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**INTERFACIAL SLIP ON A TRANSVERSE-SHEAR MODE ACOUSTIC WAVE
DEVICE**

A Thesis

Presented to

The Faculty of Graduate Studies

of

The University of Guelph

by

JONATHAN S. ELLIS

In partial fulfilment of requirements

for the degree of

Master of Science

October, 2002

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ABSTRACT

SLIP AT THE SURFACE-LIQUID INTERFACE OF A TRANSVERSE-SHEAR MODE ACOUSTIC WAVE DEVICE

**Jonathan S. Ellis
University of Guelph, 2002**

**Advisor:
Professor G. L. Hayward**

This thesis describes a mathematical relationship between the slip parameter and the slip length as boundary conditions for the transverse-shear model for a quartz acoustic device. A theory is presented to reduce the determination of slip to a one-parameter fit, showing that the magnitude and phase of the slip parameter, describing the relative displacements of the surface and liquid in the transverse-shear model, can be linked to slip length. An experiment is described, comparing the effects of liquid-surface affinity on the resonance of a TSM wave device, by applying polar and nonpolar liquids to different surfaces. The theory is validated with slip determined from the transverse-shear model, compared to slip lengths from the literature, where the agreement is within one order of magnitude. Negative liquid stiffness improves the relationship between theory and experiment, indicating that intermolecular forces contribute to resonance patterns observed in recent studies.

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1 INTRODUCTION

Piezoelectric acoustic wave devices have been used extensively to detect specific molecules in the gas and liquid phases for many years, since the work by Sauerbrey [1]. These types of sensors are highly sensitive due to their high operating frequency range, and can be used to detect masses on the order of nanograms. Quartz crystals are commonly used because of their inherent piezoelectric properties and high quality factor.

Many biological applications use acoustic wave devices configured for transverse-shear mode (TSM) operation, where the motion of the device is transverse to the direction of wave propagation. A TSM device is a thin wafer of quartz with metal electrodes on both faces, coated with a sensing polymer film. The film is selected for the specific molecule to be detected. The coated device is excited at resonance, causing sustained mechanical oscillations. The resonant frequency of the device changes as the specific molecules adsorb onto the polymer surface.

Since the substance of interest is normally in solution, the bulk liquid mass and viscoelastic coupling at the film-liquid interface all contribute to the frequency shift. If energy is expended to move the film and the liquid, less is available to move the crystal, so the resonant frequency decreases. Liquid properties can be determined by the acoustic impedance of the interface.

A major assumption used by some authors is that surface structure and interfacial characteristics play no role in the resonant characteristics of acoustic wave devices. This assertion that mass deposition is the only factor that can affect the device has become a

popular dogma. However, a large amount of experimental and theoretical work has shown that this is not the case, and it is becoming more widely accepted that mechanical, chemical, and electrical coupling between the liquid and the surface have a very significant effect on resonant characteristics of the device. This implies that in mass deposition experiments, steps must be taken to minimize changes in surface coupling. It also allows the possibility that acoustic wave devices can be used successfully as surface conformation and interfacial coupling monitors, which has important applications in the study of on-line protein conformation detection.

Hayward *et al.* [3] used a TSM sensor to measure clot dissolution time in plasminogen activators. The clot dissolution was detected by the change in viscosity of the fibrin coating, which was determined from the frequency shift of the TSM sensor. The authors observed an increase in the resonant frequency after the activator had been applied. Furtado and Thompson [4] used an on-line TSM device to detect events during oligonucleotide hybridization. The crystal was coated with oligonucleotides, using a biotinylated neutravidin binding agent. The binding of the neutravidin to the biotin was detected by shifts in the resonant frequency of the TSM device. Mutated base pairs were used to test different reaction events at the device surface, and varying resonant frequency shifts were observed. The authors found that the device sensitivity cannot be attributed to mass effects alone, and other factors, such as interfacial viscosity and charge density at the surface, play a role in the crystal motion.

The same group [5] studied interactions at the transcription level of the HIV-1 virus using a TSM device. Transcription RNA (TAR) is strongly regulated by the 86-

amino acid protein tat and HIV drug development has focused on this interaction. Chemically synthesized RNA was immobilized on the crystal surface and exposed to 12- and 40-amino acid tat-derived peptide chains and the crystal resonant frequency and resistance were measured. When exposed to certain lengths of peptide, the sensor's resonant frequency increased, which goes against the mass deposition dogma. The mass effect would predict that surface RNA mass was lost from the system, which did not occur, as shown by radio labeling of the surface RNA.

These results indicate that there is likely a change in interfacial coupling due to changes in surface energy between the film and the liquid. As coupling decreases, less energy is lost to the liquid, and the resonant frequency of the crystal increases. Ferrante *et al.* [10] and Hayward and Thompson [6] described interfacial coupling with a complex slip parameter. Strong coupling results in less slip. The contribution of interfacial interactions has been the subject of much debate over the past decade and has been attributed to many factors, including viscoelasticity factors [2,7,8,9] and interfacial slip [6,10]. Recent studies [5,11,12] have shown that both factors may play a role in the complex surface interaction.

Interfacial slip is an empirical quantity that accounts for velocity and phase differences of molecules at the surface-fluid interface. Slip is a result of reduced coupling of molecules across the interface and the velocity difference is higher for less viscous fluids [6] or hydrophilic-hydrophobic [10] interactions at the interface. Both situations have been modeled with a complex slip boundary condition. This suggests that molecular structure plays an important role in coupling at the interface and a change in

molecular conformation may cause a change in resonant characteristics, if intermolecular coupling at the interface is affected by that change.

The slip parameter has been used to successfully model slip at the surface of transverse-shear mode acoustic wave devices. It describes the displacement of one layer relative to the lower layer and is a complex number, so has magnitude and phase. Magnitude describes the relative peak displacements of the layers and phase describes the relative timing that the amplitude peaks are reached. However, the slip parameter is a phenomenological, empirical model, so cannot be predicted *a priori* from other physical models. As well, it is determined from a two-parameter, statistical fit, so it is no more valid than any other two-parameter model.

Slip has been predicted and observed in many situations involving hydrodynamic forces on small scales, for many different liquids. Most authors have used a slip-length boundary condition, introduced by Brochard-Wyart and de Gennes [13]. This method has gained a lot of credibility in the fields of tribology and nanomechanics, and consequently there is significant literature on the subject. It has become an important indicator of surface interactions and is linked to interfacial friction [14]. Slip length has been used successfully, in many cases, to model slip, and is based on underlying physics. This shows that slip can be described with a single real value, and one that can be predicted from *a priori* knowledge of other system properties. The slip parameter could therefore be represented with a one-parameter model. As well, this would show that its magnitude and phase were related.

The objectives of this research were to show that the slip parameter can be represented with the one-parameter slip length model, that the slip parameter magnitude and phase are related, and that both liquid and surface polarities play a role in determining resonant properties.

This thesis describes a mathematical relationship between the slip parameter α and the slip length b for a slip boundary condition applied to the transverse-shear model [6] for a quartz crystal acoustic wave device. An experiment is described to compare the effects of liquid-surface affinity on the resonant properties of a TSM wave device by applying different polar and non-polar liquids to surfaces of different polarity. The theory is validated with slip values determined from the transverse-shear model [6] and compared to slip length values from the literature. The fit of the theory to data is improved by adding a liquid stiffness.

This work is significant as it shows that the empirically determined complex slip parameter can be represented as a single real parameter that can be linked to interfacial viscosity and friction. There is a direct mathematical relationship between the phase and magnitude of the slip parameter, which indicates that the viscosity and elastic properties of a solid-liquid interface are related. The theory presented here provides mathematical justification for the use of a single-valued slip parameter, as proposed by McHale *et al.* [12], a limitation being that it can only be applied to purely viscous liquids, with no stiffness. However, the improved fit of the theory when a liquid stiffness is added shows that slip is dependent on elastic processes and that liquid stiffness may play a role in the interfacial acoustics.

We begin Chapter 2 with a description of the general theory of piezoelectricity, how it relates to acoustics, and how it can be used to generate waves in acoustic devices. The application to biosensors and the importance of the complex interactions at the device-liquid interface are explored. The presence of slip at the interface is elucidated. In Chapter 3, a theory is developed to show the relationship between the complex slip parameter α and the single, real-valued slip length b . Chapter 4 describes an experiment to measure the effects of liquid and surface polarity on the resonant parameters of an quartz acoustic device. The results are presented and discussed in Chapter 5, beginning with a presentation of the experimental data. The data is then compared to the model using a no-slip boundary condition to show the justification for the inclusion of slip in the model. Finally, the experimental data is compared to the model with slip and the theory relating the slip parameter to the slip length is validated. A summary of the thesis is presented in Chapter 6, followed by conclusions and recommendations for future research.

2 THEORY

The theory of piezoelectric acoustics arises from the coupling of mechanical and electrical acoustic systems in certain crystals, such as quartz. An external electric field causes a polarization of the crystal lattice dipoles in the quartz. The polarization causes electronic displacement of the crystal lattice, which is equivalent to a mechanical strain. If an oscillating electric field is applied to the quartz, an oscillating mechanical strain is produced. At a certain frequency, damping is at a minimum and the storage and reflection of energy contribute to a standing wave in the crystal; this is the resonant frequency.

An oscillating piezoelectric crystal will transfer its acoustic energy to the medium that it contacts. Acoustic energy dissipates as it travels into the contacting material, depending on the acoustic properties of the bulk medium and the interface. This is the basis of piezoelectric acoustic-wave sensors in liquid.

Before exploring the effect of damped acoustic waves in liquid, we require an explanation of basic acoustics and how it can be driven by piezoelectricity.

2.1 ACOUSTICS IN PIEZOELECTRIC CRYSTALS

An acoustic wave is generated in piezoelectric quartz due to the sustained motion of particles along an axis, in response to an electric field. Due to the crystal lattice structure of quartz and other piezoelectric crystals, when a voltage is applied to a piezoelectric crystal, the quartz molecules displace and impact upon adjacent molecules. If the voltage is alternating, displaced molecules store energy from the stressing of bonds,

which propagates through the material. Displaced molecules also reflect back as a result of prior collisions to impact upon other molecules. Near the resonant frequency, the storage and reflection of collision energy creates a standing wave in the material.

Four main types of waves can exist in a piezoelectric material, depending on the configuration of the crystal lattice relative to the electric field. The waves can be compression or shear, and longitudinal or transverse. Compression waves are characterized by particle displacement propagating linearly through the material. Particle displacement in shear waves occurs about an axis, where adjacent molecules move in opposite directions about the axis. Longitudinal waves propagate parallel to the direction of particle displacement and transverse waves propagate perpendicular to particle motion. As mentioned previously, transverse shear mode (TSM) wave devices are most common for biochemical acoustic wave sensors. The oscillation mode of a TSM resonator is shown in Figure 1.

Figure 1 – Oscillation mode of a transverse shear transducer [16]

Throughout this thesis, the following coordinate system will be used, where x is always the direction of motion of transverse-shear mode oscillations.

Figure 2 - Coordinate system used throughout analysis

In transverse shear mode, wave propagation is in the thickness direction, which is the direction of the electric field. For resonance to occur, the amplitude must be greatest at the point of reflection, which is at the end of the resonator. For a TSM wave, the thickness must be odd multiples of half wavelengths, so that the wave can reflect back on itself and cause resonance, such that

$$d_Q = \frac{n\lambda}{2} \quad (1)$$

where d_Q is the thickness, λ is the wavelength and $n = 1, 3, 5 \dots$ is the resonant harmonic. The wave velocity is the distance traveled by the wave over time. It is a function of the stiffness and density of a material, given by

$$v = \sqrt{\frac{C}{\rho}} \quad (2)$$

where v is the wave velocity, ρ is the density and C is a generalized complex shear modulus

$$C = c + e^2/\epsilon + j\omega\eta \quad (3)$$

where c is the stiffness, the e^2/ε term results from piezoelectric stiffening (e is the piezoelectric constant and ε is the dielectric constant) and η is the dissipation from the fourth-rank viscosity tensor. The stiffness and viscosity tensors apply to all viscoelastic materials. For non-piezoelectric materials, the piezoelectric stiffening term disappears, for purely viscous fluids, the stiffness c is neglected, and for purely elastic materials, the viscosity η is neglected. The wave velocity is related to the frequency, so the resonant frequency of a simple one-dimensional plate is given by

$$\omega_0 = \frac{2\pi}{d_Q} \sqrt{\frac{C}{\rho}} \quad (4)$$

where ω_0 is the radial resonant frequency. This is an approximation for a TSM sensor, since it assumes an infinite plate area. A related value is the wave number k , given by

$$k = \omega \sqrt{\frac{\rho}{C}}. \quad (5)$$

2.1.1 Resonance

For biosensor applications, the TSM device is operated at the resonant frequency because the peak amplitude is highest and thus provides the greatest device sensitivity. The energy of an oscillating material consists of three terms: viscous energy dissipation (which is very low for quartz), inertial energy storage and elastic energy storage. The viscous term is energy loss within the resonator caused by viscous dissipation. Inertial energy storage occurs when particle displacement within the standing wave is zero. At this point, particle velocity is at a maximum. Elastic energy storage occurs when particle displacement is at a maximum and velocity is zero. At this point, the particle has sufficient energy to return back to its original position. The crystal can be modeled as a

three-parameter mechanical system, consisting of a mass, representing inertial storage, an elastic spring, representing elastic storage, and a viscous damper, representing dissipation. This is shown in Figure 3.

Figure 3 - Mechanical system representation of the motional arm of a quartz resonator, showing inertial and elastic storage and internal damping

This can be described mathematically as

$$m \frac{d^2 x}{dt^2} + kx + \eta \frac{dx}{dt} = F \quad (6)$$

In the frequency domain, this becomes:

$$j\omega m + k/j\omega + \eta = F/V \quad (7)$$

F/V is a driving vector over a flow vector, which is an impedance term. This leads to the Butterworth-Van Dyke (BVD) model of the motional arm of the resonator [16]. The amount of viscous dissipation in quartz is small, but it is included as a resistance. Since, in a quartz device, motion is induced by an electric field created by two parallel plates, a parallel capacitance completes the BVD model for a quartz resonator, shown in Figure 4.

Figure 4 - Equivalent circuit for a piezoelectric quartz resonator. The motional arm has terms for inertial and elastic storage, and viscous dissipation. The parallel capacitance results from the parallel-plate metal electrodes used to drive the crystal.

Resonance will occur when the imaginary part is zero. From Bottom [16], the resonant frequencies for this system are:

$$\begin{aligned} \omega^2 &= \frac{1}{LC} & \text{and} & & \omega^2 &= \frac{1}{LC} + \frac{1}{LC_0} \\ f_R &= \frac{1}{2\pi} \sqrt{\frac{1}{LC}} & & & f_A &= \frac{1}{2\pi} \sqrt{\frac{1}{LC} + \frac{1}{LC_0}} \end{aligned} \quad (8)$$

There are two resonant frequencies because the circuit impedance model is a parallel system. The first is the series resonant frequency, and depends only on the series or motional arm of the BVD model. The parallel or anti-resonant frequency also includes the parallel capacitance C_0 . The series resonant frequency is a real resonance and will produce the highest amplitude of oscillation, so is the desired frequency for resonator applications. The anti-resonant frequency is electrical in nature and will not produce mechanical resonance.

2.2 THE PIEZOELECTRIC EFFECT

Piezoelectricity is the coupling of solid mechanics and electromagnetism. This is modeled with Tiersten's fundamental equations of piezoelectricity [17]. Two major considerations are important when developing the fundamental model for the quartz resonator: elasticity and electromagnetism.

2.2.1 Elasticity

Quartz is an anisotropic material, so its material properties depend on direction; a stress in one direction may cause a strain in multiple directions. From the conservation of linear momentum, the equation of motion due to stress in a material is:

$$\sigma_{ij,i} + F_j = \rho \frac{dv_j}{dt} \quad (9)$$

where σ_{ij} is a second-rank stress tensor, F_j is an externally applied force in direction j , ρ is the mass density and v_j is the particle velocity in direction j . By assuming no external force and that the first derivative of velocity is equal to the second time derivative of displacement, $dv_j/dt = \ddot{u}_j$ we have

$$\sigma_{ij,i} = \rho \ddot{u}_j \quad (10)$$

where u_j is the particle displacement in direction j . This is Newton's Second Law. Since a stress leads to a strain, we require the definition of the second-rank strain tensor:

$$S_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i} - u_{k,i} u_{k,j}). \quad (11)$$

For piezoelectricity, which concerns only with small deformations, the sum of the displacement gradients is much greater than their product, so $|u_{k,i} u_{k,j}| \ll |u_{i,j} + u_{j,i}|$, and

Equation 11 can be re-written as

$$S_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i}) \quad (12)$$

A strain S_{ij} is the average of the orthogonal displacement gradients. Both the stress and strain tensors exhibit symmetry, due to conservation of angular momentum, so $S_{ij} = S_{ji}$ and $\sigma_{ij} = \sigma_{ji}$.

A generalized form of Hooke's Law relates the stress and strain tensors, which combines the basic stress-strain relationship of elasticity with a viscous term added by

Reed *et al.* [7] to account for viscous losses in the quartz. The equation of motion for a viscoelastic solid is

$$\sigma_{i,j} = c_{ijkl} S_{kl} + \eta_{ijkl} \dot{S}_{kl} \quad (13)$$

where c_{ijkl} is a fourth-rank stiffness tensor, equivalent to Young's Modulus and η_{ijkl} is a fourth-rank viscosity tensor. Both fourth-rank tensors are fully symmetric.

The basis of the piezoelectric effect is that any mechanical stress is coupled to electrical motion, in the form of an electric field. A mechanical stress in the material causes an induced electrical field. This is given by the formula

$$\sigma_{i,j} = e_{ijk} E_k \quad (14)$$

where e_{ijk} is the third-rank piezoelectric stress tensor and E_k is an electric field parallel to the k -axis. This last relation forms the basis of Hooke's law for a piezoelectric viscoelastic material:

$$\sigma_{i,j} = c_{ijkl} S_{kl} + \eta_{ijkl} \dot{S}_{kl} - e_{ijk} E_k \quad (15)$$

The first term represents elastic stress, the second viscous stress and the last, piezoelectric stress. For AT-cut quartz, the most common type used for biosensor applications due to its temperature stability, $c = c_{1212}$ is the stiffness, $\eta = \eta_{1212}$ is the viscous term, and $e = e_{212}$ is the piezoelectric coefficient. The AT-cut crystal is cut along the crystallographic Y -axis and rotated approximately $-35\frac{1}{4}^\circ$ about the X -axis. In this configuration, the electric field is applied in the y -direction (subscript 2) to generate shear waves in the x -direction (subscript 1). Equation 15, which is Hooke's Law, then takes the following form:

$$\frac{\partial \sigma_x}{\partial y} = c_{1212} \frac{\partial u_x}{\partial y} + \eta_{1212} \frac{\partial^2 u_x}{\partial y \partial t} + e_{212} \frac{\partial \phi}{\partial y}. \quad (16)$$

The entire definition of Hooke's Law for an electric field along the y -axis involves similar equations for the y - and z -directions. However, for Y-cut quartz, there is only x -direction motion. This is a consequence of due stems from Equation 14 written in matrix notation, which has the form

$$\begin{bmatrix} -\sigma_{x,x} \\ -\sigma_{y,y} \\ -\sigma_{z,z} \\ -\sigma_{y,z} \\ -\sigma_{z,x} \\ -\sigma_{x,y} \end{bmatrix} = \begin{bmatrix} e_{11} & 0 & 0 \\ -e_{11} & 0 & 0 \\ 0 & 0 & 0 \\ e_{14} & 0 & 0 \\ 0 & -e_{14} & 0 \\ 0 & -e_{11} & 0 \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad (17)$$

Since the field is only in the y -direction, only the terms $-e_{14}$ and $-e_{11}$ remain, yielding shear stresses about the y - and z -axes. This corresponds to shear in the x -direction.

2.2.2 Electromagnetism

To explore electromechanical coupling in piezoelectric quartz, it is necessary to understand how the electric field is generated in the material and how this affects the mechanical characteristics.

A piezoelectric resonator is a dielectric material between two parallel electrodes and acts as a capacitor. When there is no induced electric field and no external strains or stresses, the quartz particles are arranged so that dipole moments in the crystal lattice sum to zero. For electromechanical transduction, the stress-strain characteristics of the material must be coupled to electrical parameters. The electrical parameters involve the

four Maxwell equations for stationary materials, with three material equations for a conductor, a dielectric and a magnetic material.

For a material situated within a dielectric, the divergence of the electric field $\nabla \cdot E$ is proportional to the total charge density ρ . The charge density combines the bound and free electron densities within the material. The bound charge density is the divergence of the polarization within the dielectric, and the free density is the electric flux density, and we have Gauss' Law of electric fields, in tensor form,

$$E_{i,j} = \frac{\rho}{\epsilon_0} \quad (18)$$

where ϵ_0 is the permittivity of free space. Since ρ and ϵ_0 are constant and $D = \epsilon E$, this is equivalent to

$$D_{i,j} = 0 \quad (19)$$

where D is the electric displacement. Gauss' Law of electric fields is Maxwell's first equation of electromagnetism.

Fields caused by electric currents contribute to the total magnetic field, and are caused by the magnetic fields of individual moving charges. The magnetic field B is uniform throughout a given volume with no magnetic monopoles. Therefore, there is no net magnetic flux and the divergence of B is

$$B_{i,j} = 0 \quad (20)$$

This is Gauss' Law for magnetic fields and is Maxwell's second equation of electromagnetism.

The change in the magnetic field B with time is proportional to the change in the electric field over a surface. This is shown by Faraday's Law

$$\varepsilon_{ijk} E_{k,j} + \dot{B}_i = 0 \quad (21)$$

where ε_{ijk} is the *levi-civita* symbol, such that

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

This is Maxwell's third equation for electromagnetism. The *levi-civita* symbol indicates the dependence of electric fields on magnetic fields. The dependence can be positive or negative, depending on the relative direction of the fields. If the fields are in the same direction, there is no dependence.

The dielectric equation for piezoelectricity, which relates the electric field E and the strain S to the electric displacement is given by

$$D_i = e_{ikt} S_{kt} + \varepsilon_{ik} E_k \quad (22)$$

where D_i is the electric displacement and ε_{ik} is the dielectric coefficient. For AT-cut quartz, $\varepsilon = \varepsilon_{22}$ for reasons analogous to those described by Equation 15. Finally, the electric field is related to the potential applied across it as

$$E_k = -\varphi_{,k} \quad (23)$$

where φ is the potential applied in the direction of E .

A summary of the fundamental equations of piezoelectricity is given:

$$\begin{aligned}
\sigma_{ij,i} &= \rho \ddot{u}_j \\
\sigma_{ij,i} &= c_{ijkl} u_{k,lj} - e_{ijk} E_k + \eta_{ijkl} \dot{u}_{k,li} \\
S_{ij} &= \frac{1}{2} (u_{i,j} + u_{j,i}) \\
D_i &= e_{ikl} S_{kl} + \varepsilon_{ik} E_k \\
E_k &= -\varphi_{,k} \\
D_{i,i} &= 0
\end{aligned}$$

These equations are used in many previous studies [2,6,7,8,10,18,19]. This model of piezoelectricity is significant because it is a formal continuum mechanics analysis that facilitates the coupling of a piezoelectric system with an external system such as a fluid media. Coupling with a viscoelastic media is expanded in Section 2.5.

2.3 TRANSVERSE SHEAR MODE RESONATOR

The type of resonator normally used to generate transverse shear waves is the AT-cut crystal. As mentioned above, this crystal is cut at $35\frac{1}{4}^\circ$ from the crystal axis, which is done to improve temperature stability and the direction of wave propagation. An electric field is applied parallel to the y -axis (Y-cut), the resulting strain from will be shear strains in the x - z (horizontal) plane. Figure 5 shows a typical TSM circular crystal.

Figure 5 – Circular TSM crystal, with metal electrodes on both sides. The electrodes are scattered, so oscillations are only induced in the centre.

Particle displacement is perpendicular to the direction of the applied field and to the direction of wave propagation, which is in the y -, or thickness, direction. All

coefficients must similarly be rotated from the Cartesian coordinate system to the crystal system, using rotation matrices. The rotation matrix depends on the size of the coefficient matrix being rotated. For a more complete treatment of rotations and frequency and temperature dependencies of quartz, refer to Bottom [16].

Metallic electrodes are placed on both surfaces of the quartz plate. When an alternating electric field is applied across the quartz at the series resonant frequency, the shearing stress, resulting from piezoelectric coupling, causes an alternating acoustic shear wave in the thickness direction of the quartz. The acoustic energy caused by the alternating current is stored in the quartz as the particle displacement reflects back upon itself.

For a TSM crystal, the values of the equivalent circuit components can be obtained from the material and electrical properties of quartz, using equations from Ballantine *et al.* [20]:

$$C_0 = \frac{\varepsilon A}{d_Q}, \quad (24a)$$

$$C = \frac{8Ae^2}{d_Q c_Q \pi^2}, \quad (24b)$$

$$L = \frac{c_Q d_Q \pi^2}{\omega_R^2 8Ae^2}, \quad (24c)$$

$$R = \frac{\eta_Q d_Q \pi}{8Ae^2}, \quad (24d)$$

where d_Q is the crystal thickness, A is the sensor area, ε is the dielectric permittivity, e is the piezoelectric constant, η_Q is the effective viscosity and c_Q is the shear stiffness.

These equations can be used in conjunction with Equation 8 to determine the resonant characteristics of the crystal.

2.4 FREQUENCY RESPONSE OF ADDED MASS OR FLUID

When mass is added to the top surface of the crystal, the resonant frequency drops because the wave must travel a longer distance and the crystal must expend more energy to move the added mass. The wavelength is increased due to the increase in thickness. Sauerbrey [1] found that the mass of the film added to the quartz surface causes an increase in the thickness of the oscillator. At resonance, the thickness is equal to an odd multiple of half-wavelengths, so the increased wavepath distance results in a longer wavelength at resonance. If the thickness of the film is small relative to the thickness of the quartz, the wave velocity is constant. Since the wavelength varies inversely with frequency at constant velocity, the increase in wavelength due to the film results in a decrease in frequency. Sauerbrey modeled this as:

$$\Delta f = \frac{-2f_0^2}{\sqrt{c_Q \rho_Q}} \left(\frac{\Delta m}{A} \right) \quad (25)$$

where Δf is the change in frequency for an added mass of Δm on an area A , f_0 is the unloaded resonant frequency and c_Q and ρ_Q are the stiffness and density of quartz, respectively. The film was assumed to have the same stiffness and density as quartz. This assumption is valid only for small masses or films with similar properties to quartz, such as metals, but the model overestimates the results for polymers or biological films. As well, it is not physically valid for liquids whose stiffness, viscosity and density are largely different than quartz.

Miller and Bolef [21] modeled the acoustic properties of the film by treating the loaded crystal as a compound resonator. This model accounts for the elastic properties and energy storage in the film. Lu and Lewis [22] used a one-dimensional compound resonator to simulate a crystal and film of large mass. They found that the frequency shift was related to the acoustic impedance of the film. Good agreement was found between the model and experimental data for metallic films such as those used for electrodes. They obtained a simpler form of Miller and Bolef's equation.

When the crystal is operated in a gas or liquid, acoustic energy is transferred to the fluid through viscous coupling of the quartz surface to the fluid particles. This energy transfer results in a drop in resonant frequency, because fewer oscillations can be supported due to the drop in energy stored. This can be equated to the loss in energy through viscous damping of the fluid. Kanazawa and Gordon [23] modeled a quartz resonator in contact with a fluid by coupling the properties of the fluid and the quartz. They linked the standing shear wave in the quartz with an exponentially decaying damped shear wave in the fluid. In this model, the velocity of the quartz is assumed equal to the liquid velocity at the solid-liquid interface, but decayed rapidly as the wave propagated into the fluid. This is the no-slip boundary condition, where the velocity of quartz at the interface is equal to that of the liquid layer. For a resonant frequency given by Equation 4, they derived the following equation for frequency shifts due to liquid loading

$$\Delta f = -\frac{f_0^3}{\pi} \left(\frac{\rho_L \eta_L}{\rho_Q c_Q} \right)^{1/2} \quad (26)$$

For small values of Δf , with f_0 the unloaded resonant frequency, ρ_L and η_L the density and viscosity of the liquid, respectively, and ρ_Q and c_Q the density and stiffness of the quartz. If the density of the liquid and the density and stiffness of the quartz are known, the liquid viscosity can be determined. This model agrees well with experimental results and shows the viscosity dependence of the device in liquid.

The authors explored the damping behavior of the liquid. A standing shear wave in a TSM crystal is quickly damped when transferred to the liquid. The decay is exponential and dies off with the characteristic decay length δ . This can be thought of as the thickness of the liquid rigidly bound to the crystal surface, and can be treated as added mass $\Delta\rho_L$. The effective thickness is the reciprocal of the wave constant (Equation 5) and varies with $(\eta_L)^{1/2}$. As the viscosity increases, so too does the added mass. From this analysis, the characteristic decay length for water is approximately 180 nm, on the order of 150 molecular diameters. Figure 6 shows damped oscillations in the liquid.

Figure 6 – Standing-wave oscillations in the crystal and damped oscillations as the wave progresses into the liquid. The dotted lines show the transverse resonant wave. This diagram is not to scale.

Bruckenstein and Shay [24] used a similar analysis for an electrochemical mass sensor using TSM quartz in contact with a liquid. Their experimental work analyzed the

effects of liquid viscosity and temperature, as well as the thickness of the bulk liquid. They found that temperature had a large effect on the resonant frequency, since liquid viscosity is heavily dependent on temperature. They also examined the effect of changes in double-layer structure on the resonant frequency. The double layer is the liquid mass adjacent to the crystal, whose properties cannot be lumped with the bulk liquid properties. Within the double layer, physical properties may be drastically different than the bulk liquid, which will affect the resonant frequency. The viscosity in this layer will be different, and will therefore affect the frequency response. As with the model used by Kanazawa and Gordon [23], the authors used a no-slip boundary condition.

These approaches model a shear wave propagating through a quartz resonator with an attached film or operating in a bulk fluid medium. Properties of the film or the fluid are determined by relating them to the series resonant frequency and acoustic impedance of the system. These methods partially predict the behavior of the TSM resonator, but they do not address the fundamental mechanical characteristics of the system, nor do they include the complex viscoelastic interactions at the quartz-liquid interface.

A better understanding of how acoustic waves propagate into a film or fluid permitted the development of more advanced biosensors.

2.5 TSM BIOSENSORS

As was shown in the analyses by Kanazawa and Gordon [23] and Bruckenstein and Shay [24], a liquid in contact with the crystal produces a damping effect on the resonant frequency. The damping increases with the viscosity of the liquid. Reed *et al.*

[7] applied the fundamental model described in Section 2.2, to a quartz resonator in contact with a solid film and viscoelastic liquid. They also included an elastic shear term in the fluid model to establish the mechanical admittance, which was solved by establishing a set of boundary conditions. They used the no-slip boundary condition, but acknowledged the possibility of slip at the surface-liquid interface.

To model the viscoelastic effects of the liquid, the authors included complex viscosity and shear modulus terms, given by

$$\begin{aligned}\tilde{\eta}_L &= \eta_0 \frac{1}{(1 + j\omega\tau)^\beta} \\ C &= c + e^2 / \varepsilon + j\omega\eta_0\end{aligned}\tag{27}$$

where $\tilde{\eta}_L$ is the complex viscosity and C is the complex shear modulus mentioned above. The bulk fluid viscosity is η_0 , τ is a relaxation time and β is a distribution parameter for the relaxation times. The solution involves determining τ and β from data fitting.

Martin *et al.* [8] modeled the loaded resonator in contact with a Navier-Stokes liquid to approximate a TSM resonator with mass accumulations from a contacting liquid. They used the BVD model, shown in Figure 4, adding two liquid and one solid film terms. They assumed a viscous fluid, modeled as inertial energy storage and a viscous dissipation, and a film layer modeled as an inertial storage. The expanded equivalent circuit is shown in Figure 7.

Figure 7 - Expanded equivalent circuit model, containing the film mass and fluid mass and viscous loss

The no-slip boundary condition was used, though the authors did state that there were losses due to viscous damping by the fluid. The model is effective in measuring mass loading from both fluid and film.

Hayward [9] related the viscous parameters of the fluid to the equivalent circuit of the loaded quartz crystal (Figure 7) from a solution of Stoke's second problem. This established a relationship between the physical properties of the crystal-liquid resonator and the equivalent circuit impedance, of the form

$$Z_f = \frac{\rho_q l^4 \omega^2}{16 A C \epsilon^2} (\omega \rho c / 2)^{1/2} (1 + j) \quad (28)$$

This model overestimates both the frequency response and the viscous losses, calculated from the equivalent circuit, though the overestimation may be attributed to the use of the no-slip boundary condition. This model breaks the impedance into real and imaginary terms. The real term is viscous energy dissipation and the imaginary inductance term is energy storage from fluid inertia. The real and imaginary terms are evident on the modified Butterworth-van Dyke (BVD) electrical model (Figure 7), which has an added inertial inductance for film mass.

Duncan-Hewitt and Thompson [2] reduced the fundamental equations of piezoelectricity to a system of two equations and four unknowns for the transverse-shear

displacement of the quartz surface u_1 and the electrical potential φ in transverse shear mode.

$$u_Q = [B_1 \exp(jk_Q d_Q) + B_2 \exp(-jk_Q d_Q)] \exp(j\omega t) \quad (29)$$

$$\varphi = (e/\epsilon) u_Q + (B_3 d_Q + B_4) \exp(j\omega t) \quad (30)$$

where the B values are constants of integration, d_Q is the height normal to the quartz surface, k_Q is the complex wave number for quartz from Equation 5.

They developed a four-layer model where the resonator was divided into four viscoelastic layers: the quartz and electrode, the surface-adjacent liquid, the transition liquid and the bulk liquid. The surface-adjacent layer is a highly ordered liquid with strong hydrogen bonds that takes on properties between the surface and the bulk liquid. This region will have a higher density than bulk from the higher packing ratio due to ordering effects from the surface. A thickness of one molecular diameter was used for this layer. The transition layer is less ordered than the surface-adjacent layer but still has higher density than the bulk, due to moderate packing. The transition layer can be up to ten molecular diameters thick [25]. At this point, the electrostatic interaction from the surface has very little effect, and the liquid has bulk ordering and parameters.

The authors developed the properties of the layers using thermodynamic and hydrodynamic principles governing surface wetting and interactions between liquid and a solid surface. They noted the difference in hydrophobic versus hydrophilic surfaces of quartz. The hydrophilic surface will tend to form a strong bond with the adjacent liquid, creating a thin layer of semi-crystalline liquid at the interface, resulting in a higher density than the bulk. A hydrophobic surface will not form this layer, and result in less

coupling between the quartz and liquid, thereby yielding a lower density. The surface free energy, determined by contact angles between the surfaces, can be correlated with interfacial slip parameters and will be drastically different for hydrophobic and hydrophilic surfaces. This model requires knowledge of the viscosity, density and thickness of each interfacial layer. The authors related each of these parameters to the bulk properties, resulting in a two-parameter fit of the thickness of the two interfacial layers.

Yang and Thompson [26] studied the behavior of a TSM sensor in a conductive liquid. They examined the electrical double layer and acousto-electric coupling between the double layer and ions and dipoles in the conductive solution. A double layer is a dipolar arrangement at the quartz-liquid interface caused by the electrical field. The acoustic coupling in dilute solutions results in a strong dissipation of acoustic energy and a subsequent decrease in the series resonant frequency. In concentrated solutions, the electrical double layer acts as a capacitive energy storage unit and increases energy transfer from the quartz dielectric to the double layer. This results in an increase in the dielectric capacitance and a decrease in the parallel resonance frequency.

Many models couple the motion of the quartz with the motion of an adjacent fluid layer, and are based on an infinite viscous liquid (as modeled by, for example, Landau and Lifschitz [27]). The first equation is the fluid continuity equation:

$$\dot{\rho}_L + (\rho_L \dot{u}_i)_i = 0 \quad (31)$$

where ρ_L is density and u_i is particle displacement parallel to the i -axis. The next is Hooke's law for fluids, which is the stress-strain relation for a moving fluid:

$$\sigma_{ij} = -p\delta_{ij} + \eta_B(\dot{u}_{i,j} + \dot{u}_{j,i}) + (\zeta - 0.67\eta_B)\delta_{ij}\dot{u}_{k,k} \quad (32)$$

where p is the bulk pressure, η_B is the bulk dynamic viscosity, δ_{ij} is the Kronecker delta, such that

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

and ζ is a second viscosity term from Landau and Lifschitz [27], a measure of the viscosity contribution when turbulent forces are present. In the present model, this term is neglected, since the device operates on size scales where turbulence is undefined. The final fluid equation is Newton's second law for fluids, which equates internal and external forces in the liquid:

$$\sigma_{ij,i} + F_j = \rho_B(\ddot{u}_j + \dot{u}_i\dot{u}_{j,i}) \quad (33)$$

where F_j is an external force. The non-linear term $\dot{u}_i\dot{u}_{j,i}$ was neglected, because, since the fluid is assumed isotropic, the divergence of the velocity $\dot{u}_{j,i} = 0$.

The solution to the piezoelectric solid-liquid model with no slip at the solid-liquid interface requires the following boundary conditions for a two-layer model:

1. No stress at bottom of crystal, $y = 0$:

$$\sigma(0, t) = 0 \quad (34)$$

2. Continuity-of-stress at the top of the quartz, $y = d_Q$:

$$\sigma(d_Q, t) = \sigma_{(L)}(d_Q, t) \quad (35)$$

where the subscript L refers to stress in the liquid

3. No-slip condition at the solid-liquid interface, $y = d_Q$:

$$u_{(L)x}(d_Q, t) = u_x(d_Q, t). \quad (36)$$

4. Negative potential at free surface, $y = 0$:

$$\varphi(0, t) = -\varphi_0 e^{j\omega_0 t}. \quad (37)$$

5. Positive potential at solid-liquid interface, $y = d_Q$:

$$\varphi(e, t) = +\varphi_0 e^{j\omega_0 t}. \quad (38)$$

Duncan-Hewitt and Thompson [2] solved the five boundary conditions for the fluid displacement at the interface:

$$u_B = B_5 \exp(-jk_B d_B) \exp(j\omega t), \quad (39)$$

where k_B is the complex wave number for the bulk fluid. Combined with Equations 29 and 30, this forms a system of three equations and five unknowns B_i . The final two equations for the two-layer model describe the potentials at each face of the crystal, for a device with the top face grounded:

$$(e/\varepsilon)[B_1 \exp(jk_Q d_Q) + B_2 \exp(-jk_Q d_Q)] + B_3 d_Q + B_4 = 0 \quad (40)$$

and

$$(e/\varepsilon)(B_1 + B_2) + B_4 = \varphi_0. \quad (41)$$

This establishes a system of five equations and five unknowns that can be solved to determine the frequency and motion of the quartz device, for a given configuration.

Using the no-slip boundary condition, the solution of this model agrees well with experimental data for low $\sqrt{\rho\eta}$, but overestimates the frequency shift for high viscosity and density liquids [6]. A number of theories have been postulated in an attempt to

explain the difference in experimental and theoretical results. Three prevalent explanations are liquid-trapping, the lumped impedance transmission-line model, and interfacial slip.

2.5.1 Liquid-trapping model

Martin *et al.* [28] predicted that liquid trapping in surface asperities on the electrode was the cause of deviations from values predicted from the Navier-Stokes models. For hydrophilic liquids on bare (hydrophilic) electrodes, the liquid would completely fill the cavity and would appear as added mass, since the liquid would move with the quartz and not be affected by the bulk liquid. This would lead to greater frequency shifts than expected: one component for the mass-effect (of the trapped liquid) and another for the liquid viscoelastic effect. For the hydrophobic liquid on the bare electrode, the liquid would not fill the cavity but would instead form a film over the cavity, and the cavity would remain filled with air. This situation would lead to smaller frequency shifts than the hydrophilic case, for a liquid of similar viscosity and density, since no mass effect would be observed.

However, atomic force microscopy (AFM) surface roughness measurements of hydrophilic (bare) and hydrophobic surfaces has shown that the size of the cavities on the bare surface cannot account for the entire frequency shift due to the mass effect [11]. As well, the same AFM measurements showed that the hydrophobic surface was hydrodynamically smooth, so the surface roughness on the two compared surfaces was not equal. The assumption that liquid trapping occurs on the hydrophilic surface is reasonable, but the mass effect cannot account for the discrepancy in observed frequency shifts for the hydrophilic and hydrophobic cases.

2.5.2 Lumped impedance model

Another method to account for differences between expected and observed results is the transmission-line model. Because of their very high quality-factors, piezoelectric crystals have been used extensively as frequency controllers in the electronics and telecommunications industries, and their electrical characteristics are well understood. Due to the piezoelectric properties, their electrical and acoustic properties are highly coupled, so the electrical model can be extended to load acoustic effects by adding more terms to the BVD model. The transmission line model is an electrical analogy with impedance terms representing any combination of film and liquid loading. Martin *et al.* [29] combined the crystal resonator with oscillator electronics to measure liquid density and viscosity, creating a linear sensor with a greater dynamic range. Behling *et al.* [30] explored the effect of film thickness on the lumped shear modulus of the interface G , which is a complex modulus involving elastic storage G' and viscous dissipation G'' . They also explored its relation to the electrical impedance Z . Comparisons of this model with experimental results show very good agreement. However, the lumped parameter G may cause important information to be lost, regarding the nature of the film and its interaction with an adjacent liquid.

Depending on the nature of the load, the complex impedance can take different forms [18] and the values must be determined by numerical curve fitting. While this model shows good agreement with experimental results in many cases [18,30], it is based on an electrical analogy. The transmission line model uses the classical mechanics no-slip boundary condition for the velocity at each interface. However, recent theoretical [31, 32] and experimental [33,34,35] evidence has shown that, at the micro- and

nanoscopic levels, the no-slip boundary condition is not always applicable. This is the case in many acoustic wave device applications where the motional amplitude is on the order of a few molecular diameters. For instance, Hayward and Thompson [6] calculated that, for a 9 MHz TSM crystal with a drive voltage of 0.1 V, the peak motional amplitude is 6.8 nm in air and 0.29 nm in water. An empirical formula from Borovsky *et al.* [36] shows that the displacement was 14 nm for a crystal with a 0.1 V drive and a Q of 100000. These amplitudes are very small, on the order of a few molecular diameters.

These distances are comparable to a fundamental length mentioned by Eringen [37]. The fundamental length scale is on the order of a molecular length. For classical continuum theories to apply, the fundamental length must be much smaller than the length of interest, as is the case in most macroscopic applications. However, for acoustic wave devices, the fundamental length is comparable to the length of interest, and asperities or imperfections in the system are not averaged out by the size of the system. Instead, generalizations to the classical boundary conditions must be made, and we enter into the domain of so-called non-local continuum mechanics. In fact, molecular simulations by Wittmer *et al.* [38] have shown that continuum elasticity theory breaks down below lengths of 30 to 50 molecular diameters. This is in rough agreement with the experimentally determined behavior of molecularly thin films under shear, which have been shown to have 10^5 times the viscosity of a normal bulk fluid, for films less than 5 to 10 molecular diameters [25]. This is due to the breakdown of continuum theories at small distances and separations.

In the case of the TSM crystal, we are dealing with length scales of a few molecular diameters, due to the small oscillation amplitude of the crystal. The motional amplitude is comparable to the size of a water molecule (4 Å), and much smaller than most proteins or surfactants. For this reason, the no-slip assumption of classical fluid mechanics is not applicable at this level.

For many resonator configurations, involving complex surface applications in analytical chemistry, the classical no-slip model does not agree with certain experimental results. Furtado *et al.* [6] studied the interaction of HIV-1 TAR RNA with two Tat-derived proteins of 12 and 40 amino acids, an area of interest for development of HIV drugs. They observed increases in the frequency and decreases in resistance when Tat₁₂ was bound to the surface, indicating that the Tat₁₂ changed the configuration of the TAR surface protein. If the change was from a hydrophilic configuration to a hydrophobic one, the acoustic wave would no longer propagate into the liquid and less energy is used to move the crystal, increasing the frequency and decreasing the dissipation. Similar tests with the longer protein resulted in a decrease in both frequency and resistance. This could be due to different mechanisms, one possibility being that Tat₄₀ binds fully to the TAR RNA, decreasing the frequency, but changing the surface configuration, thereby reducing the dissipation and decreasing the resistance.

The same group [39,40,41] has obtained similar results for a variety of linker-protein configurations, all involving unexpected frequency and resistance shifts. It is unlikely that any of these situations result solely from a mass deposition case, and the conventional viscoelastic model cannot explain this behavior. This has led many

researchers to speculate on the existence of slip at the sensor liquid interface [6,10,12,46], where the velocity of liquid molecules at the wall is not identical to the wall molecules themselves.

2.6 MODELS INVOLVING SLIP

The debate as to whether or not slip occurs at the solid-liquid interface has been considered in the literature for many years. It is a common question when dealing with sliding friction and lubrication, and is now at the forefront of studies involving nanomachines and nanotribology, the study of friction at very small scales [42]. In lubrication studies on the behavior of polymer flows, polymer chains can graft to the pipe wall and potentially cause slip. Brochard and de Gennes [43] predicted that the degree of slippage depends on the shear rate of the flow, with a transition from stick to slip with increasing shear rate. The authors modeled polymer chains grafted to a wall, with an identical polymer flowing across the wall. They predicted that, at low shear oscillations, the flow became entangled in the polymer film, resulting in the no-slip boundary condition. However, at higher shear rates, the flow became disentangled, resulting in significant slip. To model the slip, the authors used a conceptual slip length to relate friction to shear rate.

Slip length is commonly invoked in microscopic flow and friction modeling to represent a difference in velocity at a wall or interface. The no-slip velocity profile is stretched, so that the liquid velocity at the wall corresponds to the measured value. The profile is then extrapolated into the wall until the no-slip condition is met. The distance from the wall to the extrapolated no-slip velocity is the slip length b , shown in Figure 8 for fluid flowing at a stationary wall.

Figure 8 – Velocity profiles for a) the no slip case where the velocity at the wall $v_s = 0$ and b) the slip condition with positive slip length b , and wall velocity $v_s = v_{slip}$

Slip can also be thought of as an elastic process, where a shear stress σ at the boundary depends on the velocity of the adjacent liquid layer v_s , described by

$$\sigma = kv_s \quad (42)$$

where k is a friction coefficient (with units N.s/m^3) between the liquid and the surface.

For a Newtonian liquid with bulk viscosity η , the shear stress is caused by viscous interactions at the wall, given by

$$\sigma = \eta \left. \frac{dy}{dz} \right|_{z=0} = \eta \frac{v_s}{b} \quad (43)$$

The slip length can then be related to interfacial friction and viscosity by

$$b = \frac{\eta}{k} \quad (44)$$

Slip length is constant at constant friction and viscosity, and can be used to calculate the slip velocity if the proper velocity profile is used.

Many authors have shown the existence of slip for many cases, especially those involving non-polar liquids such as alkanes. Migler *et al.* [44] used optical techniques to

examine the local velocity of a polymer liquid near the wall. They found low slippage for strong polymer-surface interactions, which corresponds to the non-slip boundary condition, but large slip for weak polymer-surface interactions at high shear rates. This indicates that there should be a large slip length for weakly bound interfaces, which agrees with Equation 44, since the friction between two surfaces decreases with their mutual affinity. Slip is observed at high shear rates because a large velocity profile is necessary to induce observable velocities at the interface, as shown in Figure 8.

Vinogradova [31] modeled hydrodynamic slip and derived equations for pressure and hydrodynamic resistance forces for two approaching curved rigid bodies in a Newtonian liquid, using a slip length correction factor. The model permits the calculation of the pressure and hydrodynamic forces for various geometries and configurations and is accurate for low Reynolds numbers. Using the same hydrodynamic force/slip model, Horn *et al.* [45] found that a slip boundary condition could be used to describe the hydrodynamic forces of an ideal elastic fluid between two curved mica surfaces, using the surface force apparatus. They found slip lengths on the order of 30-50nm.

Molecular dynamics simulations by Barrat and Bocquet [32], of partially wetting liquids on a solid substrate wall, yielded slip lengths on the order of 30 molecular diameters, for large contact angles. A Lennard-Jones potential was used to model the interaction between molecules, with terms to represent the relative cohesiveness between phases. Low cohesiveness between the fluid and the wall yielded slip lengths of

appreciably more than a molecular diameter, even at high pressures. For higher cohesiveness, the instance of slip becomes much less prevalent.

Pit *et al.* [14] found that a simple Newtonian fluid (hexadecane) can slip at a wall coated with stearic acid while measuring slip of simple fluids between two oscillating plates. They found that the uncoated shear rate matched the coated rate when a large slip length was added, much larger than the molecular size of the hydrocarbon chain. It was predicted that similar slip should occur on the surface of a standard TSM oscillator. The same group [35] later found direct experimental evidence of slip at a hexadecane/solid interface, using the same technique as before. Hexadecane was tested on bare sapphire and octadecyltrichlorosilane (OTS).

The situation explored by this group is similar to the case of a piezoelectric acoustic device in liquid, since there is an imposed shear rate affecting the degree of slip at the interface. It is important to note that the slip lengths for a TSM will be different, due to the difference in motional amplitude and frequency.

From Craig *et al.* [34], slip can also exist in an aqueous Newtonian liquid bounded by relatively hydrophilic surfaces, the degree of slip depending on the amplitude and shear rate. The authors showed experimentally that slip length, and thus slip velocity, increased with increasing shear rate. Similar results from Zhu and Granick [33] were achieved for spheres coated with 1-hexyldecylamine or octadecyltriethoxysiloxane (OTE) immersed in tetradecane and water. The wetting case of tetradecane on bare mica agreed well with the no-slip condition but there were large deviations from the continuum situation for water on the OTE surface. Since water against an OTE surface yielded the

largest contact angle, it is evident that the surface tensions and thus surface free energy play an important role in slip behavior. As well, the authors found that slip length increases with increasing velocity.

2.6.1 Slip Models for Acoustic Wave Devices

Recently, slip has been included in various models of acoustic wave devices. McHale *et al.* [12] added slip to the lumped impedance model as a single-loop negative feedback impedance, where the forward loop is the impedance calculated for the no-slip boundary condition. This results in the slip velocity boundary condition at the interface,

$$v_i(z = z_i) = \frac{v_{i-1}(z_i)}{1 + s_i Z_L} \quad (45)$$

where $v_{i-1}(z_i)$ is the velocity of the bottom surface at the interface, s_i is the interfacial slip factor, and Z_L is the total impedance of the i th and higher layers. For a model with two layers and a slip boundary condition between the first and second layers, the load impedance is

$$Z_L = \left(\frac{Z_1 + Z_2}{1 + \frac{Z_1 Z_2}{\rho_1 G_1}} \right) \left(\frac{1 + s_2 Z_1 Z_2 (Z_1 + Z_2)}{1 + s_2 Z_2 \left(1 + \frac{Z_1 Z_2}{\rho_1 G_1} \right)} \right). \quad (46)$$

ρ_1 is the density of layer bottom layer and G_1 is a complex shear modulus

$$G = \frac{j\omega\eta c}{c + j\omega\eta}. \quad (47)$$

The authors linked slip to a dimensionless friction χ ,

$$s = \frac{1}{\chi \sqrt{\rho G}} \quad (48)$$

This relation includes the expected dependence on density and viscosity, but it does not give a specific physical context for determination of the friction coefficient. However, the authors did find agreement with experimental data [46].

Work by Krim and colleagues [46,47,48] over the past fifteen years has explored a wide range of topics relating to interfacial friction and slip on quartz oscillators. The authors explored the possibility of interfacial slip and how this contributes to interfacial viscosity. They derived the acoustic impedance of an absorbed film by adding a dissipative term, showing that the change in frequency is related to a change in mass and the change in resistance is related to the change in dissipation in the film. Dayo *et al.* [48] studied the behavior of solid nitrogen on a lead surface, at temperatures above and below its superconducting temperature, finding that friction decreased as the lead went from superconducting to non-superconducting. A decrease in friction corresponds to an increase in slip – slip corresponds to sliding of two surfaces relative to each other, and friction impedes sliding motion. Therefore, this work showed that slip can exist on the surface of a resonating quartz device.

Laschitsch and Johannsmann [49] combined a quartz resonator with an approaching small metal sphere to measure the friction forces between the surface and the sphere. The authors found that contact between the sphere and the electrode surface caused an increase in frequency, which they attributed to an increase in the effective stiffness of the crystal. In a recent report [15], the authors explored the validity of this

combined device in studying thin lubricant films adhered to the surface. Borovsky *et al.* [50] used a nano-indenter probe in contact with the crystal to completely characterize the system, including normal forces and contact area. They found that the change in resonant frequency of the crystal, with no added mass, reflects the elasticity of the interface. These studies open up an interesting area of investigation where combined devices can be used to accurately measure high-frequency friction experiments, and a more comprehensive determination of the effect of surface energy on elasticity and friction will provide a more concrete basis for more advanced and realistic studies of friction and lubrication.

2.6.2 Interfacial Slip Parameter

The slip length has proven to be useful in modeling the flow of liquids across a stationary wall. However, it is a conceptual model and not a clear representation of reality, since the slip length b represents an extrapolation length, not a real physical value. As well, for an oscillating system, the motion of a particle may be out of phase with the motion of an adjacent particle, due to the strength of intermolecular bonds and the particle mass. This is a limitation of the slip length model, when applied to an oscillating system such as a TSM device. However, Pit *et al.* [35] modeled an oscillating system with the slip length boundary condition, and found that their predictions agreed with experimental results.

The viscoelastic damping of the acoustic wave in the fluid plays an important role in the frequency shift of TSM devices, but more complex interactions may be involved. Many models assumed a no-slip boundary condition [18,26,51], where the displacement of fluid particles in contact with the surface was equal to the displacement of the surface.

Reed *et al.* [7] and Hayward [9] suggested that slip does occur but did not model it. Ferrante *et al.* [10] coupled the fundamental equations for piezoelectricity with an infinite viscous fluid using a complex interfacial slip at the quartz-liquid interface.

The slip parameter used by Ferrante *et al.* [10] is an empirically determined value indicating the relative motion of a surface-molecule and a surface-adjacent liquid molecule. The parameter is complex, allowing for differences in both amplitude and phase in the relative motion of the solid and liquid molecules. The degree of relative motion between the surface and liquid depends on many factors, including the viscosity of the surface and liquid, and the elasticity of the bond between the two. For a strong, short bond between two molecules, analogous to a rigid spring connecting two masses, little slip will occur and the slip parameter α should be close to $1 + j0$, the no-slip condition. In this case, the surface and liquid will behave as a continuum, obeying the classic no-slip condition, and the liquid will have a viscoelastic effect. However, for a weak bond, analogous to a flexible spring separating two masses, the liquid molecule will lag the surface, with lower relative motion. In this case, because the surface requires less energy to move the liquid, the resistance shift will decrease. As well, due to the weak bonds, the apparent viscoelastic liquid mass will not be as prevalent and the associated frequency shift will not be as large. By fitting α to experimental data, the authors found that, for certain low-viscosity hydrophilic liquids, α was greater than one. As well, for hydrophobic surfaces, where coupling is weak and α should be small, α values greater than unity were found. The authors offered no explanation for this.

The masses represent liquid and surface molecules and the spring is the bond between them. The motion of the surface is forced, and induces motion in the water molecule through the action of the spring. Because the spring extends as the quartz mass moves, the velocity motion of the water molecule is lower. As the spring constant k approaches zero (as the spring becomes more compliant), the amplitude of motion of the water molecule becomes zero. The spring stiffness will increase as the affinity between the surface and the liquid increases.

Hayward and Thompson [6] extended the slip parameter model to four layers, adding an elastic electrode layer and a viscoelastic polymer layer to test the effect of slip on multiple interfaces. The model allows for a complex slip at each interface, but the authors assumed slip was only present at the film-liquid interface. An interfacial slip of $\alpha = 1 + j0$ was used at the other interfaces. At the sensor-liquid interface, the real and imaginary values were fitted from the data. The authors found magnitudes as high as 1.98 with phase angles of 21.0°. With slip, the model is equivalent to Ferrante *et al.* [10]. With a no-slip boundary condition, the model yielded results similar to Kanazawa and Gordon [23]. The slip model [6], with the slip numbers from [10], underestimates experimental results while the no-slip condition overestimates them. By fitting the slip parameter to the acoustic data, the exact frequency and resistance data can be obtained. However, this model is a two-parameter fit, similar to the viscoelastic layers from [2] and the complex shear modulus G [30]. Although they are not physically similar, these models involve fitting the theory to experimental data. Determining which is most physically valid, while difficult, would provide a fuller understanding to the field of coupled microacoustics.

Hayward and Thompson [6] ignored slip at the quartz-gold and gold-polymer interfaces. The no-slip assumption at the quartz-gold interface is valid, since the quartz and gold bond ionically at the interface and are rigidly attached. However, the presence of a long-chain polymer can result in slip at the gold-polymer interface. The mechanism involved in the slip at this interface is conceptually confusing. Slip between the gold and a covalently attached polymer is unlikely. However, if the chain is flexible at or near the interface, phase-shifted motion in the polymer caused by flexing of the polymer chain could be considered slip at the interface, even if the motion of the covalently-bound polymer is continuous. This may be the case for a long chain polymer with a large bound mass at its end. Slip could occur between the surface and the polymer mass (end), and between the mass and the liquid. The situation would be similar for a long chain tightly bound to the liquid molecule at its end, except there would be no slip at the polymer-liquid interface. Note that elastic slip at the gold-polymer interface may not be dependent on the interfacial energy, as the polymer-liquid slip is. The amplitude of the liquid motion is on the order of 3 Å, which is much smaller than the width of a polymer, so bonds are not being broken and reformed; the surfaces are simply moving relative to each other.

The following equations are the solutions for the motion of the electrode layer and the polymer film layer used by Hayward and Thompson [6]:

$$u_M = [B_6 \exp(jk_M d_M) + B_7 \exp(-jk_M d_M)] \exp(j\omega t), \quad (49)$$

$$u_P = [B_8 \exp(jk_F d_M) + B_9 \exp(-jk_F d_M)] \exp(j\omega t), \quad (50)$$

where the subscript M denotes the metal layer and F denotes the film. Equations 29, 30, 39, 49 and 50 contain nine constants of integration, which must be solved with nine equations, obtained from nine boundary conditions.

Establishing boundary conditions is necessary to solve the equations of motion of the crystal. As the number of layers increases, more boundary conditions are required. The boundary conditions link the equations of motion at each interface. With the no-slip boundary condition, the equations of motion for each layer at an interface are set equal to each other. For the slip condition, the equations are set equal to each other, but modified with the slip parameter. The first three equations are obtained from the interfacial slip boundary condition for the displacements at each interface:

$$\begin{aligned} \alpha_{QM} B_1 \exp(jk_Q d_Q) + \alpha_{QM} B_2 \exp(-jk_Q d_Q) \\ = B_6 \exp(jk_M d_Q) + B_7 \exp(-jk_M d_Q) \end{aligned} \quad (51)$$

$$\begin{aligned} \alpha_{MP} B_6 \exp(jk_M d_M) + \alpha_{MP} B_7 \exp(-jk_M d_M) \\ = B_8 \exp(jk_P d_M) + B_9 \exp(-jk_P d_M) \end{aligned} \quad (52)$$

$$\begin{aligned} \alpha_{PB} B_8 \exp(jk_P d_P) + \alpha_{PB} B_9 \exp(-jk_P d_P) \\ = B_5 \exp(-jk_B d_P) \end{aligned} \quad (53)$$

where α_{ij} is the complex interfacial slip parameter between layers i and j , k_i is the complex wave number of the layer (Equation 5), and d_i is the height of interface i above the base of the crystal. The next three boundary conditions relate the stresses at each interface, which must be continuous between each layer.

$$\begin{aligned} jk_Q C_Q [B_1 \exp(jk_Q d_Q) - B_2 \exp(-jk_Q d_Q)] + eB_3 \\ = jk_M C_M [B_6 \exp(jk_M d_Q) - B_7 \exp(-jk_M d_Q)] \end{aligned} \quad (54)$$

$$\begin{aligned}
& jk_M C_M [B_6 \exp(jk_M d_M) - B_7 \exp(-jk_M d_M)] \\
& = jk_P C_P [B_8 \exp(jk_P d_M) - B_9 \exp(-jk_P d_M)]
\end{aligned} \tag{55}$$

$$\begin{aligned}
& jk_P C_P [B_8 \exp(jk_P d_P) - B_9 \exp(-jk_P d_P)] \\
& = -jk_B C_B B_5 \exp(-jk_B d_P)
\end{aligned} \tag{56}$$

Since the bottom surface of the quartz is assumed to be a free surface, there is no shear stress on the bottom face, so:

$$jk_Q C_Q (B_1 - B_2) + eB_3 = 0. \tag{57}$$

The final two equations involve the applied potential which, at the bottom surface, is:

$$(e/\epsilon)(B_1 + B_2) + B_4 = \varphi_0 \tag{58}$$

The top electrode is grounded, so the potential is 0:

$$(e/\epsilon)[B_1 \exp(jk_Q d_Q) + B_2 \exp(-jk_Q d_Q)] + B_3 d_Q + B_4 = 0 \tag{59}$$

Equations 51 through 59 form a complete set of nine equations in nine unknowns that can be used to solve for the nine constants of integration, for example, by performing Gaussian elimination on an augmented matrix. The integration constants can then be substituted into Equations 39, 49 or 50 to solve for the motion of the liquid, the metal or the film, respectively.

Ferrante *et al.* [10] characterized this system of equations as an impedance, which is the voltage across the crystal divided by the current.

$$Z = \frac{2\varphi_0}{j\omega\epsilon AB_3}. \tag{60}$$

Hayward and Thompson [6] grounded the top electrode, so (60) becomes:

$$Z = \frac{\varphi_0}{j\omega\epsilon AB_3}. \quad (61)$$

Slip can also be linked to the surface free energy of the quartz. The stronger the coupling between the quartz and liquid molecules, the more energy is transferred to the liquid. This is the case for high viscosity and hydrophilic liquids. As more energy is transferred to the liquid, less is available within the quartz to resonate and fewer oscillations can be sustained. Therefore, the resonant frequency for a strongly coupled system will be lower than for a weakly coupled system.

2.6.3 Contact Angle and Surface Free Energy

The interfacial energy is related to the amount of interaction between two different types of molecules. Charged or polar molecules will have strong interaction and will attract each other. This is the case for hydrophilic molecules and surfaces, including metals. Non-polar, spherical molecules will not strongly attract each other, but will not repel each other. They will have weak interfacial interactions. Strong interfacial interactions imply a strong bond between adjacent molecules; this bond could include electrostatic and Coulombic forces, polarization and hydrogen bonding [52]. For weak interactions, only the van der Waals force is present. Typically, polar or charged surfaces are known as strong surfaces and uncharged surfaces are considered weak or soft surfaces.

Young determined that the contact angle of an interface is an energy balance between the surface, the liquid, and its vapor. To a rough approximation, it is given by the equation

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta, \quad (62)$$

where γ_{SV} is the surface-vapor interfacial tension, γ_{SL} is the surface-liquid interfacial tension, γ_{LV} is the liquid-vapor interfacial tension, and θ is the contact angle. This is, however, a simplified description of a complex interaction. A more rigorous determination of interfacial energy depends on contact angle hysteresis and surface roughness [43,53,54]. However, contact angle measurements do provide a good estimate of the degree of interaction at an interface and are a good way to indicate how surfaces and liquids will interact.

Examination of the contact angle is a useful technique to qualitatively determine the degree of interaction at an interface and to learn how the surfaces interact with each other. Establishing a link between surface energy and slip is an essential step in furthering the combined chemical and mechanical model of the behavior of a sensor-liquid interface.

2.6.4 Elasticity and Slip

As mentioned above, slip can be thought of as an elastic process, whereby the velocity at the interface is related to the shear stress by a friction coefficient. If slip is indeed an elastic process, it should be linked to the equivalent stiffness of the interface. Therefore, a correlation between the stiffness, as determined from the slip parameter, and the slip length would further enlighten the relationship between the slip length and the slip parameter.

Hayward and Thompson [6] linked the complex viscosity used by Reed *et al.* [7] to the slip parameter to study the correlation between slip and the equivalent surface viscosity and elasticity. This is given by the relationship

$$\alpha^2 \eta_B = \eta_{EQ} - jc_{EQ}/\omega \quad (63)$$

where η_{EQ} is the interfacial viscosity and c_{EQ} the interfacial stiffness. The term on the right-hand side of the equation is the complex viscosity, C , which, for a viscoelastic liquid, has both energy storage (c) energy dissipation (η) terms. Hayward and Thompson [6] suggested that, while viscoelasticity and slip both play a role in the resonant characteristics of the sensor and can be equated, the two processes are not interchangeable. Slip dominates for low viscosity liquids, but the processes cannot be separated solely through acoustic measurement. As well, the mechanical properties of the interface affect the presence of slip, so an exploration of the link between the two is an essential step in a complete understanding of the behavior of acoustic wave sensors.

Previous work in this field has shown that slip likely exists. This work describes a model relating the slip length b to the slip parameter α , and an experiment to measure interfacial slip for various combinations of surfaces and liquids. The model is a comparison of the slip length velocity boundary condition to the slip parameter boundary condition from Hayward and Thompson [6], for a viscoelastic polymer in contact with a viscous liquid. The experiment involves the measurement of the acoustic properties of bare and coated quartz-electrode surfaces measured using a resonator-oscillator combination. The surfaces used were lyophilic, hydrophobic films designed to test the effect of surface energy and friction on the acoustic properties of the quartz device.

Short- and long-chain hydrocarbon films are used to compare the effect that film thickness has on interfacial slip. Finally, contact angles are measured for each surface-liquid combination.

3 THEORETICAL DEVELOPMENT

The slip parameter model [6,10] is a physically valid model, because it directly describes the motion of each layer through the complex slip α . It is easy to visualize the motion of a particle with reference to the magnitude and phase of the slip. However, it is a two-parameter empirical value that can be mathematically fit to experimental data without reference to any accepted quantity. This is similar to the viscoelastic layers from Duncan-Hewitt and Thompson [2] or the lumped shear parameter of Behling *et al.* [30]. For this reason, predictive models for the behaviour of complex acoustic wave systems cannot be developed using these theories, without prior calibration of the specific system.

Although the slip parameter α makes physical sense, replacing it with a single-parameter model has many advantages, provided the single parameter can be linked to quantities found in the literature. If a link between α and some other quantitative system parameter could be established, the interfacial slip could be determined *a priori*. A candidate for this is the slip length b , which is linked to the bulk viscosity and interfacial friction, as shown in Equation 44. If the bulk viscosity of a system is known, and the interfacial friction can be determined from contact angle or surface tension measurements, then α can be determined.

McHale *et al.* [12] used a single slip parameter s in the lumped-parameter model and related this to an interfacial friction, which could be determined directly from experimental data. This model showed good agreement with experimental data, so a one-parameter model is generally physically valid. At first glance, this does not take into

account the possible out-of-phase motion that is characteristic of the slip parameter model [6,10]. However, the s -model [12] involves velocity boundary conditions, versus the displacement boundary conditions of the α -model. With a difference in velocities between two particles, out-of-phase motion could occur, since particles of different layers would take different times to travel the same distances. With this concept, the out-of-phase motion from the α -model is recovered, but suggests that the phase and magnitude of the slip are dependent on each other.

The complex nature of α makes it convenient to describe the displacement of particles and to fit to experimental data. However, as shown by the one-parameter s -model, a two-parameter model may not be necessary, and the magnitude and phase may be related to each other. As noted previously, the magnitude of α likely depends on the stiffness of a bond between adjacent particles, whereas the phase depends on the length of the bonds. As the bonds are stretched due to horizontal motion, they become stiffened, affecting both the magnitude and the phase of the slip. Therefore, a difference in slip magnitude will lead to a difference in phase as well; the two should be dependent, and linked to the properties of the system. The basis of the present model is the relationship between the slip parameter displacement boundary condition and the slip length velocity boundary condition. The derivation begins with an exploration of the boundary conditions.

3.1 SLIP BOUNDARY CONDITION

The slip parameter boundary condition at the polymer-liquid interface is a displacement boundary condition, meaning that the displacements of the adjacent layers

is related by some factor, in this case α . It is based on the solutions of differential equations of motion for a viscoelastic polymer film,

$$u_p = [B_8 \exp(jk_p d) + B_9 \exp(-jk_p d)] \exp(j\omega t) \quad (64)$$

and for a purely viscous liquid,

$$u_B = -B_5 \exp(-jk_B d) \exp(j\omega t). \quad (65)$$

To establish the boundary conditions at the interface, the motions of the particles on each side of the interface are equated. The slip boundary condition at the polymer-liquid interface, from Hayward and Thompson [6], is given as

$$\alpha_{pB} [B_8 \exp(jk_p d_p) + B_9 \exp(-jk_p d_p)] = -B_5 \exp(-jk_B d_p). \quad (66)$$

To determine a relation to the slip length, which is used to form velocity boundary conditions, the previous equations of motions must be converted to velocity equations. The instantaneous velocity is simply the time derivative of the displacement, so to establish velocity equations from the transverse shear model [6], each equation is differentiated with respect to time. For the polymer film, this is

$$v_p(t, z) = \frac{du_p}{dt} = j\omega [B_8 \exp(jk_p d) + B_9 \exp(-jk_p d)] \exp(j\omega t), \quad (67)$$

and for the bulk liquid

$$v_B(t, z) = \frac{du_B}{dt} = -j\omega B_5 \exp(-jk_B d) \exp(j\omega t), \quad (68)$$

since the first exponential terms are not time-dependent. Equating the two velocities at the interface for the no-slip condition, we have

$$\begin{aligned}
v_p(t, d_p) &= v_B(t, d_p) \\
j\omega[B_8 \exp(jk_p d_p) + B_9 \exp(-jk_p d_p)] \exp(j\omega t) \\
&= -j\omega B_5 \exp(-jk_B d_p) \exp(j\omega t) \\
B_8 \exp(jk_p d_p) + B_9 \exp(-jk_p d_p) &= -B_5 \exp(-jk_B d_p)
\end{aligned} \tag{69}$$

which is equivalent to the displacement boundary condition (Equation 66), without the slip parameter. With the no-slip velocity boundary condition established, the slip length boundary condition can now be applied.

3.2 SLIP LENGTH

The slip length is applied to stretch the velocity profile, establishing a slip velocity that is different than the no-slip wall velocity. For a stationary wall, this is pictured in the Figure (8) and given by the formula

$$v_p(d_p - b) = v_B(d_p). \tag{70}$$

In this situation, the liquid velocity profile is moved into the wall to match the liquid slip velocity. However, in the case of a driving surface, we must move the velocity profile out to match the surface velocity, as shown in Figure 9.

Figure 9 - Solid and bulk liquid velocity profiles showing no-slip and slip length boundary conditions

This is described by

$$v_p(d_p) = v_b(d_p - b). \quad (71)$$

Adding the slip length to the no-slip velocity boundary condition, Equation 69 becomes

$$-B_5 \exp(-jk_B(d_p - b)) = B_8 \exp(jk_p d_p) + B_9 \exp(-jk_p d_p). \quad (72)$$

Taking the left-hand side of this equation and expanding the exponent, this becomes

$$\begin{aligned} LHS &= -B_5 \exp(-jk_B d_p) \exp(jk_B b) \\ &= -B_5 \exp(-jk_B d_p) [\cos(k_B b) + j \sin(k_B b)] \end{aligned} \quad (73)$$

and the slip length boundary condition becomes

$$\begin{aligned} B_8 \exp(jk_p d_p) + B_9 \exp(-jk_p d_p) \\ = -[\cos(k_B b) + j \sin(k_B b)] B_5 \exp(-jk_B d_p) \end{aligned} \quad (74)$$

Comparing this to Equation 66, we have

$$\alpha = \frac{1}{\cos(k_B b) + j \sin(k_B b)}. \quad (75)$$

This is a significant development, since it shows that the complex two-parameter value α can be reduced to the known liquid parameters in k_B and a single real value b .

Normalizing the denominator and using the identity $\sin^2 \theta + \cos^2 \theta = 1$, we obtain

$$\alpha = \cos \zeta - j \sin \zeta = \exp(-j \zeta), \quad (76)$$

where

$$\zeta = b k_B = b \omega \sqrt{\frac{\rho_B}{C_B}} = b \omega \sqrt{\frac{\rho_B}{j \omega \eta_B}}. \quad (77)$$

To find a complete relationship between the slip α and the slip length b , we must isolate the real and imaginary parts of the right-hand side. This is not trivial, since k_B itself contains imaginary terms. To begin, we note the identity

$$\sqrt{-j} = \frac{1-j}{\sqrt{2}}. \quad (78)$$

From this, ζ becomes

$$\zeta = \omega b \sqrt{-j \frac{\rho_B}{\omega \eta_B}} = \omega b \sqrt{-j} \sqrt{\frac{\rho_B}{\omega \eta_B}} = \frac{1-j}{\sqrt{2}} \omega b \sqrt{\frac{\rho_B}{\omega \eta_B}} = (1-j)b \sqrt{\frac{\omega \rho_B}{2 \eta_B}}, \quad (79)$$

and Equation 76 becomes

$$\begin{aligned} \operatorname{Re}(\alpha) + j \operatorname{Im}(\alpha) &= \exp(-j\zeta) \\ &= \exp(-j(1-j)\varphi) \\ &= \exp(-(1+j)\varphi) \\ &= \exp(-\varphi) \exp(-j\varphi) \\ &= \exp(-\varphi) [\cos(\varphi) - j \sin(\varphi)] \end{aligned} \quad (80)$$

where

$$\varphi = b \sqrt{\frac{\omega \rho}{2 \eta}}. \quad (81)$$

When in the form described by Equation 80, the model involves numerically fitting φ , and thus b , to the real and imaginary parts of the slip parameter α . Ideally, we should be able to predict α from b , and vice-versa. Converting the slip parameter to its polar form and collecting like terms, we obtain for the magnitude

$$\begin{aligned}
|\alpha| &= \sqrt{(\text{Re}(\alpha))^2 + (\text{Im}(\alpha))^2} \\
&= \sqrt{(\exp(-\varphi)\cos(\varphi))^2 + (\exp(-\varphi)\sin(\varphi))^2} . \\
&= \sqrt{\exp(-2\varphi)[\cos^2(\varphi) + \sin^2(\varphi)]}
\end{aligned} \tag{82}$$

With the identity used in Equation 76, this reduces to

$$|\alpha| = \exp(-\varphi) = \exp\left(-b\sqrt{\frac{\omega\rho}{2\eta}}\right). \tag{83}$$

The argument is

$$\begin{aligned}
\angle\alpha &= \tan^{-1}\left(\frac{\text{Im}(\alpha)}{\text{Re}(\alpha)}\right) \\
&= \tan^{-1}\left(\frac{-\exp(\varphi)\sin(\varphi)}{\exp(\varphi)\cos(\varphi)}\right)
\end{aligned} \tag{84}$$

Since $\sin\theta / \cos\theta = \tan\theta$, Equation 84 becomes

$$\angle\alpha = \tan^{-1}(\tan(-\varphi)) = -\varphi = -b\sqrt{\frac{\omega\rho}{2\eta}}. \tag{85}$$

Combining Equations 83 and 85,

$$|\alpha| = \exp(\angle\alpha) \tag{86}$$

we obtain a formula describing the dependence of the slip magnitude on the slip phase. It is only valid for purely viscous liquids, from Equation 65, so any elasticity in the liquid is lumped into the slip parameter calculation. However, this calculation also gives us the possibility to relate the slip parameter to the slip length, opening up a whole new area in which we can determine the slip regime from *a priori* determined interfacial properties.

4 EXPERIMENTAL METHOD

An experiment is described to compare slip parameter values across a variety of hydrophilic and hydrophobic surfaces and liquids. The liquids used were water, ethanol, hexadecane, and dodecane. The surfaces were bare gold and gold coated with hexadecanethiol, butanethiol, and 1,2-mercapto-3-propanediol. Water was selected to compare to hydrophilic and hydrophobic surfaces as most chemical studies use water as the solvent. Ethanol was used because of its low surface energy, and as well, it is used in many chemical studies. Hexadecane was selected as a hydrophobic liquid to compare it to other studies involving slip, such as Pit *et al.* [35], who showed that it slips on all surfaces. Dodecane was selected to compare to hexadecane, being a smaller hydrophobic molecule, but less flammable than shorter-chain hydrocarbons.

The bare gold surface, with proper cleaning, can be viewed as hydrophilic. Hexadecanethiol was selected to compare with results from [35], which used long-chain carbon surfaces, and to compare with the hexadecane liquid. Butanethiol was selected to as a short-chain hydrocarbon, to compare with the longer chain hexadecanethiol. Mercaptopropanediol was used because it may behave as either hydrophilic or hydrophobic surface, because of the alcohol groups.

4.1 APPARATUS

4.1.1 Experimental Setup

All measurements were performed in a painted wooden box (49×41×42 cm, with 2 cm wall thickness), with a controlled heat source to maintain the temperature of the box and a fan to ensure that the air was evenly distributed. The accuracy of heater controller

was $\pm 0.2^{\circ}\text{C}$. The box had a main door to manipulate the flow cell between experiments and an entry point to accommodate the injection inlet and outlet.

4.1.2 TSM Crystals

9-MHz AT-cut TSM quartz crystals (International Crystal Manufacturers Co, Inc, Oklahoma City, OK) with gold electrodes were used as received. As specified by the manufacturer, the crystal diameter was 1.37 cm, with an electrode diameter of 0.51 cm and thickness 1000 Å. Before use, each crystal was washed with acetone, isopropyl alcohol, 10% nitric acid, and ethanol, sonicated in ethanol for 20 minutes, and finally rinsed in ethanol and de-ionized water. The crystals were installed in a PEEK flow cell (International Crystal Manufacturers Co, Inc, Oklahoma City, OK) with a 70 μL chamber.

4.1.3 Oscillator

The oscillator used was the Maxtek PLO-10 (Maxtek, Inc, Sante Fe, CA). The oscillator was connected to a frequency counter and data acquisition card (NOSE05, designed and built in this laboratory) to measure resonant frequency and series resistance. The data were recorded by an Intel 286 computer running MS-DOS v5 (Microsoft Corp, Redmond WA), connected to the NOSE05 system via the serial port.

4.2 REAGENTS

Hexadecanethiol (HDT,92%), butanethiol (BT,99+%), 3-mercapto-1,2-propanediol (MPD,95%), hexadecane, and dodecane were all used as received from Sigma-Aldrich. Milli-Q Plus de-ionized water (Millipore Corporation, Bedford, MA) and ethanol were of analytical grade quality.

4.3 PROCEDURE

4.3.1 Surface Modification

1 mM mercaptan solutions in ethanol were prepared, for each of HDT, BT, and MPD. All surface modification was performed with the crystal in the flow cell. The crystal was dried with a stream of nitrogen, then the mercaptan solution was applied using a syringe and allowed to sit for approximately 18 hours. The solution was replaced after 2-3 hours and again after 5-6 hours to cycle the solution. After 18 hours, the crystal was washed with copious amounts of ethanol and dried for 4-6 hours with nitrogen before measurements were taken.

4.3.2 Cleaning

Before each measurement, the flow cell apparatus was rinsed with ethanol, followed by copious amounts of de-ionized water, then dried with a stream of nitrogen for 3-4 hours. After testing with hexadecane or dodecane, the apparatus was washed with hexane prior to washing with ethanol.

4.3.3 Resonant Characteristic Measurement

Prior to the initial application of the bulk liquid, the crystals were washed with ethanol and water, then dried with a stream of nitrogen. The dry, bare frequency and resistance were measured to establish a baseline. Continuous measurements were then taken without detaching the crystal from the apparatus. Measurements were performed at 29-31°C, in the temperature-controlled box. The crystal was tested in bulk liquids, before coating, in the following order: de-ionized water, ethanol, hexadecane, and dodecane. After coating, the same order was maintained.

Frequency and resistance characteristics were taken every 10 seconds, using the computer. After each application of a bulk liquid, the resonance characteristics were allowed to stabilize for 1-2 hours, until the change in frequency was less than ± 0.02 Hz/s.

4.3.4 Contact Angle Measurement

Contact angles for certain crystals were measured prior to installation in the apparatus, and then again after an entire run was complete. Others were only measured after the run was complete. The measurements were made using a custom apparatus designed and built in the Polymer Surface Interface Group laboratory (Dr. John Dutcher, Department of Physics, University of Guelph) to capture digital images of the contact angle.

Before the measurements, the crystals were washed with acetone, ethanol and de-ionized water, so as not to remove the polymer film. The contact angles were measured in the same order that resonance data was collected: water, ethanol, hexadecane and dodecane. Between each measurement, the crystals were washed with ethanol and de-ionized water.

The images were captured with a Sony XC-73 CCD camera (New York, NY), attached to an Intel Pentium computer with a frame grabber. The image capture software was Image Pro Plus (Silver Spring, MD). Once captured, the images were optically analyzed using Photoshop 5.0 (Adobe Systems Inc., San Jose, CA). Angles were measured by comparing lines drawn on the image, and measured using the image coordinate system.

5 RESULTS AND DISCUSSION

5.1 EXPERIMENTAL RESULTS

The data was collected as a continuous time-series data set, where the resonant frequency, motional resistance and chamber temperature were recorded. Figures 10 and 11 show sample runs of the time-series data. Each large frequency and resistance change indicates an injection of liquid onto the surface of the crystal, or the drying of the flow cell. For an injection, the frequency decreased and the resistance increased. During drying, the shifts are in the reverse direction.

As can be seen from Figures 10 and 11, neither the frequency nor the resistance returned to a constant baseline value. Instead, the baseline wandered frequently during drying. Without a constant baseline, it becomes more difficult to determine the shifts resulting from the presence of a contacting solvent. The causes of the wandering baseline, and the steps taken to compensate for it, are discussed in the following section.

5.1.1 Wandering baseline compensation

The crystal setup used was found to have a wandering baseline in many cases. This was due to two factors, namely the absorption of solvents into the O-ring and swelling of the O-rings due to changes in ambient conditions. The Viton® O-rings used could have absorbed the solvents while in contact with the crystal. After the flow cell was dried and before a liquid was applied, the solvent would desorb onto the crystal surface and affect the resonant parameters. To counter this situation, if the crystal had been oscillating dry for more than five hours without drying or injection, the crystal was dried for one hour to ensure that any solvent desorbed from the O-ring onto the crystal

surface would be removed by the nitrogen flow. The O-rings might also have swelled upon injection of a solvent, or due to random fluctuations in ambient conditions. Though the swelling would have been slight, it may have had an effect on the resonant characteristics of the crystal, since swelling would affect the pressure exerted on the crystal by the O-ring, affecting its mechanical properties.

To compensate for the wandering baseline, instantaneous frequency and resistance shifts were measured, instead of establishing a constant baseline. Frequency and resistance were measured after stabilizing, the solvent was injected, and the resonant parameters were allowed to come to equilibrium, normally in 1-2 hours. The instantaneous shift is the difference between the stable dry value prior to injection, and the average, stabilized value. By measuring the instantaneous shifts, errors due to incomplete drying, solvent desorption, and contamination of the free surface could be removed. Figure 12 shows an example of how Δf and ΔR_m were measured for a bare crystal in water.

Figure 10 – Full run for a crystal initially bare, then coated with hexadecane. Changes in frequency correspond to application of liquids and drying. The constant frequency for ~18 hrs. represents the mercaptan application and coating period.

Figure 11 – Same as above (Figure 10), but showing resistance shifts

5.1.2 Resonant measurements and standard error calculation

The frequency and resistance values for each solvent were recorded after having stabilized. It was found that, in almost all cases, the resistance stabilized faster than the frequency, so the limiting factor for a stable value was the frequency. Calculation of the stable values was done once the change in frequency was less than approximately ± 0.02 Hz/s. The mean of these values until drying commenced was taken as the stable frequency and resistance.

Due to the variation in the values, even once stable, a standard error was calculated for each measurement. The standard error was taken as two standard deviations from the mean value, which provides a 95% confidence interval. To evaluate the effect of the error on calculated values, all subsequent slip calculations were performed for the limits of the standard error range of the resistance and the frequency. This was performed for all four combinations of high and low resistances and frequencies.

Figure 12 – Frequency and resistance shifts for bare crystal in ethanol. The arrows show how the changes in frequency and resistance are measured.

5.1.3 Surface characterization

The model used by Hayward and Thompson [6] was found to predict the behavior of the crystal in ethanol very well using the no-slip condition. To compare the effect of the surface modification across each solvent, the frequencies and resistances of all solvents were normalized against ethanol. This was achieved by multiplying each value by the factor

$$\frac{\sqrt{\rho_{\text{EtOH}} \eta_{\text{EtOH}}}}{\sqrt{\rho_{\text{solvent}} \eta_{\text{solvent}}}}.$$

This factor is chosen since the resonant properties vary with the density and viscosity of the liquid in contact with the crystal. By normalizing the resonant properties against ethanol, which appears not to slip significantly, the surface effects can be compared on an equal footing. Figure 14 shows the averaged normalized frequency

shifts for each surface. The error bars indicate the variability among crystals, which arises from the fact that two crystals were tested and averaged for each surface. Figure 15 shows a similar plot for the resistance shifts. On both charts, lines indicate the surface from which each data point is taken. Each value is the mean of all the trials for a given solvent on a different surface. The error bars show the upper and lower values that make up the average represented by each point.

From Figure 14, we see that the MPD surface is hydrophobic. The frequency shift in water, which is hydrophilic, is similar to the shift in the other hydrophobic surfaces (HDT and BT). This could be caused by the alcohol groups being attracted to the gold, which is higher energy than the non-polar hydrocarbon chains that surround them. The non-polar hydrocarbon portion of the MPD molecules would be adjacent to the water. This possibility is supported by the frequency data. The frequency shift of the MPD coated device in water is almost the same as the shift in water of the BT and HDT devices. Similarly, the shift of the MPD device in hexadecane and dodecane was less than the shifts of the BT and HDT devices in those liquids, indicating that the slightly polar MPD coating may only partially repel the hydrophobic liquids. Figure 13 shows three possible configurations of the MPD coating. In configuration *a*), the hydroxyl groups remain in contact with the liquid, appearing as a hydrophilic surface. In *b*), the lower hydroxyl group is attracted to the surface through polar interactions. The hydroxyl group on C-3 would make this configuration partially hydrophilic. In *c*), both hydroxyl groups are polar-bound to the gold surface, making this configuration hydrophobic. Any combination of configurations may exist simultaneously on a single surface. Since the

MPD surface exhibits hydrophobic behavior, it appears that configurations *b*) and *c*) were most prevalent.

Figure 13 – *Three possible configurations for the MPD surface coating: a) more hydrophilic, b) more hydrophobic c) very hydrophobic*

The larger frequency shift of the bare device in water shows that it can be viewed as hydrophilic. The BT surface appears to be the most hydrophobic of all the surfaces, since the hydrophobic liquids showed the largest frequency shift on BT, and water showed the smallest. However, all the surface modifications led to lyophilic coatings, since there was little difference in the frequency shifts of the coated devices in any of the non-polar solvents. In the case of the resistance shifts, there is little difference across the surfaces, except for water and dodecane on bare gold. The resistance shift of the bare device in water was larger than on the coated devices, further affirming that the gold surface can be treated as hydrophilic. As well, the shift of dodecane on the bare surface was slightly smaller than on the coated devices, indicating that dodecane is being repelled by the bare gold.

Figure 14 – Frequency shifts in for different liquids normalized to ethanol.

Figure 15 – Same as above, for resistance shifts.

5.2 MODEL RESULTS – NO SLIP

To establish the validity of the experimental results, and to demonstrate a motivation for the inclusion of slip, the model was run using the no-slip boundary condition and compared to experiment of both the bare and coated devices. This shows the disagreement of certain results with the no-slip boundary condition.

The following section gives a description of the transverse shear model and discusses its implementation in this study.

5.2.1 Description of the model

The model used to determine theoretical results for the no-slip condition is described by Hayward and Thompson [6], written in the Pascal language (Borland International Inc., Scotts Valley, CA). Its main function is to determine the frequency at which the impedance is purely real and the amplitude is a maximum, which is the series resonant frequency. This is accomplished by solving the nine simultaneous equations generated from the nine boundary conditions, as explained in Section 2.6.2. A velocity profile correction, described in [6], is used, and the model is solved iteratively, using increasingly smaller frequency step sizes, until it reaches the mechanical, series, and parallel resonances. The model can solve the frequency to a resolution of 0.1 Hz. Once the frequency is found, the motional resistance and peak amplitude can be solved using Equations 61 and 29.

The four-layer model takes as input the physical properties of the crystal, the metal electrode, the polymer layer, and the liquid. The format of Table 1 lists the crystal and electrode properties used in this study.

Table 1 – Crystal and electrode model parameters used in present study

Crystal	<i>Thickness</i>	0.0001825	<i>m</i>	d_Q
	<i>Stiffness</i>	29.01×10^9	N/m^2	c_Q
	<i>Piezoelectric constant</i>	-0.0798	C/m^2	e_Q
	<i>Dielectric constant</i>	39.82×10^{-12}	$C/V \cdot m$	ϵ_Q
	<i>Viscosity</i>	0.008376	$N \cdot s/m^2$	η_Q
	<i>Density</i>	2649.0	kg/m^3	ρ_Q
Electrode	<i>Thickness</i>	1.0×10^{-7}	<i>m</i>	d_M
	<i>Stiffness</i>	50.41×10^9	N/m^2	c_M
	<i>Viscosity</i>	0.0	$N \cdot s/m^2$	η_M
	<i>Density</i>	19300.0	kg/m^3	ρ_M

5.2.2 Effect of polymer properties on resonant parameters

The properties of the polymer layer, such as its stiffness, thickness, and viscosity, are difficult to determine and must therefore be estimated. The values used throughout all calculations involving the model were based on values from Lucklum [private communication] and are listed in Table 2.

Table 2 – Polymer layer properties

<i>Density (kg/m³)</i>	1200
<i>Viscosity (cP)</i>	366
<i>Stiffness (kPa)</i>	1000
<i>Thickness (nm)</i>	5

Since these polymer properties are estimates, experimental deviations from the estimated values could cause large changes in the resonant properties. To validate the estimates, an error analysis was performed. The viscosity, stiffness and thickness were varied individually and the resulting configurations were tested with a version of the model from [6], modified to interface with an analysis program written in the Matlab scripting language (The Mathworks Inc., Natick, MA). Figures 16-18 show the changes in frequency and resistance shifts for stiffness, thickness, and viscosity.

Figure 16 shows that, in the range of stiffness from 10 kPa to 10 MPa, both the frequency and resistance change very little. Between 10^6 and $10^{6.5}$ Pa, there is a small change in frequency of 0.1 Hz, which is smaller than the standard error limits of the frequency signals measured. Figure 17 shows the effect of thickness on frequency and resistance shifts. Above 10 nm, the resonant properties change very fast, since the thickness of the polymer layer is approaching the decay length and resulting in harmonic reflections. The thickness estimate used in this study is at the point where the frequency begins to drop. However, since most hydrocarbon chains are on the order of 5-10 Å, so the estimate is likely too high and will likely not influence the results. Figure 18 shows the effect of viscosity on the resonant properties. The shift of 0.5Ω in the resistance and change of 1.5 Hz in the frequency are both within the standard error of the signals and would not have a noticeable effect on the measurements. The error analysis shows that deviations from the estimates will not have a strong effect on any comparison of experimental and theoretical results.

5.2.3 Comparison of experimental to theoretical results: No-slip condition

To evaluate the model, results for each fluid were compared with experimental results, as analyzed in Section 5.1. Figures 19, 21, and 23 show the comparison of experimental and theoretical results for frequency, and Figures 20, 22, and 24 show the results for resistance, each for a different surface modification. For each surface, two trials were performed using separate crystals, and measurements before (bare) and after surface modification were taken. The results for each trial are overlapped on the chart, to illustrate the variance among crystals. In cases where both trial results are very close, only one bar is shown. The error bars represent the standard error (see Section 5.1.2) for

each individual trial. The theoretical results from the model (see Section 5.2.1) with the no-slip condition, are indicated for each solvent and surface for ease of comparison. The liquid properties used in the model are shown in Table 3. All liquids are assumed to be purely viscous.

Figure 16 – Dependence of resonant properties on film stiffness

Figure 17 – Dependence of resonant properties on film thickness

Figure 18 – Dependence of resonant properties on film viscosity

Table 3 – Bulk liquid properties used to obtain theoretical results, from ref. [55]

	Water	Ethanol	Hexadecane	Dodecane
<i>Density (kg/m³)</i>	997.3	789.3	775.1	751.1
<i>Viscosity (cP)</i>	0.914	1.200	3.340	1.350
<i>Stiffness (kPa)</i>	0	0	0	0

It is evident from the comparison between the expected and theoretical frequencies on all surfaces, that the no-slip condition may be valid for ethanol. The average percent difference between the expected and experimental values for ethanol was only 2.45% on the bare surfaces and 2.34 % on the modified surfaces. However, the resistance values show a larger difference, on the order of 13.6% for the bare surfaces and 10.4% for the modified surfaces. There is some slip, but it is small.

There are only slight deviations between the experimental and theoretical frequency values for the bare device in water, indicating that the no-slip condition models the behavior of water on a hydrophilic coating. However, there are large deviations between the experimental and theoretical values for the coated devices in water. From Figures 14 and 15, it was apparent that all surface modifications resulted in hydrophobic surfaces, including MPD. The large deviation in frequency shift when water is in contact with the hydrophobic surfaces shows that water molecules do not interact as strongly with these surfaces as they do with the bare gold. Similarly, the decreases in resistance shifts from the bare gold to the coated devices indicate that the crystal is dissipating less energy in moving the water-hydrophobic surface combination. There is a transition from no-slip to slip when the surface is changed from hydrophilic to hydrophobic for a device operating in contact with water.

When the device is operated in contact with hexadecane, both the frequency and resistance differ from the theoretical values, irrespective of the surface modification. Moreover, there is very little difference between the bare and coated surfaces. This indicates that there is slip occurring between bulk hexadecane and the surface in all cases, as found by Pit *et al.* [35], who found slip of hexadecane on all of the solid surfaces tested by those authors. For a coated crystal oscillating at slow speeds, the hexadecane chains near the surface become entangled in the chains attached to the wall and move at the same speed as the wall, thus satisfying the no-slip condition. However, as the frequency and wall speed increase, the hexadecane molecules become disentangled from the wall. Once disentangled, they cannot move at the same speed as the rapidly oscillating wall, and slip motion occurs.

Dodecane shows a slight but consistent decrease in frequency and increase in resistance from the bare to the coated device. For MPD, the average decrease was $\Delta f = -75.5$ Hz. For BT, it was -96.1 Hz, and for HDT, $\Delta f = -108$ Hz. The increases in resistance were, for MPD, $\Delta R = 10.9 \Omega$, for BT, $\Delta R = 4.2 \Omega$, and for HDT, $\Delta R = 19.9 \Omega$. An MPD surface is less hydrophobic than BT and HDT, due to the reasons discussed in Section 5.1.3, so it is natural that the frequency and resistance shifts should be smaller when in contact with a hydrophobic liquid. This is because there is a slight hydrophilic repulsion on the MPD surface than for the more hydrophobic surfaces, leading to less energy dissipation, and therefore a lower resistance. The no-slip condition describes the coated devices in dodecane, though there are small deviations for both frequency and resistance. As opposed to the long-chain hexadecane, the shorter dodecane can maintain motion with the rapidly oscillating wall.

Figure 19 – Changes in resonant frequency from air for bare and MPD-coated crystals. In this case, three trials are shown for both the bare and coated runs, and are overlapped. In all other cases, only two trials are shown *if only one value is shown, the results were too close to show any difference in the graphic; this applies to all subsequent charts – in this case, trials 1 and 2 overlap

Figure 20 – Changes in resistance from air for bare and MPD-coated crystals. *trials 2 and 3 overlap

Figure 21 – Changes in resonant frequency from air for bare and HDT-coated crystals

Figure 22 – Changes in motional resistance air for bare and HDT-coated crystals

Figure 23 – Changes in frequency from air for bare and BT-coated crystals

Figure 24 – Changes in motional resistance from air for bare and BT-coated crystals

5.2.4 Discussion of error in resonance measurements

Due to experimental error, there are differences in the measured frequency between trials and even between different solvents for the same crystal. As mentioned in Section 5.1.1, the system suffered from a wandering baseline. Although the methods described above did help to lessen this error, it was impossible to fully remove it. Consequently, there is likely some amount of indistinguishable error between measurements on the same crystal. There are differences between the crystals used, due to electrical differences in the mounting of the devices. If the crystal had not been placed directly in the center of the O-ring, the pressure on the surface of the crystal would not have been evenly distributed, which would affect the resonance characteristics. Similarly, if the cell had not been properly tightened, the pressure on the crystal would not have been constant between crystals, also affecting the resonance characteristics and the amount by which the frequency would change.

Despite the experimental error inherent in the system, it is evident from Figures 19 through 24 that there is an important difference between experimental results and the theoretical results using the no-slip condition. This is especially noticeable for water on all modified surfaces, hexadecane on all surfaces, and dodecane on the bare electrode. As explained in Section 2.6.2, the no-slip condition involves a slip parameter $\alpha = 1 + j0$ at the polymer-liquid interface. By adjusting both the real and complex parts of the slip parameter, the experimental results can be recovered. Using an iterative algorithm explained in Section 5.3.1, slip values are determined, and are then compared to the slip length b using the model described in Section 3.

5.3 MODEL RESULTS – SLIP

As explained in Section 5.2.1, the model from [6] can contain slip at three-interfaces. In the present study, only slip at the polymer-liquid interface is assumed. The model is used in an iterative Gauss-Newton process to numerically fit the slip to experimental values of Δf_s and ΔR_m . This algorithm is described in the following section.

5.3.1 Description of Gauss-Newton method used to calculate slip

The Gauss-Newton method is an efficient non-linear least-squares algorithm, which uses the general iterative equation

$$g_{j+1}(x_i; a_i) = g_j(x_i) + \nabla g_j \cdot \Delta a_i \quad (87)$$

where the gradient is taken with respect to the parameters a_i [56]. For the present case, there are two results to fit: changes in frequency and resistance, and two parameters: changes in real and imaginary slip, so the two-parameter matrix form of the Gauss-Newton method is

$$\begin{bmatrix} \Delta f_{\text{meas}} - \Delta f_{\text{calc},j} \\ \Delta R_{\text{measured}} - \Delta R_{\text{calc},j} \end{bmatrix} = \begin{bmatrix} \Delta f_{\text{calc},j-1} \\ \Delta R_{\text{calc},j-1} \end{bmatrix} + \begin{bmatrix} \frac{\partial \Delta f}{\partial \alpha_{\text{Re}}} & \frac{\partial \Delta f}{\partial \alpha_{\text{Im}}} \\ \frac{\partial \Delta R}{\partial \alpha_{\text{Re}}} & \frac{\partial \Delta R}{\partial \alpha_{\text{Im}}} \end{bmatrix} \begin{bmatrix} \Delta \alpha_{\text{Re}} \\ \Delta \alpha_{\text{Im}} \end{bmatrix}, \quad (88)$$

where $\partial \alpha_{\text{Re}}$ and $\partial \alpha_{\text{Im}}$ were ± 0.01 . At the end of each iteration, row reduction was used to solve for $\Delta \alpha_{\text{Re}}$ and $\Delta \alpha_{\text{Im}}$, which were added to the previous value of α , and the iterations were continued. The Gauss-Newton method was implemented using Matlab, the code for which is presented in Appendix B-1 .

5.3.2 Surface-dependent slip values

Table 4 shows the average slip values as determined using the Gauss-Newton algorithm described in Section 5.3.1. The slip values in Table 4 are averaged across all crystal trials. Because the slip values are averaged across all similar trials, there is a large amount of error in some of the results. However, it is evident that the general trend remains the same. The slip magnitudes for ethanol remain constant over all surfaces, as do those for hexadecane, though the hexadecane values are smaller, since slip in hexadecane on solid surfaces is expected [35]. For water, the slip magnitude decreases from the bare device to the coated devices by a large amount. Similarly, the slip magnitude for dodecane increases from the bare device to the coated devices, though by a smaller amount.

Table 4 – Slip parameter for the various combinations of surface and bulk liquids

Bulk Liquid		Surface							
		Bare		MPD		HDT		BT	
		Mag	Phase (deg)	Mag	Phase (deg)	Mag	Phase (deg)	Mag	Phase (deg)
Water	Avg	0.894	4.307	0.663	2.624	0.648	0.788	0.675	-5.205
	±	0.17	5.78	0.30	6.63	0.02	2.55	0.07	4.53
Ethanol	Avg	0.906	3.895	0.917	2.945	0.921	5.154	0.953	0.857
	±	0.04	1.83	0.05	2.73	0.02	7.57	0.13	6.53
Hexadecane	Avg	0.848	0.707	0.828	0.424	0.835	0.833	0.844	2.019
	±	0.04	1.63	0.04	1.97	0.03	0.70	0.07	4.81
Dodecane	Avg	0.898	0.022	0.955	0.798	0.938	0.640	0.960	0.175
	±	0.08	3.37	0.06	1.70	0.03	1.96	0.01	0.00

This shows that hydrophilic-hydrophilic (water on gold) and hydrophobic-hydrophobic (dodecane on MPD, HDT and BT) interactions result in strong bonds at the interface and yield small amounts of slip. As shown in the literature [10,57,58], hydrophilic liquids on hydrophobic surfaces show less interaction due to repulsive forces

at the interface, resulting in a smaller frequency shift and more slip. The trend occurs in the reverse direction when dodecane is placed on the bare gold surface versus its behaviour on the hydrophobic surfaces. The frequency shift is smaller and there is more slip, albeit less of a difference than for water on the hydrophobic surfaces. Water is bound to the bare gold by strong hydrogen bonds, so once these no longer exist, the binding is much less and the difference in slip is large. For dodecane on hydrophobic surfaces, the only attractive forces are van der Waals and London dispersion forces. When dodecane is in contact with the bare gold, there are only repulsive van der Waals forces, so the difference between surfaces is much smaller.

There is very little slip for any coating immersed in ethanol, since ethanol has very low surface energy (see Table 5). Ethanol wetted all the surfaces, regardless of its composition. This is because ethanol has both hydrophobic and hydrophilic ends – the alcohol group is hydrophilic and the CH_2CH_3 tail is hydrophobic. Ethanol was used as the no-slip case in Section 5.1.3. Hexadecane presents the opposite case. Because it is a long chain and is difficult to move, it slips on any surface, regardless of hydrophobicity. The presence of slip agrees with results from Pit *et al.* [14,35] for hexadecane on various surfaces.

The phase shifts show a much wider variation across the surfaces than the magnitudes. However, the polar liquids, water and ethanol, have much larger phase angles than the non-polar liquids. Except for the large phase angle (2.019°) for hexadecane on the BT surface, all the averaged phase angles for the hydrophobic liquids are less than 1, and those for the polar liquids are greater than 1. In general, the level of

error in the phase shift measurements is too high to make any valid statements about phase shift effects. In some cases, the error is even larger than the value itself. There are, however, some general trends in the phase shift data, specifically the small phase shifts for the non-polar liquids and the larger ones for the polar liquids. This is likely due to friction caused by hydrogen bonds between hydrophilic surfaces and liquids produce bonds that are difficult to break, causing the liquid molecules to oscillate out-of-phase with the surface. However, a main source of error is inherent in the phase itself, which was explained in Section 5.2.4.

These results can be compared with other studies on the slip parameter, namely Ferrante *et al.* [10] and Hayward and Thompson [6]. Ferrante *et al.* obtained slips much greater than unity for a bare device in water, which physically corresponds to a larger liquid displacement than in the solid at the interface. The quartz would effectively impart elastic energy into the liquid. Some values greater than unity were obtained in the present study, though they were much lower than those found in [10]. The error in their results is likely due to the five-parameter fit used to solve their model. Hayward and Thompson also found values greater than unity, though not as drastic as in [10]. However, their values were determined by fitting the model to data from three sources where the surfaces were not characterized [9,57,58], leading to unknown effects that may have skewed the results.

5.3.3 Discussion of error in slip measurements

The phase values show a large amount of error, as indicated in Table 4. Figure 25 shows a three-dimensional plot of frequency and the complex slip parameter, which was obtained by running the model in water with no polymer layer. Both the magnitude and

the phase are indicated on the plot. As can be seen, the magnitude has a general downward slope, so as the magnitude increases, the frequency decreases. However, the phase is flat around the values of magnitude and phase that were found in this study. For this reason, when estimating the phase using the Gauss-Newton algorithm, changes in frequency produce only small deviations in the phase. Finding the physically valid phase angle for any given combination of experimental frequency and resistance is unlikely, so fitting values of the phase to the experimental data produces an inherently large amount of error.

There is also error inherent in running the model, due to deviations from the actual values of the bulk liquid properties, polymer properties and the thickness of the gold. Empirical values taken from the literature and estimates for the polymer layer may not fully characterize the true nature of the layers. This could contribute to the experimental error. The effect of the polymer layer estimation error is discussed in Section 5.2.2, and was shown to have only a small effect for the estimates used, but these errors could be compounded by deviations in the liquid layer.

A final possible source of error is the iterations involved in the Gauss-Newton algorithm. However, the amount of error is controlled, such that the iterations are continued until the error reaches a minimum value, so the amount of error is known. The only error inherent in the Gauss-Newton iteration is that the frequency and resistance difference must be calculated so, for every iteration of the algorithm, the error from the model occurs in the calculation of the values in air and the liquid. This error is minor for the magnitude, but it is considerable for the phase, as explained previously.

Figure 25 – Frequency dependence on slip magnitude and phase. The flatness of the curve with respect to phase shows that there is inherent error in the determination of phase from experimental data

5.3.4 Contact angle, surface tension and slip

Contact angles depend on the liquids and surfaces and are related to the surface tension γ (see Section 2.6.3). Surface tensions for the liquids used are given in Table 5. The highest surface tension is that of water, and is the reason that water only partially wets most surfaces ($\theta < 90^\circ$). The lower values for the other liquids explain why they generally wet most surfaces ($\theta \approx 0^\circ$). Figures 26 and 27 show the relation of the surface tension to slip magnitude and phase, respectively, for each surface. Ethanol, which has the lowest surface tension, shows very little slip on any of the surfaces. As the liquid surface tension increases, the slip magnitude decreases, meaning that amount of slip increases. This pattern is followed for all surfaces except the bare gold. When water is

in contact with the bare gold, there is almost no slip and, in fact, some trials resulted in a slip parameter greater than 1, indicating that the hydrophilic interaction between the bare gold and the water is very strong.

Table 5 – *Surface tension of liquids used in the present study; values obtained from ^aref. [55], ^bref. [14], and ^cref. [59]*

<i>Liquid</i>	<i>Surface Tension γ (mJ/m²)</i>
Water ^a	71.60
Ethanol ^a	21.89
Hexadecane ^b	27.60
Dodecane ^c	24.57

Figures 28 and 29 show the relationship of contact angle to slip magnitude and phase. For ethanol, the magnitude is not dependent on the contact angle, since it varies without a change in contact angle. For hexadecane, the contact angle has very little effect on the slip magnitude, which remains the same despite different surface interactions. The effect of contact angle on water is more pronounced, as can be seen from the sharp decrease in slip magnitude for only a small change in contact angle. Dodecane shows a reversed pattern to water and the changes are smaller.

Figure 26 – Variation in average slip magnitude with surface tension of the bulk liquid. The liquid order, from lowest tension to highest, is ethanol, dodecane, hexadecane and water

Figure 27 – Same as above, for slip phase

Figure 28 – Variation of slip magnitude with contact angle

Figure 29 – Variation of slip phase with contact angle

The comparison of contact angle and phase show an increase in phase with contact, especially in water. As the contact angle increases, this indicates an increase in

friction between the surface and the liquid – larger amounts of energy is required to break the bonds between liquid and surface. In the case of water, where internal hydrogen bonds keep water molecules attracted to each other and strongly bound to the surface, bonds would take more time to break, resulting in a larger phase angle. This trend is apparent in hexadecane and dodecane, though less prevalent, since the internal bonds and interfacial friction is less. The trend is absent in ethanol. This trend may also explain the phase trends discussed in Section 5.3.2.

5.3.5 Relation of magnitude to phase

Figures 30 to 33 show the relation of slip magnitude to phase for each liquid on the various surfaces. The slip magnitude of the device in water (Figure 30) decreases from the bare device to the coated ones. The phase decreases in the same pattern. It decreases towards zero-phase from the bare device to MPD and HDT, and then becomes negative on the BT surface, to the same degree as the result on the bare surface is positive. The device in ethanol (Figure 31) shows constant slip magnitude for all surfaces, with variable phase. However, the variable phase is likely due to the experimental error discussed in Section 5.3.3, since the two outlying trials (HDT and BT) also appear within the main distribution in other trials.

The device in hexadecane (Figure 32) also shows constant slip magnitude and clustered phase with outliers. The magnitudes are slightly less than those of ethanol, indicating more slip, and the phase angles are relatively small compared to the slip phase for the device in water. The phase distribution is similar to that of the device in ethanol. For dodecane (Figure 33), the slip magnitude increases from the bare to the coated devices, opposite of the pattern displayed for water. The phase distribution is similar to

that of water but, as with the magnitude, it is in the opposite direction, despite some experimental error. Figure 34 shows a histogram of the phase distributions for the various liquids.

Figure 30 – Dependence of slip magnitude on phase for bare and coated crystals in water

Figure 31 – Dependence of slip magnitude on phase for bare and coated crystals in ethanol

Figure 32 – Dependence of slip magnitude on phase for bare and coated crystals in hexadecane

Figure 33 – Dependence of slip magnitude on phase for bare and coated crystals in dodecane

The 'average' series on Figures 30 through 33 show the averaged values for each surface plotted against each other. Slip values for ethanol and hexadecane are not affected by the surface, as the plots do increase or decrease considerably. However, the plots for water and dodecane show an increasing dependence of the magnitude on the phase – as the phase increases, so does the magnitude. As well, the slips increase in opposite directions. For the device in water, the increase is from BT to the bare surface while, for the device in dodecane, the increase is from the bare surface to BT. The slip increases with increasing affinity.

In the slip parameter model, the liquid displacement should be lagging the solid, such that the phase should be negative. However, the experimental phase values are mostly positive, which agrees with results from Ferrante *et al.* [10] and Hayward and

Thompson [6], who found large positive phases for a device in water. The fitting algorithms used by these authors are subject to the same errors as those in the present theory. In all these studies ([6,10] and the present study), the elasticity of the liquid was neglected. Including elasticity in the fluid would be expected to produce experimental values that agree with theoretical values, as described in the following section.

5.3.6 Role of elasticity

Notwithstanding the inherent phase error, including a liquid elasticity in the model can change the analysed results. Figure 35 shows the relation of slip phase to magnitude for a bare device operating in water. The data points joined by lines represent the theoretical calculation of phase from magnitude and magnitude from phase. The solid black line is an exponential best-fit of slip from experimental data using the method described in Section 5.2.1, for a liquid stiffness of 0. Using liquid stiffnesses of 10^3 to 10^5 N/m², the experimental data is shifted to the right, away from the theoretical calculations. For negative stiffness in the range of -10^4 and -5×10^4 , the modeled data bracket the theory. These values are in the range of those calculated by Hayward and Thompson [6] from experimentally fit slip values, also described in Section 2.6.4. The Matlab script code used to analyze the different stiffnesses is shown in Appendix B-2.

The concept of a negative stiffness seems difficult to accept. It implies that an object under tensile stress will actually shorten. Contrary to the assertion from [6], this situation can exist within a Lennard-Jones molecular force model. For intermolecular forces, such as van der Waals forces, the magnitude of the force is *inversely* proportional to distance. The behavior of a simple Lennard-Jones interaction is shown in Figure 36.

Figure 34 – Histogram showing the distribution of the phases for the various liquids. The surface is not distinguished

Figure 35 – Role of liquid elasticity in slip. Each line is an exponential best-fit line of numerically fitted experimental slip values for a given liquid stiffness. The black line is the model run with no liquid stiffness. The numbers beside each line indicate the liquid stiffness. The thin black lines with data points represent the theory from Equations 83 and 85.

Figure 36 – Simple model of intermolecular interaction, the Lennard-Jones potential, where $w(r)$ (solid) is the interaction energy and the force $F(r)$ (dashed) is the derivative of energy with distance. The equilibrium separation r_e occurs at the energy minimum when the force is zero. The maximum attractive (negative) force occurs at r_s . The energy becomes negative at r_0 , the molecular radius, due to electronic repulsion. [52]

5.3.7 Validation of slip length theory

The performance of the theory describing the relationship between the slip parameter and the slip length is evaluated, and the results are compared to published results. Using atomic force microscopy, Craig *et al.* [34] found slip lengths in the range of 0 to 18 nm for aqueous sucrose solutions on 11- and 12-carbon chain coatings. Zhu and Granick [33] measured the hydrodynamic forces on two approaching spheres in liquid and found slip lengths between 0 and 2.5 μm for water and tetradecane on bare mica and various self-assembled monolayers (SAM). Pit *et al.* [35] studied the behaviour of hexadecane on solids and found slip on all the surfaces tested. The authors found a slip length of 175 nm on bare sapphire, 400 nm on a complete SAM and only 100 nm on an incomplete SAM. Unfortunately, values from the literature were not obtained using the same system. However, the systems are similar enough that comparisons will show whether Equation 83 successfully links the two theories concerning slip.

Slip length values can be calculated in two ways: using either Equation 89 or 90, both of which are repeated here in more convenient forms. These equations show the explicit calculation of the slip length b .

$$b = -\ln|\alpha| \sqrt{\frac{2\eta}{\omega\rho}} \quad (89)$$

and

$$b = -\angle\alpha \sqrt{\frac{2\eta}{\omega\rho}}. \quad (90)$$

When using Equation 90, the phase angle must be in radians. Table 6 shows values for slip length calculated from slip magnitudes and phases. Standard error values are also shown for each result, which are calculated as two standard deviations for the calculated slip length values.

Table 6 – Slip length values calculated using Equations 89 and 90, showing standard error values

Surface		Bare		MPD		HDT		BT	
Bulk Liquid		Slip Length b (nm)							
		(as calculated using)							
		Mag	Phase	Mag	Phase	Mag	Phase	Mag	Phase
Water	Avg	21.0	-782	80.8	211	78.8	-143	71.4	945
	±	34	1050	59	2528	6	462	18	82
Ethanol	Avg	23.1	-911	20.3	-689	19.3	-1205	11.6	-201
	±	10	428	12	638	6	1771	32	1527
Hexadecane	Avg	65.2	-278	74.3	-167	70.9	-328	66.7	-795
	±	18	642	21	775	14	275	31	1894
Dodecane	Avg	27.7	-6	11.7	-203	16.4	-163	10.6	-44.4
	±	23	856	16	432	8	498	2	126

As is evident from Table 6, slip lengths calculated from the magnitude yield very different results than slip lengths calculated from the phase, which have very high standard errors. This is due to the error inherent in the phase values calculated from the experimental results, as described in Section 5.2.4.

The patterns found in slip parameter magnitudes, as shown in Table 4, are still evident for the slip lengths. Low slip lengths are expected for ethanol, which is a non-wetting liquid so the no-slip condition applies. The slip length increase for water from the bare gold to the hydrophobic surfaces is considerable, showing almost a four-fold increase. Between the hydrophobic surface and water, there would be a high degree of repulsion, so a large change in slip is expected. Very low slip lengths are found for

dodecane on the hydrophobic surfaces, with a slightly higher slip on the bare hydrophilic surface. The slip of dodecane on bare gold was expected to be greater. However, because dodecane is non-polar, there is not as much repulsion between dodecane and the gold than between water and the hydrophobic surfaces. As well, the dodecane molecules may get tangled in the long-chain hydrophobic surfaces, decreasing the possibility of slip. Hexadecane shows large, fairly constant slip on all surfaces, as expected.

The large deviation among the experimental results and among the values from different literature sources can be attributed to differences in the experimental setup, specifically the flow rates reported in each case. Flow rate has a large effect on the relative amount of slip, as shown in [33], so different slip lengths would normally be found. As well, the concept of slip, and its description with the slip parameter or slip length, have not yet been fully explored and characterized. However, despite the lack of a rigorous description of slip, both theories allow for the examination of general physical trends of interfacial systems [34].

6 SUMMARY AND CONCLUSIONS

The results of this study establish a theoretical relationship between the slip parameter from the acoustic wave literature and the slip length from the hydrodynamics literature. Previous attempts to characterize the surface interaction involved two-parameter fits to experimental data. The theory presented here reduces empirical determination to a one-parameter fit. It shows that the magnitude and phase of the slip parameter α , which describes the relative motion of the surface and liquid in the transverse-shear model, can be linked to the slip length b .

The displacement boundary equations of the transverse-shear model, which involve α , were equated to the velocity boundary equations of the slip length and solved for the magnitude and phase, each in terms of the slip length. From these equations, the magnitude and phase are shown to depend upon one another. This relationship is significant in the study of acoustic wave devices, since the complex-valued slip parameter can now be represented by a single real parameter to describe the interaction at the surface-liquid interface of the device.

Experiments were performed to show that hydrophobic liquids show trends opposite to hydrophilic liquids when exposed to surfaces with different interfacial energies. Whereas hydrophilic liquids show larger frequency and resistance shifts on polar surfaces than on non-polar ones, hydrophobic liquids show larger shifts on non-polar surfaces. However, the response of hydrophobic liquids is generally smaller, likely because non-polar repulsive forces in hydrophobic liquids are weaker than polar forces or hydrogen bonding.

Results were also used to validate the slip theory by testing different liquids on a variety of surfaces. Empirical slip values determined from the transverse-shear model showed that water, hexadecane, and dodecane had similar slip magnitude-phase curves to values calculated from the theory, though the experimental slip values were shifted to the left of the theoretical curve. Results for ethanol did not agree with the theory, though it was found from the data that ethanol experiences very little slip on any surface, due to its low internal free energy. Slip length values calculated from the present theory were compared to the results from the literature, namely Zhu and Granick [33], Craig *et al.* [34], and Pit *et al.* [14,35]. Due to differences in experimental method and disagreement about how the slip length should be applied, the results could not be formally compared. However, almost perfect agreement between these results in water and results from Craig *et al.* [34] in aqueous solutions were obtained. As well, agreement within one order of magnitude was found between the results of this study for hexadecane and results reported by Pit *et al.* [14,35]. Although the methods of testing were different, the results are in agreement.

In the experiment, each surface was tested for its affinity to the liquids used. The bare gold was found to be generally hydrophilic, though there was a large amount of variance, especially in contact with water. MPD also showed a large amount of variance, due to the various configurations that the surface could adopt, depending on the location of the alcohol groups relative to surface. Both the HDT and BT surfaces were found to be hydrophobic, though BT appeared slightly more hydrophobic.

By showing that the affinity of the surface to the liquid plays a large role in the presence of slip at the interface, we establish that acoustic wave sensors can be used to detect changes in surface free energy in the absence of mass effects. This introduces an improved understanding of systems where the surface free energy changes during an experiment, such as when a protein on the surface changes configuration.

Analysis of the data shows that the slip magnitude is a better determinant of the system, and hence of the slip length, than the slip phase. There is a much larger amount of error in the phase measurements than in the magnitude, due to the flatness of the frequency curve with respect to the phase angle. As well, the slip length values calculated from the magnitude show much better agreement with data from the literature than those calculated using the phase.

The effect of adding a liquid stiffness on the agreement of theory to experiment was explored, since this was not included in the initial model runs. While positive values of stiffness shifted the data away from the theory, different values of negative stiffness bracketed the theoretical curves. This agrees with results from Hayward and Thompson [6] and the values that were closest to the theory in this study were in the range found by those authors. The concept of a negative stiffness in terms of macroscopic materials is a physical impossibility. However, it may have applications in micro- and nanoscopic science, since one side of the Lennard-Jones potential curve of intermolecular forces is analogous to a negative stiffness. Because of the application of acoustic wave devices to small-scale systems, the possibility of a negative stiffness should be further explored.

A single real-valued slip is not a new concept in the field of acoustic wave devices. In a recent article, McHale *et al.* [12] introduced slip to the lumped-impedance model for acoustic wave devices, with a real slip value s . While the results from this study showed that a single real value can be used to describe the interfacial behaviour of acoustic wave devices, the authors did not provide a mathematical justification for how it should be included in the model. The present study justifies the use of a single real slip parameter and introduces the possibility of linking the velocity and displacement boundary profiles for a slip condition.

The slip length used in the present theory can be linked to the bulk viscosity and a friction coefficient through Equation 44:

$$b = \frac{\eta}{k}.$$

Similarly, McHale *et al.* [12] linked the slip value s to the layer properties and a dimensionless friction with Equation 48:

$$s = \frac{1}{\chi \sqrt{\rho G}}.$$

The slip length equation only applies to slip at the solid-liquid interface, so only the liquid viscosity is included. The slip value s is applicable to any layer, so include a viscoelastic dependence. Future work should show that the slip length may be generalized to apply to slip of viscoelastic layers by adding an elastic term.

While these two equations are dissimilar, they both link slip to bulk parameters and some sort of interfacial friction. This interaction is important because, if it can be

determined *a priori*, changes in resonant behaviour of an acoustic device can be used to make predictions about changes at the device-liquid interface. A good indicator of interfacial energy is the contact angle between a liquid droplet and the device surface. While the contact angle is not sufficient to make predictions about the interfacial friction, some correlation between interfacial energy and friction could eventually be used to understand the complex resonance behaviour that has been observed in a number of systems [39,40,41]. If the interfacial energy is known, a theory describing the interfacial friction would be able to explain changes at the device surface, revealed through acoustic measurements.

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(<http://www.reciprocalssystem.com/ls/paper08.htm>).

APPENDIX A – NOMENCLATURE

C_Q	Quartz complex shear modulus
C_M	Metal electrode complex shear modulus
C_P	Polymer film complex shear modulus
C_B	Bulk fluid complex shear modulus
c_Q	Quartz stiffness
c_M	Metal electrode stiffness
c_P	Polymer film stiffness
c_B	Bulk fluid stiffness
ρ_Q	Quartz density
ρ_M	Metal electrode density
ρ_P	Polymer film density
ρ_B	Bulk fluid density
η_Q	Quartz viscosity
η_M	Metal electrode viscosity
η_P	Polymer film viscosity
η_B	Bulk fluid viscosity
ω	Angular frequency
f_R	Resonant frequency
R_m	Motional resistance
e	Piezoelectric constant
ϵ	Dielectric constant
k_Q	Quartz wave number
k_M	Metal electrode wave number

k_P	Polymer film wave number
k_B	Bulk fluid wave number
d_Q	Distance from bottom surface of quartz to top surface
d_M	Distance from bottom surface of quartz to top surface of metal electrode
d_P	Distance from bottom surface of quartz to top surface of polymer film
A	Electrode area
u_Q	Quartz displacement
u_M	Metal layer displacement
u_P	Polymer film displacement
u_B	Bulk fluid displacement
B_1	Integration constants (subscripts 1 to 9)
φ	Electric potential
δ	Kronecker delta
σ	Stress
b	Slip length
k	Friction coefficient
α_{QM}	Quartz-metal slip parameter
α_{MP}	Metal-polymer slip parameter
α_{PB}	Polymer-bulk fluid slip parameter
γ	Surface tension

APPENDIX B – MATLAB SCRIPT CODE

APPENDIX B-1 – GAUSS-NEWTON MATLAB SCRIPTS

```
%SlipErrAnal - script to determine slip limits for deviations in
%frequency and resistance
clear;

%frequency and resistance data and error limits stored in .slp file
data = input('Enter crystal number (3,4,7,8,9,14,15): ');
data = num2str(data);
datafile = [data '.slp'];

load(datafile);
data = ['X' data];
eval(['errors = ' data]);

fidl = fopen([data '.sp2'],'w');

%do for bare and coated
for polymer = 1:2

    %do for each surface
    for surface = 1:4

        %use surface and polymer to select model file to use
        switch surface
            case 1,
                if polymer == 2
                    inputfile = 'wapoly';
                else
                    inputfile = 'wanopoly';
                end;
            case 2,
                if polymer == 2
                    inputfile = 'etpoly';
                else
                    inputfile = 'etnopoly';
                end;
            case 3,
                if polymer == 2
                    inputfile = 'cl6poly';
                else
                    inputfile = 'cl6nopo';
                end;
            case 4,
                if polymer == 2
                    inputfile = 'cl2poly';
                else
                    inputfile = 'cl2nopo';
                end;
        end; %switch

        x = 4*(polymer-1)+surface;
```

```

freqDiff = errors(x,1);
resDiff = errors(x,2);
freqErr = errors(x,3);
resErr = errors(x,4);

alphaErr = zeros(5,2);

alphaMeas = GaussNewton(inputfile,freqDiff,resDiff);

freqUp = freqDiff + freqErr;
freqDown = freqDiff - freqErr;
resUp = resDiff + resErr;
resDown = resDiff - resErr;

alphaErr(1,:) = [real(alphaMeas) imag(alphaMeas)];

for combo = 1:4
    switch combo
        case 1,
            freqDiff = freqUp;
            resDiff = resUp;
        case 2,
            freqDiff = freqUp;
            resDiff = resDown;
        case 3,
            freqDiff = freqDown;
            resDiff = resUp;
        case 4,
            freqDiff = freqDown;
            resDiff = resDown;
    end; %switch

[alphatemp,ErrF,ErrR,itera] = GaussNewton(inputfile,freqDiff,resDiff);

    alphaErr(combo+1,:) = [real(alphatemp) imag(alphatemp)];

end; %for combo

alphaErr = transpose(alphaErr);

fprintf(fid1,['\r\n' inputfile '\r\n']);
fprintf(fid1,'% -9.8f % -9.8f\r\n',alphaErr);

end;%for surface
end;%for polymer

fclose(fid1);

```

```

function [alpha,ErrF,ErrR,itera] = GaussNewton(file,freqdiff,resdiff)

%Gauss-Newton method to numerically calculate the slip parameter from
%frequency and resistance measurements and the initial no-slip
%assumption

%to be used in conjunction with AMODEL.EXE, by Gord Hayward

```

```

%input file
inputFile = file;

%constants
alphaR = 0.01;
alphaI = 0.01;

%get initial bare frequency in air full slip:
alphaFull = 0.0 + j*0;
makeTempFile(alphaFull,inputFile);

%run model to get resonant characteristics with full slip value
[s,w] = dos('modifamo tempfile');
w = sscanf(w,'%f');
f0 = w(3)*1e6;
R0 = w(4);

alpha = 1.0 + j*0.0;

%tell user to input measured values
dFmeas = freqdiff;
dRmeas = resdiff;

%run model to get no-slip value
[s,w] = dos(['modifamo ' inputFile]);
w = sscanf(w,'%f');
dF = w(3)*1e6 - f0;
dR = w(4) - R0;

ErrF = abs(dF - dFmeas);
ErrR = abs(dR - dRmeas);

itera = 0; %initialize iteration counter

while (ErrF > 0.1) | (ErrR > 0.1)

    alphaA = alpha + alphaR;
    makeTempFile(alphaA,inputFile);

    %run model to get resonant characteristics with A slip value
    [s,w] = dos('modifamo tempfile');
    w = sscanf(w,'%f');
    dFa = w(3)*1e6 - f0;
    dRa = w(4)-R0;

    alphaB = alpha + j*alphaI;
    makeTempFile(alphaB,inputFile);

    %run model to get resonant characteristics with B slip value
    [s,w] = dos('modifamo tempfile');
    w = sscanf(w,'%f');
    dFb = w(3)*1e6 - f0;
    dRb = w(4) - R0;

    c1 = (dFa - dF)/alphaR;

```

```

c2 = (dRa - dR)/alphaR;
c3 = (dFb - dF)/alphaI;
c4 = (dRb - dR)/alphaI;

A = [c2 c4 (dRmeas-dR);c1 c3 (dFmeas-dF)];
B = rref(A);

dAlphaR = B(1,3);
dAlphaI = B(2,3);

alpha = alpha + dAlphaR + j*dAlphaI;
makeTempFile(alpha,inputFile);

%run model to get resonant characteristics with new slip value
[s,w] = dos('modifamo tempfile');
w = sscanf(w,'%f');
dF = w(3)*1e6 - f0;
dR = w(4) - R0;

ErrF = abs(dF - dFmeas)
ErrR = abs(dR - dRmeas)

itera = itera + 1

end %Do

```

```

function makeTempFile(alpha,inputFile)

alphaToFile = [real(alpha) imag(alpha)];
fid1 = fopen([inputFile '.dat'],'r');
fid2 = fopen('tempfile.dat','w');
for i = 1:24
    line = fgets(fid1);
    fprintf(fid2,line);
end
line = fgets(fid1);
fprintf(fid2,'%10.9f %10.9f\r\n',alphaToFile);
for i = 1:4
    line = fgets(fid1);
    fprintf(fid2,line);
end
fclose(fid1);
fclose(fid2);

```

APPENDIX B-2 – STIFFNESS ERROR ANALYSIS SCRIPT

```

%StifErrAnal - script to determine slip limits for deviations in
frequency and resistance for liquid stiffnesses
clear;

%frequency and resistance data and error limits stored in .slp file
load('stifn.slp');
load('stify.slp');

for a = 1:2

```

```

if a == 1
    inputfile = 'wanostf';
    errors = stifn;
else
    inputfile = 'wapostf';
    errors = stify;
end;

alphaErr = zeros(7,2)

for b = 1:7

    freqDiff = errors(b,1);
    resDiff = errors(b,2);
    freqErr = errors(b,3);
    resErr = errors(b,4);

    alphaMeas = GaussNewton(inputfile,freqDiff,resDiff);

    freqUp = freqDiff + freqErr;
    freqDown = freqDiff - freqErr;
    resUp = resDiff + resErr;
    resDown = resDiff - resErr;

    alphaErr(b,:) = [real(alphaMeas) imag(alphaMeas)];

    if a == 1
        stifn1 = alphaErr;
    else
        stify1 = alphaErr;
    end

end;%b
end;%a

save 'stifn.sp2' stifn1 -ascii -double
save 'stify.sp2' stify1 -ascii -double

```