Department of Physics

Institute for Soft Matter Synthesis and Metrology

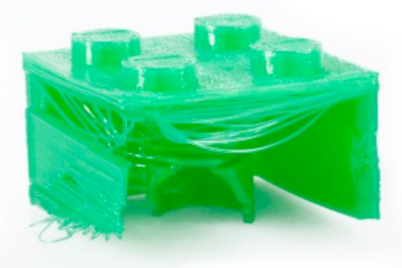
NIST
Polymers & Complex Fluids Group

GEORGETOWN UNIVERSITY

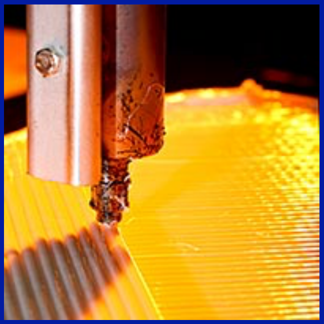
Peter Olmsted

Georgetown University

Roadmapping Workshop: Measurement Science for Polymer- Based Additive Manufacturing



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



http://web.ornl.gov/sci/manufacturing/research/additive/

Challenges in AM Processing

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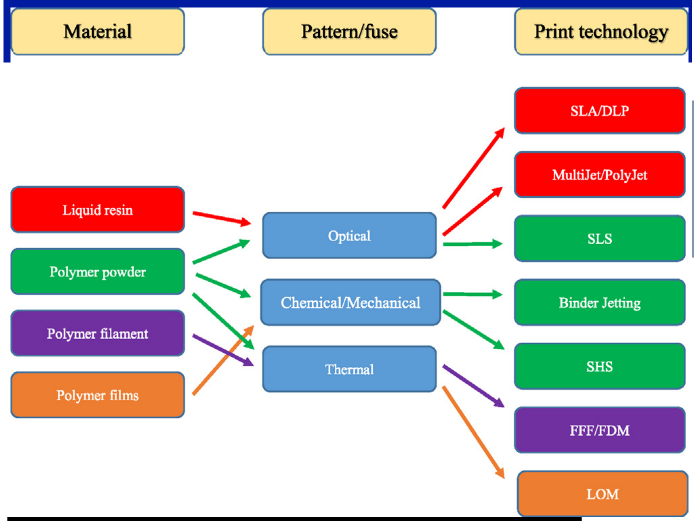
- Slow ?
- Limited combinations of materials
- Processing conditions vs materials properties
- Temperature monitor and control [non-isothermal!]
- Non-equilibrium phenomena
- Marriage of thermal and materials properties
- Mechanics, shrinkage, and morphology
- How to optimize and design shapes of materials

- Desperate need for standards!

Some polymer methods..


Material

Pattern/fuse

Print technology

Liquid resin

Polymer powder

Polymer filament

Polymer films

Optical

Chemical/Mechanical

Thermal

SLA/DLP

MultiJet/PolyJet

SLS

Binder Jetting

SHS

FFF/FDM

LOM

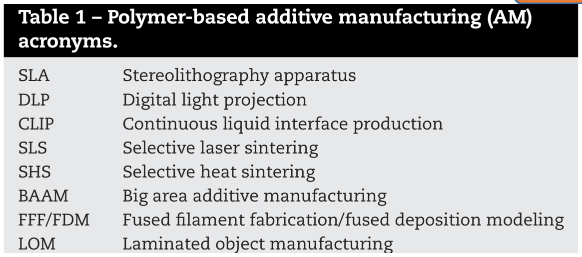
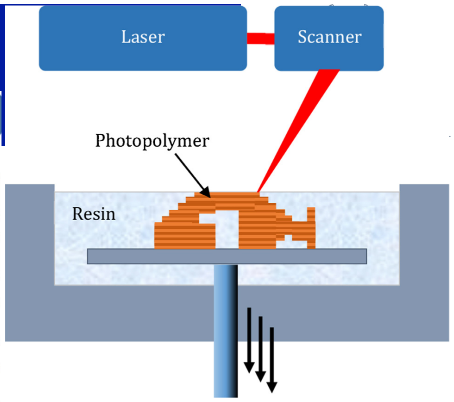
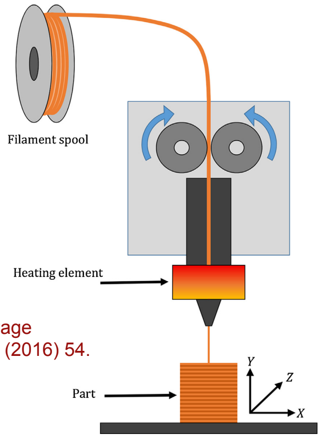


Table 1 – Polymer-based additive manufacturing (AM) acronyms.

SLA	Stereolithography apparatus
DLP	Digital light projection
CLIP	Continuous liquid interface production
SLS	Selective laser sintering
SHS	Selective heat sintering
BAAM	Big area additive manufacturing
FFF/FDM	Fused filament fabrication/fused deposition modeling
LOM	Laminated object manufacturing





Stansbury & Idacavage
Dental Materials **32** (2016) 54.

4D Printing = space + time

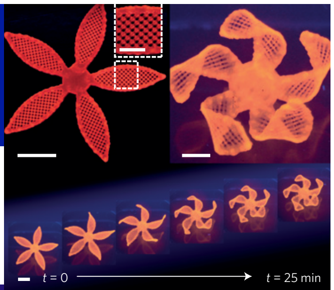

nature materials

LETTERS

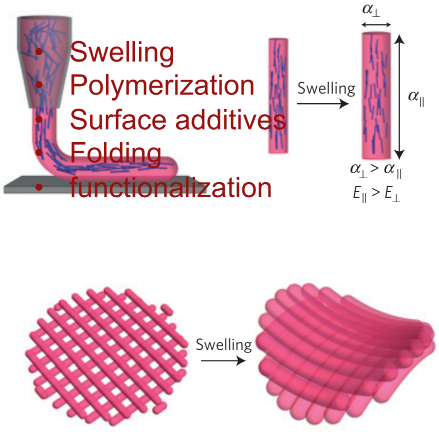
PUBLISHED ONLINE: 25 JANUARY 2016 | DOI: 10.1038/NMAT4544

Biomimetic 4D printing

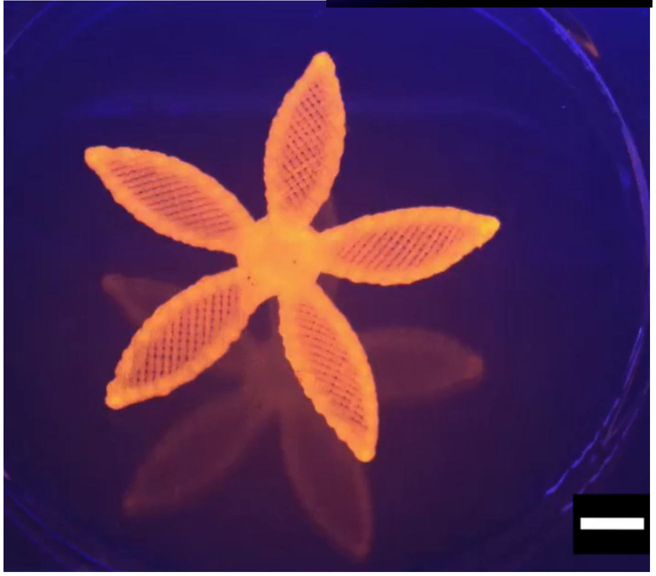
A. Sydney Gladman[1,2†], Elisabetta A. Matsumoto[1,2†], Ralph G. Nuzzo[3], L. Mahadevan[1,2,4★] and Jennifer A. Lewis[1,2★]



“time” = post-processing



- Swelling
- Polymerization
- Surface additives
- Folding
- functionalization



Fused Deposition [Filament] Modelling of Polymers (FDM, FFD, FFF)

- "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, ….?

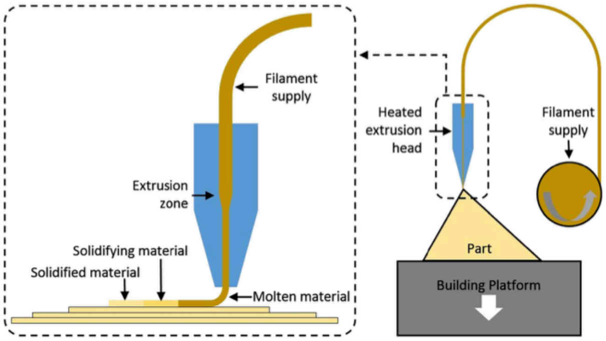
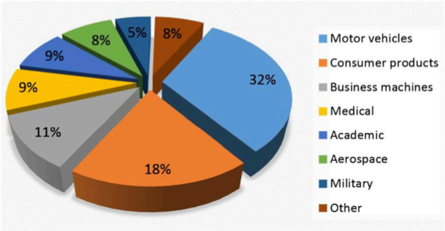


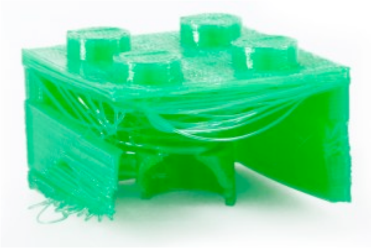
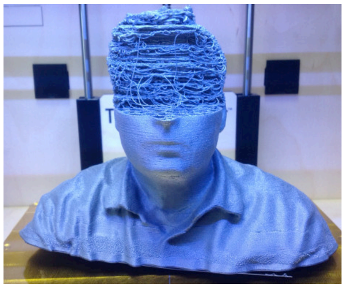
Fig. 3 Rapid prototyping worldwide 2001 [7]

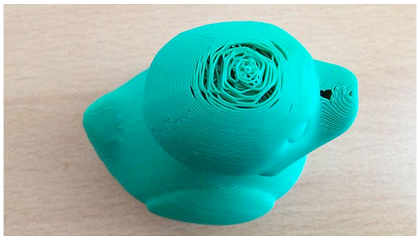
Kruth JP, Levy G, Klocke F, Childs THC (2007) Consolidation phenomena in laser and powder-bed based layered manufacturing. CIRP Ann Manuf Technol 56(2):730–759



Some Challenges in Polymer FDM

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



Polymer Materials

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Material	Transition Temperature
• Semi-crystalline polymers	
• poly-caprolactate (PCL) [biodegradeable polyester]	• Melt: 60 C
• polylactic acid (PLA) [biodegradeable]	• Melt: 150-160 C
• Amorphous polymers	
• Polycarbonate (PC)	• Glass: 147 C
• ABS: Acrylonitrile-butadiene-styrene (copolymers + rubber particles)	• Glass: 80-125 C

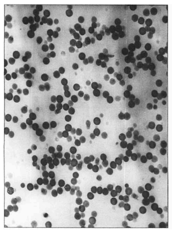


Photo 2 :ABS 1 - GD = 29%

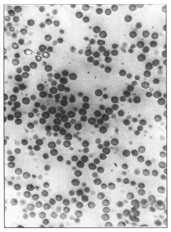
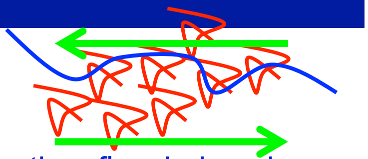
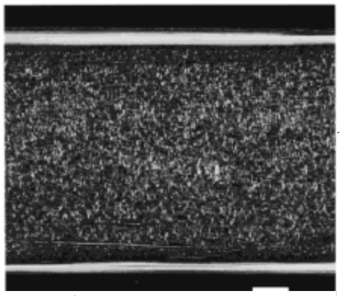


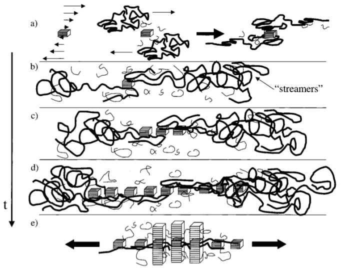
Photo 3 : ABS 3 - GD = 63%

Relevant Polymer Physics

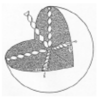


- Crystallization
  - Exothermic, structure formation, flow-induced,
- Molecular orientation in flow
  - Alignment influences welding, deposition
- Rheology of entangled polymers
  - Non-Newtonian, non-linear, . …
- Entanglement and diffusion
  - Controls weld process
- Glass transition
  - Ideally want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





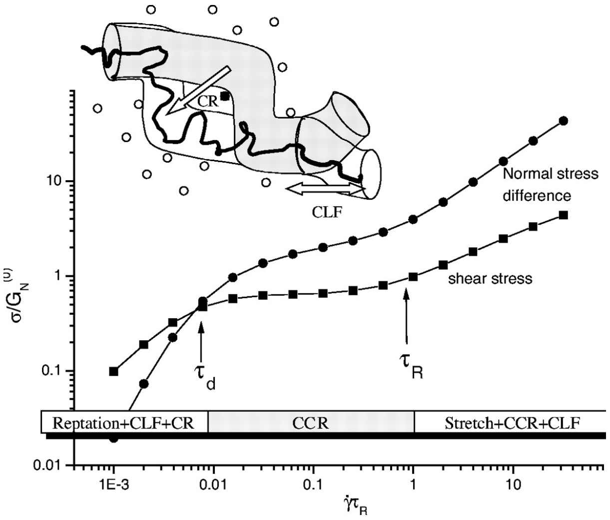
Shish-Kebab structure

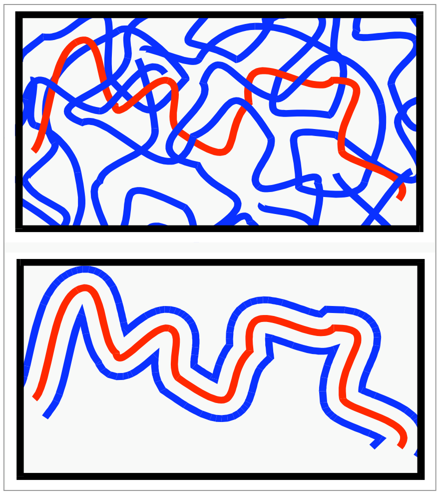


Spherulitical structure

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

Entangled Polymer Dynamics





Rouse (‘Stretch’)	$\tau_R \simeq N^2$
Reptation (‘disengagement’)	$\tau_d \simeq N^3$

Viscosity	$\eta \sim N^3$

[Doi & Edwards, Faraday Discussions II (1978-1979)]

Polymer Dynamics and Timescales: ``Weissenberg numbers”

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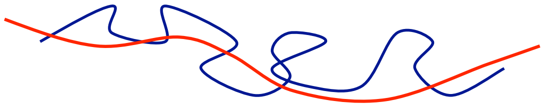


$$\mathrm{Wi}_{\mathrm{rept}} = \tau_d\dot{\gamma} \sim M^3$$

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

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

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

Significant orientation (and flow induced crystallisation)

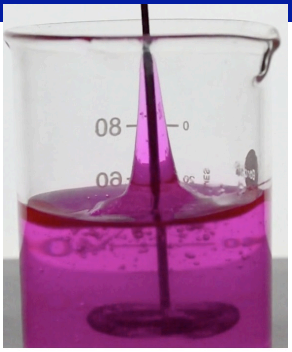
$$\mathrm{Wi}_{\mathrm{stretch}} > 10$$

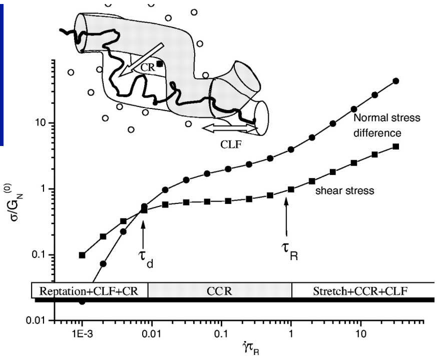
Significant stretch (and oriented crystallization)

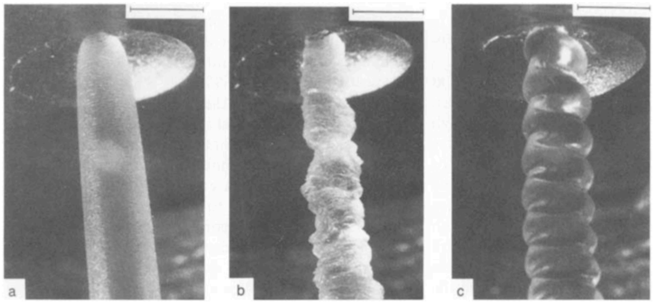
Typical nozzle parameters: $\mathrm{Wi}_{\mathrm{rept}} \simeq 100,\quad \mathrm{Wi}_{\mathrm{stretch}} \simeq 10$

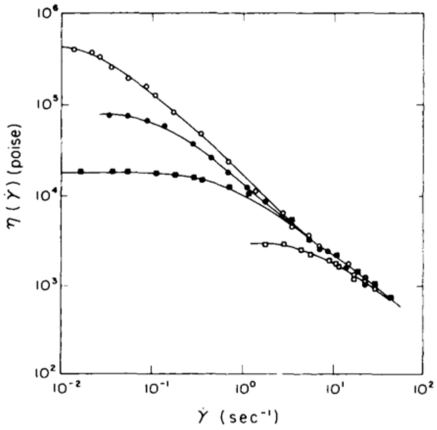
Non-Newtonian Fluid Mechanics of Polymeric Materials

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









Flow-induced crystallization during extrusion

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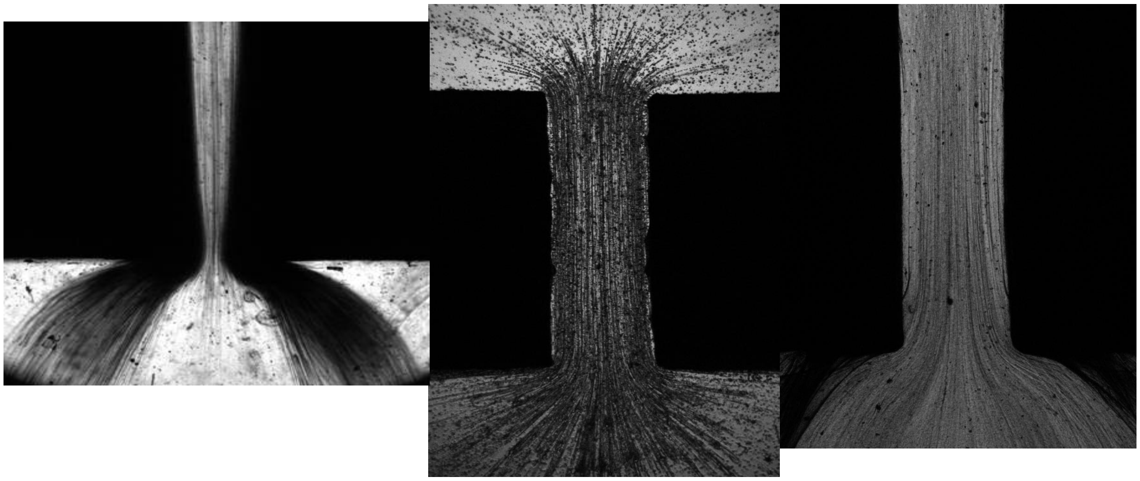
Example of polypropylene (L Scelsi, et al.. J Rheology (2009)

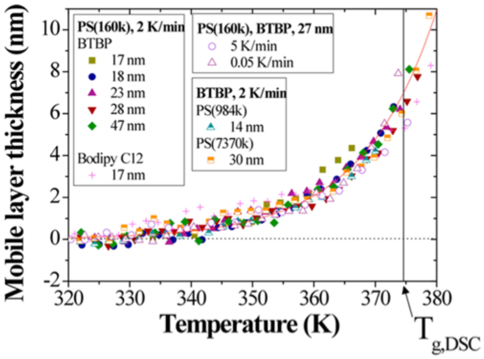


Modelling: Structure formation/crystallization, rheology, flow geometry.

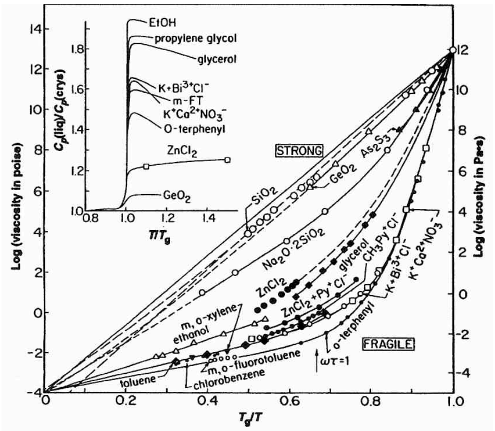
McHugh & Doufas; Fiber Spinning (JNNFM 2000);
Graham and Olmsted: flow-induced crystallization (Phys Rev Lett 2009)

Scientific Issues in FDM

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



J Forrest & M Ediger, Macromolecules 2014



A Angel, 1997

Computational/Modelling challenges

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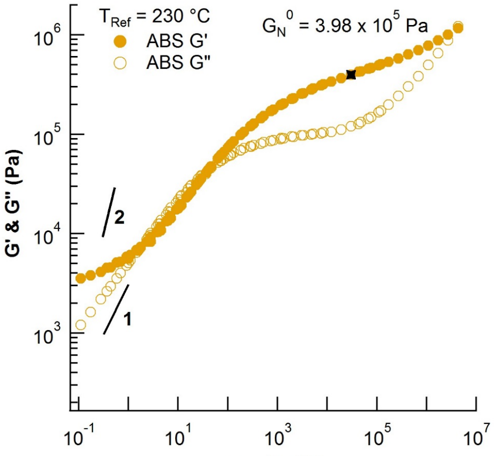
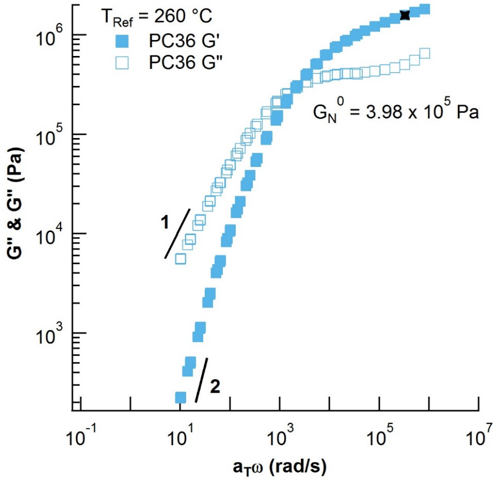
- Many coupled time-dependent quantities:
  - Molecular shape/structure/orientation/alignment
  - Temperature
  - Velocity field/deformation
  - Density
  - Moving/changing boundaries
  - Phase change materials
- Multiple scales (chemistry → polymer → mesoscale ordering → fluid mechanics of extruded filaments → bulk mechanical properties of composite FDM material).

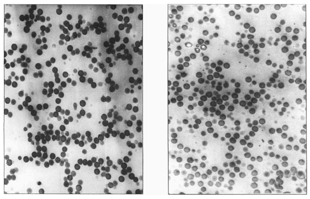
FDM Materials Polymer Rheology

ABS Moduli

Polycarbonate





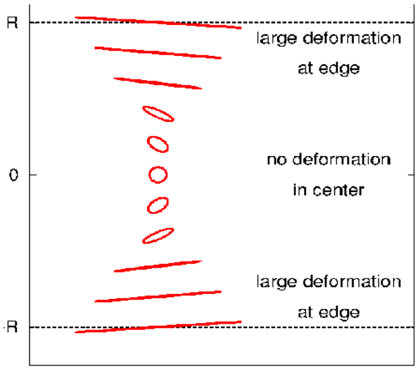


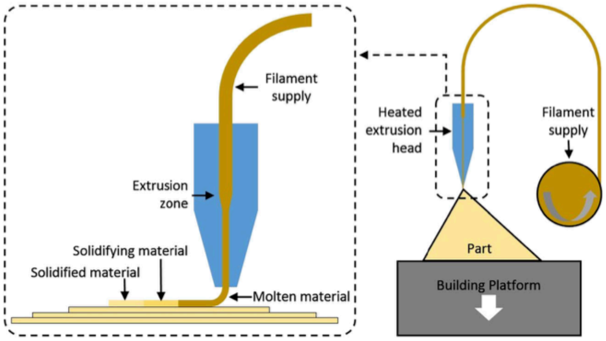
Composite (nanoparticles + copolymers)

Linear polymer melt
Reptation time

Details of extrusion

- 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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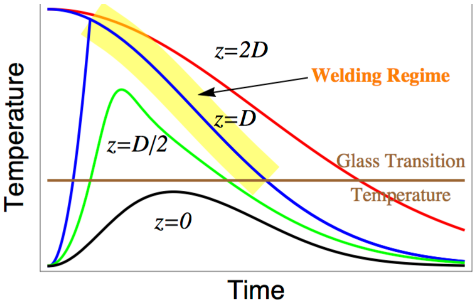
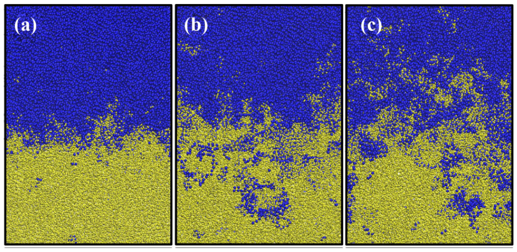
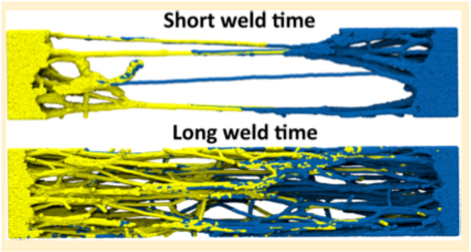




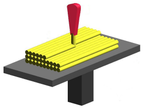


Ge, Periaha, Grest, Robbins *[ACS Nan 2013, PRE 2014]*

Printing with Polymer Melts

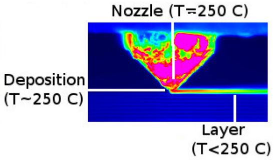
Claire McIlroy (Georgetown/NIST)

Fused Deposition Modelling



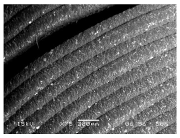
Extrusion of an **entangled polymer melt** into layers.

Infra-Red Imaging



Non-uniform **temperature profile** and glass transition.

De-bonding



Polymer alignment can **weaken welds** between layers.

Three Stages of Printing:

- **Nozzle:** Steady axisymmetric pipe flow.
  High shear rates stretch and orient the polymer.
- **Deposition:** Map axisymmetric flow to elliptical layer.
  Complex 3D polymer configurations across layer.
- **Weld:** Temperature-dependent relaxation of deformation.
  Entanglement density is key to welding characteristics.

Non-Isothermal Processes: fiber modelling: semicrystalline polymers

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

$$\boldsymbol{c}_{(1)} = -\frac{1}{\lambda_\mathrm{a}(T)}\frac{k_\mathrm{B}T}{K_0}\left((1-\alpha)\boldsymbol{\delta} + \alpha\frac{K_0}{k_\mathrm{B}T}E\boldsymbol{c}\right)\left(\frac{K_0}{k_\mathrm{B}T}E\boldsymbol{c} - \boldsymbol{\delta}\right)$$

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

$$\rho C_\mathrm{p} v_z\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{4}{D}h(T - T_\mathrm{a}) + (\tau_{zz} - \tau_{rr})\frac{\mathrm{d}v_z}{\mathrm{d}z} + \rho\Delta H_\mathrm{f} v_z\frac{\mathrm{d}\phi}{\mathrm{d}z}.$$

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

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

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

Outputs: orientation and structure of spun fibers.

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

Molecular-based kinetics of flow-induced crystallization: Graham & Olmsted (PRL 2009)

Rolie-Poly Models; apply to glassy polymers.

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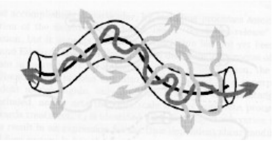
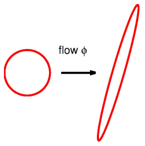
Tube Model



Deformation Tensor

$$\mathbf{A} = \frac{<\mathbf{RR}>}{3R_g^2}$$

Visualisation



Rolie-Poly Equation

$$\frac{D\mathbf{A}}{Dt} = \mathbf{K}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{K}^T - \frac{1}{\tau_d}(\mathbf{A}-\mathbf{I}) - \frac{2(1-\sqrt{3/\mathrm{tr}\mathbf{A}})}{\tau_R}\left(\mathbf{A} + \beta\left(\frac{\mathrm{tr}\mathbf{A}}{3}\right)^\delta(\mathbf{A}-\mathbf{I})\right)$$

- Reptation τ_d for **orientation**:

  e.g. Shear $= A_{r\phi}$

- Entanglements:

  $Z \approx \tau_d/3\tau_R = 37$

- Rouse time τ_R for **stretch**:

  tr$\mathbf{A} = A_{\phi\phi} + A_{\theta\theta} + A_{rr}$

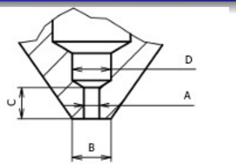
- Convective constraint release:

  $\beta = 1, \delta = -0.5$

$$\tau_d = \tau_0 \exp\left(\frac{-C_1(T-T_0)}{}\right)$$

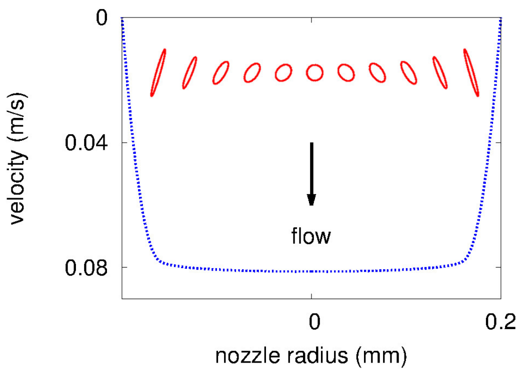
Polymer Deformation in the Nozzle

Fast Printing $v_L = 100$ mm/s



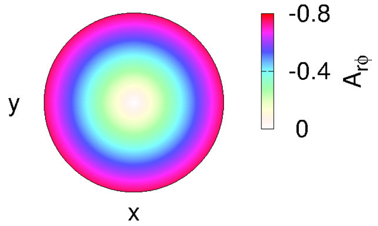
#1 Nozzle: Steady state axisymmetric pipe flow calculation for polycarbonate.
$T = 250^o$C; $v_N = 75$ mm/s; $\dot{\gamma}_w = 3600$ s^{-1}

Velocity Profile

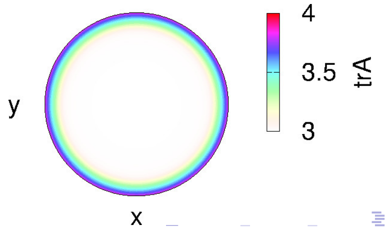


Ellipses represent how polymers become **stretched** and **oriented** near the nozzle walls.

Principle Shear: $A_{r\phi}$



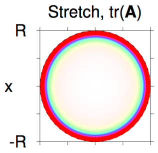
Stretch: tr**A**



Variable Entanglement Density

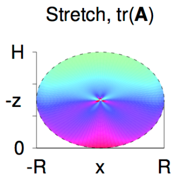
Ianniruberto & Marrucci **J. Rheol.** (2014)

#1 Nozzle: Modify entanglement density $\nu = Z/Z_{eq}$

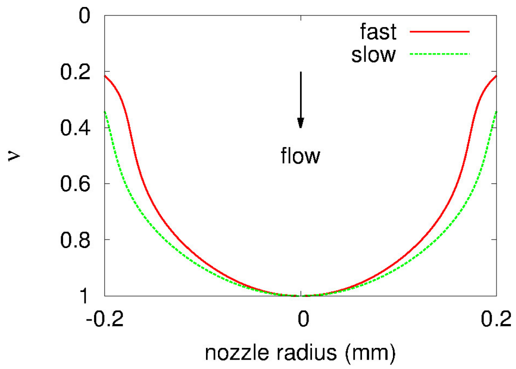


$$\frac{d\nu}{dt} = -\beta \overbrace{\left(\mathbf{K}\cdot\mathbf{A} - \frac{1}{(\mathrm{tr}\mathbf{A})}\frac{d\mathrm{tr}\mathbf{A}}{dt}\right)}^{\text{loss by convection}}\nu + \overbrace{\frac{1+\nu}{\tau_d}}^{\text{gain by diffusion}}$$

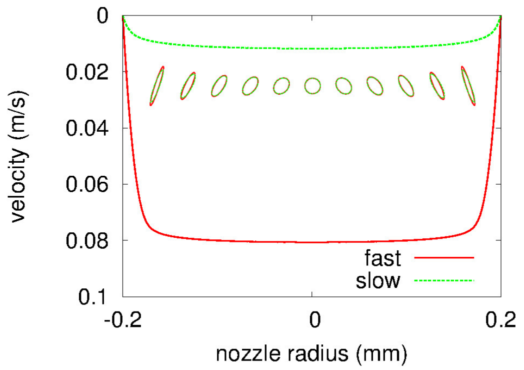
$$\tau_d = \tau_d^{eq}\nu^{1.2}$$



Entanglement Density

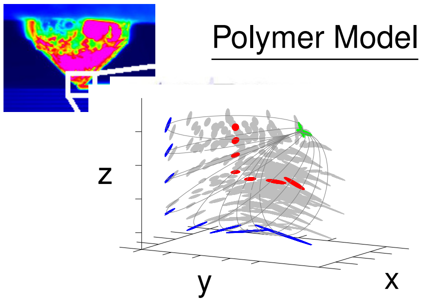


Velocity Profile

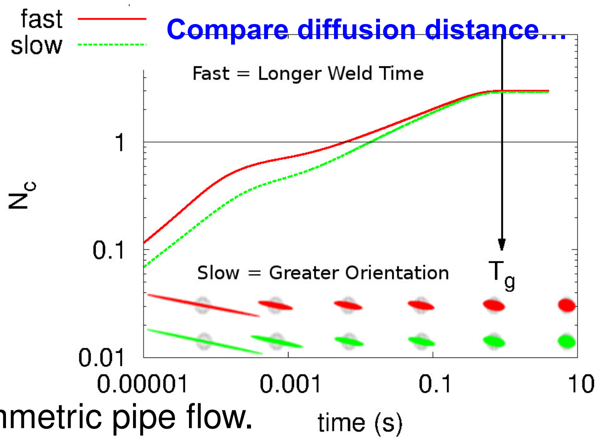


Greater **disentanglement** for **faster** printing speeds.

Printing with Polymer Melts



Polymer Model



Three Stages of Printing:

- **Nozzle:** Steady axisymmetric pipe flow. High shear rates stretch and orient the polymer.
- **Deposition:** Map axisymmetric flow to elliptical layer. Complex 3D polymer configurations across layer.
- **Weld:** Temperature-dependent relaxation of deformation. Entanglement density is key to welding characteristics.

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*Need for new/*in situ *metrologies*

GEORGETOWN UNIVERSITY

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

Time dependence!!!

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

Theory and Computational Methods/Needs

- 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

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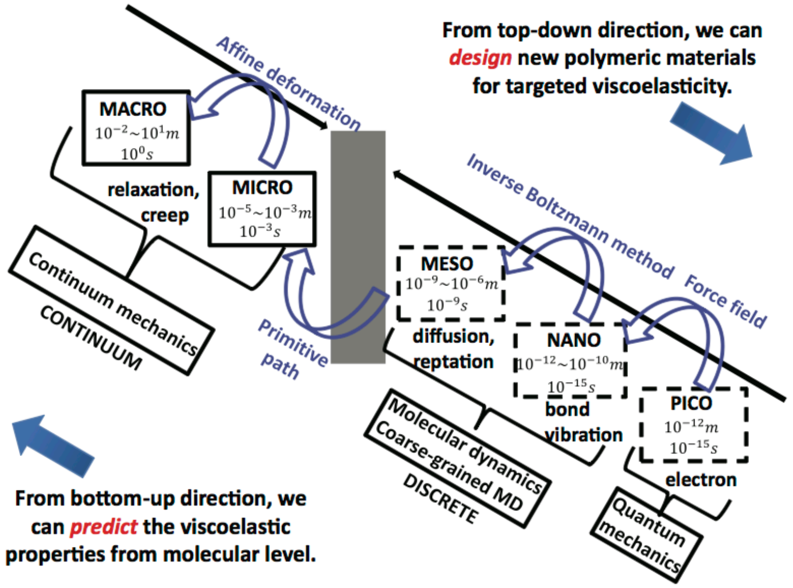
Coarse-Graining in Polymers –

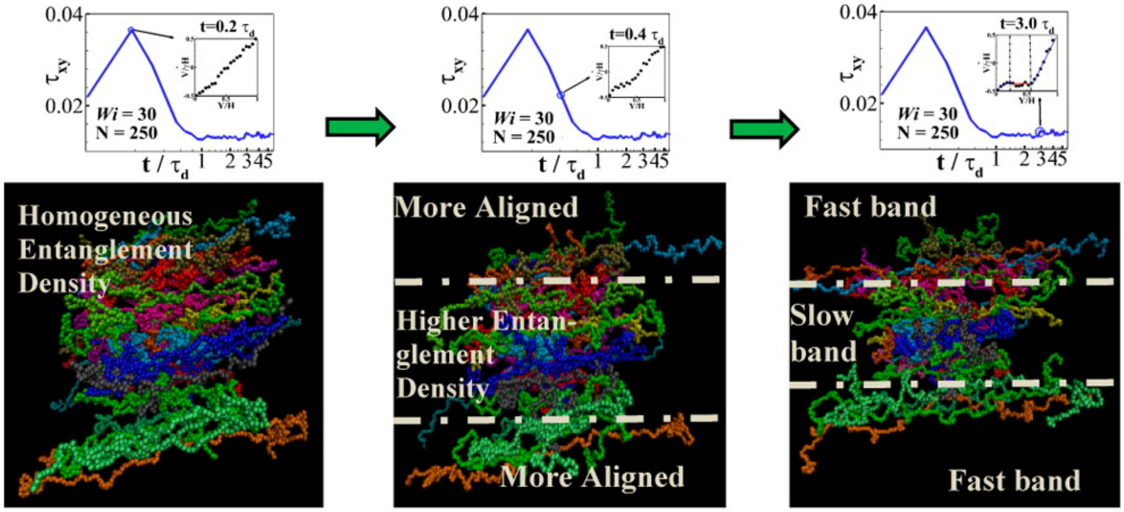
Kroger et al, Polymers 2013



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

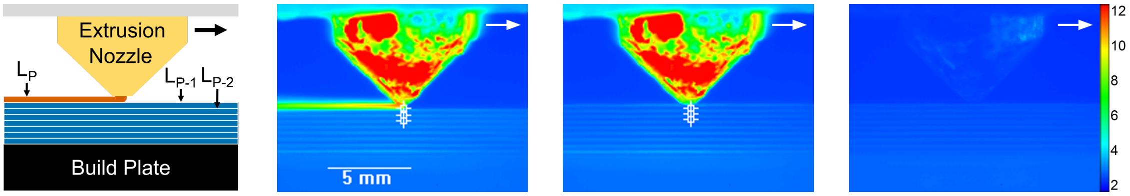
From bottom-up direction, we can *predict* the viscoelastic properties from molecular level.

Current modeling capabilities in flow

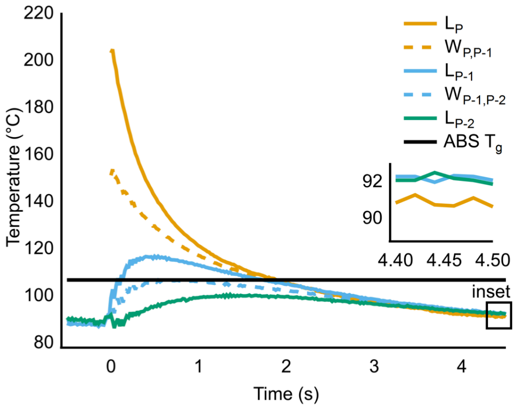


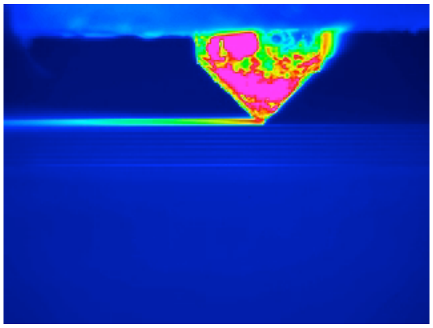
DPD Simulations, Z=17, 705 chains, startup at Wi=40 for 5 reptation times (200 strain units). [Mohagheghi & Khomani, ACS Macro Letters 2015].

Process Characterization Thermography [J Seppala, K Migler@NIST Team]



(a) Illustration (b) Extrusion (c) Hot, no extrusion (d) Cold nozzle





Infrared Image

Scientific arenas for Additive Manufacturing

1. Fundamental Scientific Issues:
    - Non-isothermal conditions. molecular alignment and welding, phase changes/glass transition, shrinkage and warping, crystallization
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.

Scientific challenges for FDM

5. Involves the most important (relevant) open questions in polymer materials and mechanics
    - The glass transition
    - Flow-induced crystallization
    - The relation of molecular structure to fracture strength and deformation.
    - …..
6. What multidisciplinary sciences are needed?
    - Chemistry, physics, metrologies, mathematics, computation, engineerings (chem, mech, …), computer science, massive data.
7. **Partnerships**
    - Academia; National Labs (NIST, Sandia, LLNL,…); Industry (materials manufacturers, AM machine developers, end users and suppliers).