Department of Physics

Institute for Soft Matter Synthesis and Metrology

NIST
Polymers & Complex Fluids Group

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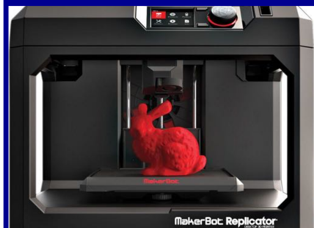
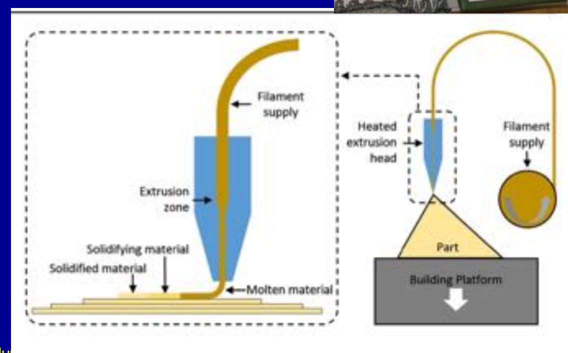


Claire McIlroy (GU → Nottingham)

Peter Olmsted

Physics Challenges in Additive Manufacturing with Polymers



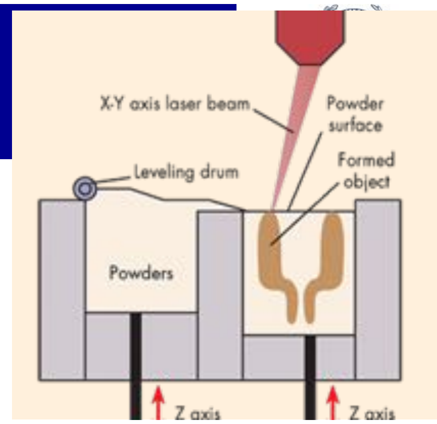
http://www.staticwhich.co.uk/media/images/in-content/makerbot-replicator-2-brick-print-failu

3D Printing with Polymers

Carbon 3D Continuous photocuring (polyurethanes)

Challenges!

- Speed!
- *in-situ* metrologies
- Non-isothermal/non-equilibrium
- Thermal gradients
- Mechanics, shrinkage, and morphology.



Selective Laser Sintering (Polyamides)

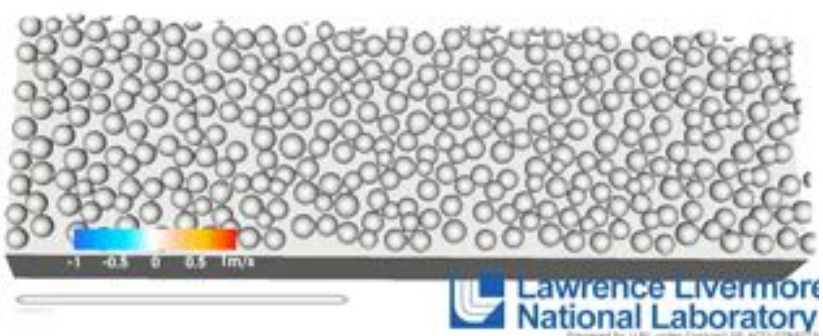
Fused Deposition Modeling/Fused Filament Fabrication
(PC, ABS, PLA)

Stereolithography (UV curing, methacrylates)

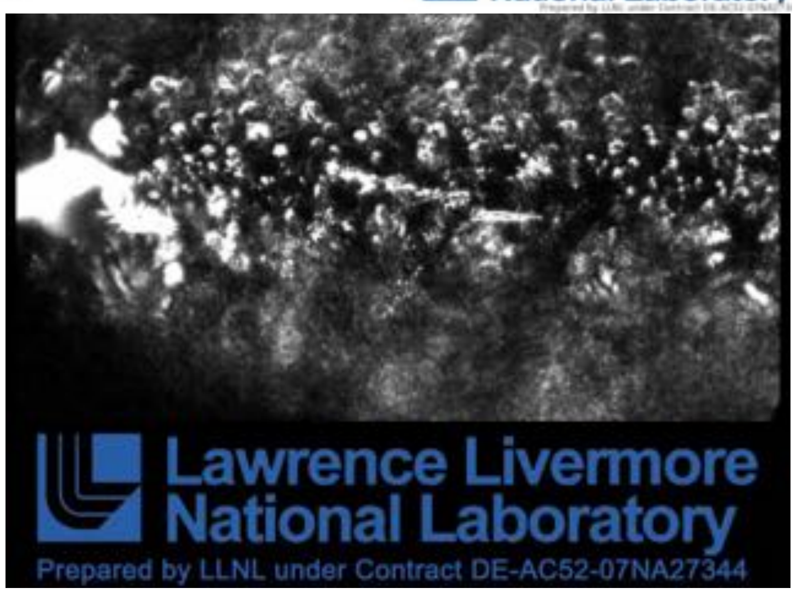
Selective Laser Melting of Metals

Stainless steel

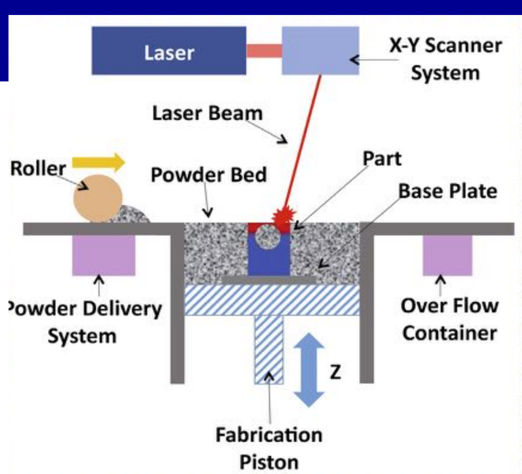
Particle Speeds 2-4 m/s
Liquid Ejection at 10 m/s



- Rapid heating/cooling
- Plasma formation
- Hydrodynamics of molten liquid meal,
- Marangoni effects
- Vapor pressure recoil
- Rapid solidification
- Non-equilibrium metastable crystal states
- Glass formation?
- Mechanical properties of welded metals, polycrystalline texture
- Alloy design
- Powder design and flows



Selective Laser Sintering



S.M. Thompson et al. / Additive Manufacturing 8 (2015) 36–62

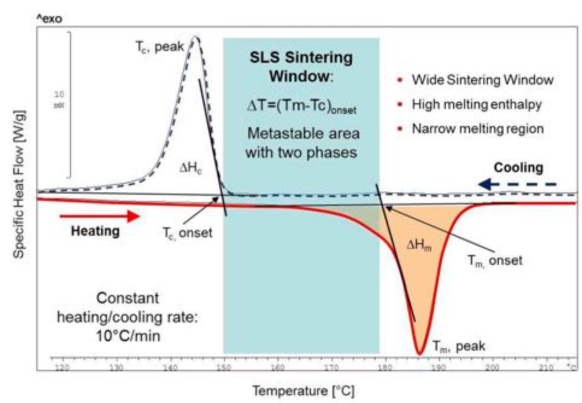
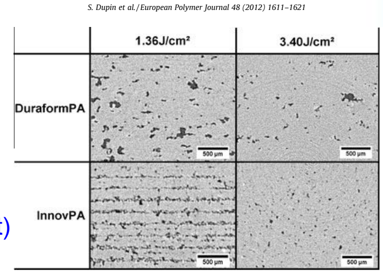


Fig. 7. Typical DSC-Thermogram with nature of 'sintering window' as LS process temperature

Wide Sintering window: to cool slowly, avoid shrinkage, mix particles.
Schmidt & Wegner, Procedia Engineering 149 (2016) 457

- **PA12** has the best (?) **sintering window**. [Tune crystal thickness and/or isoform]
- Powder flowability is crucial.
- **Porosity** due to bubble entrapment (gas diffusion in polymers important)

S. Dupin et al. / European Polymer Journal 48 (2012) 1611–1621



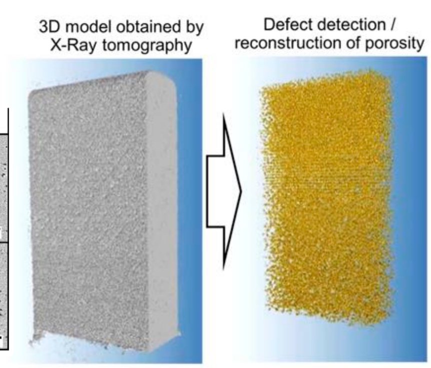
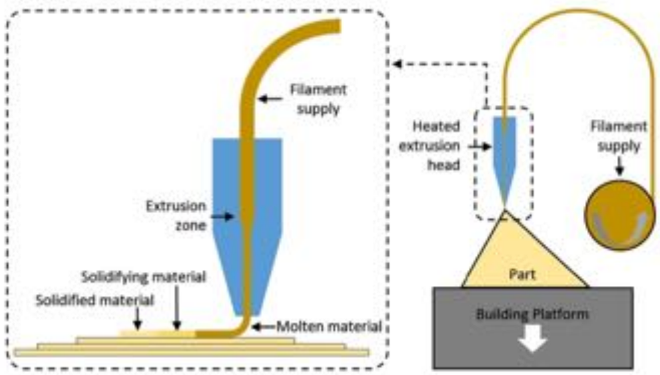


Fig. 5. Visualized CT data and detected pores (Sample size: ca. 15×8×4 mm³).
Stichel et al., Optics Las. Tech 89 (2017) 31

Fused Deposition Modelling of Polymers (FDM, FFD, FFF)



- “Hot Glue Gun” Extrusion
- Automotive, aerospace, medical devices, custom parts,….
- Rapid prototyping

Some Challenges in Polymer FDM/FFF

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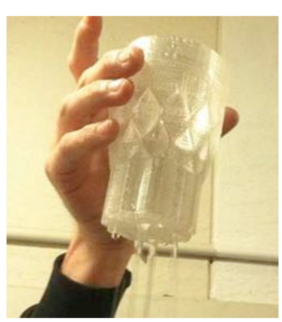
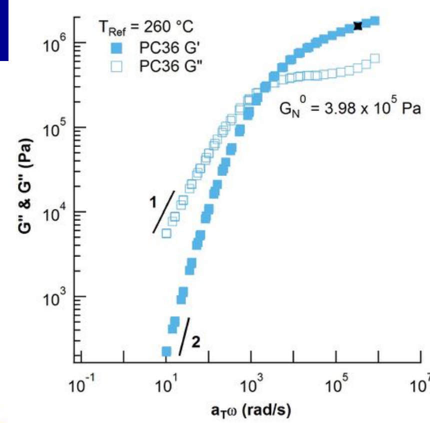
- Weak mechanical properties
- Sagging
- Poor/textured surface properties
- Porosity
- Shrinkage, warping, and debonding.



Polymer Materials

Polycarbonate



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

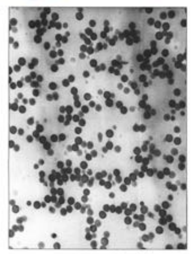
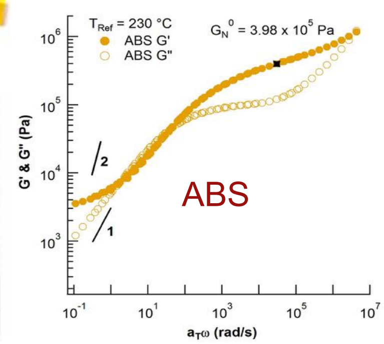
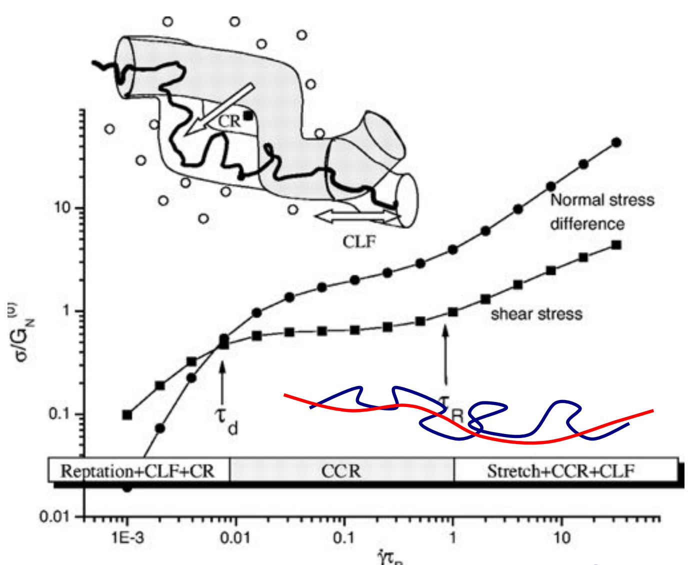
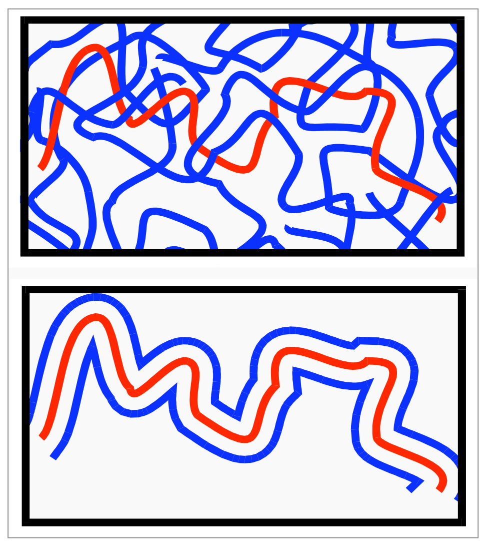


Photo 2 : ABS 1 - GD = 29%



Entangled Polymer Dynamics





Rouse $\tau_R = \tau_e Z^2$

reptation (disengagement) $\tau_d \simeq \tau_e Z^3$

Entanglement Number $Z = \frac{M_w}{M_e}$

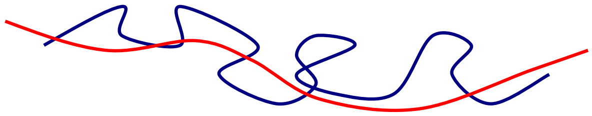
Viscosity $\eta \simeq \tau_e Z^3$

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

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

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

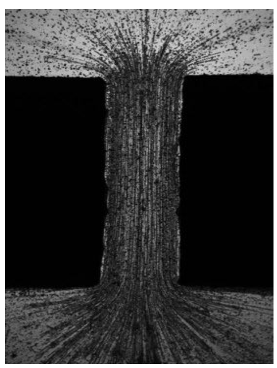
Effects of Polymer Dynamics and Timescales: Flow-induced crystallization [van Meerveld, Peters, Hutter Rheo Acta 2004]



$$\mathrm{Wi}_{\mathrm{rept}} = \tau_d \dot{\gamma} \sim M^3$$
$$\mathrm{Wi}_{\mathrm{stretch}} = \tau_R \dot{\gamma} \sim M^2$$

$\mathrm{Wi}_{\mathrm{rept}} > 1$, $\mathrm{Wi}_{\mathrm{stretch}} \lesssim 1 - 10$: Significant orientation (and flow induced crystallisation)

$\mathrm{Wi}_{\mathrm{stretch}} > 10$: Significant stretch (and oriented crystallization)



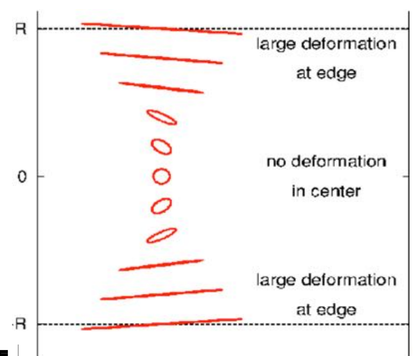
McHugh & Doufas: Fiber Spinning JNNFM 2000;
Van Meerveld Fiber Spinning, JNNFM 2008
Graham & PDO: Flow-induced crystallization PRL 2008)
Scelsi, Mackley, Klein, Visualization of FIC JOR 2009
PDO, Graham, Harlen, McLeish

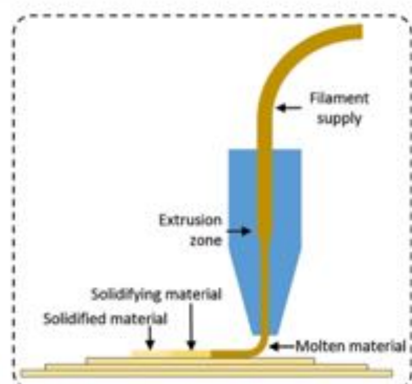
Typical maximum nozzle parameters:

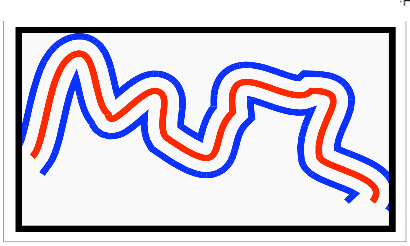
$$\mathrm{Wi}_{\mathrm{rept}} \simeq 100, \quad \mathrm{Wi}_{\mathrm{stretch}} \simeq 10$$

FDM/FFF: Details of extrusion

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

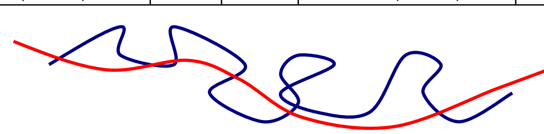




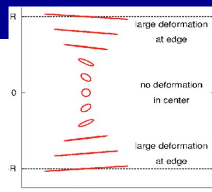


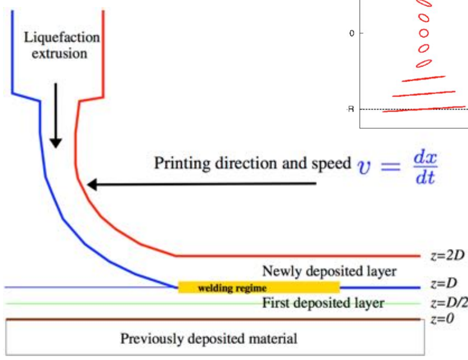
Reptation Wi	Fast	Slow	**Rouse** Wi^R	Fast	Slow
$\overline{Wi}_N$ (average)	13	2	$\overline{Wi}_N^R$ (average)	0.07	0.009
Wi_W (wall)	91	24	Wi_W^R (wall)	1.5	0.4

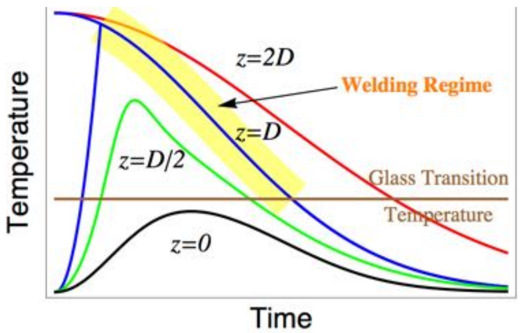
$$\mathrm{Wi}_{\mathrm{rept}} = \tau_d \dot{\gamma} \sim Z^3$$
$$\mathrm{Wi}_{\mathrm{stretch}} = \tau_R \dot{\gamma} \sim Z^2$$

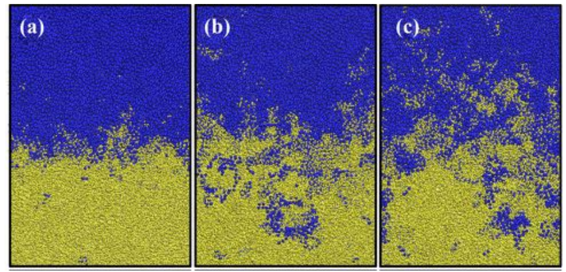


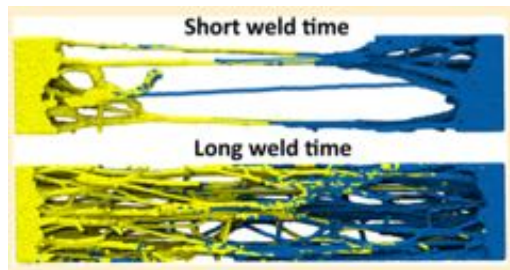
Polymer Welding – A race against time!





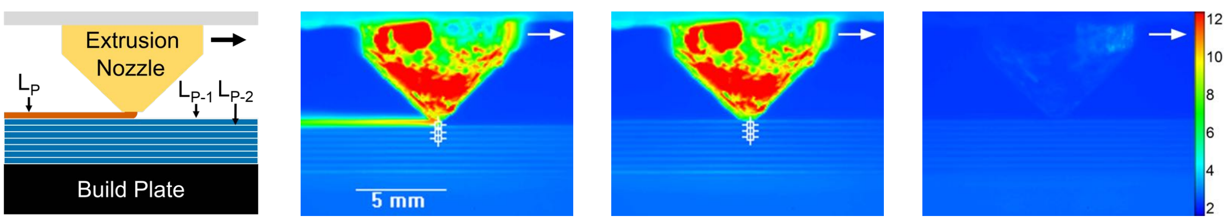




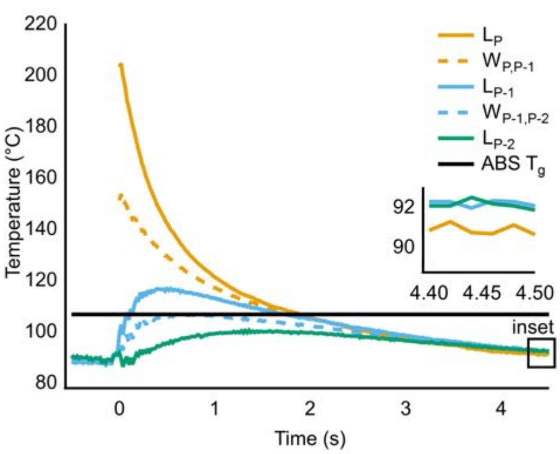


Ge, Periaha, Grest, Robbins *[ACS Nano 2013, PRE 2014]*

Measuring the temperature history [Seppala, K Migler@NIST Team]

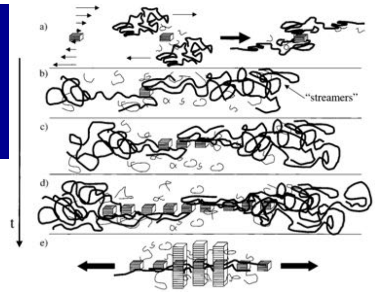


(a) Illustration (b) Extrusion (c) Hot, no extrusion (d) Cold nozzle

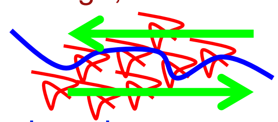


Seppala & Migler, *Additive Manufacturing* **12** (2016) 71–76

(some of the) Relevant Polymer Physics



[nonequilibrium, non-isothermal, phase change, inhomogeneous…..]



- Crystallization
  - Heat release, fibril welding, 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
  - Want sharper liquefaction above T_g (fragile glass). Mobile surface layer?

Wish List of Calculations

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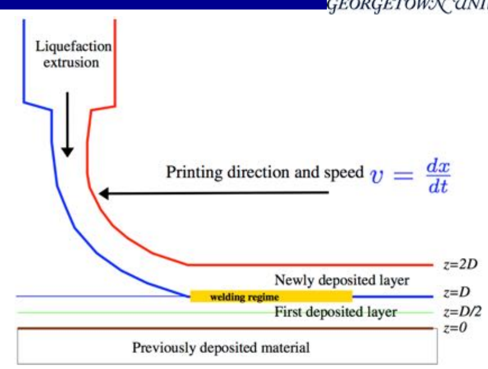
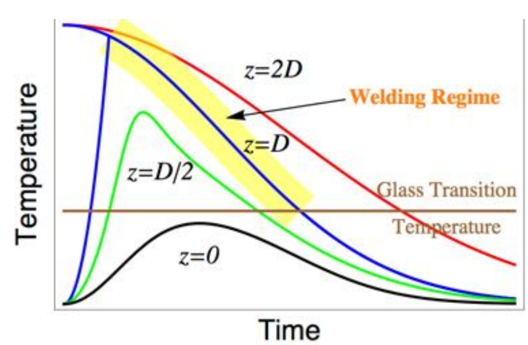
- Flows in the nozzle.
- Deformation during deposition.
- Cooling and freezing-in of alignment/disentanglement.
- Polymer welding behaviour.





FDM Modeling

C McIlroy & PDO, Journal of Rheology 61 (2017) 379

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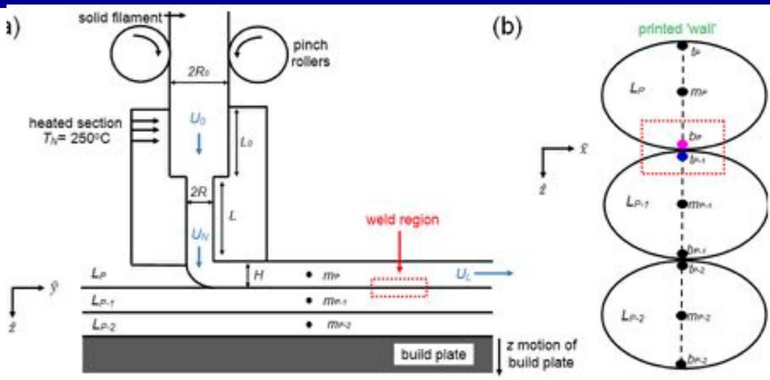

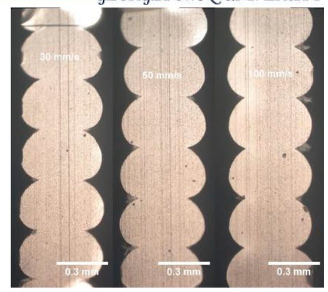

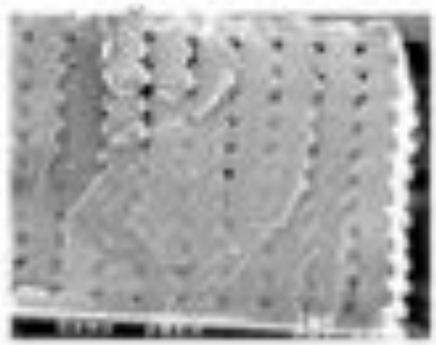

Assume:

- **Uniform Temperature across nozzle**
- **Steady state flow upon exit**
- **Final elliptical shape**

Melt rheology: Rolie-Poly model

Likhtman & Graham JNNFM 2003

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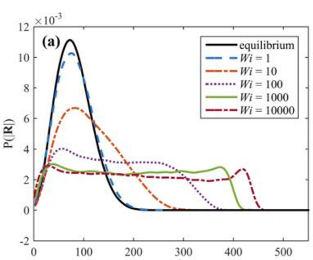
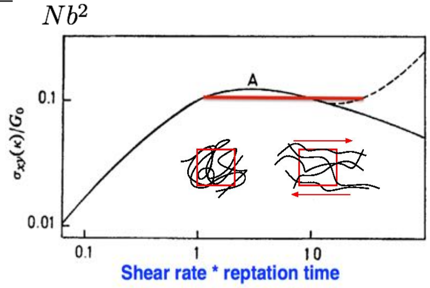
$$\frac{D\mathbf{A}}{Dt} = \mathbf{K}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{K}^T - \frac{1}{\tau_d}(\mathbf{A}-\mathbf{I}) - \frac{2(1-\sqrt{3/\mathrm{tr}\mathbf{A}})}{\tau_R}\left(\mathbf{A}+\beta\sqrt{\frac{\mathrm{tr}\mathbf{A}}{3}}(\mathbf{A}-\mathbf{I})\right)$$

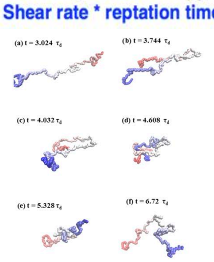
Total stress: $\mathbf{T} = G_e\mathbf{A} + 2\eta\mathbf{D}$

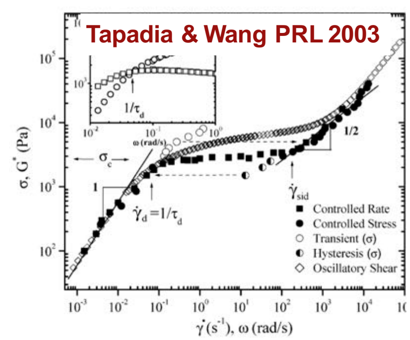
Conformation Tensor: $\mathbf{A} = \frac{3\langle\mathbf{RR}\rangle}{Nb^2}$

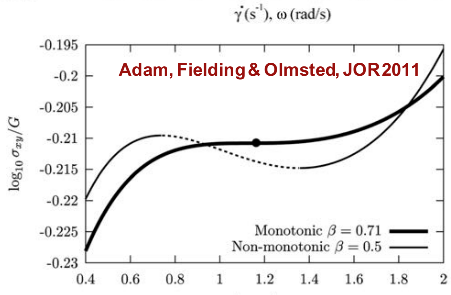
Doi-Edwards Instability, Disentanglement, …..?











C Baig et al MM2010; Mogheghagi and Khomami, ACS Macro Letters 2015; Sefiddashti, Edwards, & Khomami JOR 2015

Rolie-Poly model + disentanglement dynamics

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

Total stress: $\mathbf{T} = G_e\mathbf{A} + 2\eta\mathbf{D}$

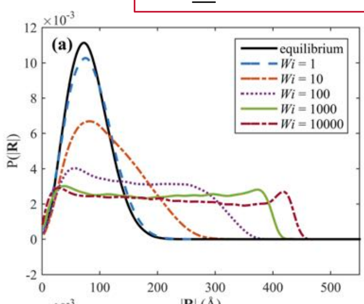
Conformation Tensor: $\mathbf{A} = \frac{3\langle \mathbf{RR}\rangle}{Nb^2}$

Modified Effective Reptation rate:

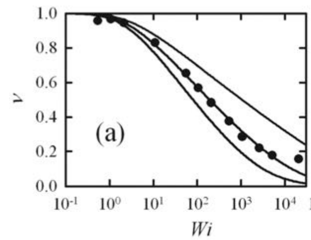
$$\frac{1}{\tau_d(T,\dot{\gamma})} = \frac{1}{\tau_d^{eq}(T)} + \beta\left(\mathbf{K} : \mathbf{A} - \frac{1}{\mathrm{Tr}\mathbf{A}}\frac{d\,\mathrm{Tr}\mathbf{A}}{dt}\right)$$

(Ianniruberto & Marrucci, 2014, 2015)

$$\boxed{\begin{aligned}\frac{d\nu}{dt} &= -\beta\left(\mathsf{K} : \mathsf{A} - \frac{1}{\mathrm{Tr}\mathsf{A}}\frac{d\,\mathrm{Tr}\mathsf{A}}{dt}\right)\nu + \frac{1-\nu}{\tau_d^{eq}(T)}\\ &= \qquad\quad \text{CCR} \qquad\qquad\qquad \text{diffusion}\end{aligned}}$$



Simulations: Sefiddashti, Edwards, Khomami JOR 2015, 2016



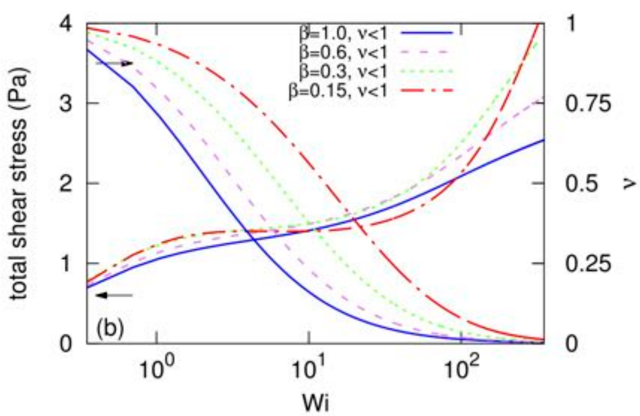
Points: Simulation Baig, Mavrantsis, Kroeger, MM 2010
Fits: Iannuruberto JOR 2015

Disentanglement in the Rolie-Poly Model

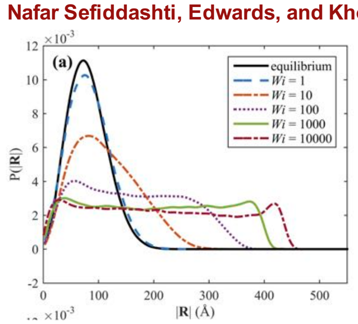
Polymer Stretch $\mathrm{Tr}A$

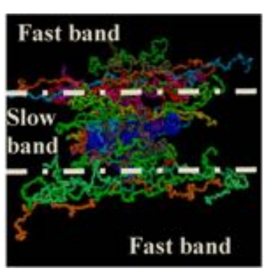
Entanglement Fraction ν

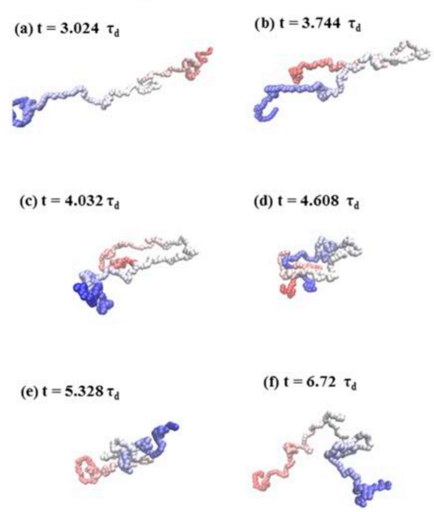
Entanglement Number $Z = 37$



Mogheghagi and Khomami, ACS Macro Letters 2015;
Nafar Sefiddashti, Edwards, and Khomami JOR 2015 & 2016, PRE 2016







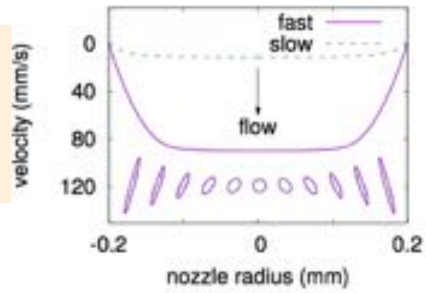
State of disentanglement still an open question:
[Baig & Kroger, Wang, Ianniruberto, Khomami, Robbins…]

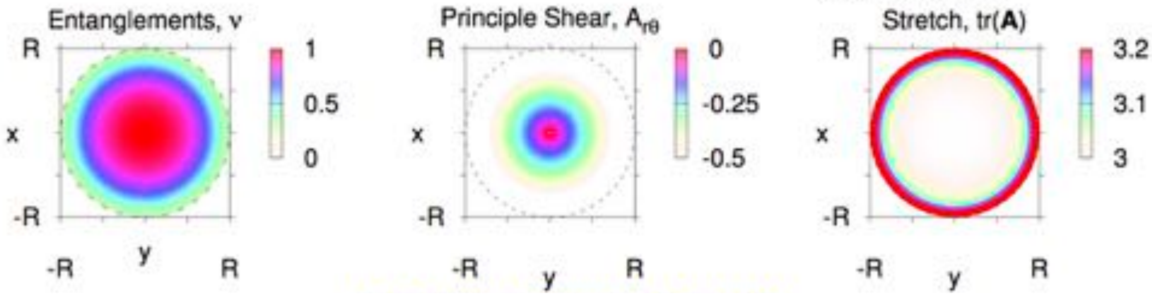
Flow through a uniaxial nozzle

axisymmetric pipe flow: $\mathbf{u} = (0, 0, w(r))$

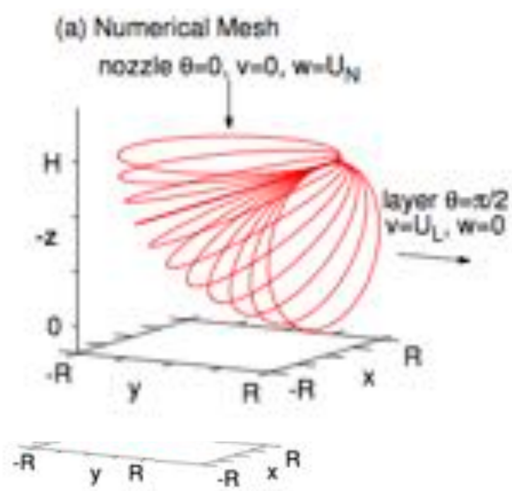
$Z = 37$ $\qquad \beta = 0.3,$

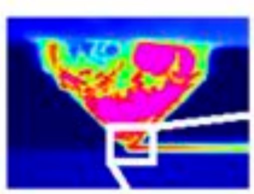
$\overline{Wi}_N = 2.0 \qquad Wi_{\text{wall}} = 24$





Map from Nozzle to Layer





- Assume **no relaxation** of polymer during deposition:
  $$\tau_d, \tau_R \gg \tau_{dep} \sim 10^{-3} \text{ s}$$
- Assume **flux** is conserved e.g. globally:
  $$\pi R^2 U_N = \pi \frac{RH}{2} U_L$$
- **Advect** polymer with velocity gradients:

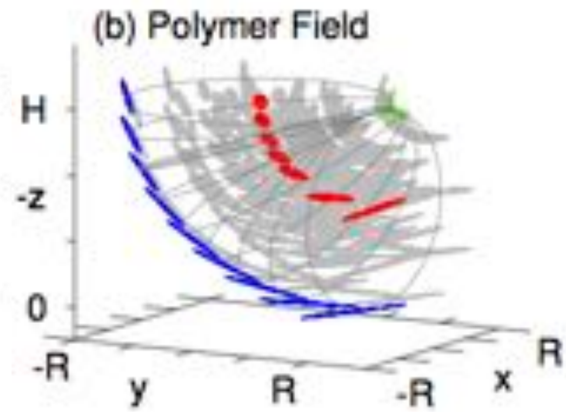
Rolie-Poly Equation

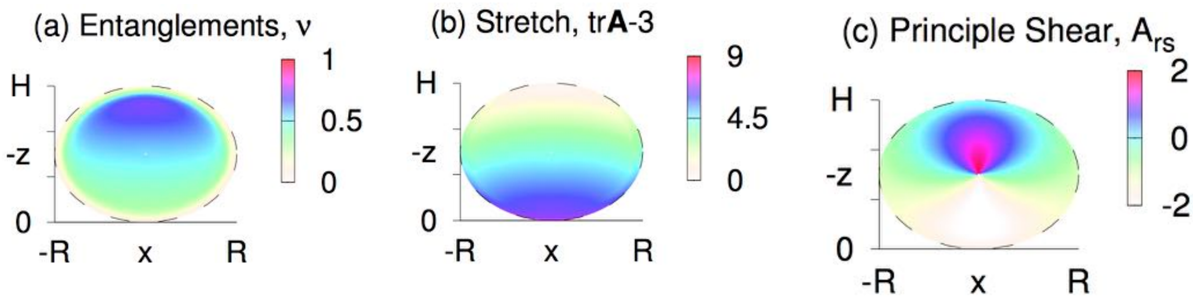
$$(\mathbf{u} \cdot \nabla)\mathbf{A} = \mathbf{K} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{K}^T.$$

Polymer deformation during deposition

$Z = 37, \beta = 0.3, \overline{Wi}_N = 2.0, Wi_{\mathrm{wall}} = 24$

- **Alignment** in flow direction.
- Larger **stretch** along the outside edge of deposition.



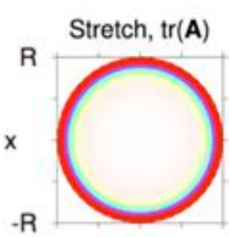


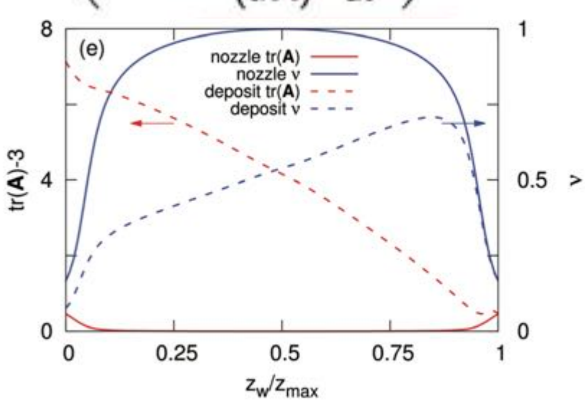
Change in Entanglement Density

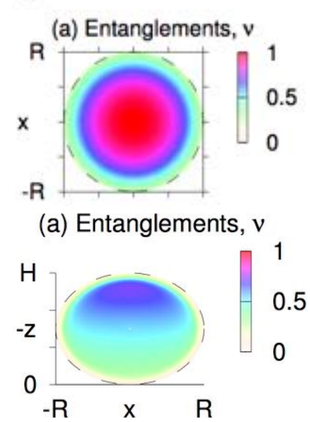
Ianniruberto & Marrucci J Rheology (2014, 2016)

Modify entanglement density $\nu = Z/Z_{eq}$

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







$Z = 37, \beta = 0.3, \overline{Wi}_N = 2.0$

McIlroy & PDO, Journal of Rheology 61 (2017) 379

Welding behavior: dynamics slows down during cooling **McIlroy & PDO Polymer (2017)**

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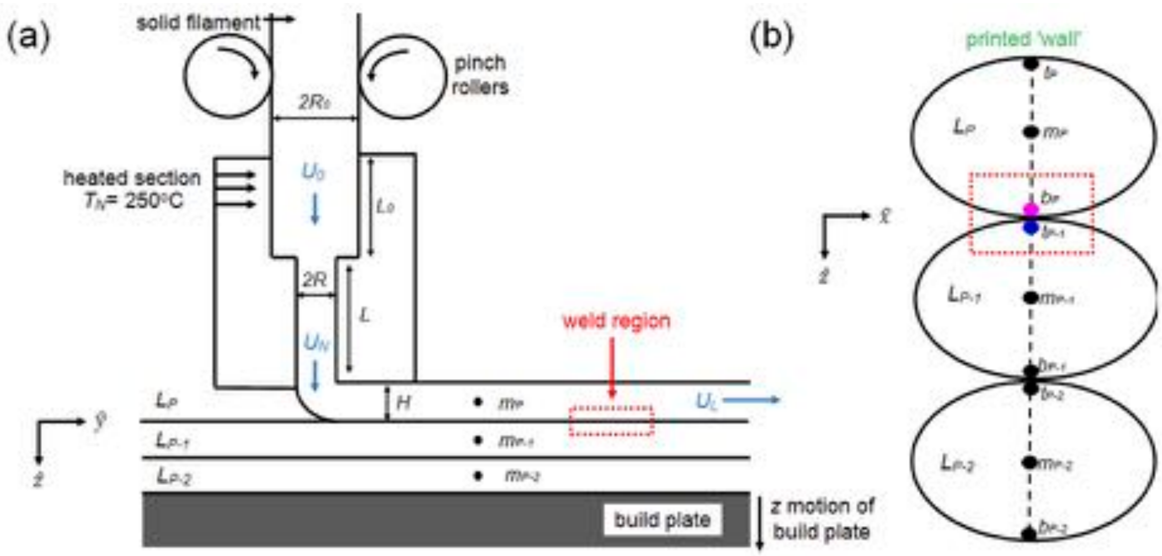

Weld strength determined by **interdiffusion** and **degree of entanglement**?

Devise T(t,z) to match experimental measurements.

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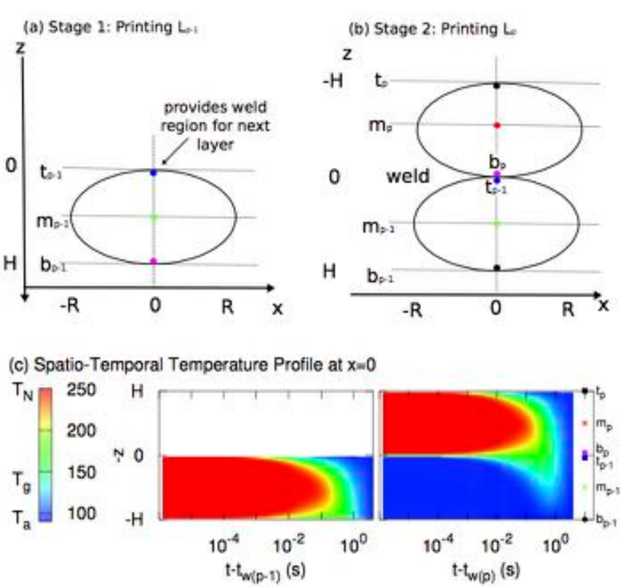
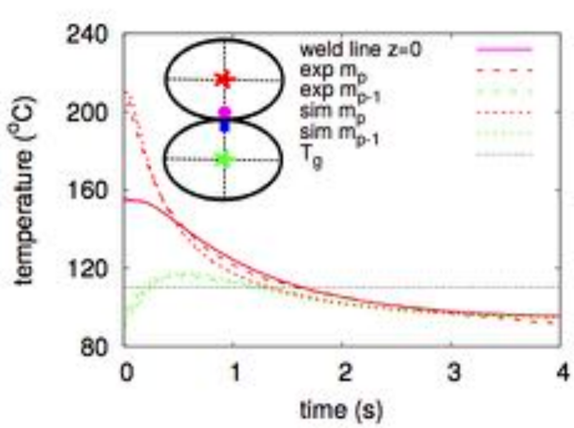
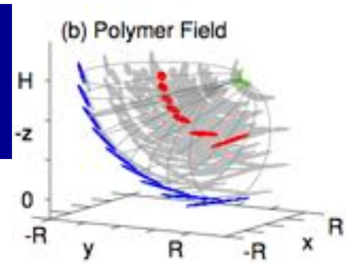


$$\frac{\partial T}{\partial t} = \alpha(T)\frac{\partial^2 T}{\partial z^2}$$

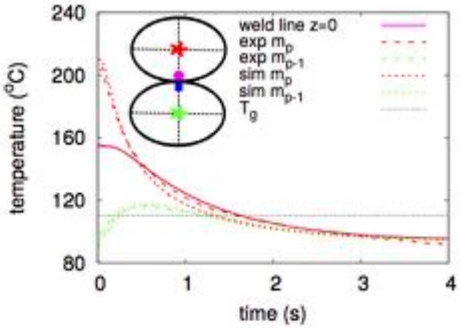


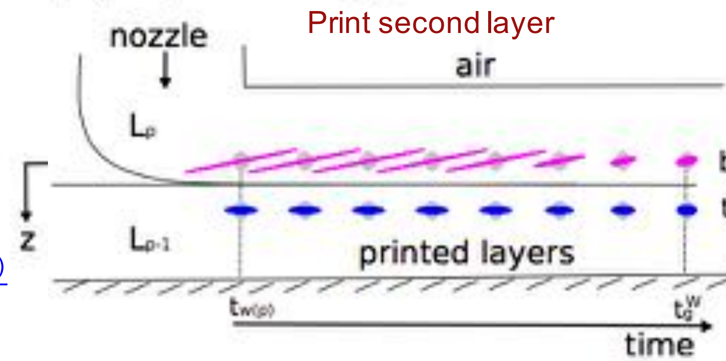
$$\tau(T) = \tau_0 \exp\left(\frac{-C_1(T-T_0)}{T+C_2-T_0}\right)$$

Cooling and freezing in of polymer orientation **McIlroy & PDO Polymer (2017)**



Seppala & Migler, *Additive Manufacturing* **12** (2016) 71–76

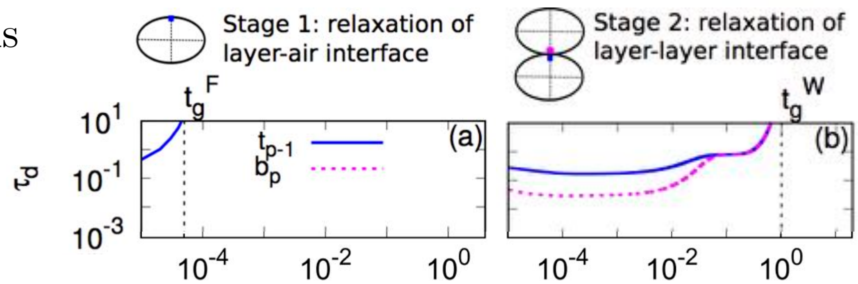




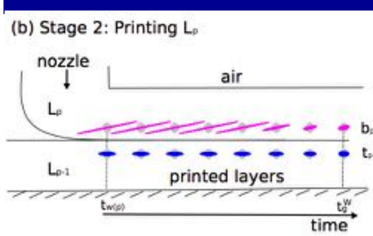
$$\tau(T) = \tau_0 e^{\frac{-C_1(T-T_0)}{T+C_2-T_0}}$$

$$\tau_d(T_N) \simeq 30\,\mathrm{ms}$$

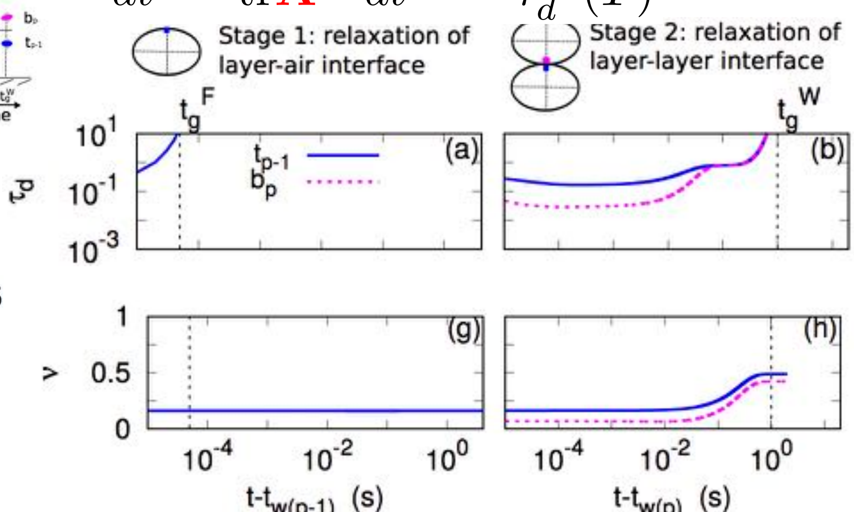
- Reptation time diverges at Tg
- 2-step evolution

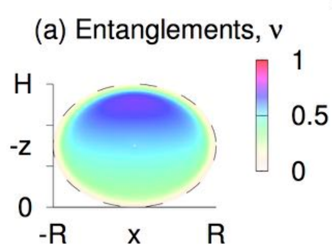


Orientation & entanglements don't fully relax



$$\frac{d\nu}{dt} = \frac{\beta\nu}{\mathrm{tr}\mathbf{A}}\frac{d\,\mathrm{tr}\mathbf{A}}{dt} + \frac{1-\nu}{\tau_d^{eq}(T)}$$





$$\tau_d(T_N) \simeq 30\,\mathrm{ms}$$

~ 50% less entangled at the weld site!

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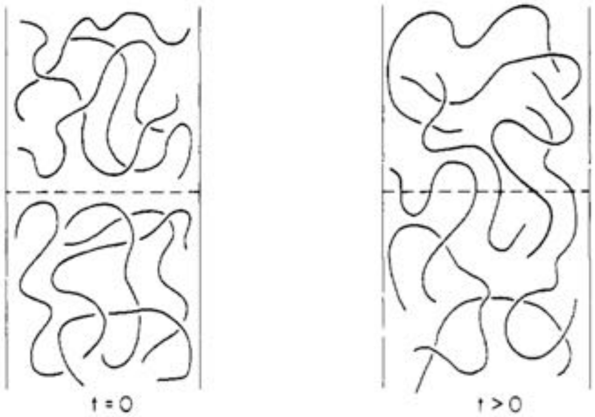
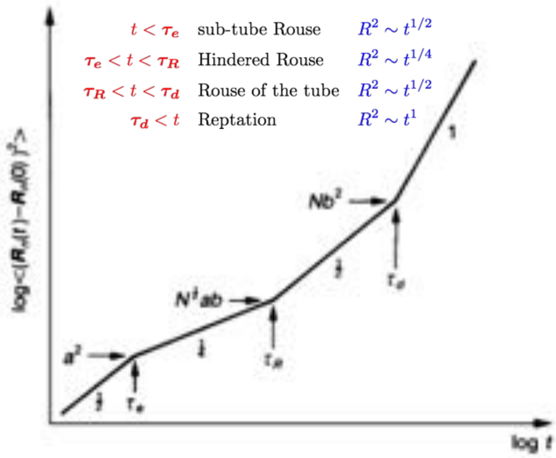
Non-isothermal welding at an interface…..[Wool 1983, …]





Governed by Rouse diffusion….

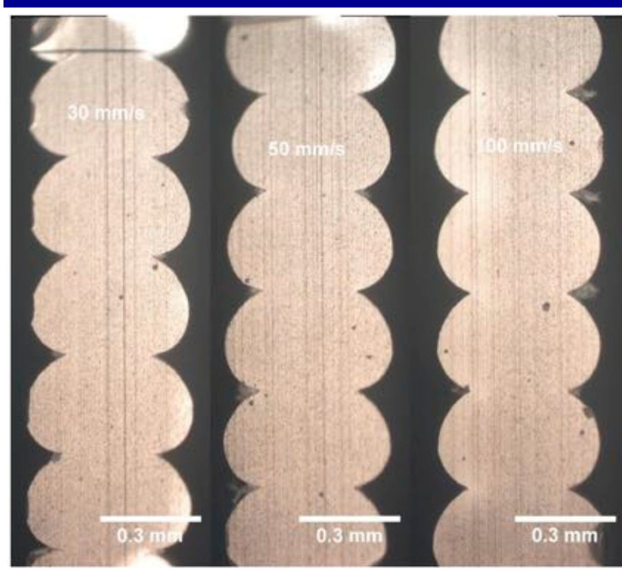
$$\tau(T) = \tau_0 e^{\frac{-C_1(T-T_0)}{T+C_2-T_0}}$$
$$= a_T(T)\,\tau(T_{\rm ref})$$

$$\langle R\rangle = \sqrt{Nb^2}\left(\frac{t}{\tau_d}\right)^{1/4}$$
$$= \sqrt{Nb^2}\left[\int_0^t \frac{dt'}{\tau_d(T(t))}\right]^{1/4}$$

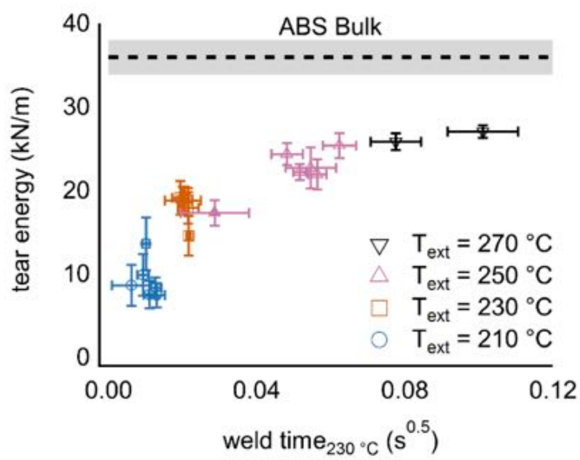
$$\boxed{\langle R\rangle = \sqrt{Nb^2}\left[\int_0^t \frac{dt'}{a_T(T)\tau_d(T_{\rm ref})}\right]^{1/4}}$$

Ge, Robbins, Perahia, Grest: ACS Mac Lett 2013, PRL 2014.

Welding behavior: cannot recover bulk strength within "weld time".



Seppala and Migler (Additive Manufacturing, 2016, Soft Matter 2017)



$$\omega(T) = \omega(T_{ref})\,/\,a(T)$$
$$\tau(T) = a(T)\,\tau(T_{ref})$$

$$\tau_w = \int_0^{t_g} \frac{dt}{a(T(t))}$$

$$a_T(T) = a_0 \exp\left(\frac{-C_1(T-T_{\rm ref})}{T+C_2-T_{\rm ref}}\right)$$

$$\boxed{\text{Strength} \sim \tau_w^{1/4}?}$$

Mechanisms for Interdiffusion…..

$$\frac{1}{\tau_d(T,\dot{\gamma})} = \frac{1}{\tau_d^{eq}(T)} - \beta \frac{1}{\mathrm{tr}\mathbf{A}} \frac{d\mathrm{tr}\mathbf{A}}{dt}$$

- **Isotropic** diffusion [Wool & O'Connor J Appl Phys (1981)]

$$\frac{\chi(t)}{\sqrt{6}R_g} = \left(2\int_{t_w}^{t_g} \frac{1}{\tau_d(t)} dt'\right)^{1/4}$$

- Modify diffusion coefficient to include **anisotropy**
  [Ilg & Kroger, JOR 2011]

$$\mathbf{D} = D_0\left(\mathbf{I} + \eta(\mathbf{A} - \mathbf{I})\right), \quad D_0 = \frac{(Na)^2}{\tau_d(T,\dot{\gamma})}$$

$$\frac{\chi_{zz}}{\sqrt{6}R_g} = \left(2\int_{t_w}^{t_g} \frac{1}{\tau_d(t)}\left(1 + \frac{1}{3}(A_{zz}(t) - 1)\right) dt'\right)^{1/4}.$$

Interdiffusion across an interface

[Kramer et al. Polymer 1984]

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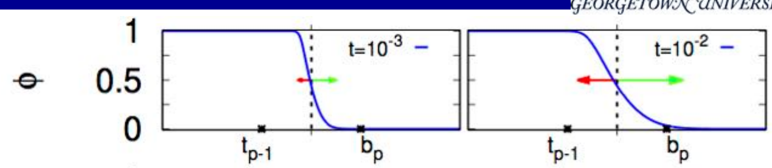


- Mutual diffusion coefficient

$$\mathbf{D}_M(t,z) = (1-\phi(t,z))\mathbf{D}^{\mathrm{R}}(t) + \phi(t,z)\mathbf{D}^{\mathrm{L}}(t),$$

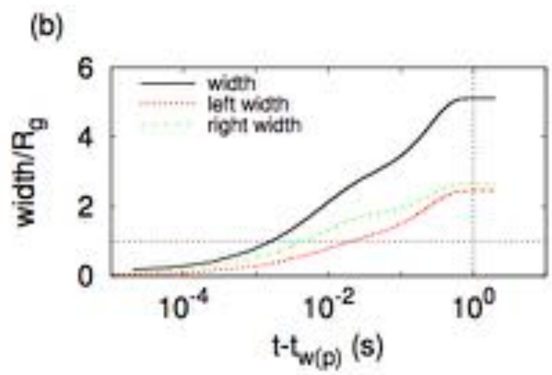
where

$$\mathbf{D}^{\mathrm{R}}(t) = \frac{(Na)^2}{\tau_d^{\mathrm{R}}(t)}\left(1 - \frac{1}{3}(A_{zz}^{\mathrm{R}}(t) - 1)\right)$$

$$\mathbf{D}^{\mathrm{L}}(t) = \frac{(Na)^2}{\tau_d^{\mathrm{L}}(t)}\left(1 - \frac{1}{3}(A_{zz}^{\mathrm{L}}(t) - 1)\right)$$

and ϕ is volume fraction of polymers on left L

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z}\left(\mathbf{D}_M(t,z)\frac{\partial \phi}{\partial z}\right),$$



- χ_M Allow inhomogeneous diffusivity along the length of the molecule

McIlroy & PDO Polymer (2017)

Diffusion seems large enough to recover bulk strength?

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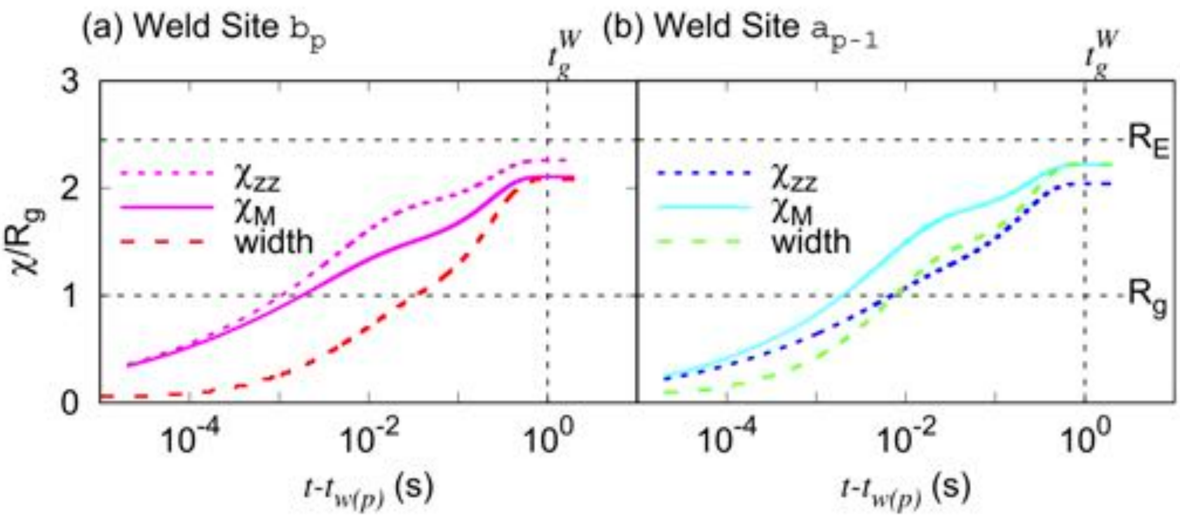

Most variants lead to a similar thickness weld

Recovery of entanglements

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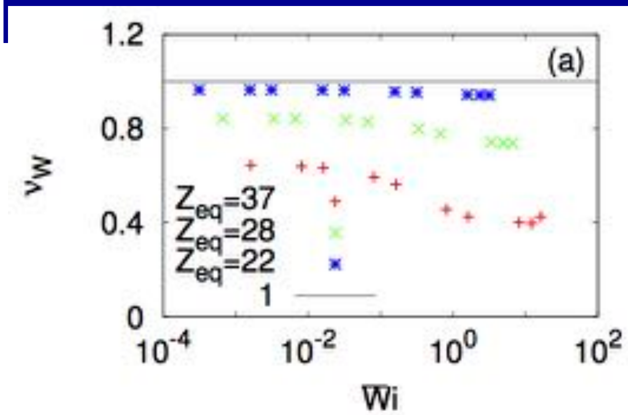
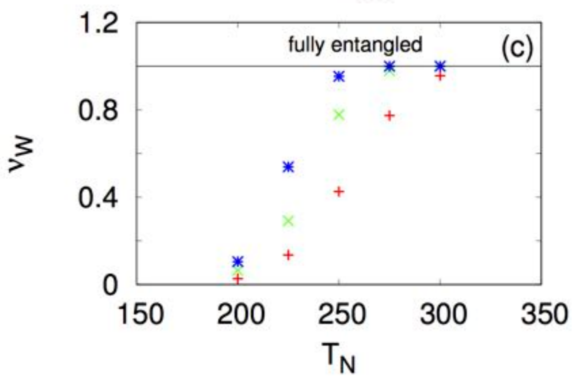


- More entanglements removed from higher *Z* melt.
- Relatively independent of nozzle speed



Full recovery at higher print temperature (diffusion enabled).

What controls weld strength?

[H Brown 1991, E Kramer 1995]

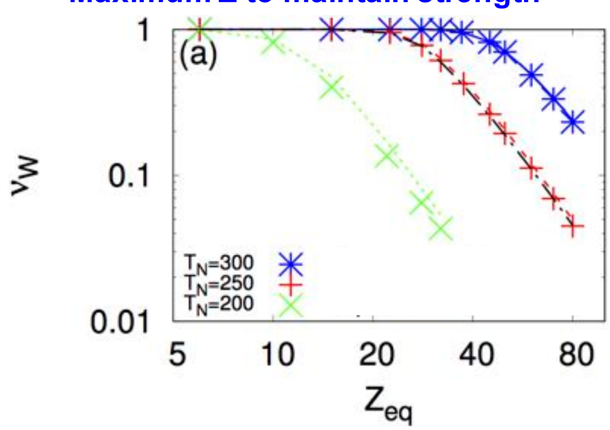
- Number of entanglements/area **Me**
- Molecular weight **Mw**

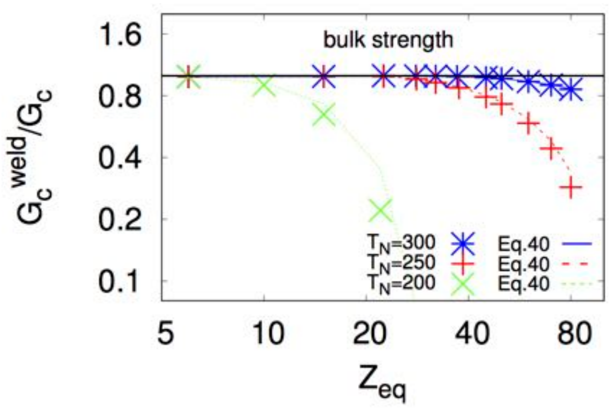
$$G_e \sim \frac{1}{M_e} \qquad \text{Strength (modulus)}$$

$$G_c \sim \left(1 - \frac{M_e}{qM_w}\right)^2 \qquad \text{toughness}$$

$$G_c^{\text{weld}} \simeq \left(1 - \frac{1}{q\nu_W Z_{eq}}\right)^2$$

Maximum Z to maintain strength

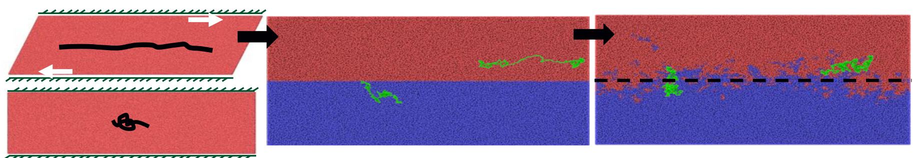


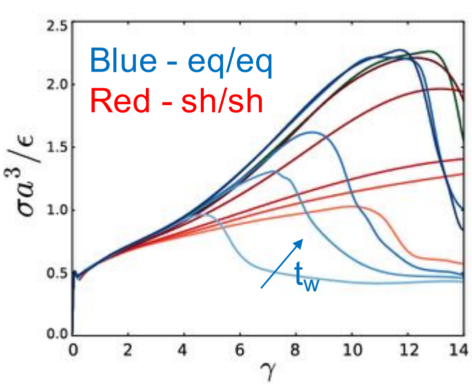


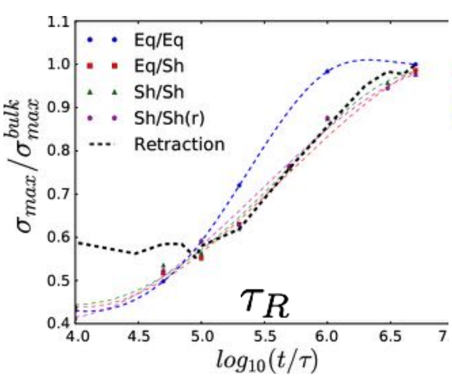
Simulations of sheared layers

Galvani & Robbins (JHU, unpublished)

Prepare layers – equilibrate together for various t







Aligned layers are much weaker **in bulk**

Summary

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- Model for understanding polymer structure in FFF using thermal history (glassy polymers).
- Thermal history at single fiber level (0.2mm) can matter!
- Disentanglement during extrusion controls weld properties.
- **Molecular weight:** short enough to diffuse, long enough to retain shape after deposition (glassy, semicrystalline) and long enough for strength
- Correct modeling of entanglement dynamics in anisotropic environments still an open question!!!
- Role of anisotropy in weld formation/strength [early simulations suggest this is very important]?

  [Marco Galvani, et al. (J Hopkins), calculations ongoing].

McIlroy & PDO, Journal of Rheology 61 (2017) 379; Polymer (2017).

Other Strategies/Avenues

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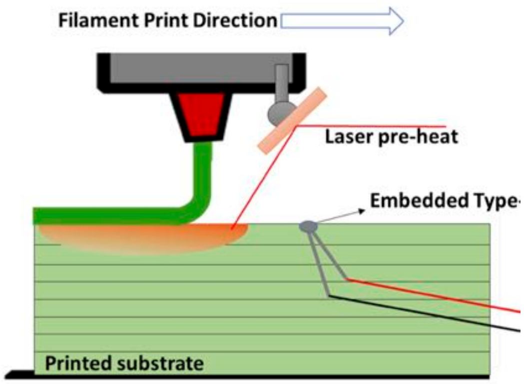
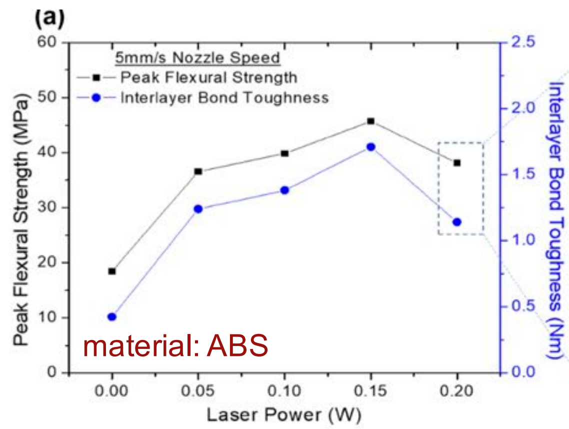
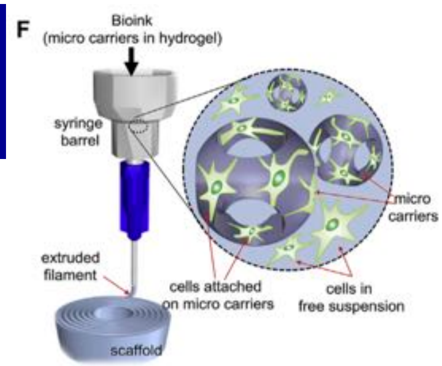
- Real parts will undergo varied and inhomogeneous temperature histories.
- ABS (nanoparticle-toughened), semicrystalline, fiber composites?
- Design dies/flow histories for better welding?
- Post-deposition heating/annealing
- Thermal limits on throughput [Mackay JOR 2017]
- Additives ?
  - Small High Mw component in many filaments (J Seppala communication)
  - Small polymers to aid diffusivity/welding/bonding (linears, stars, …) (Levenhagen & Dadmun, Polymer 2018).

Effect of laser- pre-heating on interface strength ***Deshpande, Hsu et al., Prog Additive Manufacturing 2018***

- Local annealing with a laser to enhance weld strength.







bioprinting micro-carriers
Ozbolat & Hospodiuk Biomaterials 2016

Some more Polymer Science Issues in Additive Manufacturing

- Bioprinting/colloidal inks
  - Yield stress fluids often the carrier
  - Phase separation in strong flows?
  - Depletion/slip at walls?
  - Hydrogels: Collage, fibrin, alginate, gelatin, chitosan, double networks, …
  - Viability of printed living cells
  - Syneresis/deswelling during/after deposition
- Selective laser sintering (SLS)
  - Bubble control/elimination and porosity: gas diffusion in viscoelastic media/polymers.
  - Extend the palette of materials beyond polyamides.

NSF DMREF project:
J Hopkins, Georgetown U, NIST, AFRL, ARL

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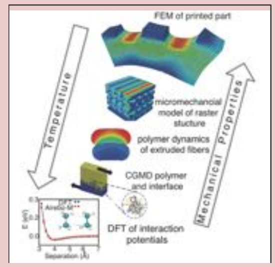
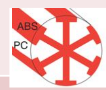
“Predictive Multiscale Modeling of the Mechanical Properties of Fused Filament Fabrication Printed Materials” [2017-2021]

Johns Hopkins University	Mechanical testing and FE modeling of final parts Molecular modeling of polymer diffusion during welding 	**V Nguyen** K Hemker SH Kang M Robbins
Georgetown University	Continuum fluid mechanics of polymer extrusion and deposition	PDO
NIST Gaitherburg	Metrologies: Raman spectroscopy and IR thermometry	K Migler
Army Research Lab (ARL)	Design custom filaments 	L Holmes
Air Force Research Labs (AFRL)	X-ray characterization of filaments	H Koener

Thanks…

NIST Polymers & Complex Fluids Group

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Claire McIlroy (Nottingham University)

NIST Team

Kalman Migler
John Seppala

NIST National Institute of Standards and Technology U.S. Department of Commerce

Johns Hopkins

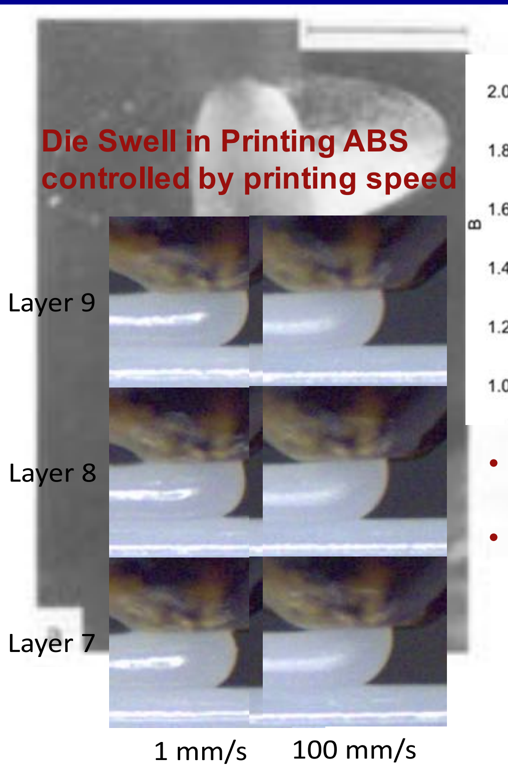
Mark Robbins
Vicky Nguyen
Kevin Hemker
Thomas O’Connor

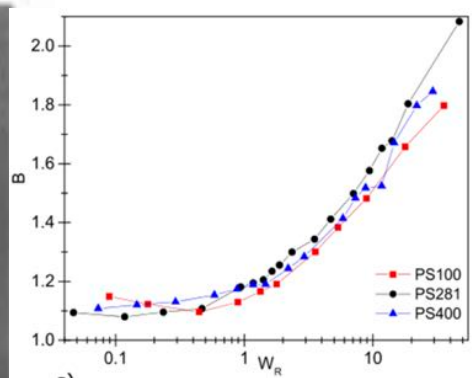
NSF DMREF

Die Swell

Robertson, Thompson, Robinson, McLeish (JOR 2017)

Die Swell in Printing ABS controlled by printing speed





- Controlled by stretch/retraction
- Upstream residence time important