SAND2018-2260C

For Presentation at the TMS2018 Annual Meeting and Exhibition, 12-15 March 2018

Challenges in gravure and ink-jet printing of nano-colloidal inks

P. Randall Schunk

National Laboratory Professor

Department of Chemical and Biological Engineering

University of New Mexico

Manager, Advanced Materials Laboratory

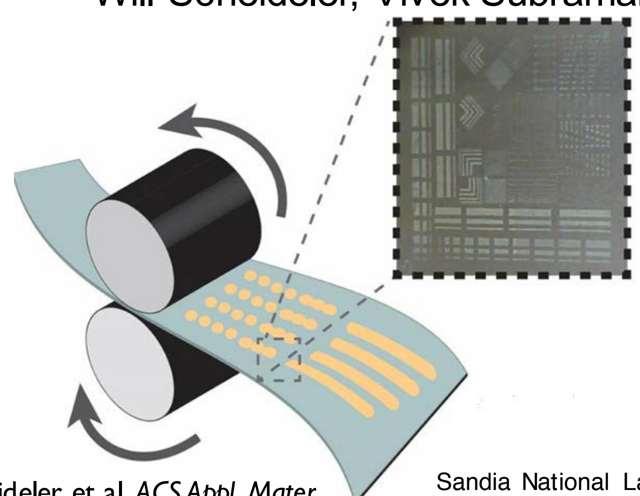
Sandia National Laboratories

Contributions:

Kristianto Tjiptowidjojo, Robert Malakhov (UNM)

Nelson Bell, Adam Cook, Sandia National Laboratories

Will Scheideler, Vivek Subramanian, UC Berkeley



Scheideler, et al, *ACS Appl. Mater. Interfaces*, 2015

http://solarindustrymag.com/midsummer-develops-sputtering-process-for-cigs-solar-cells-on-stainless-steel

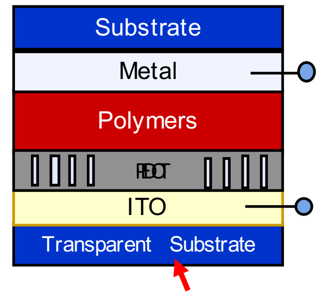
Sandia National Laboratories is a multi mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525

Sandia National Laboratories

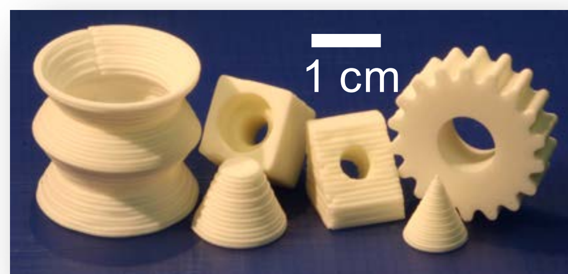
Particulate Inks for Energy, Computing/Sensing, Ceramic Piece Parts and more

- Materials/devices for energy storage, generation, conversion, sensors needed in volume – ***AM with physical template (viz. demands speed, R2R)!***
- Fully-dense ceramic piece parts and other specialized materials– ***AM with digital template (e.g. demands design flexibility - direct write)***
- Printed electronics – packaging and logic devices ***AM with digital and physical templates (demands materials flexibility and precision)***

Energy Storage/Generation Materials



Ceramics and meta-materials



Mobile computing

Flexible electronics

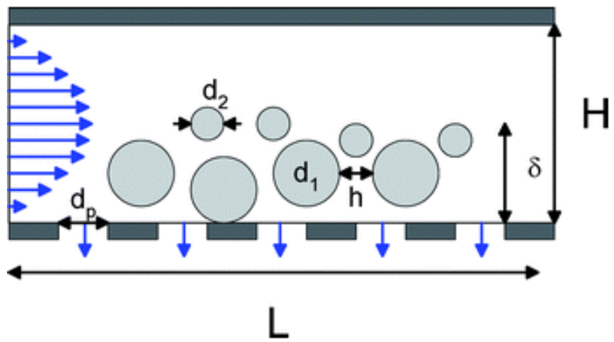
Sandia National Laboratories

Ink "generalization"

iNGk: a colored fluid used for writing, drawing, printing, or duplicating.

Simulations of confined suspension flow at multiple length scales†

R. G. M. van der Sman – Soft Matter, 2009 (5)



Mixture of particles and carrier fluid

-Particle size

-Particle size distribution

-Particle shape

-Particle material/mechanics

-Solvent/carrier rheology

-Particle loading

Ink "type"

Solution
- Dissolved species which undergo phase change upon deposition, e.g. Dye

Colloidal, nano-colloidal –
- Dispersions
  - Stabilized through long range molecular forces and short range thermal motion (brownian)

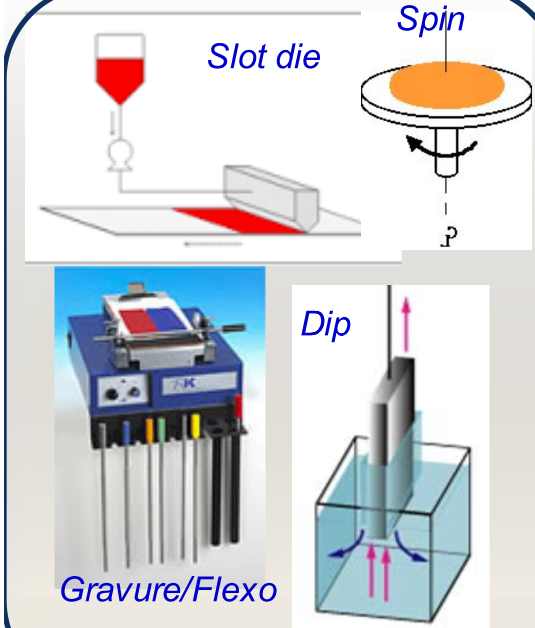
Suspensions
- Non-colloidal (>2-3 microns)
  - Dilute – settle out (sedimentation)
  - More Concentrated – sedimentation
  - Paste – viscous carrier and concentrated - stable

Dry Ink – e.g. toner (delivery through electrostatics)

Sandia National Laboratories

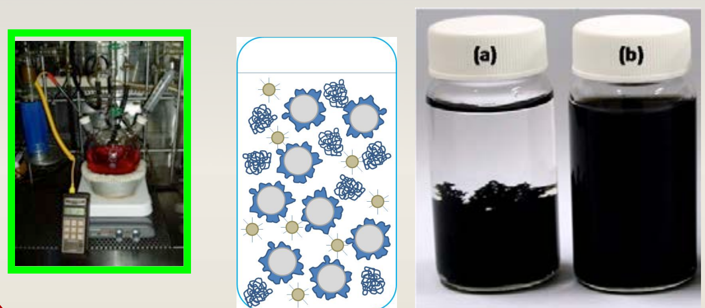
AML Materials Processing Routes

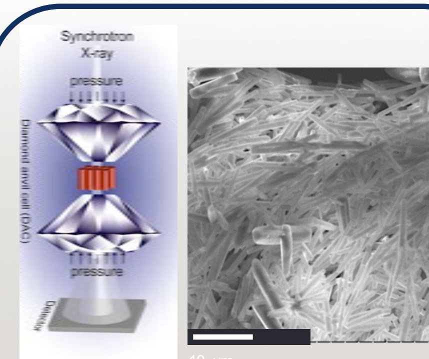
Particle effects in most of these ink processes have yet to be addressed with focused research



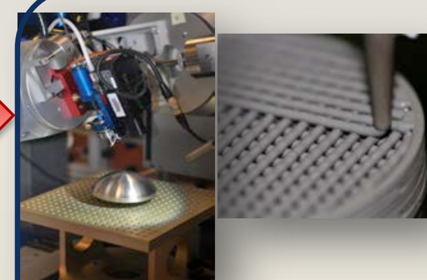
Precision thin-film coating

Chemistry -> Nanomaterials->Inks

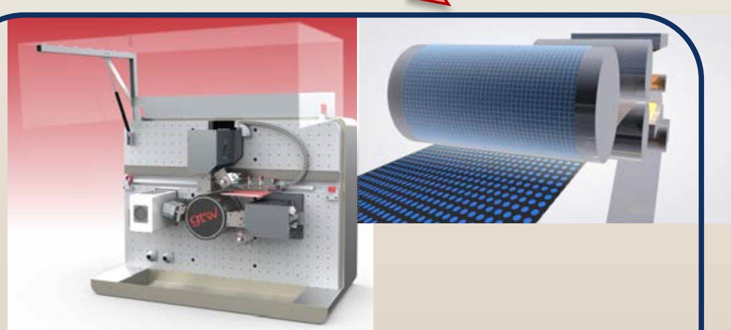




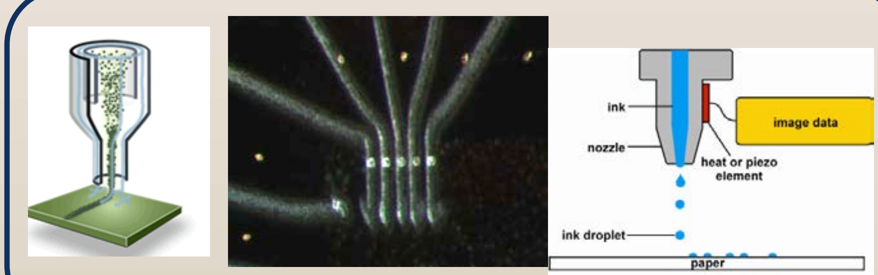
Pressure-Induced Assembly



Direct Write



microGravure Printing



Aerosol/Ink-Jet Printing

Printing Inks Carry Functionality

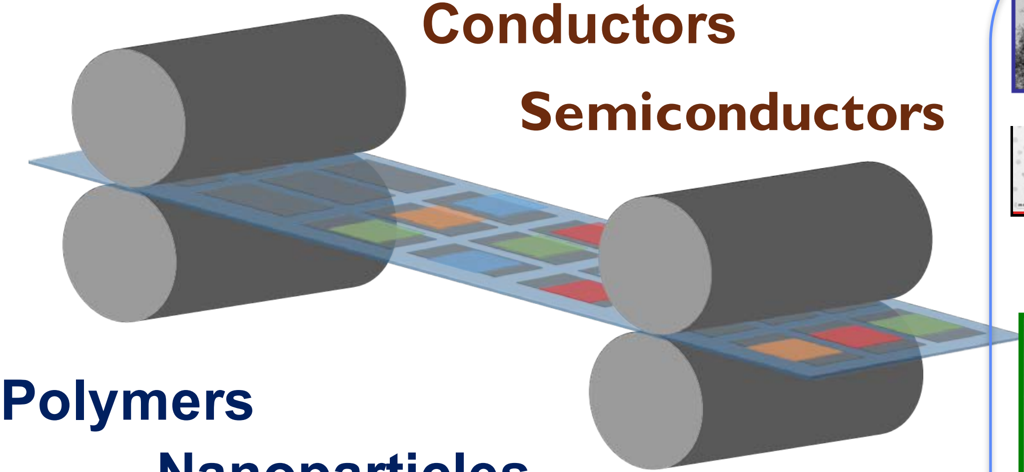
The strong suit of printed systems is the integration of diverse materials

But process design can depend on these material selections.

Dielectrics

Conductors

Semiconductors

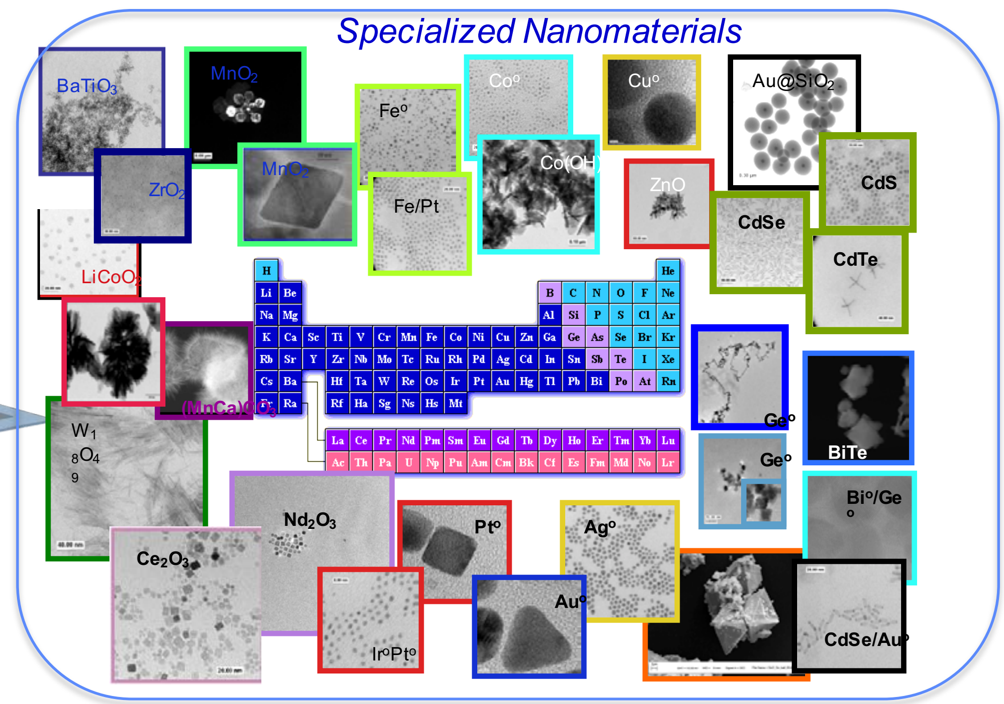


Polymers

Nanoparticles

Composites

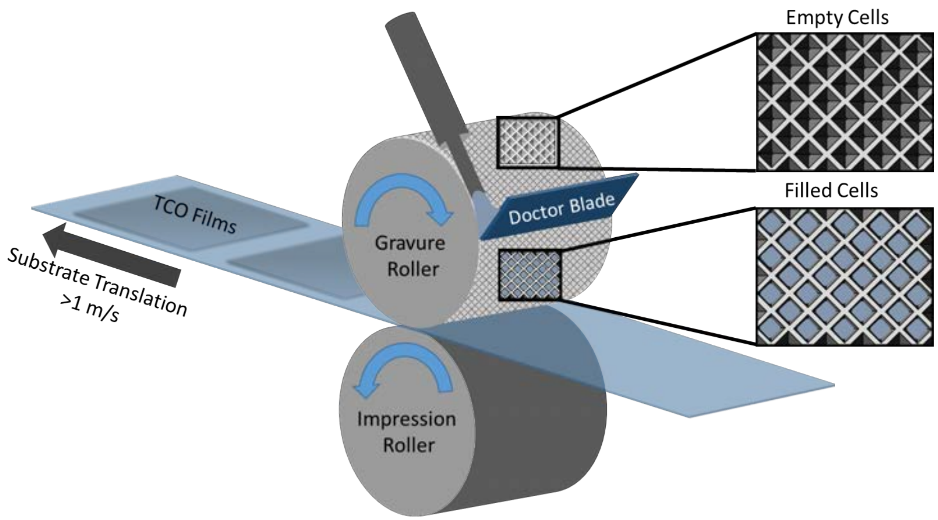
Sol-gels



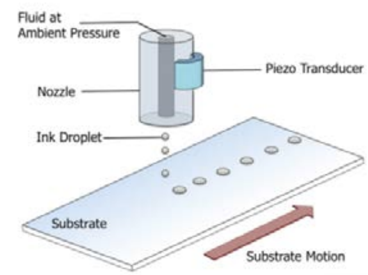
Sandia National Laboratories

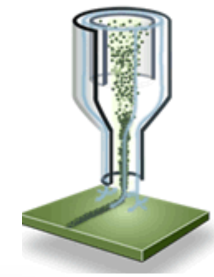
Promising Ink-based printing routes

Gravure/Flexographic Printing



Direct Write (DoD, DW, Aerosol)





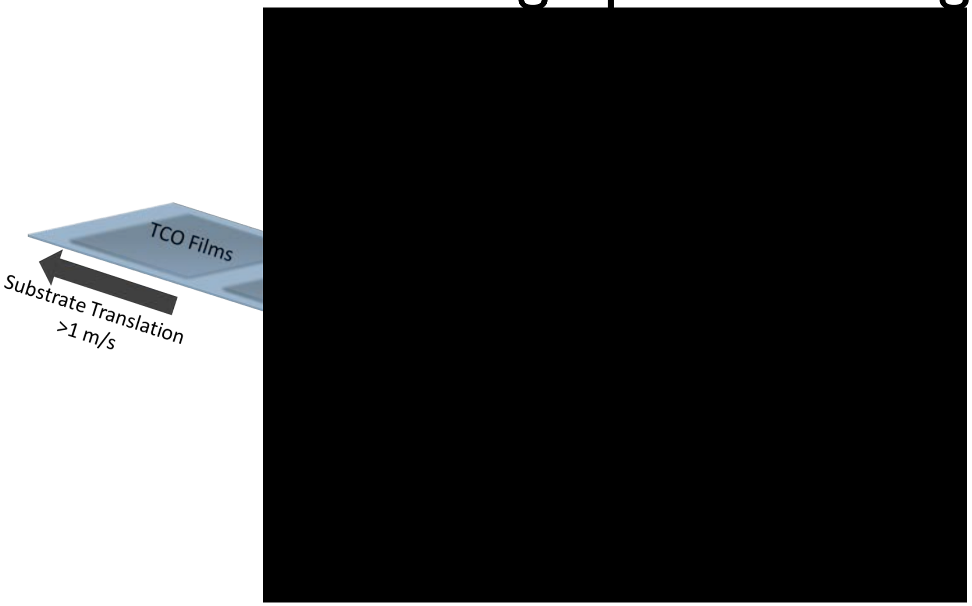
	Gravure	Direct write
Resolution	< 5 μm	< 30 μm
Speed	1 m^2/s	< 1 m^2/hr
Ink Viscosity	1-500 cP	1 cP – 10^4 P
Method	Contact	Non-Contact

Inkjet and gravure are complementary methods for low-cost fabrication

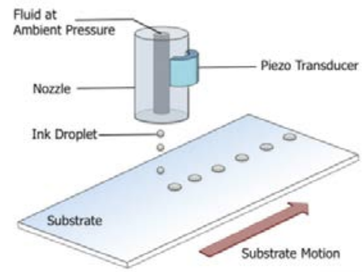
Sandia National Laboratories

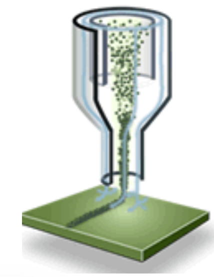
Promising Ink-based printing routes

Gravure/Flexographic Printing



Direct Write (DoD, DW, Aerosol)





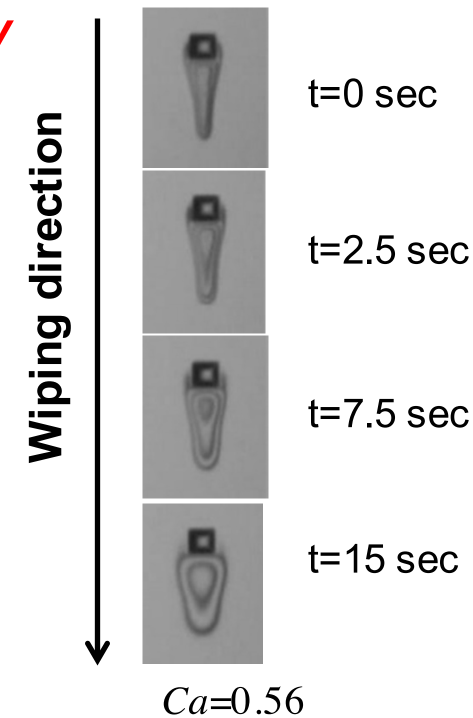
	Gravure	Direct write
Resolution	< 5 µm	< 30 µm
Speed	1 m^2/s	< 1m^2/hr
Ink Viscosity	1-500 cP	1 cP – 10^4 P
Method	Contact	Non-Contact

Inkjet and gravure are complementary methods for low-cost fabrication

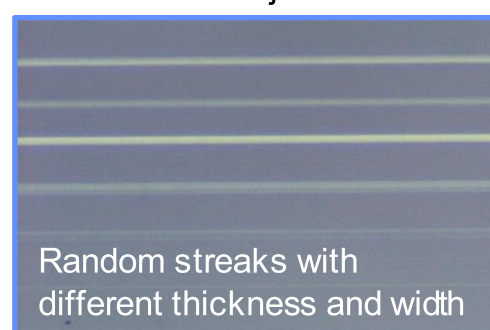
Important experimental observations on particle effects in gravure printing

Particles are both a blessing and curse: Material functionality through particle ink routes nearly limitless, BUT

- **Bulk viscosity (f(particles)) undermines feature sharpness and size** — models have confirmed this
- **Abrasion likely heightens blade and proof wear, clogs nozzles.** More deliberate experiments and modeling should be undertaken
- **Residue increases with particle size, as does streaking artifacts.** Cutoff length scale exists.
- **Particle effects on ink transfer, filling, have not been studied at all,** experimentally and theoretically.
- Virtually no experimental or computationally/theoretical work on the **bulk rheology effects of particles in inks** (complex fluid behavior like **thixotropy** and **viscoelasticity**).
- **Particles are discrete until densified, sintered, etc.** Process-Structure-Property needs extensive theoretical and experimental attention

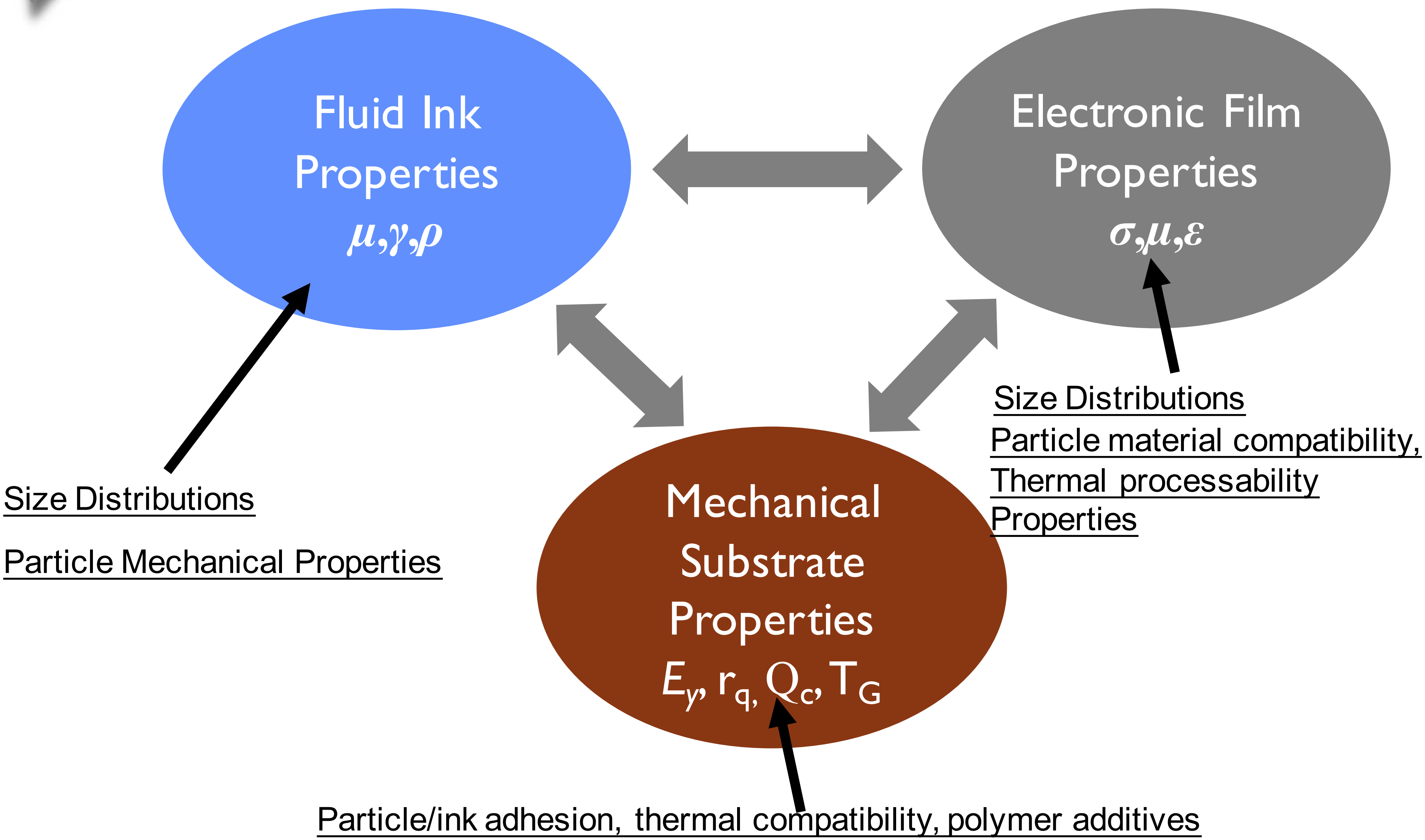


JS-B40G Inkjet Ink ~ 9cP



Sandia National Laboratories

Gravure/Ink-Jet Process science for ink-printing requires Co-Design

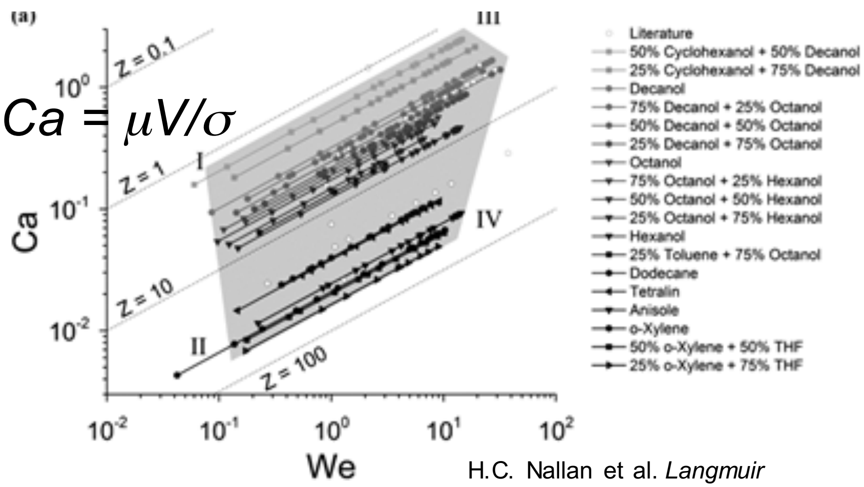


Inks, printing processes, and devices require iterative codesign

Development of Ink Compositions for Printing

- ✓ Ink Systems are formed from multiple components: Solvents (s), wetting agents, soluble polymers or micelles, & nanoparticle(s)
- ✓ Control over viscosity, surface tension, drying rate, and wetting are required.

A. Solvent compositions effects on printing window.



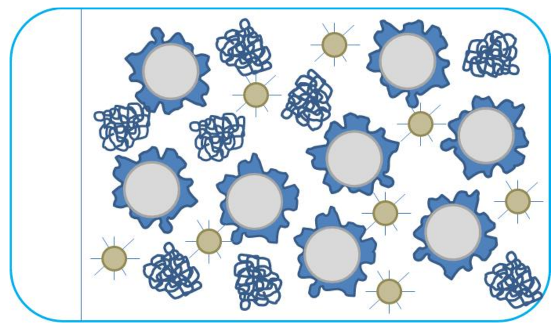
$Ca = \mu V/\sigma$

$We = \rho V^2 d/\sigma$

H.C. Nallan et al. *Langmuir* **30** (2014) 13470.

B. Effective dispersion is critical for printing using DOD or gravure/flexo printers.

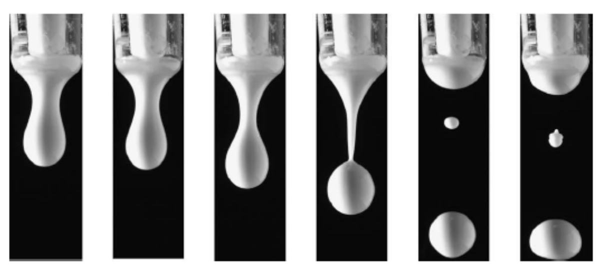
- Solids loading increased by proper dispersant choice, up to ~15-20%
- Surface tensions are low : between 15 – 40 mN/m
- Viscosity vary from 1-10 mPas.
- Surfactant concentrations tailored to surface area.

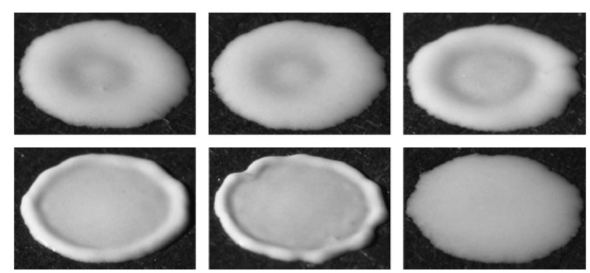


$$\mu_{rel} = \mu_{susp}/\mu_{sol} = (1 - \phi/\phi_m)^{-n}$$

C. Adjust wetting and drying agents to minimize satellite drops and surface wetting concerns.

Dependent on surface interactions with substrate, and drying rate.





R. Guo et al. *JECerS* **23** (2003) 115-122.; X. Zhao, et al. *Ceram.Intl.* **29** (2003) 887-892; N. Ramakrishnan, et al. J. Mat. Proc. Tech. 169 (2005) 372-381.; P.S.R. Krishna Prasad et al. *J. Mat. Proc. Tech.* **176** (2006) 222-229.

All experimental capabilities and SMEs exist at the AML!

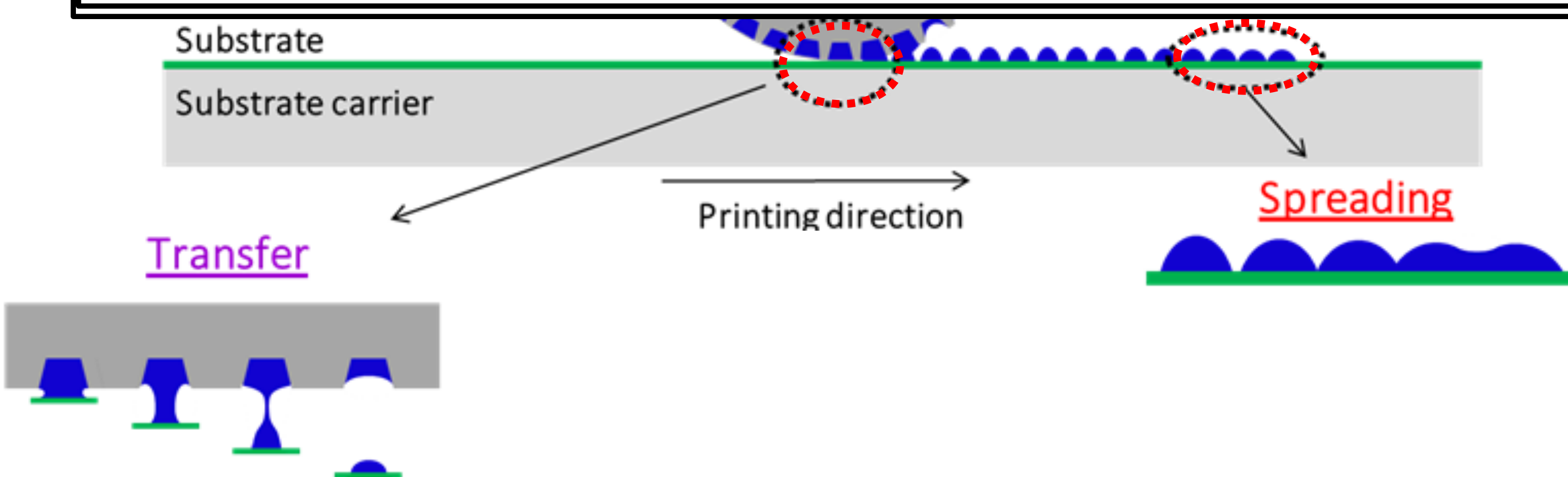
Bring to bear Computational Mechanics: What we know and don't know…

Continuum Mechanics – 3D capillary hydrodynamic solvers

- Capable amenable to Ca < 1 and various high 0<We<100.
- Complex liquid rheology (VE, Yield-Stress, etc.) - Particles
- Reduced order models for extreme geometries

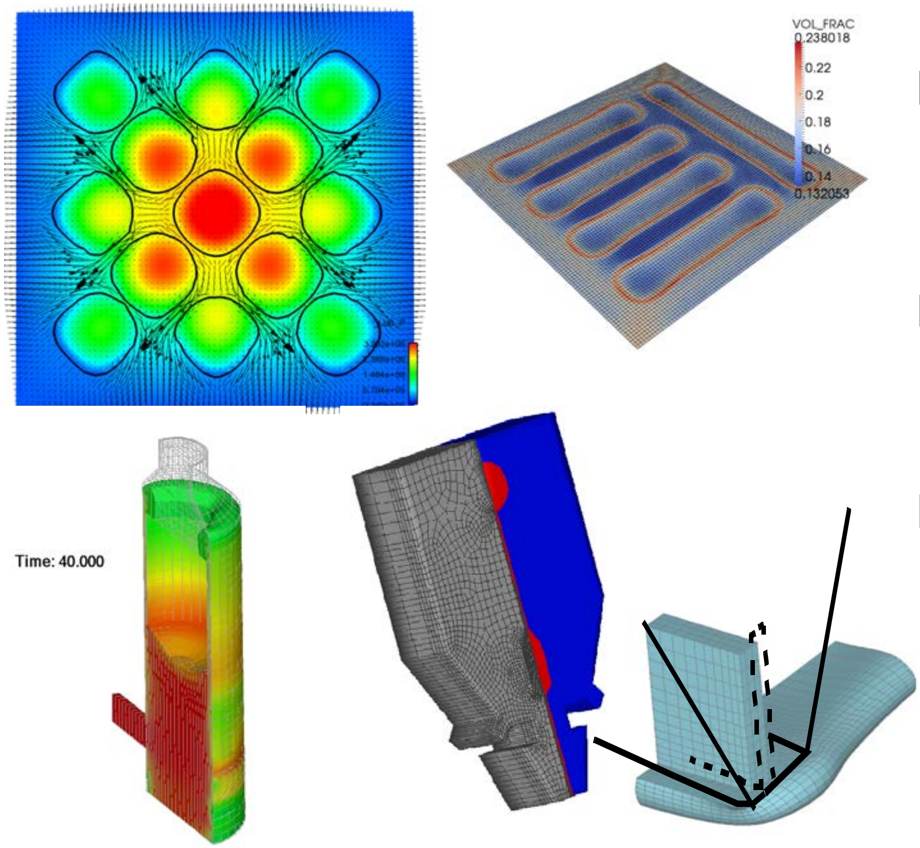
Continuum and discrete element solvers for consolidation, sintering–

- Solvent drying through porous media, consolidation (thermal, multiphase flow)
- Calendaring (thermal, mechanical, multiphase flow)
- Sintering (phase-change, reactive) - (Thermal, reactive, mechanical, fluid)



2014 R&D 100 Award Winner

Research Group Capability: Goma 6.0

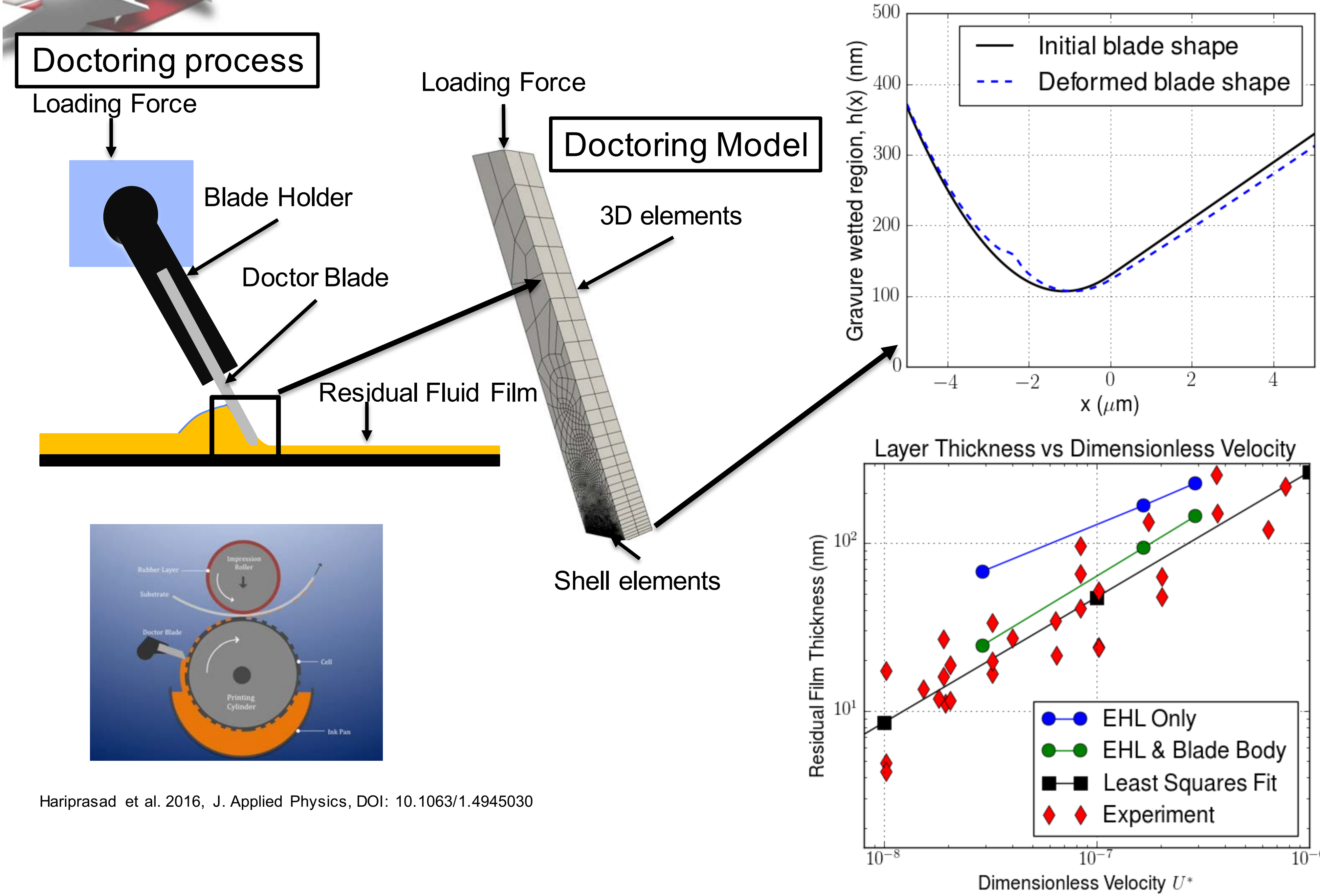


- Multiphysics ***finite element*** code, suitable for both ***research*** and ***production***
- Fully-coupled ***free*** and moving ***boundary*** parameterization – ALE, Level Set, etc.
- Modular code; ***easy to add equations*** – currently has 170+ differential equations
- ***Open source***! Available 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

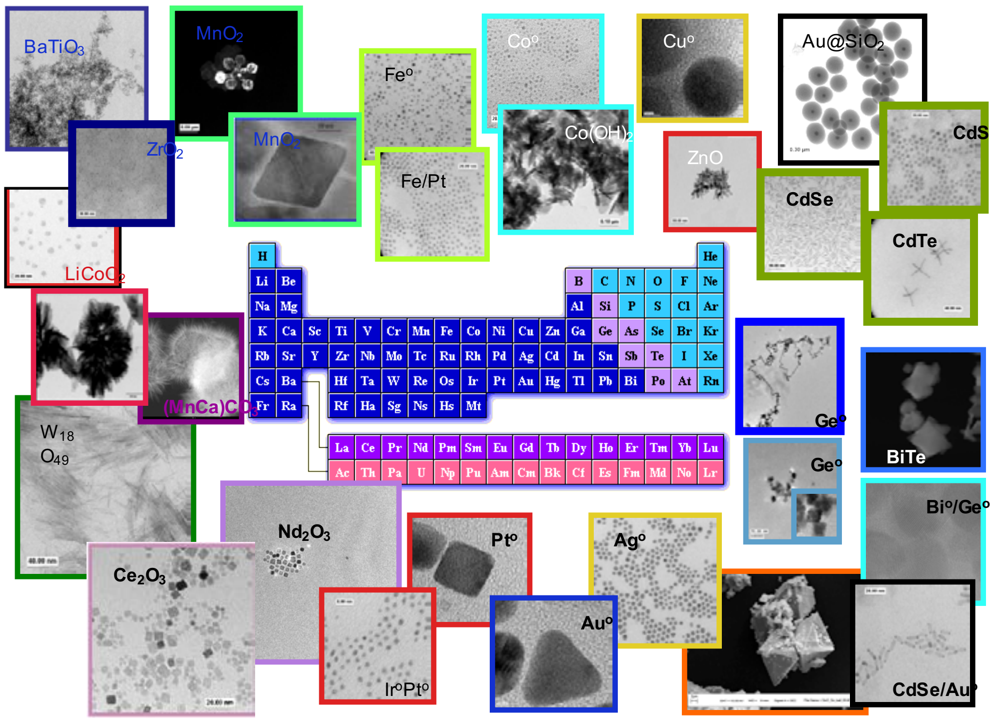
Doctoring in gravure printing

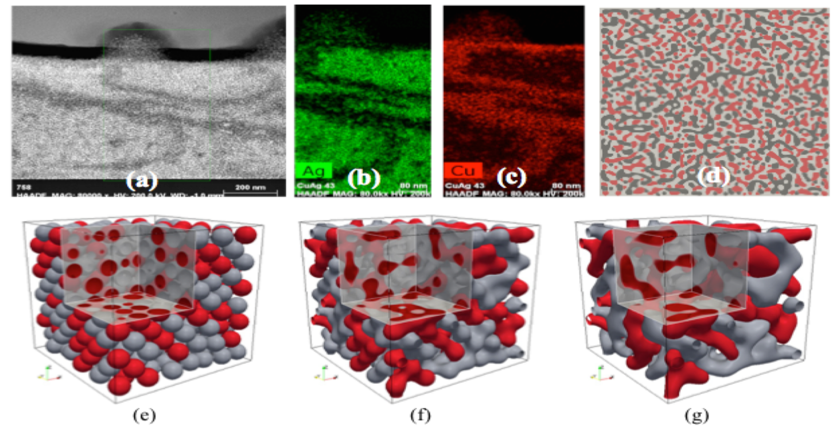


Hariprasad et al. 2016, J. Applied Physics, DOI: 10.1063/1.4945030

Solidification – Drying, consolidation, sintering…

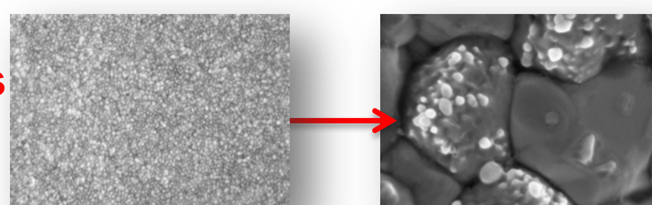
The development and study of tailored materials enable prototyping of functional components using Direct Write methods

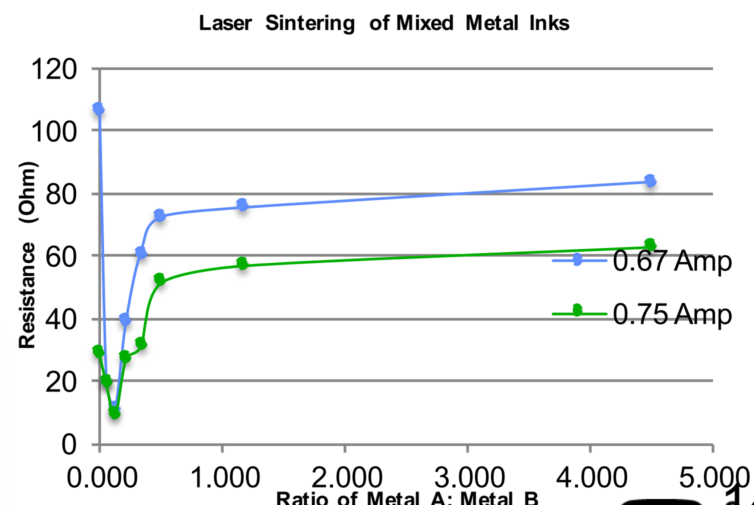




F. Abdeljawad, et al, A Diuse interface model of grain boundary faceting", *J. App. Phys*. 119, 235306 (2016)

Curing metal inks changes functionality!





Sandia National Laboratories

Sandia and Industrial Partnership for CAE tool development to assist ink design: The NanoParticle Flow Consortium (NPFC)

Comp. Part. Mech. (2014) 1:321–356
DOI 10.1007/s40571-014-0007-6

Particle dynamics modeling methods for colloid suspensions

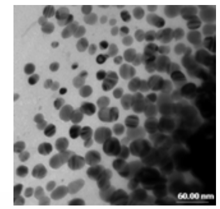
Dan S. Bolintineanu · Gary S. Grest · Jeremy B. Lechman · Flint Pierce · Steven J. Plimpton · P. Randall Schunk

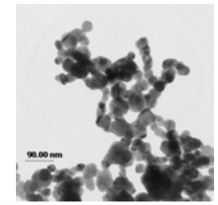
	Explicit Solvents		Implicit Solvents
	DPD	MPCD	SD-based (FLD, BD)
PREDICTIVE ABILITIES FOR SIMPLE SUSPENSIONS OF SPHERICAL PARTICLES			
Diffusion and viscosity	Well-established, but minor challenges remain in accuracy/boundary conditions; large polydispersity ratios can be computationally challenging		Well-established, but large polydispersity ratios still problematic
Microstructure prediction	Finite size of DPD particles problematic at high volume fractions/close particle contact.	Depletion effects introduce artificial inter-particle interactions.	Excellent agreement with experimental data for simple systems.
Direct mapping to physical properties	Often difficult, not all properties can be achieved simultaneously. Inherently problematic due to low Schmidt numbers and high fluid compressibility.		Simple solvent properties (e.g. viscosity, temperature) are directly input.
ADVANCED CAPABILITIES			
Non-spherical particles	DPD-colloid coupling relies on centrosymmetric potential; problematic for general case	Minor challenges exist with regard to boundary conditions/accuracy	Some simple shapes tractable. Near-field only applicable to spheres, spheroids, or particles composed of spheres; crude approximations possible for far-field.
Non-Newtonian solvent rheology	Modified algorithms can achieve certain solvent rheological properties; mapping to exact given rheology difficult		No attempts reported; requires significant development, e.g. coupling to mesh-based continuum solvers (FEM/FDM)
Complex flow geometries	Minor challenges with regard to boundary conditions/collision detection.		Boundary condition development required for confined and flow-through systems. Not suitable for arbitrary geometries.
Solvent removal (drying) and/or curing	Solvent can be readily removed to simulate drying. Capillary forces must be added. Viscosity cannot easily be adjusted during simulation.		Only simple slow drying models possible (e.g. moving wall). Capillary forces must be added. Solvent curing can be simulated by changing viscosity.

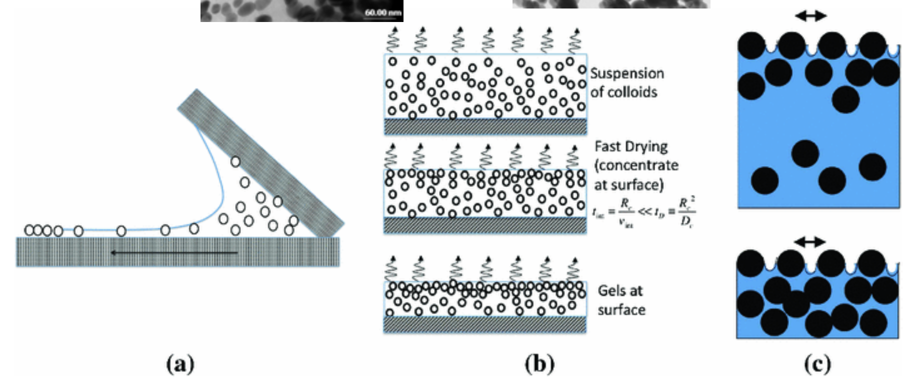
Sandia National Laboratories

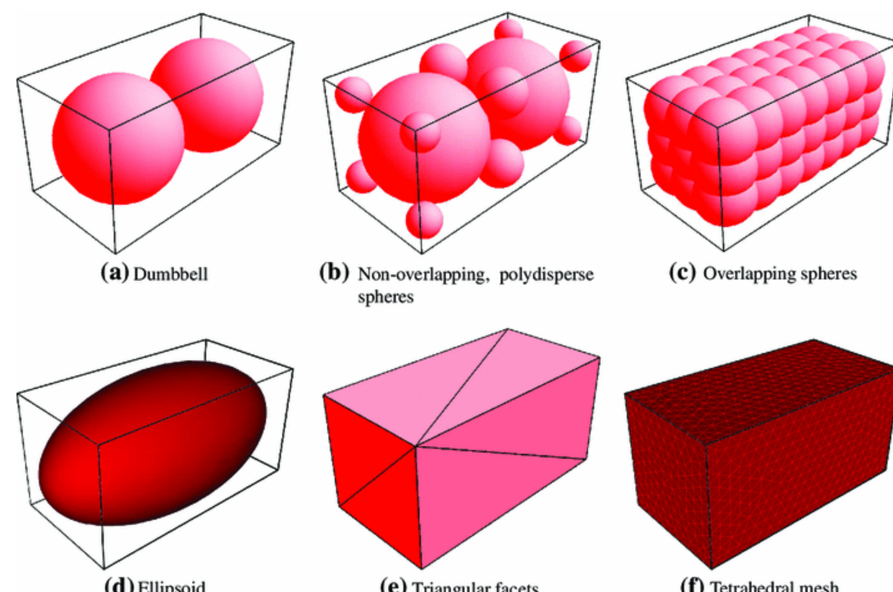
Advanced Capability Requirements for DEM Methods

- **Complications requiring advanced capabilities**
- **-Non-Newtonian solvents**
- **-Aspherical particles**
- **-Drying/solidification**
- **-Complex flow geometries**
  - Confined
  - Extreme shear
  - FSI









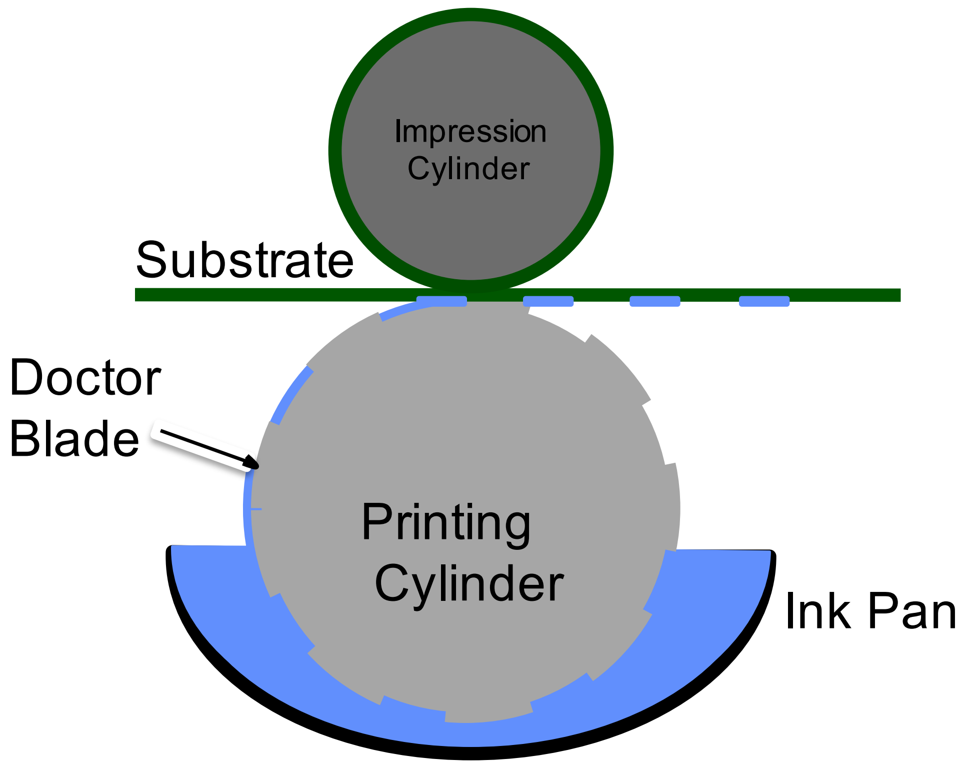
National Laboratories

Summary & Future Work

- Ink-based AM routes age-old, mature in an "Edisonian" sense
- Precision applications demand wider materials palette and colloidal materials
- Precision applications require ink-design, material properties, and substrate properties to be "co-designed" with the printing and solidification processes
- Physical barriers to higher throughput and smaller features are rooted in
  - Capillary hydrodynamics
  - Wetting and spreading
  - Structural mechanics (thin sheet)
  - Metrology (on-line/at-line)
  - Colloidal dispersion dynamics (rheology, wetting and spreading)
  - Solidification and microstructure
- Many outstanding problems in computational mechanics remain
  - DEM, Continuum, Phase-field

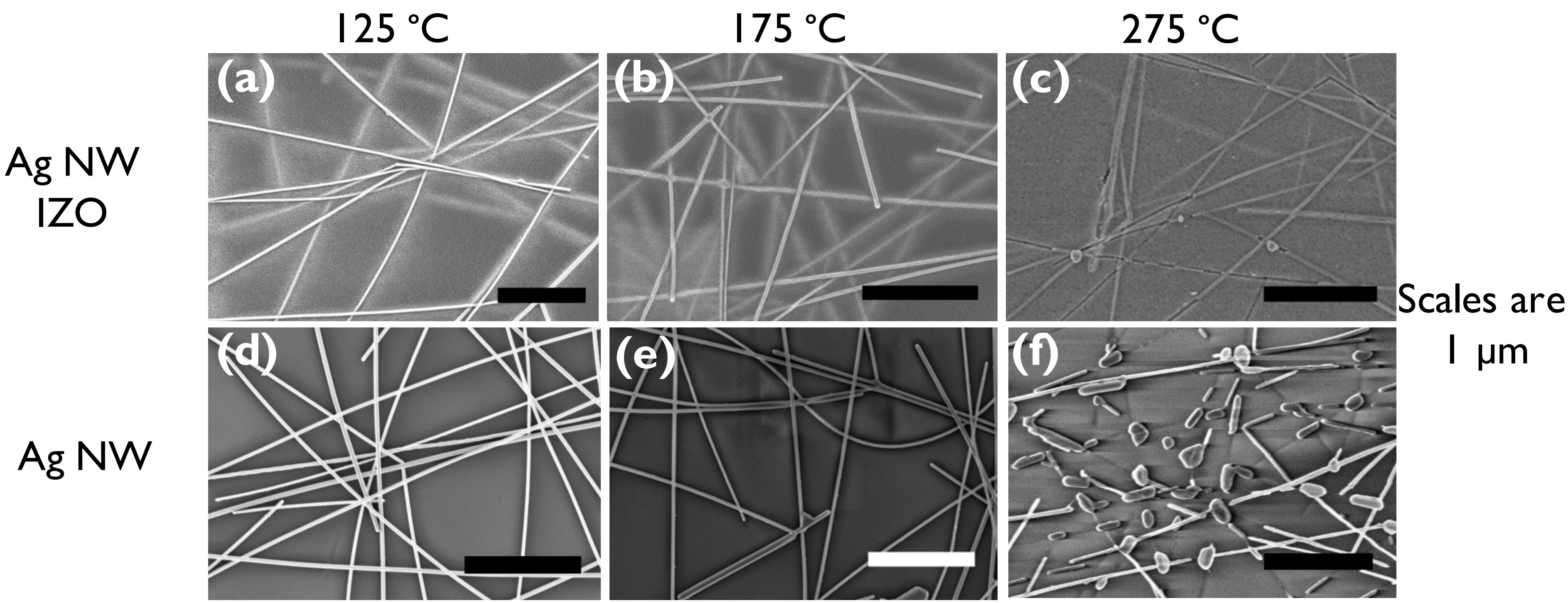
Sandia National Laboratories

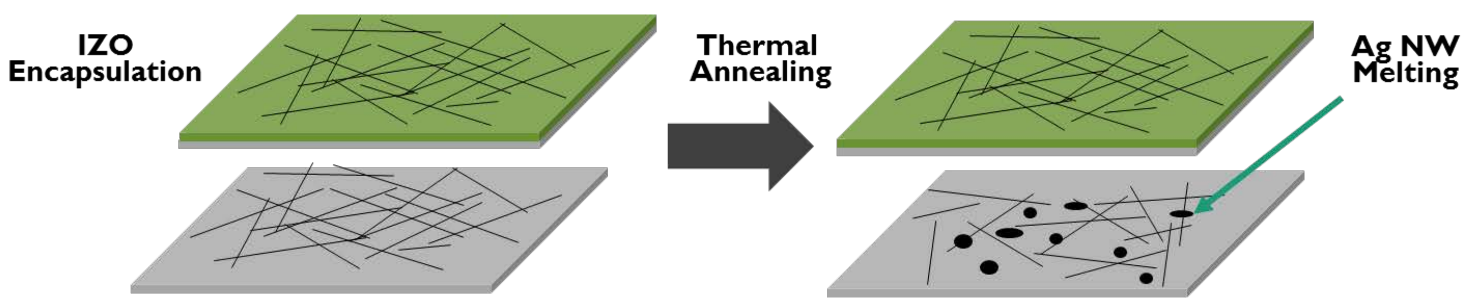
BACKUPS



Impression
Cylinder
Substrate
Doctor
Blade
Printing
Cylinder
Ink Pan

Nanowire Hybrid Encapsulation

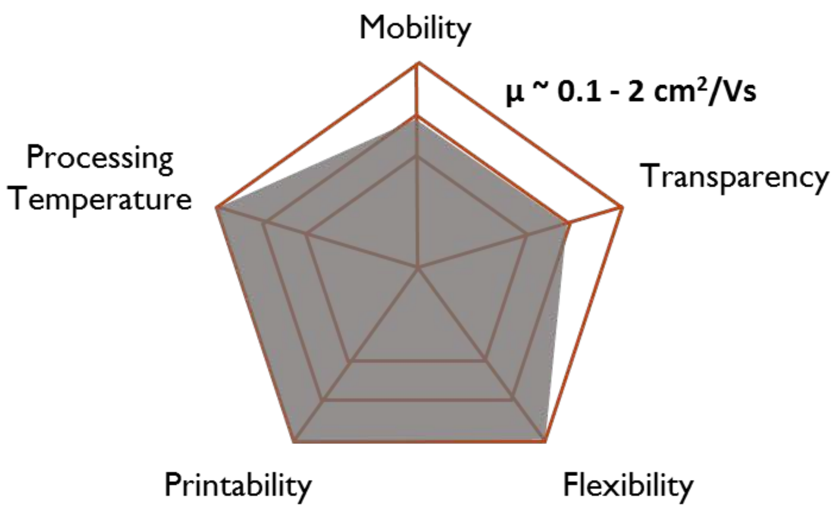


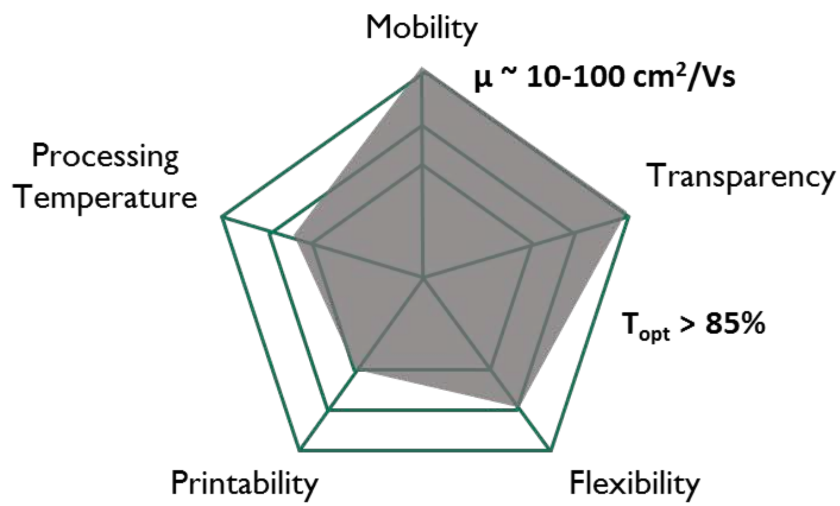


[12] Scheideler, et al. *J. Mater. Chem. C*, 2016

High Performance Printed Transistor Materials

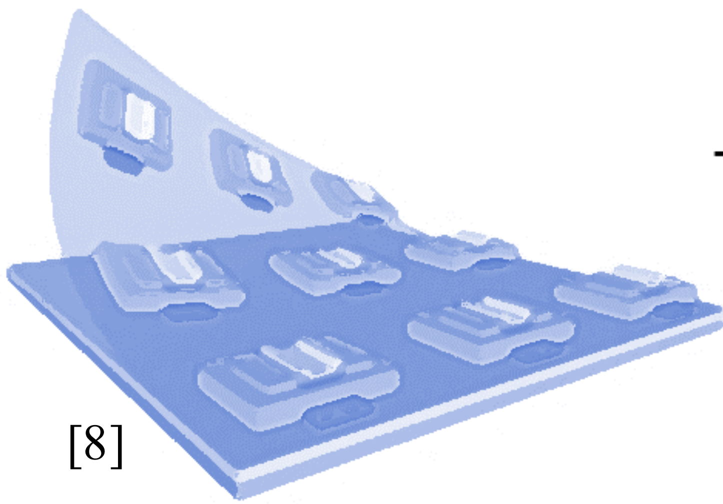
Organics	Transparent Metal Oxides

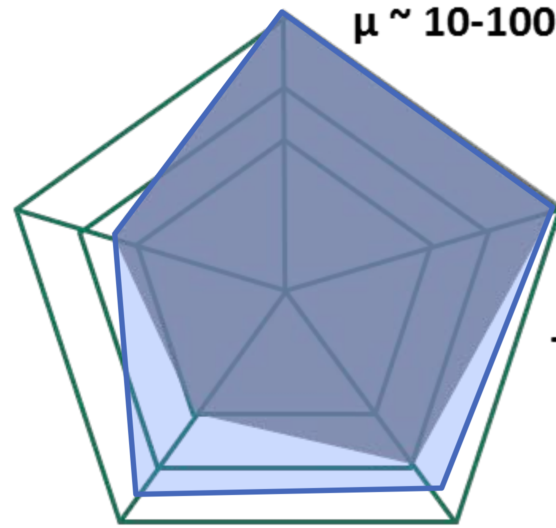




Sandia National Laboratories

Limitations of Gravure Printed TCOs (Transparent conducting oxides)





High Annealing Temperatures	Film Stress & Cracking	Mechanics of Flexible Glass

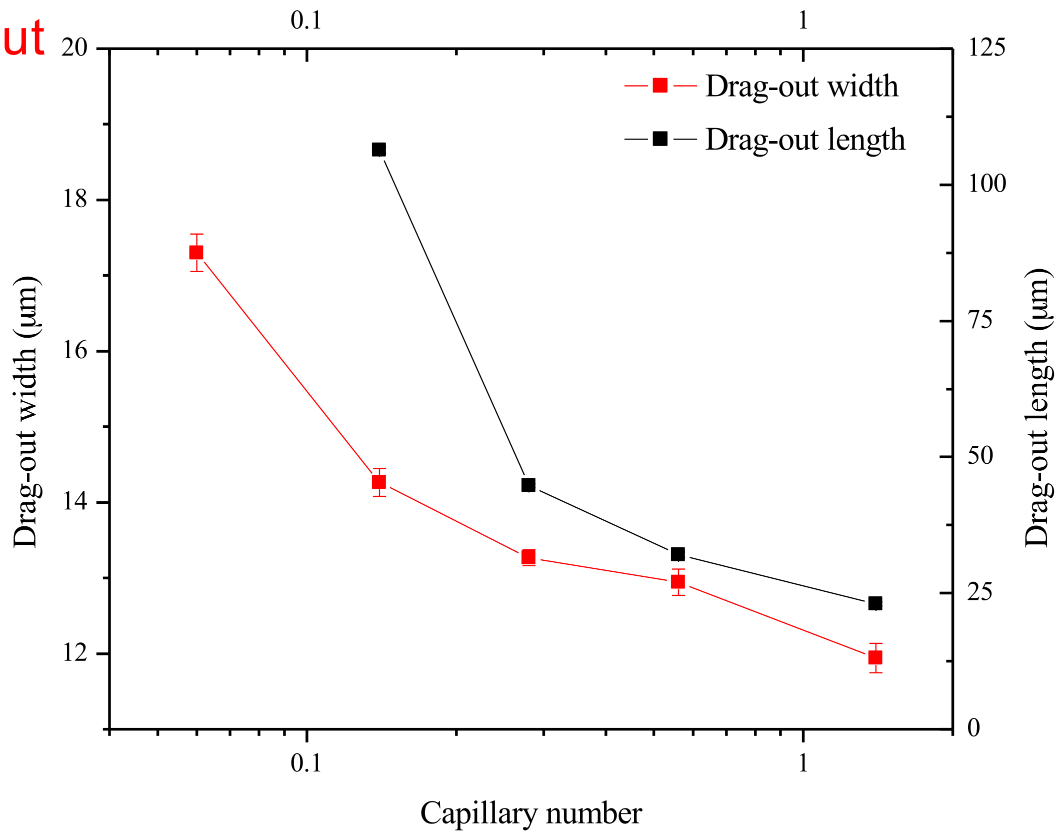
Low temperature compatible inks can solve these issues

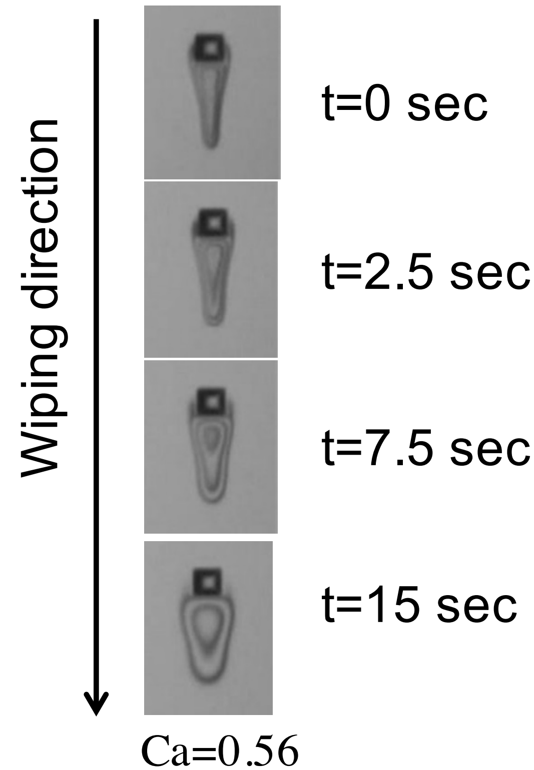
[8] Hwang, Y.H. et al, NPG Asia Mater. 2013

Sandia National Laboratories

Single-Cell Dragout Tail Features

Show Doctor-blade call-out on gravure figure

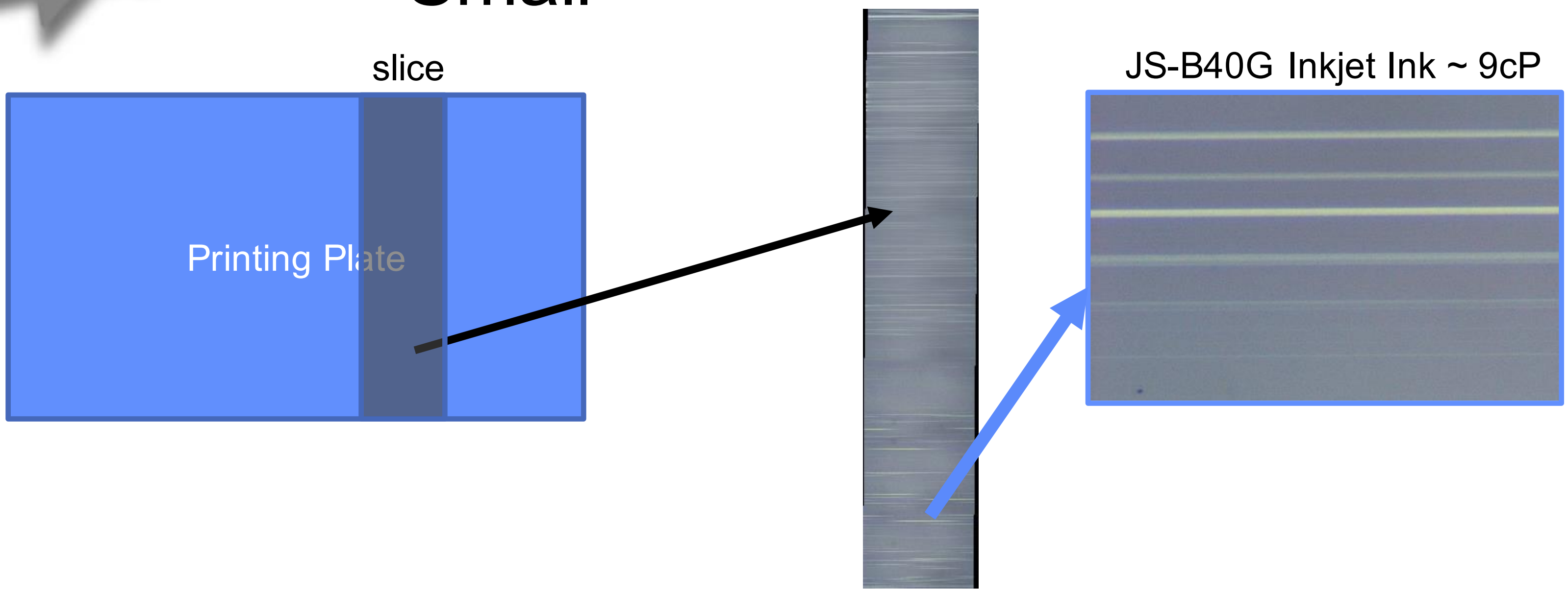




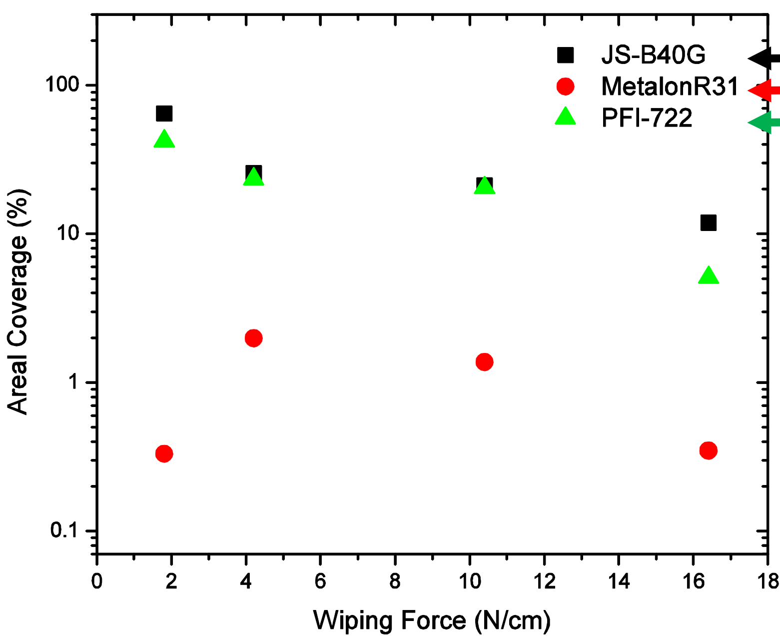
Dragout is currently one of the largest challenges for gravure patterning precise mesoscale features (OTFTs, OLEDs, sensors)

R. Kitsomboonloha, *Langmuir*, 2012

Wiping residue – Large particles vs. Small



Sparse residue film is composed of random streaks with different thickness, width, etc



9cP, size ~ 60-100nm
230cP, (0.4um – 2um)
200cP, size ~ (<0.3 um)

Wiping performed at 0.5 m/s, on glass plate. Areal coverage averaged over 2” width of plate

Particles limit feature size and resolution.
- Particle size
- Wiping speed

Sandia National Laboratories