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MICROMACHINED QUARTZ RESONATOR BASED HIGH SENSITIVITY MAGNETOMETERS

A Dissertation in
Electrical Engineering

by

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ABSTRACT
Magnetic sensor technologies are gaining further importance as they are used in smart mobile devices, navigation and especially to bio-imaging. Despite the fact that the sensitivity has been the major magnetic sensor specification, the bulkiness, overall price and the power consumption of the sensors also act as important specifications for practical applications. Micro-Electro-Mechanical Systems (MEMS) are the chip-scale actuators and sensors, which can offer very sensitive sensors that can i) operate at room temperature, ii) consume very low power iii) be manufactured in arrays iv) the overall cost is extremely cheap.

In this dissertation, two different MEMS magnetic sensors are proposed utilizing quartz micro-resonators. First sensor operates on quantifying the magnetoviscosity of ferrofluids. Magnetovisvosity is defined as the viscosity changes occurring at ferrofluids as a function of applied magnetic field. These viscosity changes as a function of magnetic field are detected utilizing micromachined AT-cut thickness Shear Mode Quartz arrays acting as micro-viscometers. Ferrofluids typically consist of 10 ± 3 nm iron oxide (Fe₂O₃) nanoparticles suspended in mineral oil. However, the high magnetic susceptibility of ferrofluid suspensions results in the modulation of the magnetoviscosity due to applied magnetic fields. These viscosity changes due to in-plane incident field shifts the at-resonance admittance characteristics of μQCR and is tracked in real time to achieve a novel magnetic sensing mechanism to detect and quantify the low frequency, low strength magnetic fields For improved sensitivity, the in-plane sensed magnetic flux density is concentrated using a high relative permeability (μr = 45000 as bulk) thin film of Metglas® (Fe₈₅B₅Si₁₀) deposited on the resonator electrode. Furthermore, by patterning the Metglas® film in a bow-tie shape and aligned at the center of the μQCR electrode 2D vector sensing is achieved. Using these improvements, a minimum detectable field of 1.5 nT/√Hz at 1 Hz has been experimentally demonstrated. Furthermore, the high frequency and small amplitude shear waves are created with the Quartz resonators and the highly magnetoviscous interface is
modeled. The ferrofluid is modeled as a viscous loading on the thickness-shear mode resonator via the modified Butterworth-Van-Dyke Model. This sensor will be referred as the magnetoviscous sensor throughout the dissertation.

Second magnetic sensor concept also exploits micro-machined quartz resonators’ admittance shifts, but the mechanism is based on the transverse force-frequency effect. Magnetostrictive Metglas® thin film coated AT-cut thickness shear mode (TSM) Quartz thin plate microresonator structures are uniquely released using focused ion beam (FIB) milling. Therefore, the whole structure is able to do flexural bending due to magnetostriction induced as a result of applied magnetic field in the magnetic thin film that is elastically coupled to the quartz microresonator. As a result of transverse loading and bending, the admittance characteristics of the resonator shifts. The transverse force-frequency sensitivity as a function of azimuth angle for magnetostrictive thin film coated AT-cut thickness shear mode (TSM) quartz thin plate are experimentally tested and successfully modeled via coupling Lee’s theory and magnetostrictive unimorph equations. The first device (500 x 500 x 19 µm) has been tested as the proof-of-concept device, where 1 µT at 10 Hz was measured. The latter thinner device (750 x 500 µm x 7.5 µm) is the optimized device, where the sensitivity is improved to 79 nT at 10 Hz input frequency inducing 94.5 nS of conductance shift. This corresponds to a frequency shift of Δf / f₀ that is equal to 1.4692 x 10⁻⁹. The ultimate expected sensitivity for this system is simulated using the coupled domain analysis. According to the theoretical model, it is predicted that low nanoTesla to high picoTesla magnetic flux densities would be detected after further thickness reduction.

To sum up, both sensors are proposed and studied as unique MEMS sensing mechanisms. They i) are relatively low power consuming devices, ii) can be manufactured in arrays, which improves the spatial density, and iii) can both operate at room temperature. All aspects of the devices, sensing mechanisms along with the experimentations and theoretical modeling will be discussed in this dissertation.
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Chapter 1

Introduction

1.1 Magnetic Sensor Technologies and Applications

Sensors, which are devices utilized to detect and measure physical quantities play a vital role in many applications. Approximately 70% of commercially available sensors in the sensor market are composed of inductive, capacitive, resistive and magnetic sensors [1]. The physical quantities measured and the roles of the sensors differ from one application to another. Furthermore, there has been a quite large interest growing towards MEMS (Micro-Electro-Mechanical Systems) sensors and actuators in the last decade. MEMS sensors and actuators can be defined as chip-scale mechanical and electrical mechanisms/transducers that are micrometer \( (10^{-6} \text{ m}) \) or even nanometer \( (<10^{-9} \text{ m}) \) sized. Many applications such as mobile devices, car industry, biomedical imaging continuously benefit from the reliability, high efficiency and compactness of MEMS sensors. Most of the widely used typical MEMS actuators and sensors can be grouped into gyroscopes, accelerometers, microphones, speakers, gas-chemical sensors, deformable micromirrors used for Digital Light processing (DLP), energy scavengers, Bulk Acoustic Wave (BAW) filters, microbolometers, inkjet printheads, pressure sensors, flow sensors, bio-sensors and magnetic sensors and actuators [2]

Magnetic sensors of any size have been widely used for many different applications. In computer technology, the magnetic actuator is the recording head for hard disks, which are used to store data. Automobiles make use of magnetic sensors to detect the position of the engine crank and wheel brakes. Airplanes and ships navigate with higher precision using very accurate magnetic compasses. In addition, non-contact magnetic switching enabled higher reliability. Biomedical devices and bio-sensors use micron sized magnetic bead separation techniques to
measure various biological signals. The critical body organs are imaged through very sensitive magnetic sensors. All of these applications require very different specifications and sensor sizes ranging from macro scale down to MEMS scale [3]. Furthermore, the physical sensing phenomena used to sense the magnetic fields vastly differ.

One of the most critical specifications of magnetic sensors is the ultimate sensitivity. As the sensors become more sensitive, the new opportunities emerge, especially in bio-imaging applications. In the following section of the introduction, different selected sensing mechanisms used for macro and micro scale magnetic devices and their sensitivity limitations will be articulated and summarized.

1.1.1 Magnetic Sensor Technologies Overview

Magnetic sensors can be divided into two parts considering the general functionality: i) Vector magnetic sensors and ii) Scalar magnetic sensors. Vector magnetometers are able to detect the direction (vector components) of the magnetic field as well as its amplitude [4], whereas scalar magnetic sensors can only measure the magnetic field amplitude.

One can immediately assume vector magnetic sensors are better and more useful than the scalar magnetic sensors since vector magnetic sensors provide additional information. However, scalar magnetic sensors are preferred over vector magnetic sensors in some applications. One example would be a sensor on a car in motion, which is detecting field changes induced due to movement of ferromagnetic objects (i.e engine cranks). Nevertheless, rotational vibrations caused by the car motion will shift earth’s field vector components, which will in turn overwhelm the signals caused by ferromagnetic objects if a vector magnetic sensor was used [4].
The sensitivities can be also categorized. The applications involve measuring: i) magnetic fields that are stronger than Earth’s magnetic field, ii) small amplitude magnetic fields caused by fluctuations in Earth’s magnetic field, iii) gradient or induced fields, iv) ultra-low amplitude magnetic fields detected in bio-imaging. Figure 1-1 shows the sensitivity ranges of different sensing devices. Hall-effect sensors, magnetodiode and magnetotransistors fall into the category where stronger magnetic fields that are larger than Earth’s magnetic field are measured (1 µT to 1 mT). AMR (Anisotropic Magnetoresistance), and GMR (Giant Magnetoresistance), sensors are able to detect low nanoTesla magnetic flux densities. SQUIDS, Atomic Magnetometers and Nitrogen Vacancy Spin sensor are all able to detect below pT magnetic flux densities and stand out as the most sensitive magnetic sensing technologies.
Hall sensors

Hall effect sensors are the most widely used magnetic sensors in the world. The principle of operation is based on the Hall effect, discovered and named by Edwin Hall (1879). A schematic of the principles of Hall effect is illustrated in figure 1-2. A voltmeter is showing the potential between the opposite two sides of a thin conductor slab, while a DC current is flowing through its length direction. When there is no applied external magnetic field, the voltmeter reads zero. On the other hand, when a magnetic field perpendicular to the current flow is applied, a potential difference between the transverse sides occurs and the voltmeter reads a value this time. This voltage difference is also named as the Hall Voltage.

![Schematics of Hall Sensor working principle. The current flowing through the conductor slab with a) no magnetic field applied, b) magnetic field applied along the transverse direction. Adapted from [5] and edited here.](image)

The charge carriers are affected by the applied magnetic and electric fields. Hall Voltage is due to the resultant force acting on the moving particles due to these fields. When the charge carriers (electrons in the case of a metal) are in motion (drifting), the total force acting on the carriers due to any magnetic or electric field is given by the equation,
\[
\vec{F} = q_o \vec{E} + q_o \vec{v} \times \vec{B}
\]  \hspace{1cm} (1.1)

Where \( \vec{F} \) is the resultant force, \( \vec{E} \) is the electric field, \( \vec{v} \) is the velocity of the particle, \( \vec{B} \) is the magnetic field and \( q_o \) is the magnitude of the charge. This equation is known as the Lorentz Force equation. The first term of the summation is the force resulting due to electric field and the second term is the magnetic force due to velocity of the particle cross product with the magnetic field. Since it is a vector multiplication, the highest force due to magnetic field is achieved when the field is perpendicular to the particle motion.

Although the magnetic field forces the charge carriers to one side of the conductor as shown in figure 1-2.b, this process is self-limiting since the excess concentration of charges accumulates on one side, resulting depletion on the other side of the conductor. This in turn induces a built-in electric field. At the equilibrium, the force on the charges due to external field is equal to the induced electric field force. Then, the force balance can be written as;

\[
\vec{F} = q_o \vec{E} + q_o \vec{v} \times \vec{B} = 0
\]  \hspace{1cm} (1.2)

where the built-in electric field along the width, \( w \), can be written as \( \vec{E} = \frac{V_H}{w} \). Substituting this into the equation and rearranging the terms, \( V_H \) can be expressed as [6];

\[
V_H = -vBw
\]  \hspace{1cm} (1.3)

From eq. (1.3), it is concluded that the Hall voltage is a function of magnetic field, the charge carrier velocity and the distance between the side sense contacts. If the substrate is metal, the conduction electrons are free to move, but the motion is random due to thermal velocities. The average rate of motion from an electric field is known as drift velocity. The drift velocity can be written as;

\[
v = \frac{I}{q_o N A}
\]  \hspace{1cm} (1.4)
where \( I \) is the current in Amperes, \( q_0 \) is the charge of an electron \((1.6 \times 10^{-19} \text{C})\), \( N \) is the carrier density in \#/cm\(^3\), \( A \) is the cross-sectional area \((w \times d)\) in cm\(^2\). If eq. 1.4 is substituted into eq. 1.3, the Hall voltage can be rewritten as;

\[
V_{H} = \frac{IB}{q_0Nd}
\]  

(1.5)

The intrinsic carrier concentration in metals is high \((8.4 \times 10^{22})\), which decreases the Hall voltage. Semiconductor materials are preferred as a material in Hall sensors due to the reasons, i) they have low intrinsic carrier density and they can be doped to any level of the carrier density, ii) the carrier can be holes or electrons. For example, in the case of 2 mA current and 0.5 Tesla of field applied to an N-type silicon Hall-effect transducer \((1000 \times 500 \times 25 \ \mu \text{m})\) with a doping concentration of \( 3 \times 10^{15} \text{cm}^{-3} \) will result in 83 mV of Hall Voltage. This transducer will have 1.36 k\( \Omega \) and therefore the power consumption will be 2.72 mW, which is modest power dissipation for electronics circuit. The thickness and current are two parameters that are engineered for optimum performance in commercial devices, but as current is increased, the power consumption increases.

The Hall sensors sensitivity range from \(10^2 \text{nT}\) up to \(100 \mu \text{T}\). Indium Antimonide is used as the material in the most sensitive sensors, They can sense DC and AC fields. The highest frequency limit is around 1 MHz. The power consumption is around 100-200 mW.

**Magnetoresistive sensors (AMR and GMR)**

In 1856, the Scottish scientist Michael Thompson (Lord Kelvin) has measured the electric resistance change \(\Delta R/R\) occurring in an iron piece due to applied magnetic field. Later, he tried Nickel and found out the resistance change was higher with respect to iron that to be around 5\%. This phenomenon is later called as the magnetoresistance. In addition, he observed
that the resistance decreased when the applied magnetic field was along the current direction. On the other hand, the resistance increased when the applied field direction was perpendicular to the current direction. Because of this direction dependence, this effect is later referred as Anisotropic MagnetoResistance (AMR). The physical origin of this phenomenon lies in the electron spin-orbit coupling [7], which is the interaction of particle’s quantum-mechanical spin with particle velocity. Spin–orbit coupling originates from the movement of electrons in a crystal’s intrinsic electric field in solid-state materials [8].

![Figure 1-3. Schematics of the working principle for Anisotropic MagnetoResistance](image)

Figure 1-3 demonstrates the schematics for the AMR principle. The magnetization vector, \( \vec{M} \), makes an angle, \( \theta \), with the current flow direction. When a perpendicular field, \( H_\perp \), is applied to the material, the magnetization vector rotates, which in turn causes the electron cloud around each nucleus to slightly deform. This deformation affects the scattering experienced by the conduction band electrons when traveling through the lattice. In the case where \( \theta \) is 0, then the magnetization is parallel to the current, the electronic orbits are perpendicular to the current, which increases the cross section for the scattering resulting in increased resistance for current flow. On the other hand, the electronic orbits are parallel to the current in the case \( \theta \) is 90° resulting in reduced resistance due to small cross section for scattering as the electronic orbits are in the plane of current. \( \theta \) changing from 0 to 90° shifts \( \Delta R/R \) from a maximum value down to 0.
For non-magnetic materials, MR effects at low fields are very small, where it can become large at high fields. MR reaches to 5% in ferromagnetic metals and alloys [9].

In 1988, some materials which are called magnetic multilayers have been utilized to demonstrate large magnetoresistance ($\Delta R/R \approx 50\%$). This is later named as Giant Magnetoresistance (GMR). This is achieved by stacking layers of magnetic and non-magnetic materials, which are nanometers thick. An example of this was Fe/Cr/Fe trilayer system, with an additional antiferromagnetic (AF) layer on top. A GMR spin valve is shown in figure 1-4. This layer is used to pin the magnetization of one of the ferromagnetic layers.

![GMR spin valve and the operation principle.](image)

Figure 1-4. GMR spin valve and the operation principle. The schematics is adapted from [4]

The ferromagnetic layers are separated with a very thin conductor. When there is no magnetic field, the free ferromagnetic layer magnetization is perpendicular to the magnetization of the pinned ferromagnetic layer as shown in figure 1-4.a. The resistance at this state is $R_0$. However, the magnetization vectors align for pinned and free ferromagnetic layers when an external field is applied in the direction shown in figure 1-4 b. When an electric current is passing through the structure (either in parallel or perpendicular direction) at this field direction, electrons experience less scattering while going from an electron band structure in one of the ferromagnets into a similar or identical electronic band structure in the other ferromagnet. This is the lower
resistance state, $R < R_0$. However, when the field direction is reversed as shown in figure 1-4.c, the magnetization of the free ferromagnet and the hard ferromagnet are in the opposite direction. The electrons in this case suffer more scattering and therefore it is high resistant state where $R > R_0$. Nevertheless, the pinned magnetization will align with the magnetic field if the field strength is increased enough to flip the magnetization of the pinned ferromagnet. This is shown in figure 1-4.d, which creates the same effect with the low resistance state $R < R_0$. The resistance change between high and low resistance states has been measured to be around 10 % [10] and 50 % at 4.2 K [11]. In 2014, Mazhar Ali [12] has reported a record high magneoresistance change that is 13,000,000 % at 14.7 Teslas at 0.53 K temperature in non-magnetic layered transition-metal dichalcogenide, WTe$_2$.

The sensitivity of the present AMR sensors range from 1 µT up to 5 mT. GMR sensitivities range from 10 nT at 1 Hz up to 100 mT. With closed loop readout electronics, the sensitivity for GMR sensors can be pushed down to 0.1 nT. This technology has certain advantages such as easy integration with electronic circuits and easy structuring. However, the stacked layers have to be smooth in order to minimize the coupling between the layers.

**Magnetic Tunnel Junction Sensors**

Practical Magnetic tunnel junction Sensors (MTJs) are first discovered in 1995 [13] even though the physical phenomenon was first suggested in 1975 by M. Julliere [14]. The device structure is identical to the GMR structure shown in figure 1-4. The device again consists of 4 stacked layers. However, two ferromagnetic layers are now separated by a thin insulator layer instead of a thin conducting layer. The insulating layer has to be thin (on the order of a few nanometers or less), so that the electrons can tunnel through if a bias is applied between two metal electrodes across the insulator. MTJs operate at the similar principle with GMR, where the
tunneling current is a function of relative magnetizations of two ferromagnetic layers. As in the GMR case, one of the ferromagnets are soft and its magnetization can be reoriented with the magnetic field direction. When the both pinned and free ferromagnetic layers’ magnetization vectors are oriented parallel and towards the same direction, the resistance to the current flow is minimum. On the other hand, the resistance is the highest when two magnetization vectors are aligned in opposite directions. Both cases are related to the spin polarization of conductance electrons.

Even though this phenomenon is known till 1975, it has not become practical since 1995-2000. One of the reasons was the percent resistance changes (ΔR/R) observed in Fe-Ge-Pb and Fe-Ge-Co junctions were too small (~10%) even at temperatures lower than 4.2 K. Another reason was it was practically very difficult to form thin insulator layers. In addition, the layer has to be smooth in order to avoid any pin-holes or metallic bridges formation when an electric field is applied to the insulator [15]. After the advancements in the manufacturing, smooth and good quality of insulator films can be deposited with techniques such as ALD (Atomic Layer Deposition). In 2006, ~200% resistance change is demonstrated for MTJ sensors with MgO insulating layers at room temperature [16, 17]. This technology has been widely used in non-volatile random access memory (MRAM)

Superconducting Quantum Interface Device (SQUIDS)

SQUIDS are the state of art magnetic sensors in terms of the sensitivity and signal to noise ratio. The noise is extremely low on these sensors since the whole sensor and the read-out electronics are cooled down to superconducting temperatures, at which there is no resistance to the current flow and therefore no/ minimal thermal noise.
Before going into details of SQUID working principle, Josephson’s junction will be explained. Josephson’s junction consists of two superconductors that are separated by a thin insulator layer, which is a few nanometers thick, so the electrons can tunnel through it. It is similar to MTJs, where in this case the two layers are superconductors. This junction is studied and proposed by Brian David Josephson in 1962, while he was a graduate student at Cambridge university. In his original paper [18], he studied the tunneling current in two superconductors that are separated from each other with a thin insulating layer and mathematically modeled the expected currents. In superconducting state, electrons form pairs which are called Cooper pairs. These pairs of electrons have opposite spin and momentum. All cooper pairs have a macroscopic wave function in the form of [19]:

\[ \varphi = |\varphi(r)|e^{iK\cdot r} \]  

(1.6)

Where \( K \) is the net wave vector of all cooper pairs and \( \Psi(\mathbf{r}) \) is the ensemble-average function when \( K = 0 \). These pairs have a probability to tunnel through the insulator barrier since the wave functions overlap. Above superconducting temperature, the net interaction between electrons is repulsive. However, individual electrons in a Cooper pair have attraction to each other at the superconducting state. This slight attraction allows electrons to drop to a lower energy state and therefore an energy gap forms. Due to this, electrons now flow through the material without being scattered by the ions of the lattice. The current proportional to the phase difference of the wavefunctions can flow in the junction, which is given by [20];

\[ I_d(t) = I_c \sin(\theta(t)) \]  

(1.7)

Where \( \theta(t) \) is the phase difference of the macroscopic wave functions of the two superconducting electrodes. It is important to emphasize this phase difference is a function of time and it affects the system physically. At no applied bias to the junction, a superconducting current flows through
the junction due to tunneling at a value between \( I_c \) and \(-I_c\). If the phase difference changes with respect to time, then a voltage drop \( (U(t)) \) is observed in the junctions given by [21];

\[
\frac{\partial \theta(t)}{\partial t} = \frac{2e}{\hbar} U(t) = \phi_0 U(t)
\]  

(1.8)

Where \( \hbar \) is the Planck’s constant and \( e \) is the charge and \( U \) is the potential. Here, the term \( 2e/\hbar \) is defined as the flux quanta and is equal to \( \phi_0 = 2.06783 \times 10^{15} \) Webers (Tesla \( \times \) m\(^2\)). This is an important conclusion that the flux is quantized at Josephson’s junction. If a DC bias, \( U_b \), is applied to the junction, the current, \( I_s \), will oscillate with the Josephson frequency \( f_j \), which is equal to \( \omega_j / 2 \pi = V / \phi_0 = V \times 483.6 \text{ MHz} / \mu \text{V} \) and \( V \) is defined as the time averaged DC voltage across the Junction [22]. In fact, Josephson’s junctions are perfect voltmeters where the applied voltage difference at the junction will change the oscillation frequency of the superconducting current. The junction itself can act as a voltage-to-frequency converter.

A DC SQUID system works on this principle where two Josephson’s junctions are manufactured in a superconductor ring structure where they are in parallel as shown in figure 1-5.a.

![Figure 1-5](image)

Figure 1-5. a) Two Josephson’s junction in parallel used in DC SQUID under no external magnetic field b) When a magnetic field is applied to the ring, a current is induced opposing the applied field direction.

When there is no field applied as in the case of figure 1-5.a, the biasing current is shared among the two parallel junctions and the current will be constant. However, if a magnetic field is applied
to the ring, it will induce a current in the loop which will oppose the external magnetic field. Therefore, the magnetic flux enclosed inside the SQUID ring will modulate $I_c$ periodically with the period of one flux quantum that is $\phi_0$. The modulation is caused by the interference of the superconducting wave functions of two junctions. As seen from equation 1.8, when both junctions are biased at $I_c$, any change in the magnetic flux will create a voltage drop across the junctions, so now the junction acts as a perfect flux-to-voltage transducer. The RF SQUID works at the similar fashion, where the junctions are inductively coupled to an RF matching circuit. Any change in the ring will shift the frequency of the matching circuit.

SQUID technology can detect magnetic fields as low as 10 fT. However, the need to use superconducting temperatures makes the device expensive. Nowadays, researchers are investigating to find out superconducting materials that show the superconductivity at temperatures at around 30 K. However, higher temperatures also increase the Johnson noise in the electronic readout circuits.

**Atomic Magnetometers**

Atomic magnetometers are also known as the optically pumped magnetometers, which work on the principle of Zeeman effect [23]. The line spectrum is defined as an image of dark or bright colored lines or bands resulting from absorption of or emission from a molecule, where each line represents one of the frequencies in the spectrum of the light source. Pieter Zeeman (1865-1943), who was a student of Hendrik Lorentz (1853-1930) observed that the spectral lines can split into two or more emission lines when an external magnetic field is applied. This effect is analogous to Stark effect [24].

Most atoms have net magnetic moment, $\vec{m}$, due to the orbiting electrons around the nucleus. Once these atoms are subjected to an external magnetic field, their magnetic moment can orient
towards certain directions. This restriction is defined as space quantization in quantum mechanics. When \( \vec{m} \) is larger, the number of orientations allowed increases. The magnetic potential energy associated to the allowed orientations can be then given by;

\[
U = -\vec{m}.B_0
\]  

(1.9)

Since the magnetic moments related to high and low energy states will have different magnitudes due to different electronic orbits, the emission of spectral lines will be different. As an example, the energy level schematics related to the excited (\( U_e \)) and the ground states (\( U_g \)) of Zinc under no magnetic field is shown in figure 1-6.a.

![Energy level schematics for Zinc under no applied magnetic field](image)

Figure 1-6. a) The energy level schematics for Zinc under no applied magnetic field b) Zeeman Effect: Spectral line splitting as a result of applied magnetic field

When an electron makes a transition from the higher energy state to the lower energy state, a photon is emitted with the frequency, \( \nu_0 \), given by ;

\[
U_e - U_g = h\nu_0
\]  

(1.10)

where \( h \) is the Planck’s constant. When a magnetic field is applied, excited energy level splits into three levels as shown in figure 1-6.b. In the case of Zinc, the ground state does not split. Now, the photons emitted from each transition at the split energies will have different frequencies with \( \nu_0 \pm \Delta \nu \), where \( \Delta \nu \) is equal to \( \pm \vec{m}B_0/\sqrt{2}h [25] \). This kind of splitting of the spectral line into three different energy levels is defined as the normal Zeeman effect. Sometimes the splitting
may be higher than three levels. This kind of phenomenon is called the anomalous Zeeman Effect.

The atomic magnetometer consists of a vapor cell, which contains Alkali metals such as Potassium, Cesium and Rubidium. These elements are preferred because the spectral splitting is respectively more pronounced and dominant. First, the vapor is spin-polarized with a pump laser to a certain direction. This creates a spin alignment with the external magnetic field that precesses with the Larmor frequency, $w_L$, that is given by [26];

$$w_L = \gamma |B_0|$$ (1.11)

where $B_0$ is the external magnetic field and $\gamma$ is the gyromagnetic constant that is defined as the ratio of the magnetic dipole moment to the angular momentum. Then, precessing transverse polarization is driven by an external magnetic field with the same Larmor frequency. The absorption coefficient of the vapor will then change. If an additional oscillating magnetic field is applied to the vapor, the magnitude of the precessing polarization is measured with a transverse probe optical field as a function of this applied magnetic field [27]. The collision between the vapor is generally causes the atoms to precess in different directions, so they decohere. In order to avoid and decrease this spin-exchange relaxation, the vapor cell is heated to 150-180 °C. Heating helps to recover the hyperfine state and cohere the precession direction.

Atomic magnetometers can measure magnetic flux densities as low as $15 \text{ fT} / \sqrt{Hz}$ [28]. Even though the technology is very promising, the cost and the bulkiness are the two things that need improvement for future. MEMS scale magnetometers are manufactured, but they also have thermal packaging and power consumption problems [29]. In addition, the sensitivity is negatively affected as the sensor size is reduced.
Nitrogen Vacancy (NV) spin sensor

Crystal defects in diamond have demonstrated interesting optical and physical properties, which attracts the attention of researchers in order to manipulate and exploit these properties for different physical, magnetic and optical sensors.

Color centers are the fluorescent defects which can form as one or several impurity atoms / vacant lattice sites [30]. These defects are extensively studied and identified via emission / absorption spectra as the defects are the reason for coloration of the precious diamond. Among different kinds of defects, Nitrogen Vacancy (NV) centers is the most prominent one. The physical structure is given in figure 1-7.

Figure 1-7. Nitrogen Vacancy in Diamond unit cell. Adapted from [31]

The electronic structure of NV consists of six electrons, where three electrons belong to three carbon atoms surrounding the vacancy, one belongs to the vacancy and two belong the nitrogen atom. The last electron is captured from the lattice and therefore NV is negatively charged. In spite of the fact that neutral and positively charged states of NV exist, only negatively charged NV demonstrates magneto-optical properties due to this single electron.

Electron Paramagnetic Resonance (EPR) is the phenomenon of exciting electron spins instead of atomic nuclei spin [32]. It is a spectroscopic technique, which is also quantified and
explained with the Zeeman effect as that is explained above in Atomic Magnetometers section. EPR detects the precession frequency optically as a function of magnetic field as it is well explained again in the same section above. As the magnetic field is applied, the excited and the ground energy levels split into three different energy sub-levels. EPR spectrum of NV center is determined via sweeping an auxiliary microwave field over the EPR resonance and applying fluorescent light through the vacancy. As the microwave frequency matches with the excitation from \( m_s = 0 \) to \( m_s = \pm 1 \) (split states) frequency, the fluorescence intensity decreases. This is defined as the Optically Detected Magnetic Resonance (ODMR) [30].

ODMRR is exploited as a very sensitive magnetic sensor and has been utilized as a nanoscale Nuclear Magnetic Resonator (NMR) very recently [33]. In this sensor configuration, a NV center is located 5 nm away from the diamond surface, where the processing protons of a poly(methyl methacrylate) (PMMA) sample that is attached at the tip of a fine tapered glass needle. The needle was attached to Quartz tuning fork in order to make gentle contacts with the surface of the diamond. The magnetic signal from the protons affects the NV center spin properties as explained above and the NMR signal is measured and quantified via the fluorescence intensity change as the sample is scanned past over the vacancy. Basically, the whole system acts similar to a nano-scale atomic magnetometer. The spatial resolution is shown to be around \(~12\) nm, which is much better spatial resolution than SQUIDs. The sensitivities are comparable with SQUIDs and may be even better as the system is improved.

**Search Coils**

Search coils are the simplest devices of detecting magnetic fields. Besides being simple, the sensitivities of search coils can go down to 20 fT [4]. Search-coils are wound circular coils with a certain number of turns which determine the inductance and resistance of the coil. The
working principle is based on Maxwell’s 3\textsuperscript{rd} law, which is known as Faraday’s law of induction. The time rate of change of magnetic flux (\(\phi\)) through the coil with turn number of \(N\) induces a voltage that is given by \([34]\):

\[
\varepsilon = -N \frac{d\phi}{dt} \quad \text{and} \quad \phi = \int_{A} \bar{B} \cdot d\bar{A} \quad (1.12)
\]

where \(\bar{B}\) is the magnetic flux density.

As equation 1.12 states, the area of the coil has to be large in order to have high flux. The number of turns is also need to be increased as much as possible. However, the inductance over resistance will determine the time constant for the coil. Also, as the rate of change increases, the induced voltage amplitude will increase. Some of these reflect as disadvantages of this technology, especially it makes it harder to minimize the technology into chip scale. The enclosed area and the number of turns are vastly reduced. The useful frequency range is generally 1 Hz to 1 MHz, but the upper limit is generally determined by the inductance of the coil. The power consumption can be around 1-10 mW.

**Fluxgate Magnetometers**

Fluxgate magnetometers are configured in ring-core or rod core design. In rod-core design, two identical ferromagnetic bars having high magnetic permeability \(\mu_s\) are placed in parallel at a distance from each other as shown in figure 1-8. Each bar is wound with a drive coil, which magnetizes the ferromagnetic core at its saturation magnetization. In addition, two cores are magnetized in opposite direction, so they cancel their magnetic field. Another coil is wound around two bars as a sense coil.
Figure 1-8. Rod-core Fluxgate Magnetometer

The device operates on magnetic induction and saturation magnetization of the ferromagnetic materials. A sinusoidal signal is applied to the excitation coil, which causes the core material to reach saturation magnetization at every half cycle. As it is well known, the magnetic flux density within the ferromagnetic core is given by;

\[ B = \mu_r \mu_0 (H + M) \]  

(1.13)

Where \( M \) is the magnetization, \( \mu_r \) and \( \mu_0 \) are relative and vacuum permeability, \( H \) is the magnetic field. As \( \mu_r \) is high, the external magnetic field due to excitation coil or environmental magnetic field will be concentrated in the core. Once the core reaches to saturation magnetization, the core reluctance will increase. Therefore, any additional magnetic field will not be concentrated at the core which is due to decreased relative permeability. On the other hand, the core will come out of saturation as the excitation current will reduce and the magnetic field will again concentrated at the core with the opposite direction. The sense coil will induce a voltage during these time varying flux collapses and recovery cycles. In practice and theory, a single component bar ferromagnetic with excitation and pick up coil would be sufficient to detect the magnetic field. However, the sense coil would pick up the excitation induction as well. That is why a two bar system of figure 1-8 is used as the excitation phase is reversed on the second bar. This way the
induced voltage from the excitation coil is canceled out. Any external field that is in the environment will cause the saturation magnetization to be achieved earlier or later with respect to no environmental field or only excitation coil field exist. The sensed field will shift the response that will be demodulated at 2f frequency if the excitation frequency is f [35].

Despite measured sensitivities of 100 pT, the B-H curve should be a perfect square to collapse and recover the flux abruptly [4]. Also, the frequency response of the system is limited with the excitation field frequency and response time of the ferromagnetic material. The maximum operating frequency for Fluxgate magnetometers are around a few tens of kHz. They can measure DC fields unlike search coils, which is one of the most important properties of these sensors. However, the power consumption of the total device is large, which is on the orders of 5-10 mW. They can be used as very sensitive compasses for navigation with accuracies of 0.1º. It is also hard to minimize these sensors on chip-scale.

*Magnetodiodes*

Magnetodiodes consist of p-n junctions with an insulator region (undoped silicon) in between, so the total device structure can be defined as the p-i-n junction as shown in figure 1-9.

Figure 1-9. The schematics of a magnetodiode and the p-i-n junction.
Upper surface of the device is interfacing with sapphire, whereas the lower surface is interfacing with SiO$_2$. Therefore, upper and lower surfaces have different surface recombinations such that $s_2 > s_1$. A potential difference is applied to the junction as shown in figure 1-9. Due to the electric field, holes and electrons drift and are injected into I region. As the magnetic field is applied in the perpendicular direction to the current flow, the charge carriers are deflected to the surfaces, $s_1$ or $s_2$, depending on the magnetic field direction due to the Lorentz force, which is given by the equation 1.1. Since the charge carriers at the silicon/sapphire boundary have a higher tendency to recombine, the resistance of the material will increase. On the other hand, if the charge carriers are deflected towards the silicon/SiO2 interface, their concentration and generation rate will increase which will increase the conductance [36]. Therefore, the overall resistance of the device is reduced.

The magnetodiodes can sense 1 order of magnitude smaller magnetic signals when compared to Hall effect sensors.

**Magnetotransistors**

The magnetotransistor has similar structure with the magnetodiodes, the only difference is being the device consists of a bipolar junction (npn). It has p-doped based and n-doped emitter and two collectors. This is the only difference from the bipolar junction transistor.

Basically, four different physical phenomena affect the fundamental operation of the magnetotransistor; injection modulation, modulation of the base transport factor, magnetoconcentration effect and carrier deflection. The details will not be discussed here but the principle will be summarized. If there is no external magnetic field applied to the device, equal number of charge carriers are collected at the collectors. However, if there is a magnetic field in
perpendicular direction to the carriers velocity direction, they are deflected to one collector or the other. If the two collector outputs are connected to a differential amplifier, the magnetic field amplitude can be sensed. The magnetotransistors can be two orders of magnitude more sensitive than the Hall effect magnetic sensors.

**MEMS based magnetometers**

MEMS based magnetometers are preferred since their low volume packaging ability, low cost, mass production in arrays and good sensitivity. The early version of MEMS magnetometers were all based on the movement / attraction of ferrous objects [37]. However, the manufacturing of ferrous thin films with the wet chemical etching and other clean room processes were challenging. It is still an issue till today.

Therefore, most of the MEMS based sensors utilize Lorentz force phenomenon, which is already explained in Hall sensors section above. The integration of planar coils, soft spring structures and magnets (the selection of materials has to be still wet etching compatible) are easier to achieve and manufacture. An example of this has been demonstrated, where a MEMS 2-axis magnetometer has been manufactured via integrating a single Lorentz force actuator with in plane capacitive sensing electrodes [38]. The device consumed 300 µW of power and demonstrated a resolution of 0.8 degrees / $\sqrt{H}$ . Another MEMS based magnetometer which is capable of measuring magnetic field with a resolution of sub 30 nT / $\sqrt{H}$ with 1 mW power consumption is proposed [39]. The device is again based on Lorentz force on current carrying spring structure, where the deflections due to force have been sensed by capacitive changes. The Q factor of the structure is listed to be around 3000-7000 in x and y axis. The sensor noise is demonstrated to have ~10x lower noise floor than the commercial Hall effect sensors.
The biggest limiting factor of MEMS based magnetometers is 1/f type noise. This reduces the sensitivity at low frequency and at DC fields. A flux concentrator mechanism that modulates the ambient field to higher frequencies is proposed in [40, 41]. The magnetic sensing element is placed in the middle region of a flux concentrator, which is manufactured out of a high magnetic permeability thin film material. Then, the flux concentrator structure is vibrated at a higher frequency, which in turn modulates the input magnetic field frequency to the sensor. This way the operating frequency is shifted to 10 kHz, which is the resonance frequency operation of the sensor. At this frequency, the noise is reduced and thus the sensitivity is increased one to three orders of magnitude.

1.2 Motivation

Most important and impactful magnetic sensors are summarized and emphasized in Section 1.1. In overall, the most sensitive technologies are SQUIDs, Atomic Magnetometers and Nitrogen Vacancy center spin sensors. These technologies emerge as the ultimate sensitivity sensors (femto-Tesla to pico-Tesla sensitivity), which can be utilized to sense low frequency weak magnetic fields such as the ones emitted from human body. Other technologies generally operate at nT to µT ranges. MEMS based magnetometers are within this category and most of them work on detecting Lorentz force through capacitive changes.

In this dissertation, two different MEMS magnetic sensors are proposed. First sensor operates on the magnetoviscosity of ferrofluids, where viscosity changes occurring at ferrofluids are detected utilizing micromachined, high frequency Quartz arrays as micro-viscometers. The high frequency and small amplitude shear waves are created with the Quartz resonators and the highly magnetoviscous interface is studied. The acoustic wave concept and Quartz crystal resonator principles are explained in detail in Chapter 2. In addition, the ferrofluid is modeled as a
viscous loading on the thickness-shear mode resonator utilizing the modified Butterworth-Van-Dyke Model. When an external magnetic field is applied to the highly ordered nano-ferro particle ordered agglomeration within the fluid, the viscosity is shifted. This in-turn shifts the impedance / admittance characteristics of the micro-Quartz crystal resonator. These shifts are monitored in real time. The sensing mechanism is offered by the author first time in the literature. This sensor will be referred as the magnetoviscous sensor throughout the thesis. The device performance and experimentation will be explained and articulated in Chapter 3.

Second sensor also exploits micro-machined Quartz resonators’ admittance shifts due to force-frequency effect. Applied external magnetic field causes magnetic domain alignment within the magnetic thin film, which in turn strains the whole film. This strain bends the Focused Ion Beam released ultra-thin Quartz resonator plate structure. The thickness shear resonance frequency is shifted due to this strain and stress. This is also a first demonstration of a released Quartz / Magnetostrictive thin film unimorph plate structure. The device is configured as a MagnetoElectric (ME) sensor, but the operating principle is different from these sensors, which basically exploits the high Quality factor of the Quartz resonator unlike ME sensors utilize the piezoelectric coupling coefficient. This sensor will be referred as the magnetostrictive sensor throughout the thesis. The device performance will be explained and articulated in Chapter 4.

Both sensors are unique in the way that they are manufactured and the way they operate. Both sensors are very low power consuming devices (<100 µW) and can be manufactured in arrays. They can both operate at room temperature. Magnetoviscous sensor is shown to detect 1.5 nT/√Hz at 1 Hz. The magnetostrictive sensor is able to detect ~79 nT of magnetic flux with an input frequency of 10 Hz. Both sensors may be utilized for different kind of applications and are open for improvement. The devices shown in here are proof-of-concept devices. The ultimate performance and sensitivities will be discussed through Chapter 3 and 4. The future work in Chapter 5 will articulate the ways to enhance the sensor performances.
Chapter 2

Acoustic Wave Propagation And Quartz Crystal Resonator Fundamentals

2.1 Acoustic Wave Equations and Strain Definition

Acoustic waves are oscillations of pressure, which can travel through solids, liquids or gas in a wave pattern with a certain velocity and wavelength. The propagation happens adiabatically.

An elastic continuous media composed of atoms or molecules can be considered as a collection of distributed mass-spring systems that are connected to each other. If any of the single elements in this network is displaced, a disturbance through the medium will propagate. For example, atoms or the molecules within a solid medium will be displaced as a result of applied force. If an infinitesimal volume of one dimensional isotropic medium of figure 2-1 is considered, any deformation or distortion from the equilibrium state will cause strain and stress on the element, which are denoted by $T_1$, $T_2$ and $S$ and the forces acting on the volume can be defined by:

$$
\begin{align*}
    dF_1 &= dAT_1 \\
    dF_2 &= dAT_2
\end{align*}
$$

(2.1)

where $dA$ is the cross sectional area that is equal to $dxdy$ multiplication. If the displacement on two particles (nodes) are equal, $u_1 = u_2$, then $L = \Delta L$ and there is no distorted region. On the other hand, if $u_1 \neq u_2$, then the distortion, $D$ can be defined as (assuming $L \approx dz$):
Figure 2-1. The particle displacement under unequal stresses and the displacement of the spring network.

\[ D = (\Delta L)^2 - (L)^2 \]
\[ = (L + \Delta u)^2 - (L)^2 \]
\[ = (L + \frac{du}{dz} L)^2 - (L)^2 \]
\[ = L^2 + 2 \frac{du}{dz} L + 2 \left( \frac{du}{dz} L \right)^2 - L^2 \]
\[ = (L)^2 \left( \frac{du}{dz} \right)^2 + 2 \frac{du}{dz} (L)^2 \]
\[ D = \frac{du}{dz} \left( \frac{du}{dz} + 2 \right)(L)^2 \]

If \( u \) does not change rapidly with position and \( du/dz << 1 \), then eq. 2.2 is simplifies to:

\[ D = 2 \frac{du}{dz} (L)^2 \]  

(2.3)

For small displacements, this is correct and the strain is defined as:
Since this is one dimensional case, the strain can be also calculated from:

\[ S = \frac{\partial u}{\partial z} \]  \hspace{1cm} (2.4)

This strain induced due to the distortion on attached molecules or nodes propagates in one dimensional solid. The net force on the volume of figure 2-1 from eq. (2.1) is:

\[ dF = [T_z - T_i]dA \]  \hspace{1cm} (2.5)

Then the equation of motion for the particles (from Newton’s second law) can be written as:

\[ \frac{\partial T}{\partial z} dzA = \rho A \Delta z \times \frac{\partial^2 u}{\partial t^2} \]

\[ \frac{\partial T}{\partial z} = \rho \frac{\partial^2 u}{\partial t^2} = \rho \frac{\partial v}{\partial t} \]  \hspace{1cm} (2.6)

Where \( \rho \) is the density in kg / m\(^3\). The particle velocity is \( v = du/dt \), and strain is given by eq (2.4). The stress, \( T \), is related to strain, \( S \), through:

\[ T = CS \]  \hspace{1cm} (2.7)

C is the stiffness coefficient. Eq. (2.8) is also known as the Hooke’s law. The time rate of change of strain is also defined as:

\[ \frac{dS}{dt} = \frac{\partial v}{\partial z} = \frac{1}{C} \frac{\partial T}{\partial t} \]  \hspace{1cm} (2.8)

One dimensional wave equation can be derived by taking the time derivative and position derivative of equations (2.9) and (2.7) respectively, which will respectively give:

\[ \frac{d^2 S}{dt^2} = \frac{\partial^2 v}{\partial z \partial t} = \frac{1}{C} \frac{\partial^2 T}{\partial t^2} \]  \hspace{1cm} (2.9)

\[ \frac{\partial^2 v}{\partial z \partial t} = \frac{1}{\rho} \frac{\partial^2 T}{\partial z^2} \]  \hspace{1cm} (2.10)
Since the terms on the left handside of equations (2.10) and (2.11) are the same, they can be equated to each other to obtain the one dimensional wave equation. It is given by [42];

$$\frac{1}{\rho} \frac{\partial^2 T}{\partial z^2} = \frac{1}{C} \frac{\partial^2 T}{\partial t^2}$$  \hspace{1cm} (2.12)

The acoustic wave propagation speed is defined as ;

$$V_a = \frac{C}{\sqrt{\rho}}$$  \hspace{1cm} (2.13)

This is different from particle velocity that is defined before. It is the velocity of the acoustic wave propagation.

Equation 2.12 is one dimensional equation. If three dimensional systems are considered, one has to first consider the stress tensor. The 3D stresses can act on the slab shown in figure 2-1 in certain directions, creating tension/compression or shear. If the slab is considered, the stress directions that can act on it will have the directions as shown in figure 2-2.

Figure 2-2. Principal and shear stresses acting on the infinitesimal volume element.

Here, $T_{xx}$, $T_{yy}$ and $T_{zz}$ are the longitudinal stress components, whereas the remaining are the shear stresses. The strain $S$ and the stress $T$ are 6 x 1 matrices, which are given by;
\[ S = \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} \quad \text{and} \quad T = \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} \quad (2.14) \]

In general, these subscripts are reduced to number notations via utilizing the symmetry such that:

\[
\begin{align*}
S_1 &= S_{xx} \\
T_1 &= T_{xx} \\
S_2 &= S_{yy} \\
T_2 &= T_{yy} \\
S_3 &= S_{zz} \\
T_3 &= T_{zz} \\
S_4 &= 2S_{yx} = 2S_{xy} \\
T_4 &= 2T_{yx} = 2T_{xy} \\
S_5 &= 2S_{xz} = 2S_{zx} \\
T_5 &= 2T_{zx} = 2T_{xz} \\
S_6 &= 2S_{xy} = 2S_{yx} \\
T_6 &= 2T_{yx} = 2T_{xy}
\end{align*}
\quad (2.15)\]

The factor of 2 comes from the sear strain definition. These notations will be used throughout the paper, especially when modeling the frequency shifts occurring in resonating Quartz under transverse loading. Remembering from equation 2-7, the position derivative of Stress acting on the particle will induce an acceleration of the particle which is multiplied by the density. The same equation in 3D can be written as:

\[ \nabla T = \rho \frac{\partial v}{\partial t} \quad (2.16) \]

where \( \nabla \) is the dell operator and \( \nabla T \) is the divergence of the matrix which is given by:

\[ \nabla T = \begin{bmatrix} \frac{\partial T_1}{\partial x} + \frac{\partial T_6}{\partial y} + \frac{\partial T_5}{\partial z} \\
\frac{\partial T_6}{\partial x} + \frac{\partial T_2}{\partial y} + \frac{\partial T_4}{\partial z} \\
\frac{\partial T_5}{\partial x} + \frac{\partial T_4}{\partial y} + \frac{\partial T_3}{\partial z} \end{bmatrix} \quad (2.17) \]

First, second and third rows are \( x, y \) and \( z \) component of the stress. In 3D, the strain, \( S \), can then be expressed as:
\[ S = \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} = \begin{bmatrix} \frac{\partial}{\partial x} & 0 & 0 \\ 0 & \frac{\partial}{\partial y} & 0 \\ 0 & 0 & \frac{\partial}{\partial z} \\ 0 & \frac{\partial}{\partial z} & \frac{\partial}{\partial y} \\ \frac{\partial}{\partial y} & \frac{\partial}{\partial x} & 0 \\ \nabla_s \end{bmatrix} \begin{bmatrix} u_x \\ u_y \\ u_z \end{bmatrix} \]  \tag{2.18}

where \( \nabla_s \) is the gradient operator. Equations 2-17 and 2-18 are 3D analogies of 2-4 and 2-7.

These equations are the wave equations obtained in a perturbed elastic media due to applied stress.

For piezoelectric materials, the acoustic waves can be generated through application of electric field. The inverse effect is also true where an electric field is induced once the material is mechanically stressed. These are known as converse and direct piezoelectric effect respectively and given by the very well known equations;

\[ S = s^E T + d_p^T E \tag{2.19} \]
\[ D = d_p T + \varepsilon^T E \tag{2.20} \]

where \( s^E, D, E, \varepsilon^T \) are the elastic modulus (under constant electric field) (Pa), electric displacement (C/m\(^2\)), electric field (V/m), dielectric constant (F / m) under constant stress respectively. Here, the piezoelectric coupling coefficient, \( d_p \), is the polarization generated per unit of mechanical stress applied to a piezoelectric material (pC / N) or, alternatively, is the mechanical displacement experienced by a piezoelectric material per unit of electric field applied (m/V). Equations 2-17 and 2-18 can be combined with 2-19 and 2-20 in order to derive the
acoustic wave equation in a piezoelectric crystal. The expression is known as the Christoffel equation. It will not be derived here, but the details can be found in [42].

The acoustic wave propagation in solid elastic medium can support different vibration modes in different directions. Therefore, the waves will have different oscillatory patterns. The vibration modes can be different as in the mass-spring-damper systems. The same is true for acoustic waves. There will be different types of acoustic modes observed through the elastic solid media. The acoustic wave propagation speed and shape will depend on the material properties and the boundary conditions. Types of the waves are shown in figure 2-3 [43]. The wave propagation direction can be same with the particle vibration direction. For example, the particles vibrate along the direction parallel to the wave direction in the case of the longitudinal (compression) waves (figure 2-3.a). The wave direction and the particle displacements are shown with black and red arrows respectively in figure 2-3. On the other hand, the particles vibrate in transverse direction with respect to the wave direction in the case of a shear wave mode as shown in figure 2-3.c. That is why this mode is also called transverse wave. Both transverse shear and longitudinal waves are Bulk Acoustic Wave (BAW) modes. As discussed before, the solid elastic media are consisting of continuous particles, which are acting as spring-mass systems. However, a particle at the free surface may act differently from the interior particles. The disturbance at the surface will induce a different acoustic mode with respect to bulk acoustic modes and this type of wave is known as the Surface Acoustic Waves (SAW). Figure 2-3.b demonstrates a SAW mode, Rayleigh wave.
The acoustic wave propagates along the black arrow and it is bound to the surface. The vibration penetration is generally a few wavelengths into the solid. Here, the particles do not vibrate in transverse or parallel direction. They follow an elliptical motion. These waves propagate at ultrasonic frequencies (10-1000 MHz) and widely used in electronic device applications such as filters, sensors, amplifiers, sensors and etc. There are cases where the particles can vibrate in both transverse and parallel directions such as in the case of the symmetrical-Lamb waves as shown in figure 2-3.d. This is also called extensional mode, where it is observed in thin plates. Here, the wave stretches and compresses the elastic medium. This is achieved when the exciting force / stress is parallel to the plate. On the contrary, asymmetrical-Lamb waves are observed when the vibration of the particles are mostly along the perpendicular to the plate and a few portion of particles vibrate along the parallel axis. This mode is also called the flexural mode and shown in figure 2-3.e. As explained above, different acoustic wave propagation modes are utilized in these sensors. Acoustic wave sensors are widely used in many sensor applications such as interfacial
layer studies, gas sensors, force sensors, pressure sensors and etc. In this dissertation, all the Quartz devices are utilized in bulk acoustic thickness-shear mode, which will be explained in detail in section

2.2 Piezoelectric crystals and equivalent modeling

*Quartz Crystal Resonator*

Quartz is single crystal SiO$_2$. It is a piezoelectric and anisotropic crystal having highly stable elastic properties with low intrinsic losses. As given in the piezoelectric eq. (2.19), when an electric field is applied to the material that is sandwiched between two electrodes, acoustic waves and therefore mechanical vibrations are generated within the bulk of the crystal.

Different acoustic wave propagation modes of figure 2-3 can be induced by applying electric fields on different cut directions of Quartz. In this work, AT-cut Quartz is utilized. AT plate is cut parallel to the crystallographic X axis, and inclined at 31°15' as shown in figure 2-4.

![Figure 2-4. AT plane cut direction with respect to Quartz crystallographic axes.](image)

AT-cut Quartz is a TSM cut. The shear wave is produced throughout the bulk of the thin plate of crystal, which reflects from top and bottom electrodes. The resonant frequency directly depends on the thickness of the plate. The wave propagation velocity, $v_s$, within the AT-cut Quartz is 3334 m/s. The frequency, $f$, and the plate thickness, $t$, multiplication will be equal to a
constant, \( N \), that is proportional to \( v_a/2 \). Then, the fundamental frequency relation with thickness can be given by [44];

\[
\frac{f}{\text{MHz}} \times \frac{t}{\mu\text{m}} = 1667
\]  

(2.21)

As an example, a 9 MHz resonator will have \( \sim 185 \mu\text{m} \) thickness. In this thesis, the Quartz resonators are micromachined down to thicknesses which are \( < 10 \mu\text{m} \). The advantages and reasoning of thinning will be discussed in the following chapters.

Quartz is used as a micro-viscometer and micro-force transducer in this dissertation because of its i) high intrinsic quality factor (\( 1.5 \times 10^6 \) at 10 MHz and \( 35 \times 10^3 \) at 300 MHz) ii) low power consumption (<50 \( \mu \text{W} \)) iii) manufacturability into arrays iv) temperature insensitivity at room temperature. The latter is the most important property because most of the piezoelectric crystals are temperature sensitive, which makes them impractical for sensor uses. This aspect will be discussed in chapter 3 in detail. AT-cut Quartz frequency deviation due to temperature is minimal. The temperature dependence of an At cut quartz resonator can be expressed by [45];

\[
\frac{\Delta f}{f} = a_0(T - T_0) + b_0(T - T_0)^2 + c_0(T - T_0)^3
\]

(2.22)

where \( a_0, b_0, c_0 \) are the first, second and third coefficient of frequency respectively. \( T_0 \) is the inflection temperature variable, which is equal to \( \sim 26 \text{C} \). The values for these coefficients are:

\[
\begin{align*}
a_0 &= -0.08583 \times 10^{-6}(\theta - \theta_0) \\
b_0 &= 0.39 \times 10^{-9}(\theta - \theta_0) - 0.07833 \times 10^{-9}(\theta - \theta_0) \\
c_0 &= 109.5 \times 10^{-12} - 0.033 \times 10^{-12}(\theta - \theta_0)
\end{align*}
\]

(2.23)

where \( (\theta - \theta_0) \) is the deviation between intended practical angle cut and the theoretical angle of cut. Figure 2-5 below shows the shift in the thickness shear resonance frequency (\( \Delta f/f \)) of AT-cut Quartz resonators as a function of ambient temperature.
Figure 2-5. AT-cut Quartz temperature vs. frequency shift characteristics.

This makes AT-cut Quartz very practical for room temperature applications since the inflection temperature is ~26°C and the frequency deviation is very minimal. In this work, Quartz is utilized at room temperature. However, the ambient temperature is increased controllably in order to measure and quantify the sensitivity of AT-cut Quartz to transverse loading. This experimental measurement will be articulated in chapter 4. Figure 2-5 is plotted for the range of the \( \theta - \theta_0 \) that is chosen as the manufacturer specifications (Boston Piezo Inc.).

As it is emphasized, Quartz is an anisotropic material. In other words, the physical properties of the crystal are highly direction dependent. For example, the piezoelectric equations of (2.19) and (2.20) can be written in charge-strain form for Quartz such that:

\[
T_{ij} = c_{ijkl} S_{kl} - e_{ijkl} E_k
\]

(2.24)

\[
D_i = e_{ijk} S_{jk} - \varepsilon_{ijk} E_k
\]

(2.25)

where \( c_{ijkl} \), \( e_{ijkl} \) and \( \varepsilon_{ijk} \) are the stiffness, piezoelectric constant and the permittivity tensors. \( T_{ij} \) is the mechanical stress tensor, \( E_k \) is the electric field vector, \( S_{kl} \) is the strain tensor and \( D_i \) is the
electric displacement vector. The subscripts ‘ijkl’ determine the rank of the tensor and the directional properties. For example, \( c_{ijkl} \) has 81 different stiffness elements, which indicate the highly anisotropic behavior of the Quartz crystal. The modeling and calculation of the detailed elastic stiffness coefficients will be discussed in chapter 4. The analytical solutions for equations (2.16),(2.24) and (2.25) are difficult to obtain. Instead, the acoustic wave propagation and strain can be analogously modeled in equivalent electrical circuits. In addition, it is easier to solve for the viscoelastic layers / liquid loaded on top of the resonators as in the case of ferrofluid loading, which will be explained in the next chapter. Later, the equivalent circuit modeling will be introduced.

**Mason model for one dimensional piezoelectric transducer**

Physical systems can be analogously modeled once the governing equations are similar. The effort and the flow within a physical domain can be analogous to the one in other physical domains. In general terms, flow is defined as the time derivative of displacement and effort is the time derivative of momentum. And the net power in the system can be defined by effort times the flow. Table 2-1 shows the analogous mapping between physical domains over the generalized description of effort and displacement. As it is shown in the table 2-1, the mechanical and acoustical waves can be modeled in electrical analogy. For modeling the work in this thesis, it can then be concluded that:

<table>
<thead>
<tr>
<th>Mechanical Tension, ( T )</th>
<th>↔</th>
<th>V, Electrical Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle velocity, ( v )</td>
<td>↔</td>
<td>I, Electrical Current</td>
</tr>
<tr>
<td>Acoustic Impedance, ( Z_{a} = \frac{T}{v} )</td>
<td>↔</td>
<td>( Z = \frac{V}{I} ), Electrical Impedance</td>
</tr>
</tbody>
</table>
Table 2-1  Mapping between physical domains depending on the general description of effort and flow. Adapted from [46]

<table>
<thead>
<tr>
<th>General</th>
<th>Definition</th>
<th>Electrical</th>
<th>Mechanical</th>
<th>Fluidic</th>
<th>Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effort (e)</td>
<td>$e = \frac{dp}{dt}$</td>
<td>Voltage, V</td>
<td>Force, F</td>
<td>Pressure P</td>
<td>Temp. difference, $\nabla T$</td>
</tr>
<tr>
<td>Flow (f)</td>
<td>$f = \frac{dq}{dt}$</td>
<td>Current, I</td>
<td>Velocity, V</td>
<td>Vol. flow Rate, Q</td>
<td>Heat Flow</td>
</tr>
<tr>
<td>Displacement (q)</td>
<td>q</td>
<td>Charge, Q</td>
<td>Displacement, x</td>
<td>Volume, V</td>
<td>Heat Q</td>
</tr>
<tr>
<td>Momentum</td>
<td>p (t)</td>
<td>-</td>
<td>Momentum, p</td>
<td>Pressure Momentum,</td>
<td>-</td>
</tr>
<tr>
<td>Resistance, R</td>
<td>R = e / f</td>
<td>Resistor, R</td>
<td>Damper, b</td>
<td>Fluidic Resistance, R</td>
<td>Thermal Resistance, R</td>
</tr>
<tr>
<td>Capacitance, C</td>
<td>C = e / q</td>
<td>Capacitor, C</td>
<td>Spring, k</td>
<td>Fluid Capacitance, C</td>
<td>Heat Capacity, mcp</td>
</tr>
<tr>
<td>Inertance, L</td>
<td>$L = e / \frac{df}{dt}$</td>
<td>Inductor, L</td>
<td>Mass, m</td>
<td>Inertance, M</td>
<td>-</td>
</tr>
<tr>
<td>Node law</td>
<td>$\Sigma f=0$</td>
<td>KCL</td>
<td>Continuity of space</td>
<td>Mass conservation</td>
<td>Heat Energy Conservation</td>
</tr>
<tr>
<td>Mesh law</td>
<td>$e = \frac{df}{dt}$</td>
<td>KVL</td>
<td>Newton's Second Law</td>
<td>Pressure is relative</td>
<td>Temperature is relative</td>
</tr>
</tbody>
</table>
A piezoelectric plate can be shown with a 3-port (two mechanical and 1 electrical) equivalent circuit known as the Mason model (Figure 2-6) using the emphasized mechanical to electrical analogy.

The impedances and the governing equations for the model can be obtained through one dimensional analysis of piezoelectric equations from (2.24) & (2.25).

\[ T = c^E \frac{\partial u}{\partial z} - eE \]  \hspace{1cm} (2.26)

\[ D = \varepsilon^s E - eS \]  \hspace{1cm} (2.27)

Equation (2.27) can be substituted into (2.26) to obtain;

\[ T = c^B S - \frac{eD}{\varepsilon^s} \]  \hspace{1cm} (2.28)

And the current can be written as

\[ I = j\omega DA \]  \hspace{1cm} (2.29)
where \( j \) is the current density, \( A \) is the area and \( \omega \) is the fundamental frequency. In order to find the voltage, equation (2.26) is rearranged to leave electric field as the single term on one side of the equation and integrated over the thickness of the plate:

\[
E = \frac{D}{\varepsilon^s} - \frac{e\hat{e}u}{\varepsilon^s \hat{e}z} \quad (2.30)
\]

\[
V = \int_{z_1}^{z_2} Edz = \frac{ Dt}{\varepsilon^s} - \frac{e}{\varepsilon^s} (u(z_2) - u(z_1)) \quad (2.31)
\]

\[
V = \frac{tl}{\varepsilon^s j \omega A} + \frac{e}{\varepsilon S j \omega} (v_1 - v_2) \quad (2.32)
\]

Rearranging this equation for the current:

\[
I = j \omega C_0 V + \frac{e}{\varepsilon^s} C_0 (v_1 - v_2) \quad (2.33)
\]

where \( C_0 \) is the static or the clamped capacitance of the Quartz plate, which is equal to \( \varepsilon^s A / t \).

The force is related to stress through eq. (2.1) and it can be rearranged for the Mason circuit as

\[
F = AcS = Ac \frac{\partial u}{\partial z} \quad (2.34)
\]

And after further derivations,

\[
F_1 = -\frac{Z}{j \sin(kt)} (v_1 - v_2) + jZ \tan \left( \frac{kt}{2} \right) v_1 + \frac{e}{\varepsilon^s j \omega} I \quad (2.35)
\]

\[
F_2 = -\frac{Z}{j \sin(kt)} (v_1 - v_2) - jZ \tan \left( \frac{kt}{2} \right) v_2 + \frac{e}{\varepsilon^s j \omega} I \quad (2.36)
\]

\( Z \) is the acoustic impedance, \( k \) is the wave number given by \( \omega / v_0 \).[47] And from KVL for the transformer side:

\[
V_{12} = \frac{I}{j \omega C_0} \quad (2.37)
\]
\[ V_{34} = \frac{e}{\varepsilon^s j \omega} I \] (2.38)

For a piezoelectric Quartz crystal resonator that is sandwiched between two thin Cr / Gold electrodes with an electric field applied in z direction, which causes a T-thickness-Shear-Mode vibration as shown in figure 2-3.a.

![Figure 2-7. AT-cut Quartz crystal plate under shear mode.](image)

This resonator is in contact with air on both electrode sides, so the Mason model parameters from (2.35) can be written as;

\[ 0 = Z_T \left( \frac{v_1}{j \sin(kt)} - \frac{v_2}{j \tan(kt)} \right) + \frac{e}{\varepsilon^s j \omega} I \] (2.39)

After further derivations, the input impedance, \( Z_{in} \), can be defined as;

\[ Z_{in} = \frac{1}{j \omega C_0} \left( 1 - k_t^2 \frac{\tan(kt / 2)}{kt / 2} \right) \text{ and } k_t^2 = \frac{ktC_0}{\omega Z} \frac{e}{\varepsilon^s} \] (2.40)
**Equivalent Butterworth-van Dyke Circuit**

Equation (2.40) implies that the resonator has a constant capacitance of $C_0$, which is in parallel with a motional branch that can be inductive or capacitive. Then, the resonator can be represented into a simpler circuit. This equivalent Butterworth-van Dyke circuit is proposed as shown in figure 2-8. The motional branch is composed of motional resistance ($R_m$), inductance ($L_m$) and capacitance ($C_m$) respectively.

![Figure 2-8. Equivalent Butterworth Van-Dyke Equivalent Circuit.](image)

The clamped or the static capacitance $C_0$ is already given in equation (2.33) and it is a constant over the Quartz plate thickness. The motional arm has a resistive term to represent the attenuation of the crystal motion and is related with the quality factor. The capacitance and the inductance impedances are highly frequency dependent and therefore the overall system will have parallel and series resonance frequencies. The components’ equivalent relations can be derived starting from equation (2.40). The detailed derivation is given in [42]. Then, the final expressions are given as;
\[ R_m = \frac{\pi \eta \varepsilon_r \varepsilon_0}{8 k' \rho A \omega V_a} \quad \text{and} \quad k'_r = \frac{e^2}{\varepsilon_s e^D} \quad (2.41) \]
\[ L_m = \frac{\pi^3 \varepsilon^2}{8k' \omega^3 \varepsilon_r \varepsilon_0 A} \quad \text{and} \quad \omega = \sqrt{\frac{1}{L_mC_m}} \quad (2.42) \]
\[ C_m = \frac{8}{\pi^2 k'_r C_0} \quad (2.43) \]
\[
Q = \frac{\text{Energy Stored}}{\text{Energy dissipated per cycle}} = \frac{\omega_r L_m}{R_m} = \frac{v_a^2 \rho}{\omega_r \eta} \quad (2.44)
\]

Where \( \omega \) is the excitation frequency, \( \omega_r \) is the resonance frequency of the crystal, \( \rho \) is the density of the Quartz crystal in this case and \( \eta \) is the acoustic viscosity.

These parameters are important to be used in equivalent modeling of the resonators used in this thesis and for the viscoelastic modeling.

**Natural Frequencies**

The electrical admittance, \( Y \), of the Butterworth-Van dyke circuit can be written as;
\[
Y = Y_m + iB_0 \quad (2.45)
\]
where \( i \) is the imaginary number, \( Y_m \) and \( B_0 \) are the admittance for the motional branch and the \( C_0 \) branch, which are equal to;
\[
B_0 = \omega C_0 \quad (2.46)
\]
\[
Y_m = \frac{1}{R_m + i\left(\omega L_m - \frac{1}{C_m}\right)} \quad (2.47)
\]
The real and imaginary parts of \( Y \) are the conductance, \( G \), and susceptance, \( B \), respectively, which can be expressed as ;
\[ \text{Re}[Y] = G = \frac{R_m}{R_m^2 + \left(\alpha L_m - \frac{1}{C_m}\right)^2} \]  
(2.48)

\[ \text{Im}[Y] = B = \left( B_0 - \frac{X_m}{R_m^2 + X_m^2} \right) \]  
(2.49)

Using equations (2.47-2.49) and knowing the fact that \( Y = G + iB \), the following relations can be written.

\[ \left( G - \frac{1}{2R_m} \right)^2 + \left( B - B_0 \right)^2 = \left( \frac{1}{2R_m} \right)^2 \]  
(2.50)

As it can be seen this is a circle equation with a radius of \( (1 / 2R_m) \) and its center is located at \( G = (1 / 2R_m), \ B = B_0 \) as shown in figure 2-9.

![Figure 2-9. Conductance and susceptance circle equation dependence on frequency](image)

The overall impedance, \( Z \), is reciprocal of the electrical admittance \( (1/Y) \). Therefore, the relations above can be similarly rearranged for the impedance such that:

\[ Z = \frac{1}{Y} = R + iX \]  
(2.51)
where \( R \) is the resistance and \( X \) is the reactance, which account for the real and imaginary portion of the impedance respectively. \( R \) and \( X \) are related to BVD circuit parameters and their relations are given as:

\[
\text{Re}[Z] = R = \frac{R_m}{(R_mB_0)^2 + \left(1 - B_0 \left(\omega L_m - \frac{1}{C_m}\right)\right)^2}
\]

\[
\text{Im}[Z] = X = \frac{-\left[R_mB_0 - \left(\omega L_m - \frac{1}{C_m}\right)\right][1 - B_0 \left(\omega L_m - \frac{1}{C_m}\right)]}{(R_mB_0)^2 + \left(1 - \left(\omega L_m - \frac{1}{C_m}\right)^2\right)^2}
\]

(2.52)

(2.53)

From figure 2N9, \( f_a \) and \( f_s \) are parallel resonance and series resonance respectively. At \( \omega = f_s \), \( G \) is max when \( B = B_0 \). At, \( \omega = f_s \), \( G \) is min when \( B = 0 \). The parameter \( f_r \) denotes the frequency at series resonance for \( B = 0 \).

Figure 2-10 below depicts 86.005 MHz micro machined resonator (that is utilized in magnetostrictive magnetic sensor experiments) admittance (\( Y \)) characteristics a function of excitation frequency, \( \omega \), acquired through an impedance analyzer (Agilent E5061B). The experimental setup is explained in Chapter 3 in detail. The vertical axis is given is milliSiemens (mS) and horizontal axis is the excitation frequency sweep in MHz.

Figure 2-11 depicts the impedance (\( Z-\theta \)) characteristics of two commercial resonators used in ferrofluidic experiments. The details can be found again in Chapter 3. Here, the characteristics are shown as an example of \( Z \) curve , whose relation is given in eq. (2.52). Here, the phase \( \theta \) is the angle between \( R \) and \( X \) and is given by:

\[
\theta = \tan^{-1}\left(\frac{X}{R}\right)
\]

(2.54)
Figure 2-10. The admittance characteristics of a 86.005 MHz micro machined resonator

Figure 2-11. The commercial 9 MHz resonator a) impedance and b) phase characteristics, which are coated with gold (blue). The commercial 9 MHz resonator c) impedance and d) phase characteristic, which are coated with and Metglas (red) thin films
The analytical expressions for \( f_s, f_r, \) and \( f_a \) are given by;

\[
f_s = \frac{1}{2\pi} \sqrt{\frac{1}{L_m(C_m + C_1)}}
\]  

(2.55)

\[
f_r = \frac{1}{2\pi} \sqrt{\frac{1}{L_mC_m}}
\]  

(2.56)

\[
f_a = \frac{1}{f_r} \sqrt{\frac{C_m + C_0}{C_0}}
\]  

(2.57)

2.3 Liquid / Viscoelastic loading and equivalent circuit model

The loading / coating on the Quartz resonators can be modeled with an extended BVD model. There will be an extra acoustic load (Surface mechanical load) at the resonator, which will shift the impedance / admittance characteristics of the resonator. Depending on the loading conditions, the resonator can be mass loaded, liquid loaded or viscoelastic layer loaded or combination of these. These are the three general loading conditions for TSM resonator. The loading can be modeled as an additional impedance, denoted by \( Z_s \), at the motional arm. This acoustic load, depending on the loading condition, can be analogously represented with the electric circuit elements. Using table 2N1, the mass loading will map as additional motional inductance and the damping will map as an additional resistance to the resonator motional arm. As an example, a liquid loading (as in the case of ferrofluids) is shown in figure 2N11, where an AT cut Quartz is loaded with a liquid. As it is shown, the mass and the damping due to loading are modeled with \( R_{\text{liq}} \) and \( L_{\text{liq}} \).
Before discussing this case in detail, a simpler case will be first analyzed here. For the case of a thin and rigid film loading, which acts as an ideal mass loading, the phase shift is assumed to be negligible. This means the film will move in phase with the resonator as it moves in thickness-shear mode. Then, the model in figure 2-11 can be simplified into a pure mass loading case (additional inductance element. \( L_{liq} \) is in series with the Quartz motional arm, where \( R_{liq} = 0 \)). Then, the reactance, \( X_{liq} \), can be written as [48];

\[
X_{liq} = \frac{N\pi \rho_s}{4K^2 \omega_s C_0 Z_q^2}
\]

(2.58)

where \( Z_q \) is the characteristic impedance of the Quartz that is given by \( Z_q = \sqrt{\frac{\rho_q \mu_q}{\omega}} \) (\( \rho_q \) and \( \mu_q \) are the quartz density and the shear stiffness), \( \rho_s \) is the mass per unit area exerted by the thin film, \( K^2 \) is the electromechanical coupling factor for Quartz, \( N \) is the harmonic number (\( N = 1, 3, 5 \ldots \)). For AT-cut Quartz, \( \rho_q = 2.643 \text{ g/cm}^3 \) and \( \mu_q = 2.947 \times 10^{11} \text{ gcm}^2\text{s}^{-2} \). This leads to the very well know Sauerbrey’s equation, which relates the expected frequency shift, \( \Delta f \), to the pure mass loading, \( \Delta m \) as [49];

\[
\Delta f = -\frac{2\omega^2}{A\sqrt{\rho_q \mu_q}} \Delta m
\]

(2.58)
where $A$ here denotes the piezoelectrically active area. This equation is used in Quartz Crystal Microbalance (QCM) applications, where very sensitive mass is detected such as the mass of the proteins.

In liquid loading case of figure 2-11, there is an additional damping or energy loss, which is denoted as $R_{\text{liq}}$ unlike in the case of mass loading where addition $R$ was zero. Here, two different fluid types will be analyzed; Newtonian fluid loading case and Maxwellian Fluid loading case. The liquid on top of the resonator can be considered as semi-infinite fluid with one dimensional plane-parallel flow. The sinusoidal acoustic shear wave propagating within the crystal resonator penetrates into the liquid as it is shown in figure 2-12 below.

![Figure 2-13. Liquid loading of the oscillating TSM Quartz resonator. The shear wave penetrates into the liquid with a acoustic decay length of $\delta$.](image)

The shear wave amplitude will decay as it gets away from the top surface and eventually attenuate. The acoustic decay length, $\delta_L$, depends on the density of the liquid, $\rho_L$, and the viscosity of the liquid, $\mu_L$, and is calculated using:

$$\delta = \sqrt{\frac{2\eta_L}{\omega \rho_L}}$$

(2.59)
When the liquids experience shear applied with a plate as in the case of figure 2-12, there will be viscous shear stresses, which will perturb the fluid particles. This shear stress, \( \tau_{xy} \), can be expressed as:

\[
T_{xy} = -\eta_x \frac{\partial v_x}{\partial y}
\]  

(2.61)

Where \( v_x \) is the velocity of the fluid particles in the x direction, \( \frac{\partial v_x}{\partial y} \) is defined as the shear strain rate (SI unit: \( 1/\text{sec} \)). A Newtonian fluid will have a viscosity, \( \eta_x \), as a constant, which is not a function of the shear strain. On the other hand, this is not true for a Maxwellian fluid. \( \eta_x \) will depend on the shear strain rate since it is a function of the shear frequency and will deviate from its original low frequency shear viscosity, \( \eta_{L,0} \). The equation is given by [48];

\[
\eta(\omega) = \eta_0 \left(1 + j\omega\tau\right)
\]

(2.62)

where \( \tau = \eta_{L,0} / G_x \). \( G_x \) is the high frequency modulus. As it is observed from the equation, the relation between \( T_{xy} \) and the shear strain will not be a linear relation anymore. In addition, for the case when \( \omega\tau \ll 1 \), then the expression above will be approximated as \( \eta_L(\omega) \approx \eta_{L,0} \), which is the Newtonian fluid case given by the equation (2.61). For the case when \( \omega\tau \approx 1 \), then some of the energy will be stored elastically and some will be dissipated (viscoelastic case). And for the case when \( \omega\tau \gg 1 \), the fluid acts as an elastic solid. Then, the additional motional resistance, \( R_{\text{liq}} \) and the reactance, \( X_{\text{liq}} \) can be written as;
\[ R_{\text{liq}} = \frac{N\pi}{4K^2\omega_0 C_0} \sqrt{\frac{\omega \rho_\text{liq} \eta_0}{2 \rho_q \eta_q}} \left[ 1 + \frac{\omega \tau}{\sqrt{1 + (\omega \tau)^2}} \right]^{1/2} \left[ \frac{1}{\sqrt{1 + (\omega \tau)^2}} \right]^{1/2} \]  

(2.63)

\[ X_{\text{liq}} = \frac{N\pi}{4K^2\omega_0 C_0} \sqrt{\frac{\omega \rho_\text{liq} \eta_0}{2 \rho_q \eta_q}} \left[ 1 + ve \frac{\omega \tau}{\sqrt{1 + (\omega \tau)^2}} \right]^{1/2} \left[ \frac{1}{\sqrt{1 + (\omega \tau)^2}} \right]^{1/2} \]  

(2.64)

The modeling of the ferrofluid loading will be discussed in section 3.5 more detail.
Chapter 3 Magnetometer Based On Magnetoviscosity Of Ferrofluids

3.1 Ferrofluids and their stability

Magnetic fluids, or better known as the ferrofluids, are emulsions of micrometer or nanometer sized ferro-particles and carrier liquid. Their rheological properties such as heat conductivity, relative permeability and most importantly viscosity can be altered as a function of magnetic field [50]. Since no natural liquid demonstrates this variable and tunable rheological properties, ferrofluids have been smart materials to be applied in many applications as active and passive elements such as tribological applications [51] (bearings, sealing, damping), biomedical applications [52] (cell sorting, magnetocytolysis), controllable heat transfer machines [53].

The stability of the ferrofluids is important factor to be implemented in applications. The stability is evaluated with i) if particles experience any sedimentation due to gravitational fields and magnetic field, ii) Any agglomeration, iii) the amplitude of particle-to-particle interactions and attractive /repulsive forces such as dipole-dipole interactions and Van Der Waals forces. The magnetic energy of the particles (E_H) under an applied magnetic field is the same equation given by eq. (1.9). The magnetic moment, m, is given by:

\[ m = M_0 \frac{\pi d^3}{6} \]

(3.1)

Where d is the particle diameter and \( M_0 \) is the spontaneous magnetization. To avoid sedimentation, the thermal energy of the particles should be large enough than the magnetic energy, \( E_T > E_H \& E_g \). Using this relation, it can be concluded that:

\[ k_b T > \mu_0 M_0 \frac{\pi}{6} d^3 H \]

(3.2)

Where \( k_b \) is the Boltzmann constant, and \( T \) is the temperature. Then, this leads to the critical diameter dimension after rearranging the equation, which is [54];
And the particles’ kinetic energy should be larger than energy in the gravitational field which leads to;

\[ d < \left( \frac{6kbT}{\mu_0 M_0 \pi H} \right)^{1/3} \]  \hspace{1cm} (3.3)

Where \( \Delta \rho \) is the density difference between the particles and the carrier liquid, \( g \) is the gravitational acceleration and \( h \) is the height. Both equations (3.3) and (3.4) will hold for particle diameter 10 nm and larger.

For agglomeration stability, the magnetic interaction energy between two parallel dipoles \((E_{ds})\) has to be smaller than the thermal energy and is given by:

\[ 2k_bT > \frac{\mu_0 M_0^2 \pi d^3}{9(2 + 2d_s / d)^5} \]  \hspace{1cm} (3.5)

where \( d_s \) is the separation distance between two particles. This leads to the critical diameter calculation of [55];

\[ d < \left( \frac{144k_b T}{\pi \mu_0 M_0^2} \right)^{1/3} \]  \hspace{1cm} (3.6)

10 nm critical diameter hold for this equation as well.

Van Der Waals forces are the second particle-particle interaction and they will cause irreversible coagulation [56]. In order to avoid Van Der Waals attraction and achieve reorientation after the application of magnetic field, a surfactant layer is coated around the nanoparticle as shown in figure 3.1. The thickness of the surfactant layer is calculated as 2 nm for 10 nm diameter particle in order to avoid Van Der Waals attraction.
Figure 3-1. Nano-ferro-particles (d=10 nm) and the surfactant layer (2 nm long)

Typical stable ferrofluids contain single domain, magnetite (Fe$_3$O$_4$) particles with a mean diameter of about 10 nm and 2 nm of surfactant layer and a total magnetic moment of 2 x10$^{19}$ Am$^2$ [54]. The volume concentration of the magnetic material reaches values up to 15 vol.% and the particles are stabilized by surfactants of about 2 nm thickness. The magnetic nanoparticles can therefore be considered as nano-magnetic dipoles in a carrier liquid. Typically synthetic oils, water and other organic solvents are used as the carrier liquids. The ferrofluid used in this work is an oil-based one having 10 nm diameter / 2 nm surfactant. (EMG 911, Ferrotec company). Other types of ferrofluids (including the water based ones) are tried in the experiments, but the best magnetoviscosity is achieved with EMG 911. This will be discussed in experimental section.

Table 3-1. EMG 911 properties

<table>
<thead>
<tr>
<th>Particle diameter</th>
<th>10 nm</th>
<th>Density @ 25 °C</th>
<th>890 kg/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation magnetization</td>
<td>11 mT (± 10%)</td>
<td>Viscosity @ 27 °C</td>
<td>2.0 mPa-s</td>
</tr>
<tr>
<td>Magnetic Particle Conc.</td>
<td>2% vol</td>
<td>Visco $@ 27 °C$</td>
<td></td>
</tr>
</tbody>
</table>

The nano ferro-particles show superparamagnetic behavior because of their size [57]. It is defined as the magnetization randomly flipping directions with enough thermal energy within a relaxation
time between two flips. The magnetization curve of an ensemble of such supermagnetic particles is hysteresis-free as shown in Figure 3-2.

![Diagram](image)

Figure 3-2.(a) Schematic illustration of a magnetic nanoparticle with a passivation shell. Typically application of magnetic field allows for such particles to spontaneously organize into ordered patterns whereas they revert to colloidal suspensions upon removal of the field. (b) Shows the typical magnetization curve for such an ensemble of superparamagnetic particles.

This has important consequences, as suspended superparamagnetic particles can be constantly manipulated within the fluid matrix using a magnetic field, and they do not agglomerate (i.e., they stay suspended) after removal of the field (see Figure 3-2a). Hence, it is very easy to switch on and off the magnetic interaction in the ferrofluid.

Treating the particles as small magnetic dipoles in a carrier fluid, the magnetization of the fluid $M$ as a function of the magnetic field strength $H$ can be given by Langevin relationship [55]

$$M = M_s \left( \coth \alpha - \frac{1}{\alpha} \right) ; \text{where } \alpha = \frac{\mu_0 m H}{k_B T} \quad (3.7)$$

where $M_s = \phi M$ is the saturation magnetization of the liquid, determined by the volume concentration of the magnetic component $\phi$ and its spontaneous magnetization $M_0$, $\mu_0$ is the vacuum permeability, $m$ is the magnetic moment of the particle, already given by equation 3.1. Hence, the magnetization curve of a ferrofluid shows the typical paramagnetic structure as shown
in Figure 3-2.b, the relaxation of the magnetization in ferrofluids can occur via two different processes: (i) Brownian relaxation (time constant, $\tau_B$) occurs in magnetically hard particles via rotation of the whole particle, and (ii) Néelian relaxation (time constant, $\tau_n$) occurs in magnetically weak particles, where thermal energy is high enough to overcome the crystallographic anisotropic energy barrier of the material. Néel relaxation depends upon the volume of the magnetic core of the particle, while Brownian relaxation is dominated by the hydrodynamic volume of the particle. Thus for small particle ($d \leq 10$ nm) $\tau_n$ will be smaller than $\tau_B$ and dominates the process. The critical diameter, where the transition occurs depends upon the viscosity of the carrier liquid, the thickness of the surfactant layer, and the magnitude of the anisotropy constant $K$.

### 3.2 Magnetoviscosity of Ferrofluids

**The background**

Magnetoviscosity is the phenomenon, where the ferrofluid viscosity changes as a function of the applied magnetic field. The classical definition is given by [58] and it is explained by the hindrance of the suspended nano-particles due to the action of the magnetic field.

Assuming the ferrofluid under a shear flow, magnetic particles will rotate due to the mechanical torque induced by the viscous forces. If the magnetic field is applied along the direction that opposes this mechanical torque, then the particles are obstructed to rotate along the mechanical torque. Because of this hinderance of rotation, the particles cannot rotate freely under viscous load. Therefore, the overall viscosity is increased as the magnetic field strength is increased. Earlier experiments on defining the phenomenon focused on measuring the viscosity with Coutte-flow type viscometers under different strengths of the magnetic field. Figure 3-3
below shows the viscosity change occurring in ferrofluid (APG 513A) as a function of applied magnetic field. Coutte-flow shear strain rate is given as 4 s\(^{-1}\) [55].

![Figure 3-3. The magnetoviscous effect in a ferrofluid (APG513A). Adapted from [55]](image)

The vertical axis shows the percent viscosity change (\(\Delta \eta / \eta_0\)) as a function of magnetic field. As it is observed from the figure, the viscosity change can go up to 50 % under an applied magnetic field strength of 30 kA / m. The magnetics principles, the relation between B and H and corresponding conversion factors are summarized in Appendix A. The reader may refer Appendix A for SI unit to CGS conversions and realize the distinction between magnetizing and induction fields.
**Magnetoviscosity experiments**

The magnetoviscosity strongly depends on both the magnitude as well as the direction of the applied magnetic field. It has been observed that as the perpendicular field strength, i.e. field normal to the surface on which the ferrofluid is placed, is increased, various structural transitions occur such that the randomly distributed collection of Brownian nano-ferroparticles transforms into a more ordered, columnar hexagonal structures [59]. The perpendicular field effect is not only limited to the alignment of the particles as the field strength increases, but also creates additional layers within these columnar structures, where the particles interact via dipolar interactions [60]. Figure 3-4 shows the experimentally obtained optical photographs of the hexagonal columnar aggregations of EMG 911 under 4 different perpendicular magnetic fields on gold surface. Clearly the areal density of the macroscopic columns formed is a function of the perpendicular field strength.

![Hexagonal Columnar Aggregations](image)

Figure 3-4. Optical photos, under identical magnification, of hexagonal columnar aggregations observed under 4 different perpendicular magnetic fields for EMG 911 on gold surface. The columns are stable after the application of the magnetic field.
Vorobiev et al [61] used neutron reflectometry to study the interfacial interaction of ferrofluid particles on a SiO$_2$ substrate. From these experiments, they have shown that under applied constant magnetic field, the SiO$_2$-ferrofluid interface is decorated with a dense magnetic double layer with a high magnetic susceptibility. When an external magnetic field is applied, the magnetic moments of the nanoparticles adjacent to this magnetic double layer experience preferential alignment parallel to the field. The attractive dipole-dipole interaction is enhanced along the field direction, while perpendicular to the field direction, the dipolar arrangement gives rise to a repulsive interaction. Thus, the perpendicular field configuration favors ordering normal to the interfaces and the compression of the surfactant layers; simultaneously it causes a separation of the nanoparticle chains within the columns. In the parallel-field configuration, ordering chains are favored parallel to the interface, while they repel each other perpendicular to the interface, giving rise to an observed expansion and disorder in the layer spacing. Thus, the interfacial double layer plays a critical role in the macroscopic ordering of the ferroparticle overlayers. To summarize, the perpendicular and in-plane fields induce different levels and shape of aggregations. In this work, we carefully tune the perpendicular bias magnetic field strength to achieve large magnetoviscous changes due to in-plane sensing fields.

### 3.3 Modeling Ferrofluid loading on AT-cut Quartz Micro-resonator

In order to model the ferrofluid loading, the relaxation time constant and the operation frequency is needed as discussed in section 2.3. For the micromachined resonators used here (TSM frequency ~ 68 MHz for micromachined resonator, 5 and 9 MHz commercial 1 inch resonators are also utilized) and ferrofluid (Table 3-1), $\omega \sim 10^7$ and the relaxation time $\tau \sim 10^6$ for ferrofluid particles [54]. From the discussion of liquid loading model of section 2.3 and the equations 2.58-2.64, Maxwellian fluid model is expected to result in a more appropriate
approximation of the loading conditions on the quartz resonator under the influence of bias magnetic field. Therefore, the additional resistance in the motional arm due to liquid, $R_{liq}$, will be given by eq. (2-63).

$R_{liq}$ given by equation (2-63) is both a function of $\rho_{liq}$ and $\eta_{liq}$. For the ferrofluid loading case, the density fluctuation as a function of applied magnetic field is assumed to be negligible with respect to viscosity changes. Therefore, the relation between the dissipation due to liquid loading ($R_{Liq}$) and the conductance maximum ($G_{max}$) can be simplified as [62];

$$\Delta R_{Liq} \approx \Delta G_{max} (R_m + R_{Liq})^2$$

(3.8)

The change in the maximum value of conductance, $G_{max}$, can now be related to a change in the viscosity of the ferrofluid (assuming that $\omega$ and $\tau$ are constants for a given resonator) as:

$$\frac{\Delta \eta_{liq}}{\eta_{liq}} \approx \frac{2 \Delta G_{max} (R_m + R_{liq})^2}{R_{liq}} \approx 2 \Delta G_{max} (R_m + R_{liq})$$

(3.9)

This method has been successfully used to monitor the density of water-glycerol mixtures and agrees well with the reported values in literature [63]. In liquid applications, the functional dependence of $\Delta f$ on the density and viscosity changes of the liquid, can be written as [64]

$$\frac{\Delta \eta_{liq}}{\eta_{liq}} + \frac{\Delta \rho_{liq}}{\rho_{liq}} = 4 \times 10^{-7}$$

(3.10)

for the ultimate resolution of viscosity and density using a QCM. Thus, quartz resonators provide a very high resolution for the measurements of density and viscosity of liquids. Furthermore, in liquid medium applications, it is important to emphasize that the shear wave rapidly damps out as it travels through the thickness of the liquid, and consequently the QCM typically samples a layer of thickness equivalent to the decay length, $\delta_{liq}$, given by eq. 2.59. If large perpendicular magnetic fields are used for the initial ordering and agglomeration of the ferrofluids, the behavior of the ferrofluid is expected to approach that of a viscoelastic interfacial layer under a liquid and
will be discussed later. We have demonstrated that high frequency micromachined quartz resonators (65 – 200 MHz) are especially suited for monitoring small changes in the viscoelastic loading on their surface [64-67]. If we consider a uniform viscoelastic layer adsorbed on the surface of a quartz resonator with a supernatant liquid layer atop, the resulting quartz resonator frequency shift and dissipation factor changes can be analyzed using a continuum mechanics approach [64, 68]. In order to model this situation, the QCM surface is considered to be in intimate contact with a layer of continuous viscoelastic slab with an infinitely thick Newtonian liquid overlayer on one of its surfaces as shown in Figure 3-5. Under the assumption that the thickness of the bulk liquid layer is much larger than the decay length of the acoustic wave in the liquid (δ_{liq} \sim 100 \text{ nm for 68 MHz resonator in ferrofluid}), the frequency, and Q-factor changes with respect to supernatant liquid only loading conditions can then be written as [63]

\[
\Delta f \approx - \frac{1}{2\pi \rho_\text{q} q} \left( t_\text{visc} \rho_\text{visc} \omega - 2 t_\text{visc} \left( \frac{\eta_{\text{liq}}}{\delta_{\text{liq}}} \right)^2 \frac{\eta_\text{visc} \omega^2}{\mu_\text{visc}^2 + \omega^2 \eta_\text{visc}^2} \right)
\]

(3.11)

Figure 3-5. Schematic representation of the model of the ferrofluid upon agglomeration and ordered arrangement of the ferroparticles due to the application of magnetic field perpendicular to the surface of the resonator.
\[ \Delta Q \approx -2\pi \omega_0 \rho_{q} \xi_{q} \left( \frac{2t_{visc} \mu_{visc} \omega}{\mu_{visc}^2 + \omega^2 \eta_{visc}^2} \right) \left[ 1 + \left( \frac{2t_{visc} \eta_{liq}}{\delta_{liq}} \right) \frac{\mu_{visc} \omega}{\mu_{visc}^2 + \omega^2 \eta_{visc}^2} \right] \]

where \( \mu_{visc}, \eta_{visc}, \) and \( \rho_{visc} \) are the elastic modulus, viscosity, and density of the viscoelastic layer, respectively, and \( t_{visc} \) is its thickness and \( \delta_{liq} \) is the penetration depth of the acoustic wave in the liquid. From these equations, it can be concluded that miniaturized resonators provide a greater resolution of the viscoelastic properties of adsorbed layers than thicker and larger resonators [63].

A large variation in the \( Q \)-factor and frequency for small changes in the viscoelastic properties of the adsorbed films is highly desirable for the accurate real-time monitoring of viscoelastic changes of ferrofluids. While magnetoviscous effect has been shown in literature to decrease as the shear rate is increased [54], and attributed mainly to the destruction of the nanoparticle chains during measurements using conventional rotating-disc type viscometers (hundreds of Hz), on the contrary low shear amplitudes and higher frequencies (tens of MHz), typical of the conditions in a \( \mu \)QCR based measurement, are shown not to decrease the magnetoviscous effect [69]. Based on our previous measurements of viscoelastic properties of globular proteins, the sensitivities (resolution) of micromachined quartz resonators for thickness, density, viscosity, and elastic modulus are listed in Table 3.2 [63]. In this thesis, we exploit this aspect of micromachined quartz resonators to sensitively monitor the changes in the viscoelastic properties of ferrofluids under the influence of external magnetic fields.

Table 3-2. 65 MHz quartz resonator sensitivities (resolution) of thickness, density, viscosity, and elastic modulus (based on the measurement of five selected proteins) [63].

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Density (kg/m³)</th>
<th>Viscosity (mPa-s)</th>
<th>Elastic Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.1 nm</td>
<td>1.98</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>
3.4 Proposed Magnetic sensor

The cross-sectional view of the packaged magnetic sensor with the ferrofluid in contact with the Metglas® top electrode and a simplified 3D illustration are shown in Figure 3-6(a). Preliminary experiments show that the high sensitivity to very small changes in in-plane magnetic field was only observed when a strong out-of-plane (perpendicular to the resonator surface) bias magnetic field was applied thus necessitated the use of the neodymium magnet in the package. For the micromachined resonators, a constant magnetic flux density of ~10 mT perpendicular (z-directed) to the surface of the resonator is applied using a neodymium magnet (5 mm diameter) placed in close proximity (~5 mm) under the µQCR as shown in Figure 3-6(b). The perpendicular field is used to pre-organize the ferroparticles and introduce some degree of spontaneous self-assembly in the ferrofluid. However, the applied field magnetizes the Metglas® electrode layer along the easy axis in the plane of the film, which in turn induces an in-plane oriented interfacial double layer and weakly coupled but ordered overlayers that decay exponentially in the ferrofluid. The low magnitude (<1 µT) and low modulation frequency (~1 Hz) field sensed magnetic fields are applied in-plane (x-direction) using Helmhloz coils (coil diameter of 15 cm and 140 turns), which perturbs this self-assembled and ordered structure including the double layer at the interface between the ferrofluid and µQCR electrode. The resulting changes in the magnetoviscosity and viscoelastic changes at the interface are monitored by the changes in the at-resonance admittance of the quartz resonator. The admittance maxima of the device was tracked and recorded as a function of the applied in-plane magnetic flux density for constant perpendicular bias field and all experiments were done at room temperature in an iron shielding box.
3.6 Magnetic Characterization Experiments and Results

**Metglas effect on ferrofluid agglomeration**

Metglas® - an iron-silicon-boron alloy (Fe\textsubscript{85}B\textsubscript{5}Si\textsubscript{10}) in amorphous thin film form has a high relative permeability which peaks at a value of $\mu_r = 25000$ and is a function of the applied magnetic field [70]. At large bias magnetic flux densities, the Metglas® film magnetizes corresponding to a low permeability state. At large magnetic fields, we expect the Metglas® film to be magnetized in the plane (along easy axis) and act as a magnet in close proximity to the ferrofluid, and thus aligning in-plane, the magnetic dipoles in the first few layers of the ferrofluid adjacent to the interface. To optically observe the effect of Metglas® on ferrofluid agglomeration,
two SiO$_2$ substrates were coated with 100 nm gold and 100 nm Metglas$^\text{®}$ films respectively. A small droplet of ferrofluid EMG 911 was placed on each of the substrates and 15 mT perpendicular magnetic flux density was applied. Figure 3-7 shows the optical image of the top view of the macroscopic ordering patterns observed in ~100 µm thick ferrofluid layer on the two substrates. From these we speculate that the strong (due to proximity), in-plane magnetization of the ferromagnetic Metglas$^\text{®}$ layer aligns the ferroparticle dipoles in the interfacial double layer in-plane. Hence, it is expected the interfacial layers ordering of the ferrofluid to be strongly influenced by the in-plane magnetization of the Metglas$^\text{®}$, whereas ordering of the layers further away from the interface is expected to be influenced by the perpendicular field as well. Thus, beyond the interfacial double layer, the over layers of ferroparticles are oriented not only in response to the external perpendicular field, but also have to arrange themselves on the in-plane oriented double layer. It can be concluded that this interaction results in the observed striated labyrinthine pattern of the overlying ferroparticle layers on Metglas$^\text{®}$ film (Fig. 3.7.b) unlike in the gold case where the absence of the in-plane oriented magnetic double layer and simply aligns the particles in the linear columns aligned to the perpendicular field and arranged in a hexagonal pattern (Fig. 3.7.a).

Figure 3-7. The agglomeration pattern of ferroparticles at 15 mT. (a) on 100 nm gold film on SiO$_2$ substrate (b) on 100 nm Metglas$^\text{®}$ film on SiO$_2$ substrate.
To quantify the effect of Metglas\textsuperscript{®} film on the response of the ferrofluids and therefore on the device sensitivity, two identical 9 MHz commercial resonators having the similar resonator characteristics (see Figure 2-10) and similar fitted BVD parameters (shown in Table 3-3) with two different electrodes; gold only and the other with gold/100 nm Metglas\textsuperscript{®} top electrodes were prepared.

Table 3-3. Butterworth Van Dyke (BVD) model parameters for two 9 MHz Quartz resonators (Inficon corp.)

<table>
<thead>
<tr>
<th></th>
<th>Only Gold</th>
<th>Gold/Metglas</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$ (Ohms)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$C_1$ (fF)</td>
<td>49.109</td>
<td>48.2937</td>
</tr>
<tr>
<td>$C_0$ (pF)</td>
<td>40.151</td>
<td>41.2284</td>
</tr>
<tr>
<td>$L_1$ (mH)</td>
<td>6.40069</td>
<td>6.47686</td>
</tr>
<tr>
<td>$F_s$ (Hz)</td>
<td>8975068.75</td>
<td>9003750</td>
</tr>
<tr>
<td>$Q$</td>
<td>72189.73664</td>
<td>73282.25371</td>
</tr>
</tbody>
</table>

Both resonators were tested under the same magnitude perpendicular bias field of 50 mT and for various in-plane sense magnetic fields. From Figure 3-8(a) it can be seen that if the resonator electrode was made of gold, the sensitivity for the same applied bias field is \(~5\) times smaller than for Metglas\textsuperscript{®} resonator electrode. Figure 3-8(b) shows the peak-to-peak conductance shifts for the two resonators at different magnetic flux densities and shows a linear dependence on the magnetic field for the gold electrode but a quadratically increasing response for the Metglas\textsuperscript{®} device. This clearly demonstrates that the actual response of the Metglas\textsuperscript{®} film to the applied magnetic flux density critically affects the interfacial ferrofluid layer.
Figure 3-8. (a) Magnetic field response of 9 MHz quartz resonators loaded with ferrofluid. Applied bias field ~50 mTesla and in-plane sensing field is 600 µTesla and quartz resonator electrode made of gold (blue curve) and Metglas® (maroon curve). Five times greater sensitivity is obtained using Metglas® electrode for identical experimental conditions. (b) Response of the gold (maroon curve) and Metglas® (blue curve) electrode resonators loaded with ferrofluid at 4 different magnetic flux densities. A larger and clearly non-linear dependence on the magnetic flux density is seen in the case of Metglas® coated resonator.

Sub-microTesla level low modulation frequency magnetic flux density detection experiments

NanoTesla level, low modulation frequency magnetic field detection experiments were performed on the micromachined 68 MHz quartz resonators with Metglas® deposited top
electrode and with 10 mT of perpendicular bias magnetic flux density. Figure 3.9(a) depicts the device response and the conductance maximum shift for the selected magnetic fields of 720 nT, 360 nT, and 60 nT for a single on/off cycle. A log-linear plot of the peak-to-peak change in conductance maximum, $\Delta G_{\text{max}}$, versus the magnetic flux density is shown in Figure 3-9(b). A continuous and monotonic response in the maximum conductance value is seen in response to the in-plane field implying a continuous perturbation in the ordering of the interfacial ferrofluid layer. The sensitivity graphs for the Metglas® coated bulk resonator, Figure 3-8(b), and micromachined resonator, Figure 3-9(b), are not linear. Instead, for the bulk resonator, a quadratic response and for the micromachined resonator, a saturating response at higher in-plane magnetic fields is observed. While the functional dependence observed in the two results seem somewhat different, there are several issues that must be considered in interpreting these results. First of all, it must be noticed that the signal magnetic flux density in Figure 3-8(b) is about three orders of magnitude larger than in the case of Figure 3-9(b). Secondly, the acoustic wave decay length of the commercial 9 MHz resonator for EMG 911 ferrofluid is 280 nm whereas it is only 100 nm for the 68 MHz micromachined resonator. This implies that the 9 MHz resonator samples a much thicker ferrofluid film above the interface and any perturbations caused by the large magnetic flux signals, in the weakly coupled overlayers beyond the interfacial double layer, are likely to have a significant influence on the admittance characteristics of this resonator.
Figure 3-9. (a) Conductance maximum as a function of time. As the magnetic field is switched on (indicated with the white bar on top), the conductance maximum is found to increase implying an associated decrease in the viscosity of the interfacial ferrofluid layer. (b) A log-linear plot of the peak-to-peak change in the conductance of the resonator as function of different square wave magnetic field amplitudes.
In what follows, it is articulated that the bias magnetic field causes the formation of a dense viscoelastic layer on the surface of the resonator with an overlaying viscous liquid present above it akin to the model presented in Figure 3-5. What is observed through modeling is that the functional dependence of conductance increase upon the incident in-plane magnetic flux density can be explained through changes in the elastic modulus of this viscoelastic layer. While the properties of the ferrofluid above and the thickness and density of the viscoelastic layer affect the absolute magnitude of the resonator $Q$-factor, they do not influence the functional dependence on the incident magnetic flux density. Thus, the presence of both a large bias and in-plane signal magnetic flux densities have the effect of agglomerating the ferroparticles in the vicinity of the resonator surface, and in turn stiffening the ferrofluid, which reflects in the increase in the overall $Q$-factor as observed. For the 9 MHz resonator, numerical evaluation of the expected $Q$-factor change using eq. (3.12), for a ferrofluid layer of viscosity 2 mPa-s, density 0.89 g/cc, and an interfacial viscoelastic layer with a viscosity of 20 mPa-s, thickness of 280 nm, and an elastic modulus varying in the range of 100 – 500 kPa, shows a near linear $Q$-factor increase as a function of the elastic modulus. This would explain the observed linear dependence for the 9 MHz resonator with no Metglas® film (gold only) electrode in Fig. 3.7(b). Linear dependence is also seen from eq. (3.9) for pure liquid loading as well, although it is articulated that this model to be less likely valid. The observed quadratic dependence in the 9 MHz Metglas® electrode resonator in Figure 3-8(b), can be only explained if an additional contribution from the Metglas® film, proportional to the applied magnetic field through a field dependent variation in its magnetization, is assumed. On the other hand, for the 65 MHz micromachined resonator, the acoustic decay length is 100 nm. Here, the perpendicular bias magnetic flux density is set to five times lower value of 10 mT and the applied signal is in the range of only a few tens to hundreds of nanoTesla. Once again, we numerically evaluate eq. (3.12), assuming all ferrofluid and viscoelastic layer properties to the same as before except for the viscoelastic layer thickness
which is now assumed to be 100 nm and the viscosity which is now assumed to be 2 mPa-s. The smaller value of the viscosity of the interfacial layer used in the simulation for the micromachined sensor reflects the smaller bias magnetic flux which induces a less dense and lower viscosity interfacial layer. Since the signals are very small in this case, the Metglas® film is not expected to make any substantial contribution through its magnetization change and thus the observed behavior is expected to follow the predicted resonator viscoelastic response which shows the saturation behavior at higher applied fields.

For the 9 MHz resonator, the numerical evaluation of the expected Q-factor change using eq. (3.12), for a ferrofluid layer of viscosity 2 mPa-s, density 0.89 g/cc, and an interfacial viscoelastic layer with a viscosity of 0.02 mPa-s, thickness of 280 nm, and an elastic modulus varying in the range of 100 – 500 kPa, is shown in Figure 3-10. A similar numerical simulation is performed for 68 MHz micro-machined resonator and the quality factor change (ΔQ) versus the rigidity shift experienced by the ferrofluid is plotted in Figure 3-11.
Figure 3-10. The elastic modulus change in the viscoelastic layer of ferrofluid at the interface resonator versus the change in Quality factor experienced by the 9 MHz Quartz resonator.

For 9 MHz Resonator
\[ t_{\text{visc}} = 280 \text{ nm}, \rho_{\text{visc}} = 1.75 \text{ g/cc} \]
\[ \eta_{\text{visc}} = 20 \text{ mPa}-\text{s}, \rho_{\text{liq}} = 0.89 \text{ g/cc} \]
\[ \eta_{\text{liq}} = 2 \text{ mPa}-\text{s}. \]

Figure 3-11. The elastic modulus change in the viscoelastic layer of ferrofluid at the interface resonator versus the change in Quality factor experienced by the 68 MHz Quartz resonator.

For 68 MHz Resonator
\[ t_{\text{visc}} = 100 \text{ nm}, \rho_{\text{visc}} = 1.75 \text{ g/cc} \]
\[ \eta_{\text{visc}} = 2 \text{ mPa}-\text{s}, \rho_{\text{liq}} = 0.89 \text{ g/cc} \]
\[ \eta_{\text{liq}} = 2 \text{ mPa}-\text{s}. \]
To summarize, the behavior of the quartz resonators under ferrofluid loading atop a Metglas® electrode shows a complex behavior and is highly sensitive to the bias magnetic flux density. The observed, at-resonance, conductance change of the quartz resonator is an outcome of the viscoelastic changes, induced within the ferrofluid layer by the Metglas® film, which in turn is a response to changes in the ambient magnetic field. The Metglas® film plays a complex role in the overall function of this sensor since its permeability and magnetization are a function of the applied magnetic flux density. Thus, depending upon the bias field, the Metglas® film is likely to act as magnetic layer adjacent to the ferrofluid and thus strongly influence the formation and viscoelastic properties of this interfacial layer. Furthermore, it is well known that the Metglas® films exhibit magnetostrictive behavior in the presence of a bias magnetic flux density. While, the effect of the magnetostriction from a 100 nm thick Metglas® layer on a commercial 9 MHz resonator (167 µm thick) is likely to be minimal, the same could not be said for a 25 µm thick 68 MHz micromachined resonator. Thus, the effect of stress arising from magnetostriction can have an influence on the response of the micromachined quartz resonators to surface loads and could also contribute to the observed behavior shown in Fig. 3.8(b). It must however be emphasized that no direct conductance shift due to magnetostriction was observed in the 68 MHz resonators coated with Metglas® with no ferrofluid atop. Further investigation is required to better understand the behavior of the device under various bias and signal conditions. Notwithstanding, from the results presented, it can be concluded that Metglas® coated micromachined resonators exhibit a more sensitive response to in-plane magnetic flux density in comparison to the commercial quartz resonators implying the improved resolution of micromachined resonators in monitoring the viscoelastic changes at the interface. At the lowest measured magnetic flux density of 60 nT, \( \Delta G_{\text{max}} \) is 0.32 µS. The noise in the conductance was measured to be 8 nS/√Hz at 1 Hz as shown in Figure 3-12, mainly originating from the Brownian motion and the thermal
energy of the ferrofluid particles. Based on these experimental measurements, the minimum detectable magnetic flux density can be calculated as 1.5 nT/√Hz.

Figure 3-12. The noise spectra for the 68 MHz micro-machined resonator.

3.7 In-plane 2D directional sensing

A further confirmation of the role played by the Metglas® layer was performed by demonstrating in-plane vector sensing of the magnetic flux density. A bow-tie shaped Metglas® pattern was aligned to the center of the circularly shaped gold top electrode of a 54.43 MHz micromachined quartz resonator as shown in Figure 3-13(a). The bow-tie shape was patterned out of Metglas® and concentrates the magnetic flux lines and focuses through the gap region. The various dimensions of the bow-tie structure fabricated are shown Figure 3-13(a). The bow-tie pattern gap is located at the center of the top gold electrode since shear displacement has its maximum value at this location and thus is the most sensitive location on quartz shear mode resonators [71, 72]. The expected directionality due to the flux concentration effect of the bow-tie
Metglas® flux concentrators has been simulated (See supplementary information) and was experimentally confirmed using 10 mT perpendicular bias field and 300 µT of in-plane magnetic flux density applied through the Helmholtz coil. The conductance maximum was recorded as the sensor was rotated with respect to the Helmholtz coils at this constant flux density. The experimentally measured conductance maximum is plotted in polar coordinates and is shown in Figure 3-13(b) which clearly demonstrates the directional response of the ferrofluid in response to the magnetic flux lines coupled to the underlying Metglas® layer. The experimentally measured ratio of the zero degree (bow-tie collinear with the in-plane flux) peak-to-peak conductance shift to the 90º (bow-tie orthogonal to the in-plane flux) peak-to-peak conductance shift is 9.55 and is comparable to the simulated ratio of 11.

Figure 3-13. (a) Schematic top-view illustration of the bow-tie shaped Metglas® flux concentrator with $w_1 = 820 \, \mu m$, $w_2 = 10 \, \mu m$, $w_3 = 45 \, \mu m$, $w_4 = 730 \, \mu m$, placed with the gap at the center of the top gold electrode of the quartz resonator. (b) Experimentally measured in-plane vector sensing of the magnetic flux density achieved using the bow-tie shape Metglas® flux concentrator.
Chapter 4

Magnetometer Based On Ultra-Thin Plate Quartz Micro-Resonator Elastically Coupled To Magnetostrictive Layer

4.1 Motivation

Transverse forces may be induced by several means in order to exploit Quartz as a sensor. In this chapter, the flexural sensitivity of Focused-Ion-Beam (FIB) released AT-cut Quartz thin plate resonators is modeled and experimentally tested as a second magnetic sensor method shown to detect low frequency and weak magnetic fields. The transverse loading causing out-of-plane bending is achieved via sputtering magnetostrictive thin film (Metglas® (Fe₈₅B₅Si₁₀) 2605SA1 with saturation magnetostriction = 27 ppm) on one side of the thin resonators and therefore straining the unimorph structure as a result of applied external magnetic field. In chapter 3, this effect of Metglas has not been observed since the whole structure was not released and Metglas had no in-situ magnetization. This magnetostrictive property of Quartz is improved and the whole device is modified to detect magnetic fields. This is a very different mechanism described in Chapter 3. Quartz force-frequency sensitivity as a function of applied magnetic field is experimentally tested, theoretically modeled and simulated by performing a split/coupled domain analysis via combining Lee’s theory and magnetostrictive unimorph theory. The magnetic sensitivity is achieved through elastically coupling a high permeability and highly magnetostrictive thin film atop. This opens up the possibility of designing very sensitive unique magnetic sensors utilizing the transverse force-frequency effect.
4.2 Force-Frequency Effect

Quartz has been introduced in chapter 2 as a good piezoelectric crystal having highly stable elastic properties with low intrinsic losses. Because of these properties, it has been widely utilized in precision control requiring applications such as timing and clocking for electronic instruments [73]. Despite having a very precise oscillation frequency, Quartz is also very sensitive to any kind of environmental disturbances as magnetoviscosity is utilized as a magnetic sensing mechanism already. Other disturbances can be also effective such as mass loading (discussed in Chapter 2 Section 2.3), external forces, bending, compression, and acceleration[43], which cause the crystal fundamental frequency to deviate, which is defined as $\Delta f/f_0$. These disturbances were indeed unwanted effects on the precision control applications and therefore early research on Quartz focused on determining frequency shifting mechanisms caused by environmental factors such as acceleration / mounting/ force and etc. One of the first frequency shifting mechanisms due to external disturbance on Quartz crystals has been experimentally found by Bottom [74] in 1947. A pair of diametric forces along the radial direction is applied to the periphery of vibrating Thickness-Shear-Mode (TSM) Quartz resonator and it is observed that the thickness-shear frequency shifts proportional to the amplitude of the forces. This phenomenon is defined as the Force-Frequency effect. Furthermore, it is found out that force-frequency effect is a function of the azimuth angle, $\Psi$, which is the in-plane angle between the crystallographic axis and the applied force direction. The crystal frequency shift, $\Delta f$, is more prominent in certain azimuth angle directions. This dependence is even exploited as to compensate the temperature-frequency variation in AT-cut resonators for determining precise location applications [75]. Ballato [76] [77] then worked on different Quartz cuts to determine and quantify the force-frequency effect and the azimuth angle dependence. The work relates initial stress produced by the mounting supports to resonance frequency changes.
Despite the fact that the initial researches are established to minimize the mounting related forces, this property of Quartz, with the availability of temperature compensated cuts, is later on realized as a sensing mechanism in recent years and successfully exploited in many sensors applications such as force sensors, acceleration sensors and pressure sensors [78-83]. A coefficient, \( K_f \), is defined and introduced by Ratajski [84] for all singly rotated crystals as a generalized metric to compare the in-plane force sensitivity of different cuts of Quartz. Force-Frequency constants are also calculated for doubly rotated Quartz using variational methods [85].

Quartz is determined to be sensitive, not only diametric forces, but also to transverse forces and flexural bending. Fletcher [86] and Mingins [87] have experimentally determined the frequency shifts due to transverse loads acting normal to the plane of Quartz circular plates. The theoretical aspects and derivation of flexural sensitivity of quartz frequency shift was given by Lee and Markenscoff [88, 89]. They explained and proved that the force-frequency effect originates from the combination of lattice deformation and non-linear elasticity.

### 4.3 Magnetostriction and Magnetostrictive coefficient Experiments

Application of magnetic fields to magnetostrictive materials causes strain and stress along the material due to change in magnetization, which is known as the Joule (Direct) effect. Also, it is true that application of stresses to magnetostrictive materials induces domain magnetization changes, which is known as the Villari (converse) effect. The constitutive equations for Direct and converse effects are given by [90]:

\[
\{\varepsilon\} = [S^H]\{\sigma\} + [d]^T H
\]

\[
\{B\} = [\mu^\sigma]\{H\} + [d]\{\sigma\}
\]
where \( \{ \varepsilon \} \) and \( \{ \sigma \} \) are strain and stress respectively. \( s^{\mu} \) is the elastic compliance under constant magnetic field and \( \mu^{\sigma} \) is the permeability under constant stress. \([d]\) represents the magnetomechanical coupling coefficient. Equation (4-1) is the direct effect and Equation (4-2) is the converse effect.

In this application, Metglas® 2605SA1 (Metglas® Inc) has been used as the magnetostrictive layer. Even though the saturation magnetostriction (27-45 ppm) is not the highest for this material when compared to Terfanol-D (850 ppm) and Galfenol (550 ppm), the magnetomechanical coupling coefficient \([d]\) is much higher [91]. At applied AC magnetic fields, the material can be strained a larger amplitudes if \([d]\) is higher. Metglas® here is sputtered through an in-house built a four gun ion beam sputtering system. Thin film thicknesses ranging from a few nanometers up to 500 nm are obtained.

A 4 gun ion-beam sputtering tool (Appendix B, Fig, B-2.) is used to sputter thin magnetic films (parameters listed in Appendix B, table B-1). During the deposition of the films, a DC magnetic field was applied in order to pole the Metglas® film in the desired orientation. The resulting magnetic characteristics of these films are characterized via Quatum Design 1802 SQUID magnetometer with a field sweep range of 5T at 305 K. The samples are digitally imaged to extract the sample area and then sewn onto SQUID straws in order to obtain the BH characteristics. In plane BH loop of two different Metglas® 2605SA1 films deposited under different DC bias fields on glass dummy substrates will differ from each other as shown in Figure 4-1depending on the lists the sputtering conditions and resulting film properties (Table 4-1). Furthermore, the crystallinity of sputtered films is investigated if the resulting film is amorphous or not. XRD is performed and it is found out that the structure is amorphous, which is necessary in order to obtain higher magnetostriction (XRD data shown in figure B-1, Appendix B).
Figure 4-1. BH loop of two different Metglas® thin films. The film thicknesses are around 150 nm.

Table 4-1. The sputtering conditions and the resulting film properties as a comparison

<table>
<thead>
<tr>
<th></th>
<th>Metglas Film 1</th>
<th>Metglas Film 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-situ Magnetization (Gauss)</td>
<td>350</td>
<td>500</td>
</tr>
<tr>
<td>Upper Coercive Field (Oe)</td>
<td>15.17</td>
<td>5.08</td>
</tr>
<tr>
<td>Lower Coercive Field (Oe)</td>
<td>-12.84</td>
<td>-3.08</td>
</tr>
<tr>
<td>Saturation magnetization (Gauss)</td>
<td>9500</td>
<td>10000</td>
</tr>
</tbody>
</table>

This was followed by the experimental characterization of the magnetomechanical coupling coefficient, [d], which represents the critical coupling between mechanical strain and external magnetic field amplitude. 300 nm Metglas® was deposited on 170 μm thick fused silica (glass) substrates which were then diced into (20 mm x 5 mm) strips and clamped on one end to create test cantilever structure. Out-of-plane deflection of the macro-cantilevers was characterized using a laser vibrometer (Polytec OFV 5000). The laser beam is focused to the tip of the cantilever. DC magnetic field sweep is performed. The strain (ppm) as a function of applied magnetic field is
obtained as shown in Figure 4-2.b. The derivative of the curve is calculated to obtain the magnetomechanical coupling coefficient, [d], which was determined to be \( \sim 4.2 \text{ ppm/Oe} \). As it is concluded, [d] for Metglas is \( \sim 1-2 \) orders of magnitude better than the values for Terfanol-D and Galfenol [91]. It has to be noted that magnetostrictive films need to be DC biased. This bias is needed to operate magnetostrictive film at the maximum sensitivity point. This can be inferred from Fig. 4-2.b, which shows that the gradient of the strain a function of the dc bias magnetic field and has a maximum value when biased at \( \sim \pm 5 \text{ Oe} \), which is already low for this type of films.

Figure 4-2. a) The strain vs DC magnetic field of macro-cantilevers b) The magnetomechanical coupling coefficient, [d]. The asymmetry is observed in many films.
4.4 Coupled domain modeling of force –frequency effect and magnetostrictive unimorph bending

The bulk acoustic wave resonance frequency changes under transverse loading of a crystal plate can be analyzed in two steps: i) Initial stress and strain due to static bending (as a result of magnetostriction induced in Metglas thin film in this case) and ii) Small oscillations of Quartz micro-resonator due to piezoelectrically actuated motion at resonance superposed on this initial bending. Here, we utilize Lee’s theory [88] to derive $\Delta f/f_0$ as a function of zeroth and first order strains and second and third order elastic coefficients and coupled this with Quartz thin plate / magnetostrictive layer unimorph beam bending theory.

3D Elasticity Equation for Finite Deformations

The position of a point Q on an elastic 3D body at a stress-free state can be denoted with Cartesian coordinates of $x_i$, $i =1,2,3$ as shown in figure 4-3. If the body is stressed at an initial state, the body is displaced and the coordinates of point Q at this state can be denoted by $y_i$. As additional oscillation or a small amplitude wave motion (incremental) is superposed onto the body, the position of the current state, which is the interest, can be denoted by $z_i$.

Figure 4-3. The deformed states of a 3D body and the corresponding strains using continuum mechanics definition.
Therefore, the total displacement at the present state with respect to the stress-free state can be denoted by $\bar{U} = z_i - x_i$, whereas the initial and the incremental displacements can be denoted by $U_i = y_i - x_i$ and $u_i = \bar{U}_i - U_i$. From the Lagrangian definition and continuum-mechanics approach, the total $E_{ij}$, initial, $E_i$, and incremental strains, $\gamma_{ij}$, are given as:

$$E_{ij} = \frac{1}{2} \left( \frac{\partial U_j}{\partial x_i} + \frac{\partial U_i}{\partial x_j} + \sum_{k=1}^{3} \frac{\partial U_k}{\partial x_i} \frac{\partial U_k}{\partial x_j} \right)$$  \hspace{1cm} (4.3)

$$E_i = \frac{1}{2} \left( \frac{\partial U_j}{\partial x_i} + \frac{\partial U_i}{\partial x_j} + \sum_{k=1}^{3} \frac{\partial U_k}{\partial x_i} \frac{\partial U_k}{\partial x_j} \right)$$  \hspace{1cm} (4.4)

$$\gamma_{ij} = \frac{1}{2} \left( \frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} + \sum_{k=1}^{3} \frac{\partial U_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} + \sum_{k=1}^{3} \frac{\partial u_k}{\partial x_i} \frac{\partial U_k}{\partial x_j} \right)$$  \hspace{1cm} (4.5)

Using variational principle of elasticity, kinetic and strain energy densities, the stresses at the initially stressed state, $T_{ij}$, and at incremental state, $t_{ij}$, can be respectively derived as:

$$T_{ij} = C_{ijkl} E_{kl} + 0.5 \left( C_{ijklmn} E_{kl} E_{mn} \right)$$

$$t_{ij} = C_{ijkl} \gamma_{kl} + C_{ijklmn} E_{kl} \gamma_{mn}$$  \hspace{1cm} (4.6)

Where $C_{ijkl}$ and $C_{ijklmn}$ are the second and third order stiffness coefficients, which will be denoted as $C_{ij}$ and $C_{ijk}$ after Voigt simplification and representation.

**Frequency Change of Quartz thin plate due to Magnetostriction – Coupled domain analysis**

Figure 4-4 depicts the 500 x 500 x 19 µm micromachined Quartz Plate schematics, which is used in magnetostriction experiments. The details of the manufacturing are briefly explained in section 4.5 and in Appendix C with details. The structure is considered as the elastic body and the corresponding Cartesian coordinates are again shown in Figure 4-4. At the stress-free state, there are no forces acting on the crystal. At initial state, it is bent with $P_{eq}$ due to external applied
magnetic field and magnetostriction. At the present state, the piezoelectrically driven plate oscillations occur with $f_0$, where the small shear amplitude is superposed on the initial strain. The stress contribution from the central region of the circular plate is the dominant component since the Bulk Acoustic Wave (BAW) shear oscillation amplitude in the mid-portion is known to be the highest [92]. Therefore, the circular plate can be readily approximated as a rectangular plate/cantilever beam as shown with dotted lines in Figure 4-4.

![Figure 4-4. The plate micro-resonator with rectangular approximation and axes defined.](image)

The 3D body studied here can be approximated with a thin plate. Then, 2D governing equations of the thin plate at the initial and incremental state can be derived by the power-series
expansions of displacements and body forces necessary for variational principle using Mindlin’s procedure of power expansion for the thin plates [93, 94]. The strain energy densities for present and incremental state can be defined. The zeroth and first order stress and strain relations for initial and incremental state can be derived by taking the partial derivatives of strain energy densities with respect to strain, which gives [88]:

\[
T_{ij}^{(0)} = 2t(C_{ijkl} + 0.5C_{ijklmn}E_{mn}^{(0)})E_{kl}^{(0)} + (t^3/3)C_{ijklmn}E_{kl}^{(1)}E_{mn}^{(1)}
\]

\[
T_{ij}^{(1)} = (2t^3/3)(C_{ijkl} + C_{ijklmn}E_{mn}^{(0)})E_{kl}^{(1)}
\]

\[
t_{ij}^{(0)} = 2t(C_{ijkl} + C_{ijklmn}E_{mn}^{(0)})K_{ij}K_{kl}^{(0)} + (2t^3/3)C_{ijklmn}K_{kl}^{(1)}E_{mn}^{(1)}
\]

\[
t_{ij}^{(1)} = (2t^3/3)C_{ijklmn}K_{kl}^{(1)}E_{mn}^{(1)} + (2t^3/3)(C_{ijkl} + C_{ijklmn}E_{mn}^{(0)})E_{kl}^{(1)}
\]

(4.7)

where \(T_{ij}^{(0)}\), \(T_{ij}^{(1)}\) are zeroth (superscript = 0) and first order (superscript = 1) initial state stress components, \(t_{ij}^{(0)}\) and \(t_{ij}^{(1)}\) are zeroth and first order incremental state stress components respectively. \(C_{ijklmn}\) are the stiffness coefficient tensor, \(K\) are the correction factors and 2\(t\) is the plate thickness.

Since the plate is very thin, the quadratic terms of strains in stress-strain relations of eq. set (4.7) can be neglected. Introducing the Voigt (abbreviated) notation, the pair of indexes \(i j, k l,\) and \(m n,\) are replaced with single index \(p, q\) and \(r\) respectively. The stress-strain relations for the initial state then can be simplified to and the stress-strain relations then can be simplified to:

\[
T_{p}^{(0)} = 2tC_{pq}E_{q}^{(0)}
\]

(4.8)

\[
T_{p}^{(1)} = (2t^3/3)C_{pq}E_{q}^{(1)}
\]

(4.9)

where \(T_{p}^{(0)}, T_{p}^{(1)}, E_{q}^{(0)}, E_{q}^{(1)}\) denote the zeroth and first order stress and strain components \((p, q = 1, 2, \ldots, 6)\) respectively and \(C_{pq}\) denotes the second order stiffness coefficients. The non-zero stress components in eq. set (4.8-4.9) are \(T_{4}^{(0)}, T_{6}^{(0)}, T_{1}^{(1)}, T_{3}^{(1)}, T_{5}^{(1)}, T_{2}^{(1)}, T_{4}^{(1)}, T_{6}^{(1)}\). The
zeroth order stresses and 3 of the first order the stresses for the rectangular cantilever shown in Fig. 4-4 are given as [93]:

\[
\begin{align*}
T_4^{(0)} &= -P \sin(\psi) / w \\
T_6^{(0)} &= -P \cos(\psi) / w \\
T_1^{(1)} &= P \cos^2(\psi)(L - \cos(\psi)x_1 - \sin(\psi)x_3) / w \\
T_3^{(1)} &= P \sin^2(\psi)(L - \cos(\psi)x_1 - \sin(\psi)x_3) / w \\
T_5^{(1)} &= P(L \cos(\psi) \sin(\psi) - \cos^2(\psi) \sin(\psi)x_1 - \cos(\psi) \sin^2(\psi)x_3) / w
\end{align*}
\]

where \( \psi \) is the azimuth angle, \( L \) is the half length of the cut plate, \( 2t \) is the plate thickness. \( P \) is the tip force that is statically equivalent to transverse distributed loading on the plate that creates flexural bending deflection. The matrix form of equations (4.8-4.10) and detailed derivations of zeroth and first order stress components and the stiffness coefficients of Quartz are all shown in Appendix D.

The bending of the unimorph due to a magnetostrictive layer as a result of applied external magnetic field can be combined with \( \Delta f / f_0 \) to predict the achievable deflection and magnetic sensitivity using this phenomenon. Before establishing this relation, the tip deflection of the elastically coupled active-inactive layers can be derived analogously to those of piezoelectric unimorphs as has been described in detail in. [95]. For a rectangular plate of width \( w \) and length \( 2L \) as described in Fig. 4-4, the deflection of a magnetostrictive unimorph along \( X_1 \) axis, \( \delta(x) \), can then be written as

\[
\delta(x) = \frac{3t_m t_q (t_q + t_m) C_{Yq} C_{Ym} x^2 dH}{C_{Yq}^2 t_q^4 + C_{Yq} C_{Ym} (4t_q t_m^3 + 6t_q^2 t_m^2 + 4t_q t_m^3) + C_{Ym}^2 t_m^4}
\]

(4.11)

where \( C_Y \) is the Young’s modulus of the materials, \( d \) is the magnetomechanical coupling coefficient of the magnetostrictive material, and \( H \) is the applied magnetic field. The subscripts \( q \) denotes for Quartz and \( m \) denotes for magnetostrictive layer (Metglas) and \( t_q = 2t \). A point load,
\( P_{eq} \) that is statically equivalent can be calculated via beam deflection formulation:

\[
\frac{3\delta_{\text{max}} C_{yu} I_u}{(2L)^3} = P_{eq}
\]

(4.12)

where subscript \( u \) denotes the material properties for unimorph (laminate) structure. \( C_{yu} I_u \) multiplication is the flexural rigidity constant for the unimorph while \( I_u \) is the second moment of area. The max. tip deflection is \( \delta_{\text{max}} = \delta(x = 2L) \). Substituting eq. (4.11) and eq. (4.12) into eqs. (4.11-4.12) by equating \( P_{eq} \) to \( P \), the zeroth and first order stress and strain components can be calculated for the plate having an elastically coupled magnetostrictive layer, where \( P_{eq} \) in this work is the statically equivalent force applied by the magnetostrictive layer on Quartz [96]. When the incremental shear displacement is superposed on the static deflection (initial state), the relationship between the frequency shift of an oscillating rectangular quartz thin plate as a result of transverse bending can be given as [89]:

\[
\frac{\Delta f}{f_0} = \frac{1}{2C_{66}} \left( 2E_{f_1}^{(0)} + C_{661} E_{f_1}^{(0)} + C_{662} E_{f_2}^{(0)} + C_{663} E_{f_3}^{(0)} + C_{664} E_{f_4}^{(0)} \right) \left( \frac{t^2}{3} (3)^{1/2} \left( \frac{\partial^2 E_{1}^{(i)}}{\partial x_1^2} + C_{163} \frac{\partial^2 E_{1}^{(i)}}{\partial x_3^2} + C_{164} \frac{\partial^2 E_{1}^{(i)}}{\partial x_3^2} \right) \right)
\]

(4.13)

Where \( C_{pqrs} \) are the third order stiffness coefficients (Please check Appendix D, table D-1). As seen in eq. (4.13), the fractional frequency change \( \Delta f/f_0 \) is a function of the zeroth and first order strains and first order strain gradients, and is related through second and third order elastic stiffnesses. By substituting eq. (4.12) into eq. (4.13) and equating \( P_{eq} = P \), the various components of \( T \) can be obtained. Following this, the strain and strain gradient components, which are a function of the magnitude of the transverse load \( P_{eq} \) induced by the magnetostrictive layer and given by eq. (4.13), can now be calculated. This approach provides a formalism for exploring the frequency dependence of quartz resonators on transverse loads generated by various inputs into a sensitive sensor concept where the load is generated through the environmental variable of interest.
4.5 Quartz Micro-Resonator Elastically Coupled with Magnetostrictive layer

AT-cut Quartz TSM micro-resonator manufactured and tested in this work is 500 µm x 500 µm x 19 µm plate resonator. Circular bulk acoustic shear wave quartz resonators made from AT-cut quartz crystal with 400 µm diameter electrodes were first micro-machined down to the thicknesses of 19 µm. The thinning is achieved through dry etching of Quartz via using a nickel hard mask. An inverted mesa resonator structure is achieved. 20/100 nm thick Cr/Gold layers were deposited and patterned using contact aligner and photolithography to define the front and back electrodes. Finally, an unpatterned and uniform layer of 300 nm thick Metglas® was sputtered using in-house built four gun ion beam deposition system on working electrode – completing the unimorph sensor structure. The resonator was packaged in a 24 pin dual-in-line ceramic package and characterized for resonance performance. In order to fully release the resonator and make it able to deflect out-of-plane, a FIB (cut parameters listed in Appendix C, table C-2) was used to mill and define the plate and cantilever structures. The SEM picture of the plate TSM micro resonators are shown Figure 4-5. The thickness shear frequency of the micro-quartz resonator laminated with Metglas is experimentally measured at ~86.05 MHz. Its manufacturing details are given in Appendix C. The admittance characteristics after release are shown in Figure 2-10.

Figure 4-5. SEM of the FIB cut plate micro-resonator. The magnetic thin film of Metglas is deposited on the other side electrode and therefore is not visible in this SEM picture.
4.6 Bimetallic Bender Test

Prior to performing a systematic investigation of magnetostrictively induced resonance perturbations, a proof-of-concept thermally induced bending sensitivity of released structures was experimentally performed. For this, the flexure sensitivity of the resonance frequency of the quartz resonator response to thermally induced bending in cantilever shaped quartz resonators was compared with those that were unreleased and clamped. We used a chip containing an array of eight inverted mesa resonators, 22 µm in thickness and a circular diameter of 1 mm and electrode diameters of 500 µm. An unpatterned, 300 nm of magnetostrictive Metglas® layer was deposited on the unetched surface of the resonator chip i.e., all the resonators. Finally, one of the edge clamped resonator was defined and released into a 500 µm long and 45 µm wide cantilever using focused ion beam milling. Figure 4-6 is an SEM picture of the fabricated cantilever device.

![SEM picture while milling out the cantilever. The Omni probe is used in order to avoid charging.](image)

The device was placed into an oven and the ambient temperature was increased. Because of coefficient of thermal expansion mismatch between quartz ($\alpha_q$=0.33 ppm/°C) and Metglas® ($\alpha_m$= 7.6 ppm/°C), the induced moment results in the bending of the cantilever. For small temperature variations around room temperature, AT-cut quartz is insensitive (<< 1 ppm of shift) to temperature fluctuations (Figure 2-5). However, thermally induced in-plane stresses and out of
plane bending are known to result in frequency shift with the effect being significantly more pronounced for out of plane bending. Figure 4-7 shows the cantilever response in terms of resonator frequency and phase shift to \( \sim 10 \, ^\circ\text{C} \) of temperature increase from room temperature. Left Y axis shows the experimentally observed frequency shift and the secondary y axis on the right shows the experimentally observed phase shift. The tip deflection for a two layer cantilever structure can be calculated using the bimetallic heat bender formulation [97],

\[
k = \frac{6b_2b_2E_1E_2t_2(t_1 + t_2)(\alpha_2 - \alpha_1)\Delta T}{\left(b_1E_1t_1^2\right)^2 + \left(b_2E_2t_2^2\right)^2 + 2b_2b_2E_1E_2t_2t_1\left(2t_1^2 + 3t_1t_2 + 2t_2^2\right)}
\]

(4.14)

\[
d = kL^2 / 2
\]

(4.15)

On the contrary the unreleased inverted mesa quartz resonator on the same chip showed a frequency shift of 250 Hz which is about 8 times smaller than that observed for the released cantilever device. The enhanced frequency response observed is a clear indication of the response to thermally induced stress in the resonator structure. Although theory predicts a linear response to small temperature changes as a result of the thermally induced out-of-plane bending, the experimentally observed increase in frequency shows an exponential dependence. This may arise due to other unintended thermal in-plane and out-of-plane stresses that are likely generated from the package due to the increase in temperature. Furthermore, even the observed frequency change for the clamped resonator is much larger than that expected for an AT-cut quartz resonator likely due to the in-plane stresses generated from the TCE mismatch between the Metglas® and quartz layers. To conclude, this test shows an enhanced response due to thermally induced flexure in released quartz resonator as compared to an unreleased one. However, a careful design of the resonator in terms of packaging and design have to be carefully considered to achieve the predicted linear behavior with temperature change. In overall, the device still demonstrates outstanding flexural sensitivity, which motivated the authors to exploit force-frequency effect.
4.7 Magnetic Characterization Experiments of Quartz Micro-Resonator Elastically Coupled with Magnetostrictive layer

The magnetic characterizations of the thin plate micro-resonator (the device in Figure 4-5 with dimensions of 500 µm x 500 µm x 19 µm) consisted of obtaining the device force-frequency/phase relation as a function of i) large DC fields and ii) the weak and low frequency AC fields. The experimental setup consists (Appendix E, Fig E-1) of a Helmholtz coil with a diameter of 15 cm and 140 turns (N=140) (Helmholtz coil design rules are shown in Appendix E, Fig. E-3) and a trilayer shield (Custom design, Magnetic Shield Cooperation) (Appendix E, Fig. E-2). The magnetic field was precisely controlled using a current source (Keithley 2400) that has low ripple. The magnetic field was switched on and off and the device characteristics are observed. The quartz plate resonator impedance characteristic at a single frequency was monitored in real-
time using an Agilent E5061B network analyzer. The s-parameters are converted into impedance parameters using a labview program. The phase shift is recorded as a function of the applied magnetic field using the admittance tracking method the authors have proposed before[98]. All the experimental setup details and Helmholtz coil details can be found in Appendix D.

Figure 4-8 (a) demonstrates the phase-frequency curve of the micro-resonator over a frequency span. Each scan is performed under different applied external DC magnetic field as the field is gradually increased from 0 to 14 Oe. While the Metglas film is strained as the magnetic field strength is increased, the Quartz is stressed and strained, which in turn results in the phase displacement (frequency shift) of the resonator as stated with equation 4.13. If only a single frequency (86.027922 MHz) is tracked on this curve instead of over a frequency span, the phase amplitude shift will have a characteristic as shown in Figure 4-8 (b). This characteristic is a typical magnetostriction behavior, similar to the behavior shown in Figure 4-2. To independently confirm the observed phase change was the result of the magnetostrictively induced flexural out-of-plane characteristics of the released plate structure, a laser vibrometer (Polytec OFV 5000 with 2 nm transverse displacement resolution and focusing optics) was utilized. Figure 4-9 depicts the laser vibrometer data that are correlated with the phase shift data of Figure 4-8 (b). As it is concluded, the flexural bending is achieved as an applied external magnetic field. From the experimental data in Fig. 5(b), the magnetomechanical coefficient of the Metglas® film on the resonator can be deduced to be ~4.6 ppm/Oe at a bias magnetic field of ~6.1 Oe.
Figure 4-8. a) The phase characteristics of device under different external magnetic fields. The arrow shows the direction of phase-frequency curve displacements as a result of increasing DC magnetic field. b) The absolute phase shift in degrees as a function of external DC magnetic field and the corresponding smooth fit. The green dots and the square show the maximum sensitivity operation location for detecting weak AC magnetic fields.
Figure 4-9. The correlation between the phase shift and the vibrometer data.

In order to detect the force-frequency and phase-frequency sensitivity of the device, the device has to be first DC biased at ~6.1 Oe, where the slope of the curve is maximum and therefore the magnetomechanical coupling coefficient, d, is the maximum (the operating point is marked with green dotted line in Figure 4-8 (b). Under this DC bias, any additional small AC signal superposed will shift the phase and therefore the frequency in a linear fashion. That’s why this region can be considered as a pseudo-linear region. Figure 4-10 shows the response of the device to magnetic flux density. The peak-to-peak change in phase exhibits a good signal amplitude with $1/f$ noise as the dominant source of noise. Via using FFT (Fast Fourier Transform), magnetic field down to ~0.01 Oe (~1 μT of magnetic flux density. See Appendix A for conversion factors) is measured. From this experiment and Figure 4-10, the phase shift is determined to be 162.3 millidegrees / Oe.
Figure 4-10. a) The device response phase shift under applied square wave magnetic flux density at 5 Hz b) peak-to-peak phase shift. The device is first DC biased at 6.1 Oe and AC magnetic field is superposed.
4.8 Numerical Analysis and Theoretical Fit

In order to perform the numerical analysis, equations (4.11) and (4.12) are first solved using the parameters stated in table 4-2. This allows for numerical computation of the equivalent point load corresponding to magnetic strain in the magnetostrictive Metglas® layer due to the application of magnetic fields. All the numerical analysis is performed using MATLAB® software.

Table 4-2. Important Simulations Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2b$</td>
<td>19 µm</td>
<td>$t_m$</td>
<td>300 nm</td>
</tr>
<tr>
<td>$2L$</td>
<td>500 µm</td>
<td>$C_{ym}$</td>
<td>110 GPa</td>
</tr>
<tr>
<td>$w$</td>
<td>180 µm</td>
<td>$d$</td>
<td>4 ppm / Oe</td>
</tr>
<tr>
<td>$f_0$</td>
<td>86 Mhz</td>
<td>$C_{yq}$</td>
<td>76.5 GPa</td>
</tr>
</tbody>
</table>

In the linear region of magnetostrictive response about a bias field of 6.1 Oe, the tip deflection was measured for a magnetic field range 2.2 Oe. The measured and theoretically calculated tip deflection from eq. (4.11) for a $d$ value of 4 ppm/Oe and the corresponding point load, $P_{eq}$ are plotted in Figure 4-11. The measured and calculated values of the tip deflection show a very close agreement with a deflection sensitivity of 3.7 nm/Oe. The equivalent point load can be computed to result in a point load equivalence of 26 µN/Oe. In terms of deflection-frequency sensitivity, it corresponds to 0.11 Hz frequency shift for 37 pm deflection.
Figure 4-11. Experimentally measured and theoretical maximum tip deflection as a function of applied magnetic flux density. The theoretical maximum tip deflection is calculated using the parameters listed in Table 1, and results in a deflection sensitivity 3.7 nm/Oe. $P_{eq}$ values for each magnetic flux density are then substituted into eq. (4.8-4.9) & eq. (4.12) in order to numerically calculate frequency shifts as a function of azimuth angle. The plate is approximated with the dotted cantilever as shown in Figure 4-4 and the corresponding parameters are again listed in Table 4-2. The cut of quartz is AT ($\theta=35^\circ 15'$). Second order and third order elastic coefficients are adapted from Ref. [99] and transformed for AT cut Quartz crystal. Figure 4-12 shows the theoretical frequency shift expected as a function of azimuth angle at different magnetic fields ranging from 0.01 Oe to 1 Oe.
Figure 4-12. The theoretical $\Delta f / f_0$ for AT cut quartz micro-resonator of figure 2 coated with magnetostrictive thin film

As it is observed from Figure 4-12, the frequency change has local maxima and minima as a function of azimuth angle. In the $\Psi=0^\circ - 180^\circ$ simulated range, the minima in response are observed for $\psi = 27^\circ$ and $153^\circ$ while a maximum response of $\Delta f/f_0 = \sim 2 \times 10^{-7}$ is observed for $\psi = 90^\circ$ for $H = 1$ Oe. The frequency shift from magnetic characterization experiments is determined to be 11 Hz for 1 Oe of applied magnetic field and corresponds to a $\Delta f/f_0$ of $1.278 \times 10^{-7}$ for the 86 MHz resonator. This value is within the theoretical calculations shown in Fig. 8 and the observed response corresponds to an azimuth angle of $\sim 70$ degrees. For this device, the cantilever pattern was not specifically aligned to the quartz crystal structure, and therefore further optimization of the obtained signal is possible by aligning the cantilever structure to the $90^\circ$ azimuth angle which is expected to result in 35% improvement in the overall signal.
Figure 4-13. The theoretical $\Delta f / B$ for different thickness and length AT cut Quartz microresonators coated with different thicknesses of magnetostrictive thin film.

The ultimate force-frequency sensitivity of the Quartz / Metglas unimorphs as a function of magnetic flux density is also simulated with varying thickness of Quartz. The parameter, $2t$, is varied from 19 µm down to 1 µm while two cases of approximated cantilever length, $2L$, with two different Metglas thickness $t_m$ is simulated. The results are shown in Figure 4-13, where the vertical axis is a normalized coefficient given by $\Delta f / B$ (Hz / µT). At 1 µm thickness of Quartz, the numerical analysis predicts a frequency shift, $\Delta f$, of 358 Hz and 716 Hz for the cases i) $2L = 500 \mu m$, $t_m = 500$ nm and ii) $2L = 1$ mm, $t_m = 500$ nm respectively. The triangle indicates the experimentally obtained $\Delta f / B$ coefficient for the current 19 µm thick plate resonator used in experimental work given in section 4.7.

In overall, a minimum detectable magnetic flux density of 1 µT with an input frequency of 10 Hz is measured by the proof-of-concept device utilizing the transverse force-frequency effect via magnetostrictive thin film. And it is theoretically shown that the sensitivity can be improved if the
resonator thickness is further reduced. Furthermore the azimuth angle can be optimized at 90° to give the highest sensitivity direction within the anisotropic crystal. This is a motivation to further thin down the Quartz resonator and increase the sensitivity. Therefore, a thinner and longer device is manufactured in order to improve the sensitivity.

4.9 Ultra-thin Micro-Resonator Magnetic sensor

Manufacturing and General Resonator Characteristics

The magnetic sensor developed next has a similar circular bulk acoustic shear wave quartz resonator made from AT-cut quartz crystal with 400 µm diameter electrodes again and but was micromachined down to 7.5 µm. It is similarly manufactured as described in section 4.5. It was manufactured by dry etching quartz down to this thickness from 100 µm thick substrate. Nickel hard mask was used during the dry etching process to realize the inverted mesa resonator structure. In order to realize extreme material properties, Quartz wafer is etched in steps of 5 minutes, which is followed by 10 minutes of cooling (Appendix C). Therefore, excessive heating and possible bowing / cracking problems are avoided. In addition, atomic smoothness is achieved ($R_a < 1$nm) via utilizing developed dry etching process recipes [100, 101]. As a result, good $Q \times f$ is obtained. 20/100 nm thick Cr/Gold layers were deposited and patterned using contact aligner and photolithography to define the front and back electrodes. Finally, an unpattered and uniform layer of 500 nm thick Metglas® was sputtered on one of the resonator faces –completing the unimorph sensor structure. The resonator was packaged in a 24 pin dual-in-line ceramic package and characterized for resonance performance. However, at this stage the thinned resonator regions are mechanically clamped along the edges due to the inverted mesa design and incompatible for flexure deflections. To realize a fully released plate resonator, focused ion beam (FIB) etching
was used to define a rectangular plate fully released on three sides and partially cut on the fourth as shown in Figure 4-14.a. The Metglas film is sputtered on the other electrode, so it is not visible in SEM picture. The micro-resonator admittance characteristics after Metglas sputtering and FIB release are depicted in Figure 4-14.b. 7.5 µm thick resonator has ~193 MHz of TSM resonance frequency after Metglas deposition. The thin micro-resonator has a quality factor of ~8250, which is practically very tough to obtain at this high resonance frequency. There is internal stresses acting on the sensor, which causes the sensor to bent out of plane at the tip especially, but this does not affect the sensitivity of the device since the incremental changes are shifting the frequency of the micro-resonator.

Figure 4-14. a) SEM pictures of the FIB released Quartz micro-plate resonator with dimensions of 750 x 500 x 7.5 µm b) The micro-resonator characteristics after Metglas deposition and FIB release
Magnetic field Characterization Experiments

The same experimental setup consists of a Helmholtz coil and the trilayer shield are used here again (Appendix E). The magnetic field was precisely controlled using a current source (Keithley 2400) that has low ripple. The magnetic field was switched on and off and the device characteristics are observed. The quartz plate resonator impedance characteristic at a single frequency was monitored in real-time using an Agilent E5061B network analyzer. The s-parameters are converted into impedance parameters using a Labview program. The experiments were performed in a high-μ material trilayer shielded box.

In order to detect small AC magnetic field, the device has to be first DC biased, where the slope of the curve is maximum and therefore the magnetomechanical coupling coefficient, [d], is the maximum. After this DC bias is applied, any additional small AC signal superposed will shift the phase in a linear fashion. That’s why this region can be considered as a pseudo-linear region. In order to determine this operating region and obtain the magnetostriction behavior, similar characterization procedure is followed as in section 4–7. The device admittance shift at a single frequency of 193.437593 MHz is recorded through the network analyzer as a function of DC magnetic flux density. Figure 4-15 depicts the device response / conductance shift at the indicated single frequency point as a function of applied DC magnetic flux. It is observed that the admittance characteristics are showing a typical magnetostriction behavior, where a sharp change in admittance is observed, which is followed by saturation. The saturation magnetization is around 9-10 Oe, which corresponds to 0.5-0.55 mS of susceptance change. The conductance peak drifts at the saturation region, which may be due to drift observed in Quartz resonators. However, the saturation conductance shift can be counted as to be around ~1.2 mS. It is also concluded that the DC magnetic flux density needed is~ 4.95 Oe, where the slope is the highest and therefore maximum magneto-mechanical coupling factor, [d], is established.
Figure 4-15. The admittance shift (Conductance and Susceptance) observed as a function of applied DC magnetic field sweep.

Later, small AC fields are superposed to test the ultimate sensitivity. Small amplitude, low frequency (<1Hz) and square wave magnetic flux densities are applied and the conductance response is recorded at the same single frequency. Figure 4-16 shows the response of the sensor to low frequency (<1Hz) and weak amplitude square wave magnetic flux density input. Down to 3 µT, the peak-to-peak conductance shift has a good signal strength at even these low frequencies, where the noise is considerably high. Therefore, the external AC magnetic field frequency is increased to 10 Hz.
Figure 4-16. The square wave magnetic flux density applied on the device. The device is first DC biased at 4.95 Oe and square wave shaped weak AC magnetic flux density is superposed.

Figure 4-17. The peak-to-peak conductance change, ∆G, a result of applied 10 Hz magnetic field. The MDFD is 79 nT.
The peak-to-peak conductance (obtained via FFT) vs. the applied AC magnetic flux density is shown in Figure 4-17. The conductance change is measured as 94.50 nS, which corresponds to experimentally measured $\Delta f$ of 0.2842 Hz at 79 nT. The normalized frequency shift ($\Delta f / f_0$) at this magnetic flux density is then equal to $1.4692 \times 10^9$. This is the minimum detectable limit with the measurement methodology proposed due to the limitations of the frequency resolution of the network analyzer.

4.10 Numerical Analysis and Theoretical Fit for Ultra-thin device

The frequency shift $\Delta f$ is normalized with the magnetic flux density in order to obtain the generalized coefficient of $\Delta f / B$, which is experimentally measured to be at $3.5535 \text{ Hz} / \mu\text{T}$. Theoretical modeling of AT-cut Quartz plate micro-resonators having different thickness utilizing the methodology explained in section 4.8 is shown in Figure 4-18.

Figure 4-18. The theoretical ultimate sensitivity of the AT-cut Quartz / Metglas heterostructures. $L$ is the longer dimension of cut length and $t_m$ stands for the Metglas thickness.
The data for 500 x 500 x 19 µm heterostructure is also included as a comparison. The blue and magenta triangles denote the experimental data points and the solid lines are the theoretical expected sensitivities for the given dimensions, where L denotes the longer dimension (2L in Figure 4-4) of FIB released plate structure and t_m denotes for the thickness of the sputtered Metglas. The straight and blue triangle is the experimental Δf / B obtained for the device utilized in the magnetic experiments in this letter (Heterostructure dimensions: 750 x 500 x 8 µm). The magenta upside down triangle represents the 500 x 500 x 19 µm heterostructure tested for transverse force-frequency sensitivity given in section 4.7 and 4.8. The theoretical and the experimental data fit well. The small difference between the experimental data and theoretical fit may be due to the calculated third order and second order elastic coefficients being off from the actual values. This is expected since these coefficients are hard to calculate and find in the literature. Further thickness reduction would give higher sensitivity for the proposed magnetic sensing mechanism. Nevertheless, this is currently practically impossible because of i) manufacturing incapabilities ii) the thin film stress due to Metglas deposition would be large enough to break Quartz. These kind of internal stresses are already observed in current device. On the other hand, annealing and smarter designs can be considered for future work to reduce stresses and optimize the performance. In general, the device holds a great promise to detect weak and low frequency signals.

4.11 Discussion

In recent years, high sensitivity Magnetostrictive/Piezoelectric composite Magnetoelectric (ME) sensors have been proposed for detecting low amplitude (nT to pT) and low frequency (<100 Hz) magnetic fields [102]. Magnetoelectric effect (ME) is the phenomenon where a dielectric polarization is induced under applied magnetic field (H) or a magnetization is
induced under an external electric field, \( E \). \cite{103} ME is first observed in \( \text{Cr}_2\text{O} \). Various single-phase materials are studied over the years and it is found out that they exhibit weak ME.

However, in heterostructures of magnetostrictive and piezoelectric composites, the effect is more promising. These sensors are generally configured as unimorph or bimorph heterostructures of magnetostrictive layers and piezolayer on top of each other. In this configuration, the elastic coupling between a magnetostrictive layer and a thin film piezoelectric is exploited, where the induced strain in the magnetostrictive layer due to external magnetic field in turn induces voltage over the piezoelectric film due to direct piezoelectric effect. The current research effort is to increase the ME coupling between the two layers, which define the effective voltage induced due to strain in the magnetostrictive layer. Voltage ME coupling coefficient for these heterostructures, \( \alpha_{\text{ME}} \), are denoted by \cite{104};

\[
\alpha_{\text{ME}} = \left. \frac{d\lambda}{dH} \right|_{\text{magnetostrictive}} \left. \frac{dE}{d\lambda} \right|_{\text{piezoelectric}} = \left. \frac{dE}{dH} \right|
\]

where \( \lambda \) is the strain induced in the magnetostrictive layer, which is given in part per million (ppm) in general. \( \alpha_{\text{ME}} \) has a unit of \( \text{V/cm}^\text{Oe} \).

Different set of magnetoelastic heterostructures are laminated together in order to improve \( \alpha_{\text{ME}} \) over the years. There are many ferrites and ferromagnetic materials that demonstrate good magnetostrictive properties. For magnetic sensor applications, a soft (magnetically) material, with low hysteresis loss is desired since the material magnetization can be abruptly switched with low magnetic field amplitudes. This wide range of material selection is also true for piezoelectric materials. In the literature, various numbers of heterostructures are presented. Piezoelectric PMN-PT / Magnetostrictive Terfenol-D layers are shown to demonstrate \( \alpha_{\text{ME}} \) of 2.2 V/cm Oe \cite{105}. Similarly, APC 840 PZT / Terfenol-D composites have shown \( \alpha_{\text{ME}} \) of 4.68 V/cm Oe \cite{106}. Later, polyvinylidene-fluoride (PVDF) / Metglas 2605 SA1
heterostructure is shown to have 7.2 V/cm Oe at low frequencies and 310 V/cm Oe under resonance operation [103]. These proof-of-concept devices are generally cm to mm sized actuators and laminated on each other using epoxy. Sol-gel derived Pb_{Zr_{0.52}Ti_{0.48}}O_{3} film and a sputter deposited Fe_{0.7}Ga_{0.3} film on Si cantilevers are demonstrated to have 1.81 V/Oe cm at the mechanical resonant frequency of 333 Hz and at DC bias magnetic field of 90 Oe. True sputtered thin film heterostructure of FeCoSiB/AlN has shown to have 737 V/cm Oe [107] at 753 Hz and requiring only 6 Oe of DC bias magnetic field. However, a different sensing mechanism of a ME heterostructure is proposed. AlN/(FeGaB/Al2O3) x 10 magnetoelectric heterostructure is shown to detect low amplitude DC (low hundreds of pT) magnetic flux densities at 215 MHz resonance utilizing the ΔE effect [108].

Table 4-3. The sputtering conditions and the resulting film properties as a comparison.

<table>
<thead>
<tr>
<th></th>
<th>Metglas Film 1</th>
<th>Metglas Film 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-situ Magnetization (Gauss)</td>
<td>350</td>
<td>500</td>
</tr>
<tr>
<td>Upper Coercive Field (Oe)</td>
<td>15.17</td>
<td>5.08</td>
</tr>
<tr>
<td>Lower Coercive Field (Oe)</td>
<td>-12.84</td>
<td>-3.08</td>
</tr>
<tr>
<td>Saturation magnetization (Gauss)</td>
<td>9500</td>
<td>10000</td>
</tr>
</tbody>
</table>

Table 4-3 is a list of the selected piezoelectric materials exploited in ME sensor applications and their properties [109-111]. For example, PVDF stands out as a soft material, but its quality factor, d_{31} coefficient and electromechanical coupling coefficient are lower with respect to PZT or PMN-PT. However, these materials have high elastic modulus, which reduces the mechanical strain. Therefore, it is quite difficult to optimize the performance. If Quartz is investigated, it has the poorest electromechanical coupling coefficient, is relatively stiff and d_{31} coefficient is very poor to utilize them in ME applications. However, it has the highest quality
factor and certain crystal cuts are temperature insensitive. Previously, bilayers of X-cut single crystal quartz and permendur (Fe-Co-V alloy) heterostructures (lengths of cm) had $\alpha_{ME}$ from 1.5 V/cm Oe at 20 Hz to ~ 185 V/cm Oe at bending resonance or electromechanical resonance corresponding to longitudinal acoustic modes [83] as x-cut Quartz has a higher $d_{31}$ coefficient.

In this paper, we propose and demonstrate MEMS scale ultra-thin Quartz plate resonator / thin film magnetostrictive Metglas unimorph heterostructures that are exploited as a sensitive magnetic sensor utilizing transverse force-frequency effect. The device is configured as a Magnetostrictive heterostructure. The sensing mechanism is, however, achieved through the transverse force-frequency effect, which utilizes the high quality factor of thickness-shear-mode (TSM) Quartz unlike traditional ME heterostructures. The external magnetic field strains the magnetostrictive layer, which is elastically coupled to the resonator. This causes the admittance characteristics of the resonator, which is mechanically vibrating in thickness-shear-mode, to shift. The frequency shifts are correlated to magnetic field strength. This sensing mechanism is advantageous over the classical ME sensors since i) the device can detect from DC to AC magnetic fields. ii) it is truly chip-scale device and all the manufacturing processes are MEMS compatible that lets the device to be integrated easily. iii) AT-cut Quartz is temperature-frequency shift is minimal (< 1ppm) at ± 10 degrees of room temperature. iv) the sensor has relatively low power consumption
Chapter 5

Conclusion, Discussion and Future Work

5.1 Summary of Research and Conclusions

This dissertation introduces two magnetic sensing mechanisms. First mechanism is based on exploiting and quantifying the magnetoviscous effect of ferrofluids, which is the viscosity shifts occurring in the ferrofluid as a function of applied magnetic field. The maximum sensitivity for this very unique technique is determined to be $1.5 \text{ nT} \sqrt{\text{Hz}}$. The second sensing mechanism is based on exploiting transverse force-frequency sensitivity of micromachined Quartz resonators via magnetostrictive thin films that is elastically coupled to the fully released unimorph structure. The minimum detectable magnetic flux density for this magnetic sensor is measured as $79 \text{ nT}$ at $10 \text{ Hz}$ input frequency.

Magnetoviscous Ferrofluid based Magnetometer

Here, Quartz is micromachined to act as a high frequency micro-viscometer. In addition to being a unique magnetic sensing mechanism, this research is also introducing the high frequency shear rate characteristics of the ferrofluids. A respectful magnetic flux density sensitivity of $1.5 \text{ nT} \sqrt{\text{Hz}}$ is achieved. Later, the device is shown to detect 2D planar sensitivity via patterning the high magnetic permeability Metglas layer as a flux concentrator, which concentrates the flux in the center of the Quartz resonator.

One drawback related to this technology is that the ferrofluid used in the experiments evaporates within a few days and the sensor loses its function. This problem can be neglected via using ionic liquids as the carrier liquid. Ionic liquids are molten salts at room temperature having organic cations and anions. The advantage of using ionic liquids is they are non-volatile. A few
trials have been performed to disperse stable ferro-particles in ionic liquids using four different ionic liquids and different dry particles, which are shown in Table 5-1. The particles used are from Ferrotec company (EMG 1200, EMG1300, EMG1400, EMG 1500, EMG 705, EMG 607, EMG 508, EMG 308). Each of these type of powder form nano ferro-particles have diameter of 10 ± 3 nm and are surrounded with different type of surfactants such as fatty acids, a type of polymer, polar and hydophobic surfactants.

Table 5-1. The ionic liquids utilized in the stable ionic-ferrofluid trials

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Short Name</th>
<th>Molecular Formula</th>
<th>Viscosity (cP)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 butyl 3 methylpyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>BMPImNTF2</td>
<td>C12H16F6N2O4S2</td>
<td>63</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>1 ethyl 3 methylimidazolium bis(fluorosulfonyl)imide</td>
<td>EMIFSI</td>
<td>C6H11F2N3O4S2</td>
<td>24.5</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>1 butyl 3 methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>BMIImNTF2</td>
<td>C10H15F6N3O4S2</td>
<td>70</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>1 butyl 3 methylimidazolium dicyanamide</td>
<td>BMIImDCA</td>
<td>C10H15N5</td>
<td>39.14</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>1 ethyl 3 methylimidazolium thiocyanate</td>
<td>BMIImSCN</td>
<td>C7H11N3S</td>
<td>22</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>

Since the surfactants are different types, the solvent has to be properly chosen in order to avoid the surfactant dissolved. Another concern is the miscibility of the solvent with the ionic liquid. Therefore, hydrophobic and hydrophilic solvents are tried out at about 50 combinations of particle / solvent and particles. The ferro-particles are first obtained in powder form from FerroTec company. They are first dissolved in hydrophilic or hydrophobic solvents (water, chloroform, butanol, toluene) that is suitable with the surfactant around the particle. Later, it is sonicated for half an hour. Ionic liquid is later added. A half an hour sonication is performed.
Finally, the solvent is evaporated in a heated vacuum oven, so particles are dispersed in ionic liquid nicely. A well dispersed ionic liquid solution is shown in Figure 5-1. As it is observed from the figure, the ferroparticles (EMG 509 nanoparticles dispersed in EMISCN) disperses well and it acts as a single phase liquid solution. When strong magnetic field is applied, the particles still protect their paramagnetic property and does not clump or agglomerate.

Figure 5-1. Unstable / Not dispersed Ionic Liquid Ferrofluid (left) vs. Stable / Well dispersed Ionic Liquid Ferrofluid.

However, the ionic liquid ferrofluid on the left (EMG 607 dispersed in EMISCN) has phase separation; the particles did not disperse very well in the ionic liquid. The possible reasons may be due to i) The destruction of the surfactant layer around the particles ii) the surfactant and the ionic liquid do not interact very well. The stable ionic ferrofluid shown in figure 5-1 has been utilized in magnetic characterization experiments that are similar to the ones explained in section 3.6. A commercial 1 inch diameter AT-cut Quartz resonator (Inficon Co.) has been used and a small amount similar to the one in section 3.6 is added atop. And the admittance is tracked in real time to record the shifts in viscosity as a function of applied magnetic flux density. Unfortunately,
no sensitivity till 1.5 mT is observed, which is orders of magnitude worse than the values measured in chapter 3 and the signal amplitude is very poor. The signal is shown in Figure 5-2.

![Graph](image.png)

Figure 5-2. The peak-to-peak conductance shift observed in a 5 MHz commercial AT-cut Quartz resonator at 1.5 mT of magnetic flux density.

The reasons of the reduced sensitivity may be articulated as i) the ionic liquids have large viscosity values compared to EMG 911, which damps the resonator and reduces the overall sensitivity. ii) The particle alignment within the ionic liquid medium may be totally different from EMG 911, which has an oil based carrier liquid. The particle alignment and chain formation needs to be investigated. Here, no further study is established by the author. As a future work, more combinations on the stability and response of the ionic ferrofluids can be studied. Once a stable ionic liquid ferrofluid is established, it will be a solution to the evaporation.
**Magnetometer based on transverse force-frequency effect of Quartz elastically coupled with magnetostrictive thin film**

Quartz resonators’ fundamental frequency shifts when they are subjected to stress and strain, which is known as the transverse force-frequency effect. In this work, AT-cut Quartz resonators are micromachined, thinned and elastically coupled to magnetostrictive thin film. To sum up, ultra-thin high quality factor TSM Quartz plate resonator / magnetostrictive Metglas heterostructure has been demonstrated as a proof-of-concept magnetic sensor exploiting transverse force-frequency effect. The device utilizes the high Quality factor operation and force-frequency displacement effect of Quartz resonator. An ultra-thin (7.5 µm) resonator has been successfully manufactured and released. A MDMFD of ~79 nT has been measured at low frequencies (<10 Hz). The advantage of this sensing mechanism is low frequency magnetic signals can be sensed. The whole device is chip-scale and room temperature operation. Since AT-cut Quartz is used, the temperature stability is much better compared to other piezoelectric materials used in magnetic sensing applications. The ultimate theoretical ultimate sensitivity is calculated through combining Lee’s theory and magnetostrictive unimorphs. The experimental data points are also compared with the theoretical sensitivity calculations.

The overall structure is FIB cut in order to achieve a unique released micro unmorph plate structure. The frequency shift ∆f is normalized with the magnetic flux density in order to obtain the generalized coefficient of ∆f / B, which is experimentally measured to be at 3.5535 Hz / µT. The minimum detectable magnetic flux density is measured as 79 nT. More importantly, the sensitivity would be an order of magnitude larger (MDMFD ~ 50 pT) if the Quartz resonator is further reduced down to 1 µm thickness and the Metglas thickness is kept constant at 500 nm as the expected ∆B / µT would be 716 Hz. Nevertheless, the manufacturing of this device is currently practically impossible because of i) manufacturing in capabilities ii) the thin film stress due to Metglas deposition would be large enough to break Quartz. These kind of internal stresses
are already observed in current device. On the other hand, annealing and smarter designs can be considered for future work to reduce stresses and optimize the performance. Another future work can be to micromachined and pattern the magnetic thin film into a flux concentrator shape, so the whole flux is concentrated in the plate region. This may improve the sensitivity one order of magnitude. In overall, the device holds a great promise to detect weak and low frequency signals.
Appendix A

Magnetics Basics and Unit Conversion Tables

Maxwell equations define the classical electromagnetism. Below is the summary of Maxwell’s Equations:

I. Faraday’s Law of Induction

\[ \oint \vec{E} \cdot d\vec{l} = -\frac{d\phi_B}{dt} \]  \hspace{1cm} (A.1)

II. Ampere’s Law

\[ \oint \vec{B} \cdot d\vec{s} = \mu_0 i + \frac{1}{c^2} \frac{\partial}{\partial t} \int \vec{E} \cdot d\vec{A} \]  \hspace{1cm} (A.2)

III. Gauss’ Law for magnetism

\[ \oint \vec{B} \cdot d\vec{A} = 0 \]  \hspace{1cm} (A.3)

IV. Gauss’ Law for electricity

\[ \oint \vec{E} \cdot d\vec{A} = \frac{q}{\varepsilon_0} \]  \hspace{1cm} (A.4)

Where;

E = Electric field (V/m) ; l = vector element ; \( \phi_B \) = Magnetic flux (Weber) ; t = time (seconds)

B = Magnetic flux density (Tesla) ; q = charge (Coulomb) ; s = vector area ; \( \mu_0 \) = Permeability of free space, \( 1.2567 \times 10^{-6} \) T m / A ; c = speed of light (m/s) ; I = current (A), A = Area (m\(^2\)) ; \( \varepsilon_0 \) = Permittivity of free space, \( 8.854 \times 10^{-12} \) F /m .
The magnetic field (Magnetizing field), \( H \) is related to magnetic flux density (magnetic induction), \( B \) in free space through the formulation;

\[
B = \mu_0 H
\]

When the generated magnetic fields pass through materials and materials contribute to magnetic field, then the relation becomes;

\[
B = \mu_r \mu_0 (H + M)
\]

Where \( M \) is the magnetization and \( \mu_r \) is the relative vacuum permability. It depends on the material property. \( \mu_r \) is related to magnetic susceptibility via;

\[
X_m = \mu_r - 1
\]

The \( H \) and \( B \) units and corresponding conversions are given in table A-1 below.

**Table A-1 Magnetic field and flux density SI and CGS units and corresponding conversion factors**

<table>
<thead>
<tr>
<th></th>
<th>Symbol</th>
<th>SI Units</th>
<th>CGS units</th>
<th>SI to CGS conversion factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic Flux Density</td>
<td>B</td>
<td>Tesla</td>
<td>Gauss</td>
<td>( 10^4 )</td>
</tr>
<tr>
<td>Magnetic Field</td>
<td>H</td>
<td>A / m</td>
<td>Oersted</td>
<td>( 4 \pi / 1000 )</td>
</tr>
</tbody>
</table>

** 1 Oersted = 100 \( \mu \)T in free space.**
Appendix B

Metglas XRD data and sputtering parameters

Figure B-1 below shows the X-Ray Diffraction Data (XRD) data of the sputtered magnetostrictive Metglas thin film using 4 gun ion beam deposition system shown in figure B-2. The large peak is associated to the gold layer that is used as the passivation layer in order to avoid oxidation. The peak around 20 degrees is amorphous iron silicon boron peak showing the sputtered films are amorphous. This structure amorphous is necessary for magnetostriction property. Therefore, the sputtering parameters are well tuned for this purpose as shown in table B-1.

Figure B-1. X-Ray Diffraction Data (XRD) data of the sputtered magnetostrictive Metglas thin film
Figure B-2. In-house built 4 gun ion beam sputtering system used to sputter magnetized magnetic thin film.

Table B-1. Sputtering parameters for Metglas thin film deposition

<table>
<thead>
<tr>
<th>Sputtering parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>30 - 50</td>
<td>µTorr</td>
</tr>
<tr>
<td>Single Gun Power*</td>
<td>6.8</td>
<td>kV</td>
</tr>
<tr>
<td>Single gun current**</td>
<td>2.8</td>
<td>mA</td>
</tr>
<tr>
<td>Deposition rate for single gun</td>
<td>0.5-1</td>
<td>nm / min</td>
</tr>
</tbody>
</table>

*Single gun deposition is not preferred. Two guns are generally used, which helps with the sputtering rate
** This current is saturated when two guns are used together. Generally, the maximum total current for 2 gun sputtering is limited to 3.5 mA
Appendix C

Cleanroom Manufacturing Methods and Sequence of Ultra-thin Quartz resonators

Figure C-1 below shows the manufacturing procedure of the released Ultra-thin plate resonator structures.

Figure C-1 a) 1st lithography b) Nickel Electroplating c) RIE etch d) Gold evaporation e) 2nd lithography f) Wet etching of electrode material g) Resist spin for 3rd lithography h) 3rd lithography using backside alignment i) Gold Evaporation j) Lift-off k) Blanket Metglas sputtering l) Packaging into 24 pin ceramic package and wire bonding m) FIB cut release
First lithography (Figure C-1(a)) defines the region that is going to be dry etched and the resonator will be established on thin region of Quartz that will be sandwiched between two electrodes later on. After lithography, nickel is electroplated on gold seed layer. (Figure C-1(b)). Nickel acts as the hard mask as the thick wafer (~100 µm) is slowly etched down (Figure C-1(c)). The most important step here is to do short etching steps in order to avoid heating, cracking and bending of the wafer that is on the submount wafer. After dry etching, all the hard mask and metal is removed via wet etch. Later, gold is evaporated on the etched side (Figure C-1(d)). The resist is sprayed for the 2nd lithography, which defines the etched side electrode pattern (Figure C-1(e)). The gold on the unwanted regions are removed in chrome and gold etchant (Figure C-1(f)). For the front side electrode, the whole wafer is submounted on the opposite side and resist is spinned on this side (Figure C-1(g)). 3rd lithography defines the opposing electrode region that is the front side (Figure C-1(h)). Chrome and Gold are evaporated respectively on the pattern (Figure C-1(i)). Then, the resist is lifted off to establish the electrode (Figure C-1(j)). The magnetostrictive Metglas layer is sputtered on the non-etched side (Figure C-1(k)). It is a blanket sputtering and not patterned. The resonator structure along with the thin film is then packaged and wire bonded into a 24 pin dual ceramic package. The middle portion of the package is water inkjet cut and removed so that the other side of the resonator can also be seen and observed during the final cut and release step (Figure C-1(l)). The Focused Ion Beam (FIB) cut is the final step to release the resonator structure as a clamped-free plate (Figure C-1(m)). This is the manufacturing procedure for the second magnetic sensor: Magnetostrictive sensor. The manufacturing steps are the same for the magnetoviscous ferrofluid magnetic sensor except the final release step. Table C-1 the detailed process flow and the details.
<table>
<thead>
<tr>
<th>Process</th>
<th>Procedure</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cleaning Quartz Wafers</td>
<td>- Dip into cleaning solution using proper wafer holders for 20-30 minutes.</td>
<td>Piranha solution (4:1::Sulphuric Acid, H2SO4:Hydrogen Per Oxide, H2O2) can be used. Piranha is not suggested to be prepared due to being a dangerous chemical to contain. Therefore, use Cyantek’s Nanostrip instead.</td>
</tr>
<tr>
<td>2. Mounting on dummy glass mounts</td>
<td>For every mounting step on glass, this procedure has to be followed.</td>
<td>- Use PR 1805 to mount 1 inch diameter Quartz wafers and soft-bake for 2-3 minutes.</td>
</tr>
<tr>
<td>3. Evaporating Cr / Au</td>
<td>Suggested thickness (15-20 nm Cr / 150 nm Au)</td>
<td>Be sure to use Cr as the sticktion layer. It is the best sticking metal to Quartz wafers. Ti has problems.</td>
</tr>
<tr>
<td>4. 1&lt;sup&gt;st&lt;/sup&gt; lithography</td>
<td>HDMS: 4000 rpm, 40 seconds SPR 220 Targeted thickness: 15 µm Spin rate: 1000 rpm Soft Bake Temperature: 115 ºC. Soft Bake Time: 5 mins Step exposures: 15 sec x 6</td>
<td>This is the lithography that defines the etch pattern and the hard mask regions. Required for thinning the Quartz wafers. Contact aligner is used for this step. SPR 220 is preferred since it is a thick resist!</td>
</tr>
<tr>
<td>6. Nickel Electroplating</td>
<td>Plating time: 3 hours Thickness: 15 µm</td>
<td>Nickel is the hard mask to be used or</td>
</tr>
<tr>
<td>7. Cr / Gold Evaporation to the backside</td>
<td>Indium wets Quartz well enough. This step may be skipped. Also, Indium and gold forms alloy at melting temperature of indium.</td>
<td></td>
</tr>
<tr>
<td>8. Mounting on 4 inches silicon wafer submount</td>
<td>Melt indium to mount Quartz</td>
<td>Indium melts around 155-160 ºC. Suggested temperature is 180 ºC. Heat slowly, don’t stress Quartz</td>
</tr>
<tr>
<td>9. Thinning down via dry etching</td>
<td>Argon flow rate: 49 sccm SF6 flow rate: 7 sccm Source Power: 2000 W Plasma Power: 400 W</td>
<td>Alcatel Oxide etching tool is used. The etching is performed in 5 minutes of steps. There is 10 minutes of cooling after each step in order to avoid bending cracking. The whole etching takes 8-10 hours depending on the thickness.</td>
</tr>
<tr>
<td>10. Releasing from the submount</td>
<td>Melt the indium back and collect quadrants of Quartz</td>
<td>Again, heat it slowly so no cracks occur and slide it through the top of the submount wafer.</td>
</tr>
<tr>
<td>11. Wet etching of metal and indium</td>
<td>Strip everything in Aqua Regia (HNO₃:HCL::1:3)</td>
<td>Since Indium may form alloys and sticks to resonator areas, wet etch everything away. Thus, Aqua Regia is used.</td>
</tr>
<tr>
<td>12. Mount Quartz</td>
<td>Etched side up.</td>
<td>Follow the procedure listed in step 2</td>
</tr>
</tbody>
</table>

Table C-1.: The process flow for manufacturing ultra-thin Quartz wafers.
<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.</td>
<td>Evaporating Cr/Au&lt;br&gt;Suggested thickness (15-20 nm Cr / 150 nm Au)&lt;br&gt;Be sure to use Cr as the sticktion layer. It is the best sticking metal to Quartz wafers. Ti has problems</td>
</tr>
<tr>
<td>14.</td>
<td>2nd lithography&lt;br&gt;Spray coating using PR 1805. Spray evenly that the PR thickness is uniform and 200-400 nm. Soft bake for 1 min at 115 ºC&lt;br&gt; Spray coating is necessary in this step. Defines the etch side electrodes. Try to control the thickness and uniformity in spray coating. This is an etch mask.</td>
</tr>
<tr>
<td>15.</td>
<td>Wet etching of Cr/Au&lt;br&gt;Gold Etchant: Transene TFA&lt;br&gt;Cr etchant: Transene 1020&lt;br&gt;~20-30 secs in gold etchant to remove 150 nm gold, 5-10 secs to remove 15-20 nm Chromium&lt;br&gt;Remove the Cr/Au in Cr and Au wet etchants. This will remove the metal everywhere except the resonator region. Control the undercut!</td>
</tr>
<tr>
<td>16.</td>
<td>Mount Quartz wafer on glass substrate&lt;br&gt;Etched side down.&lt;br&gt;Follow the procedure listed in step 2</td>
</tr>
<tr>
<td>17.</td>
<td>3rd lithography&lt;br&gt;HMDS: 4000 rpm 40 seconds&lt;br&gt;LOR 5A: 2000 rpm 40 seconds / Soft bake at 170 ºC for 3 mins&lt;br&gt;PR 1805: 4000 rpm for 40 seconds.&lt;br&gt;Soft bake: 115 ºC for 1 min.&lt;br&gt;This is a lift off mask. Backside alignment is necessary. Transparent mode is utilized.</td>
</tr>
<tr>
<td>18.</td>
<td>Oxygen Plasma clean&lt;br&gt;This is a gentle surface cleaning step.&lt;br&gt;PT 720 for 7 seconds.&lt;br&gt;Power: 300 Watt&lt;br&gt;O2 flow rate: 50 sccm&lt;br&gt;Residues may be left from the exposure and develop steps, which avoids chrome to stick on Quartz.</td>
</tr>
<tr>
<td>19.</td>
<td>Evaporating Cr/Au&lt;br&gt;Suggested thickness (15-20 nm Cr / 150 nm Au)&lt;br&gt;Be sure to use Cr as the sticktion layer. It is the best sticking metal to Quartz wafers. Ti has problems</td>
</tr>
<tr>
<td>20.</td>
<td>Lift-off&lt;br&gt;PG remover (60ºC)&lt;br&gt;1st bath in PG remover, 2nd bath in IPA.</td>
</tr>
<tr>
<td>21.</td>
<td>Package&lt;br&gt;Package using conductive epoxy</td>
</tr>
<tr>
<td>22.</td>
<td>Metglas deposition&lt;br&gt;500 nm for 7.5 µm Quartz thickness Then 20 -30 nm Au&lt;br&gt;4 gun ion beam deposition system is used. Check Table C-2. The Au acts as passivation layer to avoid any oxidation.</td>
</tr>
<tr>
<td>23.</td>
<td>FIB cut&lt;br&gt;Check table C-2 below&lt;br&gt;Releases the resonator into clamped-free plate structure.</td>
</tr>
</tbody>
</table>

Note: Demount Quartz from glass submounts using PG Remover at 60 ºC
Table C-2. Experimentally found optimum Focues Ion Beam Cut Parameters for Quartz. FEI company’s Quanta 200 3D Dual Beam FIB is utilized.

<table>
<thead>
<tr>
<th>Cut time</th>
<th>Beam energy</th>
<th>Beam current</th>
<th>Dwell Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 hours</td>
<td>30 kV</td>
<td>20 nA</td>
<td>1 µs</td>
</tr>
<tr>
<td>4 hours</td>
<td>65 kV</td>
<td>60 nA</td>
<td>1 µs</td>
</tr>
</tbody>
</table>
Appendix D

Detailed Derivation of stress and strain components for thin plate crystals And Elastic Coefficients of Quartz crystal

2D equations of a plate on the body at the intial state can be derived by the power-series expansions of displacements and body forces using Mindlin’s procedure of power expansion, which is given as:

\[ \left( \vec{U}_i, U_j, u_i \right) = \sum_n x^n \left( \vec{U}^{(n)}_i, U^{(n)}_j, u^{(n)}_i \right) \] (D.1)

Inserting (A.1) into (4.3-4.5), the relations between strain and displacement are obtained as:

\[
2E_{ij}^{(n)} = \frac{\partial U_j^{(n)}}{\partial X_i} + \frac{\partial U_i^{(n)}}{\partial X_j} + (n+1)(\alpha_{ij}U_j^{(n+1)} + \alpha_{ij}U_i^{(n+1)}) + \sum_n \left[ \frac{\partial U_i^{(n)}}{\partial X_j} + m\alpha_{ij}U_k^{(n)} \frac{\partial U_k^{(n+1)}}{\partial X_j} + (n-m+1)\alpha_{ij}U_k^{(n+1)} \right]
\]

where \( \alpha_{ij} \) is Kroniker delta. Equation (B.2) is defined for the initial stressed state where incremental state relations are similar. (B.2) can be truncated by only keeping zeroth and first order terms such that \( U_{in} \) and \( u_{in} \) are set for 0 for \( n>1 \) while disregarding \( T_{ijn} \), \( e_{ijn} \) and \( n_{ijn} \) for \( n>0 \).

2D kinetic and strain energy densities for present(\( V_0 \)) and incremental state(\( V_2 \)) can be defined through 2D variational principle. The zeroth and first order stress and strain relations for initial and incremental state can be derived through taking the partial derivates, which results as [88]

\[
T_{ij}^{(0)} = 2b(C_{ijkl} + 0.5C_{ijklmn}E_{mn}^{(0)})E_{kl}^{(0)} + \left( \frac{b^3}{3} \right) C_{ijklmn} E_{kl}^{(1)} E_{mn}^{(1)}
\]

\[
T_{ij}^{(1)} = \left( \frac{b^3}{3} \right) (C_{ijkl} + C_{ijklmn}E_{mn}^{(0)})E_{kl}^{(1)}
\]

\[
t_{ij}^{(0)} = 2b(C_{ijkl} + C_{ijklmn}E_{mn}^{(0)})K_{ij}K_{kl}\alpha_{kl}^{(0)} + \left( \frac{b^3}{3} \right) C_{ijklmn} K_{ij}K_{kl}\alpha_{kl}^{(1)} E_{mn}^{(1)}
\]

\[
t_{ij}^{(1)} = \left( \frac{b^3}{3} \right) C_{ijklmn} K_{kl}\alpha_{kl}^{(0)} E_{mn}^{(1)} + \left( \frac{b^3}{3} \right) (C_{ijkl} + C_{ijklmn}E_{mn}^{(0)})\alpha_{kl}^{(1)}
\] (D.3)
Below in equation (B.4), the matrix form of equations (4-7 and 4-8) are shown.

\[
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 & E^{(0)}_1 \\
C_{21} & C_{22} & C_{23} & C_{24} & 0 & 0 & E^{(0)}_2 \\
C_{31} & C_{32} & C_{33} & C_{34} & 0 & 0 & E^{(0)}_3 \\
C_{41} & C_{42} & C_{43} & C_{44} & 0 & 0 & E^{(0)}_4 \\
0 & 0 & 0 & 0 & C_{55} & C_{56} & E^{(0)}_5 \\
0 & 0 & 0 & 0 & C_{65} & C_{66} & E^{(0)}_6
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
0
\end{bmatrix}
\]

\[
E^{(i)}_1, \quad E^{(i)}_3, \quad E^{(i)}_5 = \frac{3}{2t} \begin{bmatrix}
C_{33}/Z & -C_{13}/Z & 0 \\
-C_{13}/Z & C_{11}/Z & 0 \\
0 & 0 & 1/C_{55}
\end{bmatrix} \begin{bmatrix}
T^{(i)}_1 \\
T^{(i)}_3 \\
T^{(i)}_5
\end{bmatrix}
\]

\[
T^{(i)}_2, \quad T^{(i)}_4, \quad T^{(i)}_6 = \frac{2}{3t^3} \begin{bmatrix}
C_{21} & C_{23} & 0 \\
C_{41} & C_{43} & 0 \\
0 & 0 & C_{65}
\end{bmatrix} \begin{bmatrix}
E^{(i)}_1 \\
E^{(i)}_3 \\
E^{(i)}_5
\end{bmatrix}
\]

(D.4)

Where \( Z = C_{11}C_{33} - C_{13}^2 \)

AT-cut Quartz Stiffness coefficients and crystal relations values are given by [112]:

\[
C_{ij} = \begin{bmatrix}
86.74 & -8.25 & 27.15 & -3.66 & 0 & 0 \\
-8.25 & 129.77 & -7.42 & 5.7 & 0 & 0 \\
27.15 & -7.42 & 102.83 & 9.92 & 0 & 0 \\
-3.66 & 5.7 & 9.92 & 38.61 & 0 & 0 \\
0 & 0 & 0 & 0 & 68.81 & 2.53 \\
0 & 0 & 0 & 0 & 2.53 & 29.01
\end{bmatrix} \times 10^9 \text{ N/m}^2
\]

(D.5)
For left-hand Quartz the third order stiffness coefficients are given by table C-1 below [99, 113, 114];

Table D-1. Third order elastic coefficients and relations for Quartz

<table>
<thead>
<tr>
<th>Stiffness Constant</th>
<th>Value (GPa)</th>
<th>Stiffness Constant</th>
<th>Value (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{111}$</td>
<td>-210</td>
<td>$C_{344} = C_{355}$</td>
<td>-110</td>
</tr>
<tr>
<td>$C_{112}$</td>
<td>-345</td>
<td>$C_{444} = -C_{455}$</td>
<td>-276</td>
</tr>
<tr>
<td>$C_{113}$</td>
<td>12</td>
<td>$C_{122}$</td>
<td>$C_{111} + C_{112} - C_{222}$</td>
</tr>
<tr>
<td>$C_{114}$</td>
<td>-163</td>
<td>$C_{156}$</td>
<td>$(C_{114} + 3C_{124})/2$</td>
</tr>
<tr>
<td>$C_{123}$</td>
<td>-294</td>
<td>$C_{166}$</td>
<td>$(-2C_{111}^2 - C_{112}^2 + 3C_{222})/4$</td>
</tr>
<tr>
<td>$C_{124} = C_{466}$</td>
<td>-15</td>
<td>$C_{224}$</td>
<td>$-C_{114} - 2C_{124}$</td>
</tr>
<tr>
<td>$C_{133} - C_{223} = C_{233}$</td>
<td>-312</td>
<td>$C_{256}$</td>
<td>$(C_{114} - C_{124})/2$</td>
</tr>
<tr>
<td>$C_{134} = -C_{234} = C_{356}$</td>
<td>2</td>
<td>$C_{266}$</td>
<td>$(2C_{111} - C_{112} - C_{222})/4$</td>
</tr>
<tr>
<td>$C_{144} = C_{255}$</td>
<td>-134</td>
<td>$C_{334}$</td>
<td>0</td>
</tr>
<tr>
<td>$C_{155} = C_{244}$</td>
<td>-200</td>
<td>$C_{366}$</td>
<td>$(C_{113} - C_{123})/2$</td>
</tr>
<tr>
<td>$C_{222}$</td>
<td>-332</td>
<td>$C_{456}$</td>
<td>$(C_{114} + C_{153})/2$</td>
</tr>
<tr>
<td>$C_{333}$</td>
<td>-815</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

AT-cut Quartz is a special case where the cut angle ($\theta=35.25^\circ$). All the third order coefficients has to be transformed into this cut direction. The procedure is given in [114], page 67-68.
Appendix E

Experimental setup, Helmholtz Coil Design and trilayer shield

The experimental setup and the data acquisition system is shown in figure E-1. Keithley 2400 LV is a low noise and low amplitude current source that is used to control the current in the Helmholtz coil. The generated magnetic field through the coil is characterized by Lakeshore Gaussmeter (Model 475) and axial / transverse probes. The network analyzer Agilent E5061B is hooked up to the device under test (DUT) and all the setup is controlled through Labview.

Figure E-1. The Experimental Setup.

The trilayer shield is custom design and the shield material is supplied by Magnetic Shield Cooperation. The shield design and the corresponding dimensions are shown in figure E-2.
Figure E-2. Technical dimensions of the tri-layer shield with the plastic rotation table and Helmholtz coils are shown.
The Helmholtz coil is designed according the equation below;

\[ B = \frac{32\pi NI}{5\sqrt{5a}} \times 10^{-7} \ T \]  
(E.1)

Where \( B \) = Magnetic Flux density (T), \( a \) = radius of the one coil and the separation distance between the coils, \( I \) = current (A), \( N \) = number of turns. Figure E-3 below shows the design rules that is followed for designing various HelmHoltz coils.

![Figure E-3 Radius, current and number of turns dependence of the HelmHoltz coil design.](image)
REFERENCES


H. F. Tiersten, "Linear Piezoelectric Plate Vibrations- Elements of the Linear Theory of Piezoelectricity and the Vibrations of Piezoelectric Plates(Linear piezoelectric plate
vibrations, Elements of linear theory of piezoelectricity and vibrations of piezoelectric plates, covering differential equations, boundary conditions, etc)," 1969.


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