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Slot-die-coating operability windows for precision thin films and particulate coatings

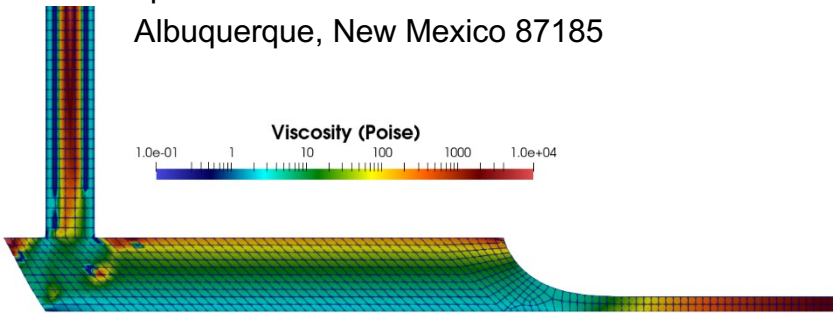
P. Randall Schunk (‡, §), Erin B. Creel (†), Kristianto Tjiptowidjojo (§), J. Alex Lee (¶), Kelsey M. Livingston (†), Nelson S. Bell (‡), Alexey Serov (†) , and David L. Wood III (†)

† Oak Ridge National Laboratory
Oak Ridge, TN 37831

§ University of New Mexico
Albuquerque, New Mexico 87131

¶ Saint-Gobain Research North America
Northborough, MA 01532

‡ Sandia National Laboratories[1]
Albuquerque, New Mexico 87185



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OUTLINE

- Motivation – Slot die coating
  - Advanced manufacturing tools for rapid process development
  - Understanding coating process window limits for new applications
- Capabilities and tools
  - Mod/sim tools and methods
  - Experimental and testing
- Low-flow limit
  - Precision applications
  - New understanding
- Particles–to-performance applications (Electrolyzers)
  - Experimental testing for single layer slot die coating
  - Coating window prediction
  - Validation
- Wrap-up and conclusions

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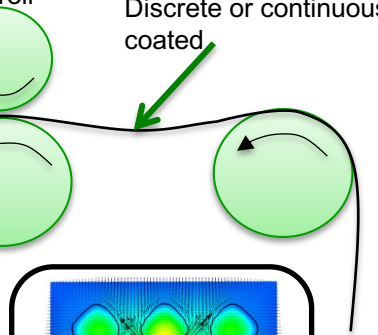
R2R Advanced Materials and Manufacturing

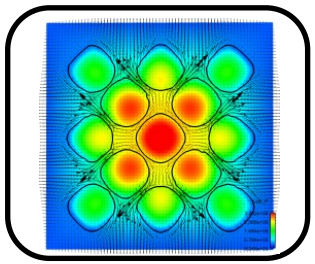
Oak Ridge National Laboratory
Argonne National Laboratory
R2R
Lawrence Berkeley National Laboratory
NREL National Renewable Energy Laboratory
Sandia National Laboratories

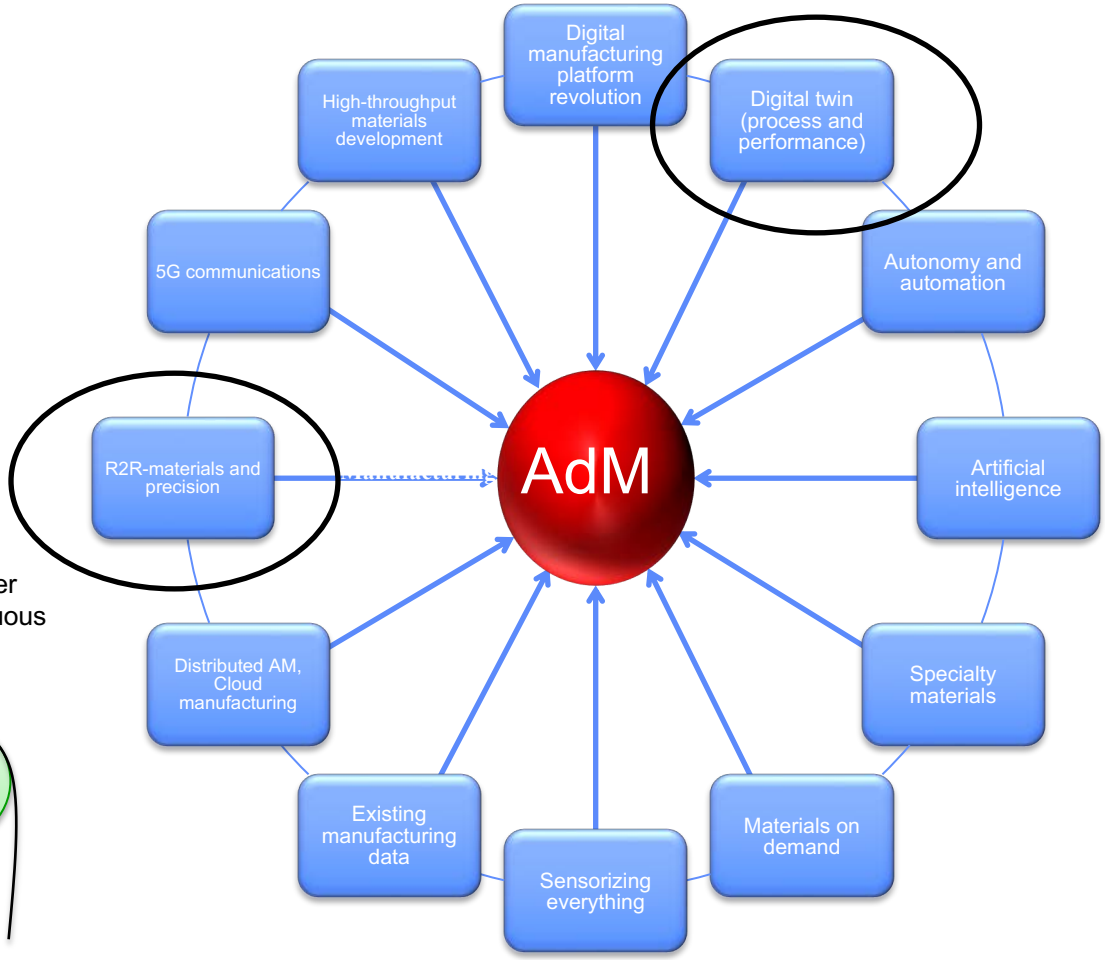
NASCENT

Imprinting/release Nip
(Gravure/patterned roll
On flexible roll)

Photoresist/polymer
Discrete or continuous
coated







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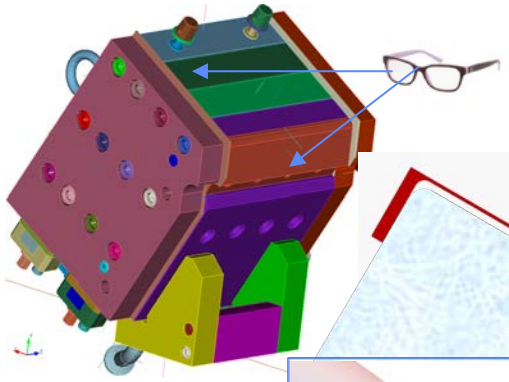
Modeling and Simulation for design and scale-up

Continuum Scale Models for process design and scale-up for energy conversion technologies (i.e. electrolyzers)

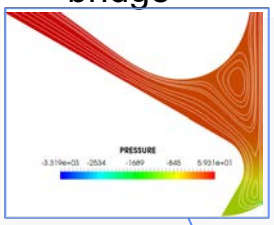
- Deposition models for single- and multi-layer slide, slot, and related coating methods
- Drying and solidification models that track thermal, diffusion, and other key physical rate processes
- Ongoing model validation from published literature and coating trials at ORNL and NREL
- Software platform based on open-source Goma 6.0 (gomafem.com) finite element software

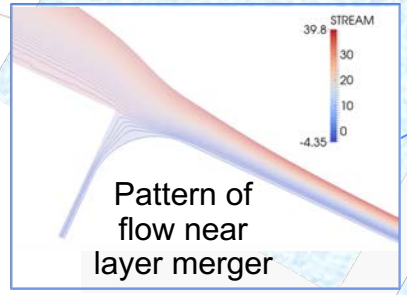


Solid Model- NREL 3 layer slide die

Coating Models of Capillary Hydrodynamics

Liquid bridge



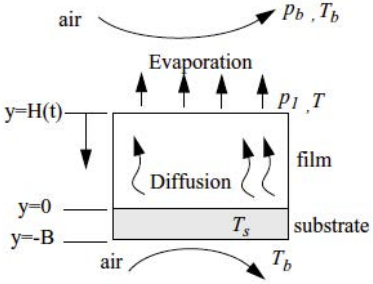


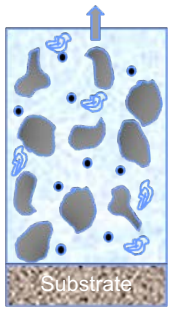
Pattern of flow near layer merger

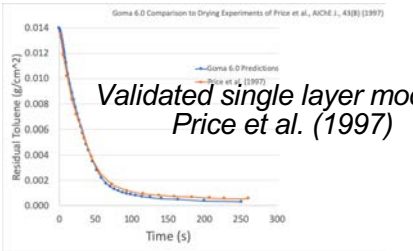
2-layer Slide die

Web

Drying Models: Reaction/diffusion/Energy transport







Validated single layer model – Price et al. (1997)

R&D 100 2014 Winner

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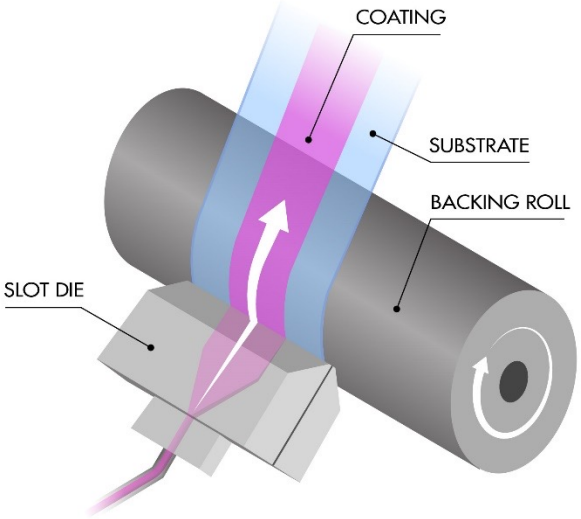
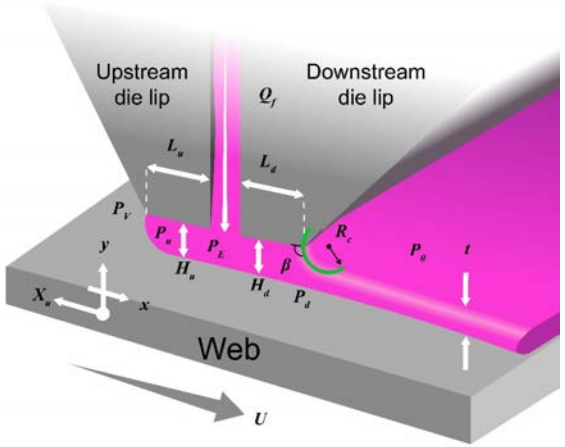
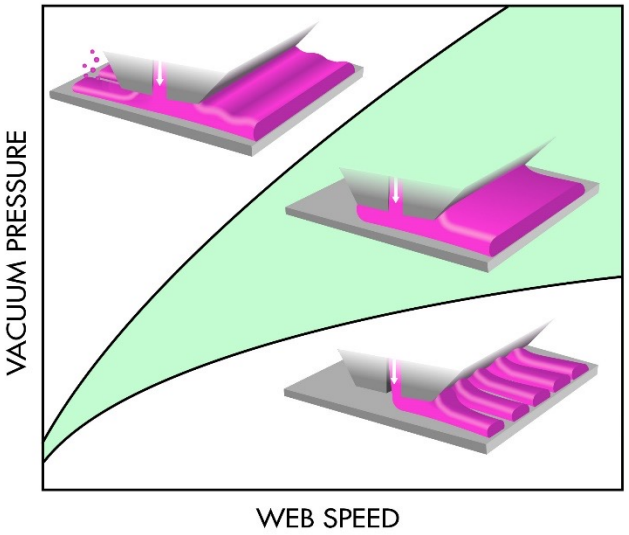
Slot-Die Coating



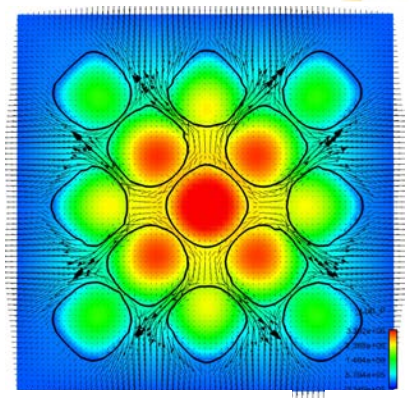


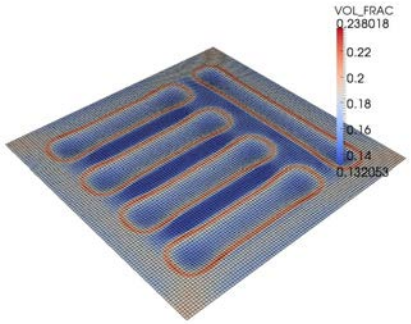


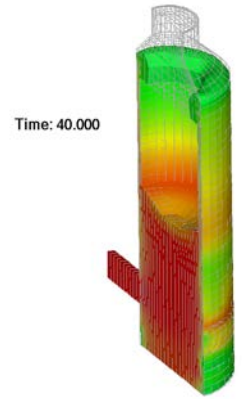
- A method ideal for ***precisely coating single or two layers***
- Thickness is set solely by flow rate and coating speed: $h = Q_f / U$ → ***premetered method***
- Coating quality, i.e. uniformity, depends on liquid properties and operating conditions – ***coating window***
- Goal: ***Predict coating window*** to guide process development

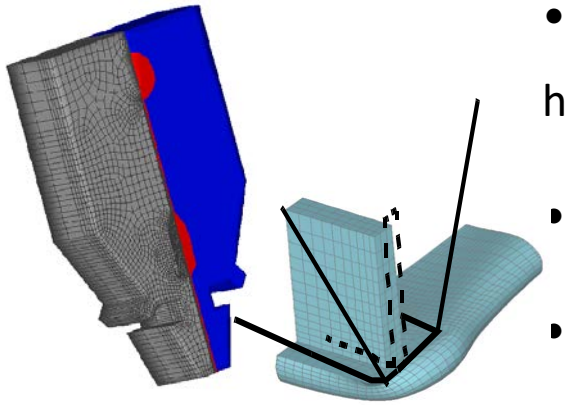
Research Group Capability: Goma 6.0

2014 R&D 100 Award Winner









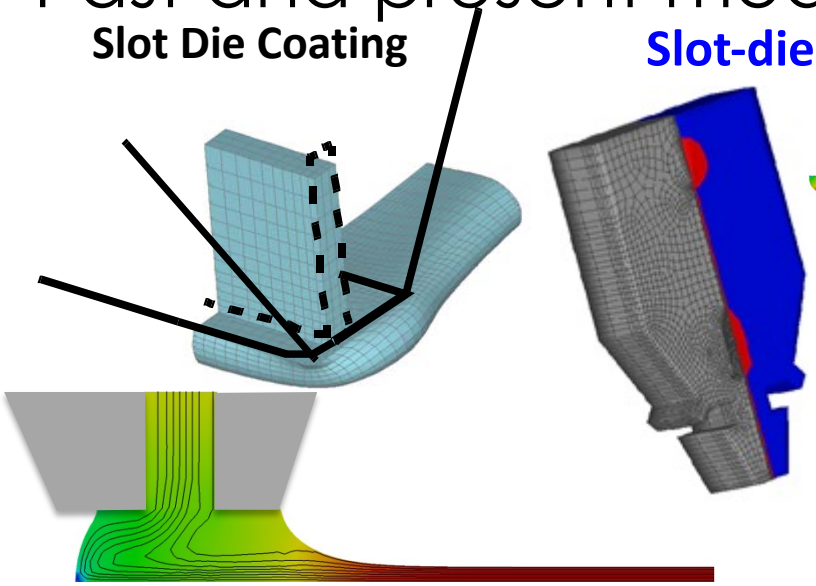
- Multiphysics ***finite element*** code, suitable for both ***research*** and ***production***
- Fully-coupled ***free*** and moving ***boundary*** parameterization – ALE, Level Set, etc.
- Modular code; ***easy to add equations*** – currently has 170+ differential equations
- ***Open source***! Available at **http://goma.github.io**
- ***Goma 6.0. training*** is available on regular basis

Goma has been used successfully in coating manufacturing for 2 decades!

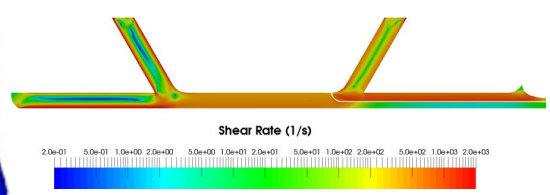
…Also a competency in LAMMPS for colloidal rheology and self/directed assembly

Past and present mod/sim efforts – Extrusion/SDC

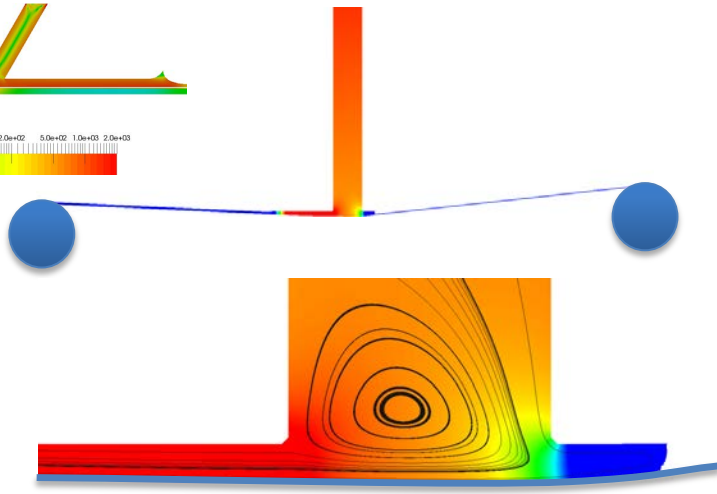
Slot Die Coating



Slot-die modalities



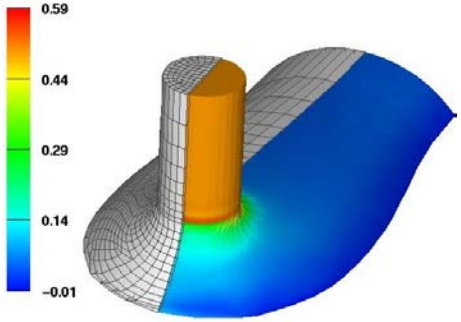
Tensioned Web over Slot Die Coating



Free Surface Tracking/Capturing

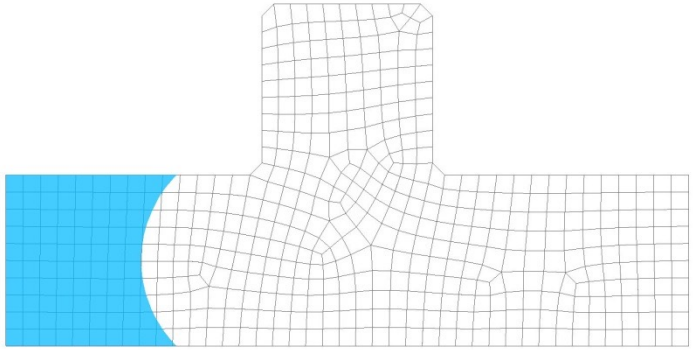
Arbitrary Lagrangian Eulerian (ALE)

Deform mesh to track free surface



Eulerian

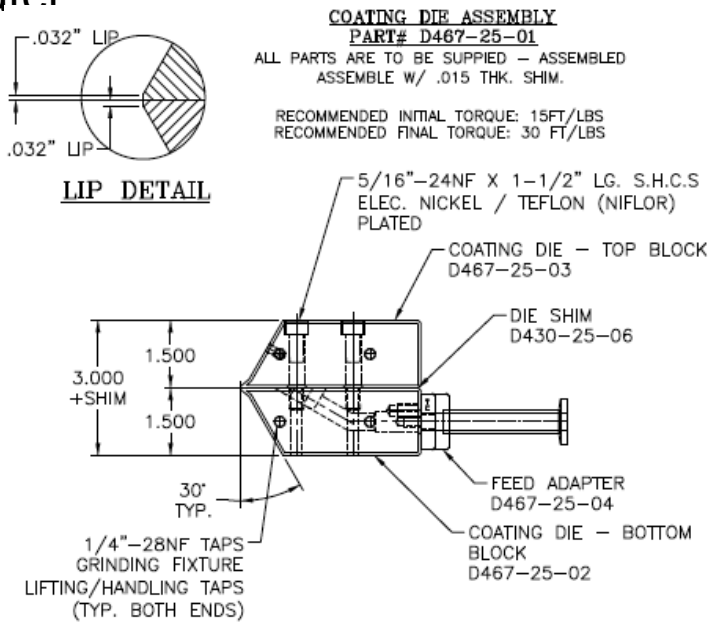
Fixed mesh, use level set to capture free surface



- ***Full 3-D simulation of continuous liquid film coating with finite element method***
- ***Capable of handling free surfaces two ways: ALE and level set method***

Coating Line – Slot-die configuration ORNL

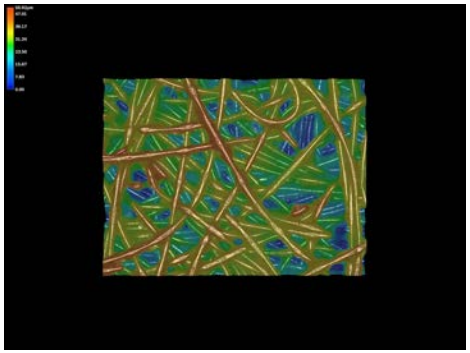
Starting geometry – ORNL Dynacoat Lab Coater



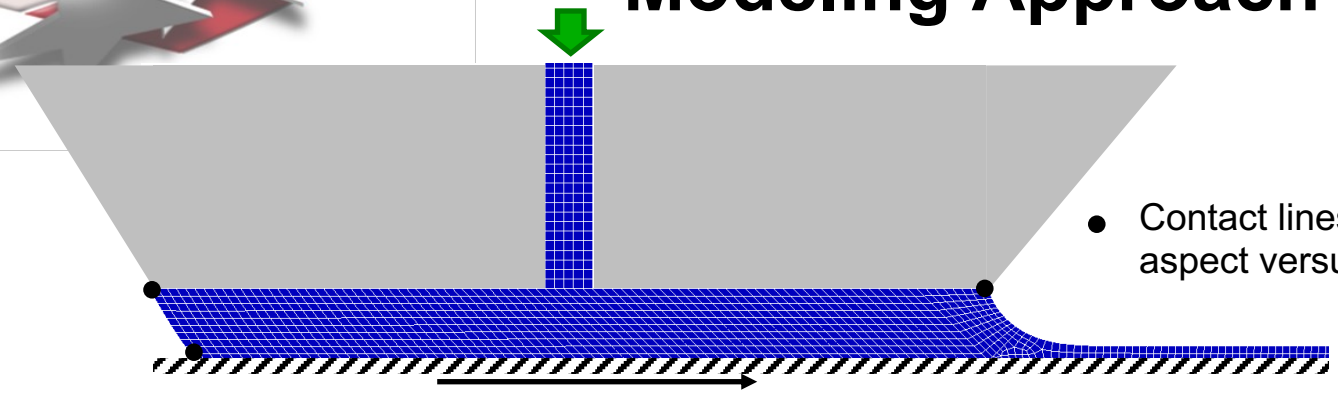
Coated side – 500x

Coated side – 2000x

Coated side – 500x

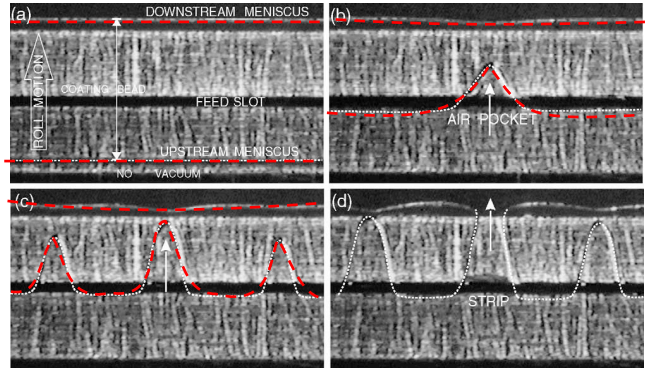


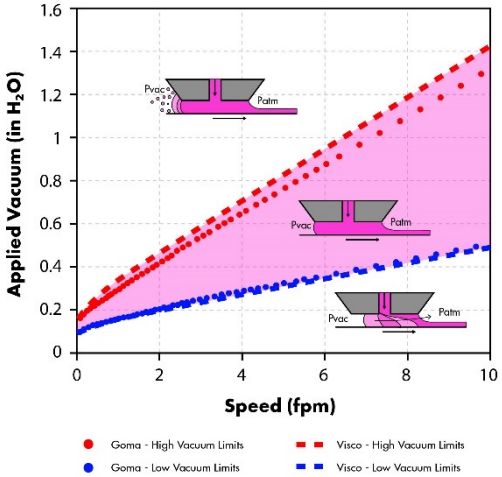
Modeling Approach



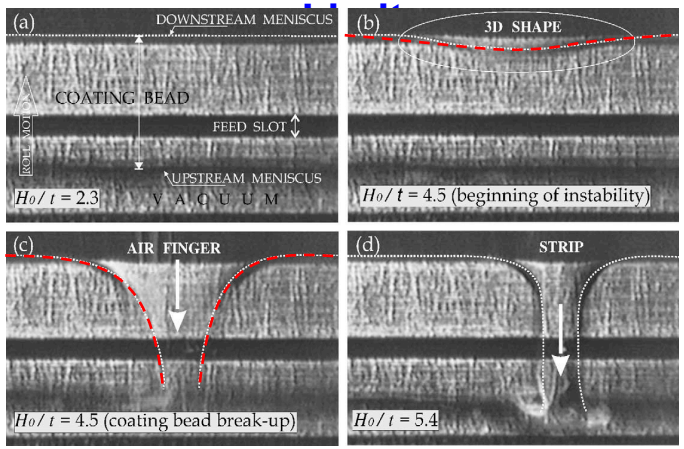
- Contact lines are not pinned; unique aspect versus literature

Low Vacuum Limit





Low Flow

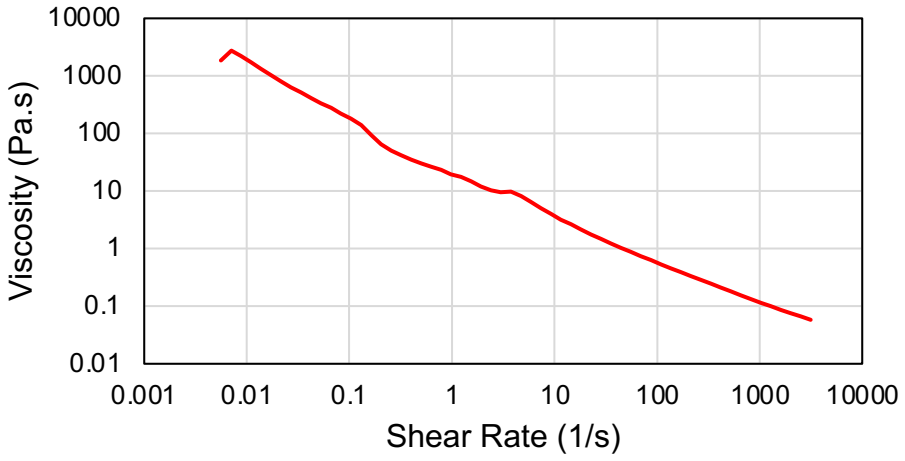


Romero et al. *Journal of Non-Newtonian Fluid Mechanics* 118.2-3 (2004): 137-156.

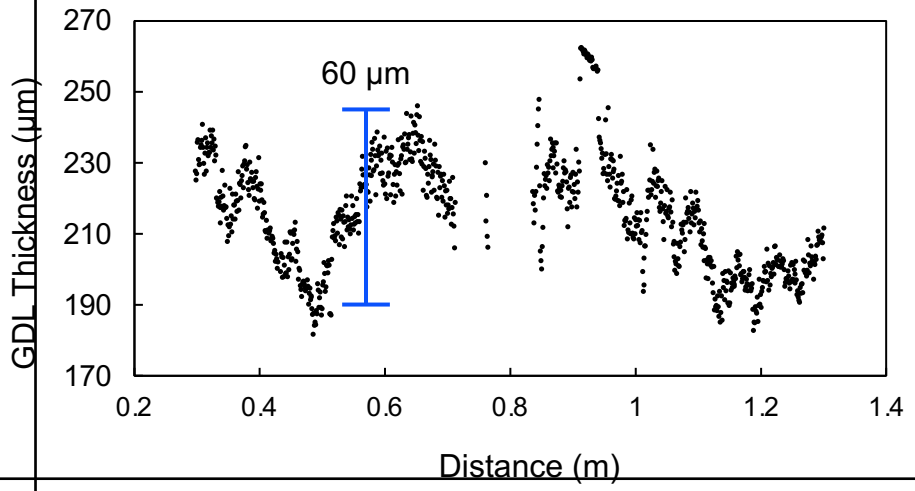
- 2-D steady state ***Navier-Stokes*** with ***arbitrary Lagrangian Eulerian*** (ALE) method to deform the mesh
- Predict coating window limits based on the ***contact lines positions***

Challenges with the Fuel Cell Cathode System

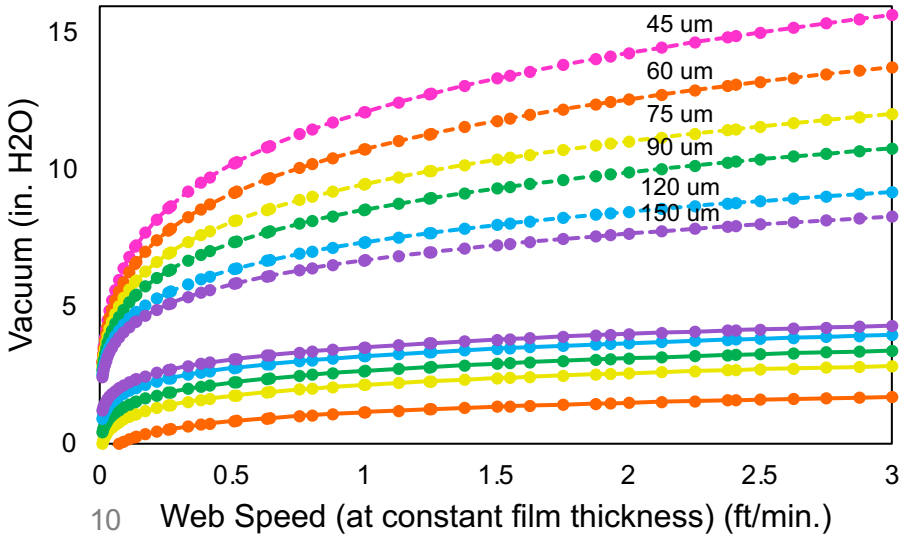
Viscosity and Shear Thinning of Ink



Variability in GDL Substrate Thickness



Window Narrows with Widening Gap



Hypothesis and Strategy

- Set minimum gap, d_{min}, knowing gap will widen during coating
- Target coating parameters in wide gap, d_{max}, window
- As the actual gap varies from d_{min} to d_{max}, we are in the window for all gaps
- First, validate model using thinner ink on uniform substrate

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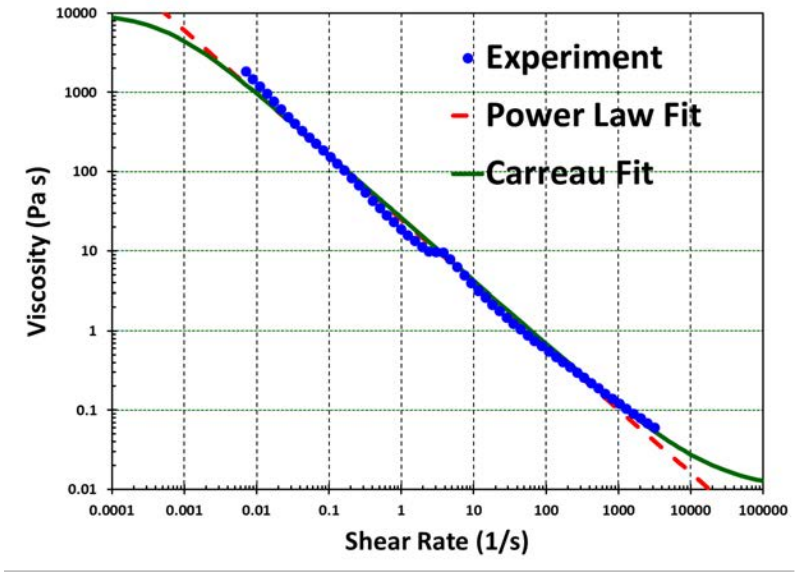
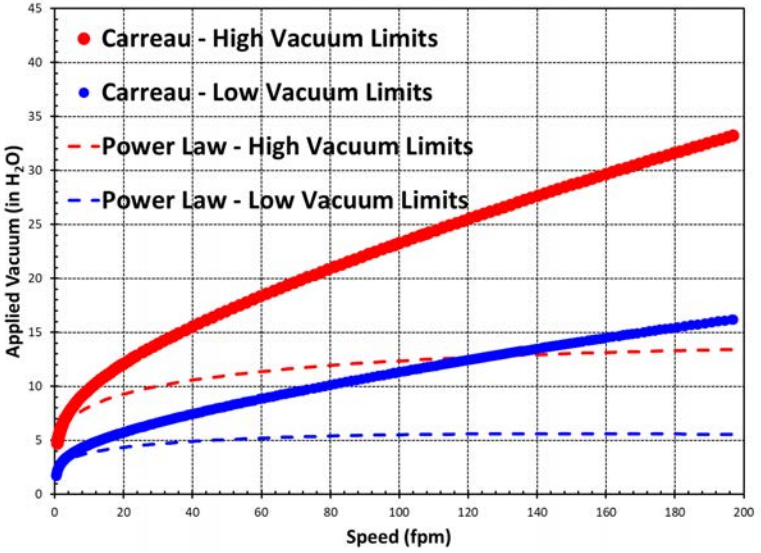
8% Pt – Wet thickness 30 µm – Gap = 150 µm

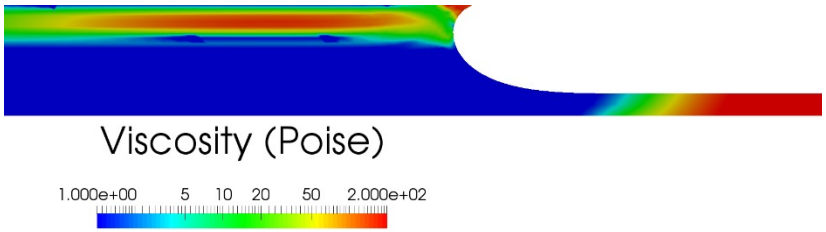
Operability Window Predictions



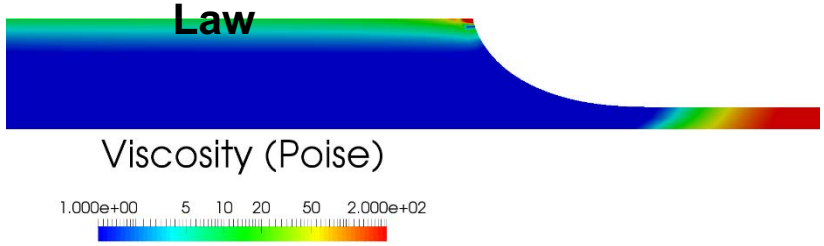


High vacuum limit – speed = 196 fpm

Carreau



Power Law



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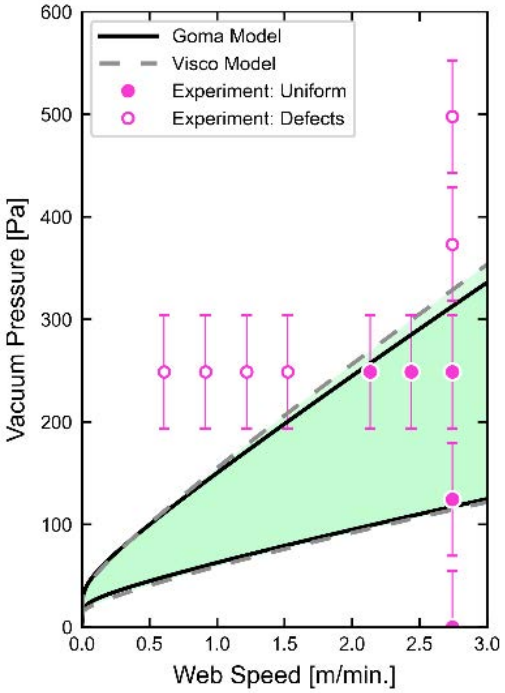
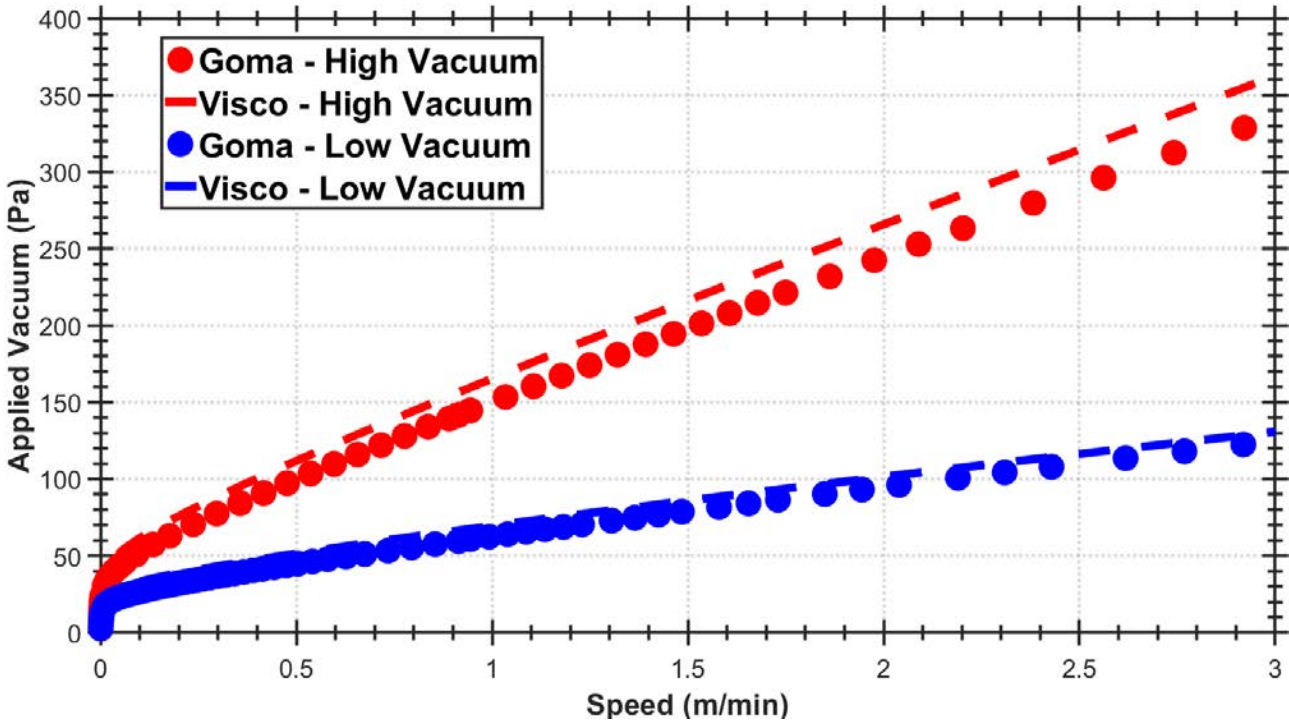
3.5 Wt% Pt – wet thickness = 60 μm, gap = 150 μm

Comparison With Experiments





- Coat on aluminum foil instead of GDL → minimize gap variation
- Prediction vacuum limits ***matches experimental observation at dilute ink*** – less shear thinning
- Viscocapillary and Goma predictions ***agree at low speed***. The discrepancy at higher speed is within each model's uncertainties

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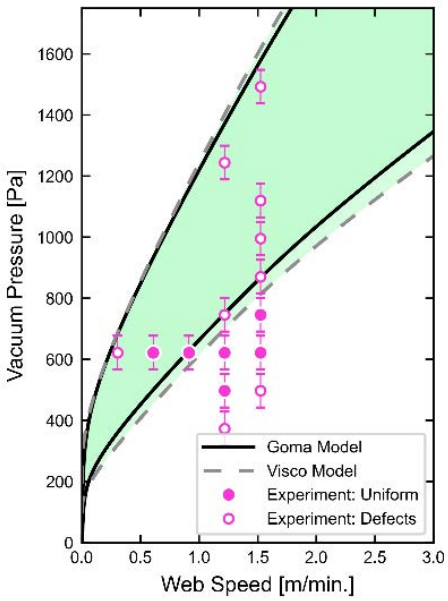
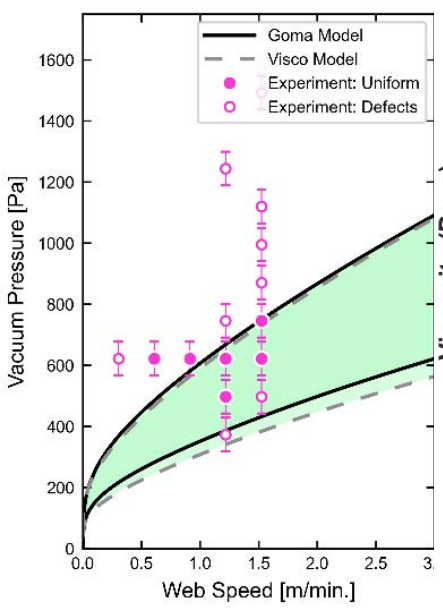
8.0 Wt% Pt – wet thickness = 30 µm, gap = 150 µm.

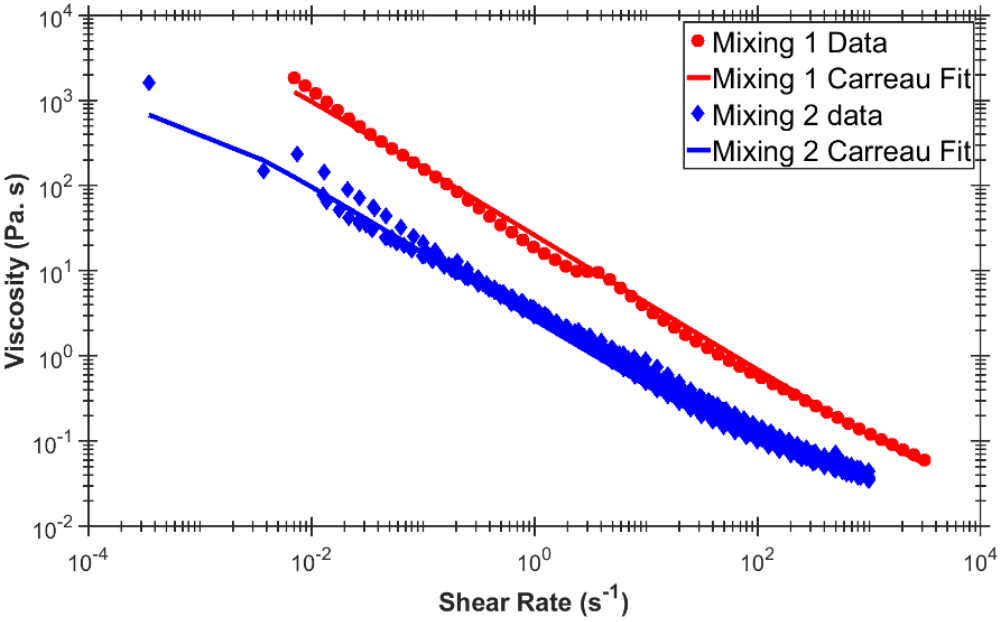
Comparison With Experiments

Rheology Fit 1



Rheology Fit 2





- Prediction of more concentrated ink is ***very sensitive to mixing procedures*** – sizes of aggregates → ink rheology
  - Viscosity 1 is measured at ORNL right after mixing procedure
  - Viscosity 2 is measured at SNL from re-mixing of samples sent from ORNL.
  - Coating trials are conducted 24 hours after mixing for de-gassing.

Enabling the Future


Decorative Films


Optical Films

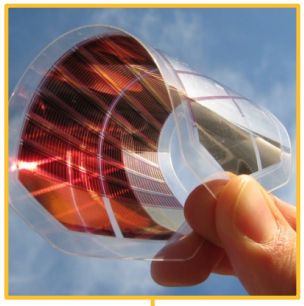
Modern Industries


Adhesives


Magnetic Films

Achieved

mm → µm
Film
Thickness


Organic Photovoltaics

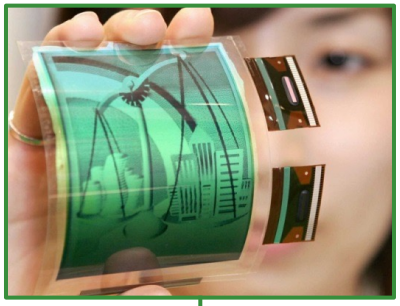
Current Innovations


Solid State Lighting

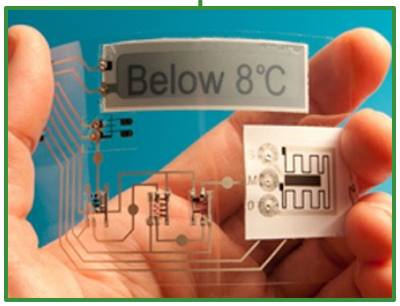
State of the Art
1-3 µm

Challenge

µm → nm
Thinner
Films!


Flexible Screens

Future Applications



Printed Electronics

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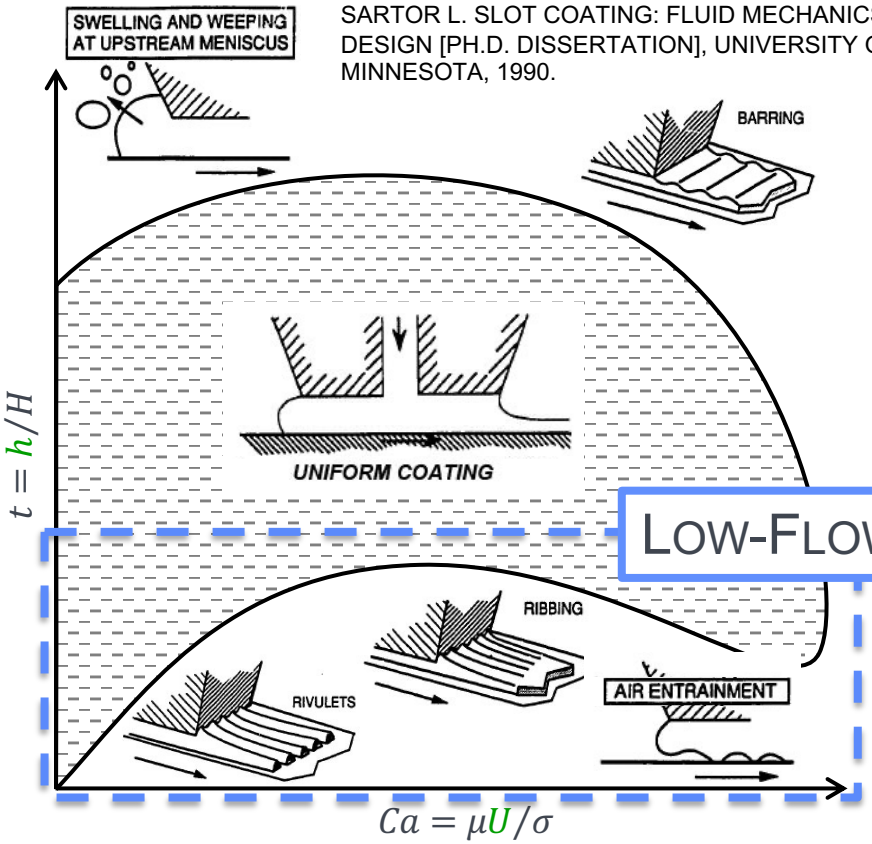
Operating Window & Coating Defects



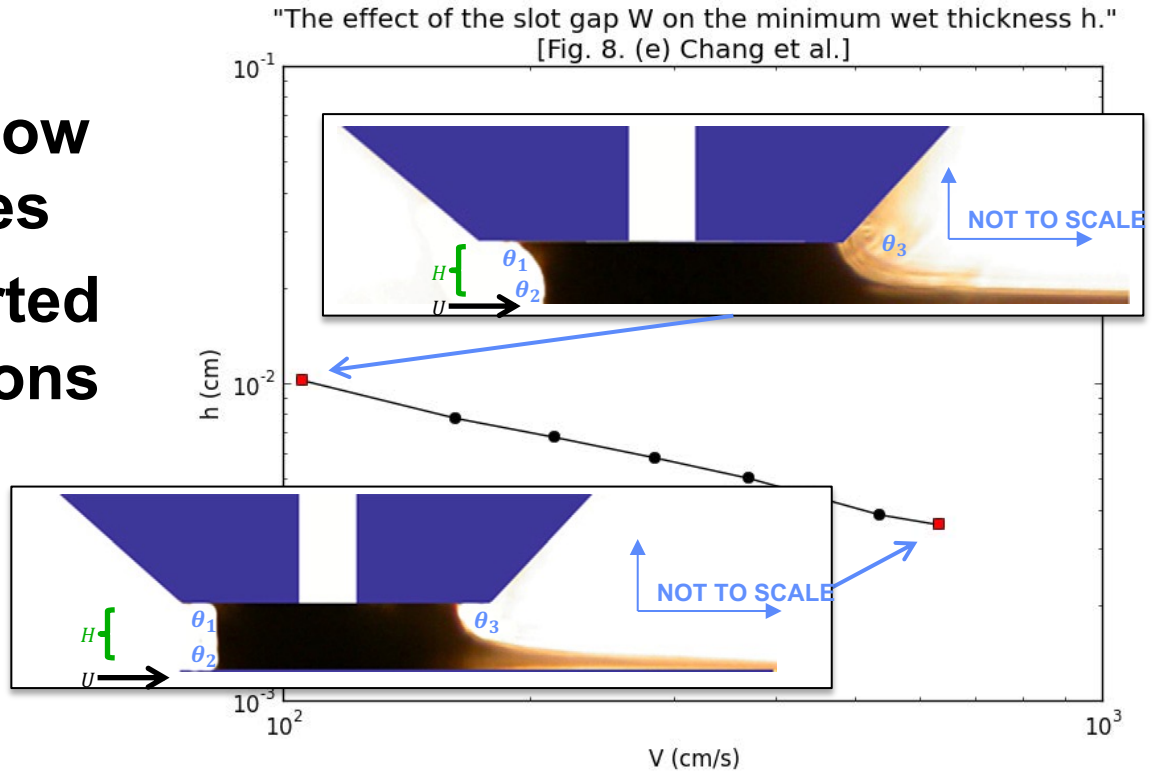
SARTOR L. SLOT COATING: FLUID MECHANICS AND DIE DESIGN [PH.D. DISSERTATION], UNIVERSITY OF MINNESOTA, 1990.

- **Window in which successful coating may be achieved**
- **Identify operating parameters that generate a thin liquid film**
- **Bound by hydrodynamic instabilities that cause defects**
  - **Weeping**
  - **Barring**
  - **Ribbing**
  - **Rivulets**
  - **Air Entrainment**

Validation

CHANG Y-R, CHANG H-M, LIN C-F, LIU T-J, WU P-Y. THREE MINIMUM WET THICKNESS REGIONS OF SLOT DIE COATING. *J COLLOID INTERFACE SCI.* 2007;308:222-230

- **Compare against experimental data**
- **Chang et al.**
  - **Reported low-flow limit thicknesses**
  - **Crucially, reported flow visualizations**



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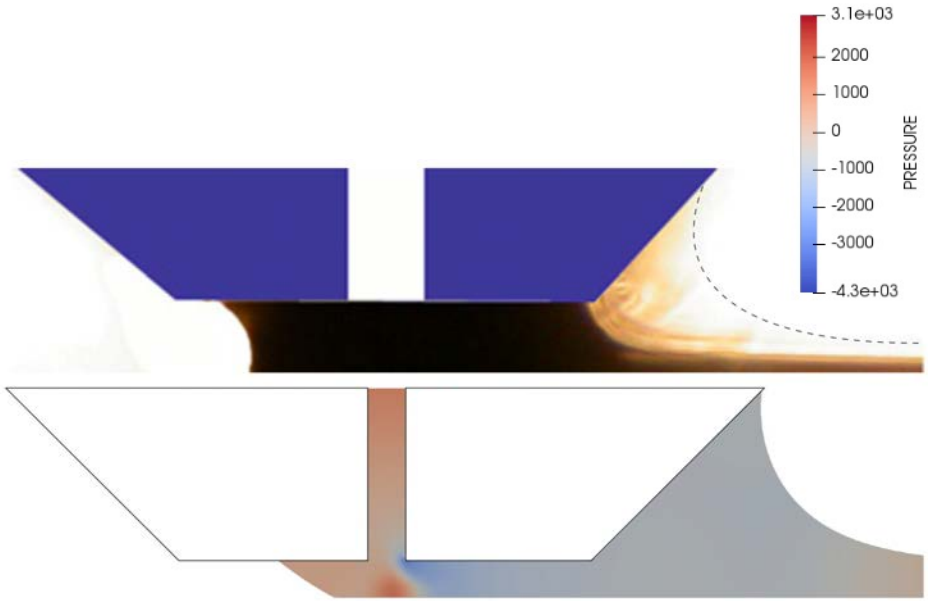
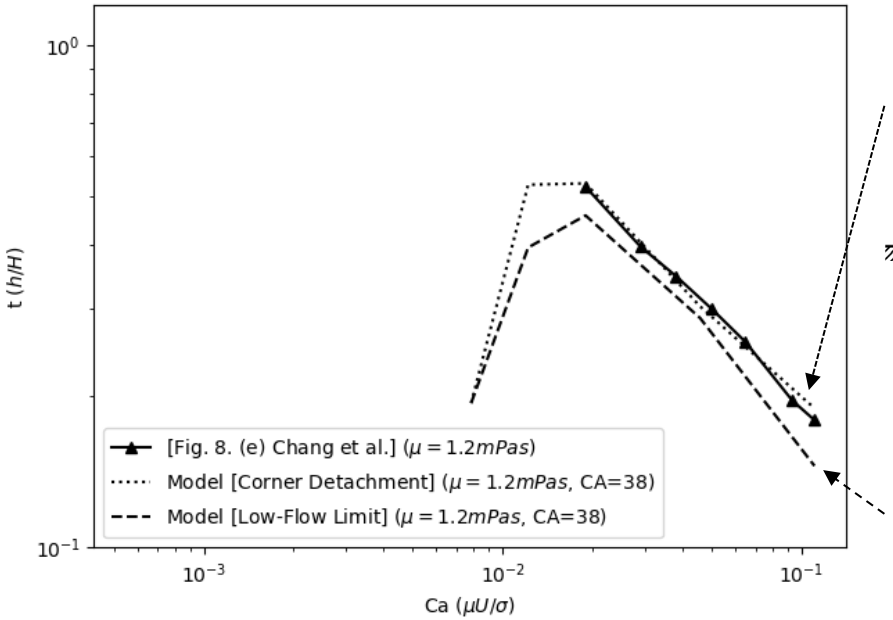
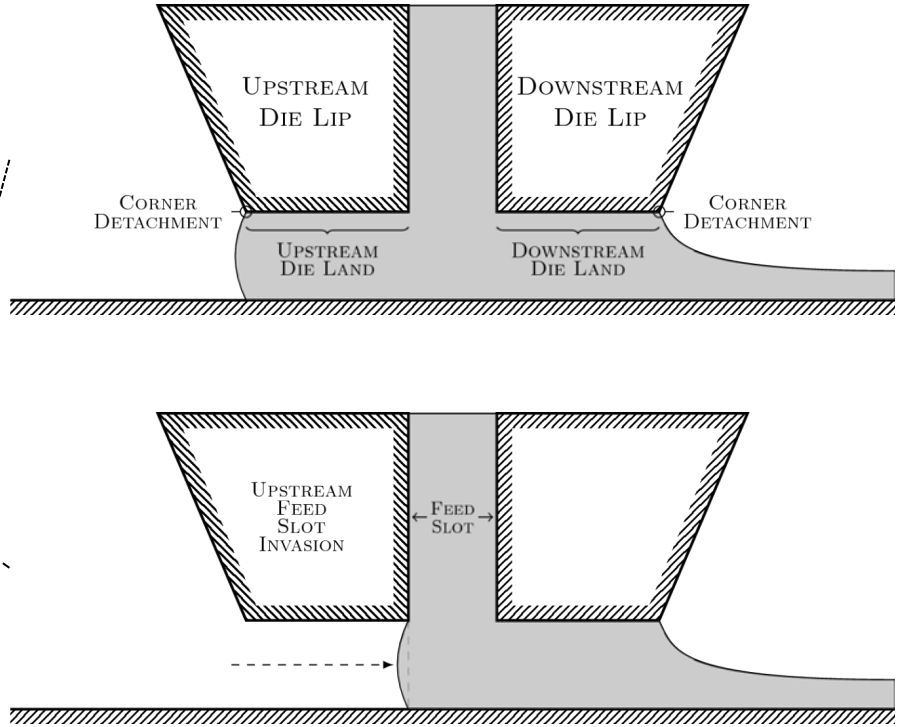
Validation

- Compare against experimental data
- Chang et al.
  - Reported low-flow limit thicknesses
  - Crucially, reported flow visualizations
- Allows direct comparison of meniscus topology
  - Not exactly aligned but encouragingly consistent

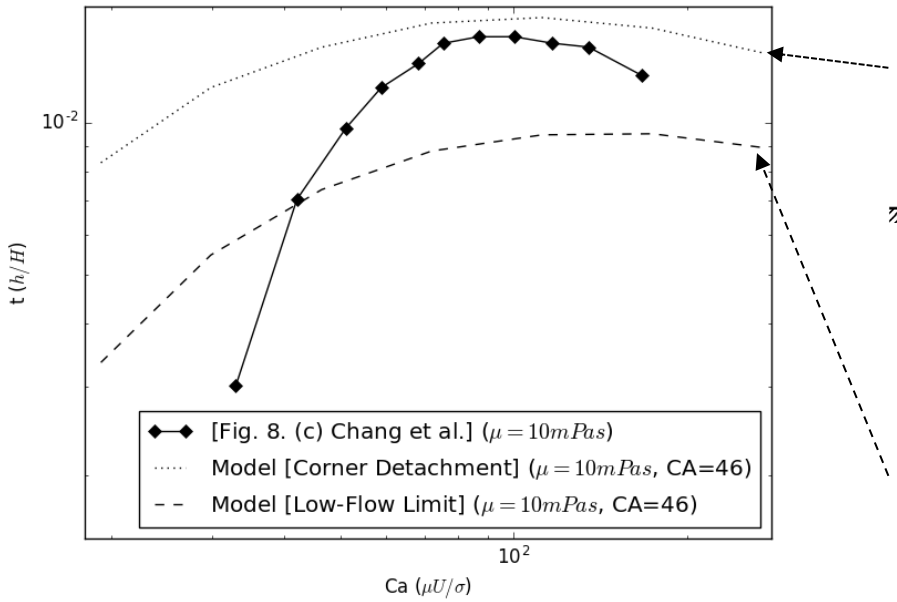


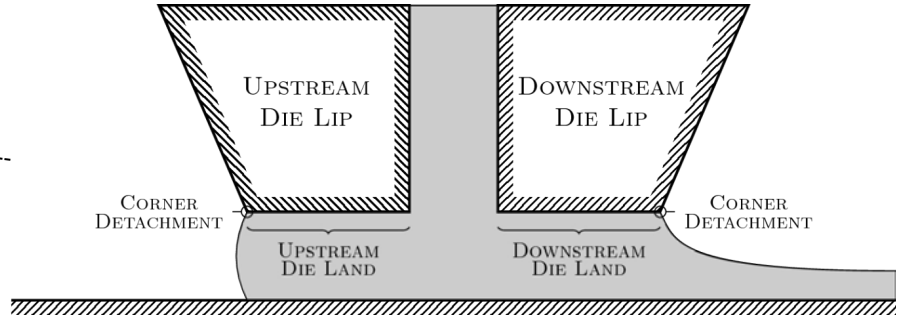
Model Validation – Low Viscosity

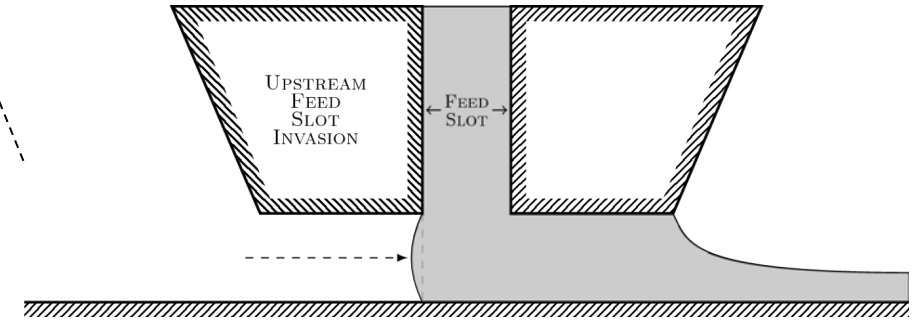




Model Validation – Mid Viscosity

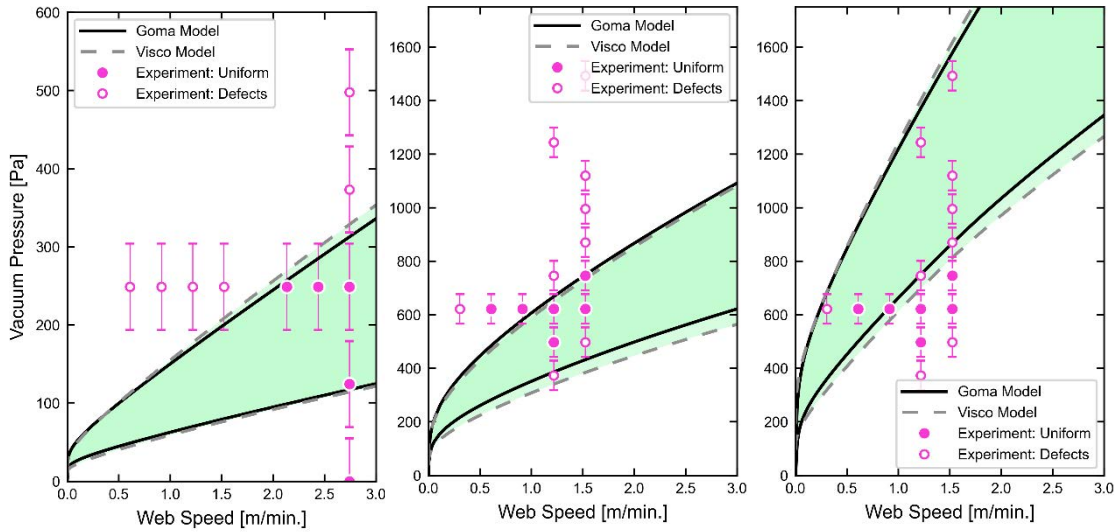






SUMMARY: Coating Window Prediction

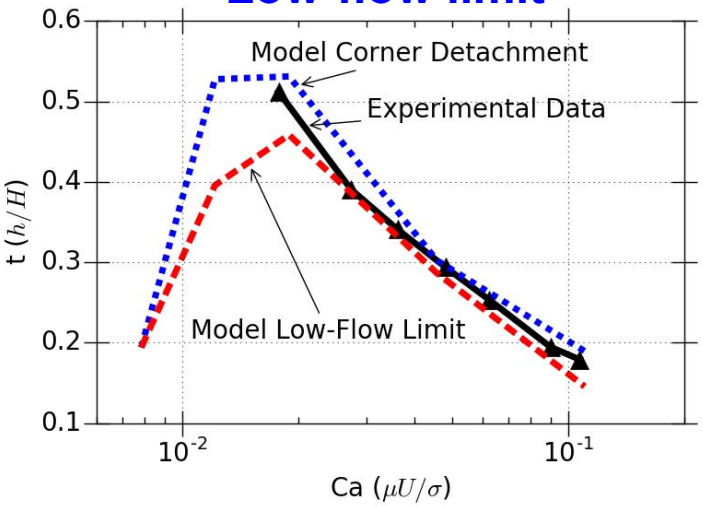
Vacuum limits



- Predicted vacuum limits of slot-coated fuel cell ink (Pt in black carbon support) – shear thinning rheology
- Prediction agrees with experimental observation

Creel et al. *Journal of Colloid and Interface Science* (2021).

Low-flow limit

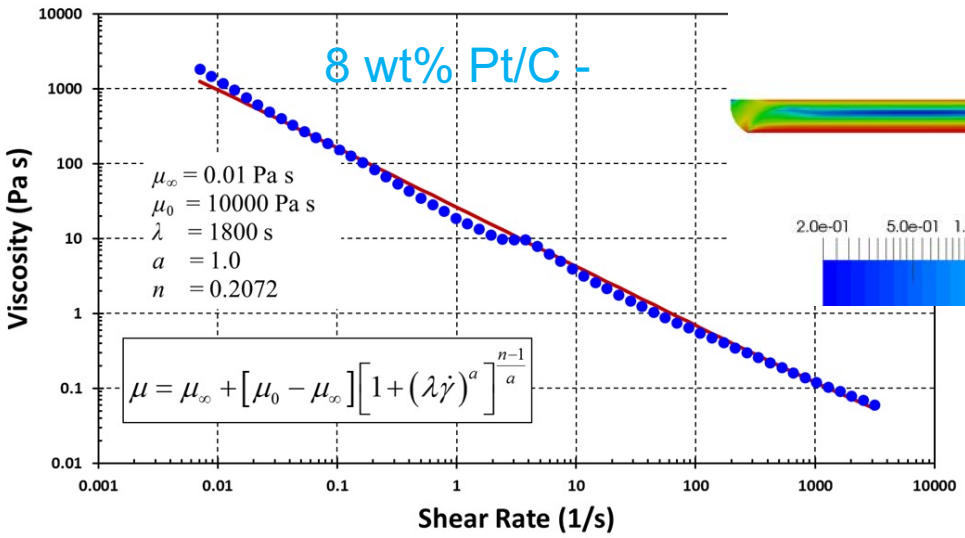


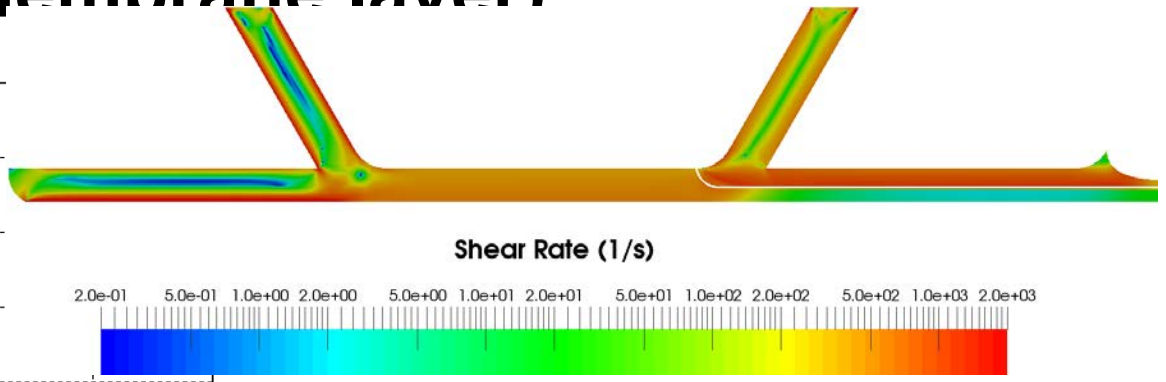
- Predicted low flow limits agrees with experimental works reported in literature
- Uncover physical mechanisms of low flow limits with no vacuum
- How to coat thinner: Smaller gap, but limited by roll runout and surface imperfection
- Another approach: Replace backing roll with tensioned web – ongoing research

Malakhov et al. *AIChE Journal* 65.6 (2019): e16593.

Backups and Future Work

Ink Rheology – MEA (catalyst layer and membrane layer)





8% (Pt/C)

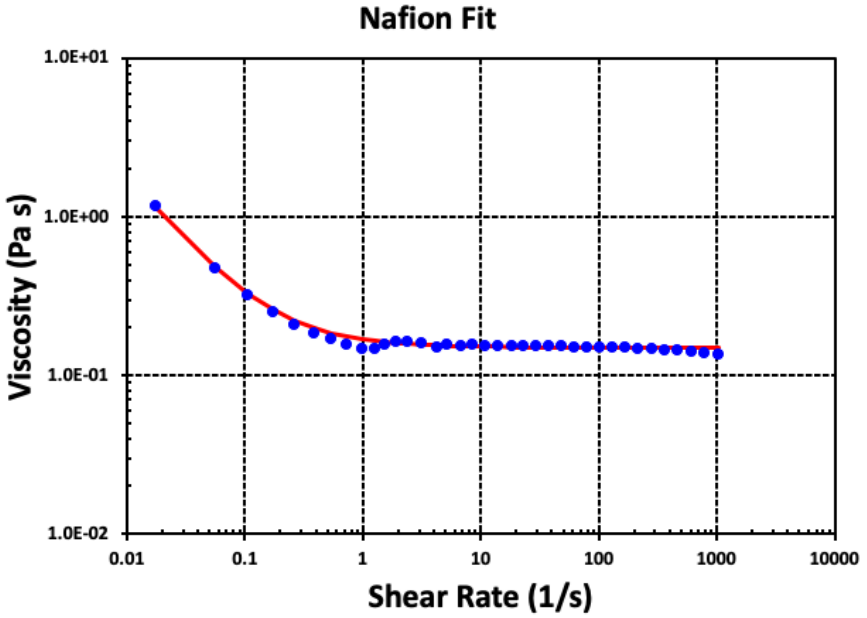
Pt/C : 32 g
Nafion : 76.64 g ≈ olid content= 76.64 g x 0.217 = **16.63 g** of Nafion
Water : 225 g
1-Propanol: 66.36 g

Total weight ≈ 400g

Total solid content: Pt/C + solid Nafion = 32 + 16.63 = **48.63 g**
% of solid content = 48.63/400 = **12.16 %**

Preparation: Shear mixed by using small shear mixture in ORNL dry room for 1.5 hours at 6000 RPM.

Slot-die coating conditions:
Pump speed (small pump cart) = 20 rpm (translate into flow rate or wet-film thickness)
Dynacoat line speed = 3 ft/min
0.584 mg-coating/cm² == 0.179 mg-Pt/cm²



SLOT-COATING SIMULATOR

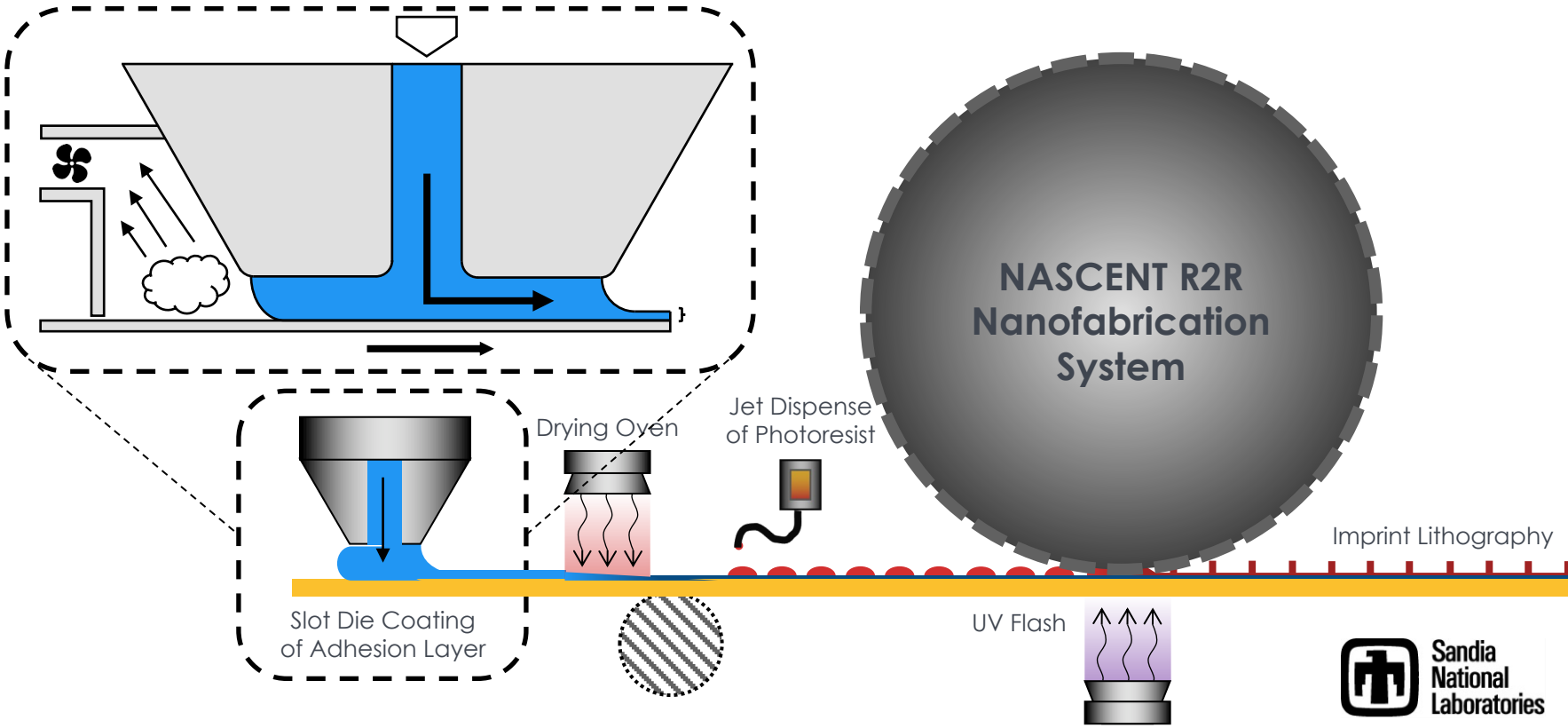
Robert Malakhov, Kris Tjiptowidjojo, Randall Schunk [UNM] (P-2E.1-K)

Goals

- Slot Die Simulator
  - Scale-up: Ultrathin coatings (1<μm)
  - Small-lot: Continuous coatings
  - Prepare surfaces for nano-imprint lithography with films of desired thickness and uniformity

Research Methods

- Navier-Stokes w/BC's model
  - Solved via FEM
    Goma 6.0
- Experimental Validation



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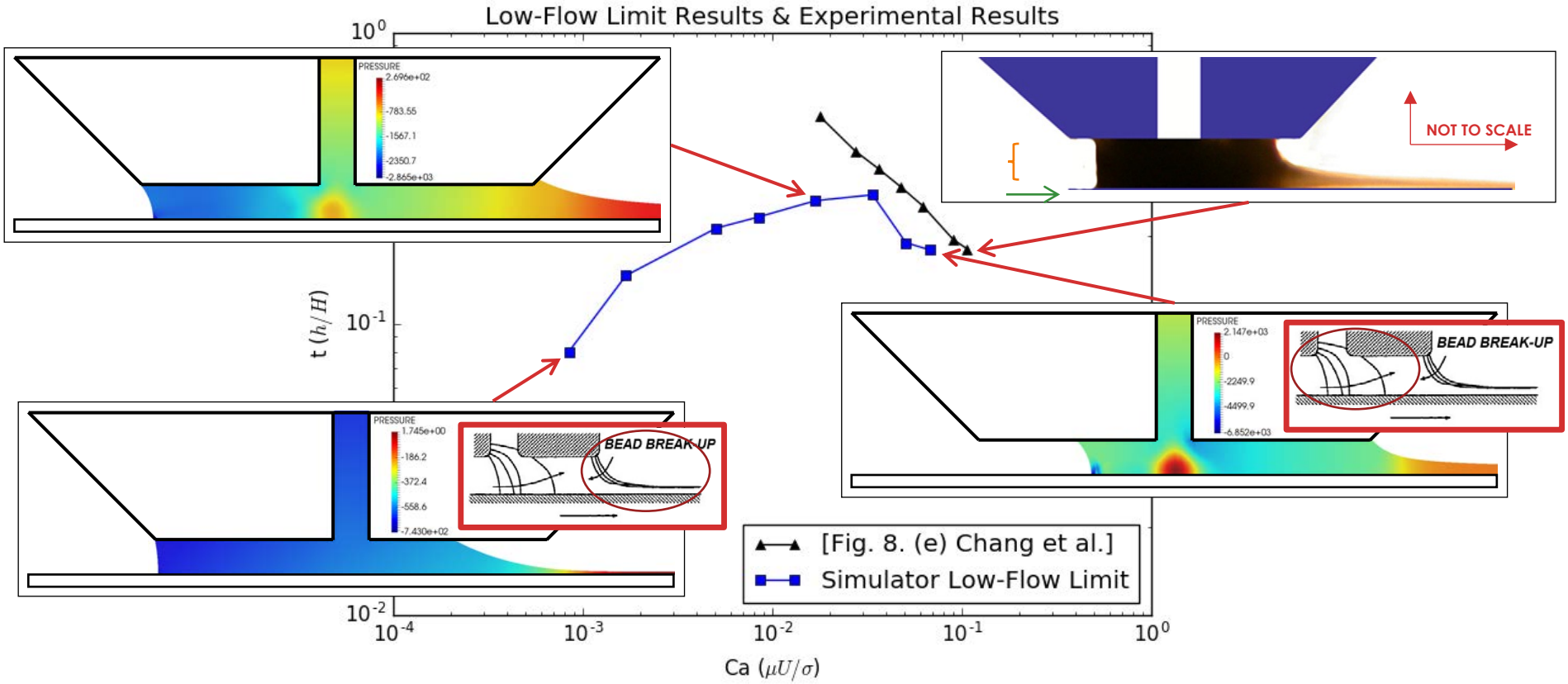
Progress Report

Low-Flow limit comparison to experimental results

- Computational results reproduce experimental film thicknesses, meniscus topologies, and failure modes



Low-Flow limit three region coexistence analysis

- Region 1 and 3 identified but region 2 not clear

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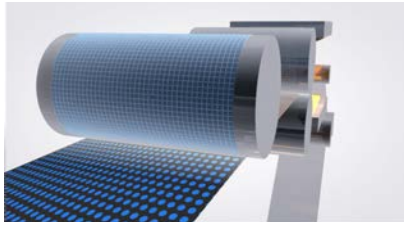
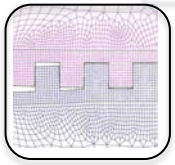
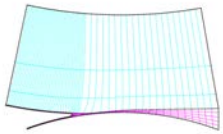
LDRD: Nanofabrication meets Roll-to-Roll = "NanoManufacturing":

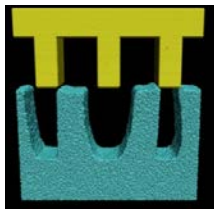


Release - peel-back, debonding



Deformable-dip, liquid-based

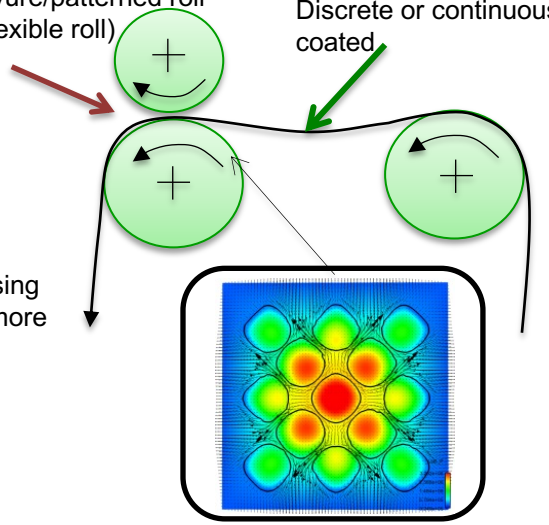




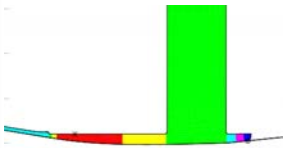
Further processing (solidification, more layers, etc.)

Imprinting/release Nip (Gravure/patterned roll On flexible roll)

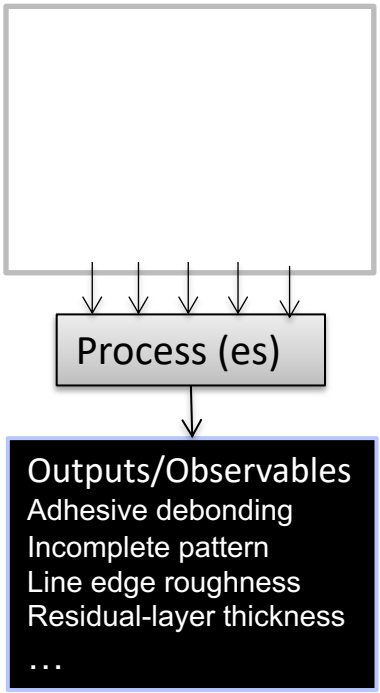
Photoresist/polymer Discrete or continuous coated



Continuous slot coating On tensioned web



Ink-Jet Discrete Coating



- Intersection of nanofabrication with *high-speed precision R2R coating/laminating/printing* -> considerable potential to spur innovation and economic growth.
- $1T / year business by 2015 (NSF).
- Coating industry alone is over $1T in 2002 (Cohen, Chemical Engineering Progress, 2002)

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