SAND2012-3516P

Computer-Aided Engineering Capabilities for Nanomanufacturing Processes

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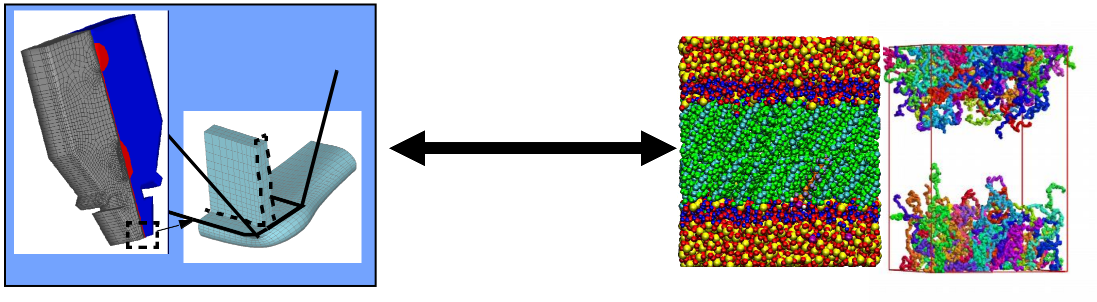


Contributions from K. Tjiptowidjojo, S. A. Roberts, J. B. Lechman, E. D. Reedy, S. J. Plimpton et al.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

OUTLINE: Retrospective to Outlook and Opportunity

- Introduction to “NanoManufacturing”
- Background on mod/sim requirements
- Survey of current capability (LAMMPS, GOMA)
- Bottom-up manufacturing with Nanoparticles
- Top-down manufacturing with SFIL
- Wrap-up -- NSF ERC on NanoManufacturing(time permitting).

NanoManufacturing: Nanostructured Materials Created Layer-by-Layer

Sandia PI: Randy Schunk Partners: UNM - Jeff Brinker et al., UT: S. V. Sreenivasan, Roger Bonnecaze, UIUC: Jon Higdon

Goal: “NanoManufacturing” => “Practical” => High-througput and Large-Area/Volume.

Concept: Produce nanostructured films layer-by-layer by two feasible approaches. 1) Proximity patterning by molding/ forming/ imprinting 2) Coating dispersions of nanoparticles.

Approach: Integrated computational toolset for underpinning mechancis. Multiscale algorithms to connect nano/atomistic scales to machine design!

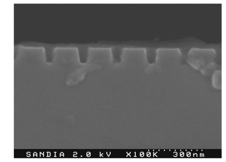
Challenges: Multiscale algorithms to predict defects over large areas (large aspect ratios, fluctuating fluids, code integration).

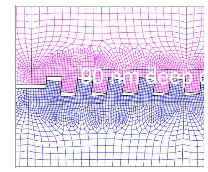
Applications: Photovoltaics, photosynthesis membranes, sensors, …

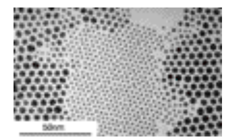
Collaborators and Partners: Industry (3M, ICI, BASF, P&G, Corning).

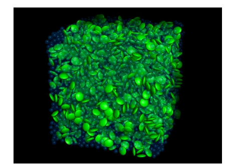
Opportunity: Numerious Undergraduate, Graduate Ph.D. level projects available!

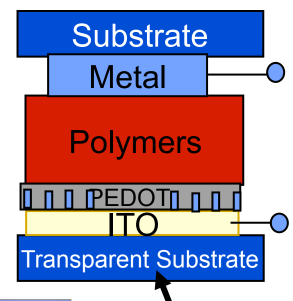
MOD/SIM LAYER-BY-LAYER



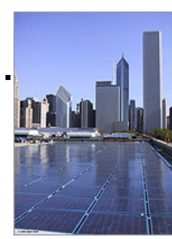








E.G. Multilayered-Films For Photovoltaics



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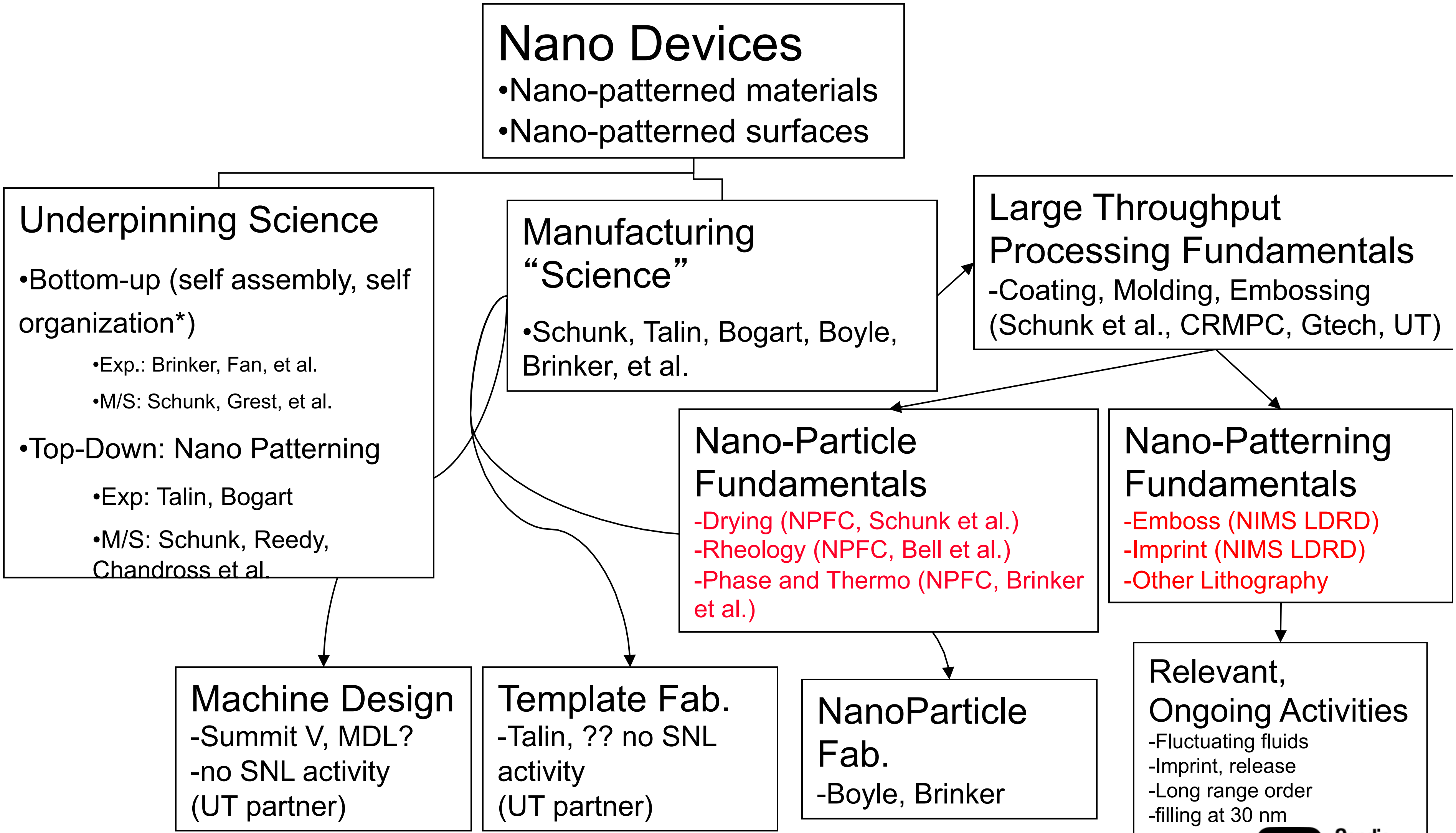
"Nano-Manufacturing" - Control of Structure in a "Practical" way



*Made practical by Pre-Processing to Concentrated form, before thermo takes over

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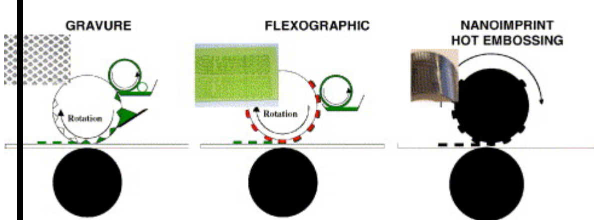
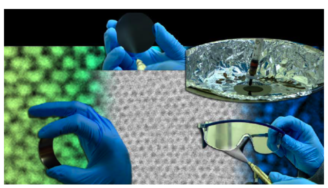
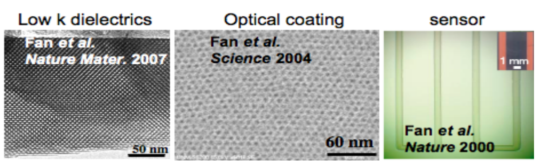
NanoEngineering: Modeling and Simulation at Sandia

"Nanotechnology" refers to a field of applied science and technology whose theme is the control of matter on the atomic and molecular scale, generally 100 nanometers or smaller, and the fabrication of devices or materials that lie within that size range (Wikipedia 2008).

NanoEngineering ⟷ NanoTechnology







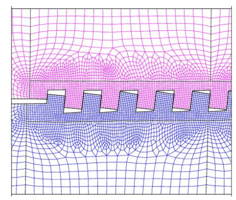
"Macro"
Nanomanufacturing
Nanomaterials
Nanodevices

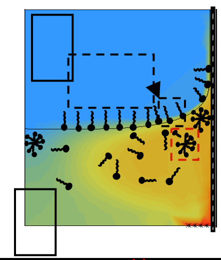
"meso"

Bridging

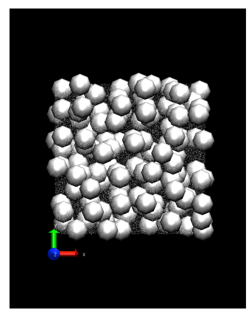
"atomistic"

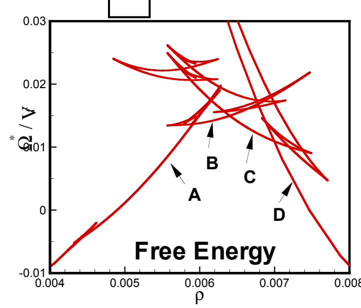
SNL's state-of-art self-assembly and nanomanufacturing capability



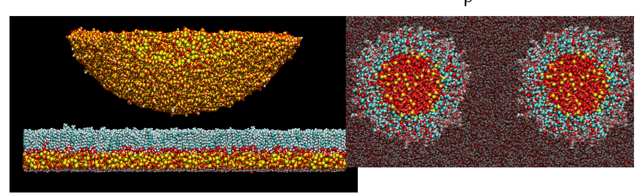


Sierra Mechanics
Goma, Aria, JAS, Adagio





Coarse-grained MD/DFT
LAMMPS, Tramonto



MD/DFT
LAMMPS, Tramonto

Quantum DFT
QUEST, SOCORRO

Length
Time scale

Nanoscience (material science)

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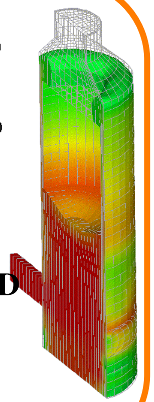
GOMA MULTIPHYSICS CODE

Contact: P. R. Schunk (prschun@sandia.gov)

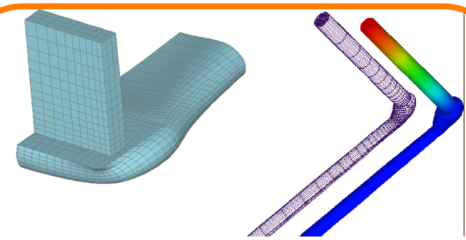
A MP FINITE ELEMENT CODE FOR MULTIPHYSICS FREE AND MOVING BOUNDARY PROBLEMS

DELIVERY OF POLYMER/CERMET ENCAPSULANTS FOR MICRO ELECTRONICS AND NEUTRON GENERATOR PERFORMANCE AND RELIABILITY



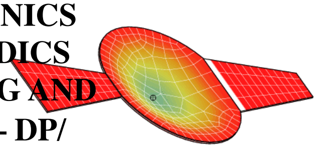
DP NG/NG TUBE FEED THROUGH

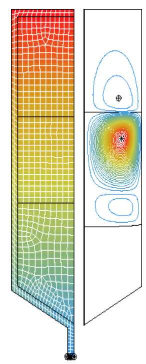
DP



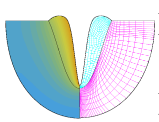
CERAMIC SLURRY EXTRUSION/ RAPID PROTO FOR NG/ PZT APPS

MICROELECTRONICS AND MEMS-FLUIDICS MANUFACTURING AND PERFORMANCE – DP/ ASCI



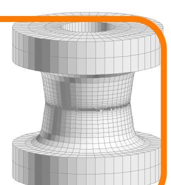


ALLOY PROCESSING CRADA



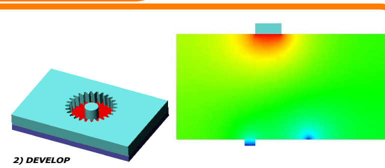
BRAZE/WELD/

SOLDER JOINT FORMATION - DP



CORROSION/ ELECTROCHEMICAL APPLICATIONS

PERFORMANCE, AGING AND RELIABILITY, LIGA

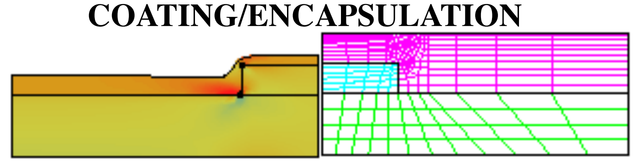


- COUPLED OR SEPARATE HEAT, N-SPECIES, MOMENTUM (SOLID AND FLUID) TRANSPORT
- FULLY-COUPLED FREE AND MOVING BOUNDARY PARAMETERIZATION
- SOLIDIFCATION, PHASE-CHANGE, CONSOLIDATION, REACTION OF PURE AND BLENDED MATERIALS
- HOST OF MATERIAL MODELS FOR COMPLEX RHEOLOGICAL FLUIDS AND SOLIDS

UNIQUE FEATURES MAKE GOMA IDEAL FOR MANUFACTURING PROCESSES IN WHICH

- FREE SURFACES ARE UBIQUITOUS
- COUPLED FLUID-SOLID MECHANICS
- COMPLEX MATERIAL RHEOLOGY/LOW SPEED
- MULTIPHASE FLOW/POROELASTICITY

COATING/ENCAPSULATION



CRMPC CRADA/DP

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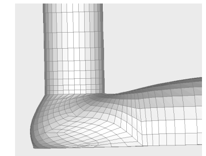
GOMA: GENERAL MECHANICS CAPABILITIES

Goma is a Great Research Tool:
Easily Extendable, but Production Oriented!



- **MATERIAL MODELS, SOLIDS**

  ELASTICITY (LINEAR, NONLINEAR, INCOMPRESSIBLE); ELASTOVISCOPLASTICITY WITH SPECIES TRANSPORT; POROELASTICITY;

- **MATERIAL MODELS, FLUIDS**

  NEWTONIAN; GENERALIZED NEWTONIAN; MULTIMODE VISCOELASTICITY; CONTINUUM SUSPENSION MODEL;

- **SPECIES TRANSPORT MODELS/PHYSICS**

  FICKIAN; NON-FICKIAN, MULTICOMPONENT; CHARGED SPECIES; FREE VOLUME THEORY;

- **PHASE CHANGE AND INTERFACIAL PHYSICS**

  IDEAL AND NONIDEAL VAPOR-LIQUID EQUILIBRIUM; VAPOR PRESSURE MODELS FOR IDEAL, NONIDEAL AND MICROPOROUS SYSTEMS; LIQUID-SOLID PHASE CHANGE (LATENT HEAT RELEASE AT LAGRANGIAN OR EULERIAN INTERFACES); MACROSEGREGATION MODELS

- **SPECIAL FLUID-SOLID, FLUID-STRUCTURE CONDITIONS**

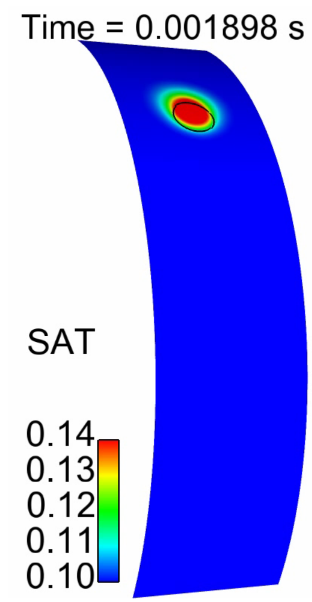
- **PARTICLE-FLUID PHYSICS**

  DISCRETE PARTICLE-CONTINUUM FLUID COUPLING

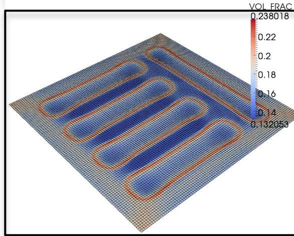
- **SPECIALIZED SHELL ELEMENT CAPABILITIES**

  STRUCTURAL SHELLS (MEMBRANES); FLUID SHELLS (LUBRICATION)

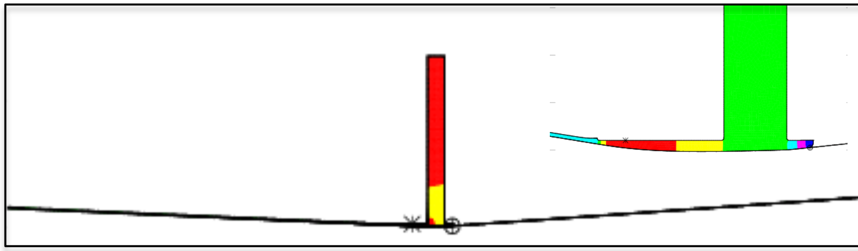
Drop Running between a impermeable and porous shell (shell thin region, LS)



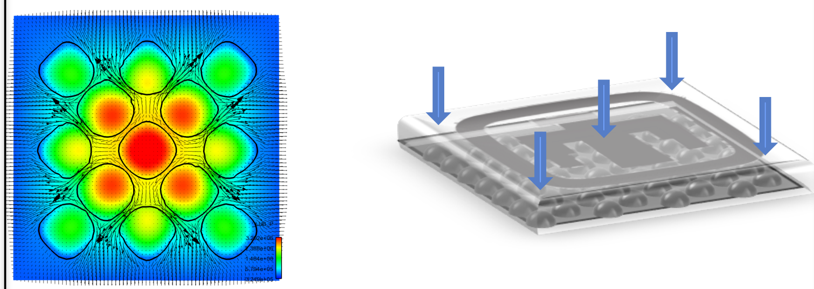
Current State-of-the-Art Capabilities: UNM/Sandia Research Group (Schunk et al.)



Thin-film Drying and surface energy patterning (full continuum and reduced order mocels)

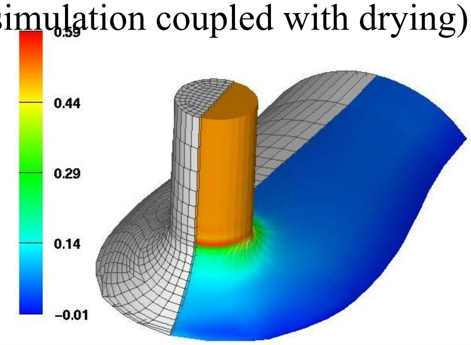


Elastohydrodynamics in coating: Reduced-order shells for webs.
Coupled Cap-Hydro continuum

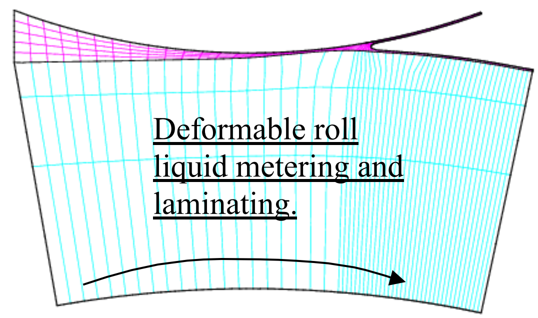


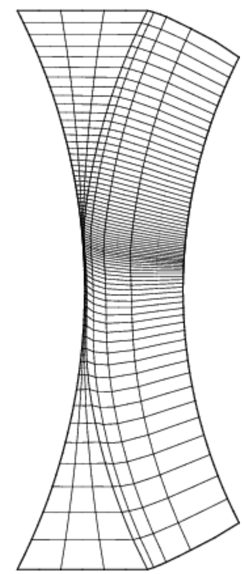
Reduced-order lubrication-shells, porous shells, Multiphase/cap-hydro -- (e.g. JFIL process)

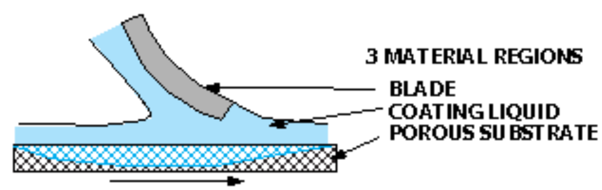
General ALE Capillary Free Surface Capability (micro-dip-pen simulation coupled with drying)



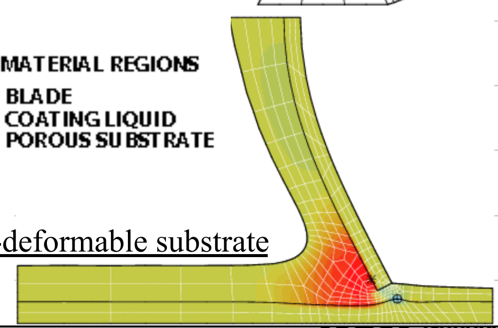
General FSI: Coupled Lagrangian or ALE solid (TALE) with full-up Navier-Stokes and ALE free-surface.
Porous Solids.







Deformable blade/porous-deformable substrate



Laboratories

GOMA Wrap-Up/Status

- Open-source someday?
- User/developer/research base at 3M, Corning, P&G, UT, CU, UNM, CCNY (past history with >10 other institutions)
- Ripe as a research tool in nanomanufacturing: mulitiscale approaches, shell techology, etc.
- Over 3000 pages of documentation (user-manual, developers manual, tutorials, etc.)
- Recent developments - full tetrahedral mesh capability together with tri-shells.

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LAMMPS Overview and Upgrades

Contact: Steve Plimpton (sjplimp@sandia.gov)

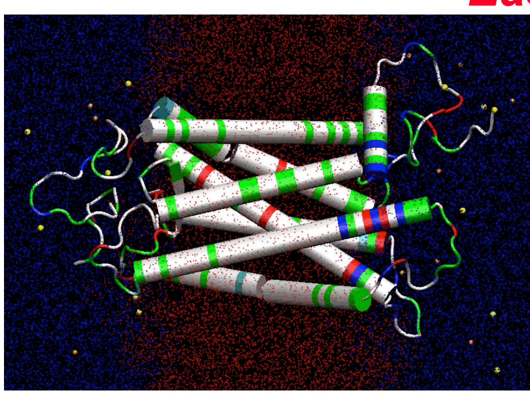
- **Classical molecular dynamics (MD) code:**
  - **serial:** fast on one processor
  - **parallel:** scalable to billions of particles on big machines

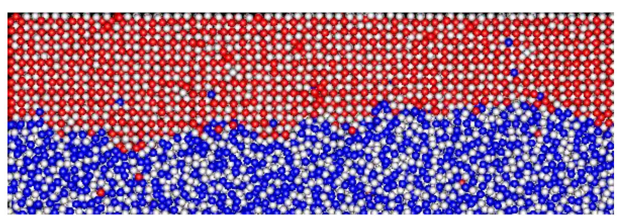
- **One foot in biomolecules and polymers**

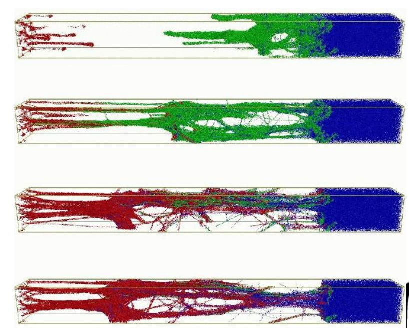
- **One foot in materials science**

- **One foot in mesoscale to continuum**
  - ***Part of that foot in nanoparticles and colloids, and coupled to bulk hydrodynamics! Another part in granular flow***

LAMMPS is a Great Research Tool:
Easily Extendable, but Production Oriented!







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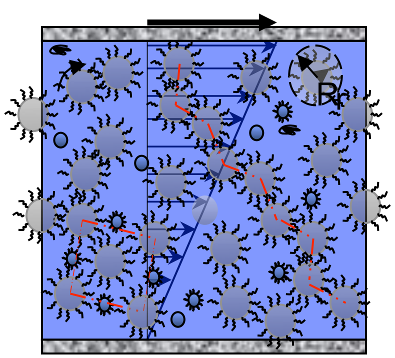
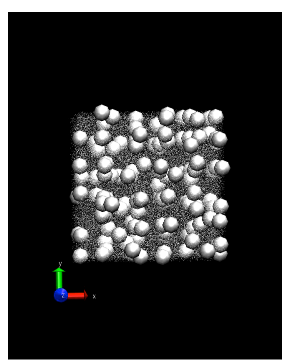
Nanoparticle Flow Project

"nanoparticle" is colloidal in nature with characteristic size of 10 nm - 500 nm.

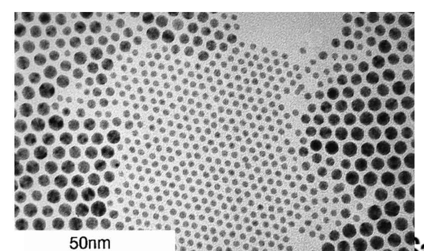
- **Project Description - "CAE Tools For NanoManufacturing"**
  - **Disperse nanoparticles in films, fibers, monolithic bulk structures for material engineering**
  - **Fluidization in liquid followed by traditional processing techniques (coating, casting, spinning) allows control of nano-building blocks at the macroscale.**
  - **Modeling and simulation of flow of dense suspensions to build process understanding and control.**
- **Partners: 3M, Corning, Procter and Gamble, BASF, ICI (Materials Manufacturing Industry)**
- **Product: Production software framework for dispersion design (rheology, stability)**





Dispersion stability: Melting of a bi-disperse lattice of nanoparticles

E.G.: Coating into functional films



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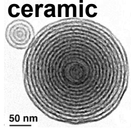
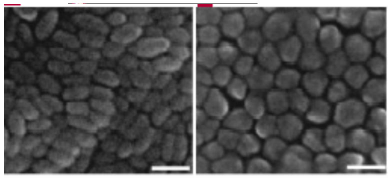
Imbedding Nanoparticles in Functional Materials : *Technology Horizon*

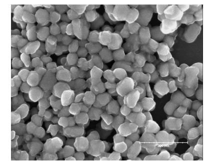
ceramic





polymer

silica



Nanoparticle Manufacture
- Solution, HighT, etc.

→ *Size/ shape* →

Nanoparticle batch characterization
- Microscopy…

→ *Distribution* →

Dispersion Chemistry
- Polymer functionalization

→

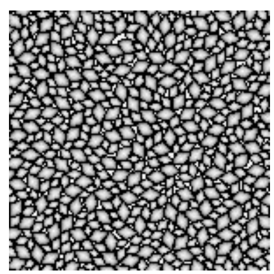
Fluidization/Processing - e.g. coating, casting…
- Rheology, Microstructure, self-assembly

Rheology, stability

(other means of processing into product do exist)

→ struct →

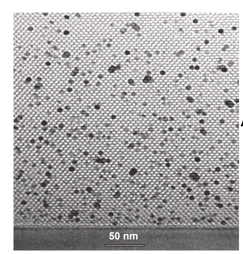
Solidification
- Drying, curing, sintering



→ struct/residual stress →

Product properties
-Thermophysical, mechanical characterization/prediction

SNL Apps: energy (fuel cells, solid state lighting, solar); high strength, lightweight composites; thermal interface materials, etc.



Ag-Silica nanocomposite

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Framework + Methods Implemented and Tested

lammps.sandia.gov

Nanoparticle Flow Project at Sandia

LAMMPS - DEM Solver

"COLLOID" Package for Pairwise Potentials (e.g. DLVO)

EXTERNAL HYDRODYNAMICS SOLVERS

MEZZO (ARIA) - Incompressible Finite element flow solver

•Coupled with LAMMPS through overset grid CDFEM.

LAMMPS PACKAGES FOR COARSE-GRAINED EXPLICIT HYDRODYNAMICS

DPD - Dissipative Particle Dynamics

•Explicit Solvent "particles". Molecular dynamics framework. Solvent potentials.

SRD - Stochastic Rotation Dynamics

•Explicit Solvent "particles". Molecular dynamics framework

LAMMPS PACKAGES FOR IMPLICIT HYDRODYNAMICS

SD - Stokesian Dynamics with FLD simplification

•Ball-Melrose pair-drag models

- ***VERIFICATION ON STANDARD TESTS***
- ***HOW MAP TO SPECIFIC PS/WATER SYSTEMS?***

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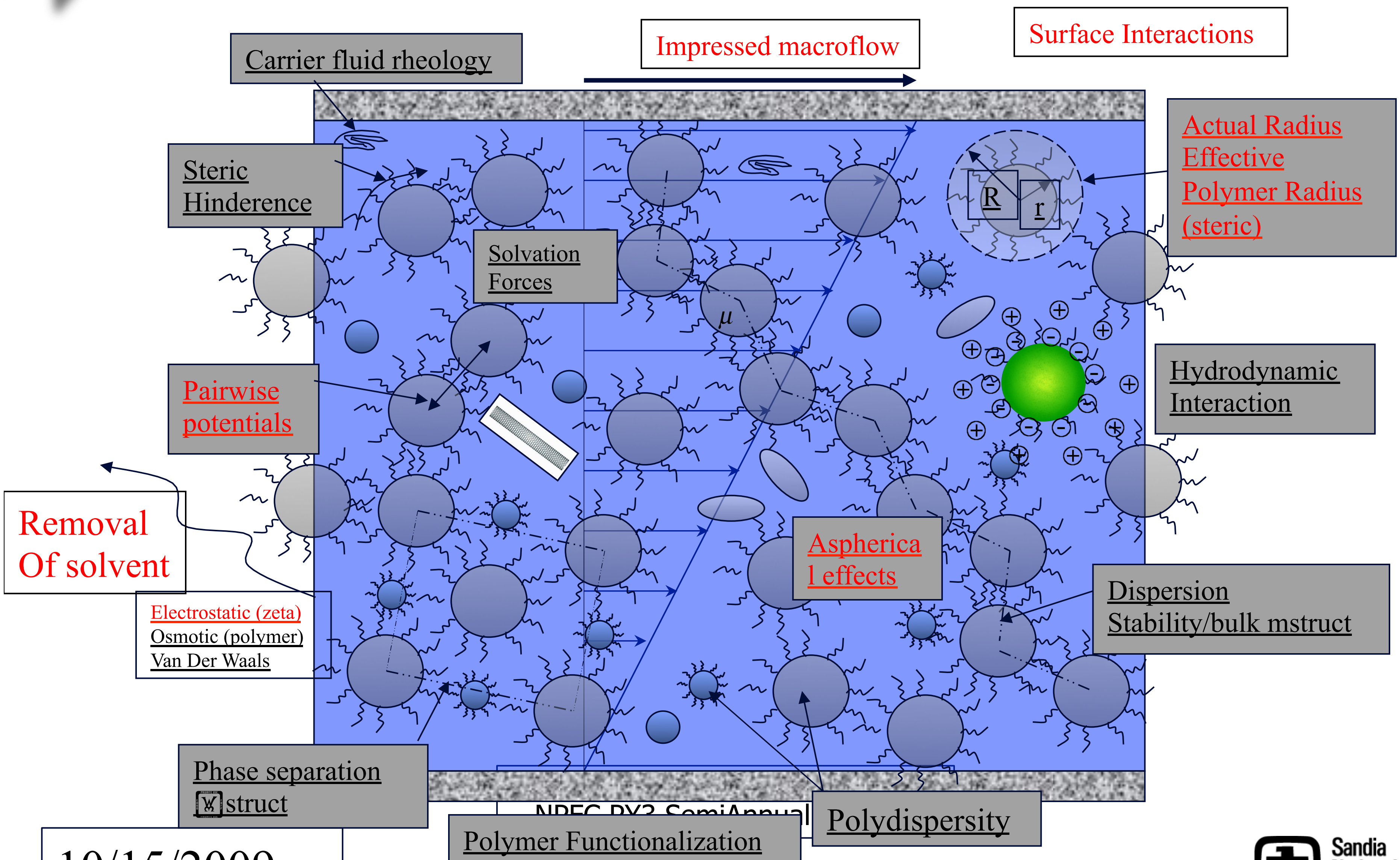
The Problem--Predictive Rheology, Microstructure (bulk and surface)



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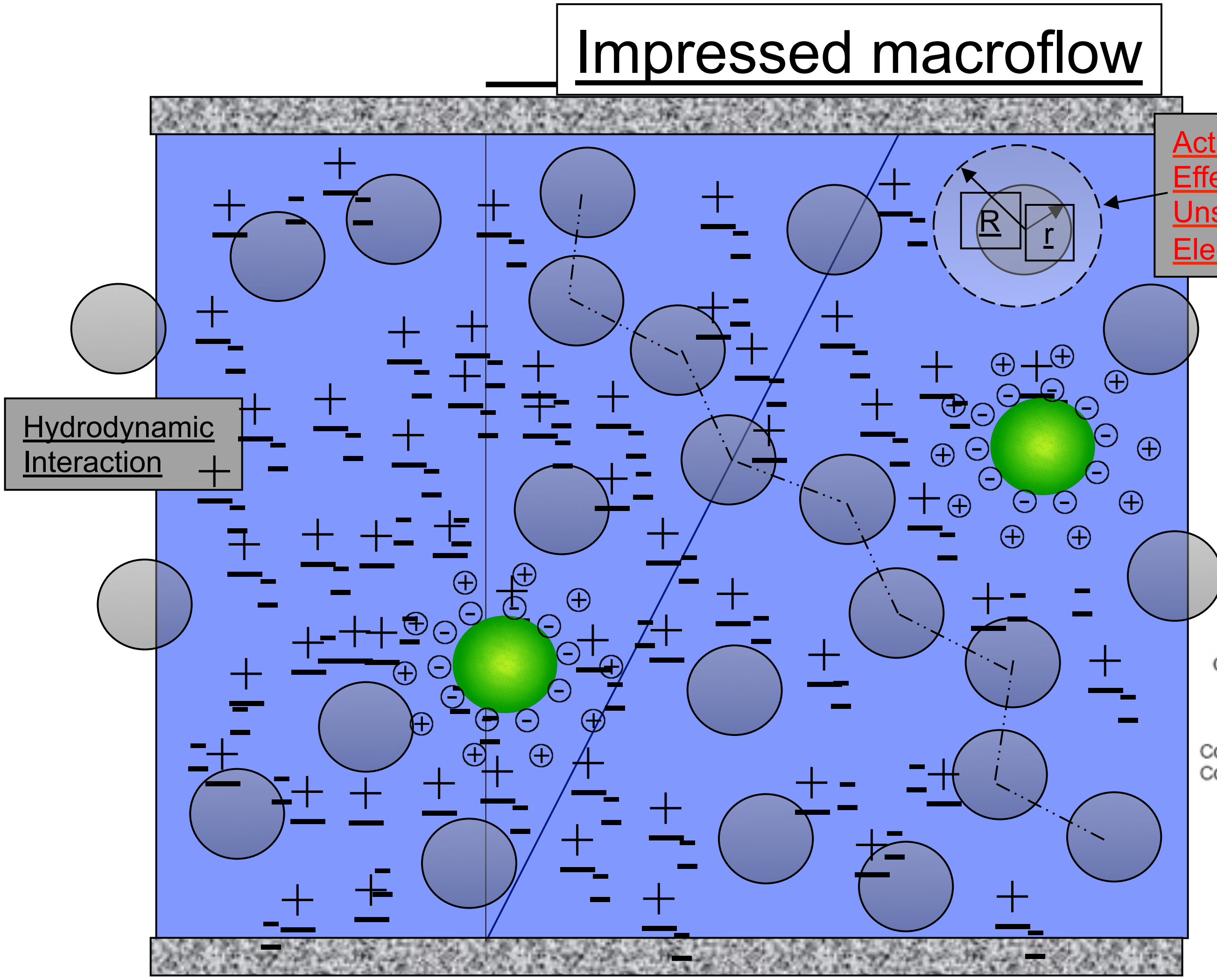
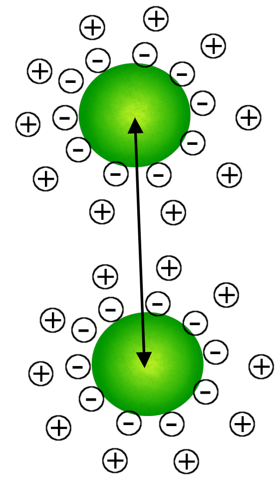
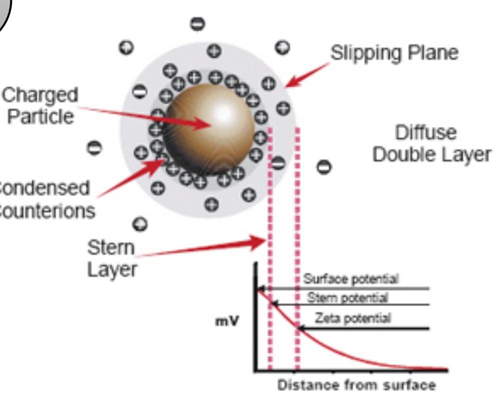
Mesoscale Models of Suspension Structure/ Dynamics- Charged Systems







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Validation Tests, Experimental Program

- **System Characteristics**
  - **Bangs Labs. Nominally 950 nm monodisperse. Required 0.003M SDS surfactant for stability. Zeta potentials measured with Malvern Zetasizer ZS (Light-scattering velocimetry)**

Salt Concentration	κ	Ψz	Ψ_0
1e-4 M	3.25e7 m^{-1}	-112.4 mV	-114 mV
1e-3 M	1.03e8 m^{-1}	-116.6 mV	-118mV
1e-2 M	3.25e8 m^{-1}	-124.2 mV	-125 mV

$$\sigma = \sqrt{\varepsilon\varepsilon_0 kT}\,\sinh\left(\frac{e\psi_0}{2KT}\right)c_{i0}^{1/2}$$

$$\sigma = \frac{2\varepsilon\varepsilon_0\kappa KT}{e}\left[\sinh\left(\frac{e\Psi_d}{2KT}\right)+\frac{2}{\kappa a}\tanh\left(\frac{e\Psi_d}{2KT}\right)\right]$$

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{1000e^2 N_{Av} c_{i0}}}$$

Particle Diffusivities

Pulsed NMR, DWS (LS Instruments)

DWS.

Dynamic Tests

–Shear/Oscillatory. RFS Rheometer (TA Instruments).

–Viscosity is reproducible, though data is very scattered at low shear rates (No indication of settling or aggregation)

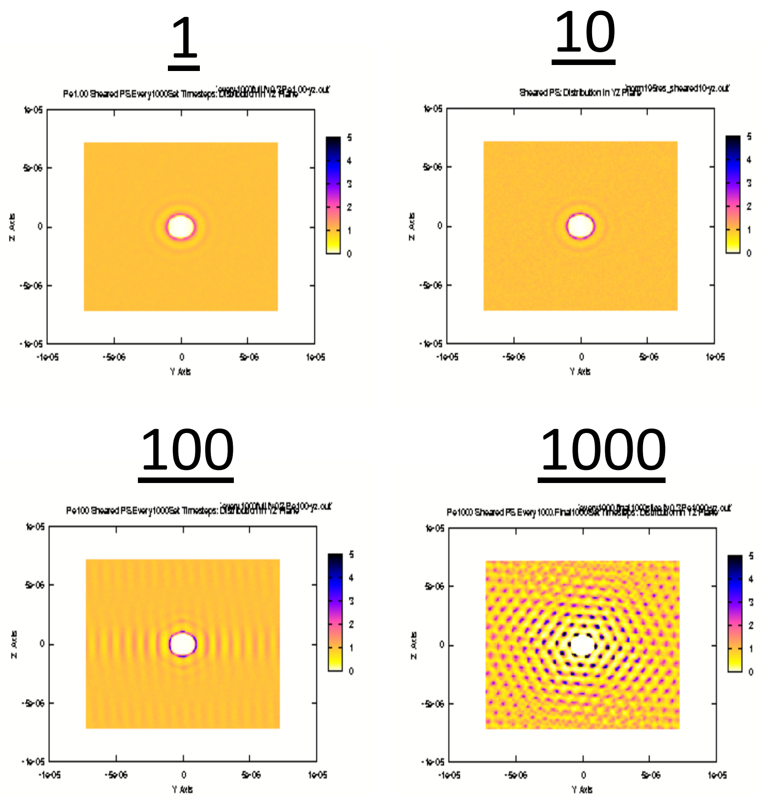
–Preshear at steady shear rate 10 s^{-1} for 300 seconds.

–Run a shear rate step test for 60s each at 1 s^{-1}, 10 s^{-1}, 100 s^{-1}, and 10 s^{-1}

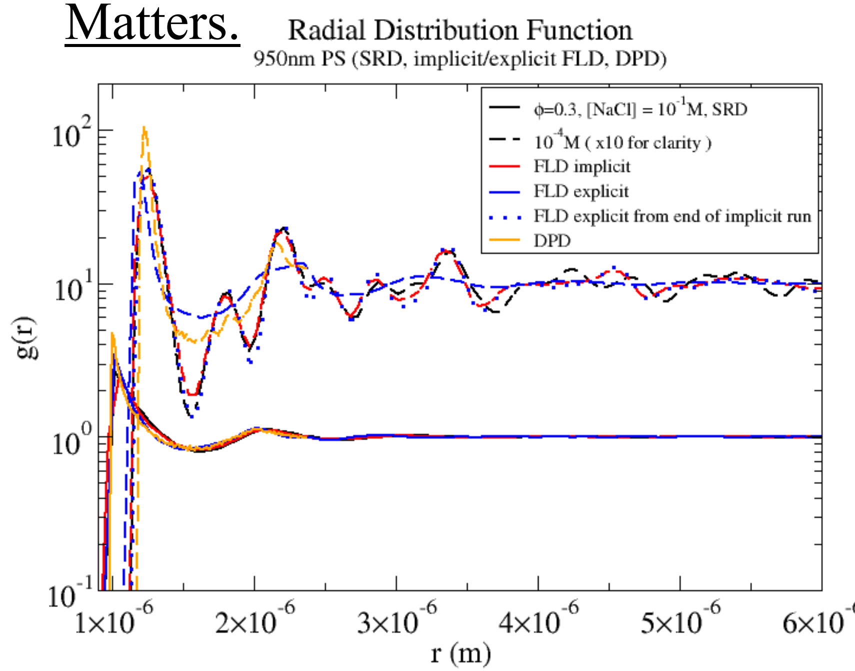
–Run a shear rate step test for 60s each at 100 s^{-1}, 200 s^{-1}, 300 s^{-1}, and 500 s^{-1}.

Structure: sheared implicit FLD g(y,z), φ=0.3, various Pe

Shear-induced Ordering
(System size effects matter!)



Equilibrated (unsheared) states can show "jamming". Initialization Matters.



Red: unsheared Green: Pe 0.10
Blue: Pe 1.00 Purple: Pe 10.0
Teal: Pe 100 Yellow: Pe 1000

Analysis by **Ethan Secor**

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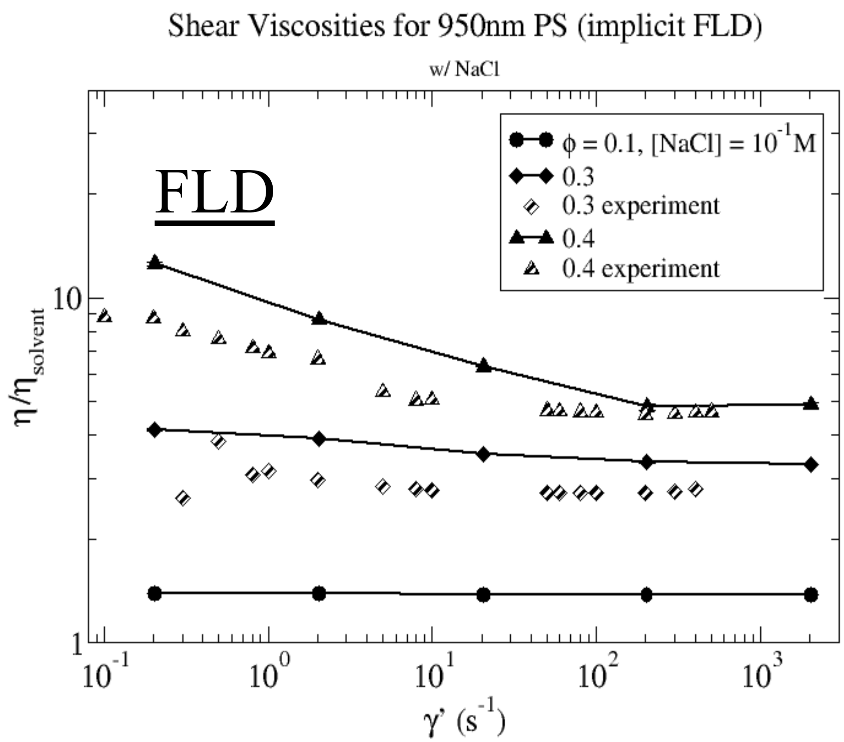
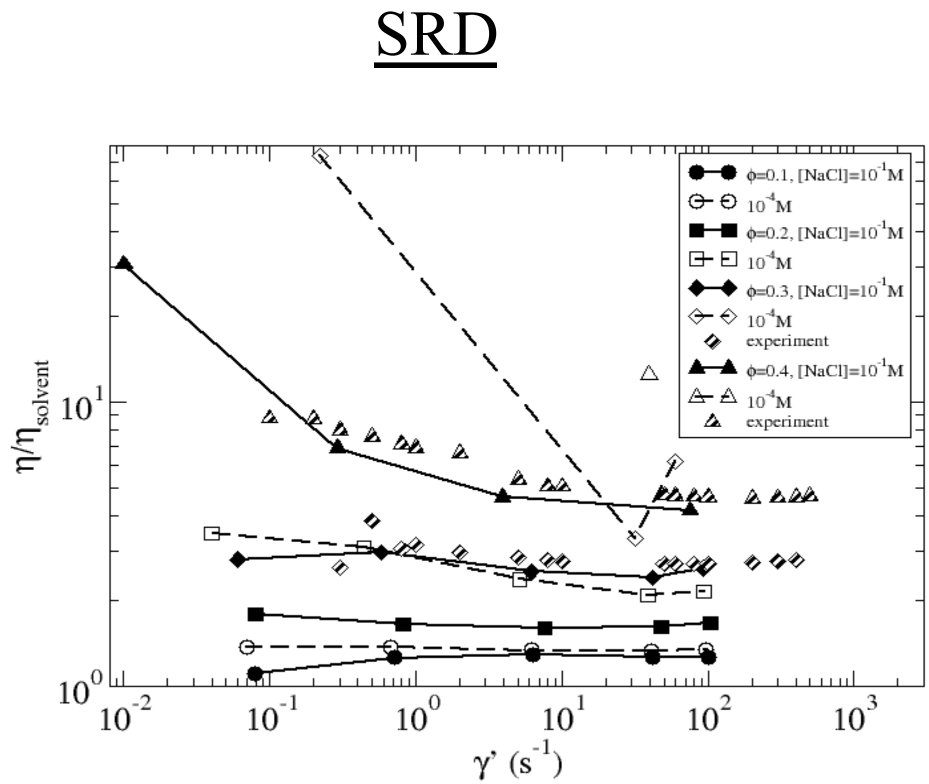
Cross-Comparison: Viscosity



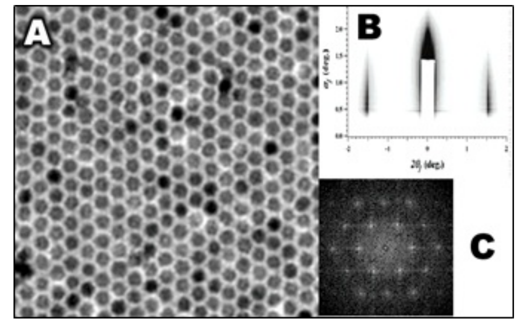


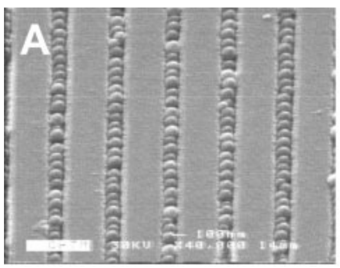
Comparison and validation at other volume fractions and salt concentrations suspect

“Manufacturing with NanoParticles”

Bottom-Up Manufacturing - Directed Assembly and/or Placement (hierarchical) of Nanoparticles (building blocks)

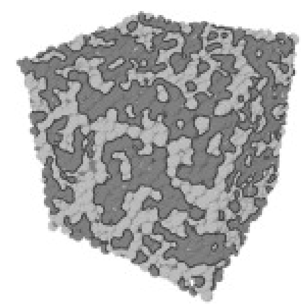
Highly ordered on particle-particle scale or placed in patterns at device scale.





Typically start as Dilute systems for mobility ⟶ *Success metric: Long-range order and non-hexagonal*

Fig. I.C.2. Silica NPs localized in lithographically defined grooves by spin coating and drying. (from Ref. 67).



Highly-loaded Nanoparticle dispersion casting and drying

Amorphous films/fibers/monolithic structures designed for tailored bulk-physical properties (conductivity, permeability, etc.) - *Success metric: Property performance and minimal residual stress*

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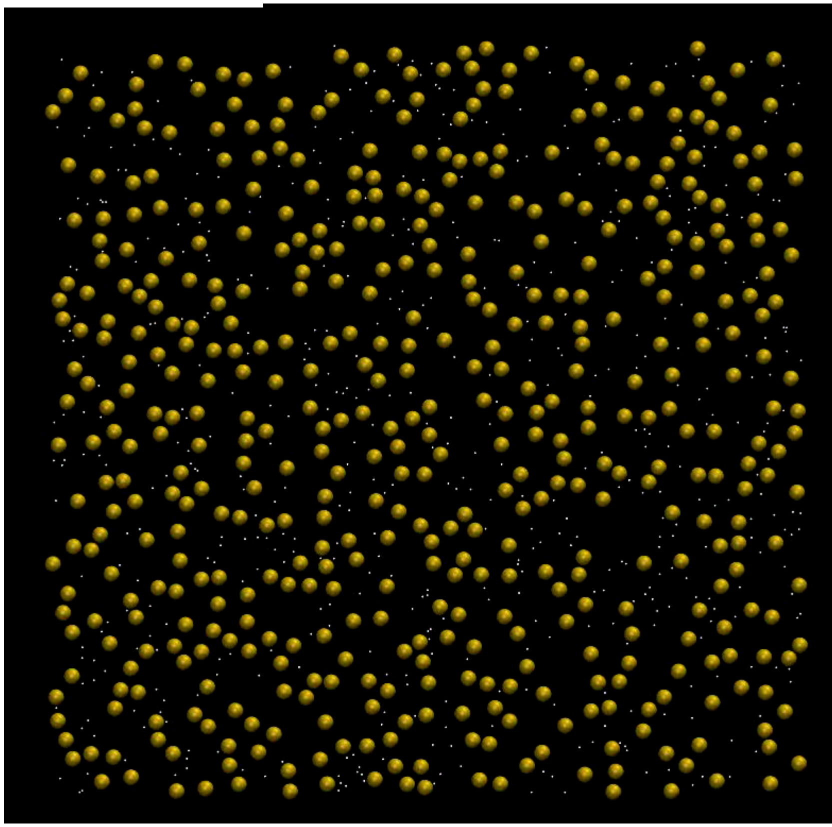
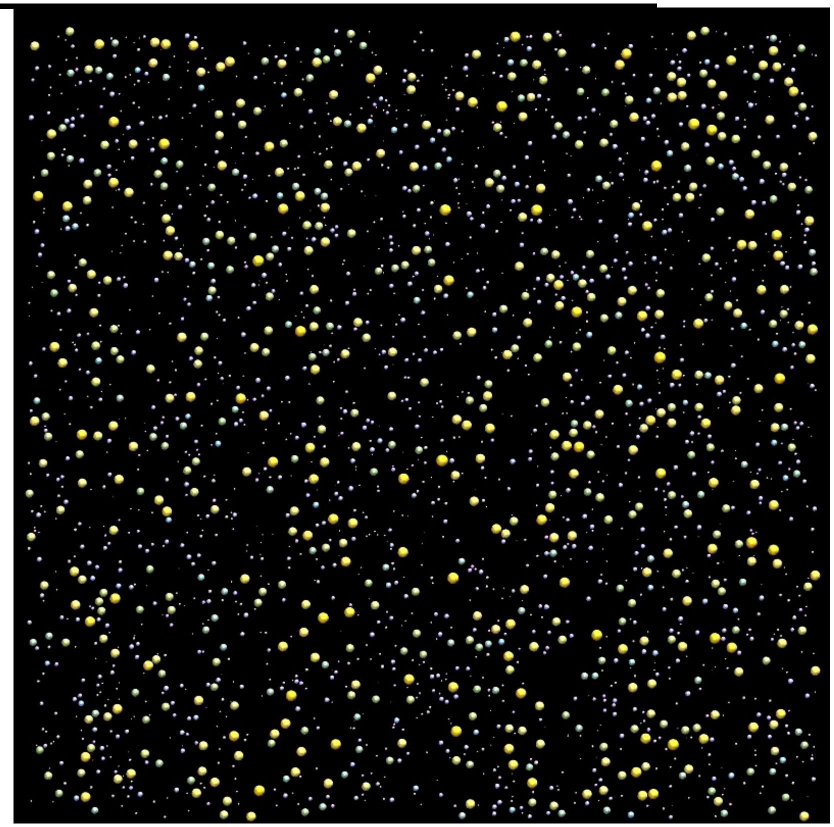
DRYING HETEROGENEOUS SYSTEMS

NEW WORK ON HIGHLY-LOADED DISPERSION

NG



BINARY 10:1 NANOPARTICLES (GOLD, THIOL



BI GAUSSIAN DISTRIBUTION (GOLD-THIOL

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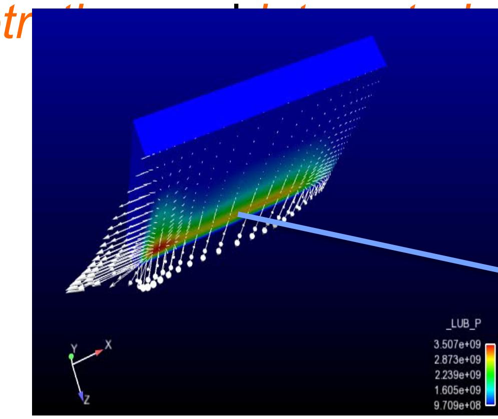
Conclusions/Status - Nanoparticle Flow Project

- Fully released in LAMMPS (www.lammps.sandia.gov)
- Website/Wiki for NPFC members maintained.
  - Tutorials
  - Example scripts
  - Verification and validation studies
- Current and potential applications at Sandia
  - Production, storage and transport of QDs for solid-state lighting/ displays
  - Algae-biofuels
  - Battery electrode fabrication (Drying)

Finite Elements and thin regions calls for Shell Elements!

- **Shell Element Technology Ideal when large-aspect-ratio regions (structures) prevail.**
  - Shell-Element: reduced-order continuum element (integrated with presumed mechanical response in one direction – membrane, inextensible shell, lubrication, porous) – *Three dimensional coordinates but only two integration coordinates*
  - We have developed and integrated true curvilinear shell capability for *lubrication* (first of its kind to our knowledge integrated with continuum codes), *porous penetr* … *tructure*.

Lubricated Slider Bearing, Melt Lubrication



Layer thickness < 5 microns, slider dimension ~10 cm

"Shell elements are also thought of as a way (data-structure, mechanism) to apply overloaded, fancy BCs"

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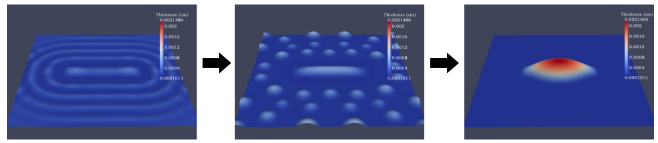
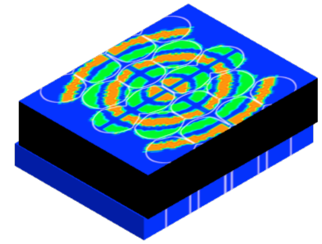
Motivation is Application Driven

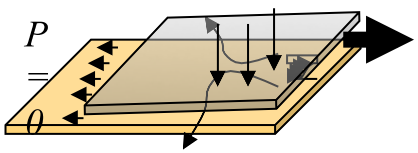
Top-down nano-manufacturing: fluid distribution, printing, mold filling in large-aspect ratio regions

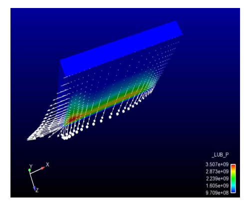




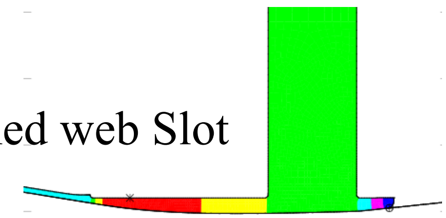
Thin-liquid film coating: film flow, metering flows, thin metering structures

Sliding Contacts: electrical brush

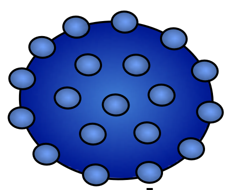


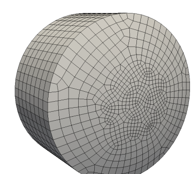


Tensioned web Slot



Capillary surface microstructure, surface rheology: emulsions, surface rheometry, oil recovery





Miscellaneous: surface microprobes (Moore et al., "Hydrophilicity and the Viscosity of Interfacial Water", submitted to Langmuir)*, tire hydro-plane etc.*

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CURRENT GOMA SHELL CAPABILITY (10/1/2011)

-Reynolds lubrication equation (highly accessorized):

$$\frac{\partial(\rho h)}{\partial t} + \nabla_{II} \bullet \left(\frac{\rho h}{2}(\underset{\sim}{U}_A + \underset{\sim}{U}_B) - \frac{\rho h^3}{K\mu}[\nabla_{II} p - \sigma\kappa\delta(\phi)\underline{n} - \rho(\phi)\underline{g} + \underline{f}] \right) - (j_A + j_B) = 0$$

Moving Control Vol (squeezing) | *Moving Walls* | *Pressure Driven* | *Capillary interfaces (multiphase)* | *Body forces* | *Exchange Fluxes*

-Shell energy equation (highly accessorized):

$$h\rho C_p \frac{\partial T}{\partial t} + h\rho C_p \underset{\sim}{u}_{II} \cdot \nabla_{II} T - hK_{eff} \nabla_{II} \cdot \nabla_{II} T + Q_{surf} + Q_{VD} + Q_{Joule} = 0$$

Ohmic Heating | *Viscous heating* | *lateral fluxes*

-Film Equations:

$$\frac{\partial h}{\partial t} + \nabla_{II} \bullet [\frac{h^3}{3\mu}(-\nabla_{II} p) + \underset{\sim}{U}_B h] + \dot{E} = 0$$

$$p = -\sigma \nabla_{II} \bullet h - \Pi$$

-Structural shells (2D only, and inextensible):

Other interoperable models:
- -Turbulence models
- -Electrostatic energy
- -Lorentz forces

CURRENT GOMA SPECIALTY SHELLS (continued):

-Porous shells

$$\frac{dS}{dt} = -\frac{1}{\phi}\frac{\kappa_{zz}}{H\mu}\frac{dP}{dz}$$

Closed pore

$$\frac{dS}{dt} = -\frac{1}{\phi}\frac{\kappa_{zz}}{H\mu}\frac{dP}{dz} + \frac{\kappa}{\mu}\nabla_{II}P$$

Open pore

$$-\phi\frac{\partial S}{\partial t} = \nabla \cdot v.$$

-Particle diffusion shells

$$\frac{\partial(\varphi h)}{\partial t} + \nabla_{II} \bullet [\frac{h^3}{3\mu}(-\nabla_{II} p)\varphi + \underset{\sim}{U}_B h\varphi] - \nabla_{II} \bullet [D\nabla_{II}(h\varphi)] = 0$$

-Evolution shells (melting, grow

$$v = (\mathbb{I} - nn) \cdot v + nn \cdot v = v_{\mathrm{II}} + v_{\mathrm{n}}.$$

$$\rho E_0 \frac{d\delta h}{dt} = H_{trans}(T - T_0)$$

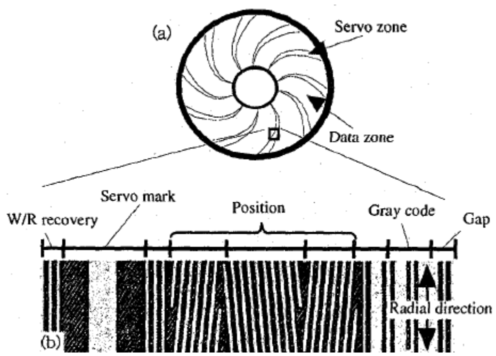
Phase Change

-Geometry Shells

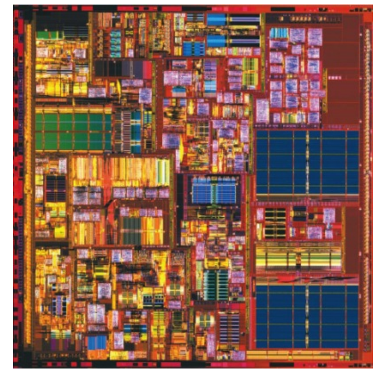
$$-h_{\mathrm{por}}\phi\frac{\partial S}{\partial t} = -\frac{h_{\mathrm{por}}}{\mu}\nabla_{\mathrm{II}} \cdot (\mathbb{K}_{\mathrm{II}} \cdot \nabla_{\mathrm{II}} p_{\mathrm{por}}) + \frac{1}{\mu}\mathbb{K}_{\mathrm{n}}\nabla_{\mathrm{n}} p_{\mathrm{por}}\Big|_{z=}$$

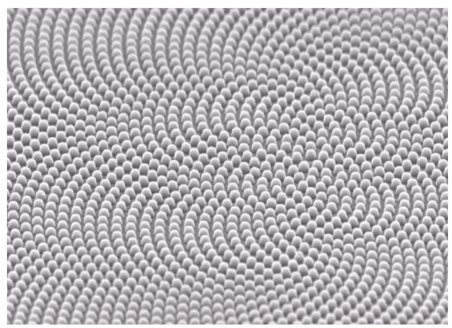
$$\kappa = -\nabla \ \mathbf{n} = -\nabla \ \frac{\nabla F}{|\nabla F|}$$

Nanoimprint Background
(Inkjet Based Jet and Flash Imprint)

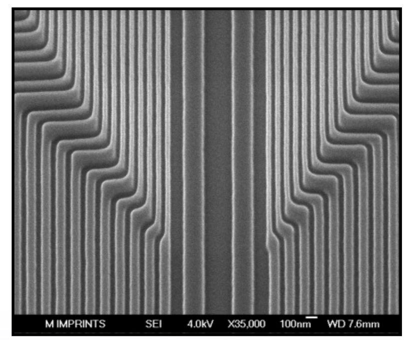


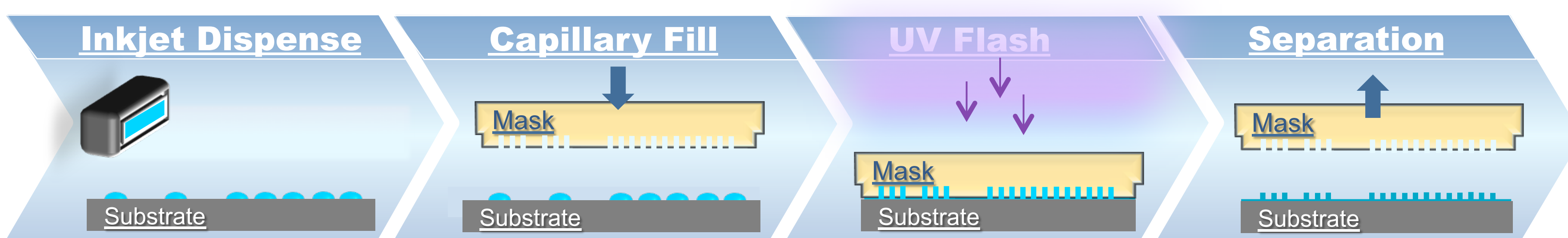
Macro-Scale
Pattern Density
Variations





Micro-Scale
Pattern Complexity





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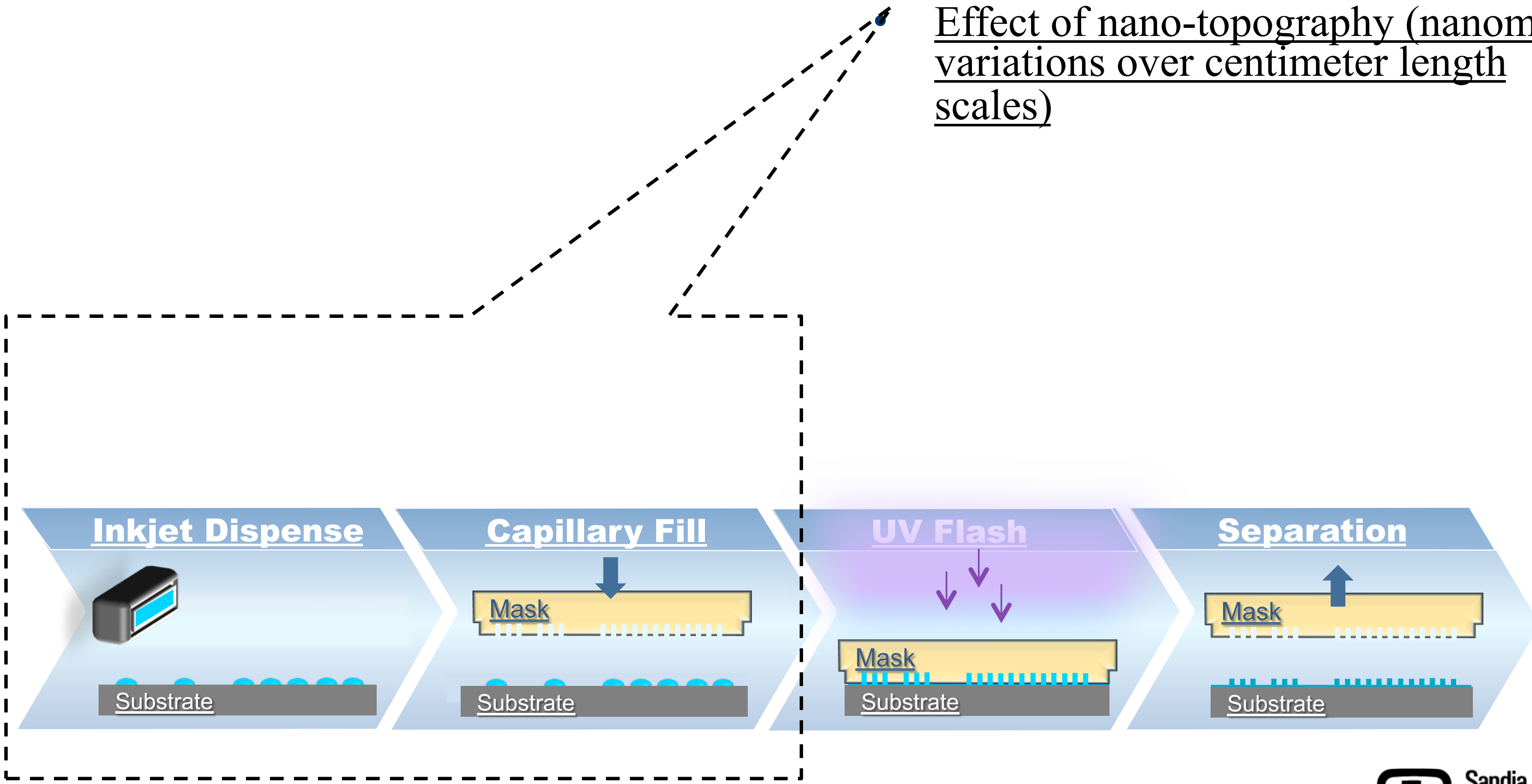
Nanoimprint Background

(Inkjet Based Jet and Flash Imprint)

Outstanding issues:

- Optimal droplet dispensing
- Minimizing residual layer thickness (RLT), ideally < 15 nm
- Effect of nano-topography (nanometer variations over centimeter length scales)



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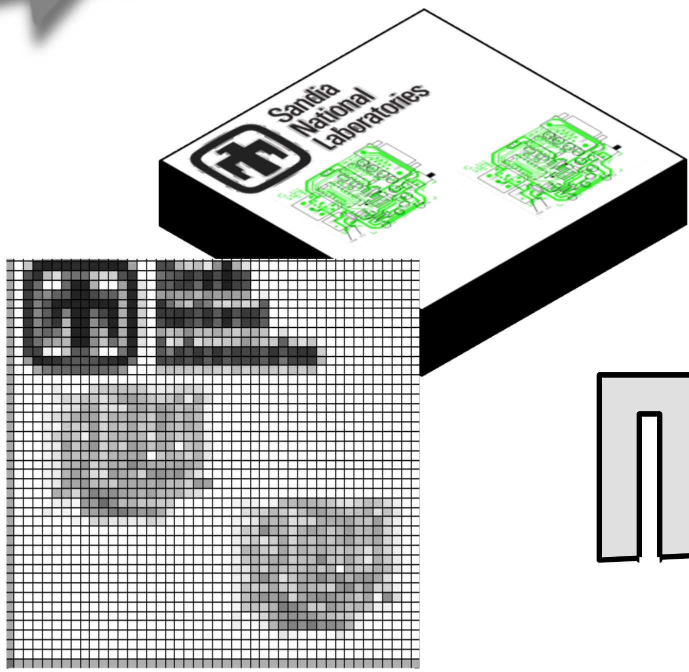
Bridging multiple scales

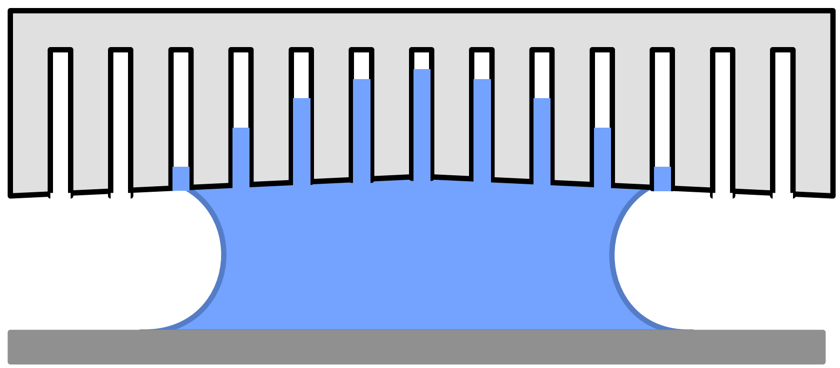
Important features:

- Six orders of magnitude difference in length scales
- Different physics at each scale



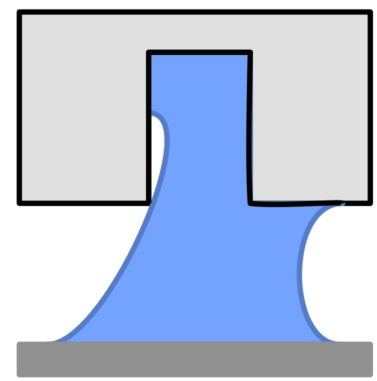
Machine-scale model

- 3-D Shell FEM
- Coarse-grained models
- Highly-parallel simulations
- 10 cm



Meso-scale model

- 3-D FEM
- Analytical model development
- Effective medium approach
- 1 μm

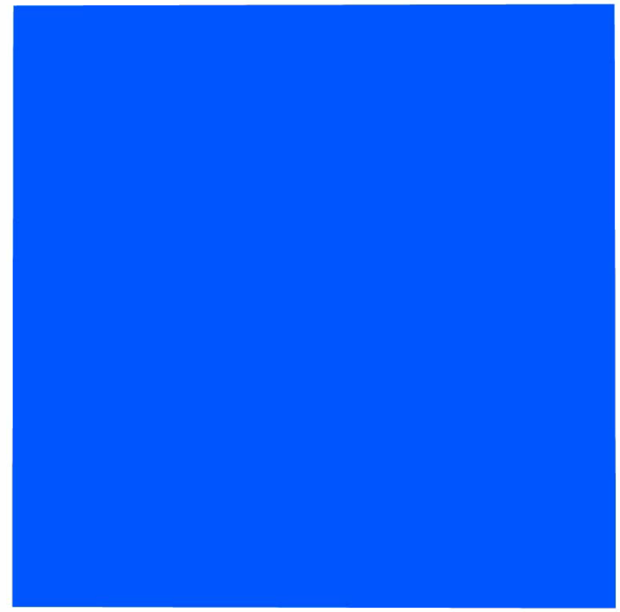


Feature Scale

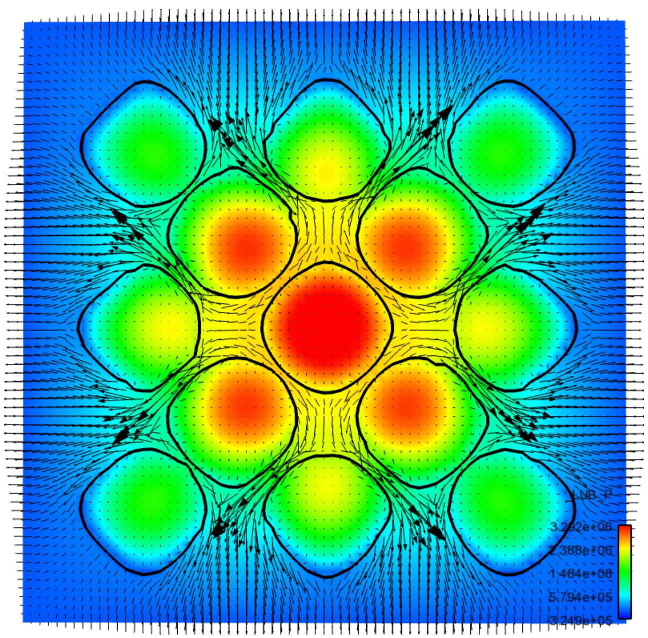
- 3-D FEM
- <u>Atomistics</u>
- 10 nm

Squeezing of multiple drops

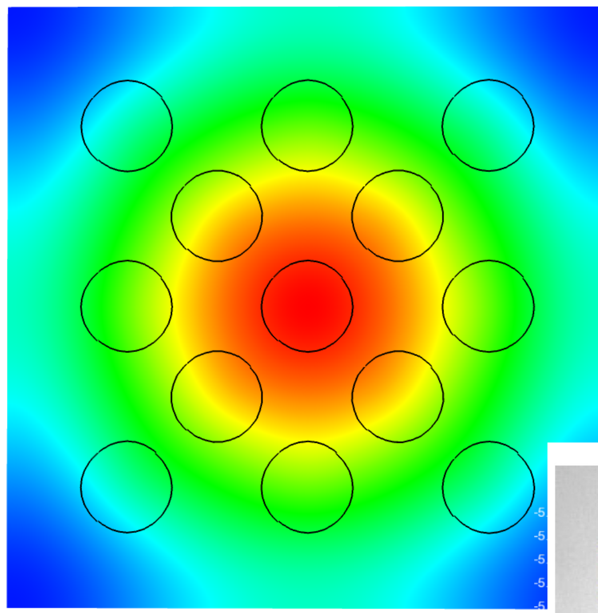
- Multiple drops do not spread symmetrically
- Dynamics of the gas phase become much more important
  - Gas must get out of the way
  - Gas can become trapped
- Template deforms over the scale of device



Pressure

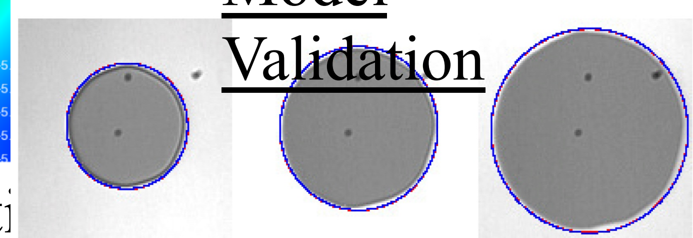


Velocity vectors



Template deflecti

Model Validation



(a) $t = 0.06$ s (b) $t = 0.12$ s (c) $t = 0.18$ s

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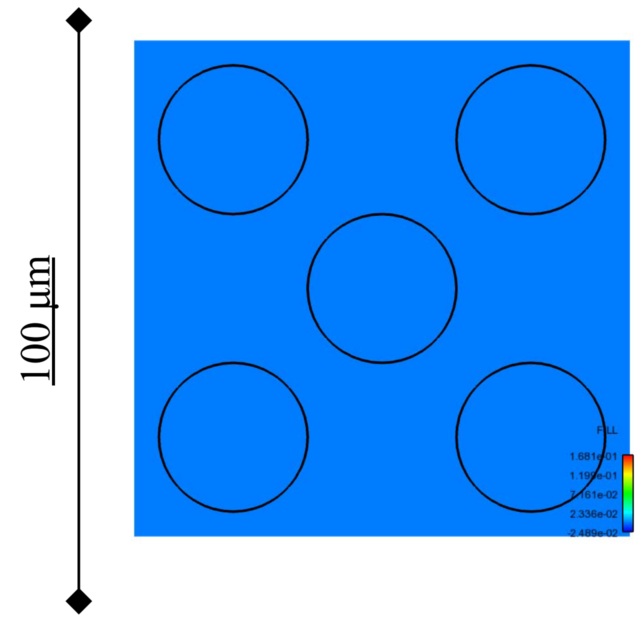
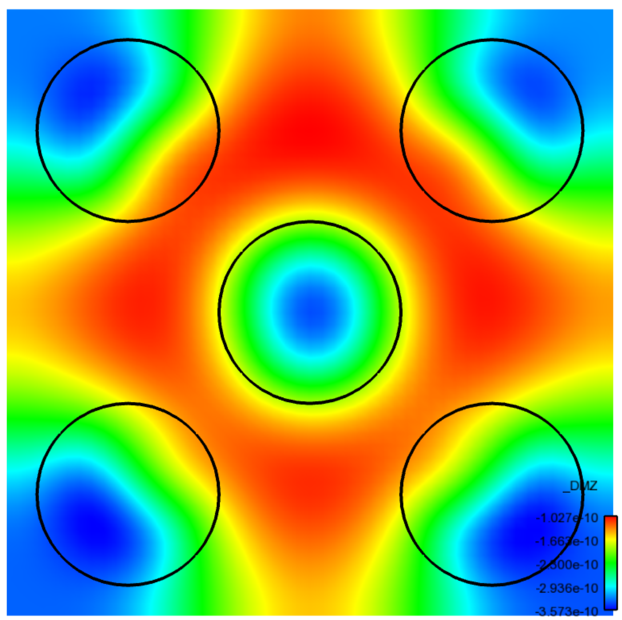
Squeezing under a patterned template

- Real templates aren't uniform, but have regions of features and regions without
- Presence of patterns have many effects:
  - Pressure profile
  - Template deflection
  - Residual layer thickness / droplet distribution

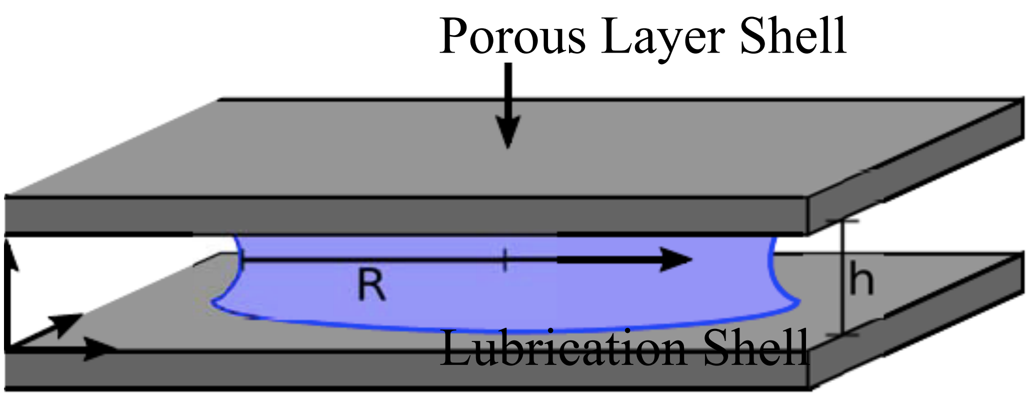


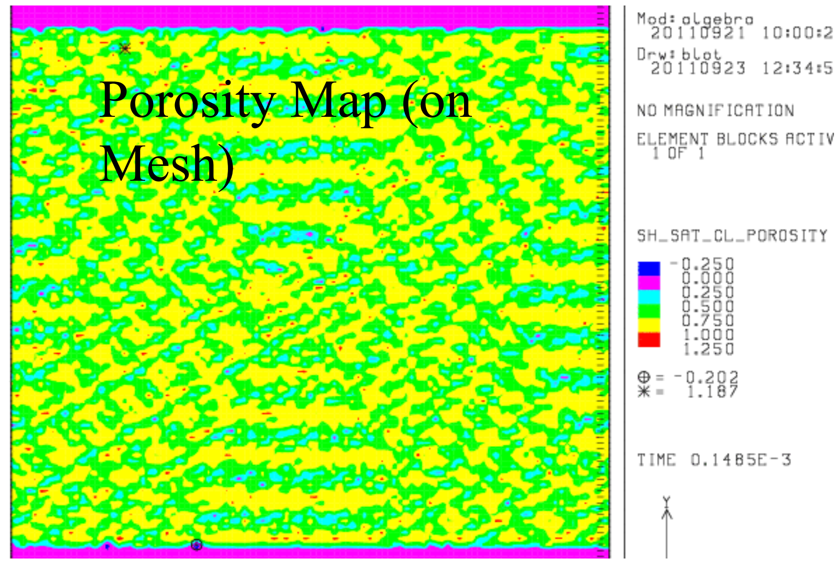
Saturation

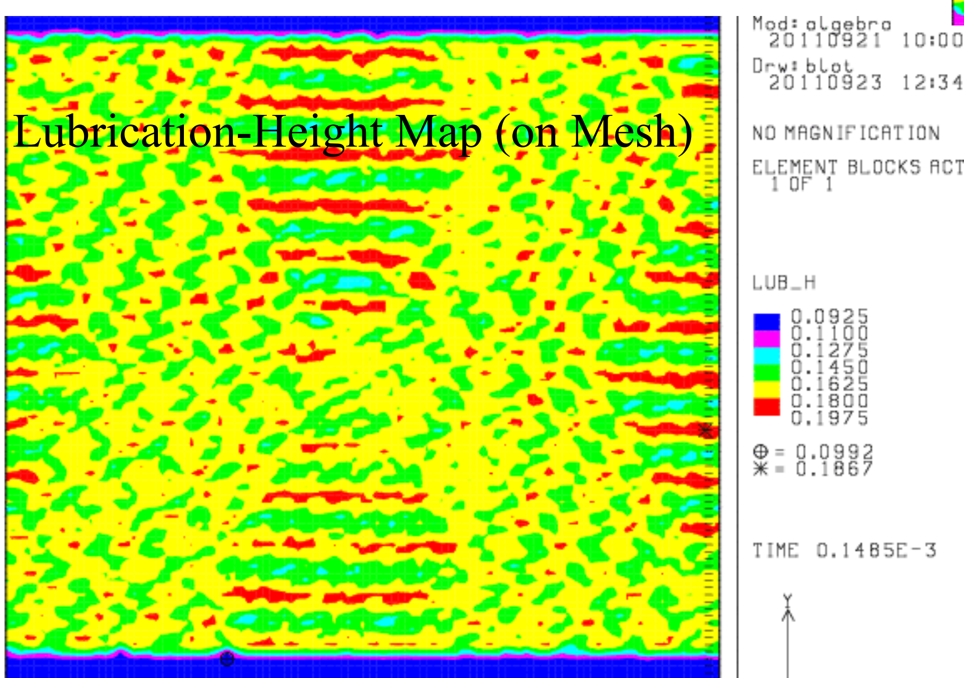


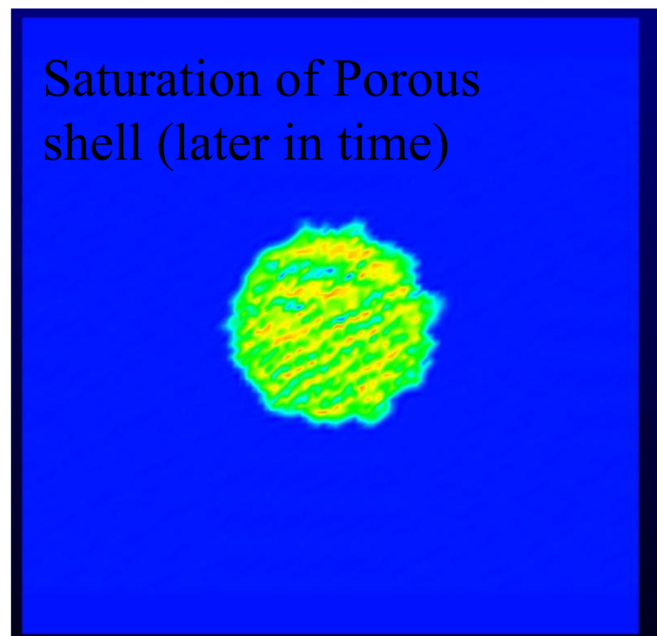
Template deflection

GOMA PIXEL-TO-IMAGE TOOL EXAMPLE, CONT'D

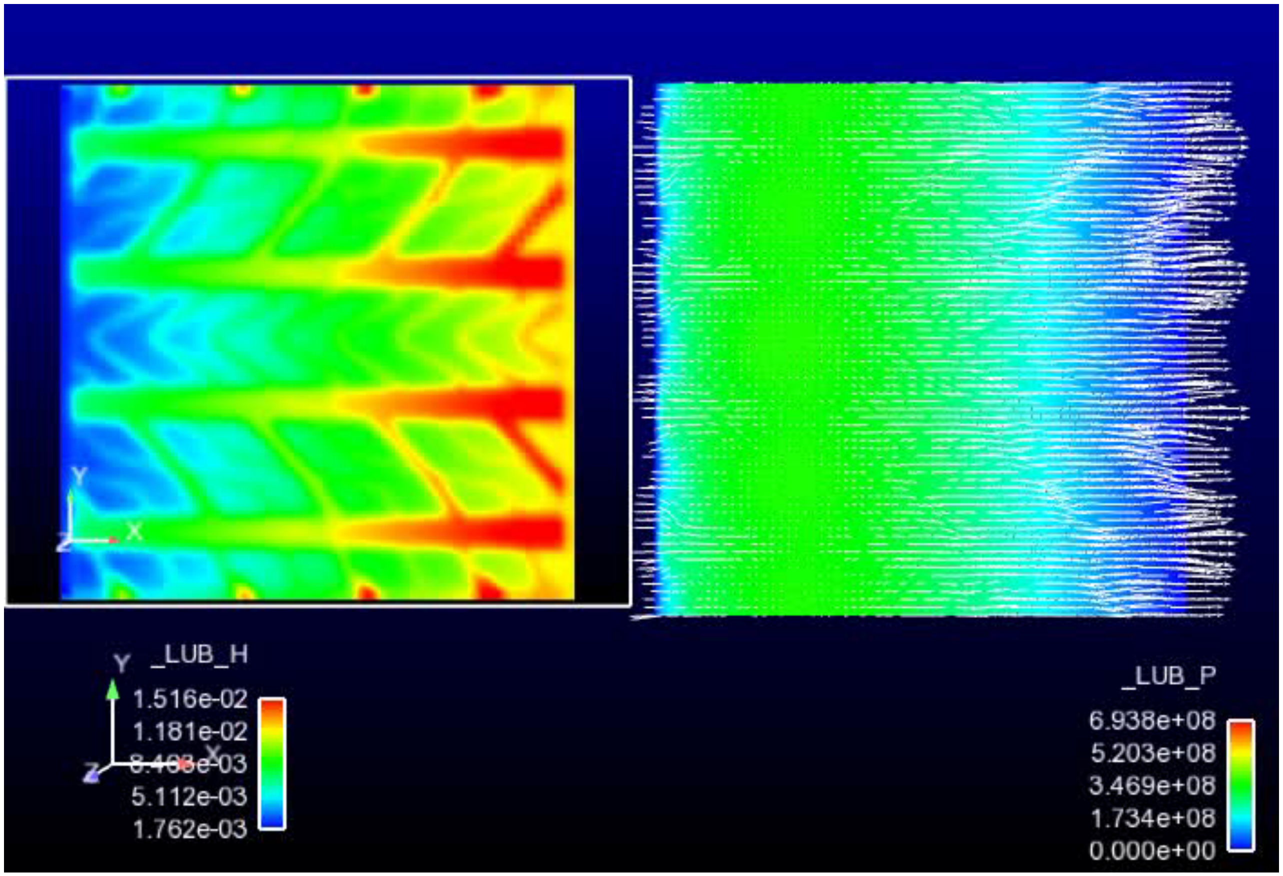








Example Application of Pattern-to-Mesh Tool: Rolling tire hydroplaning



SNL's Mod/Sim Capabilities and Activities in NanoEngineering - Retrospective and Opportunities

- **Production code platforms and multiscale activities which span all relevant scales (10 orders of magnitude) EXIST TODAY!**

- **Active programs in nanomanufacturing (NPFC and NIMS activity) - *Opportunity***

- **Software engineering which takes advantage of unique HPC environment.**

- **List of contacts:**
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