INTERFACIAL SLIP OF A QUARTZ SENSOR IN LIQUID

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ABSTRACT

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The interfacial slip parameter is a complex-valued property of the interface between the solid surface of a quartz sensor and the liquid in contact with the sensor surface. It is introduced in the theory of the quartz-liquid system by generalizing the no-slip boundary condition. The interfacial slip parameter is defined as the displacement of a particle of liquid in contact with the sensor surface divided by the displacement of a particle on the surface of the sensor.

The theoretical expression for impedance of the sensor is derived in terms of the interfacial slip parameter. The impedance of the sensor is measured by the network analysis method for hydrophilic and hydrophobic surfaces in water-glycerol solutions. The experimental values of impedance are fitted to the theory by non-linear regression analysis to find the interfacial slip parameter. A mechanical model of interfacial slip is devised which explains the variation of the interfacial slip parameter with viscosity of the liquid. The results indicate that there is considerable slip in low-viscosity liquids, near the viscosity of water, and very little slip in liquids of high viscosity, near that of glycerol.

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CHAPTER 1

INTRODUCTION

A piezoelectric quartz sensor is used to detect the presence of specific molecules in a gas or liquid. There are basically two types of quartz sensors, bulk acoustic wave (BAW) and surface acoustic wave (SAW) sensors. In this work only the BAW sensor is considered. The BAW sensor is essentially a thin plate of quartz with a very thin metal electrode on each surface of the quartz. This device is used in the communications field to control frequency, where it is called simply a quartz crystal. It is available commercially in the frequency range from about 2 to 50 MHz. Cady (1964) made major contributions to the development of quartz crystals. Bottom (1982) gives an elementary treatment of the theory of the quartz crystal.

The generic name for a device that is used for molecular recognition is a chemical sensor or biosensor. The name, biosensor, is used when the molecules to be detected are biomolecules, that is, carbon-based molecules found in living organisms. The BAW quartz sensor used for molecular recognition is an AT-cut quartz crystal. This particular cut of quartz operates in the transverse shear mode (TSM), meaning that the direction of vibration of the atoms of the quartz is transverse to the direction of propagation of the acoustic wave. In this mode the displacement of the atoms of quartz is

in the plane of the quartz plate and the wave travels in the direction normal to the plane of the plate.

The principle of operation of a chemical sensor or biosensor is simple. A molecule which reacts only with the molecule to be sensed is bound to the surface of the sensor. Then the sensor is immersed in a gas or liquid. If the molecule to be sensed is present in the gas or liquid, it will bind to the molecule on the surface of the sensor. As a consequence, the mass on the surface increases and the properties of the interface change. Electrical measurements are made to detect the changes on the surface.

The network analysis method developed by Kipling and Thompson (1990) is used to completely electrically characterize the BAW quartz sensor. This method can be used when the sensor is in a liquid of any viscosity. The network analysis method replaces the oscillator method which only partially characterizes a BAW quartz sensor and is limited to operation in liquids of low viscosity. A review article by Thompson, Kipling et al (1991) describes both the network analysis method and the oscillator method. The oscillator method is analyzed by Rajaković et al (1991).

The operation of the BAW quartz sensor in the gas phase is well understood. As mass is added to the surface of the sensor, the resonant frequency of the sensor decreases. The decrease of frequency is proportional to the increase of mass on the surface which was first explained quantitatively by

Sauerbrey (1959). When the sensor is in a gas, the acoustic wave in the quartz is completely reflected at the surface of the sensor and therefore all acoustic energy remains in the quartz. The frequency decreases as mass is added because the distance travelled by the acoustic wave from one face of the sensor to the other increases due to the thickness of the layer of added mass.

The operation of the sensor in the liquid phase is not well understood. The resonant frequency change of a sensor in a liquid is not due directly to the mass added to the surface of the sensor. Rather it is due to the change of properties of the interface between the surface of the sensor and the liquid in contact with the sensor. The nature of the interface changes when the molecule to be sensed is present in the liquid because these molecules bind to the surface and therefore this new layer of molecules is in contact with the liquid. When the sensor is in a liquid, only part of the acoustic wave which is incident on the solid-liquid interface from within the quartz is reflected back into the quartz. The rest of the wave is transmitted into the liquid and is dissipated (changes into thermal energy in the liquid). The phase and magnitude of the acoustic wave which is transmitted into the liquid is very sensitive to the properties of the solid-liquid interface. The acoustic wave carries energy and therefore some of the acoustic energy flows out of the quartz into the liquid. This energy is replaced by electrical energy

supplied to the quartz crystal that is converted by the piezoelectric effect into acoustic energy. The change of electrical energy supplied to the sensor changes the electrical characteristics measured at the terminals of the sensor.

The interfacial properties are related to three fundamental attributes of the interface: the type of molecule on the surface of the sensor, the type of molecule in the liquid which is in contact with the sensor surface and the force of attraction between the two sets of molecules. If the force of attraction is relatively strong, the surface is said to be hydrophilic and if relatively weak, the surface is hydrophobic. It is expected that there will be some slip between the molecules on the surface of the sensor and the molecules of the liquid in contact with the surface, especially when the surface is hydrophobic.

The objective of this research is to study the slip at the solid-liquid interface of a quartz sensor. A two-layer model is used, the layers being quartz and the liquid, with the interface characterized by a new property called the interfacial slip parameter. This model allows relative motion between the surface of the sensor and the liquid in contact with the surface. Reed et al (1990) used a two-layer model but with the no-slip boundary condition. Duncan-Hewitt and Thompson (1992) used a four-layer model to account for interfacial effects, where one layer is quartz and the other

three layers are different phases of the liquid, as an alternative to explicitly introducing slip at the interface.

A model of slip has been used for the case of the interface between two elastic media which are imperfectly bonded, Schoenberg (1980). The slip between the two solid regions is postulated to be linearly related to the shear stress at the interface, the slip parameter being the proportionality factor with the dimension of length/stress. In this thesis the interfacial slip parameter is defined differently.

The interfacial slip parameter appears in the theory of the two-layer model in one of the boundary conditions. The theoretical expression for impedance was found, which is a function of the interfacial slip parameter, Chapter 2. Measurements of impedance were made by the network analysis method and the experimental values of impedance were fitted to the theoretical expression for impedance using non-linear regression analysis to find the interfacial slip parameter, Chapter 3. A mechanical model of interfacial slip was devised whose predictions agree with the experimental results, Chapter 4. It is concluded that there is slip at the solid-liquid boundary of a BAW quartz sensor, Chapter 5.

The application software used in the research and in the preparation of this thesis is listed in Appendix 1.

CHAPTER 2

THEORY

Introduction

The theory of the two-layer model of a piezolectric quartz sensor is derived in terms of a new property of the interface called the interfacial slip parameter.

The two-layer model is a solid-liquid model which neglects the thickness of two other layers of material between the quartz and liquid: the metal electrode which is attached to the quartz and the chemical coating which is attached to the metal electrode. The theory also assumes that the liquid in contact with surface of the solid has the same properties, that is, it has the same structure, as the bulk liquid. The theory focuses on the interaction between the surface of the solid and the liquid in contact with the solid. The interaction is represented by the interfacial slip parameter which is introduced through one of the boundary conditions.

Three fields of physics are combined in this theory. Elasticity, Section 2.1, and electromagnetism, Section 2.2, constitute the theory of piezoelectricity, Section 2.3. The fundamental equations of elasticity and electromagnetism are coupled by the equations of the piezoelectric material. Fluid mechanics, Section 2.4, is the theory of the liquid. The boundary conditions, Section 2.5, of the solid-liquid

interface connect the equations of the piezoelectric medium and the liquid. The boundary value problem is solved, section 2.6, and then the theoretical expression for impedance is derived, section 2.7.

Subscript notation is used throughout and is described in Appendix 2.

2.1 Elasticity

There are three fundamental equations of elasticity and one equation of a viscoelastic material, Eringen (1967) and Eringen and Maugin (1990). The fundamental equations are derived from Newton's second law, conservation of angular momentum and the definition of strain. The material equation is a generalization of Hooke's law. Newton's second law and the definition of strain are non-linear equations due to the terms which are products of the variables. Two approximations are made which remove these terms and make the equations linear.

Newton's second law for a viscoelastic solid of density, ρ_m, is

$$\frac{D}{Dt}(\rho_m \dot{u}_j) = T_{ij,i} + F_{(m)j} \qquad (2\text{-}1)$$

Equation (2-1) relates the particle displacement, u_j, to the second-rank stress tensor, T_{ij}, and the external force $F_{(m)j}$. The

symbol, D/Dt, denotes the material derivative with respect to the time, t.

The total change of particle velocity, $\dot{u}_j = \dot{u}_j(x,y,z,t)$, is the total differential of $\dot{u}_j$, $d\dot{u}_j = (\partial\dot{u}_j/\partial x)dx + (\partial\dot{u}_j/\partial y)dy + (\partial\dot{u}_j/\partial z)dz + (\partial\dot{u}_j/\partial t)dt$. Divide both sides by dt and use the notation, $D\dot{u}_j/Dt$, instead of $d\dot{u}_j/dt$, for the particle acceleration. Since the components of the particle displacement, u_j, are dx_j, when the displacement is infinitely small, dx_i/dt is $\dot{u}_i$, the velocity of the particle.

$$\frac{D\dot{u}_j}{Dt} = \frac{\partial\dot{u}_j}{\partial t} + \frac{\partial\dot{u}_j}{\partial x_i}\dot{u}_i \qquad (2\text{-}2)$$

The term on the left, $D\dot{u}_j/Dt$, is the particle acceleration, the first term on the right, $\partial\dot{u}_j/\partial t$, the local acceleration and the last term, the convective acceleration. In the theory of linear viscoelasticity, meaning for small deformations of the viscoelastic medium, the magnitude of the deformation gradient is much less than one, that is, $|u_{i,j}| \ll 1$. Therefore from (2-2) the convective term, $\dot{u}_{i,j}\dot{x}_i$, is much less than the non-convective term, $\dot{v}_j$ (where $v_j = \dot{u}_j$). Thus for a linear viscoelastic theory, from (2-1), the equation of motion for a medium of uniform mass density, ρ_m, reduces to

$$\rho_m\ddot{u}_j = T_{ij,i} + F_{(m)j} \qquad (2\text{-}3)$$

From the law of conservation of angular momentum, at each

point in the medium, T_{ij} satisfies the following equation.

$$T_{ij} = T_{ji} \qquad (2\text{-}4)$$

Equation (2-4) states that the stress tensor is symmetric. This is a direct result of the conservation of angular momentum at each point of the medium.

Equation (2-3) constitutes a system of three scalar equations in the twelve dependent variables: u_1, u_2, u_3, T_{11}, T_{12}, T_{13}, T_{21}, T_{22}, T_{23}, T_{31}, T_{32}, and T_{33}. They are functions of the independent variables: the spatial coordinates, x, y, z, and the time, t. Due to the symmetry of T_{ij}, from (2-4), $T_{12} = T_{21}$, $T_{13} = T_{31}$, and $T_{23} = T_{32}$. Therefore from (2-4) there are six distinct components of T_{ij} which are T_{11}, T_{12}, T_{13}, T_{22}, T_{23}, and T_{33}. Thus the above twelve dependent variables reduce to nine dependent variables given by: u_1, u_2, u_3, T_{11}, T_{12}, T_{13}, T_{22}, T_{23}, and T_{33}.

For a given deformation of a viscoelastic medium, the general expression relating the second-rank strain tensor, S_{ij}, to the particle displacement, u_j is

$$S_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i} - u_{k,i}u_{k,j}\right) \qquad (2\text{-}5)$$

The symmetry of S_{ij} can be deduced from (2-5). Like the second-rank stress tensor, the second-rank strain tensor is a symmetric tensor, that is, $S_{ij} = S_{ji}$. For small deformations,

the magnitude of the product of two deformation gradients is much less than the magnitude of the deformation gradient alone, that is, $|u_{k,i}u_{k,j}| \ll |u_{i,j} + u_{j,i}|$. Thus (2-5) reduces to

$$S_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \qquad (2\text{-}6)$$

Due to the symmetry of S_{ij}, (2-6) constitutes a system of six scalar equations in the nine dependent variables given by: u_1, u_2, u_3, S_{11}, S_{12}, S_{13}, S_{22}, S_{23}, and S_{33}. Equations. (2-3) and (2-6), together constitute a system of nine scalar equations in the fifteen dependent variables given by: u_1, u_2, u_3, T_{11}, T_{12}, T_{13}, T_{22}, T_{23}, T_{33}, S_{11}, S_{12}, S_{13}, S_{22}, S_{23}, and S_{33}. The above system, does not constitute a complete system of equations. To complete the above system, six additional scalar equations are needed. The completion of the above system of equations is accomplished by the material equation for the viscoelastic medium. For an arbitrary viscoelastic medium, the material equation that relates the stress and strain is

$$T_{ij} = c_{ijkl} S_{kl} + \eta_{ijkl} \dot{S}_{kl} \qquad (2\text{-}7)$$

Equation (2-7) is the generalized form of Hooke's law for an arbitrary viscoelastic medium, the first term on the right being the elastic term of Hooke's law and the second term, the viscous term. The coefficients c_{ijkl} and η_{ijkl} are respectively the fourth-rank elastic coefficient tensor and the fourth-rank

viscoelastic coefficient tensor. Equation (2-7) constitutes a system of six scalar equations in no new dependent variables. Thus, (2-3), (2-4), (2-6), and (2-7) constitute a system of fifteen scalar equations in the fifteen dependent variables: u_1, u_2, u_3, T_{11}, T_{12}, T_{13}, T_{22}, T_{23}, T_{33}, S_{11}, S_{12}, S_{13}, S_{22}, S_{23}, and S_{33}. Therefore (2-3), (2-4), (2-6), and (2-7) constitutes a complete system of equations.

For an arbitrary viscoelastic medium, from the symmetry of both T_{ij} and S_{ij}, an inspection of (2-7) reveals that both c_{ijkl} and η_{ijkl} must satisfy the relations

$$c_{ijkl} = c_{ijlk} = c_{jikl} = c_{klij} \qquad \textbf{(2-8)}$$

and

$$\eta_{ijkl} = \eta_{ijlk} = \eta_{jikl} = \eta_{klij} \qquad \textbf{(2-9)}$$

The relations for c_{ijkl} and η_{ijkl} given by (2-8) and (2-9) hold for any viscoelastic medium.

The derivation of the viscoelastic wave equation for a linear viscoelastic material, is obtained by the systematic elimination of the components of the stress and strain from (2-3), (2-6), (2-7), (2-8), and (2-9). The result is the viscoelastic wave equation for u_j, given by

$$c_{ijkl}\, u_{k,li} + \eta_{ijkl}\, \dot{u}_{k,li} + F_{(m)j} = \rho_m \ddot{u}_j \qquad \textbf{(2-10)}$$

For the case of plane-wave propagation, (2-10) reduces to

Christoffel's equation.

2.2 Electromagnetism

There are four fundamental equations of electromagnetism which are called Maxwell's equations and in general, there are three equations of the material which are the equations for a conductor, a dielectric, and a magnetic material, Lorrain et al (1988).

For a stationary linear medium, Maxwell's four equations are

$$E_{i,i} = \frac{\rho}{\epsilon_o} \qquad \textbf{(2-11)}$$

$$B_{i,i} = 0 \qquad \textbf{(2-12)}$$

$$\varepsilon_{ijk} E_{kj} + \dot{B}_i = 0 \qquad \textbf{(2-13)}$$

$$\varepsilon_{ijk} B_{kj} - \frac{1}{c^2} \dot{E}_i = \mu_o J_i \qquad \textbf{(2-14)}$$

where ε_{ijk} is the levi-civita symbol defined in Appendix 2, E_i is the electric field, B_i is the magnetic field, ρ is the total charge density, J_i is the total current density, ϵ_o is the permittivity of free space, $\epsilon_o = 8.854 \times 10^{-12}$ F/m, μ_o is the

permeability of free space, $\mu_o = 4\pi\times10^{-7}$ H/m and c is the speed of light, $c = 2.998\times10^{8}$ m/s.

Equation (2-11) expresses Gauss's law in differential form. Gauss's law, in turn is a consequence of Coulomb's law. Equation (2-12) states the absence of magnetic monopoles. Equation (2-13) is the differential form of Faraday's law for time-dependent magnetic fields. Equation (2-14) is the differential form of Ampère's law for time-dependent electric fields. Maxwell's equations are relations between the fields, E_i and B_i, and the sources of the fields, ρ and J_i. The sources ρ, and J_i, are expressed in terms of the field quantities, E_i and B_i, by the equations of the material.

Maxwell's equations constitutes a system of eight scalar equations in the six dependent variables: E_1, E_2, E_3, B_1, B_2, and B_3. As a result there is some redundancy in the set of equations since there are more equations then unknowns. It is shown in Lorrain et al (1988) that equations (2-11) and (2-12) can be derived from (2-13) and (2-14). The independent variables are the time, t, and the spatial coordinates, x, y and z.

The total charge density, ρ, and the total current density, J_i, in (2-11) and (2-14) are defined by the two following equations.

$$\rho = \rho_f + \rho_b \qquad (2-15)$$

$$J_i = J_{fi} + J_{bi} + J_{Mi} \qquad \textbf{(2-16)}$$

The total charge density, ρ, is divided into two parts: the free charge density, ρ_f and the bound charge density, ρ_b. The total current density, J_t, is divided into three parts: The free charge current density, J_{fi}, the bound charge current density, J_{bi}, and the equivalent current density due to the magnetic material, J_{Mi}, which is due to the motion and spin of charge inside the atom.

The bound charge density in (2-15), ρ_b, and the current density of bound charge in (2-16), J_{bi}, are expressed in terms of the polarization, P_t. The vector, P_t, is the dipole moment per unit volume. The dipole moment is due to the displacement of positive and negative bound charges, and is defined as $|q|d$, where d is the distance between a positive charge of magnitude, $|q|$, and a negative charge of the same magnitude, $-|q|$.

The equivalent current density due to a magnetic material, J_{Mi}, in (2-16) is expressed in terms of the magnetization, M_t. The vector, M_t, is the magnetic moment per unit volume. The magnetic moment is due to circulating currents inside an atom or molecule making up the material, and is defined as IA where I is the current flowing around a loop of area A. Equations (2-15) and (2-16) in terms of P_t and M_t are

$$\rho = \rho_f - P_{i,i} \tag{2-17}$$

$$J_i = J_{fi} + \dot{P}_i + \varepsilon_{ijk} M_{kj} \tag{2-18}$$

In general, there are three equations of the material, one each, for the behaviour of the free charge, the bound charge, and the motion of the charge inside the atom.

(1) Free Charge - Conducting Materials

The material equation for a conducting material of electrical conductivity, σ, is

$$J_{fi} = \sigma E_i \tag{2-19}$$

which is called Ohm's law. The electric field, E_i, induces the current of free charge, J_{fi}, and this current is proportional to E_i, if E_i is not too large. For an insulator, $\sigma = 0$, and therefore $J_{fi} = 0$. Also for an insulator, since there are no free charges, $\rho_f = 0$.

(2) Bound Charge - Dielectric Materials

The material equation for a dielectric material of electrical susceptibility, χ_e, is

$$P_i = \epsilon_o \chi_e E_i \tag{2-20}$$

The electric field exerts a force on a positive charge in the direction of the field and a force on a negative charge in the

opposite direction. Therefore the electric field displaces positive and negative charges contained in atoms and molecules. If the electric field is not too large, then the displacement of the charges is proportional to the magnitude of the applied electric field. Therefore, the polarization, P_i, is proportional to the electric field, E_i. For all materials, $\chi_e \neq 0$.

(3) Atomic Charge - Magnetic Materials

The material equation for a magnetic material of magnetic susceptibility, χ_m, is

$$M_i = \frac{\chi_m}{\mu_o (\chi_m + 1)} B_i \qquad \textbf{(2-21)}$$

The magnetic field, B_i, orients current loops in the same direction, that is, the electron orbits and spins inside atoms and molecules are aligned with the magnetic field. The magnetization, M_i, is proportional to the magnetic field if the magnetic field is not too large, as given by (2-21). For non-magnetic materials, $\chi_m = 0$.

The general expressions for ρ and J_i, (2-17) and (2-18), in terms of E_i and B_i are, from (2-19) to (2-21)

$$\rho = \rho_f - \epsilon_o \chi_e E_{i,i} \qquad \textbf{(2-22)}$$

$$J_i = \sigma E_i + \epsilon_o \chi_e \dot{E}_i + \varepsilon_{ijk} \frac{\chi_m}{\mu_o (\chi_n + 1)} B_{kj} \qquad \textbf{(2-23)}$$

The material equations for a piezoelectric material are expressed in terms of the electric displacement, D_i, which is defined as

$$D_i = \epsilon_o E_i + P_i \qquad \textbf{(2-24)}$$

The physical significance of D_i is seen by substituting (2-17) into (2-11); the result is $(\epsilon_o E_i + P_i)_{,i} = \rho_f$. Therefore the divergence of D_i, $D_{i,i}$, is equal to the free charge density, ρ_f, that is, the free charge is the source of the field, D_i. For an insulator such as quartz, $\rho_f = 0$, and therefore as a result $D_{i,i} = 0$.

For a nonconducting ($\sigma = 0$ and $\rho_f = 0$), nonmagnetic ($\chi_m = 0$) material such as quartz, Maxwell's equations, (2-11) to (2-14), combined with the source equations (2-17) and (2-18) are expressed in terms of the field quantities E_i, B_i, and D_i, where P_i is eliminated using (2-24).

$$D_{i,i} = 0 \qquad \textbf{(2-25)}$$

$$B_{i,i} = 0 \qquad \textbf{(2-26)}$$

$$\varepsilon_{ijk} E_{k,j} = -\dot{B}_i \qquad \textbf{(2-27)}$$

$$\varepsilon_{ijk} B_{j,k} = \mu_o \dot{D}_i \qquad \textbf{(2-28)}$$

The relation, $c^2 = 1/(\mu_o \epsilon_o)$ has been used to obtain (2-28). Maxwell's equations in the form of (2-25) to (2-28) are used in the derivation of the dynamical equations of motion of a viscoelastic piezoelectric material.

The material equation for a dielectric material in terms of D_i is obtained by combining (2-20) and the definition of D_i, (2-24).

$$D_i = \epsilon_o (1 + \chi_e) E_i \qquad \textbf{(2-29)}$$

Maxwell's equations, (2-11) to (2-14) can be combined, to yield an equation for E_i and an equation for B_i, both of which are wave equations. For the case of a nonmagnetic insulator, substitute (2-22) and (2-23) into (2-11) and (2-14) with $\rho_f = 0$, $\sigma = 0$, and $\chi_m = 0$. The elimination of B_i from (2-13) and (2-14), using (2-11) results in the wave equation for E_i given by

$$E_{i,jj} = \frac{(1 + \chi_e)}{c^2} \ddot{E}_i \qquad \textbf{(2-30)}$$

Equation (2-30) constitutes a set of three scalar equations in the three variables: E_1, E_2, and E_3. By the same token, the elimination of E_i from (2-13) and (2-14), using (2-12) yields

$$B_{i,jj} = \frac{(1 + \chi_e)}{c^2} \ddot{B}_i \qquad (2\text{-}31)$$

As in (2-30), (2-31) constitutes a set of three scalar equations in the three variables: B_1, B_2, and B_3.

2.3 Piezoelectricity

The equations of motion describing the dynamics of a piezoelectric material such as quartz are obtained by combining the fundamental equations of elasticity with the fundamental equations of electromagnetism together with the material equations of elasticity and electromagnetism generalized for a piezoelectric material, Auld, Volumes I and II (1973), Kinsler et al (1982), and Tiersten (1969). The complete set of equations contains three approximations. Two have already been made when writing the equations of elasticity and one more approximation is made in this section.

One fundamental equation of elasticity is

$$T_{ij,i} = \rho_m \ddot{u}_j \qquad (2\text{-}32)$$

Equation (2-32) is equation (2-3) with $F_{(m)j} = 0$ which is Newton's second law for an arbitrary viscoelastic material. From (2-4), T_{ij} is symmetric. The second fundamental equation is given by (2-6). From (2-6), S_{ij} is symmetric.

There is one material equation of elasticity, for a piezoelectric material; it is a generalization of (2-7). For a piezoelectric material with piezoelectric stress coefficient, e_{ijk}, the material equation is

$$T_{ij} = -e_{ijk} E_k + c^E_{ijkl} S_{kl} + \eta^E_{ijkl} \dot{S}_{kl} \qquad \textbf{(2-33)}$$

The fundamental equations of electromagnetism for a nonmagnetic insulating material are Maxwell's equations given by (2-25) to (2-28). There is one material equation of electromagnetism for a piezoelectric material. It is a generalization of (2-29). For a material with dielectric strain coefficient, ϵ^S_{ik}, and piezoelectric stress coefficient, e_{ikl}, the equation is

$$D_i = \epsilon^S_{ik} E_k + e_{ikl} S_{kl} \qquad \textbf{(2-34)}$$

For a piezoelectric material the two material equations, (2-33) and (2-34), connect (or couple) the fundamental equations of elasticity and electromagnetism, since in both (2-34) and (2-44) there are elastic and electromagnetic variables.

For a nonconducting, nonmagnetic, viscoelastic, piezoelectric material in the absence of external forces, the relevant equations of motion which describe the dynamics of the medium are given by (2-6), (2-25) to (2-28), and (2-32) to (2-34). The above system of equations constitutes a system of twenty-six scalar equations in the twenty-four variables: u_i,

u_2, u_3, T_{11}, T_{12}, T_{13}, T_{22}, T_{23}, T_{33}, S_{11}, S_{12}, S_{13}, S_{22}, S_{23}, S_{33}, E_1, E_2, E_3, B_1, B_2, B_3, D_1, D_2, and D_3. The number of equations exceeds the number of variables by two, due to the redundancy of Maxwell's equations, Lorrain et al (1988); (2-25) and (2-26) can be derived from (2-27) and (2-28). Thus upon the exclusion of (2-25) and (2-26), the above set of equations constitutes a set of twenty-four scalar equations and twenty-four variables. Since the number of equations equals the number of variables, then the system is complete. The system of coupled wave equations interrelating u_i to E_i is derived from this complete set of equations, by eliminating all other variables.

The complete set of the equations of piezoelectricity are given in Table 2.1. The physical quantities of piezoelectricity are given in Table 2.2. The material properties in the equations of piezoelectricity are given in Table 2.3.

Table 2.1 Equations of Piezoelectricity

Type	Category	Name	Equation	Number
Elastic	Fundamental	Newton's second law	$T_{ij,i} = \rho_m \ddot{u}_j$	3
		Definition of strain	$S_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$	6
	Material	Hooke's law	$T_{ij} = -e_{ijk} E_k + c^E_{ijkl} S_{kl} + \eta^E_{ijkl} \dot{S}_{kl}$	6
Electromagnetic	Fundamental	Gauss's law	$D_{i,i} = 0$	1
		No magnetic monopoles	$B_{i,i} = 0$	1
		Faraday's law	$\varepsilon_{ijk} E_{k,j} = -\dot{B}_i$	3
		Ampère's law	$\varepsilon_{ijk} B_{j,k} = \mu_o \dot{D}_i$	3
	Material	Dielectric equation	$D_i = \epsilon^S_{ik} E_k + e_{ikl} S_{kl}$	3

Table 2.2 Physical Quantities of Piezoelectricity

Type	Name	Symbol	Components	Units
Elastic	particle displacement	u_i	3	m
	stress	T_{ij}	6	N/m^2
	strain	S_{ij}	6	m/m
Electromagnetic	electric field	E_i	3	N/C
	magnetic field	B_i	3	$V \cdot s/m^2$
	electric displacement	D_i	3	C/m^2

Table 2.3 Material Properties of Piezoelectricity

Type	Name	Symbol	Units
Elastic	density	ρ_m	kg/m^3
	elastic coefficient	c^E_{ijkl}	N/m^2
	viscoelastic coefficient	η^E_{ijkl}	$N \cdot s/m^2$
Electromagnetic	dielectric strain coefficient	ϵ^S_{ik}	$C/V \cdot m$
Piezoelectric	piezoelectric stress coefficient	e_{ijk}	C/m^2

In (2-34), ϵ^S_{ik}, denotes the second-rank dielectric strain coefficient tensor. The superscript 'S' refers to the measurement of ϵ^S_{ik} under conditions of constant strain. Also in (2-34), e_{ikl}, denotes the third-rank piezoelectric stress coefficient tensor. The piezoelectric stress coefficient tensor, e_{ikl}, and the second-rank dielectric strain coefficient tensor, ϵ^S_{ik}, satisfy the following symmetry relations as a consequence of the symmetry of S_{kl}; $S_{kl} = S_{lk}$.

$$e_{ikl} = e_{ilk} \tag{2-35}$$

$$\epsilon^S_{ik} = \epsilon^S_{ki} \tag{2-36}$$

From (2-35), e_{ikl}, is symmetric with respect to the indices l and k, while, ϵ^S_{ik}, is symmetric with respect to the indices i and k.

The form of the material equations for a piezoelectric material, (2-33) and (2-34), are derived as follows. For an anisotropic material, the electric susceptibility of the medium, χ_e, generalizes to the second-rank electric susceptibility coefficient tensor, $\chi^{(e)}_{ij}$. Physically the tensor character of χ_e is due to the fact that in an anisotropic medium, χ_e has different values for different directions. From (2-20), the material equation relating P_i to E_i, in an anisotropic medium generalizes to, Auld, Volume I (1973),

$$P_i = \epsilon_o \chi^{(e)}_{ij} E_j + d_{ijk} T_{jk} \tag{2-37}$$

where d_{ijk} is the third-rank strain coefficient tensor.

In (2-37) the first term on the right, $\epsilon_o \chi^{(e)}_{ij} E_j$, is the only term in (2-20). It is the part of the polarization, P_i, that is produced by the electric field, E_i. The second term, $d_{ijk} T_{jk}$, represents the other part of the polarization that is produced under the action of an applied stress, T_{jk}.

The material equation relating the strain, S_{ij}, to the electric field, E_k, and the stress, T_{kl}, is a generalization of (2-7) Auld, Volume I (1973).

$$S_{ij} = d_{ijk} E_k + s^E_{ijkl} T_{kl} \tag{2-38}$$

In (2-38), the first term, $d_{ijk} E_k$ represents part of the strain that is produced under the action of an applied electric field, E_k. The second term, $s^E_{ijkl} T_{kl}$, represents the other part of the strain that is produced under the action of an applied stress, T_{kl}. The coefficient, s^E_{ijkl}, is the fourth-rank compliance coefficient tensor, a property of the material, which is a measure of the deformation of the material materials under the action of an applied stress, T_{kl}. The superscript, E on s^E_{ijkl}, indicates that the measurement of s^E_{ijkl} is made under conditions of constant electric field, E_i.

Using (2-24) and (2-37), the expression for the electric displacement, D_i, in terms of E_i and T_{ij} is

$$D_i = \epsilon^T_{ij} E_j + d_{ijk} T_{jk} \tag{2-39}$$

where

$$\epsilon_{ij}^{T} = \epsilon_o(\delta_{ij} + \chi_{ij}^{(e)}) \tag{2-40}$$

where δ_{ij} is the kronecker delta defined in Appendix 2.

Equation (2-40) is the definition of the second-rank dielectric stress coefficient tensor, ϵ^{T}_{ij}. The superscript, T, denotes that ϵ^{T}_{ij} is measured under conditions of constant stress. From (2-38) and (2-39) the expressions relating T_{ij} and D_i to E_i and S_{ij} are

$$T_{ij} = -e_{ijk} E_k + c^{E}_{ijkl} S_{kl} \tag{2-41}$$

$$D_i = \epsilon^{S}_{ik} E_k + e_{ikl} S_{kl} \tag{2-42}$$

where c^{E}_{ijkl} is the reciprocal of s^{E}_{ijkl}, that is, $c^{E}_{ijkl} = (s^{E}_{ijkl},)^{-1}$, and

$$e_{ijk} = c^{E}_{ijkl} d_{klk} \tag{2-43}$$

$$\epsilon^{S}_{ik} = \epsilon^{T}_{ik} - d_{iij} c^{E}_{ijkl} d_{klk} \tag{2-44}$$

$$e_{ikl} = d_{iij} c^{E}_{ijkl} \tag{2-45}$$

Equations (2-43) and (2-45), are the defining equations for the third-rank piezoelectric stress coefficient tensor, e_{ijk}. Equation (2-44) expresses the relationship between ϵ^{T}_{ik} and ϵ^{S}_{ik}. Equation (2-41) is true for an elastic material and is generalized for a viscoelastic material by adding a viscous term to give the viscoelastic equation, (2-33). Equation (2-42) is one of the two piezoelectric material equations stated

earlier, (2-34). From this point forward, the superscripts 'E' and 'S' on c^{E}_{ijkl} and ϵ^{S}_{ik} respectively will be dropped, so as to simplify the notation.

In the following discussion, the system of coupled wave equations for a linear viscoelastic piezoelectric material, relating u_i to E_i, will be derived from the complete set of equations for a linear viscoelastic piezoelectric material: (2-6), (2-25) to (2-28) and (2-32) to (2-34). In addition the symmetry equations (2-8) and (2-9) are required. From (2-6), (2-8), (2-9), and (2-33), (2-32) reduces to

$$-e_{ijk} E_{k,i} + c_{ijkl} u_{k,li} + \eta_{ijkl} \dot{u}_{k,li} = \rho_m \ddot{u}_j \tag{2-46}$$

From (2-27) and (2-28), after elimination of B_i,

$$E_{j,ij} - E_{i,jj} = -\mu_o \ddot{D}_i \tag{2-47}$$

From (2-6) and (2-34), (2-47) reduces to

$$E_{j,ij} - E_{i,jj} = -\mu_o \left[\epsilon_{ik} \ddot{E}_k + \frac{1}{2} e_{ikl} (\ddot{u}_{k,l} + \ddot{u}_{l,k}) \right] \tag{2-48}$$

Equations (2-46) and (2-48) constitute a system of coupled wave equations for a linear viscoelastic piezoelectric material which interrelates u_i to E_i. The above system constitutes a complete system of six scalar equations in the six variables (unknowns): u_1, u_2, u_3, E_1, E_2, and E_3. For the case of a non-piezoelectric viscoelastic medium, $e_{ijk} = 0$, thus (2-46) and (2-48) reduce to

$$c_{ijkl}\, u_{k,li} + \eta_{ijkl}\, \dot{u}_{k,li} = \rho_m\, \ddot{u}_j \tag{2-49}$$

$$E_{j,ij} - E_{i,jj} = -\mu_o\, \epsilon_{ik}\, \ddot{E}_k \tag{2-50}$$

In the absence of external forces, (2-49) is identical to (2-10). Since $e_{ijk} = 0$, then from (2-43) and (2-45), $d_{ijk} = 0$. Thus from (2-44), $\epsilon^S_{ik} = \epsilon^T_{ik} = \epsilon_o\, (\delta_{ik} + \chi^{(e)}_{ik})$. Since the viscoelastic material is non-piezoelectric, then by necessity, the material must be isotropic. Thus for an isotropic viscoelastic material, $\delta_{ij} = 1$, $\chi^{(e)}_{ij} \rightarrow \chi_e$, and $\epsilon^S_{ik} \rightarrow \epsilon_o\, (1 + \chi_e)$, and hence (2-50) reduces to (2-30). Therefore, for an isotropic viscoelastic material, u_i and E_i decouple and the resulting equations reduce to those of an isotropic viscoelastic material.

The vector potential, A_i, is defined by the following equation.

$$B_i = \varepsilon_{ijk} A_{k,j} \tag{2-51}$$

In vector notation, (2-51) is $\mathbf{B} = \nabla \times \mathbf{A}$. Equation (2-12), $\nabla \cdot \mathbf{B} = 0$, implies that $\mathbf{B} = \nabla \times \mathbf{A}$ since $\nabla \cdot (\nabla \times \mathbf{A}) = 0$. In general the electric field, E_i, is expressed as the sum of two potentials: one scalar, and the other vector. In terms of the scalar potential, φ, and the vector potential, A_i, the expression for E_i is

$$E_i = -\varphi_{,i} - \dot{A}_i \tag{2-52}$$

The general form of E_i, given by (2-52) is a consequence of (2-13).

For an anisotropic viscoelastic material such as quartz, the frequency of elastic vibrations is many orders of magnitude greater than the corresponding frequency of pure electromagnetic vibrations. Due to the low value of piezoelectric coupling in quartz, the electromagnetic field is essentially decoupled from the elastic field. Thus the magnitude of the second term in (2-52) is much less than the magnitude of the first term in (2-52). The inequality $\|\dot{A}_i\| \ll \|\varphi_{,i}\|$ is called the quasi-static approximation. Equation (2-52) becomes

$$E_i = -\varphi_{,i} \tag{2-53}$$

In the quasi-static approximation, the equations of motion relating u_i to φ, are derived from the following equations: (2-35), (2-46), (2-48), and (2-53). From (2-53), (2-46) reduces to

$$e_{ijk}\varphi_{,ki} + c_{ijkl}u_{k,li} + \eta_{ijkl}\dot{u}_{k,li} = \rho_m \ddot{u}_j \tag{2-54}$$

Differentiating (2-48) with respect to the spatial coordinate, x_i, (2-48) reduces to

$$\epsilon_{ik}\ddot{E}_{k,i} + \frac{1}{2}e_{ikl}(\ddot{u}_{k,li} + \ddot{u}_{l,ki}) = 0 \tag{2-55}$$

From (2-35) and (2-53), (2-55) reduces to

$$e_{ikl}\ddot{u}_{k,li} - \epsilon_{ik}\ddot{\varphi}_{,ki} = 0 \tag{2-56}$$

From (2-6), (2-25), (2-34), (2-35), and (2-53), (2-25) reduces

to

$$e_{ikl}\, u_{k,li} - \epsilon_{ik}\, \varphi_{,ki} = 0 \tag{2-57}$$

From an inspection of (2-56) and (2-57), (2-56) is simply (2-57) differentiated twice with respect to the time, t. Thus in the quasi-static approximation, (2-54) and (2-57) are the dynamical equations of motion for a linear viscoelastic piezoelectric material interrelating u_i and φ. The above system of equations constitutes a complete system of four scalar equations in the four variables: u_x, u_y, u_z, and φ.

An AT-cut quartz crystal, is a rotated Y-cut quartz crystal, which has been rotated through an angle of $\theta = 35.25°$ about the X-axis. It operates in the transverse shear mode, as will be explained. The XYZ-coordinate system refers to the crystal axis coordinate system.

The rotation of the XYZ-coordinate system into the xyz-coordinate system through an angle θ, about the X-axis is given by the following rotation matrix, a_{ij},

$$a_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix} \tag{2-58}$$

In the following the prime refers to the XYZ-coordinate system. The components of the elastic coefficient tensor, c'_{ijkl}, with respect to the XYZ-coordinate system are related to the components of c_{ijkl} with respect to the xyz-coordinate system

by the following transformation.

$$c_{ijkl} = a_{im}\, a_{jn}\, a_{ko}\, a_{lp}\, c'_{mnop} \tag{2-59}$$

By the same token, the components of η'_{ijkl} are related to the components of η_{ijkl} by

$$\eta_{ijkl} = a_{im}\, a_{jn}\, a_{ko}\, a_{lp}\, \eta'_{mnop} \tag{2-60}$$

The components of the piezoelectric stress coefficient tensor, e'_{ijk}, with respect to the XYZ-coordinate system are related to the components of e_{ijk} with respect to the xyz-coordinate system by the following transformation.

$$e_{ijk} = a_{im}\, a_{jn}\, a_{ko}\, e'_{mno} \tag{2-61}$$

The components of the dielectric tensor, ϵ'_{ij}, with respect to the XYZ-coordinate system are related to the components of ϵ_{ij} with respect to the xyz-coordinate system by the following transformation.

$$\epsilon_{ij} = a_{im}\, a_{jn}\, \epsilon'_{mn} \tag{2-62}$$

For an AT-cut quartz crystal, the values for: c_{ijkl}, e_{ijk}, and ϵ_{ij} with respect to the xyz-coordinate system are given in Table 2.4, Tiersten (1969).

Table 2.4 Properties of Quartz

c_{ijkl} Elastic Coefficient		e_{ijk} Piezoelectric Stress Coefficient		ϵ_{ik} Dielectric Strain Coefficient	
Components	Values 10^9 (N/m^2)	Components	Values C/m^2	Components	Values $C/V \cdot m$
c_{1111}	86.74	e_{111}	0.171	ϵ_{11}	39.21
c_{1112}	0.0	e_{112}	0.0	ϵ_{12}	0.0
c_{1113}	0.0	e_{113}	0.0	ϵ_{13}	0.0
c_{1122}	-8.25	e_{122}	-0.152	ϵ_{22}	39.82
c_{1123}	-3.66	e_{123}	0.067	ϵ_{23}	0.68
c_{1133}	27.15	e_{133}	-0.0187	ϵ_{33}	40.42
c_{1212}	29.01	e_{211}	0.0		
c_{1312}	2.53	e_{212}	-0.095		
c_{1313}	68.81	e_{213}	0.108		
c_{2212}	0.0	e_{222}	0.0		
c_{2213}	0.0	e_{223}	0.0		
c_{2222}	129.77	e_{233}	0.0		
c_{2223}	5.7	e_{311}	0.0		
c_{2233}	-7.42	e_{312}	0.067		
c_{2312}	0.0	e_{313}	-0.0761		
c_{2313}	0.0	e_{322}	0.0		
c_{2323}	38.61	e_{323}	0.0		
c_{3312}	0.0	e_{333}	0.0		
c_{3313}	0.0				
c_{3323}	9.92				
c_{3333}	102.83				

From (2-59) to (2-62), using Table 2.4, the equations of motion for the thickness shear wave solution of an AT-cut quartz material are

$$c_{1212}\frac{\partial^2 u_x}{\partial y^2} + \eta_{1212}\frac{\partial^3 u_x}{\partial y^2 \partial t} + e_{212}\frac{\partial^2 \varphi}{\partial y^2} = \rho_q \frac{\partial^2 u_x}{\partial t^2} \tag{2-63}$$

$$c_{2322}\frac{\partial^2 u_z}{\partial y^2} + \eta_{2322}\frac{\partial^3 u_z}{\partial y^2 \partial t} + c_{2222}\frac{\partial^2 u_y}{\partial y^2} + \eta_{2222}\frac{\partial^3 u_y}{\partial y^2 \partial t} = \rho_q \frac{\partial^2 u_y}{\partial t^2} \tag{2-64}$$

$$c_{2323}\frac{\partial^2 u_z}{\partial y^2} + \eta_{2323}\frac{\partial^3 u_z}{\partial y^2 \partial t} + c_{2322}\frac{\partial^2 u_y}{\partial y^2} + \eta_{2322}\frac{\partial^3 u_y}{\partial y^2 \partial t} = \rho_q \frac{\partial^2 u_z}{\partial t^2} \tag{2-65}$$

$$e_{212}\frac{\partial^2 u_x}{\partial y^2} - \epsilon_{22}\frac{\partial^2 \varphi}{\partial y^2} = 0 \tag{2-66}$$

where c_{1312} is a component of the elastic coefficient tensor, e_{213} is a component of the piezoelectric stress coefficient tensor, η_{1312}, is a component of the viscoelastic coefficient tensor, and ϵ_{23} is a component of the dielectric strain coefficient tensor, all given in Table 2.4.

In (2-63) to (2-66), u_x, u_y, and u_z are the x,y and z components of the particle displacement in the quartz material of mass density, ρ_q, and φ is the potential. The four scalar equations (2-63) to (2-66) relate the four variables u_x, u_y, u_z, and φ. The quantities u_x and φ appear only in (2-63) and (2-66), while the quantities u_y and u_z appear only in (2-64)

and (2-65). Therefore u_y and u_z are decoupled from φ, while u_x is coupled to φ. Furthermore the dependent variables u_x, u_y, u_z, and φ are functions of the independent variables y and t only. From (2-66) if $\varphi = 0$, then from (2-63) and (2-66) $u_x = 0$, after some mathematical reasoning. If $\varphi \neq 0$, then $u_x \neq 0$ and so φ causes the displacement, u_x, which is a function of y and t only. Therefore the wave propagates in the y-direction, with the associated particle displacement in the x-direction and so the wave is a transverse wave. The AT-cut quartz is also called transverse-shear-mode (TSM) quartz for this reason. Since u_y and u_z are decoupled from φ, then if u_y and u_z are zero at some time, then they will be zero for all time.

Let $c = c_{1212}$, $\eta = \eta_{1212}$, $e = e_{212}$, and $\epsilon = \epsilon_{22}$, and denote partial differentiation with respect to y by a prime and with respect to t by a dot. Then (2-63) and (2-66) become.

$$c u_x'' + \eta \dot{u}_x'' + e \varphi'' = \rho_q \ddot{u}_x \tag{2-67}$$

$$e u_x'' - \epsilon \varphi'' = 0 \tag{2-68}$$

Equations (2-67) and (2-68) are the coupled linear partial differential equations for the thickness shear-wave solution relating the particle displacement, u_x, to the potential, φ, in the quartz.

The thickness shear-wave viscoelastic wave equation for the particle displacement, u_x, is obtained by eliminating the

potential, φ, from (2-67) and (2-68). The thickness shear-wave viscoelastic wave equation is

$$\bar{c}\, u_x'' + \eta\, \dot{u}_x'' = \rho_q\, \ddot{u}_x \tag{2-69}$$

where $\bar{c}$ is called the stiffened elastic constant of quartz , and is defined as

$$\bar{c} = c + \frac{e^2}{\epsilon} \tag{2-70}$$

From (2-6), (2-8), (2-9), (2-33), (2-34), (2-35), (2-36) and from Table 2.1, the components of T_{ij} and D_i in quartz are

$$T_{yx} = c\, u_x' + \eta\, \dot{u}_x' + e\, \varphi' \tag{2-71}$$

$$T_{zx} = c_{1312}\, u_x' + \eta_{1312}\, \dot{u}_x' + e_{213}\, \varphi' \tag{2-72}$$

$$T_{xx} = T_{yy} = T_{yz} = T_{zz} = 0 \tag{2-73}$$

$$D_x = 0 \tag{2-74}$$

$$D_y = e\, u_x' - \epsilon\, \varphi' \tag{2-75}$$

$$D_z = e_{213}\, u_x' - \epsilon_{23}\, \varphi' \tag{2-76}$$

2.4 Fluid Mechanics

There are two fundamental equations of fluid mechanics, the equation of continuity and Newton's second law applied to a liquid, Hughes and Brighton (1967), Landau and Lifshitz

(1987), and Yuan (1967). There is one equation of the material which gives the general linear relationship between the stress in the liquid medium and the corresponding deformation of the liquid medium arising from the action of the stress.

The equation of continuity for a liquid medium of mass density, ρ_l is.

$$\dot{\rho}_l + (\rho_l v_{(l)i})_{,i} = 0 \tag{2-77}$$

In (2-77), $v_{(l)i}$, denotes the i-th component of the particle velocity in the liquid medium. The general linear expression for the relation between the stress components of the liquid medium, $T_{(l)ij}$, and the components of the liquid particle velocity, $v_{(l)i}$, for a liquid medium is

$$T_{(l)ij} = -p\,\delta_{ij} + \mu\left(v_{(l)i,j} + v_{(l)j,i} - \frac{2}{3}\delta_{ij}\,v_{(l)k,k}\right) + \zeta\,\delta_{ij}\,v_{(l)k,k} \tag{2-78}$$

In (2-78), p, denotes the liquid pressure at a point in the liquid medium, μ, denotes the dynamic viscosity of the liquid medium, and ζ, denotes the second coefficient of viscosity of the liquid medium. The second coefficient of viscosity, ζ, is a measure of the viscosity of the liquid medium that arises when turbulent effects are present. From Newton's second law, the equation of motion for a liquid medium is

$$T_{(l)ij,i} + F_{(l)j} = \rho_l(\dot{v}_{(l)j} + v_{(l)i}\,v_{(l)j,i}) \tag{2-79}$$

For an incompressible liquid medium, the liquid mass density, ρ_l is considered to be constant, that is, the same at

all points. For an incompressible liquid medium, (2-77) reduces to

$$v_{(l)i,i} = 0 \tag{2-80}$$

From (2-80), with liquid pressure neglected, (2-78) reduces to

$$T_{(l)ij} = \mu (v_{(l)i,j} + v_{(l)j,i}) \tag{2-81}$$

In an incompressible liquid medium, physical effects due to turbulence, such as convection, are negligible in comparison to the translatory motion of the liquid medium. Thus the convective term in (2-79), $v_{(l)i}v_{(l)j,i}$, is negligible in comparison to the non-convective term $\dot{v}_{(l)j}$. Thus for an incompressible liquid medium with constant dynamic viscosity, μ, and mass density, ρ_l, in the absence of all external forces, from (2-80) and (2-81), (2-79) reduces to

$$\nu \, v_{(l)j,ii} = \dot{v}_{(l)j} \tag{2-82}$$

where ν is called the kinematic viscosity and is defined as

$$\nu = \frac{\mu}{\rho_l} \tag{2-83}$$

Equation (2-82) constitutes a complete system of three scalar equations in the three variables: v_x, v_y, and v_z. Equation (2-82) is the Navier-Stokes equation for an incompressible liquid medium.

Let the surface of the liquid be in contact with the plane surface of a solid material undergoing transverse oscillations in a direction parallel to the surface of the

liquid. The transverse vibratory motion of the solid will be transmitted to the surface of the liquid in contact with the solid, via contact forces, which are attractive forces between surface liquid particles and surface solid particles. A cartesian coordinate system is chosen, such that, the surface of the liquid lies in the xz-plane, with the y-axis directed into the liquid medium. The transverse motion of the solid surface in the x-direction, will produce a transverse motion of the liquid in the x-direction, with each component of the particle displacement of the liquid being a function of the spatial coordinate, y, and the time, t, only. That is: $u_{(l)x} = u_{(l)x}(y,t)$, $u_{(l)y} = 0$ and $u_{(l)z} = 0$. The x-component of the particle displacement of the liquid, $u_{(l)x}$, is the only non-vanishing component. Since $v_{(l)i} = \dot{u}_{(l)i}$, then: $v_{(l)x} = v_{(l)x}(y,t)$, $v_{(l)y} = 0$ and $v_{(l)z} = 0$. Therefore (2-82) reduces to one scalar equation in the variable, $v_{(l)x}$.

$$\nu\, v''_{(l)x} = \dot{v}_{(l)x} \tag{2-84}$$

There is also only one non-vanishing stress component of the liquid medium, $T_{(l)ij}$, from (2-81) and as a result (2-81) reduces to one scalar equation, given by

$$T_{(l)yx} = \mu\, v'_{(l)x} \tag{2-85}$$

2.5 Boundary Conditions of Solid-Liquid Model

There are five boundary conditions for the solid-liquid two-layer system shown in Figure 2.1. Two of the boundary conditions are applied at the solid-air interface, and the other three are applied at the solid-liquid interface. Figure 2.1 depicts a liquid-loaded sensor with quantities at the two interfaces, y = 0 and y = h, which appear in the following five boundary conditions.

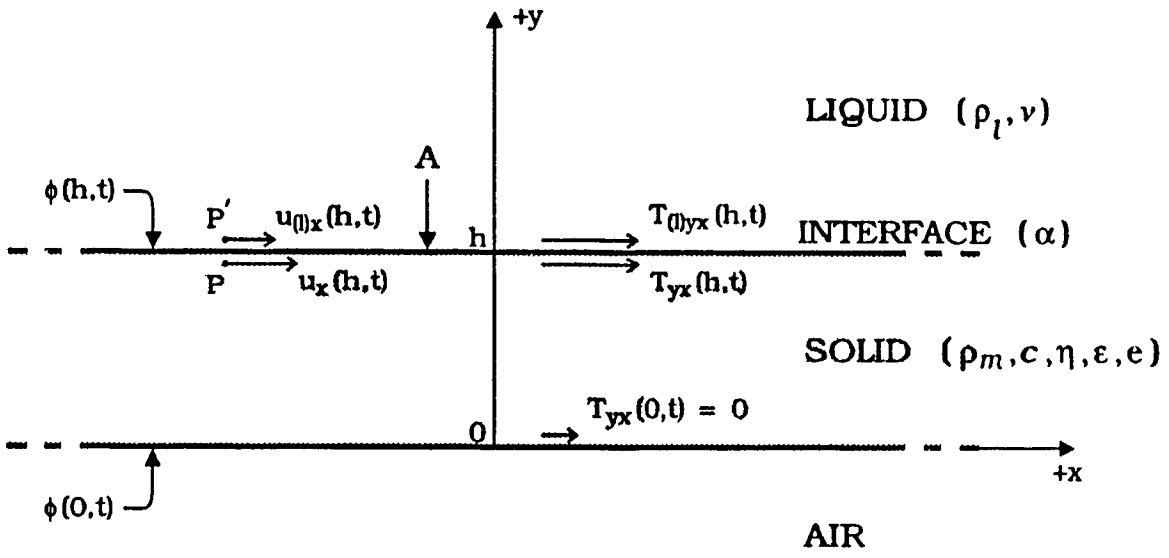


Figure 2.1 *Solid-liquid model showing quantities used to express the five boundary conditions, and showing in brackets the five properties of the solid, the two properties of the liquid and the one property of the interface.*

(1) Shear Stress At y = 0 (Stress-free boundary condition at solid-air interface interface)

$$T_{yx}(0,t) = 0 \tag{2-86}$$

Equation (2-86) states that at the solid-air interface, the air in contact with the surface of the sensor at y = 0 produces a negligible shear stress on the solid surface.

(2) Shear Stress At y = h (Continuity of stress boundary condition at solid-liquid interface)

$$T_{yx}(h,t) = T_{(l)yx}(h,t) \tag{2-87}$$

Equation (2-87) is the stress-continuity boundary condition at the solid-liquid interface. Physically the stress must be continuous at all points along the solid-liquid interface, that is, there can only be one value of stress at each point along the solid-liquid interface.

(3) Particle Displacement At y = h (Slip boundary condition at solid-liquid interface)

$$u_{(l)x}(h,t) = \alpha\, u_x(h,t) \tag{2-88}$$

The boundary condition, (2-88), defines the interfacial slip parameter, α. The interfacial slip parameter, α, is a measure of the relative displacement between two points, P in the solid at the interface and P′ in the liquid at the interface. In general α is a complex-valued quantity, which accounts for the phase difference between the displacements, $u_{(l)x}$ and u_x. The relative displacement between P and P′, is a measure of the strength of the interaction that arises between P and P′.

Thus α, may be viewed as that parameter which is a measure of the strength of the interaction between P and P′. Figure 2.1 shows points P and P′, and their respective displacements.

(4) Potential At y = 0 (Potential boundary condition at solid-air interface)

$$\varphi(0,t) = -\varphi_o e^{j\omega t} \tag{2-89}$$

Equation (2-89) specifies the value of the potential at the bottom electrode of the sensor.

(5) Potential At y = h (Potential boundary condition at solid-liquid interface)

$$\varphi(h,t) = +\varphi_o e^{j\omega t} \tag{2-90}$$

Equation (2-90) specifies the values of the potential at the top electrode of the sensor.

2.6 Solution Of Solid-Liquid Model

The following is a list of the equations needed for the solution of the boundary value problem. There are three equations of quartz: (2-67), (2-68) and (2-71). There are two equations of the liquid: (2-84) and (2-85). The quartz and liquid equations are combined with the five boundary conditions: (2-86), (2-87), (2-88), (2-89), and (2-90). In particular, two of the boundary conditions connect the quartz equations with the liquid equations: the continuity of stress boundary condition, (2-87), and the slip boundary condition,

(2-88).

From (2-69), the general plane-wave solution to the viscoelastic wave equation is

$$u_x = (a_1 e^{jk_q y} + a_2 e^{-jk_q y}) e^{j\omega t} \tag{2-91}$$

where

$$k_q = \omega \left[\frac{\rho_q}{c + \omega \eta j} \right]^{1/2} \tag{2-92}$$

In (2-91), a_1 and a_2 are complex-valued constants. The quantity, k_q, in (2-92) is complex-valued and is called the wave number for quartz.

The general plane-wave solution to (2-84) is

$$v_{(l)x} = (a_5 e^{-jk_l y} + a_6 e^{jk_l y}) e^{j\omega t} \tag{2-93}$$

where

$$k_l = \left[\frac{\omega}{j \nu} \right]^{1/2} \tag{2-94}$$

In (2-93) a_5 and a_6 denote complex-valued constants. The quantity, k_l, in (2-94) is the complex-valued wave number of the liquid medium. From (2-93) as $y \to \infty$, $\exp(-jk_l y) \to 0$, and $\exp(jk_l y) \to \infty$. Since $\exp(jk_l y) \to \infty$, then, $v_{(l)x} \to \infty$. Physically this is not possible, since for all y, $v_{(l)x}$ must be finite. Therefore in order for $v_{(l)x}$ to be finite, $a_6 = 0$. Hence (2-93) reduces to

$$v_{(l)x} = A_5 e^{-jk_l y} e^{j\omega t} \tag{2-95}$$

From (2-68) and (2-91), the expression for the potential, φ, is

$$\varphi = \frac{e}{\epsilon} u_x + (a_3 y + a_4) e^{j\omega t} \tag{2-96}$$

In (2-96), a_3 and a_4 are complex-valued constants.

The boundary value problem to be solved consists of the five boundary conditions which relate the five unknowns: a_1, a_2, a_3, a_4, and a_5.

(1) Stress-free boundary condition: (2-86)

Using (2-71), (2-91), and (2-96), the first algebraic equation is

$$a_3 e - (a_2 - a_1)\delta k_q = 0 \tag{2-97}$$

(2) Continuity of stress boundary condition: (2-87)

Using (2-71), (2-85), (2-91), (2-95), and (2-96), the second algebraic equation is

$$-\frac{\delta\left(a_2\gamma_1^2 - a_1\right)k_q - a_3 e\gamma_1}{\gamma_1} = \frac{a_5 k_l \nu \omega \rho_l}{\gamma_2} \tag{2-98}$$

(3) Slip boundary condition: (2-88)

Using $v_x = \dot{u}_x$ and $v_{(l)x} = \dot{u}_{(l)x}$, with (2-91) and (2-95), the third algebraic equation is

$$\frac{a_5}{\gamma_2} = \frac{\alpha\left(a_1 + \gamma_1^2 a_2\right)}{\gamma_1} \tag{2-99}$$

(4) Potential boundary condition: (2-89)

Using (2-91) and (2-96), the fourth algebraic equation is

$$\frac{e}{\epsilon}(a_1 + a_2) + a_4 = -\varphi_o \tag{2-100}$$

(5) Potential boundary condition: (2-90)

Using (2-91) and (2-96), the fifth and final algebraic equation is

$$\frac{e\left(a_1 + a_2\gamma_1^2\right) + \epsilon\gamma_1(h a_3 + a_4)}{\epsilon\gamma_1} = \varphi_o \tag{2-101}$$

In (2-100) and (2-101), φ_o, is the amplitude of the applied source voltage. From (2-97) to (2-101), the complex-valued quantities γ_1, γ_2, and δ are defined as

$$\gamma_1 = e^{jhk_1} \tag{2-102}$$

$$\gamma_2 = e^{jhk_2} \tag{2-103}$$

$$\delta = \eta\omega - j\bar{c} \tag{2-104}$$

The algebraic solution to (2-97) to (2-101), is found by the Macsyma program, ZIN.WP. The Macsyma program ZIN.WP is given in Appendix 3. The solution to the above system of algebraic equations follows.

$$a_1 = \frac{\alpha b_{12} + b_{11}}{\alpha b_{14} + b_{13}} \tag{2-105}$$

$$a_2 = \frac{\alpha b_{22} + b_{21}}{\alpha b_{24} + b_{23}} \tag{2-106}$$

$$a_3 = \frac{(\alpha b_{32} + b_{31})\varphi_o}{\alpha b_{34} + b_{33}} \tag{2-107}$$

$$a_4 = \frac{\alpha b_{42} + b_{41}}{\alpha b_{44} + b_{43}} \tag{2-108}$$

$$a_5 = \frac{\alpha b_{52} + b_{51}}{\alpha b_{54} + b_{53}} \tag{2-109}$$

where

$$b_{11} = -2\delta e \epsilon (\gamma_1 - 1)\gamma_1 k_q \varphi_o \tag{2-110}$$

$$b_{12} = -2 e \epsilon \gamma_1^2 k_l \nu \omega \varphi_o \rho_l \tag{2-111}$$

$$b_{13} = \delta(\gamma_1 - 1) k_q (\delta \epsilon (\gamma_1 + 1) h k_q + 2 e^2 (\gamma_1 - 1)) \tag{2-112}$$

$$b_{14} = k_l (\delta \epsilon (\gamma_1^2 + 1) h k_q + e^2 (\gamma_1 - 1)(\gamma_1 + 1)) \nu \omega \rho_l \tag{2-113}$$

$$b_{21} = 2\delta e \epsilon (\gamma_1 - 1) k_q \varphi_o \tag{2-114}$$

$$b_{22} = 2 e \epsilon k_l \nu \omega \rho_l \varphi_o \tag{2-115}$$

$$b_{23} = b_{13} \tag{2-116}$$

$$b_{24} = b_{14} \tag{2-117}$$

$$b_{31} = 2\delta^2\epsilon(\gamma_1 - 1)(\gamma_1 + 1)k_q^2 \tag{2-118}$$

$$b_{32} = 2\delta\epsilon(\gamma_1^2 + 1)k_l k_q \nu \rho_l \omega \tag{2-119}$$

$$b_{33} = b_{13} \tag{2-120}$$

$$b_{34} = b_{14} \tag{2-121}$$

$$b_{41} = -\delta^2\epsilon(\gamma_1 - 1)(\gamma_1 + 1)h k_q^2 \varphi_o \tag{2-122}$$

$$b_{42} = -k_l(\delta\epsilon(\gamma_1^2 + 1)h k_q - e^2(\gamma_1 - 1)(\gamma_1 + 1))\nu \rho_l \omega \varphi_o \tag{2-123}$$

$$b_{43} = b_{13} \tag{2-124}$$

$$b_{44} = b_{14} \tag{2-125}$$

$$b_{51} = 0 \tag{2-126}$$

$$b_{52} = 2\delta e\epsilon(\gamma_1 - 1)^2 \gamma_2 k_q \varphi_o \tag{2-127}$$

$$b_{53} = b_{13} \tag{2-128}$$

$$b_{54} = b_{14} \tag{2-129}$$

2.7 Impedance

The theoretical complex-valued expression for the impedance, Z, will be used in the analysis of the experimental results which is presented in Chapter 3. The impedance of the

sensor is defined as the voltage across the sensor, v, divided by the current through the sensor, i, shown in Figure 2.2.

The current through the sensor, i, is the time rate of change of total free charge on an electrode of the sensor. Let the total free charge on one electrode be Q_f. Then the current, i, through the sensor is, by definition

$$i = \frac{dQ_f}{dt} \tag{2-130}$$

The free charge density, ρ_f, is found by combining equation (2-11), $E_{i,t} = \rho/\epsilon_o$, equation (2-17), $\rho = \rho_f - P_{i,t}$, and the definition of the electric displacement, equation (2-24), $D_i = \epsilon_o E_i + P_i$. The result is

$$D_{i,t} = \rho_f \tag{2-131}$$

The total free charge, Q_f, is obtained by integrating (2-131) over the volume, V, of the dashed region shown in Figure 2.2. This region is a very thin box that encloses the interface between the quartz and the metal electrode. All of the free charge on the metal electrode is at the interface side of the electrode, the row of plus signs for the polarity of v which is indicated.

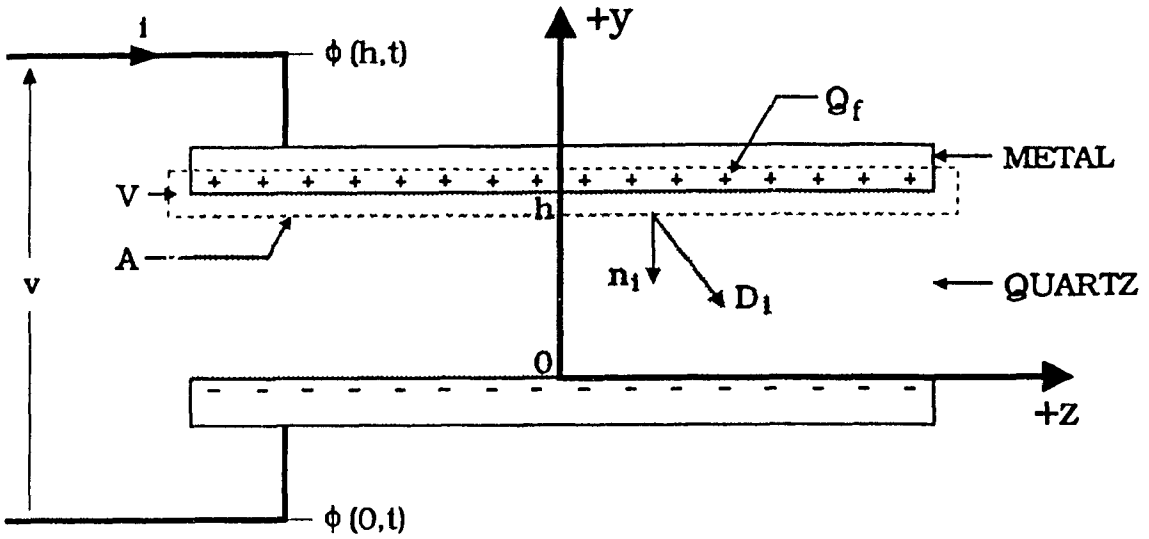


Figure 2.2 Total free charge, Q_f, found by surface integration of the electric displacement, D_i.

The result of the integration of (2-131) is

$$\int_V D_{i,i}\, dV = \int_V \rho_f\, dV \tag{2-132}$$

where the right side of (2-132) is the total free charge on the electrode, Q_f. The left side of (2-132) is converted to a surface integral over the area, A, of the region in Figure 2.2 by the application of the divergence theorem. The total free charge, Q_f, from (2-132) is

$$Q_f = \int_A D_i n_i\, dA \tag{2-133}$$

From (2-74) to (2-76), D_i lies in the yz-plane as shown in Figure 2.2. Furthermore there is only a flux of D_i through the bottom surface of the region, the surface which is in the quartz. There is no D_i in the metal electrode. The unit

normal, n_1, of the bottom surface points downward since the the unit normal points outward from the region. Therefore the components of n_1 are $n_x = 0$, $n_y = -1$ and $n_z = 0$. From (2-75), (2-91), and (2-96), (2-133) reduces to

$$Q = \epsilon A a_3 e^{j\omega t} \tag{2-134}$$

From (2-130) and (2-134), the current, i, flowing through the quartz sensor is

$$i = \frac{dQ_f}{dt} = j\omega \epsilon A a_3 e^{j\omega t} \tag{2-135}$$

The voltage across the sensor, v, is the potential at the top electrode minus the potential at the bottom electrode, Figure 2.2. Using (2-89) and (2-90),

$$v = \varphi(h,t) - \varphi(0,t) = 2\varphi_o e^{j\omega t} \tag{2-136}$$

The impedance of the sensor, Z, is defined as

$$Z = \frac{v}{i} \tag{2-137}$$

Substitute for i from (2-135) and v from (2-136).

$$Z = \frac{2\varphi_o}{j\omega \epsilon A a_3} \tag{2-138}$$

Using (2-107), (2-138) reduces to the final form for the impedance, Z, given by

$$Z = -\frac{2j}{A\omega\epsilon}\left[\frac{\alpha b_{34} + b_{33}}{\alpha b_{32} + b_{31}}\right] \qquad \textbf{(2-139)}$$

The impedance is a function of five properties of quartz, (ρ_q, c, η, ϵ, e), two properties of the liquid (ρ_l, ν), one property of the interface (α), two geometrical properties (A and h) and the angular frequency (ω). In the next chapter the interfacial slip parameter, α, will be determined by fitting the theoretical complex-valued expression for the impedance, Z, to the corresponding experimental values of Z.

CHAPTER 3

EXPERIMENT

Introduction

The interfacial slip parameter is found for sensors with hydrophilic and hydrophobic coatings in water-glycerol solutions This is done by fitting the experimental values of impedance measured by the network analysis method to the theoretical expression for the impedance derived in the last chapter.

The experimental method, Section 3.1, is the network analysis method developed by Kipling and Thompson (1990). A piezoelectric quartz sensor is completely characterized by this method by repeatedly measuring the magnitude and phase of the impedance over the resonant region of the sensor. Non-linear regression analysis, Section 3.2, is used to fit the complex-valued experimental values of impedance to the theoretical expression for impedance. The experimental data for the sensors in air are fitted to theory, Section 3.3, and the piezoelectric cofficient, e, the viscoelastic coefficient, η, thickness of the sensor, h, and effective area of the sensor, A, are found. Then the experimental data for the sensors in water-glycerol solutions are fitted to theory, Section 3.4, and the interfacial slip parameter, α, is found as well as the effective area of the sensor, A. The

interfacial slip parameter is presented and discussed in terms of the kinematic viscosity and mole fraction of the water-glycerol solutions, Section 3.5.

3.1 Experimental Method

3.1.1 Sensors and Liquid

Hydrophilic Sensor

The hydrophilic sensor, consists of a silver (Ag) plated AT-cut 9-MHz quartz crystal unit coated with a hydrophilic (water-loving) chemical coating whose chemical formula is $COOH(CH_2)_{10}SH$ and name is 1-mercapto undecanoic acid. This molecule is a chain, $COOH\text{-}CH_2\text{-}...\text{-}CH_2\text{-}SH$, with the SH strongly bonded to the silver surface and the COOH end in contact with the liquid. The COOH is polar and therefore attracts the water molecules which are also polar. Figure 3.1(a) shows the sensor with the hydrophilic coating. This sensor is designated 9AgLic.

Hydrophobic Sensor

The hydrophobic sensor, consists of a silver (Ag) plated AT-cut 9-MHz quartz crystal unit coated with a hydrophobic (water-fearing) chemical coating whose chemical formula is $CH_3(CH_2)_{15}SH$ and name is n-hexadecane thiol (or 1-mercapto hexadecane). This molecule is a chain, $CH_3\text{-}CH_2\text{-}...\text{-}CH_2\text{-}SH$, with the SH strongly bonded to the silver surface and CH_3 in contact with the liquid. Unlike the hydrophilic molecule, the

CH_3 is non-polar and therefore interacts weakly with the water molecules. Figure 3.1(b) shows the sensor with the hydrophobic coating. This sensor is designated 9AgBic.

Liquid

The liquid used in the experiment consists of water-glycerol solutions of varying concentrations ranging from pure water to pure glycerol in steps of 0.1 mole fraction of glycerol in water.

3.1.2 Experimental Arrangement

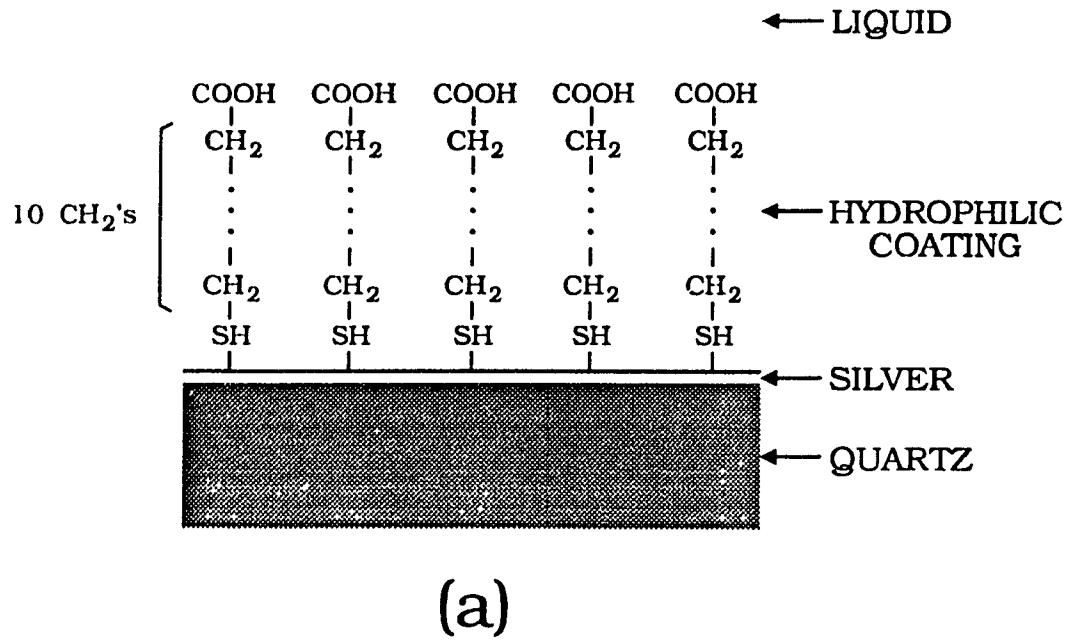
The following equipment, was used in the measurement of the magnitude and phase of the impedance, Z, for both the hydrophilic and hydrophobic sensors. Figure 3.2(a) shows the structure of the piezoelectric quartz sensor, not drawn to scale. The sensor is a thin disk of quartz with a very thin metal electrode on each surface in the shape shown in the figure. Figure 3.2(b) shows the sensor with a chemical coating attached to one of the electrodes and a liquid in contact with the coating. The network analysis system consists of the following equipment:

HP-4195A Network Spectrum Analyzer

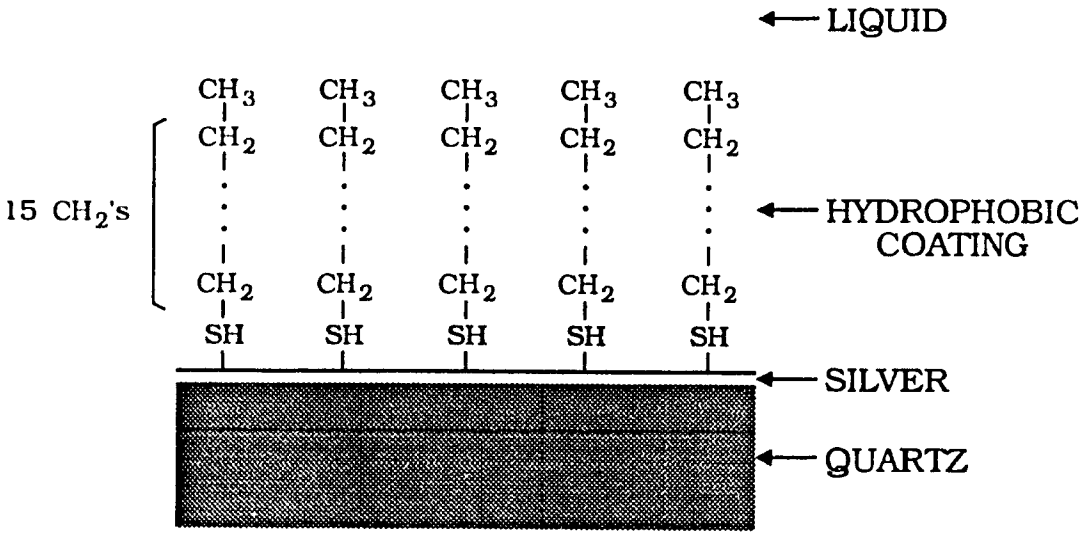
HP-41951A Impedance Test Kit

HP-16092A Spring Clip Fixture

The sensors are installed in an assembly not shown in Figure 3.2(b) and the assembly is connected to the Spring Clip Fixture.



(a)



(b)

Figure 3.1 *Sensor in liquid with (a) hydrophilic coating and (b) hydrophobic coating.*

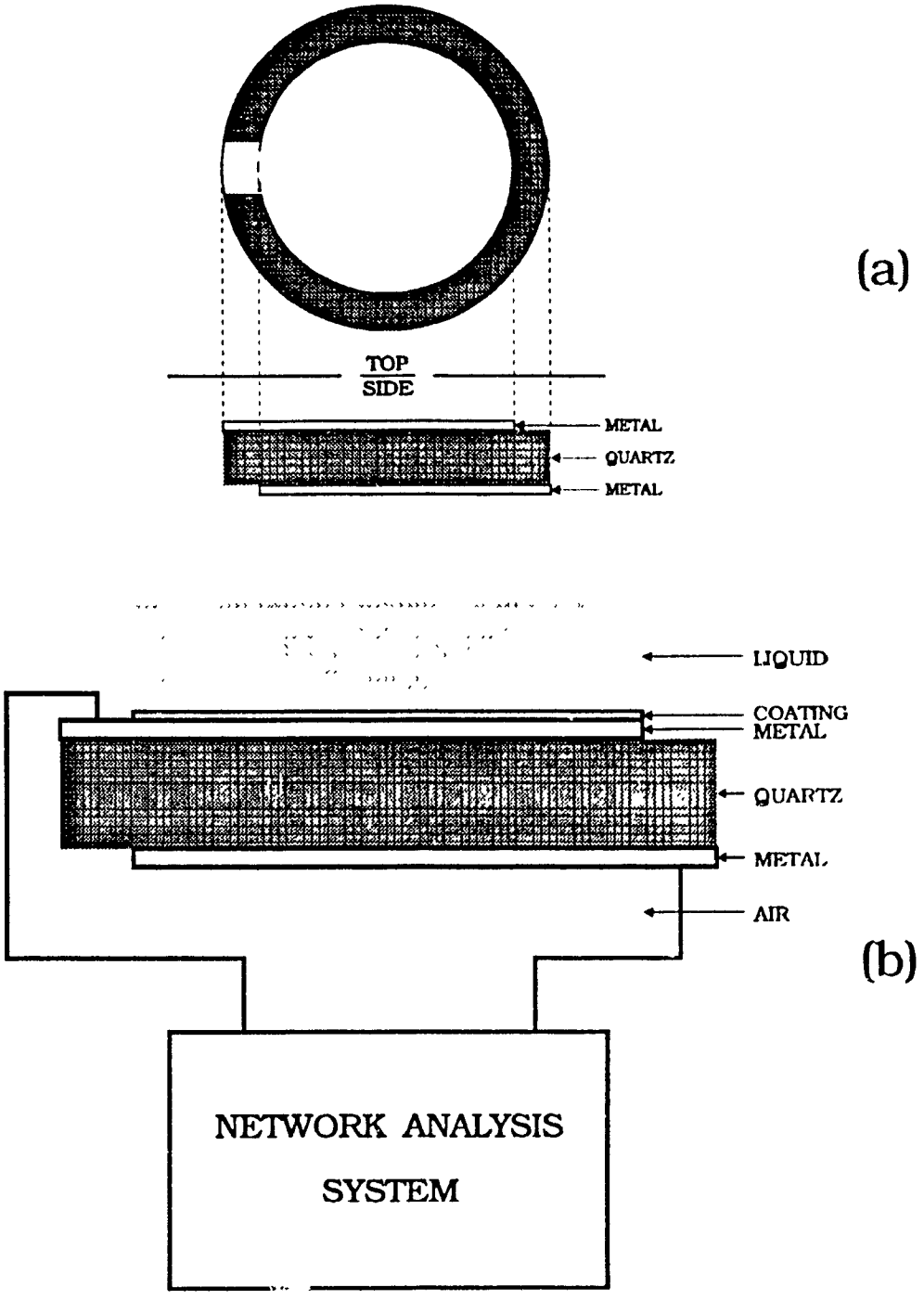


Figure 3.2 *Experimental arrangement showing (a) the top and side views of the piezoelectric quartz sensor and (b) the sensor in liquid connected to the network analysis system.*

The experimental measurement process consists of two parts: measurement in air and measurement in liquid.

Air

The magnitude, $|Z|$, and phase, θ_Z, of the impedance, Z, for both 9AgLic and 9AgBic were measured in air. The measurement of $|Z|$ and θ_Z, was carried out over the closed frequency interval $I = [f_s, f_t]$. The closed interval, I, consists of N = 401 equally spaced frequency points, in the stepsize of, $\Delta f = (f_t - f_s)/N$. The nominal resonant frequency, f_o, is midway between f_s and f_t. The difference between f_t and f_s is called the frequency span. The nominal resonant frequency is f_o = 9 MHz and the typical frequency span is 80 kHz.

Liquid

The magnitude, $|Z|$, and the phase, θ_Z, of the impedance were measured for both sensors in water-glycerol solutions of varying concentrations, ranging from pure water to pure glycerol in steps of 0.1 mole fraction. At each concentration, the closed interval I was modified, that is, the frequency span was either increased or decreased so as to ensure that measurements were made over the complete resonant region.

The preparation of the water-glycerol solutions was done 24 hours in advance so as to ensure that the solution would be in its equilbrium state. The water-glycerol solution is said to be in equilibrium when there is no diffusitory action

between water and glycerol. The liquid solution may be considered to a very good approximation to be in its equilibrium state, that is, the water-glycerol solution is homogenous throughout.

3.2 Non-Linear Regression Analysis

3.2.1 Statement of the Non-Linear Regression Analysis Problem

Given a complex-valued function $F(p_1,\ldots,p_n,\omega)$ of n complex-valued parameters, $p_1,\ldots,p_n$ and angular frequency, ω, determine $p_1,\ldots,p_n$ such that the function $F(p_1,\ldots,p_n,\omega)$ is a good fit to the experimental data.

3.2.2 Definition of Sum Of Squares Of Errors, SSE

The optimization of $F(p_1,\ldots,p_n,\omega)$, with respect to the experimental data, $\{\omega_i,y_i\}$ ($i = 1,\ldots,N$, N = the number of experimental data points), is achieved by minimizing the "Sum Of Squares Of Errors", $SSE(p_1,\ldots,p_n)$ defined by

$$SSE(p_1,\ldots,p_n) = \frac{1}{N}\sum_{i=1}^{N}\left|y_i - F(p_1,\ldots,p_n,\omega_i)\right|^2 \qquad (3\text{-}1)$$

In general, the experimental data is considered to be complex-valued, that is, $y_i \in \mathbb{C}$ (where $\mathbb{C}$ denotes the field of complex numbers) for each $i = 1,\ldots,N$. Physically the quantity, $|y_i - F(p_1,\ldots,p_n,\omega_i)|^2$ represents the square of the

distance between the two complex numbers y_i and $F(p_1,\ldots,p_n,\omega_i)$ in the complex plane $\mathbb{C}$ for each i = 1,...,N. Thus the function, SSE, is simply the sum of the squares of the distances between y_i and $F(p_1,\ldots,p_n,\omega_i)$ (i = 1,...,N). Since $SSE(p_1,\ldots,p_n) \geq 0$ for all $p_k \in \mathbb{C}^n$, where, $p_k = (p_1,\ldots,p_n)$. Then $SSE(p_1,\ldots,p_n)$ has an absolute minimum at some point, $p_{ko} \in \mathbb{C}^n$. The point, $p_{ko} = (p_{o1},\ldots,p_{on})$ is called the "best-fit point". The n coordinates , $p_{o1},\ldots,p_{on}$ are called the "n best-fit parameters". Thus at $p_k = p_{ko}$, $SSE(p_{ko}) = SSE(p_{o1},\ldots,p_{on}) = 0$.

3.2.3 Condition for SSE to be a Minimum

At $p_k = p_{ko}$, $SSE(p_k)$ as an absolute minimum. To determine the best fit point $p_k = p_{ko}$, take the total differential of $SSE(p_k)$.

$$dSSE(p_1,\ldots,p_n) = \frac{1}{N}\sum_{i=1}^{N} \frac{\partial SSE(p_1,\ldots,p_n)}{\partial p_i}\, dp_i \qquad (3\text{-}2)$$

The condition for $SSE(p_1,\ldots,p_n)$ to be a minimum is given by

$$dSSE(p_1,\ldots,,p_n) = 0 \qquad (3\text{-}3)$$

3.2.4 Definition of Normal Equations

Using condition (3-3), and the fact that the dp_i for each i = 1,...,n are all independent of each other, the normal equations from condition (3-3) are given by

$$\frac{\partial SSE(p_1, \ldots, p_n)}{\partial p_i} = 0, \qquad i = 1, \ldots, n \qquad (3\text{-}4)$$

The above system of normal equations, constitutes a system of n non-linear algebraic equations in the n unknowns, $p_1, \ldots, p_n$. The numerical solution to the above non-linear algebraic system, yields the desired best fit point $p_k = p_{k_o}$, that is

$$\frac{\partial SSE(p_{1o}, \ldots, p_{no})}{\partial p_i} = 0, \qquad i = 1, \ldots, n \qquad (3\text{-}5)$$

3.2.5 Example

In Appendix 4, Mathcad program DOC1.MCD demonstrates non-linear regression analysis. A simple example is used to show how Mathcad's **Minerr** function is used to perform a non-linear curve-fitting procedure to a non-linear multi-valued complex-valued function denoted by Z. The function Z models the electrical impedance of a series RLC circuit. Thus the function, $Z = Z(R,L,C,\omega)$, depends on three parameters, R, L, and C, which, denote respectively the resistance, inductance and the capacitance of the series RLC circuit, and the angular frequency, ω, which is defined as $\omega = 2\pi f$ where f is the frequency. The impedance, Z, is given by

$$Z = R + j\left(\omega L - \frac{1}{\omega C}\right) \qquad (3\text{-}6)$$

The resonant frequency, f, is defined as the frequency at which Z is real, or equivalently, the frequency at which the phase of Z is zero. The resonant frequency, f, is given by

$$f = \frac{1}{2\pi}\frac{1}{\sqrt{LC}} \qquad (3\text{-}7)$$

The function $Z = Z(R,L,C,\omega)$, is fitted to the complex-valued data consisting of $Z_i = Z(R,L,C,\omega_i)$, where R and L are given arbitrary values of 10.0 kΩ and 10.0 mH respectively. The value for C was computed from equation (3-7) using f = 9.0 MHz. Given that L = 10.0 mH, the value of C is, C = 0.031 pF. The function Z is computed over the closed frequency interval, I = [8.0 MHz, 10.0 MHz] and then randomized using Mathcad's **rnd** function. The exact data for Z is randomized so as to simulate an experimental data set. The interval I, is chosen, so that the centre frequency of I, corresponds to the resonant frequency of the series RLC circuit.

The non-linear curve-fitting procedure, implemented by Mathcad's **Minerr** function, implements the Levenberg-Marquardt method. The Levenberg-Marquardt method, a quasi-Newton method, is a variation of the gradient method. In Newton's method, each entry of the jacobian is computed via a numerical differentiation procedure. In contrast, in the quasi-Newton method, each entry of the jacobian is replaced by an appropriate finite-difference approximation. The Levenberg-

Marquardt algorithm uses a down-hill search method (gradient method) to obtain an initial estimate of the parameters in question. Once an initial estimate of the parameters have been made, the algorithm then uses the quasi-Newton method to refine the initial estimates of the parameters to the desired accuracy.

Mathcad's non-linear curve-fitting procedure is effectuated by providing both the function SSL(L) and the appropriate guess value L denoted by Lguess. Once the appropriate guess value for L as been given, the best fit value for L denoted by Lfit is obtained by minimizing SSE(L) via Mathcad's **Minerr** function. The value of Lfit is 10.002 mH.

From Figure 3.3, SSE(L) has only one absolute minimum in the interval [1.0 mH, 20.0 mH]. The absolute minimum of SSE(L) ocurrs at L = 10.0 mH. Since SSE has only one absolute minimum in the interval [1.0 mH, 20.0 mH], then any value for L within the above mentioned interval can serve as an appropriate guess value for L.

Figures 3.4 and 3.5 give the magnitude and phase, respectively, of the impedance of the RLC series circuit, and show the simulated experimental data produced by the Mathcad **rnd** function and the fitted curve.

3.3 Fitting of Theory to Experiment in Air

In Section 2.6 of Chapter 2, the expression for the impedance, Z, of the coated sensor in air is given by

$$Z_a = \frac{\zeta_a}{A} \tag{3-8}$$

where

$$\zeta_a = \zeta_a(e, \eta, h, \omega) = 2j \frac{b_{33}}{b_{31}} \tag{3-9}$$

with

$$b_{33} = \delta (\gamma_1 - 1) k_q (\delta \epsilon (\gamma_1 + 1) h k_q + 2 e^2 (\gamma_1 - 1)) \tag{3-10}$$

and

$$b_{31} = 2 \delta^2 \epsilon (\gamma_1 - 1) (\gamma_1 + 1) k_q^2 \tag{3-11}$$

where $\gamma_1 = \exp(jhk_q)$ and $\delta = \eta\omega - jc$

with

$$k_q = k_q(e, \eta, \omega) = \omega \left[\frac{\rho_q}{c(e) + j\omega\eta} \right]^{1/2} \tag{3-12}$$

and

$$\overline{c} = \overline{c}(e) = c + \frac{e^2}{\epsilon} \qquad (3\text{-}13)$$

From an examination of (3-9) to (3-13), ζ_a is a complex-valued function which is independent of the effective surface area, A. ζ_a in terms of rectangular coordinates in the complex plane is expressed as

$$\zeta_a = \zeta_{Re} + j\,\zeta_{Im} \qquad (3\text{-}14)$$

From (3-9) the magnitude of Z, $|Z|$, is

$$|Z| = \frac{1}{A}\sqrt{\zeta_{Re}^2 + \zeta_{Im}^2} \qquad (3\text{-}15)$$

and the phase of Z, θ_Z, is

$$\theta_Z = \arctan\left[\frac{\zeta_{Im}}{\zeta_{Re}}\right] \qquad (3\text{-}16)$$

Note that $|Z|$ is inversely proportional to A and θ_Z is independent of A.

Appendix 5 is Mathcad program DOC2.MCD which fits theory to experiment in air. The theoretical complex-valued expression for the impedance, Z, of the hydrophilic and hydrophobic coated sensor in air is fitted to the corresponding experimental data for the impedance, Z, via a

three-step process. The three steps are:

(1) The Fitting Of θ_Z To Experiment In Air

(2) The Fitting Of $|Z|$ To Experiment In Air

(3) The Fitting Of Z To Experiment In Air

In air the theoretical complex-valued expression for the impedance, Z, is given by

$$Z_a = Z_a(c, e, \epsilon, \eta, \rho_q, h, A, \omega) \qquad (3\text{-}17)$$

The values for the elastic constant of quartz, c, the dielectric stress constant of quartz, ϵ, and the mass density of quartz, ρ_q, are, from Tiersten (1969),

$$c = 29.01\ 10^9\ N/m^2$$

$$\epsilon = 39.82\ 10^{-12}\ C/V\ m$$

$$\rho_q = 2649\ kg/m^3$$

The fitting of (3-17) to the experimental data is achieved by varying four parameters: the piezoelectric stress constant of quartz, e, the visco-elastic constant of quartz, η, the thickness of the coated sensor, h, and the effective surface area of the sensor, A. The variation of the parameters e, η, h, and A is achieved by the implementation of Mathcad's **Minerr** function, via Mathcad's Solve Block facility. Below is the outline of the three-step process.

In step 1, the appropriate guess values for the piezoelectric stress constant, e, the visco-elastic constant, η, and the thickness, h, denoted respectively by eguess, ηguess, and hguess are chosen. Then the starting values for

e, η, and h, denoted respectively by estart, ηstart, and hstart, are determined by minimizing the Sum Of Squares Of Errors, SSE1(e,η,h), via Mathcad's **Minerr** function.

The values for estart, ηstart, hstart, and the guess value for the effective surface area A, denoted by Aguess are used in step 2 to determine the starting value for A, denoted by Astart. The determination of Astart is achieved by minimizing the Sum Of Squares Of Errors, SSE2(A), via Mathcad's **Minerr** function.

Finally in step 3, using the values estart, ηstart, hstart, and Astart, best-fit values for e, η, h, and A denoted respectively by efit, ηfit, hfit, and Afit, are determined by minimizing the Sum Of Squares Of Errors, SSE3(e,η,h,A), via Mathcad's **Minerr** function.

For the hydrophilic coated sensor in air, the best-fit values for e, η, h, and A, are denoted respectively by e1fit, η1fit, h1fit, and A1fit. For the hydrophobic coated sensor in air, the best-fit values for e, η, h, and A, are denoted respectively by, e2fit, η2fit, h2fit, and A2fit. Table 3.1 summarizes the final results for e, η, h, and A.

The piezoelectric stress coefficient, e, is found experimentally because if the value of e from the literature is used, it is not possible to fit the theoretical expression for θ_Z to the experimental data. From Tiersten (1969), page 60, the piezoelectric stress coefficient is e_{26} = -0.095 C/m^2 and from Table 3.1 the best-fit value of e is -0.0798 C/m^2.

It is presumed that the value of e in the literature is incorrect. The value of the viscoeleastic coefficient, η, was not found in the literature and therefore it was necessary to measure it.

Table 3.1 Summary of Results for e, η, h, and A

Physical Properties	Hydrophilic Surface (Air)			Hydrophobic Surface (Air)		
	guess values	starting values	fitted values	guess values	starting values	fitted values
e (C/m^2)	-0.079	-0.07979	-0.07980	-0.079	-0.07979	-0.07980
η ($N \cdot m/s^2$)	0.011	0.01187	0.008376	0.24	0.2438	0.2344
Geometrical Properties						
h (μm)	183.87	183.878	183.879	183.98	183.986	183.979
A (cm^2)	0.28	0.2698	0.2984	0.25	0.2533	0.2575

Figures 3.6 through 3.9 are the plots of the experimental and fitted curves for $|Z|$ and θ_Z for both the hydrophilic and hydrophobic coated sensors in air.

From Figures 3.6 through 3.9 the curves for the phase and magnitude of Z for the hydrophilic sensor in air, are less damped than the corresponding curves of the phase and

magnitude of Z for the hydrophobic sensor in air. The greater damping of the phase and magnitude of Z in the case of the hydrophobic sensor, is consistent with the results in Table 3.1. In Table 3.1 the value of η for the hydrophobic sensor in air is greater than the corresponding value of η for the hydrophilic sensor in air. The greater value of η for the case of the hydrophobic sensor in air, results in the damping effect of both the phase and magnitude of Z. Also the molecular weight of $CH_3(CH_2)_{15}SH$ (258 g/mol), the hydrophobic coating, is greater than the molecular weight of $COOH(CH_2)_{10}SH$ (218 g/mol). Thus a sensor coated with $CH_3(CH_2)_{15}SH$ is expected to exhibit greater damping than a similar sensor coated with $COOH(CH_2)_{10}SH$. However, the viscoelastic coefficient of the sensors were not measured before they were coated and so it is possible that the higher η for the hydrophobic sensor, Table 3.1, is due, in part or in total, to the mechanical characteristics of the sensor.

3.4 Fitting of Theory and Experiment in Liquid

In Section 2.6 of Chapter 2, the expression for the impedance, Z, of the liquid-loaded sensor is given by

$$Z_l = \frac{\zeta_l}{A} \qquad (3\text{-}18)$$

For a liquid-loaded sensor, the expression for ζ_1, equation (3-9), generalizes to

$$\zeta_l = 2j \frac{\alpha b_{34} + b_{33}}{\alpha b_{32} + b_{31}} \qquad (3\text{-}19)$$

where α denotes the interfacial slip parameter which is a complex-valued property of the solid-liquid interface. The interfacial slip parameter, α, expressed in rectangular coordinates of the complex plane, is

$$\alpha = \alpha_{Re} + j\alpha_{Im} \qquad (3\text{-}20)$$

It is also instructive to express α in terms of the polar coordinates in the complex plane, $|\alpha|$ and θ_α, which are called the magnitude and phase of α, respectively.

$$\alpha = |\alpha| e^{j\theta_\alpha} \qquad (3\text{-}21)$$

The polar coordinates, $|\alpha|$ and θ_α, expressed in terms of the rectangular coordinates, α_{Re} and α_{Im}, are

$$|\alpha| = \sqrt{\alpha_{Re}^2 + \alpha_{Im}^2} \qquad (3\text{-}22)$$

and

$$\theta_\alpha = \arctan\left[\frac{\alpha_{Im}}{\alpha_{Re}}\right] \qquad (3\text{-}23)$$

The expressions for b_{33} and b_{31} are given by (3-10) and (3-11) respectively. The quantities b_{32} and b_{34} are

$$b_{32} = 2\,\delta\,\epsilon\,(\gamma_1^2 + 1)\,k_l k_q\,\nu\,\rho_l\,\omega \qquad \textbf{(3-24)}$$

and

$$b_{34} = k_l\,(\delta\,\epsilon\,(\gamma_1^2 + 1)\,h\,k_q + e^2\,(\gamma_1 - 1)\,(\gamma_1 + 1))\,\nu\,\omega\,\rho_l \qquad \textbf{(3-25)}$$

where

$$k_l = k_l(\nu, \omega) = \left[\frac{\omega}{j\,\nu}\right]^{1/2} \qquad \textbf{(3-26)}$$

The expressions for $|Z|$ and θ_Z are given by equations which correspond to (3-15) and (3-16), respectively.

Appendix 6 is Mathcad program DOC3.MCD which fits theory to experiment in liquid. Using the values for e, η, h, and A found in air, the theoretical complex-valued expression for the impedance, Z, of the hydrophilic and hydrophobic coated sensor immersed in water-glycerol solutions of varying concentrations ranging from pure water to pure glycerol in steps of 0.1 mole fraction, is fitted to the corresponding experimental data for the impedance, Z.

In liquid, the theoretical complex-valued expression for the impedance, Z, is given by

$$Z_l = Z_l(c, e, \epsilon, \eta, \rho_q, \rho, \nu, \alpha, h, A, \omega) \qquad (3\text{-}27)$$

In (3-27) the same values are used for c, ϵ, and ρ_q as used in Z_a, (3-17). In addition the values of the kinematic viscosity, ν, and mass density, ρ_l, for each solution of water-glycerol which were used, are from the CRC Handbook of Chemistry and Physics, Lide (1990-91). Table 3.2 shows the values of ν and ρ_l, for each mole fraction, M_f, used in the experiments.

Table 3.2 Values for M_f, ν, and ρ_l of Water-glycerol Solutions

Mole Fraction, M_f of Glycerol in Water	Kinematic Viscosity ν (cS)	Mass Density ρ_l (kg/L)
0.0 (Water)	1.002	0.9980
0.1	2.867	1.088
0.2	7.365	1.142
0.3	16.97	1.177
0.4	39.06	1.201
0.5	67.43	1.218
0.6	142.1	1.231
0.7	330.9	1.241
0.8	572.1	1.249
0.9	986.5	1.256
1.0 (Glycerol)	1398.	1.261

The parameters that are varied in the fitting of (3-27)

to the experimental data are the interfacial slip factor, α, and the effective surface area, A. The above fitting is done for both the hydrophilic and hydrophobic coated sensors immersed in the water-glycerol solution.

For the hydrophilic coated sensor immersed in a water-glycerol solution, the guess and fitted values for α and A are summarized by the following two expressions, ($\alpha guess_{klic}$, $Aguess_{klic}$) and (αfit_{klic}, $Afit_{klic}$), for each klic = 1,...,11. The subscripted variable, klic, takes on integral values from 1 to 11 inclusive, with klic = 1 representing pure water and klic = 11 representing pure glycerol. For the hydrophobic coated sensor immersed in a water-glycerol solution, the guess and fitted values for α and A are summarized by the following two expressions, ($\alpha\alpha guess_{kbic}$, $AAguess_{kbic}$) and ($\alpha\alpha fit_{kbic}$, $AAfit_{kbic}$) for each kbic = 1,...,7. The subscripted variable kbic, takes on integral values from 1 to 7 inclusive, with kbic = 1 representing pure water and kbic = 7 representing pure glycerol. For the case of the hydrophobic coated sensor immersed in the water-glycerol solution, four of the eleven data files for the magnitude and phase of Z, were corrupted, likely due to a poor electrical connection during the measurement process.

For the hydrophilic sensor immersed in the water-glycerol solution, for each, klic = 1,...,11, the determination of the best-fit values for α and A denoted by (αfit_{klic}, $Afit_{klic}$), is achieved by minimizing the Sum Of Squares Of Errors,

SSElic(α_{klic}, A_{klic}, klic) via Mathcad's **Minerr** function. For the hydrophobic sensor immersed in the water-glycerol solution, for each, kbic = 1,...,7, the determination of the best-fit values for α and A denoted by ($\alpha\alpha fit_{kbic}$, $AAfit_{kbic}$), is achieved by minimizing the Sum Of Squares Of Errors, SSEbic(α_{kbic}, A_{kbic}, kbic) via Mathcad's **Minerr** function. Tables 3.3 through 3.6 summarize the results for the guess and fitted values of α and A for both the hydrophilic and hydrophobic coated sensors in water-glycerol solutions.

Table 3.3 Interfacial Slip Parameter, α, for Hydrophilic Sensor

	Interfacial Slip Parameter, α Hydrophilic Sensor				
	guess values	fitted values			
Mole Fraction, M_f of Glycerol in Water		α_{Re}	α_{Im}	$\lvert\alpha\rvert$	θ_α (deg)
0.0 (Water)	3.76+2.30j	3.774	2.299	4.419	31.35
0.1	2.6+1.3j	2.631	1.246	2.911	25.34
0.2	1.9+0.6j	1.914	0.6510	2.022	18.79
0.3	1.6+0.4j	1.680	0.4000	1.727	13.39
0.4	1.4+0.2j	1.432	0.2130	1.447	8.461
0.5	1.3+0.1j	1.316	0.1180	1.321	5.110
0.6	1.1+0.07j	1.172	0.06900	1.174	3.393
0.7	0.92+0.01j	0.9370	0.01600	0.9370	1.000
0.8	0.8-0.003j	0.8930	-0.004000	0.8930	-0.2850
0.9	0.8-0.04j	0.8420	-0.04800	0.8440	-3.234
1.0 (Glycerol)	0.8-0.06j	0.8300	-0.06600	0.8320	-4.556

Table 3.4 Effective Surface Area, A, for Hydrophilic Sensor

Mole Fraction, M_f of Glycerol in Water	Effective Surface Area, A (cm^2) Hydrophilic Sensor	
	guess values	fitted values
0.0 (Water)	0.4	0.4115
0.1	0.39	0.3911
0.2	0.34	0.3494
0.3	0.34	0.3509
0.4	0.34	0.3433
0.5	0.33	0.3316
0.6	0.32	0.3271
0.7	0.33	0.3255
0.8	0.32	0.3242
0.9	0.32	0.3236
1.0 (Glycerol)	0.32	0.3221

Table 3.5 Interfacial Slip Parameter, α, for Hydrophobic Sensor

Mole Fraction, M_f of Glycerol in Water	Interfacial Slip Parameter, α Hydrophobic Sensor				
	guess values	fitted values			
		α_{Re}	α_{Im}	$\lvert\alpha\rvert$	θ_α (deg)
0.0 (Water)	4.9+2.3j	5.003	2.290	5.503	24.60
0.1	3.2+1.2j	3.268	1.256	3.501	21.03
0.2	2.3+0.7j	2.346	0.6910	2.446	16.42
0.4	1.3+0.1j	1.398	0.1490	1.405	6.086
0.6	1.1+0.00093j	1.176	0.003000	1.176	0.1420
0.8	0.8-0.05j	0.8670	-0.04300	0.8680	-2.855
1.0 (Glycerol)	0.7-0.11j	0.8150	-0.1170	0.8230	-8.202

Table 3.6 Effective Surface Area, A, for Hydrophobic Sensor

Mole Fraction, M_f of Glycerol in Water	Effective Surface Area, A (cm^2) Hydrophobic Sensor	
	guess values	fitted values
0.0 (Water)	0.36	0.3681
0.1	0.37	0.3731
0.2	0.35	0.3584
0.4	0.34	0.3409
0.6	0.35	0.3526
0.8	0.33	0.3346
1.0 (Glycerol)	0.32	0.3399

Figures 3.10 to 3.17 are plots of the experimental and fitted curves for θ_Z and $|Z|$ versus frequency, f.

3.5 Interfacial Slip Parameter, α

3.5.1 Plots of α

Figures 3.18 to 3.25 plot the variation of the real part of α, α_{Re}, the imaginary part of α, α_{Im}, the magnitude of α, $|\alpha|$, and the phase of α, θ_α, versus kinematic viscosity, ν, and mole fraction, M_f. In Appendix 7, Mathcad program DOC4.MCD performs a non-linear curve-fitting procedure to the experimental data consisting of α_{Re}, α_{Im}, $|\alpha|$, and θ_α, versus ν and M_f by fitting the experimental data to the power law model, $F(a,b,c,x) = ax^b + c$, for the case of α_{Re}, α_{Im}, $|\alpha|$, θ_α versus ν and to the exponential law model, $G(a,b,c,x) = ae^{bx} + c$, for the case of α_{Re}, α_{Im}, $|\alpha|$, θ_α versus M_f.

3.5.2 Numerical Computation of the Real Part of $u_{(l)x}$ and u_x

Appendix 8 is Mathcad program DOC5.MCD which numerically computes the real part of $u_{(l)x}$ and u_x. Using the values for ρ_q, c, e, ϵ, η, h, and A for the hydrophilic and hydrophobic sensor in air and the values for α and A corresponding to the different mole fractions of glycerol in water for the hydrophilic and hydrophobic sensor in the water-glycerol solution, the real part of u_x and $u_{(l)x}$ is computed over the time interval $[t_s, t_f]$ in time steps of Δt for each klic = 1,...,11 for the case of the hydrophilic sensor and for each kbic =

1,...,7 for the case of the hydrophobic sensor. The maximum displacement of the real part of u_x and $u_{(1)x}$ for the case of the hydrophilic and hydrophobic sensor was computed by Mathcad's **max** function. The resulting data for the maximum displacement of the real part of u_x and $u_{(1)x}$ versus ν was then fitted to the power law model F(a,b,c,x) by Mathcad's **Minerr** function for both the hydrophilic and hydrophobic sensor.

3.5.3 Discussion of the Variation of α versus Low Values of ν

In the plots shown in Figures 3.18 and 3.20 at low viscosity values, for the case of the hydrophilic coated sensor immersed in pure water, both $\alpha_{\lambda c}$ and $|\alpha|$ are approximately equal to 3.8 and 4.4, respectively. For the case of the hydrophobic coated sensor immersed in pure water, both α_{Rc} and $|\alpha|$ are approximately equal to 5.0 and 5.5, respectively.

The results at low viscosities for the hydrophilic and hydrophobic surfaces can be interpreted in terms of the greater strength of electrical attraction between a water molecule and a hydrophilic molecule than between a water molecule and a hydrophobic molecule. As the force between the water molecule and the surface molecule increases, the motion of the water molecule will more closely follow the motion of the molecule on the surface, that is, $|\alpha|$ will approach 1. From Figure 3.20, this is indeed the case; $|\alpha|$ for the hydrophilic sensor is closer to 1 than $|\alpha|$ for the hydrophobic

sensor. From Figure 3.21 the sign of the phase, θ_a, for both the hydrophilic and hydrophobic sensors means that the liquid particle displacement $u_{(l)x}$, leads the quartz particle displacement u_x, at the interface. Because $u_{(l)x}$ leads u_x, $u_{(l)x}$ will achieve its maximum displacement at an earlier time than u_x. Figure 3.26 depicts the time variation of the real part of u_x and $u_{(l)x}$ both for the hydrophilic and hydrophobic sensor immersed in pure water. Notice that for both the hydrophilic and hydrophobic sensor, the real part of $u_{(l)x}$ leads the real part of u_x. Also from Figure 3.26 the maximum displacement of the real part of $u_{(l)x}$ for the case of the hydrophilic sensor is greater than the maximum displacement of the real part of $u_{(l)x}$ for the case of the hydrophobic sensor. By the same token the maximum displacement of the real part of u_x for the case of the hydrophilic sensor is greater than the maximum displacement of the real part of u_x for the case of the hydrophobic sensor. This result is to be expected, since for the case of the hydrophobic sensor, the molecular weight of the hydrophobic coating is greater than the molecular weight of the hydrophilic coating in the case of the hydrophilic sensor. The greater molecular weight of the hydrophobic coating induces a greater mass-loading effect than that induced by the hydrophilic coating. A greater mass-loading effect in the case of the hydrophobic sensor, means that for a given input voltage drop across the sensor, the electric field generated, will produce a transverse particle

displacement inversely proportional to the mass of the coating in question. Thus in the case of the hydrophobic sensor the maximum displacement of the real part of the transverse particle displacement, u_x will be less than the corresponding maximum displacement of the real part of u_x for the case of the hydrophilic sensor.

Also from Figures 3.18 and 3.20, at low viscosity values, the fact that $|u_{(0)x}| \neq |u_x|$ at the solid-liquid interface, implies that there is slip between the top surface of the coating in contact with the bottom surface of the liquid. Thus at low viscosity values, the interfacial slip parameter, α, satisfies the slip condition given by

$$\alpha \neq 1 \qquad (3\text{-}28)$$

Figure 3.27 depicts the plots of the maximum displacement of the real part of u_x and $u_{(0)x}$ versus ν for both the hydrophilic and hydrophobic sensor. From Figure 3.27, for low values of viscosity ν, the maximum displacement of the real part of $u_{(0)x}$ for the case of the hydrophilic sensor is greater than the maximum displacement of the real part of $u_{(0)x}$ for the case of the hydrophobic sensor. Again this result is expected, since for the case of pure water, the hydrophilic interaction that occurs at the solid-liquid interface is greater than the corresponding hydrophobic interaction. The traction force between the wheels of a car and a dry road

produces a greater displacement of the car, than the displacement that would occur if the wheels of the same car were in contact with an icy road. In much the same way, the greater strength of the hydrophilic interaction between the hydrophilic surface and the water molecules at the solid-liquid interface will produce a greater displacement of the water molecules in the vicinity of the interface than the displacement that would occur if the interaction at the solid-liquid interface were hydrophobic in character. Thus the displacement of the water molecules in the vicinity of a hydrophobic interface is less than the displacement of the water molecules in the vicinity of a hydrophilic interface.

3.5.4 Discussion of the Variation of α versus High Values of ν

From Figures 3.18 and 3.20, as the kinematic viscosity, ν, increases towards higher values of viscosity, both α_{Re} and $|\alpha|$ approach unity for both the hydrophilic and hydrophobic coated surfaces. However from Figure 3.19 as ν increases towards higher values of viscosity, α_{Im} approaches zero. This is to be expected, since the strength of the interaction at the solid-liquid interface between water molecules in contact with the coating molecules at the interface, increases as ν increases towards higher values of viscosity. For values of $\nu \gg 1$, from Figures 3.18, 3.19, and 3.20, $\alpha_{Re} \approx 1$, $\alpha_{Im} \approx 0$, and $|\alpha| \approx 1$ respectively. From Figure 3-21 as ν increases towards higher values of viscosity, θ_α decreases until, at some

critical value for kinematic viscosity, $\nu = \nu_c$, $\theta_\alpha = 0$. From (3-23) $\theta_\alpha = 0$ when $\alpha_{Im} = 0$. As noted above, from Figure 3.20, for high values of kinematic viscosity, ν, the $|\alpha| = 1$, which implies that $|u_{(l)x}| = |u_x|$, which in turn implies that $u_{(l)x} = u_x$. The condition, $u_{(l)x} = u_x$ implies that at the solid-liquid interface, there is no slip. The no slip condition is given by

$$\alpha = 1 \qquad \textbf{(3-29)}$$

From Figure 3.27 over the entire viscosity range from pure water to pure glycerol the maximum displacement of the real part of $u_{(l)x}$ for the case of the hydrophilic sensor is greater than the maximum displacement of the real part of $u_{(l)x}$ for the case of the hydrophobic sensor. The same holds true for the maximum displacement of the real part of u_x. This is to be expected since the strength of the interaction of a hydrophilic surface in contact with a water-glycerol solution at the interface, on the average will be greater than the strength of the interaction between a hydrophobic surface and the water-glycerol solution in question.

3.5.5 Variation of α with Mole Fraction, M_f

The results for α_{Re}, α_{Im}, $|\alpha|$, and θ_α versus mole fraction, M_f, plotted in Figures 3.22 through 3.25 are the same as the results for α_{Re}, α_{Im}, $|\alpha|$, and θ_α versus kinematic viscosity, ν, as plotted in Figures 3.18 through 3.21. The fact that the

above two results are the same can be seen from Figure 3.28. From Figure 3.28, low values of mole fraction correspond to low values of kinematic viscosity, whereas high values of mole fraction correspond to high viscosity values. From Figure 3.28, $M_f = 0$ corresponds to pure water with a viscosity value of $\nu = 1.00$ cS, and $M_f = 1$ corresponds to pure glycerol with a viscosity value of $\nu = 1400$ cS. Thus the variation between ν and M_f as plotted in Figure 3.28, is such that the variation of α_{Re}, α_{Im}, $|\alpha|$, and θ_α versus M_f and ν are similar.

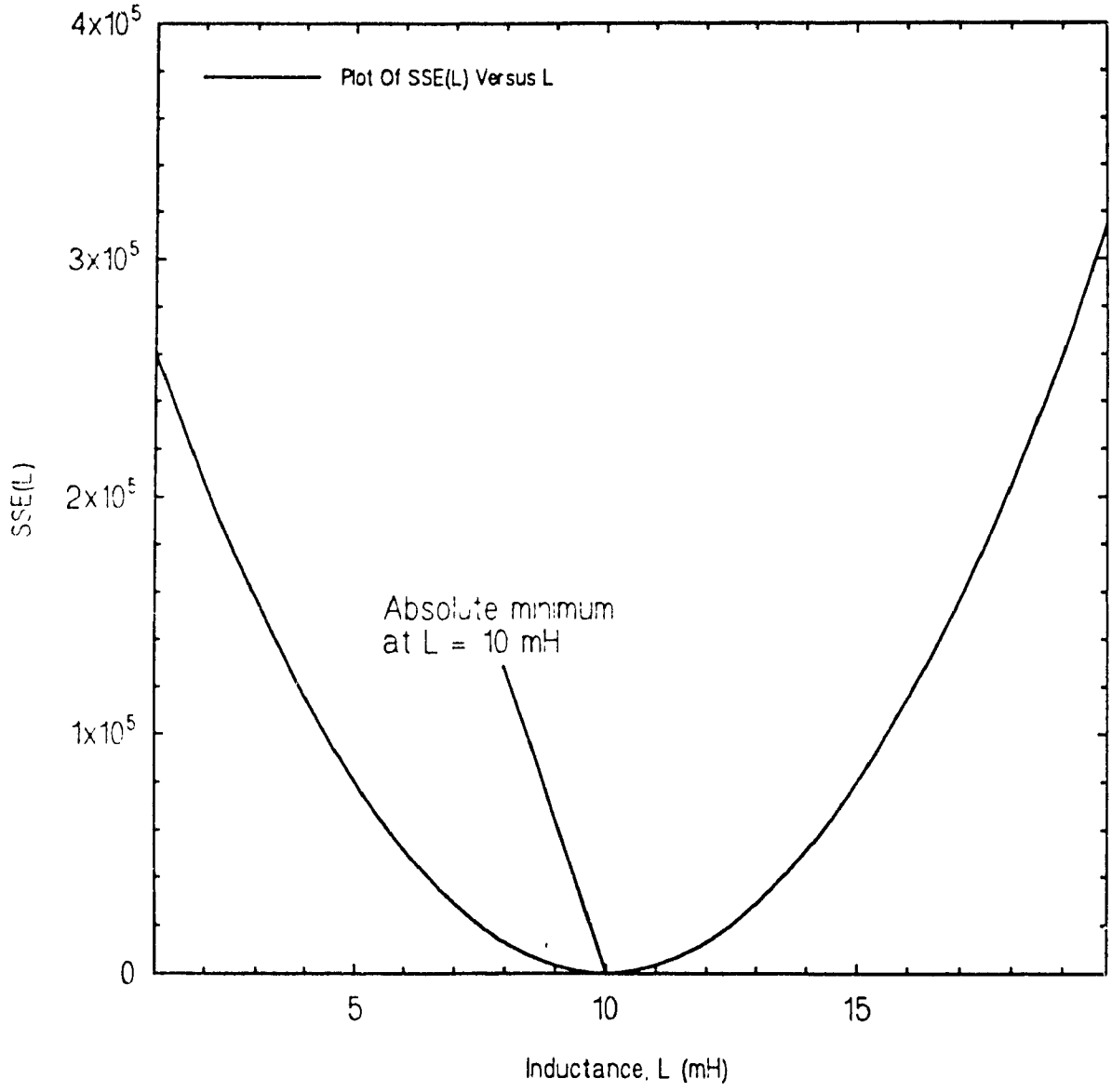


Figure 3.3 Sum Of Squares Of Errors for a series RLC circuit.

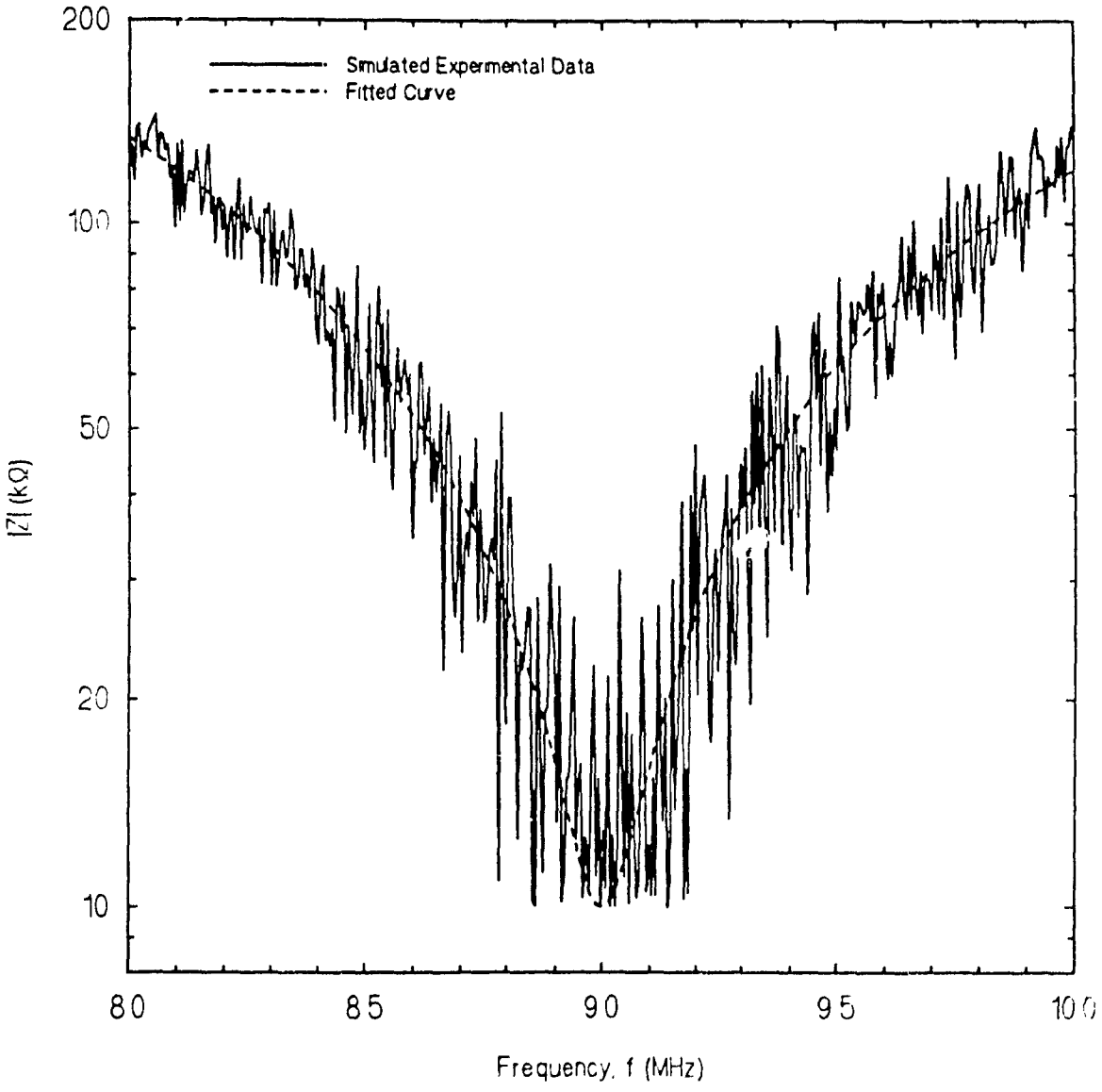


Figure 3.4 Magnitude of impedance for a series RLC circuit.

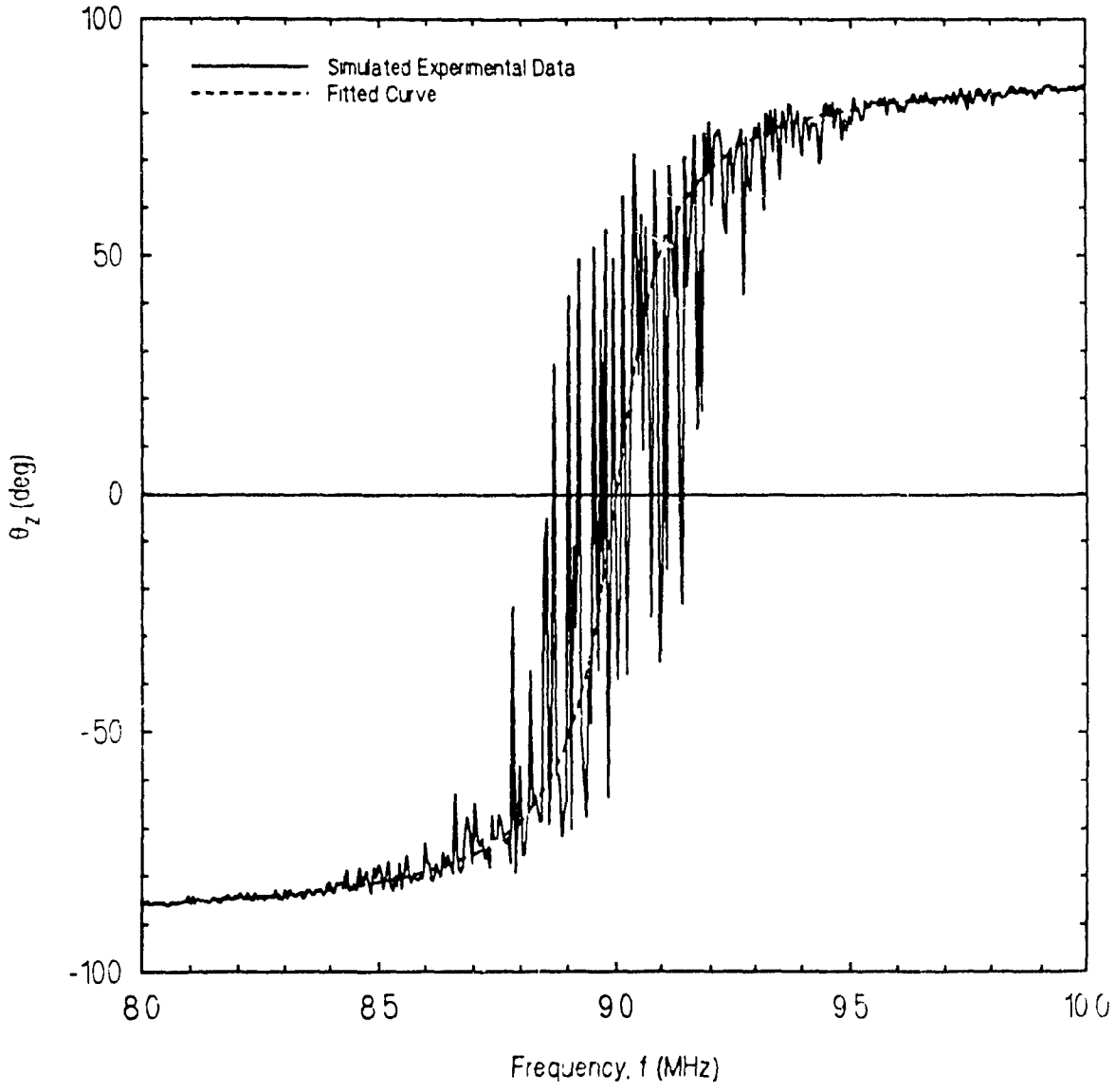


Figure 3.5 Phase of impedance for a series RLC circuit.

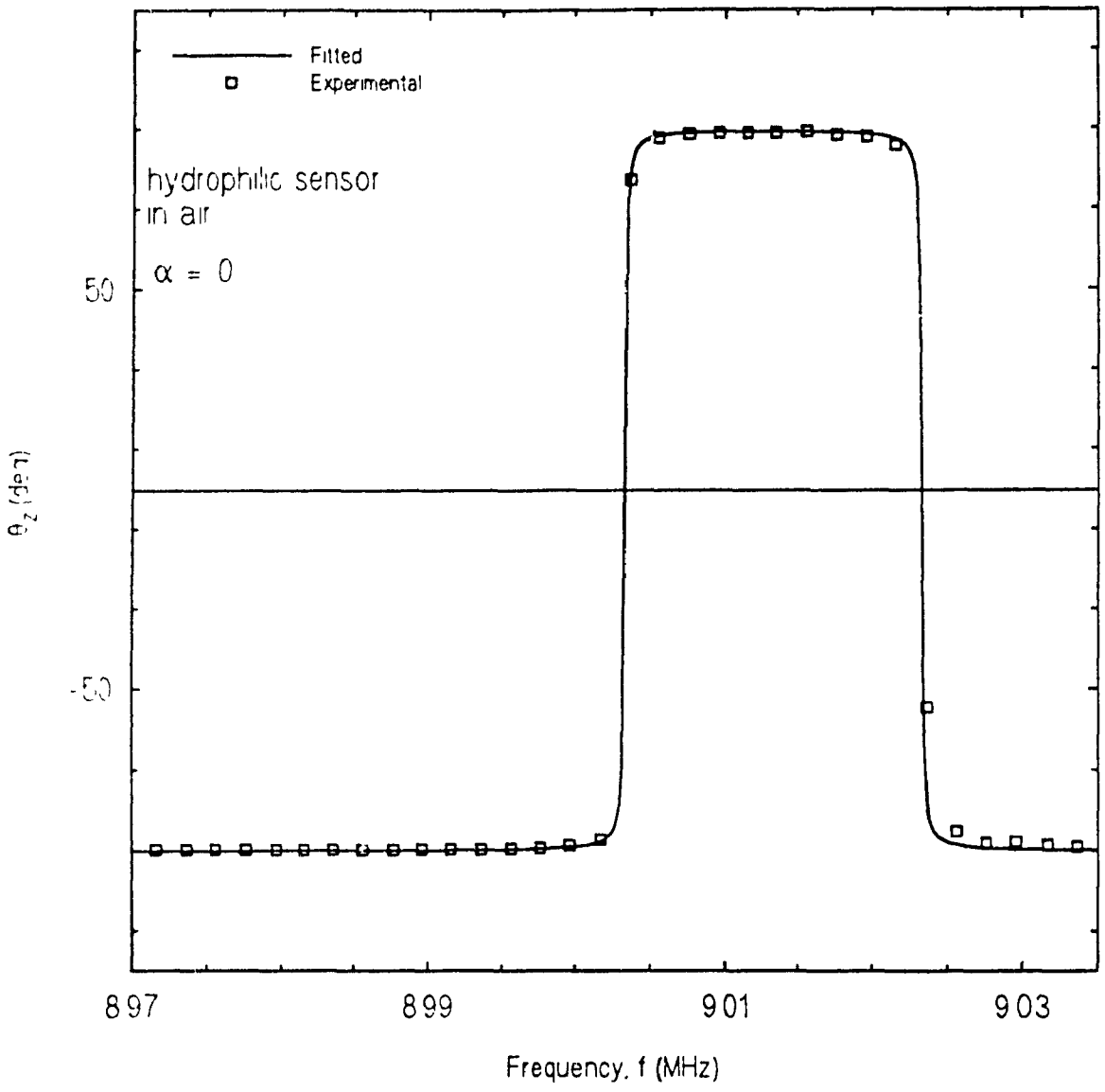


Figure 3.6 Phase of impedance of the hydrophilic sensor in air.

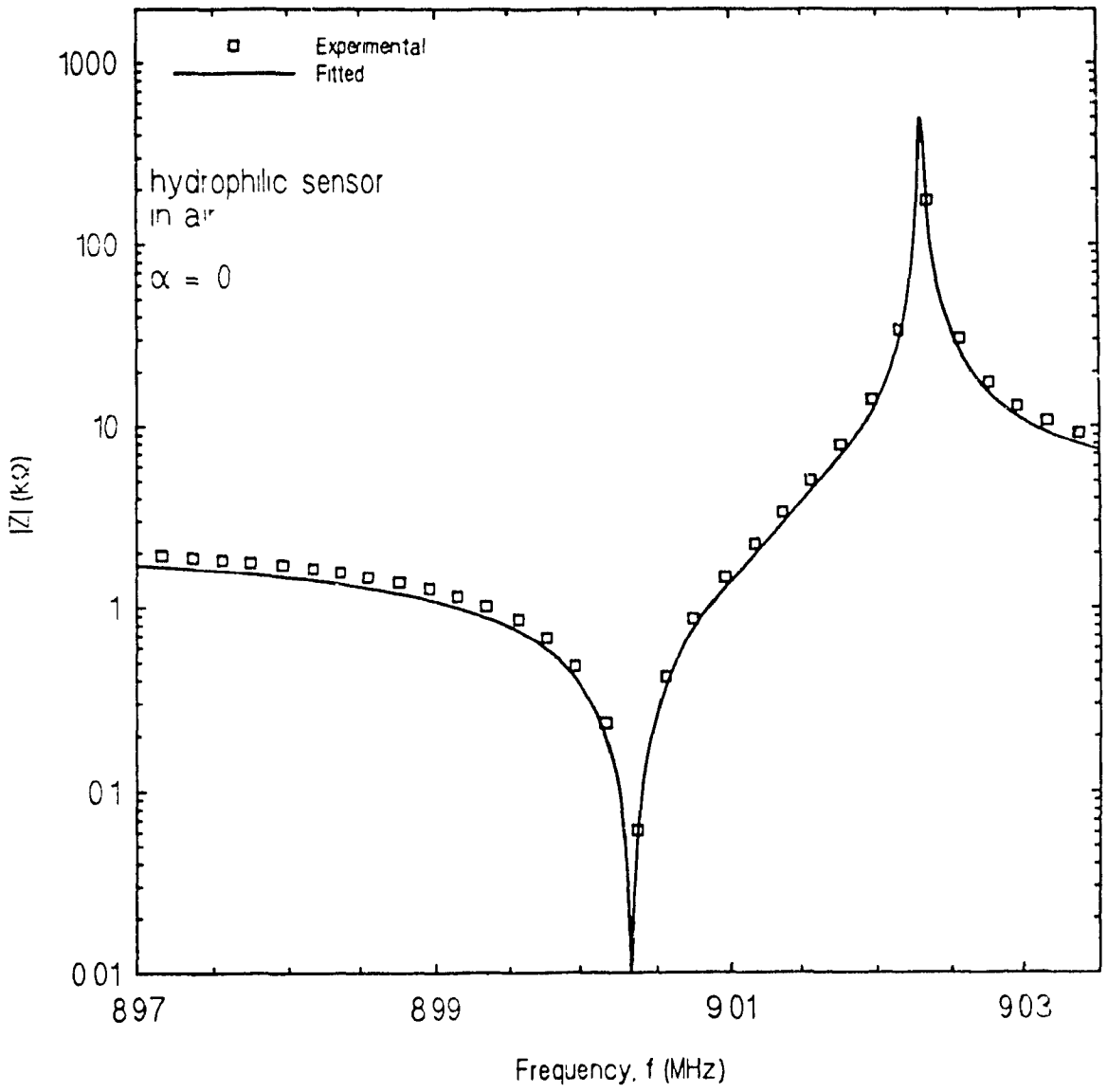


Figure 3.7 Magnitude of impedance of the hydrophilic sensor in air.

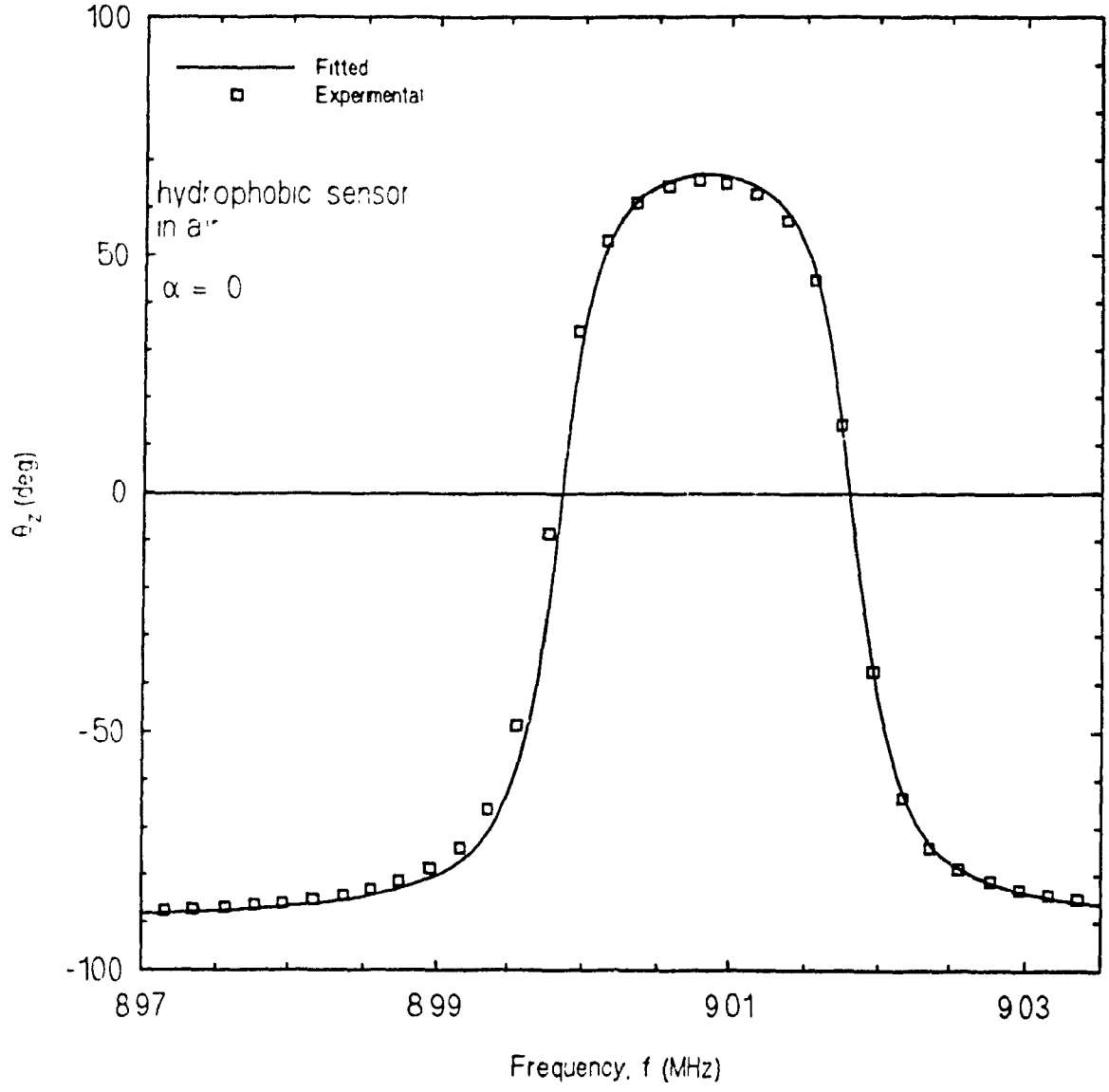


Figure 3.8 Phase of impedance of the hydrophobic sensor in air.

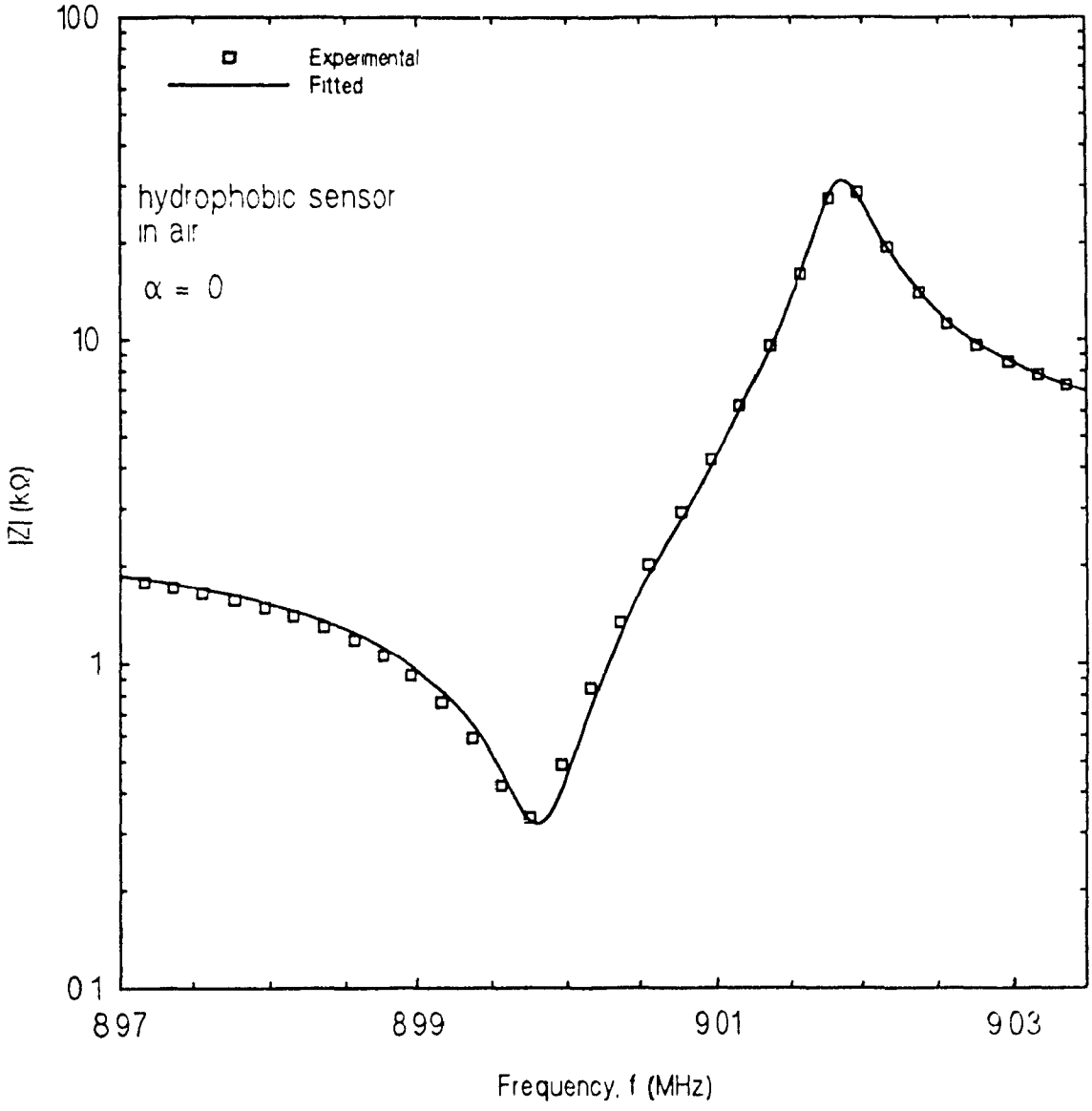


Figure 3.9 Magnitude of impedance of the hydrophobic sensor in air.

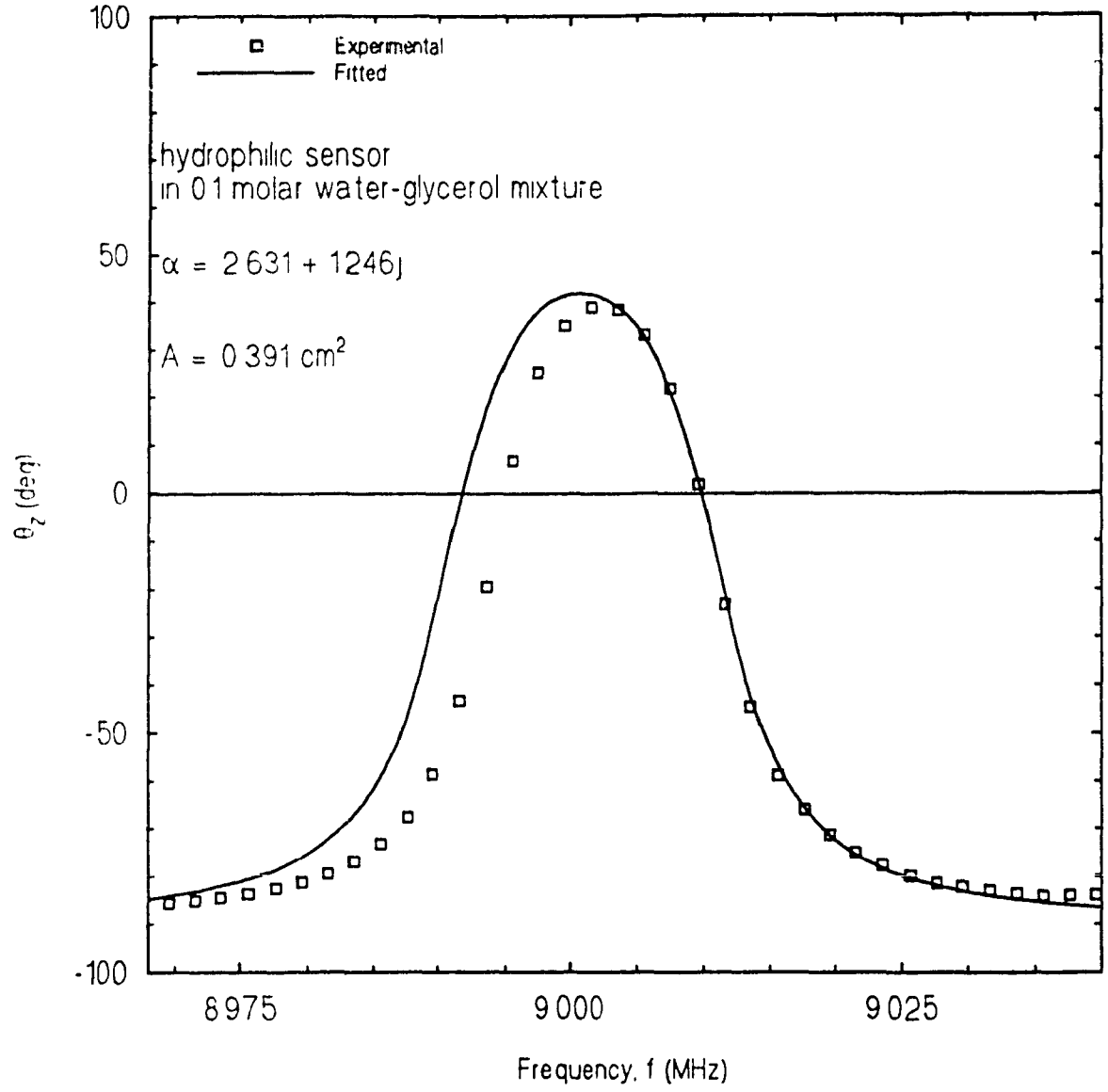


Figure 3.10 Phase of impedance of the hydrophilic sensor in 0.1 molar water-glycerol solution.

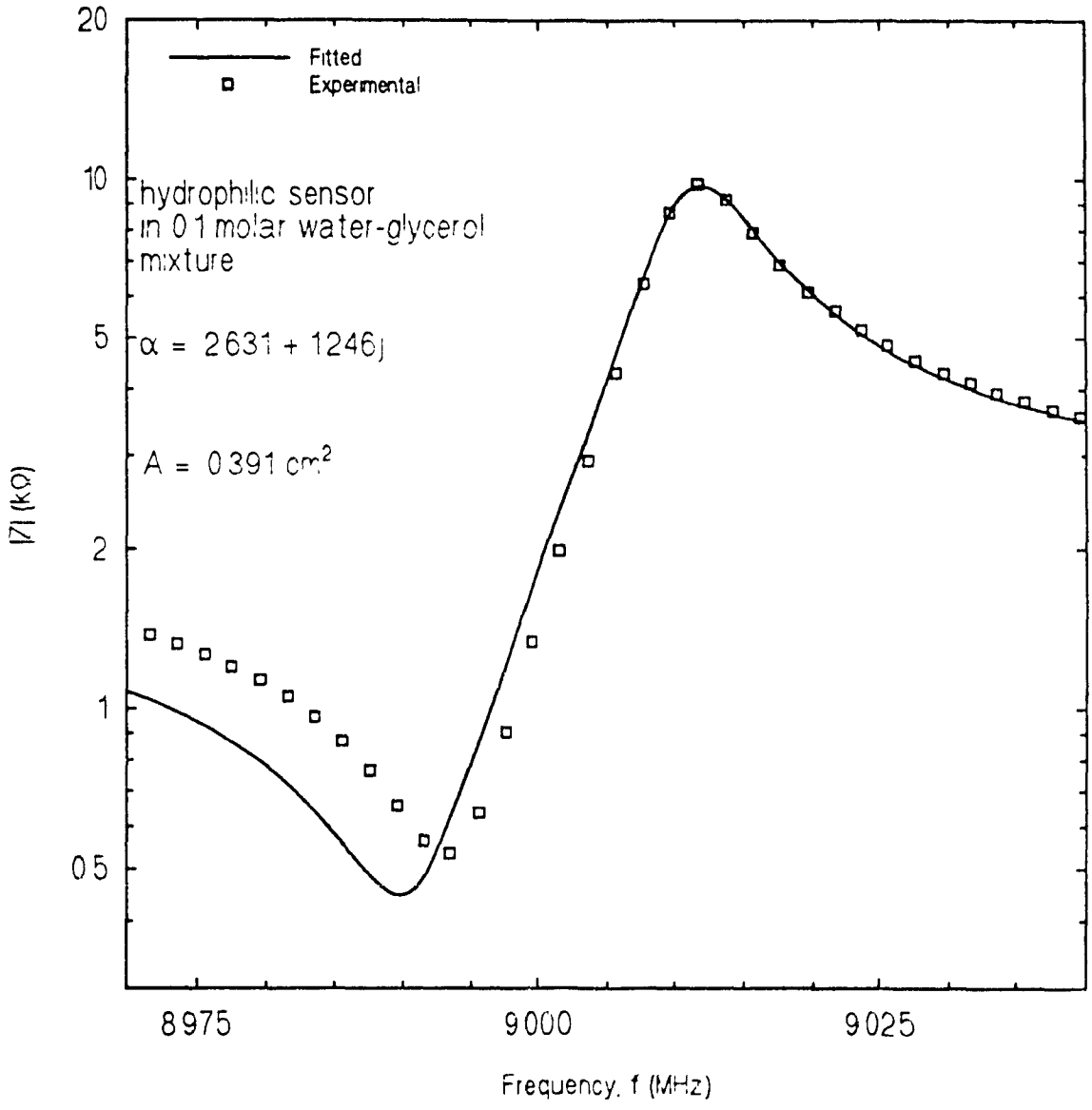


Figure 3.11 Magnitude of impedance of the hydrophilic sensor in 0.1 molar water-glycerol solution.

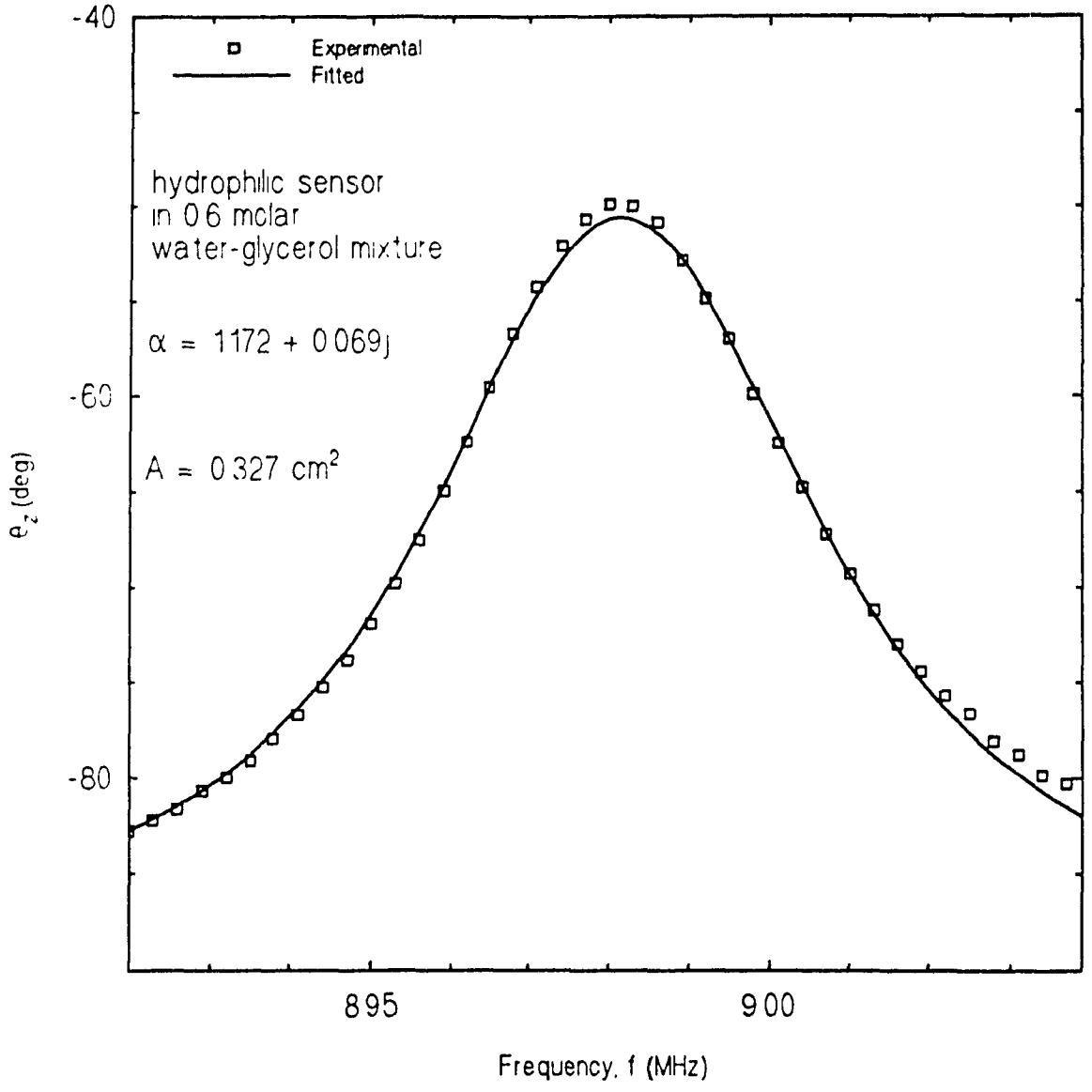


Figure 3.12 Phase of impedance of the hydrophilic sensor in 0.6 molar water-glycerol solution.

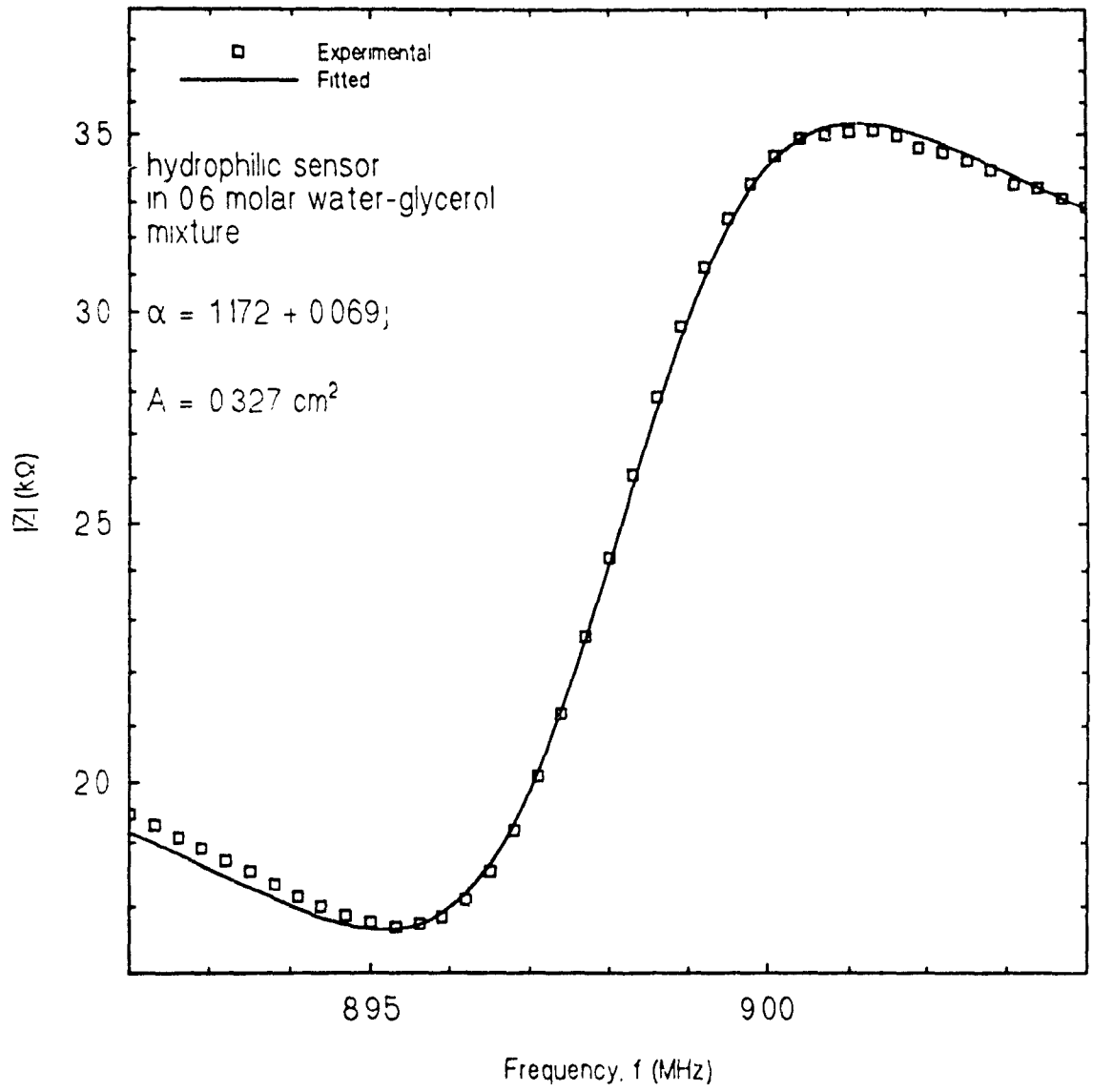


Figure 3.13 Magnitude of impedance of the hydrophilic sensor in 0.6 molar water-glycerol solution.

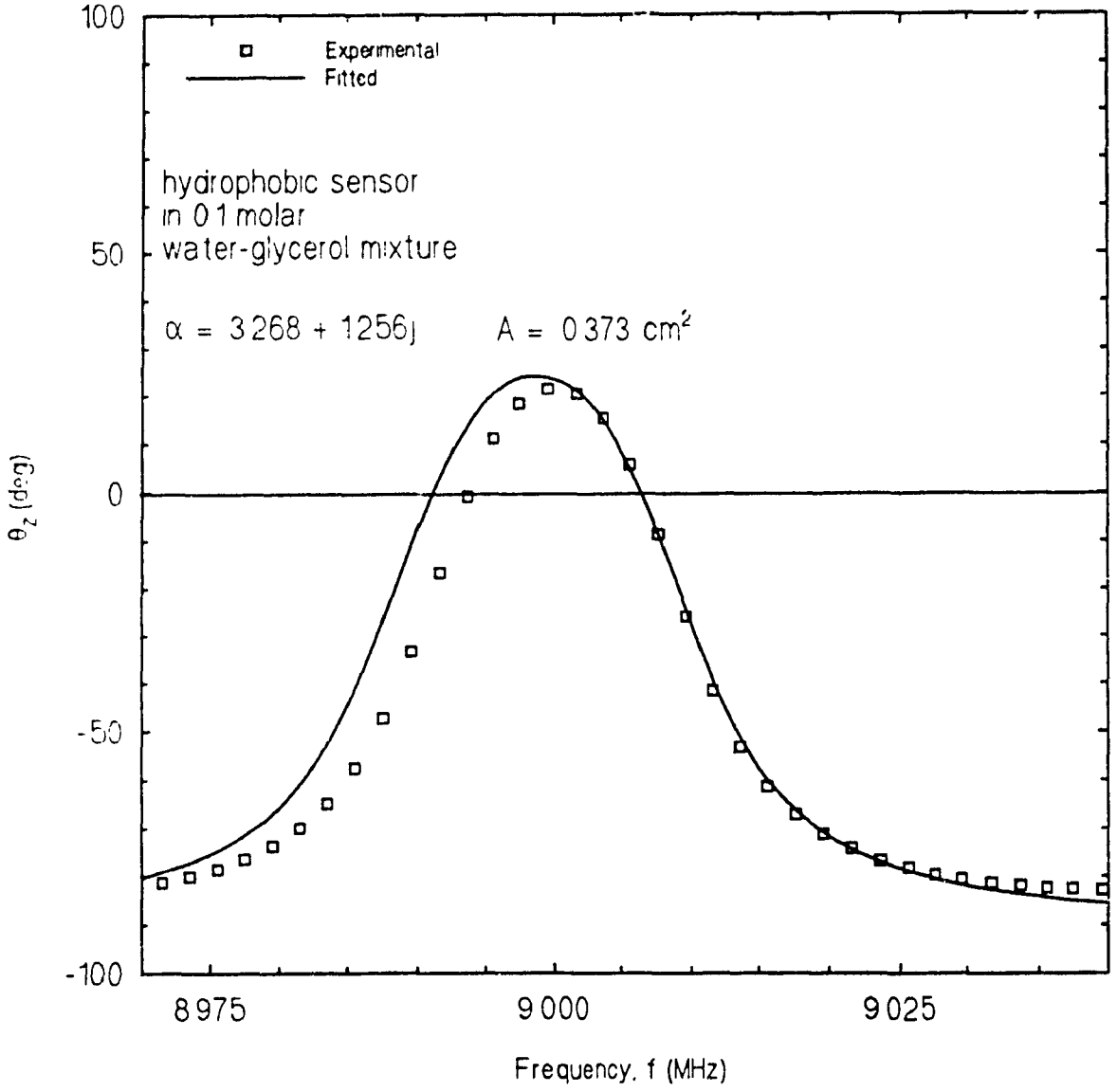


Figure 3.14 Phase of impedance of the hydrophobic sensor in 0.1 molar water-glycerol solution.

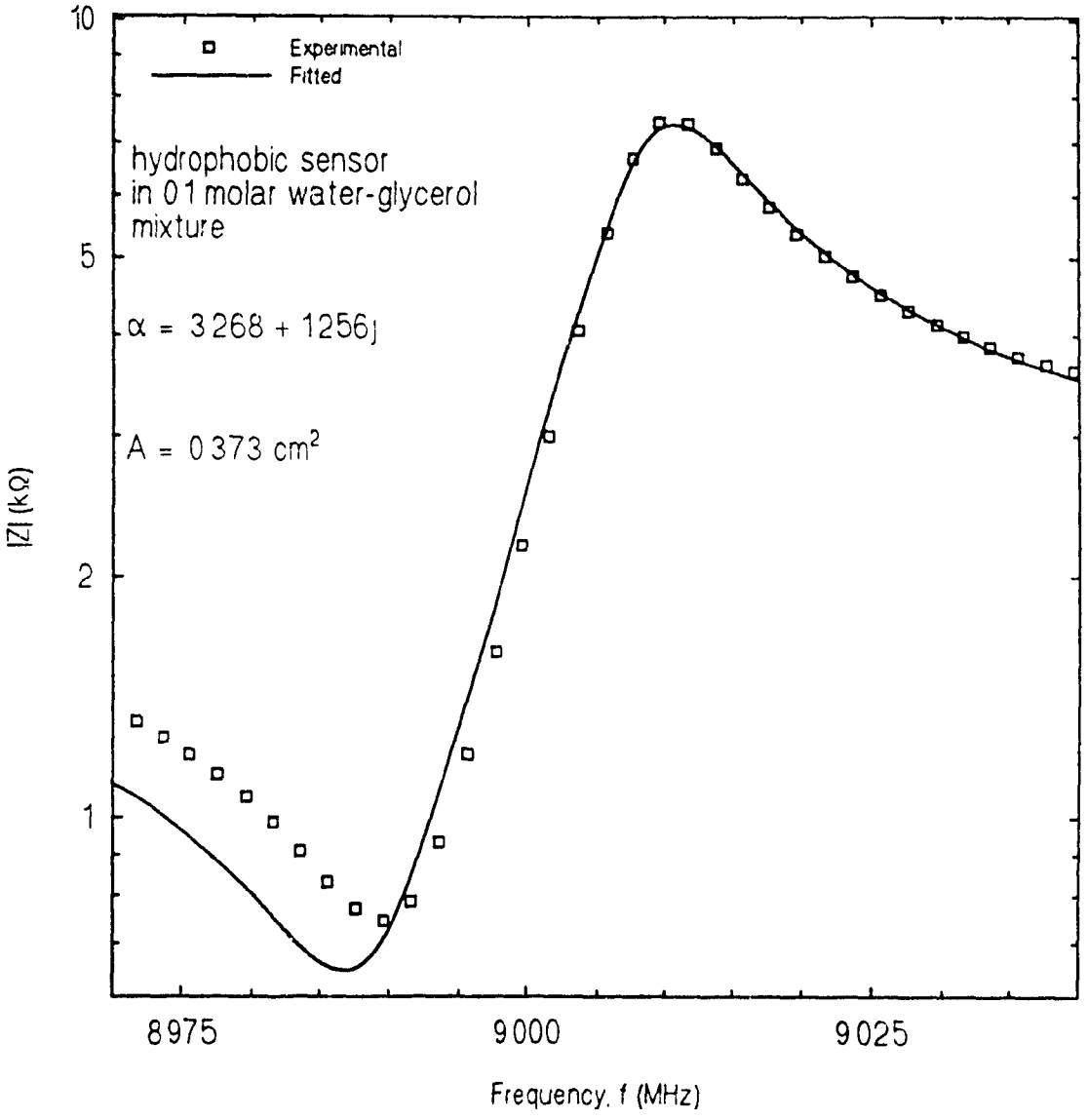


Figure 3.15 Magnitude of impedance of the hydrophobic sensor in 0.1 molar water-glycerol solution.

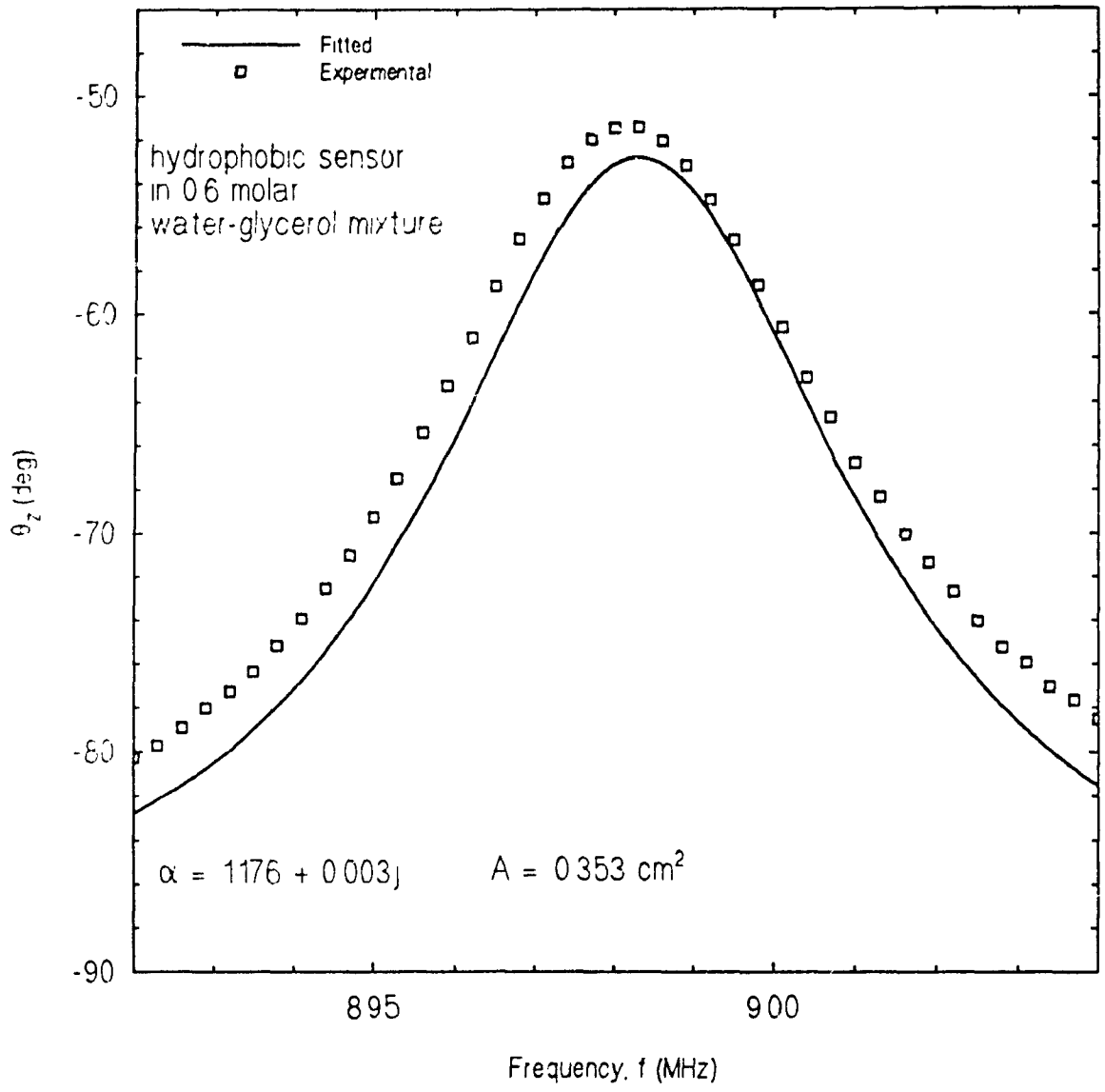


Figure 3.16 Phase of impedance of the hydrophobic sensor in 0.6 molar water-glycerol solution.

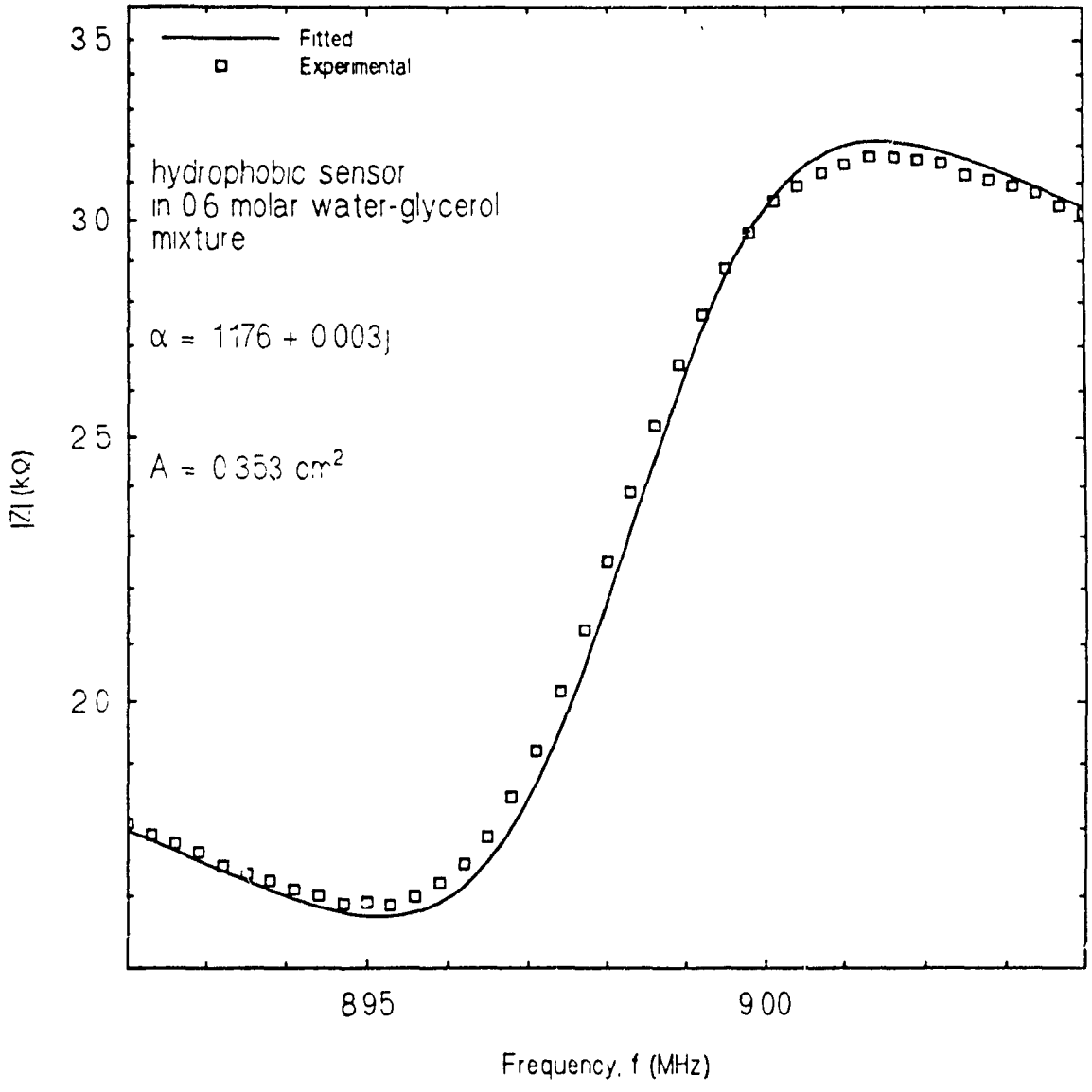


Figure 3.17 Magnitude of impedance of the hydrophobic sensor in 0.6 molar water-glycerol solution.

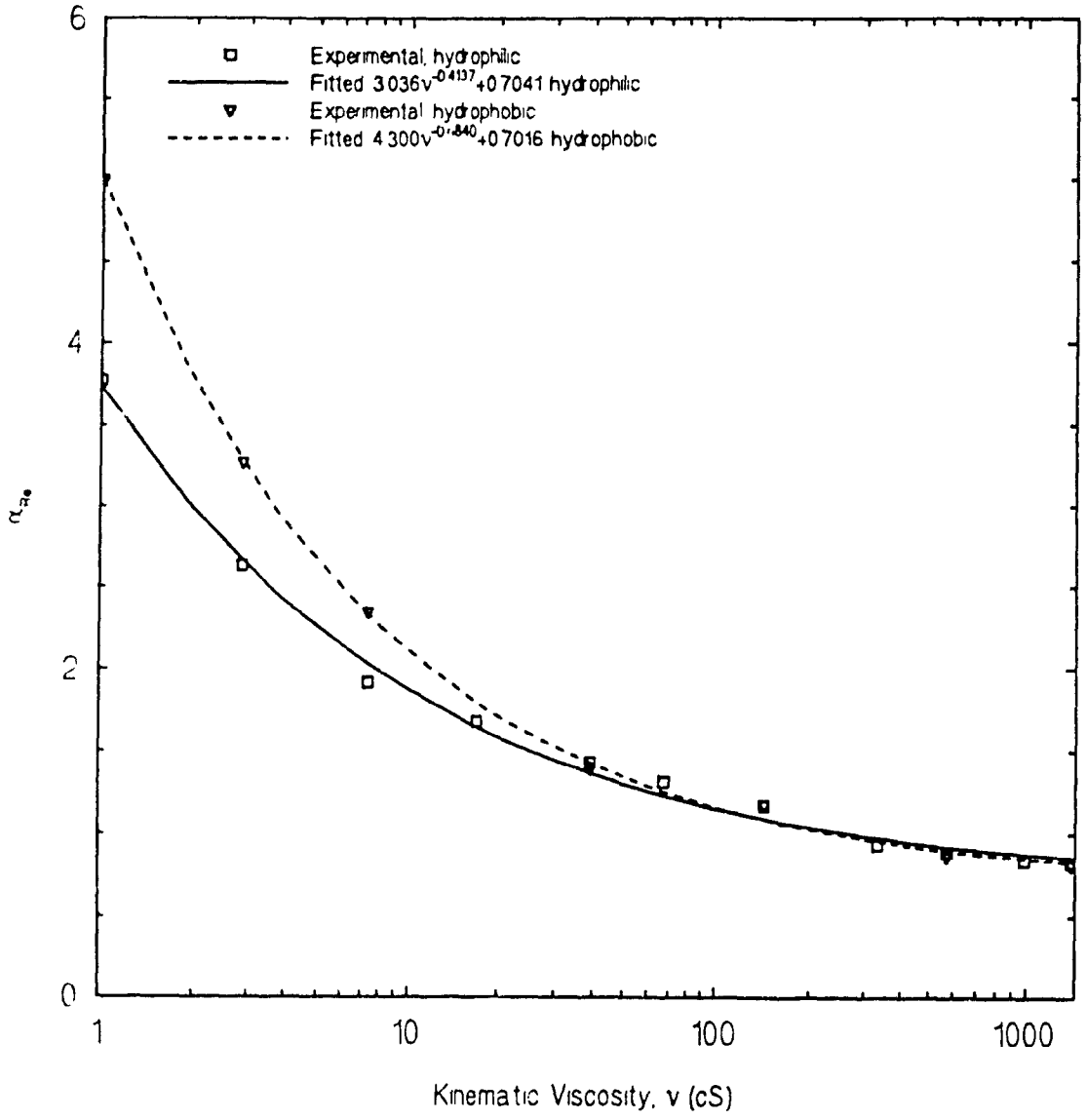


Figure 3.18 Real part of interfacial slip parameter versus kinematic viscosity for the hydrophilic and hydrophobic sensor in liquid.

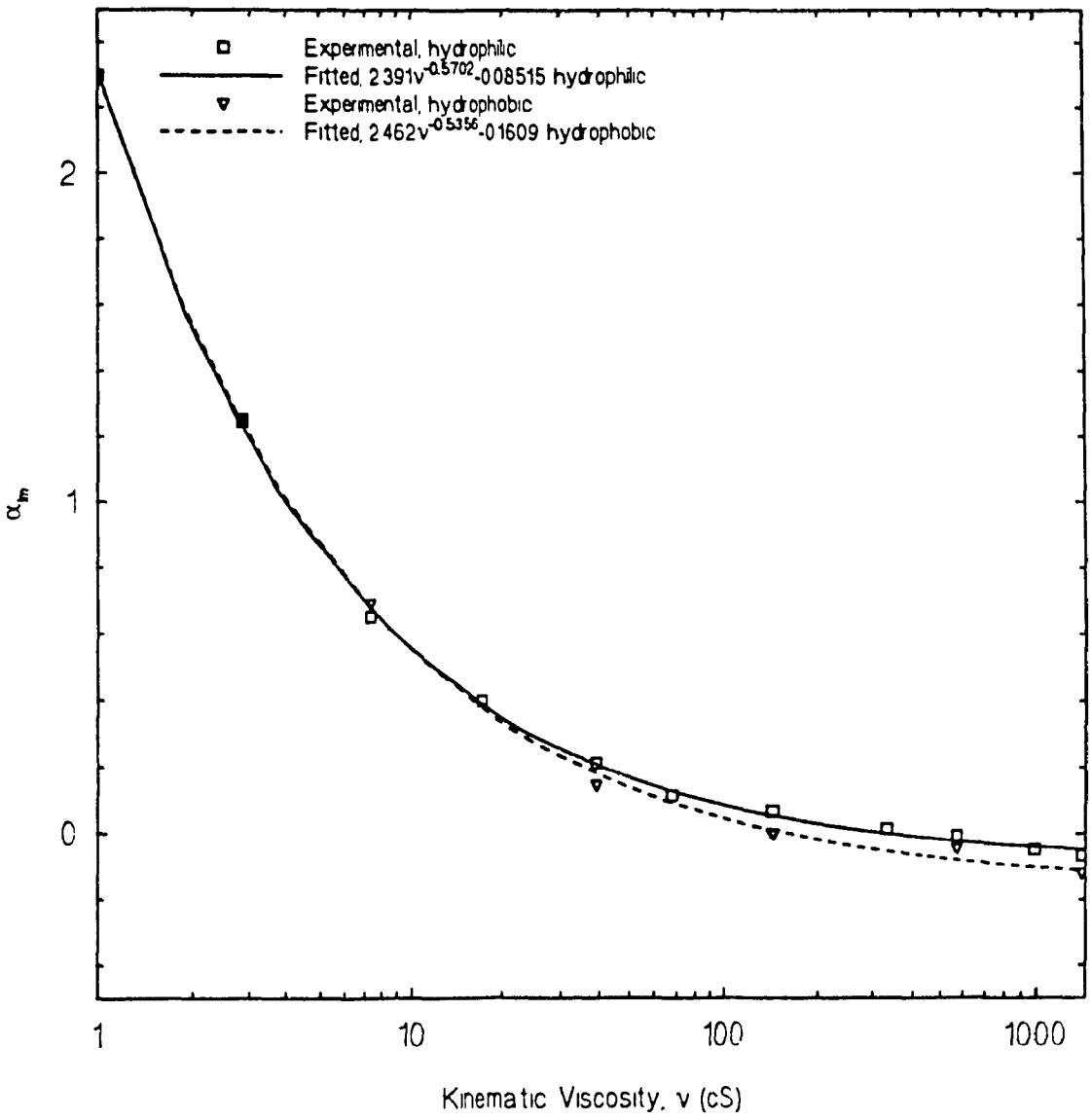


Figure 3.19 Imaginary part of interfacial slip parameter versus kinematic viscosity for the hydrophilic and hydrophobic sensor in liquid.

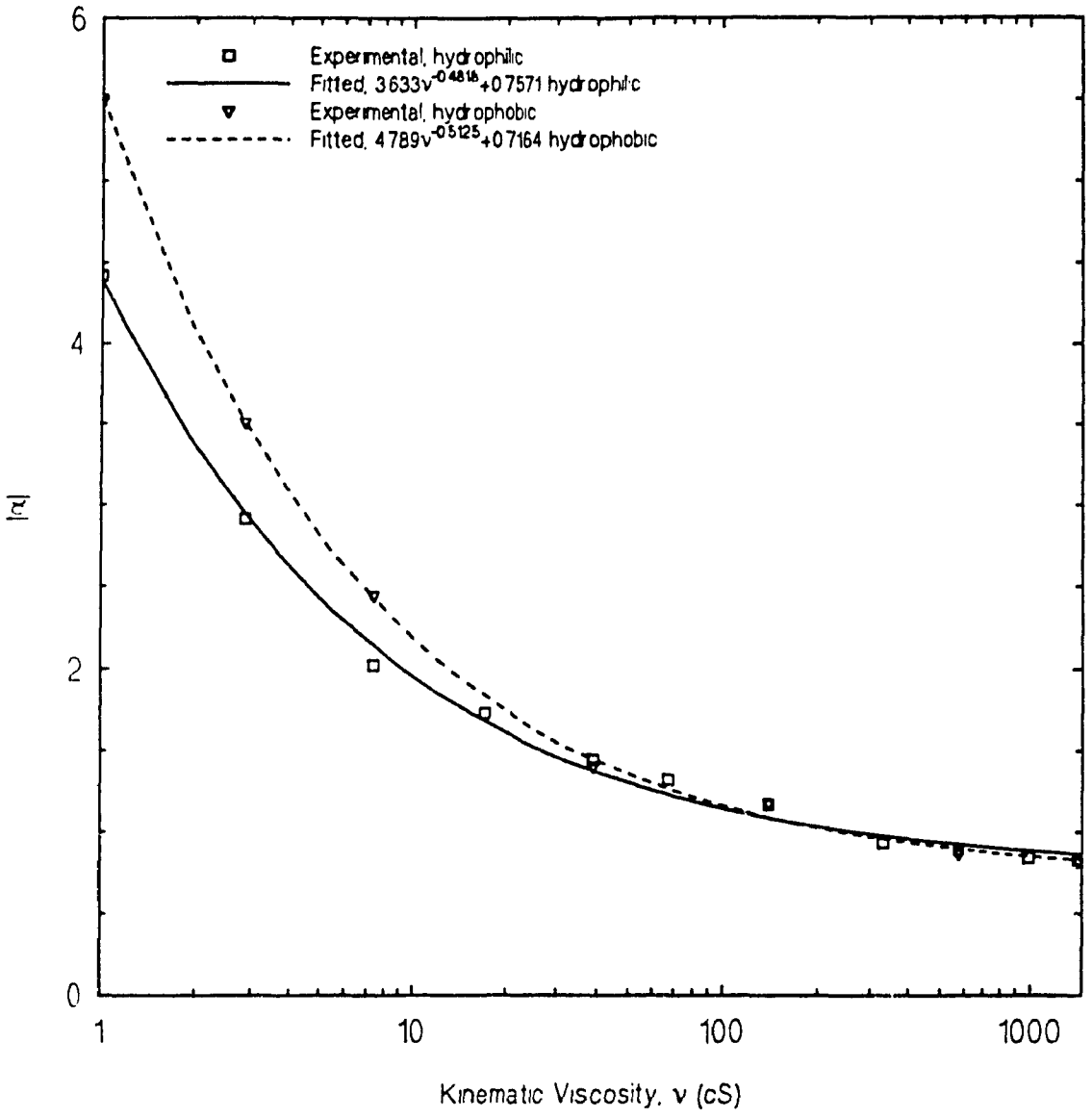


Figure 3.20 Magnitude of interfacial slip parameter versus kinematic viscosity for the hydrophilic and hydrophobic sensor in liquid.

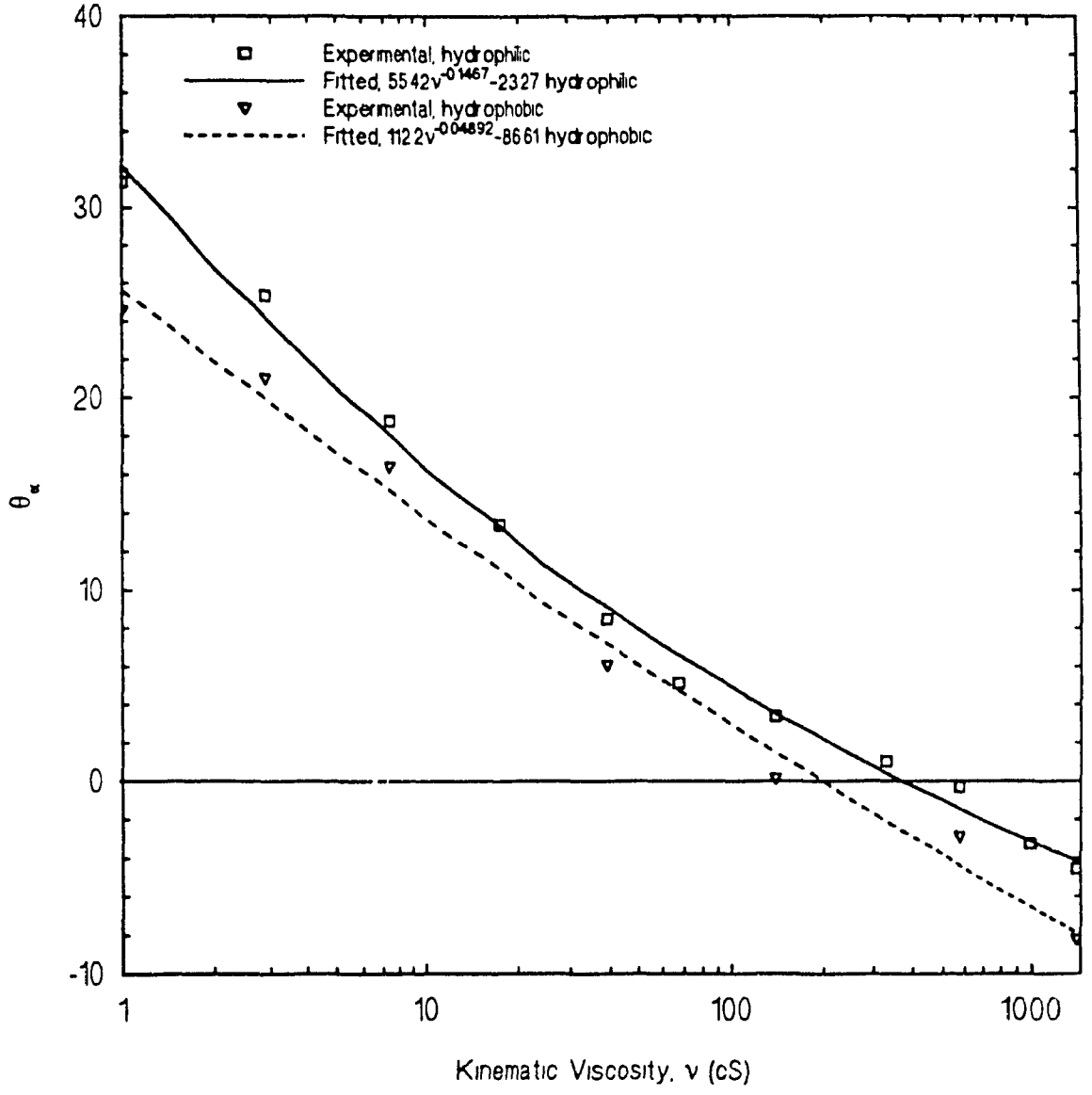


Figure 3.21 Phase of interfacial slip parameter versus kinematic viscosity for the hydrophilic and hydrophobic sensor in liquid.

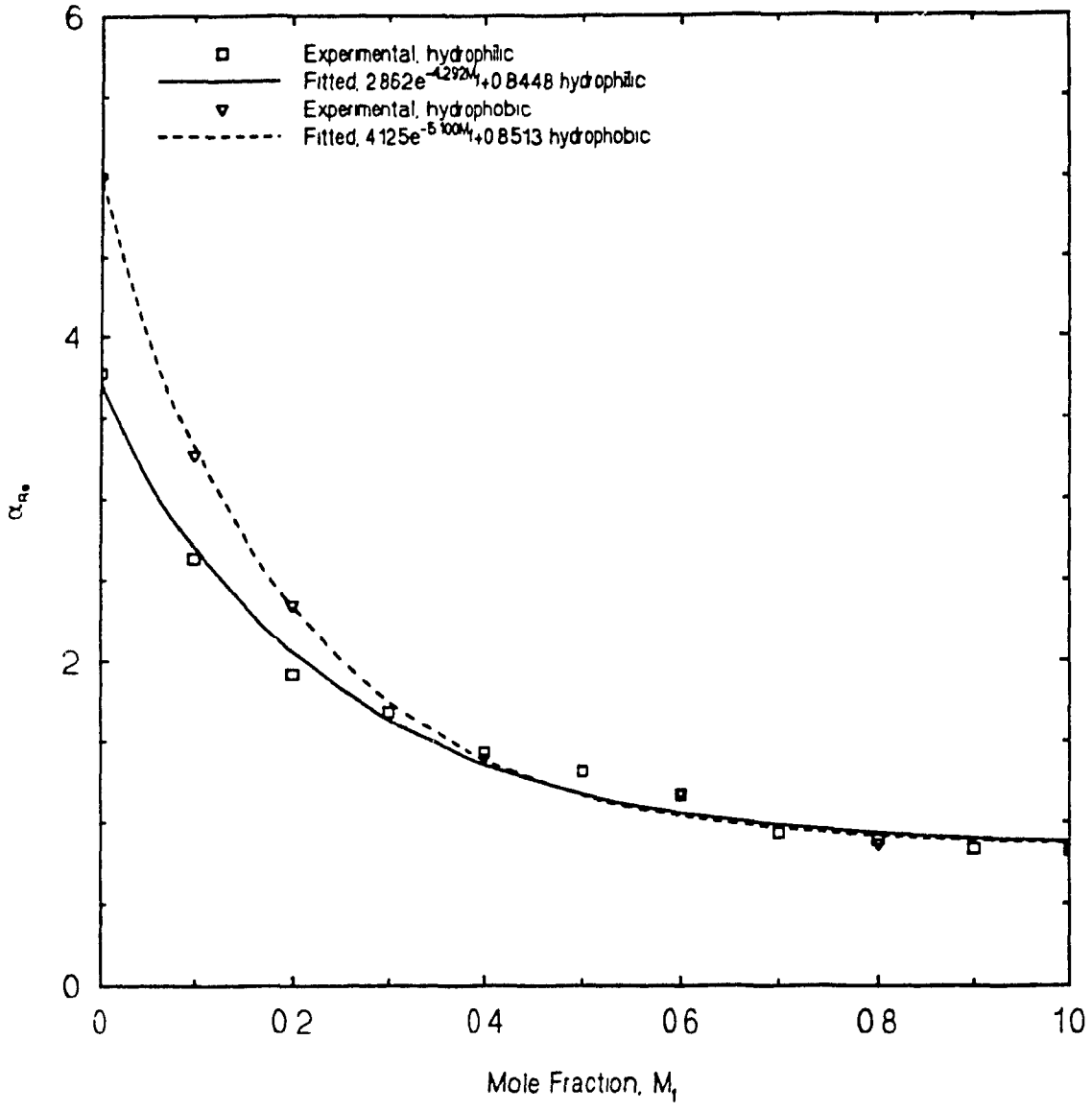


Figure 3.22 Real part of interfacial slip parameter versus mole fraction for the hydrophilic and hydrophobic sensor in liquid.

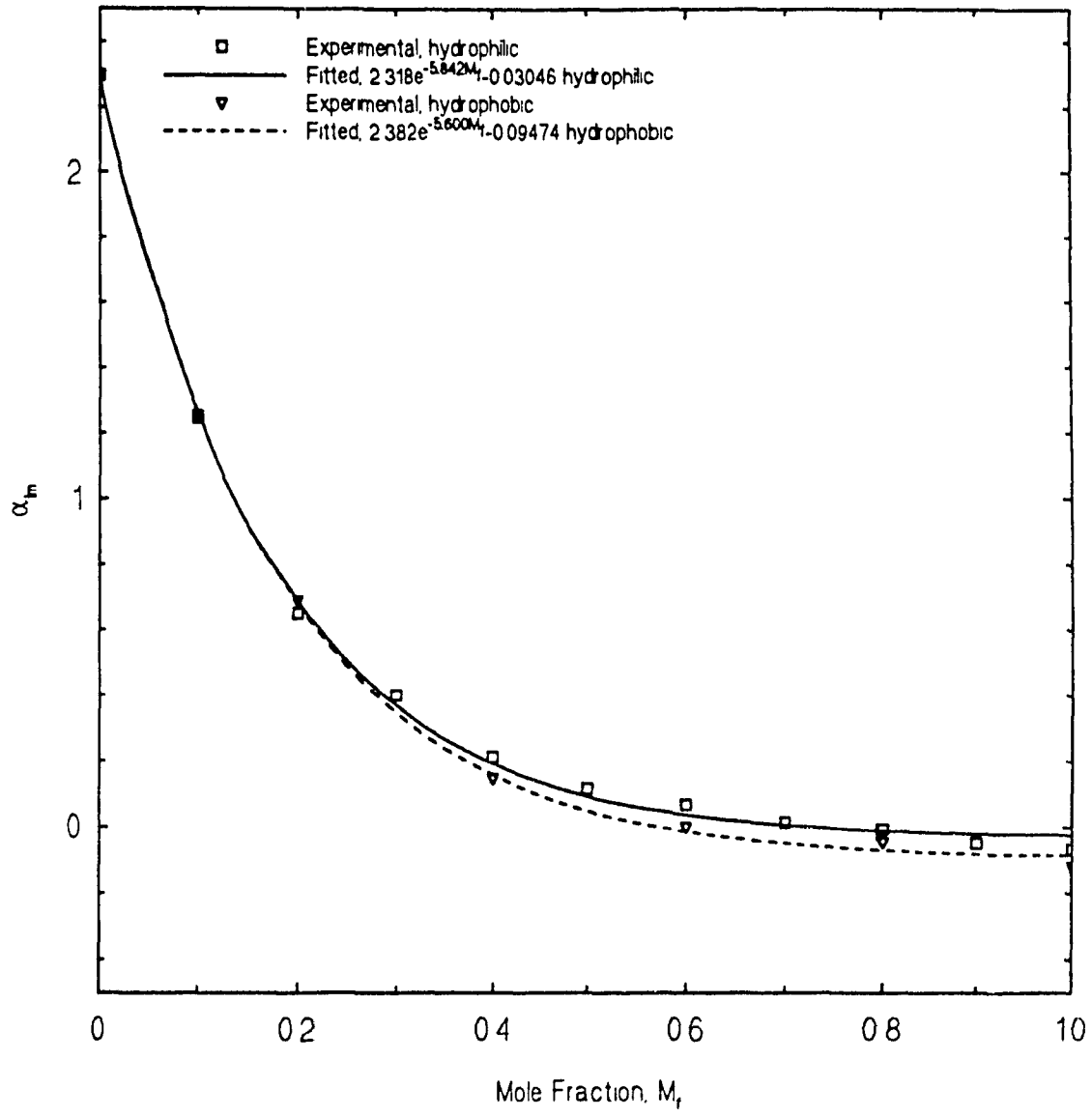


Figure 3.23 Imaginary part of interfacial slip parameter versus mole fraction for the hydrophilic and hydrophobic sensor in liquid.

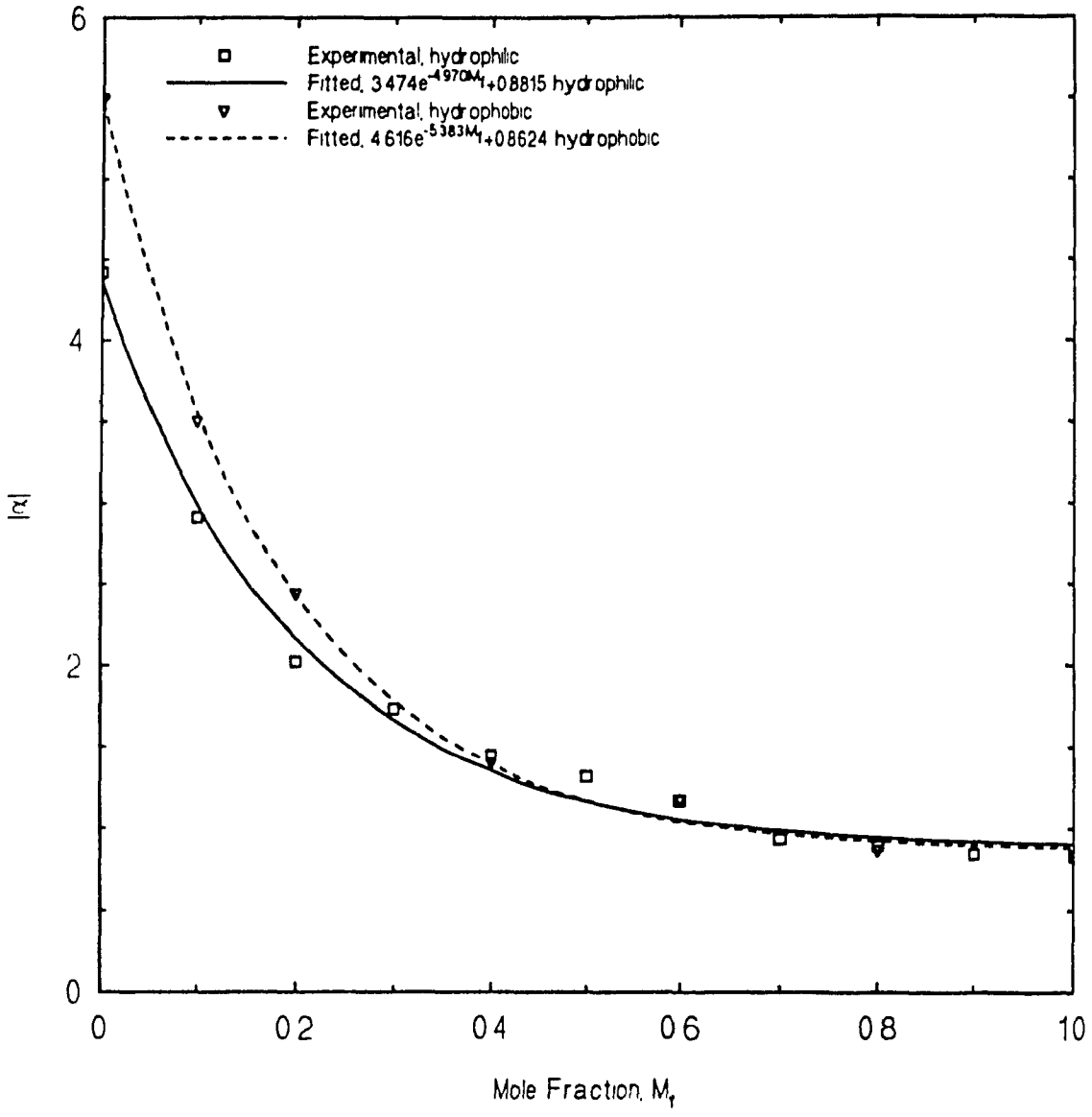


Figure 3.24 Magnitude of interfacial slip parameter versus mole fraction for the hydrophilic and hydrophobic sensor in liquid.

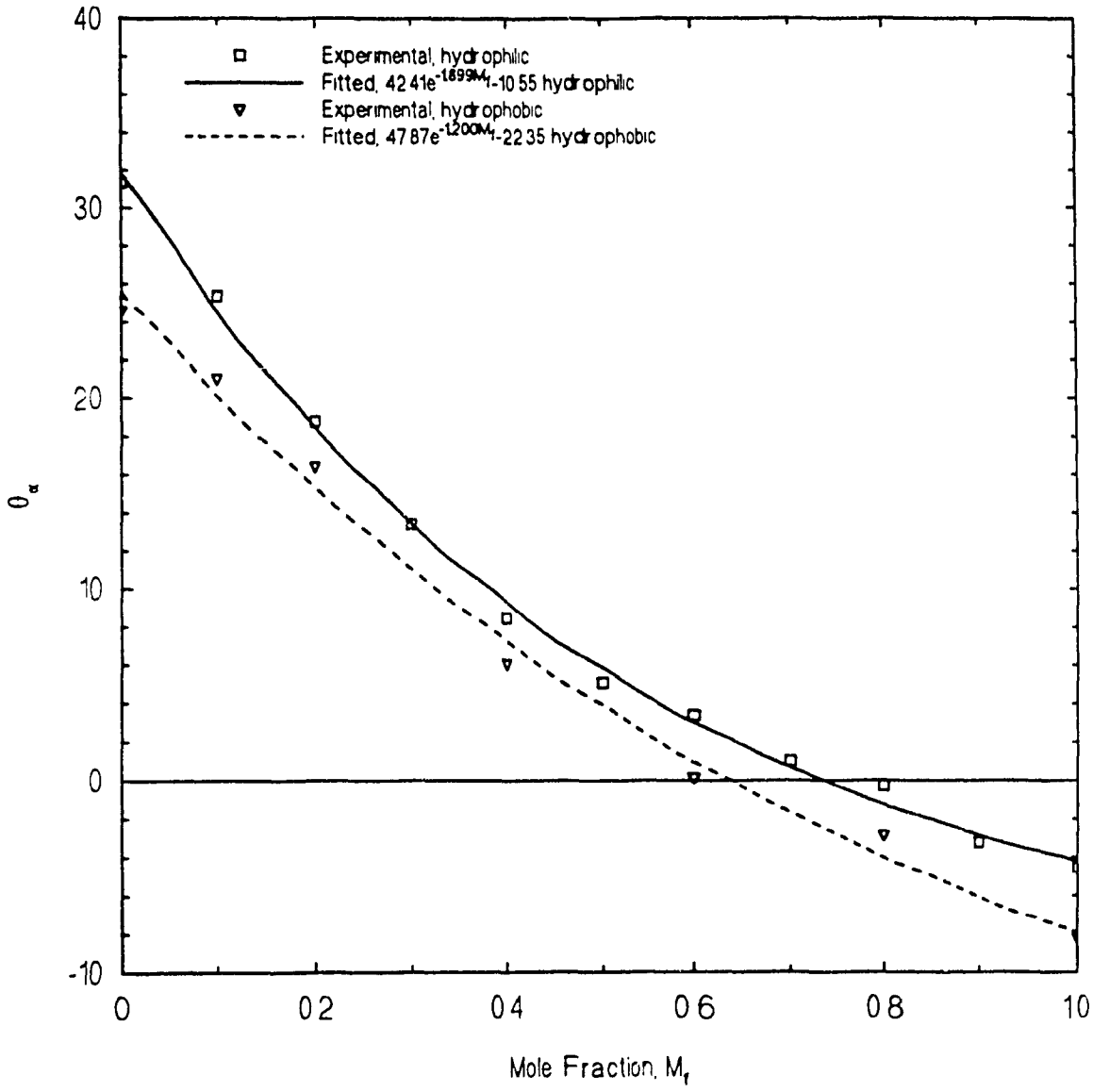


Figure 3.25 Phase of interfacial slip parameter versus mole fraction for the hydrophilic and hydrophobic sensor in liquid.

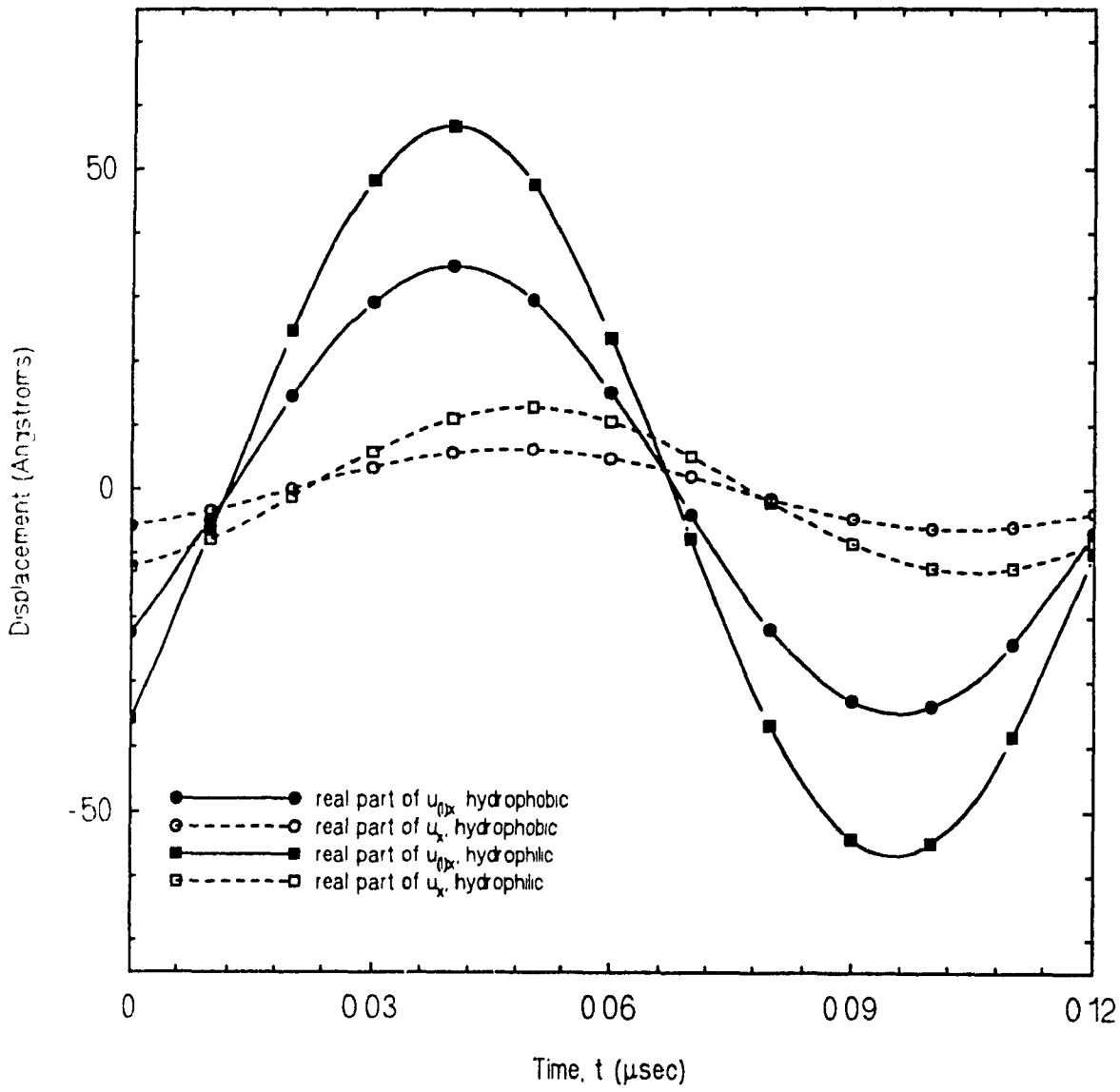


Figure 3.26 Solid and liquid particle displacement at the solid-liquid interface for the hydrophilic and hydrophobic sensor in liquid.

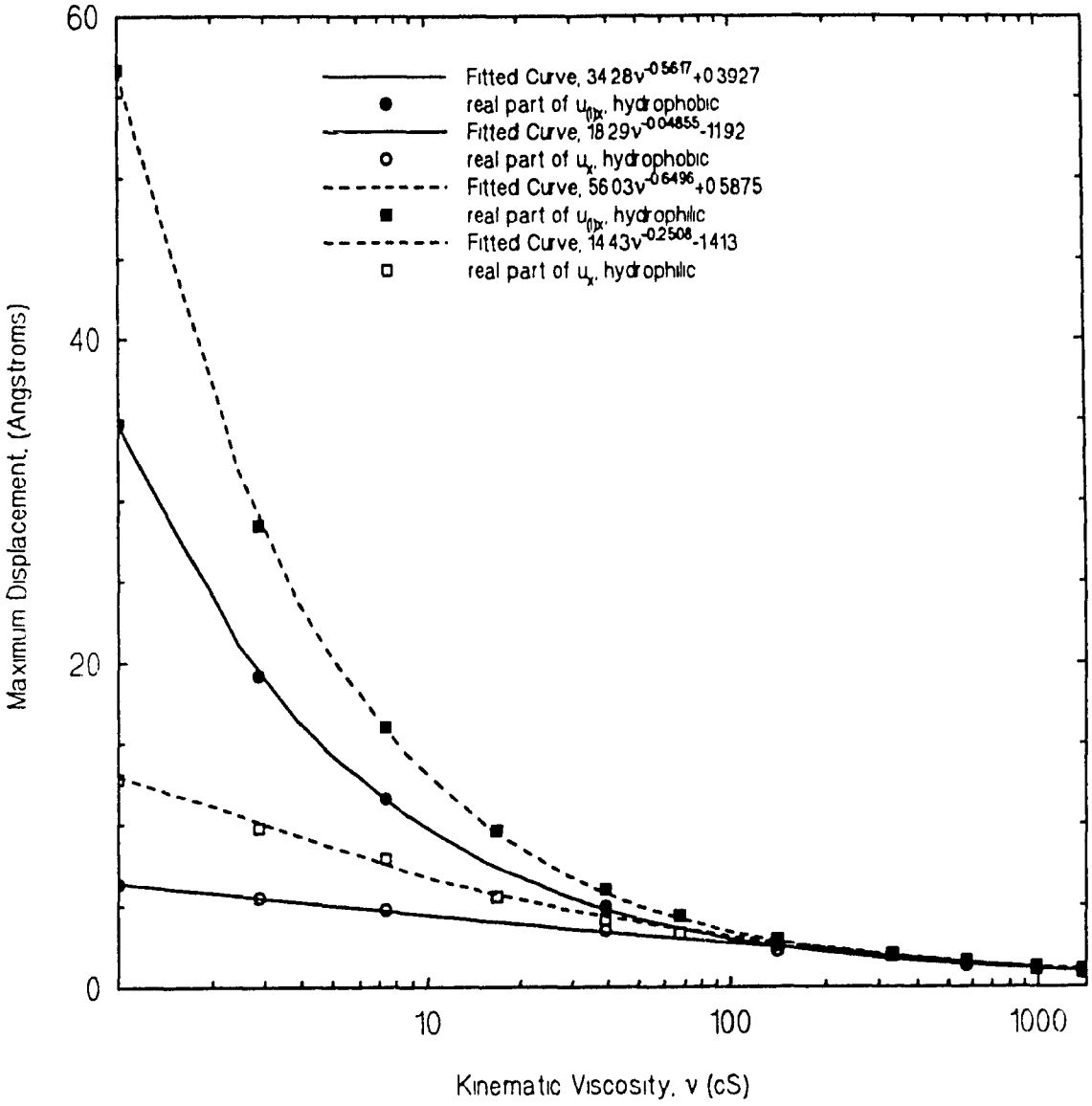


Figure 3.27 Maximum values of solid and liquid particle displacements at the solid-liquid interface for both the hydrophilic and hydrophobic sensor in liquid.

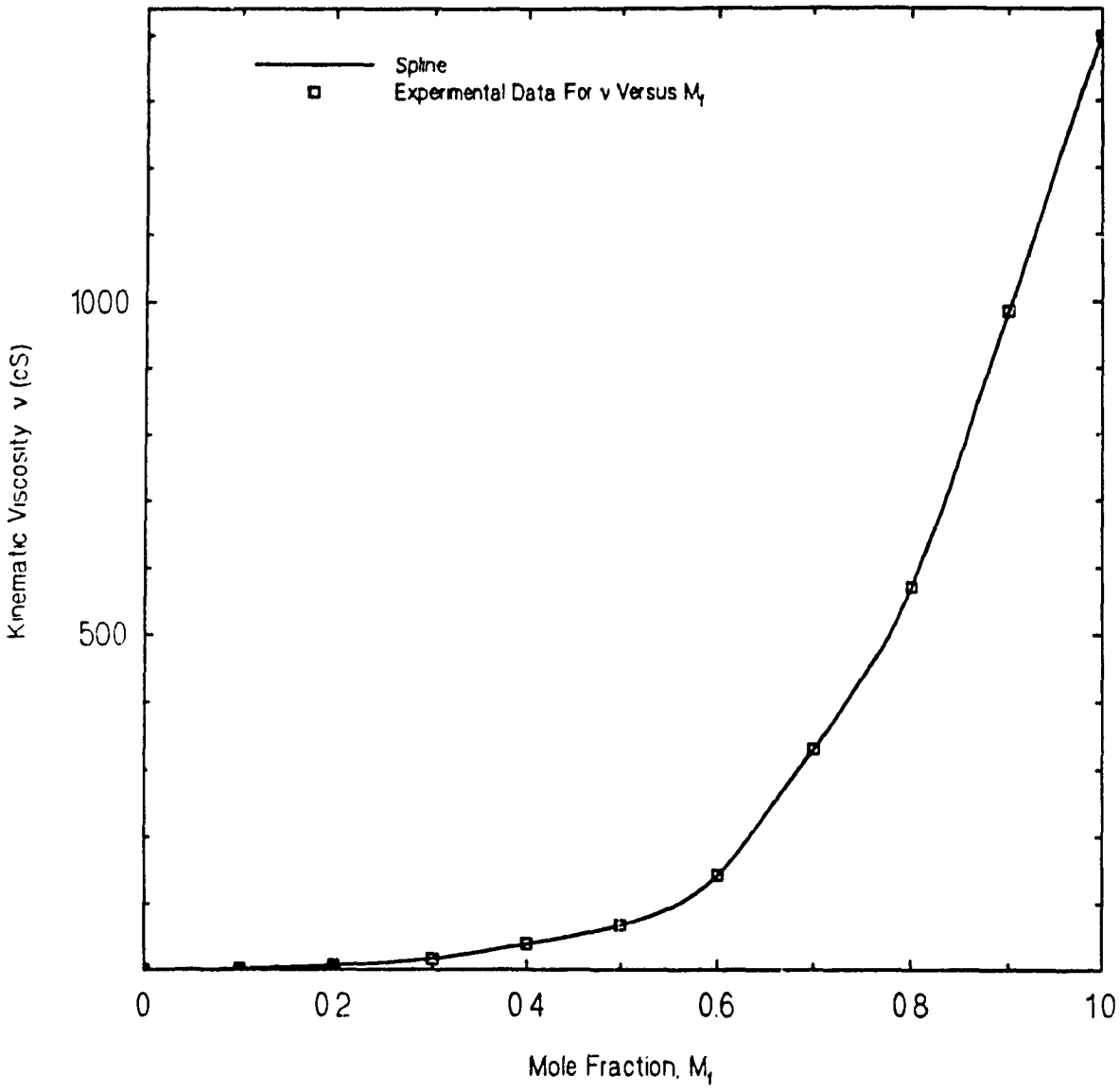


Figure 3.28 Kinematic viscosity versus mole fraction for water-glycerol solution.

CHAPTER 4

MODEL

Introduction

A mechanical model of slip at the solid-liquid interface of a quartz sensor has been devised. A parameter of the model corresponds to the interfacial slip parameter which was found by fitting experiment and theory in the last chapter.

The mechanical model of interfacial slip is defined and the equation of motion of the system is found by writing the Lagrangian of the system, Section 4.1. The equation of motion of the system cannot be solved analytically since it is nonlinear. Therefore it is necessary to solve the equation by a numerical procedure, Section 4.2.

4.1 Interfacial Slip Model

4.1.1 Description of Model

The interfacial slip is modeled by a spring-mass system consisting of two masses m_1 and m_2, and a spring of force constant, k, connecting the two masses as shown in Figure 4.1. The two masses m_1 and m_2 are constrained to move along the x-direction, which lies in the plane of the spring-mass system.

In the interfacial slip model, mass, m_1, represents the mass of a liquid particle, in contact with the top surface of

the sensor, while mass, m_2, represents the mass of a solid particle on the surface of the sensor. The motion of the masses in the x-direction corresponds to the transverse shear mode (TSM) of AT-cut quartz. The spring connecting masses m_1 and m_2 represents the force of interaction that occurs between the liquid molecules and the solid molecules which are in contact at the top surface of the sensor. The quantity, k, represents the strength of the force of interaction that occurs at the solid-liquid interface. The interaction that occurs at the solid-liquid interface arises primarily due to electromagnetic forces that occur between liquid molecules in contact with solid molecules at the top surface of the sensor coating. This model is the first step in the understanding of the experimental variation of α_{Re}, α_{Im}, $|\alpha|$ and α_θ versus kinematic viscosity, ν, and mole fraction, M_f.

The relation between the elements of the mechanical model and the solid-liquid interface is summarized in Table 4.1.

Table 4.1 Model and Interface

Mechanical Model	Solid-liquid Interface
m_1	mass of liquid particle
m_2	mass of solid particle
k	force of attraction between solid and liquid particles
motion in x-direction	transverse shear mode (TSM)

4.1.2 Statement of Problem

The displacement of mass, m_2, is $x_2 = x_2(t) = A\cos(\omega t + \phi)$, with A, ω, and ϕ denoting respectively the amplitude, the angular frequency, and the phase angle of the displacement. It is required to find the displacement of mass m_1, given by, $x_1 = x_1(t)$, at any time, t. The quantities $x_1(t)$ and $x_2(t)$ are shown in Figure 4.1.

In Figure 4.1, l and l´ denote respectively the nonextended length of the spring at time = 0, and the extended length of the spring at time = t. At time = 0 the motion of masses m_1 and m_2 start from rest, at their respective equilibrium positions.

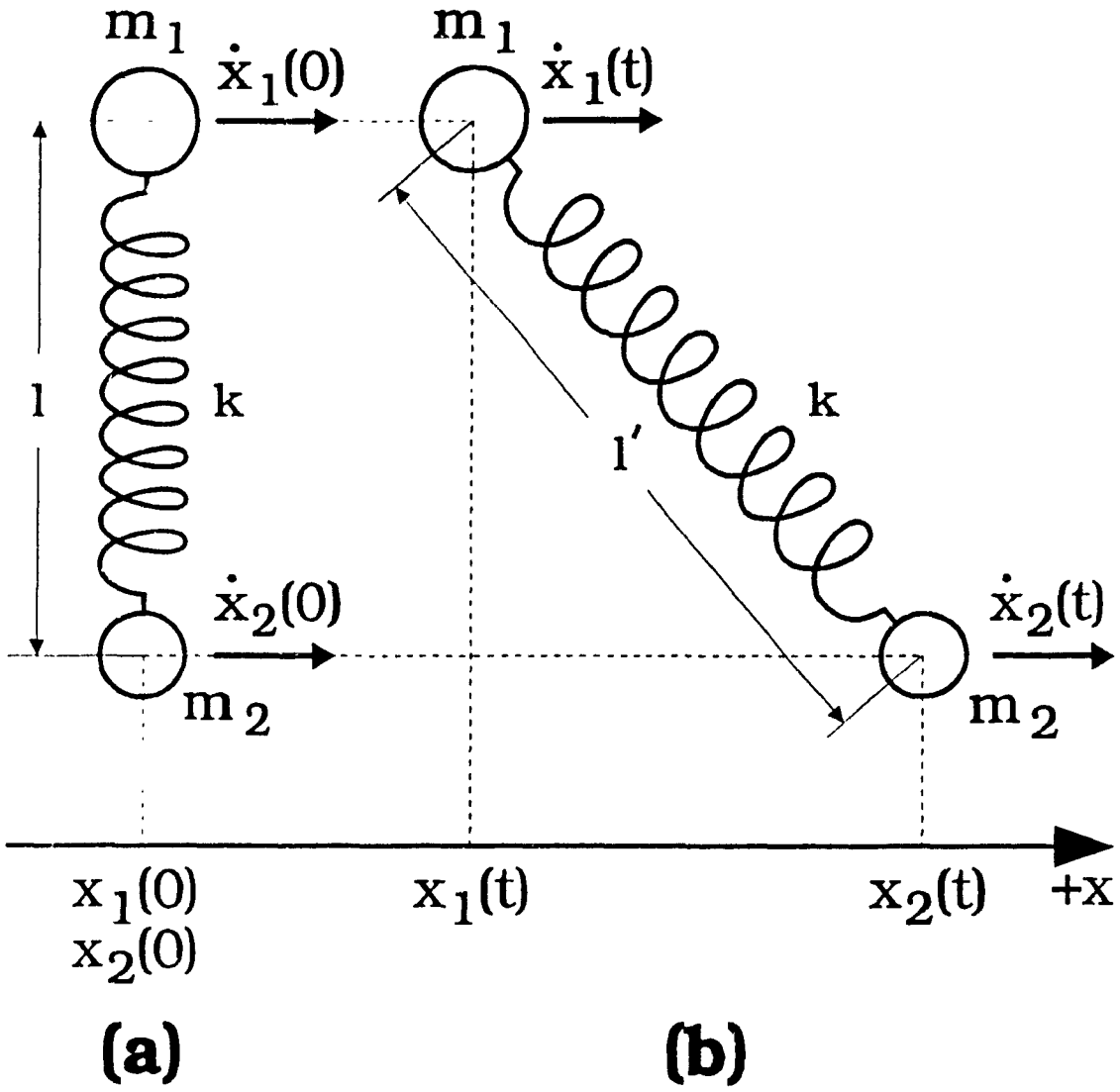


Figure 4.1 *Mechanical model of interfacial slip showing masses m_1 and m_2 connected by a spring of force constant, k, at (a) time = 0 and (b) time = t.*

4.1.3 Derivation of the Equations of Motion for the Interfacial Slip Model

The equation of motion for mass, m_1, is obtained from the Lagrangian, $\mathcal{L}$, of the spring-mass system at time = t. From Figure 4.1, the elongation, $s = l' - l$, of the spring at time = t, is given by

$$s = \sqrt{l^2 + (x_2 - x_1)^2} - l \tag{4-1}$$

The potential energy, V, and the kinetic energy, T, of the spring-mass system at time = t, are given by

$$V = \frac{1}{2} k s^2 = \frac{1}{2} k \left(\sqrt{l^2 + (x_2 - x_1)^2} - l\right)^2 \tag{4-2}$$

$$T = \frac{1}{2} (m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2) \tag{4-3}$$

The spring in the model, has zero mass since it represents the electrical force between masses m_1 and m_2. The Lagrangian, $\mathcal{L}$, of the spring mass system is given by

$$\mathcal{L} = T - V = \frac{1}{2} (m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2) - \frac{1}{2} k \left(\sqrt{l^2 + (x_2 - x_1)^2} - l\right)^2 \tag{4-4}$$

Given that $x_2 = x_2(t) = A\cos(\omega t + \phi)$, equation (4-4) reduces to

$$\mathcal{L} = \frac{1}{2}\left(m_1\dot{x}_1^2 + m_2A^2\omega^2\sin^2(\omega t + \phi)\right) - \frac{1}{2}k\left(\sqrt{l^2 + (A\cos(\omega t + \phi) - x_1)^2} - l\right)^2 \qquad (4\text{-}5)$$

Lagrange's equation of motion for mass, m_1, is given by

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{x}_1} = \frac{\partial \mathcal{L}}{\partial x_1} \qquad (4\text{-}6)$$

From equations (4-5) and (4-6), the equation of motion for mass m_1 is given in terms of γ which is defined as $\gamma = x_2 - x_1 = A\cos(\omega t+\phi) - x_1$.

$$\ddot{x}_1 = \frac{k}{m_1}\frac{(\sqrt{l^2 + \gamma^2} - l)\gamma}{\sqrt{l^2 + \gamma^2}} \qquad (4\text{-}7)$$

Note that (4-7) is a second-order differential equation which is highly non-linear.

4.2 Numerical Solution of the Equations of Motion

4.2.1 Description of Runge-Kutta's Method

The fourth-order Runge-Kutta method, is used to solve equation (4-7) numerically for x_i as a function of the time, t. A system of n first-order differential equations in n unknowns $u_0,\ldots,u_n$ is given by

$$\dot{u}_i = F_i(u_i, t) \tag{4-8}$$

For each j = 0,1,...,N - 1 where N, is the number of time steps, the following four functions K_1, K_2, K_3, and K_4 implement the fourth-order Runge-Kutta method of stepsize, h. In the four equations below, $u_{ij} = u_i(t_j)$.

$$K_{1_{ij}} = hF_i(t_j, u_{ij}) \tag{4-9}$$

$$K_{2_{ij}} = hF_i(u_{ij} + \frac{1}{2}K_{1_{ij}}, t_j + \frac{h}{2}) \tag{4-10}$$

$$K_{3_{ij}} = hF_i(u_{ij} + \frac{1}{2}K_{2_{ij}}, t_j + \frac{h}{2}) \tag{4-11}$$

$$K_{4_{ij}} = hF_i(u_{ij} + K_{3_{ij}}, t_{j+1}) \tag{4-12}$$

For each i = 0,1,...,n and j = 0,1,...,N - 1 the following recursive procedure, performs a weighted average.

$$u_{i,j+1} = u_{ij} + \frac{1}{6}\left(K_{1_{ij}} + 2K_{2_{ij}} + 2K_{3_{ij}} + K_{4_{ij}}\right) \qquad \textbf{(4-13)}$$

Equation (4-7), may be rewritten as a first-order system consisting of two equations in the two unknowns u_0, u_1. Let

$$u_0 = x_1 \qquad \textbf{(4-14)}$$

$$u_1 = \dot{x}_1 \qquad \textbf{(4-15)}$$

$$\dot{u}_1 = \ddot{x}_1 \qquad \textbf{(4-16)}$$

The following set of two equations will be solved by Mathcad. The first equation is obtained by substituting (4-14) into (4-15). The second equation is (4-7) written using (4-14) and (4-16).

$$\begin{aligned} \dot{u}_0 &= u_1 \\ \dot{u}_1 &= \frac{k}{m_1}\,\frac{\left(\sqrt{1^2 + \gamma^2} - 1\right)\gamma}{\sqrt{1^2 + \gamma^2}} \end{aligned} \qquad \textbf{(4-17)}$$

The system of two equations, (4-17), are solved numerically by

the Mathcad program described in the next subsection.

4.2.2 Numerical Solution of Interfacial Slip Model

In Appendix 9, Mathcad document DOC6.MCD implements the fourth-order Runge-Kutta method for the numerical solution of the equation of motion of mass, m_1. The displacement, x_1, of mass, m_1, is computed over five periods of the motion, that is, the closed time interval I = [0, 5/f], for several values of the ratio, k/m_1, starting with a numerical value of 1 and ending with a numerical value of 10^9 metric units. In the interval, I, the frequency, f = 9.0 MHz, is the oscillating frequency of mass, m_2. Mass, m_2, starts its motion from rest, with an amplitude, A, of one metric unit, and a phase angle, ϕ, of $-\pi/2$ radians. The motion of masses m_1 and m_2 both start at time t = 0. The displacement, x_1, of mass, m_1, was computed over the closed interval, I, in time steps of, $\Delta t = 0.001\ \mu s$. The total number of points computed was N = 555. At each value of k/m_1, the maximum displacement, x_{1max}, was computed over the closed interval, I, using Mathcad's **max** function. The maximum displacement, x_{1max}, is defined as the greatest displacement of mass, m_1, over the closed interval, I. A two-dimensional data vector of data pairs, with each pair consisting of the $\log(k/m_1)$ versus x_{1max}, was created in a semi-interactive manner using Mathcad's **WRITEPRN** and **APPENDPRN** functions. The data file X1MAX.PRN, which is a result of applying the functions **WRITEPRN** and **APPENDPRN**, contains the data pairs consisting of $\log(k/m_1)$ versus x_{1max}. Figure 4.2

shows the variation of the maximum displacement of mass m_1 versus the $\log(k/m_1)$. From Figure 4.2 at a certain critical value of k/m_1, the maximum displacement of mass m_1 achieves its maximum value, therefore the spring-mass system is in resonance at this value.

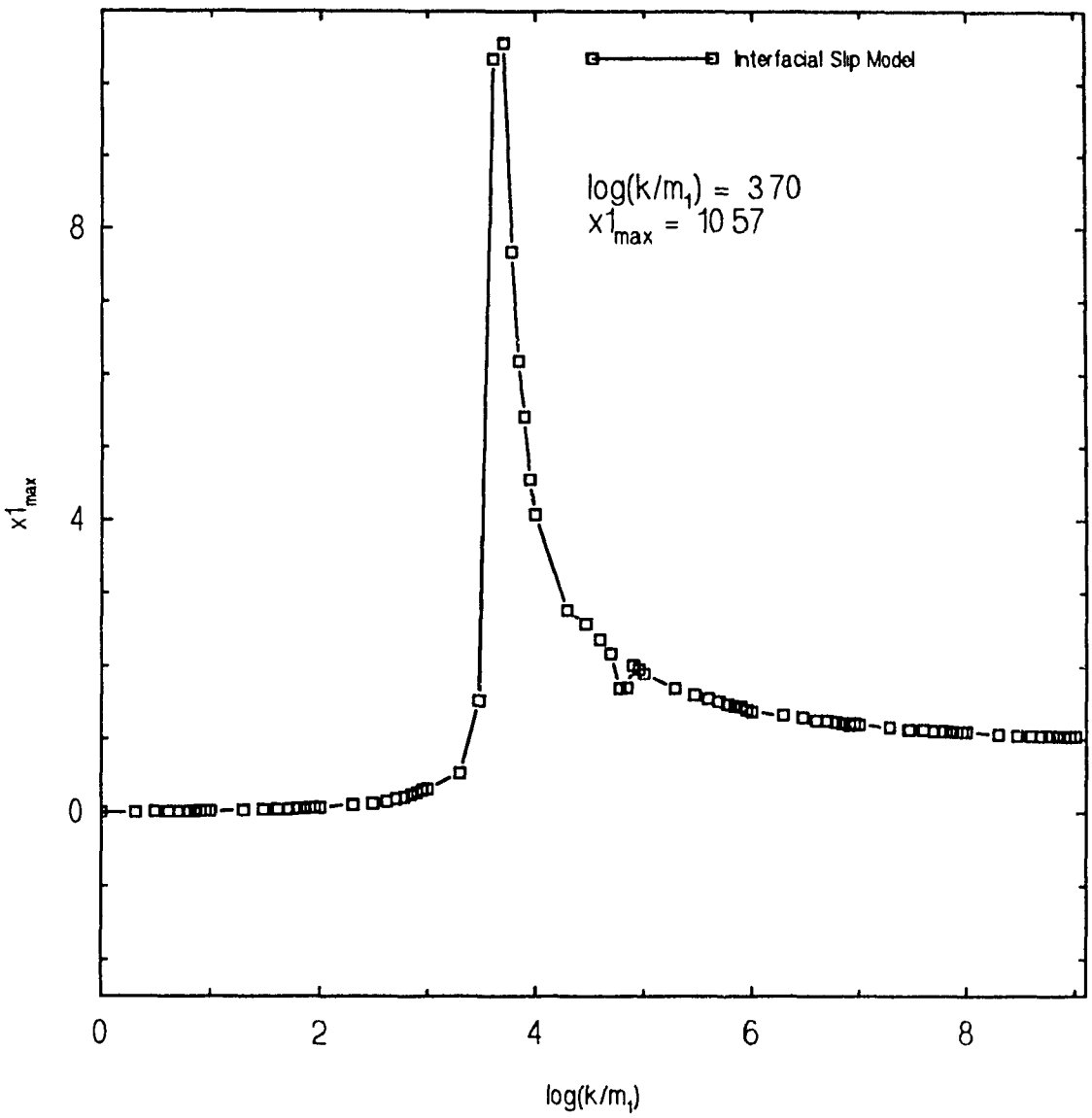


Figure 4.2 *Maximum displacement of mass m_1 versus the logarithm of the spring constant, k, divided by the mass, m_1, for the mechanical model of interfacial slip. The maximum displacement of mass m_2 is unity.*

CHAPTER 5

CONCLUSIONS

A new property of the interface called the interfacial slip parameter was introduced in the theory of the sensor in order to account for the slip between the surface of a sensor vibrating in the transverse shear mode and a liquid which is in contact with the surface of the sensor. The theoretical expression for the impedance was derived which is a function of the interfacial slip parameter. The impedance of sensors with hydrophilic and hydrophobic coatings was measured in water-glycerol solutions using the network analysis method. Then the interfacial slip parameter was found by fitting the experimental values of impedance to the theoretical expression for impedance using non-linear regression analysis.

The interfacial slip parameter, α, is defined as $\alpha = u_{(l)x}/u_x$, where $u_{(l)x}$ is the displacement of a liquid particle in contact with the solid surface of the sensor and u_x is the displacement of a solid particle on the surface of the sensor. If the force between the liquid particle and solid particle is very strong, their displacements will be the same and so $\alpha = 1$. In this case there is no slip at the interface between the solid and liquid. At the other extreme, if the force between the liquid and solid is zero, then there is no connection between the solid and liquid. In this case when the solid particles on the surface of the sensor move, the liquid

particles do not move, that is, $\alpha = 0$. Intuitively, one expects that the magnitude of α should be between 0 and 1.

The measurements of impedance were made for the sensors in both air and liquid, and the experimental values of impedance were fitted to the theoretical expression for impedance using nonlinear regression analysis. In air, α was set equal to zero since the connection between the molecules on the surface of the solid and the molecules in air is very weak. Two properties of the quartz were found by fitting theory and experiment in air: the piezoelectric stress coefficient, e, and the viscoelastic coefficient, η. The value of e found for both the hydrophilic and hydrophobic sensors is the same: $e = -0.0798\ C/m^2$, from Table 3.1. This is significantly different than the value of e in the literature: $e = -0.095\ C/m^2$. Since 401 measurements of impedance, each at a different frequency, were used to find e, and the value of e was the same for both sensors, it is speculated that the value of e in the literature is incorrent. The value of η for quartz was also found by fitting theory and experiment in air since η was not found in the literature. The value of η was not the same for both sensors.

The interfacial slip parameter, α, was found by fitting the experimental values of impedance found in water-glycerol solutions with the theoretical expression for impedance. The magnitude of α, $|\alpha|$, is plotted versus kinematic viscosity of water-glycerol solutions in Figure 3.20 for hydrophilic and

hydrophobic sensors. At high viscosities, where the interaction between the solid surface and the liquid is strong, $|\alpha|$ is near 1, as expected. At low viscosities, however, the magnitude of α is larger than 1, not less than 1 as expected when the interaction at the interface is weak. Furthermore, at low viscosities, $|\alpha|$ for the hydrophobic surface is greater than $|\alpha|$ for the hydrophilic surface, as seen from the left side of Figure 3.20. This means that the amplitude of the liquid particle is greater when the interaction between the liquid particle and solid particle is smaller.

This behaviour is explained by a mechanical model which was invented to represent the interaction between particles on the surface of the sensor and particles of the liquid in contact with the surface. The model is drawn in Figure 4.1. Two masses connected by a spring are constrained to move transversely. One mass, m_2, represents a solid particle on the sensor surface which moves sinusoidally with time at a constant frequency and at constant amplitude, which is choosen as unity. The other mass, m_1, represents a liquid particle in contact with the solid particle. The spring, with spring constant, k, represents the force of attraction between the two particles. The system was analyzed to find the displacement of the liquid particle in terms of its mass, m_1, and the spring constant, k.

The variation of maximum displacement (the amplitude) of

the liquid particle in the model as a function of the log of the (spring constant)/(mass of liquid particle) is given in Figure 4.2. As expected, as the spring constant approaches zero, the amplitude of the liquid particle approaches zero. At this extreme, the liquid particle and solid particle are diconnected. As the spring constant becomes very large, the amplitude of the liquid particle becomes 1, the same as the solid particle. This is the other extreme where the liquid and solid particles are rigidly connected together. In between the two extremes there is a resonant region of the spring-mass system. The amplitude of the liquid-particle mass is a maximum at a particular value of the ratio of the spring constant, k, and the mass of the liquid particle, m_l. In Figure 4.2 the frequency is 9.0 MHz and k/m_l is expressed in metric units. The mass of the solid particle, m_2, does not influence the motion of m_l in this model because it is driven (forced to oscillate) at a constant unit amplitude.

The amplitude of the liquid-particle in Figure 4.2 is numerically equal to the magnitude of the interfacial slip parameter in Figure 3.20, since the amplitude of the solid-particle is unity. The spring constant, k, in Figure 4.2 corresponds to the kinematic viscosity of the liquid in contact with the surface of the sensor in Figure 3.20. The mass, m_l, in Figure 2 corresponds to the mass of the liquid particle in contact with the sensor surface. In Figure 4.2 the log of k/m_l is plotted and in Figure 3.20 the kinematic

viscosity is plotted on a log scale.

It is clear from the results of the analysis of the mechanical model given in Figure 3.20 that an increase of k, say by a factor of two, has exactly the same effect as a decrease of m_1 by the same factor of two. In the experiments, various water-glycerol solutions were in contact with the sensor surface, starting with pure water and ending with pure glycerol. The viscosity of water is 1 cS and the viscosity of glycerol is 1400 cS which corresponds to the spring constant, k, in the model. But as the water is replaced by the glycerol, the mass of the liquid molecules in contact with the sensor surface also increases, corresponding to the mass, m_1, in the model. The molecular weight of water, H_2O, is 18 and the molecular weight of glycerol, $C_3H_8O_3$, is 92. As the solution changes from water to glycerol, the viscosity increases by a factor of 1400 whereas the molecular weight increases by only a factor of about 5. So the increase of viscosity is offset somewhat by the mass of the liquid molecules. However, when comparing Figure 3.20 and Figure 4.2, the mass of the liquid particles can be regarded as constant.

The shape of the curve to the right of the resonant peak of the model in Figure 4.2 is the same as the shape of the curve of the experimental results in Figure 3.20. In Figure 3.20, $|\alpha| \approx 5$ for kinematic viscosity = 1 and $|\alpha| \approx 1$ for kinematic viscosity $\approx 10^3$. In Figure 4.2, $x1_{max}$ (which is

numerically the same as $|\alpha|$) has the value of 5 at $k/m_l \approx 10^4$, and $x1_{max}$ drops to about 1 at $k/m_l \approx 10^7$. So very roughly, a kinematic viscosity of 1 corresponds to a k/m_l of 10^4 and the two quantities are roughly proportional to each other.

The separation of the curves for the hydrophilic and hydrophobic sensors in Figure 3.20 can also be interpreted in terms of the model of Figure 4.2. At low viscosity $|\alpha|$ for the hydrophobic sensor is larger than $|\alpha|$ for the hydrophilic sensor. At a given viscosity, that is, for a given water-glycerol solution in the experiments, the force of interaction between the liquid and a hydrophobic surface is less than between the same liquid and a hydrophilic surface. Therefore the value of k in Figure 4.2 is lower and so the value of $x1_{max}$ (which equals $|\alpha|$) is larger, which is in agreement with the larger $|\alpha|$ in Figure 3.20. Effectively, the hydrophobic sensor surface corresponds to a region of Figure 4.2 which is to the left of the region for the hydrophilic sensor surface.

In summary, there is good qualitative agreement between the experimental results and the predictions of the mechanical model of interfacial slip. For both the hydrophilic and hydrophobic sensors, there is considerable slip when the liquid in contact with the surface is water (low viscosity) and very little slip when the liquid is glycerol (high viscosity).

APPENDIX 1 Application Software

The application software that was used to do the research and prepare the thesis is listed below. IBM-compatible 386 and 486 computers were used to run the software. The computer used in the Physics research laboratory is an IBM-compatible 486DX, 33 MHz with 32 MB of RAM. It is connected to a Hewlett-Packard LaserJet III printer which was used to print the thesis. The application software is the following.

(1) Windows 3.1
(2) WordPerfect 5.1 for Windows
(3) CoreDraw 2.0 for Windows
(5) EasyPlot for DOS
(4) Mathcad 3.1 for Windows
(6) Macsyma 417.125 for Windows

Windows 3.1 is the operating system.

WordPerfect 5.1 is a word processing program. The text was typed, and the equations and tables were made with WordPerfect. WordPerfect was also used as described below.

CorelDraw 2.0 is a graphics (or drawing) program. The diagrams were made with CorelDraw and then the .cdr files were exported to .tif files using File/Export in CorelDraw. A WordPerfect macro was used to add the diagrams to WordPerfect files by using Graphics/Figure/Retrieve and then formatting the diagrams by Graphics/Figure/Position and then setting, Anchor to: Character and Size: Auto Both.

EasyPlot is a plotting (or presentation) program. The graphs were made by EasyPlot from text files of the data from the network analyzer. The graphs were plotted by EasyPlot. Then the captions and page numbers were printed on the graphs by WordPerfect.

Mathcad 3.1 is a numerical mathematics program. The Mathcad programs were printed by Mathcad. Then the titles and page numbers were printed on the Mathcad pages by WordPerfect.

Macsyma 417.125 is a symbolic mathematics program. The source code and the output of the Macsyma program are text files which were printed by WordPerfect.

APPENDIX 2 Subscript Notation

Subscript (also called tensor) notation is used instead of symbolic (also called vector) notation because the equations of piezoelectricity include tensor quantities of rank two and greater. Although symbolic notation can be used to state the equations, the equations cannot be easily manipulated using this notation.

The conventions of the notation for cartesian tensors are stated, the kronecker delta and levi-civita symbol are defined, and examples of tensor quantities and notation are given.

Conventions

The numbers 1, 2 and 3 label the x, y and z directions, respectively. The coordinates of a point (x,y,z) are written (x_1, x_2, x_3). The components of a vector, the particle displacement for example, (u_x, u_y, u_z) are written (u_1, u_2, u_3). The indices i,j,k . . . are used to represent the x, y and z directions and they take the values 1, 2 and 3.

(1) Range Convention: single subscript
Subscript i that occurs once in a term takes all three values of 1,2,3. For example,

$$u_i \quad means \quad u_1,\ u_2,\ u_3$$

(2) Summation Convention: repeated subscript
Subscript i that occurs twice (or more) in a term is summed over 1,2,3. For example,

$$a_{ij}\,u_j \quad means \quad \sum_{j=1}^{3} a_{ij}\,u_j$$

(3) Partial derivative convention: subscript comma
Subscript ,i denotes partial differentiation with respect to the ith coordinate, x_i. For example,

$$u_{i,j} \quad means \quad \frac{\partial u_i}{\partial x_j}$$

Kronecker Delta, δ_{ij}

The kronecker delta by definition is

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

For example, $\delta_{11} = 1$ and $\delta_{12} = 0$.

Levi-civita Symbol, ε_{ijk}

The levi-civita symbol, also called the permutation symbol, by defintion is

$$\varepsilon_{ijk} = \begin{cases} 1 & \textit{if } (ijk) \textit{ is an even permutation of } (123) \\ -1 & \textit{if } (ijk) \textit{ is an odd permutation of } (123) \\ 0 & \textit{if any two indices are equal} \end{cases}$$

For example, $\varepsilon_{123} = 1$, $\varepsilon_{213} = -1$ and $\varepsilon_{113} = 0$.

The levi-civita symbol is related to the kronecker delta by the following identity.

$$\varepsilon_{ijk}\varepsilon_{ipq} = \delta_{jp}\delta_{kq} - \delta_{jq}\delta_{kp}$$

The following two relations are a consequence of the identity above.

$$\varepsilon_{ijk}\varepsilon_{ijl} = 2\delta_{kl}$$

$$\varepsilon_{ijk}\varepsilon_{ijk} = 3!$$

Examples

The examples of tensors in Table A2.1 are from the equations of piezoelectricity. The rank of a tensor quantity is equal to the number of subscripts on the quantity.

Table A2.1 Examples of Tensors

Tensor		Quantity	
Rank	Name	Symbol	Name
0	scalar	φ	scalar potential
1	vector	E_i	electric field
		u_i	particle displacement
2		T_{ij}	stress
		S_{ij}	strain
		ϵ_{ik}	dielectric strain coefficient
3		e_{ijk}	piezoelectric stress coefficient
4		c_{ijkl}	elastic coefficient

The examples of notation in Table A2.2 are from the equations of piezoelectricity. In the symbolic notation, a single dot indicates summation over a single subscript and a double dot, summation over two subscripts. The symbolic notation does not indicate the rank of the tensor. This is the symbolic notation used by Auld, Volume I (1973).

Table A2.2 Examples of Notation

Name	Symbolic Notation	Subscript Notation
gradient	$\nabla\varphi$	$\varphi_{,i}$
divergence	$\nabla\cdot\mathbf{E}$	$E_{i,i}$
curl	$\nabla\times\mathbf{E}$	$\varepsilon_{ijk}E_{k,j}$
	$\nabla\mathbf{u}$	$u_{i,j}$
	$\nabla\cdot\mathbf{T}$	$T_{ij,i}$
	$\mathbf{e}\cdot\mathbf{E}$	$e_{ijk}E_k$
	$\mathbf{e}:\mathbf{S}$	$e_{ijk}S_{kl}$

APPENDIX 3 Solution of Boundary Value Problem, Macsyma Program ZIN.WP

MACSYMA SOURCE CODE

```
     (clearscreen(),kill(all),fancy_display:false)$

     /*  Determine the electrical input impedance Zin for
the liquid loaded AT-Cut

         quartz sensor...  */

     /* establish dependencies for uq,ul, and vl. */

     (ratfac:true,
      depends([uq,ul,vl.phi],[y,t]),
      depends([f1,f2,f3],y),
      assume(nu>0,omega>0))$


/* The equation of motion for the transverse particle
displacement uq in the quartz sensor
          is
        given by...*/

     eq1:cbar*diff(uq,y,2) + eta*diff(uq,y,2,t,1) -
rhoq*diff(uq,t,2) = 0;

     /* The potential phi and the transverse particle
displacement uq are related to each
        other by the following relation...*/

     eq2:e*diff(uq,y,2) - epsilon*diff(phi,y,2) = 0;

     /* Let uq = f1(y)*exp(%i*omega*t) and phi =
f2(y)*exp(%i*omega*t), equation eq1
     reduces to...*/

     (expr1:ev(eq1,uq =
f1*exp(%i*omega*t),diff,ratsimp)/exp(%i*omega*t),
      expr1:ratsimp(expr1,diff(f1,y,2)),
      disp(expr1))$

     /* Let f1 = exp(%i*r*y), the general solution to
equation eq1  is given by...*/

     (expr1:factor(ev(expr1,f1 =
exp(%i*r*y),diff,ratsimp)/exp(%i*r*y)),
      sol1:solve(expr1,r),
      disp("The christoffel equation to equation eq1 is
given by...",
           expr1,
           "The solution to the above christoffel equation
```

```
is given by...",
          sol1))$

     /* Let kq denote the complex wave number for the quartz
sensor, kq is defined as
     follows...*/

     cwq:kq = rhs(sol1[2]);

     /* The general solution to equation eq1 is given
by...*/

     (sol1:subst(kq,rhs(sol1[2]),sol1),
      gen_sol1:uq =
sum(concat(a,i)*exp(%i*rhs(sol1[i])*y),i,1,2)*exp(%i*omega*t
),
      disp(gen_sol1))$

     /* From equation eq2 the potential phi is given by...*/

     (expr2:expand(ev(eq2,[phi =

f2*exp(%i*omega*t),gen_sol1],diff,ratsimp)/exp(%i*omega*t)),
      expr2:ode(expr2,f2,y),
      expr2:subst(a3,%k2,expr2),
      expr2:rhs(expand(subst(a4,%k1,expr2))),
      gen_sol2:ev(phi = expr2*exp(%i*omega*t),sol2),
      disp(gen_sol2))$


/* Perform a check to determine if gen_sol1 and gen_sol2
satisfy equations eq1 and
          eq2...*/

     (check1:ev([eq1,eq2],[gen_sol1,gen_sol2],diff,ratsimp),
      check1:ev(check1,cwq,ratsimp),
      map(disp,check1))$


     /* The equation of motion for the transverse particle
velocity vl in the liquid medium is
        given by...*/

     eq3:mu*diff(vl,y,2) - rhol*diff(vl,t,1) = 0;

     /* With mu = nu*rhol and vl = diff(ul,t,1), then
equation eq3 reduces to...*/

     eq3:expand(ev(eq3,[mu = nu*rhol,vl =
diff(ul,t,1)],diff)/rhol);

     /* Let ul = f3(y)*exp(%i*omega*t), then equation eq3
```

```
reduces to...*/

     expr3:factor(ev(eq3,ul =
f3*exp(%i*omega*t),diff,ratsimp)/exp(%i*omega*t));

     /* Let f3 = exp(%i*r*y), then the general solution to
equation eq3 is given by...*/

     (expr3:factor(ev(expr3,f3 =
exp(%i*r*y),diff,ratsimp)/exp(%i*r*y)),
      sol3:solve(expr3,r),
      disp("The christoffel equation to equation eq3 is
given by...",
           expr3,
           "The solution to the above christoffel equation
is given by...",
           sol3))$

     /* Let kl denote the complex wave number for the
liquid-medium, kl is defined as
     follows...*/


     cwl:kl = rhs(sol3[2]);


     /* The general solution equation eq3 is given by...*/


     (sol3:subst(kl,rhs(sol3[2]),sol3),
      gen_sol3:ul =
sum(concat(a,i+4)*exp(%i*rhs(sol3[i])*y),i,1,2)*exp(%i*omega
*t),
      disp(gen_sol3))$


     /* Perform a check to determine if gen_sol3 satisfies
equation eq3...*/

     (check3:ev(eq3,gen_sol3,diff,ratsimp),
      check3:ev(check3,cwl,ratsimp),
      disp(check3))$


     /* Physically as y -> infinity, ul -> 0, therefore
consider the limit as y -> infinity of
        each of the two terms exp(%i*kl*y) and exp(-%i*kl*y)
seperately...*/

     (term1:exp(%i*kl*y),
      term1:ev(term1,cwl,ratsimp),
      term1:factor(rectform(term1)),
```

```
      disp(term1))$

     /* take the limit of the magnitude of the above
expression as y -> infinity...*/

     (term1:trigsimp(cabs(term1)),
      limit1:'limit(term1,y,inf) = limit(term1,y,inf));

     (term2:exp(-%i*kl*y),
      term2:ev(term2,cwl,ratsimp),
      term2:factor(rectform(term2)),
      disp(term2))$

     /* take the limit of the magnitude of the above
expression as y -> infinity...*/

     (term2:trigsimp(cabs(term2)),
      limit2:'limit(term2,y,inf) = limit(term2,y,inf));


     /* As y -> infinity exp(%i*kl*y) -> infinity while
exp(-%i*kl*y) -> 0.
        Therefore in order for ul to remain finite for all y
a6 must be set to zero.
        Thus for finite ul, a6=0. */

     gen_sol3:ev(gen_sol3,a6=0,ratsimp);


     /* The shear stresses Tq and Tl are given by... */


(Tq:c*diff(uq,y,1)+eta*diff(uq,y,1,t,1)+e*diff(phi,y,1),
      Tl:mu*diff(vl,y,1),
      Tl:ev(Tl,[vl = diff(ul,t,1),mu = nu*rhol],diff),
      display(Tq,Tl))$

     /* Substituting gen_sol1,gen_sol2, and gen_sol3 into
the expression for Tq and Tl.
        Tq and Tl reduce down to...*/

     (Tq:ev(Tq,[gen_sol1,gen_sol2],diff,ratsimp),

Tq:factorsum(ratsimp(ratsubst(cbar,c+e^2/epsilon,Tq))),
      Tl:factorsum(ev(Tl,gen_sol3,diff,ratsimp)),
      display(Tq,Tl))$

     /* Implement the boundary conditions...*/

     /* Stress free boundary condition: Tq(0,t) = 0   */
```

```
BC1:ratsimp(ev(Tq=0,y=0,ratsimp)/exp(%i*omega*t),a1,a2,a3,a4
,a5,kq,kl);


     /* continuity of stress across interface: Tq(h,t) =
Tl(h,t)  */

     BC2:ratsimp(ev(Tq =
Tl,y=h,ratsimp)/exp(%i*omega*t),a1,a2,a3,a4,a5,kq,kl);


     /* Potential at bottom surface of quartz sensor:
phi(0,t) = -phi0*exp(%i*omega*t)  */

     (phi:rhs(gen_sol2),
      BC3:ratsimp(ev(phi =

-phi0*exp(%i*omega*t),y=0,ratsimp)/exp(%i*omega*t),a1,a2,a3,
a4,a5,kq,kl));


     /* Potential at top surface of quartz sensor: phi(h,t)
= phi0*exp(%i*omega*t)  */


     BC4:ratsimp(ev(phi =

phi0*exp(%i*omega*t),y=h,ratsimp)/exp(%i*omega*t),a1,a2,a3,a
4,a5,kq,kl);


     /* slip boundary condition: ul(h,t) = alpha*uq(h,t)  */


     (uq:rhs(gen_sol1),
      ul:rhs(gen_sol3),
      BC5:ratsimp(ev(ul = alpha*uq, y=h,
ratsimp)/exp(%i*omega*t),a1,a2,a3,a4,a5,kq,kl));
     (pause(),
      clearscreen(),
      disp("Let",gamma1 = exp(%i*h*kq), gamma2 =
exp(%i*h*kl), delta =
     eta*omega-%i*cbar),
      pause(),
      clearscreen())$

     (BC:expand([BC1,BC2,BC3,BC4,BC5]),
      BC:ratsubst(gamma1,exp(%i*h*kq),BC),
      BC:ratsubst(gamma2,exp(%i*h*kl),BC),
      BC:ratsimp(ratsubst(delta, eta*omega-%i*cbar,BC)),
      map(disp,BC),
      pause(),
```

```
      clearscreen())$


     /* The solution to the above boundary value problem is
given by...*/

     (solBC:linsolve(BC,[a1,a2,a3,a4,a5]),
      solBC1:rhs(solBC[1]),
      solBC2:rhs(solBC[2]),
      solBC3:rhs(solBC[3]),
      solBC4:rhs(solBC[4]),
      solBC5:rhs(solBC[5]),
      solBC1num:num(solBC1),
      solBC1denom:denom(solBC1),
      solBC2num:num(solBC2),
      solBC2denom:denom(solBC2),
      solBC3num:num(solBC3),
      solBC3denom:denom(solBC3),
      solBC4num:num(solBC4),
      solBC4denom:denom(solBC4),
      solBC5num:num(solBC5),
      solBC5denom:denom(solBC5),
      pause(),
      clearscreen(),
      disp("Let",
           b11 = factorsum(ratcoef(solBC1num,alpha,0)),
           b12 = factorsum(ratcoef(solBC1num,alpha,1)),
           b13 = factorsum(ratcoef(solBC1denom,alpha,0)),
           b14 = factorsum(ratcoef(solBC1denom,alpha,1)),
           "Therefore...",
           a1 = (b11 + alpha*b12)/(b13 + alpha*b14)),
      pause(),
      clearscreen(),
      disp("Let",
           b21 = factorsum(ratcoef(solBC2num,alpha,0)),
           b22 = factorsum(ratcoef(solBC2num,alpha,1)),
           b23 = factorsum(ratcoef(solBC2denom,alpha,0)),
           b24 = factorsum(ratcoef(solBC2denom,alpha,1)),
           "Therefore...",
           a2 = (b21 + alpha*b22)/(b23 + alpha*b24)),
      pause(),
      clearscreen(),
      disp("Let",
           b31 =
factorsum(ratcoef(ratcoef(solBC3num,alpha,0),phi0)),
           b32 =
factorsum(ratcoef(ratcoef(solBC3num,alpha,1),phi0)),
           b33 = factorsum(ratcoef(solBC3denom,alpha,0)),
           b34 = factorsum(ratcoef(solBC3denom,alpha,1)),
           "Therefore...",
           a3 = ((b31 + alpha*b32)*phi0)/(b33 + alpha*b34)),
      pause(),
```

```
       clearscreen(),
       disp("Let",
            b41 = factorsum(ratcoef(solBC4num,alpha,0)),
            b42 = factorsum(ratcoef(solBC4num,alpha,1)),
            b43 = factorsum(ratcoef(solBC4denom,alpha,0)),
            b44 = factorsum(ratcoef(solBC4denom,alpha,1)),
            "Therefore...",
            a4 = (b41 + alpha*b42)/(b43 + alpha*b44)),
       pause(),
       clearscreen(),
       disp("Let",
            b51 = factorsum(ratcoef(solBC5num,alpha,0)),
            b52 = factorsum(ratcoef(solBC5num,alpha,1)),
            b53 = factorsum(ratcoef(solBC5denom,alpha,0)),
            b54 = factorsum(ratcoef(solBC5denom,alpha,1)),
            "Therefore...",
            a5 = (b51 + alpha*b52)/(b53 + alpha*b54)))$

     /* The electric displacement D in the quartz sensor is
given by... */

     (D:e*diff('uq,y,1) - epsilon*diff('phi,y,1),
      display(D))$

     /* Substituting uq and phi into D we get... */

     (D:ev(D,diff,ratsimp),
      display(D))$

     /* The total surface charge Q of the quartz sensor is
given by... */

     Q:D*A;

     /* The instataneous current i is given by... */

     i:diff(Q,t,1);

/* The electrical input impedance of the liquid-loaded
AT-cut quartz sensor is given by...
          */

     (Zin:(-phi0*exp(%i*omega*t) - phi0*exp(%i*omega*t))/i,
      a3:((b31 + alpha*b32)*phi0)/(b33 + alpha*b34),
      Zin:ratsimp(ev(Zin)),
      display(Zin))$
```

MACSYMA OUTPUT

```
>> Executing: D:\MACSYMA\MACSYMA.EXE D:\MACSYMA\MACSYMA.CLO
This is Macsyma 417.125 for Intel 80386/486 Series
Computers.
Copyright (c) 1982 - 1992 Macsyma Inc.  All rights reserved.
Portions copyright (c) 1982 Massachusetts Institute of
Technology.
All rights reserved.
Type "DESCRIBE(TRADE_SECRET);" to see important legal
notices.
Type "HELP();" for more information.

D:\macsyma\system\init.lsp being loaded.
←¦$LABEL(-1,15,Times New Roman,)Batching the file
D:\macsyma\mac-init.mac
Batchload done.
(c1) display2d:false$
(c2) batch("D:\\MACSYMA\\ZIN.TXT");

(c3) (clearscreen(),kill(all),fancy_display:false)$

(c1) /*  Determine the electrical input impedance Zin for
the liquid loaded AT-Cut

    quartz sensor...  */

/* establish dependencies for uq,ul, and vl. */

(ratfac:true,
 depends([uq,ul,vl,phi],[y,t]),
 depends([f1,f2,f3],y),
 assume(nu>0,omega>0))$

(c2) /* The equation of motion for the transverse particle
displacement uq in the quartz sensor is
   given by...*/

eq1:cbar*diff(uq,y,2) + eta*diff(uq,y,2,t,1) -
rhoq*diff(uq,t,2) = 0;

(D2)
cbar*'DIFF(uq,y,2)-rhoq*'DIFF(uq,t,2)+eta*'DIFF(uq,t,1,y,2)
= 0

(c3) /* The potential phi and the transverse particle
displacement uq are related to each
   other by the following relation...*/

eq2:e*diff(uq,y,2) - epsilon*diff(phi,y,2) = 0;

(D3) e*'DIFF(uq,y,2)-epsilon*'DIFF(phi,y,2) = 0
```

```
(c4) /* Let uq = f1(y)*exp(%i*omega*t) and phi =
f2(y)*exp(%i*omega*t), equation eq1 reduces to...*/

(expr1:ev(eq1,uq =
f1*exp(%i*omega*t),diff,ratsimp)/exp(%i*omega*t),
 expr1:ratsimp(expr1,diff(f1,y,2)),
 disp(expr1))$

f1*omega^2*rhoq+'DIFF(f1,y,2)*(%i*eta*omega+cbar) = 0


(c5) /* Let f1 = exp(%i*r*y), the general solution to
equation eq1 is given by...*/

(expr1:factor(ev(expr1,f1 =
exp(%i*r*y),diff,ratsimp)/exp(%i*r*y)),
 sol1:solve(expr1,r),
 disp("The christoffel equation to equation eq1 is given
by...",
      expr1,
      "The solution to the above christoffel equation is
given by...",
      sol1))$

"The christoffel equation to equation eq1 is given by..."


omega^2*rhoq-%i*eta*omega*r^2-cbar*r^2 = 0


"The solution to the above christoffel equation is given
by..."


[r = -omega*sqrt(rhoq/(%i*eta*omega+cbar)),r =
omega*sqrt(rhoq/(%i*eta*omega
+cbar))]


(c6) /* Let kq denote the complex wave number for the quartz
sensor, kq is defined as follows...*/

cwq:kq = rhs(sol1[2]);

(D6) kq = omega*sqrt(rhoq/(%i*eta*omega+cbar))

(c7) /* The general solution to equation eq1 is given
by...*/

(sol1:subst(kq,rhs(sol1[2]),sol1),
 gen_sol1:uq =
sum(concat(a,i)*exp(%i*rhs(sol1[i])*y),i,1,2)*exp(%i*omega*t
```

```
),
 disp(gen_sol1))$

uq = %e^(%i*omega*t)*(a2*%e^(%i*kq*y)+a1*%e^-(%i*kq*y))


(c8) /* From equation eq2 the potential phi is given by...*/

(expr2:expand(ev(eq2,[phi =
f2*exp(%i*omega*t),gen_sol1],diff,ratsimp)/exp(%i*omega*t)),
 expr2:ode(expr2,f2,y),
 expr2:subst(a3,%k2,expr2),
 expr2:rhs(expand(subst(a4,%k1,expr2))),
 gen_sol2:ev(phi = expr2*exp(%i*omega*t),sol2),
 disp(gen_sol2))$
D:\macsyma\ode\ode.fas being loaded.
D:\macsyma\ode\odeaux.fas being loaded.
D:\macsyma\ode\ode2.fas being loaded.

phi =
%e^(%i*omega*t)*(a2*e*%e^(%i*kq*y)/epsilon+a1*e*%e^-(%i*kq*y
)/epsilon
+a3*y+a4)


(c9) /* Perform a check to determine if gen_sol1 and
gen_sol2 satisfy equations eq1 and eq2...*/

(check1:ev([eq1,eq2],[gen_sol1,gen_sol2],diff,ratsimp),
 check1:ev(check1,cwq,ratsimp),
 map(disp,check1))$

0 = 0


0 = 0


(c10) /* The equation of motion for the transverse particle
velocity vl in the liquid medium is
   given by...*/

eq3:mu*diff(vl,y,2) - rhol*diff(vl,t,1) = 0;

(D10) mu*'DIFF(vl,y,2)-rhol*'DIFF(vl,t,1) = 0

(c11) /* With mu = nu*rhol and vl = diff(ul,t,1), then
equation eq3 reduces to...*/

eq3:expand(ev(eq3,[mu = nu*rhol,vl =
diff(ul,t,1)],diff)/rhol);
```

```
(D11) nu*'DIFF(ul,t,1,y,2)-'DIFF(ul,t,2) = 0

(c12) /* Let ul = f3(y)*exp(%i*omega*t), then equation eq3
reduces to...*/

expr3:factor(ev(eq3,ul =
f3*exp(%i*omega*t),diff,ratsimp)/exp(%i*omega*t));

(D12) omega*(f3*omega+%i*'DIFF(f3,y,2)*nu) = 0

(c13) /* Let f3 = exp(%i*r*y), then the general solution to
equation eq3 is given by...*/

(expr3:factor(ev(expr3,f3 =
exp(%i*r*y),diff,ratsimp)/exp(%i*r*y)),
 sol3:solve(expr3,r),
 disp("The christoffel equation to equation eq3 is given
by...",
      expr3,
      "The solution to the above christoffel equation is
given by...",
      sol3))$

"The christoffel equation to equation eq3 is given by..."


-omega*(%i*nu*r^2-omega) = 0


"The solution to the above christoffel equation is given
by..."


[r = -sqrt(-%i)*sqrt(omega)/sqrt(nu),r =
sqrt(-%i)*sqrt(omega)/sqrt(nu)]


(c14) ,* Let kl denote the complex wave number for the
liquid-medium, kl is defined as follows...*/


cw1:kl = rhs(sol3[2]);

(D14) kl = sqrt(-%i)*sqrt(omega)/sqrt(nu)

(c15) /* The general solution equation eq3 is given by...*/


(sol3:subst(kl,rhs(sol3[2]),sol3),
 gen_sol3:ul =
sum(concat(a,i+4)*exp(%i*rhs(sol3[i])*y),i,1,2)*exp(%i*omega
*t),
```

```
 disp(gen_sol3))$

u1 = %e^(%i*omega*t)*(a6*%e^(%i*k1*y)+a5*%e^-(%i*k1*y))


(c16) /* Perform a check to determine if gen_sol3 satisfies
equation eq3...*/

(check3:ev(eq3,gen_sol3,diff,ratsimp),
 check3:ev(check3,cw1,ratsimp),
 disp(check3))$

0 = 0


(c17) /* Physically as y -> infinity, u1 -> 0, therefore
consider the limit as y -> infinity of
   each of the two terms exp(%i*k1*y) and exp(-%i*k1*y)
seperately...*/

(term1:exp(%i*k1*y),
 term1:ev(term1,cw1,ratsimp),
 term1:factor(rectform(term1)),
 disp(term1))$

%e^(sqrt(omega)*y/(sqrt(2)*sqrt(nu)))*(%i*sin(sqrt(omega)*y/
(sqrt(2)*sqrt(nu
)))+cos(sqrt(omega)*y/(sqrt(2)*sqrt(nu))))


(c18) /* take the limit of the magnitude of the above
expression as y -> infinity...*/

(term1:trigsimp(cabs(term1)),
 limit1:'limit(term1,y,inf) = limit(term1,y,inf));
D:\macsyma\share\trigsimp.fas being loaded.

(D18) 'limit(%e^(sqrt(omega)*y/(sqrt(2)*sqrt(nu))),y,inf) =
inf

(c19) (term2:exp(-%i*k1*y),
 term2:ev(term2,cw1,ratsimp),
 term2:factor(rectform(term2)),
 disp(term2))$

-%e^-(sqrt(omega)*y/(sqrt(2)*sqrt(nu)))*(%i*sin(sqrt(omega)*
y/(sqrt(2)*sqrt
(nu)))-cos(sqrt(omega)*y/(sqrt(2)*sqrt(nu))))


(c20) /* take the limit of the magnitude of the above
expression as y -> infinity...*/
```

```
(term2:trigsimp(cabs(term2)),
 limit2:'limit(term2,y,inf) = limit(term2,y,inf));

(D20) 'limit(%e^-(sqrt(omega)*y/(sqrt(2)*sqrt(nu))),y,inf) =
0

(c21) /* As y -> infinity exp(%i*kl*y) -> infinity while
exp(-%i*kl*y) -> 0.
   Therefore in order for ul to remain finite for all y a6
must be set to zero.
   Thus for finite ul, a6=0. */

gen_sol3:ev(gen_sol3,a6=0,ratsimp);

(D21) ul = a5*%e^(%i*omega*t-%i*kl*y)

(c22) /* The shear stresses Tq and Tl are given by... */

(Tq:c*diff(uq,y,1)+eta*diff(uq,y,1,t,1)+e*diff(phi,y,1),
 Tl:mu*diff(vl,y,1),
 Tl:ev(Tl,[vl = diff(ul,t,1),mu = nu*rhol],diff),
 display(Tq,Tl))$

tq = c*'DIFF(uq,y,1)+eta*'DIFF(uq,t,1,y,1)+e*'DIFF(phi,y,1)


tl = nu*rhol*'DIFF(ul,t,1,y,1)


(c23) /* Substituting gen_sol1,gen_sol2, and gen_sol3 into
the expression for Tq and Tl.
   Tq and Tl reduce down to...*/

(Tq:ev(Tq,[gen_sol1,gen_sol2],diff,ratsimp),
 Tq:factorsum(ratsimp(ratsubst(cbar,c+e^2/epsilon,Tq))),
 Tl:factorsum(ev(Tl,gen_sol3,diff,ratsimp)),
 display(Tq,Tl))$

tq =
-(kq*(eta*omega-%i*cbar)*(a2*%e^(2*%i*kq*y)-a1)-a3*e*%e^(%i*
kq*y))*%e^
(%i*omega*t-%i*kq*y)


tl = a5*kl*nu*omega*rhol*%e^(%i*omega*t-%i*kl*y)


(c24) /* Implement the boundary conditions...*/

/* Stress free boundary condition: Tq(0,t) = 0    */

BC1:ratsimp(ev(Tq=0,y=0,ratsimp)/exp(%i*omega*t),a1,a2,a3,a4
```

```
,a5,kq,kl);

(D24)
a3*e-kq*(a2*(eta*omega-%i*cbar)+a1*(%i*cbar-eta*omega)) = 0

(c25) /* continuity of stress across interface: Tq(h,t) =
Tl(h,t)  */

BC2:ratsimp(ev(Tq =
Tl,y=h,ratsimp)/exp(%i*omega*t),a1,a2,a3,a4,a5,kq,kl);

(D25)
-%e^-(%i*h*kq)*(kq*(a2*(eta*%e^(2*%i*h*kq)*omega-%i*cbar*%e^
(2*%i*h*kq))+a1*
(%i*cbar-eta*omega))-a3*e*%e^(%i*h*kq)) =
a5*kl*%e^-(%i*h*kl)*nu*omega*rhol

(c26) /* Potential at bottom surface of quartz sensor:
phi(0,t) = -phi0*exp(%i*omega*t)  */

(phi:rhs(gen_sol2),
 BC3:ratsimp(ev(phi =
-phi0*exp(%i*omega*t),y=0,ratsimp)/exp(%i*omega*t),a1,a2,a3,
a4,a5,kq,kl));

(D26) (a4*epsilon+a2*e+a1*e)/epsilon = -phi0

(c27) /* Potential at top surface of quartz sensor: phi(h,t)
= phi0*exp(%i*omega*t)  */


BC4:ratsimp(ev(phi =
phi0*exp(%i*omega*t),y=h,ratsimp)/exp(%i*omega*t),a1,a2,a3,a
4,a5,kq,kl);

(D27)
%e^-(%i*h*kq)*(a2*e*%e^(2*%i*h*kq)+a3*epsilon*h*%e^(%i*h*kq)
+a4*epsilon*%e^
(%i*h*kq)+a1*e)/epsilon = phi0

(c28) /* slip boundary condition: ul(h,t) = alpha*uq(h,t)
*/


(uq:rhs(gen_sol1),
 ul:rhs(gen_sol3),
 BC5:ratsimp(ev(ul = alpha*uq, y=h,
ratsimp)/exp(%i*omega*t),a1,a2,a3,a4,a5,kq,kl));

(D28) a5*%e^-(%i*h*kl) =
alpha*%e^-(%i*h*kq)*(a2*%e^(2*%i*h*kq)+a1)
```

```
(c29) (pause(),
 clearscreen(),
 disp("Let",gamma1 = exp(%i*h*kq), gamma2 = exp(%i*h*kl),
delta = eta*omega-%i*cbar),
 pause(),
 clearscreen())$
Pausing. Press Enter to continue.


"Let"


gamma1 = %e^(%i*h*kq)


gamma2 = %e^(%i*h*kl)


delta = eta*omega-%i*cbar

Pausing. Press Enter to continue.


(c30) (BC:expand([BC1,BC2,BC3,BC4,BC5]),
 BC:ratsubst(gamma1,exp(%i*h*kq),BC),
 BC:ratsubst(gamma2,exp(%i*h*kl),BC),
 BC:ratsimp(ratsubst(delta, eta*omega-%i*cbar,BC)),
 map(disp,BC),
 pause(),
 clearscreen())$

a3*e-(a2-a1)*delta*kq = 0


-((a2*delta*gamma1^2-a1*delta)*kq-a3*e*gamma1)/gamma1 =
a5*kl*nu*omega
*rhol/gamma2


(a4*epsilon+(a2+a1)*e)/epsilon = -phi0


(a3*epsilon*gamma1*h+a2*e*gamma1^2+a4*epsilon*gamma1+a1*e)/(
epsilon*gamma1)
= phi0


a5/gamma2 = alpha*(a2*gamma1^2+a1)/gamma1

Pausing. Press Enter to continue.
```

```
(c31) /* The solution to the above boundary value problem is
given by...*/

(solBC:linsolve(BC,[a1,a2,a3,a4,a5]),
 solBC1:rhs(solBC[1]),
 solBC2:rhs(solBC[2]),
 solBC3:rhs(solBC[3]),
 solBC4:rhs(solBC[4]),
 solBC5:rhs(solBC[5]),
 solBC1num:num(solBC1),
 solBC1denom:denom(solBC1),
 solBC2num:num(solBC2),
 solBC2denom:denom(solBC2),
 solBC3num:num(solBC3),
 solBC3denom:denom(solBC3),
 solBC4num:num(solBC4),
 solBC4denom:denom(solBC4),
 solBC5num:num(solBC5),
 solBC5denom:denom(solBC5),
 pause(),
 clearscreen(),
 disp("Let",
      b11 = factorsum(ratcoef(solBC1num,alpha,0)),
      b12 = factorsum(ratcoef(solBC1num,alpha,1)),
      b13 = factorsum(ratcoef(solBC1denom,alpha,0)),
      b14 = factorsum(ratcoef(solBC1denom,alpha,1)),
      "Therefore...",
      a1 = (b11 + alpha*b12)/(b13 + alpha*b14)),
 pause(),
 clearscreen(),
 disp("Let",
      b21 = factorsum(ratcoef(solBC2num,alpha,0)),
      b22 = factorsum(ratcoef(solBC2num,alpha,1)),
      b23 = factorsum(ratcoef(solBC2denom,alpha,0)),
      b24 = factorsum(ratcoef(solBC2denom,alpha,1)),
      "Therefore...",
      a2 = (b21 + alpha*b22)/(b23 + alpha*b24)),
 pause(),
 clearscreen(),
 disp("Let",
      b31 =
factorsum(ratcoef(ratcoef(solBC3num,alpha,0),phi0)),
      b32 =
factorsum(ratcoef(ratcoef(solBC3num,alpha,1),phi0)),
      b33 = factorsum(ratcoef(solBC3denom,alpha,0)),
      b34 = factorsum(ratcoef(solBC3denom,alpha,1)),
      "Therefore...",
      a3 = ((b31 + alpha*b32)*phi0)/(b33 + alpha*b34)),
 pause(),
 clearscreen(),
 disp("Let",
      b41 = factorsum(ratcoef(solBC4num,alpha,0)),
```

```
      b42 = factorsum(ratcoef(solBC4num,alpha,1)),
      b43 = factorsum(ratcoef(solBC4denom,alpha,0)),
      b44 = factorsum(ratcoef(solBC4denom,alpha,1)),
      "Therefore...",
      a4 = (b41 + alpha*b42)/(b43 + alpha*b44)),
 pause(),
 clearscreen(),
 disp("Let",
      b51 = factorsum(ratcoef(solBC5num,alpha,0)),
      b52 = factorsum(ratcoef(solBC5num,alpha,1)),
      b53 = factorsum(ratcoef(solBC5denom,alpha,0)),
      b54 = factorsum(ratcoef(solBC5denom,alpha,1)),
      "Therefore...",
      a5 = (b51 + alpha*b52)/(b53 + alpha*b54)))$
Pausing. Press Enter to continue.


"Let"


b11 = -2*delta*e*epsilon*(gamma1-1)*gamma1*kq*phi0


b12 = -2*e*epsilon*gamma1^2*kl*nu*omega*phi0*rhol


b13 =
delta*(gamma1-1)*kq*(delta*epsilon*(gamma1+1)*h*kq+2*e^2*(ga
mma1-1))


b14 =
kl*(delta*epsilon*(gamma1^2+1)*h*kq+e^2*(gamma1-1)*(gamma1+1
))*nu*omega
*rhol


"Therefore..."


a1 = (alpha*b12+b11)/(alpha*b14+b13)

Pausing. Press Enter to continue.


"Let"


b21 = 2*delta*e*epsilon*(gamma1-1)*kq*phi0


b22 = 2*e*epsilon*kl*nu*omega*phi0*rhol
```

```
b23 =
delta*(gamma1-1)*kq*(delta*epsilon*(gamma1+1)*h*kq+2*e^2*(ga
mma1-1))


b24 =
kl*(delta*epsilon*(gamma1^2+1)*h*kq+e^2*(gamma1-1)*(gamma1+1
))*nu*omega
*rhol


"Therefore..."


a2 = (alpha*b22+b21)/(alpha*b24+b23)

Pausing. Press Enter to continue.


"Let"


b31 = 2*delta^2*epsilon*(gamma1-1)*(gamma1+1)*kq^2


b32 = 2*delta*epsilon*(gamma1^2+1)*kl*kq*nu*omega*rhol


b33 =
delta*(gamma1-1)*kq*(delta*epsilon*(gamma1+1)*h*kq+2*e^2*(ga
mma1-1))


b34 =
kl*(delta*epsilon*(gamma1^2+1)*h*kq+e^2*(gamma1-1)*(gamma1+1
))*nu*omega
*rhol


"Therefore..."


a3 = (alpha*b32+b31)*phi0/(alpha*b34+b33)

Pausing. Press Enter to continue.


"Let"


b41 = -delta^2*epsilon*(gamma1-1)*(gamma1+1)*h*kq^2*phi0
```

```
b42 =
-kl*(delta*epsilon*(gamma1^2+1)*h*kq-e^2*(gamma1-1)*(gamma1+
1))*nu
*omega*phi0*rhol


b43 =
delta*(gamma1-1)*kq*(delta*epsilon*(gamma1+1)*h*kq+2*e^2*(ga
mma1-1))


b44 =
kl*(delta*epsilon*(gamma1^2+1)*h*kq+e^2*(gamma1-1)*(gamma1+1
))*nu*omega
*rhol


"Therefore..."


a4 = (alpha*b42+b41)/(alpha*b44+b43)

Pausing. Press Enter to continue.


"Let"


b51 = 0


b52 = 2*delta*e*epsilon*(gamma1-1)^2*gamma2*kq*phi0


b53 =
delta*(gamma1-1)*kq*(delta*epsilon*(gamma1+1)*h*kq+2*e^2*(ga
mma1-1))


b54 =
kl*(delta*epsilon*(gamma1^2+1)*h*kq+e^2*(gamma1-1)*(gamma1+1
))*nu*omega
*rhol


"Therefore..."


a5 = (alpha*b52+b51)/(alpha*b54+b53)
```

```
(c32) /* The electric displacement D in the quartz sensor is
given by... */

(D:e*diff('uq,y,1) - epsilon*diff('phi,y,1),
 display(D))$

d = e*'DIFF(uq,y,1)-epsilon*'DIFF(phi,y,1)


(c33) /* Substituting uq and phi into D we get... */

(D:ev(D,diff,ratsimp),
 display(D))$

d = -a3*epsilon*%e^(%i*omega*t)


(c34) /* The total surface charge Q of the quartz sensor is
given by... */

Q:D*A;

(D34) -a*a3*epsilon*%e^(%i*omega*t)

(c35) /* The instataneous current i is given by... */

i:diff(Q,t,1);

(D35) -%i*a*a3*epsilon*omega*%e^(%i*omega*t)

(c36) /* The electrical input impedance of the liquid-loaded
AT-cut quartz sensor is given by... */

(Zin:(-phi0*exp(%i*omega*t) - phi0*exp(%i*omega*t))/i,
 a3:((b31 + alpha*b32)*phi0)/(b33 + alpha*b34),
 Zin:ratsimp(ev(Zin)),
 display(Zin))$

zin =
-2*%i*(alpha*b34+b33)/(a*(alpha*b32+b31)*epsilon*omega)


(c37) /* 6:25PM  1/9/93 */
```

APPENDIX 4 Non-linear Regression Analysis Example of a Series RLC circuit, Mathcad program DOC1.MCD

Non-linear regression analysis of the theoretical complex-valued expression of the impedance for a series RLC-circuit.

Introduction

The following is a demonstration of how Mathcad's **Minerr** function can be used to perform a non-linear regression analysis procedure on a multi-valued non-linear complex-valued function, Z. Mathcad's **Minerr** function implements a modified version of the Levenberg-Marquardt method . The the Levenberg-Marquardt method, a quasi-Newton method, is a variation of the gradient method.

Given a system of n non-linear algebraic equations in n unknows, at each step in the iterative procedure Newton's method computes the jacobian of the non-linear system. Each component of the jacobian is computed by a numerical differentiation procedure. On the other hand, in the quasi-Newton method, each component of the jacobian is replaced by an appropriate finite-difference approximation.

Mathcad's Levenberg-Marquardt algorithm was obtained from the public-domain MINPACK algorithms developed and published by the Argonne National Laboratory in Argonne, Illinois

Complex-Valued Function

The impedance, Z, of a series RLC circuit is chosen as the multi-valued non-linear complex-valued function. The expression for the impedance, Z, in terms of the resistance, R, the inductance, L, the capacitance, C, and the angular frequency, ω, is

$$(1)\quad Z(R,L,C,\omega) := R + j\cdot\left(\omega\cdot L - \frac{1}{\omega\cdot C}\right)$$

The resonant frequency, f, of the series RLC circuit, is given by

$$(2)\quad f := \frac{1}{2\cdot\pi}\cdot\frac{1}{\sqrt{L\cdot C}}$$

Let the resonant frequency, f, be 9.0 MHz. $f = 9.0\cdot MHz$

Let the inductance, L, be 10.0 mH. $Lexact = 10.0\cdot mH$

From equation (2), the numerical value for the capacitance, C, is.

$$(3)\quad Cexact = \frac{1}{4\,Lexact\,\pi^2 \cdot f^2}$$

$$Cexact = 0.031 \cdot pF$$

Let the numerical value of the resistance, Rexact, be 10.0 kΩ. $Rexact = 10.0\,k\Omega$

Procedure

A simulated set of N experimental data points of the form (ω_i, $Zexp_i$) is generated from (1) via Mathcad's **rnd** function. The best fit value for L denoted by Lfit, is determined by fitting the theoretical complex-valued expression for the impedance, Z = Z(R, L, C, ω) to the simulated experimental data, $Zexp_i$. The fitting of Z to $Zexp_i$ is achieved by minimizing the Sum Of Squares Of Errors, SSE(L) via Mathcad's **Minerr** function.

Enter number of experimental data points $N = 401$

Enter the closed interval, $I = [f_s, f_t]$

Enter numerical value for f_s $fs = 8.0\,MHz$

Enter numerical value for f_t $ft = 10.0\,MHz$

Compute step size Δf $\Delta f = \frac{ft - fs}{N}$ $\Delta f = 4.988 \cdot kHz$ $f_1 = fs$ $i = 1 \ldots N$

$$f_{i+1} = f_i + \Delta f \quad ff_i = f_i$$

Using Mathcad's **rnd** function generate a set of N experimental data points using the theoretical complex-valued expression for Z. The experimental data $Zexp_i$ is generated by perturbing the value of Lexact at each of the N = 401 data points. The perturbation of Lexact is done by Mathcad's **rnd** function. Mathcad's random function,, **rnd**(x), generates uniformly distributed random numbers between 0 and x inclusive.

The perturbation of Lexact is accomplished by the expression below.

$$(4)\quad L\_perturbed_i = \frac{(Lexact + rnd(1) \cdot mH) + (Lexact - rnd(1)\,mH)}{2}$$

Using values for Rexact, Lexact, and Cexact, compute the exact values for the impedance, Z, for each of the N = 401 data points.

$$(5)\quad Zexact_i = Z\left(Rexact, Lexact, Cexact, 2\cdot\pi\cdot f_i\right)$$

Using the perturbed values for Lexact, and the values for Rexact and Cexact, compute the simulated experimental data for the impedance Z.

$$(6)\quad Zexp_i = Z\left(Rexact, L\_perturbed_i, Cexact, 2\,\pi\cdot f_i\right)$$

From equations (5) and (6) compute the magnitude and phase of both Zexact and Zexp versus frequency f.

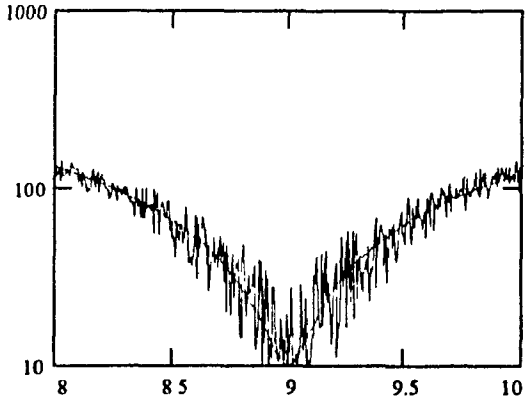
$$(7)\quad MZexact_i = \left|Zexact_i\right|$$

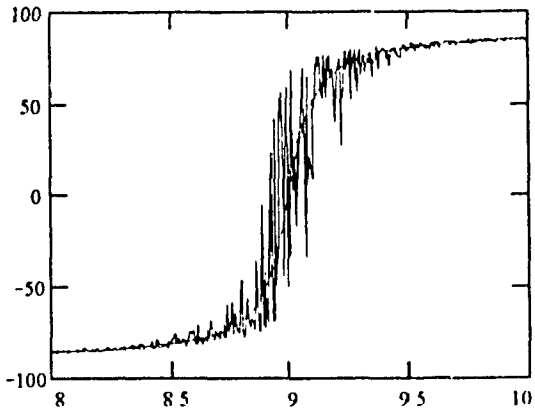
$$(8)\quad MZexp_i = \left|Zexp_i\right|$$

$$(9)\quad \theta Zexact_i = \arg\left(Zexact_i\right)$$

$$(10)\quad \theta Zexp_i = \arg\left(Zexp_i\right)$$

Plot the magnitude and phase of both Z and Zexp versus frequency f.





-- |Zexact| versus f
— |Zexp| versus f

Generate data files of the magnitude and phase of both Zexact and Zexp versus frequency f.

-The data for the magnitude of Zexact versus frequency f is stored in the data file MZEXACT.PRN.
-The data for the magnitude of Zexp versus frequency f is stored in the data file MZEXP.PRN.
-The data for the phase of Zexact versus frequency f is stored in the data file THEXACT.PRN.
-The data for the phase of Zexp versus frequency f is stored in the data file THEXP.PRN.

$$(11)\quad \mathrm{WRITEPRN(MZEXACT)} := \mathrm{augment}\left(\frac{f}{\mathrm{MHz}}, \frac{MZexact}{k\Omega}\right)$$

$$(12)\quad \mathrm{WRITEPRN(MZEXP)} := \mathrm{augment}\left(\frac{f}{\mathrm{MHz}}, \frac{MZexp}{k\Omega}\right)$$

$$(13)\quad \mathrm{WRITEPRN(THEXACT)} := \mathrm{augment}\left(\frac{f}{\mathrm{MHz}}, \frac{\theta Zexact}{\mathrm{deg}}\right)$$

$$(14)\quad \mathrm{WRITEPRN(THEXP)} := \mathrm{augment}\left(\frac{f}{\mathrm{MHz}}, \frac{\theta Zexp}{\mathrm{deg}}\right)$$

The Sum Of Squres Of Errors, SSE(L) is given by

$$(15)\quad SSE(L) := \frac{1}{N}\sum_{i}\left(\left|\frac{Zexp_i}{k\Omega} - \frac{Z\left(Rexact, L, Cexact, 2\cdot\pi\cdot f_i\right)}{k\Omega}\right|\right)^2$$

Compute SSE(L) over the closed interval [1.0 mH, 20.0 mH] in steps of $\Delta L = 0.1$ mH

Enter numerical value for ΔL $\quad \Delta L := 0.1$ mH

Enter numerical value for Linitial $\quad$ Linitial := 1.0 mH

Enter numerical value for Lterminal $\quad$ Lterminal := 20.0 mH

From the values for ΔL, Linitial, and Lterminal, compute the number of interval subdivisions, NL. The expression for NL is

$$(16)\quad NL := floor\left(\frac{(Lterminal - Linitial)}{\Delta L}\right)$$

The value of NL is NL = 190

The variable k takes on integral values from 1 to NL $\quad k := 1 \ldots 190$ inclusive.

$$(17)\quad L_1 := Linitial$$

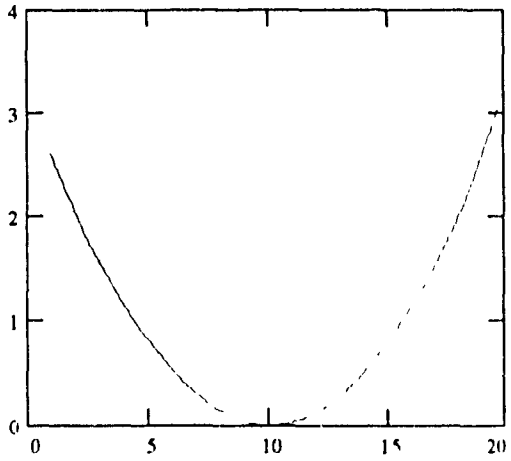
$$(18)\quad L_{k+1} := L_k + \Delta L \quad LI_k := L_k$$

Expression (18) generates NL equally spaced subinterval for the above closed interval.

For each k = 1, . . . , NL, compute SSE(L) for each L_k. The data for SSE(L) is stored in the one dimensional array, SSE_exp_k.

$$(19)\quad SSE\_exp_k := SSE\left(L_k\right)$$

Plot the data for SSE(L) versus L



— SSE(L) versus L

Store the data for SSE(L) versus L in the data file SSEL.PRN

$$(20) \quad \text{WRITEPRN(SSEL)} := \text{augment}\left(\begin{matrix} LL \\ mH \end{matrix}, SSE\_exp\right)$$

From the above plot of SSE(L) versus L, SSE as an absolute minimum in the closed interval [1.0 mH, 20.0 mH]. The absolute minimum of SSE(L) occurs when L = 10.0 mH. Since SSE(L) has only one absolute minimum in the above closed interval, then any value in the above closed interval may be used as a guess value for L. In fact, any value outside the above closed interval will serve as a guess value for L.

In view of the above, to implement MathCAD's Minerr function via MathCAD's Solve Block facility, enter any positive guess value for L.

Enter numerical value for Lguess. Lguess = 15.0·mH

---------- Mathcad Solve Block ----------

Given

(21) $SSE(Lguess) = 0$

(22) $Lfit := Minerr(Lguess)$

The result of the Solve Block, Lfit is given by

$$Lfit = 10.02 \cdot mH$$

Compute the residual error, ERR, given by ERR = SSE(Lfit)

$$ERR = 135.515$$

Using the values for Rexact, Lfit, and Cexact, compute the best fit values for Z denoted by Zfit.

(23) $Zfit_i := Z(Rexact, Lfit, Cexact, 2\pi f_i)$

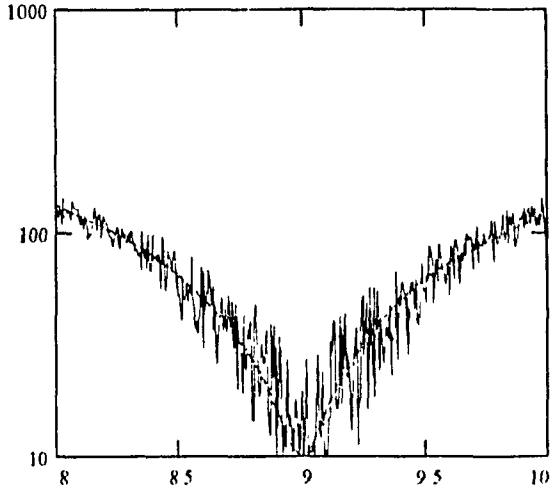
From equation (23) compute the magnitude and phase of Zfit.

(24) $MZfit_i := |Zfit_i|$

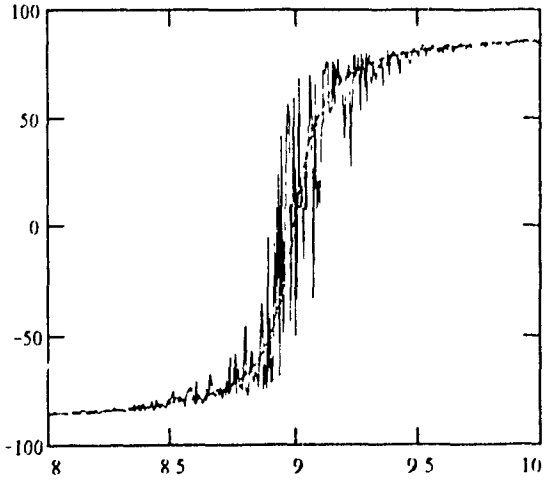
(25) $\theta Zfit_i := \arg(Zfit_i)$

Plot the magnitude and phase of Zexp, Zexact, and Zfit versus frequency f.

Plot the magnitude and phase of Zexp, Zexact, and Zfit versus frequency f.



— |Zexp| versus f
|Zexact| versus f
– |Zfit| versus f



— |Zexp| versus f
|Zexact| versus f
– |Zfit| versus f

APPENDIX 5 Non-linear Regression Analysis of Sensor in Air, Mathcad Program DOC2.MCD

Non-linear Regression Analysis of the Theoretical Complex-Valued Expression of the Impedance for the Hydrophilic and Hydrophobic Sensor in Air.

The best-fit values for e,η,h, and A will be determined by fitting the theoretical complex-valued expression of the impedance, Z, to the corresponding experimental data for the hydrophilic and hydrophobic sensor in air. The fitting is done by using the THREE STEP PROCEDURE, which is outlined below.

In step 1 the starting values for e, η, and h are determined by fitting the theoretical expression of the phase of Z, θ_Z, to the corresponding experimental data.

In step 2 the starting values for e, η, and h found in step 1 will be used to the determine the starting value for the effective surface area, A, by fitting the theoretical expression of the magnitude of Z, |Z|, to the corresponding experimental data.

In step 3 the starting values for e, η, h and A found in steps 1 and 2 will be used to determine the best-fit values of e, η, h and A by fitting the theoretical complex-valued expression of Z to the corresponding experimental data.

The impedance, Z, of an AT-cut quartz sensor in air is given in terms of the following nine expressions.

$$\mathrm{cbar}(e) := c + \frac{e^2}{\varepsilon}$$

$$\delta(e,\eta,\omega) := \eta\,\omega - j\,\mathrm{cbar}(e)$$

$$kq(e,\eta,\omega) := \omega \cdot \sqrt{\frac{\rho q}{\mathrm{cbar}(e) + j\cdot\omega\,\eta}}$$

$$\gamma 1(e,\eta,h,\omega) := \exp(j\,h\,kq(e,\eta,\omega))$$

$$\lambda 1(e,\eta,h,\omega) := \gamma 1(e,\eta,h,\omega) - 1$$

$$\lambda 2(e,\eta,h,\omega) := \gamma 1(e,\eta,h,\omega) + 1$$

$$b31(e,\eta,h,\omega) := 2\,\delta(e,\eta,\omega)^2 \cdot e\,\lambda 1(e,\eta,h,\omega)\,\lambda 2(e,\eta,h,\omega)\,kq(e,\eta,\omega)^2$$

$$b33(e,\eta,h,\omega) := \delta(e,\eta,\omega)\,\lambda1(e,\eta,h,\omega)\cdot kq(e,\eta,\omega)\left(\begin{matrix}\delta(e,\eta,\omega)\,\varepsilon\,\lambda2(e,\eta,h,\omega)\,h\,kq(e,\eta,\omega)\\ +2\cdot e^2\,\lambda1(e,\eta,h,\omega)\end{matrix}\right)$$

$$\xi a(e,\eta,h,\omega) := -\frac{2\,j}{\omega\,\varepsilon}\cdot\frac{b33(e,\eta,h,\omega)}{b31(e,\eta,h,\omega)}$$

The expression of the impedance, Za, is

$$Za(e,\eta,h,A,\omega) := \frac{1}{A}\cdot\xi a(e,\eta,h,\omega)$$

The expression of the magnitude of Za, |Za|, is

$$MZa(e,\eta,h,A,\omega) := |Za(e,\eta,h,A,\omega)|$$

The expression of the phase of Za, θ_{Za}, is

$$\theta Za(e,\eta,h,\omega) := \operatorname{atan}\left(\frac{Im(\xi a(e,\eta,h,\omega))}{Re(\xi a(e,\eta,h,\omega))}\right)$$

Enter the number of experimental data points N. N := 401

The range variable, i, iterates through the N experimental data points.

i := 1 .. N

To start the three-step procedure, read in the experimental data for |Z| and θ_Z in air for the hydrophilic and hydrophobic sensors.

Experimental Data for Hydrophilic Sensor in Air

Read in data array flicAir for frequency, f, an array of 401 values of f.

flicAir := READPRN(FLICAIR) MHz

Read in data array MZlicAir for the magnitude of Z, |Z|, an array of 401 values of |Z|.

MZlicAir := READPRN(ZLICAIR) kΩ

Read in data array θZlicAir for the phase of Z, θ_Z, an array of 401 values of θ_Z.

θZlicAir := READPRN(THLICAIR)

Experimental Data for Hydrophobic Sensor in Air

Read in data array fbicAir for frequency, f, an array of 401 values of f.

$$fbicAir := READPRN(FBICAIR)\cdot MHz$$

Read in data array MZbicAir for the magnitude of Z, |Z|, an array of 401 values of |Z|.

$$MZbicAir := READPRN(ZBICAIR)\cdot k\Omega$$

Read in data array θZbicAir for the phase of Z, θ_Z, an array of 401 values of θ_Z.

$$\theta ZbicAir := READPRN(THBICAIR)$$

Using the above frequency data flicAir and fbicAir, compute the corresponding angular frequency data ωlicAir and ωbicAir.

$$\omega licAir := 2\cdot\pi\cdot flicAir$$

$$\omega bicAir := 2\cdot\pi\cdot fbicAir$$

Using the experimental data for |Z| and θ_Z, for each i = 1,...,N compute the corresponding experimental data for ZlicAir and ZbicAi, using the exponential form for the complex number Z = |Z|exp(jθ_Z).

$$ZlicAir_i := MZlicAir_i\cdot\exp\left(j\ \theta ZlicAir_i\cdot deg\right)$$

$$ZbicAir_i := MZbicAir_i\exp\left(j\cdot\theta ZbicAir_i\cdot deg\right)$$

The above experimental data for |Z| and θ_Z consists of 401 points measured at 401 equally spaced frequencies. The resonant region of the quartz sensor is chosen as the frequency interval.

Enter numerical value for the mass density of quartz.

$$\rho q := 2649\ \frac{kg}{m^3}$$

Enter numerical value for the elastic constant of quartz.

$$c := 29.01\cdot 10^9\cdot\frac{newton}{m^2}$$

Enter numerical value for the dielectric constant of quartz.

$$\varepsilon := 39.82\ 10^{-12}\ \frac{coul}{volt\ m}$$

Non-Linear Regression Analysis of Hydrophilic Sensor in Air.

Step 1. Determine starting values for e, η and h using the experimental data for θ_Z.

To perform Step 1, define the Sum Of Squares Of Errors, SSE1_1(e,η,h).

$$SSE1\_1(e,\eta,h) := \frac{1}{N}\sum_{i}\left(\theta ZhcAir_i - \frac{\theta Za\left(e,\eta,h,\omega hcAir_i\right)}{deg}\right)^2$$

To start the non-linear curve-fitting procedure,, enter guess values for e, η and h.

$$e1\_guess := -0.079\,\frac{coul}{m^2}$$

$$\eta 1\_guess := 0.011\,newton\,\frac{sec}{m^2}$$

$$h1\_guess := 183.87\,\mu m$$

Use Mathcad's Minerr function to perform the non-linear curve fitting procedure.

---------- Mathcad Solve Block ----------

Given

$$SSE1\_1(e1\_guess,\eta 1\_guess,h1\_guess)=0$$

$$1=1$$

$$1=1$$

$$\begin{pmatrix} e1\_start \\ \eta 1\_start \\ h1\_start \end{pmatrix} := Minerr(e1\_guess,\eta 1\_guess,h1\_guess)$$

In the above Mathcad Solve Block, Mathcad needs two dummy equations, 1 = 1, to form a complete system of three non-linear algebraic equations in the three unknowns e, η and h.

The result of the Solve Block, e1_start, η1_start and h1_start is.

$$e1\_start = -0.0798 \cdot \frac{coul}{m^2}$$

$$\eta 1\_start = 0.0119 \cdot newton\ \frac{sec}{m^2}$$

$$h1\_start = 183.878 \cdot \mu m$$

Compute the residual error, ERR, given by ERR = SSE1_1(e1_start,η1_start,h1_start).

$$ERR = 1.945$$

Step 2. Use e1_start, η1_start, h1_start and the experimental data for |Z| to determine the starting value for the effective surface area, A.

To perform Step 2, define the Sum Of Squares Of Errors, SSE1_2(A).

$$SSE1\_2(A) := \frac{1}{N} \cdot \sum_i \left(\frac{MZlicAir_i}{k\Omega} - \frac{MZa\left(e1\_start, \eta 1\_start, h1\_start, A, \omega licAir_i\right)}{k\Omega} \right)^2$$

To start the non-linear curve-fitting procedure, enter the guess value for A.

$$A1\_guess := 0.28 \cdot cm^2$$

Use Mathcad's Minerr function to perform the non-linear curve-fitting procedure.

---------- Mathcad Solve Block ----------

Given

$$SSE1\_2(A1\_guess) = 0$$

$$A1\_start := Minerr(A1\_guess)$$

The result of the Solve Block, A1_start, is.

$$A1\_start = 0.2701 \cdot cm^2$$

Compute the residual error, ERR, given by SSE1_2(A1_start).

$$ERR = 110.993$$

Step 3. Use el_start, η1_start, h1_start, A1_start and the experimental data for Z to compute best-fit values for e, η, h and A.

To perform Step 3, define the Sum Of Squares Of Errors, SSE1_3(e,η,h,A). The quantity summed, is the product of a complex number and its conjugate.

$$SSE1\_3(e,\eta,h,A) := \frac{1}{N}\sum_{i}\left(\left|\frac{Zhc_{Air_i}}{k\Omega} - \frac{Za\left(e,\eta,h,A,\omega hc_{Air_i}\right)}{k\Omega}\right|\right)^2$$

Use Mathcad's Minerr function to perform the non-linear curve-fitting procedure.

---------- Mathcad Solve Block ----------

Given

nested solve block

$$SSE1\_3(el\_start,\eta1\_start,h1\_start,A1\_start) = 0$$

$$i = 1$$

$$i = 1$$

$$i = 1$$

$$\begin{bmatrix} el\_fit \\ \eta1\_fit \\ h1\_fit \\ A1\_fit \end{bmatrix} := Minerr(el\_start,\eta1\_start,h1\_start,A1\_start)$$

The result of the Solve Block, el_fit, η1_fit, h1_fit and A1_fit is.

$$el\_fit = -0.0798 \cdot \frac{coul}{m^2}$$

$$\eta1\_fit = 0.0084 \cdot newton \cdot \frac{sec}{m^2}$$

$$h1\_fit = 183.879 \cdot \mu m$$

$$A1\_fit = 0.2985 \cdot cm^2$$

Compute the residual error, ERR, given by ERR = SSE1_3(el_start, η1_start, h1_start, A1_start).

$$ERR = 60.727$$

Non-Linear Regression Analysis of Hydrophobic Sensor in Air.

For the hydrophilic sensor the value for e is the same as the value that is used for the hydrophobic sensor. On physical grounds , the value of e is expected to be independent of the type of chemical coating that is placed on the surface of the sensor. Therefore the value of e for the hydrophilic and hydrophobic sensor is the same.

Step 1. Determine starting values for η and h using the experimental data for θ_Z.

To perform Step 1, define the following Sum Of Squares Of Errors SSE2_1(η,h) .

$$SSE2\_1(\eta,h) := \frac{1}{N}\sum_i \left(0ZbicAir_i - \frac{0Za\left(e1\_fit,\eta,h,\omega bicAir_i\right)}{deg}\right)^2$$

To start the non-linear curve-fitting procedure, enter guess values for η and h.

$$\eta2\_guess := 0.24\cdot newton\cdot\frac{sec}{m^2}$$

$$h2\_guess := 183.98\ \mu m$$

Use Mathcad's Minerr function to perform the non-linear curve-fitting procedure.

---------- Mathcad Solve Block ----------

Given

$$SSE2\_1(\eta2\_guess,h2\_guess)=0$$

$$1=1$$

$$\begin{pmatrix}\eta2\_start\\h2\_start\end{pmatrix} := Minerr(\eta2\_guess,h2\_guess)$$

The result of the Solve Block, η2_start and h2_start is.

$$\eta2\_start = 0.2439\cdot newton\cdot\frac{sec}{m^2}$$

$$h2\_start = 183.986\cdot\mu m$$

Compute the residual error, given by ERR = SSE2_1(e1_fit,η 2_start,h2_start).

$$ERR = 5.351$$

Step 2. Use η2_start, h2_start and the experimental data for |Z| to determine the starting value for the effective surface area, A.

To perform Step 2, define the Sum Of Squares Of Errors, SSE2_2(A).

$$SSE2\_2(A) := \frac{1}{N}\cdot\sum_{i}\left(\frac{MZbicAir_i}{k\Omega} - \frac{MZa\left(e1\_fit,\eta2\_start,h2\_start,A,\omega bicAir_i\right)}{k\Omega}\right)^2$$

To start the non-linear curve-fitting procedure, enter the guess value for A.

$$A2\_guess := 0.25\ cm^2$$

Use Mathcad's Minerr function to perform the non-linear curve-fitting procedure.

---------- Mathcad Solve Block ----------

Given

$$SSE2\_2(A2\_guess) = 0$$

$$A2\_start := Minerr(A2\_guess)$$

The result of the Solve Block, A2_start, is.

$$A2\_start = 0.2533\cdot cm^2$$

Compute the residual error, ERR, given by SSE2_2(A2_start).

$$ERR = 0.311$$

Step 3. Use h2_start, η2_start, A2_start and the experimental data for Z to compute best-fit values for η, h and A.

To perform Step 3, define the Sum Of Squares Of Errors, SSE2_3(η,h,A). The quantity summed, is the product of a complex number and its conjugate.

$$SSE2\_3(\eta,h,A) := \frac{1}{N}\cdot\sum_i\left(\left|\frac{ZbicAir_i}{k\Omega}-\frac{Za\left(el\_fit,\eta,h,A,\omega bicAir_i\right)}{k\Omega}\right|\right)^2$$

Use Mathcad's Minerr function to perform the non-linear curve-fitting procedure.

---------- Mathcad Solve Block ----------

Given

$$SSE2\_3(\eta2\_start,h2\_start,A2\_start)=0$$

$$l=1$$

$$l=1$$

$$\begin{pmatrix}\eta2\_fit\\h2\_fit\\A2\_fit\end{pmatrix} := Minerr(\eta2\_start,h2\_start,A2\_start)$$

The result of the Solve Block, η2_fit, h2_fit and A2_fit is.

$$\eta2\_fit = 0.2345\cdot newton\,\frac{sec}{m^2}$$

$$h2\_fit = 183.979\cdot\mu m$$

$$A2\_fit = 0.2575\cdot cm^2$$

Compute the residual error, ERR, given by ERR = SSE2_3(el_fit,η2_start,h2_start,A2_start).

$$ERR = 0.057$$

Compute |Z| and θ_Z for the hydrophilic sensor in air.

$$MZa1\_fit_i := MZa(e1\_fit, \eta1\_fit, h1\_fit, A1\_fit, \omega hicAir_i)$$

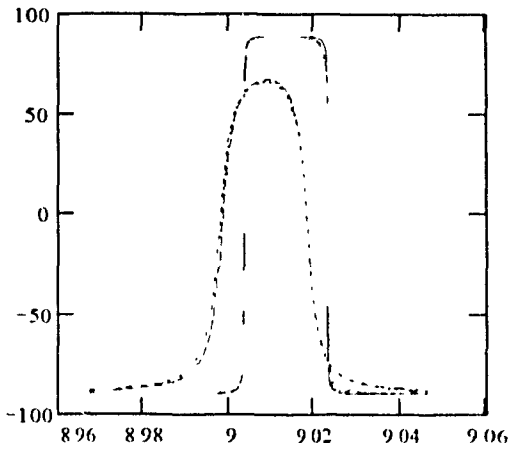
$$\theta Za1\_fit_i := \theta Za(e1\_fit, \eta1\_fit, h1\_fit, \omega hicAir_i)$$

Compute |Z| and θ_Z for the hydrophobic sensor in air.

$$MZa2\_fit_i := MZa(e1\_fit, \eta2\_fit, h2\_fit, A2\_fit, \omega hicAir_i)$$

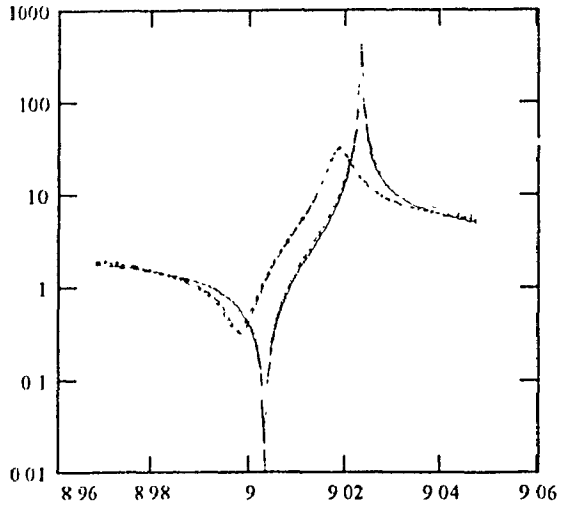
$$\theta Za2\_fit_i := \theta Za(e1\_fit, \eta2\_fit, h2\_fit, \omega hicAir_i)$$

Plot of θ_Z versus f for the hydrophilic and hydrophobic sensor in air.



— Hydrophilic Sensor (Fitted Curve)
Hydrophilic Sensor (Experimental Curve)
-- Hydrophobic Sensor (Fitted Curve)
· · Hydrophobic Sensor (Experimental Curve)

Plot of |Z| versus f for the hydrophilic and hydrophobic sensor in air.



Hydrophilic Sensor (Fitted Curve)
Hydrophilic Sensor (Experimental Curve)
Hydrophobic Sensor (Fitted Curve)
Hydrophobic Sensor (Experimental Curve)

Summary of results for hydrophilic sensor

$$\varepsilon 1\_fit = 0.0798 \cdot \frac{coul}{m^2}$$

$$\eta 1\_fit = 0.0084 \cdot newton \frac{sec}{m^2}$$

$$h1\_fit = 183.879 \cdot \mu m$$

$$A1\_fit = 0.2985 \cdot cm^2$$

Summary of results for hydrophobic sensor

$$\varepsilon 1\_fit = 0.0798 \cdot \frac{coul}{m^2}$$

$$\eta 2\_fit = 0.2345 \cdot newton \frac{sec}{m^2}$$

$$h2\_fit = 183.979 \cdot \mu m$$

$$A2\_fit = 0.2575 \cdot cm^2$$

Store data for the hydrophilic and hydrophobic sensor in air.

$$SENSOR1 := \begin{pmatrix} \frac{e1\_fit}{\left(\frac{coul}{m^2}\right)} \\ \frac{\eta 1\_fit}{\left(newton\ \frac{sec}{m^2}\right)} \\ \frac{h1\_fit}{\mu m} \\ \frac{A1\_fit}{cm^2} \end{pmatrix} \qquad SENSOR1 = \begin{pmatrix} -0.08 \\ 0.008 \\ 183.879 \\ 0.298 \end{pmatrix} \qquad WRITEPRN(SENSOR1) := SENSOR1$$

$$SENSOR2 := \begin{pmatrix} \frac{e1\_fit}{\left(\frac{coul}{m^2}\right)} \\ \frac{\eta 2\_fit}{\left(newton\ \frac{sec}{m^2}\right)} \\ \frac{h2\_fit}{\mu m} \\ \frac{A2\_fit}{cm^2} \end{pmatrix} \qquad SENSOR2 = \begin{pmatrix} 0.08 \\ 0.231 \\ 183.979 \\ 0.257 \end{pmatrix} \qquad WRITEPRN(SENSOR2) := SENSOR2$$

Store fitted and experimental data of $|Z|$ and θ_Z for the hydrophilic and hydrophobic sensor in air.

$$WRITEPRN(TZLICAIR) := augment\left(\frac{flicAir}{MHz}, augment\left(\frac{\theta Za1\_fit}{deg}, \theta ZlicAir\right)\right)$$

$$WRITEPRN(MZLICAIR) := augment\left(\frac{flicAir}{MHz}, augment\left(\frac{MZa1\_fit}{k\Omega}, \frac{MZlicAir}{k\Omega}\right)\right)$$

$$WRITEPRN(TZBICAIR) := augment\left(\frac{fbicAir}{MHz}, augment\left(\frac{\theta Za2\_fit}{deg}, \theta ZbicAir\right)\right)$$

$$WRITEPRN(MZBICAIR) := augment\left(\frac{fbicAir}{MHz}, augment\left(\frac{MZa2\_fit}{k\Omega}, \frac{MZbicAir}{k\Omega}\right)\right)$$

APPENDIX 6 Non-linear Regression Analysis of Sensor in Liquid, Mathcad Program DOC3.MCD

Non-Linear regression analysis of the theoretical complex-valued expression of the impedance for the hydrophilic and hydrophobic sensor in water-glycerol solution.

The best-fit values for the interfacial slip parameter, α, and the effective surface area, A, will be determined by fitting the theoretical complex-valued expression of Z to the experimental data for the hydrophilic and hydrophobic sensors in water-glycerol solutions of varying concentrations ranging from pure water to pure glycerol in steps of 0.1 mole fraction. The fitting of theory to experiment will be done by minimizing the appropriate Sum of Squares Of Errors, SSE, by using Mathcad's Minerr function.

The theoretical complex-valued expression of the impedance, Z, for the liquid loaded AT-cut quartz sensor in terms of the sixteen expressions is:

$$\text{cbar} = c + \frac{e^2}{\varepsilon}$$

$$\delta(\eta,\omega) = \eta\ \omega\ \ j\ \text{cbar}$$

$$kq(\eta,\omega) = \omega \sqrt{\frac{\rho q}{\text{cbar} + j\ \omega\ \eta}}$$

$$kl(\nu,\omega) = \sqrt{\frac{\omega}{j\ \nu}}$$

$$\gamma 1(\eta,h,\omega) = \exp(j\ h\ kq(\eta,\omega))$$

$$\gamma 2(\nu,h,\omega) = \exp(j\ h\ kl(\nu,\omega))$$

$$\lambda 1(\eta,h,\omega) = \gamma 1(\eta,h,\omega) - 1$$

$$\lambda 2(\eta,h,\omega) = \gamma 1(\eta,h,\omega) + 1$$

$$\lambda 3(\eta,h,\omega) = \gamma 1(\eta,h,\omega)^2 + 1$$

$$b31(\eta,h,\omega) \quad 2\ \delta(\eta,\omega)^2\ \varepsilon\ \lambda 1(\eta,h,\omega)\ \lambda 2(\eta,h,\omega)\ kq(\eta,\omega)^2$$

$$B31(\eta,h,\omega) = \omega\ \varepsilon\ b31(\eta,h,\omega)$$

$$b32(\eta,\nu,\rho l,h,\omega) = 2\ \delta(\eta,\omega)\ \varepsilon\ \lambda 3(\eta,h,\omega)\ kl(\nu,\omega)\ kq(\eta,\omega)\ \nu\ \rho l\ \omega$$

$$B32(\eta,\nu,\rho l,h,\omega) = \omega\ \varepsilon\ b32(\eta,\nu,\rho l,h,\omega)$$

$$b33(\eta,h,\omega) := \delta(\eta,\omega)\,\lambda1(\eta,h,\omega)\,kq(\eta,\omega)\begin{pmatrix}\delta(\eta,\omega)\,\varepsilon\,\lambda2(\eta,h,\omega)\,h\,kq(\eta,\omega)\\ +2\,e^2\,\lambda1(\eta,h,\omega)\end{pmatrix}$$

$$b34(\eta,v,\rho l,h,\omega) := k1(v,\omega)\begin{pmatrix}\delta(\eta,\omega)\,\varepsilon\,\lambda3(\eta,h,\omega)\,h\,kq(\eta,\omega)\\ +e^2\,\lambda1(\eta,h,\omega)\,\lambda2(\eta,h,\omega)\end{pmatrix} v\,\omega\,\rho l$$

$$\zeta l(\eta,v,\rho l,\alpha,h,\omega) := -2\,j\left(\frac{\alpha\,b34(\eta,v,\rho l,h,\omega)+b33(\eta,h,\omega)}{\alpha\,B32(\eta,v,\rho l,h,\omega)+B31(\eta,h,\omega)}\right)$$

The expression of the impedance, Zl, is

$$Zl(\eta,v,\rho l,\alpha,h,A,\omega) := \frac{1}{A}\,\zeta l(\eta,v,\rho l,\alpha,h,\omega)$$

The expression of the magnitude of Zl, |Zl|, is

$$MZl(\eta,v,\rho l,\alpha,h,A,\omega) \quad |Zl(\eta,v,\rho l,\alpha,h,A,\omega)|$$

The expression of the phase of Zl, θ_{Zl}, is

$$\theta Zl(\eta,v,\rho l,\alpha,h,\omega) \quad \operatorname{atan}\left(\frac{Im(\zeta l(\eta,v,\rho l,\alpha,h,\omega))}{Re(\zeta l(\eta,v,\rho l,\alpha,h,\omega))}\right)$$

Enter the number of experimental data points N. N := 401

The range variable, i, iterates through the N experimental data points.

$$i := 1\ldots N$$

Experimental Data for Hydrophilic Sensor in Water-Glycerol Solution

Read in data array flicAir for frequency, f, an array of 401 values of f.

$$flic := READPRN(FLIC)\ MHz$$

Read in data array MZlicAir for the magnitude of Z, |Z|, an array of 401 values of |Z|.

$$MZlic := READPRN(ZLIC)\ k\Omega$$

Read in data array θZlicAir for the phase of Z, θ_Z, an array of 401 values of θ_Z.

$$\theta Zlic := READPRN(THLIC)$$

Experimental Data for Hydrophobic Sensor in Water-Glycerol Solution

Read in data array flicAir for frequency, f, an array of 401 values of f.

$$fbic = READPRN(FBIC)\ MHz$$

Read in data array MZlicAir for the magnitude of Z, |Z|, an array of 401 values of |Z|.

$$MZbic = READPRN(ZBIC)\ k\Omega$$

Read in data array θZlicAir for the phase of Z, θ_Z, an array of 401 values of θ_Z.

$$\theta Zbic = READPRN(THBIC)$$

Using the above frequency data flic and fbic, compute the corresponding angular frequency data ωlic and ωbic.

$$\omega lic = 2\pi\, flic$$

$$\omega bic = 2\pi \cdot fbic$$

For each i = 1,...,401 and klic = 1,...,11 compute the experimental data of the impedance, Z, using the exponential form for the complex number $Z = |Z|\exp(j\theta_Z)$ for the hydrophilic sensor in water-glycerol solution.

$$klic = 1..11$$

$$Zlic_{i,klic} = MZlic_{i,klic}\cdot \exp\left(j\cdot \theta Zlic_{i,klic}\ deg\right)$$

For each i = 1,...,401 and kbic = 1,...,7 compute the experimental data of the impedance, Z, using the exponential form for the complex number $Z = |Z|\exp(j\theta_Z)$ for the hydrophobic sensor in water-glycerol solution.

$$kbic = 1..7$$

$$Zbic_{i,kbic} = MZbic_{i,kbic}\cdot \exp\left(j\ \theta Zbic_{i,kbic}\ deg\right)$$

For each water-glycerol concentration, the above experimental data for |Z| and θ_Z consists of 401 points measured at 401 equally spaced frequencies. At each concentration level, the resonant region of the quartz sensor was modified so as to achive a full characterization of the quartz sensor.

Data for Hydrophilic and Hydrophobic Sensor

Enter numerical value for the mass density of quartz.

$$\rho q := 2649 \frac{kg}{m^3}$$

Enter numerical value for the elastic coefficient of quartz.

$$c := 29.01 \cdot 10^9 \frac{newton}{m^2}$$

Enter numerical value for the best-fit piezoelectric stress coefficient of quartz.

$$e := 0.0798007 \frac{coul}{m^2}$$

Enter numerical values for the best-fit viscoelastic coefficient of quartz.

$$\eta lic\_fit := 0.0083762\ newton \frac{sec}{m^2}$$

$$\eta bic\_fit := 0.2344606\ newton \frac{sec}{m^2}$$

Enter numerical values for the best-fit thickness.

$$hlic\_fit := 183.8790101\ \mu m$$

$$hbic\_fit := 183.9794329\ \mu m$$

Enter numerical value for the dielectric constant of quartz.

$$\varepsilon := 39.82 \cdot 10^{-12} \frac{coul}{volt\ m}$$

Water-Glycerol Solution for Hydrophilic Sensor

Read in data array vlic for kinematic viscosity, ν, an array of eleven values of ν.

$$vlic := READPRN(NULIC)\ cS$$

Read in data array ρlic for kinematic viscosity, ρ, an array of eleven values of ρ.

$$\rho lic := READPRN(RHOLIC) \frac{kg}{liter}$$

Water-Glycerol Solution for Hydrophobic Sensor

Read in data array vbic for kinematic viscosity, v, an array of eleven values of v.

$$vbic := READPRN(NUBIC)\ cS$$

Read in data array ρbic for kinematic viscosity, ρ, an array of eleven values of ρ.

$$\rho bic := READPRN(RHOBIC)\cdot\frac{kg}{liter}$$

Hydrophilic Sensor

For each i = 1,...,401 and klic = 1,...,11 compute the four complex-valued functions B31, B32, b33 and b34. The two-dimensional arrays B31_lic, B32_lic, b33_lic and b34_lic store the 401x11 values of the complex-valued functions B31, B32, b33 and b34 respectively.

$$B31\_lic_{i,klic} := B31\left[\eta lic\_fit, hlic\_fit, \left(\omega lic^{<klic>}\right)_i\right]$$

$$B32\_lic_{i,klic} := B32\left[\eta lic\_fit, vlic_{klic}, \rho lic_{klic}, hlic\_fit, \left(\omega lic^{<klic>}\right)_i\right]$$

$$b33\_lic_{i,klic} := b33\left[\eta lic\_fit, hlic\_fit, \left(\omega lic^{<klic>}\right)_i\right]$$

$$b34\_lic_{i,klic} := b34\left[\eta lic\_fit, vlic_{klic}, \rho lic_{klic}, hlic\_fit, \left(\omega lic^{<klic>}\right)_i\right]$$

$$\zeta lic(\alpha,k,i) := -2\cdot\left(\frac{\alpha\ b34\_lic_{i,k} + b33\_lic_{i,k}}{\alpha\ B32\_lic_{i,k} + B31\_lic_{i,k}}\right)$$

From the above expression for ζlic, the expression for the impedance, fZlic, is.

$$fZlic(\alpha,A,k,i) := \frac{1}{A}\cdot\zeta lic(\alpha,k,i)$$

The expressions for the magnitude of fZlic, |fZlic|, and the phase of fZlic, $f\theta_Z lic$, are.

$$MfZlic(\alpha,A,k,i) := \left|fZlic(\alpha,A,k,i)\right|$$

$$f\theta Zlic(\alpha,k,i) := atan\left(\frac{Im(\zeta lic(\alpha,k,i))}{Re(\zeta lic(\alpha,k,i))}\right)$$

Hydrophobic Sensor

For each ı = 1,...,401 and kbıc = 1,...,7 compute the four complex-valued functions B31, B32, b33 and b34. The two-dimensional arrays B31_bic, B32_bıc, b33_bıc and b34_bıc store the 401x7 values of the complex-valued functions B31, B32, b33 and b34 respectively.

$$B31\_bic_{ı,kbıc} := B31\left[\eta bıc\_fit, hbıc\_fit, \left(\omega bıc^{\langle kbıc\rangle}\right)_ı\right]$$

$$B32\_bıc_{ı,kbıc} := B32\left[\eta bıc\_fit, vbıc_{kbıc}, \rho bıc_{kbıc}, hbıc\_fit, \left(\omega bıc^{\langle kbıc\rangle}\right)_ı\right]$$

$$b33\_bic_{ı,kbıc} := b33\left[\eta bic\_fit, hbıc\_fit, \left(\omega bıc^{\langle kbıc\rangle}\right)_ı\right]$$

$$b34\_bıc_{ı,kbıc} := b34\left[\eta bic\_fit, vbıc_{kbıc}, \rho bıc_{kbıc}, hbıc\_fit, \left(\omega bıc^{\langle kbıc\rangle}\right)_ı\right]$$

$$\zeta bıc(\alpha,k,ı) := -2\,j\left(\frac{\alpha\, b34\_bıc_{ı,k} + b33\_bıc_{ı,k}}{\alpha\cdot B32\_bıc_{ı,k} + B31\_bıc_{ı,k}}\right)$$

From the above expression for ζbıc, the expression for the ımpedance, fZbıc, ıs.

$$fZbıc(\alpha,A,k,ı) := \frac{1}{A}\,\zeta bıc(\alpha,k,ı)$$

The expressions for the magnitude of fZbıc, |fZbıc|, and the phase of fZbıc, $f\theta_Z bic$, are.

$$MfZbıc(\alpha,A,k,ı) := \left|fZbıc(\alpha,A,k,ı)\right|$$

$$f\theta Zbıc(\alpha,k,ı) := \operatorname{atan}\left(\frac{Im(\zeta bıc(\alpha,k,ı))}{Re(\zeta bıc(\alpha,k,ı))}\right)$$

Hydrophilic Sensor

The following Sum Of Squares Of Errors, SSElic(α,A,k), will be used in the fitting of the experimental data to the theoretical complex-valued expression of the ımpedance, Z, given by the function fZlıc. The results from the fitting procedure will consist of eleven best-fit values for α and A, one value of α and A for each concentration of glycerol ın water.

$$SSElıc(\alpha,A,k) := \frac{1}{N}\sum_ı \left|\left|\frac{\left(Zlıc^{\langle k\rangle}\right)_ı}{k\Omega} - \frac{fZlıc(\alpha,A,k,ı)}{k\Omega}\right|\right|^2$$

Hydrophobic Sensor

The following Sum Of Squares Of Errors, SSEbic(α,A,k), will be used in the fitting of the experimental data to the theoretical complex-valued expression of the impedance, Z, given by the function fZbic. The results from the fitting procedure will consist of seven values best-fit for α and A, one value of α and A for each concentration of glycerol in water.

$$SSEbic(\alpha,A,k) := \frac{1}{N}\sum_{i}\left|\left|\frac{(Zbic^{<k>})_i}{k\Omega} - \frac{fZbic(\alpha,A,k,i)}{k\Omega}\right|\right|^2$$

Hydrophilic Sensor

Determination of α in pure water.

Enter guess values for α and A.

$\alpha 1\_guess := 3.76 + 2.30j$

$A1\_guess := 0.4\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEhc(\alpha 1\_guess, A1\_guess, 1) = 0$$

$$l := 1$$

$$\begin{pmatrix} \alpha 1\_fit \\ A1\_fit \end{pmatrix} := Minerr(\alpha 1\_guess, A1\_guess)$$

The result of the solve block, α1_fit and A1_fit, is.

$$\alpha 1\_fit = 3.774 + 2.299i$$

$$A1\_fit = 0.4115 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSElic(α1_fit,A1_fit,1).

$$ERR = 0.131$$

Hydrophilic Sensor

Determination of α in 0.1 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 2\_guess = 2.6 + 1.3\,j$

$A2\_guess = 0.39\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSElic(\alpha 2\_guess, A2\_guess, 2) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha 2\_fit \\ A2\_fit \end{pmatrix} = Minerr(\alpha 2\_guess, A2\_guess)$$

The result of the solve block, α2_fit and A2_fit, is.

$$\alpha 2\_fit = 2.631 + 1.246i$$

$$A2\_fit = 0.3911 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSElic(α2_fit,A2_fit,2).

$$ERR = 0.088$$

Hydrophilic Sensor

Determination of α in 0.2 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 3\_guess := 1.9 + 0.6\,i$

$A3\_guess := 0.34\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSElic(\alpha 3\_guess, A3\_guess, 3) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha 3\_fit \\ A3\_fit \end{pmatrix} := Minerr(\alpha 3\_guess, A3\_guess)$$

The result of the solve block, α3_fit and A3_fit, is.

$$\alpha 3\_fit = 1.9145 + 0.6513\,i$$

$$A3\_fit = 0.3494 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSElic(α3_fit,A3_fit,3).

$$ERR = 0.043$$

Hydrophilic Sensor

Determination of α in 0.3 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 4\_guess = 1.6 + 0.4j$

$A4\_guess = 0.34\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEllc(\alpha 4\_guess, A4\_guess, 4) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha 4\_fit \\ A4\_fit \end{pmatrix} = Minerr(\alpha 4\_guess, A4\_guess)$$

The result of the solve block, α4_fit and A4_fit, is.

$$\alpha 4\_fit = 1.68 + 0.3999i$$

$$A4\_fit = 0.3509 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEllc(α4_fit,A4_fit,4).

$$ERR = 0.036$$

Hydrophilic Sensor

Determination of α in 0.4 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 5\_guess = 1.4 + 0.2j$

$A5\_guess = 0.34\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEllc(\alpha 5\_guess, A5\_guess, 5) = 0$$

$$I = 1$$

$$\begin{pmatrix} \alpha 5\_fit \\ A5\_fit \end{pmatrix} = Minerr(\alpha 5\_guess, A5\_guess)$$

The result of the solve block, $\alpha 5\_fit$ and A5_fit, is.

$$\alpha 5\_fit = 1.432 + 0.213i$$

$$A5\_fit = 0.3433 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEllc(α5_fit,A5_fit,5).

$$ERR = 0.012$$

Hydrophilic Sensor

Determination of α in 0.5 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 6\_guess = 1.3 + 0.1j$

$A6\_guess = 0.33\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEhc(\alpha 6\_guess, A6\_guess, 6) = 0$$

$$l = 1$$

$$\begin{pmatrix} \alpha 6\_fit \\ A6\_fit \end{pmatrix} = Minerr(\alpha 6\_guess, A6\_guess)$$

The result of the solve block, α6_fit and A6_fit, is.

$$\alpha 6\_fit = 1.316 + 0.118i$$

$$A6\_fit = 0.3316 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEhc(α6_fit, A6_fit, 6).

$$ERR = 0.003$$

Hydrophilic Sensor

Determination of α in 0.6 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 7\_guess = 1.1 + 0.07i$

$A7\_guess = 0.32\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEhc(\alpha 7\_guess, A7\_guess, 7) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha 7\_fit \\ A7\_fit \end{pmatrix} = Minerr(\alpha 7\_guess, A7\_guess)$$

The result of the solve block, α7_fit and A7_fit, is.

$$\alpha 7\_fit = 1.172 + 0.069i$$

$$A7\_fit = 0.3271 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEhc(a7_fit,A7_fit,7).

$$ERR = 0.001$$

Hydrophilic Sensor

Determination of α in 0.7 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 8\_guess := 0.92 + 0.01j$

$A8\_guess := 0.33\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEllc(\alpha 8\_guess, A8\_guess, 8) = 0$$

$$l = 1$$

$$\begin{pmatrix} \alpha 8\_fit \\ A8\_fit \end{pmatrix} := Minerr(\alpha 8\_guess, A8\_guess)$$

The result of the solve block, $\alpha 8\_fit$ and A8_fit, is.

$$\alpha 8\_fit = 0.937 + 0.016i$$

$$A8\_fit = 0.3255 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEllc($\alpha 8\_fit$,A8_fit,8).

$$ERR = 0.002$$

Hydrophilic Sensor

Determination of α in 0.8 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 9\_guess := 0.8 - 0.003j$

$A9\_guess := 0.32\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEhc(\alpha 9\_guess, A9\_guess, 9) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha 9\_fit \\ A9\_fit \end{pmatrix} := Minerr(\alpha 9\_guess, A9\_guess)$$

The result of the solve block, α9_fit and A9_fit, is.

$$\alpha 9\_fit = 0.8935 - 0.0044i$$

$$A9\_fit = 0.3242 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEhc(α9_fit,A9_fit,9).

$$ERR = 0.002$$

Hydrophilic Sensor

Determination of α in 0.9 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha 10\_guess := \begin{pmatrix} 0.8 \\ 0.04 \end{pmatrix}$

$A10\_guess := 0.32\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSElic(\alpha 10\_guess, A10\_guess, 10) = 0$$

$$l := 1$$

$$\begin{pmatrix} \alpha 10\_fit \\ A10\_fit \end{pmatrix} := Minerr(\alpha 10\_guess, A10\_guess)$$

The result of the solve block, $\alpha 10\_fit$ and $A10\_fit$, is.

$$\alpha 10\_fit = 0.842 - 0.048i$$

$$A10\_fit = 0.3236 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSElic($\alpha 10\_fit, A10\_fit, 10$).

$$ERR = 0.003$$

Hydrophilic Sensor

Determination of α in pure glycerol.

Enter guess values for α and A.

$\alpha 11\_guess := 0.8 - 0.06\,j$

$A11\_guess := 0.32\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEhc(\alpha 11\_guess, A11\_guess, 11) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha 11\_fit \\ A11\_fit \end{pmatrix} := Minerr(\alpha 11\_guess, A11\_guess)$$

The result of the solve block, α11_fit and A11_fit, is.

$$\alpha 11\_fit = 0.83 - 0.066\,i$$

$$A11\_fit = 0.3221 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEhc(α11_fit,A11_fit,11).

$$ERR = 0.001$$

Hydrophobic Sensor

Determination of α in pure water.

Enter guess values for α and A.

$\alpha\alpha 1\_guess := 49 + 23j$

$AA1\_guess := 0.36\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEbic(\alpha\alpha 1\_guess, AA1\_guess, 1) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha\alpha 1\_fit \\ AA1\_fit \end{pmatrix} := Minerr(\alpha\alpha 1\_guess, AA1\_guess)$$

The result of the solve block, $\alpha\alpha 1\_fit$ and AA1_fit, is.

$$\alpha\alpha 1\_fit = 3.02 + 1.446i$$

$$AA1\_fit = 0.368 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEbic($\alpha\alpha 1$ fit,AA1_fit,1).

$$ERR = 0.056$$

Hydrophobic Sensor

Determination of α in 0.1 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha\alpha 2\_guess = 3.2 + 1.2j$

$AA2\_guess = 0.37\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEbic(\alpha\alpha 2\_guess, AA2\_guess, 2) = 0$$

$$I = 1$$

$$\begin{pmatrix} \alpha\alpha 2\_fit \\ AA2\_fit \end{pmatrix} = Minerr(\alpha\alpha 2\_guess, AA2\_guess)$$

The result of the solve block, αα2_fit and AA2_fit, is.

$$\alpha\alpha 2\_fit = 2.192 + 0.795i$$

$$AA2\_fit = 0.3728 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEbic(αα2_fit,AA2_fit,2).

$$ERR = 0.048$$

Hydrophobic Sensor

Determination of α in 0.2 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha\alpha 3\_guess := 2.3 + 0.7j$

$AA3\_guess := 0.35\,cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEbic(\alpha\alpha 3\_guess, AA3\_guess, 3) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha\alpha 3\_fit \\ AA3\_fit \end{pmatrix} := Minerr(\alpha\alpha 3\_guess, AA3\_guess)$$

The result of the solve block, $\alpha\alpha 3\_fit$ and AA3_fit, is.

$$\alpha\alpha 3\_fit = 1.707 + 0.417i$$

$$AA3\_fit = 0.3581 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEbic($\alpha\alpha 3$ _fit,AA3_fit,3).

$$ERR = 0.026$$

Hydrophobic Sensor

Determination of α in 0.4 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha\alpha4\_guess = 1.3 + 0.1\,j$

$AA4\_guess = 0.34\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEbic(\alpha\alpha4\_guess, AA4\_guess, 4) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha\alpha4\_fit \\ AA4\_fit \end{pmatrix} = Minerr(\alpha\alpha4\_guess, AA4\_guess)$$

The result of the solve block, αα4_fit and AA4_fit, is.

$$\alpha\alpha4\_fit = 1.135 + 0.037i$$

$$AA4\_fit = 0.341 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEbic(αα4_fit,AA4_fit,4).

$$ERR = 0.005$$

Hydrophobic Sensor

Determination of α in 0.6 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha\alpha5\_guess := 1.1 \cdot 9.3 \cdot 10^{-4}$

$AA5\_guess := 0.35\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEbic(\alpha\alpha5\_guess, AA5\_guess, 5) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha\alpha5\_fit \\ AA5\_fit \end{pmatrix} := Minerr(\alpha\alpha5\_guess, AA5\_guess)$$

The result of the solve block, $\alpha\alpha5\_fit$ and $AA5\_fit$, is.

$$\alpha\alpha5\_fit = 1.043 - 0.053i$$

$$AA5\_fit = 0.3529 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEbic($\alpha\alpha5$ _fit,AA5_fit,5).

$$ERR = 0.011$$

Hydrophobic Sensor

Determination of α in 0.8 molar water-glycerol solution.

Enter guess values for α and A.

$\alpha\alpha 6\_guess = 0.8 - 0.05\,i$

$AA6\_guess = 0.33\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEbic(\alpha\alpha 6\_guess, AA6\_guess, 6) = 0$$

$$I = 1$$

$$\begin{pmatrix} \alpha\alpha 6\_fit \\ AA6\_fit \end{pmatrix} = Minerr(\alpha\alpha 6\_guess, AA6\_guess)$$

The result of the solve block, αα6_fit and AA6_fit, is.

$$\alpha\alpha 6\_fit = 0.801 - 0.073\,i$$

$$AA6\_fit = 0.3345 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEbic(αα6_fit,AA6_fit,6).

$$ERR = 0.013$$

Hydrophobic Sensor

Determination of α in pure glycerol.

Enter guess values for α and A.

$\alpha\alpha7\_guess := 0.7 \cdot (0.1)^1$

$AA7\_guess := 0.32\ cm^2$

---------- Mathcad Solve Block ----------

Given

$$SSEbic(\alpha\alpha7\_guess, AA7\_guess, 7) = 0$$

$$1 = 1$$

$$\begin{pmatrix} \alpha\alpha7\_fit \\ AA7\_fit \end{pmatrix} := Minerr(\alpha\alpha7\_guess, AA7\_guess)$$

The result of the solve block, αα7_fit and AA7_fit, is.

$$\alpha\alpha7\_fit = 0.7703 - 0.1344i$$

$$AA7\_fit = 0.3399 \cdot cm^2$$

Compute the residual error, ERR, given by ERR=SSEbic(αα7_fit,AA7_fit,7).

$$ERR = 0.03$$

Data for Hydrophilic and Hydrophobic Sensor

$$\alpha\_hydrophilic := \begin{vmatrix} \alpha1\_fit \\ \alpha2\_fit \\ \alpha3\_fit \\ \alpha4\_fit \\ \alpha5\_fit \\ \alpha6\_fit \\ \alpha7\_fit \\ \alpha8\_fit \\ \alpha9\_fit \\ \alpha10\_fit \\ \alpha11\_fit \end{vmatrix} \qquad A\_hydrophilic := \begin{bmatrix} A1\_fit \\ A2\_fit \\ A3\_fit \\ A4\_fit \\ A5\_fit \\ A6\_fit \\ A7\_fit \\ A8\_fit \\ A9\_fit \\ A10\_fit \\ A11\_fit \end{bmatrix}$$

Store the data for α_hydrophilic and A_hydrophilic in the data files ALPLIC.PRN and ALIC.PRN.

$$\text{WRITEPRN(ALPLIC)} \quad \alpha\_\text{hydrophilic}$$

$$\text{WRITEPRN(ALIC)} \quad \frac{\text{A\_hydrophilic}}{\text{cm}^2}$$

For each i = 1,...,401 and klic = 1,...,11 compute the magnitude and phase of Z.

$$\text{MZlic\_fit}_{i,klic} = \text{MZl}\left(\eta\text{lic\_fit}, \nu\text{lic}_{klic}, \rho\text{lic}_{klic}, \alpha\_\text{hydrophilic}_{klic}, \text{hlic\_fit}, \text{A\_hydrophilic}_{klic}, \left(\omega\text{lic}^{\cdot klic}\right)_i\right)$$

$$\theta\text{Zlic\_fit}_{i,klic} = \theta\text{Zl}\left(\eta\text{lic\_fit}, \nu\text{lic}_{klic}, \rho\text{lic}_{klic}, \alpha\_\text{hydrophilic}_{klic}, \text{hlic\_fit}, \left(\omega\text{lic}^{\cdot klic}\right)_i\right)$$

Store the data for MZlic_fit and θZlic_fit in the data files MZLICFIT.PRN and TZLICFIT.PRN

$$\text{WRITEPRN(MZLICFIT)} \quad \frac{\text{MZlic\_fit}}{\text{k}\Omega}$$

$$\text{WRITEPRN(TZLICFIT)} \quad \frac{\theta\text{Zlic\_fit}}{\text{deg}}$$

$$\alpha\_\text{hydrophobic} \quad \begin{bmatrix} \alpha\alpha1\_\text{fit} \\ \alpha\alpha2\_\text{fit} \\ \alpha\alpha3\_\text{fit} \\ \alpha\alpha4\_\text{fit} \\ \alpha\alpha5\_\text{fit} \\ \alpha\alpha6\_\text{fit} \\ \alpha\alpha7\_\text{fit} \end{bmatrix} \qquad \text{A\_hydrophobic} \quad \begin{bmatrix} \text{AA1\_fit} \\ \text{AA2\_fit} \\ \text{AA3\_fit} \\ \text{AA4\_fit} \\ \text{AA5\_fit} \\ \text{AA6\_fit} \\ \text{AA7\_fit} \end{bmatrix}$$

Store the data for α_hydrophobic and A_hydrophobic in the data files ALPBIC.PRN and ABIC.PRN.

$$\text{WRITEPRN(ALPBIC)} = \alpha\_\text{hydrophobic} \qquad \text{WRITEPRN(ABIC)} \quad \frac{\text{A\_hydrophobic}}{\text{cm}^2}$$

For each i = 1,...,401 and kbic = 1,...,7 compute the magnitude and phase of Z.

$$\text{MZbic\_fit}_{i,kbic} = \text{MZl}\left(\eta\text{bic\_fit}, \nu\text{bic}_{kbic}, \rho\text{bic}_{kbic}, \alpha\_\text{hydrophobic}_{kbic}, \text{hbic\_fit}, \text{A\_hydrophobic}_{kbic}, \left(\omega\text{bic}^{\cdot kbic}\right)_i\right)$$

$$\theta\text{Zbic\_fit}_{i,kbic} = \theta\text{Zl}\left(\eta\text{bic\_fit}, \nu\text{bic}_{kbic}, \rho\text{bic}_{kbic}, \alpha\_\text{hydrophobic}_{kbic}, \text{hbic\_fit}, \left(\omega\text{bic}^{\cdot kbic}\right)_i\right)$$

APPENDIX 7 Plots of Interfacial Slip Parameter, Mathcad Program DOC4.MCD

Data Analysis of Interfacial Slip Parameter, α, Versus Kinematic Viscosity, ν, and Mole Fraction, M_f.

The power law model given by $F(a,b,c,x)=ax^b+c$ will be fitted to the experimental data consisting of the real part of α, α_{Re}, imaginary part of α, α_{Im}, the magnitude of α, $|\alpha|$, and the phase of α, θ_α versus kinematic viscosity, ν.

The exponential law model given by $G(a,b,c,x)=ae^{bx}+c$ will be fitted to the experimental data consisting of the real part of α, α_{Re}, imaginary part of α, α_{Im}, the magnitude of α, $|\alpha|$, and the phase of α, θ_α versus mole fraction, M_f.

Hydrophilic Sensor

Read in data array αlic for interfacial slip parameter, α, an array of eleven values of α.

αlic := READPRN(ALPLIC)

αlic := αlic$^{\langle 1\rangle}$ + i αlic$^{\langle 2\rangle}$

Read in data array νlic for kinematic viscosity, ν, an array of eleven values of ν.

νlic := READPRN(NULIC) cS

Read in data array MFlic for mole fraction, M_f, an array of eleven values of M_f.

MFlic := READPRN(MOLLIC)

Hydrophobic Sensor

Read in data array αbic for interfacial slip parameter, α, an array of seven values of α.

αbic = READPRN(ALPBIC)

$\alpha bic = \alpha bic^{\langle 1 \rangle} + j\,\alpha bic^{\langle 2 \rangle}$

Read in data array νbic for kinematic viscosity, ν, an array of seven values of ν.

νbic = READPRN(NUBIC)·cS

Read in data array MFbic for mole fraction, M_f, an array of seven values of M_f.

MFbic = READPRN(MOLBIC)

Hydrophilic Sensor

The arrays αRelic, αImlic, αMaglic and θαlic store respectively α_{Re}, α_{Im}, $|\alpha|$ and θ_α. Compute α_{Re}, α_{Im}, $|\alpha|$ and θ_α.

$$\alpha Relic \quad Re(\alpha lic)$$

$$\alpha Imlic \quad Im(\alpha lic)$$

$$\alpha Maglic \quad |\alpha lic|$$

$$\theta\alpha lic \quad \frac{\operatorname{atan}\left(\frac{\alpha Imlic}{\alpha Relic}\right)}{deg}$$

The subscript klic takes on integral values from 1 through 11 inclusive. Each value of klic corresponds to a different concentration of glycerol in water.

Hydrophilic Sensor

klic = 1 corresponds to pure water.
klic = 2 corresponds to 0.1 molar water-glycerol solution.
klic = 3 corresponds to 0.2 molar water-glycerol solution.
klic = 4 corresponds to 0.3 molar water-glycerol solution.
klic = 5 corresponds to 0.4 molar water-glycerol solution.
klic = 6 corresponds to 0.5 molar water-glycerol solution.
klic = 7 corresponds to 0.6 molar water-glycerol solution.
klic = 8 corresponds to 0.7 molar water-glycerol solution.
klic = 9 corresponds to 0.8 molar water-glycerol solution.
klic = 10 corresponds to 0.9 molar water-glycerol solution.
klic = 11 corresponds to pure glycerol.

Nlic corresponds to the number of experimental data points given by

$$Nlic := 11$$

$$klic := 1 \ldots Nlic$$

Hydrophobic Sensor

The arrays αRelic, αImbic, αMagbic and θαbic store respectively α_{Re}, α_{Im}, $|\alpha|$ and θ_{α}. Compute α_{Re}, α_{Im}, $|\alpha|$ and θ_{α}.

$$\alpha Rebic := Re(\alpha bic)$$

$$\alpha Imbic := Im(\alpha bic)$$

$$\alpha Magbic := \overrightarrow{|\alpha bic|}$$

$$\theta\alpha bic := \frac{\overrightarrow{atan\left(\frac{\alpha Imbic}{\alpha Rebic}\right)}}{deg}$$

The subscript kbic takes on integral values from 1 through 7 inclusive. Each value of kbic corresponds to a different concentration of glycerol in water.

Hydrophobic Sensor

kb1c = 1 corresponds to pure water.
kb1c = 2 corresponds to 0.1 molar water-glycerol solution.
kb1c = 3 corresponds to 0.2 molar water-glycerol solution.
kb1c = 4 corresponds to 0.4 molar water-glycerol solution.
kbic = 5 corresponds to 0.6 molar water-glycerol solution.
kbic = 6 corresponds to 0.8 molar water-glycerol solution.
kl1c = 7 corresponds to pure glycerol.

Nb1c corresponds to the number of experimental data points given by

$$Nb1c = 7$$

$$kbic = 1 \quad Nb1c$$

For the hydrophilic and hydrophobic sensors, the mathematical model $F(a,b,c,x) = ax^b+c$ will be used to fit the experimental data consisting of α_{Re}, α_{Im}, $|\alpha|$ and θ_α versus kinematic viscosity, ν. For the experimental data consisting of α_{Re}, α_{Im}, $|\alpha|$ and θ_α versus mole fraction, M_f, the mathematical model $G(a,b,c,x) = ae^{bx}+c$ will be used.

The following Sum Of Squares Of Errors will be used in the non-linear curve-fitting process SSE1lic(a,b,c),...,SSE8lic(a,b,c) and SSE1b1c(a,b,c),...,SSE8b1c(a,b,c) .

Power Law Model

$$F(a,b,c,x) = a\,x^b + c$$

Exponential Law Model

$$G(a,b,c,x) = a\,e^{b\,x} + c$$

Hydrophilic Sensor

Non-Linear Regression Analysis of α_{Re} vs V

$$SSEllic(a,b,c) := \frac{1}{Nllc}\sum_{klic}\left(\alpha Relic_{klic} - F\left(a,b,c,\frac{vlic_{klic}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

allc_guess := 1

bllc_guess := 0.1

cllc_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSEllic(allc\_guess, bllc\_guess, cllc\_guess) = 0$$

$$l := 1$$

$$l := 1$$

$$\begin{pmatrix} allc\_fit \\ bllc\_fit \\ cllc\_fit \end{pmatrix} := Minerr(allc\_guess, bllc\_guess, cllc\_guess)$$

---

allc_fit = 3.0298

bllc_fit = -0.4182

cllc_fit = 0.7142

Compute the residual error, ERR, given by ERR = SSEllic(allc_fit,bllc_fit,cllc_fit).

ERR = 0.0036

Hydrophilic Sensor

Non-Linear Regression Analysis of α_{Im} vs ν

$$SSE2hc(a,b,c) := \frac{1}{Nhc}\cdot\sum_{khc}\left(\alpha Imhc_{khc} - F\left(a,b,c,\frac{\nu hc_{khc}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

a2hc_guess := 1

b2hc_guess := -0.1

c2hc_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE2hc(a2hc\_guess, b2hc\_guess, c2hc\_guess) = 0$$

$$l = 1$$

$$l = 1$$

$$\begin{pmatrix} a2hc\_fit \\ b2hc\_fit \\ c2hc\_fit \end{pmatrix} := Minerr(a2hc\_guess, b2hc\_guess, c2hc\_guess)$$

$$a2hc\_fit = 2.3904$$

$$b2hc\_fit = -0.5718$$

$$c2hc\_fit = 0.0838$$

Compute the residual error, ERR, given by ERR = SSE2lic(a2lic_fit,b2lic_fit,c2lic_fit).

$$ERR = 2.4244 \cdot 10^{-4}$$

Hydrophilic Sensor

Non-Linear Regression Analysis of |α| vs v

$$SSE3lic(a,b,c) := \frac{1}{Nlic}\cdot\sum_{klic}\left(\alpha Maglic_{klic} - F\left(a,b,c,\frac{vlic_{klic}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

a3lic_guess := 1

b3lic_guess := 0.1

c3lic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE3lic(a3lic\_guess,b3lic\_guess,c3lic\_guess)=0$$

$$1=1$$

$$1=1$$

$$\begin{pmatrix} a3lic\_fit \\ b3lic\_fit \\ c3lic\_fit \end{pmatrix} := Minerr(a3lic\_guess,b3lic\_guess,c3lic\_guess)$$

---

a3lic_fit = 3.6292

b3lic_fit = -0.484

c3lic_fit = 0.7619

Compute the residual error, ERR, given by ERR = SSE3lic(a3lic_fit,b3lic_fit,c3lic_fit).

ERR = 0.0041

Hydrophilic Sensor

Non-Linear Regression Analysis of θ_α vs v

$$SSE4lic(a,b,c) := \frac{1}{Nlic}\cdot\sum_{klic}\left(\theta\alpha lic_{klic}\cdot deg - F\left(a,b,c,-\frac{vlic_{klic}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

a4lic_guess := 1

b4lic_guess := -0.01

c4lic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE4lic(a4lic\_guess, b4lic\_guess, c4lic\_guess) = 0$$

$$l := 1$$

$$l := 1$$

$$\begin{pmatrix} a4lic\_fit \\ b4lic\_fit \\ c4lic\_fit \end{pmatrix} := Minerr(a4lic\_guess, b4lic\_guess, c4lic\_guess)$$

$$a4lic\_fit = 0.8113$$

$$b4lic\_fit = -0.2101$$

$$c4lic\_fit = 0.2303$$

Compute the residual error, ERR, given by ERR = SSE4lic(a4lic_fit,b4lic_fit,c4lic_fit).

$$ERR = 3.5861\cdot10^{-4}$$

Hydrophobic Sensor

Non-Linear Regression Analysis of α_{Re} vs v

$$SSE1bic(a,b,c) := \frac{1}{Nbic}\sum_{kbic}\left(\alpha Rebic_{kbic} - F\left(a,b,c,\frac{vbic_{kbic}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

a1bic_guess := 1

b1bic_guess := 0.1

c1bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE1bic(a1bic\_guess, b1bic\_guess, c1bic\_guess) = 0$$

$$1 = 1$$

$$1 = 1$$

$$\begin{pmatrix} a1bic\_fit \\ b1bic\_fit \\ c1bic\_fit \end{pmatrix} := Minerr(a1bic\_guess, b1bic\_guess, c1bic\_guess)$$

---

a1bic_fit = 2.3621

b1bic_fit = -0.4143

c1bic_fit = 0.663

Compute the residual error, ERR, given by ERR = SSE1bic(a1bic_fit,b1bic_fit,c1bic_fit).

ERR = 0.0013

Hydrophobic Sensor

Non-Linear Regression Analysis of α_{Im} vs v

$$SSE2bic(a,b,c) := \frac{1}{Nbic}\cdot\sum_{kbic}\left(\alpha Imbic_{kbic} - F\left(a,b,c,\frac{vbic_{kbic}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

a2bic_guess := 1

b2bic_guess := -0.1

c2bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE2bic(a2bic\_guess, b2bic\_guess, c2bic\_guess) = 0$$

$$l := 1$$

$$l := 1$$

$$\begin{pmatrix} a2bic\_fit \\ b2bic\_fit \\ c2bic\_fit \end{pmatrix} := Minerr(a2bic\_guess, b2bic\_guess, c2bic\_guess)$$

---

a2bic_fit = 1.6247

b2bic_fit = 0.5201

c2bic_fit = -0.1664

Compute the residual error, ERR, given by ERR = SSE2bic(a2bic_fit,b2bic_fit,c2bic_fit).

$$ERR = 4.9071\cdot10^{-4}$$

Hydrophobic Sensor

Non-Linear Regression Analysis of |α| vs v

$$SSE3bic(a,b,c) := \frac{1}{Nbic}\sum_{kbic}\left(\alpha Magbic_{kbic} - F\left(a,b,c,\frac{vbic_{kbic}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

a3bic_guess := 1

b3bic_guess := 0.1

c3bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE3bic(a3bic\_guess, b3bic\_guess, c3bic\_guess) = 0$$

$$1 = 1$$

$$1 = 1$$

$$\begin{pmatrix} a3bic\_fit \\ b3bic\_fit \\ c3bic\_fit \end{pmatrix} := Minerr(a3bic\_guess, b3bic\_guess, c3bic\_guess)$$

---

a3bic_fit = 2.6548

b3bic_fit = -0.4648

c3bic_fit = 0.6995

Compute the residual error, ERR, given by ERR = SSE3bic(a3bic_fit,b3bic_fit,c3bic_fit).

ERR = 0.0014

Hydrophobic Sensor

Non-Linear Regression Analysis of θ_α vs v

$$SSE4bic(a,b,c) := \frac{1}{Nbic}\cdot\sum_{kbic}\left(\theta\alpha bic_{kbic}\cdot deg - F\left(a,b,c,\frac{vbic_{kbic}}{cS}\right)\right)^2$$

Enter guess values for a,b and c.

a4bic_guess := 1

b4bic_guess := -0.1

c4bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE4bic(a4bic\_guess, b4bic\_guess, c4bic\_guess) = 0$$

$$l = 1$$

$$l = 1$$

$$\begin{pmatrix} a4bic\_fit \\ b4bic\_fit \\ c4bic\_fit \end{pmatrix} := Minerr(a4bic\_guess, b4bic\_guess, c4bic\_guess)$$

---

a4bic_fit = 0.8075

b4bic_fit = 0.2057

c4bic_fit = -0.3292

Compute the residual error, ERR, given by ERR = SSE4bic(a4bic_fit,b4bic_fit,c4bic_fit).

$$ERR = 6.272\cdot10^{-4}$$

Hydrophilic Sensor

Non-Linear Regression Analysis of α_{Re} vs M_f

$$SSE5hc(a,b,c) := \frac{1}{Nhc}\sum_{khc}\left(\alpha Rehc_{khc} - G\left(a,b,c,MFhc_{khc}\right)\right)^2$$

Enter guess values for a,b and c.

a5hc_guess := 1

b5hc_guess := 2

c5hc_guess := 1

------ ------------------- Mathcad Solve Block ------------------------

Given

$$SSE5hc(a5hc\_guess,b5hc\_guess,c5hc\_guess)=0$$

$$1=1$$

$$1=1$$

$$\begin{pmatrix} a5hc\_fit \\ b5hc\_fit \\ c5hc\_fit \end{pmatrix} := Minerr(a5hc\_guess,b5hc\_guess,c5hc\_guess)$$

---

a5hc_fit = 2.8631

b5hc_fit = -4.2491

c5hc_fit = 0.8387

Compute the residual error, ERR, given by ERR = SSE51c(a51c_fit,b51c_fit,c51c_fit).

ERR = 0.0073

Hydrophilic Sensor

Non-Linear Regression Analysis of α_{Im} vs M_f

$$SSE6hc(a,b,c) := \frac{1}{Nhc}\sum_{khc}\left(\alpha Imhc_{khc} - G(a,b,c,MFhc_{khc})\right)^2$$

Enter guess values for a,b and c.

a6hc_guess := 1

b6hc_guess := -0.1

c6hc_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE6hc(a6hc\_guess,b6hc\_guess,c6hc\_guess)=0$$

$$l=1$$

$$l=1$$

$$\begin{pmatrix} a6hc\_fit \\ b6hc\_fit \\ c6hc\_fit \end{pmatrix} := Minerr(a6hc\_guess,b6hc\_guess,c6hc\_guess)$$

---

a6hc_fit = 2.3159

b6hc_fit = -5.7621

c6hc_fit = 0.0354

Compute the residual error, ERR, given by ERR = SSE6lic(a6lic_fit,b6lic_fit,c6lic_fit).

$$ERR = 6.7774\cdot10^{-4}$$

Hydrophilic Sensor

Non-Linear Regression Analysis of $|\alpha|$ vs M_f

$$SSE7hc(a,b,c) := \frac{1}{Nhc}\sum_{khc}\left(\alpha Maghc_{khc} - G\left(a,b,c,MFhc_{khc}\right)\right)^2$$

Enter guess values for a,b and c.

a7hc_guess := 1

b7hc_guess := -1

c7hc_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE7hc(a7hc\_guess, b7hc\_guess, c7hc\_guess) = 0$$

$$1 = 1$$

$$1 = 1$$

$$\begin{pmatrix} a7hc\_fit \\ b7hc\_fit \\ c7hc\_fit \end{pmatrix} := Minerr(a7hc\_guess, b7hc\_guess, c7hc\_guess)$$

---

a7hc_fit = 3.473

b7hc_fit = -4.8874

c7hc_fit = 0.8714

Compute the residual error, ERR, given by ERR = SSE7lic(a7lic_fit,b7lic_fit,c7lic_fit).

ERR = 0.0089

Hydrophilic Sensor

Non-Linear Regression Analysis of θ_α vs M_f

$$SSE8hc(a,b,c) := \frac{1}{Nhc}\sum_{khc}\left(\theta\alpha hc_{khc}\,deg - G(a,b,c,Mfhc_{khc})\right)^2$$

Enter guess values for a,b and c.

a8hc_guess := 1

b8hc_guess := -0.1

c8hc_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE8hc(a8hc\_guess,b8hc\_guess,c8hc\_guess)=0$$

$$1=1$$

$$1=1$$

$$\begin{pmatrix} a8hc\_fit \\ b8hc\_fit \\ c8hc\_fit \end{pmatrix} := Minerr(a8hc\_guess,b8hc\_guess,c8hc\_guess)$$

---

a8hc_fit = 1.0236

b8hc_fit = 0.9586

c8hc_fit = 0.5074

Compute the residual error, ERR, given by ERR = SSE81c(a81c_fit,b81c_fit,c81c_fit).

$$ERR = 7.0692\cdot10^{-4}$$

Hydrophobic Sensor

Non-Linear Regression Analysis of α_{Re} vs M_f

$$SSE5bic(a,b,c) := \frac{1}{Nbic}\cdot\sum_{kbic}\left(\alpha Rebic_{kbic} - G\left(a,b,c,MFbic_{kbic}\right)\right)^2$$

Enter guess values for a,b and c.

a5bic_guess := 1

b5bic_guess := 2

c5bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE5bic(a5bic\_guess, b5bic\_guess, c5bic\_guess) = 0$$

$$l := 1$$

$$l := 1$$

$$\begin{pmatrix} a5bic\_fit \\ b5bic\_fit \\ c5bic\_fit \end{pmatrix} := Minerr(a5bic\_guess, b5bic\_guess, c5bic\_guess)$$

---

a5bic_fit = 2.2309

b5bic_fit = -4.378

c5bic_fit = 0.7751

Compute the residual error, ERR, given by ERR = SSE5bic(a5bic_fit,b5bic_fit,c5bic_fit).

ERR = 0.0022

Hydrophobic Sensor

Non-Linear Regression Analysis of α_{Im} vs M_f

$$SSE6bic(a,b,c) := \frac{1}{Nbic}\cdot\sum_{kbic}\left(\alpha Imbic_{kbic} - G\left(a,b,c,MFbic_{kbic}\right)\right)^2$$

Enter guess values for a,b and c.

a6bic_guess := 1

b6bic_guess := -0.1

c6bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE6bic(a6bic\_guess, b6bic\_guess, c6bic\_guess) = 0$$

$$l = 1$$

$$l = 1$$

$$\begin{pmatrix} a6bic\_fit \\ b6bic\_fit \\ c6bic\_fit \end{pmatrix} := Minerr(a6bic\_guess, b6bic\_guess, c6bic\_guess)$$

---

a6bic_fit = 1.5698

b6bic_fit = -5.2243

c6bic_fit = 0.1297

Compute the residual error, ERR, given by ERR = SSE6bic(a6bic_fit,b6bic_fit,c6bic_fit).

$$ERR = 3.1137\cdot10^{-4}$$

Hydrophobic Sensor

Non-Linear Regression Analysis of $|\alpha|$ vs M_f

$$SSE7bic(a,b,c) := \frac{1}{Nbic}\cdot\sum_{kbic}\left(\alpha Magbic_{kbic} - G\left(a,b,c,MFbic_{kbic}\right)\right)^2$$

Enter guess values for a,b and c.

a7bic_guess := 1

b7bic_guess := 2

c7bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE7bic(a7bic\_guess,b7bic\_guess,c7bic\_guess)=0$$

$$1=1$$

$$1=1$$

$$\begin{pmatrix} a7bic\_fit \\ b7bic\_fit \\ c7bic\_fit \end{pmatrix} := Minerr(a7bic\_guess,b7bic\_guess,c7bic\_guess)$$

---

a7bic_fit = 2.5396

b7bic_fit = -4.8354

c7bic_fit = 0.793

Compute the residual error, ERR, given by ERR = SSE7bic(a7bic_fit,b7bic_fit,c7bic_fit).

ERR = 0.0024

Hydrophobic Sensor

Non-Linear Regression Analysis of θ_α vs M_f

$$SSE8bic(a,b,c) := \frac{1}{Nbic}\cdot\sum_{kbic}\left(\theta\alpha bic_{kbic}\cdot deg - G\left(a,b,c,MFbic_{kbic}\right)\right)^2$$

Enter guess values for a,b and c.

a8bic_guess := 1

b8bic_guess := 2

c8bic_guess := 1

---------- Mathcad Solve Block ----------

Given

$$SSE8bic(a8bic\_guess,b8bic\_guess,c8bic\_guess)=0$$

$$1=1$$

$$1=1$$

$$\begin{pmatrix} a8bic\_fit \\ b8bic\_fit \\ c8bic\_fit \end{pmatrix} := Minerr(a8bic\_guess,b8bic\_guess,c8bic\_guess)$$

---

a8bic_fit = 0.7646

b8bic_fit = -1.7386

c8bic_fit = 0.3113

Compute the residual error, ERR, given by ERR = SSE8bic(a8bic_fit,b8bic_fit,c8bic_fit).

$$ERR = 4.1297\cdot10^{-4}$$

Plot the fitted and experimental data for α_{Re}, α_{Im}, $|\alpha|$ and θ_α versus v and M_f.

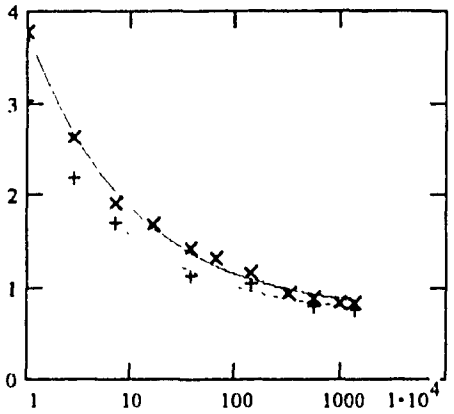
Plot α_{Re}, α_{Im}, $|\alpha|$ amd θ_α versus v and M_f for the hydrophilic and hydrophobic sensor.

v 10 cS, 20 cS 1400 cS

Mf 0,001 1

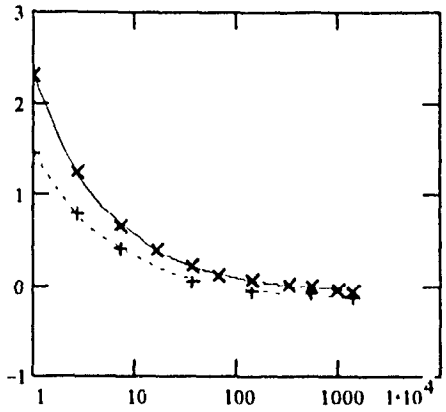
Hydrophilic and Hydrophobic Sensor

Plot of α_{Re} versus v (Hydrophilic and Hydrophobic Sensor)



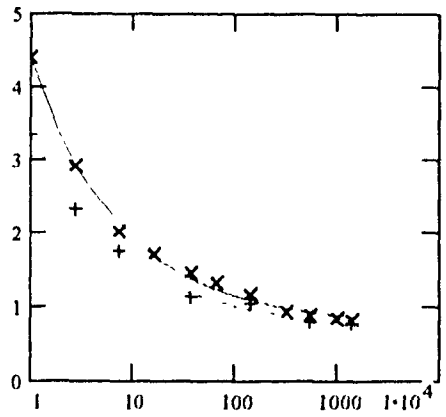
× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
- - Hydrophobic Sensor (Fitted Curve)

Plot of α_{Im} versus v (Hydrophilic and Hydrophobic Sensor)



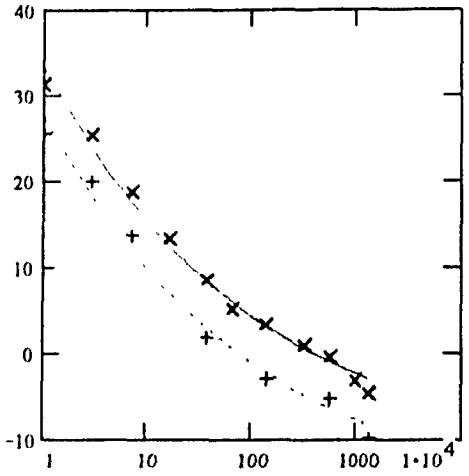
× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
- - Hydrophobic Sensor (Fitted Curve)

Plot of |α| versus v (Hydrophilic and Hydrophobic Sensor)



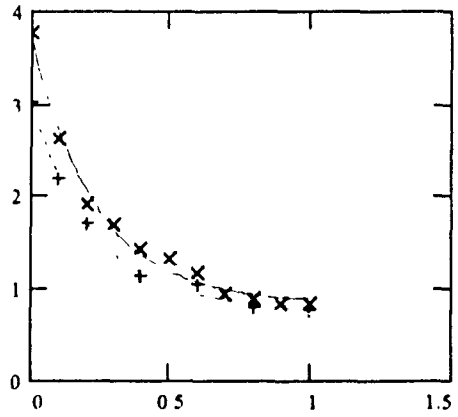
× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
- - Hydrophobic Sensor (Fitted Curve)

Plot of θ_α versus ν (Hydrophilic and Hydrophobic Sensor)



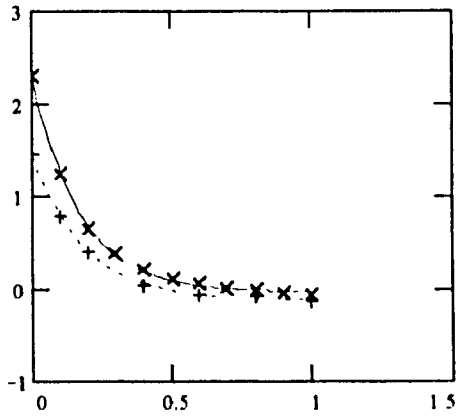
× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
Hydrophobic Sensor (Fitted Curve)

Plot of α_{Re} versus M_f (Hydrophilic and Hydrophobic Sensor)



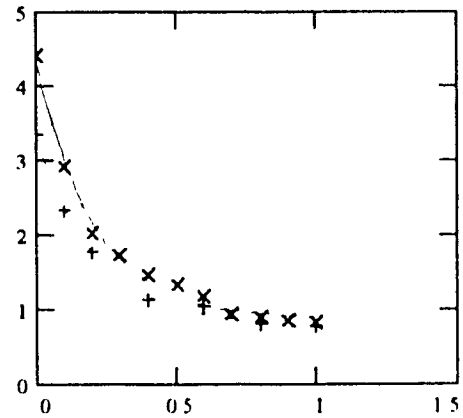
× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
Hydrophobic Sensor (Fitted Curve)

Plot of α_{Im} versus M_f (Hydrophilic and Hydrophobic Sensor)



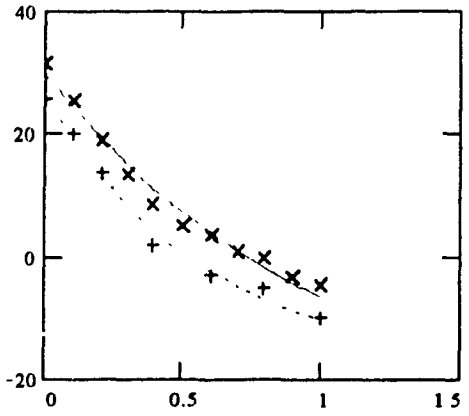
× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
Hydrophobic Sensor (Fitted Curve)

Plot of $|\alpha|$ versus M_f (Hydrophilic and Hydrophobic Sensor)



× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
Hydrophobic Sensor (Fitted Curve)

Plot of θ_α versus M_f (Hydrophilic and Hydrophobic Sensor)



× Hydrophilic Sensor (Experimental Curve)
— Hydrophilic Sensor (Fitted Curve)
\+ Hydrophobic Sensor (Experimental Curve)
· Hydrophobic Sensor (Fitted Curve)

APPENDIX 8 Particle Displacement of Sensor in Liquid, Mathcad Program DOC5.MCD

Numerical Solution of the Maximum Values of the Real Part of u_x and $u_{(1)x}$ Versus Kinematic Viscosity, ν, for the Hydrophilic and Hydrophobic Sensor in Water-Glycerol Solution

The maximum value of the real part of the liquid particle displacement, $u_{(1)x}$, and the quartz particle displacement, u_x, will be computed at the interface over the time interval, $I=[0,5/f_o]$ for the hydrophilic and hydrophobic sensor.

The following seventeen complex-valued expressions constitute the expression for the particle displacement, u_x, of the quartz sensor.

$$cbar := c + \frac{e^2}{\varepsilon}$$

$$\delta(\eta,\omega) := \eta\cdot\omega - j\cdot cbar$$

$$kq(\eta,\omega) := \omega\sqrt{\frac{\rho q}{cbar + j\,\omega\,\eta}}$$

$$kl(\nu,\omega) := \sqrt{\frac{\omega}{j\,\nu}}$$

$$\gamma 1(\eta,h,\omega) := \exp(j\cdot h\ kq(\eta,\omega))$$

$$\gamma 2(\nu,h,\omega) := \exp(j\ h\ kl(\nu,\omega))$$

$$\lambda 1(\eta,h,\omega) := \gamma 1(\eta,h,\omega) - 1$$

$$\lambda 2(\eta,h,\omega) := \gamma 1(\eta,h,\omega) + 1$$

$$\lambda 3(\eta,h,\omega) := \gamma 1(\eta,h,\omega)^2 + 1$$

$$b11(\eta,h,\omega) := -2\cdot\delta(\eta,\omega)\ e\ \varepsilon\ \lambda 1(\eta,h,\omega)\ \gamma 1(\eta,h,\omega)\ kq(\eta,\omega)\ \phi 0$$

$$b12(\eta,\nu,\rho l,h,\omega) := -2\ e\ \varepsilon\ \gamma 1(\eta,h,\omega)^2\ kl(\nu,\omega)\ \nu\ \omega\ \phi 0\ \rho l$$

$$b13(\eta,h,\omega) := \delta(\eta,\omega)\ \lambda 1(\eta,h,\omega)\ kq(\eta,\omega)\left(\begin{matrix}\delta(\eta,\omega)\ \varepsilon\ \lambda 2(\eta,h,\omega)\ h\ kq(\eta,\omega)\\ +2\ e^2\cdot\lambda 1(\eta,h,\omega)\end{matrix}\right)$$

$$b14(\eta,\nu,\rho l,h,\omega) := kl(\nu,\omega)\left(\begin{matrix}\delta(\eta,\omega)\cdot\varepsilon\ \lambda 3(\eta,h,\omega)\cdot h\ kq(\eta,\omega)\\ +e^2\ \lambda 1(\eta,h,\omega)\ \lambda 2(\eta,h,\omega)\end{matrix}\right)\ \nu\ \omega\ \rho l$$

$$b21(\eta,h,\omega) := 2\cdot\delta(\eta,\omega)\cdot e\,\varepsilon\,\lambda1(\eta,h,\omega)\,kq(\eta,\omega)\cdot\phi0$$

$$b22(\eta,\nu,\rho l,h,\omega) := 2\,e\,\varepsilon\,kl(\nu,\omega)\cdot\nu\cdot\omega\cdot\rho l\cdot\phi0$$

$$a1(\eta,\nu,\rho l,\alpha,h,\omega) := \left(\frac{\alpha\,b12(\eta,\nu,\rho l,h,\omega)+b11(\eta,h,\omega)}{\alpha\,b14(\eta,\nu,\rho l,h,\omega)+b13(\eta,h,\omega)}\right)$$

$$a2(\eta,\nu,\rho l,\alpha,h,\omega) := \left(\frac{\alpha\cdot b22(\eta,\nu,\rho l,h,\omega)+b21(\eta,h,\omega)}{\alpha\cdot b14(\eta,\nu,\rho l,h,\omega)+b13(\eta,h,\omega)}\right)$$

The particle displacement, u_x, of the quartz sensor at the solid-liquid interface is.

$$ux(\eta,\nu,\rho l,\alpha,h,\omega,t) := \left(\begin{matrix}a1(\eta,\nu,\rho l,\alpha,h,\omega)\cdot\exp(-j\cdot kq(\eta,\omega)\cdot h)\ \ldots\\ +a2(\eta,\nu,\rho l,\alpha,h,\omega)\cdot\exp(j\cdot kq(\eta,\omega)\cdot h)\end{matrix}\right)\cdot\exp(j\cdot\omega\,t)$$

From the slip boundary condition, the liquid particle displacement, $u_{(l)x}$, at the solid-liquid interface is.

$$ulx(\eta,\nu,\rho l,\alpha,h,\omega,t) := \alpha\,ux(\eta,\nu,\rho l,\alpha,h,\omega,t)$$

Data for Hydrophilic and Hydrophobic Sensor

Enter numerical value for the mass density of quartz.

$$\rho q := 2649\ \frac{kg}{m^3}$$

Enter numerical value for the elastic coefficient of quartz.

$$c := 2901\ 10^9\cdot\frac{newton}{m^2}$$

Enter numerical value for the best-fit piezoelectric stress coefficient of quartz.

$$e := -0.0798007\cdot\frac{coul}{m^2}$$

Enter numerical values for the best-fit viscoelastic coefficient of quartz.

$$\eta lic\_fit := 0.0083762\ newton\ \frac{sec}{m^2}$$

$$\eta bic\_fit := 0.2344606\ newton\ \frac{sec}{m^2}$$

Enter numerical values for the best-fit thickness.

$$hlic\_fit := 183.8790101\ \mu m$$

$$hbic\_fit := 183.9794329\ \mu m$$

Enter numerical value for the dielectric constant of quartz.

$$\varepsilon := 39.82\ 10^{-12}\ \frac{coul}{volt\ m}$$

Water-Glycerol Solution for Hydrophilic Sensor

Read in data array vlic for kinematic viscosity, ν, an array of eleven values of ν.

$$vlic := READPRN(NULIC)\ cS$$

Read in data array plic for kinematic viscosity, ρ, an array of eleven values of ρ.

$$\rho lic := READPRN(RHOLIC)\ \frac{kg}{liter}$$

Read in data array αlic for interfacial slip parameter, α, an array of eleven values of α.

$$\alpha lic := READPRN(ALPLIC)$$

$$\alpha lic := \alpha lic^{\langle 1 \rangle} + j\,\alpha lic^{\langle 2 \rangle}$$

Water-Glycerol Solution for Hydrophobic Sensor

Read in data array vbic for kinematic viscosity, ν, an array of eleven values of ν.

$$vbic := READPRN(NUBIC)\ cS$$

Read in data array ρbic for kinematic viscosity, ρ, an array of eleven values of ρ.

$$\rho bic := READPRN(RHOBIC)\ \frac{kg}{liter}$$

Read in data array αbic for interfacial slip parameter, α, an array of seven values of α.

$$\alpha bic := READPRN(ALPBIC)$$

$$\alpha bic := \alpha bic^{\langle 1 \rangle} + j\,\alpha bic^{\langle 2 \rangle}$$

Using the nominal resonant frequency, f_o, of the quartz sensor, compute $u_x(h,t)$ and $u_{(1)x}(h,t)$ over the time interval $[0, 5/f_o]$.

Enter numerical value for nominal resonant frequency, f_o. $fo = 9.0\ MHz$

The corresponding angular frequency, ω_o, is given by. $\omega o = 2 \cdot \pi \cdot fo$

Enter starting value for the time t, t_s. $ts = 0\ sec$

Enter terminal value for the time t, t_f. $tf = \frac{5}{fo}$ $tf = 0.556 \cdot \mu sec$

Enter numerical value for the time step Δt. $\Delta t = 0.001 \cdot \mu sec$

The number of data points, N, is. $N = floor\left(\frac{tf - ts}{\Delta t}\right)$ $N = 555$

In the above expression for N, Mathcad's floor function, converts a real number into the smallest integer corresponding to that real number.

The range variable, i, takes on integral values from 1 to N inclusive.

$$i = 1 \ldots N$$

Generate a partition of N equally spaced time points, t_i, each of width Δt.

$$t_1 = ts$$

$$t_{i+1} = t_i + \Delta t$$

$$tt_i = t_i$$

Hydrophilic Sensor

Compute the real part of u_x and $u_{(1)x}$ over the time interval $[0, 5/f_o]$ for each i=1,...,N and klic=1,...,11.

klic = 1 11

$$uxRe\_hydrophilic_{i,klic} = Re\left(ux\left(\eta lic\_fit, vlic_{klic}, \rho lic_{klic}, \alpha lic_{klic}, hlic\_fit, \omega_o, t_i\right)\right)$$

$$ulxRe\_hydrophilic_{i,klic} = Re\left(ulx\left(\eta lic\_fit, vlic_{klic}, \rho lic_{klic}, \alpha lic_{klic}, hlic\_fit, \omega_o, t_i\right)\right)$$

Using Mathcad's max function, compute the maximum values of the real parts of u_x and $u_{(1)x}$ over the time interval $[0, 5/f_o]$ for each klic=1,...,11.

$$uxmax\_lic_{klic} = \max\left(uxRe\_hydrophilic^{<klic>}\right)$$

$$ulxmax\_lic_{klic} = \max\left(ulxRe\_hydrophilic^{<klic>}\right)$$

Store the one-dimensional arrays uxmax_lic and ulxmax_lic in the respective data files UXMAXLIC.PRN and ULMAXLIC.PRN.

$$WRITEPRN(UXMAXLIC) = augment\left(\begin{matrix} vlic \\ cS \end{matrix}, \begin{matrix} uxmax\_lic \\ angstrom \end{matrix}\right)$$

$$WRITEPRN(ULMAXLIC) = augment\left(\begin{matrix} vlic \\ cS \end{matrix}, \begin{matrix} ulxmax\_lic \\ angstrom \end{matrix}\right)$$

Hydrophobic Sensor

Compute the real part of u_x and $u_{(1)x}$ over the time interval [0,5/fo] for each i=1,...,N and kbic=1,...,7.

kbic 1..7

$$uxRe\_hydrophobic_{i,kbic} = Re\left(ux\left(\eta bic\_fit, vbic_{kbic}, \rho bic_{kbic}, \alpha bic_{kbic}, hbic\_fit, \omega o, t_i\right)\right)$$

$$ulxRe\_hydrophobic_{i,kbic} = Re\left(ulx\left(\eta bic\_fit, vbic_{kbic}, \rho bic_{kbic}, \alpha bic_{kbic}, hbic\_fit, \omega o, t_i\right)\right)$$

Using Mathcad's max function, compute the maximum values of the real parts of u_x and $u_{(1)x}$ over the time interval $[0,5/f_o]$ for each kbic=1,...,7.

$$uxmax\_bic_{kbic} = \max\left(uxRe\_hydrophobic^{\langle kbic\rangle}\right)$$

$$ulxmax\_bic_{kbic} = \max\left(ulxRe\_hydrophobic^{\langle kbic\rangle}\right)$$

Store the one-dimensional arrays uxmax_bic and ulxmax_bic in the respective data files UXMAXBIC.PRN and ULMAXBIC.PRN.

$$WRITEPRN(UXMAXBIC) = augment\left(\frac{vbic}{cS}, \frac{uxmax\_bic}{angstrom}\right)$$

$$WRITEPRN(ULMAXBIC) = augment\left(\frac{vbic}{cS}, \frac{ulxmax\_bic}{angstrom}\right)$$

For the case of the hydrophilic and hydrophobic sensors immersed in pure water, store the data for the real part of ux and u(1)x versus the time t in the respective data files UXRELIC.PRN, UXREBIC.PRN, ULRELIC.PRN and ULREBIC.PRN.

$$WRITEPRN(UXRELIC) = augment\left(\frac{tt}{\mu sec}, \frac{uxRe\_hydrophilic^{\langle 1\rangle}}{angstrom}\right)$$

$$WRITEPRN(UXREBIC) = augment\left(\frac{tt}{\mu sec}, \frac{uxRe\_hydrophobic^{\langle 1\rangle}}{angstrom}\right)$$

$$WRITEPRN(ULRELIC) = augment\left(\frac{tt}{\mu sec}, \frac{ulxRe\_hydrophilic^{\langle 1\rangle}}{angstrom}\right)$$

$$WRITEPRN(ULREBIC) = augment\left(\frac{tt}{\mu sec}, \frac{ulxRe\_hydrophobic^{\langle 1\rangle}}{angstrom}\right)$$

Use the power law model $F(a,b,c,x)=ax^b+c$ to fit the data consisting of uxmax_lic, uxmax_bic, ulxmax_lic and ulxmax_bic.

$$F(a,b,c,x) := a\,x^{b} + c$$

The following Sum Of Squares Of Errors, SSEUXLIC(a,b,c), SSEULXLIC(a,b,c), SSEUXBIC(a,b,c) and SSEULXBIC(a,b,c) will be used in the following non-linear curve-fitting procedure.

$$SSEUXLIC(a,b,c) := \frac{1}{11}\sum_{klic}\left(\frac{uxmax\_lic_{klic}}{angstrom} - F\left(a,b,c,\frac{vlic_{klic}}{cS}\right)\right)^2$$

$$SSEULXLIC(a,b,c) := \frac{1}{11}\sum_{klic}\left(\frac{ulxmax\_lic_{klic}}{angstrom} - F\left(a,b,c,\frac{vlic_{klic}}{cS}\right)\right)^2$$

$$SSEUXBIC(a,b,c) := \frac{1}{7}\sum_{kbic}\left(\frac{uxmax\_bic_{kbic}}{angstrom} - F\left(a,b,c,\frac{vbic_{kbic}}{cS}\right)\right)^2$$

$$SSEULXBIC(a,b,c) := \frac{1}{7}\sum_{kbic}\left(\frac{ulxmax\_bic_{kbic}}{angstrom} - F\left(a,b,c,\frac{vbic_{kbic}}{cS}\right)\right)^2$$

To start the non-linear curve-fitting procedure, enter guess values for a,b and c.

Enter guess value for a. aguessux_lic = 14

Enter guess value for b. bguessux_lic = -0.2

Enter guess value for c. cguessux_lic = -1.4

---------- Mathcad Solve Block ----------

Given

$$SSEUXLIC(aguessux\_lic, bguessux\_lic, cguessux\_lic) = 0$$

$$1 = 1$$

$$1 = 1$$

$$\begin{pmatrix} afitux\_lic \\ bfitux\_lic \\ cfitux\_lic \end{pmatrix} = Minerr(aguessux\_lic, bguessux\_lic, cguessux\_lic)$$

The result of the Solve Block, afitux_lic, bfitux_lic and cfitux_lic is.

afitux_lic = 14.523

bfitux_lic = -0.246

cfitux_lic = -1.529

Compute the residual error, ERR, given by ERR = SSEUXLIC(afitux_lic,bfitux_lic,cfitux_lic).

ERR = 0.057

To start the non-linear curve-fitting procedure, enter guess values for a,b and c.

Enter guess value for a. aguessulx_lic = 56

Enter guess value for b. bguessulx_lic = -0.6

Enter guess value for c. cguessulx_lic = 0.5

---------- Mathcad Solve Block ----------

Given

$$SSEULXLIC(aguessulx\_lic, bguessulx\_lic, cguessulx\_lic) = 0$$

$$l = 1$$

$$l = 1$$

$$\begin{pmatrix} afitulx\_lic \\ bfitulx\_lic \\ cfitulx\_lic \end{pmatrix} = Minerr(aguessulx\_lic, bguessulx\_lic, cguessulx\_lic)$$

The result of the Solve Block, afitulx_lic, bfitulx_lic and cfitulx_lic is.

afitulx_lic = 56.032

bfitulx_lic = 0.649

cfitulx_lic = 0.577

Compute the residual error, ERR, given by ERR = SSEULXLIC(afitulx_lic,bfitulx_lic,cfitulx_lic).

ERR = 0.036

To start the non-linear curve-fitting procedure, enter guess values for a, b and c.

Enter guess value for a. aguessux_bic = 18

Enter guess value for b. bguessux_bic = -0.04

Enter guess value for c. cguessux_bic = -11

---------- Mathcad Solve Block ----------

Given

$$SSEUXBIC(aguessux\_bic, bguessux\_bic, cguessux\_bic) = 0$$

$$l = 1$$

$$l = 1$$

$$\begin{pmatrix} afitux\_bic \\ bfitux\_bic \\ cfitux\_bic \end{pmatrix} = Minerr(aguessux\_bic, bguessux\_bic, cguessux\_bic)$$

The result of the Solve Block, afitux_bic, bfitux_bic and cfitux_bic is.

afitux_bic = 19.311

bfitux_bic = -0.081

cfitux_bic = -10.043

Compute the residual error, ERR, given by ERR = SSEUXBIC(afitux_bic,bfitux_bic,cfitux_bic).

ERR = 0.051

To start the non-linear curve-fitting procedure, enter guess values for a,b and c.

Enter guess value for a. aguessulx_bic := 34

Enter guess value for b. bguessulx_bic := -0.5

Enter guess value for c. cguessulx_bic := 0.3

---------- Mathcad Solve Block ----------

Given

$$SSEULXBIC(aguessulx\_bic, bguessulx\_bic, cguessulx\_bic) = 0$$

$$l := 1$$

$$l := 1$$

$$\begin{pmatrix} afitulx\_bic \\ bfitulx\_bic \\ cfitulx\_bic \end{pmatrix} := Minerr(aguessulx\_bic, bguessulx\_bic, cguessulx\_bic)$$

The result of the Solve Block, afitulx_bic, bfitulx_bic and cfitulx_bic is.

afitulx_bic = 31.284

bfitulx_bic = 0.536

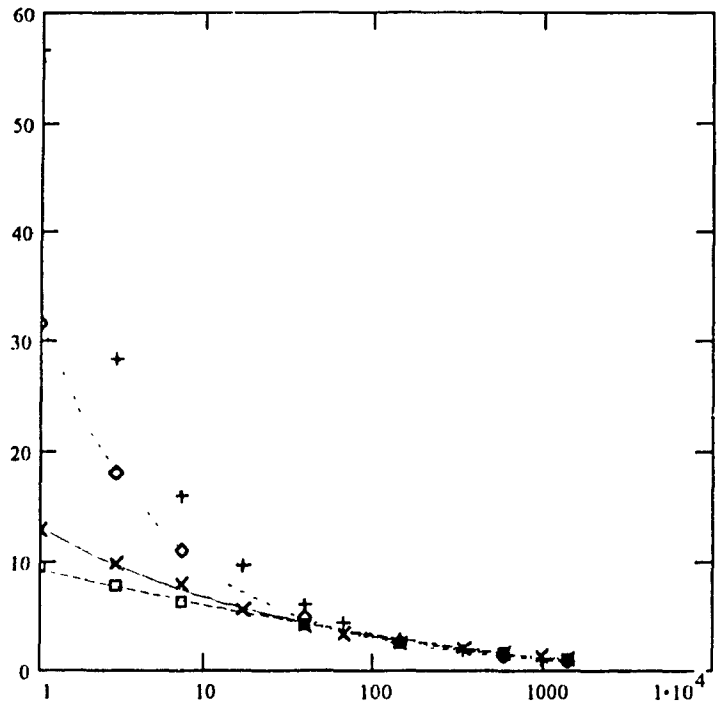
cfitulx_bic = 0.308

Compute the residual error, ERR, given by ERR = SSEULXBIC(afitulx_bic,bfitulx_bic,cfitulx_bic).

ERR = 0.01

Plot of the maximum displacement of the real part of u_x and $u_{(1)x}$ versus n for the hydrophilic and hydrophobic sensor.

x := 1 0,2 .. 1400



× Maximum displacement of the real part of ux, hydrophilic
— Fitted Curve
\+ Maximum displacement of the real part of ulx, hydrophilic
Fitted Curve
□ Maximum displacement of the real part of ux, hydrophobic
--- Fitted Curve
◇ Maximum displacement of the real part of ul, hydrophobic
Fitted Curve

APPENDIX 9 Numerical Solution of Interfacial Slip Model, Mathcad Program DOC6.MCD

Numerical Solution of the Equation of Motion of Mass m_1 using Runge-Kutta's Fourth Order Method.

The numerical computation of the displacement, x_1, of mass m_1 will be performed by using a fourth-order Runge-Kutta method. Using a semi-interactive method, the displacement x_1, will be computed over the time interval [0,5/f], for several values of the ratio of spring constant and mass of liquid particle, k/m_1, starting with 10^2 and ending with 10^9. Using the above data for x_1, the maximum displacement of xl_{max} will be computed for each value of k/m_1. The maximum displacement x_{1max} is defined as the largest displacement of mass m_1 in the time interval [0,5/f].

Implementation of Runge-Kutta's Method Using Mathcad

Let $x_1(t)$ denote the displacement of the liquid particle of mass m_1 from its equlibrium position at time t.

Let $x_2(t)$ denote the displacement of the solid particle of mass m_2 from its equlibrium position at time t.

Let $v_1(t)$ denote the velocity of mass m_1 at time t.

Let $v_2(t)$ denote the velocity of mass m_2 at time t.

Let l denote the length of the spring connecting masses m_1 and m_2.

Let k denote the force constant of the spring.

Let A denote the amplitude of the displacement of mass m_2.

Let ϕ denote the phase angle of the displacement of mass m_2.

STATEMENT OF PROBLEM

Given that $x_2 = x_2(t) = A\cos(\omega t+\phi)$, determine $x_1 = x_1(t)$ numerically over the closed time interval $[t_i, t_f]$.

$x1 = x1(t)$ satisfies the following non-linear second-order differential equation.

$$\frac{d^2}{dt^2} x1(t) = \frac{k}{m1} \frac{\left[\sqrt{(A\cos(\omega t+\phi) - x1(t))^2 + l^2} - l\right](A\cos(\omega t+\phi) - x1(t))}{\sqrt{(A\cos(\omega t+\phi) - x1(t))^2 + l^2}}$$

To determine $x1 = x1(t)$ numerically, a Runge-Kutta method of stepsize Δt will be used.

Enter numerical value for the amplitude A of the displacement of mass m_2.

$$A = 1$$

Enter numerical value for the phase angle ϕ of the displacement of mass m_2.

$$\phi = -\frac{\pi}{2}$$

Enter numerical value for the driving frequency f of mass m_2.

$$f = 9$$

The corresponding angluar frequency ω of mass m_2 is given by.

$$\omega = 2\cdot\pi f$$

Enter initial value for the time t. $ti = 0$

Enter terminal value for the time t. $tf = \frac{5}{f}$

Enter time increment dt. $dt = 0.001$

The number of time increments N is given by. $N = \text{floor}\left(\frac{tf - ti}{dt}\right)$ $N = 555$

Enter initial values for the displacement and velocity of mass m_1.

Initial values... $u^{<0>} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$ ...Initial displacement of mass m_1.
...Initial velocity of mass m_1.

The derivative vector $\mathbf{F}(t,\mathbf{u})$ is given by.

$$F(t,u) \equiv \begin{bmatrix} u_1 \\ \dfrac{k}{ml}\left[\sqrt{\left(A\cdot\cos(\omega t+\phi)\ \ u_0\right)^2+l^2}-l\right]\left(A\cos(\omega t+\phi)\ \ u_0\right) \\ \hline \sqrt{\left(A\cos(\omega t+\phi)-u_0\right)^2+l^2} \end{bmatrix}$$

The four functions K_1, K_2, K_3, and K_4 implement the Runge-Kutta method.

$$K1(t,u,F,dt) \equiv F(t,u)$$

$$K2(t,u,F,dt) \equiv F\left(t+\frac{dt}{2},u+\frac{dt}{2}K1(t,u,F,dt)\right)$$

$$K3(t,u,F,dt) \equiv F\left(t+\frac{dt}{2},u+\frac{dt}{2}K2(t,u,F,dt)\right)$$

$$K4(t,u,F,dt) \equiv F(t+dt,u+dt\,K3(t,u,F,dt))$$

The function RK computes the weighted average of the above four functions.

$$RK(t,u,F,dt) \quad \frac{dt}{6}\left(K1(t,u,F,dt)+2\,K2(t,u,F,dt)+2\,K3(t,u,F,dt)+K4(t,u,F,dt)\right)$$

For each $i = 1,\ldots,N$ compute the displacement, x_i, and velocity, v_i, of mass m_i at each time t_i using the recurrence relation given below.

$i \equiv 1\ \ N$

$$t_i \equiv ti+(i-1)\cdot dt$$

$$u^{\langle i\rangle} \equiv u^{\langle i-1\rangle}+RK\left(t_{i-1},u^{\langle i-1\rangle},F,dt\right)$$

From the above recurrence relation, $u_{(0,1)}$ and $u_{(1,1)}$ correspond to $x_1 = x_1(t_1)$ and $v_1 = v_1(t_1)$ respectively.

The displacement of mass m_1 at each $t = t_1$ is given by.

$$x1_i = u_{0,i}$$

Compute the displacement of mass m_2 at each $t = t_1$.

$$x2_i = A \cdot \cos(\omega t_i + \phi)$$

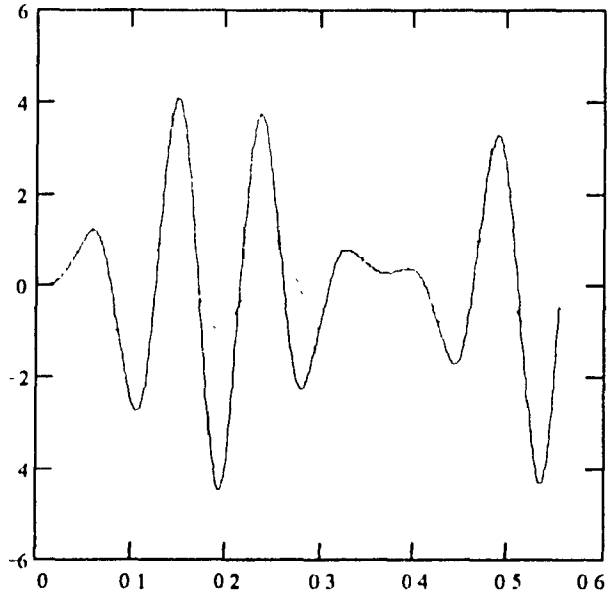
To initiate the numerical computation of $x_1(t_i)$, enter appropriate numerical values for the mass m_1, the length of the spring l and the force constant, k, of the spring.

Enter numerical value for mass m_1. $m1 \equiv 1$

Enter numerical value for the length l of the spring. $l \equiv 1$

Enter numerical value for the force constant k of the spring. $k \equiv 10^4$

Plot the displacements of masses m_1 and m_2 versus the time t.



— displacement of mass m1 versus time
displacement of mass m2 versus time

Numerical Computation Of x_{1max}

The above mentioned semi-interactive method is described below.

Mathcad's **max** function will be used to compute x_{1max} for each value of k in the interval $[10^2, 10^9]$. For $k/m_1 = 10^2$ Mathcad's **WRITEPRN** function will store the first pair $(\log(k/m_1), x_{1max})$ in the data file X1MAX.PRN. Disabling the function **WRITEPRN**, Mathcad's function **APPENDPRN** will then append succeeding pairs $(\log(k/m_1), x_{1max})$ to the data fileX1MAX.PRN for each value of k/m_1.

$$\text{WRITEPRN(X1MAX)} \quad \left(\begin{matrix}\log\left(\frac{k}{m1}\right) \\ \max(x1)\end{matrix}\right)^T$$

$$\text{APPENDPRN(X1MAX)} \quad \left(\begin{matrix}\log\left(\frac{k}{m1}\right) \\ \max(x1)\end{matrix}\right)^T$$

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