq.0) write (*,30)
if (info.eq.1) write (*,40)
if (info.eq.2) write (*,50)
if (info.eq.3) then
  write (*,60)
  write (*,40)
  write (*,50)
endif
if (info.eq.4) write (*,70)
if (info.eq.5) write (*,80)
if (info.eq.6) write (*,90)
if (info.eq.7) write (*,100)
30 format (' info= 0, improper input parameters',/)
40 format (' info= 1, algorithm estimates that the relative error',
  & '/,' in the sum of squares is at most tol',/)
50 format (' info= 2, algorithm estimates that the relative error',
  & '/,' between x and the solution is at most tol',/)
60 format (' info= 3, conditions for info=1 and info=2 both hold',/)
70 format (' info= 4, fvec is orthogonal to the columns of the',
  & '/,' jacobian to machine precision',/)
80 format (' info= 5, number of calls to fcn has reached or'
  & '/,' exceeded 200*(n+1)',/)
90 format (' info= 6, tol is too small. no further reduction in'
  & '/,' the sum of squares is possible',/)
100 format (' info= 7, tol is too small. no further improvement in'
  & '/,' the approximate solution x is possible',/)

c
Output parameters.

c
write (3,*) 'm =',m
write (3,*) 'tol =',tol
write (3,*) 'tau_o (hr) =',x(1)
write (3,*) 'tau_p (hr) =',x(2)
print *, '... done'
end
This subroutine computes the vector of differences between the measured and calculated concentrations of moisture in the oil.

```fortran
subroutine fcn(m,n,x,fvec,iflag)
implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0)
parameter (max=250)

integer m,n,iflag
double precision Kf
complex*16 ecp,ecm,erfc
dimension x(n),fvec(m)
dimension te(max),coe(max)

common /param/rm,Kf,cof,cb
common /data/te,coe

Determine nature and value of etas.

to = x(1)
tp = x(2)
rt = to/tp
fac = 1.+Kf/rm
eta = Kf/(2.*rm*rt)
sq = eta*eta-1./rt
if (sq) 10,20,30
10 ecp = dcmplx(eta,dsqrt(-sq))
ecm = dcmplx(eta,-dsqrt(-sq))
goto 40
20 PI2 = dsqrt(PI)
goto 40
30 erp = eta+dsqrt(sq)
erm = eta-du sqrt(sq)

Compute value of moisture concentration in oil.

do 90 i = 1, m
   t = te(i)/tp
   t2 = dsqrt(t)
   if (sq) 50,60,70
50 co = dreal(herfc((ecp*t2),(ecp*ecp*t))/(ecp*(ecp-ecm)))
   co = co*2./rt
   goto 80
60 co = (2.*eta*eta-t-1.)*erfcc((eta+t2),(eta*eta+t))
90 continue
```

Appendix M: fcn.for
co = co-2.*eta*t2/PI2
goto 80

co = erfcc((erp*t2),(erp*erp*t))/erp
co = (co-erfcc((erm*t2),(erm*erm*t))/erm)/(rt*(erp-erm))

co = 1.-fac*(1.+co)
fvec(i) = coe(i)-(co*cb+cof)

continue
return
end
This subroutine reads the input parameters and computes
the characteristic lengths and critical ratios of the
Couette Facility.

Parameters:

C: Conversion factor
Tk: Offset for kelvin scale
p0: Density of oil at T0p (kg/m^3)
T0p: Base temperature for po (K)
beta: Coefficient of thermal expansion of oil (1/K)
ppa: Apparent density of paper (kg/m^3)
ro: Mass ratio of oil absorbed in dry paper (%)

subroutine inest()

implicit double precision (a-h,o-z)
parameter (C=2.54D-2,Tk=273.)
parameter (p0=0.885D3,T0p=288.,beta=0.75D-3)
parameter (ppa=1.00D3,ro=24.)

character outfile=10
double precision Ki,Kf
common /out(outfile,na
common /param/ rm,Kf,cof,cb

Enter input parameters.

print *, 'Enter output file name: ', read 10, outfile
format(a10)
na = index(outfile, '-1)
if (na .lt. 0) na = 10
print *, 'Enter outer radius (inches): ', read *, R2
R2 = R2*C
print *, 'Enter inner radius (inches): ', read *, R1
R1 = R1*C
print *, 'Enter paper thickness (inches): ', read *, del
del = del*C
print *, 'Enter final temperature (C): ', read *, T
T = T + Tk
print *, 'Enter initial concentration in oil (ppm): '
read *, coi  
coi = coi*1.D-6  
print *, 'Enter final concentration in oil (ppm):'  
read *, cof  
cof = cof*1.D-6  
print *, 'Enter initial concentration in paper (%):'  
read *, cpi  
cpi = cpi/100.

Compute parameters.

p0 = p0/(1.+beta*(T-T0p))  
d = (R2/R1)*R2-R1  
pp = ppa*(1.+ro/100.)  
rm = pp*2.*del/(po*d)  
Ki = coi/cpi  
Kf = cof/cpi  
cfi = (rm*Ki)/(rm*Kf)  
Kf = cof/(cfi*cpi)  
cb = 1.D6*(coi-cof)  
cof = 1.D6*cof

Write parameters to output file.

open (unit=3,file=outfile(:na))  
print *, 'Writing ', outfile(:na), ' ...'  
write (3,*) 'R2 (inches) =', R2/C  
write (3,*) 'R1 (inches) =', R1/C  
write (3,*) 'Delta (inches) =', del/C  
write (3,*) 'T (C) =', T-Tk  
write (3,*) 'c_o_i (ppm) =', coi/1.D-6  
write (3,*) 'c_o_f (ppm) =', cof  
write (3,*) 'c_p_i (%) =', cpi*100.  
write (3,*) 'rho_o (kg/m^-3) =', po  
write (3,*) 'rho_p (kg/m^-3) =', pp  
write (3,*) 'r_m =', rm  
write (3,*) 'K_i =', Ki  
write (3,*) 'K_f =', Kf  
write (3,*) 'c_p_f/c_p_i =', cfi  
end
This subroutine reads the input parameters and computes
the characteristic lengths and critical ratios of the
Couette Facility.

Parameters:

C: Conversion factor
Tk: Offset for kelvin scale
p0: Density of oil at T0p (kg/m^3)
T0p: Base temperature for po (K)
beta: Coefficient of thermal expansion of oil (1/K)
ppa: Apparent density of paper (kg/m^3)
rc: Mass ratio of oil absorbed in dry paper (%)
tol: tolerance for apparent equilibrium time (%)

subroutine inexp()

implicit double precision (a-h,o-z)
parameter (C=2.54D-2,Tk=273.)
parameter (p0=0.885D3,T0p=288.,beta=0.75D-3)
parameter (ppa=1.00D3,rc=24.)
parameter (tol=5)

c
character outfile*10
double precision Ki,Kf
c
common /out(outfile,na
common /param/Kf,rm,rt
common /norm/Ki,cfi,cpi,tp

c
Enter input parameters.

c
print *, 'Enter output file name: '
read 10, outfile
format(a10)
na = index(outfile,')'-1
if (na .lt. 0) na = 10
print *, 'Enter outer radius (inches): '
read *, R2
R2 = R2*C
print *, 'Enter inner radius (inches): '
read *, R1
R1 = R1*C
print *, 'Enter paper thickness (inches): '
read *, del
del = del*C
print *, 'Enter final temperature (C): '  

Appendix M: inexp.for
read *, T
T = T + Tk
print *, 'Enter initial concentration in oil (ppm):'
read *, coi
coi = coi*1.D-6
print *, 'Enter final concentration in oil (ppm):'
read *, cof
cof = cof*1.D-6
print *, 'Enter initial concentration in paper (%):'
read *, cpi
cpi = cpi/100.
print *, 'Enter value of to (hr):'
read *, to
print *, 'Enter value of tp (hr):'
read *, tp

Compute parameters.

po = p0/(1.+beta*(T-T0p))
d = (R2/R1)*R2-R1
pp = ppa*(1.+ro/100.)
rm = pp*2.*del/(po*d)
rt = to/tp
Ki = coi/cpi
Kf = cof/cpi
cfi = (rm+Ki)/(rm+Kf)
Kf = cof/(cfi*cpi)
err = tol*(Ki/Kf-1.)/(Ki/rm+1.)

Write parameters to output file.

open (unit=3,file=outfile(:na))
print *, 'Writing ', outfile(:na), ' ...'
write (3,*) 'R2 (inches) =', R2/C
write (3,*) 'R1 (inches) =', R1/C
write (3,*) 'Delta (inches) =', del/C
write (3,*) 'T (C) =', T-Tk
write (3,*) 'c_o_i (ppm) =', coi/1.D-6
write (3,*) 'c_o_f (ppm) =', cof/1.D-6
write (3,*) 'c_p_i (%) =', cpi*100.
write (3,*) 'rho_o (kg/m^3) =', po
write (3,*) 'rho_p (kg/m^3) =', pp
write (3,*) 'tau_o (hr) =', to
write (3,*) 'tau_p (hr) =', tp
write (3,*) 'r_m =', rm
write (3,*) 'r_tau =', rt
write (3,*) 'K_i =', Ki
write (3,*) 'K_f =', Kf

Appendix M: inexp.for
write (3,*) 'c_p_f/c_p_i =', cfi
write (3,*) 'Error (%) =', err
end
This subroutine reads the input parameters and computes
the characteristic lengths, time constants, and critical ratios
of the Couette Facility.

Parameters:

C: Conversion factor
Bc: Boltzmann constant
Ec: Electronic charge
Tk: Offset for kelvin scale
p0: Density of oil at T0p (kg/m^-3)
T0p: Base temperature for po (K)
beta: Coefficient of thermal expansion of oil (1/K)
v0: Base kinematic viscosity of oil at T0v (m^-2/s)
T0v: Base temperature for vo (K)
Wo: Activation temperature for vo (K)
D0: Base diffusion coefficient of water in paper at T0d (m^-2/s)
T0d: Base temperature for Dp (K)
Wp: Activation temperature for Dp (K)
ppa: Apparent density of paper (kg/m^-3)
ro: Mass ratio of oil absorbed in dry paper (%)
tol: tolerance for apparent equilibrium time (%)

subroutine input()

implicit double precision (a-h,o-z)
parameter (PI=3.141592653589793D0,C=2.54D-2)
parameter (Bc=1.38066D-23,Ec=1.6022D-19,Tk=273.)
parameter (p0=0.885D3,T0p=288.,beta=0.75D-3)
parameter (v0=20.9D-6,T0v=298.,Wo=3394.)
parameter (D0=1.71D-13,T0d=298.,Wp=8074.)
parameter (ppa=1.00D3,ro=24.)
parameter (tol=5)

character outfile*10
double precision Ki,Kf
common /out/outfile,na
common /param/Kf,rm,rt

Enter input parameters.

print *, 'Enter output file name: '
read 10, outfile
format(a10)
na = index(outfile,' ') - 1
if (na .lt. 0) na = 10
print *, 'Enter outer radius (inches): '  
read *, R2  
R2 = R2*C  
print *, 'Enter inner radius (inches): '  
read *, R1  
R1 = R1*C  
print *, 'Enter paper thickness (inches): '  
read *, del  
del = del*C  
print *, 'Enter rotational speed (rpm): '  
read *, O  
O = 0.2*PI/60.  
print *, 'Enter final temperature (C): '  
read *, T  
T = T + Tk  
print *, 'Enter initial concentration in oil (ppm): '  
read *, coi  
coi = coi*1.D-6  
print *, 'Enter final concentration in oil (ppm): '  
read *, cof  
cof = cof*1.D-6  
print *, 'Enter initial concentration in paper (%): '  
read *, cpi  
cpi = cpi/100.

Compute parameters.

po = p0/(1.+beta*(T-T0p))  
vo = v0*dexp(Wo*(1./T-1./T0v))  
Do = (1.5D-11/(po*vo))*(Bc*T/Ec)  
S = vo/Do  
d = R2-R1  
Ry = 0*R2*d/vo  
tw = 0.1*po*(D*R2)**2/dsqrt(Ry)  
u = dsqrt(tw/ps)  
dd = 11.7*vo/((S**(1./3.))*u)  
Dp = D0*dexp(Wp*(1./T0d-1./T))  
pp = ppa*(1.+ro/100.)  
td = dd*d/Do  
to = dd/(2.*Do)  
up = del*del/Dp  
rm = pp*2.*del/(po*d)  
rt = to/up  
Ki = coi/cpi  
Kf = cof/cpi  
cfi = (rm*Ki)/(rm*Kf)  
Kf = cof/(cfi*cpi)  
err = tol*(Ki/Kf-1.)/(Ki/rm+1.)
Write parameters to output file.

open (unit=3, file=outfile(:na))
print *, 'Writing ', outfile(:na), ' ...
write (3,*) 'R2 (inches) =', R2/C
write (3,*) 'R1 (inches) =', R1/C
write (3,*) 'Delta (inches) =', del/C
write (3,*) 'Omega (rpm) =', 0*30./PI
write (3,*) 'T (C) =', T-Tk
write (3,*) 'c_o_i (ppm) =', coi/1.D-6
write (3,*) 'c_o_f (ppm) =', cof/1.D-6
write (3,*) 'c_p_i (%) =', cpi*100.0
write (3,*) 'rho_o (kg/m^3) =', po
write (3,*) 'nu_o (m^-2/s) =', vo
write (3,*) 'D_o (m^-2/s) =', Do
write (3,*) 'S = ', S
write (3,*) 'R_y = ', Ry
write (3,*) 'tau_w (Nt/m^-2) =', tw
write (3,*) 'v_* (m/s) =', u
write (3,*) 'delta_d (microns) =', dd/1.D-6
write (3,*) 'D_p (m^-2/s) =', Dp
write (3,*) 'rho_p (kg/m^3) =', pp
write (3,*) 'tau_d (s) =', td
write (3,*) 'tau_o (min) =', to/60.
write (3,*) 'tau_p (hr) =', tp/3600.
write (3,*) 'r_m =', rm
write (3,*) 'r_tau =', rt
write (3,*) 'K_i =', Ki
write (3,*) 'K_f =', Kf
write (3,*) 'c_p_f/c_p_i =', cfi
write (3,*) 'Error (%) =', err
end
isot.for

This program reads apparent equilibrium time data from the input file and interpolates given iso-t_star lines.

Input file:

infile: this file contains the coordinates (rm,rt) and the associated values of the apparent equilibrium time.

Output file:

infile.tstar: this is a plot file describing the apparent equilibrium time normalized to the diffusion time in the paper as a function of the ratios r_\tau and r_m.

Parameters:

xacc: accuracy of root
MAX: maximum number of grid points

program isotstar

implicit double precision (a-h,o-z)
parameter (xacc=1.D-9)
parameter (MAX=100)

character infile*11,outfile*11
double precision iso(10)
dimension rm(MAX),rt(MAX),t(MAX,MAX)
dimension y(MAX),y2(MAX)
dimension xi(MAX),yi(MAX)
external splint
common /param/\H,rm,y,y2,tstar

Enter input parameters.

print *, 'Enter input file name: '
read 10, infile
format(a10)
na = index(infile,' ') - 1
if (na .lt. 0) na = 10
print *, 'Enter number of iso lines: '
read *, N1
if (N1 .gt. 10) STOP 'Number of lines exceeds maximum (10)
print *, 'Enter iso values for tass: '
read *, (iso(i),i=1,N1)
Read parameters from input file.

open (unit=3, file=infile)
read (3, *) N
N = N + 1
if (N .gt. MAX) STOP 'Matrix size exceeds maximum size (100)'
do 30 j = 1, N
   do 20 i = N, 1, -1
      read (3, *) rm(j), rt(i), t(i, j)
   20 continue
30 continue

Interpolate t_star.

open (unit=4, file=infile(/na)/'.tstar')
print *, 'Writing ', infile(/na)/'.tstar', ' ...'
write (4, *) 'label left "log_{10} r_\tau"'
write (4, *) 'label bottom "log_{10} r_m"'
do 60 i = 1, N
   1 = 0
tstar = iso(i)
write (4, *) '# t_star = ', tstar
write (4, *) 'plot spline'
do 50 j = 1, N
   do 40 k = 1, N
      y(k) = t(j, k)
   40 continue
50 continue
call spline(rm, y, N, 1.D30, 1.D30, y2)
rm1 = rtbis(splint, rm(1), rm(N), xacc)
if (rm1 .gt. dmax1(dabs(rm(1)), dabs(rm(N))))) goto 50
write (4, *) rm1, rt(j)
1 = 1 + 1
xi(1) = rm1
yi(1) = rt(j)
50 continue
call ratint(xi, yi, 1, rm(N), rti, err)
write (4, *) rm(N), rti
60 continue
print *, '... done'
end
leastbx.for

This program reads in a stream of (x,y) pairs and computes the least-squares estimates and the uncertainty of the coefficient B in the expression

\[ y = Bx \]

The program assumes equal uncertainty in the measurements of y and virtually no uncertainty in the measurements of x.

program leastbx

implicit double precision (a-h,o-z)
double precision x(1000), y(1000)

do 10 i = 1, 1000
    read (5,*,err=20,end=20) x(i), y(i)
10 continue

n = i-1
if (n .le. 2) STOP 'number of points less than three'
print *, 'n = ', n
sx = 0.
sy = 0.
sx2 = 0.
sxy = 0.
do 30 i = 1, n
    sx = sx + x(i)
    sy = sy + y(i)
    sx2 = sx2 + x(i)**2
    sxy = sxy + x(i)*y(i)
30 continue

slope = sxy/sx2
sxy2 = 0.
sxyb = 0.
sxb2 = 0.
syb2 = 0.
do 40 i = 1, n
    sxy2 = sxy2 + (y(i)-slope*x(i))**2
    sxyb = sxyb + (x(i)-sx/n)*(y(i)-sy/n)
    sxb2 = sxb2 + (x(i)-sx/n)**2
    syb2 = syb2 + (y(i)-sy/n)**2
40 continue

sigmay = dsqrt(sxy2/(n-1))
sigmaslope = sigmay/dsqrt(sx2)
r = sxyb/dsqrt(sxb2*syb2)
print *, 'slope = ', slope
print *, 'sigma_slope = ', sigmaslope
print *, 'sigma_y =', sigmay
print *, 'r =', r
end
leastexp.for

This program reads in a stream of \((x,y)\) pairs and computes the least-squares estimates and the uncertainty of the coefficients \(A\) and \(B\) in the expression

\[ y = A e^{-Bx} \]

The program assumes equal uncertainty in the measurements of \(y\) and virtually no uncertainty in the measurements of \(x\).

program leastexp

implicit double precision (a-h,o-z)
double precision x(1000),y(1000),z(1000)

print *, 'y = A exp(Bx)' print *, 'log_10 y = C + Dx'
do 10 i = 1, 1000
   read (5,*,err=20,end=20) x(i), y(i)
   z(i) = dlog10(y(i))
10 continue

n = i-1
if (n .le. 2) STOP 'number of points less than three'
print *, 'n =', n
sx = 0.
sz = 0.
sy2 = 0.
sy2z = 0.
sxy2 = 0.
sxy2z = 0.
sx2y2 = 0.
do 30 i = 1, n
   sx = sx + x(i)
   sz = sz + z(i)
   sy2 = sy2 + y(i)*y(i)
   sy2z = sy2z + y(i)*y(i)*z(i)
   sxy2 = sxy2 + x(i)*y(i)*y(i)
   sxy2z = sxy2z + x(i)*y(i)*y(i)*z(i)
   sx2y2 = sx2y2 + x(i)*x(i)*y(i)*y(i)
30 continue

xb = sx/n
zb = sz/n
delta = sy2*sy2z-sxy2*sxy2
C = (sx2y2*sy2z-sxy2*sxy2)/delta
D = (sy2*sxy2z-sxy2*sy2z)/delta
beta = dlog10(dexp(1.D0))
sigy = 0.
szzb = 0.
sxb2 = 0.
szb2 = 0.
do 40 i = 1, n
   sigy = sigy + y(i)*y(i)*(z(i)-c-d*x(i))*2
   szzb = szzb + (x(i)-xb)*(z(i)-zb)
sxb2 = sxb2 + (x(i)-xb)**2
   szb2 = szb2 + (z(i)-zb)**2
40 continue
sigmay = dsqrt(sigy/(n-2))/beta
r = szzb/dsqrt(szb2*sxb2)
call sigma(x,y,z,n,sgmac,sgmad)
sgmac = sgmac*sigmay
sgmad = sgmad*sigmay
a = 10.**c
b = d/beta
sgmac = a*sgmac/beta
sgmad = sgmad/beta

c
print *, 'c =', c
print *, 'd =', d
print *, 'sgmac =', sgmac
print *, 'sgmad =', sgmad
print *, 'r =', r
print *, 'a =', a
print *, 'b =', b
print *, '1/b =', 1./b
print *, 'sgma =', sgma
print *, 'sgmb =', sgmb
print *, 'sgma/1/b =', sgma/(b*b)
print *, 'sgmy =', sigmay
end

subroutine sigma(x,y,z,n,sgmac,sgmad)

implicit double precision (a-h, o-z)
double precision x(1000),y(1000),z(1000)
parameter(epsilon=1.e-9)

c
call param(x,y,z,n,c0,d0)
sgmac = 0.0
sgmad = 0.0
do 10 i = 1, n
   ysav = y(i)
   zsave = z(i)
   y(i) = (1.+epsilon)*y(i)
   if (y(i) .eq. 0.0) y(i) = epsilon
   z(i) = dlog10(y(i))
10 continue
deltay = y(i)-ysave
        call param(x,y,z,n,C,D)
        C = (C-C0)/deltay
        sigmaC = sigmaC+C*C
        D = (D-D0)/deltay
        sigmaD = sigmaD+D*D
        y(i) = ysave
        z(i) = zsave
        continue
        sigmaC = dsqrt(sigmaC)
        sigmaD = dsqrt(sigmaD)
        return
        end

        subroutine param(x,y,z,n,C,D)

        implicit double precision (a-h,o-z)
        double precision x(1000),y(1000),z(1000)

        c
        sy2 = 0.
        sy2z = 0.
        sxy2 = 0.
        sxy2z = 0.
        sx2y2 = 0.
        do 10 i = 1, n
           sy2 = sy2 + y(i)*y(i)
           sy2z = sy2z + y(i)*y(i)*z(i)
           sxy2 = sxy2 + x(i)*y(i)*y(i)
           sxy2z = sxy2z + x(i)*y(i)*y(i)*z(i)
           sx2y2 = sx2y2 + x(i)*x(i)*y(i)*y(i)
        10       continue
        delta = sy2*sx2y2-sxy2*sxy2
        C = (sx2y2*sy2z-sxy2*sxy2z)/delta
        D = (sy2*sxy2z-sxy2*sy2z)/delta
        return
        end
This program reads in a stream of (x,y) pairs and computes the least-squares estimates and the uncertainty of the coefficients A and B in the expression
\[ y = A + Bx \]

The program assumes equal uncertainty in the measurements of y and virtually no uncertainty in the measurements of x.

Program leastsq

```
implicit double precision (a-h,o-z)
double precision x(1000), y(1000)

do 10 i = 1, 1000
   read (5,*,err=20,end=20) x(i), y(i)
10 continue
n = i-1
if (n .le. 2) STOP 'number of points less than three'
print *, 'n = ', n
sx = 0.
sy = 0.
sx2 = 0.
sxy = 0.
do 30 i = 1, n
   sx = sx + x(i)
   sy = sy + y(i)
   sx2 = sx2 + x(i)*x(i)
   sxy = sxy + x(i)*y(i)
30 continue
slope = (n*sxy-sx*sy)/(n*sx2-sx*sx)
yint = (sx2*sy-sx*sxy)/(n*sx2-sx*sx)
sxy2 = 0.
sybx = 0.
sxb2 = 0.
sybx2 = 0.
do 40 i = 1, n
   sxy2 = sxy2 + (y(i)-yint-slope*x(i))*y(i)
   sxyb = sxyb + (x(i)-sx/n)*y(i)-y/n)
   sxb2 = sxb2 + (x(i)-sx/n)*y(i)
   syb2 = syb2 + (y(i)-y/n)*y(i)
40 continue
sigmay = dsqrt(sxy2/(n-2))
sigmaslope = sigmay/dsrt(sx2-sx*sx/n)
sigmayint = sigmay*dsqrt(sx2/(n*sx2-sx*sx))
r = sxyb/dsqt(sxb2+syb2)
```
print *, 'y-int =', yint
print *, 'slope =', slope
print *, '1/slope =', 1./slope
print *, 'sigma_y =', sigmay
print *, 'sigma_yint =', sigmayint
print *, 'sigma_slope =', sigmaslope
print *, 'sigma_1/slope =', sigmaslope/(slope*slope)
print *, 'r =', r
end
This subroutine gets the necessary information for the numerical aspects of the computations of the diffuse double layer.

subroutine num()

integer N1,N2
integer k,N,nmax
double precision he,err

Store variables in memory.

common /tin1/N1,N2
common /tin/k,N,nmax
common /herr/he,err

N1: Maximum number of collocation points
N2: Number of Cn computed

N: Number of summation terms in admittance calculation (= N2)
k: Number of collocation points (< N1)

N1=50
N2=1000
print *, 'NUMERICAL INPUTS:'
print *, 'Input number of summation terms: ', read 10, N
format(I4)
N = min0(N,N2)
print *, 'N = ', N
N2 = N
print *, 'Input number of collocation points: ', read 10, k
k = min0(k,N1)
print *, 'k = ', k

Setup integration parameters for double layer.
he: thickness of space varying region
err: error tolerance

print *, 'Input thickness normalized to the Debye length: ', read 20, he
print *, 'he = ', he
print *, 'Input error tolerance for integration: ', read 20, err
print *, 'err = ', err

Appendix M: num.for
format (E9.0)
c
c  Echo inputs to output file.
c
  write (3,30)
30  format ('NUMERICAL INPUTS:')
   write (3,40) k
40  format ('Number of collocation points = ',I3)
   write (3,50) N
50  format ('Number of summation terms = ',I4)
   write (3,60) he
60  format ('Thickness of integration region = ', 1PE10.3)
   write (3,70) err
70  format ('Error tolerance for integration = ', 1PE10.3)
   write (3,80)
80  format ('**************************************************************************')
   return
end
This subroutine performs rational function interpolation on tabulated data. It is a double precision version of the subroutine ratint.for in Section 3.2 of Numerical Recipes by W.H. Press et al.

subroutine ratint(xa,ya,n,x,y,dy)

implicit double precision (a-h,o-z)
parameter (nmax=100,tiny=1.e-25)
dimension xa(n),ya(n),c(nmax),d(nmax)
s=1
hh=abs(x-xa(1))
do 10 i=1,n
   h=abs(x-xa(i))
   if (h.eq.0.)then
      y=ya(i)
      dy=0.0
      return
   else if (h.lt.hh) then
      ns=i
      hh=h
   endif
   c(i)=ya(i)
   d(i)=ya(i)+tiny
10 continue
y=ya(ns)
ns=ns-1
do 30 m=1,n-1
   do 20 i=1,n-m
      w=c(i+1)-d(i)
      h=x(i+m)-x
      t=(x(i)-x)*d(i)/h
      dd=t-c(i+1)
      if(dd.eq.0.) STOP 'There is a pole at x'
      dd=w/dd
      d(i)=c(i+1)*dd
      c(i)=t*dd
20 continue
   if (2*ns.lt.n-m)then
      dy=c(ns+1)
   else
      dy=d(ns)
      ns=ns-1
   endif
   y=y+dy
30 continue
return
end
rtbis.for

This subroutine finds the root of the function func known to lie between the extremes x1 and x2 using the bisection method. It is a double precision version of the subroutine rtbis.for in Section 9.1 of Numerical Recipes by W.H. Press et al.

double precision function rtbis(func,x1,x2,xacc)

implicit double precision (a-h,o-z)
parameter (jmax=50)
func=func(x2)
f=func(x1)
if(f*fmid.ge.0.)then
  rtbis = 2.*dmax1(dabs(x1),dabs(x2))
  return
endif
if(f.lt.0.)then
  rtbis=x1
  dx=x2-x1
else
  rtbis=x2
  dx=x1-x2
endif
do 10 j=1,jmax
  dx=dx*.5
  xmid=rtbis+dx
  fmid=func(xmid)
  if(fmid.lt.0.)rtbis=xmid
  if(dabs(dx).lt.xacc .or. fmid.eq.0.) return
10 continue
STOP 'too many bisections'
end
rtsafe.f0r

This subroutine finds the root of the function funcd known to lie between the extremes x1 and x2 using a combination of the Newton-Raphson and bisection methods. It is a double precision version of the subroutine rtsafe.f0r in Section 9.4 of Numerical Recipes by W.H. Press et al.

double precision function rtsafe(funcd,x1,x2,xacc)

implicit double precision (a-h,o-z)
parameter (maxit=100)
call funcd(x1,f1,df)
call funcd(x2,fh,df)
if(f1*fh.ge.0.) STOP 'root must be bracketed'
if(f1.lt.0.)then
  x1=x1
  xh=x2
else
  xh=x1
  x1=x2
  swap=f1
  f1=fh
  fh=swap
endif
rtsafe=.5*(x1+x2)
dxold=abs(x2-x1)
dx=dxold
call funcd(rtsafe,f,df)
do 10 j=1,maxit
   if((((rtsafe-xh)*df-f)*((rtsafe-x1)*df-f)).ge.0.
      .or. abs(2.*f).gt.abs(dxold*df) ) then
      dxold=dx
      dx=0.5*(xh-x1)
      rtsafe=x1+dx
      if(x1.eq.rtsafe)return
   else
      dxold=dx
      dx=f/df
      temp=rtsafe
      rtsafe=rtsafe-dx
      if(temp.eq.rtsafe)return
   endif
10   if(abs(dx).lt.xacc) return
call funcd(rtsafe,f,df)
if(f1.lt.0.) then
  x1=rtsafe
  f1=f

Appendix M: rtsafe.f0r
else
  xh=rtsafe
  fh=f
endif
continue
STOP 'RTSAFE exceeding maximum iterations'
end
This subroutine computes the surface capacitance density for a diffuse double layer. The double layer is always the first layer.

subroutine scap(C)

parameter (PI=3.141592654)
integer k,N,nmax,N1,N2,m
real h,g,eox,LAM,YLOAD
real e,d,A12,A22
complex tmp,Ckmin,C(1000)

Get variables from memory.

common /comp2/e,d
common /flot/h,g,eox,LAM,YLOAD
common /tin/k,N,nmax
common /tin1/N1,N2

Functions definitions:

A12(m)=(e/eox)*2*PI*m/sinh(2*PI*m*d)
A22(m)=(e/eox)*2*PI*m/tanh(2*PI*m*d)

do 10 m = 1, N2
   call dd2Cn (m,C(m))
   C(m) = C(m)*LAM/eox
   if ((2*PI*m*d) .lt. 44) then
      C(m) = A22(m)-(A12(m)**2)/(C(m)+A22(m))
   else
      C(m) = A22(m)
   end if

Find out when Cn/km approaches a limit.

if (m .eq. 1) goto 10
   tmp = C(m-1)/(2*PI*(m-1))
   tmp = tmp - C(m)/(2*PI*m)
   if (abs(aimag(tmp)) .lt. 1.E-20) tmp = cmplx(real(tmp),0.0)
   if (cabs(tmp) .lt. 1.E-5) goto 20
10  continue
nmax = N2
return
20  nmax = m
   Ckmin = C(nmax)/nmax
do 30 m = nmax+1, N2
C(m) = C_{\text{min}}^m
continue
return
end
This subroutine gets necessary information about the
dielectric layer above the electrodes.

subroutine scapinfo()

real e, d, eox, LAM, g, h, YLOAD

common /comp2/e,d
common /flot/h,g,eox,LAM,YLOAD

print *, 'DIELECTRIC INPUTS:'
print *, 'Input thickness: '
read 10, d
10 format (E9.0)
print *, 'd =', d
d = d/LAM
print *, 'Input permittivity: '
read 10, e
print *, 'e =', e

Echo inputs.

write (3,20)
20 format ('DIELECTRIC INPUTS:')
write (3,30) d*LAM
30 format ('Thickness = ',1PE8.2)
write (3,40) e
40 format ('Permittivity = ',1PE8.2)
write (3,50)
50 format ('**************************************************')
return
end
setfreq.for

This subroutine sets the appropriate set of frequencies equally spaced on a log scale.

subroutine setfreq(f,freq)

integer i,f
real c,fn,fmin,fmax,freq(100)

Enter frequency bounds.

print *, 'FREQUENCY INPUTS:
print *, 'Input lowest frequency: '
read 10, fmin
print *, 'f_min =', fmin
print *, 'Input highest frequency: '
read 10, fmax
print *, 'f_max =', fmax
format(E9.0)

Setup lowest frequency and determine order of magnitude.

f = 1
freq(f) = fmin
if (fmin .eq. fmax) return
c = aint(alog10(fmin))
if (fmin .lt. 1.0) c = c - 1.

Determine next frequency in sequence.

fn=alog10(fmin/(10.***(c)))
do 20 i = 1, 10
   if (fn .lt. (0.1*i)) then
      f = f + 1
      freq(f) = 10.***(0.1*i+c)
goto 30
   endif
20 continue

If already passed upper bound exit.

30 if (freq(f) .gt. fmax) then
   freq(f) = fmax
   return
endif

Determine rest of frequencies up to upper bound.
c
40  f = f + 1
    i = i + 1
    if (i .gt. 10) then
      o = o + 1.
      i = 1
    endif
    freq(f) = 10.**(0.1*i+o)
    if (freq(f) .gt. fmax) then
      freq(f) = fmax
      return
    else
      goto 40
    endif
end

Appendix M: setfreq.for
spline.for

This subroutine computes the second derivatives of the interpolating function at the tabulated points x(i). It is a double precision version of the subroutine spline.for in Section 3.3 of Numerical Recipes by W.H. Press et al.

subroutine spline(x,y,n,yp1,ypn,y2)

implicit double precision (a-h,o-z)
parameter (nmax=100)
dimension x(n),y(n),y2(n),u(nmax)
if (yp1.gt..99e30) then
  y2(1)=0.
  u(1)=0.
else
  y2(1)=-0.5
  u(1)=(3./(x(2)-x(1)))*((y(2)-y(1))/(x(2)-x(1))-yp1)
endif

do 10 i=2,n-1
  sig=(x(i)-x(i-1))/(x(i+1)-x(i-1))
  p=sig*y2(i-1)+2.
  y2(i)=(sig-1.)/p
  u(i)=(6.*((y(i+1)-y(i))/(x(i+1)-x(i))-(y(i)-y(i-1))
       /(x(i)-x(i-1)))/(x(i+1)-x(i-1))-sig*u(i-1))/p
10 continue

if (ypn.gt..99e30) then
  qn=0.
  un=0.
else
  qn=0.5
  un=(3./(x(n)-x(n-1)))*(ypn-(y(n)-y(n-1))/(x(n)-x(n-1)))
endif

y2(n)=(un-qn*u(n-1))/(qn*y2(n-1)+1.)
do 20 k=n-1,1,-1
  y2(k)=y2(k)*y2(k+1)+u(k)
20 continue

return
end
This subroutine computes the difference between the desired
and the calculated value of the apparent equilibrium time, tstar.
It is a modified double precision version of the subroutine
splint.for in Section 3.3 of Numerical Recipes by W.H. Press et al.

double precision function splint(x)

implicit double precision (a-h,o-z)
parameter (max=100)
common /param/n,xa,ya,y2a,tstar
dimension xa(max),ya(max),y2a(max)
klo=1
khi=n
10 if (khi-klo.gt.1) then
   k=(khi+klo)/2
   if(xa(k).gt.x) then
      khi=k
   else
      klo=k
   endif
   goto 10
endif
h=xa(khi)-xa(klo)
if (h.eq.0.) STOP 'bad xa input.'
a=(xa(khi)-x)/h
b=(x-xa(klo))/h
y=a*ya(klo)+b*ya(khi)+
* ((a**3-a)*y2a(klo)+(b**3-b)*y2a(khi))*(h**2)/6.
splint=y-tstar
return
end
This subroutine defines the transcendental function and its derivative used to compute the eigenvalues that describe the moisture concentrations in the Couette Facility.

subroutine trans(x,f,df)

implicit double precision (a-h,o-z)
double precision Kf
common /param/Kf,rm,rt

f = x*dcos(x)-(rm/Kf)*(rt*x*x-1.)*dsin(x)
df = (1.-(rm/Kf)*(rt*x*x-1.))*dcos(x)-(1.+2.*rt*rm/Kf)*x*dsin(x)
return
end
This program maps the apparent equilibrium time for a range of values of the ratios \( r_m \) and \( r_{\tau} \).

Output file:

\texttt{outfile}: this file contains the coordinates \((r_m, r_{\tau})\) and the associated values of the apparent equilibrium time.

\textbf{Parameter:}

\texttt{xacc}: accuracy of root

\textbf{Program \texttt{tstar}}

\begin{verbatim}
implicit double precision (a-h,o-z)
parameter (PI=3.14159265358979323846D0)
parameter (xacc=1.D-9)

character outfile*10
double precision Kf
external coil
common /param/Kf,rm,rt

Enter input parameters.

print *, 'Enter output file name: '
read 10, outfile
format(a10)
na = index(outfile,')'-1
if (na .lt. 0) na = 10
open (unit=3, file=outfile(:na))
print *, 'Enter Kf: '
read *, Kf
print *, 'Enter lower value of \( r_m \): '
read *, rmin
rmin = dlog10(rmin)
print *, 'Enter upper value of \( r_m \): '
read *, rmax
rmax = dlog10(rmax)
print *, 'Enter lower value of \( r_{\tau} \): '
read *, rltmin
rltmin = dlog10(rltmin)
print *, 'Enter upper value of \( r_{\tau} \): '
read *, rltmax
rltmax = dlog10(rltmax)
print *, 'Enter number of grid points: '
end run
\end{verbatim}
read *, N
write (3,*) N

c Determine apparent equilibrium time using Newton-Raphson method
and errors associated with concentrations in the oil and the paper.
c
delrm = (rmax-rmin)/N
delrt = (tmax-rtmin)/N
tstart = 1.D0

do 30 j = 0, N
   rm = 10.D0**(rmin+j*delrm)
   tmax = tstart
   do 20 i = 0, N
      rt = 10.D0**(rtmax-i*delrt)
      t = rtstarp(coil,0.D0,tmax,xacc)
      write (3,*) dlog10(rm),dlog10(rt),t
      if (i .eq. 0) tstart = tmax
tmax = 1.5*t
20    continue
30 continue

print *, '... done'
end
This subroutine updates the eigenvalue matrix elements and the parameters that depend on the temporal frequency.

subroutine update()

integer i
real w1
double precision wb, kb, w
double precision ar(8,8), ai(8,8)
complex*16 sp, sm, sn, Gd(4)

common /flot2/w1
common /sig/ar, ai, Gd
common /wk/wb, kb
common /sjr/sp, sm, sn

Only ai(6,2), ai(7,3), and ai(8,4) are affected.

w = wb * w1
ai(6,2) = -w
ai(7,3) = w
ai(8,4) = -w

Update parameters sp, sm, sn.

sp = dcmplx(0.0D0, -w)
sm = dcmplx(0.0D0, w)
sn = dcmplx(0.0D0, -w)

return
end
Bibliography

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[62] Personal communication: Michael A. Franchek, EHV-Weidmann Industries, Inc., P.O. Box 278, Route 5, St. Johnsbury, VT 05819-0903, (802) 748-8106.


[88] Low Conductivity IC Sensor, Fourteen Inch, Model 022S, Micromet Instruments, Inc., 7 Wells Avenue, Newton Centre, MA 02159, (617) 969-5060.


