International Conference on Nanotechnology for Renewable Materials

POLYMER COMPOSITE &
MATERIALS LABORATORY
PCML

Rheological considerations for advanced manufacturing with cellulose nanocrystals

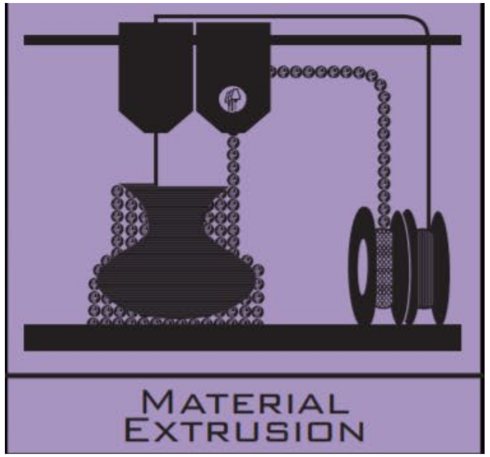
June 13, 2023

Prof. Michael J. Bortner
Dept. of Chemical Engineering, Virginia Tech
mbortner@vt.edu

TAPPI
NANO
DIVISION

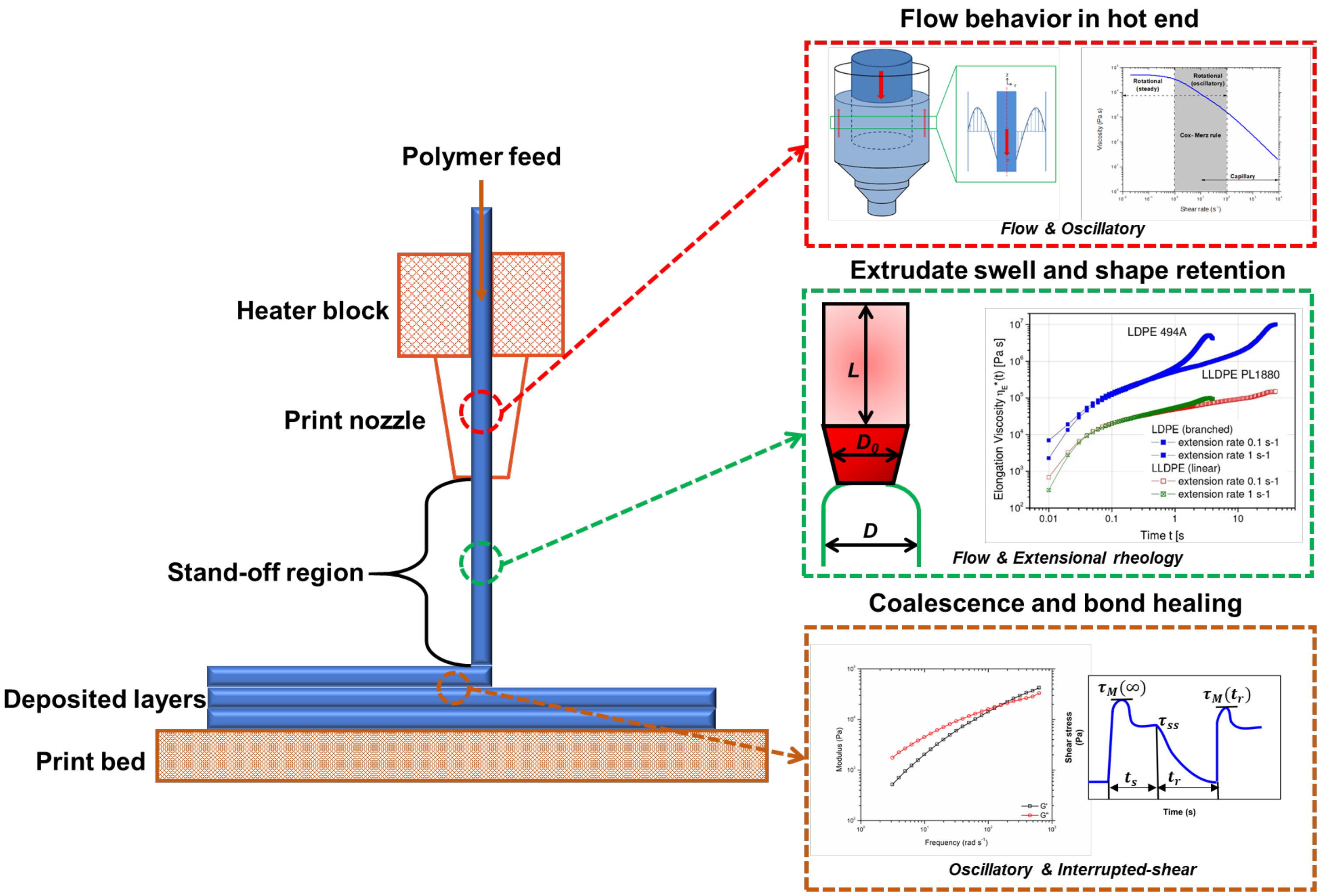
12-16 JUNE 2023 • VANCOUVER, B.C. CANADA

7 Additive Manufacturing Modalities



https://www.additivemanufacturing.media/cdn/cms/7_families_print_version.pdf

Modeling and Rheology of the MatEx process



AM mode depends on RT flow behavior/thermal transitions

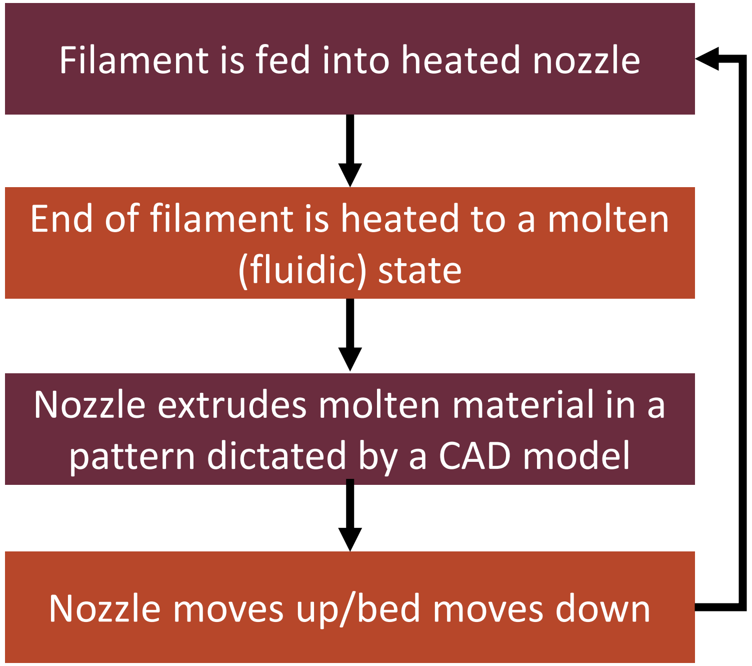
- Will a material extrude?
- What happens when it exits the nozzle?
- What are the dynamics driving interlayer adhesion?
- How do all of these couple to final part properties?

http://blog.capinc.com/2014/12/design-for-3d-printing-success/

A. Das, E.L. Gilmer, S. Biria, and M.J. Bortner, "Importance of Polymer Rheology on Material Extrusion Additive Manufacturing: Correlating Process Physics to Print Properties", *ACS Applied Polymer Materials*, (2021)

Fused Filament Fabrication (FFF)

- Material extrusion AM
- Filament feedstock
- Continuous process

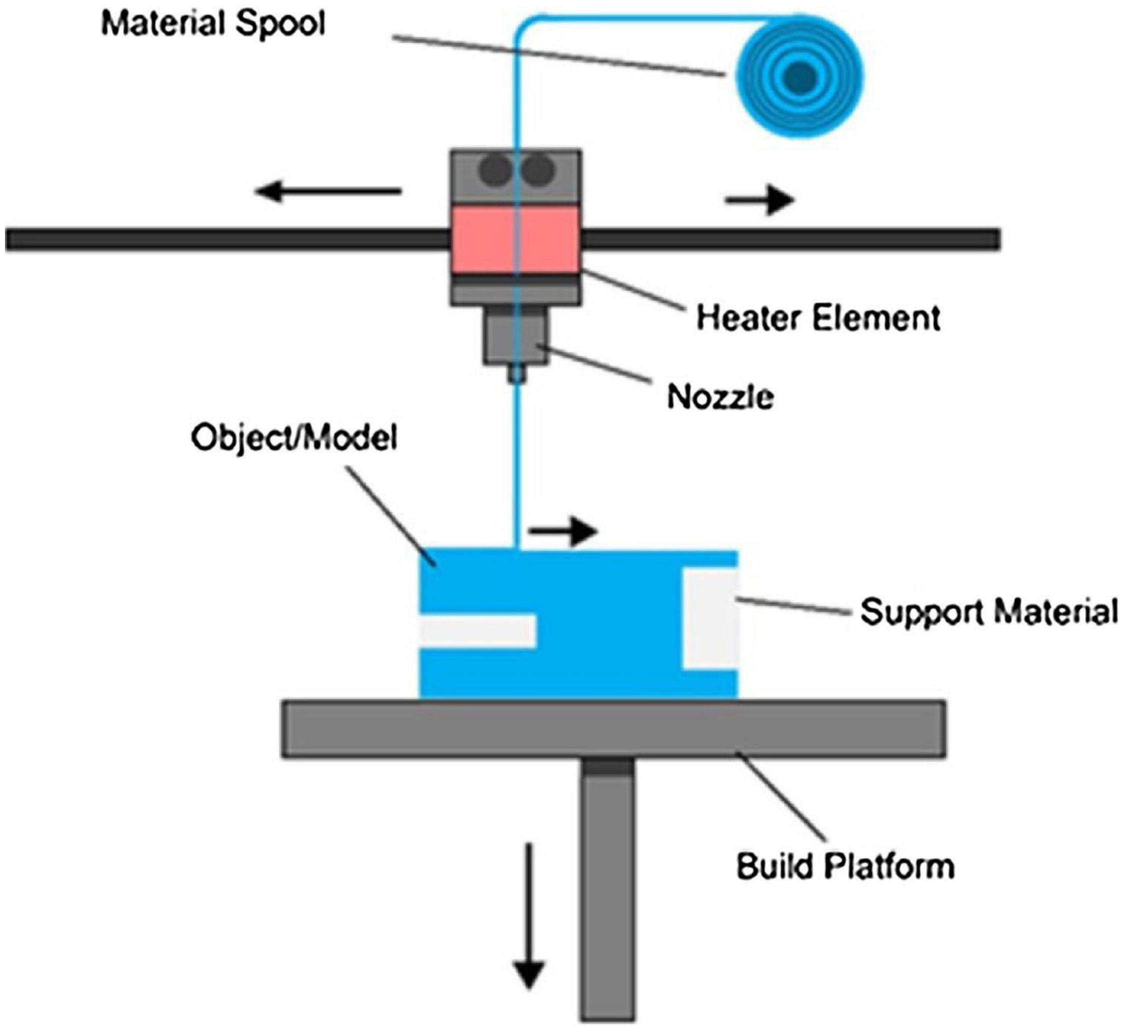


Filament is fed into heated nozzle

End of filament is heated to a molten (fluidic) state

Nozzle extrudes molten material in a pattern dictated by a CAD model

Nozzle moves up/bed moves down



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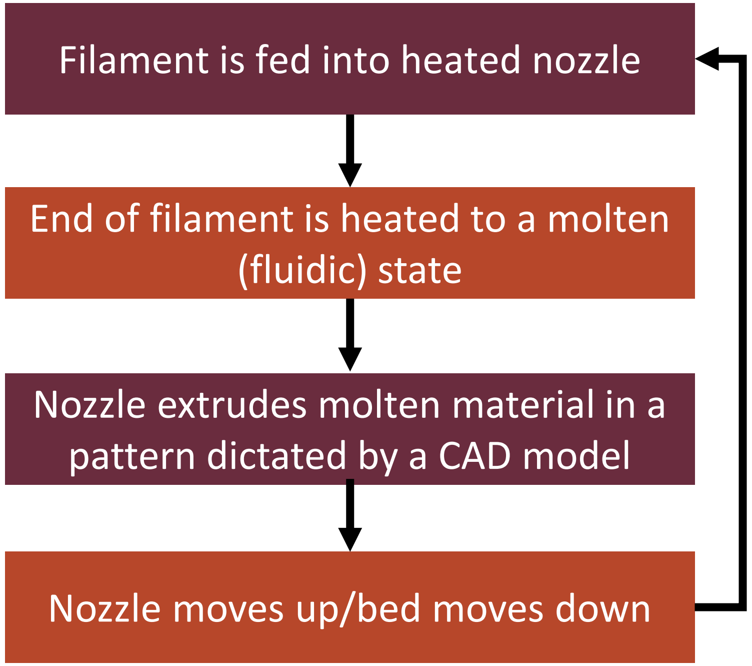

Filament is fed into heated nozzle

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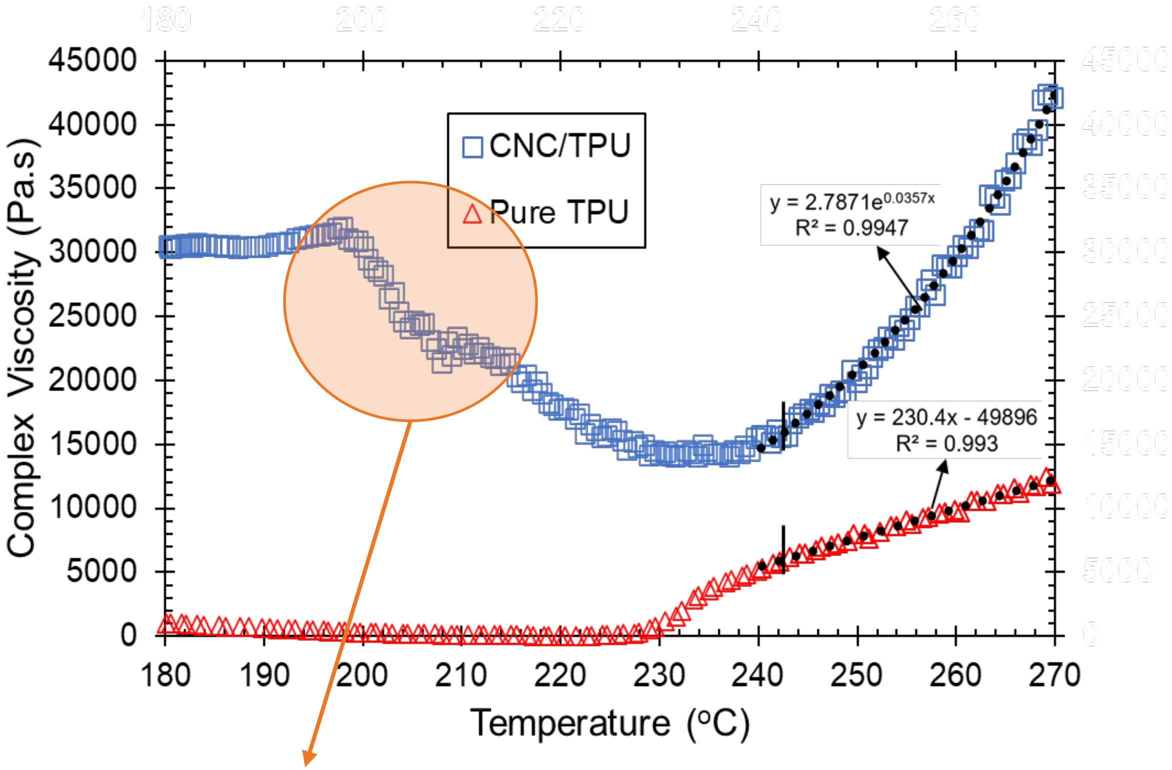
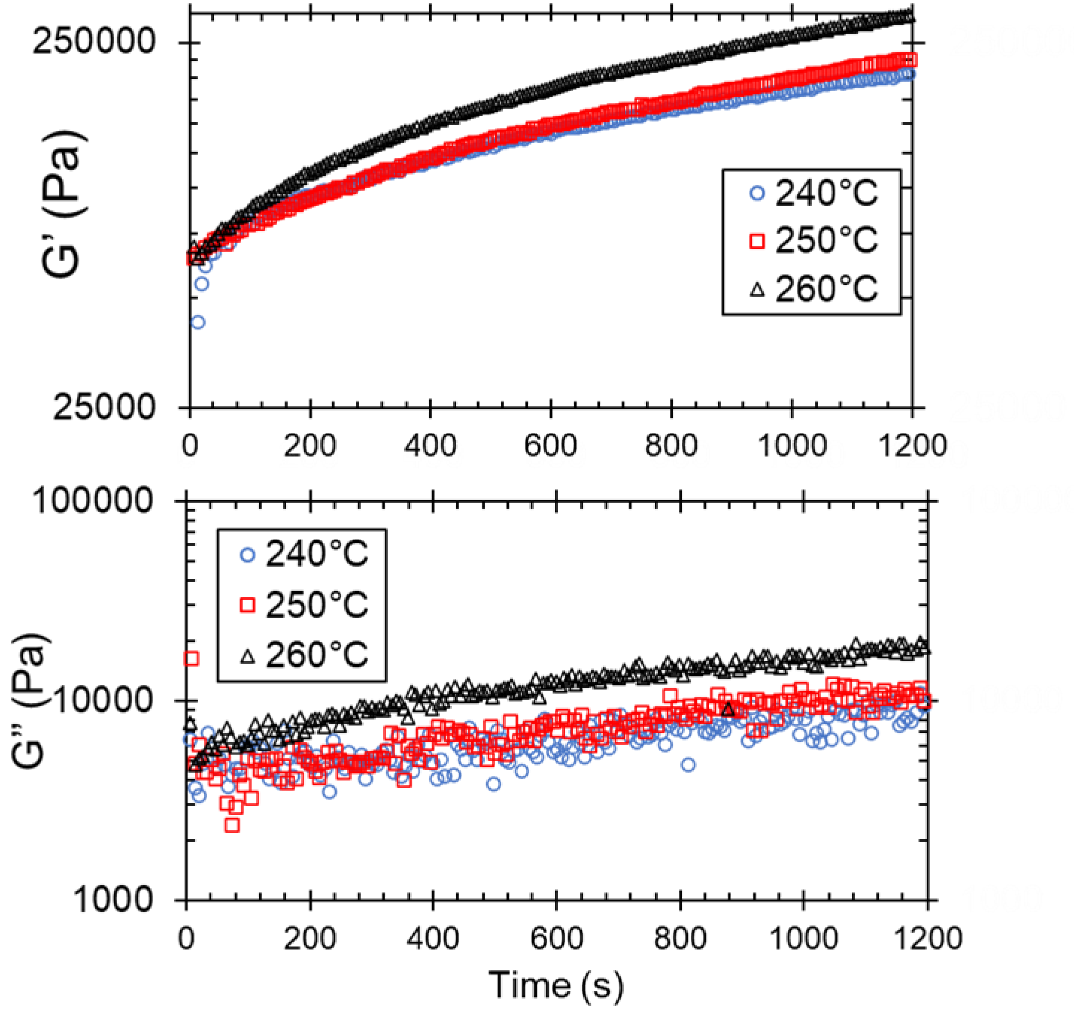
Nozzle extrudes molten material in a pattern dictated by a CAD model

Nozzle moves up/bed moves down

Chemorheology: Oscillatory Time/Temp Sweeps



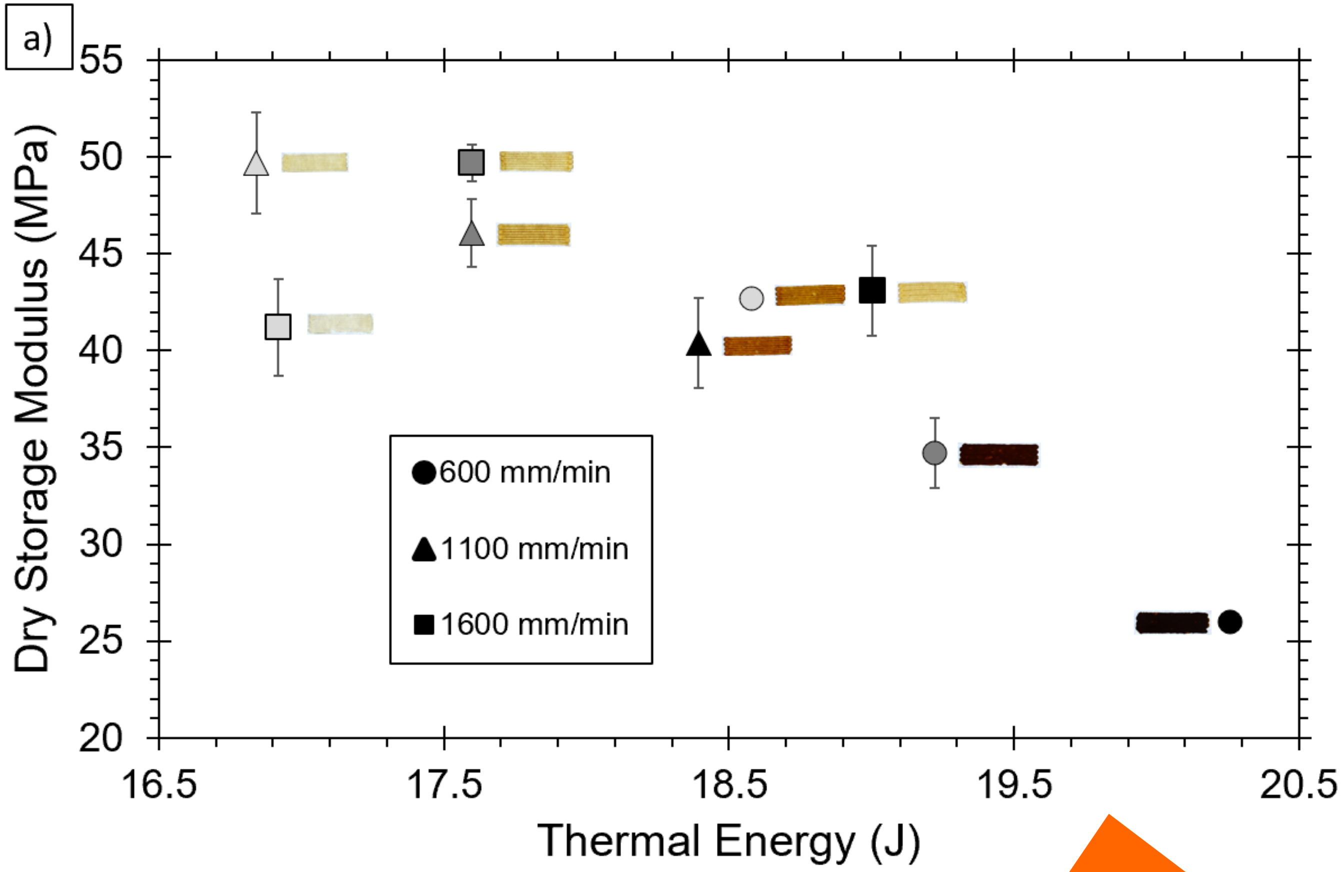
Flow state but no degradation?

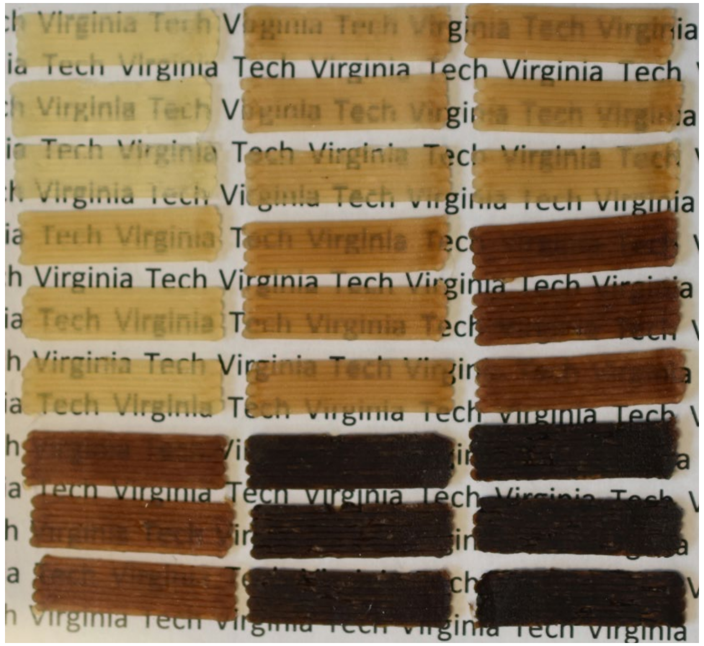


T. Seguine M.S. Thesis (2021)

T. Seguine et. al., *Green Materials*, https://doi.org/10.1680/jgrma.20.00066 (2021)

Thermal Energy Analysis: Balancing Interlayer Adhesion with Mechanical Performance





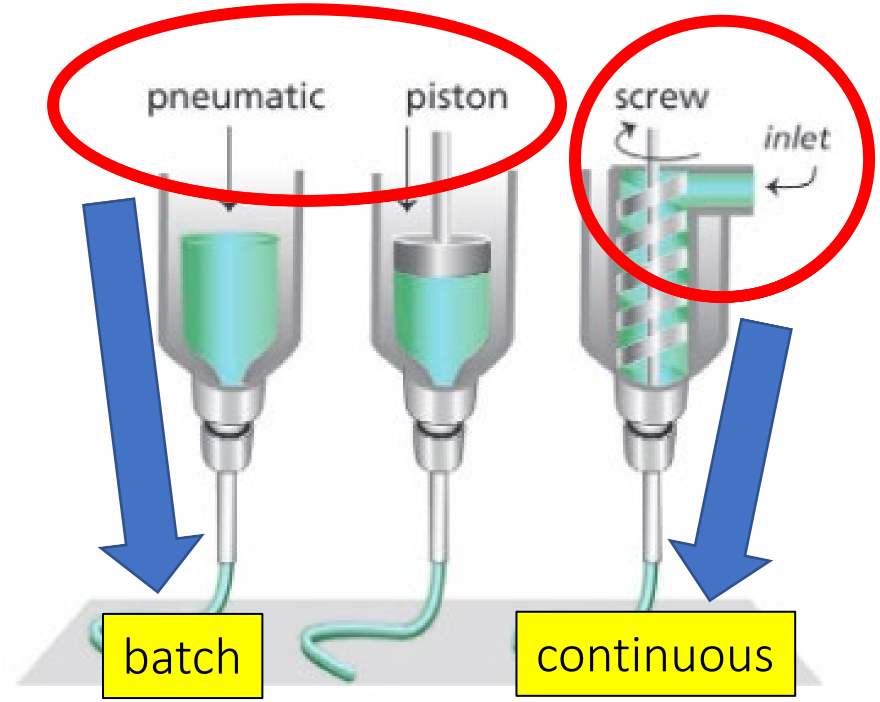
Heat energy increasing

More degradation

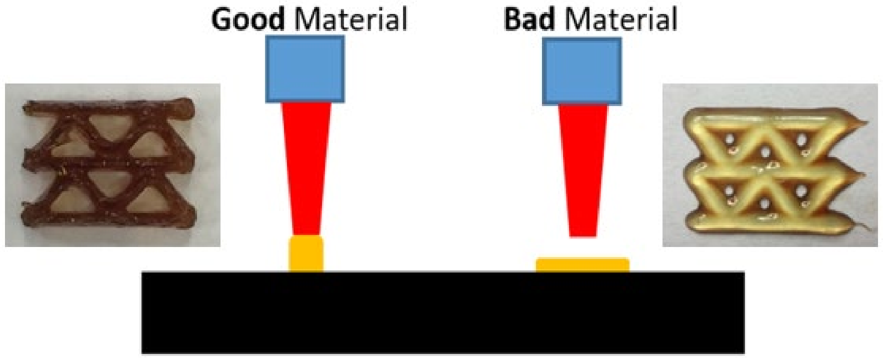
Heat energy increasing

T. Seguine et. al., *Green Materials*, https://doi.org/10.1680/jgrma.20.00066 (2021)

Introduction to Direct Ink Write MatEx



Step 1: Flow Through Nozzle → **Step 2:** Solidification

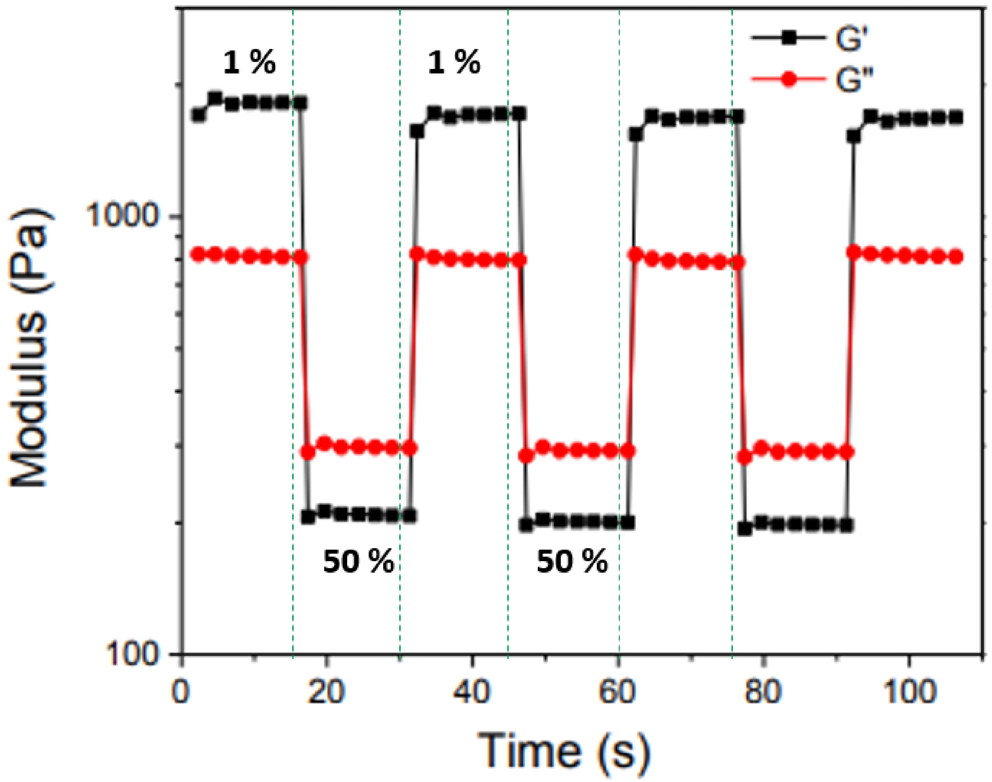


Solidification Mechanisms Include:

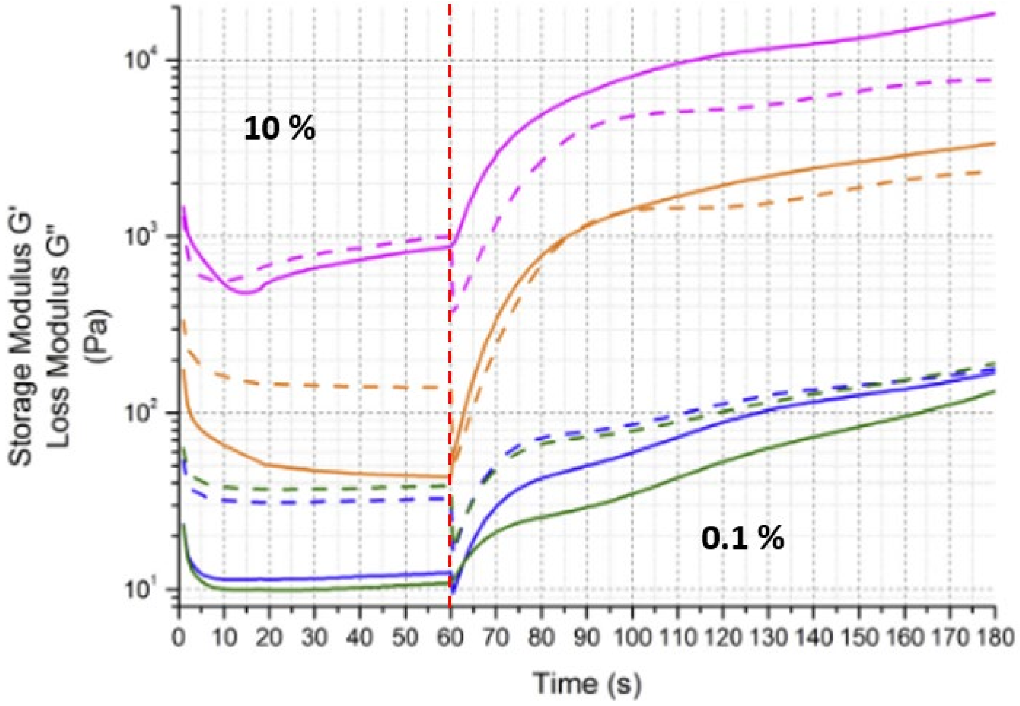
- Materials with a Yield Stress
- Solvent Evaporation
- Chemical Reaction

Malda, Jos, et al. "25th anniversary article: engineering hydrogels for biofabrication." *Advanced materials* 25.36 (2013): 5011-5028.

Thixotropy, Yield Stress and Recovery



Optimal Recovery



Slow Recovery

Li, Longyu, et al. "Hierarchical Co-Assembly Enhanced Direct Ink Writing." *Angewandte Chemie* 130.18 (2018): 5199-5203.

Franchin, Giorgia, et al. "Direct ink writing of geopolymeric inks." *Journal of the European Ceramic Society* 37.6 (2017): 2481-2489.

Interactions Between CNCs

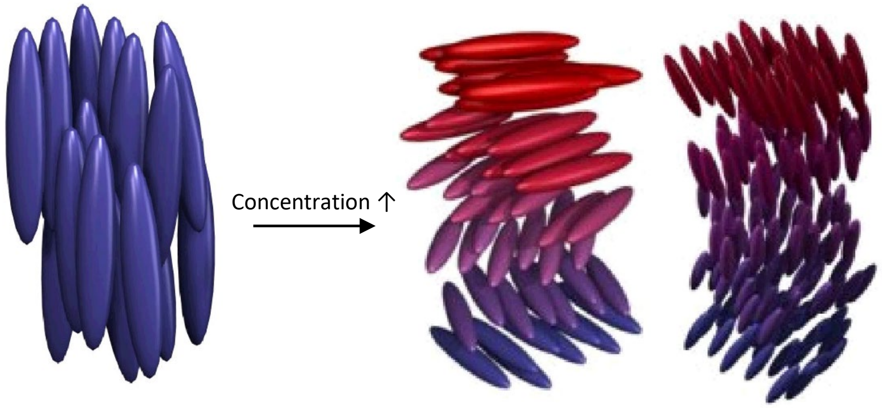
Derjaguin-Landau-Verwey-Overbeek (DLVO)

- *van der Waals Force*
  - Attractive force between rods
  - Promotes ∥ orientation
- *Electrostatic Double Layer Force*
  - Repulsive force between similarly charged rods
  - Promotes ⊥ orientation
- *Parameters affecting interactions*

Aspect ratio ↑	rotational diffusivity ↓
Surface charge density ↑	Ionic strength ↑
Ionic strength ↑	κ^{-1} ↓
$pH < 2$ or $pH < 11$	Ionic strength ↑, κ^{-1} ↓

Debye Length[1] $\kappa^{-1} \approx 4.25\ nm$ at pH $2 - 10$

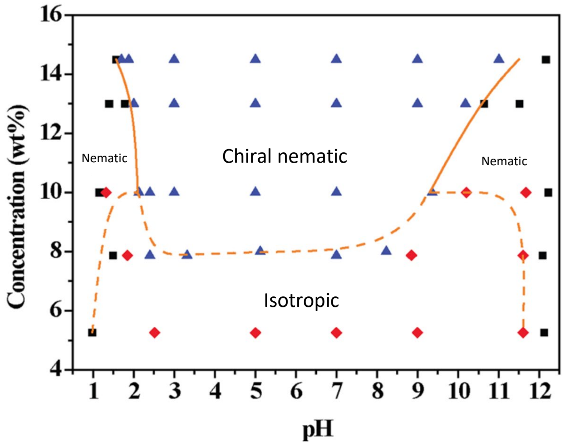
Liquid Crystalline Order of CNCs



Nematic

Chiral Nematic

Entropy and sterically driven phase transitions

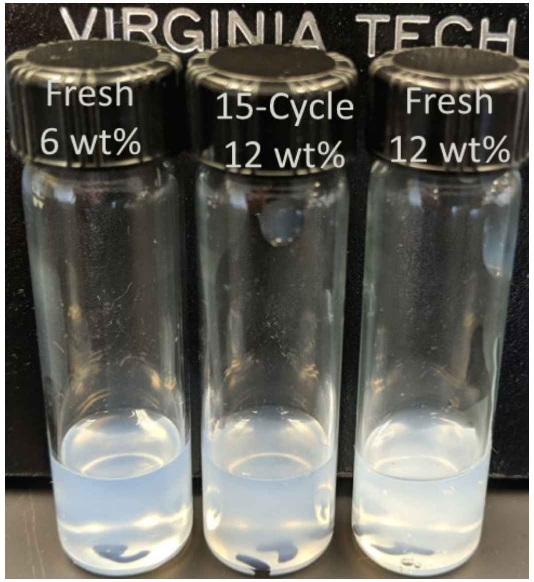


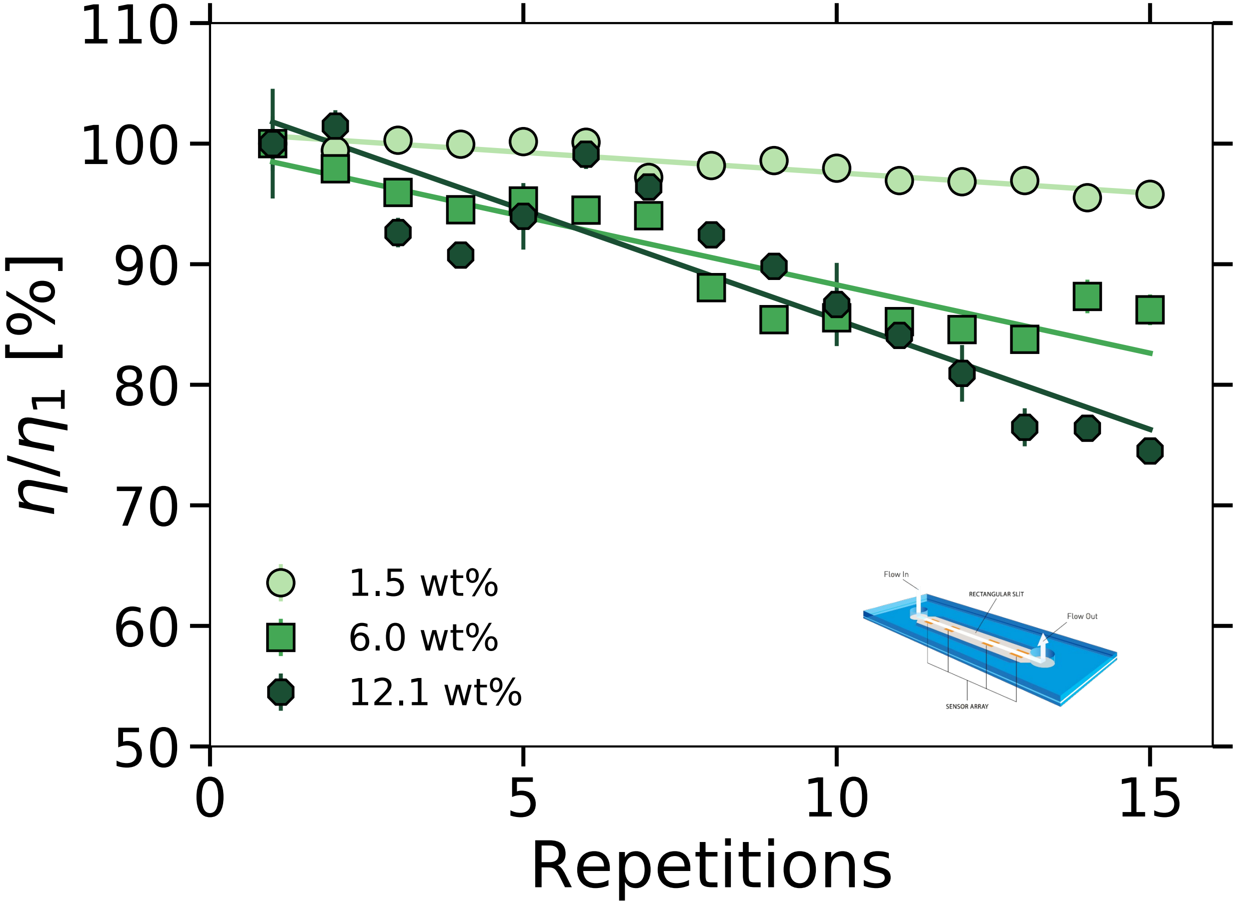
Control of DLVO interactions governs phase at a given CNC concentration

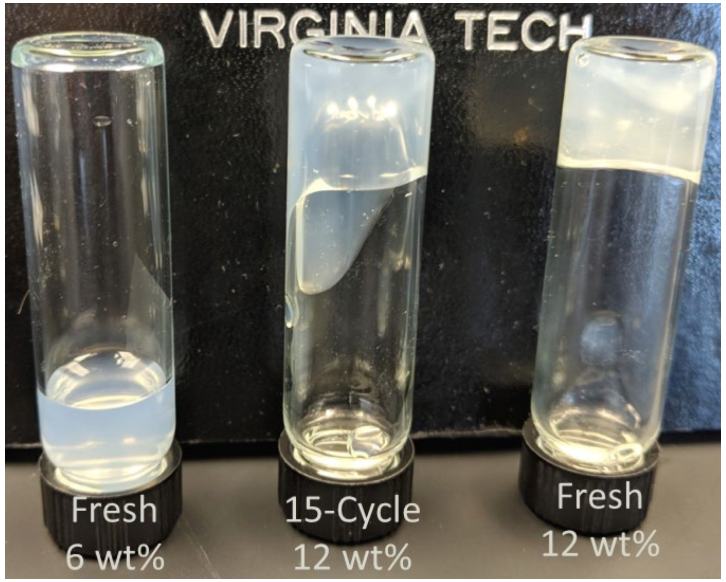
M. Li, Q.Wu, R.J. Moon, M.A. Hubbe, and M.J. Bortner, "Rheological Aspects of Cellulose Nanomaterials: Governing Factors and Emerging Applications", Advanced Materials, 33 (21), 2006052 (2021)

Li, C., et al., *Sci* Rep, 2019. 9(1): p. 11290.

CNC - Prolonged Shear Experiments







η = viscosity at a given run

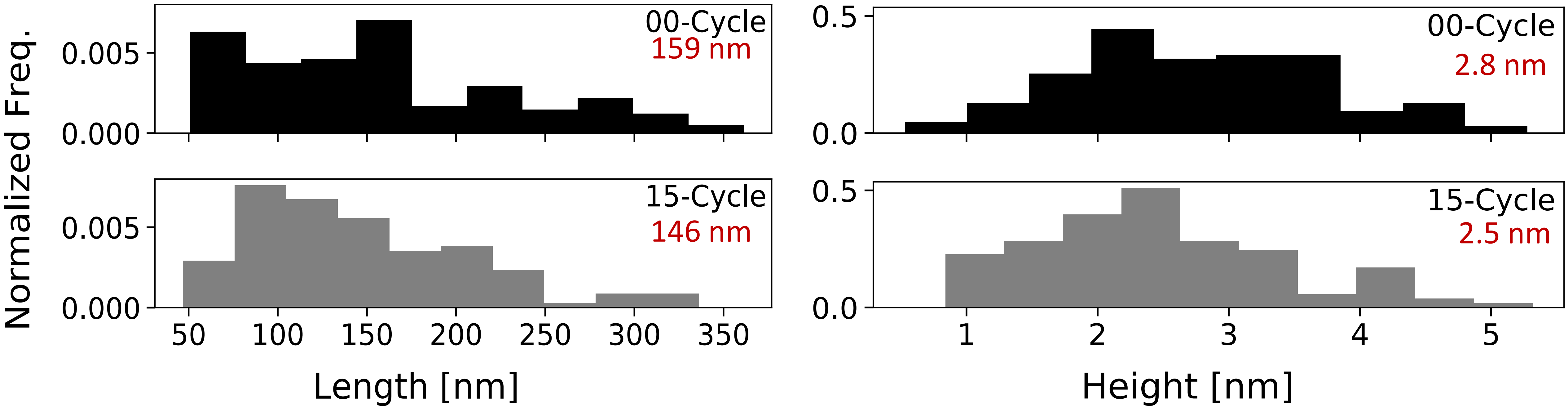
η_1 = viscosity of run 1

Sutliff, B. P.; Das, A.; Youngblood, J.; Bortner, M. J.. *Carbohydr. Polym.* **2020**, *231*, 115735.

mVROC – E05 chip – 50 µm x 3000 µm

CNC-12.1 wt% decreases in length and height

CNC



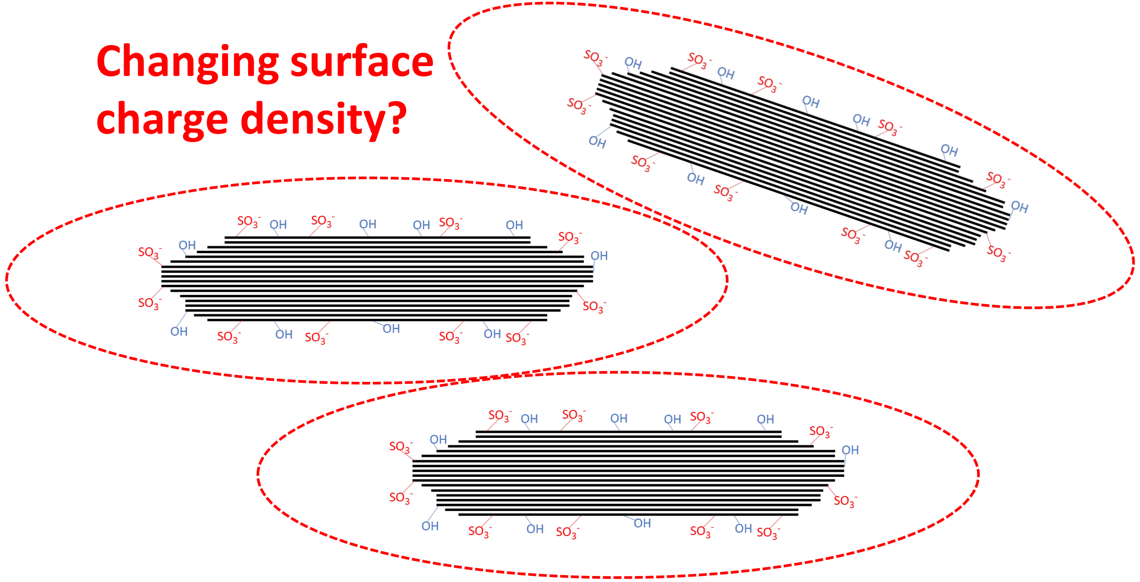
12.1 wt% samples from Forest Products Lab (UMaine) @ 800,000 s^{-1}

Asylum Research MFP-3D-Bio AFM, 1 Hz, 512x512 scans/line, AC200, r=7nm, 9N/m

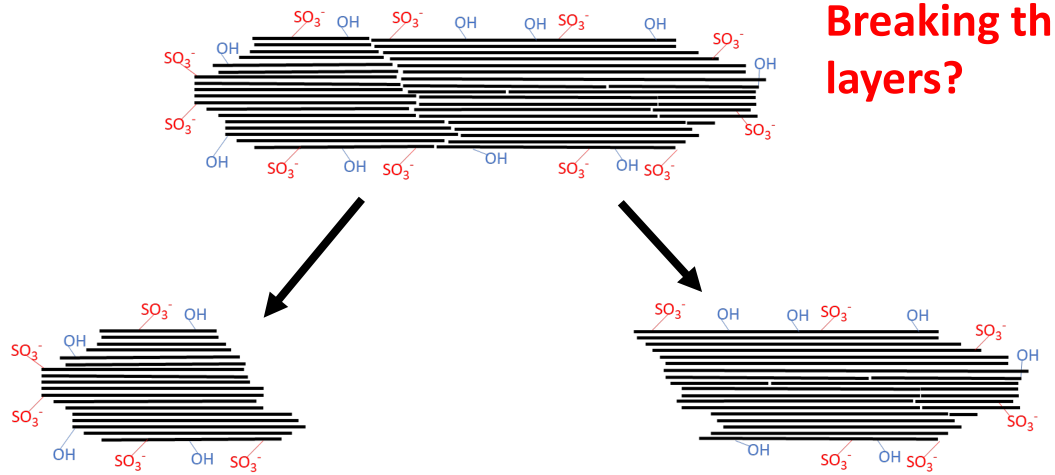
Sutliff, B. P.; Das, A.; Youngblood, J.; Bortner, M. J.. *Carbohydr. Polym.* **2020**, *231*, 115735.

CNC – Potential causes of viscosity decrease

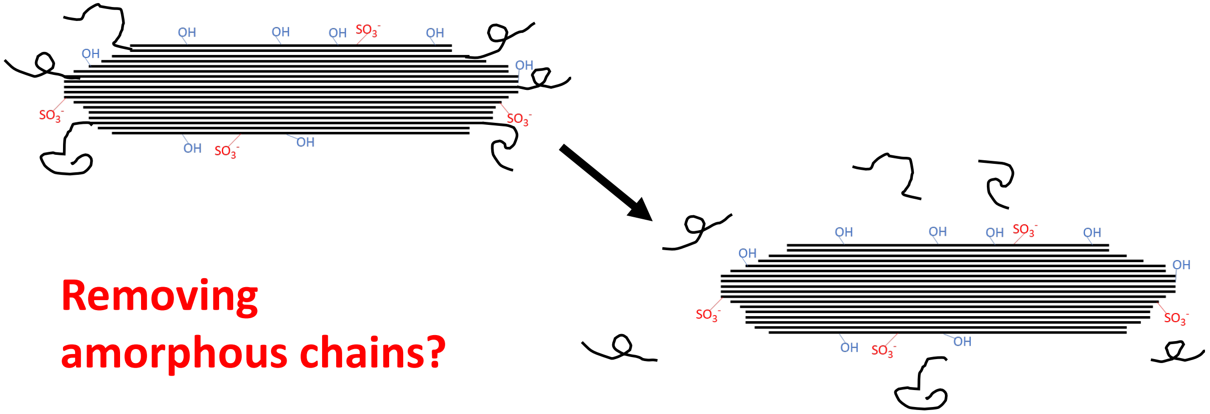
Changing surface charge density?



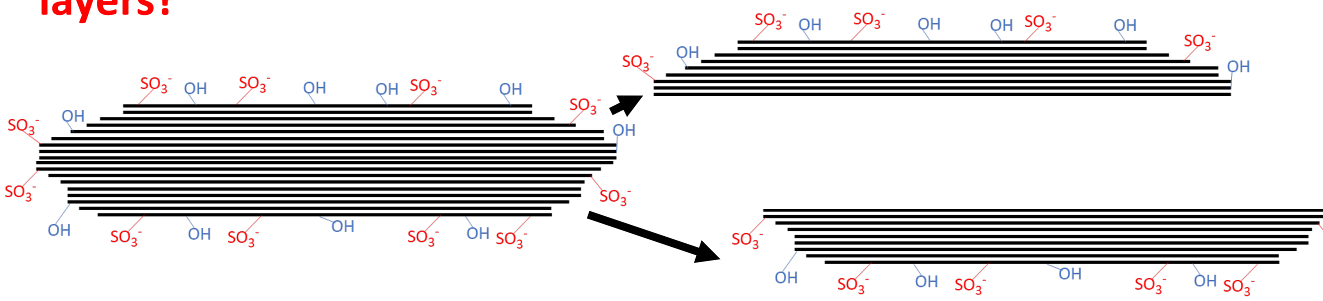
Breaking through layers?



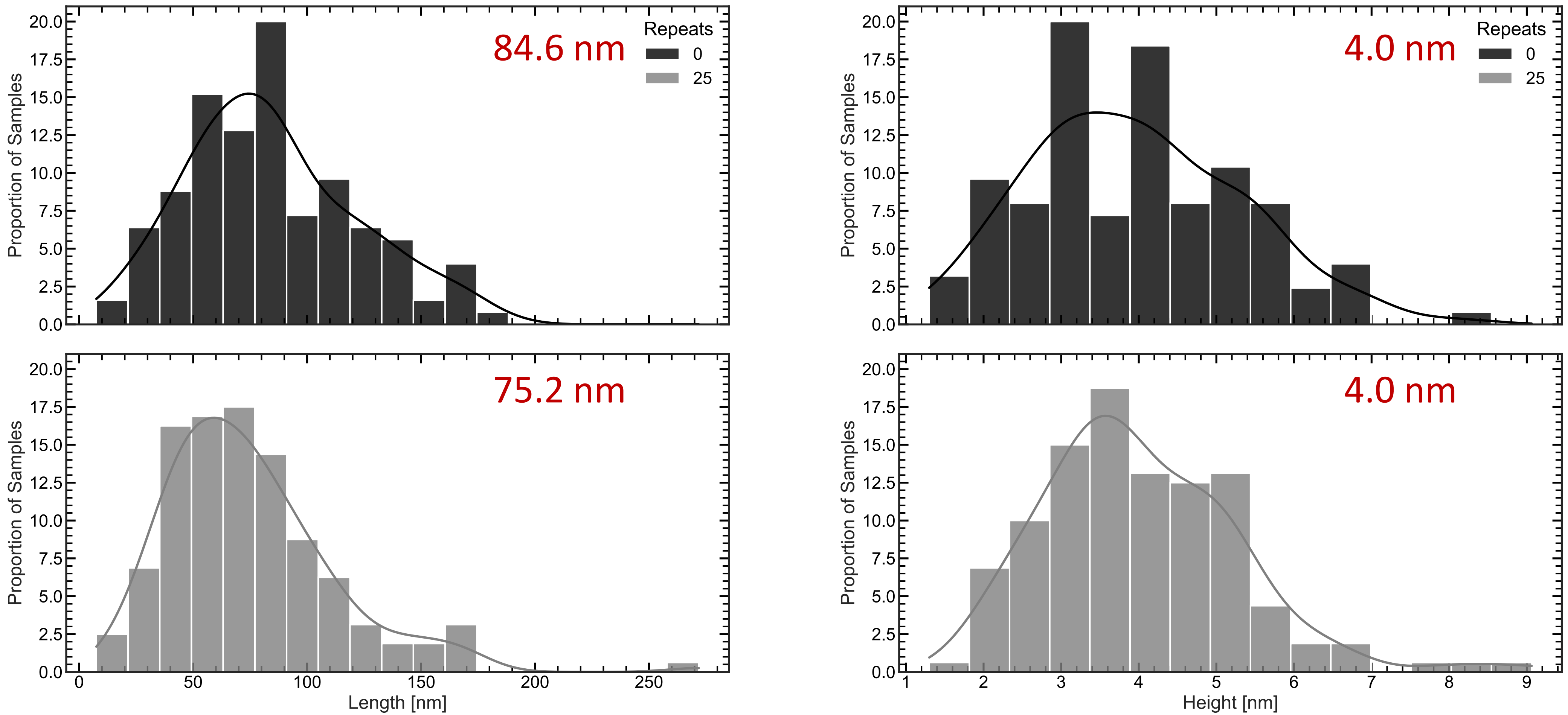
Removing amorphous chains?



Breaking between layers?



CNC–6.0 wt% samples decrease in length only



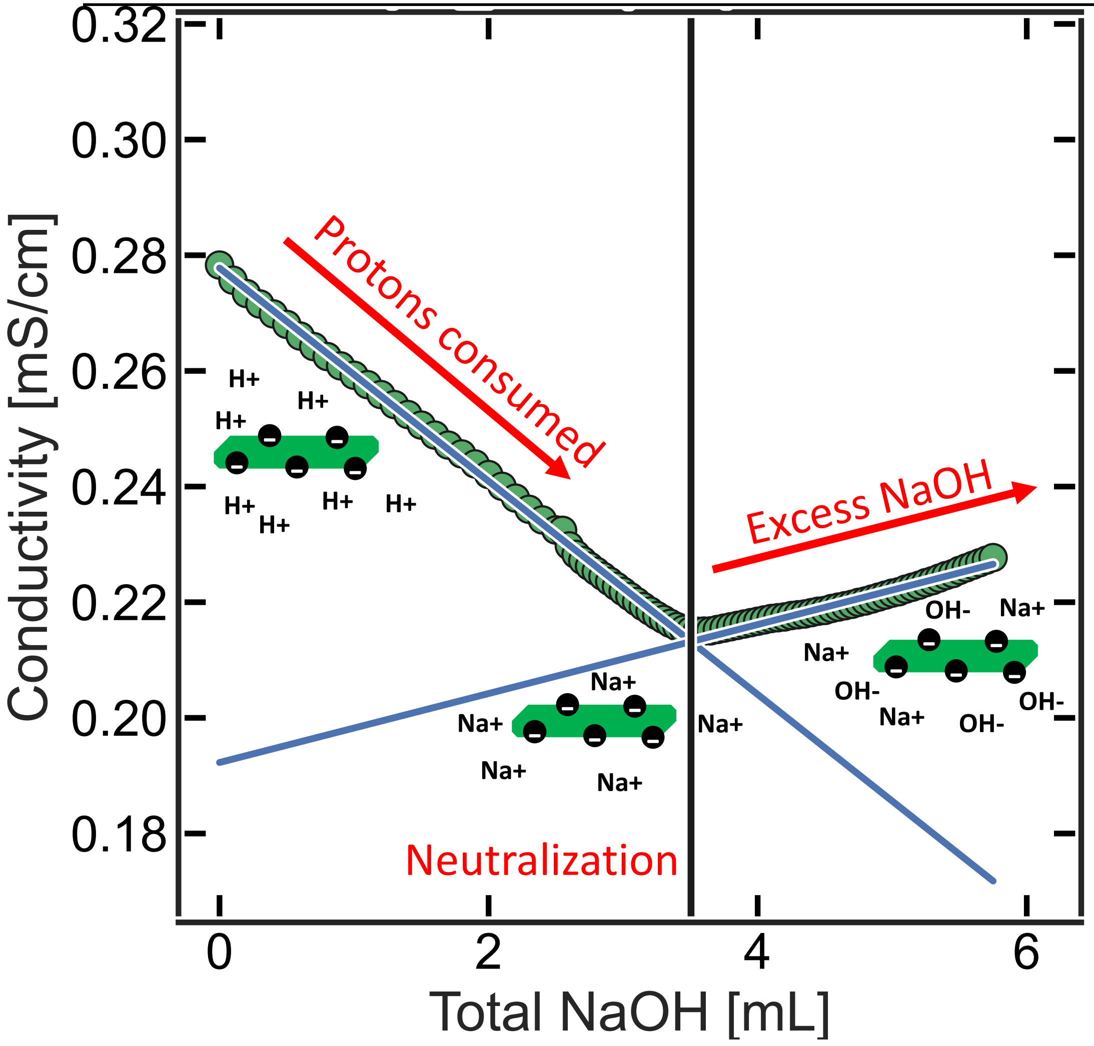
6.0 wt% samples from Celluforce @ 316,000 s^{-1}

Asylum Research Jupiter AFM, 1 Hz, 512x512 scans/line, AC200, r=7nm, 9N/m

Sutliff, B. P.; Farrell, C.; Martin, S.M.; Bortner, M. J.. *Carbohydr. Polym.* **2022**, *In preparation*.

CNC–Sulfate density does not change

CNC



Null Hypothesis: $\bar{\mu}_{00} = \bar{\mu}_{25}$

~~Alternative Hypothesis: $\bar{\mu}_{00} \neq \bar{\mu}_{25}$~~

$p = 0.58$

Repeats	CNC [g]	NaOH Conc. [mMol]	Sulfate Density [mmol/kg]	Mean Sulfate Density [mmol/kg]
0	0.150	21	325	449
0	0.149	21	528	
0	0.149	21	494	
25	0.149	21	505	490
25	0.149	21	524	
25	0.178	21	440	

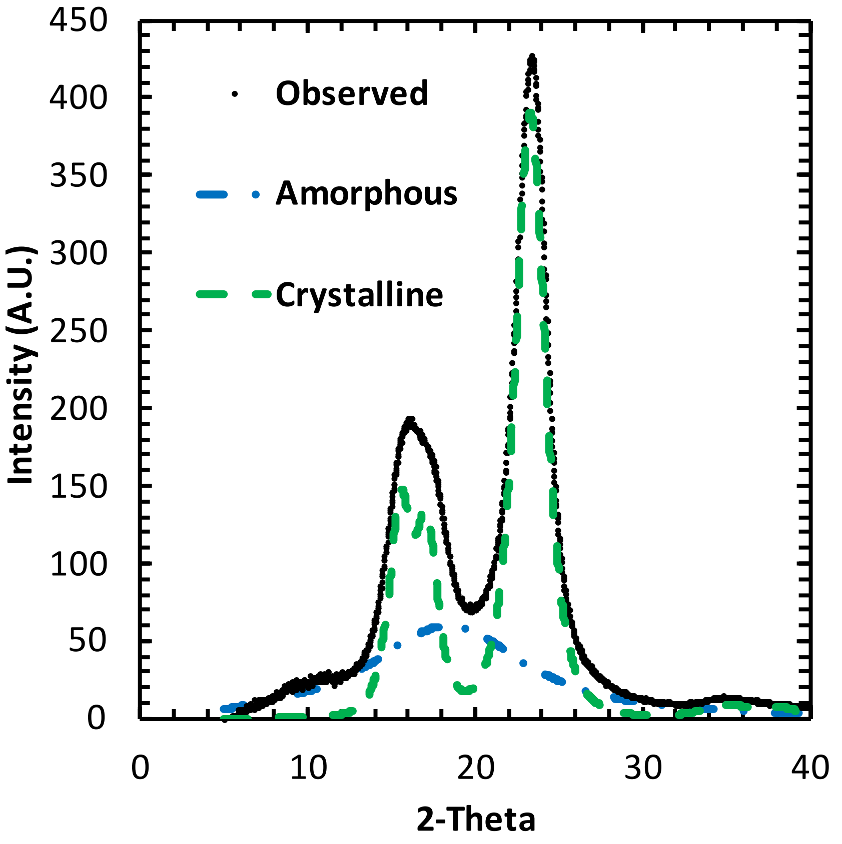
+5 mL of 0.5M NaCl

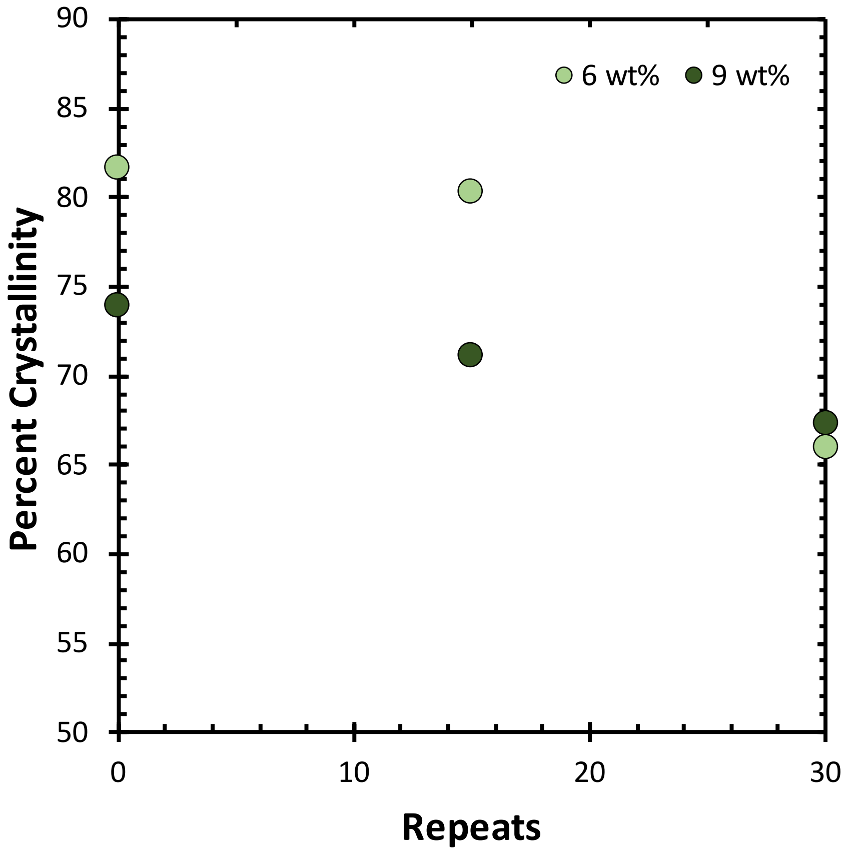
+ ~300 mL DI H_2O

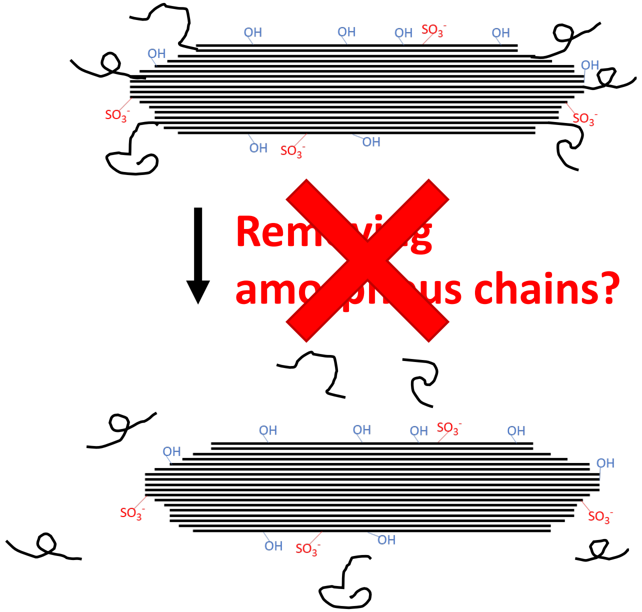
Sutliff, B. P.; Farrell, C.; Martin, S.M.; Bortner, M. J.. *Carbohydr. Polym.* **2023**, *In preparation*.

Metrohm 905 Titrando automatic titrator + Metrohm 800 Dosino automatic doser + Metrohm 856 conductivity module

CNC – XRD indicates: less crystalline!



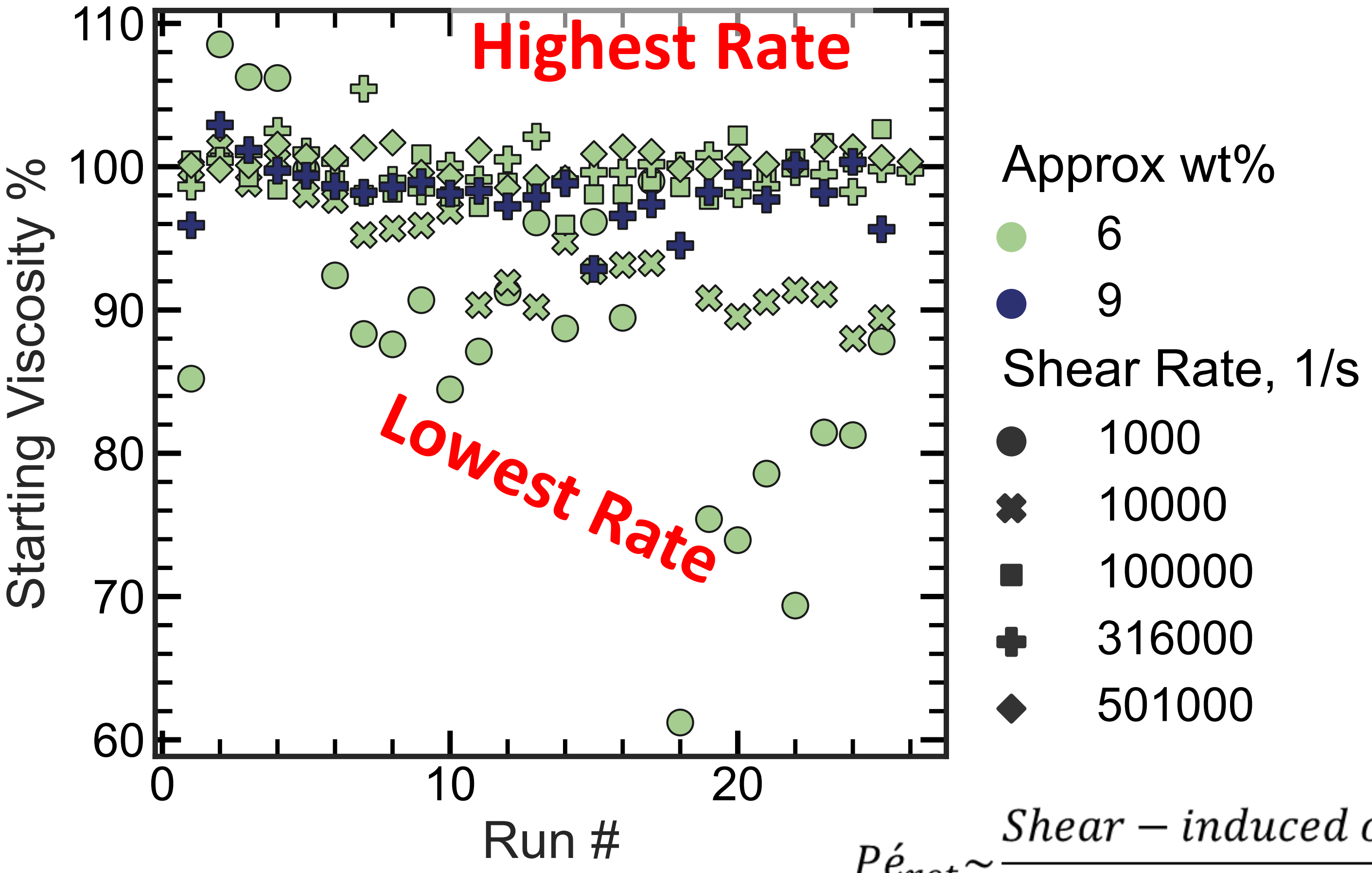


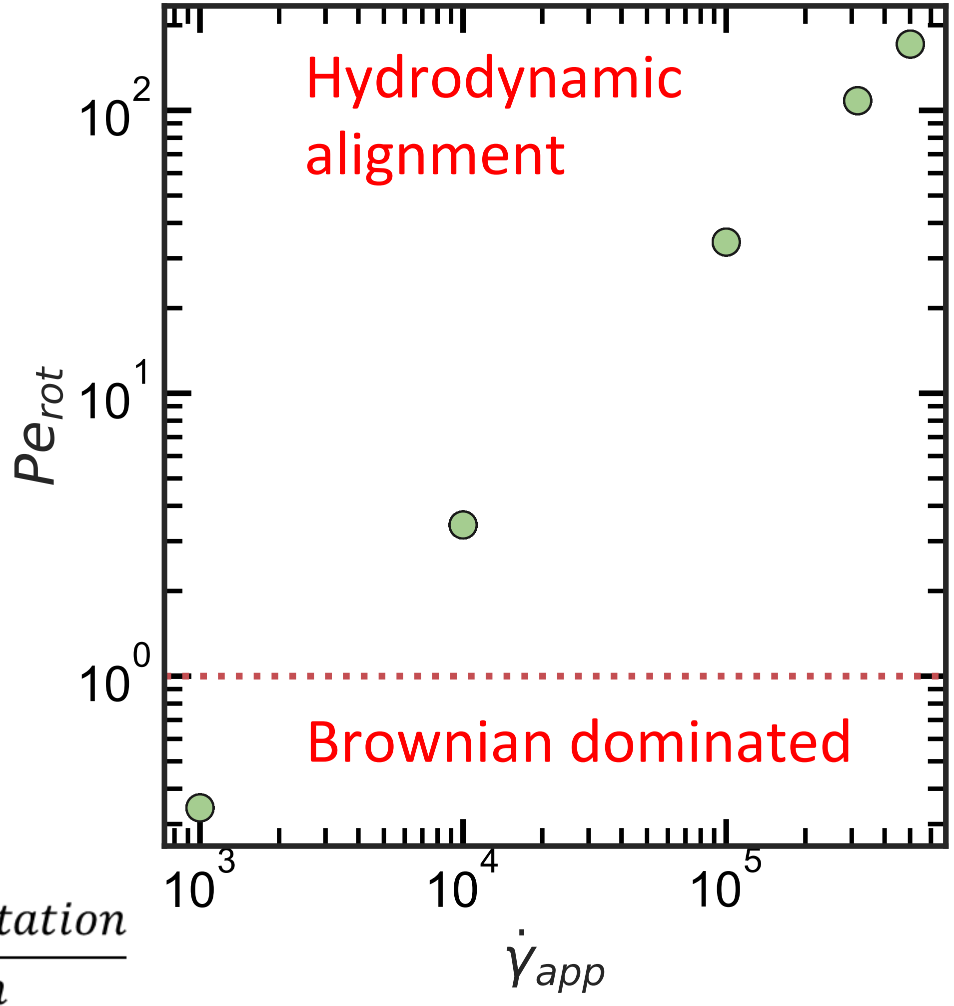


Bruker D2-Phaser, 30 kV, 10 mA, Cu Kα radiation source, single Si crystal zero-background specimen holder

Foster, E. J.; Moon, R. J.; Agarwal, U. P.; Bortner, M. J.; Bras, J.; Camarero-Espinosa, S.; Chan, K. J.; Clift, M. J. D.; Cranston, E. D.; Eichhorn, S. J.; et al. *Chem. Soc. Rev.* **2018**, *47* (8), 2609–2679.
Sutliff, B. P.; Farrell, C.; Martin, S.M.; Bortner, M. J.. *Carbohydr. Polym.* **2023**, *In preparation*.

CNC concentration/stress rate dependence on attrition



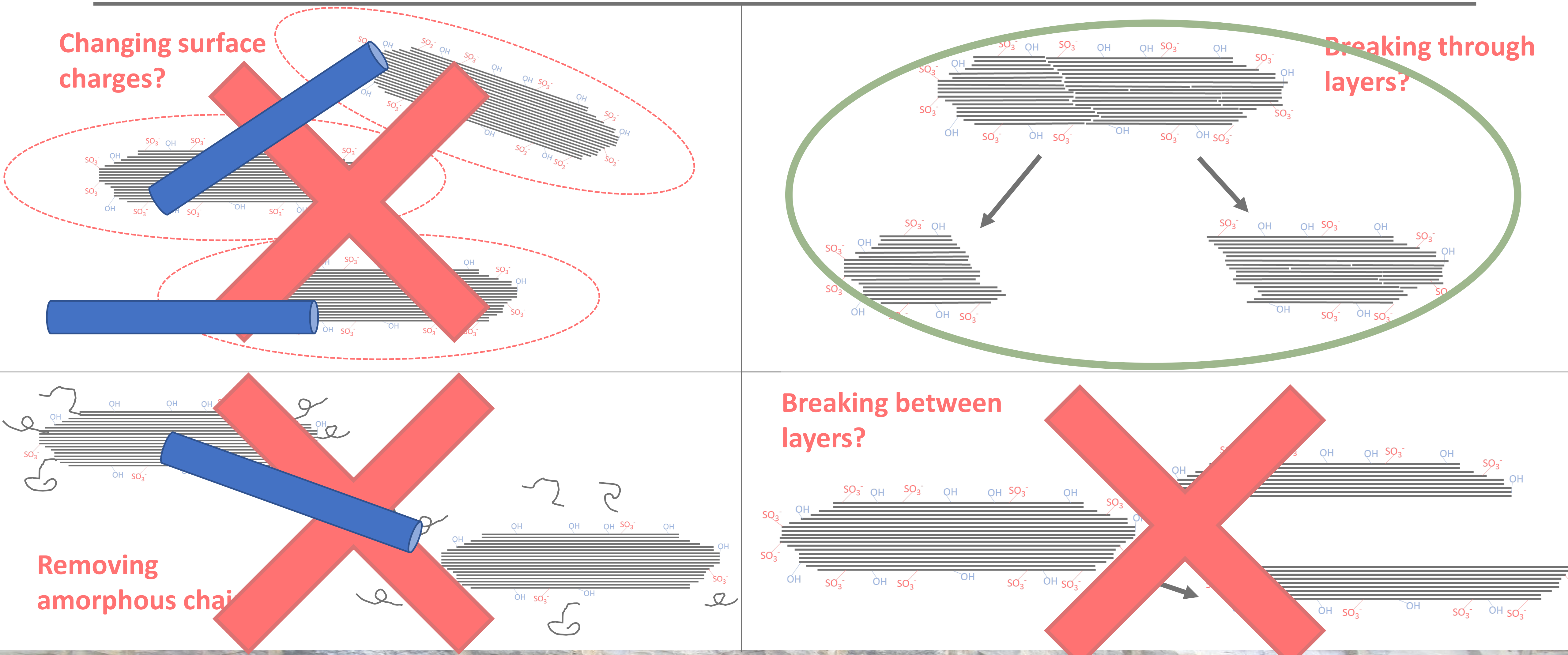


$$P\acute{e}_{rot} \sim \frac{Shear - induced\ orientation}{Brownian\ motion}$$

Sutliff, B. P.; Farrell, C.; Martin, S.M.; Bortner, M. J.. *Carbohydr. Polym.* **2023**, *In preparation*.

mVROC – E05 chip – 50 µm x 3000 µm

CNC – Potential causes of viscosity decrease



Changing surface charges?

Breaking through layers?

Removing amorphous chai

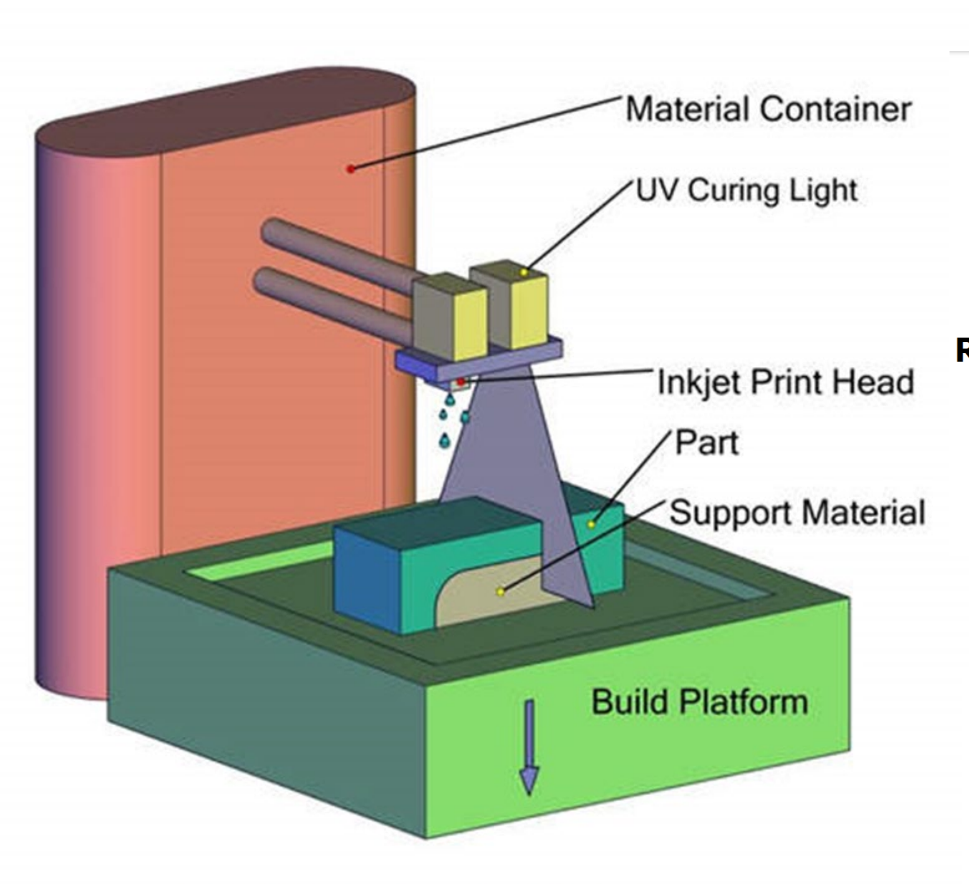
Breaking between layers?

Sutliff, B. P.; Farrell, C.; Martin, S.M.; Bortner, M. J.. *Carbohydr. Polym.* **2023**, *In preparation*.

7 Additive Manufacturing Modalities

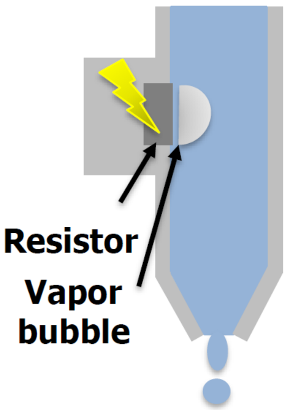
https://www.additivemanufacturing.media/cdn/cms/7_families_print_version.pdf

Material Jetting Overview



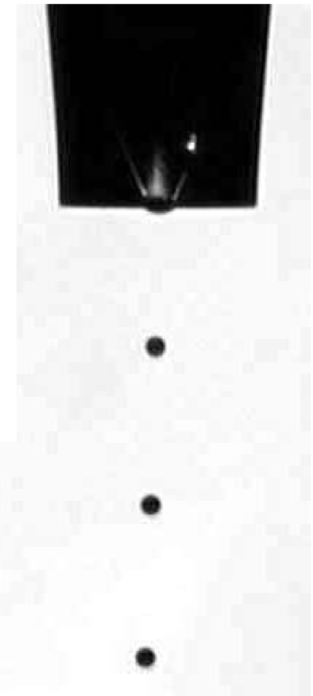
Material Jetting 3D Printing

Thermal inkjet print head



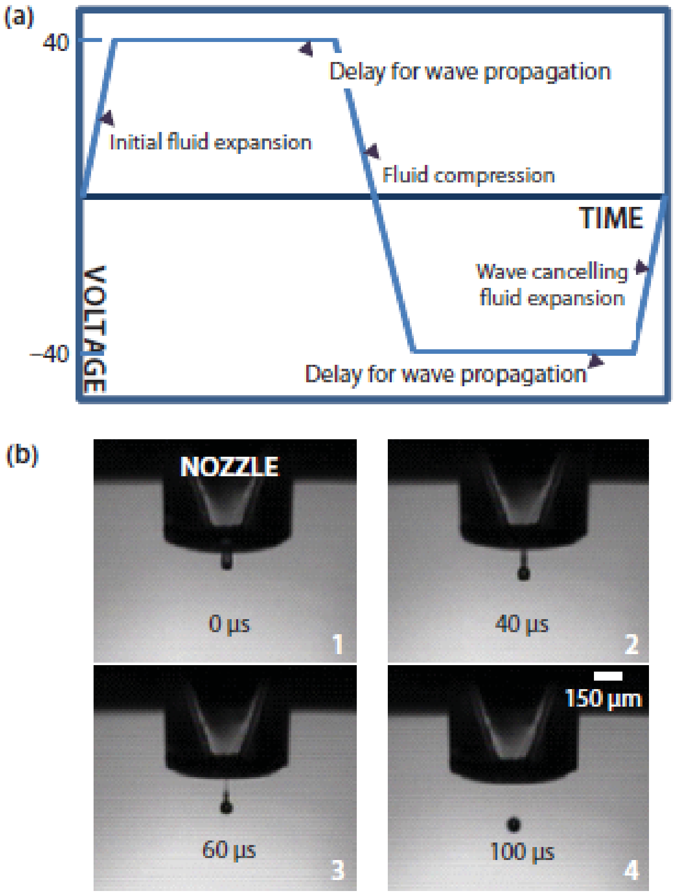
Electrical pulses heat the resistor to produce a vapor bubble

The vapor bubble forces a drop out of the nozzle



$$Oh = \frac{\eta_0}{\sqrt{\rho \sigma R_0}}$$

Piezo Process



https://www.tanerxun.com/principle-of-3d-printing-mj/.html

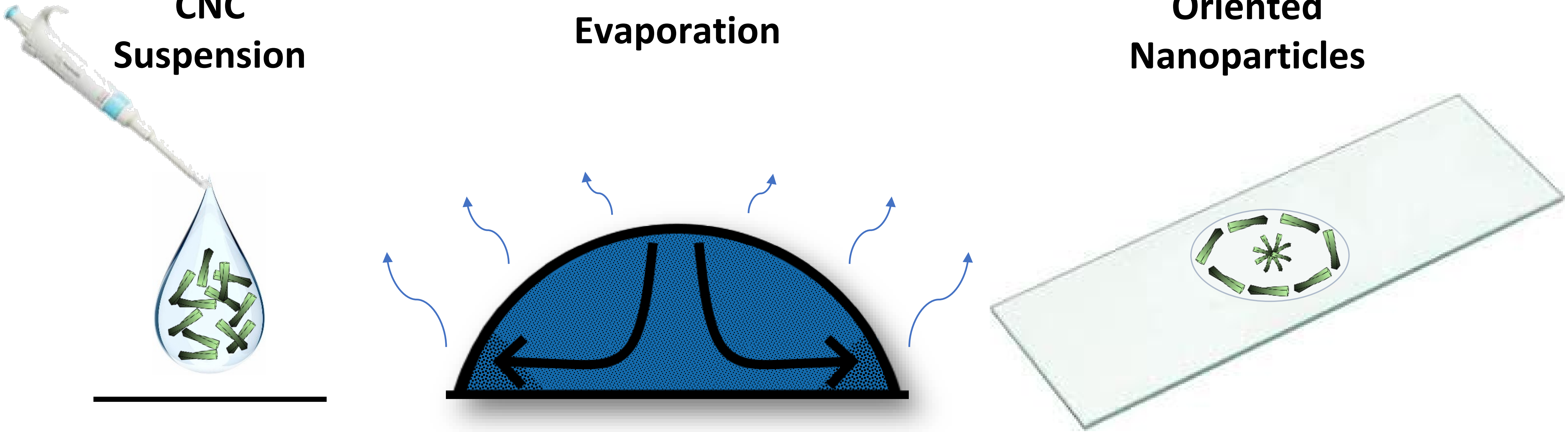
Telle et. al.; J. Eur. Ceram. Soc.; 2010, 30, 1669-1678.

Halley and Mackay, P. Eng. Sci., 36 (5) 1996

Droplet Evaporation

Novel droplet-based patterning method for rod-shaped particles

- Low energy input
- Multi-axis control
- Planar orientation -> no orientation normal to substrate



CNC Suspension

Evaporation

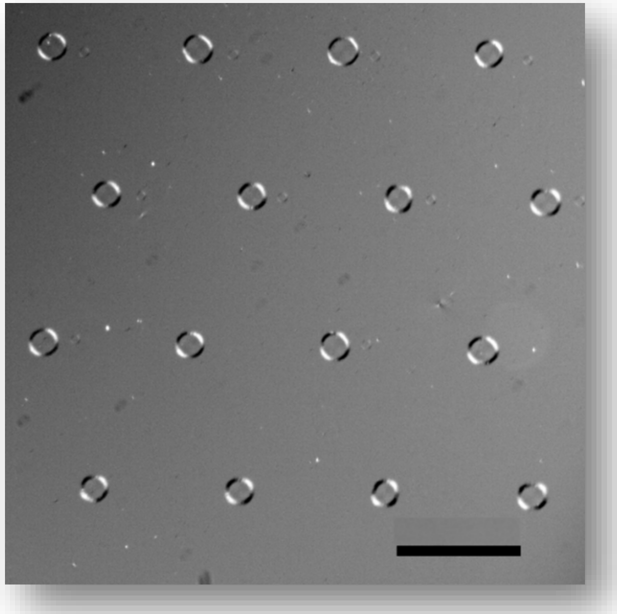
Oriented Nanoparticles

C.Q. Pritchard, F. Navarro, M. Roman, and M.J. Bortner, "Multi-axis alignment of Rod-like cellulose nanocrystals in drying droplets", Journal of Colloid and Interface Science, 603, 450-458 (2021)

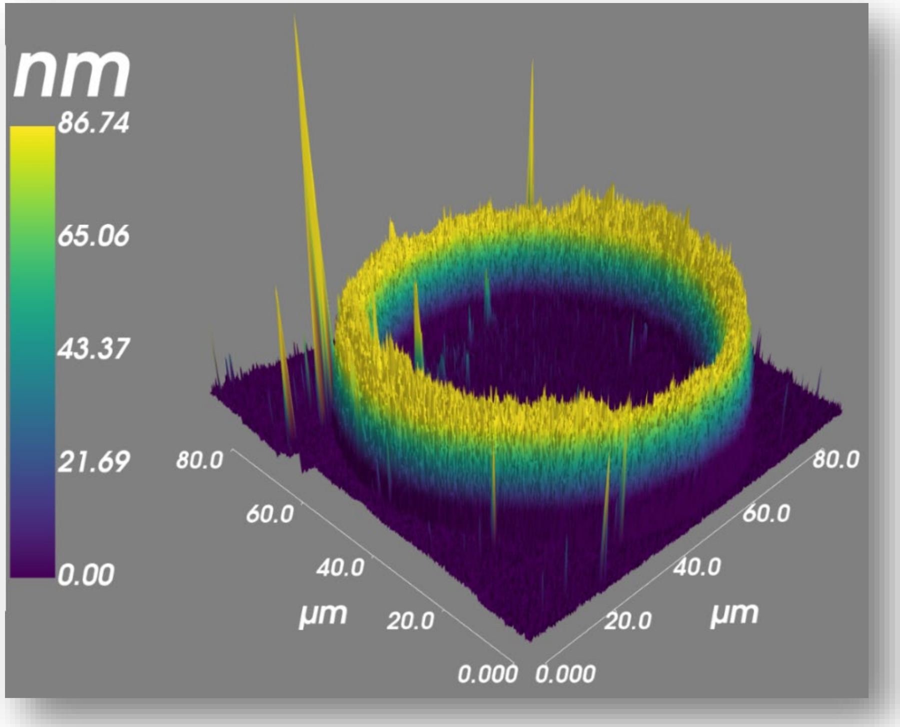
CNC Coffee Ring Deposition

- Deposition on CNC suspensions hydrophilic glass slides
  - $\theta = 30.1°$
- Constant contact area evaporation
  - pinned contact line

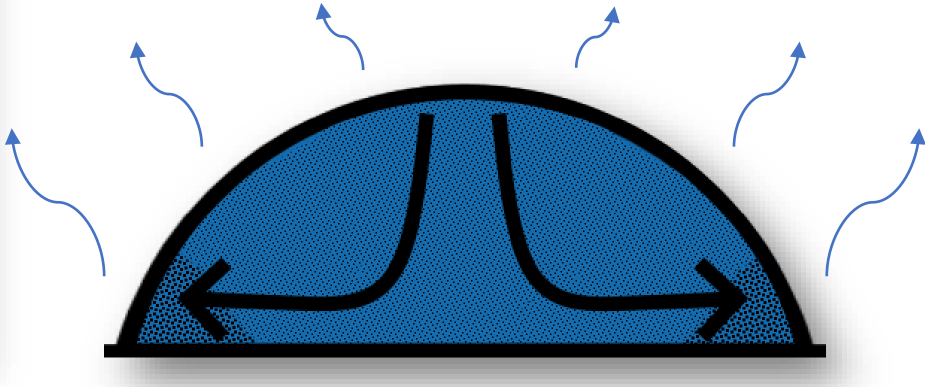
“3D-printed” CNC suspension



AFM Height Profile



Coffee-ring effect

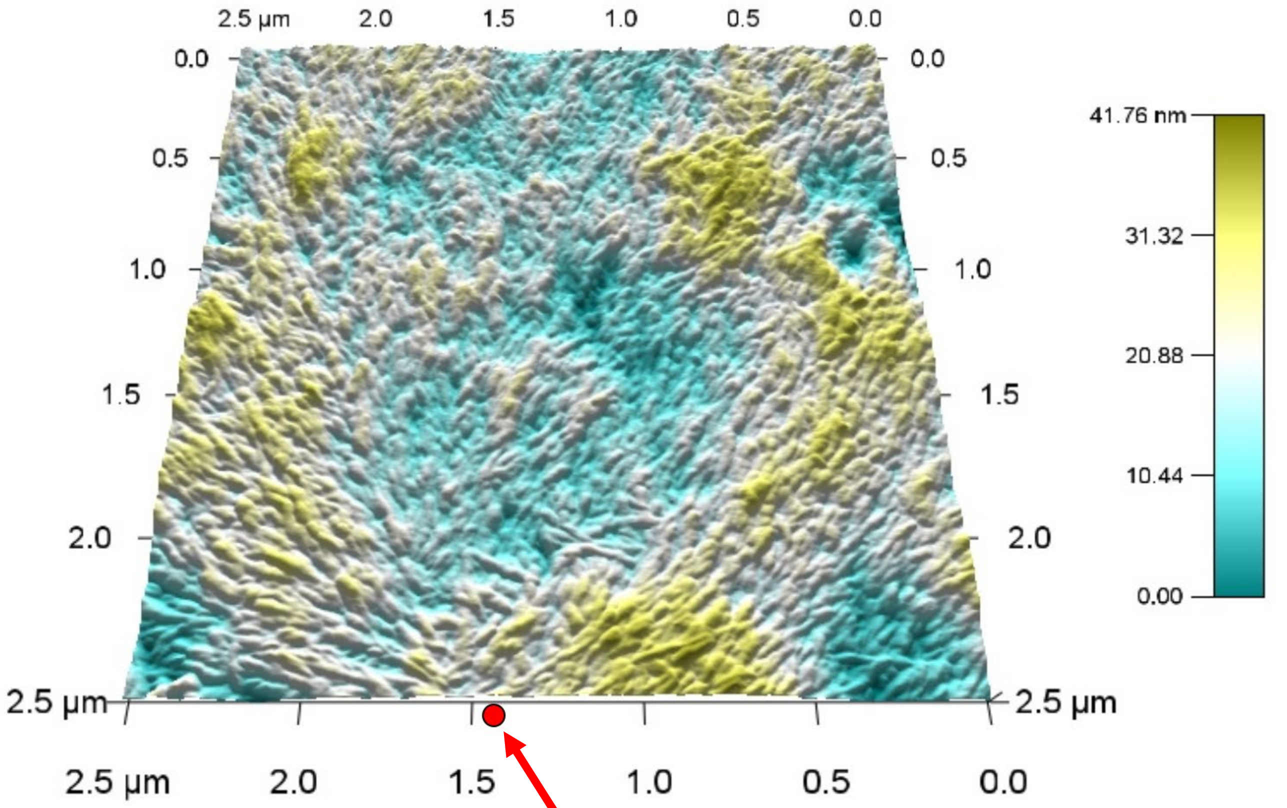


C.Q. Pritchard, F. Navarro, M. Roman, and M.J. Bortner, "Multi-axis alignment of Rod-like cellulose nanocrystals in drying droplets", Journal of Colloid and Interface Science, 603, 450-458 (2021)

CNC Orientation in Dried Droplets

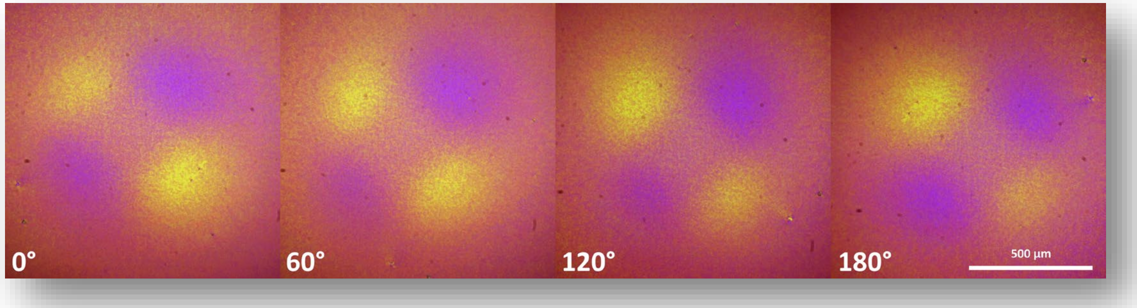
Inkjet-printed droplet height profile

Radial orientation near droplet center



Droplet center point

Polarized light microscopy +
1st order retardation plate (550 nm)



Radial Orientation

C.Q. Pritchard, F. Navarro, M. Roman, and M.J. Bortner, "Multi-axis alignment of Rod-like cellulose nanocrystals in drying droplets", Journal of Colloid and Interface Science, 603, 450-458 (2021)

Rotational Péclet Number

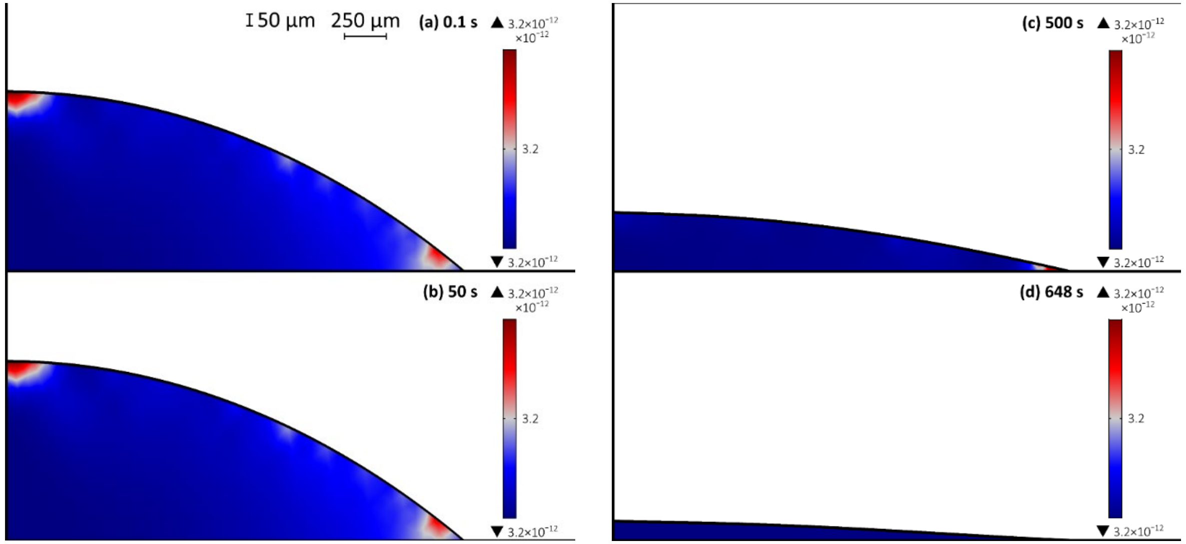
$$Pé_{rot} \sim \frac{Shear - induced\ orientation}{Brownian\ motion}$$

$$Pe_{rot} = \tau_{rot}\dot{\gamma}$$

$$\tau_{rot}^{-1} = \frac{3k_BT\left(ln2r_p - 0.5\right)}{8\pi\eta_s a^3}$$

- Pé$_{rot}$ > 1: shear flow drives orientation
- Pé$_{rot}$ < 1: Random orientation resulting from Brownian motion

CFD analysis of Pé$_{rot}$(t)



Evaporation Stage	**Shear Rate (s^{-1})**	**Pé$_{rot}$**
Pinned Contact Line	1.2×10^{-8}	3.2×10^{-12}
Receding Contact Line	100	0.15

C.Q. Pritchard, F. Navarro, M. Roman, and M.J. Bortner, "Multi-axis alignment of Rod-like cellulose nanocrystals in drying droplets", Journal of Colloid and Interface Science, 603, 450-458 (2021)

CNC Orientation Evolution

After placement

Tangential CNC orientation develops

Contact line depins

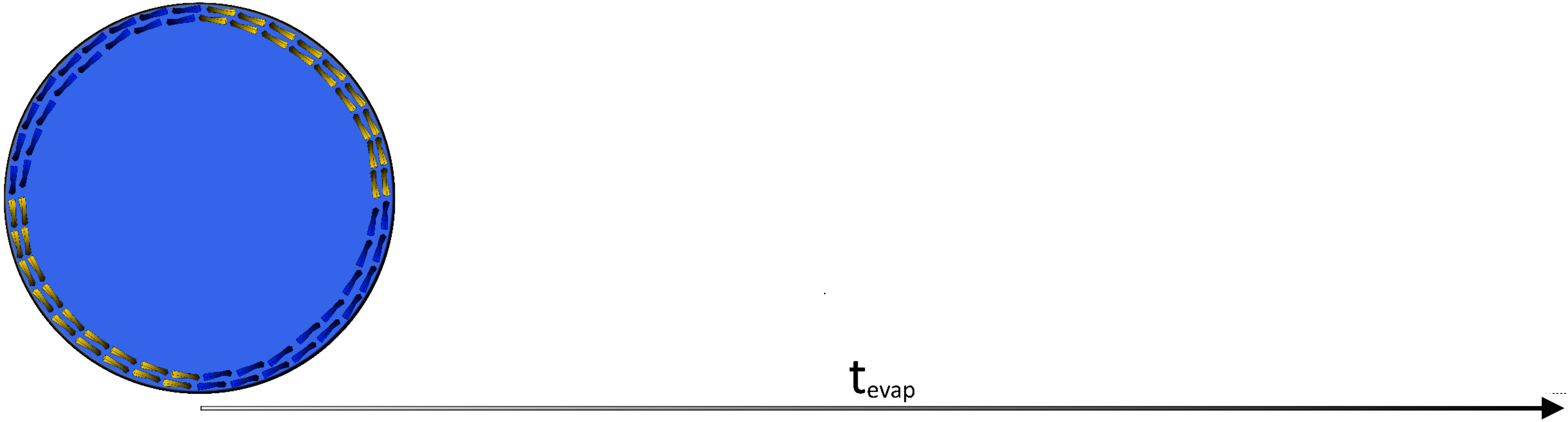
Radial CNC orientation in the vicinity of the contact line

Low CNC Concentration

CNCs lose neighbor interactions and maintain radial alignment imparted from contact line

Final Confinement

CNCs are compacted and interact once more resulting in generally tangential alignment



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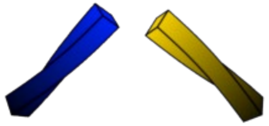
CNC Orientation Evolution

CNC Orientation Key



16x Playback Speed

0.25 µL droplet of a 2 wt % CNC suspension on an Alconox cleaned glass slide

Takeaway Messages

- AM rheological considerations strongly depend on AM modality
- CNCs - highly tailorable, wide range of rheological properties
- Chemorheology - thermal process windows/CNC degradation in high T processes (e.g. FFF, BAAM)
- Transient rheology – flow/solidification (yield stress/thixotropy) in low T ink printing (e.g. DIW)
  - CNC suspension chemistry/formulation
  - Yield stress sensitivity – apparent CNC breakage at low/moderate (likely because of Brownian driven rotation)
- Peclet/CFD analysis + microscopy - hydrodynamic alignment for drop-on-demand processes (e.g. material jetting)

Sutliff, B. P.; Kaplan, A.; Stutz, S.; Oxley, S.; Bortner, M. J.. *Cellulose.* **2023**, *under review*

Sutliff, B. P.; Farrell, C.; Martin, S.M.; Bortner, M. J.. *Carbohydr. Polym.* **2023**, *In preparation*.

Acknowledgements



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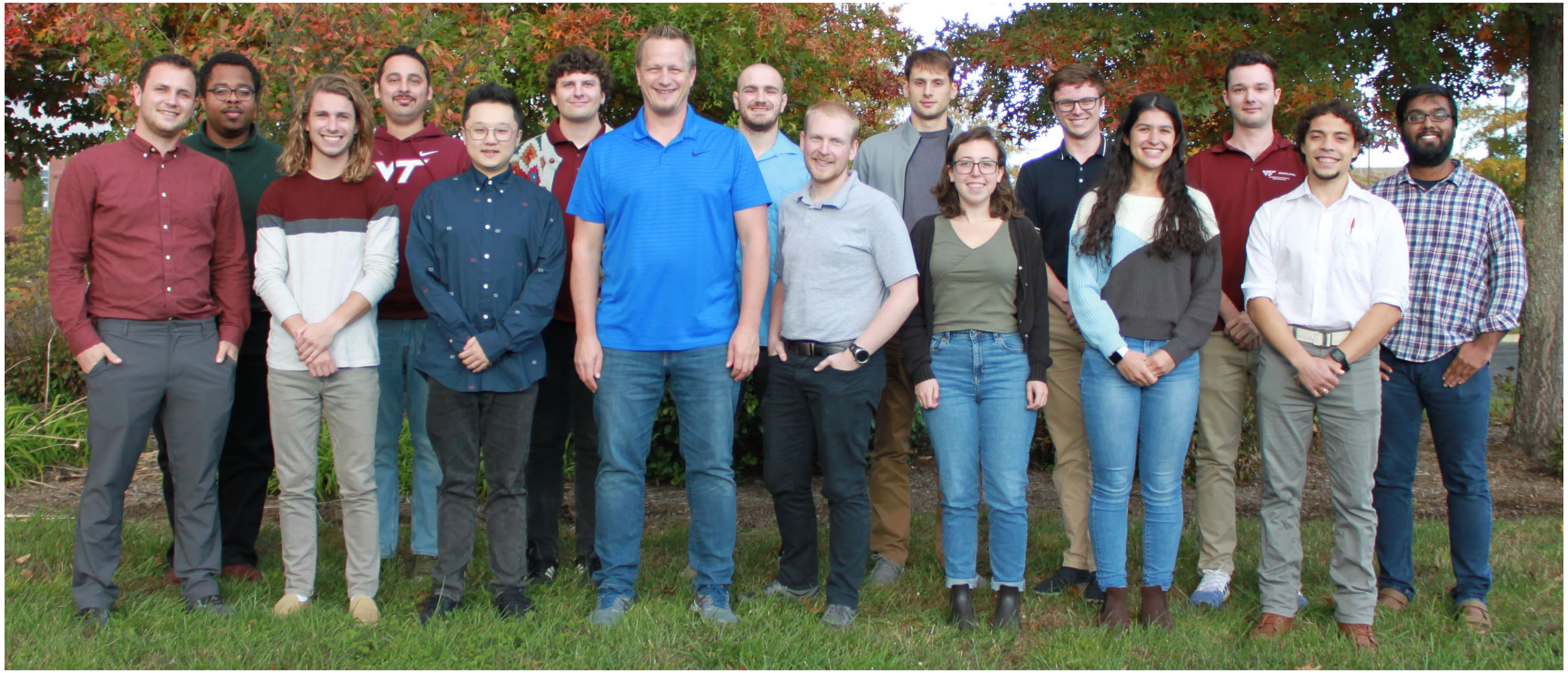

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