Experimental and theoretical approaches to investigating bulk and nanoscale properties of ferroelectrics

Ng, Nathaniel

2008

Ng, N. (2008). Experimental and theoretical approaches to investigating bulk and nanoscale properties of ferroelectrics. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/13540>

<https://doi.org/10.32657/10356/13540>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**EXPERIMENTAL AND THEORETICAL APPROACHES
TO INVESTIGATING BULK AND NANOSCALE
PROPERTIES OF FERROELECTRICS**

NATHANIEL NG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2008

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School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2008

Acknowledgments

The author wishes to thank Professor Freddy Boey, Assoc Prof Ma Jan, Asst Prof Su Haibin, Asst Prof Chen Lang, Asst Prof Lee Pooi See, Dr Rajeev Ahluwalia, Asst. Prof Joachim Loo, Dr. Li Tao, Dr. Erwin Wouterson, Willy, Alfred Chia, Yesie, Yang Lyn and George for their kind support in making this possible. I would especially like to thank my wife, Charmaine, for her support and encouragement to me throughout my entire Ph.D, especially when things were not easy. Most of all, I would like to thank God who was with me til the end.

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List of Symbols

γ	=	deformation angle
ϵ_0	=	permittivity of free space, 8.85×10^{-12} farad/m
ϵ^T	=	permittivity of the material at constant stress
ϵ_r	=	relative permittivity of the material
φ	=	rotation angle
ρ_{tube}	=	density of the tube (IEC, 1976)
σ_{ij}	=	Cauchy stress tensor
ν_{ij}, ν, σ	=	Poisson's ratio
ω	=	rotational speed of the motor
ζ	=	bending displacement of tube as measured from the mean position
a, b	=	wave numbers
d, d_{ij}	=	piezoelectric constant (IEC, 1976)
D_{tube}	=	outer diameter (OD) of piezoelectric tube
d_{tube}	=	inner diameter (ID) of piezoelectric tube
D	=	electric displacement (IEC, 1976)
E	=	electric field strength (IEC, 1976)
F	=	force
f_r	=	resonance frequency (IEC, 1976)
f_a	=	antiresonance frequency (IEC, 1976)
f_n	=	frequency of maximum impedance / minimum admittance (IEC, 1976)
f_m	=	frequency of minimum impedance / maximum admittance (IEC, 1976)
Δf	=	frequency bandwidth at 3dB
G	=	shear modulus
I	=	moment of inertia
k_{ij}	=	electromechanical coupling coefficient
k_{shape}	=	shape factor
K	=	dimensionless radius of gyration of the tube
l_{nodal}	=	position of the nodal point as measured from the end of the tube
L_{tube}	=	length of tube
m	=	mass
M	=	bending moment
M_{ij}	=	electrostrictive constant with respect to strain
P_i	=	polarization vector

P_r	=	remnant polarization
Q	=	electrostrictive constant with respect to polarization
Q_m	=	Mechanical quality factor
r_{contact}	=	contact radius
s	=	slenderness ratio of the beam, $s = \frac{1}{K} = \frac{4L}{\sqrt{D^2 + d^2}}$
s_{ij}	=	elastic compliance of the material
S, S_i	=	mechanical strain (IEC, 1976)
T_{melting}	=	melting point of the material
T_g	=	glass transition temperature
T	=	mechanical stress (IEC, 1976)
V	=	voltage applied across the tube's electrodes
v_v	=	vibration velocity
Y^E	=	Young's Modulus of the piezoelectric tube

Summary

The rapid development of piezoelectric ceramics in the recent years, has led to a wide range of possible applications, particularly in the area of miniaturized applications where significant advances have been made. Piezoelectric tubular transducers are key components for microactuating devices such as ultrasonic motors and devices utilizing piezoceramics outperform their electromagnetic counterparts at miniaturized scales. Traditional tubular ultrasonic transducers have been reported to produce rotational speeds up to about 300rpm with torque in the μNm to mNm range, but recently, an ultrasonic tubular transducer reaching a speed of 4000rpm has been developed. Constitutive relationships are formulated using classical Timoshenko beam theory to describe the performance of such motors as a function of the electrical inputs, the material properties such as the piezoelectric constant and mechanical quality factor, and geometry. Experimental work is carried out to support this theoretical derivation, as well as to improve the understanding of the frequency-dependent and geometric-dependent behavior of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT) as well as polyvinylidene fluoride (PVDF) copolymers, a recent development in the field of ferroelectric polymers which allows the benefits of increased strain and energy density.

The advances in the field of biomedical engineering have led to new devices incorporating piezoelectrics, which operate at the micron and nano-scales. However, due to the limitations of piezoelectric theory at the macroscopic scale, an analysis of the material behavior at much smaller scales are required. Hence, a phase-field model at the meso-scale using the Landau-Ginzburg-Devonshire approach, incorporating the Time-Dependent Ginzburg-Landau (TDGL) equations is introduced, which is used to explain size effects, thickness-dependence, as well as the role of charged defects in the thin film. The results of the present findings will finally lead to a proposal for

improving the performance of the piezoelectric ultrasonic motor, as well as to further improve understanding towards the development of sub-micron or nano-scale devices based on piezoelectric materials.

1. Introduction

Ever since the discovery of the piezoelectricity, many applications have been made possible. In recent years, the need for high power applications has increased, and particularly, materials with high piezoelectric constants and high mechanical quality factor are in high demand. Miniaturized devices on a micron or nano-scale (where the length-scales are such that surface effects play a major role) have also been receiving an increasing amount of research interest, and the development of such devices, as well as their mathematical modeling will pave the way for further advancement in this field.

A development by Li et al (2003) has seen piezoelectric ultrasonic motors reach speeds of up to 4000 rpm, a speed well above those reported in current literature, as well as that of commercial ultrasonic motors, with speeds typically in the vicinity of 300 rpm or so. This has led to the exploration of the possibility of using such a motor in a heart pump application, which is currently being investigated. Recent tests have shown that such a motor is capable of generating a flow rate exceeding 0.55 litres/minute at 2000 rpm when connected in series with a 15mm diameter inducer. However, the desire to further improve the device, so as to apply it in more challenging applications is driving research towards a greater understanding and control of the present knowledge & technology.

The piezoelectric ultrasonic transducer's performance depends primarily on two key material properties, the piezoelectric constant, d_{31} , which governs the strain per unit of voltage input to the material, and the mechanical quality factor, Q_m , which can be described as the inverse of the damping in the material to mechanical loss such as internal friction. Piezoelectric material can be doped to facilitate domain motion

reorientation thereby improving its piezoelectric properties (such as the d_{31} and d_{33} constants) (Chen, 2004), but this comes at the expense of Q_m , whose physical meaning can be defined as the reciprocal of the internal friction of the dipoles (Huang, 2004). Data from commercial vendors (APC 2004, Boston Piezo Optics 2004, Channel Industries 2004, Morgan Electroceramics 2004, Piezo Technologies 2004, Piezo Kinetics 2004, Saint-Gobain Quartz 2004) have also shown that materials with high mechanical quality factor comes at the expense of a lower d_{31} piezoelectric constant, and vice versa. Materials that balance these two properties fall into the class of “hard” PZT material, which preferred for high power applications, and this can be most significantly achieved by doping the PZT material with rare-earth elements (Yu, 1997. Rukmini, 1998. Ryu, 2003).

The high speed and torque of piezoelectric ultrasonic motors, over electromagnetic motors of the same size, confers the advantages of many applications that would otherwise not be possible. Applications which require a smaller form factor than that which electromagnetic motor technology is able to provide may exist, particularly in the biomedical sector. For such applications, not only are good material properties required, but also a thorough understanding of the physics, mathematical model (such as time-dependent Ginzburg-Landau theory), and working principles involved. In addition, material properties scale with both the frequency and the geometry of the device and understanding this mechanism would thereby be important in scaling ultrasonic motors for micro-electromechanical systems (MEMS) applications, as well as applications in ferroelectric random access memories (FRAMs) and capacitors.

1.1. Objectives

The objective of this project is two-fold. Firstly, to develop an understanding of the mechanism that links the no-load speed of piezoelectric ultrasonic motors to the material properties. Secondly, based on these material properties, to improve the material formulation and optimize processing thereby developing the material for this application. And in parallel to this, to understand how the material properties scale with the geometry, through the Timoshenko Beam theory at the macroscale, and the time-dependent Ginzburg-Landau (TDGL) theory at the nanoscale, which will pave the way to knowhow on how material properties and processing technology may be developed for miniaturized applications.

2. Literature Review

2.1. Ferroelectric Ceramics

2.1.1. Introduction to Ceramics

Since ancient times, ceramics have been formed from by taking naturally occurring raw materials as clay minerals and quartz sand, shaping the material and then hardening it by firing at high temperatures to form a final product. Ceramics can be described as the class of substances which have as their essential component, inorganic non-metallic materials (Moulson, 2003). These substances display a wide range of properties; compared to metals, ceramics typically have the following properties: brittleness, high strength and hardness at elevated temperatures, low thermal and electrical conductivity, low thermal expansion, low density, low toughness, and high elastic modulus. Ceramic materials may be classified into “traditional ceramics” such as pottery, and the industrial ceramics (sometimes called engineering ceramics or advanced ceramics) (Kalpakjian, 1995), which are tailored to the rigorous demands of engineering applications today. Another way to classify ceramic materials is as shown below:

Figure 2-1: Classification of Ceramics

2.1.2. Introduction to Ferroelectric Ceramics

A class of advanced ceramics (see Figure 2-1 above) exhibit the piezoelectric effect, a phenomenon discovered in 1880 by Jacques and Pierre Curie (Morgan, 2004a). They found that by applying a stress to certain crystals, a charge could be detected on the crystal surface, and that the degree of polarization due to the charge build-up was proportional to the applied strain. This phenomenon was named as the piezoelectric effect. Conversely, the application of an external electric field to the material, resulted in a strain being induced in the material, and this phenomenon was called the inverse-piezoelectric effect.

The materials exhibiting these properties were found to have a crystal structure without a centre of symmetry, caused by the shift of the cation/anion in the centre of the structure. On the other hand, no materials possessing a centrosymmetric crystal structure were found to be piezoelectric.

Figure 2-2: Material Crystal Classes

The figure above shows that of the non-centrosymmetric crystal classes, 20 exhibit piezoelectric properties. Of the centro-symmetric materials classes, none display piezoelectric, pyroelectric, or ferroelectric properties.

2.1.3. Pyroelectricity, Ferroelectricity and the Electrostrictive Effect

Similar to the piezoelectric effect is the pyroelectric effect, which is exhibited by materials which exhibit spontaneous polarization in the absence of an electric field, and experience a change in its polarization with temperature. The change in polarization is proportional to the temperature change and the proportionality constant is the pyroelectric coefficient. Ten of the 20 piezoelectric crystal classes are pyroelectric, having a single polar axis and being spontaneously polarized.

Like pyroelectric materials, ferroelectric materials exhibit spontaneous polarization in the absence of an electric field, and this polarization is reversible by the application of an electric field. Ferroelectric materials are named as such due to its analogy with ferromagnetic materials.

All electrical nonconductors (i.e. dielectrics) exhibit the electrostrictive effect. When an electric field is applied to electrostrictive materials, a strain is generated that is proportional to the square of the field applied, and this mechanical deformation is

independent of the polarity of the field. The constant of proportionality in this case is the electrostrictive coefficient and the relationship is given by Strain, $S_i = M_{ij}E_j^2$, where E_j is the electric field vector and M_{ij} is the electrostrictive coefficient. In ferroelectric material, which has a spontaneous polarization, the expression: Strain, $S_i = Q_{ij}P_j^2$, may also be used. This expression is more useful than the former because the constant M_{ij} tends to depend on the amplitude of the electric field, but the constant Q_{ij} does not.

Unlike the piezoelectric effect, the expansion of material is independent of the polarization of the electric field, as shown in the figure below.

Figure 2-3: Difference between the Electrostrictive and Piezoelectric Effects

In ferroelectric material which exhibit a spontaneous polarization, the piezoelectric effect can also be understood as a consequence of the electrostrictive effect. From the definition of the piezoelectric constant, $d = \partial S / \partial E$, we have:

$d = \partial / \partial E (QP^2) = 2QP(\partial P / \partial E)$. Hence, for a poled material with remnant polarization, $P = P_r$, the piezoelectric constant is related to the electrostrictive constant through the relationship: $d = 2QP_r(\partial P / \partial E)_{P=P_r}$. Conversely, an unpoled material with $P = 0$, will have a piezoelectric constant $d = 0$. It therefore follows that a ferroelectric material may operate in piezoelectric mode (with Strain, $S = d \times E$ where $d = 2QP_r(\partial P / \partial E)_{P=P_r}$)

without polarization switching, and in electrostrictive mode with polarization switching (with Strain, $S = QP^2$).

2.1.4. PZT and the Perovskite Structure

The crystal structures that give rise to the piezoelectric effect in ceramics come from a shift in the cation or anion in the centre of the structure, whereby a dipole is formed. Perhaps one of the better known material classes exhibiting piezoelectric behavior is PZT, or lead zirconate titanate. The structure of this material is the perovskite structure, a tetragonal / rhombohedral structure very close to cubic. At the centre of the unit cell is a central tetravalent metal ion; at the corners, the divalent metal ions, and at the 6 faces, the oxygen anions as shown in Figure 2-4 below.

(a) Cubic lattice above T_c

(b) Tetragonal lattice below T_c

Figure 2-4: Perovskite structure above and below T_c

Above a certain temperature, T_c , defined as the Curie Temperature (IRE, 1962), the structure is cubic, and the material is paraelectric (i.e. non-ferroelectric). However, when the temperature is brought below T_c , the structure takes on a tetragonal symmetry and a crystallographic phase change occurs from centrosymmetric to asymmetrical, non-centrosymmetric, and the positive and negative charge sites no longer coincide. Each of these sites form an electric dipole, and neighbouring dipoles tend to align with each other, forming regions of local alignment, or Weiss domains.

Within the Weiss domain, all dipoles are aligned, giving a net dipole moment to the domain, and hence a net polarization.

To make the piezoelectric material useful, the initially randomly oriented domains [Figure 2-5 (a)] are aligned during a process called poling. During poling, an electric field is applied which causes the domains most nearly aligned [Figure 2-5 (b)] with the field to grow at the expense of other domains [Figure 2-7]. After poling, the domains remain locked in approximate alignment [Figure 2-5 (c)], giving the material a remnant polarization and a permanent deformation.

Figure 2-5: Domain Orientations: (a) Random Orientations before Poling, (b) Aligned Domains During Poling, and (c) Alignment retained After Poling

The following curve shows how hysteresis in the P-E (Polarization – Electric Field) curve, implies that, upon the removal of a strong electric field, a remnant polarization remains.

Figure 2-6: Illustration of Remnant Polarization in a Piezoelectric Material

Figure 2-7 below shows how domains closely oriented to the direction of the electric field grow at the expense of other domains during poling.

Figure 2-7: Domain Orientations & Sizes Before & After Poling

Before poling, the ceramic material is isotropic. After poling, the material takes on anisotropic properties and the direction of polarization becomes an axis with an infinite order of symmetry which is chosen as the z (or 3) axis (IEC, 1976).

2.1.5. Properties of Piezoelectric Ceramics and Characterization

Upon the completion of the poling process, piezoelectric ceramics are characterized to determine their material properties. The experimental techniques involved are outlined in international standards, such as the IEC 302, 444, and 483 standards (IEC, 1969, 1973, 1976), and the ANSI/IEEE 176-1987 standard, as well as the standard procedures used by various vendors, such as Morgan Electro Ceramics (Morgan, 2004b), which are also in compliance with the international standards.

2.1.5.1. The Piezoelectric Constants

Poled piezoelectric ceramics, upon the application of a mechanical stress, experience a polarization proportional to that stress. In the inverse-piezoelectric effect, a strain in the material is observed upon the application of an electric field, and the magnitude of that strain is proportional to the field applied.

The piezoelectric response is the sum of the intrinsic contributions from the lattice deformation of individual grains, plus the extrinsic contributions due to changes in the ferroelectric domain populations (Hall, 2004, Li, 1991). The domain walls have a significant influence on the properties of PZT ceramics (Zhang, 1994)—under the application of an electric field, the domain walls move to minimize the domain energy, thereby influencing the domain structure (size, shape & population), resulting in a change in the net strain and polarization. (Sherrit, 1997). Mobile domain walls tend to result in properties characteristic of soft PZT (Zhang, 1988), whereas domain walls are pinned by impurities result in properties characteristic of hard PZT.

The electrical behaviour of an unstressed medium in the presence of an electric field is given by:

$$D = \epsilon E \text{ (Charge Density = Permittivity} \times \text{Electric Field)} \dots\dots\dots (2.1)$$

The mechanical behaviour of the same medium under zero field is given by Hooke's Law:

$$S = sT \text{ (Strain = Compliance} \times \text{Stress)} \dots\dots\dots (2.2)$$

Piezoelectricity involves the combined effect of the two mediums and the general form of the constitutive relationships is:

$$\{S\} = [s^E]\{T\} + [d]\{E\} \dots\dots\dots (2.3)$$

$$\{D\} = [d]^t\{T\} + [\epsilon^T]\{E\} \dots\dots\dots (2.4)$$

Here, the superscript, E, in s^E denotes the condition of constant electric field, or short-circuit condition, whereby the electrodes on the piezoelectric material are short-circuited to keep the electric field constant. Similarly, the superscript, T, in ε^T denotes the condition of constant stress. The matrix $[d]^t$ denotes the transpose of the matrix, $[d]$.

For tetragonal PZT or BaTiO₃, as well as any other material that belongs to the 4mm (C_{4v}) point group, $d_{31} = d_{32}$, and $d_{15} = d_{42}$ with the remaining constants equal to zero (ANSI-IEEE 176-1987). For these materials, the piezoelectric $[d]$ matrix consists of 3 independent constants, d_{31} , d_{33} and d_{15} as follows:

$$[d] = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \text{ m.V}^{-1} \dots\dots\dots (2.5)$$

By convention, the direction in which the ceramic element is polarized is designated as direction 3. Directions 1 & 2, both perpendicular to direction 3, are equivalent. It follows that:

1. d_{33} is the induced polarization in direction 3 per unit stress applied in direction 3,
or the induced strain in direction 3 per unit electric field applied in direction 3.
2. d_{31} is the induced polarization in direction 3 per unit stress applied in direction 1
or the induced strain in direction 1 per unit electric field applied in direction 3.
3. d_{15} represents the induced polarization in direction 1 per unit shear stress applied
about direction 2 or induced shear strain about direction 2 per unit electric field
applied in direction 1.

2.1.5.2. Characterization of the Piezoelectric Constant, d_{31}

The strain in the piezoelectric material is proportional to the electric field applied, and this is given by the relationship:

$$S_1 = d_{31}E_3, \dots \dots \dots (2.6)$$

where E_3 is the electric field in the polarization direction,

d_{31} is the piezoelectric constant, and

S_1 is the strain in the direction perpendicular to the electric field.

The piezoelectric constant, d_{31} , may thereby be obtained from the gradient of the Strain-Electric Field curve. For piezoelectric tubes, the 4 electrodes of the tube are short-circuited by the application of silver paste. A voltage is applied across the inner and outer electrodes, and the strain measured by a displacement-measuring device such as the fonic sensor.

Figure 2-8: Setup for the Characterization of d_{31}

The relationship between these two properties is used to plot the Strain-Electric Field curve whereby the piezoelectric constant, d_{31} , is obtained. Normally, a low electric

field is used to avoid hysteresis, which will cause an inaccurate measurement of d_{31} to be obtained.

2.1.5.3. Hysteresis Loops

Ferroelectric material has the ability to exhibit a spontaneous polarization, and the ability to switch its polarization state upon application of an electric field. This is exhibited by the polarization-electric field (P-E) hysteresis loops in the material. Polarization reversal in ferroelectric material is distinguished from behavior in capacitors and conductors as illustrated in the current-voltage and polarization-electric field graphs below (IEEE UFFC, 2003):

Figure 2-9: Effect of Polarization Reversal on Current-Voltage characteristics of the material (top row) and Polarization-Electric Field characteristics of the material (bottom row).

2.1.5.4. Electromechanical coupling coefficient

The electromechanical coupling coefficient, k , measures the ability of the material to change energy from one form to another. When a piezoelectric crystal is compressed

to generate a charge on its surface, the electromechanical coupling coefficient is given by:

$$k^2 = \frac{\text{mechanical energy converted to electric charge}}{\text{input mechanical energy}} \dots\dots\dots (2.7)$$

For the inverse piezoelectric effect, the coefficient is given by:

$$k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \dots\dots\dots (2.8)$$

and is numerically identical to the earlier value of k^2 .

There are four electromechanical coupling coefficients, k_{33} for the vibration of thick specimens along the direction of polarization, k_{31} for the transverse vibration (vibration perpendicular to the direction of polarization), k_p for the radial vibration of a thin disc, and k_t for vibration of thin specimens along the direction of polarization.

2.1.5.5. Concept of Equivalent Circuit

When the electrical impedance of a piezoelectric material is measured as a function of frequency, the impedance begins as a pure resistance, and becomes inductive with increasing the frequency. When the frequency is increased further, the impedance once more becomes a pure resistance, but at a higher resistance level, and then returning to its capacitive state. This behaviour is often represented by the following equivalent circuit with capacitances C_0 and C_1 , inductance, L , and resistance R .

Figure 2-10: Piezoelectric Equivalent Circuit

The constants L_1 and C_1 are related to the mass and elastic compliance of the crystal, multiplied by a factor representing the piezoelectric effect. The mechanical damping of the crystal is represented by R_1 . The ratio C_1 / C_0 is indicative of the strength of the piezoelectric effect. This method is often used to find the resonance frequency of a piezoelectric transducer.

2.1.5.6. Mechanical Quality Factor

This analogy of the equivalent circuit allows another parameter to be introduced, the mechanical quality factor, Q_m . Q_m is given by:

$$Q_m = \frac{\text{energy stored in a period (in } L \text{ and } C)}{\text{energy dissipated in a period (in } R)} \dots\dots\dots (2.9)$$

This quantity is also a measurement of the sharpness of the resonance peak and may be calculated from:

$$Q_m = \frac{f_r}{\Delta f} \dots\dots\dots (2.10)$$

where $f_r = \frac{1}{2\pi\sqrt{LC}}$ is the resonance frequency, and Δf is the band width at 3dB corresponding to an amplitude reduction of $1/\sqrt{2}$ in relation to the resonance as shown in Figure 2-11 below.

Figure 2-11: Q_m as a Measurement of the Sharpness of the Resonance Peak

Using this analogy of the equivalent circuit, the mechanical quality factor may be obtained by plotting a displacement versus frequency curve (instead of admittance versus frequency). This quantity has a similar physical meaning, the ratio of energy dissipated per cycle to the energy dissipated per cycle, but may not be necessarily equal to the former. In a physical sense, it is a measure of the mechanical loss due to internal friction during vibration, and it is an important material property in the characterization of piezoelectric ceramics.

2.1.5.7. Characterization of the Mechanical Quality Factor

The mechanical quality factor is obtained through the relationship:

$$Q_m = \frac{f_a^2}{2\pi R_1 (C_0 + C_1) f_r (f_a^2 - f_r^2)}, \dots\dots\dots (2.11)$$

where C_0 , C_1 , and R_1 are the capacitances and resistances in the piezoelectric equivalent circuit (Figure 2-10):

To obtain the values of L_1 , C_1 , R_1 and C_0 of the piezoelectric equivalent circuit, the impedance analyzer, HP4194A (Masys 2003) may be used. This equipment measures the impedance data and carries out a curve fit in order to estimate the equivalent

circuit constants. For $Q_m > 3$, an alternative way to obtain the mechanical quality

factor uses the sharpness of the resonance peak, i.e. $Q_m = \frac{f_r}{\Delta f}$, as mentioned earlier.

2.1.5.8. Density

The density of the piezoelectric tube, ρ_{tube} , may be obtained by measurement from a densimeter, or from its mass and volume ($\rho_{\text{tube}} = \text{mass} / \text{volume}$), using an electronic balance, and digital vernier caliper or micrometer. A second way to obtain the density may be obtained is through the relationship:

$$\frac{\rho_{\text{tube}}}{\rho_{\text{water}}} = \frac{m_{\text{air}}}{m_{\text{air}} - m_{\text{water}}} \dots\dots\dots (2.12)$$

where m_{air} is the mass of the object in air on an electronic balance, m_{water} is the measurement when the object is submerged in water, and ρ_{water} is the density of water.

In both techniques, measuring the densities of the sintered tubes before the electrodes are added will increase the accuracy of the measurement. This is especially the case when the piezoelectric tube walls are thin, as the thickness of the electrodes becomes significant.

2.1.5.9. Young's Modulus

The Young's Modulus is a measure of the stiffness of the material. Using the resonance method, the value of the Young's Modulus may be obtained from the length, resonance frequency and the density of a piezoelectric tube from the relationship:

$$\text{Young's Modulus, } Y^E = 4L_{\text{tube}}^2 f_r^2 \rho_{\text{tube}} \dots\dots\dots (2.13)$$

2.1.6. Modifications of properties

The properties of PZT are primarily dependent on two factors—firstly, the material composition, which includes the dopants added to the material, and secondly the processing method used to fabricate the material. Some of the materials PZT has been doped with include Lanthanum, Sodium (Rukmini, 1998), and various rare earth elements.

In ferroelectric polymers, the material properties are dependent on factors such as the composition, the mole fraction of the copolymer (or terpolymer), branching, crystallinity, as well as the material processing.

2.1.7. Hard and Soft Piezoelectric Materials

Small quantities of a *donor dopant* added to a ceramic formulation create metal (cation) vacancies in the crystal structure. The result of such doping gives rise to *soft ceramics*. *Acceptor dopants*, on the other hand, create oxygen (anion) vacancies in the crystal structure, and these are done to produce *hard ceramics*. Thus, piezoelectric materials may sometimes be classified into categories of “Hard” materials, and “Soft” materials (Morgan, 2004a). The properties of hard ceramics are generally opposite to those of soft ceramics. High power “Hard” ceramics can withstand high levels of electrical excitation and mechanical stress. They are thus suited for high voltage or high power generators and transducers. High sensitivity “Soft” ceramics have high sensitivity and permittivity, but are susceptible to self-heating beyond their operating temperature range. These find applications in sensors, low-power motor-type transducers, receivers, and low power generators.

Soft ceramics are characterized by large electromechanical coupling factors, large piezoelectric constants, low mechanical quality factors and poor linearity. They are easier to polarize or depolarize than hard ceramics, but are generally more unstable

and have a lower Curie Temperature. A comparison of the differences between soft and hard piezoelectric material is shown in the table below.

Table 2-1: Comparison of Hard and Soft Piezoelectric Material

Characteristic	Soft Ceramic	Hard Ceramic
Piezoelectric Constants	larger	smaller
Permittivity	higher	lower
Dielectric Constants	larger	smaller
Dielectric Losses	higher	lower
Electromechanical Coupling Factors	larger	smaller
Electrical Resistance	very high	lower
Mechanical Quality Factors	low	high
Coercive Field	low	higher
Linearity	poor	better
Polarization / Depolarization	easier	more difficult

2.1.8. Fabrication of Piezoelectric Ceramic Material

There are various methods of fabricating PZT material including the machining of PZT tubes from raw billets, the hydrothermal method, gel-casting (Guo, 2003), electrophoretic deposition (Li, 2003), slip casting, injection molding (Li, 2003) and extrusion (Li, 2003). Some of these methods are described in the following sections.

2.1.8.1. Electrophoretic Deposition (Li, 2003. Ma, 2004)

In electrophoretic deposition, ceramic bodies are formed directly from a stable colloid suspension by a DC (direct current) electric field (Chan, 1997. Gani, 1994. Sarkar, 1996). Through the effect of the electric field, charged particles in the suspension move towards an oppositely charged electrodes where they are deposited.

The starting materials are prepared from raw oxide powders of PbO, ZrO₂ and TiO₂ which are dried for 24 hours to remove the water content. The powders are then weighed according to the desired composition, and mixed together. To homogenize

the materials, the powders are ball-milled with ZrO_2 balls and ethanol for about 24 hours. They are then dried and the mixed powders are calcined at a high temperature. Next, the powders are removed and then planetary ball milled in ethanol. Upon completion, the powders are sieved to remove the large agglomerates.

From the starting PZT material, a suspension of the ceramic powder is formed, by adding it to an organic solvent such as ethanol, acetone, or water. The suspension is dispersed ultrasonically and a stabilizer is added such as ether glycol.

The suspension, held in a metal (or other conducting material) container, is placed on a magnetic stirrer, and a rod, normally graphite inserted into the fluid medium. The magnetic stirrer inhibits the sedimentation of the particles in the suspension, and keeps the suspension uniform.

The rod is connected to the terminal of a power supply, and the container to the second terminal. The power supply provides a predetermined DC voltage which produces an electric field whereby particles are moved to deposit themselves onto the rod. After a timed interval (about 3-10 minutes, depending on the thickness, concentration, and voltage), the graphite rod is removed, now with a layer of particles deposited on it.

The deposited particles are then heat treated to form the final piezoelectric tube. The particles are heat treated to a first temperature (normally between 500 and 1000 deg C). This solidifies the particles onto the surface of the rod, and burns off the rod, the tube at this stage is closed off at one end. The particles are then heated to a second, higher temperature (typically between 850 and 1300 deg C) in a process called sintering. The closed end of the tube is cut off and the final tube is obtained.

2.1.8.2. Ultrasonic Machining (Secondary Process)

Sometimes, tubes may be formed from raw billets and machined to the desired dimensions. In this project, the tubes used were purchased commercially from Boston Piezo Optics, which machined them from select, void free, high quality, homogeneous PZT billet material via a Sonic Milling machine (Boston Piezo, 2004).

In this process, called ultrasonic machining, material is removed from a surface by erosive process of fine abrasive grains (Kalpakjian, 1995). The abrasive slurry is injected between the workpiece and the tool. The tip of the tool vibrates at low amplitude (12.5-75 μ m), with a frequency of about 20kHz, and does not come into contact with the workpiece.

Figure 2-12: Ultrasonic Machining Process

The vibration transmits a high velocity to the abrasive grains in the slurry between the tool and the workpiece. Due to the short “time of contact” between the particles and the surface (10-100 μ s), and the small area of contact, the impact stresses created are sufficient to cause microchipping and erosion of the workpiece surface.

The key advantage of using a ultrasonic machining, is that the process is much gentler to the walls of the tube, minimizing surface imperfections that could eventually result in cracks or breakage. This process does not produce a heat-affected zone, nor does it cause any chemical / electrical alterations on the workpiece surface. It is best suited for materials that are hard and brittle, such as ceramics, carbides, precious stones, and hardened steels.

A variation of traditional ultrasonic machining is rotary ultrasonic machining (Li, Z. 2004, Hu, 2002) which is a hybrid material removal process. combining the removal mechanisms of diamond grinding and ultrasonic machining.

2.1.8.3. Slip Casting

In order to prepare the PZT starting powders, the raw powders (PbO, ZrO₂, TiO₂, and any dopants, such as La₂O₃) are first weighed out according to the stoichiometric ratio. The powders are then placed in a bottle, and mixed with zirconia balls & ethanol, to be ball milled. The powders are then dried and heated to a temperature of about 800 deg C and then cooled back to room temperature. Next, the PZT powders is added to ethanol to form a slurry. Two to three drops of dispersant are added. Gas bubbles (if any), are then removed from the slurry by placing it in a vacuum chamber. The slurry is then placed in the ultrasonic cleaner for about 30 minutes, and then magnetically stirred for 30 minutes. The slurry is then poured into a CaSO₄ mold. When no more slurry can be added, the mold is left for drying. The tube is then removed from the mold and sintered.

With normal slip casting, particles with a higher density tend to sink to the bottom, resulting in tubes of non-uniform properties. In order to keep these properties as uniform as possible, sometimes the tubes may be “rolled” during slip casting process.

During this process, however, it is important to minimize the formation of bubbles & pores.

2.1.8.4. Adding of Electrodes and the Poling Process

The next stage of the process involves the addition of electrodes to the tube by applying metallic paste to the inner & outer surfaces of the tube. Poling the tube is then carried out to form a transducer, normally done by applying an electrical field with a voltage of about 2-4 kV/mm to the electrodes. The voltage is applied for a duration between 20 to 120 minutes, and a temperature typically between 100 and 150 deg C. Poling is carried out in a silicone oil bath to reduce the risk of short circuit.

2.1.9. Applications of Piezoelectric Ceramics

2.1.9.1. Introduction

Applications of piezoelectric ceramics generally fall into four categories – generators, sensors, actuators, and transducers.

Figure 2-13: Applications of Piezoelectric Ceramics

As *generators*, piezoelectric ceramics can produce voltages sufficient to spark an electrode gap, and thus find applications as ignitors in fuel lighters, gas stoves, or welding equipment. Sometimes the electrical energy generated is stored, allowing the possibility for generators to be used as solid state batteries for electronic circuits. Piezoelectric *sensors* convert physical parameters, such as acceleration or pressure, into an electrical signal. *Actuators* convert an electrical input into a physical displacement, or a mechanical force. These find applications as micro-pumps,

hydraulic valves or as motors. Piezoelectric *transducers* convert electrical energy into vibrational mechanical energy, which is used to perform a task. Applications of piezoelectric transducers include ultrasonic cleaning, atomizing liquids, or the drilling & milling of ceramics.

2.1.9.2. Piezoelectric Actuators and Transducers

The focus of this research is on piezoelectric actuators and transducers, whereby electrical energy is converted to a form of mechanical energy. Various types of piezoelectric actuators (Uchino, 1993) were developed from this inverse-piezoelectric effect—multilayer actuators, and bending displacement-type actuators in the bimorph family, the monomorph, unimorph, and bimorph. Bimorph actuators use two piezoelectric plates with an electrode bonded in between, and two electrodes on the outside of the plates (Hayashi, 1991). Unimorph actuators, on the other hand, use just one piezoelectric plate, bonded to a non-piezoelectric material. Functionally gradient materials have also been reported to be used to create monomorph-type piezoelectric actuators (Wang, 1999), using electrophoretic deposition.

2.1.9.3. Tubular-Type Actuators

In a different category from these bending-displacement type actuators is the tubular-type actuators. Instead of a flat layer of piezoelectric material sandwiched between electrodes, a tube of piezoelectric material is coated internally and externally with a layer of electrode. By dividing the outside electrode layer of the piezoelectric tube into four quadrants, and the inside with a single electrode all round, appropriate voltages can be applied to create an electric field to cause a strain in the material, inducing a bending action.

Piezoelectric tubular actuators are commonly used in applications such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), and lateral force

microscopy (LFM) (Gan, 2000). Other piezoelectric actuator applications, that do not use a tube include printer heads (Uchino, 1997), 3-D positioners (Uchino, 2002), multi-layer actuators (Yao, 2001).

When the voltages induced are changed sinusoidally, and if the voltage between each electrode the next has a 90° degree phase lag behind the other, a jiggling motion is induced as follows (Boey, 2004. Boey 2005. Li, 2003. Li, 2004b. Li, 2005):

Figure 2-14: Jiggling Motion of a Piezoelectric Tube

The jiggling motion of the piezoelectric tube causes the end cap on the top to rotate in the manner shown above, and if the end cap is attached to a shaft, the rotational motion can be converted to useful output.

2.1.9.4. The Piezoelectric Heart Pump

(Boey, 2004. Boey 2005. Li, 2003. Li, 2004b. Li, 2005)

The piezoelectric heart pump leverages on the technology of tubular type actuators, by the addition of an axial-inducer mounted onto the shaft (rotor). This rotational motion generated can be converted into the forward motion of a fluid. The device is encased in a biocompatible housing as shown below:

Figure 2-15: Cross Section of Heart Pump

Figure 2-16: 3D Model of the Axial Inducer of the Heart Pump

The entire assembly is encased in a housing that isolates the piezoelectric tube from the fluid medium, which would otherwise introduce an additional damping to the jiggling motion of the tube. In this manner, the device functions as continuous flow cardiovascular heart pump, and by assisting the heart in pumping fluid throughout the body, the heart is given a chance to recover (Cooper, 1995. Dreyfus, 1996. Lachat, 1999. Lonn, 1995. Meyns, 1995. Sweeney, 1996. Waldenberger, 1995). Currently, no existing heart pump design incorporates piezoelectric ceramic (such as PZT) or piezoelectric polymer material as the means by which mechanical power (or hydraulic power) is generated.

The technologies involved in the pump may be described in Figure 2-17:

Figure 2-17: Overview of the Technologies Involved in the Piezoelectric Heart Pump

The portion of the design involving the technology of the inducer and fluid mechanics (Gharib, 2003), as well as hemocompatibility (ASTM, 1997. Viole, 2003), and is beyond the scope of this report.

2.2. Ferroelectric and Electroactive Polymers

Electroactive polymers (EAPs) are a recent development competing with existing ferroelectric ceramics in actuator and transducer applications. Properties such as improved strain and energy densities in EAPs compared to ferroelectric ceramics (Chu, 2006), as well as other advantages such as low cost, biocompatibility and the fact that the material is lead-free, have led to considerable interest in this area.

EAPs may be defined as materials that change their shape in response to electrical stimulation. These polymers are typically classified into two major categories based on their activation mechanism: ionic EAPs (activated by an electrically-induced

transport of ions or molecules), and electronic EAPs (activated by an external electric field or by Coulomb forces) (Bar-Cohen, 2004). The former category includes polyelectrolyte gels, ion polymer metal composites (IPMCs), conducting polymers, and carbon nanotubes (Bao, 2004) and devices typically consist of two electrodes and an electrolyte. These can be activated by very low voltages (in the order of 1 V), but there is a need to maintain their wetness and they can be operated only within a surrounding electrolyte medium. Furthermore, ionic EAPs which involve water content cannot be operated at voltages above 1.23V, due to damage to the material through hydrolysis (Bao, 2004). Except for conductive polymers, ionic EAPs experience a difficulty in sustaining a constant displacement under DC voltage (Bao, 2004).

The latter category of electronic EAPs includes ferroelectric / piezoelectric polymers, electrostrictive polymers, dielectric elastomers, and liquid crystal polymers (Zhang, 2002b), and require typically high driving electric field, in the order of 10-100MV/m, but they have a number of key advantages. These include a faster response, operability in air (conductive polymers require a protective layer to prevent oxidation), and the ability to hold the induced displacement under a dc voltage. Among these, poly(vinylidene fluoride) or PVDF and its copolymers are the most exploited ferroelectric polymers. They consist of a partially crystalline component in an inactive amorphous phase. Large applied AC fields (~ 200 MV/m) induce electrostrictive (non-linear) strains of nearly $\sim 2\%$. P(VDF-TrFE), a PVDF polymer which has been subject to electron radiation has shown electrostrictive strain as high as 5% at 2 Hz, 150 MV/m (Zhang, 2002b).

Zhang et al (2002b) have demonstrated that the energy density of electron-irradiated piezoelectric polymers with an appropriate dielectric filler can be up to

0.13 J/cm³ at an electric field of only 13MV/m, which is comparable to the best performing piezoelectric and electrostrictive ceramics. 100 % PVDF materials have also been reported to achieve up to 0.13 J/cm³ of electromechanical energy (Xia, 2002. Xia, 2006). Later, the same group reported energy densities of up to 9 J/cm³ in P(VDF-TrFE-CFE) 58.3/34.2/7.5 mol% and 17 J/cm³ in P(VDF-CTFE) 91-9 mol% (Chu, 2006). This shows that PVDF-based electroactive polymers have potential to replace traditional PZT in some piezoelectric devices, as well as expand to areas previously not possible. The use of copolymer with VDF content between 60 and 70%, for a stable beta phase (Chen, 1998), over pure PVDF allows higher electromechanical coupling coefficient ($k = 0.20$ versus 0.11) (Lovinger, 1983), fast polarization reversal (Furukawa, 1997), and higher crystallinity. The copolymer crystallizes directly into the beta phase upon cooling from the melt, and hence does not require mechanical drawing which changes the existing morphology and may introduce artifacts such as voids and defects (Lovinger, 1979). Molecular dynamics simulations have shown that the copolymer exhibits a lower threshold stress and higher mobility at the interface between polar and nonpolar phases under uniaxial stress (Su, 2004).

Piezoelectric polymers have gained considerable interest since the discovery of strong piezoelectricity in poly(vinylidene fluoride), or PVDF, by Kawai et al. in 1969. Very large piezoelectric coefficients, 6-7 pC/N⁻¹, were observed in poled thin films of PVDF, 10 times larger than that observed in any other polymer (Kawai, 1969). In fact, among known synthetic organic materials, this class of polymer currently possesses the highest electromechanical responses over a broad temperature range (Zhang, 2002a). Since then, most research work on this class of polymers has been focused on areas such as the reduction of the Curie temperature, the narrowing of the

polarization-hysteresis loop, as well as the generation of large electromechanical response at ambient temperature (Petchsuk, 2003).

PVDF has a glass transition well below room temperature ($T_g = -35^\circ\text{C}$) and is typically 50-60% crystalline (Harrison, 2002). It comprises of ordered regions of monomer units (crystallites) surrounded by an amorphous sea of scrambled, spaghetti-like chains (Zhang, 2002a). Samples are typically prepared from a melt (Figure 2-18a), mechanically stretched, to orient the molecular chains (Figure 2-18b), and poled under tension (Figure 2-18c) to give it its piezoelectric properties.

Figure 2-18: Processing of PVDF (Harrison, 2002).

Stretching the PVDF polymer aligns the amorphous strands in the plane of the film and this facilitates uniform rotation of the crystallites by an electric field (Harrison, 2002). Figure 2-19 shows the change in the XRD peak profile before and after stretching.

Figure 2-19: XRD Peak Profile Before & After Mechanical Stretching (Zhang, 2002)

During this process, an electric field of about 50-100MV/m is applied to the polymer under tension, thereby giving PVDF its piezoelectric properties. This process would typically take about 2 hours, at a stretch ratio of 5:1, 85-100°C (Vinogradov, 2002). PVDF has the structural formula $-(CH_2-CF_2)_n-$ as shown:

Figure 2-20: Structure of PVDF

2.2.1. Synthesis of PVDF

In polymer synthesis, reaction kinetics usually follow two main routes—*step-growth* polymerization (also called polycondensation) and *chain-growth* polymerization (also called polyaddition). Polyvinylidene fluoride (and its copolymers) follow the polyaddition route, where the chain is extended by the addition of a monomer to an active chain. This is in contrast to polycondensation which occurs with a random reaction of molecules which may be any combination of monomer, oligomer, or a longer chain molecule.

By the successive addition of vinylidene fluoride (1,1-difluoroethylene) monomer units, PVDF is synthesized using the following reaction (Ferren, 1988): $n(CH_2=CF_2) \rightarrow -(CH_2-CF_2)_n-$ at high temperature (50-150°C) and high pressure (10-300atm).

Reactions start with an initiation step whereby the initiator (e.g. I—I) forms a radical species, usually by dissociation ($I-I \rightarrow 2I^*$), for example, benzoyl peroxide:

Figure 2-21: Dissociation of Benzoyl Peroxide

This follows with the addition of a single monomer to that species:

The chains propagate with the addition of subsequent monomers to the active species:

Termination occurs with either combination ($P_n^* + P_m^* \rightarrow P_n-P_m$), or disproportionation ($P_n^* + P_m^* \rightarrow P_n^= + P_m$) depending on the conditions and the monomer used.

This reaction is usually carried out in emulsion polymerization, with a dispersing medium such as water (Ferren, 1988), which provides better heat dissipation as compared to bulk polymerization. The copolymer, P(VDF-TrFE) is synthesized in a similar manner (Yagi, 1979).

Chains typically take up orientations of :

—CH₂CF₂CH₂CF₂— (head to tail),

—CH₂CF₂CF₂CH₂— (tail to tail), and

—CF₂CH₂CH₂CF₂— (head to head)

Most of the chains end up in “head-to-tail” orientation—the percentage of defects (tail to tail or head to head) is present in the order of about 10% (Wilson, 1968). Other defects come from side reactions such as chain transfer to monomer/solvent/polymer. PVDF is the principal commercially-available piezoelectric polymer and is typically produced in the form of thin films of thickness ranging from 9 to 800 μm (Vinogradov, 2002). Other configurations are also possible; it has been extruded as a tubular film by Xu, 2004.

Unlike previously reported piezoelectric polymers which possessed a ∞2 symmetry, the polymers investigated by Kawai, 1969, have a mm2 symmetry and

piezoelectric constants d_{31} , d_{32} , d_{33} , d_{15} and d_{24} . The piezoelectric matrix for poled PVDF after uniaxial stretching is (Fukada, 1981b):

$$d_{ij} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

If the poling is carried out without stretching, the 1 and 2 directions are equivalent and the matrix for the material of C_v symmetry is (Fukada, 1981b):

$$d_{ij} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Typical properties of PVDF are $d_{33}=20\text{pC/N}$, $d_{31}= -5$ to -16 pC/N, $d_{32}= -3$ to -5pC/N , $\epsilon_r= 9$ to 11 . (Piezotech, S.A.), $T_{\text{melting}} = 175$ °C (Davis, 1993), density 1780 kg/m³, $Y_1^E = 2.56\text{GPa}$, $Y_2^E = 2.6\text{GPa}$, (Vinogradov, 2002), $\nu_{21}\sim 0.1$ and $\nu_{31}\sim 0.8$ (Tasaka, 1981).

The piezoelectric properties of PVDF arise from the positioning of the fluorine atoms relative to the carbon atoms in the carbon chain. The dipole moment of the C-F bond is about 1.4 D (Debye units) (Murayama, 1976). In PVDF, rotation about the carbon-carbon skeletal bond results in a change in potential energy (Figure 2-22). The angle of rotation is zero when all four carbon atoms lie on the same plane. At this point, the repulsion is greatest, and the potential energy is a maximum. Rotating by an angle of about 60° and 300° , the structure takes on the *gauche* G and $\bar{G}$ conformations, and at an angle of 180° , the structure takes on the *trans* conformation (Figure 2-22).

Figure 2-22: Interactions between fluorine and hydrogen atoms on adjacent carbon atoms in PVDF polymer chains lead to changes in the potential energy as the bond connecting the carbon atoms is rotated. (Zhang, 2002a).

Figure 2-23: PVDF α , β , and γ forms

The crystal structures of PVDF are described by: (1) the conformations of the chains (as a series of trans (T) or gauche (G) linkages), (2) the orientation of the chain sequences about the chain axis (parallel or antiparallel), and (3) the relative directions of adjacent chains, i.e. up-up (same direction) or down-down (opposite direction) as shown below.

Figure 2-24: Trans & Gauche linkages

There are four major crystalline forms of PVDF (Lovinger, 1982). Form I is the β phase, consisting of chains in an all-trans planar zigzag configuration (Figure 2-24). This form is polar, having a net dipole of 2.1 Debye per monomer unit (Zhang, 2002a, Fukada, 1981b). Both the α phase (form II) and δ phase (form IV) consist of alternating *trans* and *gauche* sequences (TGT $\overline{G}$). In the α phase, the individual carbon-fluorine bond orientations cancel each other out, while in the δ phase, they are oriented in one direction around the chain direction to form a net dipole (Bachmann, 1980). The γ phase (form III), had chain conformations in the sequence TTTGTTT $\overline{G}$ (Figure 2-24). The data for each of these phases is shown below:

Table 2-2: Lattice Constants & Point Groups of PVDF (Fukada, 1981b)

Form	Lattice Constants				Point Group
	a (nm)	b (nm)	c (nm)	Others	
Form I (β phase)	0.858	0.491	0.256		C_{2v} or $mm2$ (orthorhombic)
Form II (α phase)	0.496	0.964	0.462		C_{2h} or $2/m$ (monoclinic)
Form III (γ phase)	0.866	0.493	0.258	$\beta = 97^\circ$	C_2 or 2 (monoclinic)

2.2.2. Processing of PVDF (Zhang, 2002a).

PVDF takes on the α phase when cooled from a melt, or cast from solutions of an organic solvent. In order to get the useful β phase, which has the net dipole moment, it is necessary to mechanically tension the PVDF film to convert the TGT $\overline{G}$ chains into the polar all-*trans* β phase. Typically, samples are stretched to up to 4 times its original length and this goes up to stretch ratios of up to 7:1 (Ramos, 2005). Alternatively, the β phase may be obtained from quenching melted PVDF under high pressure or casting from hexamethylphosphoric triamide solutions (Zhang, 2002a).

Once the β phase is obtained, the material must be poled via either: (a) electroding the polymer surfaces with a metal, followed by application of an electric field, or (b) using a corona discharge, whereby a needle electrode is placed a centimeter or two from the film. In the latter case, no electroding is required. A typical poling condition is about 60 MV/m (Ramos, 2005). The behavior of PVDF under poling has also been investigated using atomistic modeling. Calculations on a PVDF chain of 20 repeat units by Ramos, et al. (2005) showed a transition from the α to the β zigzag form beginning at about 37% mechanical strain without electric field. Without any mechanical strain, an α to β transition could be induced under high electric fields of 100 MV/m. It should be noted that poling cannot correct for head-head or tail-tail defects occurring during processing nor does it influence the degree of crystallinity in the material; the main effect is the partial rotation of the chains and to optimize the α to β transition that occurs under mechanical stretching (Ramos, 2005).

Noda, 2003, have also used the VDF oligomer, $\text{CF}_3(\text{CH}_2\text{CF}_2)_{17}\text{I}$ evaporated onto metal surfaces at approximately liquid-nitrogen temperatures, whereby large remnant polarization ($P_r = 130\text{mC/m}^2$) has been reported. The $\text{CF}_3(\text{CH}_2\text{CF}_2)_{17}\text{I}$ oligomer is

commercially synthesized using the telomerization method by companies such as Daikin Kogyo Co., Ltd (Noda, 2001, Noda, 2000).

2.2.3. P(VDF-TrFE)

PVDF also forms random copolymers with trifluoroethylene (TrFE) and tetrafluoroethylene (TFE) (Bune, 1998), which are currently the state of the art in piezoelectric polymers and are currently the only commercially available piezoelectric polymers (Harrison, 2001). Of particular interest is the P(VDF-TrFE) copolymer, with structural formula $\text{---}(\text{CH}_2\text{---CF}_2)_x\text{---}(\text{CHF---CF}_2)_{1-x}\text{---}$ with x typically in the range of 0.50 to 0.75 for commercially available copolymers. Unlike PVDF, it does not have to be mechanically drawn in order to obtain the ferroelectric β -phase (Zhang, 2002a, Harrison, 2002). Both PVDF and P(VDF-TrFE) are polymorphic and exist in several crystal forms (Lovinger, 1982), but P(VDF-TrFE) crystallizes to a larger extent than PVDF (up to 90% crystallization versus 50-60%). It also yields a higher remnant polarization, a lower coercive field, and sharper hysteretic loops than PVDF (Harrison, 2002).

An increase in the TrFE content improves both crystallinity and remnant polarization in the P(VDF-TrFE) copolymer (Figure 2-25):

Figure 2-25: Change in (a) crystallinity and (b) remnant polarization, P_r & coercive field E_c with TrFE content. (Zhang, 2002a).

The result is an improvement in properties, most evident at about 70-80 mol% VDF (20-30 mol% TrFE) (Koga, 1986). This is a balance between VDF content for good ferroelectric properties, and TrFE content for crystallinity (Cheng, 2001, El-Hami, 2003). The addition of TrFE results in a first-order ferroelectric-paraelectric phase transition, connected with the conversion of all-*trans* chains to mixtures of *trans* and *gauche* bonds with little or no net dipole moment) (Bune, 1998), illustrated in the following phase diagram (Figure 2-26).

Figure 2-26: Phase diagram of P(VDF-TrFE) copolymer (Zhang, 2002). T_m and T_c stand for the melting point and Curie point respectively.

It was discovered that high-energy electron irradiation on the P(VDF-TrFE) copolymer converts the room-temperature ferroelectric phase to resemble a macroscopically paraelectric phase (Lovinger, 1985). Furthermore, Maachi (1990) and Odajima (1985) observed that via irradiation, the dielectric constant peak from the ferroelectric-paraelectric phase transition could be broadened and moved to near room temperature. In fact, the normal ferroelectric P(VDF-TrFE) copolymers are converted into a relaxor ferroelectric with high electrostrictive strains (Bharti, 1998, Bharti, 2000, Cheng, 2000, Zhang, 1998, Zhang, 2000).

Electron irradiation disrupts the coherence of polarization domains, consisting of all-trans chains. The result is the formation of localized polar regions, which are nanometer-sized, all-trans chains interrupted by trans & gauche bonds. (Harrison, 2002). The irradiated material exhibits behavior analogous to that of relaxor ferroelectric systems in inorganic materials (Harrison, 2002). The strains in irradiated P(VDF-TrFE) have been observed at magnitudes of 4% upwards, compared to typical strains in the order of 0.1% in piezoelectric ceramics (Cheng, 2000). This is about two orders of magnitude greater than piezoceramics (Bar-Cohen, 2001). However, it should be noted that at high VDF content, it is more difficult to eliminate polarization hysteresis to generate electrostrictive strain (Cheng, 2001).

The electrostrictive constant κ is defined by: $\kappa = \partial D / \partial S \partial E = \partial^2 T / \partial E^2$ and as a fourth-rank tensor quantity, it appears in all substances regardless of their symmetries (Fukada, 1981b). This effect may be described by the equation Strain, $S_{ij} = Q_{ijkl} P_k P_l$, for a material under zero or constant stress, where Q is the electrostrictive constant, and P is the polarization. For an isotropic polymer, $S_3 = Q_{33} P^2$ and $S_1 = Q_{13} P^2$ where S_1 and S_3 are the strains along and perpendicular to the polarization direction. For an isotropic polymer, $Q_{33} < 0$ and $Q_{13} > 0$. Elongated PVDF exhibits the largest electrostrictive effect among polymers, particularly when the strain is given along the elongation direction (Fukada, 1981b).

2.2.4. Synthesis of P(VDF-TrFE)

Kubouchi et al (1989) describe a process for the synthesis of the P(VDF-TrFE) copolymer using free radical polymerization at 22°C using 3,5,6-trichloroperfluorohexanoyl peroxide as initiator.

In free-radical copolymerization between two monomers, M_1 and M_2 , the following reactions may occur during the propagation stage (Fried, 2003):

The Mayo-Lewis Equation (Mayo, 1944), also called the copolymerization equation, gives the molar ratios of the monomers in the resulting copolymer as a function of the reactivity ratios:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} = \frac{1+r_1 \frac{[M_1]}{[M_2]}}{1+r_2 \frac{[M_2]}{[M_1]}} \dots\dots\dots (2.14)$$

where r is the ratio of the homopolymerization to copolymerization propagation rate given by $r_1 = \frac{k_{11}}{k_{12}}$ & $r_2 = \frac{k_{22}}{k_{21}}$, and $[M_1]$ & $[M_2]$ denote the concentrations of monomers M_1 & M_2 in solution.

Or in terms of the feed ratios, the copolymerization equation becomes:

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \dots\dots\dots (2.15)$$

where $f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$ and $F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]}$

The azeotrope occurs at (Fried, 2003):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} = \frac{1-r_2}{1-r_1} \text{ or } f_1 = \frac{1-r_2}{2-r_1-r_2} \dots\dots\dots (2.16)$$

In the case of P(VDF-TrFE), $r_1(\text{VDF}) = 0.7$ and $r_2(\text{TrFE}) = 0.5$ (Kubouchi, 1989, Petchsuk, 2003) and the azeotrope occurs at a VDF content of $F_1 = f_1 = 62.5$ mol%. Generally, random copolymers (also called statistical copolymers) are favored when r_1 and r_2 are close to 1. Alternating copolymers are favored when r_1 and r_2 are close to

zero and block copolymers are favored when $r_1 > 1$ and $r_2 > 1$. When r_1 is large compared to r_2 and r_2 is small, the monomer M_1 tends to homopolymerize and vice versa for M_2 .

In the free radical polymerization, NMR results obtained by Kubouchi (1989) indicate 90% VDF/VDF dyad, 75% VDF-TrFE or TrFE-VDF dyad, and 50% TrFE-TrFE dyad. In his findings, the arrangement of comonomers was found to be statistically random and the head-to-tail connection predominates. X-ray and DSC results by Kubouchi, 1989, indicated that the VDF/TrFE copolymers are in the crystalline state for the whole range of polymer compositions. The dipole moment is 1.96 Debye in the VDF monomer, and 1.63 Debye in TrFE (Kubouchi 1989). The glass transition temperature, T_g , slightly higher than that in PVDF, is -20°C (Kubouchi, 1989).

2.2.5. Processing of P(VDF-TrFE):

Processing methods of P(VDF-TrFE) mentioned in literature include melt crystallization as well as crystallization and recrystallization from cast solutions of organic solvents. The polymer, typically in powder or pellet form, is dissolved in liquids such as dimethylacetamide (DMA) (Zhang, 2002a), dimethylformamide (DMF), (Guo, 2005, Tsutsumi, 2004, Zhang, 2002a), cyclohexanone (Zhang, 2002a), or MEK (Kiumura, 2004, Tsutsumi, 2004). The solutions are then stirred or ultrasonically agitated, sometimes at elevated temperatures.

Some of the processes include spin coating (thickness is a function of rpm and concentration), but AFM, SEM results indicate that the samples are not uniform. Other methods mentioned include solution cast (Barique, 2001, Guo, 2003. Guo, 2004, Tang, 2001, Xu, 2005), and hotpressing (Bharti, 2001). After this, the P(VDF-

TrFE) film may undergo mechanical drawing to enhance chain orientation. However, results by Sencadas (2004) show that mechanical stretching does not change the degree of crystallinity, evidenced by the unchanged melting peak obtained by differential scanning calorimetry. The ferroelectric-paraelectric peak decreases in area and temperature indicating a damage of the ferroelectric phase.

P(VDF-TrFE) has also been fabricated layer by layer at the molecular level using the Langmuir-Blodgett method (LB method), described by Lee (2002). According to Richardson (1989), the “resulting degree of control over film thickness and molecular architecture (using LB deposition) is unsurpassed by any other deposition technique”. Langmuir determined that certain films on water had the thickness of only one molecule. In this method, the P(VDF-TrFE) powders / pellets would be dissolved into a volatile organic solvent which will not react with or dissolve in the subphase. This solution is then placed on the surface of the subphase, and when the solvent evaporates, a layer of P(VDF-TrFE), one molecule thick will be left on the surface of the subphase.

The P(VDF-TrFE) thin films are then immersed in distilled water, and removed from the substrate. After drying, the films are annealed to increase the crystallinity. Annealing temperatures typically range from 120°C (Tsutsumi, 2004) to 160°C (Kimura, 2004).

Figure 2-27 shows the AFM images of P(VDF-TrFE) thin film observed during the annealing process at (Fukuma, 2000).

Figure 2-27. AFM Images of spin-coated P(VDF-TrFE) 73-27 mol% film showing the growth of crystallites during the annealing process at (a) 25°C, (b) 96°C, (c) 123°C and (d) 136°C (1 $\mu\text{m} \times 1 \mu\text{m}$).

Bune et al (1998) have shown that Langmuir-Blodgett deposited ferroelectric polymer films of P(VDF-TrFE 70:30) of 2 monolayers have the same first-order phase transition as the bulk material at $\sim 80^\circ\text{C}$, and there is no apparent critical (minimum) thickness, implying that ferroelectric LB-deposited polymer films may be essentially two-dimensional ferroelectrics (Bune 1998).

2.2.6. Irradiation of P(VDF-TrFE)

Irradiated P(VDF-TrFE) copolymers have been observed to show exceptionally large longitudinal strain of about 4% and energy storage of up to 170 J/kg (Guo, 2004b). Irradiation is typically carried out in a nitrogen atmosphere at elevated temperatures (Harrison, 2002), and the effect of irradiation dosages ranging from 30 to 150 Mrad is shown in Figure 15 (Bharti, 2001). Coherence of polarization domains, containing all-*trans* chains, is disrupted and localized polar regions are formed, containing all-*trans*

chains interrupted by *trans* and *gauche* bonds (Harrison, 2002). In practice, radiation doses above 80 Mrad are to be avoided, as the material becomes brittle and easy to break down mechanically (Tang, 2001).

Figure 2-28: Effect of irradiation on the polarization loop for P(VDF-TrFE) 65/35 mol% film. (Cheng, 2001)

Figure 2-29: Effect on the polarization hysteresis loop for P(VDF-TrFE) 50/50 mol% copolymer 25µm films irradiated at 120 deg C with 3 MeV electrons (Bharti, 2001).

2.2.7. Electroding

Electroding of the polymer is typically carried out using aluminum, gold, or combinations of gold and chromium / platinum, with (Xu, 2005) or without a shadow mask. Aluminum electrodes have been coated on film using vacuum deposition / evaporation (Guo, 2005, Guo, 2004b, Tsutsumi, 2004). In the case of Tsutsumi, the evaporation was carried out before annealing at 120 °C for 4 hours.

Gold electrodes (Kutnjak, 2005, Ma, 2005, Xu, 2005) have been sputtered at thicknesses of about 40nm (Cheng, 2001) to 100nm (Xu, 2005). Xu also utilized the gold layer as a reflective surface for the displacement characterization. Sometimes, the gold is sputtered over an initial layer of another metal. Piezotech, S.A., France produces P(VDF-TrFE) films with electroding carried out by sputtering gold over platinum. Guo et al mentions the sputtering of a chromium/gold electrode (Guo, 2003b), in one case with 100 to 200Å chromium buffer layer, under a 400 to 600Å gold upper layer (Guo, 2004a). A thin copper wire was glued to the electrode, with the use of conductive silver paint.

Electroding with conductive polymers may also be possible. Bliznyuk et al. (2005) reported surface and volume modification on PVDF by polyaniline (PANI) to create a 2D conductive network of about 8µm thickness. This network had a conductivity ranging from 10^{-8} to 10^{-3} S/cm and non-linear I-V characteristics possibly explained by the surface conductive network of PANI being alternated with β-crystalline PVDF microdomains. Other possibilities include poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) dissolved in dimethyl sulfoxide [PEDOT/PSS (DMSO)] implemented by Lee (2005), which was screen-printed onto IAR-modified (ion-assisted-reaction modified) PVDF. IAR (Han, 1999, Koh, 1995) is used to increase the adhesion on the hydrophobic surface of the PVDF. The PEDOT/PSS electrodes performed better under fatigue than the inorganic ITO and Pt electrodes which were either mechanically or electrically damaged under a vibration of 1MHz / 200Vrms, suggesting that the conductive polymers may be more mechanically compatible to PVDF than the organic ITO and Pt electrodes. To make the bimorph layers, Lee et al. (2005) used screen-printed epoxy adhesive (Araldite standard, Ciba-Geigy Corp) of 40µm thickness and dried for 1 hr at 70°C.

2.2.8. Electrical Poling

Polymers are normally poled using a direct contact method or corona discharge (Harrison, 2002). In the corona discharge method, contacting electrodes are not required and samples of large surface area can be poled continuously (Harrison, 2002). Poling by means of sandwiching polymer film between polished metal plates under a vacuum has been reported (Harrison, 2002). In this process, an electric field of the order of 50MV/m is applied across the thickness of the polymer, to effect crystalline orientation (Harrison, 2002).

Commercial poling methods, includes the ISL-Bauer process—US Patent No. 4,684,337, (Bauer, 1987) in which an alternating electric field is applied (frequency between 0.001 to 1 Hz, and amplitude gradually increasing from 0 to $\pm E_N$, at a rate of 0.05 MV/cm/min with E_N just above the coercive force E_c , of the material).

Figure 2-30: Notation for Poling & Stretched Directions for Ferroelectric Polymers

For a poled and mechanically stretched piezopolymers, the tensor directions are designated as follows (Figure 2-30): directions 1 & 3 represent the stretching and poling directions respectively and direction 2 is the axis perpendicular to directions 1 & 3. The shear planes about axes “1”, “2” & “3” are designated as “4”, “5” & “6” respectively. (Harrison, 2002).

Figure 2-31. The piezoelectric response images ($8\ \mu\text{m} \times 8\ \mu\text{m}$) of P(VDF-TrFE) obtained (a) immediately after the poling process and after thermal annealing at (b) 110°C , (c) 115°C and (d) 120°C .

Fukuma et al. studied the ferroelectric properties of copolymer ultrathin films during thermal processes using piezoelectric response imaging. A local “positive poling” area with a size of $10\ \mu\text{m} \times 10\ \mu\text{m}$ was formed using a scan with a tip bias voltage of 10V with the conductive substrate grounded. A smaller “negative poling” area was formed within this region with a size of $4\ \mu\text{m} \times 4\ \mu\text{m}$ using a tip bias of -10V. At a temperature of 120°C , no difference could be observed between the “positive poling” and “negative poling” regions (Figure 2-31).

2.2.9. Applications of Ferroelectric Polymers

P(VDF-TrFE) copolymers have applications in piezoelectric and pyroelectric devices, such as pyroelectric detectors, broad-band transducers, medical ultrasound, nonlinear optics (Brown, 2000, Ohigashi, 1988), devices for minimally invasive surgery (MIS) (Frecker, 2004), artificial muscles and biomimetics (Bar-Cohen, 2004, Zhang, 2002b), smart skins for drag reduction (Zhang, 2002b), and as a polymer-based microfluidic system (Xu, 2005) for drug delivery (Zhang, 2002b).

As a pyroelectric device, the piezopolymer may be used as an infrared detector, as a pyrovidicon, or as a laser calorimeter (Kubouchi, 1989). Other applications include audio frequency transducers (headphones, tweeter speakers, telephone transmitters, medical sensors, accelerometers), ultrasonic transducers (hydrophone, ultrasonic medical transducer), electromechanical transducer (typewriter and keyboard, pressure sensor, telephone dial, impact detector) (Kubouchi, 1989).

As an actuator, devices take the form of bimorph or monomorph actuators, suitable for applications in requiring relatively large deflections and small forces (Frecker, 2004). An actuation mode of particular interest is the segmented actuator, which allows more precise control over its curvature, as both convex and concave curvature along its length is allowed. This would be useful in an impedance pump device whereby an active ferroelectric layer is placed perpendicularly across a channel to induce a deflection.

Of considerable interest are piezoelectric tubular ultrasonic transducers (Boey, 2004, Boey 2005, Li, 2003 Li, 2004b Li, 2005), which have not been fabricated using piezoelectric polymers to date. Hence, the potential of developing an all-polymer piezoelectric tubular transducer has not been explored so far. The advantages of an all-polymer device would include high energy density (Chu, 2006, Zhang, 2002b), light weight, flexibility, low cost, as well as biocompatibility which has already been explored in PVDF polymers by Ryu (2005). These have also attracted attention as possible biomedical devices, including actuators for surgery and cardiovascular pumps. These transducers operate in bending vibration mode and are excited sinusoidally with two sets of voltages 90 degrees phase apart applied to quartered outer electrodes. These transducers differ from those by Dameron (1981/82) and Linvill (1986) which operate in the longitudinal vibration mode. The bending

vibration mode allows operation in a 2-D plane, as opposed to the longitudinal displacement mode which allows motion only along a 1-D axis, thereby facilitating more actuator applications, such as the rotational motion described in this work. It is also noted that important parameters which characterize the frequency-dependent behavior of the tube have not been extensively studied. Hence, much work remains to address this knowledge gap through an investigation into the dynamic behavior of the piezoelectric constant, d_{31} , in tubular transducers. In addition, operation of tubular transducers in electrostrictive mode has not been reported so far. Hence, a study into this operation mode, together with the dynamic behavior of the electrostrictive coefficients, Q_{13} and M_{13} will allow this to be addressed.

The potential applications of P(VDF-TrFE) are further broadened, due to its performance under high mechanical load. It has been reported that irradiated P(VDF-TrFE) electrostrictive polymers are able to maintain high strain levels under high external stresses. At tensile stress levels up to 40MPa, the strain of the material remains almost the same as that without load (Figure 2-32).

Figure 2-32: Effect of Tensile Stress on Transverse Strains, S_1 , for stretched P(VDF-TrFE) 65/35 mol% copolymer film irradiated at 95 deg C with 60Mrad dose using 2.55 MeV electrons (Zhang, 2002)

Stress-dependent behaviour of ferroelectric materials have been investigated through experiments as well as the use of time-dependent Ginzburg-Landau (TDGL) theory, though not extensively. Currently, no work has been done to explain the ability of irradiated P(VDF-TrFE) copolymers to maintain these large strains under high mechanical load using TDGL.

Unrelated to piezoelectric actuators, another interesting result by Fukada (1981a) indicated an influence in bone growth due to electric polarization. In an experiment involving PVDF film, which is biocompatible (Ryu, 2005), wrapped around the femur of a monkey, formation of new bone was observed within weeks. This was attributed to the motion of the animal which caused deformation of the film, thereby producing a neutralizing ionic current in the surrounding tissue. It is believed that this small current stimulates the metabolic activity of the bone cells.

2.2.10. Other Electroactive Polymers

Various other copolymers of PVDF have also been investigated, such as PVDF/HFP (hexafluoropropylene) (He, 2005) at IMRE, Singapore. The results by Petchsuk (2003) at Penn State University involve the incorporation of chloro-containing monomers of chlorotrifluoroethylene (CTFE), 1,1 and 1,2-chloro-fluoroethylene (CFE), 1-chloro-2,2-difluoroethylene (CDFE) into P(VDF-TrFE) to form terpolymers. Ideally, this reduces the polar domain size (without changing crystallinity), thereby reducing the energy barrier for the F-P (ferroelectric-paraelectric) phase transition, and bringing it nearer to room temperature. Work carried out by Petschuk (2003) involved functionalizing the chains to enhance adhesion with pseudo-living radical polymerization techniques involving (i) functionalized borane/oxygen initiators, and (ii) the iodine transfer polymerization (ITP) method which is based on the combination of a reversible addition-fragmentation chain transfer (RAFT) process, and an α,ω -

diiodoperfluoroalkane (I-R_F-I) chain transfer agent, where R_F includes CF₂CF₂, CF₂CF₂CF₂CF₂, CF₂CFCl, CF₂CF(CF₃). In this method, chains are terminated at both ends by iodine groups, of which the CF₂-I bond can be easily cleaved for future functionalization.

Besides PVDF and its copolymers/terpolymers containing the TrFE, CTFE, CFE, CDFE, and/or HFP monomers, other polymers have been shown to be piezoelectric. A comparison of PVDF to these polymers showing the glass transition temperature, T_g , the melting point, T_m , the maximum usable temperature, $T_{\max \text{ use}}$, is as follows:

Table 2-3: List of Piezoelectric Polymers

Polymer	Structure	T_g (°C)	T_m (°C)	$T_{\max \text{ use}}$ (°C)	d_{31}	P_r (mCm ²)
PVDF	$\left(\begin{array}{c} \text{F} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{F} \end{array} \right)_n$	-35	175	80	20-28	-
PTrFE	$\left(\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{CH}- \\ \\ \text{F} \end{array} \right)_n$	32	150	90-100	12	-
Nylon-11	$\left(\begin{array}{c} \text{O} \\ \\ -\text{NH}-(\text{CH}_2)_{10}-\text{C}- \\ \\ \text{O} \end{array} \right)_n$	68	195	185	3 @25°C 14 @107°C	-
Polyurea-9	$\left(\begin{array}{c} \text{O} \\ \\ -(\text{CH}_2)_9-\text{HN}-\text{C}-\text{HN}- \\ \\ \text{O} \end{array} \right)_n$	50	180	-	-	-
PVC	$\left(\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{H} \end{array} \right)_n$	80	-	-	5	16
PAN	$\left(\begin{array}{c} \text{C N} \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{H} \end{array} \right)_n$	90	-	-	2	25
PVAc	$\left(\begin{array}{c} \text{CH}-\text{CH}_2- \\ \\ \text{O} \\ \\ \text{O}-\text{C}-\text{CH}_3 \end{array} \right)_n$	30	-	-	-	5
P(VDCN-VAc)	$\left(\begin{array}{c} \text{C N} \quad \text{C N} \\ \quad \quad \\ -\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}- \\ \quad \quad \\ \text{C N} \quad \text{O} \\ \\ \text{O}-\text{C}-\text{CH}_3 \end{array} \right)_n$	170	-	-	10	50
PPEN	$\left(\begin{array}{c} \text{C N} \\ \\ \text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O} \end{array} \right)_n$	145	-	-	-	12
(β-CN) APB/ODPA	$\left(\begin{array}{c} \text{C N} \quad \text{C N} \quad \text{C N} \\ \quad \quad \\ \text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{N} \end{array} \right)_n$	220	-	-	5 @150°C	20

Piezoelectricity has also been investigated in a number of naturally occurring materials as shown below.

Table 2-4: Naturally Occurring Materials Exhibiting Piezoelectricity (Fukada, 1968)

Material	Crystallographic Symmetry	Piezoelectric Tensor
Cellulose	monoclinic C_2	$\begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & d_{36} \end{bmatrix}$
Wood (highly oriented and crystallized cellulose fibres)		$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}, d_{14} \approx -d_{15}$
Bone (oriented collagen fibres with enmeshed hydroxyapatite) and Tendon (close-packed oriented collagen fibres)	hexagonal C_6	$\begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$

Material	Piezoelectric moduli (10^{-8} cgs esu)			
	d_{14}	d_{15}	d_{33}	d_{31}
Wood (maple)	-0.26	0	0	0
Ramie bundle	-0.73	0	0	0
Rayon bundle	-0.08	0	0	0
Silk bundle	-3.30	0.70	0.07	0.06
Wool bundle	-0.20	0.20	0.01	0.03
Horse femur	-0.65	0.13	0.01	0.01
Horse Achilles tendon	-5.70	1.60	0.20	0.04
Bovine Achilles tendon	-8.00	4.20	0.26	0.20

2.3. Size Effects in Ferroelectrics

2.3.1. Ferroelectric Thin Films under Inhomogeneous Electric Fields – Lateral Size and Thickness Dependence

The current advancement in nanotechnology and device miniaturization, has led to significant interest in studying size effects in ferroelectrics. The properties of nano-scale ferroelectric thin films substantially differ from the bulk (Tagantsev, 2006), and

it has been shown that strong depolarization effects can completely suppress ferroelectricity below a critical thickness. In fact, thickness dependence of ferroelectric behavior has been well studied both theoretically and experimentally (Streiffer, 2002. Junquera, 2003), but not much attention has been devoted to the role of lateral size. Scanning probe techniques such as the Piezoresponse Microscopy (PFM) allows the polarization to be switched locally and arrays of these locally switched domains are the building blocks of ferroelectric memory devices (e.g. ferroelectric capacitors and dynamic random access memory (DRAM) applications). In such devices, the main limitation on lateral width is due to fringing electric fields (Scott, 1998), and reduction of the lateral size is key to allowing very high-density memories to be achieved (Buhlmann, 2002).

Apart from the technological interest, it is also important to understand the role of the complex long-range elastic as well as electrostatic interaction on selectively switched domains. Fringing of the electric field (Scott, 1998) as well as inhomogeneous elastic deformations will crucially influence the behavior of the locally switched domains. These long-range interactions will influence the local polarizations in the neighborhood of the domains, thereby influencing the effective properties such as the polarization vs. electric field response (P-E). For example, in a recent work, Chen et. al. (2004c) studied the local 180° degree switching in epitaxial PZT by PFM. They found that the 90° degree domain formation relaxes the internal stresses associated with inhomogeneous electric fields. This underscores the importance of studying the effect of finite lateral width from a theoretical point of view to understand the underlying mechanisms. Such a study may provide a guideline to choose the optimal thickness and widths of the selectively switched domains.

The effect of lateral size in ferroelectric films was studied experimentally by Lee (2006a) and Chen (2004c), as well as analytically by Wang (1995), and Roytburd (2000). The analysis by Wang and Roytburd, however, did not incorporate domains and domain wall motion. In fact, both models neglected electrostatic effects (equations 3.34 and 3.35), and Wang's model neglected elastic effects (equations 3.36 and 3.38). A TDGL frame work that takes into account elastic as well electrostatic long-range interacts is a useful technique to study the domain switching under inhomogeneous electric fields. Hence, in section 6.4, we use the TDGL framework to study lateral size and thickness dependence of selectively switched domains.

3. Theory

3.1. Performance of Piezoelectric Ultrasonic Transducers - Derivation of Vibration Velocity

The performance of a piezoelectric ultrasonic motor is governed by the performance of the piezoelectric tube (i.e. the piezoelectric tubular transducer). The key parameter of interest is the vibration velocity of this tube in its bending vibration mode. This is numerically equivalent to the velocity of a point on the extreme end of the piezoelectric tube, and it is the parameter that governs the rotational speed of the motor. In order to determine which material is best suited to achieve a high vibration velocity, v_v , a relationship must be first be derived linking v_v to the material properties. The methodology to derive the vibration velocity involves the derivation for the expression of the resonance frequency and the bending displacement using the solution given by the Timoshenko beam theory. The Timoshenko model can be apply to both piezoelectric ceramic tube as well as a piezozelectric polymer version, as long as the appropriate material constants (e.g. ρ_{tube} , Y_{11}^E , Y_{12}^E , Y_{33}^E , ϵ_{11} , ϵ_{33} , etc.) are changed. The solution based on the Timoshenko beam theory is outlined in the following sections.

3.1.1. Timoshenko Beam Theory

In Timoshenko beam theory (Coleman, 1993. Farchaly, 1995. Han, 1999. Lee, 1994. Mindlin, 1955. Tan, 1995. Timoshenko, 1921), an element of the beam is modeled having a transverse motion with a shear deformation and a rotation. Under the action of a shear force, F , and a bending moment, M , a transverse displacement, ζ , and a rotation, φ , are produced, and the element deforms by an angle γ . This is illustrated in Figure 3-1 below:

Figure 3-1:Element undergoing a shear force, F , and a bending moment, M .

The equation of motion given by the Timoshenko model is:

$$Y^E I \frac{\partial^4 \zeta}{\partial x^4} + \rho_{tube} A \frac{\partial^2 \zeta}{\partial t^2} - \rho_{tube} I \left(1 + \frac{Y^E}{k_{shape} G} \right) \frac{\partial^4 \zeta}{\partial x^2 \partial t^2} + \frac{\rho_{tube}^2 I}{k_{shape} G} \frac{\partial^4 \zeta}{\partial t^4} = 0 \dots\dots\dots (3.1)$$

where I is the moment of inertia given by $I = \frac{\pi}{64} (D_{tube}^4 - d_{tube}^4)$,

A is the cross sectional area,

k_{shape} is the shape factor, and

G is the shear modulus.

The solution to the Timoshenko beam model (Han, 1999) is of the form:

$$\begin{bmatrix} \zeta(x) \\ \phi(x) \end{bmatrix} = \begin{bmatrix} C_1 \\ D_1 \end{bmatrix} \sin ax + \begin{bmatrix} C_2 \\ D_2 \end{bmatrix} \cos ax + \begin{bmatrix} C_3 \\ D_3 \end{bmatrix} \sinh bx + \begin{bmatrix} C_4 \\ D_4 \end{bmatrix} \cosh bx \dots\dots\dots (3.2)$$

$$\text{where } \begin{cases} a = \sqrt{\left(I + \frac{1}{k'G}\right) \frac{\rho_{tube} \omega^2}{2} + \sqrt{\left(I - \frac{1}{k'G}\right)^2 \frac{\rho_{tube}^2 \omega^4}{4} + \rho_{tube} A \omega^2}} \\ b = \sqrt{-\left(I + \frac{1}{k'G}\right) \frac{\rho_{tube} \omega^2}{2} + \sqrt{\left(I - \frac{1}{k'G}\right)^2 \frac{\rho_{tube}^2 \omega^4}{4} + \rho_{tube} A \omega^2}} \end{cases} \dots\dots\dots (3.3)$$

and C_i & D_i ($i = 1$ to 4) are constants related by the equations:

$$\begin{cases} D_1 = -\frac{k'GAa^2 - \rho_{tube}A\omega^2}{k'GAa} C_2 \\ D_2 = \frac{k'GAa^2 - \rho_{tube}A\omega^2}{k'GAa} C_1 \\ D_3 = \frac{k'GAb^2 + \rho_{tube}A\omega^2}{k'GAb} C_4 \\ D_4 = \frac{k'GAb^2 + \rho_{tube}A\omega^2}{k'GAb} C_3 \end{cases} \dots\dots\dots (3.4)$$

Applying the boundary conditions for the free-free end conditions:

$$\begin{cases} \frac{d\zeta}{dx} - \varphi = 0 & \text{at } x = 0, \text{ and } x = 1 \\ \frac{d\varphi}{dx} = 0 & \text{at } x = 0, \text{ and } x = 1 \end{cases} \dots\dots\dots (3.5)$$

From equations 3.2, 3.3, 3.4 and 3.5, the following relationships can be obtained (Li, 2003):

$$\begin{cases} \zeta = C_3 \left[\frac{a}{b} \sin ax + \sinh bx + \alpha \left(\frac{1}{\eta} \cos ax + \cosh bx \right) \right] \\ \varphi = k_{shape} C_3 \left[\alpha \left(-\frac{b}{a} \sin ax + \sinh bx \right) + \eta \cos ax + \cosh bx \right] \\ \eta = \frac{a^2 + b^2 \gamma^2}{b^2 + a^2 \gamma^2} \\ \alpha = \frac{\frac{a}{b} \eta \sin a - \sinh b}{\cosh b - \cos a} \\ k_{shape} = \frac{b^2 + a^2 \gamma^2}{(1 + \gamma^2)b} \end{cases} \dots\dots\dots (3.6)$$

Here, $\zeta(x)$ gives the mode shape equation, and the resonance frequency and bending displacement may also be obtained as explained in the following sections.

3.1.2. Resonance Frequency

Based on the solutions to the differential equation, from equations 3.2 to 3.6, the bending-mode resonance frequency (Li, 2003) may be expressed as:

$$f_r = \frac{1}{2\pi L_{tube}} \sqrt{\frac{Y^E}{\rho_{tube}}} \sqrt{\frac{a^2 - b^2}{5 + 3\nu}} \dots\dots\dots (3.7)$$

where ν = Poisson's ratio,

and the wave numbers a and b are to be obtained from:

$$\left\{ \frac{(a^2 - b^2)(a^2 + b^2 + \gamma^2 ab - ab)(a^2 + b^2 - \gamma^2 ab + ab)}{2ab(b^2 + \gamma^2 a^2)(a^2 + \gamma^2 b^2)} \sin a \sinh b - \cos a \cosh b + 1 = 0 \right. \dots\dots\dots (3.8)$$

$$\left. \frac{(\gamma^2 b^2 + a^2)(\gamma^2 a^2 + b^2)}{(a^2 - b^2)(1 + \gamma^2)} = s^2 = \frac{16L_{tube}^2}{D_{tube}^2 + d_{tube}^2} \right\}$$

where s is the shape factor,

L_{tube} is the tube length, and

D_{tube} and d_{tube} are the tube's outer and inner diameters respectively.

Therefore, the expressions in equation 3.8 must be solved simultaneously:

The solutions for a and b corresponding to the different values of the shape factor s are first obtained by numerical methods [see Appendix, section 10.2 for procedure]. Based on the result of this calculation, the parameter, $\sqrt[3]{(a^2 - b^2)}$, is plotted against $1/s$ and the curve fitted to a degree-6 polynomial.

Figure 3-2: Curve fit for Wave Number parameter, $\sqrt{a^2 - b^2}$, as a function of $1/s$ for $\sigma = 0.3$

The degree-6 polynomial obtained gives the formula:

$$\sqrt{a^2 - b^2} \approx 151105s^{-6} - 109072s^{-5} + 30029.1s^{-4} - 3478.30s^{-3} - 18.4379s^{-2} + 54.9410s^{-1} - 0.0025671 \quad \dots (3.9)$$

with $R^2 = 0.9999997$

*Other curve fits are also possible, but the degree-6 polynomial was chosen for reasons explained in the Appendix, Section 10.3.

Next, by substituting $\gamma = \sqrt{4 + 3\sigma}$, the resonance frequency formula becomes:

$$f_r = \frac{\sqrt{Y^E} \sqrt{a^2 - b^2}}{2\pi L_{tube} \sqrt{\rho_{tube} (5 + 3\sigma)}} \quad \dots (3.10)$$

This expression gives an exact constitutive relationship for the currently investigated tubular transducer.

For practical purposes, the degree-6 polynomial curve fit may be used as an estimate for $\sqrt[3]{(a^2 - b^2)}$, which gives the following expression:

$$f_r \approx \frac{\sqrt{Y^E} \left(151105s^{-6} - 109072s^{-5} + 30029.1s^{-4} - 3478.30s^{-3} - 18.4379s^{-2} + 54.9410s^{-1} - 0.0025671 \right)}{2\pi L_{tube} \sqrt{\rho_{tube}} (5 + 3\sigma)} \dots\dots\dots (3.11)$$

3.1.3. Bending Displacement

Similarly, by applying the mode shape equation derived from the free-free boundary conditions, the formula for the bending displacement at resonance (Li, 2003) may be evaluated as:

$$\zeta = Q_m \frac{16d_{31}V \times l_{nodal} \times (L_{tube} - l_{nodal}) \cos \beta}{\pi(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \dots\dots\dots (3.12)$$

The bending displacement relationship may be extended to include the effect of an external blocked force and bending moment, as well as the introduction of the electrostrictive mode in ferroelectric polymers. The following result may be derived in a similar manner from the strength of materials approach using the piezoelectric relationship, Strain, $S_1 = d_{31}E_3 + M_{13}E_3^2$. The resulting equation has been derived as follows:

$$\zeta = l_{nodal} (L_{tube} - l_{nodal}) \left[\begin{aligned} & \frac{2d_{31}(V_2 - V_1) \cos \beta}{\pi(r_{ou}^2 + r_{in}^2) \ln(r_{ou}/r_{in})} \\ & + \frac{4M_{13}(V_2^2 - V_1^2) \cos \beta}{\pi(r_{ou}^2 + r_{in}^2)(r_{ou} + r_{in}) [\ln(r_{ou}/r_{in})]^2} \\ & + \frac{2s_{11}^E (M_{FF} - F_{FF} l_{nodal})}{\pi(r_{ou}^4 - r_{in}^4)} \end{aligned} \right] \dots\dots\dots (3.13)$$

where r_{ou} and r_{in} are the outer and inner radius respectively, V_2 and V_1 are the voltages applied to the outer and inner surface, s_{11}^E is the material property which is

the inverse of the Young's Modulus, and M_{13} is the electrostrictive coefficient. Here, M_{FF} is the bending moment, and F_{FF} is force applied externally to the ends of the beam. This relationship may also be extended to derive an expression for torque.

3.1.4. Vibration Velocity

Several modes of vibration of the piezoelectric tube exist. Of these, however, only the bending vibration mode results in the circular motion of a point in the tube.

Figure 3-3: Bending Vibration Mode of a Piezoelectric Tube

When the tube is coupled to a shaft, this circular motion causes the shaft to rotate.

Figure 3-4: Locus of Rotation for a Point on a Piezoelectric Tube

A point on the PZT tube under bending oscillates in a circular fashion, with the radius of rotation equal to the bending displacement. The maximum speed of the shaft is determined by the vibration velocity, the speed of this rotational motion.

Thus, the vibration velocity is given by:

$$v_v = \omega \times r = (2\pi \times \text{resonance frequency}) (\text{bending displacement at resonance})$$

$$v_v = 2\pi f_r \zeta \dots\dots\dots (3.14)$$

Expressing equation 3.14 in a general form, the vibration velocity may be rewritten as a function of three parameters:

Vibration Velocity, $v_v = f(\text{geometry, electrical, materials})$

$$v_v = 2\pi f_r \zeta$$

$$= 2\pi \left(\frac{1}{2\pi L_{tube}} \sqrt{\frac{Y^E}{\rho_{tube}}} \sqrt{\frac{a^2 - b^2}{5 + 3\sigma}} \right) \left(Q_m \frac{16d_{31} \times l_{nodal} \times (L_{tube} - l_{nodal}) \times V \cos \beta}{\pi(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right) \dots\dots\dots (3.15)$$

$$= \frac{16}{\pi} (V \cos \beta) \underbrace{\left(Q_m d_{31} \sqrt{\frac{Y^E}{\rho_{tube} (5 + 3\sigma)}} \right)}_{\text{Material Factor}} \underbrace{\left(\frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}} \right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right)}_{\text{Geometric Factor}}$$

Electrical Factor
Material Factor
Geometric Factor

$$v_v = \text{Electrical Factor} \times \text{Material Factor} \times \text{Geometric Factor} \dots\dots\dots (3.16)$$

where,

$$\text{Electrical Factor} = V \cos \beta \dots\dots\dots (3.17)$$

$$\text{Material Factor} = Q_m d_{31} \sqrt{\frac{Y^E}{\rho_{tube} (5 + 3\sigma)}} \dots\dots\dots (3.18)$$

$$\text{Geometric Factor} = \frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}}\right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \dots\dots\dots (3.19)$$

Because the term, $\sqrt{a^2 - b^2}$ is a function of $1/s$ and σ , and can only be obtained by numerical methods, it is sometimes easier to use the estimate in equation (3.9):

$$\sqrt{a^2 - b^2} \approx 151105s^{-6} - 109072s^{-5} + 30029.1s^{-4} - 3478.30s^{-3} \\ - 18.4379s^{-2} + 54.9410s^{-1} - 0.0025671$$

The geometric factor therefore becomes:

$$\text{GeometricFactor} = \frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}}\right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \\ \approx \frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}}\right) \left(\begin{array}{l} 151105s^{-6} - 109072s^{-5} + 30029.1s^{-4} \\ - 3478.30s^{-3} - 18.4379s^{-2} \\ + 54.9410s^{-1} - 0.0025671 \end{array} \right)}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \dots\dots\dots (3.20)$$

$$\text{where } \frac{1}{s} = \frac{\sqrt{D_{tube}^2 + d_{tube}^2}}{4L_{tube}}$$

Thus, the vibration velocity, v_v , may be written as:

$$v_v = \frac{16}{\pi} \times \text{ElectricalFactor} \times \text{MaterialFactor} \times \text{GeometricFactor} \\ = \frac{16}{\pi} (V \cos \beta) \left(Q_m d_{31} \sqrt{\frac{Y^E}{\rho_{tube} (5 + 3\sigma)}} \right) \left(\frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}}\right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right) \dots\dots\dots (3.21)$$

Hence, vibration velocity can be expressed in terms of three factors, the first one purely a function of the electrical inputs. The second term is primarily a function of the material properties, and the third term primarily a function of the geometric properties.

The exceptions to these are the cross-coupled terms: the nodal point term, $\frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}}\right)$, and the wave number term, $\sqrt{a^2 - b^2}$, which depend slightly on the material property—the Poisson ratio, σ . However, the Poisson ratio in piezoelectric ceramics does not vary much within commercially available tubes. If this value is fixed at $\sigma = 0.3$, the variation in these two properties is less than 3% for $\sqrt{a^2 - b^2}$, and less than 1% for $\frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}}\right)$. This is explained further in the Appendix, sections 10.4 and 10.5. Hence, in order to select or optimize a material for piezoelectric tubular ultrasonic motor applications, the material should have the largest possible material factor.

3.2. Theoretical Maximum for the Rotational Speed of the Motor

The rotational speed of the motor, under “no slip” condition, is directly related to the vibration velocity by the relationship (Chen, 1994):

$$\omega = \frac{60 f_r \zeta}{r_{contact}} \dots\dots\dots (3.22)$$

where $r_{contact}$ is the contact radius of the coupling between the piezoelectric tube and the end cap.

This formula is easily derived using the assumption that the speed of a point on the contact edge of the PZT tube is the same as the speed of a point on the end cap. The coupling mechanism is shown in Figure 3-5 below.

Figure 3-5: Coupling Mechanism between Piezoelectric Tube and End Cap

If we let:

v_1 = velocity of a point on the contact edge of the *jiggling PZT tube*

v_2 = velocity of a point on the contact edge of the *end cap*

A point at the end of the PZT tube, moves at a speed given by:

$$v_1 = \omega_1 r = 2\pi f_r \zeta$$

A point at the contact edge of the end cap moves at a speed (assuming no slip occurs):

$$v_2 = v_1 = 2\pi f_r \zeta$$

Hence the angular velocity of the end cap is given by:

$$\omega_2 = \frac{v_2}{r_{\text{contact}}} = \frac{2\pi f_r \zeta}{r_{\text{contact}}} \text{ (in rad/s)}$$

$$\omega = \frac{60}{2\pi} \cdot \frac{2\pi f_r \zeta}{r_{\text{contact}}} = \frac{60 f_r \zeta}{r_{\text{contact}}} \text{ (in rpm)}, \dots\dots\dots (3.23)$$

since $2\pi \text{ rad/s} = 1 \text{ rev/s} = 60 \text{ rpm}$

In this simple derivation, the no-slip speed of an ultrasonic motor can be calculated from the frequency of excitation, the bending displacement, and the contact radius.

It should be noted that sometimes, a diameter reducer is added to reduce the contact radius, thereby increasing the rotational speed of the motor. In such a case, the contact radius, r_{contact} , is defined as shown in Figure 3-6:

Figure 3-6: Reduction of Contact Radius

3.3. Other Tube Parameters

3.3.1. Blocking Force

The blocking force of a piezoelectric tubular transducer is defined as the external equivalent force, when applied to the tip of the transducer, which is sufficient to maintain that tip at its fixed original position. The strength of an actuator is normally characterized by the magnitude of its blocking force. This parameter is important because it directly relates to the maximum output torque of a piezoelectric motor.

Under the free-free boundary condition, the blocking force for a piezoelectric tubular transducer is given by (Li, 2003):

$$F_{FF} = - \frac{(L_{tube} - l_{nodal}) d_{31} Y^E V \cos \beta \times \frac{1}{4} (D_{tube}^2 - d_{tube}^2)}{l_{nodal} \ln \frac{D_{tube}}{d_{tube}} \times (\frac{1}{2} L_{tube} - \frac{2}{3} l_{nodal})} \dots\dots\dots (3.24)$$

3.4. The Material Factor

3.4.1. Isolating the Parameter for the “Material Factor”

Based on the derivation of vibration velocity, the “material factor” for a particular material may be obtained by experiment. Isolating the material factor allows the verification of the materials formulation for optimum performance, independently from the geometry of the tube.

The vibration velocity is given as follows:

$$v_v = \frac{16}{\pi} \times (V \cos \beta) \times MaterialFactor \times GeometricFactor$$

$$\frac{dv_v}{dV} = \frac{16 \cos \beta}{\pi} \times MaterialFactor \times GeometricFactor \dots\dots\dots (3.25)$$

Plotting $\frac{dv_v}{dV}$ against geometric factor, and keeping β constant at 45° ($\beta = 45^\circ$ for a tube with four electrodes) gives a straight line graph with a gradient of:

$$\frac{16 \cos \beta}{\pi} \times MaterialFactor = 3.6012 \times MaterialFactor$$

$$= const \times MaterialFactor$$

Due to the cross-coupled terms of $\sqrt{a^2 - b^2}$ and $\frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}} \right)$ in the geometric

factor, which are also functions of the material properties, this relationship will not

hold exactly. However, as explained in the Appendix, section 10.4 and 10.5, these terms each do not vary by more than 3% within the typical range of values of the Poisson ratio in commercial piezoelectric tubes. Hence, determining the material factor in a given material will provide a good indication of its performance that is independent of the geometry.

3.5. Introduction to Time-Dependent Ginzburg-Landau (TDGL) Theory

Landau theory is a mean-field framework to study phase transitions, based solely on symmetry considerations (Chandra, 2007). In 1954, Devonshire adapted Landau's model to ferroelectrics, whereby he described thermodynamic behavior in the BaTiO₃ system, which is now called the Landau-Ginzburg-Devonshire (LGD) approach to ferroelectrics. This was later used by Haun et al (1989) to develop a thermodynamic theory of the PZT system. This model has been shown to be able to explain properties such as the spontaneous polarization of the material, the intrinsic coercive field (Ducharme, 2000), and hysteresis loops (Ducharme, 2000). The kinetics of the LGD approach are investigated with the time-dependent Ginzburg-Landau (TDGL) equation (also called the Allen-Cahn relaxational equation) (Chen, 2002), which can be used to obtain important properties such as the ferroelectric d_{ij} constants, temperature-dependent characteristics, stress-induced degradation of the piezoelectric constants, thickness-dependent behavior, and domain size dependence (Ahluwalia, 2005).

The basic idea of the Landau theory is that the free energy of a system, can be written as a Taylor expansion in terms of an order parameter, ϕ , given as:

$$\Delta G = f = a_1\phi + a_2\phi^2 + a_3\phi^3 + a_4\phi^4 + a_5\phi^5 + a_6\phi^6 + \dots, \dots\dots\dots (3.26)$$

where $\Delta G = f$ is the free energy, and the coefficients, $a_1, a_2, a_3, \dots$ may be obtained from experiment or first principles / atomistic calculations (Chandra, 2007). Here, the order parameter is chosen to be a unit cell property that varies across a phase transition. For example, in ferroelectrics, this order parameter, ϕ , is identified with the polarization, P , which changes at the domain wall boundaries, and across the paraelectric to ferroelectric transition. It is assumed that the order parameter is small, and higher order terms may be truncated. Typically, this is done at either the 4th or 6th order in existing models, as is the case in the investigations by Haun (1989), Ducharme (2000), Bell (2001), Iwata (2005), and Ishibashi (2005).

The Landau polynomial expansion must also agree with the symmetry of the system. For example, if the $[100]$ and $[\bar{1}00]$ directions have the same free energy, which is the case in cubic or tetragonal BaTiO_3 and PZT systems, then $f(P) = f(-P)$. By retaining only symmetry-compatible terms in the Landau expansion, the coefficients of the odd powers are zero, and the free energy expansion may be reduced to: $f = a_2 P^2 + a_4 P^4 + a_6 P^6 + \dots$. From here, the state of the system may be determined by minimizing the free energy with respect to the order parameter, ϕ , and the thermodynamic functions may be obtained by differentiating the free energy accordingly (Chandra, 2007). This free energy applies to a homogeneous system, but non-homogeneous systems may be handled with an additional term to account for the energy of an interface.

In ferroelectrics, the constant a_2 is usually assumed to be temperature dependent and therefore written as $a_0(T - T_0)$ to be consistent with the Curie-Weiss law in ferroelectrics:

$$\chi = C/(T - T_0), \dots \dots \dots (3.27)$$

where $1/\chi = \kappa$, the dielectric stiffness, T is the temperature, T_0 is a critical temperature, and C is the Curie constant.

With an additional term for the energy due to the electric field, PE , the 6th order Taylor expansion for the free energy may be written as:

$$\Delta G = F_0 + \alpha/2 P^2 + \beta/4 P^4 + \gamma/6 P^6 - PE, \dots \quad (3.28)$$

where $\alpha = \alpha_0(T - T_0)$, β and γ are the coefficients of the polynomial expansion, P is the polarization, E , is the electric field, and F_0 is the free energy density of the paraelectric phase at zero electric field.

In all known ferroelectrics, α_0 and γ are always positive (Chandra, 2007), and β is positive for a second order transition at $T = T_0$, and negative for a first order transition at the same temperature (Chandra, 2007). Plotting the free energy as a function of the order parameter results in a double-well potential below a certain critical temperature, T_c (Figure 3-7). Above a critical temperature, only one free minima exists at $P = 0$, corresponding to the paraelectric cubic phase. For a second order transition, the two cases of $T < T_c$ and $T > T_c$ are illustrated in Figure 3-7.

Figure 3-7: Plot of the free energy polynomial expansion as a function of polarization for the cases of $T < T_c$ and $T > T_c$.

At temperatures above T_c , the material assumes the paraelectric cubic phase, where the central Ti atom remains at the centre of the perovskite structure, as shown in Figure 3-7A. This state is stable, due to the free energy minimum at $P = 0$, but when the system is brought to a temperature below T_c , this state becomes unstable, and any small perturbation (e.g. thermal, etc.) will drive the system towards either of the two free energy minima at $P = \pm P_s$ (Figure 3-7B & C), where P_s is the spontaneous polarization. The spontaneous polarization is the result of the displacement of the central Ti cation relative to the centre of the unit cell and the material assumes the tetragonal ferroelectric phase.

The system may be switched from one polarization state to the other (i.e. from one minima to the other) by application of an electric field that is sufficiently large to overcome the energy barrier between the two states. Application of an electric field modifies the free energy of the system as shown in Figure 3-8, where it can be seen that with a sufficiently large field, the energy barrier to switch the polarization state may be overcome:

Figure 3-8: Hysteresis loop (polarization vs. electric field loop) in an idealized ferroelectric and the plots of the free energy corresponding to various points of the hysteresis curve.

The minima of the free energy are obtained by setting:

$$\partial \Delta G / \partial P = \alpha P + \beta P^3 + \gamma P^5 - E = 0 \text{ with } E = 0. \dots\dots\dots (3.29)$$

Solving for P , we obtain the spontaneous polarization,

$$P_s = \pm \sqrt{\frac{-\beta(1 + \sqrt{1-t})}{2\gamma}} \dots\dots\dots (3.30)$$

where $t = 4\alpha\gamma/\beta^2$ (Ducharme, 2000). Similarly, the intrinsic coercive field may be obtained from equation 6.4, i.e. $E = \alpha P + \beta P^3 + \gamma P^5$, and setting $\partial E / \partial P = 0$. By this method, Ducharme (2000) gives the intrinsic coercive field as:

$$E_c = 6/25 \sqrt[3]{5} (|\beta|^{5/2} / \gamma^{3/2})^{1/\sqrt{2}} [1 + (1 - 5/9t)^{1/2}]^{1/2} [1 + (1 - 5/9t)^{1/2} - 5/3t] \dots\dots\dots (3.31)$$

3.5.1. Extending the Model to 3D

The previous analysis considered only one ferroelectric variant, $P_x = \pm P_s$, as shown in Figure 3-7. In general, however, there are 6 polarization variants ($P_x = \pm P_s$, $P_y = \pm P_s$,

$P_z = \pm P_s$) for the cubic to tetragonal (paraelectric to ferroelectric) transition, as seen in Figure 3-9:

Figure 3-9: Six Polarization Variants for the Cubic to Tetragonal (Paraelectric to Ferroelectric) Phase Transition. Here, a_c is the lattice constant for the cubic phase, while a_T and c_T are the lattice constants for the tetragonal phase.

This leads to a free energy term as a function of the three polarizations (Bell, 2001, Haun, 1989) given by:

$$\begin{aligned}
 F(P_x, P_y, P_z) = & \frac{1}{2}\alpha_0(T - T_c)(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}\alpha_{11}(P_x^4 + P_y^4 + P_z^4) + \frac{1}{2}\alpha_{12}(P_x^2 P_y^2 + \\
 & P_y^2 P_z^2 + P_z^2 P_x^2) + \frac{1}{2}\alpha_{112}[P_x^4(P_y^2 + P_z^2) + P_y^4(P_x^2 + P_z^2) + P_z^4(P_x^2 + P_y^2)] + \\
 & \frac{1}{6}\alpha_{111}(P_x^6 + P_y^6 + P_z^6) + \frac{1}{2}\alpha_{123}P_x^2 P_y^2 P_z^2, \dots \dots \dots (3.32)
 \end{aligned}$$

where T_c is a critical temperature, and α_0 , α_{11} , α_{12} , α_{111} , α_{112} , and α_{123} are the polarization interaction dielectric stiffness coefficients (Haun, 1989) in the Landau polynomial expansion. Note that the expression in equation 3.32 is invariant under the symmetry operations for a cubic system.

In the paraelectric phase, this free energy term has only one minima, corresponding to $P_x = P_y = P_z = 0$, whereas in the tetragonal ferroelectric phase, the free energy has

six minima corresponding to $P_x = \pm P_s$, $P_y = \pm P_s$, $P_z = \pm P_s$, where P_s is the spontaneous polarization.

3.5.2. Domain Wall Energetics

The previous analysis applies entirely to homogeneous systems, but this may be extended to include inhomogeneities, such as domain walls which are usually formed during ferroelectric transitions. The energy cost due to domain walls can be included by adding a gradient term to free energy. The Ginzburg term, $F_{\text{Ginzburg}} = K/2 |\nabla P_i|^2$, where K is a constant, denotes the energy of an interface, and represents the energy cost when the polarizations are not parallel. This energy is related to the domain wall energy (Ahluwalia, 2005), and is analogous to the $|\nabla M|^2$ term for magnetic domain walls, where M is the magnetization. For simplicity, from this point onwards, we will work in 2D, whereby the full inhomogeneous free energy can be expressed as:

$$F_{\text{LG}}(P_x, P_y) = F_{\text{Landau}} + F_{\text{Ginzburg}}, \text{ or}$$

$$F_{\text{LG}}(P_x, P_y) = \frac{1}{2}\alpha_0(T - T_c)(P_x^2 + P_y^2) + \frac{1}{4}\alpha_{11}(P_x^4 + P_y^4) + \frac{1}{2}\alpha_{12}(P_x^2 P_y^2) + \frac{1}{2}\alpha_{112}(P_x^4 P_y^2 + P_y^4 P_x^2) + \frac{1}{6}\alpha_{111}(P_x^6 + P_y^6) + \frac{K}{2}[|\nabla P_x|^2 + |\nabla P_y|^2]. \dots\dots\dots (3.33)$$

3.5.3. Electrostatic Constraints

In general, a spontaneous polarization is associated with an internal depolarizing electric field, which results in an electrostatic energy. The electrostatic constraint is incorporated by including the electrostatic energy given as (Ahluwalia, 2005):

$$F_{\text{electrostatic}} = -(\mathbf{E} \cdot \mathbf{P} + \frac{1}{2}\epsilon_0 \mathbf{E} \cdot \mathbf{E}), \dots\dots\dots (3.34)$$

where ϵ_0 is the permittivity of a vacuum, $\mathbf{P}$ is the polarization vector, and $\mathbf{E} = -\nabla\phi$, the internal electric field, is obtained by solving Gauss's Law, which is one of the four Maxwell equations, given by (Joshi, 1992, Zhang, 2005a):

$$\nabla \cdot \mathbf{D} = \nabla \cdot (\epsilon_0 \mathbf{E} + \mathbf{P}) = \nabla \cdot (-\epsilon_0 \nabla \phi + \mathbf{P}) = \rho, \dots \dots \dots (3.35)$$

where ρ is the space charge, and $\mathbf{D}$ is the electric displacement vector.

These electrostatic interactions significantly influence the microstructures of ferroelectric materials.

3.5.4. Elastic Constraints

As we have seen in Figure 3-9, the paraelectric to ferroelectric (cubic to tetragonal) phase transitions is accompanied by a distortion of the unit cell. This leads to a spontaneous strain, $(a_T - a_c) / a_c$, which is coupled to the polarization. This can be expressed by introducing an elastic energy, $F_{elastic}(\mathbf{P})$ which describes the electromechanical coupling (Cao, 1991), and is given by:

$$F_{elastic}(\bar{P}) = \frac{C_{11}}{2} (\tilde{\epsilon}_{xx}^2 + \tilde{\epsilon}_{yy}^2) + C_{12} \tilde{\epsilon}_{xx} \tilde{\epsilon}_{yy} + \frac{C_{44}}{2} \tilde{\epsilon}_{xy}^2 \dots \dots \dots (3.36)$$

$$\text{where } \tilde{\epsilon}_{ij} = \epsilon_{ij} - Q_{ij} P_i P_j, \text{ i.e. } \begin{cases} \tilde{\epsilon}_{xx} = \epsilon_{xx} - (Q_{11} P_x^2 + Q_{12} P_y^2) \\ \tilde{\epsilon}_{yy} = \epsilon_{yy} - (Q_{11} P_y^2 + Q_{12} P_x^2) \\ \tilde{\epsilon}_{xy} = \epsilon_{xy} - Q_{44} P_x P_y \end{cases}$$

Here, C_{11} , C_{12} , and C_{44} are the strain/compliance constants, Q_{11} , Q_{12} , and Q_{44} are the electrostrictive coefficients, and ϵ_{ij} is the strain in the material.

The values for the strains, ϵ_{ij} , are obtained by solving the elastic stress equation of motion (Joshi, 1992):

$$\nabla \cdot \sigma = \sigma_{ij,j} = \rho \ddot{u}, \dots \dots \dots (3.37)$$

where σ (and σ_{ij}) is the stress tensor, ρ is the density, and $\ddot{u}$ is the acceleration vector.

We use the assumption of mechanical equilibrium, which is commonly used by others

such as Chen (2002), Zhang (2005), Ahluwalia (2000). Hence, $\ddot{u} = 0$, so equation 3.37 may be written in full as:

$$\sigma_{xx,x} + \sigma_{xy,y} = 0 \text{ and } \sigma_{xy,x} + \sigma_{yy,y} = 0, \dots \quad (3.38)$$

In this equation, the comma in the notation denotes a derivative, i.e. $\sigma_{xx,x}$ means $\partial\sigma_{xx}/\partial x$, $\sigma_{xy,y}$ means $\partial\sigma_{xy}/\partial y$, etc. The stresses may be obtained from the strains using:

$$\begin{aligned} \sigma_{xx} &= \frac{\delta F_{el}}{\delta \tilde{\epsilon}_{xx}} \frac{\delta \tilde{\epsilon}_{xx}}{\delta \epsilon_{xx}} = C_{11} \tilde{\epsilon}_{xx} + C_{12} \tilde{\epsilon}_{yy} \\ \sigma_{yy} &= \frac{\delta F_{el}}{\delta \tilde{\epsilon}_{yy}} \frac{\delta \tilde{\epsilon}_{yy}}{\delta \epsilon_{yy}} = C_{11} \tilde{\epsilon}_{yy} + C_{12} \tilde{\epsilon}_{xx} \dots \quad (3.39) \\ \sigma_{xy} &= \frac{\delta F_{el}}{\delta \tilde{\epsilon}_{xy}} \frac{\delta \tilde{\epsilon}_{xy}}{\delta \epsilon_{xy}} = C_{44} \tilde{\epsilon}_{xy} \end{aligned}$$

3.5.5. Kinetics – the TDGL Equation

The previous analysis up to this point only covers the thermodynamics of the phase transition. However, in order to study microstructural evolution, we need a framework to study the kinetics of domain formation and evolution. This is given by the time-dependent Ginzburg-Landau (TDGL) model described by the relaxational equation (Ahluwalia, 2005):

$$\frac{\partial P_i}{\partial t} = -\Gamma \frac{\delta F_T}{\delta P_i}, \dots \quad (3.40)$$

where P_i is the polarization vector, t is time, Γ is a dissipative coefficient, and F_T is the free energy of the system, given by:

$$F_T = \int d\vec{r} \left[F_{LG}(\vec{P}) + F_{elastic}(\vec{P}) + F_{electrostatic}(\vec{P}) \right], \dots \quad (3.41)$$

Note that equation 3.40 is an overdamped equation that leads to $\frac{\delta F_T}{\delta P} \rightarrow 0$ in the long

time limit ($t \rightarrow \infty$). These equations have been shown to be a powerful technique to

simulate microstructural evolution. Substitution of equation 3.41 into 3.40 leads to the full TDGL equations:

$$\frac{\partial P_x}{\partial t} = \Gamma \left[\begin{array}{l} -\alpha_1 P_x - \alpha_{11} P_x^3 - \alpha_{12} P_x P_y^2 - \alpha_{111} P_x^5 \\ -\alpha_{112} (P_x P_y^4 + 2P_x^3 P_y^2) + K \nabla^2 P_x \\ -\phi_{,x} - [2(Q_{11} \sigma_{xx} + Q_{12} \sigma_{yy}) P_x + Q_{44} \sigma_{xy} P_y] \end{array} \right] \dots\dots\dots (3.42)$$

$$\frac{\partial P_y}{\partial t} = \Gamma \left[\begin{array}{l} -\alpha_1 P_y - \alpha_{11} P_y^3 - \alpha_{12} P_x^2 P_y - \alpha_{111} P_y^5 \\ -\alpha_{112} (P_y P_x^4 + 2P_y^3 P_x^2) + K \nabla^2 P_y \\ -\phi_{,y} - [2(Q_{11} \sigma_{yy} + Q_{12} \sigma_{xx}) P_y + Q_{44} \sigma_{xy} P_x] \end{array} \right] \dots\dots\dots (3.43)$$

Here, the polarizations are influenced by the electrostatic and elastic constraints which are given as $\nabla \cdot (-\epsilon_0 \nabla \phi + \mathbf{P}) = \rho$ (equation 3.35), and $\nabla \cdot \sigma = \sigma_{ij,j} = 0$ (equation 3.38) respectively. With these constraints, equations 3.42 and 3.43 may be used to predict the microstructures of ferroelectric materials.

4. Ferroelectric Ceramic PZT

4.1. Experimental Procedure for Ceramic PZT

4.1.1. Device Fabrication / Assembly

Sintered, electroded, and poled ceramic PZT tubular transducers were purchased from Boston Piezo Optics (BPO), and mounted in rubber O-rings purchased from RS components. The tubes were then placed horizontally onto metal jigs (Figure 4-1). Wires were wrapped around the O-rings and connected to the outer quartered-electrodes on the tubes and electric contact was further ensured by application of silver adhesive paste between the wires and the electrodes. Verification of the electrical contact was carried out with a connectivity test using a digital multimeter.

Figure 4-1: Jig Assembly for Mounting of PZT Tubular Transducer using O-rings located at the nodal positions.

4.1.2. Obtaining the Vibration Velocity

The vibration velocity is determined indirectly from the experimental measurement of the resonance frequency and bending displacement. From the following relationship, the vibration velocity, v_v , may be obtained as follows:

$$v_v = \omega \times r = (2\pi \times \text{resonance frequency}) (\text{bending displacement at resonance})$$

$$v_v = 2\pi f_r \zeta \dots\dots\dots (4.1)$$

In order to carry this out, the following setup is used, which allows the measurement of both the resonance frequency and the bending displacement:

Figure 4-2: Experimental Setup for Measurement of Bending Displacement and Resonance Frequency. The tube is mounted horizontally as in Figure 4-1.

The function generator generates two sinusoidal waveforms, with 90 degrees phase difference, which are each amplified by the two high voltage amplifiers. The amplified waveforms are each applied to opposite pairs of electrodes across a piezoelectric tube, causing it to oscillate in its bending vibration mode. The displacement of the tube is picked up by the fotonic sensor, and output as a voltage. The displacement of the tube is sinusoidal, and the magnitude and frequency of the displacement signal may be obtained by the oscilloscope. The oscilloscope also measures the voltage output by the two Trek PZD2000 amplifiers.

4.1.3. Obtaining the Resonance Frequency using the Impedance Analyzer

Before carrying out the setup in Figure 4-2 above, the resonance frequency must be obtained from the minimum point of the impedance-frequency curve, and similarly, the anti-resonance frequency from the maximum point of the curve. The impedance analyzer, the HP4194A (Tanasoiu, 1999, Masys 2003), measures the impedance of the piezoelectric tube, as a function of frequency, with the connections as shown in Figure 4-3 below:

Figure 4-3: Characterization with the Impedance Analyzer

The data is collected using PRAP software (TASI Technical Software Inc.) and a typical output from such a setup includes impedance-frequency and phase-frequency curves as shown in Figure 4-4 below:

Figure 4-4: Typical Phase-Frequency and Impedance Frequency Curves for a Piezoelectric Tube

In this case, the data was obtained from a piezoelectric tube of dimensions: $10 \times 8 \times 20$ mm (OD $\times$ ID $\times$ Length), as measured by a HP 4194A Impedance Analyzer. The measurement of the impedance is carried out by placing the probes on opposite sides of the tube at the nodal points. As there are four sides to the tubes, measurement may be carried out by choosing either pair of electrodes (sides 0 and 2, or sides 1 and 3).

Figure 4-5: Electrode Positions on a Piezoelectric Tube with 4 Equally Spaced Electrodes

Due to the non-uniformity of the tube, a slight difference may be observed between, depending on which pair of electrodes are used for the measurement. However, this difference has been verified to be small—in the graph below, the resonance frequency values are obtained from the raw data as 57.80, 57.89, 57.83, 57.88 kHz, or 57.85 ± 0.05 kHz, which indicates a variation within 0.1%, -regardless of the method used.

Figure 4-6: Impedance-Frequency Relationships when changing the Probe Contact Positions.

Sometimes, multiple resonance peaks on the impedance analyzer are observed, so it may sometimes be necessary to determine which peak refers to the bending displacement mode. In order to do so, the frequencies are normally verified with simulation, or checked against the formula for resonance frequency. The equation

$$f_r = \frac{\sqrt{Y^E} \sqrt{a^2 - b^2}}{2\pi L_{tube} \sqrt{\rho_{tube} (5 + 3\sigma)}} \text{ may therefore be rearranged as:}$$

$$2\pi L_{tube} f_r \sqrt{\frac{\rho_{tube}}{Y^E}} = \frac{\sqrt{a^2 - b^2}}{\sqrt{5 + 3\sigma}} \dots\dots\dots (4.2)$$

The term on the right hand side is the frequency term, and the term on the left hand side is primarily a function of the geometry. Hence, by plotting the dimensionless

frequency term, $2\pi L_{tube} f_r \sqrt{\frac{\rho_{tube}}{Y^E}}$, against the geometric term, $\frac{1}{s} = \frac{\sqrt{D_{tube}^2 + d_{tube}^2}}{4L_{tube}}$ for

both the experimental and theoretical frequencies, it can be determined whether the mathematical model agrees with the experiment.

4.1.4. Obtaining the Bending Displacement at Resonance

Figure 4-7: Obtaining the Bending Displacement at Resonance

Once the resonance frequency is obtained, it is keyed in to the function generator, which generates two sinusoidal waveforms of equal amplitude, but with a phase difference of 90 degrees. This output is amplified via the Trek PZD2000 amplifiers to power the piezoelectric tubes. This will cause the tubes to oscillate in the bending displacement mode, and the bending displacement is obtained using the fotonic

sensor, an optical device that provides non-contact measurement of the displacement of the piezoelectric tube.

The fonic sensor emits light from the probe which is reflected off a metallic strip on the piezoelectric tube. The intensity of the light reflected back into the probe changes with the position of the tube, and the fonic sensor outputs a voltage proportional to the position of the tube. This voltage is then captured by the oscilloscope and the bending displacement is obtained.

In practice, the resonance frequency obtained using the impedance analyzer is not always the frequency of maximum bending displacement. This is because the resonance frequency of the tube experiences a slight shift with the voltage. Hence, the frequency was further fine-tuned, to achieve a maximum signal (of the bending displacement) on the fonic sensor. Since the resonance frequency shifted slightly with the voltage, for every increment of the voltage, the frequency was readjusted as required.

4.1.5. Determining the Material Factor

The vibration velocity of a piezoelectric tube is a product of a constant multiplied by three factors: the electrical factor, the material factor, and the geometric factors. For a given geometry, and electrical input, the performance of the piezoelectric tube is directly proportional to the material factor. Hence, in the selection of materials for piezoelectric tubular ultrasonic motors, materials should be chosen which provide the highest possible material factors. To determine the material factor, the following relationship derived earlier is used:

$$v_v = \frac{16}{\pi} \times \text{ElectricalFactor} \times \text{MaterialFactor} \times \text{GeometricFactor}, \text{ or}$$

$$v_v = \frac{16}{\pi} (V \cos \beta) \left(Q_m d_{31} \sqrt{\frac{Y^E}{\rho_{tube} (5 + 3\sigma)}} \right) \left(\frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}} \right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right)$$

$$\Rightarrow \frac{dv_v}{dV} = \frac{16 \cos \beta}{\pi} \left(Q_m d_{31} \sqrt{\frac{Y^E}{\rho_{tube} (5 + 3\sigma)}} \right) \left(\frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}} \right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right) \dots\dots\dots (4.3)$$

First, vibration velocity is plotted against voltage for each tube. The gradient of this

curve, $\frac{dv_v}{dV}$, is then plotted against the geometric factor, $\left(\frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}} \right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right)$.

Therefore, the above relationship for the vibration velocity may be verified by confirming that the $\frac{dv_v}{dV}$ vs. geometric factor plot is a straight line, with the gradient being a constant that is proportional to the material factor, and the constant of proportionality being numerical equal to $(16 \cos \beta) / \pi$.

4.2. Results and Discussion for Ferroelectric Ceramics

4.2.1. Results for the Resonance Frequency & Bending Displacement

The resonance frequencies and bending displacements (peak-to-peak) measured for each of the PZT tubes with various geometries (see Table 4-1), are shown in Table 4-2 and Table 4-3.

Table 4-1: Dimensions of Tubular Transducers Investigated

Material Used	Length (mm)	Outer Diameter (mm)	Inner Diameter (mm)
PZT Navy Type III	35	10	8
	35	10	9
	50	20	18
PZT Navy Type VI	35	10	8
	42	15	13
	50	20	18

Table 4-2: Resonance Frequencies & Vibration Velocities for PZT Navy Type VI:**VI 50-20-18 (mm, Length x OD x ID)**

V (V)	f_r (kHz)	ζ (10^{-6} m)	v_v (m/s)
0	-	0	0.00000
5	16.797	0.575	0.03034
10	16.737	1.085	0.05705
15	16.706	1.585	0.08319
20	16.71	1.98	0.10394
40	16.5	3.54	0.18350
60	16.4	4.23	0.21794
80	16.3	5.55	0.28420
100	16.4	4.455	0.22953

Theoretical f_r : 16.893**VI 42-15-13**

V (V)	f_r (kHz)	ζ (10^{-6} m)	v_v (m/s)
0	-	0	0.00000
5	19.013	0.645	0.03853
10	18.98	1.165	0.06947
15	18.945	1.71	0.10177
20	18.9	2.21	0.13122
40	18.6	4.115	0.24045
60	18.4	5.5	0.31793
80	18.2	6.6	0.37737
100	18	7.25	0.40998

Theoretical f_r : 18.927**VI 35-10-8**

V (V)	f_r (kHz)	ζ (10^{-6} m)	v_v (m/s)
0	-	0	0.00000
5	20.119	0.835	0.05278
10	20.09	1.54	0.09720
15	20.03	2.105	0.13246
20	20.015	2.585	0.16254
40	19.7	4.47	0.27665
60	19.6	5.85	0.36022
80	19.5	7.3	0.44721
100	19.3	8.95	0.54266

Theoretical f_r : 19.785

Table 4-3: Resonance Frequencies & Vibration Velocities for PZT Navy Type III:**III 50-20-18 (mm, Length x OD x ID)**

V (V)	f_r (kHz)	ζ (10^{-6} m)	v_v (m/s)
0	-	0	0.00000
5	24.295	0.595	0.04541
10	24.25	1.105	0.08418
15	24.245	1.585	0.12073
20	24.24	2	0.15230
30	24.4	3.155	0.24185
50	24.3	5.5	0.41987
80	24.2	7.58	0.57628

Theoretical f_r : 17.227**III 35-10-8**

V (V)	f_r (kHz)	ζ (10^{-6} m)	v_v (m/s)
0	-	0	0.00000
5	20.119	0.835	0.05278
10	20.09	1.54	0.09720
15	20.03	2.105	0.13246
20	23.831	2.625	0.19653
40	23.8	5.1	0.38133
60	23.7	7.1	0.52864
80	23.7	9.35	0.69616
100	23.7	10.6	0.78923

Theoretical f_r : 20.177**III 35-10-9**

V (V)	f_r (kHz)	ζ (10^{-6} m)	v_v (m/s)
0	-	0	0.00000
5	24.295	0.595	0.04541
10	24.25	1.105	0.08418
15	24.245	1.585	0.12073
20	24.24	2	0.15230
30	24.4	3.155	0.24185
50	24.3	5.5	0.41987
80	24.2	7.58	0.57628

Theoretical f_r : 25.822

A comparison of the normalized resonance frequency parameter, $2\pi L_{tube} f_r (\rho_{tube}/Y^E)^{1/2}$ (equation 4.2) as a function of the inverse of the shape factor, $1/s = \sqrt{(D_{tube}^2 + d_{tube}^2)} / 4L_{tube}$, is shown in Figure 4-8 (Ng, 2006).

Figure 4-8: Theoretical and Measured Resonance Frequencies for Tubular Transducers of various geometries (specified in mm as length-OD-ID-material, where OD refers to the tubular outer diameter, ID refers to inner diameter, and the material “III” indicates PZT Navy Type III while “VI” indicates PZT Navy Type VI).

4.2.2. Discussion on the Resonance Frequency and Bending Displacement

As Figure 4-8 shows, there is a good experimental agreement between the dimensionless resonance frequency parameter, $2\pi L_{tube} f_r (\rho_{tube}/Y^E)^{1/2}$, and the curve predicted by the Timoshenko model. A slight shift in the resonance frequency is experienced as the voltage is increased, but this shift is small enough that the experimental values do not deviate significantly from those obtained theoretically. However, a mathematical model accommodating for this shift in the resonance frequency would further improve the correlation.

The experimental bending displacement, on the other hand, does not agree with the relationship implied by equation 4.3 (which is derived from the Timoshenko model). This is because the material property data obtained from the vendor, in particular the mechanical quality factor and piezoelectric constant, d_{31} , is based on two assumptions. Firstly, it is assumed that the material properties obtained using the IEC standards,

which utilizes low voltage characterization, is the same as that obtained at higher voltages. Secondly, that these material properties are independent of the frequency, which is a function of the vibration mode used as well as the geometry of the sample.

Characterization is often carried out using the radial vibration mode of a disc-shaped sample of the material. If the bending vibration mode was used for characterization of a tube-shaped sample of the same material, the properties obtained would not necessarily be the same:

Figure 4-9: Radial Vibration Mode of a Disc-Shaped Sample

These assumptions imply that the mechanical quality factor and the piezoelectric constant, d_{31} , is not purely a function of the material formulation and processing, but is also a function of the geometry of the sample, the vibration mode used, and/or the voltage applied. If this is so, knowing how this factor, Q_m , scales with the geometry, electric field and other parameters is therefore important when optimizing a material for a different geometry or a different vibration mode.

4.2.3. Vibration Velocity vs. Geometrical Factor

The gradient of the vibration velocity was plotted against the geometric factor in Figure 4-10 (Ng, 2006).

Figure 4-10: Gradient of Vibration Velocity vs. Voltage Curve Plotted Against Geometric Factor for PZT III and PZT VI (geometry specified as length-OD-ID material) and with various resonance frequencies (indicated on graph in Hz).

Figure 4-10 shows the plot of dv_v/dV versus the geometric factor,

$$\left(\frac{L_{tube} \times \frac{I_{nodal}}{L_{tube}} \left(1 - \frac{I_{nodal}}{L_{tube}} \right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right) \text{ with a least squares regression line connecting the data points}$$

for PZT Navy Type III and a second least squares regression line connecting the data points for PZT Navy Type VI. These results, including Figure 4-8 and Figure 4-10 have been published in the *Journal of Electroceramics* (Ng, 2006). Due to the larger values of the factor $Q_m \times d_{31}$ in hard PZT, the vibration velocities in PZT III are expectedly higher.

According to the theoretical relationship obtained earlier, the following relationship is expected.

$$\frac{dv_v}{dV} = \frac{16 \cos \beta}{\pi} \times MaterialFactor \times GeometricFactor \dots\dots\dots (4.4)$$

From the above graph, a deviation is observed from the expected relationship for both materials, particularly PZT Navy Type III.

This deviation may be addressed through observation of the following assumptions. One assumption made is that for materials PZT Navy Type III and PZT Navy Type VI, the “material factor” is constant with geometry, voltage, and frequency. [see Appendix, section 10.1, for specifications of PZT Navy Type III, PZT Navy Type VI]. However, this assumption is not always valid, as previous research has shown that the material properties are a function of domain wall mobility, and there is an increased difficulty in changing the alignment of the domain walls at high frequency (Masys, 2003) which occurs at higher values of the geometric factor. We also note that the domain wall mobility is higher in soft piezoelectric materials, but lower in hard piezoelectric materials where the domain walls are pinned by impurities. Since the piezoelectric response requires the motions of domain walls, we would expect that at sufficiently high frequencies, there will be insufficient time for the motion of domain walls, resulting in a reduced piezoelectric response. It also follows that materials with higher domain wall mobilities (e.g. soft PZT) would require less switching time than those with lower domain wall mobilities (e.g. hard PZT).

4.2.4. Influence of Domain Wall Mobility on the Mechanical Quality Factor and d_{31}

While domain wall mobility affects the material properties, its influence is only significant on a few of these properties. Of the material properties: Y^E , ρ_{tube} , d_{31} , Q_m , σ , and the shape factor, s , which is a function of σ , we can eliminate the variables: Y^E , ρ_{tube} , σ , due to the matching of the theoretical and experimental values of the

resonance frequency, $f_r = \frac{\sqrt{Y^E} \sqrt{a^2 - b^2}}{2\pi L_{tube} \sqrt{\rho_{tube}(5 + 3\sigma)}}$, as explained in Section 4.2.1.

Furthermore, the shape factor, s , is also an unlikely candidate, since results [see Appendix, section 10.4] have shown that s does not vary significantly with σ .

This leaves us with the two factors most likely to be influenced by the domain wall mobility, the mechanical quality factor, Q_m and the piezoelectric constant, d_{31} . Since domain wall mobility has a frequency dependence (Cain, 1998), and since this resonance frequency is a function of the geometry, an understanding of how Q_m scales with the resonance frequency or the geometry of a sample is important in the development of piezoelectric material for a different form factor or for a different size. Would the material formulation or processing have to be optimized in a different way if the form factor or size of the sample is changed? Existing literature indicates that very high mechanical quality factors can be achieved in single-crystalline ferroelectric materials, but this is difficult to achieve in PZT (as compared to BaTiO₃, for example). Moreover, the behavior of these material properties (in particular d_{31} and Q_m) when incorporated into a tubular transducer as opposed to other geometries has not been fully investigated.

4.2.5. Maximum Vibration Velocity vs. Geometric Factor

Given the relationship for the vibration velocity, v_v , given by equation 3.21, the maximum vibration velocity achievable, *for a given geometry*, is given by:

$$(v_v)_{\max} = \frac{16}{\pi} (V_{\max} \cos \beta) \left(Q_m d_{31} \sqrt{\frac{Y^E}{\rho_{tube} (5 + 3\sigma)}} \right)_{\max} \times \left(\frac{L_{tube} \times \frac{l_{nodal}}{L_{tube}} \left(1 - \frac{l_{nodal}}{L_{tube}} \right) \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \right) \dots\dots\dots (4.5)$$

Hence, there are two parameters governing the maximum vibration velocity:

- (1) the magnitude of the material factor, $Q_m d_{31} \sqrt{\frac{Y^E}{\rho_{tube} (5 + 3\sigma)}}$
- (2) the magnitude of the electrical voltage, V

For any tube, there is a maximum electric field that the material can take before it breaks down. This, in turn, sets an upper limit on the maximum voltage that can be applied. Therefore, there is a constant, $V_{\max}$, which sets an upper limit that is dependent on the material.

For this reason, the maximum vibration velocity obtained for each tube was plotted against the geometric factor as shown below:

Figure 4-11: Plot of Maximum Vibration Velocity vs. Geometric Factor

The above graph indicates that, for a given material, there is an “optimum” geometric factor that will provide the largest vibration velocity. This may be important in future, when optimizing the vibration velocity of an actuator for a given material formulation. Alternatively, it should be noted that where the tube wall thickness drops from 2mm to 1mm, the points deviate from the original trend. This could also indicate a geometric dependence of the material properties.

4.2.6. Frequency Dependent Properties

The piezoelectric constants of the PZT tubes described in Table 4-1 were also obtained as a function of frequency, based on the relationship for the vibration velocity, v_v , in equation 3.21. The material constants used were based on the commercial data listed in Appendix 10.1, and the vibration velocities were obtained

experimentally using the techniques described in Section 4.1. Figure 4-12 shows a plot of the effective d_{31} constant ($Q_m \times d_{31}$) as a function of frequency as follows:

Figure 4-12: Effective Piezoelectric Constant as a Function of Frequency in Tubular Transducers of Hard & Soft PZT.

Figure 4-12 shows that in hard PZT, there is a reduction of the piezoelectric response at higher frequencies, as evidenced by the decrease in the effective d_{31} constant. This result is important in the development of piezoelectric tubular transducers as the reduced piezoelectric response would affect the optimal design of such devices. Currently, no work on the frequency-dependent characteristics of piezoelectric tubular transducers has been published so far. However, degradation of the d_{33} constant (but not d_{31} constant) in thin films at high frequencies has been observed by Damjanovic, 1998 as shown below:

Figure 4-13: Frequency dependent behavior of ferroelectric thin film by Damjanovic for (a) the direct piezoelectric effect in Nb-doped PZT, and (b) converse piezoelectric effect in PZT.

It should be noted that these results by Damjanovic (1998), were obtained for thin film, with corrections for the clamping effects due to the substrate. The key similarities and differences between these results by Damjanovic and this project are outlined as follows in Table 4-4:

Table 4-4: Similarities and differences between the results by Damjanovic and this project

	Damjanovic, D.	NTU
Form Factor	Thin Film	Bulk Tubular Transducer
Materials Investigated	Nb-doped PZT (direct effect) and PZT (converse effect)	Hard PZT-III & soft PZT-VI (converse effect)
Material Property	d_{33}	d_{31}
Trend	Linear	Linear
Frequency-dependence	Decreases with frequency	Decreases with frequency

4.3. Summary of Chapter 4

In summary, relationships for the resonance frequency, bending displacement, and vibration velocity have been derived for ceramic piezoelectric tubular transducers, whereby the device performance is governed mainly by the term $Q_m \times d_{31}$. In hard PZT-III, both the vibration velocity, v_v , and $Q_m \times d_{31}$ are larger in magnitude, compared to soft PZT-VI. Furthermore, we observe frequency-dependent behavior in hard PZT-III which is believed to be due to the lower mobility of the domain walls.

5. Ferroelectric Polymers

5.1. Experimental Procedure for Ferroelectric Polymers

Poled P(VDF-TrFE) 25 μ m film in 70-30 mol% ratio purchased from Piezotech, France, was electroded using Au sputtering, which was chosen over alternate electroding methods, such as silver paste. Silver paste was avoided partly due to the unknown effects of the organic solvent in which the silver paste was dissolved in, and partly due to observed swelling in the film when excessive amounts of silver paste were added. The film was rolled into tubes of various sizes, the edges of the film being held together using adhesive or heat. The application of heat was preferred over adhesive, due to the possible effects of the adhesive on the dynamic behaviour of the tube. Potential problems would include the acoustic impedance mismatch between the two materials, due to the different densities, Poisson ratio, and Young's modulus. On the other hand, while the application of heat would allow this issue to be circumvented, this would change the thermal history in one section of the tube, namely the location where the film edges overlap. However, this thermal history could be reset by annealing and repoling the material. Other processing methods to fabricate tubes were explored, such as casting, using a metal jig, but this method had a number of disadvantages such as: (a) the difficulty of electroding the inner wall of the tube, and (b) the large minimum wall thicknesses which would require the application of very large electric fields of at least 40 times that required in thin films. Annealing of the tubes was carried out at 135°C, which is below the melting point of the film, which is about 140°C in literature. This temperature was reconfirmed in the current films using differential scanning calorimetry (DSC) with thermogravimetric analysis (TGA), whereby the latter was used to confirm the maximum allowable temperature

for the DSC measurement, and the DSC characterization used to determine the melting point of the material.

Measurement of the film thickness was verified using an elcometer, in conjunction with a digital micrometer. The elcometer had the advantage over the digital micrometer, due to its ability to measure film thickness in polymers without compressing the film (and hence reducing the measurement), but had one disadvantage—the polymer film thicknesses were smaller than the optimum measurement range of the instrument. However, the difference in measurement between the two instruments was only about 1-2 microns in a 40 micron thin film, with the digital micrometer consistently obtaining the smaller reading (Note that a measurement of 40 μ m in thickness via elcometer and 38-39 μ m via micrometer, translates into an error of at most $(\frac{1}{38} - \frac{1}{40}) = 0.13\%$ in the coercive field value). This was expected because the digital micrometer would be expected to compress the film slightly. Measurement of the film thickness using a surface profiler were not used, as the readings were about 3 times those measured by the digital micrometer and elcometer, the likely reason being an air gap between the film and the glass substrate below it. Hence, surface profiler film thickness measurements would only be possible for film processed in-house, and not for the commercially-obtained film purchased from Piezotech, S. A., France.

Figure 5-1: Summary of Main Steps in the Experimental Procedure for P(VDF-TrFE) Film

Characterization of the ferroelectric properties was carried out in the same way as ferroelectric ceramic PZT, which is described as follows. At the pre-calculated nodal points (calculated using the mode shape equation, i.e. equation 10.3 in the Appendix), $\phi 50\mu\text{m}$ wire was taped to the tube using copper conductive adhesive (purchased from RS components). Characterization with a Radiant Technologies RT6000HVA/S ferroelectric tester was used to obtain the polarization-electric field (P-E) hysteresis loops while the MTI2000 Fotonic Sensor provided optical non-contact measurement of the displacement. The tube was vertically-mounted and operated in longitudinal extension mode to obtain the piezoelectric constant, d_{31} , which was verified against the data provided by the commercial supplier. The Young's Modulus was measured using a Instron microtester.

A second tube of $\phi 6.0 \times L 18.7\text{mm}$ was electroded with a single inner electrode and quartered outer electrodes and mounted at the pre-calculated nodal points based on the Timoshenko Beam Theory ($J_{nodal}/L_{tube} = 0.223$ and 0.776) to simulate the free-free boundary condition. The tube was powered by a 2-channel Yokogawa FG300 function generator coupled to two Trek PZD2000 high-voltage amplifiers. Peak-to-peak displacement was obtained using the MTI2000 sensor, and the displacement frequency verified as identical to the frequency of the input voltage before measurement. A frequency sweep was performed whereby the resonance frequency was obtained. In addition to these measurements, displacement versus voltage loops were obtained over a range of frequencies. In order to induce the electrostrictive mode in P(VDF-TrFE) tubular transducers, the applied electric field was increased to values exceeding the coercive field, E_c . As an additional check, films were tested to confirm that properties such as breakdown voltage, remnant polarization, and coercive field and hysteresis loop shapes remained unchanged before sputtering (using aluminum plates as electrodes) & after sputtering (using the Au coating as the electrode and wires taped to the coating with conductive adhesive tape). For further checks on the film quality, hysteresis loops were compared with published experimental results as well as theoretically derived hysteresis loops using a prediction based on a Maxwell-Boltzmann model as explained in the next section.

5.1.1. The Maxwell-Boltzmann Model

5.1.1.1. Polarization as a function of Electric Field

The hysteresis loops obtained in a ferroelectric material may be estimated theoretically using the relationship by Takahashi (1980):

$$\text{Polarization, } P(E) = P_{\max} \langle \cos \theta \rangle = P_{\max} \int_0^{\pi} \cos \theta \cdot f(\theta, E) d\theta \dots\dots\dots (5.1)$$

where $P_{\max}$ is the maximum polarization in the material, $f(\theta, E)$ is the distribution function of the dipoles as a function of the electric field, E , and where $f(\theta, E)$ must satisfy the equation: $\int_0^{\pi} f(\theta, E) d\theta = 1$.

If we assume that the dipoles follow the Boltzmann distribution function, then $f(\theta, E)$ is given by (Takahashi, 1980):

$$f(\theta, E) = \exp\left(\frac{E\mu \cos \theta}{kT}\right) \left[\int_0^{\pi} \exp\left(\frac{E\mu \cos \theta}{kT}\right) d\theta \right]^{-1} \dots\dots\dots (5.2)$$

where μ is the dipole moment of CF_2 and k is the Boltzmann constant.

5.1.1.2. Calculation of $P_{\max}$

Evaluation of Equation 5.1 requires the calculation of $P_{\max}$, the maximum polarization in the material, and this may be obtained from the dipole moment of β -PVDF (Lovinger, 1983, Furukawa, 1997), given by $\mu = 7.0 \times 10^{-30}$ C-m or 2.1 Debye. The direction of the dipole relative to the polymer chain is as shown in Figure 5-2:

Figure 5-2: Dipole Moment of β -PVDF

There are two chains per unit cell of PVDF (Lovinger, 1983) which come from the two carbon-fluorine (C-F) bonds. PTrFE has three C-F bonds, but the third C-F bond is in the opposite direction of the first two C-F bonds, reducing the effective number of dipole moments per unit cell from 2 to 1. Hence the number of chains per unit cell of P(VDF-TrFE) 70-30 mol% is $2 \times 70\% + 1 \times 30\% = 1.7$.

The maximum polarization occurs when the maximum number of dipoles are aligned in the same direction. Hence, $P_{\max} (\text{C/m}^2) = N\mu$, where μ is the dipole moment per unit cell (C-m), and N is the number of unit cells per m^3 of polymer. The variable, N , may be calculated using, $N = 1 \text{ m}^3 / \text{unit cell volume (in m}^3\text{)}$, where the unit cell volume for the beta phase = $8.58 \times 4.91 \times 2.56 \times 10^{-30} \text{ m}$ (since the lattice constants are $a = 8.58 \text{ \AA}$, $b = 4.91 \text{ \AA}$, and $c = 2.56 \text{ \AA}$ by Furukawa (1997), Lovinger (1981), and Kepler (1978). The average dipole moment per unit cell of P(VDF-TrFE) is $\mu = 1.7 \times 7.0 \times 10^{-30} \text{ C-m}$. This calculation may be summarized in the relationship (Furukawa, 1997):

$$P_{\max} = n\mu/abc, \dots\dots\dots (5.3)$$

with n , the number of dipoles per unit cell equal to 1.7 ($n = 2$ in the case of PVDF in the paper by Furukawa, 1997), whereby we obtain $P_{\max} = 0.110 \text{ C/m}^2$. Since the

amorphous phases do not contribute to the polarization, we multiply $P_{\max}$ by crystallinity (e.g. if the crystallinity is 80% , $P_{\max} = 0.088 \text{ C/m}^2$). In general,

$$P_{\max} = \frac{\mu \times (2x_{\text{VDF}} + x_{\text{TrFE}})}{(a \times b \times c)} \times \text{Crystallinity} \dots\dots\dots (5.4)$$

where x_{VDF} is the mole fraction (mol%) of the VDF monomer and x_{TrFE} is the mole fraction of the TrFE monomer. In the above expression, $(2x_{\text{VDF}} + x_{\text{TrFE}})/(abc)$ is equal to number of dipoles per unit volume.

Making use of the relationship $x_{\text{TrFE}} = 1 - x_{\text{VDF}}$, equation 5.4 may be simplified as:

$$P_{\max} = \frac{\mu \times (1 + x_{\text{VDF}})}{(a \times b \times c)} \times \text{Crystallinity} \dots\dots\dots (5.5)$$

5.1.1.3. Modifications to the Model by Takahashi

To obtain the full polarization-electric field (P-E) hysteresis loop, we substitute equation 5.2 into 5.1 and calculate the integral using Simpson's rule. The results of the integration were further verified by comparing the numerical integration using the trapezium rule (first order approximation), Simpson's rule (second order approximation) and Boole's rule (fourth order approximation) whereby the same result was obtained to 6 significant figures.

Initial results showed that the Boltzmann distribution function suggested by Takahashi (1980) could not fully explain our experimentally-obtained hysteresis loops. Hence, we found it necessary to include a scale factor, α , such that equation 5.2 becomes:

$$f(\theta, E) = \exp\left(\frac{\alpha E \mu \cos \theta}{kT}\right) \left[\int_0^\pi \exp\left(\frac{\alpha E \mu \cos \theta}{kT}\right) d\theta \right]^{-1} \dots\dots\dots (5.6)$$

In addition, in order to obtain values for the negative electric field, we reflect the P-E curve about the origin, as well as adding a phase shift between the polarization and the

electric field to obtain the hysteresis curve. The phase shift, ϕ , was added by replacing the electric field values, E , with E' where

$$E' = E_0 \cos[\cos^{-1}(E/E_0) + \phi] \dots\dots\dots (5.7)$$

Using this relationship, it can be easily seen that E' will be equal to E when $\phi = 0$. The phase shift was then adjusted such that the theoretical coercive field matched the experimental coercive field.

5.2. Results and Discussion for Ferroelectric Polymers

5.2.1. Results – Hysteresis Loops

Calculation of $P_{\max}$ using equation 5.5 is compared with experimental data obtained from the Radiant Ferroelectric Tester, as well as with existing literature as shown in Table 5-1:

Table 5-1: Comparison of theoretical & experimental values of $P_{\max}$

Description	$P_{\max}$ (C/m ²)
Theory / Calculation	0.088
Experimental Data	0.083
Literature (Takahashi, 1980)	0.090
Literature (Bauer, 1994)	0.075

The crystallinity used in the calculation was 80%, based on the experimental DSC data for the P(VDF-TrFE) 70-30 mol% thin film. The corresponding Boltzmann distribution function, $f(\theta, E)$, evaluated from equation 5.6 for different values of αE , is as shown:

Figure 5-3: Boltzmann distribution function, $f(\theta, \alpha E)$, for various electric field strengths
 Evaluation of equation 5.1 using the above Boltzmann distribution function yielded the following graph of polarization versus αE :

Figure 5-4: Polarization versus αE as calculated from equation 5.1 where $f(\theta, E)$ is the Boltzmann distribution function

Figure 5-4 is converted into a hysteresis loop by reflecting the curve about the origin, and adding a phase lag of 29° which is the correction required to remove the phase lag

between the forward & reverse curves of the experimental hysteresis loop as shown in Figure 5-5:

Figure 5-5: Phase Shift Correction required to minimize the difference between the forward and reverse curves of the P-E hysteresis loop.

Hence, by adding a 29° phase correction, and adjusting α to fit the experimental E_c of the curve, a reasonably close fit between the calculated & experimental P-E loops may be obtained. The graph of the polarization versus electric field (i.e. the hysteresis loop) for the P(VDF-TrFE) 70-30 mol% copolymer (as obtained from the Radiant Ferroelectric tester) is shown in Figure 5-6. The calculated theoretical curve using the Maxwell-Boltzmann assumption, with $\alpha = 34$, is also shown.

Figure 5-6: Experimental Hysteresis Loops for commercial P(VDF-TrFE) 70-30 mol% 25 μm film, with theoretical hysteresis loop shown for comparison.

Based on these results, the experimentally obtained hysteresis loops show reasonable agreement with the theoretically-predicted hysteresis loops, particularly in the prediction of the remnant polarization, P_r , which is the polarization at zero electric field (i.e. the vertical intercept). A likely reason for the differences between the two results near the coercive field (i.e. the horizontal intercepts) would be that the assumption of a Maxwell-Boltzmann distribution (i.e. equation 5.6) does not hold in that region. This issue can be addressed using the time-dependent Ginzburg-Landau (TDGL) model which is described in detail in chapter 6. Lastly, the meaning of the fitting for the constant $\alpha = 34$ in equation 5.6 is expected to be related to the formula by Scott (1998) where he mentions a Maxwell Boltzmann distribution of defect energies, $n(E) = n_0 \exp[bE/kT]$, where b is a temperature independent parameter with dimensions of an effective charge. Hence, the constant, α , is an indication of the defects in the material whereby the coercive field is reduced from the intrinsic coercive field.

5.2.2. Results – Piezoelectric Mode

The performance for the tubular transducer ($L = 14.5\text{mm}$, $\phi = 4.0\text{mm}$, $t = 25\mu\text{m}$) operating in piezoelectric mode showed a linear relationship between the longitudinal strain and the applied electric field. The plot of the strain vs. electric field was linear up to about 1.5kV (60 MV/m), whereby the piezoelectric constant was obtained as $d_{31} = 5.3\text{ pC/N}$ as shown in Figure 5-7 (Ng, 2007):

Figure 5-7: Strain as a Function of Electric Field for a Piezoelectric Tubular Transducer of length 14.5mm, ϕ 4.0mm

Beyond 60MV/m , strain-electric field butterfly curves were obtained, indicating switching in the material. For the tube in bending displacement mode, the best response at low frequency occurred around 25Hz . A dynamic displacement of 0.5 microns was obtained at about 25MV/m as shown in Figure 5-8 for $V=0$ to 627V (about 25MV/m) (Ng, 2007).

Figure 5-8: Bending Displacement as a Function of Electric Field for a Piezoelectric Tubular Transducer

Displacement measurement repeatability was verified at several frequency ranges up to 2kHz, but a lack of repeatability was observed in the 9-15kHz range, probably due to instabilities resulting from the thin wall of the tube as well as the emission of audible acoustic energy in this range. Matching of the electrical input frequency with the frequency of the displacement output from the photonic sensor was not observed in frequencies above 20-30 kHz. Resonance peaks were observed near the resonance frequency predicted by Timoshenko Beam Theory (11.9 kHz, for Poisson Ratio $\sigma = 0.4$). At electric fields greater than the coercive field, E_c , the tube maintains its circular motion in a 2-D plane, but operates in an electrostrictive mode with strain and displacement proportional to the square of the electric field ($S_1 = M_{13}E_3^2$, where S_1 is the strain, M_{13} is the electrostrictive coefficient and E_3 is the electric field). This allows greater strain than the piezoelectric mode with strain directly proportional to the electric field ($S_1 = d_{31}E_3$). At fields of $E = 90\text{MV/m} > E_c$, a maximum peak-to-peak bending displacement of $4\text{ }\mu\text{m}$ was obtained for a 18.7 mm length tubular

transducer of 7mm diameter. These results in section, including Figure 5-7 and Figure 5-8 have been published in the journal, *Electrochemical & Solid State Letters*, (Ng, 2007). In the next section, the results are discussed in greater detail as follows.

5.2.3. Results – Electrostrictive mode

The results in Figure 5-9 below show the tubular transducer peak-to-peak displacements when operating in electrostrictive mode (electric field > coercive field of the material) for the P(VDF-TrFE) 70-30 mol% tubular transducer ($\phi 7\text{mm}$, $L_{tube} = 18.7\text{mm}$, $thickness = 25\mu\text{m}$). The quadratic shape of the curve is due to the quadratic characteristic of the electrostrictive strain.

Figure 5-9: Peak-to-Peak Displacement – Voltage Characteristics for a Electrostrictive Mode P(VDF-TrFE) 70-30 mol% Tubular Transducer of 7mm diameter, 18.7mm length.

5.2.3.1. Results - Frequency Dependent Properties of Tubular Transducer Device

The shape of the displacement-voltage relationship for the polymer tube as a function of frequency (ranging from 0.02Hz to 20Hz) is shown:

Figure 5-10: Shape of the Displacement – Voltage Curve for a P(VDF-TrFE) polymer tubular transducer for the frequencies: 20 mHz, 50 mHz, 0.1Hz, 0.2 Hz, 0.5 Hz, 1 Hz, 2 Hz, 5 Hz, 10 Hz and 20Hz.

From the above results, the peak-to-peak displacements in microns may also be plotted as a function of the frequency of the sinusoidal electrical inputs:

Figure 5-11: Peak-to-Peak Displacement – Frequency Characteristics for a Ferroelectric Polymer in Electrostrictive Mode

Figure 5-12: Electrostrictive Coefficient as a function of Frequency

A discussion on these results is covered in the following section.

5.3. Discussion

5.3.1. Discussion – Piezoelectric Mode

The displacement vs. electric field result in Figure 5-7 showed a linear tubular response at 1.5kV (60MV/m), and the d_{31} value of 5.3pC/N is close to the commercial specification of 6 pC/N $\pm$ 20% (i.e. 6 $\pm$ 1.2 pC/N). In bending displacement mode, a linear relationship is obtained which is agreement with theory, when a Q value of about 0.18 is used. The effect of air resistance is believed to be negligible at 25Hz measurement range, as it would cause a deviation from the linear relationship observed. Furthermore, the tubular vibration velocity was small (40 μ m/s). However, this may not be the case near the Timoshenko resonance frequency of 11kHz (with vibration velocity of 3.4 mm/s). Air resistance could be a factor in the lack of repeatability of the data in the 9-15 kHz range, as well as the lack of matching between the electrical input frequency & displacement output frequency above 20-30 kHz.

The linear bending displacement curve in Figure 5-8 deviates with a slight quadratic component at higher electric fields, indicating the possibility of an electrostrictive component and/or Maxwell stress component to the displacement³. The Maxwell stress is due to the electrostatic forces between the charges and contributes a strain, $S_1 = \frac{1}{2}K\epsilon_0 E_3^2(1+2\sigma)/Y^E$, where K is the relative dielectric constant, E_3 is the electric field, σ is the Poisson ratio, and Y^E is the Young's modulus (Zhang, 2002b). For large electric fields, the magnitude of this component should be incorporated into the present constitutive relationships, but it is believed that this is not required for the voltage ranges tested, as the displacement for the tube under longitudinal mode was linear. The operating principle of the tubular transducer with quartered electrodes requires the extension of one segment of the quartered tube and the contraction of the opposite segment via the piezoelectric effect. The effect of electrostriction and Maxwell stress is proportional to the square of the electric field, would increase the extension of one segment, but reduce the contraction on the opposite segment. The calculated strain due to this effect ($S_1 = \frac{1}{2}K\epsilon_0 E_3^2(1+2\sigma)/Y^E$) was about 10% of the piezoelectric strain ($S_1 = d_{31}E_3$) at 250V, but 20% at 500V. Tubular performance and displacement measurement at higher voltages were not carried out as the piezoelectric relationship is only linear at lower electric fields, and at the elastic regime of the polymer. With an appropriate change in the driving method applied to the electrodes, it is possible for the tube to be operated in the electrostrictive regime. The higher electric fields would result in increased strain and energy densities, but at the expense of greater polarization fatigue.

5.3.2. Discussion – Electrostrictive Mode

The tubular performance in the electrostrictive mode (Figure 5-9) allowed greater displacements than the piezoelectric mode (Figure 5-8), and therefore confers the benefits of greater transducer performance. The quadratic relationship of the peak-to-peak displacement versus voltage curves is indicative of the quadratic nature of the electrostrictive effect. Due to the phase lag in the polarization-electric field relationship, there is also an experimentally-observed phase lag between the displacement and the electric field.

To use the former relationship however, an understanding of the relationship between the polarization, P , a function of the electric field, E , is required. This may be obtained in three different ways, using the Maxwell Boltzmann assumption (as described in section 5.1.1), Landau theory for homogeneous systems (described later in chapter 6), and the time-dependent Ginzburg-Landau (TDGL) model discretized over a $n \times n$ grid, with n = an integer such as 64, or 128 (also described later in chapter 6). Using this third model allows a prediction of the material behavior with the introduction of “defects” into the grid, which result in a change in the behavior of the polarization-electric field curve.

In addition, thickness-dependent and size-dependent materials behavior may be derived by reducing one of the grid dimensions to a certain critical size. An understanding of ferroelectric materials behavior at the nanoscale has significant importance in the development of miniaturized devices for applications in areas such as the biomedical industry. On another note, in the semiconductor industry, interest in miniaturized ferroelectric memory devices has developed, due to its potential to replace existing magnetic memory devices (Scott, 2005). For these two reasons, a

mathematical model to understand ferroelectric materials behavior at sub-micron and nano-scales is developed. The details are described later in chapter 6.

5.4. Comparison with Ceramic PZT

In these studies, it can be seen that both hard PZT and P(VDF-TrFE) exhibit frequency dependent behavior, with a reduction in the effective material constants as a function of frequency (Figure 4-12 for PZT and Figure 5-12 for P(VDF-TrFE)). In terms of the suitability of these materials for applications based on tubular transducers, P(VDF-TrFE) versions achieve higher displacements at low frequencies, due to the quadratic relationship between displacement and voltage. At higher frequencies, however, there was a significant degradation in the material constants in addition to stability issues. For this reason, PZT versions would be more suitable for applications requiring high-frequency operation or high vibration velocities.

5.5. Summary of Chapter 5

The feasibility of fabricating P(VDF-TrFE) tubular transducer equivalents of their ceramic counterparts for bending-mode operation has been demonstrated. In these devices an (almost) linear relationship between bending displacement and driving voltage is observed, with a deviation due to a quadratic component resulting from electrostriction and Maxwell stress. We demonstrate the ability of these tubes to operate in electrostrictive mode with a quadratic relationship between bending displacement and electric field is observed, in contrast to the linear relationship of the ceramic PZT equivalents.

6. Theoretical Modeling of Ferroelectrics

6.1. Motivation

Recent advances in technology are pushing the size of practical devices down to nanometer length scales (Tagantsev, 2006). Devices at this length scale have diverse applications, ranging from biosensors to ferroelectric random access memory (FRAM) devices. However, while theories have been developed for bulk ferroelectric materials, behavior at the nanoscale is poorly understood, as at these length scales, size-effects can no longer be ignored (Tagantsev, 2006). The motivation for this section is therefore to understand the behavior of state-of-the-art nanoscale devices based on ferroelectric material, and here, we describe a theoretical framework to study microstructural evolution in ferroelectrics at the nanoscale. With this model, we demonstrate domain formation in ferroelectrics as well as its ability to predict and explain properties of nanoscale ferroelectrics, which is useful for practical applications in the biomedical and electronics industries.

6.1.1. Motivation – Existing Nanoscale Devices Based on Ferroelectric Materials

FRAM devices are already outperforming their existing magnetic based counterparts in the laboratory (Dawber, 2005. Scott, 2005), and in fact are already in commercial production. For example, a Fujitsu 8-kbit PZT-based FRAM is used in every Sony Playstation 2 and Matsushita has developed 4-MBit strontium bismuth tantalate (SBT) FRAMs (Scott, 2005). Unlike magnetic random access memory (MRAM) devices, their power & current requirements scale with size (Scott, 2005), and we note the recent publication by Li (2004e) citing switching speeds of 220ps, which significantly

exceeds the 25ns state-of-the art access speed of MRAMs (Dawber, 2005. Scott, 2005). Furthermore, if these devices can be miniaturized to a lateral size of 1nm (about 2 lattice constants), this corresponds to a device density near to 100Tb/cm², which is about a million times larger than existing dynamic random access memory (DRAM) devices today (Ahn, 2004). Scott (2005) and Dawber (2004) mention several advantages of FRAM devices which are outlined below:

Table 6-1: Comparison of MRAMs and FRAMs:

Company	Size	Design rule (feature size)	Speed (access speed)
MRAM			
NEC/Toshiba	1 Mb	0.18 μm	70 ns
IBM	16 Mb		
Matsushita	4 Mb		
Sony	8 kb		
Cypress	256 kb	0.09 μm 8F ²	25 ns
Motorola	4 Mb		
State-of-the-art	16 Mb		
FRAM			
Fujitsu (in Toshiba memory for SONY Playstation 2)	32 kb	0.18 μm (PZT) (SBT)	100 ns
Samsung	32 Mb		60 ns
Matsushita	4 Mb		60 ns
Laboratory			0.2 ns [†]

[†]J. Li, B. Nagaraj, H. Liang, W. Cao, Chi. H. Lee, and R. Ramesh, "Ultrafast Polarization Switching in Thin-Film Ferroelectrics," *Appl. Phys. Lett.*, **84**, 1174-6 (2004). FRAM, ferroelectric random access memories; MRAM, magnetic random access memories; PZT, lead zirconate titanate; SBT, strontium bismuth tantalate.

Biomedical devices also benefit from miniaturization. For example, Zandonella (2003) reports the development of nanoscale cantilever arrays which incorporate piezoelectric crystals to measure forces between a drug and a receptor molecule. Another application includes molecular recognition devices which incorporate a selective coating on the tip of a cantilever, where the presence of a virus (or other biomolecule) which attaches itself to the cantilever changes the effective mass at the end of the beam, resulting in a downward shift in the resonant frequency (Polla, 1998). These can be used for genetic testing, or detecting viruses such as influenza and

rhinovirus (Polla, 1998). Drug delivery systems incorporating nanoscale fluidics with a peristaltic piezoelectric voltage drive have also been developed (Scott, 2005). In inhaler units, these would have the advantage of being able to deliver uniform submicrometer droplets, which are able to penetrate the bronchia or lungs without being stuck in the windpipe (Scott, 2005).

Besides biosensors and FRAM devices, many more potential applications based on nano-scale ferroelectric material exist, such as microelectromechanical systems (MEMS) and microfluidics. However, regardless of the application, it still remains necessary to find a relevant and appropriate theoretical model to understand the material properties. These new devices are expected to be fabricated at length scales ranging from 10nm to 1 μ m, which is not accessible to purely atomistic methods (Chandra, 2007), hence for our methodology, we choose the Landau-Ginzburg-Devonshire (LGD) theory, as this approach is considered one of the most powerful methods to study microstructures of materials undergoing phase transitions (Damjanovic, 1998. Chen, 2002). The details of this theory are described in the next section.

6.2. Methodology for the Time-Dependent Ginzburg-Landau (TDGL) Model

6.2.1. Novelty of the Present Approach

Currently, existing models by L. Q. Chen (2002) as well as others incorporate a Fourier-transform based method to solve the TDGL equations subject to the electrostatic and elastic constraints. However, these models are generally restricted to periodic boundary conditions, which are convenient for computation, but not for application (Zhang, 2005a). In this work, we introduce a novel approach to the TDGL

model, whereby we use a real-space solver which allows virtually arbitrary boundary conditions (e.g. stress-free, clamped, fixed strains, space charge layers, inactive layers, periodic / free polarizations, periodic / free electrostatic potential, etc).

We note that a similar real-space method has been developed and introduced by Zhang (2005), except that we work with displacement fields, while Zhang works directly with strain fields. Zhang's method requires solving an additional strain compatibility equation (i.e. $\varepsilon_{11,11} + \varepsilon_{22,22} - 2\varepsilon_{12,12} = 0$), which we avoid in our model by working with displacements. This way, we can ensure compatibility at every time step, without the additional computational load incurred by the strain compatibility equation.

6.2.2. Methodology for Solving the TDGL Equations

These TDGL equations are usually rescaled (i.e. made dimensionless) for numerical convenience. Here, we rescale the coefficients for BaTiO₃, Pb(Zr_{1-x}Ti_x)O₃, and P(VDF-TrFE) as follows. In rescaled units, we put $P'_x = P_x / P_0$, $P'_y = P_y / P_0$, for the polarizations, where P_0 is set to the spontaneous polarization of the material (e.g. $P_0 = 0.260 \text{ C/m}^2$ for BaTiO₃, and 0.647 C/m^2 for PZT). The length scale is rescaled as $x' = x / \delta$, $y' = y / \delta$, where δ is chosen such that the simulation widths agree with the experimentally observed domain wall widths. As the simulation shows domain wall thicknesses of about one grid cell, we note that δ is approximately equal to the domain wall width, which is about 1.3 nm (Choudhury, 2005). This is close to the value in the simulation by Choudhury et al. (2005), whereby the width is set arbitrarily as $\delta = 1.0 \text{ nm}$. We set $\phi' = \phi / \phi_0$, where $\phi_0 = \theta[(P_0\delta)/\varepsilon_0]$, for the electrostatic potential, where θ is a dimensionless parameter, arbitrarily chosen as 1.0. For the space charge, ρ , we used $\rho = \rho_0\rho'$, where $\rho_0 = P_0/\delta$. The elastic constants are

rescaled as $C'_{ij} = C_{ij} / C_{11}$, while the electrostrictive constants are rescaled as $Q'_{ij} = Q_{ij} / Q_{11}$. For the strains, we use the rescaling, $\varepsilon'_{ij} = \varepsilon_{ij} / \varepsilon^0$, and $\tilde{\varepsilon}'_{ij} = \tilde{\varepsilon}_{ij} / \varepsilon^0$, where $\varepsilon^0 = Q_{11}P_0^2$, and for the stresses, the rescaling is $\sigma'_{ij} = \sigma_{ij} / \sigma_0$, where $\sigma_0 = C_{11}\varepsilon^0 = C_{11}Q_{11}P_0^2$. Hence equations 3.42 and 3.43 may be written in rescaled form as follows:

$$\frac{\partial P'_x}{\partial t} = \Gamma |\alpha_1| \left[-\frac{\alpha_1}{|\alpha_1|} P'_x - \frac{\alpha_{11}P_0^2}{|\alpha_1|} P'^3_x - \frac{\alpha_{12}P_0^2}{|\alpha_1|} P'_x P'^2_y - \frac{\alpha_{111}P_0^4}{|\alpha_1|} P'^5_x - \frac{\alpha_{112}P_0^4}{|\alpha_1|} (P'_x P'^4_y + 2P'^3_x P'^2_y) + \frac{K}{|\alpha_1|\delta^2} \nabla'^2 P'_x - \frac{\theta}{\varepsilon_0 |\alpha_1|} \phi'_{,x'} - \frac{C_{11}Q_{11}^2 P_0^2}{|\alpha_1|} [2(\sigma'_{xx} + Q'_{12}\sigma'_{yy})P'_x + Q'_{44}\sigma'_{xy}P'_y] \right] \dots\dots\dots (6.1)$$

$$\frac{\partial P'_y}{\partial t} = \Gamma |\alpha_1| \left[-\frac{\alpha_1}{|\alpha_1|} P'_y - \frac{\alpha_{11}P_0^2}{|\alpha_1|} P'^3_y - \frac{\alpha_{12}P_0^2}{|\alpha_1|} P'^2_x P'_y - \frac{\alpha_{111}P_0^4}{|\alpha_1|} P'^5_y - \frac{\alpha_{112}P_0^4}{|\alpha_1|} (P'_y P'^4_x + 2P'^3_y P'^2_x) + \frac{K}{|\alpha_1|\delta^2} \nabla'^2 P'_y - \frac{\theta}{\varepsilon_0 |\alpha_1|} \phi'_{,y'} - \frac{C_{11}Q_{11}^2 P_0^2}{|\alpha_1|} [2(\sigma'_{yy} + Q'_{12}\sigma'_{xx})P'_y + Q'_{44}\sigma'_{xy}P'_x] \right] \dots\dots\dots (6.2)$$

where the constant $\Gamma|\alpha_1|$ may be absorbed into the time scale (Bray, 1994).

In a similar manner, Gauss's Law (equation 3.35) was rescaled as:

$$(P'_{x,x'} + P'_{y,y'}) - \theta(\phi'_{,x'x'} + \phi'_{,y'y'}) - \rho' = 0, \dots\dots\dots (6.3)$$

and the equilibrium equation (equation 3.38) was rescaled as:

$$\begin{cases} \sigma'_{xx,x'} + \sigma'_{xy,y'} = 0 \\ \sigma'_{xy,x'} + \sigma'_{yy,y'} = 0 \end{cases} \dots\dots\dots (6.4)$$

The simulation of the TDGL model is carried out using equations 6.1, 6.2, with the two constraints of electrostatics (equation 6.3) and elasticity (equation 6.4), both of which are solved at each time step, before proceeding to the next time step. To solve

equations 6.3 and 6.4, an iterative method was used (as proposed by Zhang, 2005), as we found inverse matrix methods too slow for this problem. The Landau, electrostrictive, and elastic coefficients are obtained from the journal papers by Haun (1989) for the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ system, Bell, A. J. (2001) for BaTiO_3 , and Iwata (2005) and Ishibashi (2005) for P(VDF-TrFE) 65-35 mol%.

Traction-free boundary conditions were used ($\sigma_{ij} = 0$) along the x and y surfaces, with no polarization gradients ($P_{i,j} = 0$) and no gradients in the electrostatic potential ($\phi_{i,j} = 0$). When an electric field is applied to the material, the boundary conditions for the electrostatic potential are changed from $\phi_{i,j} = 0$ to $\phi = V_0 \cos \omega t$ at the top electrode and $\phi = -V_0 \cos \omega t$ at the bottom electrode. In the case of a short circuit condition, the boundary condition for the electrostatic potential is $\phi = 0$ at both the top and bottom electrode.

The TDGL equations are solved using a simple second-order symmetric finite difference method on a uniform spatial grid (of sizes such as 128×128 , 512×128 , and 256×64) and explicit time-stepping, which is a method typically used in many phase field simulations (Chen, 2002). The polarizations at every point inside the grid are set either to zero with a small initial random thermal noise, or to the spontaneous polarization of the material under investigation. The polarization at each point is updated at every time step using the equations 6.1 and 6.2. For the hysteresis loop, which is the most studied behavior (Damjanovic, 1998), and from the application point of view, one of the most interesting properties of ferroelectric materials, we plot the average polarization in the poled region against the average electric field, E_y . Similarly, the butterfly loop is obtained by plotting the average strain, ϵ_{yy} , in the poled region against the average electric field.

Implementation of the model was carried out in Microsoft Visual C++ Express edition, and run on one of three computers in the Windows XP environment: (a) Intel 3.0 GHz Pentium 4 Desktop, 512MB RAM, (b) Intel 2.8 GHz Pentium 4 Desktop, 1GB RAM, and (c) Fujitsu S7110, Intel T2400 1.83 GHz Centrino Duo Laptop, 1GB RAM. For the numerical computation, all calculations were carried out in double-precision, in order to minimize numerical errors. The code was not parallelized, though it is known that iterative solvers can be efficiently parallelized for large computations (Zhang, 2005). However, the dual-core nature of the laptop & desktop allowed two simulations to be run in parallel, without any noticeable drop in the speed of computation. Code was written to generate the vector fields of the polarizations and scalar fields of the strains, stresses, and electrostatic potentials as bitmaps. In addition, the raw polarization, electric field, and strain data were saved into ASCII files.

Simulation of domain patterns using the model are presented later in section 6.3. We demonstrate the capabilities of this model, by the methodology for three separate studies as follows. In section 6.4, we study size effects and inhomogeneous poling in ferroelectric thin films, which to date, has not been investigated so far. Section 6.5 uses the same model to investigate the influence of space charge on the evolution of the domain structure material, which also has not yet been investigated.

6.3. Simulation of Domain Evolution using the TDGL Model

In this work, the approach to the TDGL model is different from that in existing literature (as mentioned in section 6.2.1), as we are moving from a Fourier transform based method to a real-space method. Hence, we found it necessary to compare our simulated domain patterns with existing theory as well as experiments. We test the

ability of the model to demonstrate experimentally observed features such as 90° and 180° domain walls, and no charged walls (i.e. no head-to-head or tail-to-tail orientations in the polarization vectors) which is required to minimize the electrostatic energy (Pompe, 1993).

6.3.1. Simulation of Domain Evolution Without Incorporating Electrostatic and Elastic Constraints

In order to simulate the domain structure of a ferroelectric material, the TDGL model was discretized on a 128 x 128 grid from an initial state with polarization equal to zero plus a small random thermal noise. The purpose of adding this noise into the simulation is to ensure that domain structures nucleate from the artificially-injected noise, rather than from errors in the numerical solver. For the first set of verification tests, we use the free energy, $F_{Landau}(\vec{P}) + F_{Ginzburg}(\vec{P})$, which is equivalent to the free energy in equation 3.41 without the electrostatic and elastic effects. For the colour scheme, we use white to represent regions where the polarization vector points to the left, red to represent regions where the vector points to the right, blue for the downwards direction, and green for the upwards direction. The results using the parameters for PZT by Haun, 1989, are as shown:

(a)

(b)

Figure 6-1: Domain State after (a) 2000 iterations, and (b) 4000 iterations

Figure 6-2: Domain State After 8000 iterations (left image) and 16000 iterations (right image)

Figure 6-3: Domain State After 32,000 iterations (left image) and 64,000 iterations (right image)

The above results show the ability of the simulation to predict curved domain structures, in which the domain walls move to minimize domain wall energies. The next section shows the effect of adding the electrostatic energy term, $F_{\text{electrostatic}} = \mathbf{E} \cdot \mathbf{P} + \frac{1}{2}\epsilon_0 \mathbf{E} \cdot \mathbf{E}$, to the free energy, where $\mathbf{E}$ is calculated from the Maxwell Equation, $\nabla \cdot (\epsilon_0 \mathbf{E} + \mathbf{P}) = \rho = 0$ (i.e. equation 3.35).

6.3.2. Simulation of Domain Evolution with only Electrostatic Constraints

In the case where electrostatic effects (but not elastic effects) are taken into consideration, the free energy term from equation 3.41 becomes $F_{\text{Landau}}(\vec{P}) + F_{\text{Ginzburg}}(\vec{P}) + F_{\text{electrostatic}}(\vec{P})$, subject to the electrostatic constraint in equation 3.35 (i.e. Gauss's Law). The results of the simulation using the parameters for PZT by Haun et al (1989) are as follows:

Figure 6-4: Domain State after 4000 iterations (left image) and 8000 iterations (right image). Red shading is used for negative electrostatic potential and blue shading for positive electrostatic potential. Black shading is used for zero potential.

(a)

(b)

Figure 6-5: Domain State after (a) 16,000 iterations and (b) 32,000 iterations. The area bounded by the white rectangle in (b) is shown in Figure 6-7 below.

Figure 6-6: Domain State after 64,000 iterations (left image) and 150,000 iterations (right image).

Figure 6-7: Enlarged region of Figure 6-5(b), showing the polarization vectors and 90° domain walls (angled at 45°) and 180° domain walls (angled horizontally or vertically).

In Figure 6-7, polarization vectors are drawn in yellow for the upwards direction, blue for the downwards direction, red for the right direction and white for the left direction. Dots are drawn at regions where the polarization vector is effectively zero. Note that

the regions where the arrows point head-to-head, or tail-to-tail are minimized. Shading is red for negative values of the electrostatic potential, ϕ , and blue for positive values with the red and blue intensities scaled between 0 and 255 according to the magnitude of ϕ .

The above results show the ability of the simulation to predict the formation of 90° and 180° degree domain walls, as well as the minimization of head-head and tail-tail polarization vectors, which is in agreement with the known behavior of the material (Pompe, 1993). In the case of 90° domain walls, in order for electrostatic energy to be minimized, there must be no net charge at the domain walls, hence the normal component of the polarization vectors are conserved across a domain wall boundary (Pompe, 1993), which can also be observed in Figure 6-7. Comparison of this result with the previous result showing curved domain walls shows that electrostatic effects play a role in the formation of the 90° and 180° domain walls, which are not present when only the Landau-Ginzburg free energy, F_{LG} , is used.

6.3.3. Simulation of Domain Evolution with only Elastic Constraints

In the case where elastic effects (but not electrostatic effects) are taken into consideration, the free energy from equation 3.41 is $F_{Landau}(\vec{P}) + F_{Ginzburg}(\vec{P}) + F_{elastic}(\vec{P})$, subject to the elastic constraint (equation 3.38). Based on this free energy and using the constants for PZT by Haun et al (1989), the domain evolution is obtained as follows:

Figure 6-8: Domain state after 4000 iterations (left image) and after 8000 iterations (right image).

Blue shading refers to positive values of $\tilde{\varepsilon}_{xy}$, while red shading refers to negative

values of $\tilde{\varepsilon}_{xy}$.

Figure 6-9: Domain state after 16,000 iterations (left image) and after 32,000 iterations (right image).
The region enclosed by the white box is shown in Figure 6-12 below.

Figure 6-10: Domain state after 64,000 iterations (left image) and after 128,000 iterations (right image).

Figure 6-11: Domain state after 256,000 iterations

Figure 6-12: Magnified region of Figure 6-9(b) showing the domain state after 32,000 iterations.

In these results (Figure 6-8 to Figure 6-12), we observe the development of 90° domain walls (angled at 45°), but not 180° domain walls. This is in agreement with existing literature (Damjanovic, 1998). 180° domain walls are termed as ferroelectric domain walls because they minimize the electrostatic energy, and 90° domain walls are termed as both ferroelectric and ferroelastic, because they minimize both the electrostatic and elastic energies (Damjanovic, 1998). We note that in Figure 6-7 which is calculated based on electrostatics, we obtain both 90° and 180° domain walls,

whereas in Figure 6-12 which is calculated purely based on minimizing the elastic energy, only 90° domain walls can form. In addition, the minimization of the elastic energy does not eliminate the charged walls (i.e. walls where the polarization vectors point head-to-head or tail-to-tail) in Figure 6-12, but these are eliminated in Figure 6-7 where the electrostatic energy is minimized.

6.3.4. Simulation of Domain Evolution with both Electrostatic and Elastic Constraints

In this last investigation, we use the full free energy term from equation 3.41,

$$F_{LG}(\vec{P}) + F_{elastic}(\vec{P}) + F_{electrostatic}(\vec{P}), \quad \text{which includes both elastic and electrostatic}$$

effects. Based on this free energy, the domain evolution is as follows:

Figure 6-13: Initial domain state (left) and domain state after 4000 iterations (right)

Figure 6-14: Domain state after (a) 8,000 iterations and (b) 16,000 iterations.

The region enclosed by the white box is shown in Figure 6-16.

Figure 6-15: Domain state after 32,000 iterations (left) and 128,000 iterations (right)

Figure 6-16: Enlarged region of Figure 6-14, showing both 90° and 180° domain walls.

In Figure 6-16, we again observe both 90° and 180° domain walls, which is in agreement with observations by Zhang (2005a). Both of these kind of domain wall

structures are also present when we used the BaTiO_3 parameters by Bell, 2001. For comparison, the domain structures from the TDGL simulation (Figure 6-18) are shown beside domain structures in single crystalline BaTiO_3 (Figure 6-17), which were experimentally observed by Hooton (1955):

Figure 6-17: (a) Experimentally observed domain structures by Hooton, 1955, and (b) the corresponding domain structures.

Figure 6-18: Domain structures from TDGL simulation using BaTiO_3 parameters by Bell, 2001. Hence, we can see that the current model is able to show domain structures which are in agreement with experimental observations.

6.3.5. Discussion – Assumptions & Limitations of the TDGL Model

We note that Landau theory inherently assumes spatial averaging of local fluctuations (Chandra, 2007), and hence there is a minimum length scale below which the theory is

no longer valid. Continuum theories are generally expected to be valid on length scales much larger than a lattice constant, and while we expect this to be the case also for ferroelectrics, we note the observation by Ahn (2004), that this model has been repeatedly shown to be useful for films and heterostructures down to the nanoscale, and that many of the characteristics of nanoscale ferroelectrics can be faithfully reproduced. The simulation grid step size, δ , must therefore be above a certain minimum value, and we restrict ourselves from using values below that of other authors in literature – e.g. Chen (2005), uses a value of $\delta = 1\text{nm}$. For lower length scales, molecular dynamics or atomistic modeling are suggested. On the other hand, larger length scales are limited by the ability of the simulation to handle large grid sizes.

The TDGL model is only as good as its parameters, which are typically obtained from experiment or from first-principles calculations. The work in this project makes use of Bell's (2001) parameters for BaTiO_3 , Haun's (1989) parameters for PZT, and Iwata (2005) and Ishibashi's (2005) parameters for P(VDF-TrFE) , all of which are experimentally derived. None of these authors publish the value of the dissipative constant, Γ , used in equation 3.40, hence we absorb the constant, $\Gamma|\alpha_1|$ into the time-scale, as suggested by Bray (1994), and measure the progress of the simulation in time-steps. From here, simulation data can be fit to existing experimental data. In PZT, domain wall velocities are estimated as 40m/s (at 45MV/m) by Grigoriev (2006) using time-resolved x-ray microdiffraction, and $0.3\text{-}1.0\text{m/s}$ (at 7.8MV/m) by Gruverman (2005) using piezoforce microscopy and these can give a rough estimate on the time scale used in the TDGL simulation.

For simplicity, our model uses the same assumption as Chen (2002), Zhang (2005), Ahluwalia (2000), which is the condition of mechanical equilibrium (equation 3.38).

This is a reasonable assumption given that elastic deformations propagate at velocities in the order of several km/s (Grigoriev, 2006), which is orders of magnitude larger than the ferroelectric domain wall velocities of 40m/s (Grigoriev, 2006) and 0.3-1.0m/s (Gruverman, 2005) cited in literature. Furthermore, the condition of mechanical equilibrium is sufficient to show domain evolution mechanisms and switching phenomena which agree with experimental observations as has been the case in the work by many authors in this field such as Ahluwalia (2000) and Zhang (2005).

Another point to note is that the current TDGL model has been developed in 2D and not 3D, although for future work, a 3D model is possible. Hence, the model is only able to capture a “slice” of the domain structures in the material investigated, but this is sufficient to reproduce experimentally observed domain structures (e.g. Figure 6-17 by Hooton et al). Also, using a 2D model restricts our investigations to cubic, tetragonal, orthorhombic, and hexagonal phases, but not rhombohedral phases which involve polarizations in the [111] directions. Hence, in this work, investigations which involve phase transitions such as rhombohedral to cubic / tetragonal / etc, are avoided.

Lastly, our model does not incorporate the ability to investigate polycrystalline material but is restricted only to materials such as single-crystalline BaTiO₃, epitaxial PZT, or single-crystalline P(VDF-TrFE). However, all of these materials are experimentally achievable, at least in thin film form.

In this thesis we demonstrate the capabilities of this model by applying it to study size effects (section 6.4), the role of charged defects in ferroelectric thin films (section 6.5), and domain evolution in P(VDF-TrFE) (section 6.6).

6.4. Ferroelectric Thin Films under Inhomogeneous Electric Fields – Lateral Size and Thickness Dependence

The effects of inhomogeneous poling are of interest in studying size effects in ferroelectric thin film, as mentioned in Section 2.3. To improve on these theoretical investigations by Roytburd (2000) and Wang (1994), we investigate the 2D domain evolution using an LGD approach with the TDGL relaxational equations with both electrostatic and elastic effects (equations 3.34, 3.35, 3.36 and 3.38). We also note of the ability of our model to investigate other important phenomena, such as the stability of submicron capacitor structures (Ganpule, 1999) at zero field, which is an indication of their capability to retain the polarization state over long periods of time.

6.4.1. Methodology

To investigate this phenomenon, we focus on parallel-plate capacitor geometry (electrode-ferroelectric-electrode) which is the building block of many devices (Xiao, 2005). A sinusoidal voltage is applied, to a thin film with a different lateral size of the poling width, w_{poling} , and film thickness, t_{film} , as shown below:

Figure 6-19: Ferroelectric Thin Film Dimensions and Poling Conditions

The grid sizes used are 256×64 , and 256×16 , and we use $w_{\text{poling}} = 10, 32$, and 64 grid steps, which correspond to approximately $13, 41.6$, and 83.2 nm, respectively, based on $\delta \approx$ domain wall thickness $= 1.3\text{nm}$ (Choudhury, 2005) in PZT. Kalinin, et al, 2007, noted that recent developments in piezoforce microscopy (PFM) imaging has brought down the resolution to the sub-10nm level, and that fabricating devices below

the 10nm level can quite complicated (Ganpule, 1999). Hence we use 10nm as our minimum lateral width, to ensure experimental verifiability and that the results are applicable to existing PFM setups. The lower limit of the thickness is chosen as 16 grid steps (corresponding to 20.8nm). The results are shown below.

6.4.2. Results

6.4.2.1. Hysteresis Loops

The polarization – electric field hysteresis loops for the methodology in section 6.4.1 are as follows:

Figure 6-20: Average polarization versus average electric Field in rescaled units for the smaller thickness ($t_{\text{film}} = 16$, $w_{\text{poling}} = 10, 32, 64$)

Figure 6-20 shows a plot of the rescaled polarization, $P' = P/P_0$, (where $P_0 = 0.647$ C/m² is the spontaneous polarization), versus the rescaled electric field, $E' = E / E_0$, where $E_0 = \phi_0/\delta = \theta[P_0/\epsilon_0]$. It can be seen that no switching occurs for the case of $w_{\text{poling}} = 10$, and that the coercive field (i.e. the electric field for which the polarization

is zero) for $w_{\text{poling}} = 32$ is larger than that for $w_{\text{poling}} = 64$. When we increase the film thickness, a similar result is obtained as shown in Figure 6-21:

Figure 6-21: Polarization versus Electric Field for $t_{\text{thickness}} = 64$, $w_{\text{poling}} = 10, 32, 64$

As shown in Figure 6-21, we are still unable to pole the film in the case of $w_{\text{poling}} = 10$, and again, the coercive field is larger for the $w_{\text{poling}} = 32$ case, compared to the case of $w_{\text{poling}} = 64$.

Figure 6-22: Polarization versus Electric Field for $w = 10$, $t = 16$ & 64

In this last result with the smallest poling width, $w_{\text{poling}} = 10$, for both cases of film thicknesses ($t_{\text{film}} = 16$ and $t_{\text{film}} = 64$), it can be seen that there are no hysteresis loops, which is due to the fact that no switching occurs. The slight difference in slope corresponds to a change in the effective dielectric constant of the material.

Also, for the cases of $t_{\text{film}} = 16$, $w_{\text{poling}} = 32, 64, 180$ direct switching was observed, without any observable 90° domain structures. However, for the case of $t_{\text{film}} = 64$, similar domain patterns were observed for $w_{\text{poling}} = 32, 64$. These results are summarized in below in Table 6-2:

Table 6-2: Effects of Lateral Width and Film Thickness in the Poling of Ferroelectric Thin Films

	$t_{\text{film}} = 16$	$t_{\text{film}} = 64$
$w_{\text{poling}} = 10$	no switching	no switching
$w_{\text{poling}} = 32$	180° switching	90° & 180° switching
$w_{\text{poling}} = 64$	180° switching	90° & 180° switching

6.4.2.2. Domain Evolution

From Table 6-2, the only results with interesting domain structures involved those with both 90° and 180° switching, i.e. $t_{\text{film}} = 64$, $w_{\text{poling}} = 32, 64$, for which both cases yielded similar results. This was because the “no switching” cases (i.e. $t_{\text{film}} = 16$, and 64, $w_{\text{poling}} = 10$) yielded domain structures which remained virtually unchanged throughout the application of the electric field, while the “direct switching” cases (i.e. $t_{\text{film}} = 16$, $w_{\text{poling}} = 32$, and 64) yielded no domain structures except a reversal of the polarizations at the electrodes (shown in red) as follows:

Figure 6-23: Domain structure for $t_{\text{film}} = 16$, $w_{\text{poling}} = 32$ before poling.

Figure 6-24: Domain structure for $t_{\text{film}} = 16$, $w_{\text{poling}} = 32$ after poling.

Hence, for the domain evolution, we only study the 90° and 180° switching case, where the domain structures are shown later in Figure 6-27 to Figure 6-42. Also, each of these domain structures (Figure 6-27 to Figure 6-42) is labeled on the polarization–electric field hysteresis loop in Figure 6-25 below:

Figure 6-25: Hysteresis Loop: Average Polarization versus Average Electric Field in Rescaled Units (the rescaled polarization, P/P_0 , where $P_0 = 0.647 \text{ C/m}^2$ is plotted against the rescaled electric field, $E' = E/E_0$, where $E_0 = \theta[P_0/\epsilon_0]$).

Here, the points A to P correspond to the domain structures in Figure 6-27 to Figure 6-42. In a similar manner, the same points A to P are also labeled in the strain–electric field butterfly loop in Figure 6-26 below.

Figure 6-26: Strain – Electric Field Butterfly Loop in Rescaled Units.

The domain evolution for $w_{\text{poling}} = 32$, is as shown below. The polarizations point downwards in the blue regions, upwards in the yellow regions, left in the white regions, and right in the red regions. The red line drawn at the top and bottom of the figures indicates the position of the electrode:

Figure 6-27: Domain Evolution With Inhomogeneous Poling: Initial polarization state before application of the electric field at $t = 20k$. (Point A of Figure 6-25 & Figure 6-26)

Figure 6-28: Domain Evolution With Inhomogeneous Poling: $t = 82.5k$ time steps. Formation of 90° domain wedges angled at approximately 45°, due to the fringing effects with the inhomogeneous electric field. (Point B of Figure 6-25 & Figure 6-26)

Figure 6-29: Domain Evolution With Inhomogeneous Poling: $t = 85k$ time steps. Merging of original domain wedges at the centre of the film thickness. (Point C of Figure 6-25 & Figure 6-26)

Figure 6-30: Domain Evolution With Inhomogeneous Poling: $t = 85.5k$ time steps. (Point D of Figure 6-25 & Figure 6-26)

Figure 6-31: Domain Evolution With Inhomogeneous Poling: $t = 86k$ time steps. (Point E of Figure 6-25 & Figure 6-26)

Figure 6-32: Domain Evolution With Inhomogeneous Poling: $t = 90k$ time steps. Formation of the reversed domains. (Point F of Figure 6-25 & Figure 6-26)

Figure 6-33: Domain Evolution With Inhomogeneous Poling: $t = 100k$ time steps. Disappearance of 90° domain structures. (Point G of Figure 6-25 & Figure 6-26)

Figure 6-34: Domain Evolution With Inhomogeneous Poling: $t = 102.5k$ time steps. Poled domain structure. (Point H of Figure 6-25 & Figure 6-26)

Figure 6-35: Domain Evolution With Inhomogeneous Poling: $t = 480k$ time steps. Reversal of electric field leading to the formation of domain wedges at the electrode edges. (Point I of Figure 6-25 & Figure 6-26). This is the converse of Figure 6-28, but with extra 180° domain walls

Figure 6-36: Domain Evolution With Inhomogeneous Poling: $t = 482.5k$ time steps, showing the interface between the 45° domain wedges and the 180° domain wall. (Point J of Figure 6-25 & Figure 6-26)

Figure 6-37: Domain Evolution With Inhomogeneous Poling: $t = 485k$ time steps. Collapse of 180° domain wall. (Point K of Figure 6-25 & Figure 6-26)

Figure 6-38: Domain Evolution With Inhomogeneous Poling: $t = 486k$ time steps. Further collapse of 180° domain wall. (Point L of Figure 6-25 & Figure 6-26)

Figure 6-39: Domain Evolution With Inhomogeneous Poling: $t = 486.5k$ time steps. Growth of 90° Domains and Domain reversal at the centre region. (Point M of Figure 6-25 & Figure 6-26)

Figure 6-40: Domain Evolution With Inhomogeneous Poling: $t = 487.5k$ time steps. (Point N of Figure 6-25 & Figure 6-26)

Figure 6-41: Domain Evolution With Inhomogeneous Poling: $t = 490k$ time steps. (Point O of Figure 6-25 & Figure 6-26)

Figure 6-42: Domain Evolution With Inhomogeneous Poling: $t = 492.5k$ time steps. (Point P of Figure 6-25 & Figure 6-26)

For the case of $w_{\text{poling}} = 64$, similar domain evolution is observed, with the same nucleation of 45° wedges.

6.4.3. Discussion

From these results we can see at least four characteristics in the behavior of the ferroelectric thin film, fringing in the electric field, a slight asymmetry in the switching loops, lateral size effects, and thickness dependence.

6.4.3.1. Fringing of the Electric Field

The fringing of the electric field, mentioned by Scott (1998), is due to edge effects at the edge of the poled region. By plotting the solution to the Maxwell equation (equation 6.11) at $t = 80k$, the fringe effects at the edges of the electric field can be clearly seen as shown in Figure 6-43:

Figure 6-43: Electric field vectors at $t = 80k$ time steps.

White lines represent the equipotential contours of the electrostatic potential, ϕ , which is given a red shading for negative values and a blue shading for positive values. Arrows are colored according to the orientation of the polarization vector but not

scaled with its magnitude (the magnitude of the electric field is proportional to the spacing between the equipotential contours).

Two consequences arise from the fringing electric fields – firstly, a lateral size-dependence (i.e. a dependence on the value of w_{poling}) on the material behavior, and secondly, the edge effects create nucleation points for domain wedges to form as shown below:

Figure 6-44: 90° Domain wedges angled at 45° for $t = 82.5k$ time steps, and the resulting electrostatic potential.

The electrostatic potential is shaded as blue (for negative values) and red (for negative values), with white lines showing the equipotentials.

It is believed that for smaller lateral sizes, the electric field becomes more and more inhomogeneous, and that the material becomes more and more difficult to pole (i.e. the effective coercive field of the material has increased). For this reason, we see the lowest coercive field in the case of $w_{\text{poling}} = 64$, an intermediate value in $w_{\text{poling}} = 32$, and in the case of $w_{\text{poling}} = 10$, the coercive field may be too large for the electric field applied to cause switching in the material. The implication of this result is that there is a minimum lateral width below which the material can no longer be poled. This is expected, due to a similar result by Wang (1995), where a minimum critical lateral width of 7.4nm for PbTiO_3 and 9.1nm for BaTiO_3 was proposed.

6.4.3.2. Thickness Dependent Behavior

In the case of the thinner film (with $t_{\text{film}} = 16$), there is an absence of 90° domains, unlike the case of the thicker film. A possible explanation for this is the experimental observations by Buhlmann (2002) and Lee (2006a) which have shown the disappearance of domain structures below a certain critical domain size. Furthermore, these results are in line with experimental observations by Nagarajan et al (2003) who showed that 90° domain walls disappeared below a certain minimum critical thickness in their $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ films.

6.4.3.3. Slight Asymmetry in the Switching Loops

Lastly, we wish to address the reason for the asymmetry in the switching loops, by recalling the following hysteresis loop, which was shown earlier:

Figure 6-45: Hysteresis Loop for Inhomogeneously Poled Thin Film

The domain evolution starts with a completely poled material (Point A), with domain wedges nucleating at (B), and growing at (C) and (D). At point (E), reverse polarization domains start to appear, and the disappearance of the domain wedges

occurs at points (F) & (G), to form the fully poled domain structure at (H). Nucleation of the wedges begins again at points (I) & (J) as the electric field is reversed. At point (K), these wedges intersect with the 180° domain wall, forming the complicated structures at points (L) & (M). Point (N) is the point for the completion of the reversal of the polarizations at the centre of the film. At points (O) & (P), the remaining side structures quickly disappear. Here, it should be noted that points (F), (G), and (H) are opposite points (N), (O), and (P) in the hysteresis loop, and for a symmetrical hysteresis loop, we would expect the domain structures at (N), (O), and (P) to be the converse of those at (F), (G), and (H). However, this is not so if we observe points (F), (G), (H) in Figure 6-32 to Figure 6-34, and compare these to points (N), (O), (P), which are in Figure 6-40 to Figure 6-42. In fact, what is observed is the formation of a 180° domain wall stabilized by domain wedges at (F), (G), and (H), and the collapse of what was originally a 180° domain wall at (N), (O), and (P). It should be also noted that Chen et al (2004c) also observed the formation of 90° elastic domains which formed to stabilize the 180° domain walls in an experimental PFM setup similar to Figure 6-46B below. The importance of these results is relevant for ferroelectric memory devices incorporating either a ferroelectric capacitor (Figure 6-46A), or a scanning probe approach (Figure 6-46B) as shown:

Figure 6-46: Ferroelectric memory devices incorporating (A) the traditional capacitor structure, and (B) an approach using an array of nanoscale scanning probe cantilevers. (Ahn, 2004).

In conclusion, these results show (a) 180° intrinsic switching for films below a certain critical thickness, and 90° domain wedges which nucleate due to fringing in an inhomogeneous electric field in thicker films (b) 180° domain walls stabilized by 90° domain wedges, which is similar to observations by Chen (2004c), (c) a minimum lateral width whereby it becomes nearly impossible to pole the material, and (d) asymmetric hysteresis loops due to 180° domain walls. This result is important because it allows for a better understanding of structures in ferroelectric capacitors and memory devices at the nanoscale, as well as the domain structures observed in piezoforce microscopy experiments.

6.5. The Influence of Space Charge on Domain Structures in Ferroelectric Thin Film

6.5.1. Introduction & Motivation

Ferroelectric perovskites can be treated as p-type wide band-gap semiconductors (Scott, 1998), where depletion layers at the electrodes influence the polarization profile (Xiao, 2005). At the interface between the ferroelectric material and the electrode, a Schottky barrier with a depletion layer (a region depleted of charge carriers) is formed, the properties of which depend on the work functions of the two

materials (Damjanovic, 1998). While the length of this depletion layer may not be important in bulk materials, this is not so in ferroelectric thin films whose thicknesses may be of the same order as that of the depletion layer. The thickness of the depletion layers is estimated as a fraction of a micrometer (Damjanovic, 1998), and we note that the actual thickness has been a subject of debate, with some authors believing film to be fully depleted, due to their insulating nature, and others believing the films to be only partially depleted, due to the semiconductor behavior observed in thin films (Zubko, 2006).

Interest in the effects of space charge has led to a number of studies on these depletion layers, including a recent analytical study by Zubko (2006). Zubko, however, studied only the monodomain case, and hence did not investigate domain structures in the material. Furthermore, Zubko (2006) used an analytical approach, and hence used a 1D Landau expansion of the free energy to the 4th order, with only electrostatic effects. In our model, however, the parameters for PZT by Haun (1989) incorporate a 2D Landau expansion of the free energy to the 6th order, which allow us extend Zubko's work to study the domain structures, and in addition, we are able to consider both electrostatic and elastic effects via equations 3.35 and 3.38 respectively.

6.5.2. Methodology

In order to investigate the influence of space charge on the grid, we use the TDGL equations with equation 6.3 set with $\rho' = \rho/\rho_0 = \delta q N_d / P_0$, where $\rho_0 = P_0/\delta$, δ is the grid step size, $q = 1.6 \times 10^{-19}$ C is the electronic charge and N_d is the dopant concentration. Here N_d is $1.8 \times 10^{19} \text{ cm}^{-3}$ for a 250nm PZT thin film, and other typical values have been used, such as $N_d = 10^{18} \text{ cm}^{-3}$ (Xiao, 2005), and $N_d = 2 \times 10^{19} \text{ cm}^{-3}$

(Zubko, 2006). To study the effect of the magnitude of space charge, we arbitrarily set values between $\rho' = 0.0064$, corresponding to the value used by Zubko (2006) up to $\rho' = 0.1024$. The value of ρ' was applied to the top 16 layers and bottom 16 layers of the grid (i.e. the top 20.8 and bottom 20.8nm, approximately) and zero at all other regions. The simulation was run for 10,000 time steps under the short-circuit condition to allow the system to stabilize, before applying a sinusoidal voltage to the top and bottom layers, with the hysteresis loop divided into 200,000 time steps. After completion of the hysteresis loop, the system was allowed to run for an additional 5,000 time steps.

6.5.3. Results & Discussion

The hysteresis loop showing the average polarization plotted against the average electric field in rescaled units is as shown below:

Figure 6-47: Plot of the rescaled polarization, P_y/P_0 , where $P_0 = 0.647 \text{ C/m}^2$ against the rescaled electric field, $E_y' = E_y/E_0$, where $E_0 = \theta[P_0/\epsilon_0]$. The domain structures for points A to Q are shown in Figure 6-49 to Figure 6-65 below.

Here, we can see that the influence of space charge tilts (and narrows) the hysteresis loop, a phenomenon observed by Damjanovic (1998) in experiments, as well as in the analytical study by Zubko (2006).

The domain evolution is as shown in Figure 6-48 to Figure 6-65:

Figure 6-48: Domain Evolution with Space Charge: Initial polarization at $t = 0$.

After 10,000 time steps (at $t = 10k$), the space charge in the material sets up an internal electric field which results in the formation of 180° domain walls (Figure 6-49), a phenomena observed by Ahluwalia (unpublished results), in studies involving thickness dependence in ferroelectric thin films. This is expected because incomplete neutralization of an internal field (which is the consequence of the space charge introduced into our model) results in the presence of striped domains patterns (i.e. 180° domain wall structures) (Streiffer, 2002). Applying an electric field of sufficient magnitude to neutralize the internal field, would result in the disappearance of such domain structures.

Figure 6-49: Domain Evolution with Space Charge: Initial polarization before application of the electric field at $t = 10k$, showing 180° walls. (Point A of Figure 6-47)

Figure 6-50: Domain Evolution with Space Charge: $t = 20k$. Growth of yellow regions ($P_y = P_0$) at the expense of blue regions ($P_y = -P_0$). (Point B of Figure 6-47)

Figure 6-51: Domain Evolution with Space Charge: $t = 34k$. Disappearance of blue regions and 180° domain walls. (Point C of Figure 6-47)

Figure 6-52: Domain Evolution with Space Charge: $t = 40k$. (Point D of Figure 6-47)

Figure 6-53: Domain Evolution with Space Charge: $t = 50k$. Disappearance of domain wedges. (Point E of Figure 6-47)

Figure 6-54: Domain Evolution with Space Charge: $t = 85k$. Nucleation of domain wedges from the bottom edge. (Point F of Figure 6-47)

Figure 6-55: Domain Evolution with Space Charge: $t = 100k$. Growth of domain wedges. (Point G of Figure 6-47)

Figure 6-56: Domain Evolution with Space Charge: $t = 110k$. Formation of domains of opposite polarizations (blue regions) where $P_y = -P_0$. (Point H of Figure 6-47)

Figure 6-57: Domain Evolution with Space Charge: $t = 115k$. Growth of blue regions at the expense of other regions, and the formation of 180° walls. (Point I of Figure 6-47)

Figure 6-58: Domain Evolution with Space Charge: $t = 120k$. (Point J of Figure 6-47)

Figure 6-59: Domain Evolution with Space Charge: $t = 125k$. Disappearance of yellow regions ($P_y = P_0$). (Point K of Figure 6-47)

Figure 6-60: Domain Evolution with Space Charge: $t = 130k$. (Point L of Figure 6-47)

Figure 6-61: Domain Evolution with Space Charge: $t = 135k$. Disappearance of domain wedges. (Point M of Figure 6-47)

Figure 6-62: Domain Evolution with Space Charge: $t = 140k$. (Point N of Figure 6-47)

Figure 6-63: Domain Evolution with Space Charge: $t = 195k$. Nucleation of domain wedges from the top edge. (Point O of Figure 6-47)

Figure 6-64: Domain Evolution with Space Charge: $t = 205k$. Growth of domain wedges from the top edge. (Point P of Figure 6-47)

Figure 6-65: Domain Evolution with Space Charge: $t = 213k$. Growth of yellow opposite poled regions ($P_y = P_0$). (Point Q of Figure 6-47).

The formation of 90° domain wedges (angled at 45°) shown in Figure 6-55 and Figure 6-63, are of interest due to experimental results showing very similar structures in single crystalline BaTiO_3 , which were observed by Little (1955) as well as Merz (1954), using optical techniques (Figure 6-66):

FIG. 5. 90° wedge nucleation in a $[100]$ crystal: (a) positive field, and (b) negative field.

Figure 6-66: Domain wedge structures in BaTiO_3 as observed by Little (1955)

It is also noted that Little (1955) suggested that the bright regions in her domain structures consisted of space charge which was responsible for the formation of the domain structures observed.

In conclusion, we have shown that space charge tilts and narrows the ferroelectric hysteresis loops, which is in agreement with observations by Damjanovic (1998) and Zubko (2006). Furthermore, wedge-like domain structures nucleating from the space charge regions are observed suggesting that observations of these by Little (1955) and Merz (1954), could be due to the influence of space charge. We also note that in existing theoretical work, we have not seen any published results showing these wedge-like structures using the TDGL model (or any other model), which further points to the novelty of this work.

6.6. Domain Evolution in P(VDF-TrFE)

6.6.1. Introduction

Recently, Iwata (2005) and Ishibashi (2005) used an LGD approach to investigate the P(VDF-TrFE) 65-35 mol% system. To our knowledge, they are obtained the Landau parameters for the 2D free energy function experimentally, and used it to study the behavior of the phase transition in the material. They did not, however, use these parameters to study domain evolution in the material, and to our knowledge, no work has been done in this area before.

6.6.2. Methodology

To study domain evolution in P(VDF-TrFE), we use the form of the free energy given by Iwata (2005) and Ishibashi (2005), which allows for anisotropy between the x and y directions. This anisotropy requires the term F_{Landau} in equation 3.33 to be modified to:

$$F_{\text{Landau}}(P_x, P_y) = \frac{1}{2}\alpha_1(P_x^2 + P_y^2) + \frac{1}{4}\alpha_{11}(P_x^4 + P_y^4) + \frac{1}{2}\alpha_{12}P_x^2P_y^2 + \frac{1}{2}\alpha_{112a}P_x^4P_y^2 + \frac{1}{2}\alpha_{112b}P_x^2P_y^4 + \frac{1}{6}\alpha_{111a}P_x^6 + \frac{1}{6}\alpha_{111b}P_y^6 \dots (6.5)$$

for the Landau free energy polynomial expansion. From here, we solve equations 6.1 & 6.2, with the constraints of electrostatics (equation 6.3) and elasticity (equation 6.4). The TDGL equations are discretized onto a 256×256 grid, and the resulting domain structures are shown in the next section.

6.6.3. Results & Discussion

The domain structures are obtained as follows:

Figure 6-67: Domain Structures for P(VDF-TrFE) at $t = 2000$ (left image) and $t = 4000$ (right image).

Figure 6-68: Domain Structures for P(VDF-TrFE) at $t = 8000$ (left image) and $t = 16000$ (right image).

Figure 6-69: Domain Structures for P(VDF-TrFE) at $t = 32000$. The region enclosed by the white box is shown below.

Figure 6-70: Domain Structures in P(VDF-TrFE).

Unfortunately, the domain structures (Figure 6-70) predicted by the Landau parameters of Iwata (2005) and Ishibashi (2005) have not been observed experimentally. Hence, it is difficult to verify the accuracy of the Landau parameters proposed by them. However, this results show the flexibility of our TGDL model to

be adapted to materials such as P(VDF-TrFE) which involve an anisotropic free energy proposed by these authors in equation 6.5, as well as a hexagonal ferroelectric phase.

6.7. Summary of Chapter 6

In this chapter, a theoretical framework to solve the Time-Dependent Ginzburg-Landau (TDGL) equations in real space is demonstrated, whereby we are able to obtain experimentally observed domain structures, including twin 90° domain walls and ferroelectric 180° domain walls. Application of this model to study lateral-size effects in inhomogeneously poled thin films allows the observation of the fringing electric fields. At very small lateral sizes, the fringing effects become more significant whereby the coercive field becomes very large, and the film becomes virtually impossible to pole. In studies on the effect of space charge, a reduction in the remnant polarization and coercive field is observed, in agreement with observations by Damjanovic (1998). The inclined 90° domain wedges observed have similarities with experimental observations by Little (1955), indicating that these domain structures could be the result of a space-charge layer. Lastly, the flexibility of our model to handle materials with a hexagonal symmetry is demonstrated, using the material constants for P(VDF-TrFE) suggested by Iwata (2005) and Ishibashi (2005).

7. Conclusions

In summary:

1. In this report, a relationship has been derived, showing that $Q_m \times d_{31}$ is the primary material property that relates to the performance of the piezoelectric tube and this applies to both ferroelectric ceramic PZT as well as the ferroelectric polymer P(VDF-TrFE). It has also been noted that the material properties, Q_m and d_{31} , are related to domain wall mobility, which in turn has an electric-field dependence as well as frequency dependence.
2. Results indicate a deviation of $Q_m \times d_{31}$ from expected values, and these two parameters are related to domain wall mobility which is known to be both frequency-dependent and electric field dependent. Scaling the geometry of the transducer changes its resonance frequency, and this would influence these parameters, and the same would happen if the transducer was operated under a high electric field.
3. Relationships resonance frequency and the material properties have been derived and experimentally verified. Expressions for bending displacement, and the tube vibration velocity have also been derived.
4. The feasibility of P(VDF-TrFE) tubular transducers in bending displacement mode has been established. Like their piezoceramic counterparts, P(VDF-TrFE) tubular transducers perform linearly with the voltage under low electric field. At higher electric fields, there is a small quadratic component, indicating the possibility that the constitutive relationships could be further developed. The performance of the current tube has the potential to exceed that of piezoceramics, provided it is operated at large electric field (70MV/m), or at low electric field but using

- piezopolymer tubes with dielectric filler³. Further work is recommended to characterize the performance of such tubes using stretched or irradiated P(VDF-TrFE) polymers, as well as at different VDF to TrFE mol% ratios.
5. The electrostrictive mode in P(VDF-TrFE) tubular transducers has also been investigated, and frequency-dependent characteristics area also observed.
 6. A theoretical framework to solve the TDGL equations in real space with both elastic and electrostatic effects has been introduced, and shown to be able to predict both 90° and 180° domain structures in ferroelectric material which is in agreement with both experimental observations and theory.
 7. Inhomogeneous poling due to fringing electric fields contributes to lateral size effects with the formation of domain wedges at the electrode edges. The fringing effect becomes more pronounced at very small lateral sizes, whereby there is a minimum lateral width below which a material may become almost impossible to pole.
 8. The effect of space charge results in tilted hysteresis loops, with a reduction in the coercive field and the remnant polarization which is in agreement with Damjanovic (1998). We show that a possible explanation for the domain wedges observed by Little (1955) could be due to a space charge layer, and that space charge can create domain structures similar to those observed by Little (1955), which has not been observed before.
 9. A phase field model for P(VDF-TrFE) 65-35 mol% using the Landau parameters by Iwata (2005) and Ishibashi (2005) has been introduced, showing the flexibility of our model to handle the anisotropy of the free energy, as well as the hexagonal ferroelectric phase.

8. List of Publications & Original Work

8.1. List of Publications

1. Ng, N., Ma, J., Boey, F., (2007). “Polymer Piezoelectric Tubular Transducers”, *Electrochemical and Solid-State Letters*, 10 (2), P5-P7.
2. Ng, N., Li, T., Ma, J., Boey, F., (14 Dec 2006). “Behavior of piezoelectric ultrasonic tubular transducers in relation to tube geometry”, *Journal of Electroceramics*, 16, 307-311.

8.2. Novelty of this Work

List of Original Contributions

1. Application of the Timoshenko model to piezoelectric tubular transducer devices in bending mode, whereby we:
 - (a) write the vibration velocity of the tube as a function of three independent components, an electrical factor, a materials factor, and a geometric factor,
 - (b) use this relationship to investigate the behavior of the material constants, $Q_m \times d_{31}$, as a function of frequency for PZT
2. Fabrication of piezoelectric tubular transducer devices of P(VDF-TrFE) 70-30 mol% copolymer, with quartered electrodes, for which:
 - (a) the bending displacement is characterized for the piezoelectric mode (electric field < coercive field, E_c) and compared with the Timoshenko model,

- (b) the bending displacement is characterized for the electrostrictive operation modes (electric field $> E_c$),
 - (c) the frequency dependent behavior of the bending displacement and effective electrostrictive coefficients are characterized.
3. A theoretical framework to investigate microstructural evolution in ferroelectric perovskites and polymers using the TDGL equations with both elastic and electrostatic effects has been introduced, which:
 - (a) improves on traditional Fourier-space methods by allowing the TDGL equations to be solved in real space, without requiring the strain compatibility equation,
 - (b) and is able to reproduce experimentally-observed domain structures such as 90° and 180° domain walls and 90° domain wedges (inclined at 45°).
 4. Investigation of the effects of inhomogeneous poling due to fringing electric fields as a function of lateral size and film thickness using the TDGL model, whereby a minimum lateral size requirement is observed. As mentioned in section 2.3, our model improves on work by Wang (1995) and Roytburd (2000) by adding electrostatic effects, and incorporating an investigation of the domain evolution.
 5. Investigation of the effect of space charge in ferroelectric thin film on the domain evolution, using the TDGL model. As mentioned in section 6.5.1, our model improves on work by Zubko (2006), who only investigated the 1D case without elastic effects, by investigating domain structures in 2D and incorporating both elastic and electrostatic effects.

6. Investigation of domain structures in the P(VDF-TrFE) 65-35 mol% system, to improve on work by Iwata (2005) and Ishibashi (2005) who applied the TDGL model to the system, but did not study microstructural evolution, as mentioned in section 6.6.1.

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10. Appendices

10.1. Piezoelectric Materials Data

Table 10-1: Piezoelectric Material Data for Commercial Tubes Purchased

	Boston Piezo Optics	
Coupling Coefficients	Navy Type VI High Density	Navy Type III
K_{33}	.750	.640
K_{31}	.440	.300
K_{15}	.680	.550
k_p	.750	.510

Piezoelectric Constants		
d_{33} (x 10 ⁻¹² m/V)	650	225
d_{31}	-320	-97
d_{15}	810	330
g_{33} (x 10 ⁻³ Vm/N)	19.0	24.0
g_{31}	-9.5	-10.9
g_{15}	27.0	-28.9

Free Dielectric Constant		
K_{33}^f	3800	1000
K_{11}^f		1290

Elastic Constants		
S_{33}^E (x 10 ⁻¹² m ² /N)	21.0	13.5
S_{11}^E	16.6	10.0

Young's Modulus (x 10 ¹⁰)	6.4	9.9
Poisson Ratio	0.31	0.31
Density (kgm ⁻³)	7800	7500
Q_M	30	1000
Q_E	21	250
Curie Point (°C)	250	300

Frequency Constants		
N_t (Hz-m) thickness	1940	2180
(KHz in)	76.4	86
N_s (Hz-m) shear	1180	1400
(KHz in)	46.5	55
N_r (Kz-m) radial	2085	2310
(KHz in)	82	91

Table 10-2: Properties of Commercially Available Piezoelectric Materials

(APC, 2004. Boston, 2004. Morgan, 2004. Piezo Kinetics 2004. Saint-Gobain 2004)

Properties of Piezoelectric Materials			Physical Properties				Piezoelectric Properties		
Vendor	Material	Product No	Young's Modulus		Poisson Ratio	Density	Mechanical Quality Factor	Strain Constant	
			Y_{11}^E (kg·m ⁻¹ ·s ⁻²)	Y_{33}^E (kg·m ⁻¹ ·s ⁻²)	σ -	ρ (kg·m ⁻³)	Q_m -	-d ₃₁ (m·V ⁻¹)	
1	American Piezo		840	8.0E+10	6.8E+10	0.30	7600	500	1.25E-10
2			841	7.6E+10	6.3E+10	0.30	7600	1400	1.09E-10
3			850	6.3E+10	5.4E+10	0.30	7700	80	1.75E-10
4			855	5.9E+10	5.1E+10	0.30	7700	65	2.76E-10
5			856	5.8E+10	4.5E+10	0.30	7500	72	2.60E-10
6			880	9.0E+10	7.2E+10	0.30	7600	1000	9.50E-11
7	Boston Piezo Optics	Navy Type I		7.8E+10		0.31	7600	400	1.22E-10
8		Navy Type II		6.6E+10		0.31	7500	100	1.71E-10
9		Navy Type II High Density		5.3E+10		0.31	7700	80	1.90E-10
10		Navy Type VI		6.4E+10		0.31	7500	65	2.65E-10
11		Navy Type VI High Density		4.9E+10		0.31	7800	30	3.20E-10
12		Navy Type III		9.9E+10		0.31	7500	1000	9.70E-11
13	Morgan Electroceramics	PZT, Navy Type I	402	8.20E+10	6.60E+10	0.31	7600	500	1.22E-10
14		PZT, Navy Type I	403	7.50E+10	5.90E+10	0.31	7600	600	1.35E-10
15		PZT, Navy Type I	404	7.50E+10	5.90E+10	0.31	7600	600	1.35E-10
16		PZT, Navy Type I	406	Not Available		0.30	7800	750	1.30E-10
17		PZT, Navy Type II	5A4			0.35	7900	80	1.95E-10
18		PZT, Navy Type III	805			0.30	7800	1000	1.00E-10
19		PZT, Navy Type V	5J1	6.20E+10	4.40E+10	0.31	7400	75	2.20E-10
20		PZT, Custom	PZT501	6.10E+10	n/a	0.31	7600	75	1.85E-10
21		PZT, Custom	PZT502	6.20E+10	n/a	0.31	7800	80	1.95E-10
22		PZT, Custom	PZT503	Not Available		0.30	7800	75	2.15E-10
23		PZT, Custom	PZT504			0.30	7800	75	2.00E-10
24		PZT, Custom	PZT507			0.30	7800	65	2.80E-10
25		PZT, Custom	PZT407			0.30	7900	1200	1.50E-10
26		PZT, Custom	PZT701	9.30E+10	7.20E+10	0.31	7700	600	6.00E-11
27		PZT, Custom	PZT702	9.20E+10	n/a	0.31	7600	500	1.00E-10
28		PZT, Custom	PZT703	Not Available		0.30	7800	80	1.50E-10

29	PiezoKinetics	PZT, Navy Type I	402	7.6E+10		0.31	7600	500	1.20E-10	
30		PZT, Navy Type I	406	7.2E+10		0.22	7700	600	1.50E-10	
31		PZT, Navy Type II	502	7.1E+10		0.31	7700	80	1.75E-10	
32		PZT, Navy Type III	802	7.2E+10		0.31	7600	900	1.00E-10	
33		PZT, Navy Type III	804	7.3E+10		0.25	7700	900	1.00E-10	
34		PZT, Navy Type V	532	6.3E+10		0.31	7600	75	2.30E-10	
35		PZT, Navy Type VI	552	6.0E+10		0.31	7600	75	2.70E-10	
36		PZT, Navy Type VI	556	5.8E+10		0.22	7800	65	3.10E-10	
37		PZT, PKI 700	700	8.6E+10		0.25	7600	600	6.00E-11	
38		PNN, PKI 906	906	5.5E+10		0.22	7800	55	3.10E-10	
39	St Gobain	Barium Titanate, Navy IV	T57	1.1E+11	9.4E+10	0.28	5300	500	4.50E-11	
40			P1 60	6.0E+10	4.6E+10	0.30	7500	80	1.75E-10	
41		Lead Titanate Zirconate, Navy I	P7 62	8.2E+10	6.0E+10	0.29	7550	600	1.30E-10	
42			P4 68	5.8E+10	4.6E+10	0.30	7400	80	2.20E-10	
43		Lead Titanate Zirconate, Navy II	P1 88	Not Available			0.30	7700	80	1.86E-10
44		Lead Titanate Zirconate, Navy III	P1 89				0.31	7650	1000	1.08E-10
45		Lead Titanate Zirconate, Navy VI	P1 91				0.34	7410	60	2.47E-10
46			P1 94				0.35	7900	60	3.05E-10

10.2. Numerical Methods

10.2.1. Obtaining the Solution to the Wave Number Equation

The wave number equation is:

$$\left\{ \begin{array}{l} \frac{(a^2 - b^2)(a^2 + b^2 + \gamma^2 ab - ab)(a^2 + b^2 - \gamma^2 ab + ab)}{2ab(b^2 + \gamma^2 a^2)(a^2 + \gamma^2 b^2)} \sin a \sinh b - \cos a \cosh b + 1 = 0 \\ \frac{(\gamma^2 b^2 + a^2)(\gamma^2 a^2 + b^2)}{(a^2 - b^2)(1 + \gamma^2)} = s^2 = \frac{16L_{tube}^2}{D_{tube}^2 + d_{tube}^2} \end{array} \right. \quad .. (10.1)$$

In order to solve the above equation, the following numerical method was used. First, let:

$$\begin{aligned} f_1 &= \frac{(a^2 - b^2)(a^2 + b^2 + \gamma^2 ab - ab)(a^2 + b^2 - \gamma^2 ab + ab)}{2ab(b^2 + \gamma^2 a^2)(a^2 + \gamma^2 b^2)} \sin a \sinh b - \cos a \cosh b + 1 \\ f_2 &= \frac{(\gamma^2 b^2 + a^2)(\gamma^2 a^2 + b^2)}{(a^2 - b^2)(1 + \gamma^2)} - s^2 \end{aligned} \quad .. (10.2)$$

A solution to the equation requires: $f_1 = f_2 = 0$, so the steps to solve the above equation are as follows:

1. Start with an initial seed for the values of wave numbers a and b
2. Minimize the parameter, $f_1^2 + f_2^2$, by calculating $f_1^2 + f_2^2$ for the points $(a, b + \Delta b)$, $(a, b - \Delta b)$, $(a + \Delta a, b)$, and $(a - \Delta a, b)$, and determining which has the lowest value
3. Repeat the process until $f_1^2 + f_2^2$ remains unchanged from the previous iteration. In such a case, the step values of Δa and Δb are halved and the process repeated until $f_1^2 + f_2^2 = 0$ is obtained.

10.2.2. Obtaining the Solution for the Nodal Points

The solutions for the nodal point equation for different values of the Poisson Ratio, σ , and shape factor $1/s$ were obtained using the Newton Raphson Method.

The nodal points for the tube bending displacement are obtained by solving the mode shape equation (Li, 2003) for $\zeta = 0$:

$$\left\{ \begin{array}{l} \zeta = C_3 \left[\frac{a}{b} \sin ax + \sinh bx + \alpha \left(\frac{1}{\eta} \cos ax + \cosh bx \right) \right] = 0 \\ \text{where } \eta = \frac{a^2 + b^2 \gamma^2}{b^2 + a^2 \gamma^2}, \text{ and } \alpha = \frac{\frac{a}{b} \eta \sin a - \sinh b}{\cosh b - \cos a} \end{array} \right. \dots\dots\dots (10.3)$$

The Newton Raphson method is given by (Kreyszig, 1993):

$$x_{k+1} = x_k - \frac{f(x_k)}{f'(x_k)} \dots\dots\dots (10.4)$$

Differentiating the mode shape equation,

$$\frac{d\zeta}{dx} = C_3 \left[\frac{a^2}{b} \cos ax + b \cosh bx + \alpha \left(-\frac{a}{\eta} \sin ax + b \sinh bx \right) \right] \dots\dots\dots (10.5)$$

Thus,

$$x_{k+1} = x_k - \frac{\left[\frac{a}{b} \sin ax_k + \sinh bx_k + \alpha \left(\frac{1}{\eta} \cos ax_k + \cosh bx_k \right) \right]}{\left[\frac{a^2}{b} \cos ax_k + b \cosh bx_k + \alpha \left(-\frac{a}{\eta} \sin ax_k + b \sinh bx_k \right) \right]} \dots\dots\dots (10.6)$$

The values of a and b as a function of the shape factor $1/s$ and Poisson Ratio, obtained earlier in Section 10.2.1, were tabulated and substituted into the equation.

With an initial seed value of 0.22, the first nodal point could be obtained to 4 decimal places within five iterations. Using the seed value of 0.776, the second nodal point could be obtained to the same accuracy within five iterations.

10.3. Curve Fitting for Wave Numbers , $\sqrt{a^2 - b^2}$

The wave numbers a and b , obtained earlier numerically, were tabulated, and the resulting value of $\sqrt{a^2 - b^2}$ plotted against the shape factor, $1/s$ as follows:

Figure 10-1: Wave Number parameter, $\sqrt{a^2 - b^2}$ plotted as a function of $1/s$

To find the best curve fit, an attempt was made to fit the above graph to various equations. The curve fit to degree-2, 3, 4, 5 & 6 polynomials with $R^2 = 0.9977576$, 0.999978, 0.999978, 0.9999958, 0.9999997 respectively. Power, logarithmic, linear, and exponential fits performed worse, with $R^2 = 0.9752498$, 0.9584295, 0.9293955, and 0.7033854 respectively. Of these, the curve fit to a degree-6 polynomial performed the best, and hence was chosen to provide an approximation to the parameter $\sqrt{a^2 - b^2}$.

10.4. Effect of Poisson Ratio on the Wave Numbers, $\sqrt{a^2 - b^2}$

Strictly speaking, the geometric factor, $\frac{L_{tube} \sqrt{a^2 - b^2}}{(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}}$, is not purely a function

of the geometrical properties. The wave numbers, a and b are obtained by solving the simultaneous equations:

$$\begin{cases} \frac{(a^2 - b^2)(a^2 + b^2 + \gamma^2 ab - ab)(a^2 + b^2 - \gamma^2 ab + ab)}{2ab(b^2 + \gamma^2 a^2)(a^2 + \gamma^2 b^2)} \sin a \sinh b - \cos a \cosh b + 1 = 0 \\ \frac{(\gamma^2 b^2 + a^2)(\gamma^2 a^2 + b^2)}{(a^2 - b^2)(1 + \gamma^2)} = s^2 = \frac{16L_{tube}^2}{D_{tube}^2 + d_{tube}^2} \end{cases} \quad (10.7)$$

which involve γ and s^2 .

Since $\gamma = \sqrt{4 + 3\sigma}$ and $s^2 = \frac{16L_{tube}^2}{D_{tube}^2 + d_{tube}^2}$, a and b are functions of σ , L_{tube} , D_{tube} , and

d_{tube} , i.e. $(a, b) = f(\sigma, L_{tube}, D_{tube}, d_{tube})$.

To determine the effect of Poisson ratio on the parameter $\sqrt{a^2 - b^2}$, $\sqrt{a^2 - b^2}$ is plotted against $1/s$ for the typical range of values [see Section 10.1] of the Poisson Ratio, σ , in PZT.

Figure 10-2: $\sqrt{a^2 - b^2}$ as a function of $\frac{1}{s} = \frac{\sqrt{D_{tube}^2 + d_{tube}^2}}{4L_{tube}}$ for different Poisson Ratios

From Table 10-2: Properties of Commercially Available Piezoelectric Materials (APC, 2004. Boston, 2004. Morgan, 2004. Piezo Kinetics 2004. Saint-Gobain 2004), the Poisson ratio of the PZT materials listed was found to average around 0.30 with a minimum of 0.22 and a maximum of 0.35.

Figure 10-3: Frequency Distribution of the Poisson Ratio of Commercial Piezoceramic Material

Based on Table 10-2, the frequency of occurrence of each Poisson Ratio was plotted in the table above. Over 75% of the values fell within the range $\sigma = 0.30$ to 0.31 .

Figure 10-4: Percentage change in $\sqrt{(a^2-b^2)}$ as a function of Poisson ratio and shape factor.

Figure 10-4 above shows that if a Poisson Ratio of $\sigma = 0.3$ is assumed, the values of $\sqrt{(a^2-b^2)}$ will not vary by more than 3%, since in most commercial PZT material, Poisson Ratio, σ , falls within the range of 0.22 to 0.35.

10.5. Effect of Poisson Ratio and Shape Factor on the Nodal Points

The nodal points for the tube bending displacement are obtained by solving the mode shape equation (Li, 2003) for $\zeta = 0$ using numerical methods:

$$\left\{ \begin{array}{l} \zeta = C_3 \left[\frac{a}{b} \sin ax + \sinh bx + \alpha \left(\frac{1}{\eta} \cos ax + \cosh bx \right) \right] = 0 \\ \text{where } \eta = \frac{a^2 + b^2 \gamma^2}{b^2 + a^2 \gamma^2}, \text{ and } \alpha = \frac{\frac{a}{b} \eta \sin a - \sinh b}{\cosh b - \cos a} \end{array} \right. \quad \dots\dots\dots (10.8)$$

The positions of the first and second nodal points as functions of shape factor, $1/s$ and Poisson Ratio, σ , are given by:

Figure 10-5: Position of First Nodal Point as a Function of Poisson Ratio, σ , and $1/s$

Figure 10-6: Position of Second Nodal Point as a Function of Poisson Ratio, σ , and $1/s$

When the nodal points are plotted on the same scale, it can be seen that the nodal point positions do not vary much with shape factor or Poisson's ratio.

Figure 10-7: Positions of Nodal Points as a Function of Shape Factor and Poisson Ratio

Since bending displacement is given by:

$$\zeta = Q_m \frac{16d_{31}V \times l_{nodal} \times (L_{tube} - l_{nodal}) \cos \beta}{\pi(D_{tube}^2 + d_{tube}^2) \ln \frac{D_{tube}}{d_{tube}}} \dots\dots\dots (10.9)$$

Bending displacement is proportional to the parameter, $l_{nodal}/L_{tube}(1-l_{nodal}/L_{tube})$, which varies with Poisson Ratio and shape factor as shown in the Figure 10-8 below.

Figure 10-8: Effect of Poisson Ratio and Shape Factor on the Parameter, $l_{nodal}/L_{tube}(1-l_{nodal}/L_{tube})$

Figure 10-9: Error in the parameter, $l_{nodal}/L_{tube}(1-l_{nodal}/L_{tube})$, if Poisson Ratio $\sigma = 0.30$ is Assumed

From the preceding graphs, it can be seen that assuming a Poisson Ratio of $\sigma = 0.30$ will not affect the estimate of the parameter, $l_{nodal}/L_{tube}(1-l_{nodal}/L_{tube})$, by more than 1%, for values of $1/s = 0.02$ to 0.20 , and $\sigma = 0.20$ to 0.40 .

As a reference, the mode shape curve is plotted for varying values of Poisson Ratio, σ , and for varying values of $1/s$, to show that the nodal points do not change significantly:

Figure 10-10: Effect of Poisson Ratio on the Mode Shape Equation

Figure 10-11: Effect of Shape Factor on the Mode Shape Equation