Electrohydrodynamic Control Systems for Nanomanufacturing



Electrospray Ionization

- Electrospray ionization occurs when:
 - a strong electric field is applied in the vicinity of a liquid
 - enough charge accumulates on the surface of a liquid to overcome the surface tension





Destabilization at the surface

- Destabilization at the surface occurs when:
 - enough charge accumulates in a small region of the liquid to overcome the surface tension
 - the solvent evaporates (volume abruptly decreasing)
- The liquid elongates into a "Taylor cone" and an aerosol spray of positively charged droplets is formed



Rayleigh Limit of a Charged Droplet

- In 1882, Lord Rayleigh published on stability limits of electrically charged liquid droplets
- Maximum amount of charge a droplet may hold before Coulomb Fission occurs (<u>Rayleigh limit</u> (Q_{ray}):

$$Q_{ray} = 8\pi \sqrt{\alpha} \epsilon_0 r_d^3$$

 α = surface tension ϵ_0 permittivity of free space r_d = radius of droplet



Coulomb Fission

- Coulomb fission: droplet explosions due to evaporation and pressure (droplet radius decreases) while surface charges get closer (electrostatic repulsion breaks the surface tension)
- During fission, the droplet loses a small percentage of its mass (1.0–2.3%) along with a relatively large percentage of its charge (10–18%)
- Bernoulli's principle due to increasing velocities



What is Electrospinning?

Decrease the electric field or increase the viscosity ...

 Electrohydrodynamic & viscoelastic process
 Easy to produce nanofibers

- Jet solidifies during trajectory
- Variable rheological properties
- <u>Random deposition</u>



Idea: Deflect the Charged Jet

- Grounded intermediate electrode attracts jet
- Positive intermediate electrodes deflect jet









- Several intermediate electrodes
- Electric lensing decreases spot size



Is this Possible with Current Resources?



Will need:

- Vacuum tubes
- Function generators
- Oscilloscope
- High voltage probes
- High voltage power supplies
- Copper
- Miscellaneous electronics/wiring
- Syringe pump
- Teflon/HDPE/Nylon stock

Not sure how to build a tube circuit?

- Go to the library annex
- Read books from the 1940s



Switching High Voltage



 Choose circuit components based on amplifier requirements and power supply ratings



- Drawing the load lines for quiescent conditions using the transfer characteristic curves
- Common-cathode configuration: high input impedance, medium-to-low output impedance, relatively high gain, good frequency response



CAD + Simulations to Understand & Automate the Electrohydrodynamic Deflection Process





Goals:

- Test current mathematical models
- Control deposition
- Develop feedback control
- data





Space Charge Effects: Mass-
Spring-Damper Model
$$\vec{F}_{coulomb_i} = k_e \sum_{j=1, j \neq i}^{N} \frac{q_i q_j}{R_{ij}^2} \left[\frac{(x_i - x_j)}{R_{ij}} \hat{e_x} + \frac{(y_i - y_j)}{R_{ij}} \hat{e_y} + \frac{(z_i - z_j)}{R_{ij}} \hat{e_z} \right],$$

where N is the number of beads in the system, x_i , y_i , z_i and x_j , y_j , z_j , are the current positions of each corresponding element, which promotes each j^{th} effect on the i^{th} charge, and R_{ij} is the distance between them (note that $i \neq j$):

•
$$R_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}.$$





Viscous & Elastic Effects
•
$$\vec{F}_{viscoelastic_i} = \vec{F}_{fi} + \vec{F}_{bi},$$

 $\vec{F}_{bi} = \pi a_{bi}^2 \sigma_{bi} \left[\frac{(x_i - x_j)}{s_{bi}} \hat{e}_x + \frac{(y_i - y_j)}{s_{bi}} \hat{e}_y + \frac{(z_i - z_j)}{s_{bi}} \hat{e}_z \right].$

- a_{bi} = cross sectional radius between i & i-1
- σ_{bi} = longitudinal stress pulling m_i backward



$$s_{bi} = \left[(x_{i-1} - x_i)^2 + (y_{i-1} - y_i)^2 + (z_{i-1} - z_i)^2 \right]^{\frac{1}{2}}.$$
$$\frac{d\sigma_{bi}}{dt} = G \frac{1}{s_{bi}} \frac{ds_{bi}}{dt} - \frac{G}{\mu} \sigma_{bi},$$

- G = Elastic modulus (vary in time)
- μ = viscosity (vary in time)

 $\pi a_{bi}{}^2s_{bi} = \pi a_0{}^2L.$

- L = Initial filament Length
- a₀ = Initial filament cross sectional radius

Surface Tension

$$\vec{F}_{tension_i} = -\alpha \pi a_{average}{}^2 k_i \hat{p}_i,$$

where α is the surface tension coefficient, k_i is the curvature of the jet with respect to the the coordinates of m_{i-1} , m_i , and m_{i+1} , \hat{p}_i is a unit vector from the i^{th} element toward the center of curvature (with respect to i + 1 and i - 1), and the average radius, $a_{average}$, at the i^{th} element is given by,

$$a_{average} = \frac{a_{fi} + a_{bi}}{2}$$

Simulations Require Rheological Measurements

 Using FSAD's Advanced Rheometer 200 & KSV Sigma 701 Instruments



Figure 14: This image shows measurements of the elastic modulus (G') of PEO 10% using a frequency sweep from 1 to 10Hz, with 20 sample points, at $25^{\circ}C$ with a strain percentage of .6% using an Advanced Rheometer AR 2000.



Figure 13: This image shows viscosity measurements of a 10% (w/w) mixture of deionized (DI) water and Polyethylene Oxide (PEO), with a molecular weight of $M_w = 600,000$, at 20°C over 4 minute intervals at shear rates ranging between $(0 - 180)\frac{1}{s}$ using an Advanced Rheometer AR 2000.

Measured	Parameters for PEO 10%	05
Variable	Definition	Value
μ	Viscosity	$4-42 Pa \cdot s$
α	Surface Tension	$30.95 \frac{m \cdot N}{m}$
G	Elastic Modulus	$190 - 1020 \ Pa$
ρ	Mass Density	$1.02 \frac{g}{cm^3}$

•
$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_{external_i} + \vec{F}_{coulomb_i} + \vec{F}_{viscoelastic_i} + \vec{F}_{tension_i}$$

 $\hat{r}_i = x_i \hat{e}_x + y_i \hat{e}_y + z_i \hat{e}_z.$

$$\vec{F}_{external_i} = q_i \vec{E}_i,$$

Must be more specific to electrode architecture and relative distances



Importing CAD models into Comsol

Cross sectional analysis of 3D electrode architecture





More CAD -> Machine Shop

• HDPE, Nylon, Delrin, & Teflon to insulate v_{cc} from high voltage









High voltage power supply (0-30kV, 0-200μA);
 High Voltage DC power supply (0 to -40kV, 0-7.5mA);
 Polymer solution (PEO & PEO + Carbon Black.
 Precision DC power supply (0-60V, 2.5A);
 Syringe pump 70-3005 with ±0.25% accuracy;
 Nintendo controller;
 Electronic controls for stepper motors;
 Function generators;
 Oscilloscopes;
 10MHz reference clock sign

The Injection Chamber



(Left) The injection chamber, which includes: 1. Stepper motor; 2. Vacuum tube amplifier; 3. Syringe needle/driving mechanism; 4. Electrode driving mechanism; 5. 10M resistor; 6. Collector (½" thick, 6061 8" diameter Aluminum plate)

Guiding the Nanofiber in 2-D



Drawing a Triangle:

• f = 10Hz pulses, $D_N = 33.3\%$ duty cycle. The 2nd and 3rd pulses are $\phi_2 = 33.3$ ms and $\phi_3 = 66.6$ ms, out of phase from ϕ_1 , respectively.







Printing a Hexagon



Voltage and Distance Dependence





PEO 10%	$\frac{\Delta V}{\Delta Z}$ Dependency	
Frequency (f)	15 Hz	15Hz
Nozzle Position from Origin (Z_N)	-76.2mm	-114.3mm
Collector Position from Origin (Z_C)	76.2mm	114.3mm
Nozzle Voltage (V_N)	13kV	13kV
Collector Voltage (V_C)	-2.6kV	-9.2kV
Intermediary-electrode Position from Z-axis	19.1mm	19.1mm
Deposition Diameter (D_{Dep})	$\sim 30mm$	$\sim 20mm$

Frequency Dependence







PEO 10%	f Dependency	
Electrode Pulsing Frequency (f)	30Hz	45Hz
Nozzle Position from $\operatorname{origin}(Z_N)$	-114.3mm	-114.3mm
Collector Position from origin (Z_C)	57.2mm	57.2mm
Nozzle Voltage (V_N)	13kV	13kV
Collector Voltage (V_C)	-7kV	-7kV
Intermediary-electrode Position from z-axis	12.7mm	12.7mm
Deposition Diameter (D_{Dep})	$\sim 10 mm$	$\sim 7.5 dmm$

Goal: 2D and 3D Print Aligned Nanofibrous Structures





Future Work: Actuated Quadrupole Mass Spectrometer

- Single point of actuation
- No need for calibration or motors







• Decrease spot size



Thank you!