# Designing complex fluids

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$$\rho \frac{D\underline{v}}{Dt} = \rho \underline{g} - \nabla p + \nabla \cdot \underline{\underline{\sigma}}$$

A small step away from Newtonian fluid creates an explosion in the range of possibilities.

#### **Complex Fluid:**

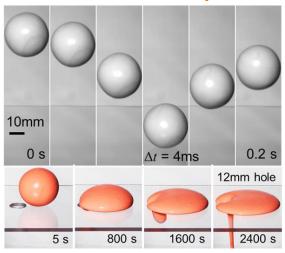
non-Newtonian constitutive behavior (rheology)

#### Design:

- 1. to create, fashion, execute, or construct according to plan
- 2. to conceive and plan out in the mind

# The 4 Key Phenomena of Rheology\*

#### 1. Viscoelasticity



#### 3. Extensional-Thickening



\*Macosko (1994)
(and more! Thixotropy, Shear-Thickening, ...)
Photos & Videos from
Ewoldt Research Group YouTube Channel

#### 2. Shear-Thinning

'yield-stress fluid' = extreme shear-thinning



#### 4. Rod-Climbing



# The 4 Key Phenomena of Rheology\*

\*Macosko (1994)

Photos & Videos from





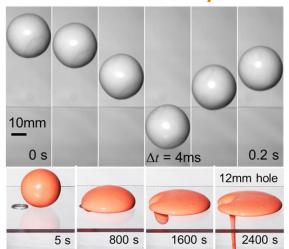
R.B. Bird R. C. Armstrong O. Hassager

D.D. Joseph

# The 4 Key Phenomena of Rheology\*

#### 1. Viscoelasticity



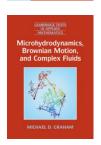












M.D. Graham



\*Macosko (1994)

(and more! Thixotropy, Shear-Thickening, ...) Photos & Videos from

Ewoldt Research Group YouTube Channel





2. Shear-Thinning

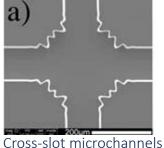
'yield-stress fluid' = extreme shear-thinning

### Design and optimization in fluid mechanics

$$\rho \frac{D\underline{v}}{Dt} = \rho \underline{g} - \nabla p + \nabla \cdot \underline{\underline{\sigma}}$$

#### Designing the...

Geometry

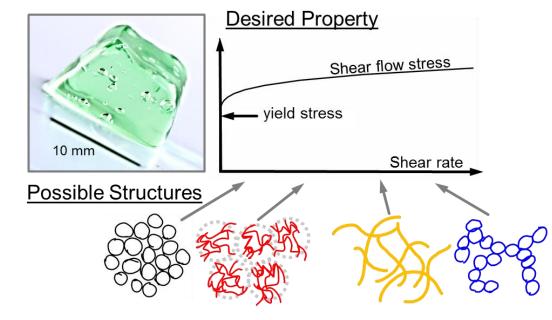


(F.J. Galindo-Rosales et al. 2014)

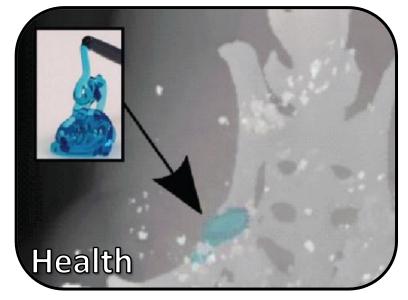
**Kinematics** 



#### Fluid

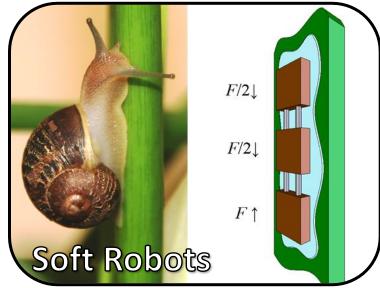


# Complex fluids to achieve diverse objectives



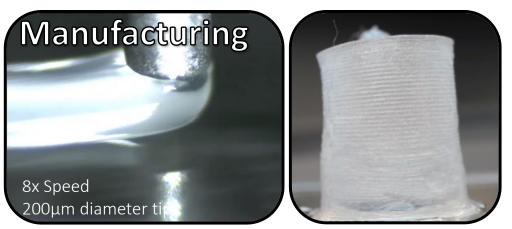






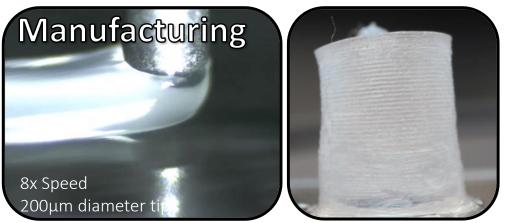
# Motivation: Design with yield-stress fluids





Oil-in-water Emulsion [Rauzan and Nelson et al. Adv. Func. Matls. 2018]

# Motivation: Design with yield-stress fluids



Oil-in-water Emulsion [Rauzan and Nelson et al. Adv. Func. Matls. 2018]



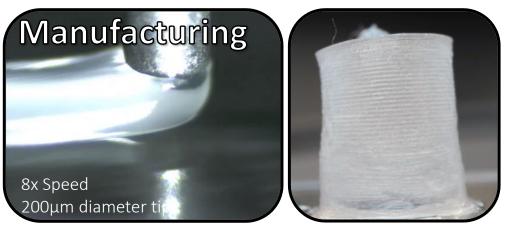
Adhesive/Coating

Fingering Instability - The Rheology Zoo



[Curtis-Fisk et al. 2013] [Nelson et al. *Submitted*]

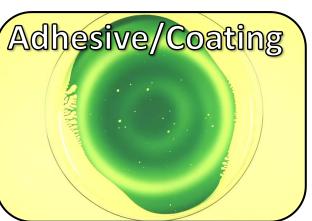
# Motivation: Design with yield-stress fluids



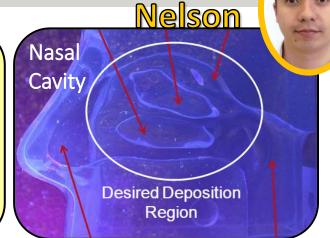
Oil-in-water Emulsion [Rauzan and Nelson et al. Adv. Func. Matls. 2018]



Orbitz Drink Hubba Bubba Bubble Tape [Nelson et al. *JOR* 2018]



Fingering Instability - The Rheology Zoo



[Curtis-Fisk et al. 2013] [Nelson et al. *Submitted*]



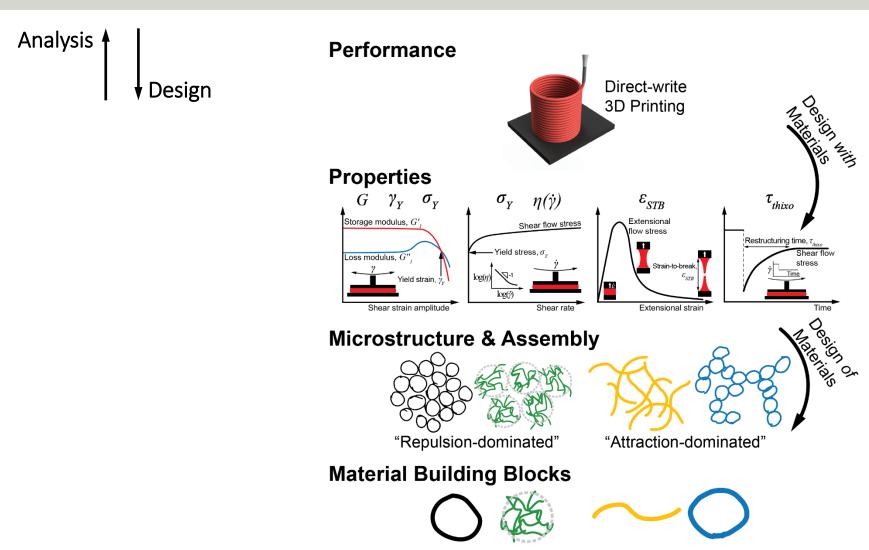
Mystic Smoke



Octopalm



### Design perspective...



$$\rho \frac{D\underline{v}}{Dt} = \rho \underline{g} - \underline{\nabla} p + \underline{\nabla} \cdot \underline{\underline{\sigma}}$$

Continuum fluid physics

- What properties desired?
- Quantitative targets agnostic to microstructure/building blocks?

Microstructural fluid physics

- How many ways to achieve the target properties?
- Quantitative prediction?

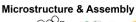


#### Design-based organization of knowledge



#### Shear-Thinning









Current Opinion in Solid State & Materials Science 23 (2019) 100758



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#### Designing and transforming yield-stress fluids





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# How many ways to get a yield-stress fluid?

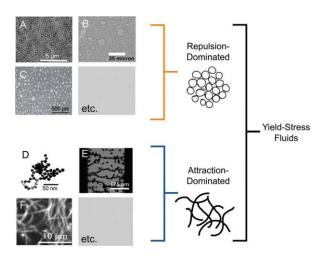


Table 1. An incomplete list of the many ways to engineer an effective yield-stress fluid

Reported

Material Class	Material System Details/Additive	Yield Stress Range	Design Guidelines
Crowded hard particles	Brownian: PMMA spheres[53], silica sphere mixtures[54,55], anisotropic polystyrene[56] non-Brownian: polystyrene beads[57], glass beads[58], sand[58]	1-500 Pa 1-1000 Pa	High moduli Low yield strain Low thixotropic time High volume fraction
Effectively-crowded charged particles	Laponite in water (also reported as a gel)[59,60]	10-500 Pa	Low volume fractions Few practical examples
Crowded soft particles	Carbopol microgels in water[61,62] poly-NIPAM microgels in water[63,64] polybutadiene stars[65] dendrimers[66] diblock, triblock copolymer mixture in oil[67]	0.1 – 200 Pa	Low-moderate moduli, critical shear rate, and thixotropic time Low weight fractions with microgels Can be transparent
Crowded micelles and vesicles	Pluronic F127 in water[68,69] poly(oxyethylene-oxybutylene) in water[70] Triton X-100 in water[71]	0.1 – 500 Pa	Low thixotropic time Surface active additives
Crowded emulsions	silicone oil-in-water stabilized with SDS[72] water-in-mineral oil stabilized with Span- Tween[14]	0.03 – 1000 Pa	Low critical shear rate Low thixotropic time High volume fraction dispersed phase Allows encapsulation Robust in confinement Can be transparent
Foams	nitrogen in microgel solution[73] nitrogen in water/glycerol stabilized with TTAB, dodecanol[74]	0.1 – 20 Pa	Low moduli Often need supplementary stabilizing structure
Particulate gels	bentonite in water[14] silica in organic solvents[75,76] titanium dioxide in water [77] carbon black in oil[78] metal oxide nanoparticles in water[79] rod-shaped virus particles in water[80]	0.06 -500 Pa	High critical shear rate High thixotropic time (except high aspect- ratio particles) Low volume fraction Often highly tunable properties
Electrorheological fluids	titanium dioxide in silicone oil[81] silica spheres in corn oil[82]	0 (no applied field) – 120 kPa	High yield stress Active control
Magnetorheological fluids	carbonyl iron in mineral oil[83] carbonyl iron in grease[84]	0 (no applied field) – 80 kPa	High yield stress Active control Commercially available
Associating polymers or fibrils	nanofibrillated cellulose in water[9] xanthan gum in water[14]	1 – 500 Pa	High thixotropic time (at low concentrations) High yield strain Low volume fraction Very few predictive models



#### Can we predict properties from formulation and structure?

Nelson & Ewoldt, Soft Matter (2017)

**Table 1** Structure-rheology scaling relationships and equations for yield-stress fluid material classes. These relationships are useful for concept evaluation and synthesis as they allow one to predict the resulting yield-stress to varying degrees. See Table 2 for the definitions of all variables

Material class	Scaling relationship	(Eqn #)	Notes
Hard spheres <sup>87</sup>	$\sigma_{ m Y} = \sigma_{ m Crit} + 112 \sqrt{\phi - \phi_{ m Crit}}$	(1)	$\phi > \phi_{ m Crit}$
Charged particles <sup>88</sup>	$\sigma_{ m Y} pprox K \Biggl( rac{W(r_{ m m}) - k_{ m B}T}{\left(r_{ m m}/2 ight)^3} \Biggr)$	(2)	$r_{ m m} < d_{ m eff} \ K = { m constant}$
Soft particles <sup>61</sup>	See reference		
Emulsions and foams <sup>57</sup>	$\sigma_{\rm Y} = \frac{\Gamma}{R_{\rm mean}} \phi^{\frac{1}{3}} Y(\phi)$	(3)	$\phi > 0.9069$
Particulate gels <sup>89</sup>	$egin{aligned} \sigma_{ m Y} &\sim rac{\phi^2}{a^2} W_{ m max}' \ \sigma_{ m Y} &\sim  \phi arepsilon_0 arepsilon_S eta^2 E^2 f_{ m max} \end{aligned}$	(4)	$\phi < 0.64$
Electrorheological fluids <sup>78</sup>	$\sigma_{\rm Y} \sim \phi \varepsilon_0 \varepsilon_{\rm S} \beta^2 E^2 f_{\rm max}$	(5)	
Magnetorheological fluids <sup>80</sup>	$\sigma_{ m Y} \sim H^2$	(6)	Low field strength
	$\sigma_{ m Y} = \sqrt{6} \phi \mu_0 M_{ m S}^{1/2} H^{3/2}$	(7)	Intermediate field strength
	$\sigma_{\rm Y}^{\rm Sat}=0.086\phi\mu_0 M_{\rm S}^{\ 2}$	(8)	Fully-saturated induced dipoles

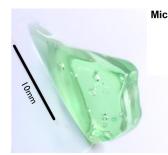


# Design-based organization of knowledge

- Organizes research efforts across diverse material classes
- Reviews current **microstructure** fluid physics knowledge to support the design process
- Similar 'rheology-to-structure' inverse organization for other rheological phenomena?



#### **Shear-Thinning**









Nelson

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- Microstructure-level fluid physics: more needed beyond scaling laws
- Continuum-level fluid physics: target properties, agnostic to structure?

#### stress fluids





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Biotechnology and Health, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden



# MICROSTRUCTURE-AGNOSTIC RHEOLOGY TARGETS?



# VISCOPLASTIC IMPACT:

Blackwell et al., JNNFM (2016)

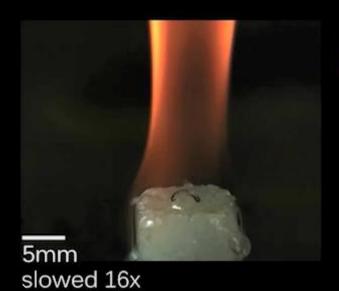
Blackwell et al., Phys Fl. (2015)

Blackwell, Ph.D. thesis (2017)

Sen et al., *JFM* (2019)

Sen et al. *arXiv* (2020)

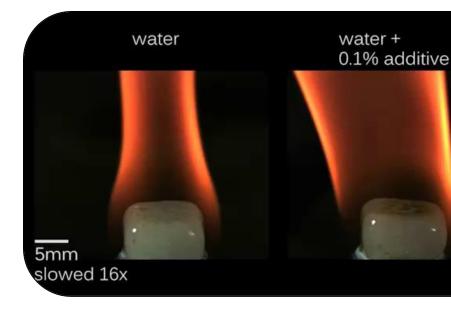
water



water + 0.1% additive



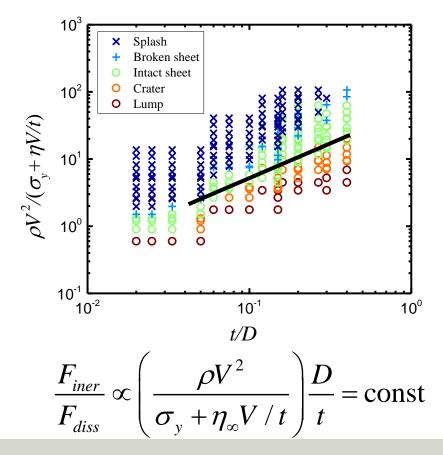
# Droplet coating: microstructure-agnostic rheology target?



Blackwell et al., JNNFM (2016) Blackwell et al., Phys Fl. (2015) Blackwell, Ph.D. thesis (2017) Sen et al., JFM (2019) Sen et al. arXiv (2020) What is target rheology for enhanced fire suppression? or droplet coating?

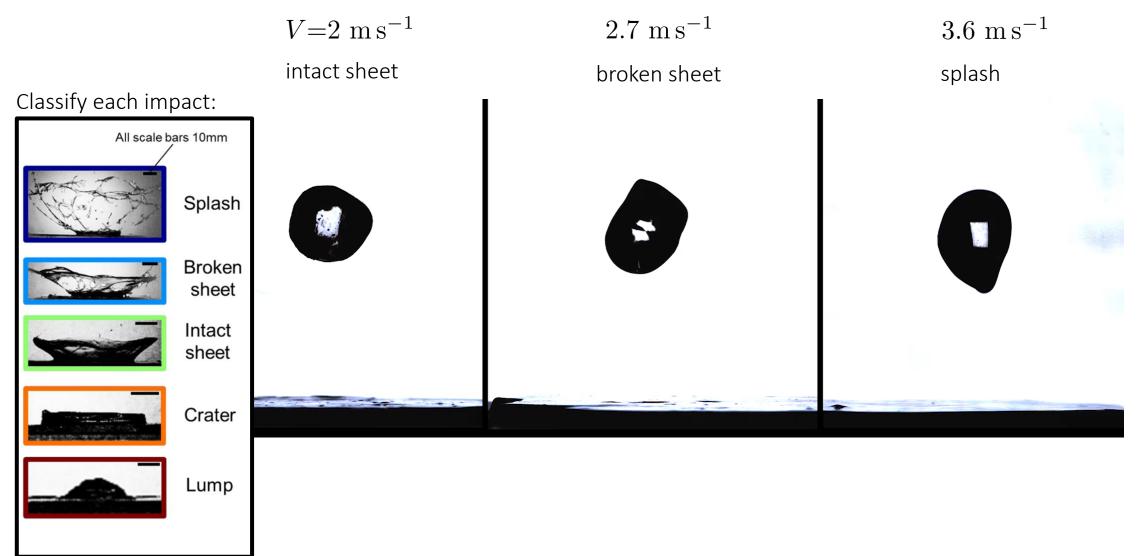
- → yield stress fluid (function of dynamic conditions)
- → low thixotropy







# Drop impact tests for (unaged) Laponite

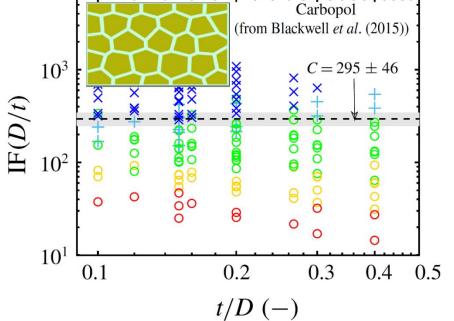


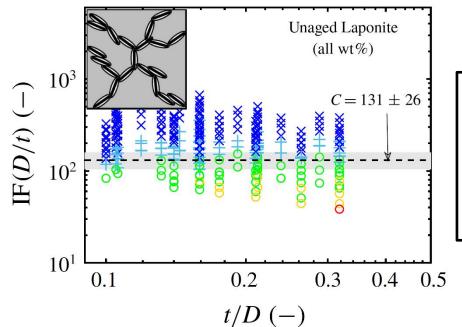


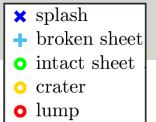
#### Microstructure does not matter (sort of)

A single dimensionless group to understand splash regimes:

$$\operatorname{IF}\left(\frac{D}{t}\right) \equiv \frac{\rho V^2 D}{[\sigma_{y} + K(V/t)^{0.5} + \eta_{\infty} V/t]t} \approx C$$







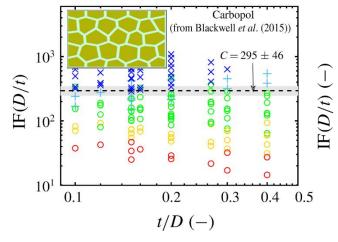


This scaling with IF works for both **Carbopol** and **(unaged) Laponite**, but the *C* are different

#### Microstructure-agnostic targeting

- Enables design targets for 'stick' versus 'splash',
   with fluid physics revealed in a dimensionless group
- Target rheology, even with complex formulations
- More opportunities
  - Some dependence on microstructure, or more complex rheological properties
  - Analysis may fail for very thin or thick coatings
  - Additional effects from surface tension with very small droplet sizes
  - Thixotropic effects not previously studied (until now! see **Z03.08**)
- What if properties more complex? (e.g. shapes of rheological material functions)

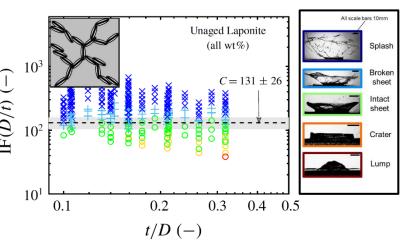
$$\operatorname{IF}\left(\frac{D}{t}\right) \equiv \frac{\rho V^2 D}{[\sigma_{y} + K(V/t)^{0.5} + \eta_{\infty} V/t]t} \approx C$$















#### Linear viscoelastic design targets





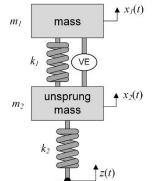
$$\rho \frac{D\underline{v}}{Dt} = \rho \underline{g} - \underline{\nabla} p + \underline{\nabla} \cdot \underline{\underline{\sigma}}$$

$$\underline{\underline{\sigma}}(t) = \int_{-\infty}^{t} G(t - t') \dot{\underline{y}}(t') dt'$$

$$\rightarrow \text{Optimization techniques for } shapes \text{ of function}$$

- → Optimization techniques for *shapes* of functions
- $\rightarrow$  Design freedom is NOT G', G''
- → Models may be independent of microstructure (in a good way)

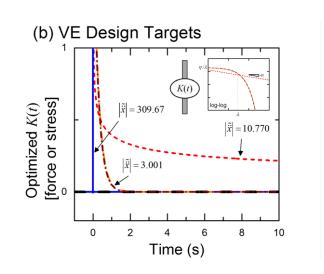




$$G(t) = \sum_{i=1}^{M} G_i \exp\left(-\frac{t}{\lambda_i}\right)$$

$$G(t) = \{G_e\} + \int_{-\infty}^{\infty} \frac{H(\tau) \exp(-t/\tau) d \ln \tau}{\cot \tau}$$

$$\cot \tau$$

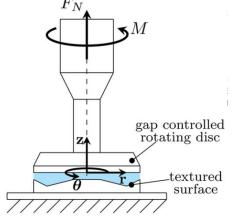


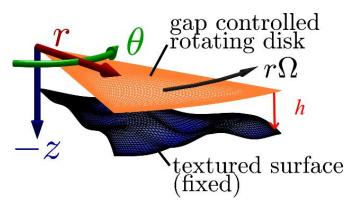


#### Surface topography design with Newtonian fluid

$$\rho \frac{D\underline{v}}{Dt} = \rho \underline{g} - \underline{\nabla} p + \underline{\nabla} \cdot \underline{\underline{\sigma}}$$

$$\underline{\underline{\sigma}} = \mu \dot{\underline{\gamma}} = \mu \left(\underline{\nabla} \underline{v} + (\underline{\nabla} \underline{v})^T\right)$$

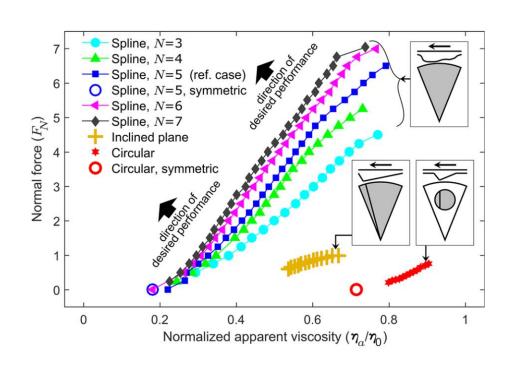




#### Viscous lubrication

- → Optimization of *arbitrary shapes*
- → Manufacturing constraints
- → Newtonian Stokes flow (lubrication flow) solver







# Co-design of surfaces and rheological functions

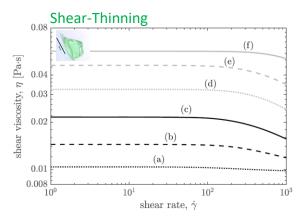
$$\rho \frac{D\underline{v}}{Dt} = \rho \underline{g} - \underline{\nabla} p + \underline{\nabla} \cdot \underline{\underline{\tau}} \qquad \text{CEF: } \underline{\underline{\tau}} = \eta (\dot{\gamma}) \underline{\underline{\gamma}}_{(1)} - \frac{1}{2} \Psi_1 (\dot{\gamma}) \underline{\underline{\gamma}}_{(2)} + \Psi_2 (\dot{\gamma}) \left( \underline{\underline{\gamma}}_{(1)} \cdot \underline{\underline{\gamma}}_{(1)} \right) \\ \text{or } \\ \text{Giesekus: } \lambda_k \left( \frac{\partial \underline{\underline{\tau}}_{p_k}}{\partial t} + (\underline{u} \cdot \underline{\nabla}) \underline{\underline{\tau}}_{p_k} - \left[ (\underline{\nabla} \underline{u})^{\mathsf{T}} \cdot \underline{\underline{\tau}}_{p_k} + \underline{\underline{\tau}}_{p_k} \cdot (\underline{\nabla} \underline{u}) \right] \right) \\ \text{(multi-mode)} \\ + \underline{\underline{\tau}}_{p_k} + \frac{\lambda_k \alpha_k}{\eta_{p_k}} \left( \underline{\underline{\tau}}_{p_k} \cdot \underline{\underline{\tau}}_{p_k} \right) = \eta_{p_k} \underline{\underline{\dot{\gamma}}},$$

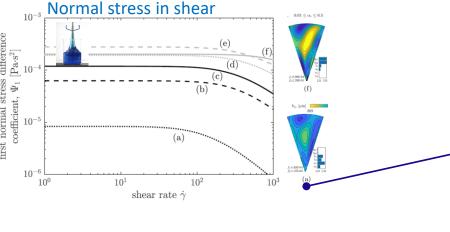


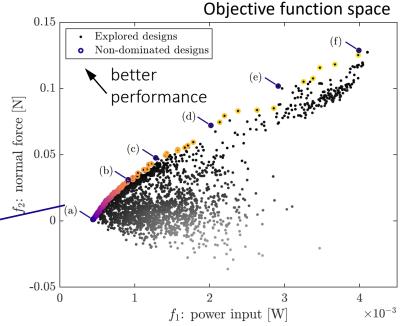
Schuh



- Sliding friction reduction with nonlinear viscoelasticity, e.g. polymer added to oil
- Optimization (inverse) problem is computationally expensive → use surrogate modeling
- Identify a family of optimal combinations of *surface topography* and *rheology*









# Co-design of surfaces and rheological functions

$$\rho \frac{D\underline{v}}{Dt} = \rho \underline{g} - \underline{\nabla} p + \underline{\nabla} \cdot \underline{\tau} \qquad \text{CEF: } \underline{\underline{\tau}} = \eta (\dot{\gamma}) \underline{\gamma}_{\equiv (1)} - \frac{1}{2} \Psi_{1} (\dot{\gamma}) \underline{\gamma}_{\equiv (2)} + \Psi_{2} (\dot{\gamma}) \left( \underline{\gamma}_{\equiv (1)} \cdot \underline{\gamma}_{\equiv (1)} \right)$$
or
$$Giesekus: \quad \lambda_{k} \left( \frac{\partial \underline{\tau}_{p_{k}}}{\partial t} + (\underline{u} \cdot \underline{\nabla}) \underline{\tau}_{p_{k}} - \left[ (\underline{\nabla} \underline{u})^{\mathsf{T}} \cdot \underline{\tau}_{p_{k}} + \underline{\tau}_{p_{k}} \cdot (\underline{\nabla} \underline{u}) \right] \right)$$

$$+ \underline{\tau}_{p_{k}} + \frac{\lambda_{k} \alpha_{k}}{\eta_{p_{k}}} \left( \underline{\tau}_{p_{k}} \cdot \underline{\tau}_{p_{k}} \right) = \eta_{p_{k}} \underline{\dot{\gamma}},$$

$$\text{(multi-mode)}$$

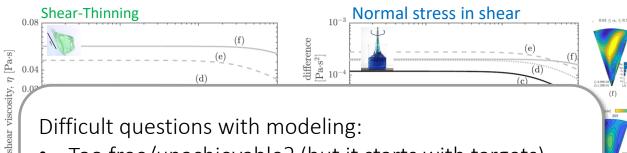






**Yong Hoon** Lee

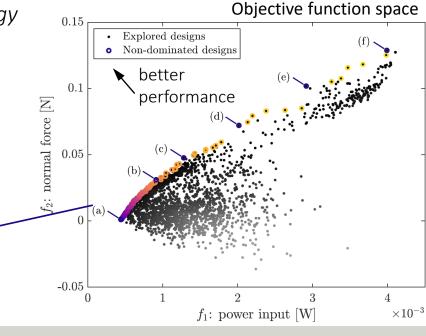
- Sliding friction reduction with nonlinear viscoelasticity, e.g. polymer added to oil
- Optimization (inverse) problem is computationally expensive  $\rightarrow$  use surrogate modeling
- Identify a family of optimal combinations of surface topography and rheology



Difficult questions with modeling:

- Too free/unachievable? (but it starts with targets)
- Too restrictive?

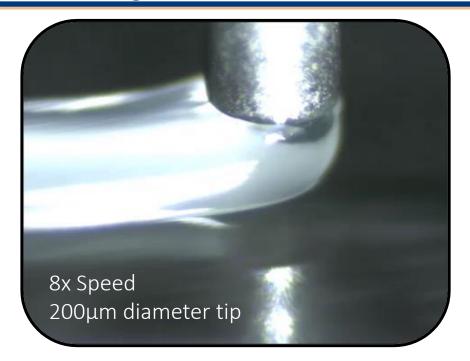
Yes! e.g. there exists behavior outside of current modeling paradigms...

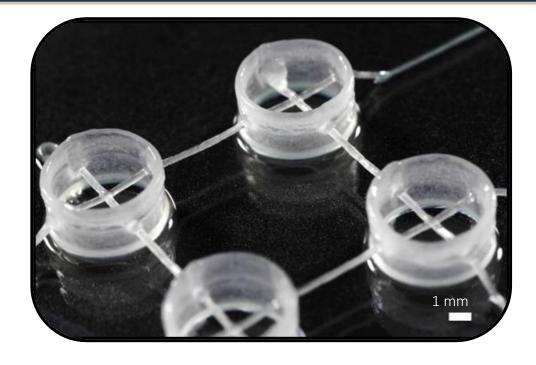






#### Rheological Design of Direct-Write 3D Printing Inks





What is the rheology for a "good" 3D Printing Ink?

Yield-stress fluid

Extensibility..?

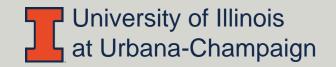


**Shear-Thinning** 



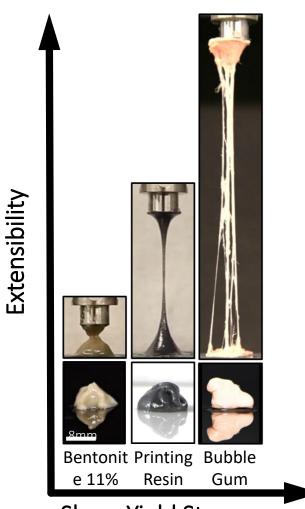
**Extensional-Thickening** 

Rutz et al. 2015 Shepherd et al. 2011 Blackwell et al. 2015 Dinec et al. *in Preparation* 



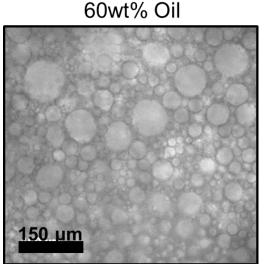
#### **Extensible yield-stress fluids** (new paradigm, new model material)





**Shear Yield Stress** 

Architecture concept: silicone oil-in-water emulsion (yield stress) + poly(vinyl alcohol) network transiently crosslinked with borate ions (extensibility)



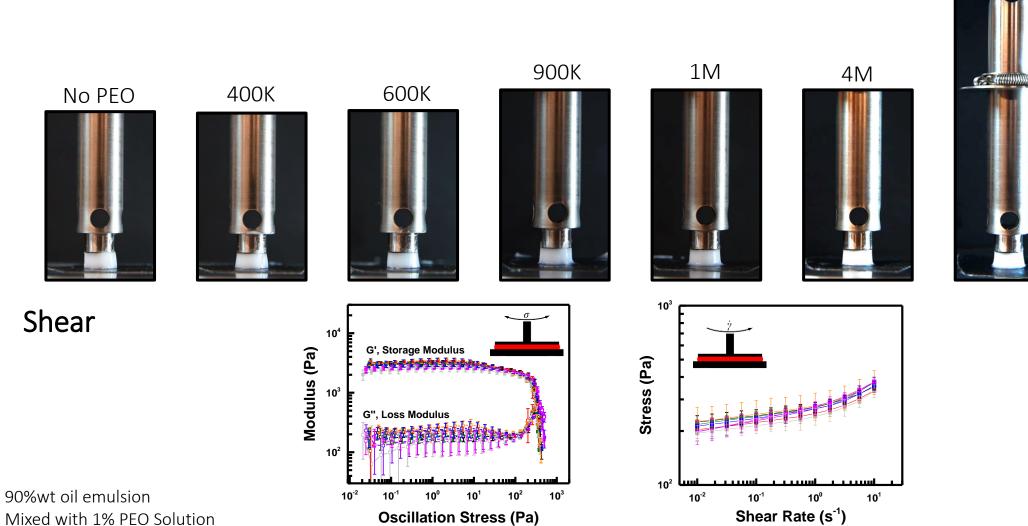
PVA molecular weight 85,000 – 124,000 Emulsified on stand mixer at 300rpm Mixed with sodium tetraborate solution



Material

Silicone oil-in-water emulsion with varying molecular weight of poly(ethylene oxide)

#### **Extension**

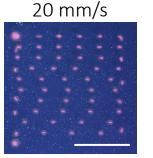


Arif Nelson | Ewoldt Research Group

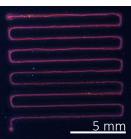
8M

5M

#### Faster printing with extensible yield-stress fluids

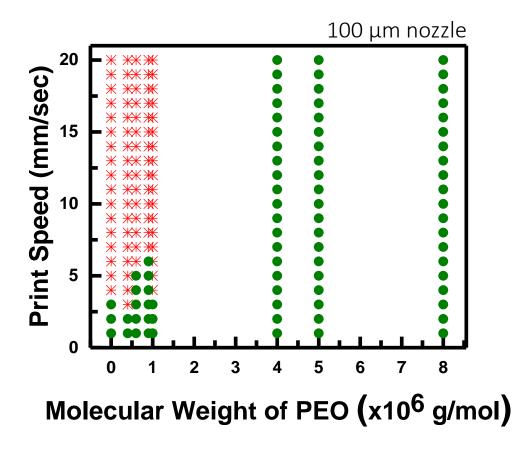






1 mm/s

Arif Nelson | Ewoldt Research Group



Design Target:

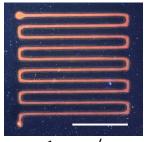
 $\varepsilon_{STB}$  > 500% to achieve max available print speed





8M PEO

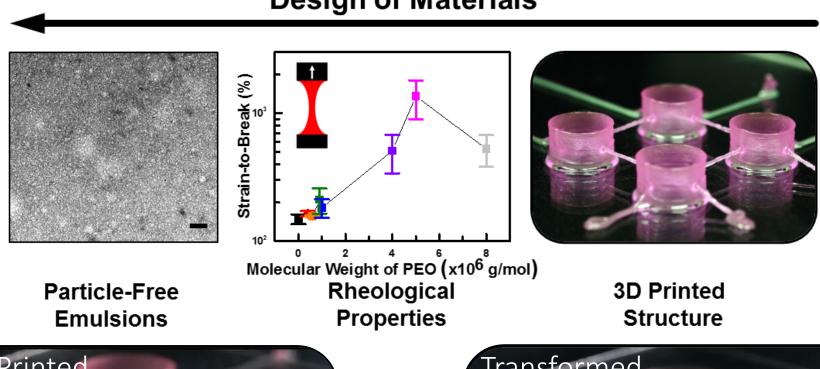




1 mm/s

# Chemical transformation may be required

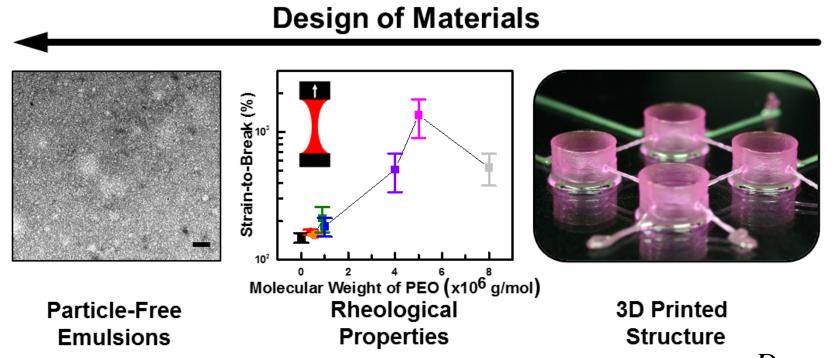








### Success here, but there's a bigger picture...



Continuum-level: target properties may be non-obvious (not yet in constitutive models) ho –

- High extensibility allows higher print speeds and increased gap spanning
- Material-level: we formulated a model direct-write 3D printing ink
- Particle-free emulsions allow for patterning of a buildable material below 10µm
- Post-printing transformations provide a method for greatly improving mechanical properties

# Vision for Designing Complex Fluids

- Many inspiring materials: yield-stress fluids, thixotropic fluids, flow battery working fluids, ...
- Design engineers need **intuition** for this complex behavior
- Many open questions for the "engineering toolbox" for design & inverse problems
- Will require scientific understanding and predictive equations: structure-to-rheology (material-level fluid physics) & rheology-to-flow (continuum-level fluid physics)



# Inverse methods: adjoint-based sensitivity



#### Local Chair: Jon Freund

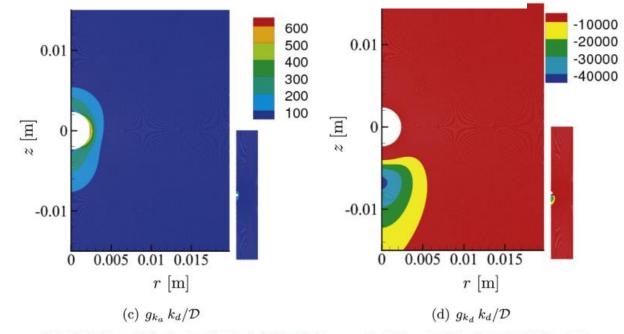


#### Field sensitivity of flow predictions to rheological parameters

J.B. Freund\*,a,b, J. Kima, R.H. Ewoldta

- → Example: drag on sphere
- → Sensitivity to parameters at every location in space
- → inspires design (local change? Heating? Other?)

$$\delta \mathcal{D} = \underbrace{\left(\frac{\partial \mathcal{D}}{\partial \vec{\theta}}\right) \odot \delta \vec{\theta}}_{\delta \mathcal{D}_{\theta}} + \underbrace{\left(\frac{\partial \mathcal{D}}{\partial \vec{q}}\right) \odot \delta \vec{q}}_{\delta \mathcal{D}_{q}},$$



**Fig. 10.** Field sensitivity for the thixotropic fluid (38): (a)  $g_{\eta_{\infty}} \eta_{\infty}/\mathscr{D}$ , (b)  $g_{\eta_1} \eta_1/\mathscr{D}$ , (c)  $g_{k_a} k_a/\mathscr{D}$ , and (d)  $g_{k_d} k_d/\mathscr{D}$ .

$$\delta \mathcal{D} = \delta \mathcal{D}_{\theta} + \left\langle \vec{q}^*, \delta \vec{\mathcal{N}}_{\theta} \right\rangle + \delta \mathcal{D}_{q} + \left\langle \vec{q}^*, \delta \vec{\mathcal{N}}_{q} \right\rangle$$



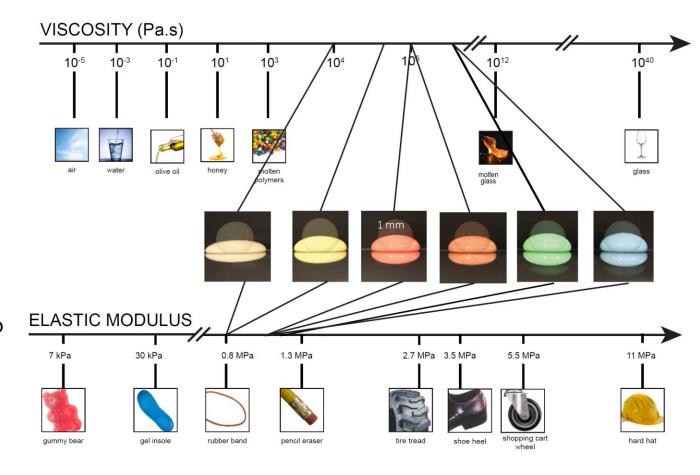
#### Viscoelastic design intuition





#### Model materials

- → Feel modulus? viscosity? timescale?
- → Pipkin maps
- → Low-dimensional descriptions
- → Ashby-style property maps



[Corman & Ewoldt, Appl Rheol (2019)]

### Flow battery working fluids

Physics of Fluids

ARTICLE

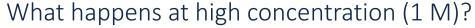
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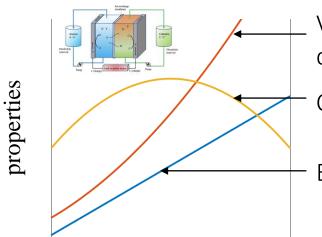
Cite as: Phys. Fluids 32, 083108 (2020); doi: 10.1063/5.0010168 Submitted: 7 April 2020 • Accepted: 20 July 2020 • Published Online: 18 August 2020











concentration

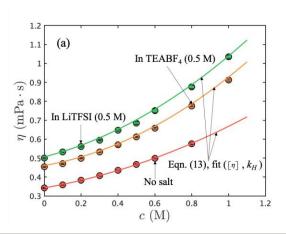
Viscosity increases dramatically 💮

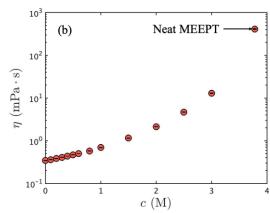
Conductivity decreases 😔

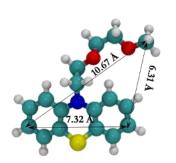
Wang

DFD G03.17

Energy density increases 😳







What are limits to energy density and conductivity?

Other fluids based on polymeric or colloidal structures have more complex rheology/conductivity/energy density design trade offs



# Vision for Designing Complex Fluids

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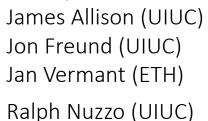
### Acknowledgements



Arif **Nelson** 



Samya Sen



Gareth McKinley (MIT)

Chris Macosko (U MN)

Peko Hosoi (MIT)

Vivek Sharma (UIC)

Faculty:

U.S. Department of Energy, Office of Science, Basic Energy Science, Joint Center for Energy Storage Research



Rebecca Corman

**Jonathon** 

**Yong Hoon** 

Schuh

Lee



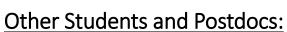
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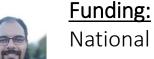
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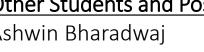
Olivia Carey-De La Torre



National Science Foundation CARFFR CBET-1351342; CMMI-1463203

(JCESR), an Energy Innovation Hub

ETH-Zurich sabbatical support



Gaurav Chaudhary

Tanver Hossain

Luca Martinetti

Nabil Ramlawi

Piyush Singh

Carolyn Darling Michael Johnston

Jaekwang Kim

Jiahui (Carrie) Liang







P&G

