MIT 3.071
Amorphous Materials

6: Glass Shaping

Juejun (JJ) Hu

After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 20
- Introduction to Glass Science and Technology
  - Ch. 13





Crystal

Glass

"Viscosity makes things happen essentially in slow motion. If you are trying to melt a crystalline solid (like ice or an aluminum oxide ceramic), as soon as you reach the melting point, a drop of liquid forms and falls away from the melting surface. Glass, on the other hand, … gradually transforms from a hard solid to a slowly softening liquid. This soft liquid gradually stiffens as it cools (because of its increasing viscosity), allowing glass blower time to shape and manipulate the glass."

http://madsci.org/posts/archives/2007-09/1188944613.Ph.r.html

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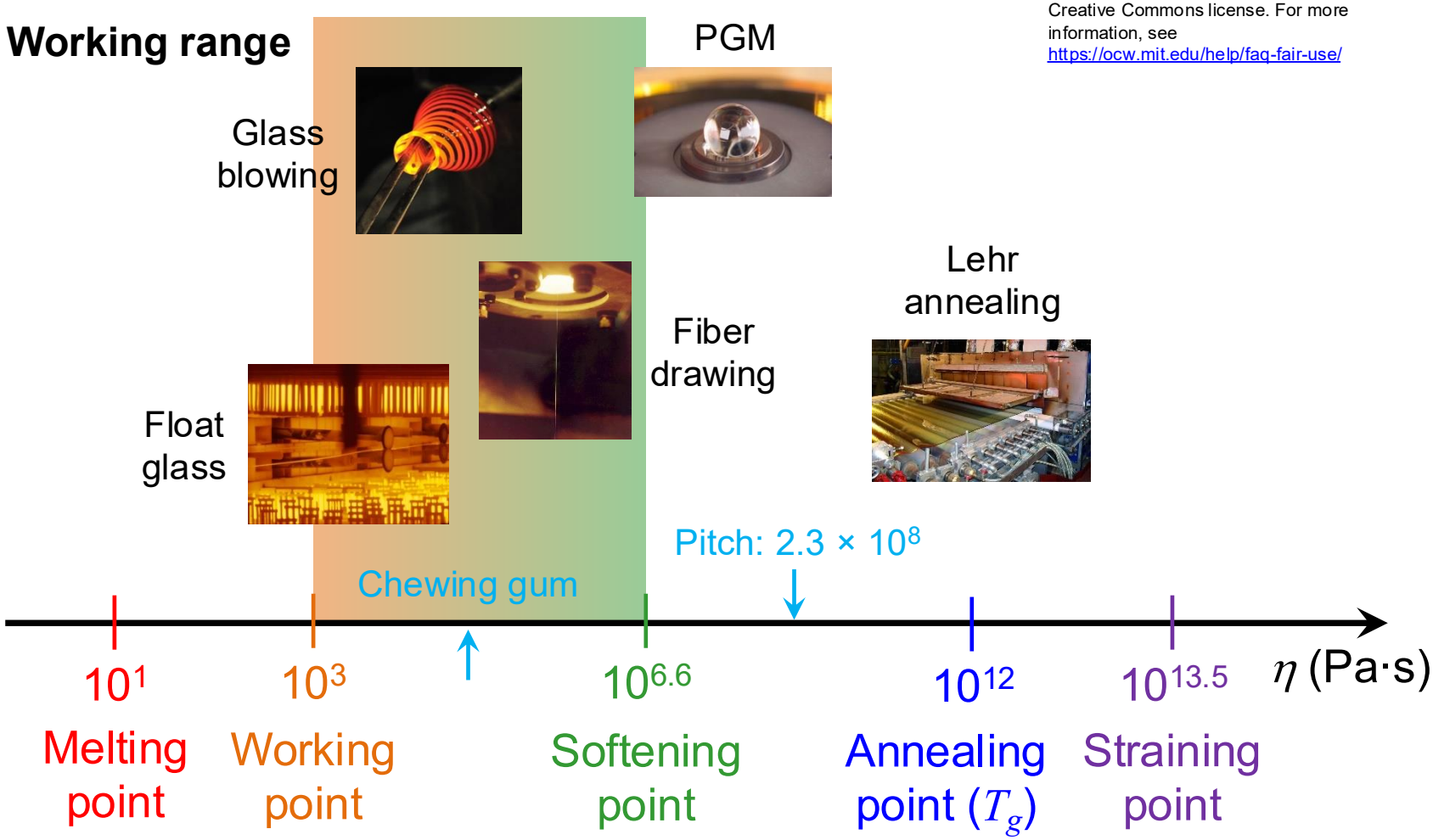
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Viscosity reference points

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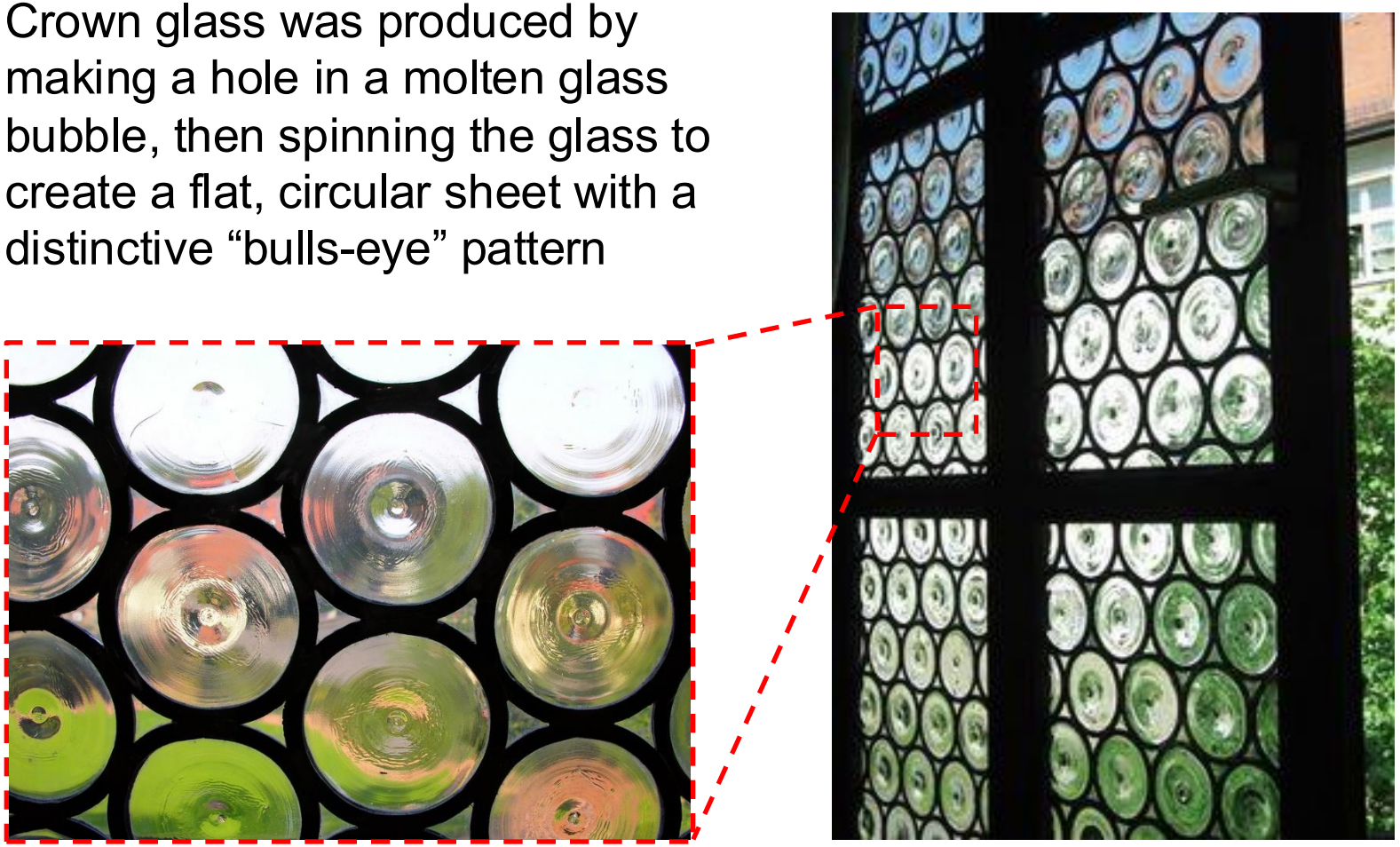
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Basic properties of common silicate glasses

	Soda-lime	Borosilicate	Fused silica
CTE (ppm/°C)	9.2	3.2	0.5
Working point (°C)	1005	1252	N/A
Softening point (°C)	696	821	1650
Annealing point (°C)	510	560	1140
Strain point (°C)	475	510	1070

Early flat glass process: crown glass

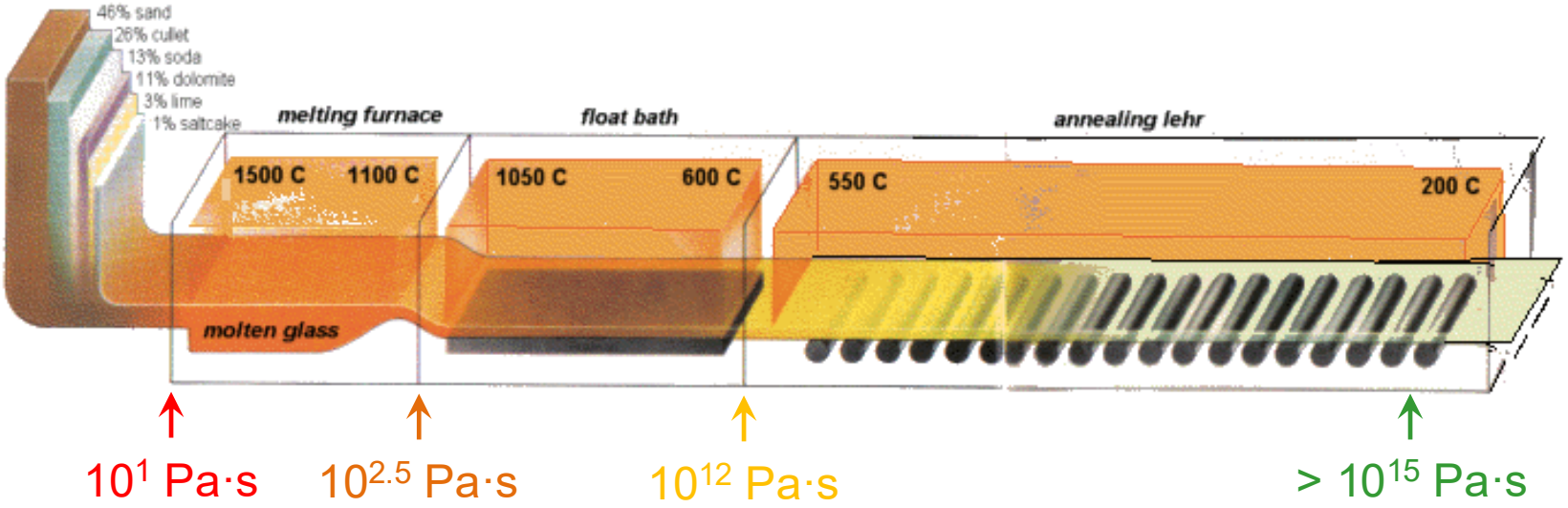
- Crown glass was produced by making a hole in a molten glass bubble, then spinning the glass to create a flat, circular sheet with a distinctive “bulls-eye” pattern



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Flat glass manufacturing: float glass process

- Forming of a continuous ribbon of glass using a molten tin bath
  - Melting and refining (homogenization and bubble removal)
  - Float bath: glass thickness controlled by flow speed
  - Annealing: stress release
  - Inspection, cutting and shipping

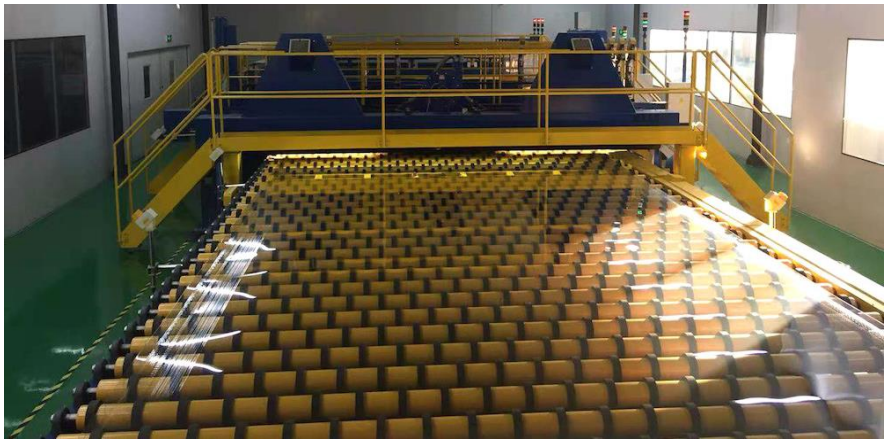


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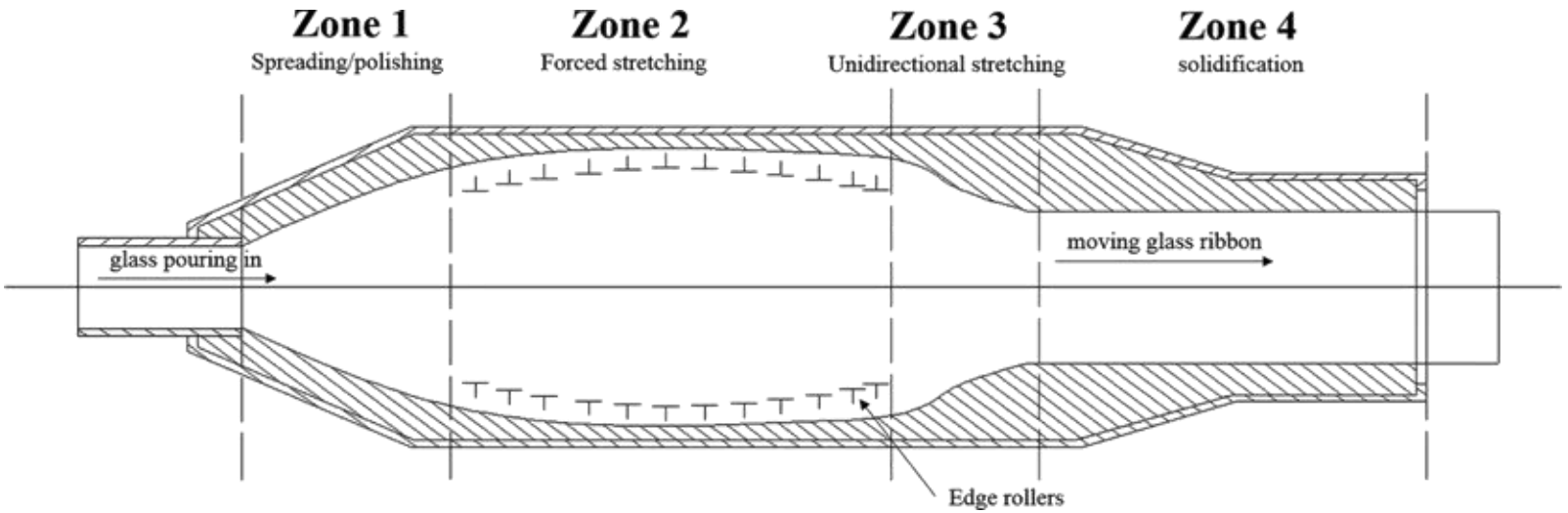
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Ultra-thin, ultra-wide glass by float stretching



0.12 mm thick, 4 m wide float glass

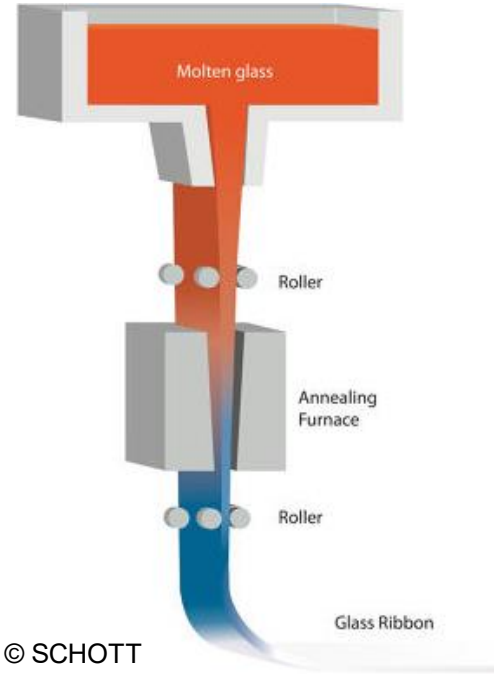
Int. J. Appl. Glass Sci. **10**, 275 (2019)



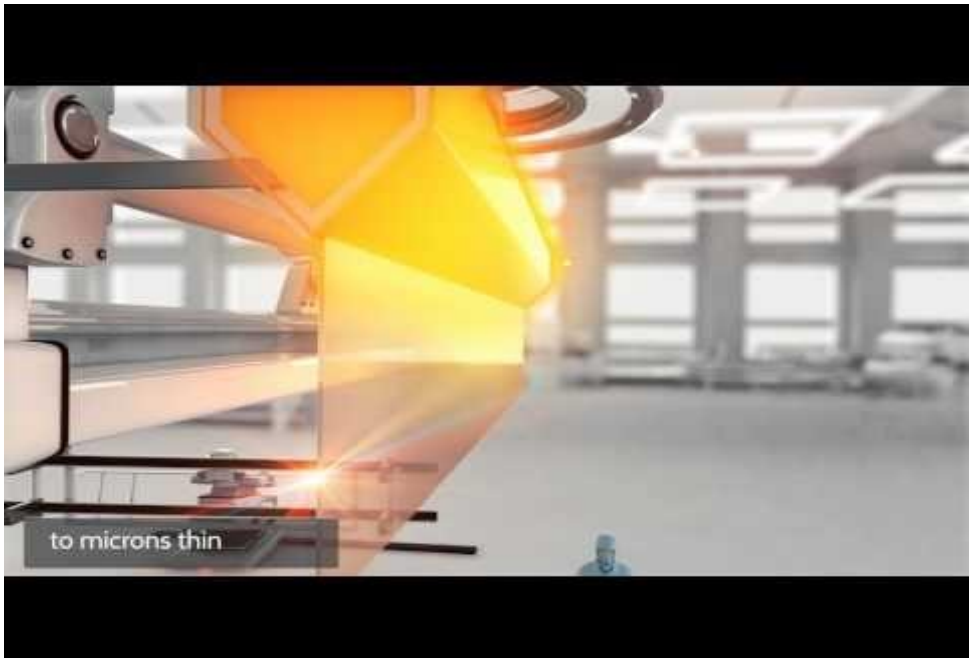
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Flat glass manufacturing: down-draw methods

- Preserves pristine surfaces: no subsequent polishing required
- Broad range of thicknesses from millimeter to tens of microns
- Mostly used for flat panel display glasses



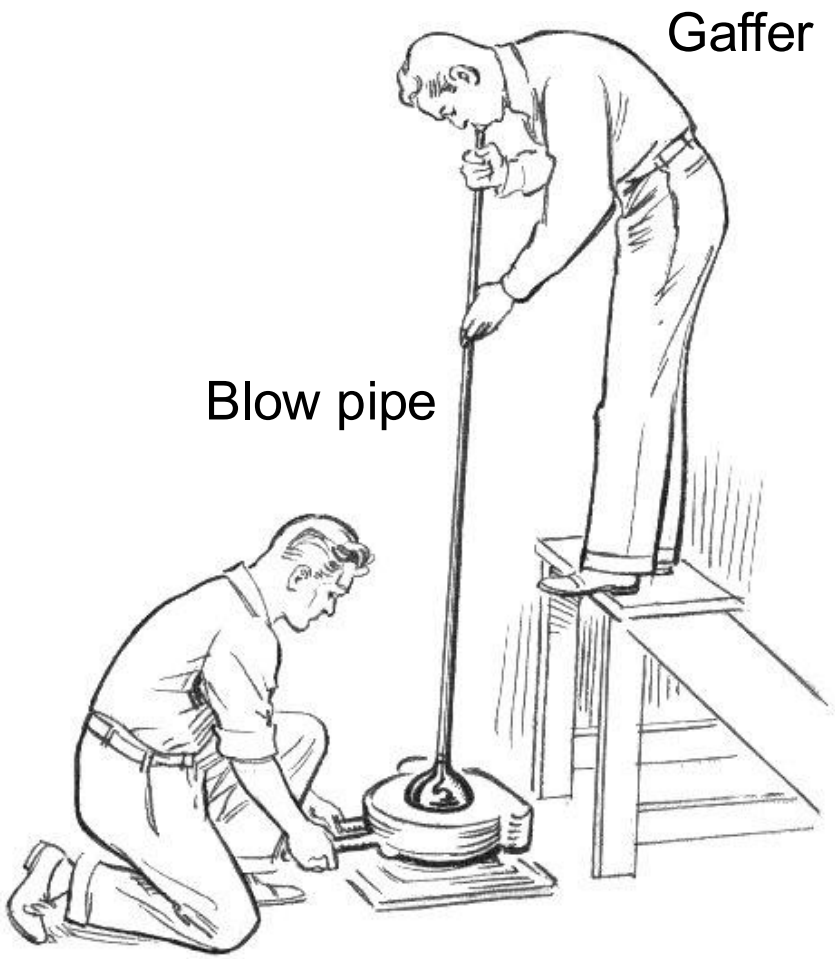
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Glassblowing



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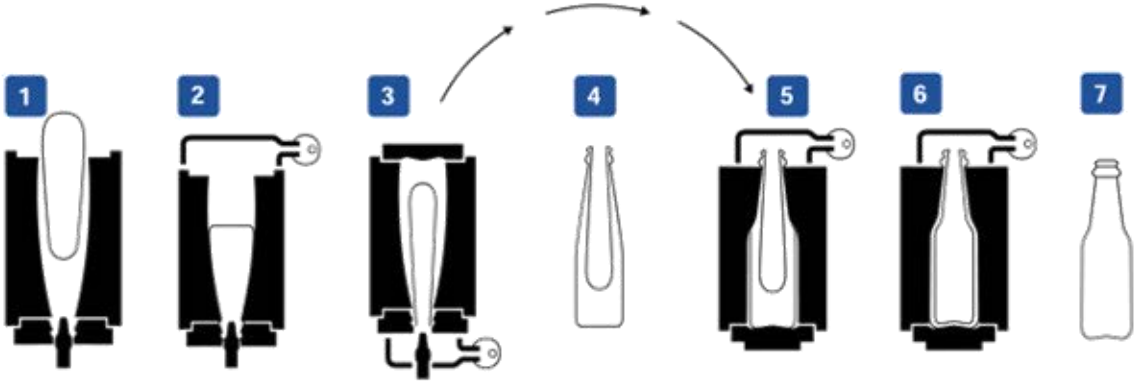
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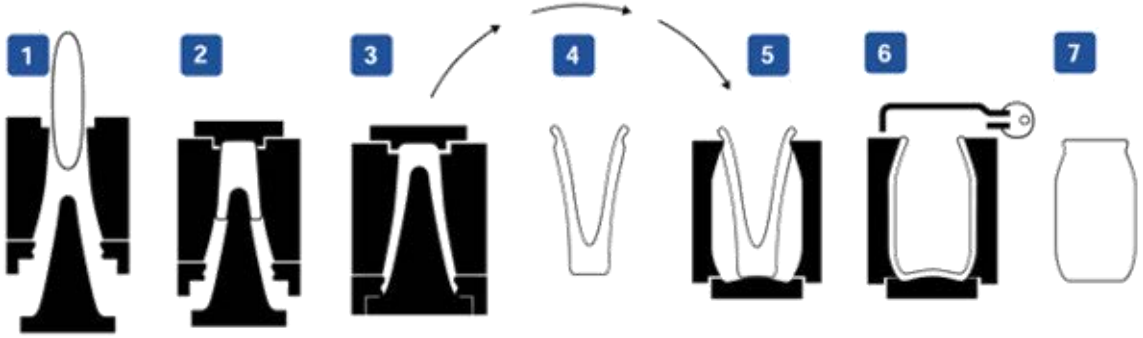
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Glass container production

- Narrow-neck containers (e.g., bottles): blow-and-blow process



- Wide-mouthed jars: press-and-blow process



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http://www.beatsonclark.co.uk/

Glass container production



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Glass caneworking



Reticello



Zanfirico

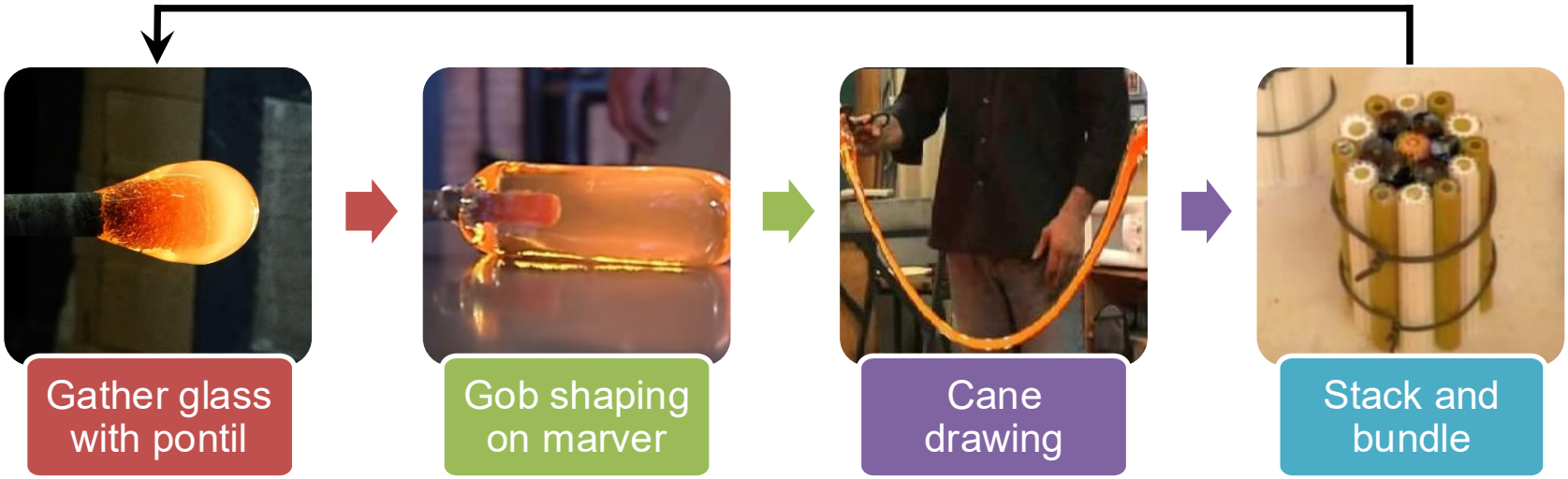


Millefiori

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Glass caneworking

- Canes: thin glass rods (often with color); can be of a single color, or contain multiple strands arrayed in a pattern (murrine)
- Basic glass work technique for adding intricate stripe patterns to glassware or blown glass

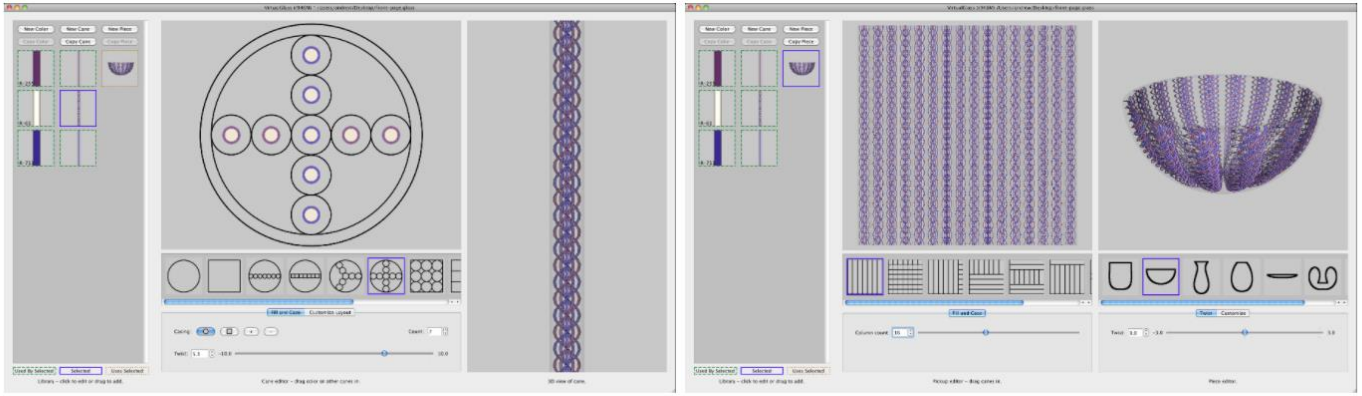


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VirtualGlass

virtualglass.org

computer-aided design of blown glass, specifically glass cane



Download this design: front-page.glass

Source: Public Domain

The **Virtual Glass software** lets anyone, with any or no glass experience, design and visualize glass cane, and to get a sense of what that cane will look like on a blown piece, all on your computer (without lifting a pipe!). The goal is to allow the exploration of cane designs, especially new cane designs, and settle on a nice-looking design before going through the effort of making it.

Status

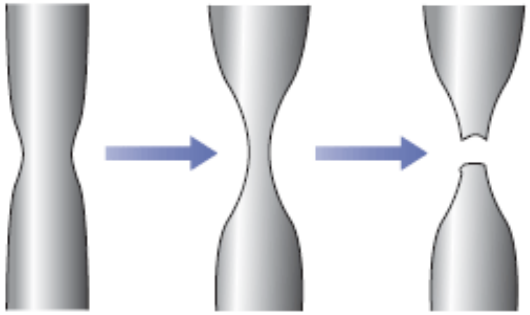
The software is freely available and open source. We offer versions for both Windows and MacOS, and the software runs on Linux as well. The software is the early stages of development, so it lacks certain features (for instance, pickup customization) and certain compatibility (graphics acceleration is only supported on reasonable NVIDIA graphics cards).

Millefiori – “1,000 flowers”



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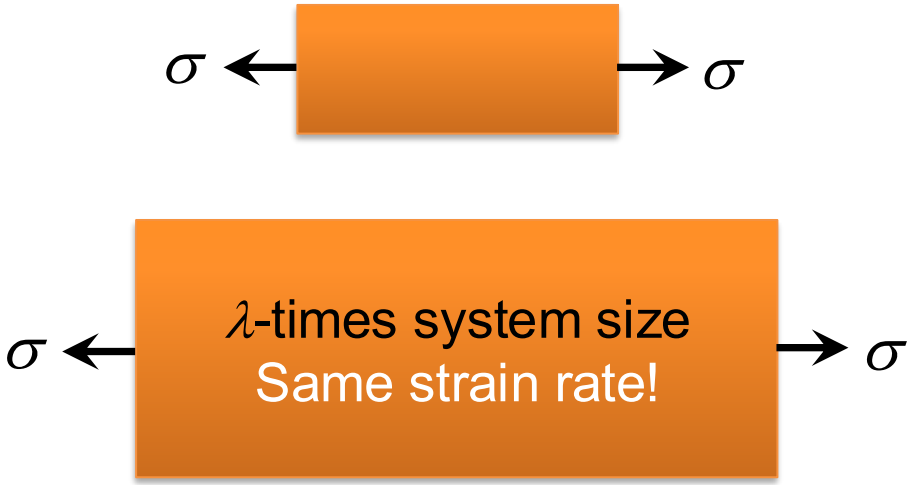
Stability of drawn cane structures



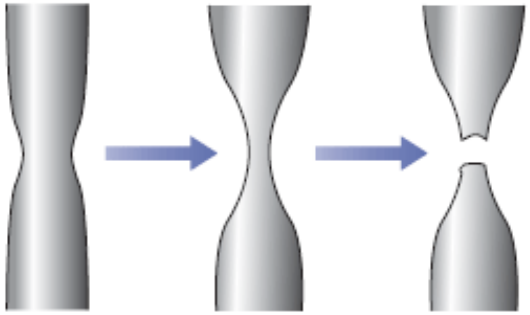
Scaling analysis

- Scale-invariance of viscous flow: strain rate $\dot{\varepsilon}$ remains invariant if the externally applied stresses are kept constant regardless of system size





Stability of drawn cane structures



Cane diameter D change:

$$\frac{\partial D}{\partial t} \propto \frac{1}{\eta D}$$

Necking develops if viscosity is independent of diameter D

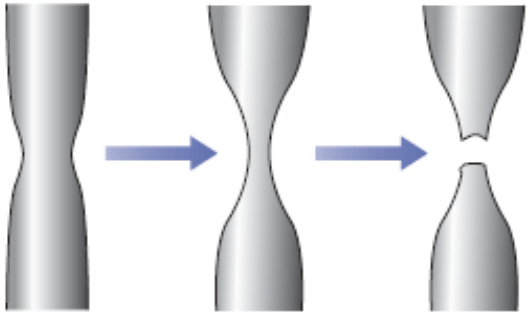


$F,\ \sigma$ ← → $F,\ \sigma$

$F,\ \sigma/\lambda^2$ ← λ-times system size → $F,\ \sigma/\lambda^2$

$$\&_\lambda = \&t\lambda^2$$

Stability of drawn cane structures



Stability threshold:

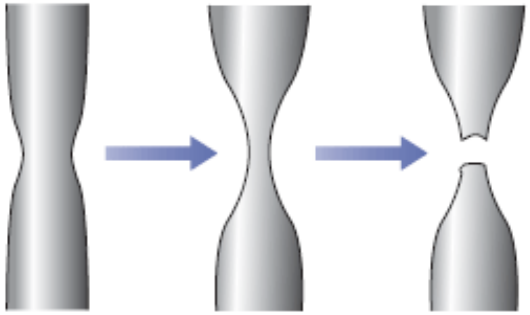
$$\dot{\varepsilon} = \frac{1}{D}\frac{\partial D}{\partial t} \propto \frac{1}{\eta D^2} = \text{constant}$$



$F,\ \sigma$ ← → $F,\ \sigma$

$F,\ \sigma/\lambda^2$ ← λ-times system size $\dot{\varepsilon}_\lambda = \dot{\varepsilon}\lambda^2$ → $F,\ \sigma/\lambda^2$

Stability of drawn cane structures





Now consider heat dissipation:

- Radiative heat transfer dominates
- Stefan-Boltzmann law

  Heat flux: $q = e\sigma T^4$ e : emissivity

  $\sigma = 5.67 \times 10^{-8}$ W/m^{2}K^4
- Temperature change rate

$$\frac{\partial T}{\partial t} = -\frac{qS}{c_P V} = -\frac{4e\sigma T^4}{c_P D}$$

- Viscosity dependence on temperature

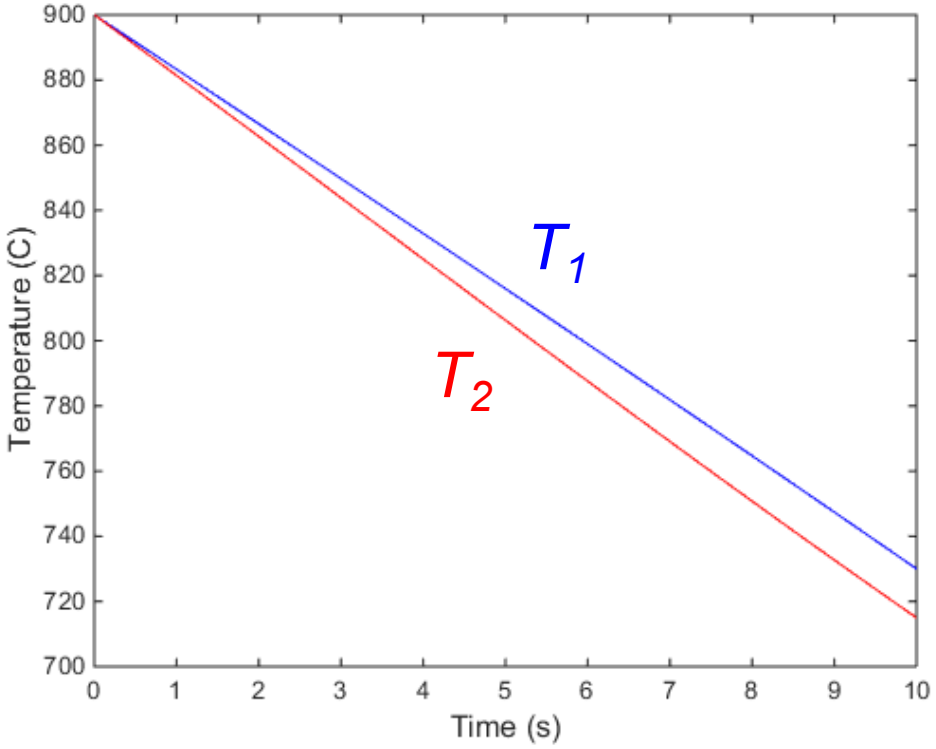
$$\eta = \eta_0 \exp\left[\frac{\Delta E_a(T)}{k_B T}\right]$$ High T range

Modeling outcome

Assumptions:

- Uniform temperature distribution along the cane cross-section
- No heat or mass exchange between cane sections
- Only considers radiative heat transfer from glass cane to the surroundings
- Constant drawing speed



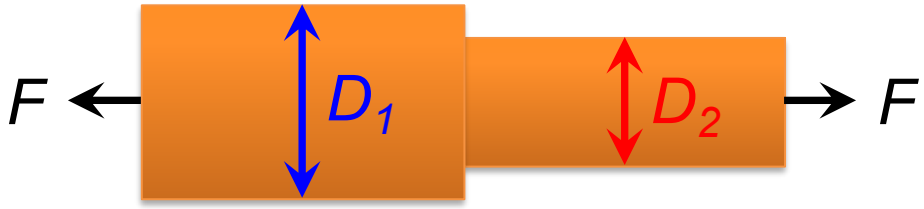


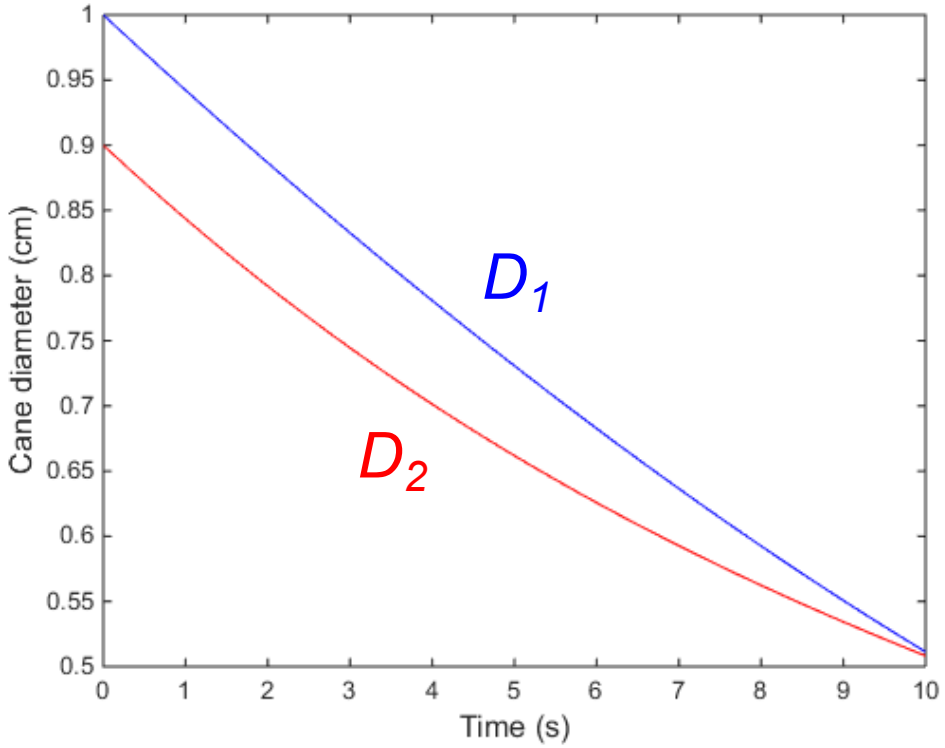
Modeling outcome

Conclusions:

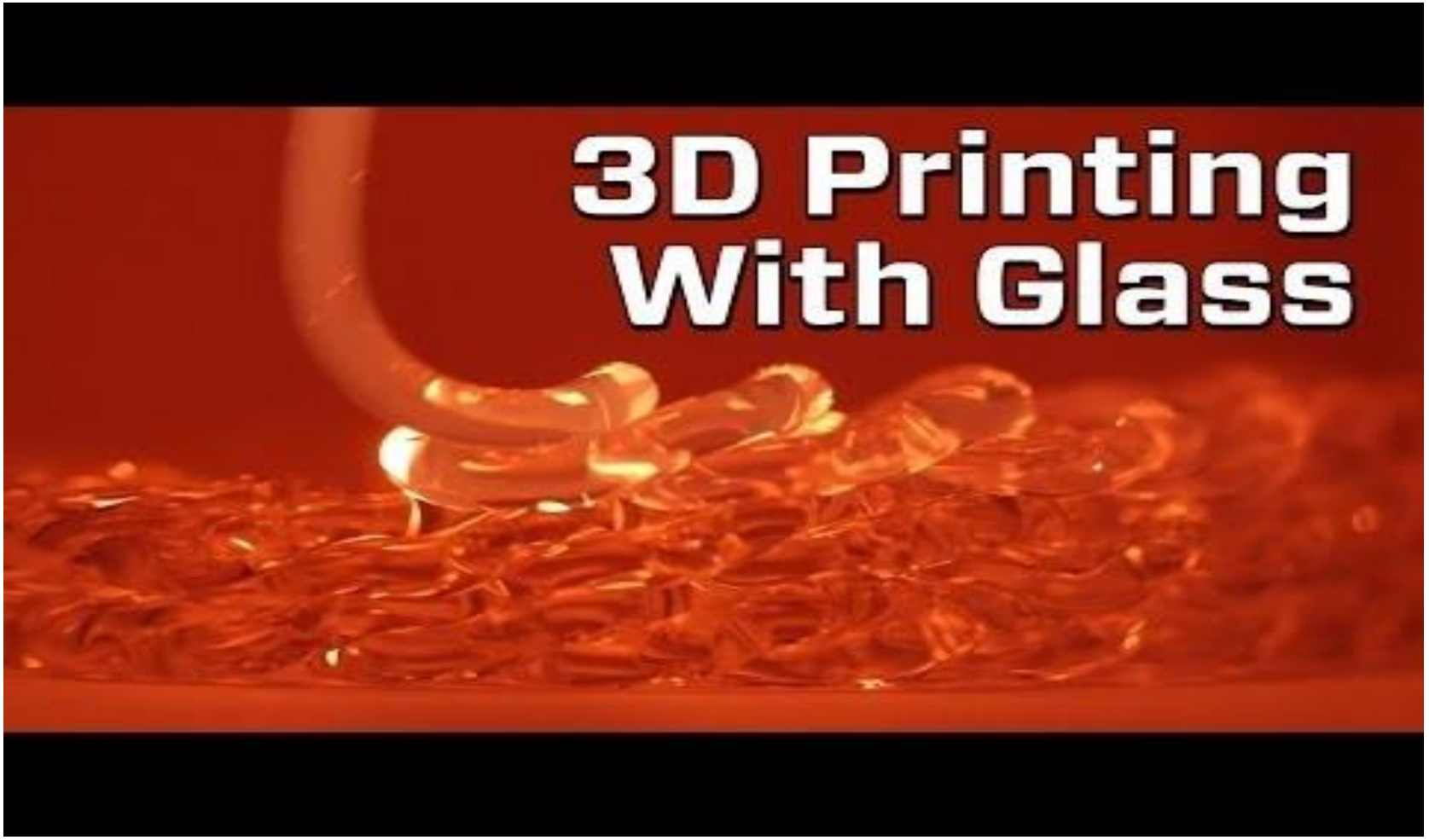
- Thinner section cools faster
- Viscosity increase in thinner section prevents necking
- Cane diameter non-uniformity damps out





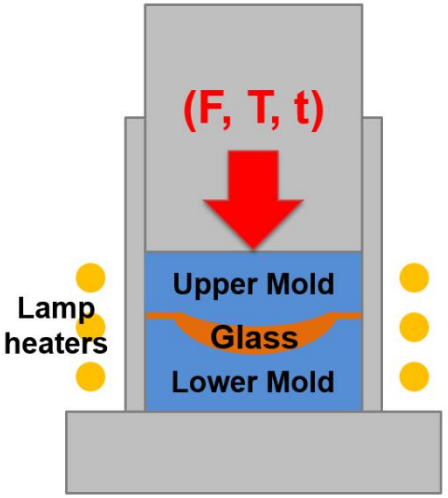


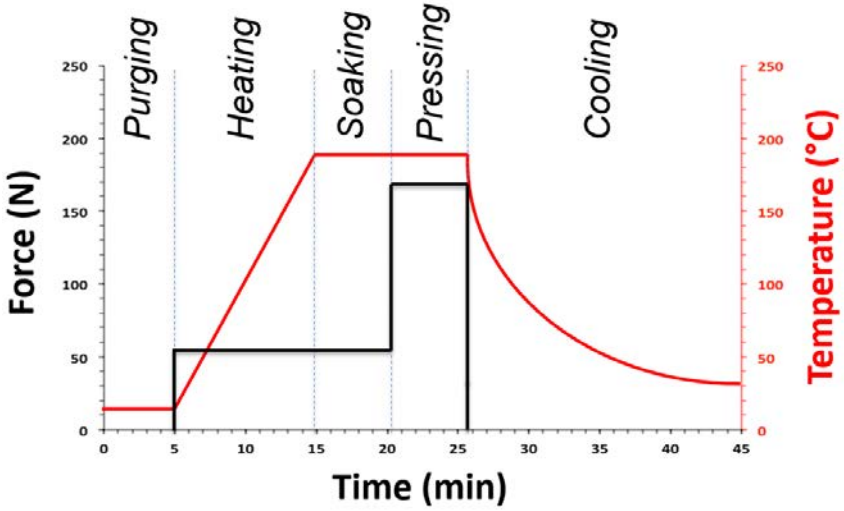
3-D glass printing



Precision glass molding (compression molding)





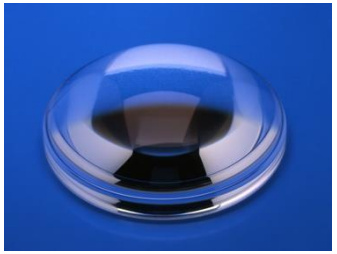


- Viscosity: $10^{6.6}$ – 10^{8} Pa·s; pressure: ~ MPa
- Mold sticking and damage: TiN or SiC low friction coatings
- Non-uniform temperature distribution
- Post-molding deformation: thermal shrinkage, viscoelasticity

http://www.rpoptics.com/wp-content/uploads/2015/01/Precision-Glass-Molding-Technical-Brief_21.pdf

Comparison of key properties between molded glass and plastic optics

Property	Glass	Plastic
Available material options	>100	<10
	Quantitative properties	
Index of refraction (n_d)	$1.434 < n_d < 2.144$	$1.491 < n_d < 1.682$
Abbe number (v_d)	$17.8 < v_d < 95.0$	$18.9 < v_d < 58.5$
CTE (α) (10^{-7}/°C)	$49 < \alpha < 160$	$558 < \alpha < 720$
Glass transition temperature (T_g) (°C)	$288 < T_g < 618$	$77 < T_g < 210$
dn/dt (10^{-4}/°C)	$10.9 < dn/dt < 23.4$	$-14.3 < dn/dt < -8.5$
Specific gravity (SG)	$2.4 < SG < 7.1$	$1.0 < SG < 1.3$
	Qualitative properties	
Environmental durability	Excellent	Poor–Good
Integrated features	Limited	Extensive
	Typical commercial product properties	
Focal length (%)	±1	±2–3
Radius of curvature (%)	±1	±2–3
Power/irregularity (fringes)	3/1	5/2
Scratch/dig	40/20	60/40
Center thickness (mm)	±0.050	±0.050

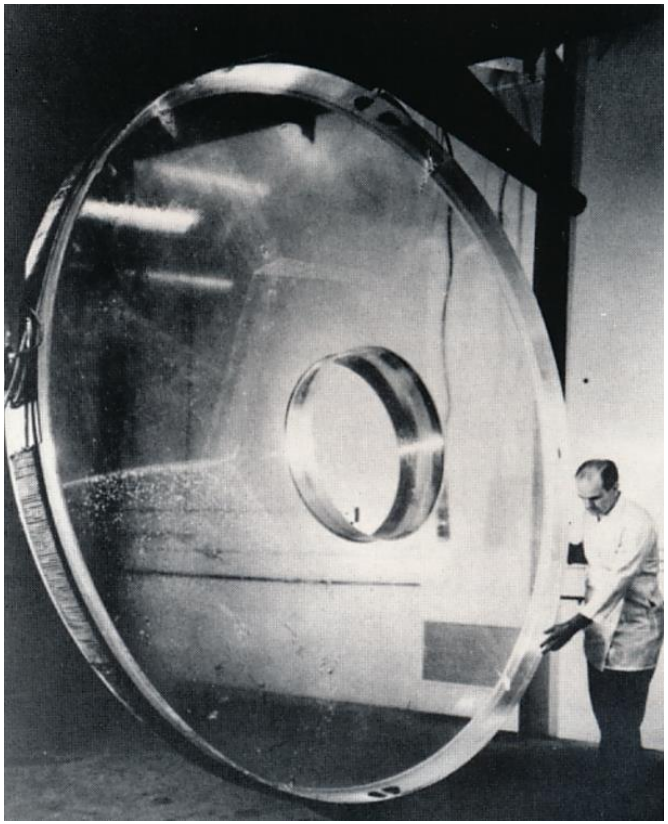


PGM glass asphere lens

LFW **47**, 42-45 (2011)

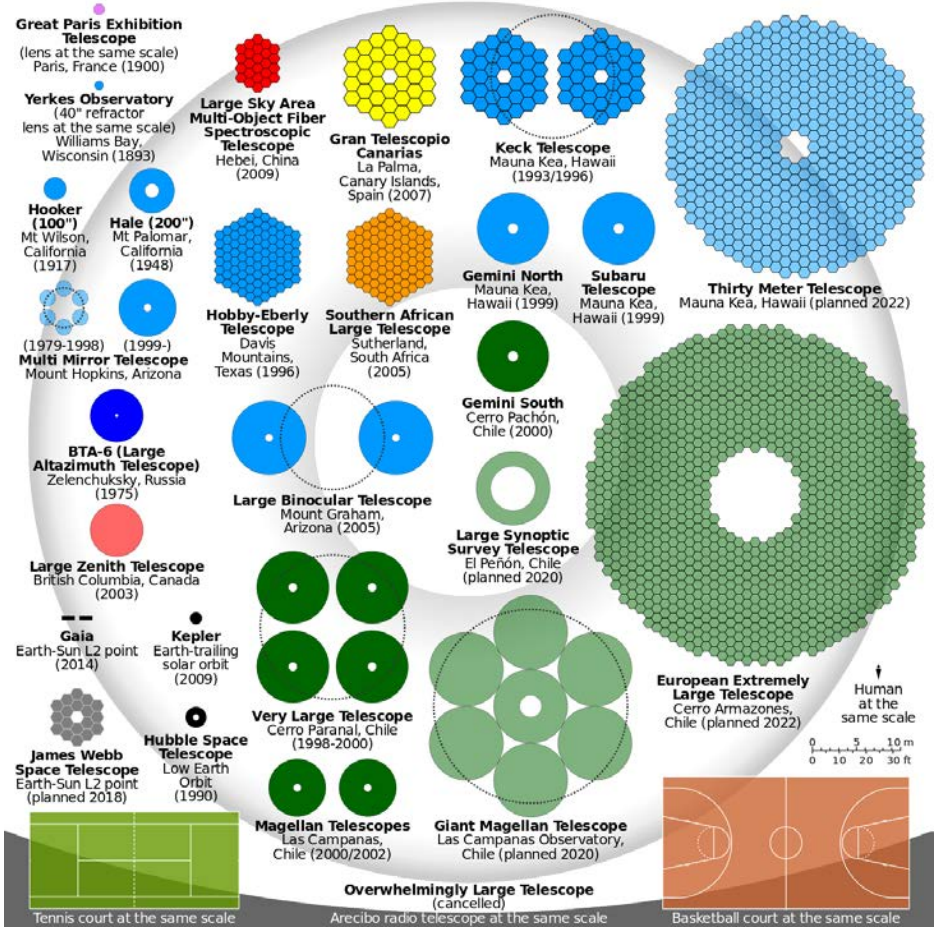
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Making extremely large telescope mirrors



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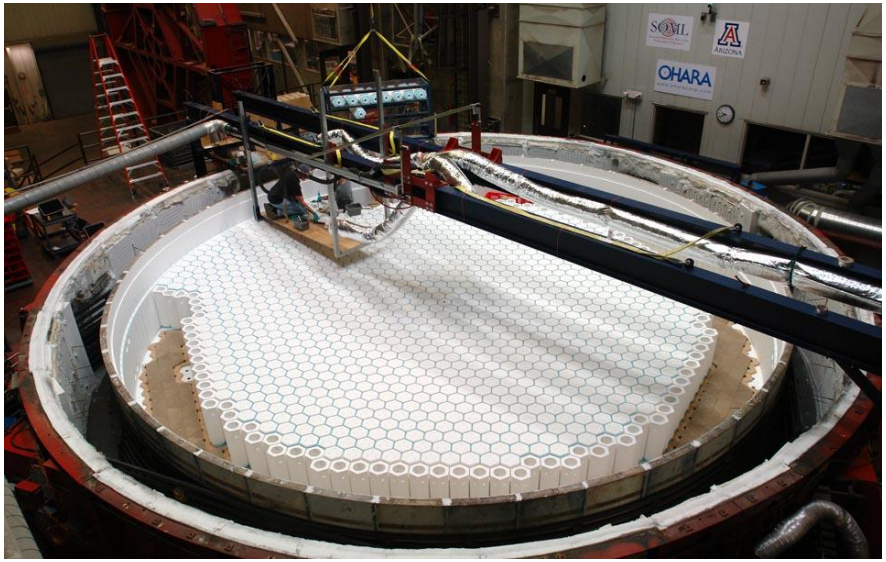
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Making extremely large telescope mirrors



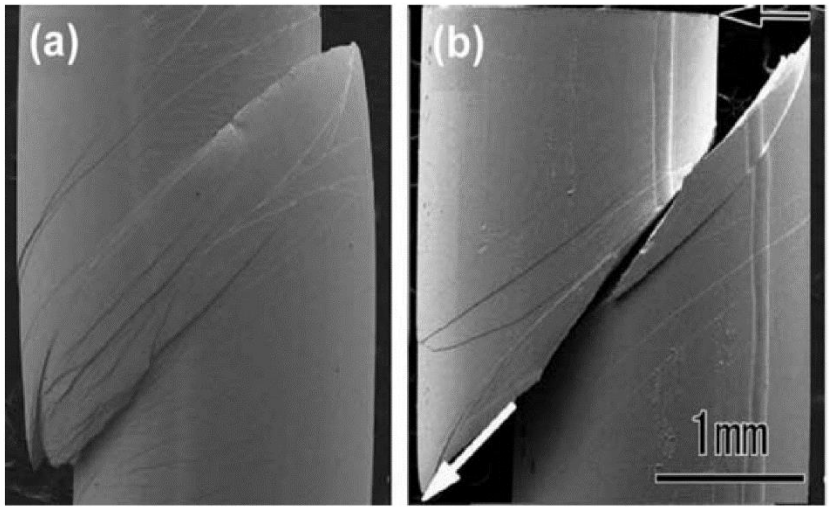


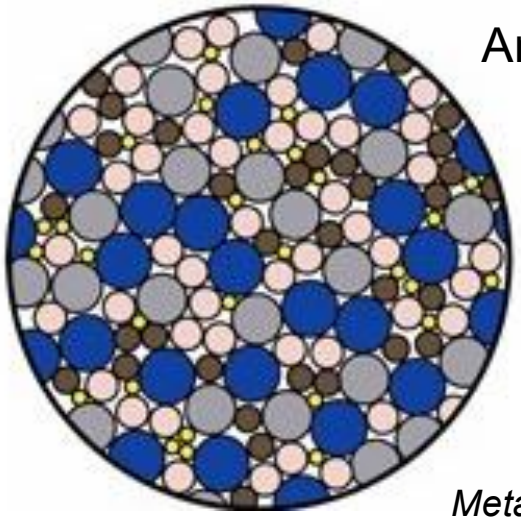
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- **Initial paraboloidal shape is formed by casting the mirror in the spinning furnace, followed by milling and polishing down to 25 nm accuracy**
- **A honeycomb mirror structure leads to low weight and high stiffness**

Mechanical properties of bulk metallic glass (BMG)





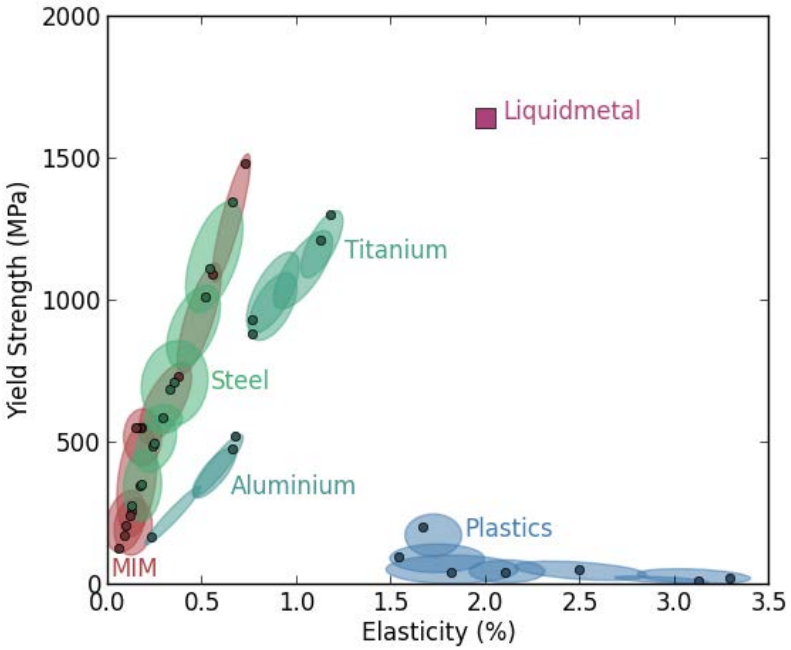
Amorphous metal

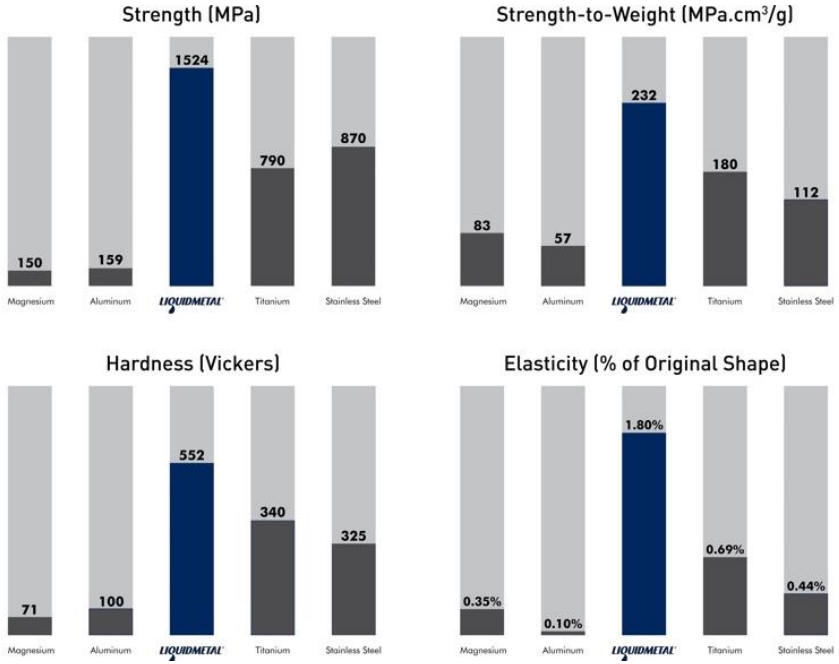
Metals **3**, 1 (2013)

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- Absence of dislocations and slip planes/directions in BMG
  - Large elastic limit and high yield strength (2% and 2 GPa in Zr-based BMGs)
  - Poor global plasticity: absence of strain hardening, strong tendency towards shear localization
- Cold working is not a viable processing solution

Mechanical properties of a commercial BMG



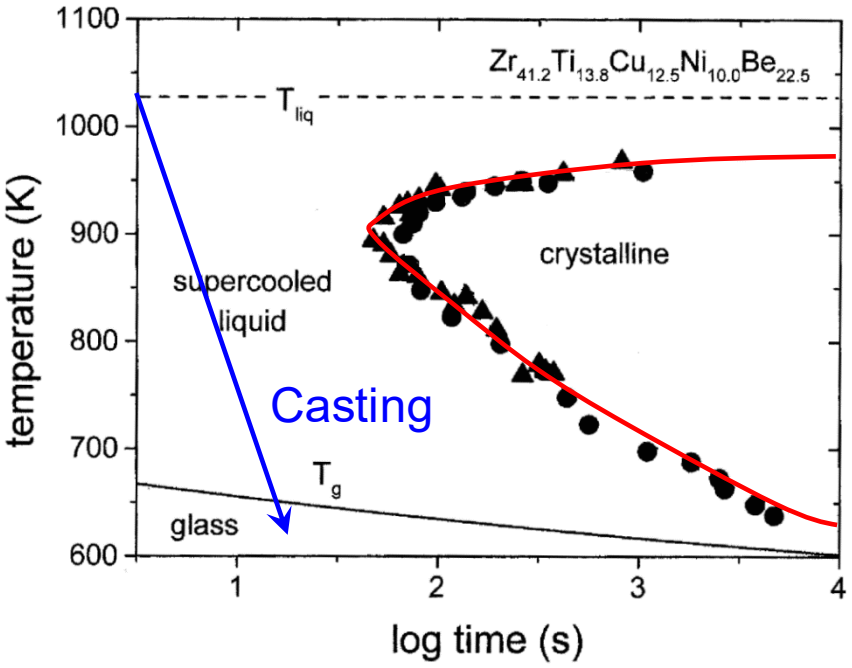


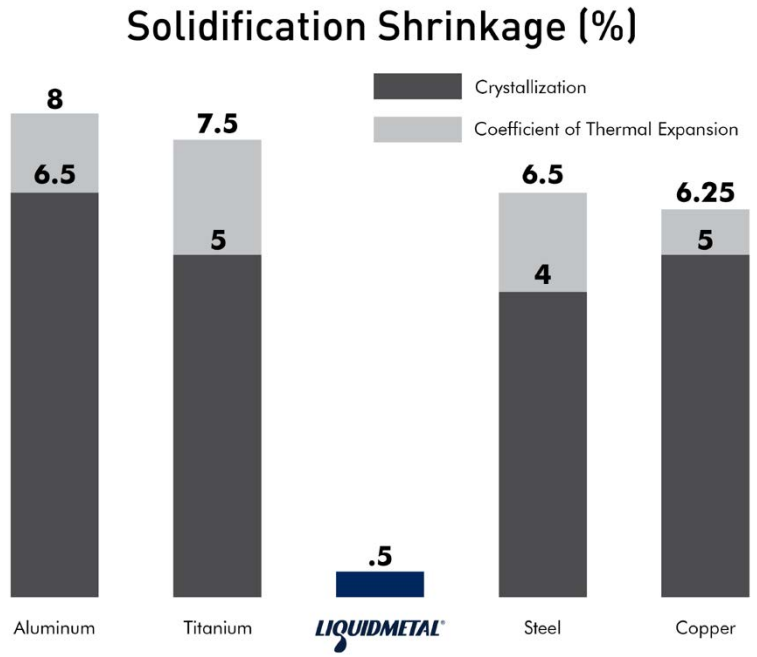
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✓ High yield strength, hardness, and elasticity

BMG process design



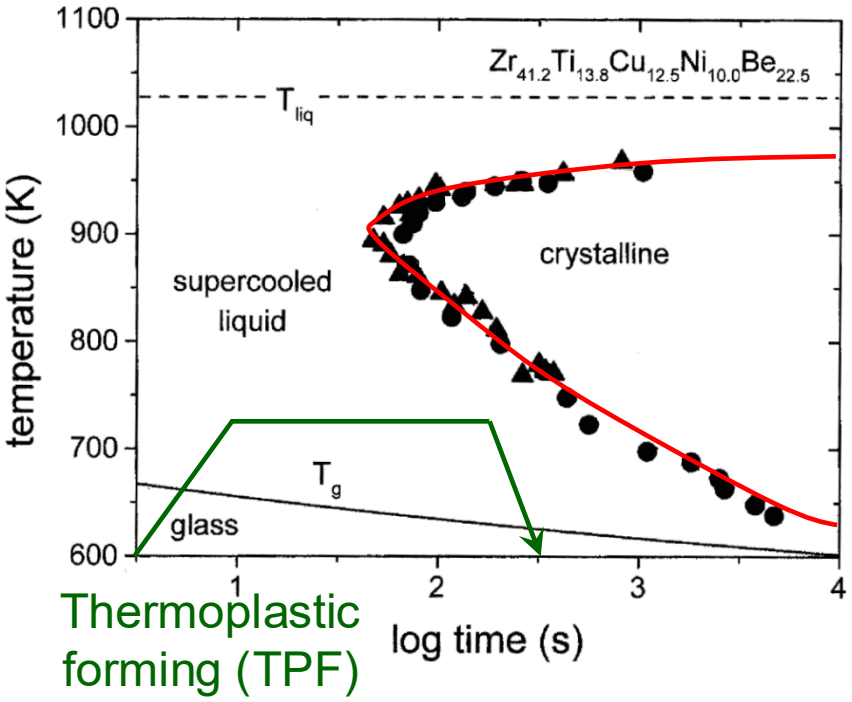


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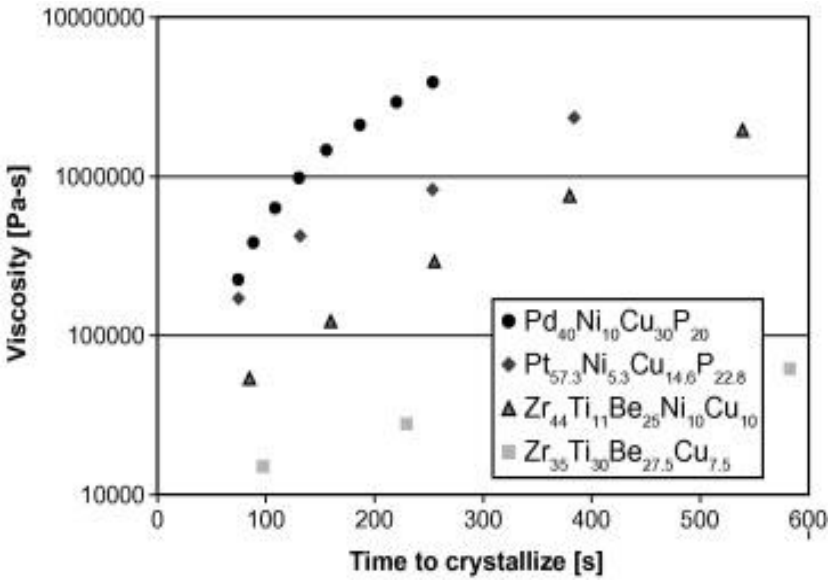
- Casting: suction casting, die casting
  - Reduced volume shrinkage (< 1%): net-shape forming
  - Cooling rate control: mold filling and crystallization mitigation

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BMG process design



Thermoplastic forming (TPF)

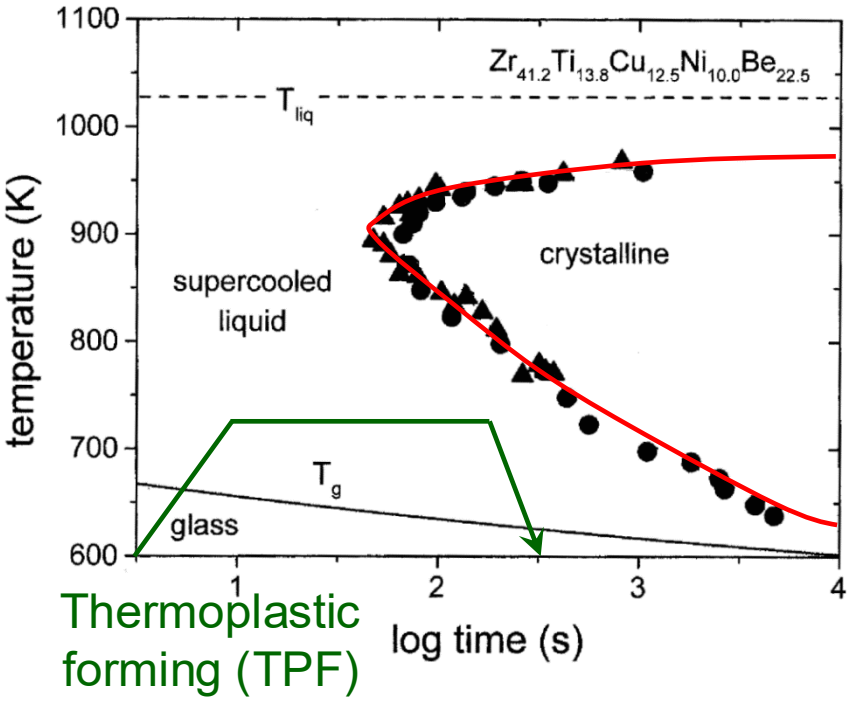


Scripta Mater. **60**, 160 (2009)

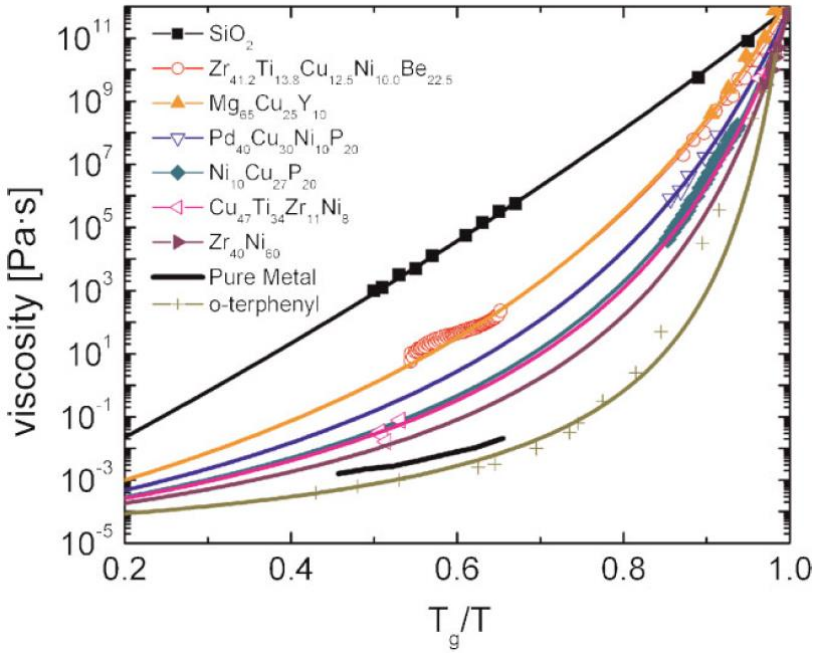
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- Thermoplastic forming: compression & injection molding, extrusion, rolling, blow molding, 3-D printing
  - Thermal embrittlement: free volume decrease

BMG process design



Thermoplastic forming (TPF)

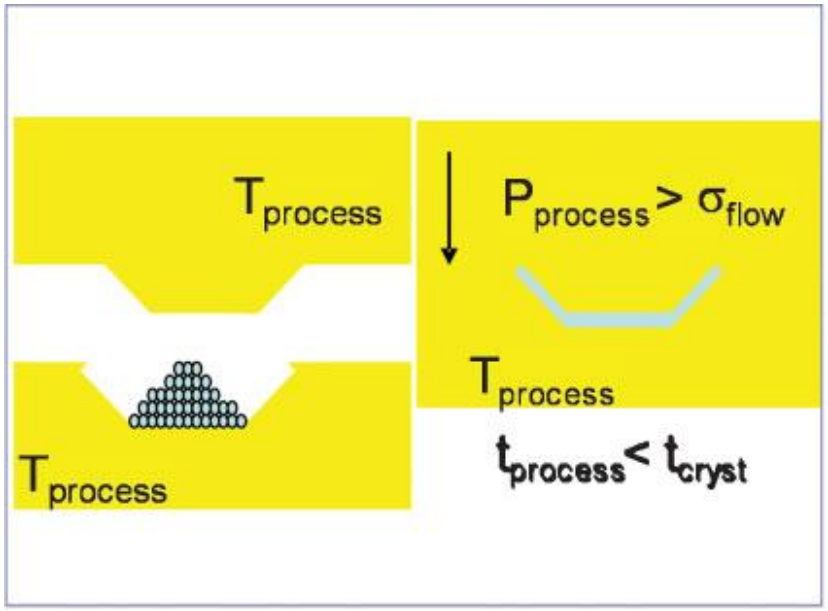


Adv. Mater. **22**, 1566 (2010)

- Glass-forming liquid fragility
  - Liquids with low fragility have better temperature tolerance

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Compression molding



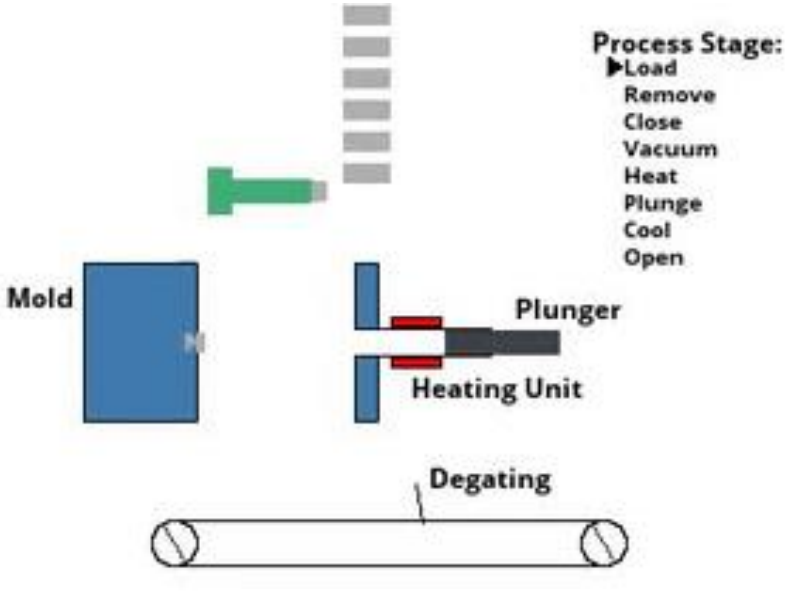


Sample size	Shape	Aspect ratio	Issues
mm to cm	Open structures	1 to 10	Mold release and mold wear

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Injection molding



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Sample size	Shape	Aspect ratio	Issues
mm to cm	Open structures	1 to 10	Mold release and mold wear

Blow molding

Parameter	Materials	
	Plastics	BMG
Processing temperature [°C]	160 – 260	160 (Au-based)
		280 (Pt-based)
		350 (Pd-based)
		430 (Zr-based
Processing pressure [Pa]	$1 – 10 \times 10^5$ Pa	$1 – 4 \times 10^5$ Pa
Maximum strain [%]	∞	~10 000
Typical strain rate [s^{-1}]	$10^{-1} – 1$	10^{-1}
κ [W/mK]	0.3	10

Parison Final shape

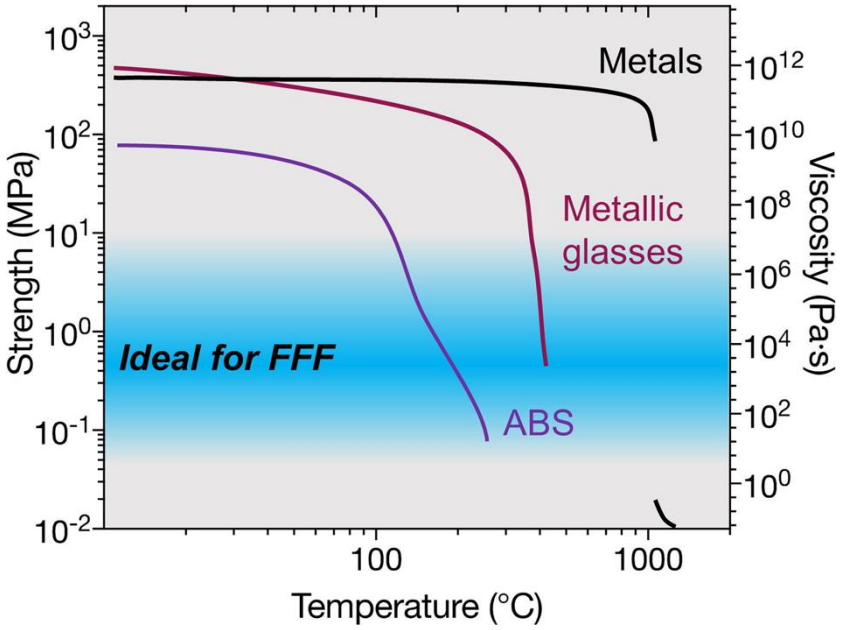


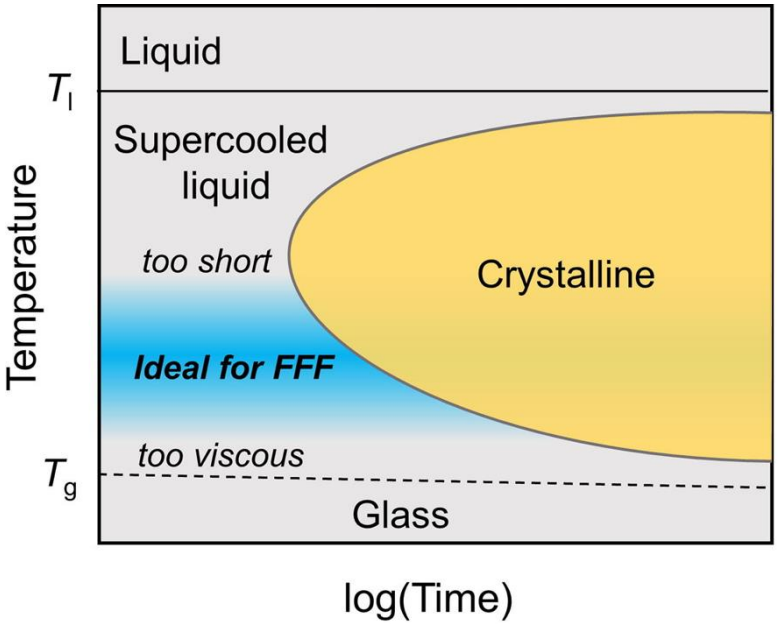
Sample size	Shape	Aspect ratio	Issues
10 μm to cm	Hollow shapes	10 to 1,000	Temperature control, mold sticking

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3-D printing of BMG



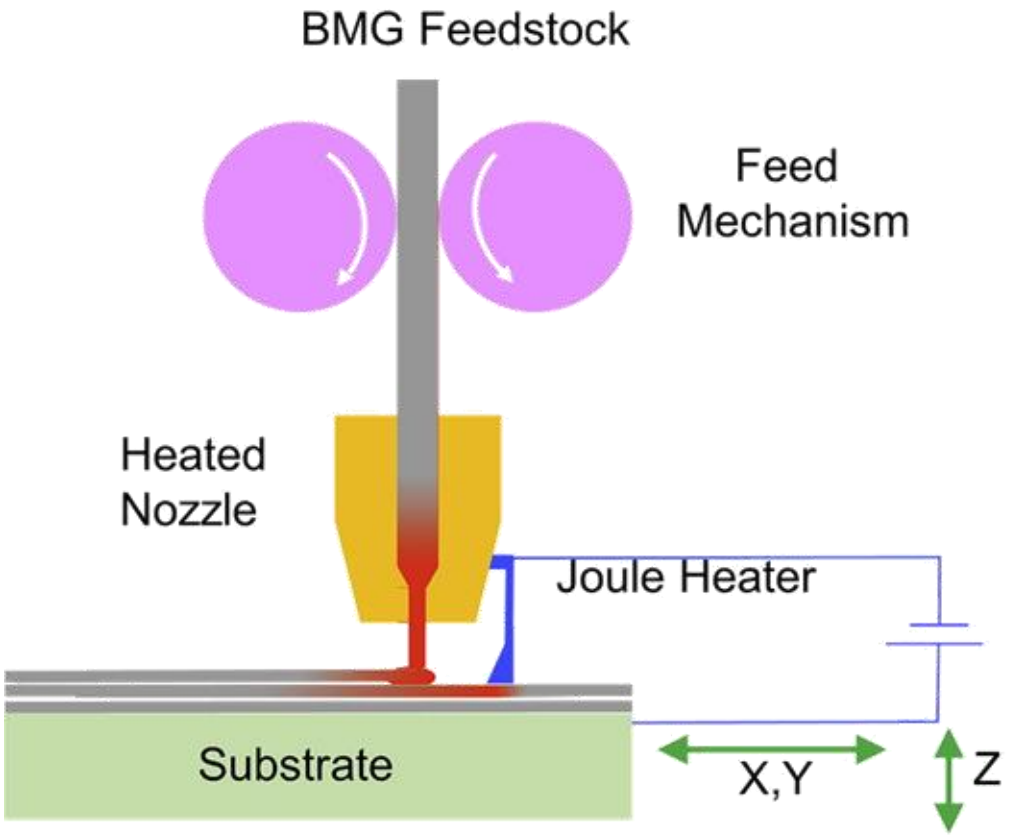


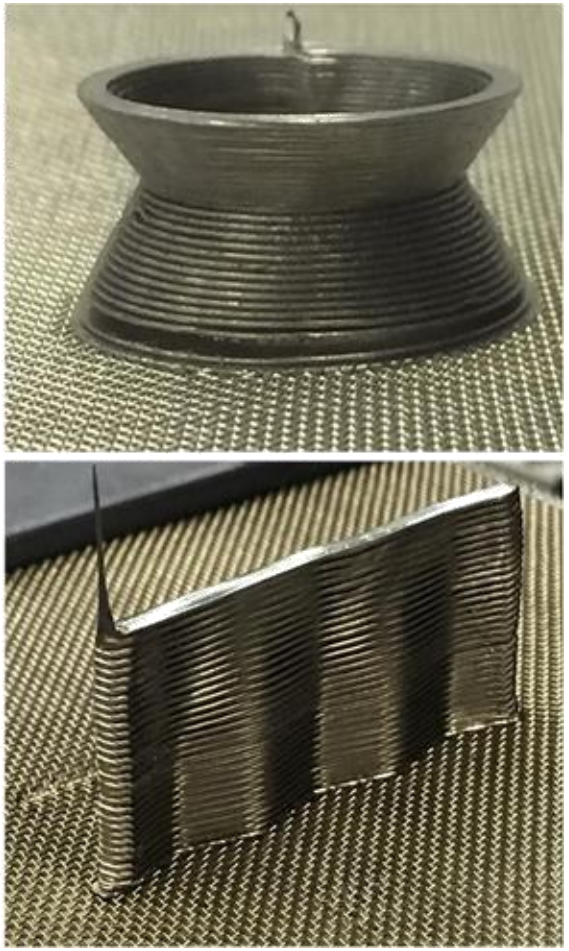
Continuous softening behavior of BMGs enables extrusion-based 3-D printing through fused filament fabrication (FFF)

Mater. Today **21**, 697 (2018)

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3-D printing of BMG





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