Department of Physics

Institute for Soft Matter Synthesis and Metrology

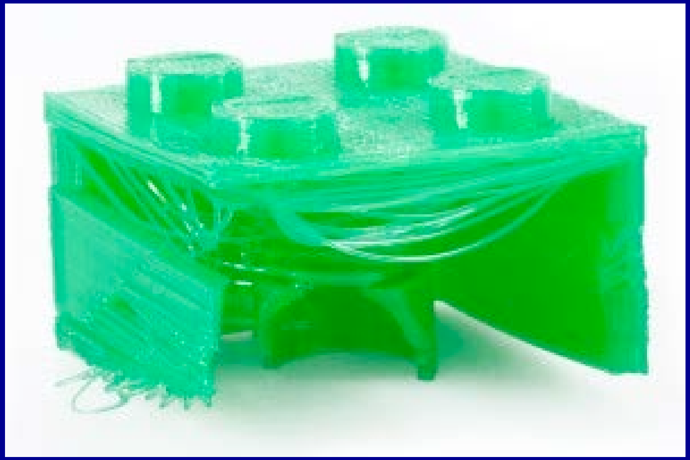
NIST
Polymers & Complex Fluids Group

GEORGETOWN UNIVERSITY

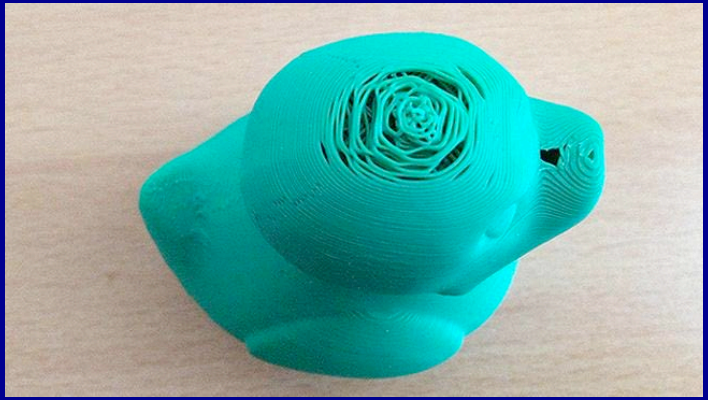
Peter Olmsted, Claire McIlroy (Georgetown University)

***NIST Team:* K Migler, J Seppala, A Kotula, R Sheridan, G Gillen, A Forster, J Bennett, J Kilgore, R Ricker**

Challenges in Additive Manufacturing of Soft Materials: Polymer-based Fused Deposition Modeling



http://www.staticwhich.co.uk/media/images/in-content/makerbot-replicator-2-brick-print-failure-323301.jpg



http://www.news.com.au/technology/science/when-3d-printing-fails-beautiful-things-can-happen/

- Selective lithography
- Laser sintering

Fused Deposition Modelling of Polymers (P-FDM)

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- "Hot Glue Gun" Extrusion
- Molten polymers: glassy or semi-crystalline
- Non-isothermal process..
- Rapid prototyping
- Poor mechanical properties?
- Great potential to expand to biopolymers, medical devices, mechanically strong materials, ….?

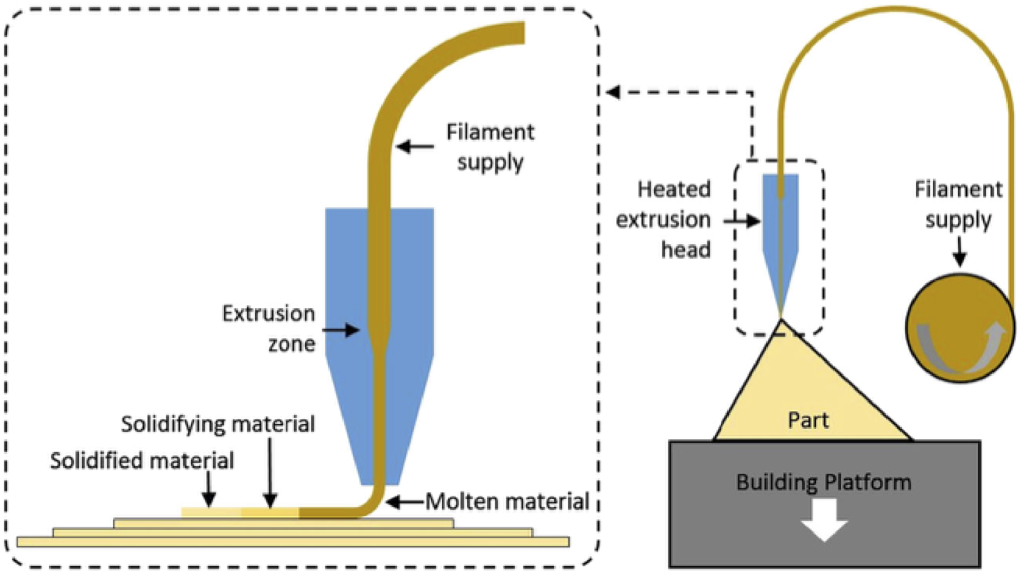
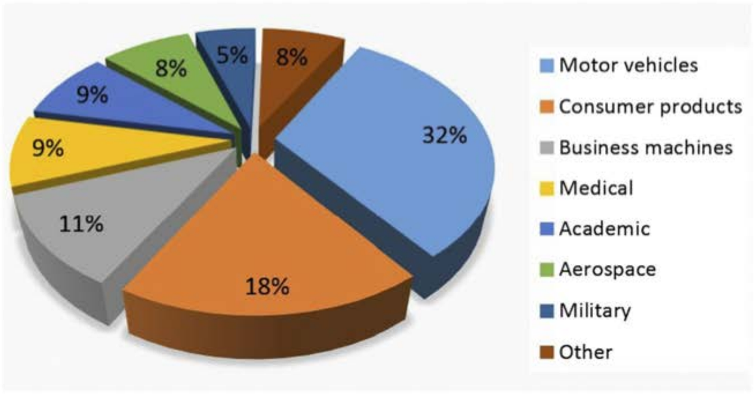


Fig. 3 Rapid prototyping worldwide 2001 [7]

Kruth JP, Levy G, Klocke F, Childs THC (2007) Consolidation phenomena in laser and powder-bed based layered manufacturing. CIRP Ann Manuf Technol 56(2):730–759



Challenges in Polymer FDM (P-FDM)

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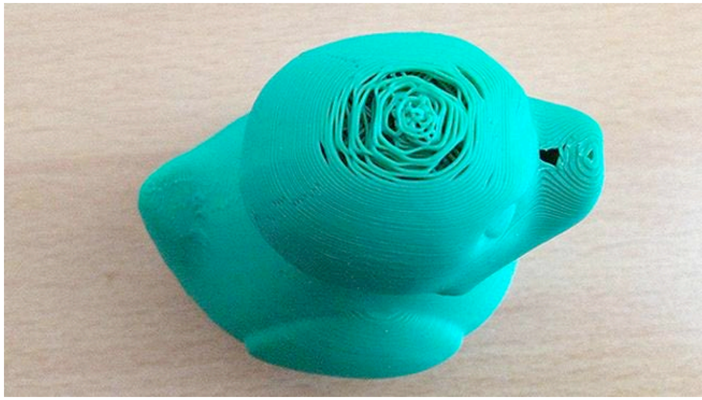
- Weak mechanical properties
- Sagging
- Poor/textured surface properties
- Porosity
- Shrinkage, warping, and debonding.



Polymer Materials

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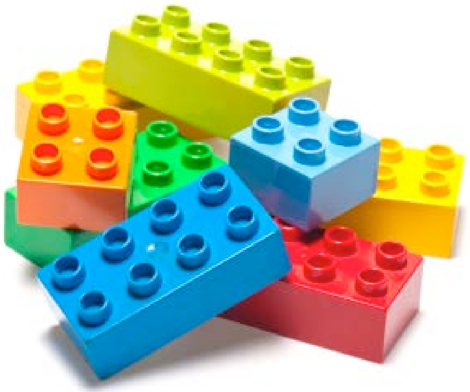
Material

- Semi-crystalline polymers
  - poly-caprolactate (PCL) [biodegradeable polyester]
  - polylactic acid (PLA) [biodegradeable]
- Amorphous polymers
  - Polycarbonate (PC)
  - ABS: Acrylonitrile-butadiene-styrene (copolymers + rubber particles)

Transition Temperature

- Melt: 60 C
- Melt: 150-160 C

- Glass: 147 C
- Glass: 80-125 C



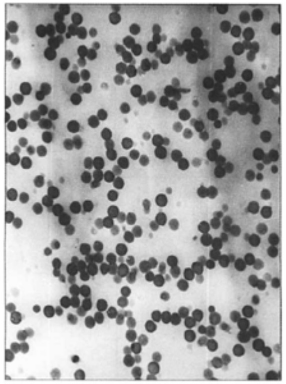


Photo 2 :ABS 1 - GD = 29%

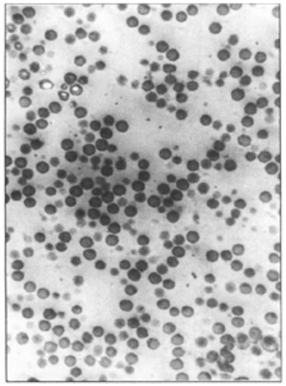
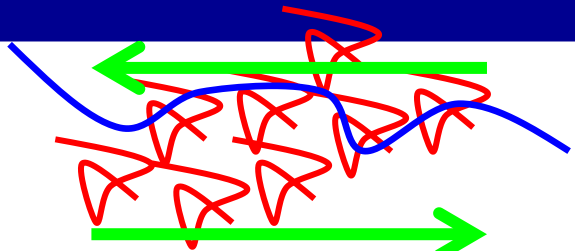
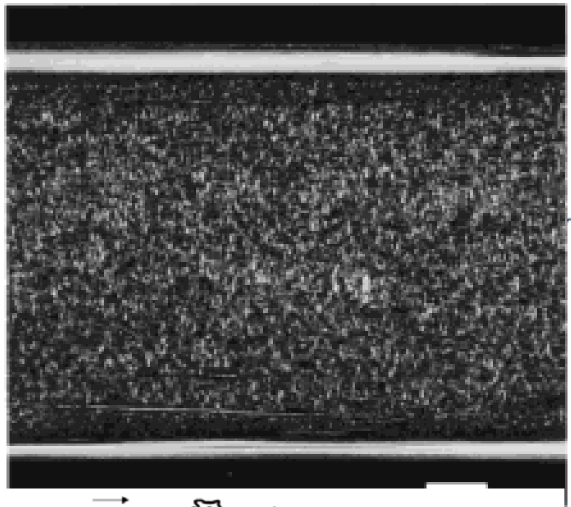


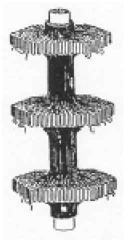
Photo 3 : ABS 3 - GD = 63%

Relevant Polymer Physics

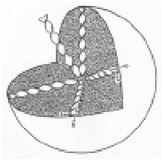




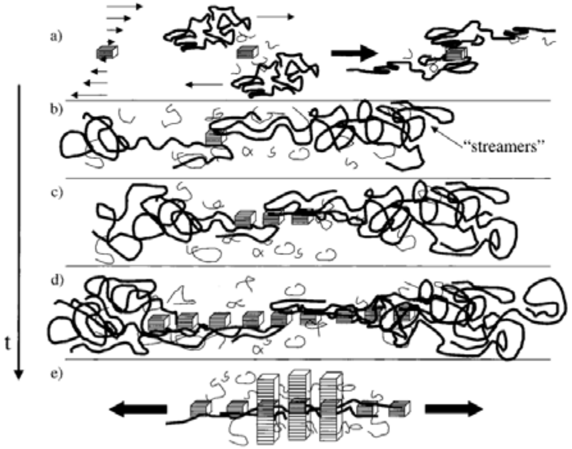
- Crystallization
  - Exothermic, structure formation, flow-induced,
- Molecular orientation in flow
  - Alignment influences welding, deposition
- Rheology of entangled polymers
  - Non-Newtonian, non-linear, . …
- Entanglement and diffusion
  - Controls weld process
- Glass transition
  - Ideally want sharper liquefaction above T_g (strong glass)



Shish-Kebab structure

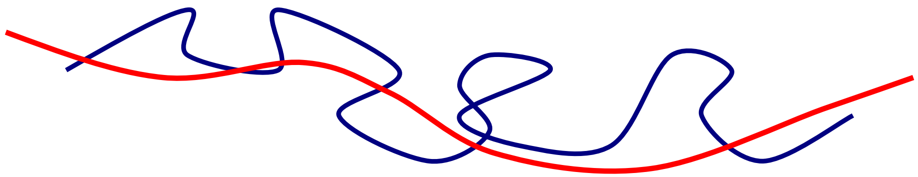


Spherulitical structure



[PLLA (Grade 4043D, Mw=111kg/mole, Z=12 Entanglements]

Polymer Dynamics and Timescales: ``Weissenberg numbers''



$$\mathrm{Wi}_{\mathrm{rept}} = \tau_d \dot{\gamma} \sim M^3$$

$$\mathrm{Wi}_{\mathrm{stretch}} = \tau_R \dot{\gamma} \sim M^2$$

$$\mathrm{Wi}_{\mathrm{rept}} > 1$$

$$\mathrm{Wi}_{\mathrm{stretch}} \lesssim 1 - 10$$

Significant orientation (and flow induced crystallisation)

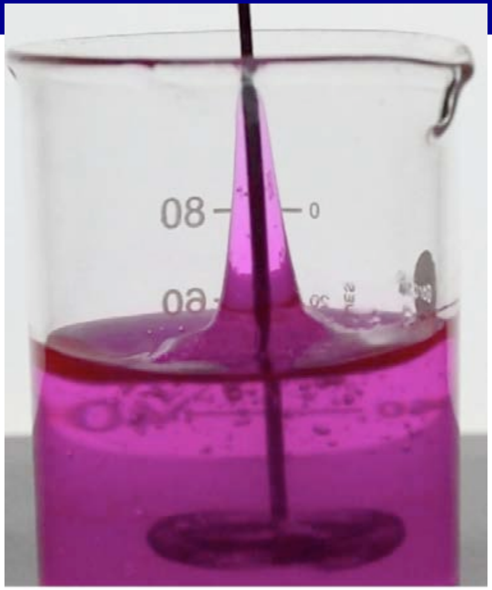
$$\mathrm{Wi}_{\mathrm{stretch}} > 10$$

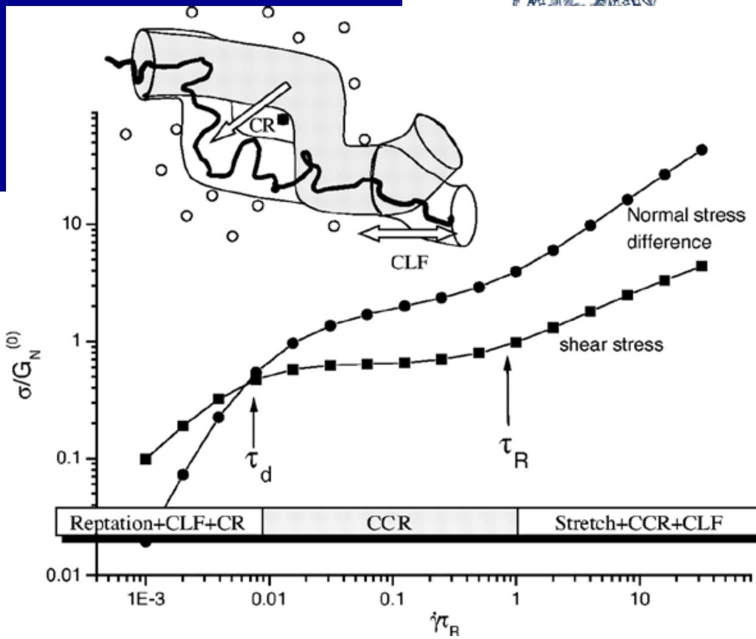
Significant stretch (and oriented crystallization)

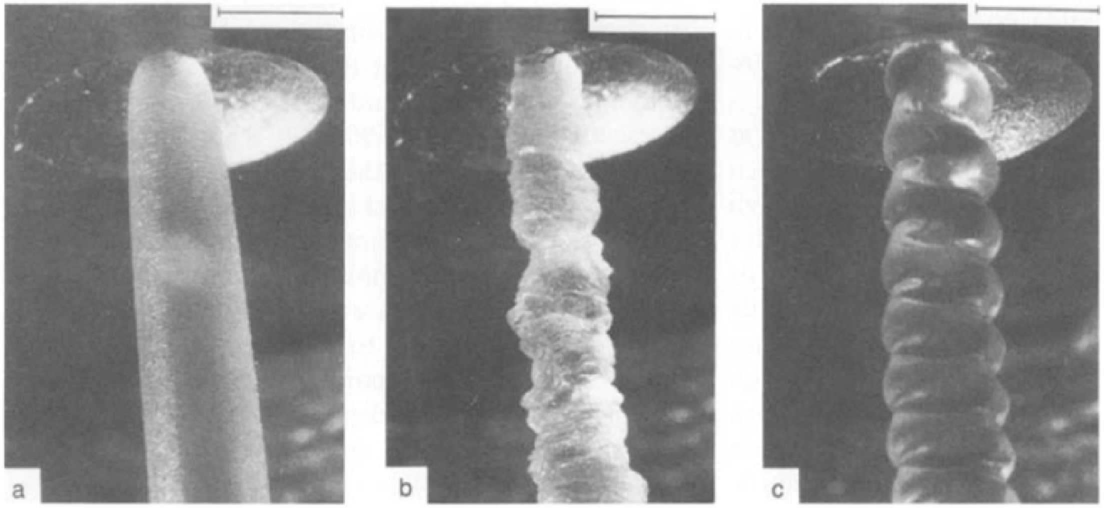
Typical nozzle parameters: $\mathrm{Wi}_{\mathrm{rept}} \simeq 100, \quad \mathrm{Wi}_{\mathrm{stretch}} \simeq 10$

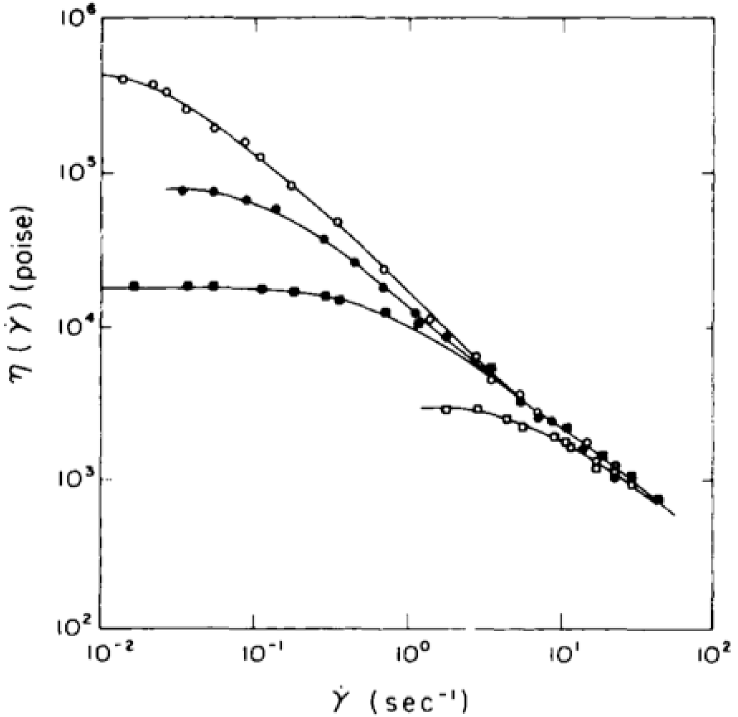
Non-Newtonian Fluid Mechanics of Polymeric Materials

- Shear Thinning
- Rod Climbing
- Die Swell
- Spurt and slip









Flow-induced crystallization during extrusion

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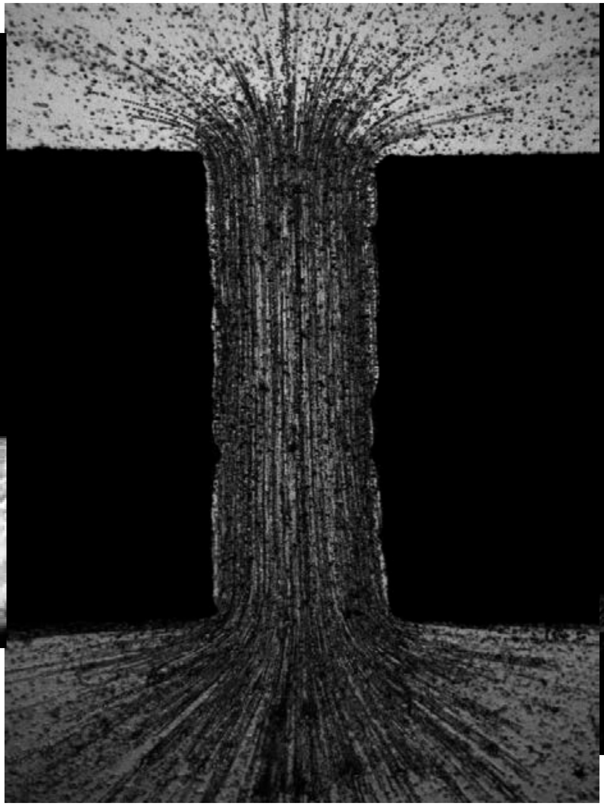
Example of polypropylene (L Scelsi, et al.. J Rheology (2009)


Modelling: Structure formation/crystallization, rheology, flow geometry.

McHugh & Doufas; Fiber Spinning (JNNFM 2000);
Graham and Olmsted: flow-induced crystallization (Phys Rev Lett 2008)

Scientific Issues in P-FDM

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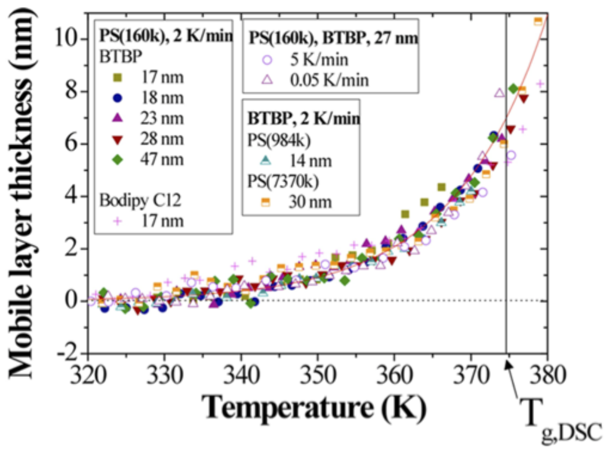
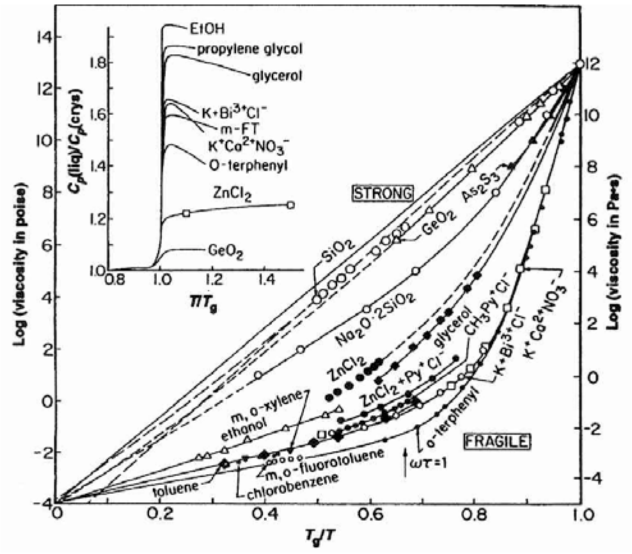
- Glass transition
- Polymer welding
- Crystallization
- Non-isothermal processes

J Forrest & M Ediger, Macromolecules 2014





A Angel, 1997

Computational/Modelling challenges

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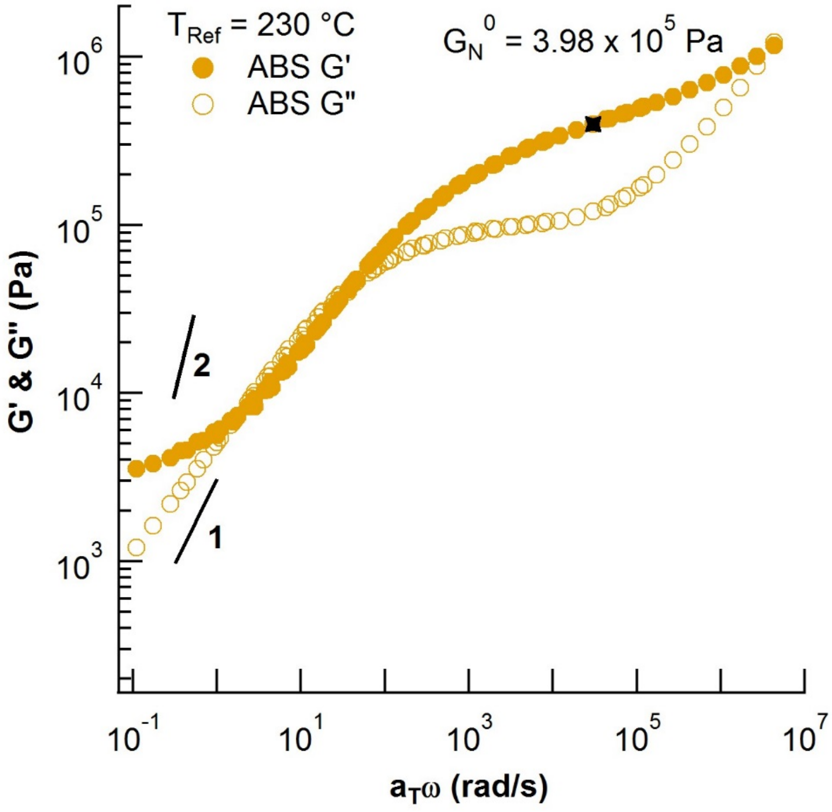
- Many coupled time-dependent quantities:
  - Molecular shape/structure/orientation/alignment
  - Temperature
  - Velocity field/deformation
  - Density
  - Moving/changing boundaries
  - Phase change materials

- Multiple scales (chemistry → polymer → mesoscale ordering → fluid mechanics of extruded filaments → bulk mechanical properties of composite FDM material).

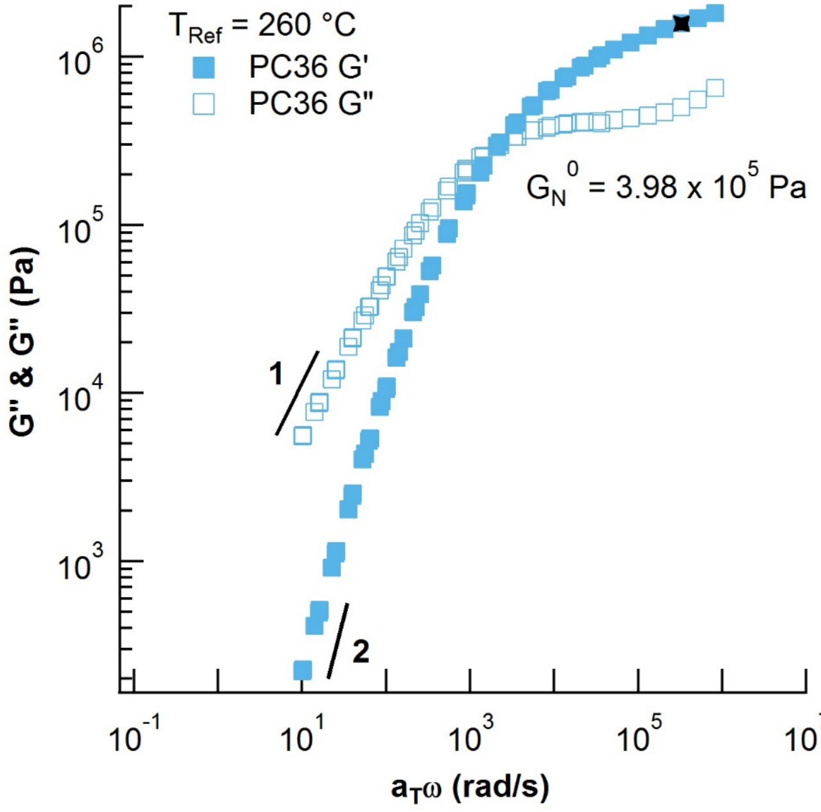
FDM Materials Polymer Rheology

ABS Moduli



Composite (nanoparticles + copolymers

Polycarbonate



Linear polymer melt
Reptation time

Details of extrusion

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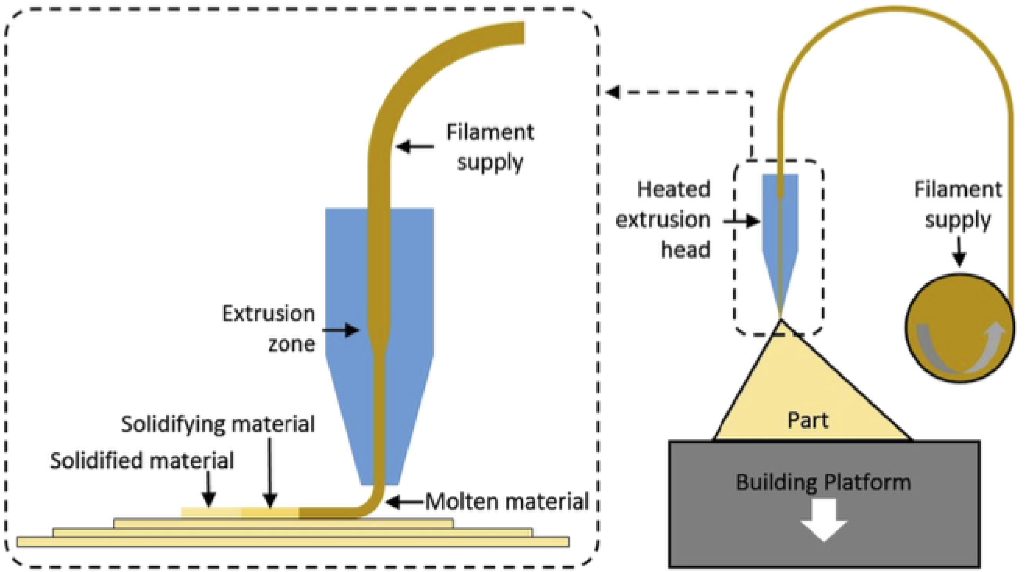
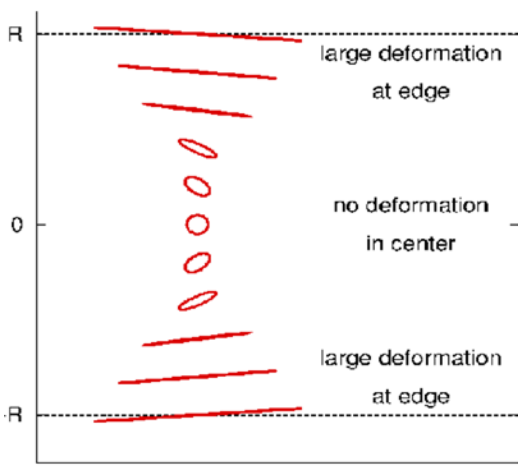
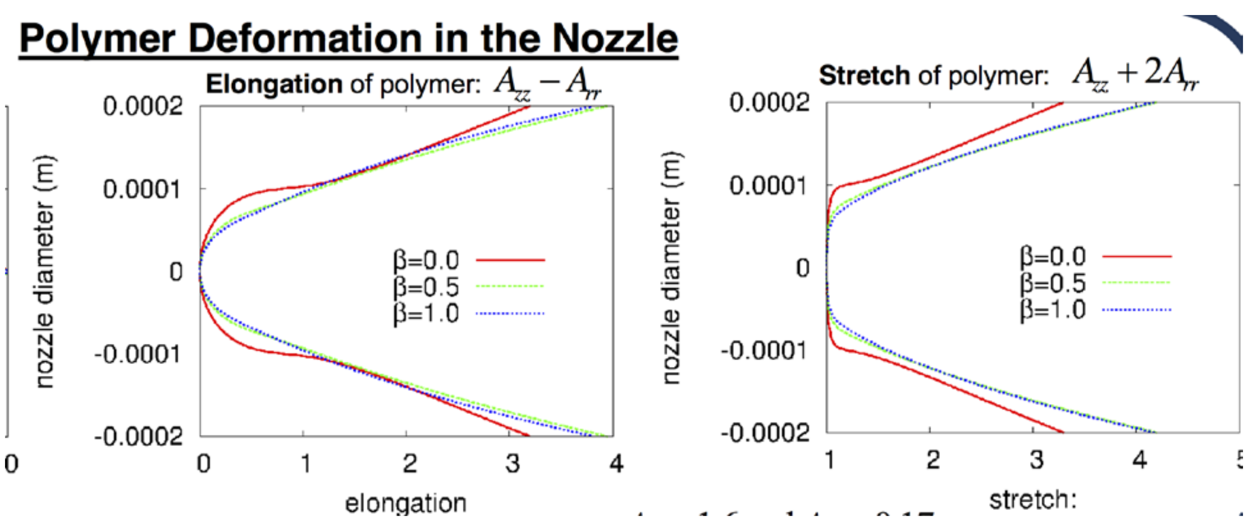
- Strong alignment and orientation in the nozzle.
- Molecular `skin' layer remains well-aligned upon extrusion and deposition.







Polymer Welding – A race against time!

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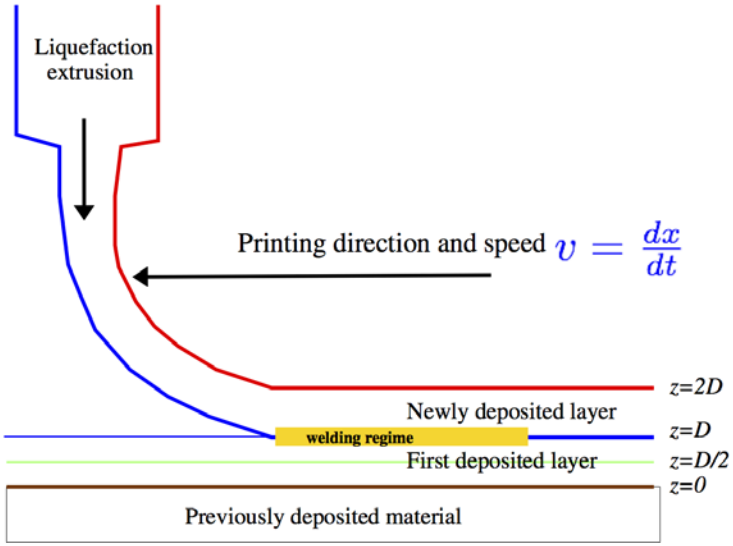

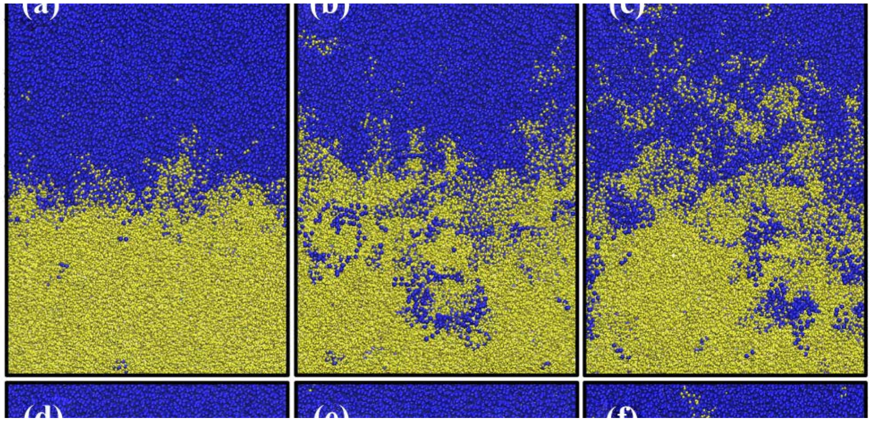

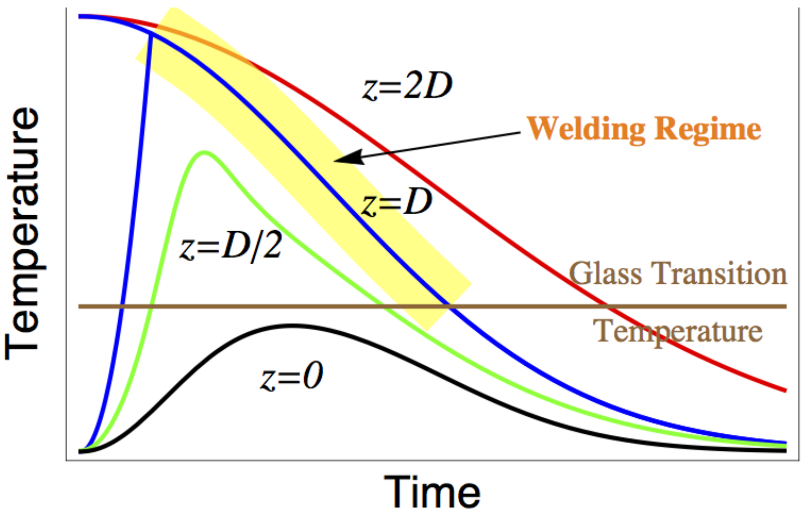

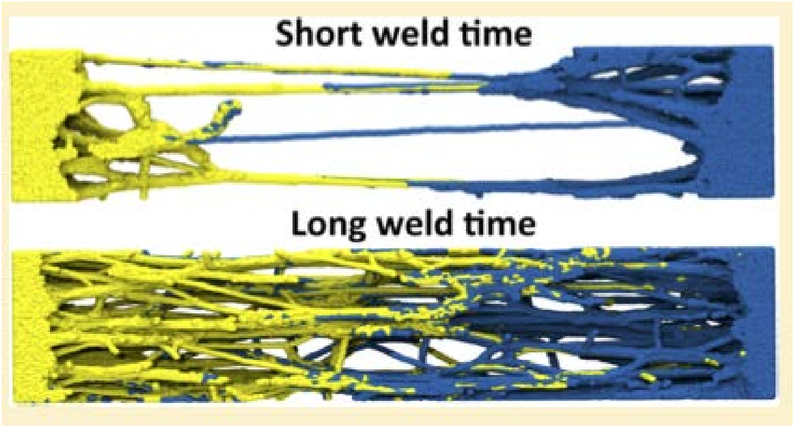

Ge, Periaha, Grest, Robbins *[ACS Nan 2013, PRE 2014]*

Non-Isothermal Processes: fiber modelling

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$$W\frac{\mathrm{d}v_z}{\mathrm{d}z} = \frac{\mathrm{d}}{\mathrm{d}z}[A(\tau_{zz} - \tau_{rr})] - \pi B\mu_a(v_z - v_d) + \rho g A + \frac{1}{2}\pi s\frac{\mathrm{d}D}{\mathrm{d}z}$$

$$\boldsymbol{c}_{(1)} = -\frac{1}{\lambda_a(T)}\frac{k_B T}{K_0}\left((1-\alpha)\boldsymbol{\delta} + \alpha\frac{K_0}{k_B T}E\boldsymbol{c}\right)\left(\frac{K_0}{k_B T}E\boldsymbol{c} - \boldsymbol{\delta}\right)$$

$$\boldsymbol{\tau}_{sc} = 3nk_B T(\boldsymbol{S} + 2\lambda_{sc}(\nabla\boldsymbol{v})^T : \langle\boldsymbol{uuuu}\rangle).$$

$$\rho C_p v_z\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{4}{D}h(T - T_a) + (\tau_{zz} - \tau_{rr})\frac{\mathrm{d}v_z}{\mathrm{d}z} + \rho\Delta H_f v_z\frac{\mathrm{d}\phi}{\mathrm{d}z}.$$

$$\frac{\mathrm{D}x}{\mathrm{D}t} = mK_{av}(T)[-\ln(1-x)]^{(m-1)/m}(1-x)\exp\left(\xi\frac{\mathrm{tr}\,\boldsymbol{\tau}}{G}\right),$$

$$\lambda_a(x, T) = \lambda_{a,0}(T)(1-x)^2,$$

- Momentum
- Conformation
- Stress Constitutive Relation
- Heat Flow
- Crystallinity
- Timescales

Outputs: orientation and structure of spun fibers.

[Doufas, McHugh, & Miller, JNNFM 92 (2000) 27-66]

Polymer Processing from the ground up – an example

μPP^2

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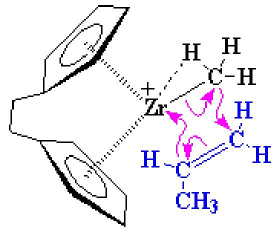
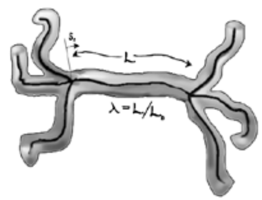
Reaction Chemistry



Molecular shape



Melt Rheology

"Good processing"

processing projects [2001-2008]

μPP²

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- Universities of Leeds (Prof TCB McLeish), Cambridge, Durham, Bradford, Sheffield, Oxford, Eindhoven.
- Many industrial players.

BASF, Innovene, Mitsubishi, Dow, DSM, ICI, Lucite

- Polymer rheology, flow-induced crystallization, instabilities, design for process, materials, and product properties.
- Close collaboration with industry.

EPSRC

Engineering and Physical Sciences Research Council

Linking theory, chemistry, experiment, and industrial materials.

μPP²
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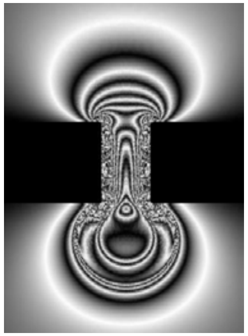
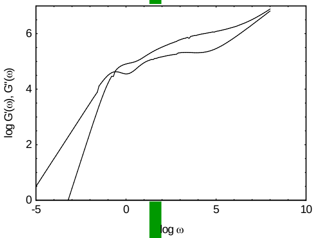
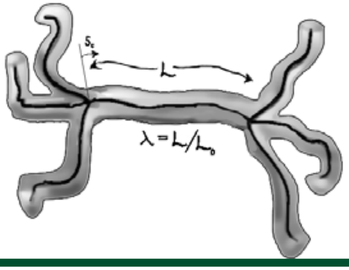
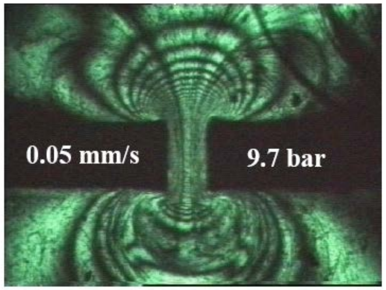
THEORY

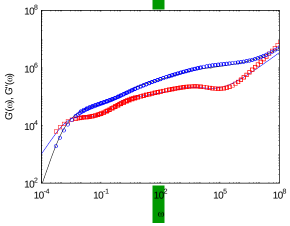


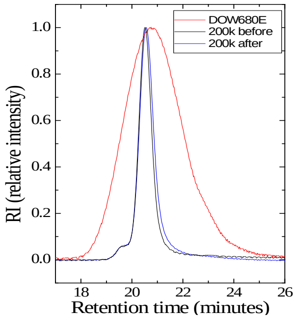




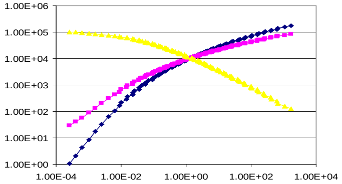
MODEL MATERIALS

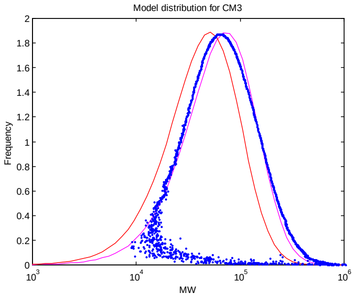






INDUSTRIAL RESINS





*Need for new/*in situ *metrologies*

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- Temperature
- Molecular conformation/shape
- Welding/interfacial properties
- Mechanical properties: elastic moduli, fracture strength and toughness, anisotropy, plasticity, ..
- Crystallinity

- Spectroscopies (IR, X-ray, neutron, Raman, fluorescence)
- Microscopies (light, Raman, TEM, SEM, …)
- Interfacial characterization (neutron scattering)

Process Characterization Thermography [J Seppala@NIST Team]

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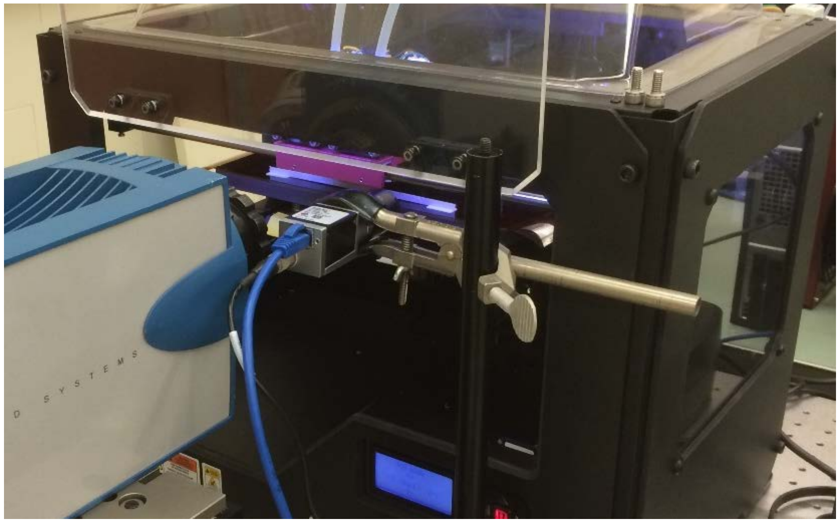

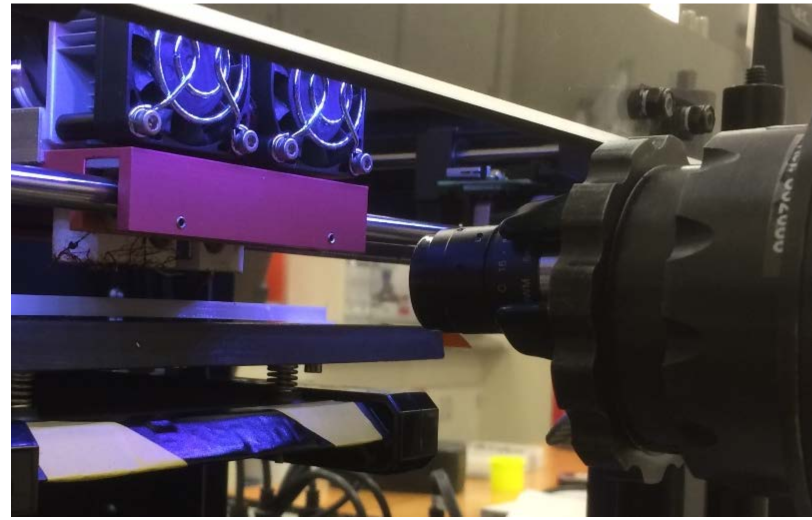

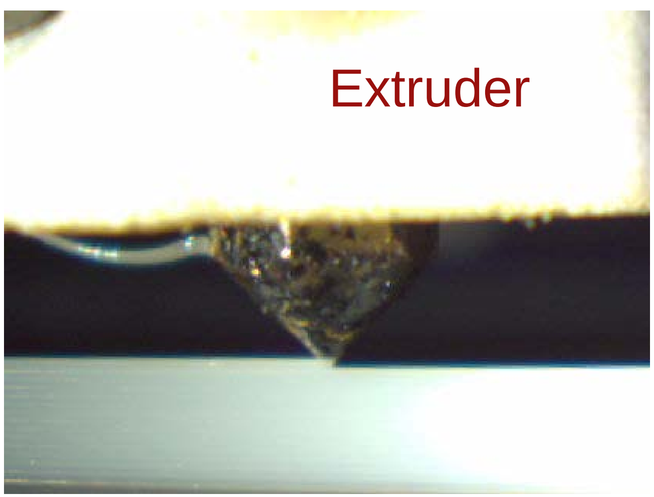

J Seppala (NIST team)

Infrared Image

IR Intensity Profiles

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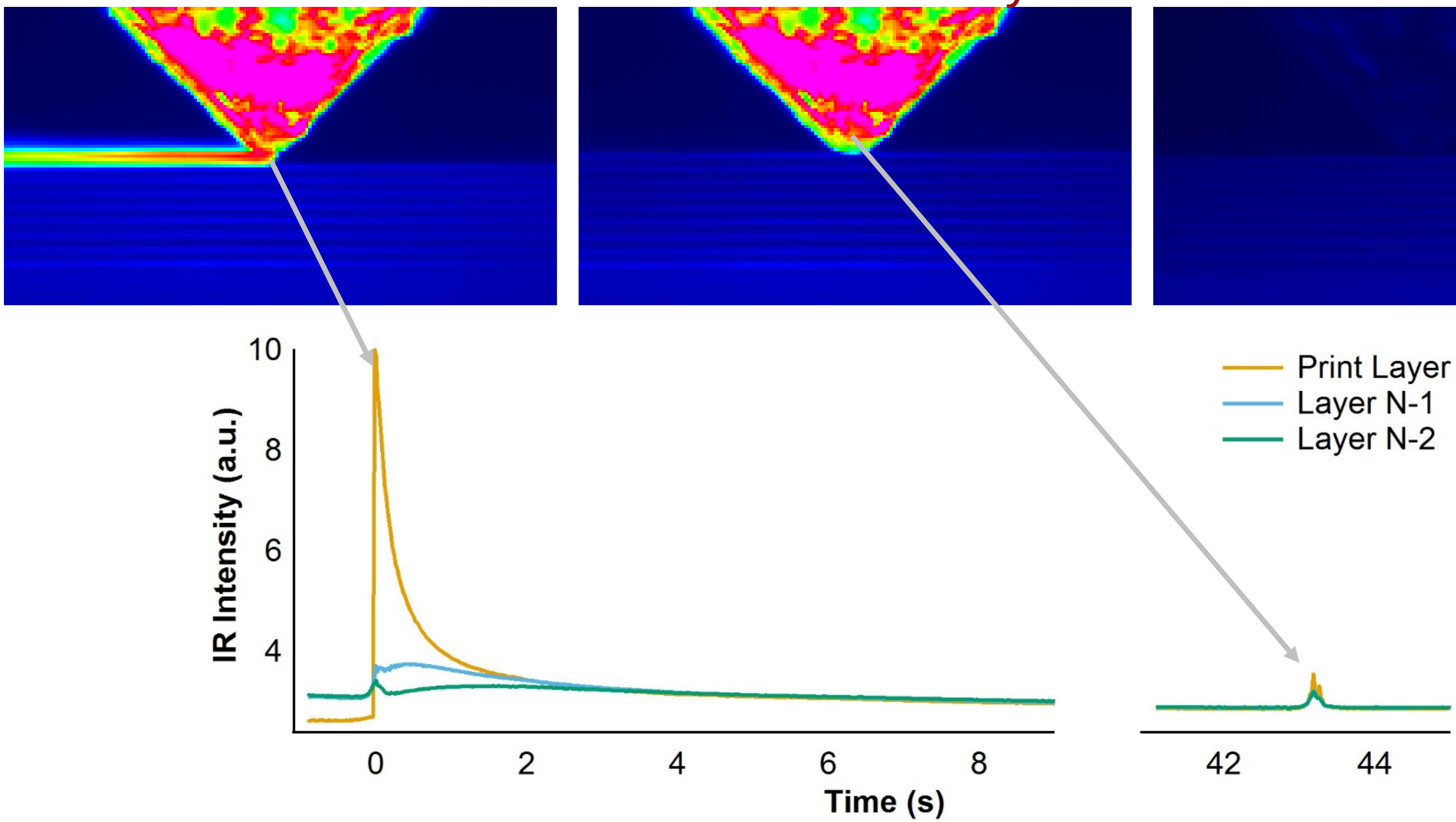
Printing Pass Emission + Reflection	Non-Printing Pass Reflection Only	Cold Pass No Reflection



Reflection + Emission Intensity

Reflection Intensity

Reflection Correction

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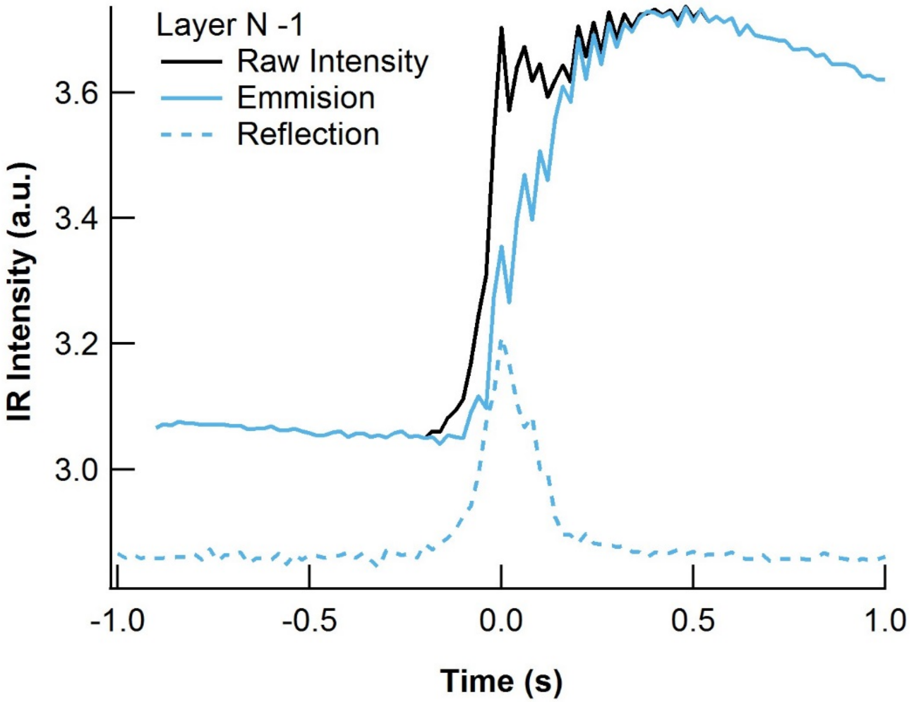
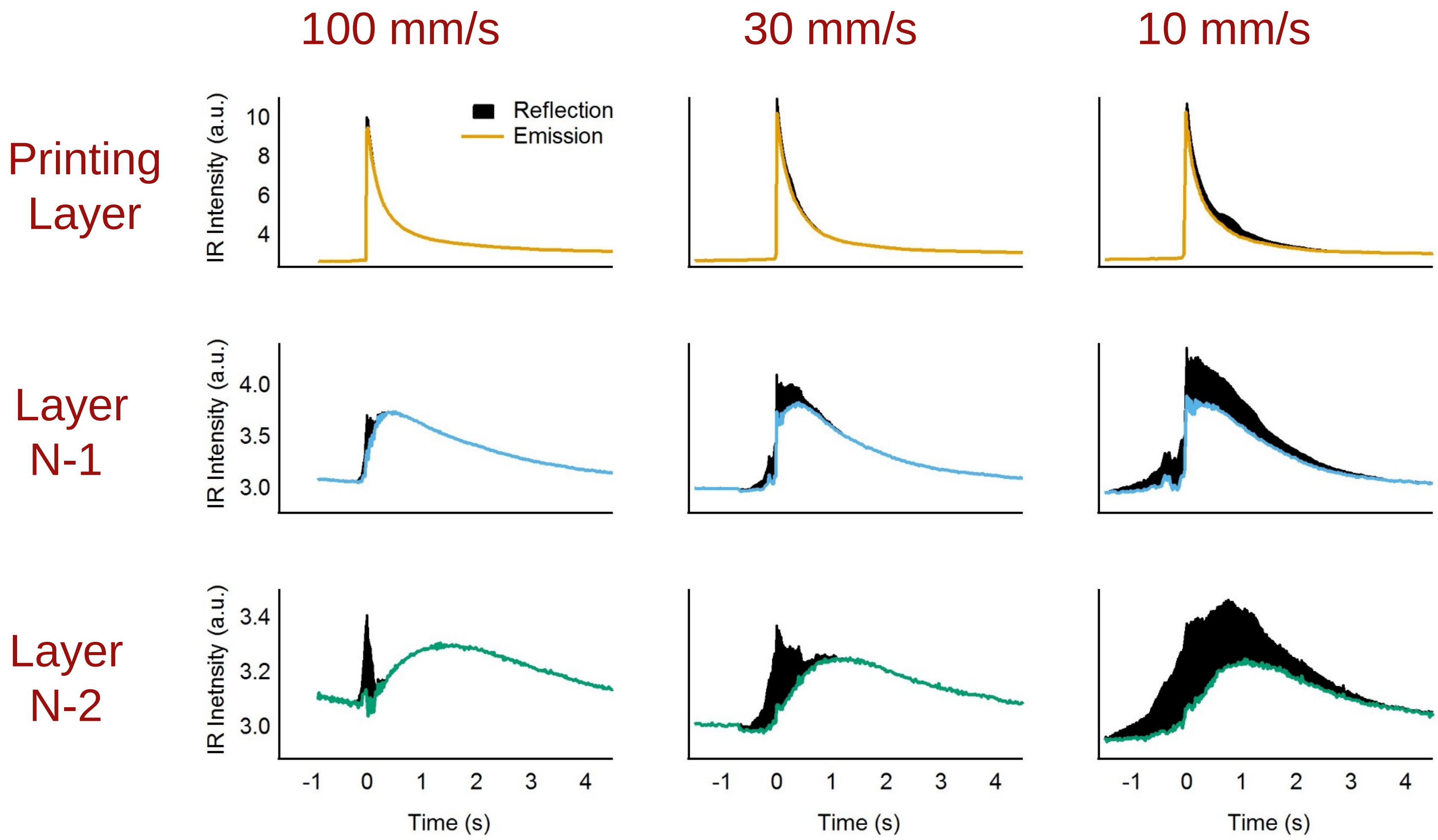


Reflection Correction

Decreasing Print Speed, Increasing Reflection



Linkam-IR Camera Calibration Curve

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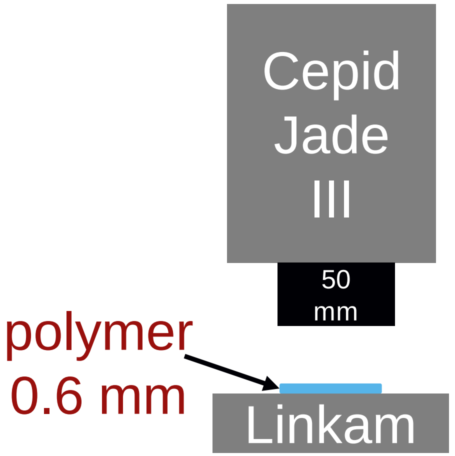
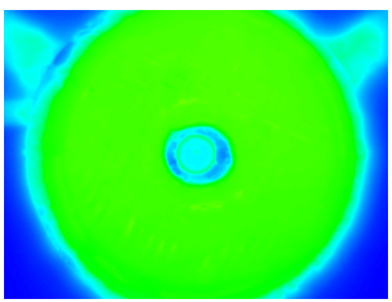
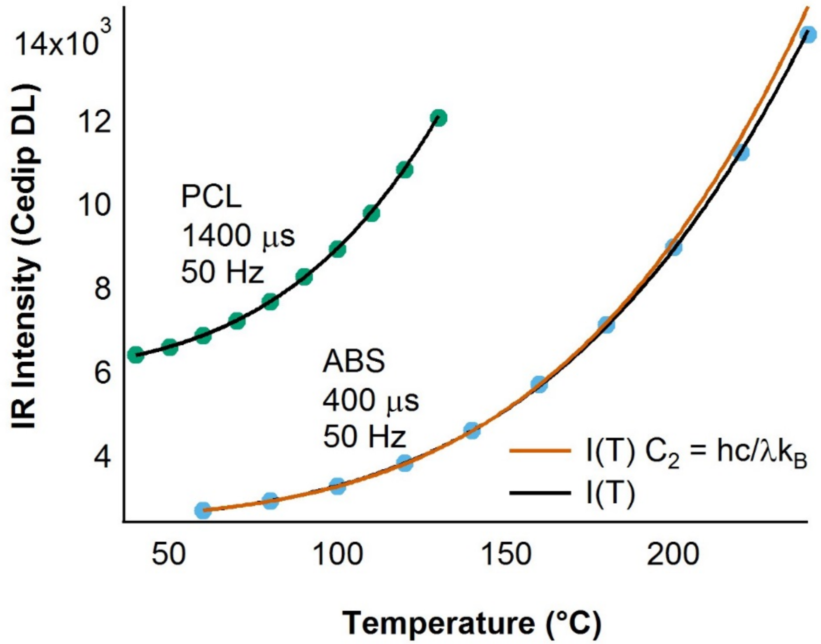


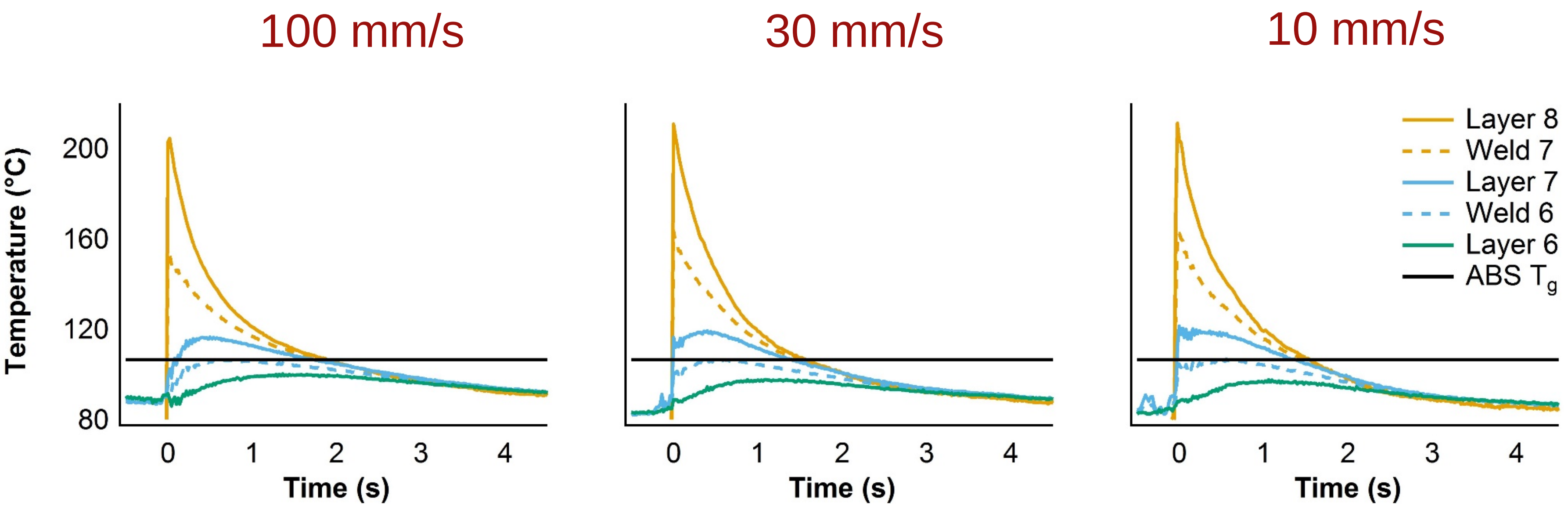


IR image polymer "washer" at 200 ° C



Polymer	C_1	C_2	C_3
ABS	1.2367×10^7	3572.2	2428.1
PCL	4.2487×10^7	3561.0	5911.6

Temperature Profiles



Weld Temperature

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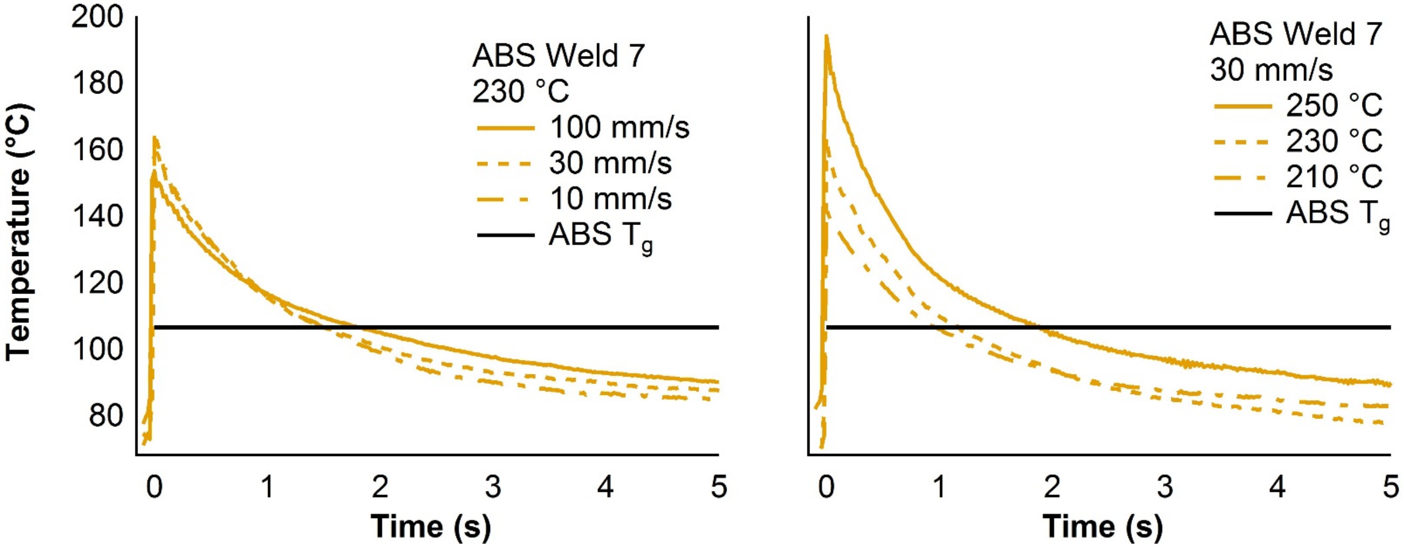
Vary Print Speed

Vary Extrusion Temperature



NIST: Materials Genome Initiative (MGI)

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- Develop predictive materials database for AM.
- Predict mechanical properties, prototype speed, resolution, and processing parameters based on polymeric properties.
- Develop tight seamless link between advanced metrologies, computation and prediction, and materials properties.
- Shorten times for development of new protocols and products.

Theory and Computational Methods/Needs

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- Develop coupled molecular and thermodynamic fields (temperature, mass, velocity, crystallinity, orientation, …). Micron scale
- Polymeric atomistic (or united atom model) simulation: welding, deformation of materials. nm scale
- Experimental inputs: temperature, extrusion conditions, build protocols, ….
- Build theory and prediction around model materials; in conjunction with `wild' materials.
- Finite element simulations of parts/pieces; compare with experiment on deformation, fracture, yield. mm scale

Coarse-Graining in Polymers

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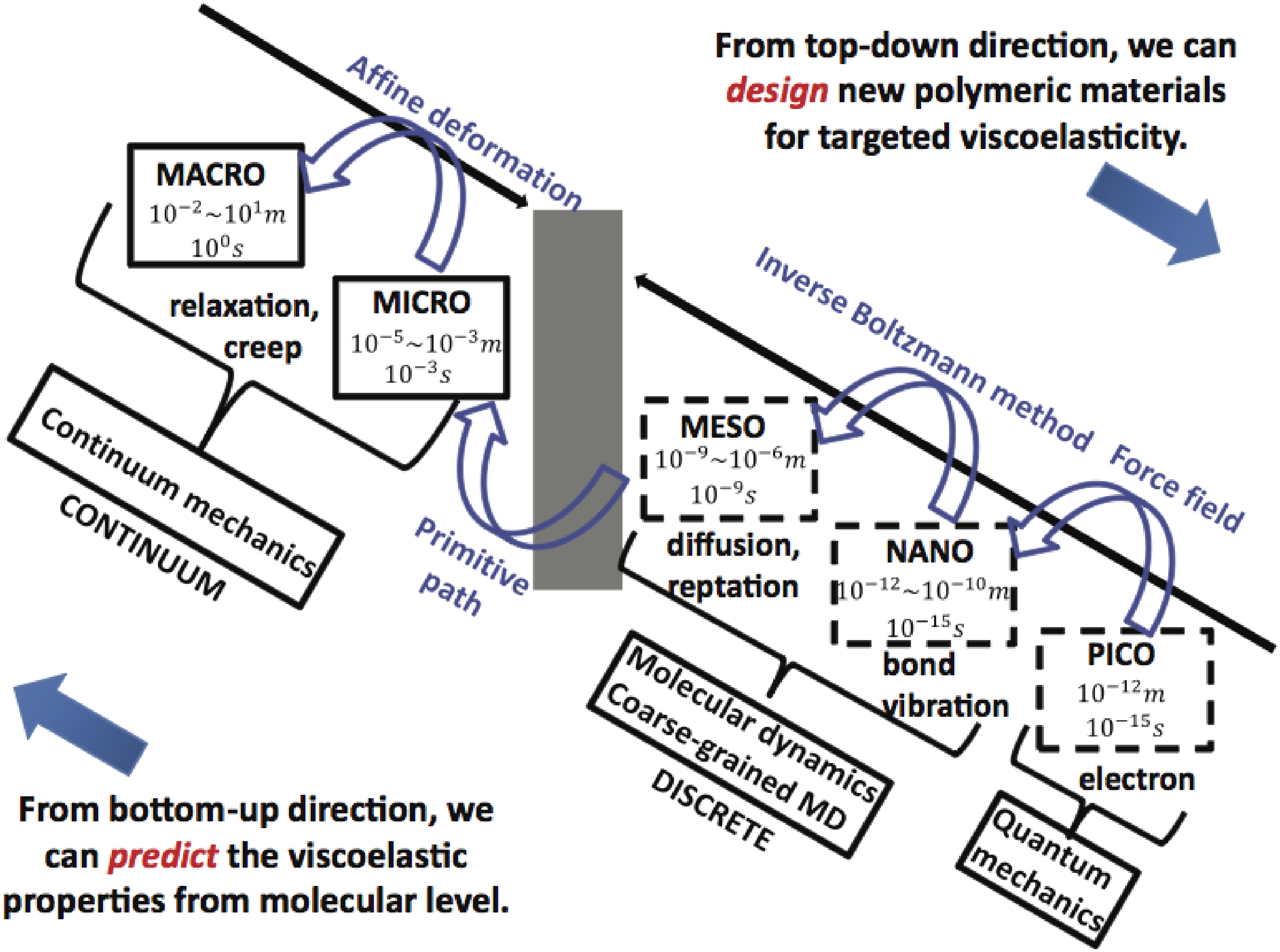
Kroger et al, Polymers 2013

From top-down direction, we can *design* new polymeric materials for targeted viscoelasticity.



From bottom-up direction, we can *predict* the viscoelastic properties from molecular level.

Main questions for P-FDM

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1. Fundamental Scientific Issues:
   - Non-isothermal conditions. molecular alignment and welding, phase changes/glass transition, shrinkage and warping
2. Unique Fundamental Theory/Computational approaches
   - Multiple scales (molecular [nm] to part size [cm])
   - Multiple dynamic fields (temperature, velocity, deformation)
   - Complex molecular and non-linear rheology/constitutive relations
3. Mathematical Models/Validation
   - Rheology: advanced models for polymer deformation.
   - Computation: flow-solvers for complex non-isothermal constitutive models for different build protocols.
   - Experimental: in situ characterization of T, orientation, etc; weld properties, mechanical performance.

Main questions for P-FDM

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5. Most important (relevant) open questions in materials and mechanics
   - The glass transition
   - Flow-induced crystallization
   - The relation of molecular structure to fracture strength and deformation
6. Does AM require unique fundamental research ?
   - Glass transition, polymer dynamics, interfaces, …
7. What multidisciplinary sciences are needed?
   - Mathematics, computation, engineering (chem, mech, …), metrology, physics, chemistry.
8. Partnerships?
   - National Labs (NIST, …); Industry (polymer manufacturers, AM developers).

Other Soft AM Methods

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- Stereo Lithography
- Selective Laser Sintering