PRESSURE CONTROL SYSTEM FOR THE ELECTROSPINNING PROCESS:  
NON-INVASIVE FLUID LEVEL DETECTION USING INFRARED AND 
ULTRASONIC SENSORS  

A Thesis 
Presented to 
The Graduate Faculty of the University of Akron  

In Partial Fulfillment 
of the Requirements for the Degree 
Masters of Science  

Charles J Druesedow  
August, 2008
PRESSURE CONTROL SYSTEM FOR THE ELECTROSPINNING PROCESS:
NON-INVASIVE FLUID LEVEL DETECTION USING INFRARED AND
ULTRASONIC SENSORS

Charles J Druesedow

Thesis

Approved:  

Advisor
Dr. Celal Batur

Co-Advisor
Dr. Miko Cakmak

Committee Member
Dr. Nathan Ida

Accepted:  

Dean of the College
Dr. George K. Haritos

Dean of the Graduate School
Dr. George R. Newkome

Date

Department Chair
Dr. Celal Batur
ABSTRACT

Electrospinning is a method for producing micro and nano sized synthetic fibers through the use of electrostatic forces. This phenomenon has been known since early in the 20th century, but has had an increase in interest since the 1990’s due to their potential applications in textiles, electronics, and the biomedical field. To make electrospinning a commercially viable fiber production method requires the high volume production of continuous, uniform diameter fibers that are free of defects. To achieve greater control over the process variables that affect the fiber formation, a scaleable closed loop control system that can maintain a constant pressure at the capillary tip was designed.

Two sensing technologies, infrared and ultrasonic, were used and compared for their ability to detect the height of the polymer solution in the electrospinning fluid container. The air pressure above the solution was measured with a pressure transducer and adjusted through a controllable syringe pump that was controlled through a custom LABVIEW program. A simulation of the jet formation was also performed by programming the derived equation of motion of the electrospun jet in MATLAB.

The closed loop electrospinning system was successful at controlling and maintaining a constant pressure at the capillary tip to within 2% of the specified
pressure over a 24-hour period. The control system was also able to create a defect free fiber mat when the pressure and voltage at the capillary tip were carefully selected. The adjustments of the pressure at the capillary tip did not show a strong correlation to controlling the fiber diameter or uniformity.

Though a closed loop electrospinning control system was designed and implemented, the use of pressure control at the capillary tip to create a closed loop control system for the electrospinning process may not be the optimal solution for controlling the diameter of the produced fibers.

The simulation of the jet using MATLAB’s differential equation solver, ode45, was successful but limited in accuracy by the number of beads that could be used in the simulation.
ACKNOWLEDGEMENTS

I would like to extend my sincere gratitude and appreciation to both of my advisors, Dr. Batur and Dr. Cakmak, for their support, guidance, and patience. Their accessibility, professionalism, and willingness to work with me, was not only encouraging, but impressive. Thanks to Dr. Ida, for his contributions and discussions on non-invasive sensing technologies, and Cliff Bailey for always finding the time to answer questions and help in anyway he can. Thanks to both the Mechanical and Polymer Engineering departments for providing me with the financial support, which allowed me to attend graduate school on a full time basis.

Thanks to Baris Yalcin and Bart Hamilton for helping me on a daily basis and making sure I always had the supplies and materials I needed. Also, thanks to two great friends, Jesse Robbins and Todd Lewis, which I meet in graduate school but am sure their friendship will last a lifetime.

Lastly I want to thank my parents, Charles and Frances Druesedow, my sister, Carrie, and cousin Alex, for their endless support and encouragement, not only over the last two years, but everyday year after year.
# TABLE OF CONTENTS

| LIST OF TABLES | viii |
| LIST OF FIGURES | ix |

## CHAPTER

I. INTRODUCTION .................................................................1
   1.1. Statement of Problem ..............................................1
   1.2. Summary of Approach ..............................................1

II. LITERATURE REVIEW ......................................................4
   2.1. Fundamental Theory ..............................................5
   2.2. Applications .......................................................6
   2.3. Process Variable Studies .......................................6
   2.4. Simulation and Modeling .......................................9
   2.5. Control System Design .........................................13

III. EXPERIMENTAL SETUP ...............................................17
   3.1. Mechanical Setup ...............................................17
   3.2. Controller ........................................................24
   3.3. Calibration .......................................................26
   3.4. Sensor Comparison ..............................................30
   3.5. Simulation Setup and Coding .................................33
IV. RESULTS AND DISCUSSION

4.1. Infrared and Ultrasonic Sensor Comparison

4.2. Ultrasonic Testing and Observed Trends

4.3. Dripping and Set Point Choice for Long Run Test

4.4. Humidity Effects

4.5. Simulation

V. CONCLUSION

REFERENCES

APPENDICES

APPENDIX A. MAIN PROGRAM

APPENDIX B. SUBROUTINE
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1. Air Pressure Sensor Calibration</td>
<td>26</td>
</tr>
<tr>
<td>3.2. Jet Initial Conditions for N Beads</td>
<td>37</td>
</tr>
<tr>
<td>3.3. Format of Equations to be Integrated by ode45</td>
<td>39</td>
</tr>
<tr>
<td>4.1. Solution Flow Rates and Jet Current</td>
<td>53</td>
</tr>
<tr>
<td>4.2. Predicted Fiber Diameters (µm)</td>
<td>56</td>
</tr>
<tr>
<td>4.3. Experimental Fiber Diameters (µm)</td>
<td>57</td>
</tr>
<tr>
<td>4.4. Flow Rate Data Over: 24-Hour Period</td>
<td>64</td>
</tr>
<tr>
<td>Set Point = 3”of H₂O and Voltage = 8 kV</td>
<td></td>
</tr>
<tr>
<td>4.5. Set Point, Current, and Voltage Variations: 24-Hour Period</td>
<td>64</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1. Horizontal Electrospinning</td>
<td>16</td>
</tr>
<tr>
<td>3.1. Infrared Sensor Setup</td>
<td>18</td>
</tr>
<tr>
<td>3.2. Ultrasonic Sensor Setup</td>
<td>19</td>
</tr>
<tr>
<td>3.3. Ultrasonic Sensor Electronics Box</td>
<td>20</td>
</tr>
<tr>
<td>3.4. New Era Pump and Air Pressure Sensor</td>
<td>21</td>
</tr>
<tr>
<td>3.5. Exposed Air Pressure Sensor</td>
<td>21</td>
</tr>
<tr>
<td>3.6. Electrospinning Experimental Control System Setup</td>
<td>23</td>
</tr>
<tr>
<td>3.7. Electrospinning Control System Diagram</td>
<td>24</td>
</tr>
<tr>
<td>3.8. Air Pressure Sensor Calibration</td>
<td>27</td>
</tr>
<tr>
<td>3.9. Infrared Sensor Calibration Curve</td>
<td>28</td>
</tr>
<tr>
<td>3.10. Infrared Detector and Emitter</td>
<td>29</td>
</tr>
<tr>
<td>3.11. Ultrasonic Sensor Calibration</td>
<td>30</td>
</tr>
<tr>
<td>3.12. Filtered and Unfiltered Infrared Sensor Output Signal</td>
<td>32</td>
</tr>
<tr>
<td>3.13. Initial Position of Jet</td>
<td>37</td>
</tr>
<tr>
<td>3.14. Jet Curvature Diagram</td>
<td>41</td>
</tr>
<tr>
<td>4.1. Ultrasonic and Infrared Sensor Solution Measurements</td>
<td>44</td>
</tr>
<tr>
<td>4.2. Infrared Sensor Volume and Set Point Comparison</td>
<td>45</td>
</tr>
<tr>
<td>4.3. Stable Jet vs. Dripping Jet Current Comparison</td>
<td>47</td>
</tr>
</tbody>
</table>
4.4. Polymer Solution Bad at Capillary Tip.................................................................47
4.5. Jet Varicose Instabilities .......................................................................................49
4.6. Infrared Sensor Fiber Mat: Set Point = 8” of H\textsubscript{2}O and Voltage = 12 kV ....................50
4.7. Ultrasonic Sensor Fiber Mat: Set Point = 8” of H\textsubscript{2}O and Voltage = 12 kV .............51
4.8. Fiber Diameter Spacing, excerpt from Figure 4.5 .................................................51
4.9. Solution Flow Rates at Applied Voltage ..............................................................54
4.10. Jet Current at Applied Voltage ...........................................................................54
4.11. 15 Second Fiber Mat: Set Point = 2” of H\textsubscript{2}O and Voltage = 8 kV .......................55
4.12. 15 Second Fiber Mat: Set Point = 2” of H\textsubscript{2}O and Voltage = 12 kV ....................55
4.13. Theoretical and Experimental Fiber Dia. Comparison: Voltage = 8 kV .................57
4.14. Theoretical and Experimental Fiber Dia. Comparison: Voltage = 12 kV .................58
4.15. Fiber Diameter Distribution at Constant Set Point = 2” of H\textsubscript{2}O .......................59
4.16. Fiber Diameter Distribution at Constant Set Point = 8” of H\textsubscript{2}O .......................59
4.17. Fiber Diameter Distribution at Constant Voltage = 8 kV .......................................60
4.18. Fiber Diameter Distribution at Constant Voltage = 12 kV .....................................60
4.19. Fiber Mat; Set Point = 2” of H\textsubscript{2}O and Voltage = 8 kV ........................................61
4.20. Fiber Mat; Set Point = 2” of H\textsubscript{2}O and Voltage = 12 kV ........................................61
4.21. Fiber Mat; Set Point = 8” of H\textsubscript{2}O and Voltage = 8 kV ........................................62
4.22. Fiber Mat; Set Point = 8” of H\textsubscript{2}O and Voltage = 12 kV ........................................62
4.23. Polymer Solution Flow Rates .............................................................................63
4.24. Set Point Variation over 24 Hour Period .............................................................65
4.25. Solution Volume Change over 24 Hour Period ...................................................66
4.26. Current Variation over 24 Hour Period ................................................................66

x
4.27. Voltage Variation over 24 Hour Period .................................................................66
4.28. No Drip Defect; Set Point = 3” of H₂O and Voltage = 8 kV ..............................67
4.29. Drip Defect; Set Point = 2” of H₂O and Voltage = 6 kV .................................67
4.30. Low RH: 24.5°C and 47% RH ............................................................................68
4.31. High RH: 23.3°C and 64% RH ...........................................................................68
4.32. High RH after 72 Hour Period ..........................................................................69
4.33. High RH: 22.7°C and 57% RH .........................................................................71
4.34. High RH: 22.7°C and 57% RH, 50% zoom .....................................................71
4.35. Low RH: 24.5°C and 47% RH .........................................................................72
4.36. Solution Convergence Time ............................................................................73
4.37. Time = 0.01 seconds, # of Beads = 50 ...............................................................75
4.38. Time = 0.02 seconds, # of Beads = 50 ...............................................................75
4.39. Time = 0.03 seconds, # of Beads = 50 ...............................................................76
4.40. Time = 0.04 seconds, # of Beads = 25 ...............................................................76
4.41. Time = 0.05 seconds, # of Beads = 25 ...............................................................77
1.1. Statement of Problem

Electrospinning is a method for producing long polymer fibers with micro and nano sized diameters. Due to their high surface area to volume ratio and superior mechanical performance [1], these fibers have the potential for many important applications. However, to be able to bring this technology to industry on a production scale, several obstacles must first be overcome. The three major obstacles to be solved [1] with electrospinning are: low deposition (production) rate of fibers, producing fibers with consistent and controllable diameters, and producing defect free mats, i.e. no dripping of polymer solution from the tip of the capillary. Simply put, to make electrospinning a commercially viable fiber production technique, it has to be able to produce a high volume of continuous, uniform diameter nanofibers that are free of defects.

1.2. Summary of Approach

The objective of this thesis is to create an electrospinning control system that can produce consistent diameter electrospun fiber mats without any defects caused by dripping polymer solution from the capillary tip. Keeping in mind the other obstacle of electrospinning, fiber production rates, the control system must be able to control individual bottles and jets so that when production scale up does happen, the control over
fiber morphology achieved with the single setup can be reproduced on a larger scale. Additionally, it is desired that the electrospinning process happen in the vertical direction so it can be implemented on typical industrial machines, such as a film-casting machine.

In order to achieve this goal, the control system must continuously maintain a constant pressure at the electrified capillary tip. The pressure at this point is dependent on two factors: the pressure head of the polymer solution and the air pressure above the polymer solution. Hence, the pressure at the capillary tip is the addition of the pressure head and air pressure.

The air pressure can easily be measured using a miniature amplified low-pressure sensor. Continuously measuring the amount of polymer solution in the bottle without contacting the electrified solution is a more challenging task. To achieve this goal, two non-invasive sensing technologies are used: infrared and ultrasonic. Both sensors can measure the distance to the polymer solution/air interface. The return signal from the sensor is then used to calculate the corresponding pressure head of the polymer solution.

The infrared sensor is a compact distance sensor that contains both the infrared light emitter and detector, along with the electronics to process the signal. The emitter is a light-emitting diode (LED) and the detector is a photodiode also known as a position-sensing device (PSD). To measure the distance between the sensor and the object, the LED emits a 850 ± 70nm wavelength. When the emitted light reaches a reflective surface, some of it is reflected back and received by the PSD. Depending on where the reflected light hits the PSD, the distance from the sensor is calculated by the signal processing circuit and output as an analog voltage. The output voltage is sent to the
National Instruments data acquisition system and then to LabVIEW, which converts the signal into a calibrated amount of solution volume.

The ultrasonic sensor uses a piezoelectric material, in operation the electronics box generates and electronic signal, which is sent to the sensor and is then converted to an ultrasonic burst. The burst then travels through the medium (polymer solution), and when it reaches the polymer/air interface, it is reflected back to the sensor. The reflected echo is then converted to an electronic signal, which is then sent back to the electronics box. The transit time of the ultrasonic burst is then calculated, which is directly proportional to the height of the polymer solution, and sent to the electronics box output as a voltage. The voltage is then sent to the data acquisition box and LabVIEW, which then converts the voltage to a calibrated volume of polymer solution.
CHAPTER II
LITERATURE REVIEW

It has been known since the beginning of the 20th century that electrostatic forces applied to a solution could be used to create synthetic fibers. Rayleigh and Zeleny investigated this phenomenon independently, but the first patent for an electrostatic spinning apparatus was given to Formhals in 1934 [1-4]. In the 1960’s, Taylor studied the formation of the conical shape that a solution makes when an electric field is applied [5]. In this work, Taylor theoretically and experimentally showed that the conical shape the solution takes when an electric field is applied has a semi-vertical angle of 49.3°, this has since been referred to as the Taylor cone. A resurgence of interest in electrically formed fibers came about in the 90’s due to the increased interest in nanofibers and their potential applications. Since then, much work has been done dealing with each aspect of the electrospinning process. This work can be subdivided into 5 categories:

a. Fundamental Theory
b. Applications
c. Process Variable Studies
d. Simulation and Modeling
e. Control System Design
Some detailed reviews of electrospinning history, theory, applications, and fiber collection can be found in references [1-3, 6].

2.1. Fundamental Theory

The formation of the Taylor cone and the emitted jet of solution from its apex has been observed and well documented. [6, 7] In a typical electrospinning process, a pendent of polymer solution is held at the tip of a capillary needle by the solution's surface tension. To start the electrospinning process, a high voltage is applied to the polymer solution causing the surface of the solution to become highly charged. The pendent drop will elongate and form into the well-known conical shaped Taylor cone due to the competition between the surface tension forces and the mutual surface charge repulsion, which acts directly opposite to the surface tension. In addition to these two forces, the drop will also experience the Coulombic force interaction due to the external field. As the forces try to balance each other and form a stable shape, the drop will continue to elongate but once the strength of the electric field has surpassed a critical value, the electrostatic forces overcome the surface tension forces and stable shape can no longer be maintained and thus a liquid jet is emitted from the apex of the Taylor cone, [6]. Once the jet is emitted from the Taylor cone, the charges in the jet accelerate the solution towards the collector plate due to the external electric field, completing the electrical circuit. The diameter of the jet is reduced as the jet travels towards the collection surface, due to stretching of the jet by the mutual charge repulsion of the jet and the evaporation of the solvent from the polymer solution. Additionally, small perturbations in the jet due to the mutual charge repulsion and the interaction with the
external electric field cause the onset of the jet whipping instability, which further
decreases the final collected fiber diameter [2, 6].

2.2. Applications

There are many potential applications for electrospun fibers, especially since the
interest in the field of nanotechnology has greatly increased in recent years. Currently,
the most available process for producing electrospun fibers is in the form of non-woven
mats, which is what will be focused on in this thesis. For a review of collection methods
and their applications, see reference [3]. These non-woven mats can be used for filtration
membranes, nanofiber composites, catalytic nanofibers, and protective fabrics and
textiles. This technology also has many possible applications in the biomedical and
electronics fields. Some of the possible biomedical applications are wound dressing,
tissue scaffolding, artificial blood vessels, and drug delivery systems. In the electronics
field, electrospun materials have possible applications in sensors, batteries, storage cells,
electrically conductive fibers, solar cells and supercapacitors. Surely, as the process and
availability of this technique are refined and proliferated, many additional potential
applications will be discovered. [1, 2, 6-10].

2.3. Process Variable Studies

When producing electrospun fibers and mats, the goal is to produce long, continuous
fibers with a uniform fiber diameter and the absence of beads and defects. There are
many variables that have an effect on the electrospinning process and the final fiber
morphology, mainly final fiber diameter and the presence/absence of beaded fibers.
These parameters can be broken up into three categories: process variables, solution
properties, and ambient conditions.
The process variables that affect the properties of the electrospun fibers are: the applied voltage, distance from electrode to ground plate, and solution flow rate. The effect the solution flow rate has on the fiber diameter has been well documented. The fiber diameter is shown to increase when the solution flow rate increases; this has been shown \cite{11, 12} while spinning a polystyrene solution. The solution flow rate can typically be changed directly, syringe pump flow rate, or indirectly, the applied voltage. Increasing the applied voltage is shown to increase the polymer flow rate from the Taylor cone due to the higher charge repulsion forces \cite{1, 2}. Additionally, an increase in applied voltage has been shown to produce thinner fiber diameters \cite{11, 12}. The reason for this is at higher voltages, the charge carried by the jet is increased imposing larger surface charge repulsion forces, which draws down the diameter of the fiber \cite{1}. It has also been shown that increasing the applied voltage also increases the occurrence of beaded fibers in the mat \cite{13}.

The distance from capillary tip to ground plate has a correlation with the jets deposition time, evaporation rate, and whipping/instability interval \cite{2}. It has been shown \cite{11}, when spinning polystyrene and varying the distance to the collector from 9 to 26 cm that larger diameter fibers occur at larger collection distances. Though it was noted that flow rate and not collection distance was the dominant factor in determining fiber diameter. Another group, \cite{12}, also spun polystyrene fibers with varying collection distance from 35 to 15 cm, and did not see any significant change in fiber diameters. The formation of beaded fibers was noticed at distances less than 30 cm.

The critical solution properties are surface tension, viscosity, conductivity, and dielectric permittivity. These properties are dependent on the type of polymer,
concentration, and solution used; contribute to the behavior of the electrospun jet and the final morphology of the fiber.

Many different polymers and solutions have been processed using the electrospinning technique. One of the most commonly tested polymer solutions is polyethylene oxide and water. The concentrations tested usually vary from 3 to 10% [13, 14]. Polystyrene is another polymer that has been frequently tested in different solvents. The effects the process variables have on the PS fiber morphology has been well documented [11, 12]. Some other commonly tested polymers are: polyacrylic acid (PAA), polyvinyl alcohol (PVA), polyurethane (PU), polycaprolactone (PCL), polycarbonate (PC), and polymethyl-methacrylate (PMMA) [12, 15]. Some common solvents other than water that have been used are: Acetone, tetrahydrofuran (THF), dimethylformamide (DMF), methylene chloride (MC), chloroform, cyclohexane, and toluene [12, 15]. For a comprehensive review of polymer solutions that have been electrospun, see reference [1] and [2].

The viscosity of the solution has a large effect on the final fiber diameter and the formation of beaded defects. The viscosity of the solution is dependent on the concentration of the polymer used, the higher concentration the more viscous the solution will be. The correlation between polymer concentration and the final fiber diameter has been well documented [1, 2, 6, 12, 13], showing higher concentration solutions result in larger diameter fibers. The viscosity of the polymer solution resists rapid changes in shape and supports the formation of smooth fibers without bead defects [6]. The more viscous the solution, the less likelihood beaded fiber defects will occur. [1, 2, 6, 13]
The surface tension of the polymer solution has a large effect on the formation of beads in the fiber since the surface tension forces cause the minimization of the surface area of the jet [14]. It can be seen from references [8] and [14] that the surface tension is mainly dependent on the solution and not the concentration of the polymer. Reference [14] shows that the surface tension can be lowered by the addition of ethanol to the solution. The lower the surface tension of the polymer solution, the less likely the formation of beaded fibers will be [14].

Polymer solutions are conductive, and the charge carried by the jet is highly influential on the jet formation. The more conductive the solution, the more charge the jet can carry. The electrostatic repulsion of the charges carried by the jet, located on the surface of the jet, want to maximize the surface area and cause the jet to thin and create smaller, uniform fiber diameters [6]. It has been well documented, [1, 13], that the charge carried by the jet increases as the applied voltage is increased. Reference [14] also shows that the addition of NaCl decreases the solution resistivity, which allows for more current to be carried by the jet, hence decreasing the formation of beaded fibers.

Additionally, the ambient conditions that affect the electrospinning process are the surrounding air temperature, humidity, and velocity [7].

2.4. Simulation and Modeling

Several groups have developed mathematical models in an attempt to describe and better understand the electrospinning process. One model created by Reneker and Yarin [4], treats the jet as a series of beads connected together by viscoelastic dumbbells. Each bead has a mass \( m \) and possesses a charge \( e \). The jet trajectory and velocity is determined by equating the forces acting on the beads to the beads mass times acceleration according
to Newton’s second law. The forces acting on each bead are: the Coulomb, Electric Field, Viscoelastic, and Surface Tension.

The net Coulomb force (1) acting on bead $i$ is dependent on the position of all the other individual beads. The 3 dimensional distance, $R_{ij}$, between two beads is defined (2).

$$f_c = \sum_{j=1,N, j \neq i} e^2 \frac{e^2}{R_{ij}^2} \left[ \frac{x_i - x_j}{R_{ij}} + j \frac{y_i - y_j}{R_{ij}} + k \frac{z_i - z_j}{R_{ij}} \right]$$

$$R_{ij} = \left[ (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \right]^{1/2}$$

The electric force (3) imposed on bead $i$ is created by the potential difference between the applied voltage, $V_0$, and the distance from the capillary tip and the collector plate, $h$.

$$f_y = -e \frac{V_0}{h}$$

The viscoelastic force (4) acting on bead $i$ has two components. The first term on the right hand side of the equation is from the bead above, or up $(i+1)$, and the second term from the bead below, or down $(i-1)$.

$$f_{ve} = \pi a_u^2 \sigma_{ui} \left[ \frac{i}{\ell_{ui}} \frac{x_{i+1} - x_i}{\ell_{ui}} + j \frac{y_{i+1} - y_i}{\ell_{ui}} + k \frac{z_{i+1} - z_i}{\ell_{ui}} \right]$$

$$- \pi a_d^2 \sigma_{di} \left[ \frac{i}{\ell_{di}} \frac{x_{i-1} - x_i}{\ell_{di}} + j \frac{y_{i-1} - y_i}{\ell_{di}} + k \frac{z_{i-1} - z_i}{\ell_{di}} \right]$$

Where the viscoelastic stress between two beads is defined (5a) and (5b), and the length by (6a) and (6b).

$$\frac{d\sigma_{ui}}{dt} = G \frac{1}{\ell_{ui}} \frac{dl_{ui}}{dt} - \frac{G}{\mu} \frac{\sigma_{ui}}{\ell_{ui}}$$

$$\frac{dl_{ui}}{dt} = \frac{1}{G \ell_{ui}} \left( \sigma_{ui} - \sigma_{di} \right)$$
\[
\frac{d\sigma_{di}}{dt} = G \frac{1}{l_{di}} \frac{dl_{di}}{dt} - \frac{G}{\mu} \sigma_{di}
\]

(5b)

\[L_{ui} = [(x_{i+1} - x_i)^2 + (y_{i+1} - y_i)^2 + (z_{i+1} - z_i)^2]^{1/2}
\]

(6a)

\[L_{di} = [(x_i - x_{i-1})^2 + (y_i - y_{i-1})^2 + (z_i - z_{i-1})^2]^{1/2}
\]

(6b)

The jet radii \( a_{ui} \) and \( a_{di} \) in (4) can be calculated from mass conservation and neglecting the solution evaporation, yielding \( a_{ui} = a_0 \sqrt{L/\ell_{ui}} \) and \( a_{di} = a_0 \sqrt{L/\ell_{di}} \). The initial jet cross section radius \( a_0 \) is given in [4] and the length scale is also defined as \( L = \sqrt{e^2/\pi a_0^2 G} \).

Lastly, the surface tension force acting on bead \( i \) is defined by (7). The force is negative because the surface tension force wants to restore the rectilinear shape of the bent jet.

\[f_{cap} = -\alpha \pi (a^2)_{av} k_i \cdot \left| j \right| x_i \cdot \text{sign}(x_i) + \left| j \right| y_i \cdot \text{sign}(y_i) \]

(7)

The average jet radius is defined as \( (a^2)_{av} = (a_{ui} + a_{di})^2/4 \), and the curvature \( k_i \) is calculated using the x and y locations of beads \( i, i+1 \) and \( i-1 \). The calculation of \( k_i \) will be discussed in more detail in Chapter 3.5. The sign convention is defined in (8a-8c). The use of sign is to make sure that the resultant surface tension force in (7) is straightening the jet curvature by acting towards the x and y centerlines.

\[\text{sign}(x) = 1, \text{ if } x > 0 \quad (8a)\]

\[\text{sign}(x) = -1, \text{ if } x < 0 \quad (8b)\]

\[\text{sign}(x) = 0, \text{ if } x = 0 \quad (8c)\]

The resulting equation of motion (9) takes on the following form according to Newton’s second law: \( m \cdot a = f_c + f_o + f_{ve} + f_{cap} \), where \( r_i = ix_i + jy_i + kz_i \).
\[ m \frac{d^2 r_i}{dt^2} = \sum_{j=1}^{N} \frac{e^2}{R_{ij}^3} (r_i - r_j) - e \frac{V_o}{h^2} k + \frac{\pi \alpha u^2 \sigma_{ul}}{l_{ul}} (r_{i+1} - r_i) \]  

\[ - \frac{\pi \alpha^2 \sigma_{dl}}{l_{dl}} (r_i - r_{i-1}) - \frac{\alpha \pi (a^2)_{en}}{l_{en}} k_i \]

\[ \times [i x_i \text{sign}(x_i) + j y_i \text{sign}(y_i)] \]

Another model was developed by a research group at MIT, [16, 17]. In this model, the jet is treated as a long, slender object. The equation of motion for the jet is derived from Newton’s second law and the jet’s conservation of mass, conservation of charge, and momentum balance, see equations 81-85 in reference [16]. From this derivation, three types of instabilities were identified; Rayleigh mode, electric field induced axisymmetric, and whipping instabilities. It was observed that the Rayleigh mode is dominant at lower charge density where the surface tension is the larger force. The whipping instability is the dominant mode at higher charge densities in the jets when the force due to surface charge repulsion is larger than the surface tension force. The whipping instability mode is the critical mode in electrospinning because it is responsible for the thinning of the jet diameter, due to mass and charge conservation.

This same group with the help of Fridrikh, [18], reexamined these equations for the nonlinear whipping instability regime, to determine how thin the jet diameter can become. Equations 81-85 are simplified by eliminating derivatives with respect to s when h/R and h/L<<L, which is true in the late whipping stages. The equation of motion for the jet then becomes:

\[ \rho \pi h \dot{x}^2 = 2 \pi h \sigma_{en} E_{en} \dot{\vec{z}} + \left( \pi \gamma + \frac{h \sigma}{2} \beta (E_{en} \cdot \dot{i})^2 + \frac{2 \pi^2 h \sigma^2}{\sigma} (3 - 2 \ln \chi) \right) \frac{h}{R} \]  

12
The stability of the jet is then summarized as a competition between the surface tension and surface charge repulsion. The following inequality is then achieved by taking the whole second term on the right hand side of (10), and neglecting the electric field force:

$$\pi \gamma \geq 2\pi^2 h(z)\sigma_0(z)^2 (2\ln \chi - 3)/\bar{e}$$

(11)

The terminal jet diameter is then written implicitly, by solving this inequality for $h$ and substituting $\sigma_0 = hl/2Q$, which comes from the charge and volume conservation of the jet when the advection current dominates, into (11).

$$h_t = \left(\frac{\gamma \bar{e} Q^2}{I^2 \pi (2\ln \chi - 3)}\right)^{\frac{1}{3}}$$

(12)

2.5. Control System Design

As stated earlier in section 3, the electrospun fiber diameters are dependent on many process and solution variables, and maintaining control over these variables is critical to producing consistent and repeatable fiber diameters over the production cycle. Most current electrospinning setups run as open-loop systems, similar to the setups used in references [8, 15], with no feedback control. These open loop systems typically have a programmable syringe pump that supplies the polymer solution to the capillary tip at constant flow rate. To give greater control and flexibility to the electrospinning process it is desirable to have a real-time closed loop control system. Most attempts to develop a real-time control system have revolved around using digital cameras to capture the shape of the Taylor cone and the emerging jet. A group from Clemson University, [10], has proposed, but not tested, the use of a CCD camera and a Fresnel lens to capture images of the fiber jet, which will then be transferred to a computer for further processing and
analysis. To generate the error signal, the captured modes of bending instability will be compared with their derived mathematical model of a stable jet, which is based on the Yarin, Reneker [4] viscoelastic jet model. The resulting error signal is then sent to an adaptive controller that can adjust the voltage, solution flow rate, and distance from tip to collector to achieve the desired bending instability mode. A similar approach, but more extensive, has been developed by the MIT research group that also worked on references [16, 17]. In their approach, 3 CMOS cameras are used to measure the Taylor cone volume, upper jet diameter, the length of the straight jet, and the angle of the whipping region. In addition to this, the current conducted to the collector plate is measured and recorded. The computer system can control the solution flow rate and applied voltage. For a given flow rate, the voltage is adjusted to achieve the desired Taylor cone volume, based on the image data from the CMOS camera. Even though the images are displayed real-time, they are not feedback to a computer to create a closed loop system. It appears that the user must manually adjust the voltage to achieve the desired Taylor cone shape. The testing results show that at higher voltages and lower flow rates, the fiber diameters are smaller and have less variation, and at low voltages and higher flow rates, the fiber distribution is larger; suggesting that a closed loop control system based on the Taylor cone volume could reduce fiber diameter fluctuations.

Another proposed method for determining the quality of the electrospun jet and fibers, that can be used to create a closed loop control system, is to measure the current carried to the collector surface as in [8, 19]. In particular, [8] shows that by observing the current real-time, the type of jet and the morphology of the fibers can be determined. In their research, 4 distinct relations between current and the jet were observed; a fluctuating
jet with large variations in current, a stable jet with very small changes in current, a stable jet but with dripping polymer solution resulting in current surges in the normally stable current reading, and lastly, multiple jets emerging from the Taylor cone with an increase in current proportional to the number of jets.

As outline above, both digital imaging and jet current measurements can be used individually or together to create a closed loop electrospinning control system. The problem with both of these schemes is that they most likely would be impractical for a production scale up control system. Image based control systems are limited by the cost of expensive camera equipment and the ability to properly image the Taylor cone or jet in a dense field of electrospinning nozzles. The use of jet current measurement is limited by the ability to measure the current of an individual jet when multiple jets are being collected on surface, such as a film-casting machine.

Mitchell and Sanders [9] had an alternative approach to creating a closed loop control system for electrospinning. In their setup the variables that they have control over are distance between electrodes, distance from nozzle to collector, applied voltage, temperature of melt, collection surface dielectric strength, and collection surface area.

In addition to being able to adjust the morphology of the electrospun jet, another reason for developing a closed loop control system is to be able to prevent dripping of the polymer solution from the tip of the capillary. This phenomenon has not widely been reported in literature, except for [8] when referring to fluctuations in jet current and the resulting spherical beads that are found in the collected fiber. A drop of polymer solution will form at the tip of the capillary when the solution flow rate to the tip is greater than the emitted jet flow rate. This equation is summarized nicely in [19].
\[ \dot{V}_{\text{cone}} = Q_{\text{pump}} - Q_{\text{jet}} \] (13)

It can be seen from this equation that the ideal non-dripping operating condition is where \( Q_{\text{jet}} = Q_{\text{pump}} \), and that if \( Q_{\text{jet}} < Q_{\text{pump}} \), the Taylor cone will increase in size until a volume of solution is present to form a drop. Some groups have set up the electrospinning apparatus to spin horizontally and collect on a mat that is hung vertically, as shown below in Figure 2.1. In this case, if a drop of solution is released it will fall in the direction of gravity and not be collected on the mat. For industrial applications such as film casting, this is not an optimal solution since electrospinning in the vertical direction is necessary for integration with the existing machine.

![Figure 2.1: Horizontal Electrospinning](image)

Figure 2.1: Horizontal Electrospinning
CHAPTER III
EXPERIMENTAL SETUP

3.1. Mechanical Setup

The experimental setup consists of the typical electrospinning components plus the addition of the non-invasive level sensors. The high voltage is supplied from a Spellman high voltage power supply (Model# CZE30RN10 24V in 0-30kV out) and connected to a 20-gauge (0.036” OD, 0.025” ID) stainless steel needle. The collector plate is a 12” x 6” x 0.020” steel plate with a 10kΩ resistor connected between the ground plate and the ground connection. The measured voltage drop across the resistor allows for the electrical current carried by the jet to be calculated using Ohm’s law. The distance from the capillary tip to the collector plate has an adjustable range of 0 to 15 cm.

The polymer solution is contained in Teflon bottles. A custom Teflon bottle was designed and fabricated for use with the Infrared sensor (Sharp GP2D120), as shown in Figure 3.1. For the ultrasonic sensor (Cosense 092-10003), a standard 120 ml Teflon bottle (TJ-120) from Science Gear was modified so the air pressure fitting and luer lock tubing and lock valve for the needle could be threaded to the bottle cap and bottle bottom respectively, see Figure 3.2 for the ultrasonic bottle and setup. Both sensors are used to determine the height of the polymer solution in the bottle, which is then used to calculate the pressure due the fluid height.
The air pressure above the solution is measured using an All Sensors 10” D2-4V mini pressure transducer, and the air pressure can be regulated using a controllable New Era NE-50X syringe pump with a 1” diameter BD 60ml syringe, Figure 3.4 and 3.5.

Figure 3.1: Infrared Sensor Setup
Figure 3.2: Ultrasonic Sensor Setup
Figure 3.3: Ultrasonic Sensor Electronics Box
Figure 3.4: New Era Pump and Air Pressure Sensor

Figure 3.5: Exposed Air Pressure Sensor
All the sensors are connected to a National Instruments Signal Conditioning Connector Block (SC 2345) and Analog Input and Output voltage modules (SCCAI03/04 and SCCAO10). The Ultrasonic signal is first sent to its own processing electronics box (Cosense 092-20001), Figure 3.3, which converts the electronic pulses into a voltage, before it is sent to the SC 2345. The electronics box can be accessed by the user to define or modify the parameters that control the operation of the ultrasonic sensor. The repetition rate, which defines the frequency at which the readings are taken, is set to 5 milliseconds or 200 Hertz. For more information about the controlling parameters, see the Cosense user’s manual.

Additionally, the voltage drop across the 10kΩ resistor is measured using a special Analog Input module (SCCAI07) for millivolt voltages. The connector block is then connected to a data acquisition box (NI-USB 6259), which then sends the information to the computer (Dell Optiplex 745). The data is then sent to a custom program written in LabVIEW 7.1, which processes the data and then sends a control signal to the syringe pump.
Figure 3.6: Electrospinning Experimental Control System Setup
3.2. Controller

The New Era Syringe Pump movement is controlled using LabVIEW 7.1 and a standard virtual instrument program that was written for the pump. The program was downloaded from the National Instruments website under the NI Developer Zone/Instrument driver network. The program had to be modified so the pump direction could be controlled by the readings from level sensors and air pressure sensor. The pump movement is controlled through an on/off closed-loop control scheme. Figure 3.7 shows the block diagram of the closed loop control system.

\[ h = \frac{4 \cdot Volume}{\pi \cdot d^2} \]  

Figure 3.7: Electrospinning Control System Diagram

The LabVIEW program and control system work as follows. The distance between the polymer solution and either the infrared or ultrasonic sensor is measured, which produces an output voltage, which is then relayed to the program. This voltage is then read by the program and converted to a calibrated volume of polymer solution, and is then converted, using the container diameter to a corresponding solution height, h.
The height value is then used, along with the solution density, to calculate the hydrostatic solution pressure, $P_s$.

$$ P_s = \rho \cdot g \cdot h $$  \hspace{1cm} (15)

At the same time the solution pressure is being measured and calculated, the air pressure above the polymer solution, $P_a$ is measured and these two values are added together to calculate the pressure at the tip of the capillary needle. The system setpoint (SP) is the desired pressure at the tip of the capillary needle. The error signal, which determines the syringe pump movement, is calculated by comparing the system set point and the measured polymer solution pressure and air pressure as follows:

$$ Error = SP - (P_s + P_a) $$  \hspace{1cm} (16)

If the error signal is positive, the pump will infuse, if the error signal is negative, the pump will withdraw. There is no pause or hold state programmed into the pump movement. The sampling rate of each sensor is 1000 Hz. Due to the large amount of data that would collect if every sensor sample were saved, the statistical variation of each sensor’s signal is calculated using a root mean square (RMS) algorithm that is standard in LabVIEW. The sample time for the RMS calculation is one second, so 1000 samples are collected for each calculation.

By controlling the pressure at the tip of the capillary, it is believed that a more consistent fiber diameter will be produced over the duration of the electrospinning experiment, since the pressure at the capillary tip and the voltage are both directly controlled through the LabVIEW program. Whereas, the typical setup for an electrospinning system, as discussed in Chapter 2.5, is to use a syringe pump and set a constant flow rate. This method does not provide any method for generating a feedback
signal, which could be used to develop a closed loop control system. The use of the infrared or ultrasonic sensor to measure the height of solution in the container allows for the creation of a closed loop control system that controls the pressure at the capillary tip.

3.3. Calibration

The pressure sensor was calibrated using a Magnehelic 0-5” of H₂O gauge pressure gauge. The syringe pump was adjusted so that the pressure gauge would change in increments of 0.5” of H₂O, from 0-5” of H₂O. The corresponding sensor output voltages for the varying pressure values were set in LabVIEW. Since the response of the sensor is linear and a greater calibration range than the 0-5” of H₂O provided by the Magnehelic gauge is needed, the equation of the pressure versus voltage was calculated from the obtained values in Table 3.1.

Table 3.1: Air Pressure Sensor Calibration

<table>
<thead>
<tr>
<th>Air Pressure (gauge) inches of H₂O</th>
<th>Sensor Output Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>0.0000</td>
<td>2.2450</td>
</tr>
<tr>
<td>0.5000</td>
<td>2.3435</td>
</tr>
<tr>
<td>1.0000</td>
<td>2.4416</td>
</tr>
<tr>
<td>1.5000</td>
<td>2.5396</td>
</tr>
<tr>
<td>2.0000</td>
<td>2.6367</td>
</tr>
<tr>
<td>2.5000</td>
<td>2.7355</td>
</tr>
<tr>
<td>3.0000</td>
<td>2.8333</td>
</tr>
<tr>
<td>3.5000</td>
<td>2.9323</td>
</tr>
<tr>
<td>4.0000</td>
<td>3.0272</td>
</tr>
<tr>
<td>4.5000</td>
<td>3.1256</td>
</tr>
<tr>
<td>5.0000</td>
<td>3.2250</td>
</tr>
</tbody>
</table>

Air Pressure vs. Voltage Trendline: \( y = 0.196 \cdot x + 2.246 \quad (17) \)
Using (17), the rest of the pressure readings were calibrated by moving the syringe pump to predicted sensor output voltage. The final air pressure calibration is from -11 to 12” of H$_2$O as shown in Figure 3.8.

![Pressure Sensor Calibration Curve](image)

Figure 3.8: Air Pressure Sensor Calibration

The calibration of the Infrared Sensor involves one of the main drawbacks to using this device for this application. The sensor was originally calibrated relying on the air/solution interface to reflect the emitted infrared wavelength, but this lead to a weaker signal that was unresponsive at fluid volumes below 20 ml. After several failed attempts to recalibrate the sensor, it was determined that the use of a foam float on top of the fluid was necessary to achieve a strong and repeatable signal. Polyimide foam disks were cut
to a 1” diameter and used as floats. The polyimide foam was chosen because of its good resistance to solvents.

The calibration was done as follows. The bottle was filled with 35 ml of a 3% PEO and water solution, a low viscosity solution was used to make the calibration time shorter than if a high viscosity solution was used. The solution was drained from the bottle in increments of 1 ml; the corresponding infrared sensor output voltage was recorded in the LabVIEW program.

Figure 3.9: Infrared Sensor Calibration Curve

Figure 3.9 shows the response of the sensor is nonlinear due to the way the emitter and detector function. Since the detector judges change in distance from the sensor by
the changing angle of the return beam, the change in distance is a non-linear trigonometric function.

![Figure 3.10: Infrared Detector and Emitter](image)

The calibration for the Ultrasonic Sensor was done in much the same was as the infrared sensor. The Teflon bottle was filled with 77mL of a 5% PEO and water solution, and drained from the container in increments of 1 mL. At each increment of volume, the corresponding sensor voltage output was recorded. The voltage output of the ultrasonic sensor has a linear response as shown in the Figure 3.11. Due to the nature of the ultrasonic sensor, there is a minimum distance that it can detect, and in this configuration, the sensor cannot detect volume changes below 34 mL of volume. This will be discussed in more detail in the next section.
3.4. Sensor Comparison

It has been discussed briefly in the previous sections that both sensors have their advantages and disadvantages. Central to the practicality of implementing either one of these sensors into a functional control system is their ability to accurately and repeatedly measure the distance between the sensor and the air/solution interface. In the calibration section both sensors were shown to be able to measure this distance, but the infrared requires the use of an invasive float to achieve a strong signal. The ultrasonic sensor is the better technology in this respect since it can non-invasively measure the height of the polymer solution. Along with measuring distances, each sensor is limited by a useable detection range. The infrared sensor can measure distances ranging from 4 to 30 cm (1.8 to 11.8”) and the ultrasonic sensor has an operational range of 1.25 to 15.3 cm (0.5 to 6”).
The minimum sensing distance of both sensors has an effect on how they are applied. For the infrared sensor, since it is measuring from the top of the container down, the polymer solution has to be at least 4 cm away from the sensor, limiting the maximum amount of fluid to 35 ml. If the bottle needs to hold more fluid it could just be made longer, up to 30 centimeters. Since the ultrasonic sensor is mounted on the bottom of the bottle, the minimum sensing distance limits how low the solution level can get before it can no longer detect any changes in fluid. As shown in the calibration section, the minimum volume the ultrasonic sensor can detect is 34 ml of solution.

The Infrared sensor can detect a range of solution pressure head from 5.41” to 3.00” of H2O, with a total change in liquid pressure of 2.41” of H2O. The Ultrasonic sensor can detect a range of 4.37” to 3.60” of H2O, with a total change of liquid pressure of 0.77” of H2O. Since the bottle diameter of the ultrasonic sensor is larger (2-3/32”) than the diameter of the infrared sensor bottle diameter (1-1/16”), the change in solution pressure head per milliliter of solution is less for the ultrasonic system than it is for the infrared system.

Another important aspect of implementing these sensors is their cost, since it is desirable to use one of these technologies to create a mass production electrospinning control system. The infrared sensor has the advantage of being cheap, costing $12 each, and having the required electronics built into the sensor. On the other hand the ultrasonic sensor costs $200 and requires the use of an external electronics box that costs an additional $1600. The cost of the ultrasonic system may be too expensive and make it cost prohibitive for mass production situations.
Some other issues that should be considered when comparing the infrared and ultrasonic sensors are discussed here. In addition to the float being undesirable because it is in contact with the polymer solution, the float also has some other limitations. Since the float is made of foam, it soaks up the solution like a sponge and can affect the concentration of the polymer solution. Additionally, the float does not work well with high viscosity solutions because the solution gets between the disk edge and the bottle wall and tends to hold it in a stationary position. Another problem with the infrared sensor was the output signal has a 12 Hz periodic cycle caused from the emitting and detecting of the infrared light. A low pass filter with a 5Hz cutoff was used to filter the signal and obtain a consistent output value. Figure 3.12 shows the difference between filtered and unfiltered infrared output signal.

![Infrared Sensor Output Signal: Unfiltered and Low Pass Filter](image)

Figure 3.12: Filtered and Unfiltered Infrared Sensor Output Signal
The ultrasonic sensor reading is very sensitive to disturbances that cause movement of the solution inside the container, since the sensor must be parallel to the measured interface for the return signal to be received. In some electrospinning applications it may be desirable to have the bottle and sensor mounted on a linear actuator to allow for the fibers to be distributed evenly over a wide area. In the case of this setup, the ultrasonic sensor and container will most likely not work for this application due to the movement of the solution as the actuator moves. Though the higher viscosity of solution used, the less severe this problem would be.

Both systems had problems with the bottles and air lines having slow leaks causing the pump to constantly withdraw to compensate for the loss of pressure and run out of travel during a long experiment. Sealing all of the hose connections with a silicon sealant and using O-rings at the bottle and cap interfaces solved this problem.

3.5. Simulation Setup and Coding

The simulation of the electrospun jet will follow very closely to the work presented in [4]. To solve the equation of motion of the jet following the procedure presented in [4], equation (9) in Chapter 2.4 is simulated. A MATLAB script, ode45 will be used to integrate these equations. The first step is to rewrite (9) separately in terms of the x, y, and z directions by substituting \( r_i = ix_i + jy_j + kz_k \) into (9).

\[
\frac{m}{dt^2} = \sum_{j=1}^{N} \frac{e^2}{R_j} (x_i - x_j) + \frac{\pi a^2 \sigma_{ui}}{l_{ui}} (x_{i+1} - x_i) \\
- \frac{\pi a^2 \sigma_{di}}{l_{di}} (x_i - x_{i-1}) - \frac{\alpha \pi (a^2)_{wi} k_i}{(x_i^2 + y_i^2)^{1/2}} \times |x_i| \text{sign}(x_i)
\]
\[ m \frac{d^2 y_i}{dt^2} = \sum_{j=1, N(i)} \frac{e^2}{R_{ij}} (y_i - y_j) + \frac{\pi a_{ui}^2 \sigma_{ui}}{l_{ui}} (y_{i+1} - y_i) \]  
(19)

\[- \frac{\pi a_{di}^2 \sigma_{di}}{l_{di}} (y_i - y_{i-1}) - \alpha \pi (a^2)^{3/2} k_i \times \text{sign}(y_i) \]

\[ m \frac{d^2 z_i}{dt^2} = \sum_{j=1, N(i)} \frac{e^2}{R_{ij}^3} (z_i - z_j) - e \frac{V_o}{h} \]

\[ + \frac{\pi a_{ui}^2 \sigma_{ui}}{l_{ui}} (z_{i+1} - z_i) - \frac{\pi a_{di}^2 \sigma_{di}}{l_{di}} (z_i - z_{i-1}) \]  
(20)

Since these equations of motion are second order partial differential equations, the stress term is a function of strain rate as (24a) and (24b) shows; they are converted into a system of first order ordinary differential equations in order to use existing MATLAB routines such as ode45. Conversion is done as follows:

\[ z_{i,1} = x_i \quad \text{x position of bead i} \]  
(21a)

\[ \dot{z}_{i,1} = \dot{x}_i = z_{i,2} \quad \text{x velocity of bead i} \]  
(21b)

\[ \ddot{z}_{i,1} = \ddot{x}_i \quad \text{x acceleration of bead i} \]  
(21c)

\[ z_{i,3} = y_i \quad \text{y position of bead i} \]  
(22a)

\[ \dot{z}_{i,3} = \dot{y}_i = z_{i,4} \quad \text{y velocity of bead i} \]  
(22b)

\[ \ddot{z}_{i,3} = \ddot{y}_i \quad \text{y acceleration of bead i} \]  
(22c)

\[ z_{i,6} = z_i \quad \text{z position of bead i} \]  
(23a)

\[ \dot{z}_{i,6} = \dot{z}_i = z_{i,7} \quad \text{z velocity of bead i} \]  
(23b)

\[ \ddot{z}_{i,6} = \ddot{z}_i \quad \text{z acceleration of bead i} \]  
(23c)
\( z', z'', z''' \) are dummy variables and are only used to relate \( x \) to \( \dot{x} \) and \( \ddot{x} \), and similarly for \( y \) and \( z \). Any name or letters could be used to designate each individual \( x, y, z \) case. The format of the conversion is as follows: one prime, \( z' \) represents the \( x \) variable, two primes, \( z'' \) represents the \( y \) variables, and three primes, \( z''' \) represents the \( z \) variables. Furthermore, subscript one is used to indicate the bead position and subscript two is used to indicate the bead velocity.

Additionally, the stress on bead \( i \) due to the beads directly above and below must be calculated using the viscoelastic forces, defined by (5a) and (5b). These equations will also be solved using ode45. The rates of strain, \( \frac{dl_{ui}}{dt} \) and \( \frac{dl_{di}}{dt} \), are defined by (24a) and (24b), where the partial derivatives of (6a) and (6b) are taken as shown below to define the right hand side of the equations.

\[
\frac{dl_{ui}}{dt} = \frac{\partial l_{ui}}{\partial x_{i+1}} \cdot \frac{dx_{i+1}}{dt} + \frac{\partial l_{ui}}{\partial x_i} \cdot \frac{dx_i}{dt} + \frac{\partial l_{ui}}{\partial y_{i+1}} \cdot \frac{dy_{i+1}}{dt} + \frac{\partial l_{ui}}{\partial y_i} \cdot \frac{dy_i}{dt} + \frac{\partial l_{ui}}{\partial z_{i+1}} \cdot \frac{dz_{i+1}}{dt} + \frac{\partial l_{ui}}{\partial z_i} \cdot \frac{dz_i}{dt} \tag{24a}
\]

\[
\frac{dl_{di}}{dt} = \frac{\partial l_{di}}{\partial x_i} \cdot \frac{dx_i}{dt} + \frac{\partial l_{di}}{\partial x_{i-1}} \cdot \frac{dx_{i-1}}{dt} + \frac{\partial l_{di}}{\partial y_i} \cdot \frac{dy_i}{dt} + \frac{\partial l_{di}}{\partial y_{i-1}} \cdot \frac{dy_{i-1}}{dt} + \frac{\partial l_{di}}{\partial z_i} \cdot \frac{dz_i}{dt} + \frac{\partial l_{di}}{\partial z_{i-1}} \cdot \frac{dz_{i-1}}{dt} \tag{24b}
\]

These equations can be simplified by substituting (6a) and (6b) into (24a) and (24b) respectively.

\[
\frac{dl_{ui}}{dt} = \frac{1}{l_{ui}} \left( (x_{i+1} - x_i) \cdot \dot{x}_{i+1} + (-x_{i+1} + x_i) \cdot \dot{x}_i + (y_{i+1} - y_i) \cdot \dot{y}_{i+1} + (-y_{i+1} + y_i) \cdot \dot{y}_i + (z_{i+1} - z_i) \cdot \dot{z}_{i+1} + (-z_{i+1} + z_i) \cdot \dot{z}_i \right) \tag{25a}
\]
\[
\frac{dl_{di}}{dt} = \frac{1}{l_{di}} \left( \begin{array}{c}
(x_i - x_{i-1}) \cdot \dot{x}_i + (-x_i + x_{i-1}) \cdot \dot{x}_{i-1} \\
+ (y_i - y_{i-1}) \cdot \dot{y}_i + (-y_i + y_{i-1}) \cdot \dot{y}_{i-1} \\
+ (z_i - z_{i-1}) \cdot \dot{z}_i + (-z_i + z_{i-1}) \cdot \dot{z}_{i-1}
\end{array} \right)
\]  
(25b)

Now that the partial differential equations are converted into a system of ordinary differential equations and the viscoelastic stresses are defined, they can be solved using ode45 in MATLAB. The program that solves ode45 requires the use of a main program and a subroutine. In the main program, the integration time interval, number of beads N, wavelength of perturbation \( \lambda \), length scale L (defined in Chapter 2.4), and the distance from the tip to the collector, h, are defined. Subsequently, the initial position and velocity of each bead can be calculated in all three dimensions as well as the initial stress on each bead.

To calculate the initial jet position, the jet is considered to be a long rectilinear filament from \( 0<z<h \), that is perturbed by moving it laterally in the x and y direction. The positions of the beads are defined by (26) and (27). The perturbation is used to simulate the start of the bending instabilities of the jet. The number of beads (N) can be specified to increase the accuracy of the solution, reference [4] uses approximately 12500 beads per meter in the z direction; therefore a good estimate of the number of beads that should be used in the simulation is \( N=12500*h \). Additionally at \( t = 0 \), the initial bead velocity and stresses are zero. See Figure 3.13 for initial position of a single perturbed jet.

\[
x = 10^{-3} L \cos \left( \frac{2\pi}{\lambda} z \right) \frac{h-z}{h}
\]  
(26)

\[
y = 10^{-3} L \sin \left( \frac{2\pi}{\lambda} z \right) \frac{h-z}{h}
\]  
(27)
A row of eight data points is created representing these defined values; the string is then concatenated to produce a data column, which gets sent to the subroutine along with the integration time. The data column contains the information shown in Table 3.2.

<table>
<thead>
<tr>
<th>Variable</th>
<th>MATLAB name</th>
<th>Physical Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>zt1</td>
<td>x position</td>
</tr>
<tr>
<td>\dot{x}</td>
<td>zt2</td>
<td>x velocity</td>
</tr>
<tr>
<td>y</td>
<td>zdt1</td>
<td>y position</td>
</tr>
<tr>
<td>\dot{y}</td>
<td>zdt2</td>
<td>y velocity</td>
</tr>
<tr>
<td>z</td>
<td>ztt1</td>
<td>z position</td>
</tr>
<tr>
<td>\dot{z}</td>
<td>ztt2</td>
<td>z velocity</td>
</tr>
<tr>
<td>\sigma_u</td>
<td>su</td>
<td>stress caused from bead above</td>
</tr>
<tr>
<td>\sigma_d</td>
<td>sd</td>
<td>stress caused from bead below</td>
</tr>
</tbody>
</table>
The initial data column is named zt0 in the main program, and once it is sent in the subroutine, project1, the column is renamed zt for each successive integration. Since all the position and stress data contained in this column is in the form:

\[ zt(x, \dot{x}, y, \dot{y}, z, \dot{z}, \sigma_u, \sigma_d) \Rightarrow zt(i, i+1, i+2, i+3, i+4, i+5, i+6, i+7) \]  

(28)

To access this information for use in the subroutine, the variables need to be indexed with respect to bead \( i \), where \( i \) represents the x position, \( i+1 \) is the x velocity, \( i+2 \) is the y position and so forth, as in (28). Moreover, if the position, velocity, or stress of the beads up (\( u \)) or down (\( d \)) to bead \( i \) need to be used, they can be referenced similarly. For example: x position of the up bead is \( zt(i-8) \); y velocity of the up bead is \( zt(i-5) \); x position of the down bead is \( zt(i+8) \); y velocity of the down bead is \( zt(i+11) \) and so forth.

The data column (zt) is used to define the right hand sides of the system of ordinary differential equations defined in (18-20) and (21-23), and the viscoelastic stresses defined in (5a) and (5b). Thus a set of 8 equations is defined and can be solved by integration; ode45 uses an explicit Runge-Kutta method. The general format for this set of equations is shown in Table 3.3.
Table 3.3: Format of Equations to be Integrated by ode45

<table>
<thead>
<tr>
<th>Variable</th>
<th>MATLAB name</th>
<th>Physical Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_u$</td>
<td>sudot</td>
<td>viscoelastic stress from bead above</td>
</tr>
<tr>
<td>$\sigma_d$</td>
<td>sddot</td>
<td>viscoelastic stress from bead below</td>
</tr>
<tr>
<td>$\dot{x}$</td>
<td>zt1dot</td>
<td>x velocity</td>
</tr>
<tr>
<td>$\ddot{x}$</td>
<td>zt2dot</td>
<td>x acceleration</td>
</tr>
<tr>
<td>$\dot{y}$</td>
<td>zdt1dot</td>
<td>y velocity</td>
</tr>
<tr>
<td>$\ddot{y}$</td>
<td>zdt2dot</td>
<td>y acceleration</td>
</tr>
<tr>
<td>$\dot{z}$</td>
<td>ztt1dot</td>
<td>z velocity</td>
</tr>
<tr>
<td>$\ddot{z}$</td>
<td>ztt2dot</td>
<td>z acceleration</td>
</tr>
</tbody>
</table>

To completely define the right hand side of the x, y, and z acceleration equations, some other properties and variables need to be defined, such as the bead mass $m$, charge $e$, length scale $L$, elastic modulus $G$, viscosity $\mu$, initial cross section radius $a_0$, and surface tension $\alpha$ are defined. These quantities are all given or defined in the program shown in Appendix B. The variables defined in the subroutine are the voltage $V_0$, distance from capillary tip to collector $h$, and the number of beads $N$. For the simulation run for this thesis, the specified voltage is 10 kV and the distance from tip to collector is 2 meters. The number of beads $N$ used in the simulation will be discussed in the chapter 4.5.

The net Coulomb force, equation 1, interaction and jet curvature need to be defined as well. Since the net Coulomb force on any given bead is dependent on all the other bead
locations a nested “for loop” must be used to calculate all of the charge interactions. This matrix becomes very large when a large amount of beads are used. To limit the size of the matrix, the data column (zt) is used to create a \( \{1 \times N\} \) position matrix for each bead at x, y, and z location. Now the net Coulomb force on each bead can be calculated using (1) and (2) from Chapter 2.4. Below is an excerpt of the code from the subroutine that shows the Coulomb force calculation.

```matlab
Rx=zt(1:8:end);  
Ry=zt(3:8:end);  
Rz=zt(5:8:end);  
for i=1:N+1;  
    for j=1:N+1;  
        if i~=j;  
            R(I,j)=sqrt((Rx(i)-Rx(j))^2+(Ry(i)-Ry(j))^2+(Rz(i)-Rz(j))^2);  
            Fcx(I,j)=((e^2/R(I,j)^3)*(Rx(i)-Rx(j)));  
            Fcy(I,j)=((e^2/R(I,j)^3)*(Ry(i)-Ry(j)));  
            Fcz(I,j)=((e^2/R(I,j)^3)*(Rz(i)-Rz(j)));  
        end  
    end  
end
```

As stated in Chapter 2.4, the jet curvature \( k_i \) is calculated by using the locations of the beads above (up) and below (down) the bead that is being analyzed, bead \( i \). When calculating the curvature only the x and y directions are taken into account. The curvature is approximated by (29). The change in angle \( \Delta \alpha \) is calculated using (30) and the distance between beads (\( \Delta s_1 \) and \( \Delta s_2 \)) are calculated with the Pythagorean theorem.

\[
K = \left| \frac{d\alpha}{ds} \right| \approx \frac{\Delta \alpha}{\Delta s_1 + \Delta s_2} \quad (29)
\]

\[
\Delta \alpha = \tan^{-1} \left( \frac{m_2 - m_1}{1 + m_1 m_2} \right) \quad (30)
\]
Figure 3.14 depicts the change in angle ($\Delta \alpha$) and the distance ($\Delta s_1$ and $\Delta s_2$) between beads. The slope of line 1 ($i-1$ to $i$) and line 2 ($i$ to $i+1$), are defined as $m_1$ and $m_2$ in (30). A sample calculation for determining $\Delta s_2$ and $m_2$ are shown in (31) and (32).

\[
\Delta s_2 = \sqrt{(x_{i+1} - x_i)^2 + (y_{i+1} - y_i)^2} \tag{31}
\]

\[
m_2 = \frac{y_{i+1} - y_i}{x_{i+1} - x_i} \tag{32}
\]

Once the right hand side of all 8 equations in Table 4.3 has been defined, the program can now integrate them according to the Runge-Kutta method. The program runs through the integration once and the calculated values become the inputs into the right hand side of the equation. This is done repeatedly until the equations are converged to within a range determined by ode45. The output of the program is the $x$, $y$, and $z$ position and velocity and the stress, up and down, for each bead.
CHAPTER IV
RESULTS AND DISCUSSION

4.1. Infrared and Ultrasonic Sensor Comparison

Central to this thesis is the comparison of the two sensing technologies and their ability to be used in a real time control system. As discussed in chapter 3.4, both sensors have their own inherit advantages and disadvantages. The infrared sensor is low cost but cannot accurately measure the fluid height without the use of a float to reflect the signal. The ultrasonic sensor can measure liquid height non-invasively but the sensor and electronics are expensive. To determine the functionality of each sensor in application two variables will be manipulated, voltage and pressure set point, and their effect on the mass flow rate and current carried by the jet will be analyzed. Moreover, the electrospun fiber mats collected using both control systems at the same test conditions can be compared.

Using a 7% PEO/water solution at a set point of 4” of H$_2$O and an applied voltage of 8kV, both the ultrasonic and infrared systems were tested. The fluid volume data was normalized so a comparison between the flow rates of each system could be made; the results are shown in Figure 4.1. The ultrasonic sensor shows a gradual decrease in volume of 0.35 ml over a 2-hour period, which corresponds to a flow rate of 0.0029 ml/min, and a change in solution pressure head of 0.0062 inH$_2$O.
The ability of the infrared sensor and float system to detect volume change is clearly flawed as Figure 4.1 shows. The sensor is registering an increase of 2 ml of volume over the 2-hour period, which is physically impossible since a visible electrospun mat is being created, and the solution volume is actually decreasing. The increase in the volume reading corresponds to what the program calculates as a solution pressure increase of 0.14” of H$_2$O, and the control system responds by adjusting the vacuum pressure by the same amount. Since the infrared volume reading is not representative of the actual amount of solution volume in the container, it is impossible for the program to accurately control the setpoint pressure at the capillary tip.

Another interesting observation is that the float position changes as the set point of the control system is adjusted. Figure 4.2 shows that the infrared reading (float position) decreases when the set point is increased to 8” of H$_2$O from 7500 to 8000 seconds and then again decreases dramatically from 8300 to 8700 seconds when the set point is again increased to 8” of H$_2$O. The corresponding height change from 8300 to 8700 seconds is 0.40”, which is 15% of the total detectable height change (6.12”) for the infrared system. Since the float position varies with the set point, it is not possible to calculate any reasonable flow rate value.

It is possible that when the set point is increased, the float is being pushed into the polymer solution, causing the large changes in volume observed in Figure 4.2. Since the calibration in Chapter 3.3 with the float and 3% PEO/water solution did not have the same issues observed in this test, it appears that higher viscosity solutions have an effect on how well the float works. It has been observed that when the higher viscosity solution gets between the float and the Teflon bottle wall, a gap of 1/32”, the solution will hold...
the float in place, preventing the float from moving down with the solution as volume decreases. After observing these issues with the float and the higher viscosity solution, calibration without the float, as done in Chapter 3.3 Figure 3.9, appears to be a more reliable method for determining the correct volume of solution with any reasonable accuracy.

The design of the float could also be improved to potentially solve the problems discussed here. Instead of using a foam disk, an inert plastic disk could be designed that has enough buoyancy to float on top of the liquid. The top surface of this disk could be coated with a material that reflects infrared light, such as aluminum.

![Normalized Flow Rate Comparison](image)

**Figure 4.1: Ultrasonic and Infrared Sensor Solution Measurements**
Figure 4.2: Infrared Sensor Volume and Set Point Comparison

Another issue critical to the electrospinning process that was observed during the comparison of the two sensors was the phenomenon of dripping polymer solution from the capillary tip. This situation happens when more polymer solution is supplied to the tip then is being electrospun away in the fiber jet. Dripping will be discussed in more detail in part III of this chapter.

When a stable, non-dripping jet is being produced the current carried by the jet will maintain at a constant value, as show in Figure 4.3. When a dripping situation occurs, the current carried by the jet slowly decreases as a bead of solution at the capillary tip develops and increases in volume, Figure 4.4. As the bead grows in size, the surface tension forces become more dominant than the electrostatic repulsion forces, reducing the
jet mass flow rate. Once enough fluid is at the tip and the bead drops, the current returns back to its normal operational level. Four distinct drips with the infrared system can be observed in Figure 4.3. Since the ultrasonic system did not cause any drips during the experiment and the infrared did, it shows the importance of being able to accurately measure the polymer solution in the container.

The dripping of the polymer solution with the infrared system occurred between 2000 and 4500 seconds, as shown in Figure 4.3. After the last drip, the current starts to stabilize and ends up at approximately the same value as the ultrasonic sensor example. Figure 4.3, is not showing the differences in measured current with respect to the ultrasonic or infrared sensor, rather it is showing the difference in measured current between a dripping and non-dripping electrospinning situation. If the infrared control system were working correctly, the current measurement graph would be the same as the ultrasonic measurements.

The reason for the occurrence of drips can be explained by the increase in the infrared sensor volume reading as discussed above. When the sensor is measuring 22.5 ml or 4.55” of H2O of solution pressure, the pump is adjusting the vacuum pressure to be 0.55” of H2O, but the dripping stops once the solution volume reading increases to 24.5 ml or 4.69” of H2O, and the pump has to adjust for this and increase the vacuum pressure to 0.69” of H2O. The average current for both signals is the same, 2.94e-7 amps.
Figure 4.3: Stable Jet vs. Dripping Jet Current Comparison

Figure 4.4: Polymer Solution Bead at Capillary Tip
To compare each sensor’s ability to produce fibers, a comparison of the electrospun mats created at a set point of 8” of H$_2$O and voltage of 12 kV was done. Interestingly, even with the infrared sensor issues, both mats appear to be very similar in fiber density (number of fibers in a given area) and morphology (diameter and uniformity). Two distinct fibers can be seen in Figures 4.6 and 4.7, thinner fibers with more fluctuations in fiber diameter around 0.5 to 0.6 µm, and larger more uniform fibers with diameters approximately from 0.750 to 0.850 µm. The possible reason for this will be discussed in the next section.

Another interesting observation about the fiber morphology in Figures 4.5 and 4.6 is the periodic fluctuations in fiber diameters. There is a possibility that these fluctuations are caused by the competition between the two instabilities, varicose and whipping, identified in [16], where the varicose instabilities are causing the fluctuations in the diameter of the fiber. The distance between fluctuations have an approximate spacing of 2.0 µm, as seen in Figure 4.7. If an equation with the form $e^{ikx} = \cos kx + is\sin kx$ is used to approximate the periodic variations, then the period of fluctuations can be defined as $kx = 2\pi$. A wave number, k, of 0.03 µm$^{-1}$ is calculated using 2.0 µm for the period, x. The dimensionless external field can be calculated according to [16] and (33).

$$\Omega_0 = \frac{E_0}{E_\infty} = \frac{E_\infty}{\sqrt{\gamma / (\varepsilon - \varepsilon) \rho_0}}$$ (33)

The applied electric field, $E_\infty$, is calculated from the applied voltage (12 kV) divided by the distance from the tip of the capillary to the collector plate (0.15 m). The surface tension of the solution is approximated as water, 0.0728 N/m. The dielectric constant of the fluid, $\varepsilon$, is also approximated as water, 80.4 F/m. The dielectric constant of the
outside medium, $\varepsilon$, air is 1.00059 F/m. The capillary tip diameter, 0.32 mm, is used to define the length scale, $r_0$. The dimensionless external field is calculated as; $\Omega_0 = 0.14$.

Using Figure 4.5 from, [16], and the approximated wave number and dimensionless external field, the jets instability can be estimated. The solid and dotted lines represent the external fields in the form, $\Omega^2_0 = 0, 0.97, 1.93, 2.90, 3.8$, from uppermost to lowermost, respectively. The experimentally calculated external field of $\Omega^2_0 = 0.02$ is very close to zero which is represented as the uppermost solid line in Figure 4.5.

Figure 4.5: Jet Varicose Instabilities

It appears from this analysis, since the calculated dimensionless external field is small; that the experiments are operating in a range where the varicose instabilities are likely to occur. Though, the calculated wave number for the fiber diameter fluctuations is relatively small, $k = 0.03 \, \mu m^{-1}$, where the varicose instabilities are suppressed. Reference [18] states that the formation of the fiber diameter is heavily dependent on the force balance between surface tension and surface charge repulsion. The surface tension forces definitely are effecting the final fiber formation, due to the presence of the semi-spherical
beads in the thinner diameter fibers. It can safely be assumed that the fluctuations in the fiber diameters are caused by the varicose instability mode, but this mode is not the dominant instability. The whipping instability is most likely the dominant mode, having a greater affect on the final fiber morphology.

Another potential cause of the fiber diameter fluctuations could be due to variations of the polymer concentration or molecular weight in the solution. Since none of the theoretical equations have any concentration or molecular weight dependency, an estimation of there effects cannot be calculated.

Figure 4.6: Infrared Sensor Fiber Mat; Set Point = 8” of H$_2$O and Voltage = 12 kV
4.2. Ultrasonic Testing and Observed Trends

Due to the issues with the infrared sensor discussed in the previous section, it is clear that the use of the infrared sensor is not advisable for obtaining a more detailed understanding of the electrospinning control system. For the rest of testing the ultrasonic system will be used to collect experimental data.
As discussed in Chapter 2.3, the process parameters that can be adjusted to control the electrospun fiber diameters are the applied voltage, distance from tip to collector, and the solution flow rate. In this experimental setup, the solution flow rate is not controlled by a syringe pump as is typically done, but through maintaining a constant pressure set point at the tip of the capillary. In these tests the effects of changing the applied voltage and the pressure at the capillary tip, or pressure set point, are demonstrated, with the distance from the tip to the collector set to 15 centimeters.

The effects of changing the applied voltage to the polymer solution are shown below in Table 4.1 and Figures 4.9 and 4.10. The flow rate is calculated by dividing the total change in solution volume over the length of time of the experiment. The current carried by the jet is calculated according to Ohm’s law, \( I = V/R \). As stated in Chapter 3.1, the voltage drop (V) across the 10k\( \Omega \) resistor connected between the collector plate and ground is measured through the National Instruments and LabVIEW interface. Each test was run for a duration of 2 hours.

The flow rate increases between 40-50% when the applied voltage is increased by 50% from 8 to 12kV. Figures 4.11 and 4.12 shows the difference in mat density for samples collected for 15 seconds at 8 and 12 kV. The applied voltage also has a large effect on the current carried by the electrospun jet. By increasing the applied voltage by 50% the current carried by the jet increases by over 3 times. However, the current carried by the jet is not nearly as sensitive to set point changes as it is to voltage changes. Changing the set point in increments of 2” of H\(_2\)O only increases the current carried by the jet by 5%, as seen in Figure 4.8.
This small increase in current with respect to the set point changes is unexpected, since a large increase in flow rate is observed for the same set point changes, as seen in Figure 4.9. The current carried by the jet is expected to increase as the set point is increased because the current carried by the jet has two components, conduction and surface charge advection [18].

\[
I = 2\sigma_0 \frac{Q}{h} + \pi E, Kh^2
\]

If the second term is ignored, then the only way that the current \(I\) is not increasing as the flow rate \(Q\) is increased, is that \(\sigma_0/h\) is decreasing, but there is experimental evidence that the fiber diameters only increase slightly when the set point is increased, Table 4.3. Therefore, it is left to conclude that either \(\sigma_0\) is decreasing when the set point is increased, which there is no way of verifying, or that the current measurements are unreliable. It appears that due to the small currents being measured and the large changes in current over time, Figure 4.26, that the current measurement is not accurate.

<table>
<thead>
<tr>
<th>Set Point</th>
<th>Flow Rate (ml/min)</th>
<th>Flow Rate (m³/sec)</th>
<th>Jet Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 kV</td>
<td>12 kV</td>
<td>8 kV</td>
</tr>
<tr>
<td>2</td>
<td>0.00219</td>
<td>0.00310</td>
<td>3.65E-11</td>
</tr>
<tr>
<td>3</td>
<td>0.00275</td>
<td>0.00379</td>
<td>4.58E-11</td>
</tr>
<tr>
<td>4</td>
<td>0.00295</td>
<td>0.00505</td>
<td>4.91E-11</td>
</tr>
<tr>
<td>6</td>
<td>0.00434</td>
<td>0.00617</td>
<td>7.24E-11</td>
</tr>
<tr>
<td>8</td>
<td>0.00536</td>
<td>0.00697</td>
<td>8.93E-11</td>
</tr>
</tbody>
</table>
Figure 4.9: Solution Flow Rates at Applied Voltage

Figure 4.10: Jet Current at Applied Voltage
Figure 4.11: 15 second Fiber Mat; Set Point = 2” of H₂O and Voltage = 8 kV

Figure 4.12: 15 Second Fiber Mat; Set Point = 2” of H₂O and Voltage = 12 kV
Due to the changes in flow rate and current based on changing the process parameters, and referencing (12) from [18], it can be assumed that some changes in the fiber morphology should be observed. For a given applied voltage, Figures 4.9 and 4.10 shows that the flow rate, Q, increases and the current, I, remains almost constant. From this, it is expected that experimental fiber diameters should increase significantly as the set point is increased. To calculate the predicted fiber diameters, the experimental flow rates, Q, and jet current, I, from Table 4.1 are used. The surface tension of the polymer solution is mostly dependent on the solution used; in this case the solution is water, which has a surface tension of 72.8 dyne/cm. Reference [14] shows that the solution surface tension changes very little when the PEO concentration is varied, so for the calculations below, an average value of 77 dyne/cm is used. The dielectric constant of the outside medium, air is 1.00059 F/m. Table 4.2 below shows the predicted fiber diameters for 8 and 12 kV at varying L/r (jet length to jet diameter) ratios of 10, 100, and 1000. Since the ln(L/r) ratio is logarithmic, it varies slowly so the exact value of L/r used is not critical. Since the L/r ratio of 10 predicts the largest fiber diameters, this will be used for the comparison to the experimental results.

Table 4.2 Predicted Fiber Diameters (µm)

<table>
<thead>
<tr>
<th>Set Point</th>
<th>8 kV</th>
<th>12 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L/r=10</td>
<td>L/r=100</td>
</tr>
<tr>
<td>2</td>
<td>0.172</td>
<td>0.109</td>
</tr>
<tr>
<td>3</td>
<td>0.222</td>
<td>0.141</td>
</tr>
<tr>
<td>4</td>
<td>0.196</td>
<td>0.125</td>
</tr>
<tr>
<td>6</td>
<td>0.262</td>
<td>0.167</td>
</tr>
<tr>
<td>8</td>
<td>0.283</td>
<td>0.180</td>
</tr>
<tr>
<td>Max Change</td>
<td>0.112</td>
<td>0.071</td>
</tr>
</tbody>
</table>
Table 4.3 shows the variation in the experimental fiber diameters resulting from varying the set point from 2 to 8” of H₂O and voltage from 8 to 12 kV. Interestingly, the changes in fiber diameters does not show a definite decrease when the voltage is changed from 8 to 12 kV, as the prediction shows. There is a slight increase in diameter as the pressure at the capillary tip is increased from 2 to 8, with the exception of the 12 kV minimum values.

Table 4.3 Experimental Fiber Diameters (µm)

<table>
<thead>
<tr>
<th>Set Point</th>
<th>8kV</th>
<th>12kV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>2</td>
<td>0.417</td>
<td>0.686</td>
</tr>
<tr>
<td>8</td>
<td>0.467</td>
<td>0.733</td>
</tr>
<tr>
<td>Max Change</td>
<td>0.051</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Theoretical and Experimental Fiber Diameter Comparison: Voltage 8 kV

Figure 4.13: Theoretical and Experimental Fiber Dia. Comparison: Voltage = 8 kV
Theoretical and Experimental Fiber Diameter Comparison: Voltage 12 kV

For each condition that was tested, a sample of the collected mat was analyzed. For each mat 15 fibers were picked at random from different locations on the mat and measured. Each fiber was measured in 3 locations and the average of those numbers was used to calculate the diameter for that fiber. The figures below show the distribution of the fiber diameters in increments of 0.1 µm for each condition. The charts show that when the set point is increased the distribution of the diameters increases. Also, larger fiber diameters occur when the set point is at 8” of H₂O, regardless of the applied voltage.

Figure 4.14: Theoretical and Experimental Fiber Dia. Comparison: Voltage = 12 kV
Figure 4.15: Fiber Diameter Distribution at Constant Set Point = 2” of H₂O

Figure 4.16: Fiber Diameter Distribution at Constant Set Point = 8” of H₂O
Figure 4.17: Fiber Diameter Distribution at Constant Voltage = 8 kV

Figure 4.18: Fiber Diameter Distribution at Constant Voltage = 12 kV
Figure 4.19: Fiber Mat; Set Point = 2” of H₂O and Voltage = 8 kV

Figure 4.20: Fiber Mat; Set Point = 2” of H₂O and Voltage = 12 kV
Figure 4.21: Fiber Mat; Set Point = 8” of H₂O and Voltage = 8 kV

Figure 4.22: Fiber Mat; Set Point = 8” of H₂O and Voltage = 12 kV
4.3. Dripping and Set Point Choice for Long Run Test

Another goal of this thesis was to be able to prevent dripping of the polymer solution by controlling the hydrostatic pressure, or the set point, at the tip of the capillary needle. Figure 4.23 shows that the flow rate of the polymer solution from the capillary tip with no applied voltage and the flow rate of the jet under 8 and 12 kV’s. This data is the same data from Table 4.1, with the addition of the free flow rate, which is the solution flow rate at zero applied voltage. This data was collected from 2 hour-long tests. From Figure 4.23, it can be seen that the flow rate at 8 kV is only slightly greater than the flow rate at zero applied voltage, from this it can be determined that a stable jet with no dripping issues as discussed earlier in this chapter in section I and Figures 4.3 and 4.4, as long as the applied voltage is at or above 8 kV’s. This information is used in the next section to determine the correct set point and voltage to perform a 24 hour-long electrospinning test.

![Polymer Solution Flow Rates](image)

**Figure 4.23: Polymer Solution Flow Rates**
To demonstrate that an electrospun mat with no dripping defects can be made by controlling the set point and having a jet flow rate greater than the free flow rate, a 24 hour long test was run at a set point of 3” of H₂O and a voltage of 8kV. The results and data from this no drip test are summarized in Tables 4.4, 4.5 and Figures 4.24 – 4.27.

Table 4.4 Flow Rate Data Over: 24-Hour Period
Set Point = 3”of H₂O and Voltage = 8 kV

<table>
<thead>
<tr>
<th>Total Volume Change (ml)</th>
<th>4.366</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (ml/min)</td>
<td>0.00303</td>
</tr>
<tr>
<td>Flow Rate (m³/s)</td>
<td>5.054E-11</td>
</tr>
</tbody>
</table>

Table 4.5 Set Point, Current, and Voltage Variations: 24-Hour Period

<table>
<thead>
<tr>
<th>Measured Pressure at Capillary Tip (inH₂O)</th>
<th>Current (A)</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>3.069</td>
<td>2.682E-07</td>
</tr>
<tr>
<td>Min</td>
<td>2.942</td>
<td>1.533E-07</td>
</tr>
<tr>
<td>Difference</td>
<td>0.128</td>
<td>1.149E-07</td>
</tr>
<tr>
<td>Average</td>
<td>3.000</td>
<td>2.19E-07</td>
</tr>
</tbody>
</table>

Table 4.5 and Figure 4.24 show that the control system is able to maintain a constant set point over the length of the experiment within 2% accuracy, or a maximum variance of 0.128”of H₂O. Figure 4.25 also shows that the solution flow is maintained at a constant rate as the set point is maintained at a constant value. Interestingly, the current carried by the electrospun jet varies from 20-30% of the average value, even though the applied voltage is maintained with a maximum change from the average value of 5%. Since all of the other properties are maintained within 5% of their average value, it appears that the current carried by the jet is influenced by some additional external...
variables, possibly the ambient air conditions, or as discussed earlier in this chapter, the current measurements may just be unreliable.

A mat with no dripping defects was created at a set point = 3” of H₂O and a voltage of 8kV, as shown in Figure 4.28. In comparison, an attempt was made to make a mat at a lower voltage, 6 kV, and a set point = 2” of H₂O, but as Figure 4.29 shows, this attempt was unsuccessful. It appears that when using a 20-gauge needle, that it will be very difficult to make mats without at any dripping defects at lower voltages than 8 kV. If a lower voltage is required in the process than a higher gauge (smaller diameter) needle should be used.

![Set Point Variation over 24 Hour Period](image)

Figure 4.24: Set Point Variation over 24 Hour Period
Solution Volume Change
Set Point = 3 inH₂O Voltage = 8 kV

Figure 4.25: Solution Volume Change of 24 Hour Period

Figure 4.26: Current Variation over 24 Hour Period

Figure 4.27: Voltage Variation over 24 Hour Period
4.4. Humidity Effects

It was mentioned in the literature review that the ambient air conditions have an effect on the resultant electrospun fibers. The dramatic effect of the surrounding air humidity is shown below in Figures 4.30 and 4.31. Figure 4.30 shows a 7% PEO/water solution spun at a capillary tip pressure (set point) of 6” of H$_2$O, voltage of 8kV, and tip to collector distance of 15cm. The air conditions were 24.5 C and 47% relative humidity. Figure 4.31 shows a collected mat spun with the same polymer solution and the exact same conditions, with the exception of the air condition at 23.3 C and 64% RH. Both pictures were taken under 10X magnification and collected on a 1” 304 stainless steel disk mesh (0.55 mm square with 0.1 mm diameter wire).
Figure 4.30: Low RH: 24.5 C and 47% RH

Figure 4.31: High RH: 23.3 C and 64% RH
The difference between these two samples can be easily seen. The fibers spun at low relative humidity are long, continuous, relatively straight fibers with uniform diameters and very few beaded defects. The fibers spun under high relative humidity conditions are curved, discontinuous, and very thin and contain a concentration of beaded defects. It appears that in the case of excess humidity, the solution is not evaporating from the jet as it travels towards the collector plate and since the fibers are still wet with solvent, the surface tension of the water remains a dominant force resulting in the formation of the beads in the fibers, since surface tension wants to minimize the surface area of the jet into spheres. In addition to this, supporting the theory that the fibers are collecting on the mat in a wet state is that after 72 hours, the mat of the Figure 4.32 was inspected again and only a few fibers remained at the corners of the mesh grid and the center was empty. It appears that when the solution evaporated the fibers fell apart and through the mesh grid leaving behind only a few fibers in the corners.

Figure 4.32: High RH after 72-Hour Period
More detail about the difference between fibers caused by the air’s humidity can be obtained by looking at the fibers under a higher magnification. Figure 4.33 shows a high humidity sample made at a Set Point = 6”of H₂O and Voltage = 8 kV, under a 50X magnification and 100% zoom. It can be seen that average fiber diameter is about 0.75 µm and the beaded defects are typically about 2X the diameter of the nominal fiber diameter. Also, Figure 4.34 shows the highly curved, short, and discontinuous fibers; 50% zoom is used to show larger area of fiber mat.

In comparison the properties of the fibers spun at low relative humidity, but at the same Set Point and Voltage as the last sample, are straight, continuous, and uniform. The distribution of the fiber diameters are 1, 0.8, and 0.6 µm, but the fibers have a consistent diameter through without any bead formations. Even the smaller diameter, 0.6 µm, fibers don’t have the presence of beads in the fibers like the 0.75 µm diameter fibers spun at the high humidity. There are some fluctuations in the small fibers, where they become thicker and thinner, but nothing as severe as seen at the higher humidity. These fluctuations in the fiber diameter could be removed by spinning a higher concentration PEO or spinning at a lower voltage.
Figure 4.33: High RH: 22.7 °C and 57% RH

Figure 4.34: High RH: 22.7 °C and 57% RH, 50% zoom
4.5. Simulation

The output of ode45 once a converged solution has been achieved is the x, y, z position and velocity for each bead in the jet, and the viscoelastic stress on each bead due to the above and below beads. The main limitations of the program are the solution computation time and the limited memory error that become a problem when the number of beads in the solution is increased.

Figure 4.36, the solution time increased dramatically as the number of beads used in the solution is increased. The solution time follows a power law relationship; this could be used to predict required times for solutions containing more than 65 beads. A solution
could not be achieved for a simulation with 70 beads, because a memory error was encountered.

![Program Convergence Time Graph](image)

**Figure 4.36: Solution Convergence Time**

In addition to the long solution computation time, the real limitation of the program is the maximum number of beads than can be used before the program stops due to a lack of available memory. The error encountered is listed below:

```matlab
??? Error using ==> horzcat
Out of memory. Type HELP MEMORY for your options.

Error in ==> ode45 at 495
yout = [yout, zeros(neq,chunk,dataType)];

Error in ==> main_project at 38
[t,zt]=ode45('project1',tspan,zt0);
```

This error resides with MATLAB’s ode45 program, and is not a result of the computer hardware not having enough available memory. Each integration that is
performed to reach a converged solution is saved in the data column \( zt \), which is the final output of the program. Since each bead has 8 equations to be solved, a \([8\times N \times \text{(\# of integrations to reach convergence)})\] matrix is created. Since the Runge-Kutta method used by ode45 only requires the knowledge of the present integrated value, the memory error can probably be resolved if somehow the matrix could be simplified to the following form \([8\times N \times \text{(Present Integration Value)})\]. This change most likely would have to be made in the code for ode45.

Despite these limitations, a simulation of the jet development was performed using the values and variables outlined in [4]. The distance from the capillary tip to the collect, \( h \), is specified as 2 meters, and the applied voltage 10kV. The initial simulations from time = 0.01 to 0.03 seconds uses 50 beads. After that time interval, the number of beads used in the simulation was decreased to 25 beads because the “out of memory” error was encountered. Clearly, the number of beads used in these simulations is far below the desired number outlined in Chapter 3.5. In this case with \( h = 2 \) meters, approximately 25,000 beads should be used in the simulation.

Figures 4.37 through 4.41 show an x-z plane cross section of the simulated electrospun jet. The applied electric field forces the beads to move down, in the negative z direction. As the simulation time increases and the beads are moved under the applied electric field, and become closer together, where the Coulombic force between the beads then causes the zig zag pattern seen in Figure 4.39. Figure 4.41 shows that jet is starting to form the familiar electrospinning jet shape, with a stable straight jet at the top and the whipping jet, inverted cone shape, at the bottom. Since only 25 beads are used in the
solution, the shape is very rough, but if this simulation was done with more beads the stable straight jet and whipping jet areas would be well defined.

Figure 4.37: Time = 0.01 seconds, # of Beads = 50

Figure 4.38: Time = 0.02 seconds, # of Beads = 50
Figure 4.39: Time = 0.03 seconds, # of Beads = 50

Figure 4.40: Time = 0.04 seconds, # of Beads = 25
Figure 4.41: Time = 0.05 seconds, # of Beads = 25
CHAPTER V
CONCLUSION

The goal of this research project was to develop a closed loop electrospinning control system that could maintain a constant pressure at the capillary tip. By controlling the pressure at the capillary tip, it was hoped that more control over the fiber diameters could be achieved and that a defect free mat could be produced. Additionally, the design of the control system and its components should be able to be implemented into a large-scale production while maintaining control over each electrospun jet. Two different sensors, infrared and ultrasonic, were compared for their functionality in a closed loop control system. The following conclusions are specific for a PEO/water solution and may not necessarily be true for solutions composed from different polymers and solvents.

The testing shows the ultrasonic sensor is the more capable sensor for creating a closed loop control system. The infrared sensor produced unreliable readings that were affected by the float position in the container and the viscosity of the solution used. Also, the ultrasonic sensor is truly a non-invasive sensor, since it does not require any floats or instrumentation inside the bottle to determine the height of the solution. The drawback to the ultrasonic sensor is the cost ($1800) of the sensor and its required electronics box. In the case of a large-scale electrospinning setup, the infrared sensor at $12 a piece would clearly be the more desirable choice if the technical difficulties could be resolved.
The rest of the testing done with the ultrasonic sensor shows that very little control over the fiber diameters can be achieved by changing the pressure at the capillary tip. It was observed that when the set point was increased that the distribution of fiber diameters increased as well, and that larger diameter fibers were more likely to occur. One factor that did have a large effect on the final fiber morphology is the relative humidity of the surrounding air. It appeared from the testing done at high relative humidity that the surface tension forces are more dominant, increasing the effect of the varicose instability compared to the whipping instability, due to the solution not evaporating as quickly, forming more beaded fibers.

The comparison of the predicted fiber diameters and the experimental diameters show that the predicted fiber diameters are smaller than the collected fiber diameters, but both cases show approximately the same increases in fiber diameter as the set point is increased. This is an interesting result since the current measurements of the jet current appear to be unreliable, but yet there is some agreement between the experimental and predicted fiber diameter results.

The control system was able to maintain a constant pressure at the capillary tip over a 24-hour period. During this test a fiber mat was made without any defects caused from dripping polymer solution. The control system can also maintain the pressure at the capillary tip when no voltage is applied, to prevent solution dripping during experimental setup and break down.

Since it was shown that very little control over the fiber diameter is achieved by controlling the pressure at the tip of the capillary needle, a control system based on the
pressure at the Taylor cone may not be the most optimal solution for controlling the final morphology of the electrospun mat.

The simulation of the electrospun jet produces very minimal results that can be used to develop a greater understanding of the electrospinning process. If the program can be modified to run and converge with 25,000 beads, then it can be used to accurately simulate the jet.
REFERENCES


% Initial Conditions for 1 jet centered at x=0 and y=0.
clear;
t0=0;
tfinal=9.9e-3;
tspan=[0 tfinal];
N=20;
L=.00319;
lambda=2.9979e6;
h=.15;

zi=[0 0 0 0 2 0 0 0];

for i=1:N

    % z initial position
    ztt1(i,:)-h-(h/N)*i;
    % z initial velocity
    ztt2(i,:)=0;
    % x initial position
    ztt1(i,:)-10^-3*L*cos((2*pi)/lambda)*ztt1(i,:)*(h-ztt1(i,:))/h;
    % x initial velocity
    ztt2(i,:)=0;
    % y initial position
    ztt1(i,:)-10^-3*L*sin((2*pi)/lambda)*ztt1(i,:)*(h-ztt1(i,:))/h;
    % y initial velocity
    ztt2(i,:)=0;
    % Stress up from bead i
    su(i,:)=0;
    % Stress down from bead i
    sd(i,:)=0;

    z(i,:)-[ztt1(i,:),ztt2(i,:),ztt1(i,:),ztt2(i,:),su(i,:),sd(i,:)]';
    zi=[zi,z(i,:)];
end

zt0=zi';
[t,zt]=ode45('project1',tspan,zt0);

% 3D plot generation
for i=1:8;8*N+8
    A(i,:)=zt(end,i);
    B(i,:)=zt(end,i+2);
    C(i,:)=zt(end,i+4);
end
Az=A(1:9,8*N+8);
Bz=B(1:9,8*N+8);
Cz=C(1:9,8*N+8);
plot3(Az,Bz,Cz)
APPENDIX B

SUBROUTINE
function stdot=project1(t,zt)
%
known system properties
m=0.283e-8;
e=2.83e-9;
Vo=10000;
h=.15;
L=3.19e-3;
G=10e4;
u=1000;
alpha=0.7;
lambda=2.9979e6;
N=20; % number of beads
stdot=[0 0 0 0 0 0 0 0];

Rz=zt(1:8:end);
Rx=zt(3:8:end);
Ry=zt(5:8:end);
for i=1:N+1;
    for j=1:N+1;
        if i==j,
            R1(i,j)=sqrt((Rx(1)-Rx(j))^2+(Ry(1)-Ry(j))^2+(Rz(1)-Rz(j))^2);
            Fcx(i,j)=((e^2/R(1,j)^3)*(Rx(1)-Rx(j)));
            Fcy(i,j)=((e^2/R(1,j)^3)*(Ry(1)-Ry(j)));
            Fcz(i,j)=((e^2/R(1,j)^3)*(Rz(1)-Rz(j)));
        end
    end
end
for j=1:N+1
    Fx(j)=sum(Fcx(j,:));
    fy(j)=sum(Fcy(j,:));
    Hz(j)=sum(Fcz(j,:));
end
fc=[fx;zeros(1,N+1);fy;zeros(1,N+1);Hz;zeros(3,N+1)];
Fc=fc';
for i=1:8:8*N+8;
    l1(i)=sqrt((zt(1)-zt(1))^2+(zt(i-6)-zt(i+2))^2+(zt(i-4)-zt(i+4))^2);
    u(i)=sqrt(((ao*2*L)/l1(i)));
end
for i=1:8:8*N;
    ld(i)=sqrt((zt(1)-zt(i+8))^2+(zt(1+2)-zt(i+10))^2+(zt(i+4)-zt(i+12))^2);
    ad(i)=sqrt((ao*2*L)/ld(i));
end
i=1; % first bead
sudot(1,:)=[0;
    sddot(1,:)=(G(l1d(i))^2)*((zt(1)-zt(i+8))*zt(i+1)+(-zt(i)+zt(i+8))*zt(i+9)+((zt(i+2)-zt(i+10))*zt(i+3))+(zt(i+2)+zt(i+10))*zt(i+11)+((zt(i+4)-zt(i+12))*zt(i+5)+(-zt(i+4)+zt(i+12))*zt(i+13))-G/mu)*zt(i+7);
    ztd1dot(1,:)=-zt(i+1);
    ztd2dot(1,:)=-zt(i+2);
    zd1dot(1,:)=-zt(i+3);
    zd2dot(1,:)=-zt(i+4);
ztt1dot(1,:)=zt(1+5);
ztt2dot(1,:)=zt(1+6);

zt(1,:)=zt1dot(1,:); zt2dot(1,:); ztt1dot(1,:); ztt2dot(1,:)

sudot(1,:); eddot(1,:);

for i=9:8:8*N,
% middle beads
if zt(1+4)<0;
    zt(1+4)=0;
end
if zt(1)>0;
    signx=1;
end
if zt(1)<0;
    signx=-1;
end
if zt(1+2)>0;
    signy=1;
end
if zt(1+2)<0;
    signy=-1;
end

m1(1)=(zt(1+2)-zt(1+10))/(zt(1)-zt(1+8));
m2(1)=(zt(1-6)-zt(1+2))/(zt(1-8)-zt(1));

dxu(1)=abs(zt(1-8)-zt(1));
dyu(1)=abs(zt(1-6)-zt(1+2));
dxd(1)=abs(zt(1)-zt(1+9));
dyd(1)=abs(zt(1+2)-zt(1-10));

dsu(1)=sqrt(dxu(1)^2+dyu(1)^2);
ds(1)=sqrt(dxd(1)^2+dyd(1)^2);

k(1)=atan((m2(1)-m1(1))/(1+m1(1)*m2(1)))/1d(1)+sudot(1,:); eddot(1,:);

sd1(1,:)=G/(lu(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
sdot(1,:)=G/(ld(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1)+zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
zt1dot(1,:)=zt(1+1);
zt2dot(1,:)=Pc(1)-((pi*(au(1)^2)*zt(1+6))/1u(1))*(zt(1-8)-zt(1))*((pi*(ad(1)^2)+zt(1+7))*zt(1-7)/1d(1))*zt(1-8));
zt(1)=zt(1+2))+(zt(1-4)+(4)^2)/4)*k(1))/sqrt((zt(1)^2+zt(1+2)^2));

k(1)=atan((m2(1)-m1(1))/(1+m1(1)*m2(1)))/1d(1)+sudot(1,:); eddot(1,:);

sd1(1,:)=G/(lu(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
sdot(1,:)=G/(ld(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1)+zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
zt1dot(1,:)=zt(1+1);
zt2dot(1,:)=Pc(1)-((pi*(au(1)^2)*zt(1+6))/1u(1))*(zt(1-8)-zt(1))*((pi*(ad(1)^2)+zt(1+7))*zt(1-7)/1d(1))*zt(1-8));
zt(1)=zt(1+2))+(zt(1-4)+(4)^2)/4)*k(1))/sqrt((zt(1)^2+zt(1+2)^2));

k(1)=atan((m2(1)-m1(1))/(1+m1(1)*m2(1)))/1d(1)+sudot(1,:); eddot(1,:);

sd1(1,:)=G/(lu(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
sdot(1,:)=G/(ld(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1)+zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
zt1dot(1,:)=zt(1+1);
zt2dot(1,:)=Pc(1)-((pi*(au(1)^2)*zt(1+6))/1u(1))*(zt(1-8)-zt(1))*((pi*(ad(1)^2)+zt(1+7))*zt(1-7)/1d(1))*zt(1-8));
zt(1)=zt(1+2))+(zt(1-4)+(4)^2)/4)*k(1))/sqrt((zt(1)^2+zt(1+2)^2));

k(1)=atan((m2(1)-m1(1))/(1+m1(1)*m2(1)))/1d(1)+sudot(1,:); eddot(1,:);

sd1(1,:)=G/(lu(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
sdot(1,:)=G/(ld(1))^2*(((zt(1)-8)-zt(1))*zt(1-7))+(zt(1)+zt(1-8)+zt(1))*zt(1+1)+((zt(1-6)-zt(1-2))*zt(1-5))+(zt(1)+zt(1-2)+zt(1-3))*zt(1)+((zt(1-4)-zt(1-4))*zt(1-3))+(zt(1+4)+zt(1+4))*zt(1+5));
zt1dot(1,:)=zt(1+1);
zt2dot(1,:)=Pc(1)-((pi*(au(1)^2)*zt(1+6))/1u(1))*(zt(1-8)-zt(1))*((pi*(ad(1)^2)+zt(1+7))*zt(1-7)/1d(1))*zt(1-8));
zt(1)=zt(1+2))+(zt(1-4)+(4)^2)/4)*k(1))/sqrt((zt(1)^2+zt(1+2)^2));
ztdot(1,:)=[zt1dot(1,:), zt2dot(1,:), zt3dot(1,:), zt4dot(1,:)]
sudot(1,:) ssdot(1,:); ztadot=[ztadot,ztadot(1,:)]
end
ztmdot=ztmdot(:,9:8*N);

i=8*N+1; % last bead
if zt(i+4)<0;
    zt(i+4)=0;
end
if zt(i)>0;
    signm=1;
end
if zt(i)<0;
    signm=-1;
end
if zt(i+2)>0;
    signy=1;
end
if zt(i+2)<0;
    signy=-1;
end
ml(1)=zr(i+2)/zt(1);
ml(1)=(zt(1-6)-zt(1+2))/(zt(1-8)-zt(1));
dsxu(1)=abs(zt(1-8)-zt(1));
dsyu(1)=abs(zt(1-6)-zt(1+2));
dsxu(1)=abs(zt(1));
dsyd(1)=abs(zt(1+2));
dsdu(1)=sqrt(dsdxu(1)^2+dsyu(1)^2);
dsd(1)=sqrt(dsxu(1)^2+dsyd(1)^2);
k(1)=atan((ml(1)-m2(1))/(1+m1(1)*ml(1)))/(dsd(1)+dsd(1));
sudot(1,:)=G/(lu(1)^2)*((zt(1-8)-zt(1))*zt(1-7))+((zt(1-6)-zt(1))*zt(1-5))+((zt(1-4)-zt(1-3))+((zt(1-4)+zt(1-5)))-(G/mu)*zt(1+6);
sudot(1,:)=0;
zt1dot(1,:)=zt(1-1);
zt2dot(1,:)=(Pc(1)-((pi*(au(1)^2)*zt(1+6))/lu(1)))*((zt(1-8)-zt(1))-(alpha*pi*((au(1)^2)*V/4)*1)))*(sqrt(zt(1)^2+zt(1+2)^2))*(abs(zt(1))*signx)/m;
zt1dot(1,:)=zt(1+3);
zt1dot(1,:)=(Pc(i+2)+((pi*(au(1)^2)*zt(i+6))/lu(1)))*zt(1-6)-zt(1+2))-((alpha*pi*((au(1)^2)*V/4)*1)))*(sqrt(zt(i)^2+zt(i+2)^2))*(abs(zt(i+2))*signy)/m;
zt1dot(1,:)=zt(1+5);
zt3dot(1,:)=(Pc(i)+4-1*Vo)*h+((pi*(au(1)^2)*zt(i+6))/lu(1)))*zt(1-4)-zt(1+4))/m;
zt1dot(1,:)=zt1dot(1,:); zt2dot(1,:); zt3dot(1,:); zt1dot(1,:); zt2dot(1,:); zt1dot(1,:); zt2dot(1,:); zt1dot(1,:))
ssdot(1,:) ssdot(1,:);
ztmdot=[ztmdot,ztmdot(1,:)]';
89