SAND2020-8979C

Multilayer Slide Coating Model for Manufacturing of PEMFC

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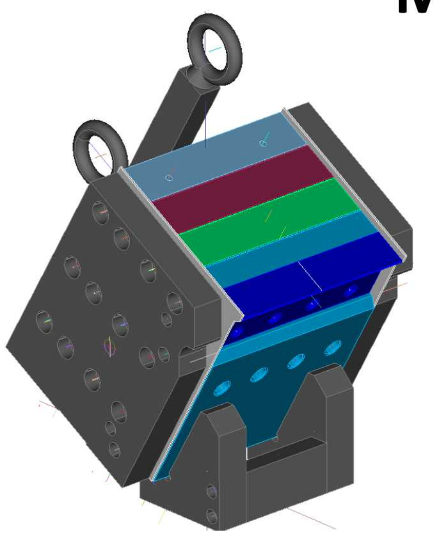

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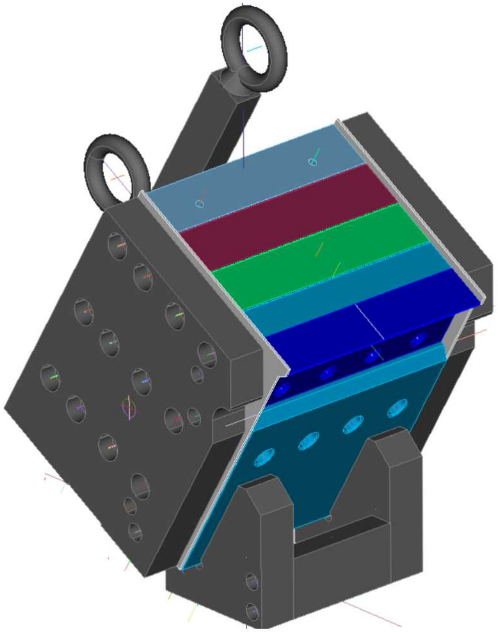
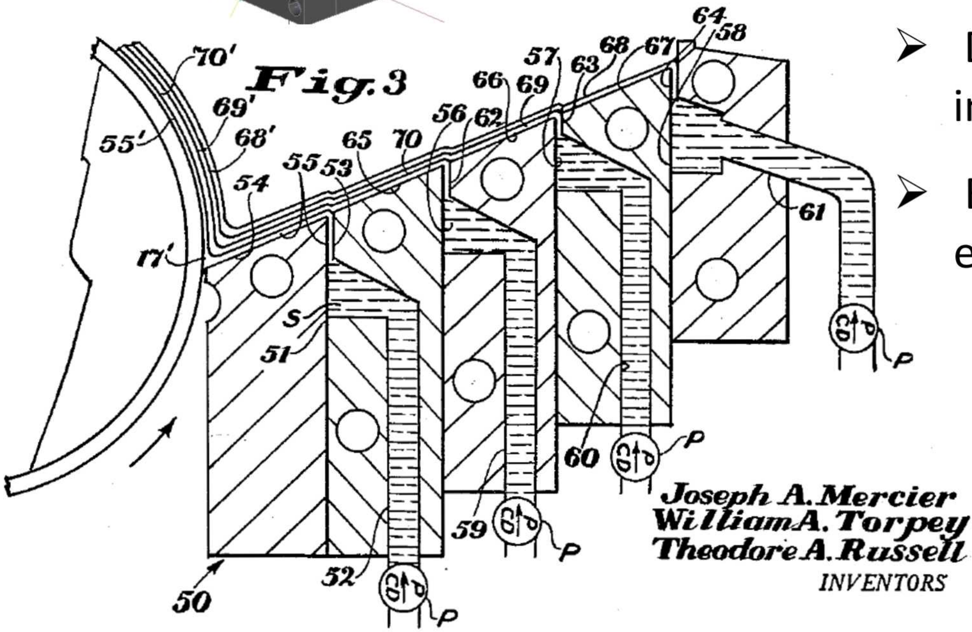
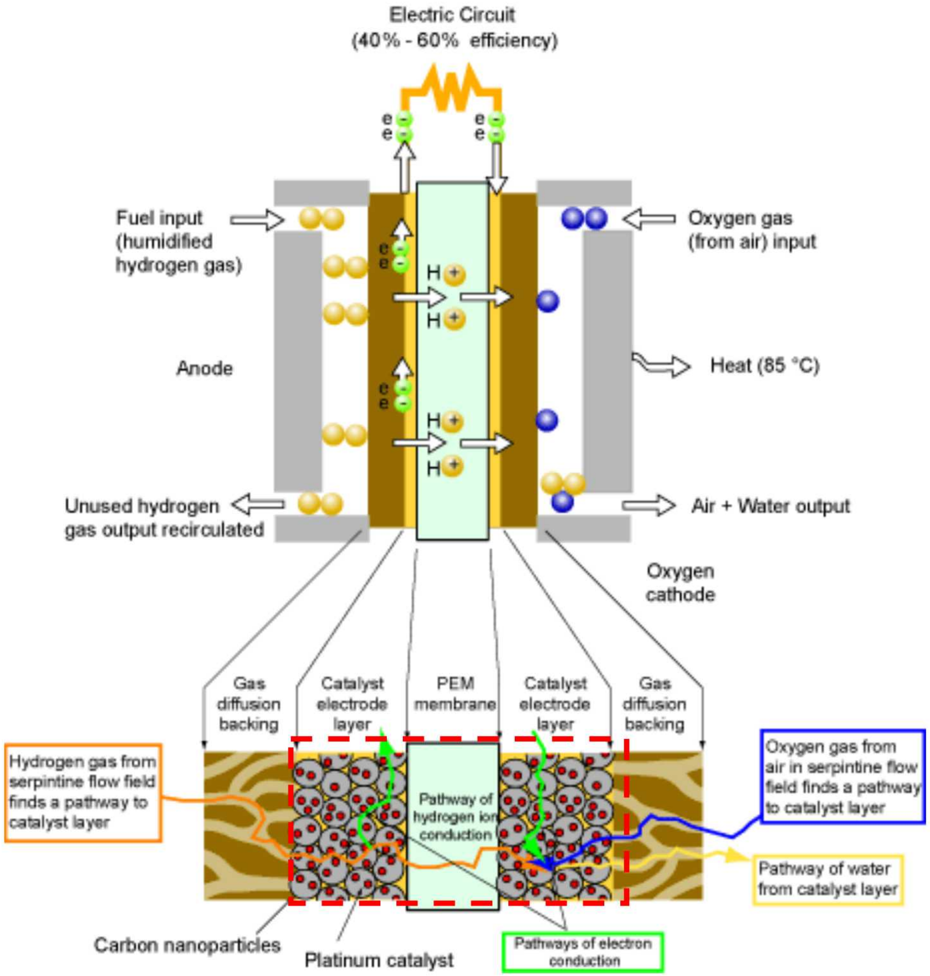
Slide Coating





- A method ideal for ***precisely coating multiple layers*** or more
- Stack multiple layers via ***gravity driven flow*** and coat them simultaneously on a moving substrate.
- ***Premetered method*** → thickness is set by flow rate and coating speed
- Developed originally by photographic film industries
- Emerging application: Multilayer structures for energy -> ***polymer membrane fuel cell (PEMFC)***

Polymer Electrolyte Membrane Fuel Cells (PEMFC)



https://www.physics.nist.gov/MajResFac/NIF/pemFuelCells.html

Anode Reaction

Convert hydrogen gas into protons and electrons

$$2H_2 \rightarrow 4H^+ + 4e^-$$

Ions Transport

- Transport protons ***through the membrane***
- Transport electrons ***around the membrane*** through external circuit → electricity

Cathode Reaction

Combine protons, electrons, and oxygen to form water and heat

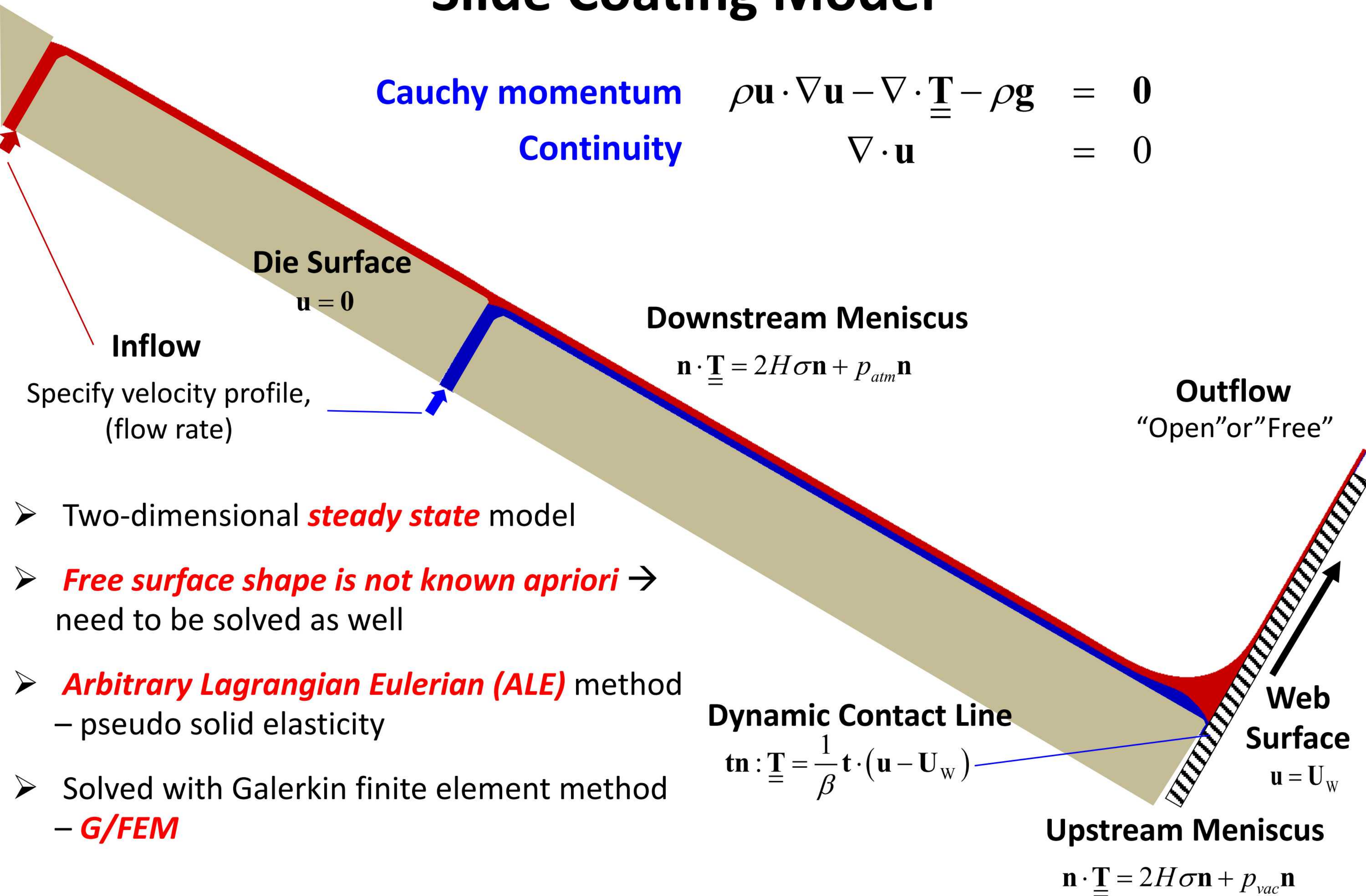
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

- Use slide coating to manufacture ***membrane-electrode-assembly (MEA)***
- Target speed: ***1- 10 min/min***
- Target wet thicknesses:
  - Anode/cathode: ***60 – 150 µm***.
  - Membrane:***250 µm***

Slide Coating Model

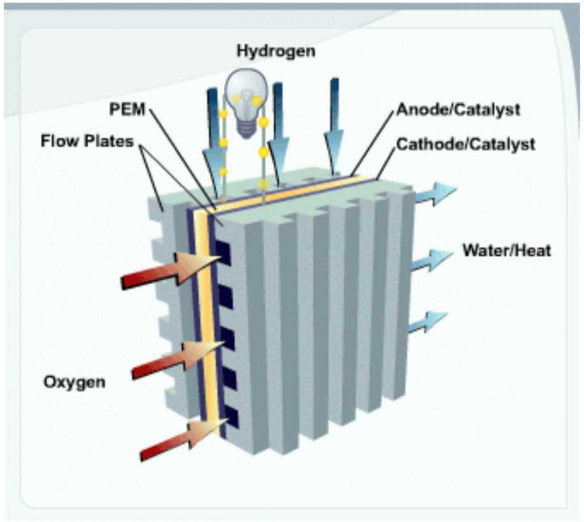
Cauchy momentum $\rho \mathbf{u} \cdot \nabla \mathbf{u} - \nabla \cdot \underline{\underline{\mathbf{T}}} - \rho \mathbf{g} = \mathbf{0}$

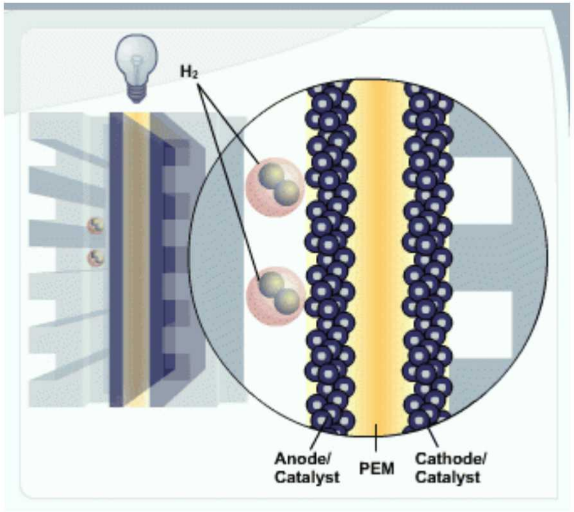
Continuity $\nabla \cdot \mathbf{u} = 0$



- Two-dimensional ***steady state*** model
- ***Free surface shape is not known apriori*** → need to be solved as well
- ***Arbitrary Lagrangian Eulerian (ALE)*** method – pseudo solid elasticity
- Solved with Galerkin finite element method – ***G/FEM***

Coating Materials





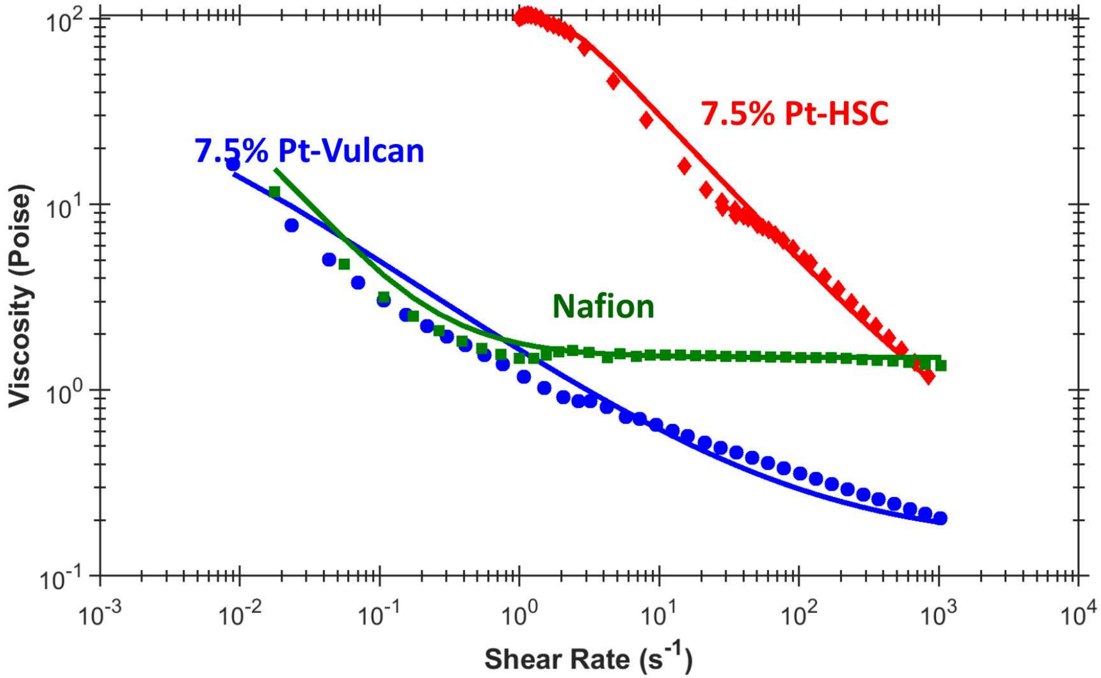
https://www.energy.gov/eere/fuelcells/fuel-cell-animation-text-version

Anode/Cathode:

- Platinum – Vulcan 3% or 7.5%, 1-propanol 10%, I/C 1.05
- Platinum – High Surface Carbon (HSC) 3% or 7.5%, 1-propanol 10%, I/C 1.05

Membrane:

- Nafion™ D2020 – Ionomer 20%, Water 34%, 1 Propanol 46%



- ➢ Particles-laden ink system – highly ***shear thinning***
- ➢ All layers are miscible→ ***no interfacial tension***
- ➢ Wide ranges of viscosity values → ***tailor ink rheology*** to improve coatability

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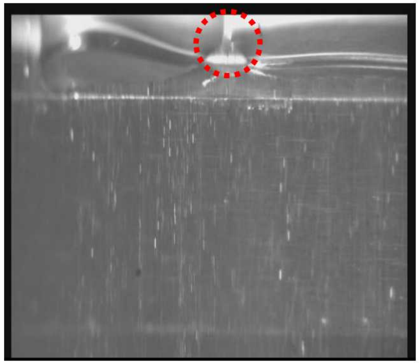
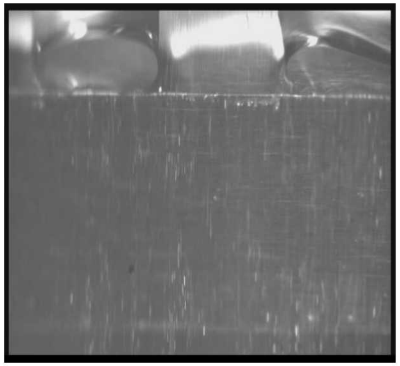
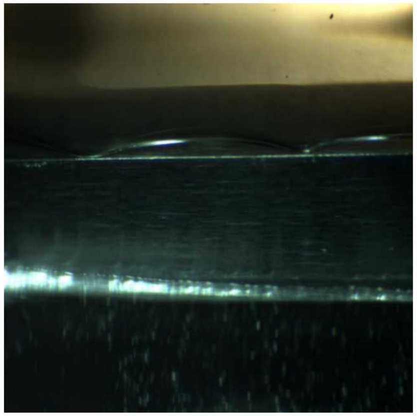
Mapping Vacuum Limits

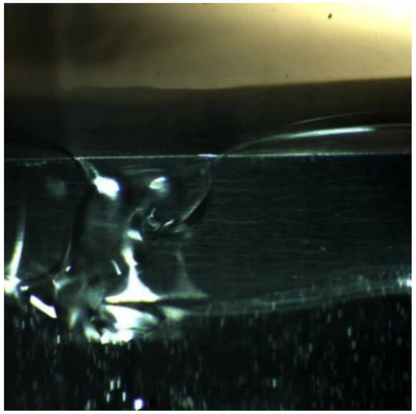
Front View of Bead – Low Vacuum Limits





Front View of Bead – High Vacuum Limits



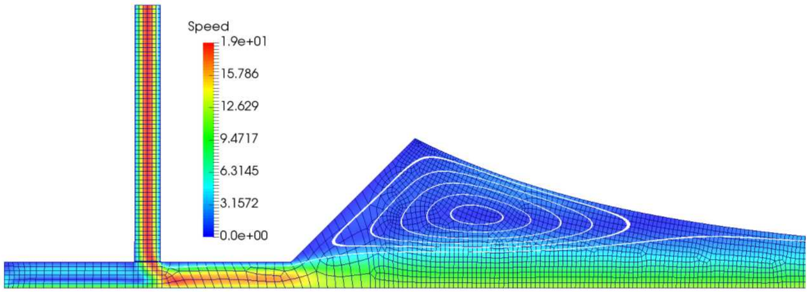


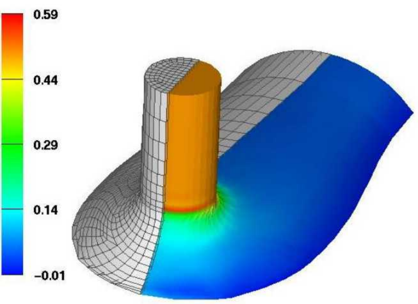
Tjiptowidjojo, K., & Carvalho, M. S. (2011). Operability limits of slide coating. *Chemical Engineering Science*, 66(21), 5077-5083.

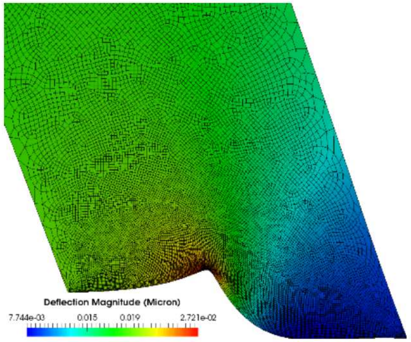
- Typically a "vacuum" pressure is applied on upstream meniscus to ***stabilize the bead***
- Too little vacuum → ***rivulets*** – ***low vacuum limit***
- Too high vacuum → ***weeping, leakage*** – ***high vacuum limit***
- Strongly correlates with ***upstream meniscus*** (contact lines) ***location***
- Solve ***an augmenting condition*** for vacuum pressure needed to place upstream contact line in either edge of die face → ***solve for vacuum limits***.

Simulation Tool: Goma 6.0

2014 R&D 100 Award Winner





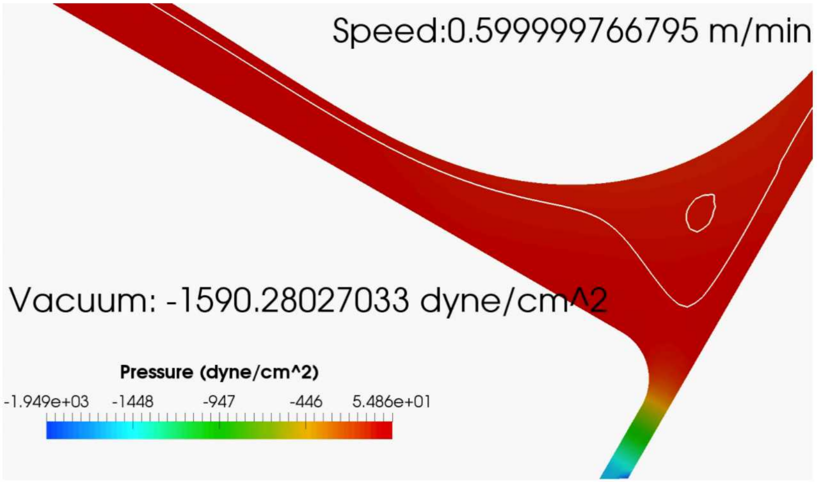


- Multiphysics ***finite element*** code, suitable for both ***research*** and ***production***
- Fully-coupled and segregated ***free*** and moving ***boundary*** parameterization – ALE, Level Set, etc.
- Modular code; ***easy to add equations*** – currently has 200+ differential equations
- ***Open source***! Available at http://goma.github.io
- ***Goma 6.0. training*** is available!

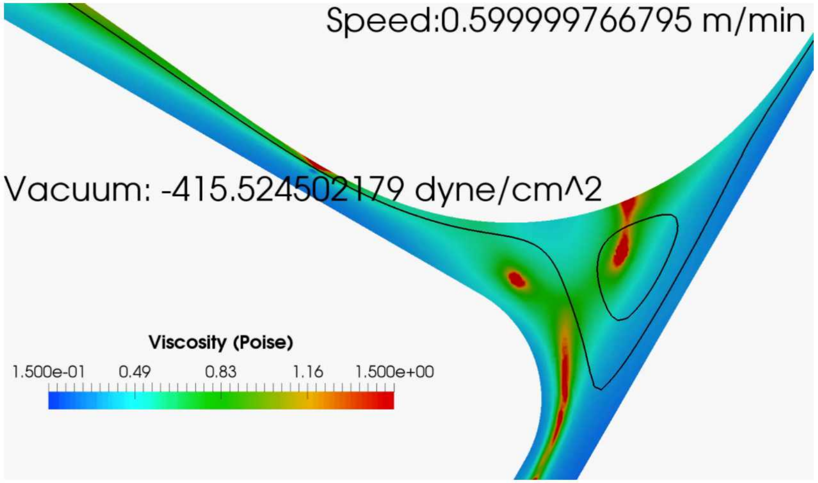
Goma has been used successfully in coating manufacturing for 3 decades!

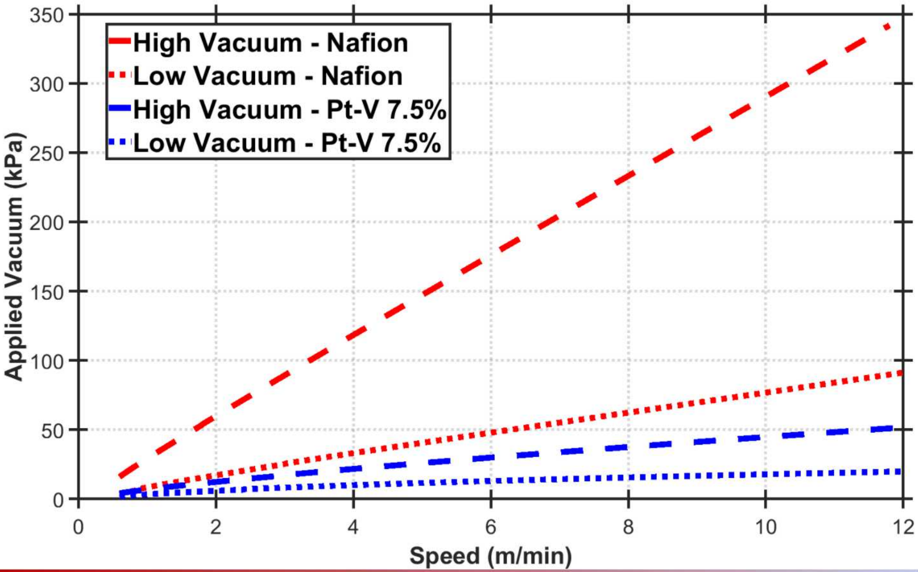
Single Layer – Vacuum Limits

Nafion – h_{wet} = 250 μm



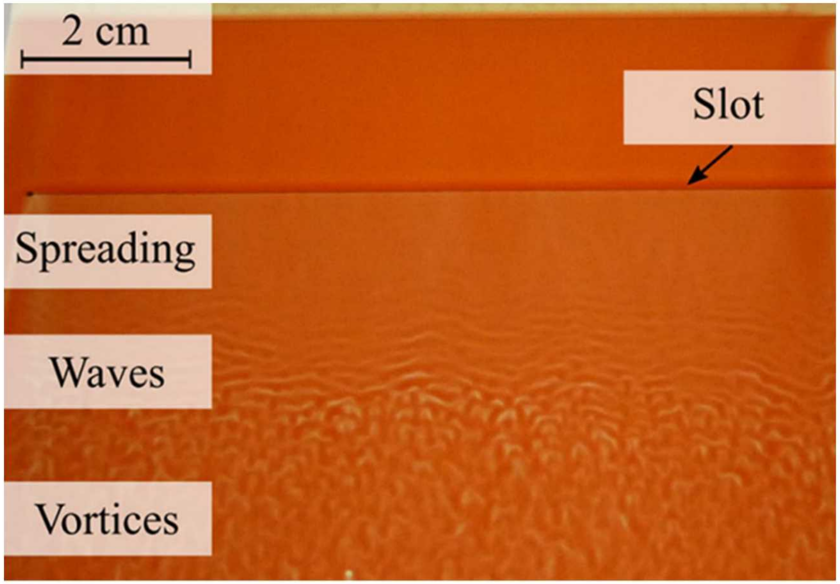
Pt-V 7.5% – h_{wet} = 64 μm





- Increase speed with constant h_{wet} → ***calculate flow field and required applied vacuum*** to keep upstream static contact line at either die face edge
- Downstream vortex disappear at higher speed (and vacuum)
- Nafion vacuum limits are higher than Pt-V 7.5% due to ***shear thinning*** of catalyst ink

Stability of Flow



Buerkin, Cornelia K., et al. "Investigation of interfacial instabilities with a two-layer slide coating process." *Journal of Coatings Technology and Research* 14.5 (2017): 991-1001.

- Predict vacuum limits – ***onset of 3-D flow instabilities*** with ***heuristics*** from visualization
- Enable ***prediction*** of vacuum limits with a ***2-D model***.
- Other defects commonly found in multilayer slide coating: ***Interfacial instabilities***. Manifestation: Dewetting, waves, vortices
- No known heuristics to predict onset, some rules of thumbs available → Buerkin et al. (2017).

Predict stability of flow with 2-D base flow model → linear stability analysis

Linear Stability Analysis

Examining flow behavior due to ***infinitesimally small*** disturbances

Governing equations:

$$\rho\left[\frac{\partial \mathbf{u}}{\partial t}+\mathbf{u}\cdot\nabla\mathbf{u}\right]-\nabla\cdot\underline{\underline{\mathbf{T}}}-\rho\mathbf{g} = \mathbf{0} \quad ; \quad \mathbf{T}=-p\mathbf{I}+\mu\left[\nabla\mathbf{u}+\nabla\mathbf{u}^{T}\right]$$

$$\nabla\cdot\mathbf{u} = 0$$

Express solution in terms of base (steady state) solution and ***small*** disturbance:

$$\mathbf{u} = \mathbf{u}_0 + \varepsilon\mathbf{u}_1$$
$$p = p_0 + \varepsilon p_1$$

Base (steady) Disturbance

Substitute into PDE, eliminate $o(\varepsilon^2)$ and higher order terms, discretize with G/FEM:

$$\underline{\underline{\mathbf{M}}}\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix}\mathbf{u}\\ p\end{bmatrix} = \underline{\underline{\mathbf{J}}}\begin{bmatrix}\mathbf{u}\\ p\end{bmatrix}$$

Express solution in terms of eigenmodes: $\begin{bmatrix}\mathbf{u}\\ p\end{bmatrix}=\sum_{i=1}^{N}\mathbf{x}_i\exp\left(\lambda_i t\right)$

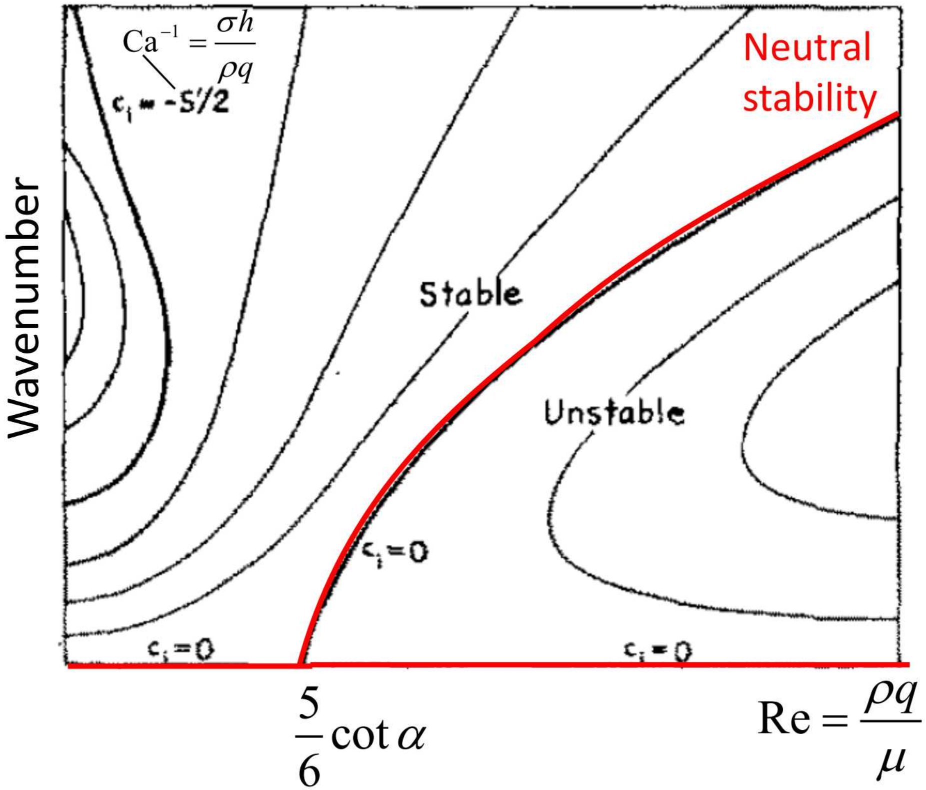
Generalized eigenvalue problem:

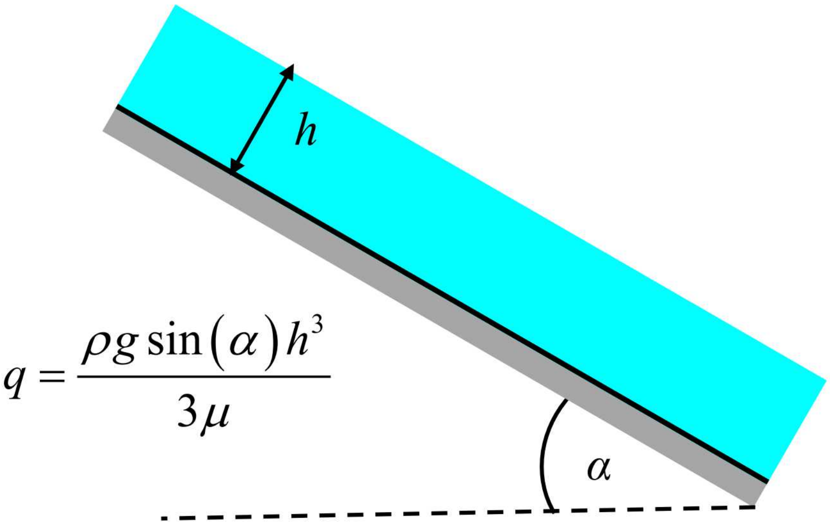
$$\boxed{\lambda_i\underline{\underline{\mathbf{M}}}\mathbf{x}_i = \underline{\underline{\mathbf{J}}}\mathbf{x}_i}$$

Re(λ) > 0 → *unstable mode*

Re(λ) < 0 → *stable mode*

Previous Work – Single Layer



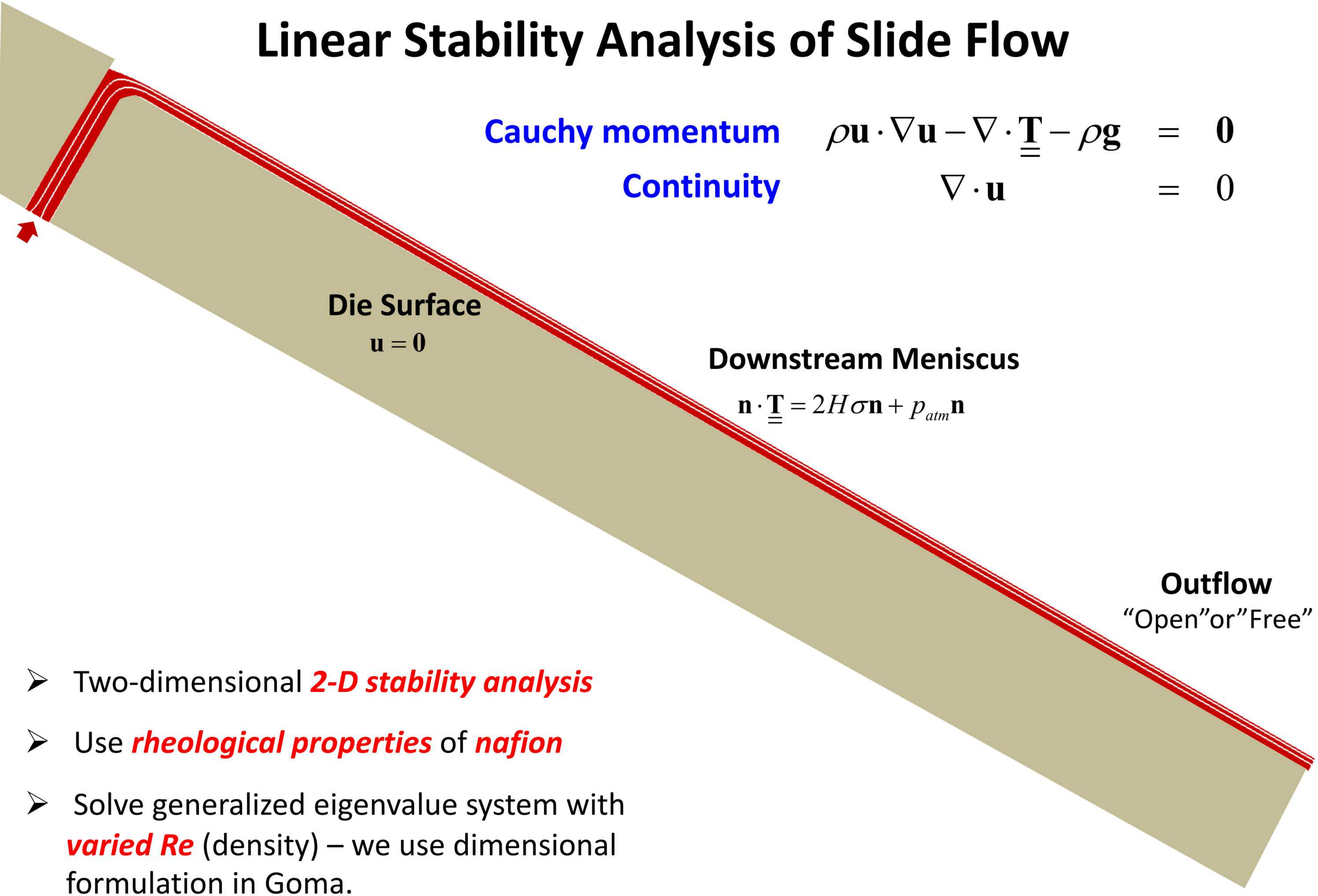


Yih, C.S. (1963) "Stability of liquid flow down an inclined plane." *The Physics of Fluids* 6(3): 321-334.

- Fully developed Newtonian flow down an inclined plane – ***2-D linear stability of 1-D flow***
- Neutral stability curve ($\mathrm{Re}(\lambda) = 0$) ***depends on plane inclination*** α.
- Small wavenumber (***long wavelength***) modes are ***most unstable***. Smaller wavelength modes are dampened with surface tension
- For inclination of $30°$, critical $\mathrm{Re} = 1.44$

Linear Stability Analysis of Slide Flow

Cauchy momentum	$\rho \mathbf{u} \cdot \nabla \mathbf{u} - \nabla \cdot \underline{\underline{\mathbf{T}}} - \rho \mathbf{g}$	$=$	$\mathbf{0}$
Continuity	$\nabla \cdot \mathbf{u}$	$=$	0



- Two-dimensional ***2-D stability analysis***
- Use ***rheological properties*** of ***nafion***
- Solve generalized eigenvalue system with ***varied Re*** (density) – we use dimensional formulation in Goma.

Conclusions

- Complete single layer and two-layer slide coating flow model
- Augment the flow model to solve for applied vacuum pressure needed to locate upstream contact line at either die face edge → expedite vacuum limits mapping by continuing in speed and vacuum simultaneously
- Verify linear stability analysis implementation with single-layer slide flow study

Research Plans

- Complete three-layer slide coating flow model
- Complete stability analysis of two-layer and three-layer slide flow
- Use the model and stability analysis to guide ink and process condition selections

References

Funding Support

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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Back Up Slides

Linear Stability Analysis

Examining flow behavior due to i***nfinitesimally small*** disturbances

Governing equations:

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$$\nabla\cdot\mathbf{u} = 0$$

Express solution in terms of base (steady state) solution and ***small*** disturbance:

$$\mathbf{u} = \mathbf{u}_0 + \varepsilon\mathbf{u}_1$$

$$p = p_0 + \varepsilon p_1$$

Base (steady) Disturbance

Substitute into PDE and eliminate $o(\varepsilon^2)$ or higher order terms

$o(1)$ term:

$$\rho\mathbf{u}_0\cdot\nabla\mathbf{u}_0-\nabla\cdot\underline{\underline{\mathbf{T}}}_0-\rho\mathbf{g} = \mathbf{0}$$

$$\nabla\cdot\mathbf{u}_0 = 0$$

Solve base flow fields $\mathbf{u}_0$ and p_0 with finite element method

$o(\varepsilon)$ term:

$$\rho\left[\frac{\partial \mathbf{u}_1}{\partial t}+\mathbf{u}_0\cdot\nabla\mathbf{u}_1+\mathbf{u}_1\cdot\nabla\mathbf{u}_0\right]-\nabla\cdot\mathbf{T}_1 = \mathbf{0}$$

$$\nabla\cdot\mathbf{u}_1 = 0$$

Use base flow solution to solve for disturbance flow fields.

Generalized Eigenvalue Problem

Finite element method transforms the PDEs into a system of differential algebraic equations

$$\underline{\underline{\mathbf{M}}}\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix}\mathbf{u}\\ p\end{bmatrix} = \underline{\underline{\mathbf{J}}}\begin{bmatrix}\mathbf{u}\\ p\end{bmatrix}$$

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Generalized eigenvalue problem: $\lambda_i \underline{\underline{\mathbf{M}}}\mathbf{x}_i = \underline{\underline{\mathbf{J}}}\mathbf{x}_i$

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