MIT 3.071 Amorphous Materials

5: Viscosity of Glass

Juejun (JJ) Hu

After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 9
- Introduction to Glass Science and Technology
  - Ch. 6

The pitch drop experiment

- The pitch drop experiment is a long-term experiment which measures the flow of a piece of pitch (asphalt)
- The most famous version of the experiment was started in 1927 by Professor Thomas Parnell of the University of Queensland in Brisbane, Australia. The eighth drop fell on 28 November 2000, allowing the experimenters to calculate that pitch has a viscosity approximately 230 billion times that of water.

Is glass a solid or a viscous liquid?

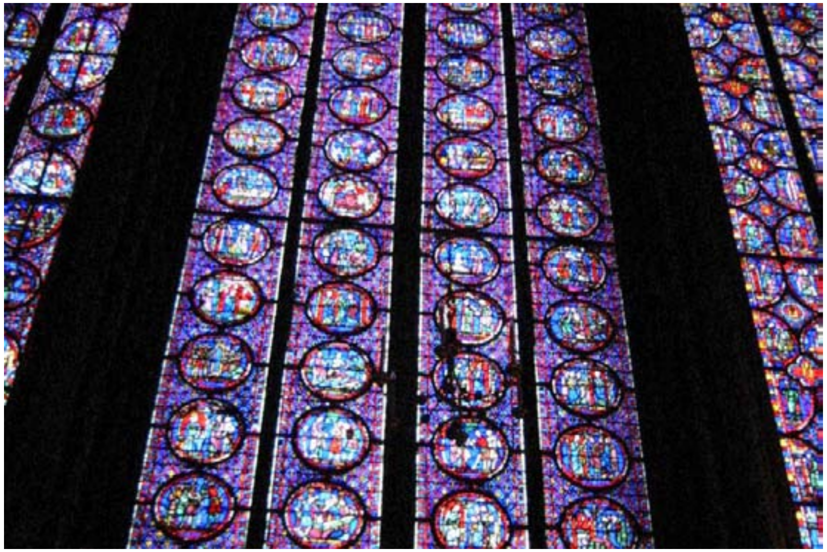
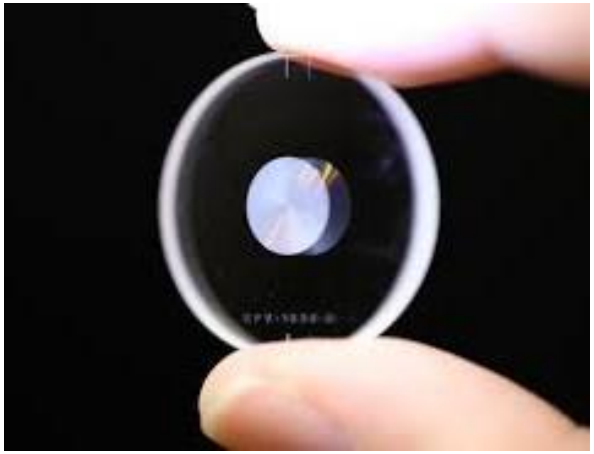


Image is in the public domain. Source: Wikimedia Commons.

"It is well known that panes of stained glass in old European churches are thicker at the bottom because glass is a slow-moving liquid that flows downward over centuries."

"Successful read/write of digital data in fused silica glass with a recording density equivalent to Blu-ray Disc™, enabling both greater capacity using 100 recording layers and long storage life of 300 million years."

Hitachi Ltd. Press Release 2014



Is glass a solid or a viscous liquid?

Solid

Elasticity

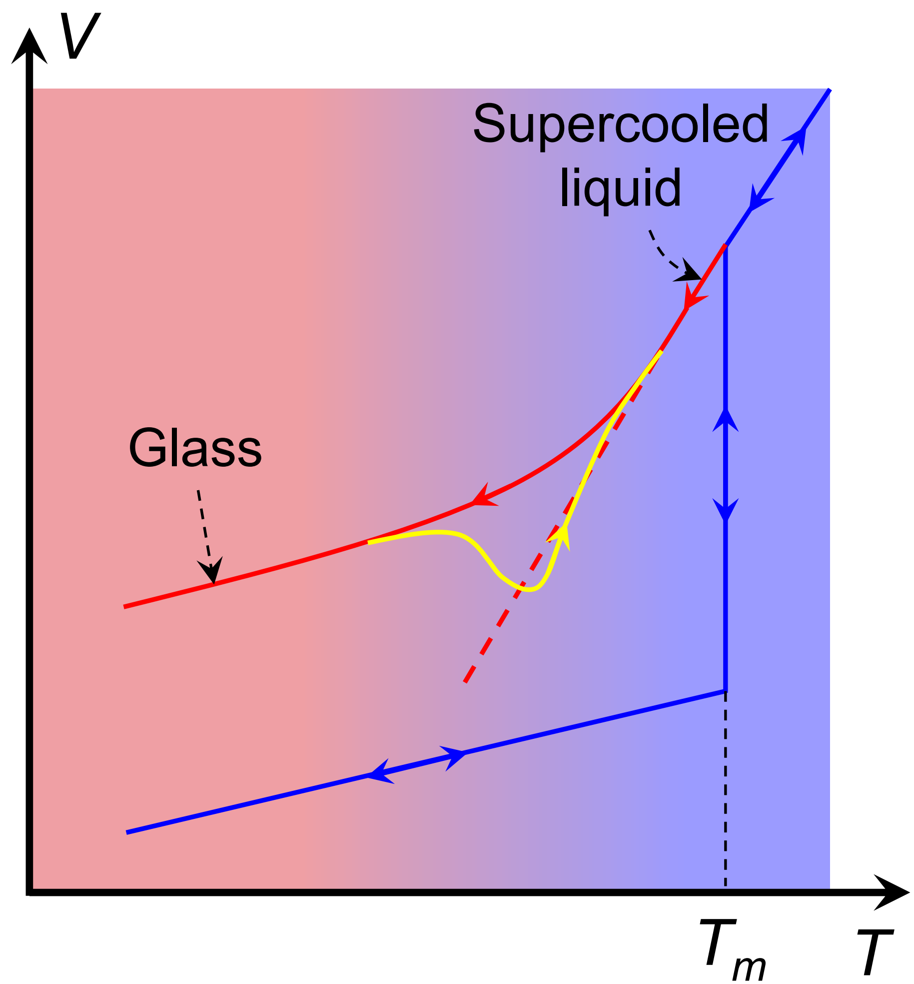
instantaneous, transient

$$\sigma_x = E\varepsilon_x$$

$$\sigma_{xy} = G\varepsilon_{xy}$$

E : Young's modulus

G : shear modulus



Liquid

Viscosity

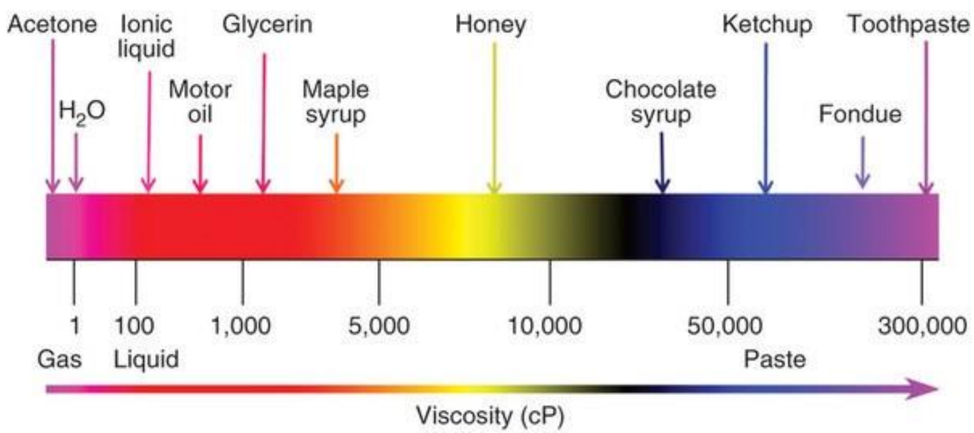
time-dependent, permanent

$$\sigma_{xy} = \eta \cdot \frac{\partial \varepsilon_{xy}}{\partial t}$$

η : viscosity (unit: Pa·s or Poise)

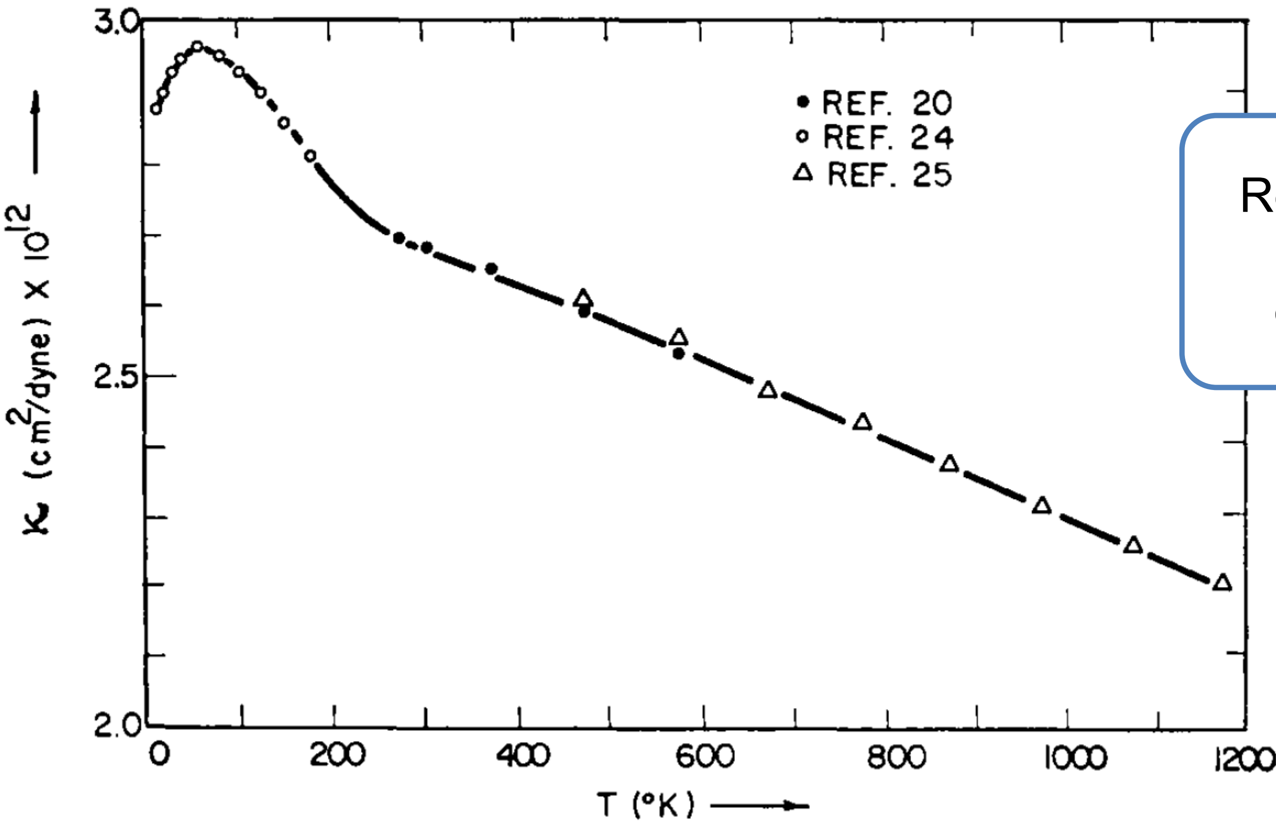
Microscopic origin of elasticity and viscosity

- Elasticity: attractive and repulsive forces between atoms
- Viscosity: motion of atoms/molecules relative to their neighbors (**relaxation**)
  - Conformation change of (macro)molecules
  - Vacancy diffusion
  - Dislocation motion



- ✓ Different relaxation mechanisms have distinctive relaxation time scales
- ✓ Strong inter-atomic/molecular bonds give rise to high viscosity

Temperature dependence of elasticity



Relatively weak temperature dependence

M. R. Vukcevich, *J. Non-cryst. Sol.*, **11**, 25-63 (1972).

Temperature dependence of viscosity

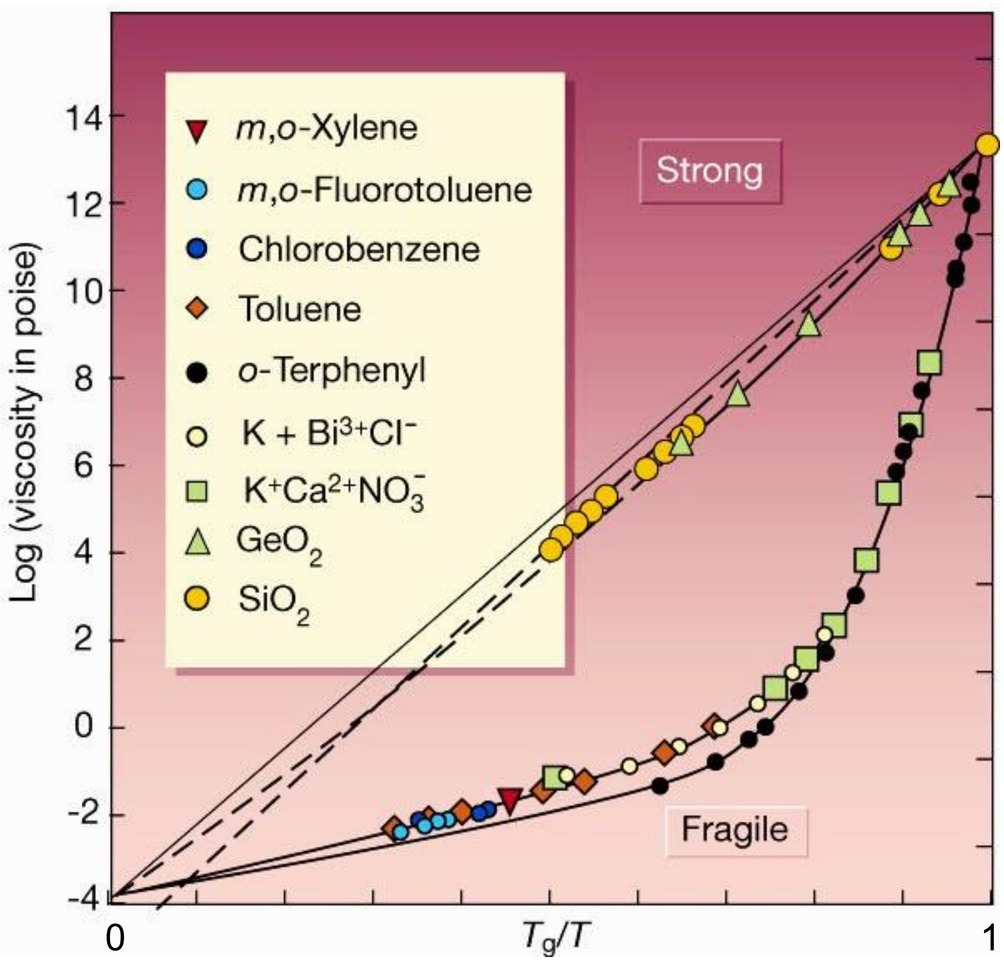
- Viscous flow is a thermally activated process

$$\eta \propto \exp\left[-\frac{\Delta E_a(T)}{k_B T}\right]$$

Glass	Activation energy (kcal mol^{-1})	Temperature range (°C)
Vitreous silica	170	1,100–1,400
	123	1,600–2,500
Vitreous germania	75	540–1,500
Vitreous P_2O_5	41.5	545–655
Vitreous B_2O_3	83–12	26–1300

In general, the activation energy ΔE_a is temperature dependent

The Angell plot and fragility



- Glass transition temperature T_g

  $\eta = 10^{12}\ \mathrm{Pa \cdot s}$

- Fragility parameter

$$m \equiv \left. \frac{\partial \log_{10} \eta}{\partial \left(T_g / T \right)} \right|_{T = T_g}$$

Fragility has nothing to do with mechanical properties of glass!

Science **267**, 1924-1935 (1995)

Strong vs. fragile glass forming liquids

Strong liquids

- Arrhenius equation

$$\eta = \eta_0 \exp\left(-\frac{\Delta E_a}{k_B T} \right)$$

- Covalent glass forming liquids
- Fragility often exhibits a minimum at the rigidity percolation threshold ($\langle r \rangle = 2.4$)

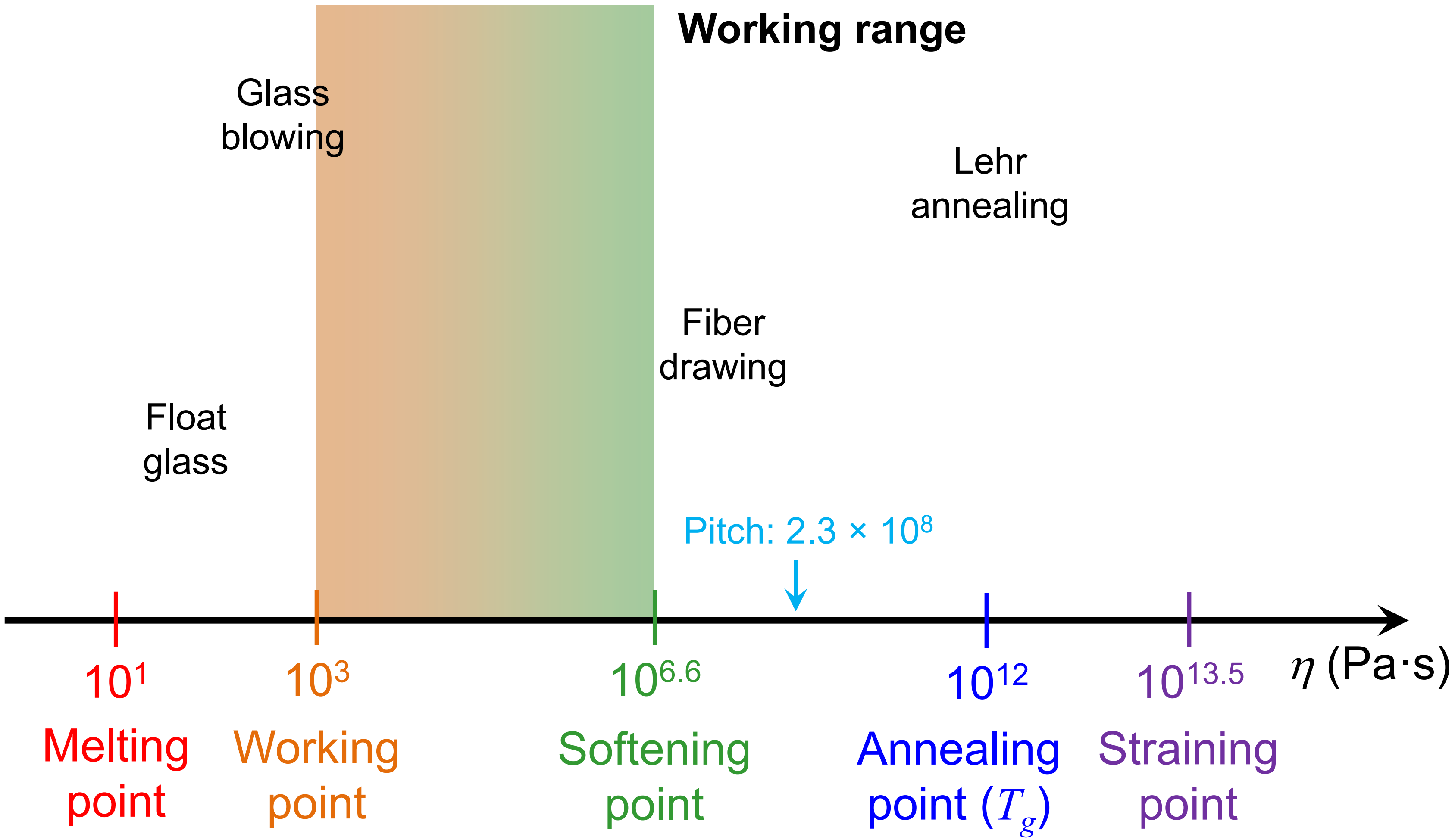
Fragile liquids

- Vogel-Fulcher-Tammann (VFT) equation

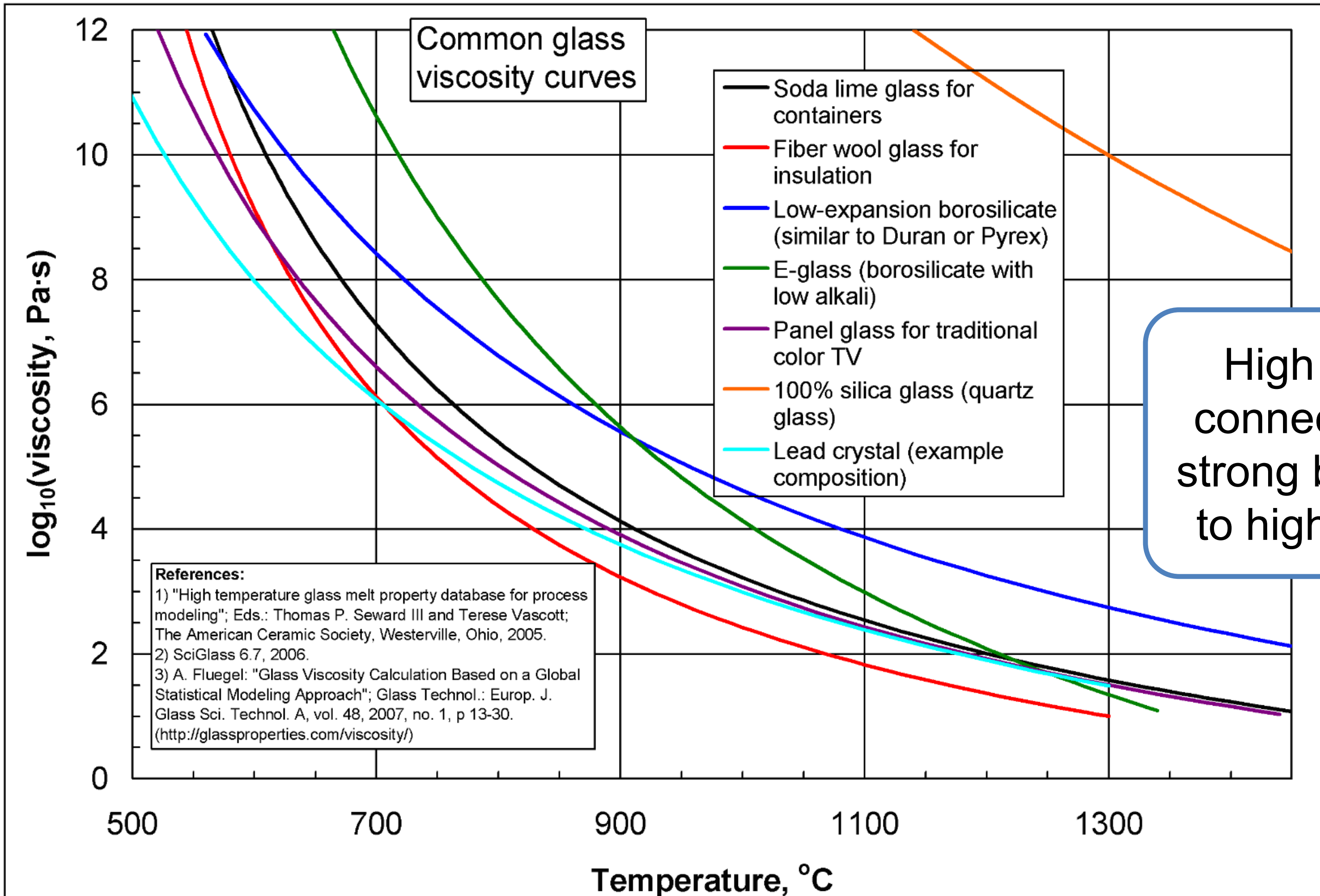
$$\eta = \eta_0 \exp\left(-\frac{A}{T - T_{VFT}} \right)$$

- Ionic and molecular liquids
- Decrease of molecular cluster size as temperature rises

Viscosity reference points



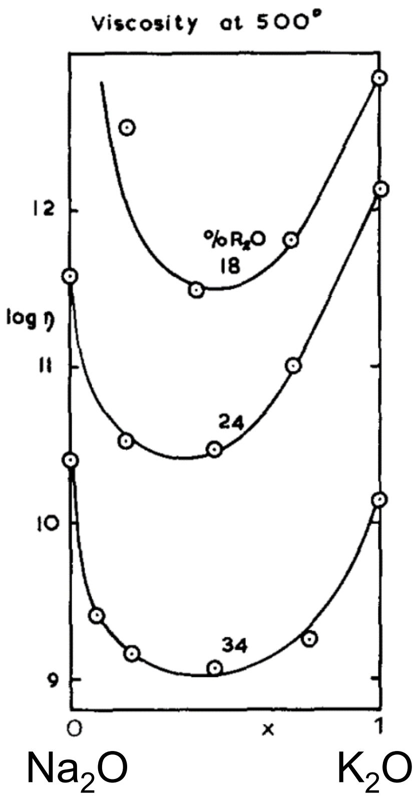
Composition dependence of viscosity

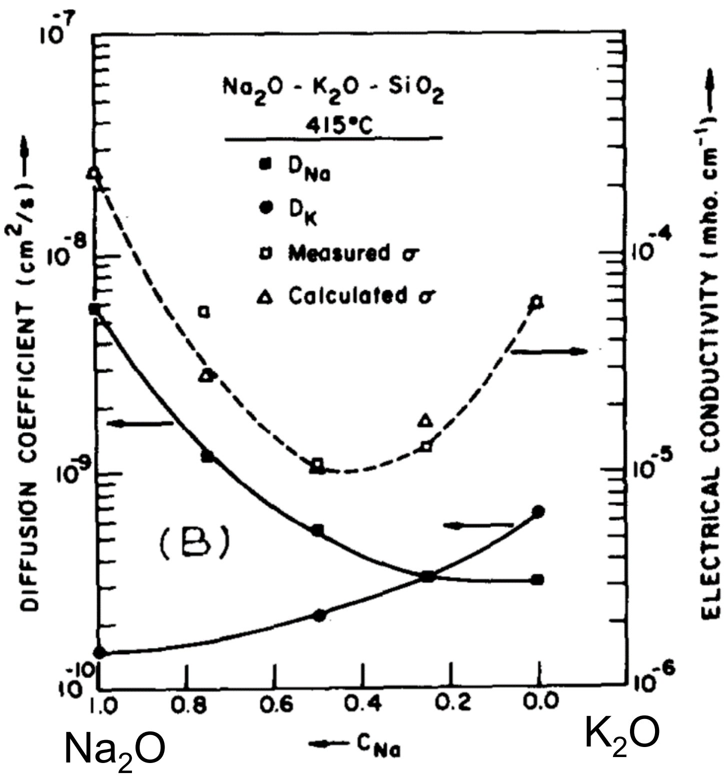


High network connectivity and strong bonds lead to high viscosity

Mixed alkali effect

- Simultaneous presence of two alkali modifiers in glass leads to non-additive behavior (in particular transport properties)

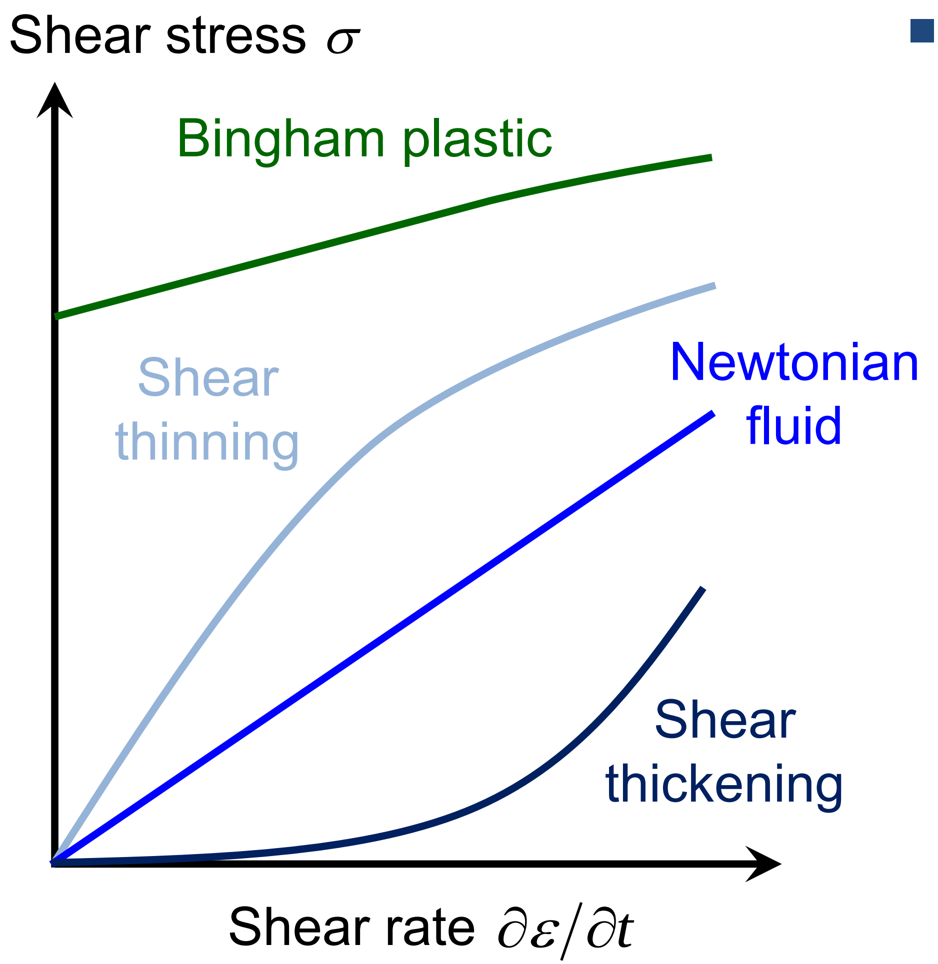




Possible mechanism: mutual blocking of transport pathways by the two ions

J. Non-Cryst. Solids **1**, 235 (1969);
J. Non-Cryst. Solids **21**, 343 (1976);
Phys. Rev. Lett. **90**, 155507 (2003).

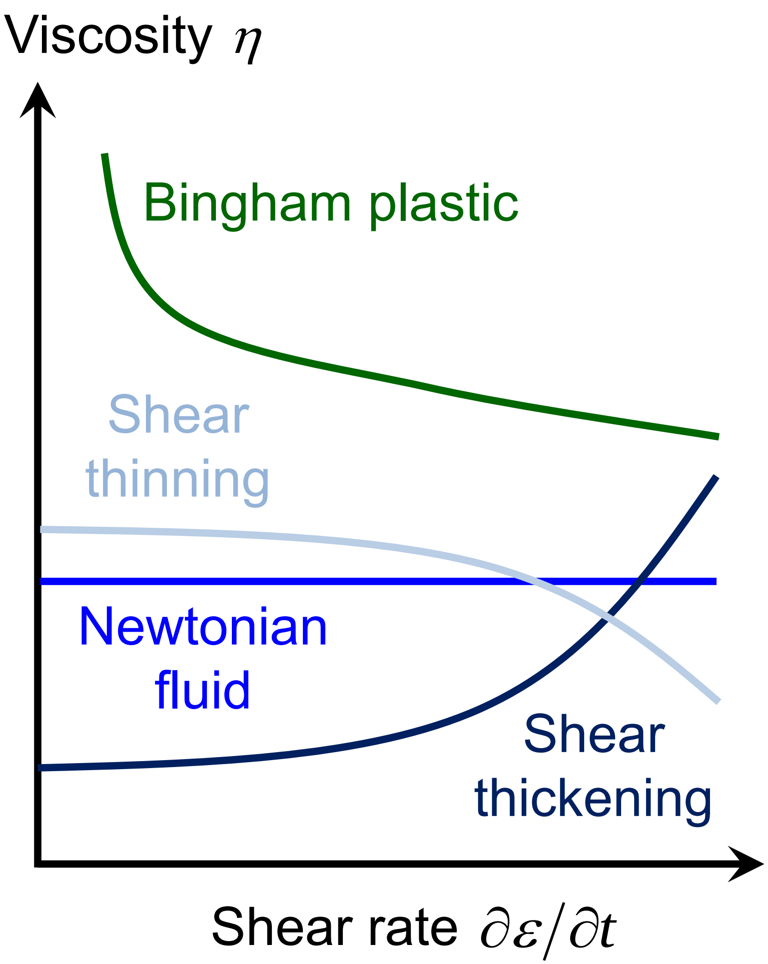
Non-Newtonian behavior



- Rate dependent viscosity

$$\sigma_{xy} = \eta\left(\frac{\partial \varepsilon_{xy}}{\partial t}\right)\cdot\frac{\partial \varepsilon_{xy}}{\partial t}$$

Non-Newtonian behavior

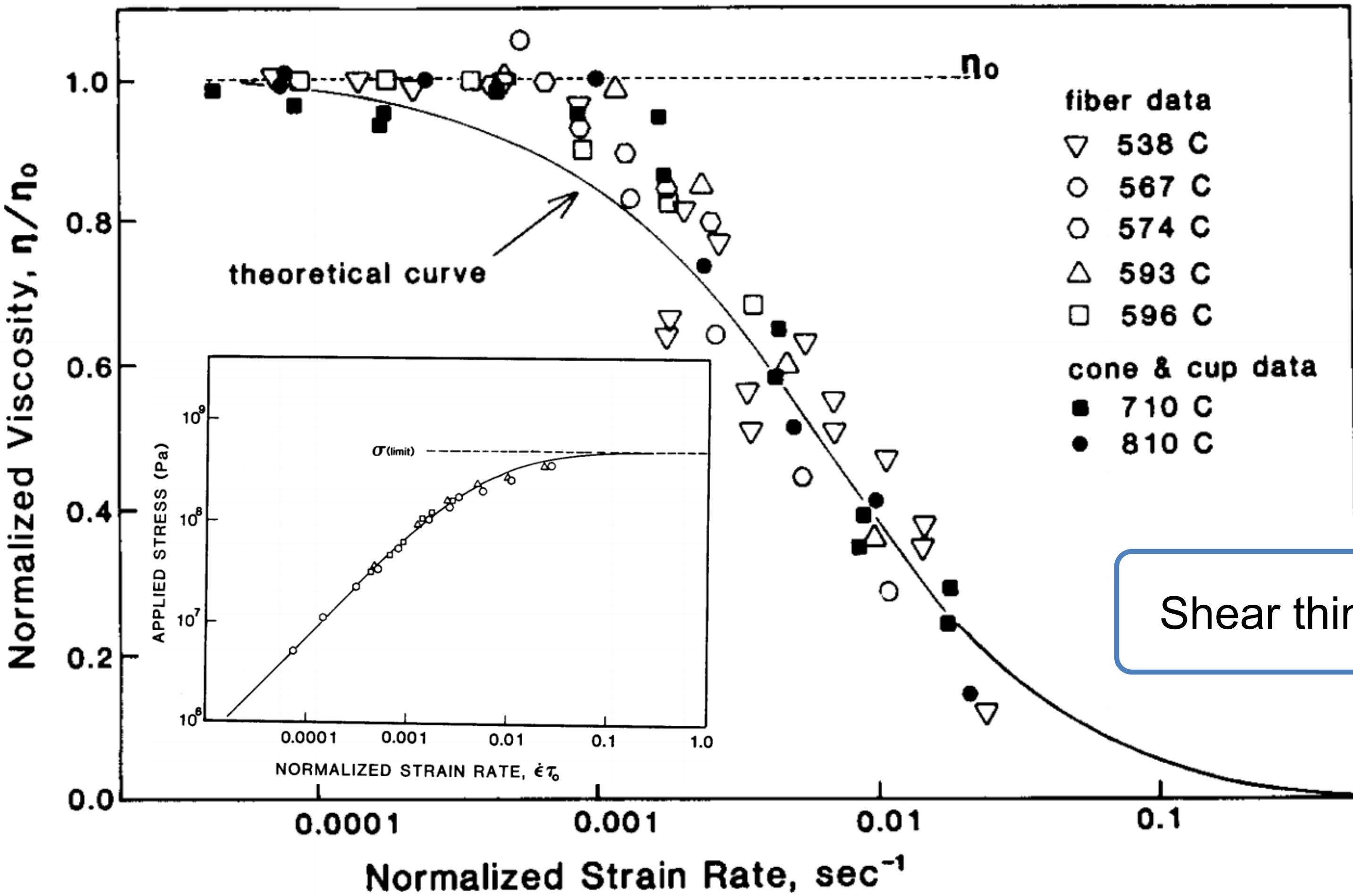


- Rate dependent viscosity

$$\sigma_{xy} = \eta\left(\frac{\partial \varepsilon_{xy}}{\partial t}\right)\cdot\frac{\partial \varepsilon_{xy}}{\partial t}$$

Schematics of direct-write 3D technique figure removed due to copyright restrictions. See Figure 3: "Three-dimensional printing of freeform helical microstructures: A review." *Nanoscale* 6 (2014): 10470-10485.

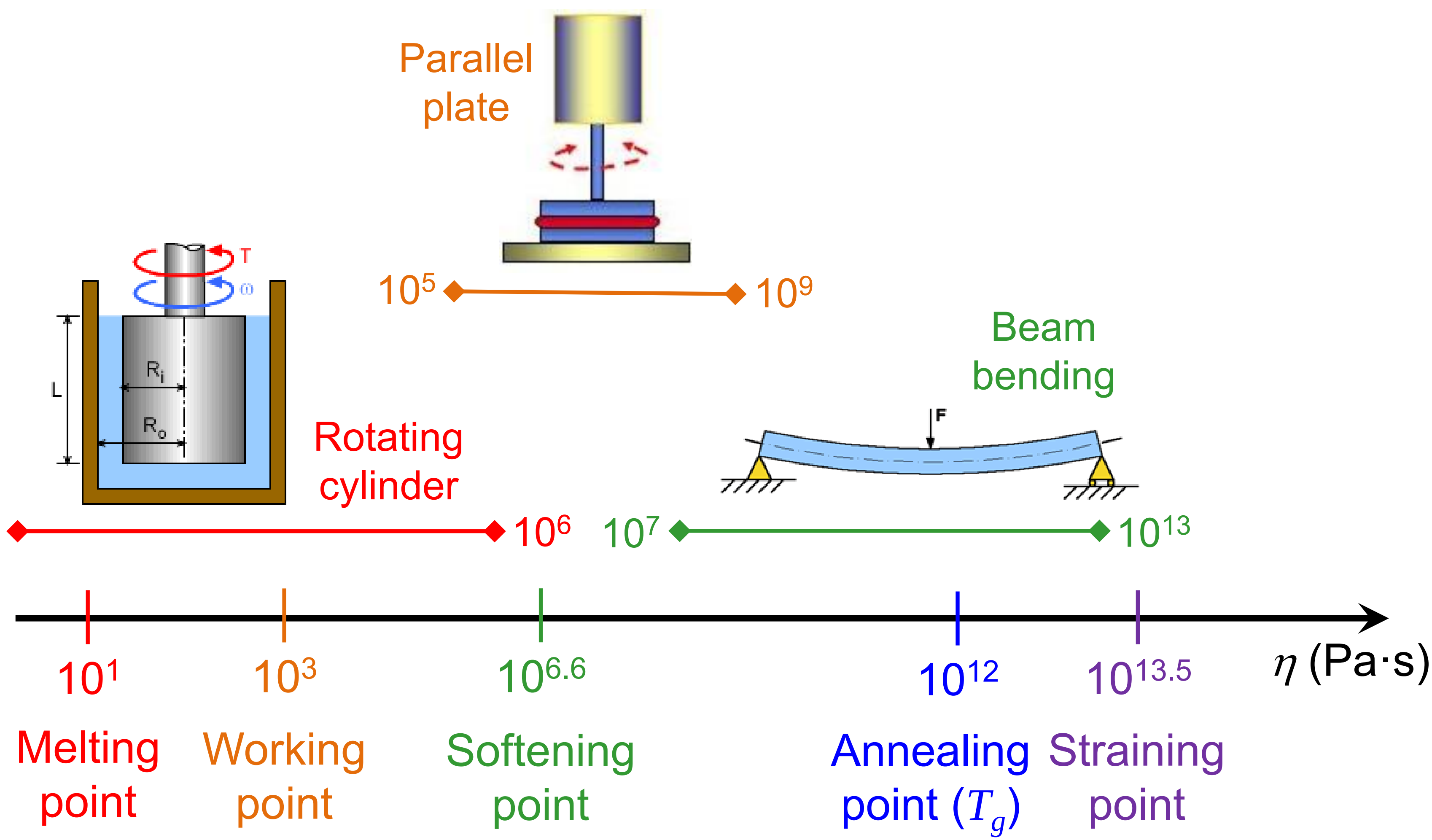
Non-Newtonian behavior of soda-lime glass



Shear thinning

J. Non-Cryst. Solids **105**, 313-322 (1988)

Viscosity measurement: viscometry



Precision viscometry based on optical interferometry

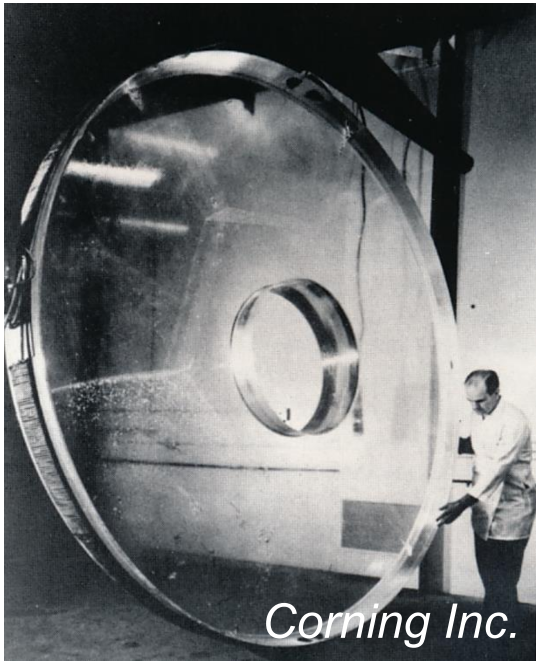


Figure removed due to copyright restrictions. See Figure 1: Vannoni, M., A. Sordini, G. Molesini. "Relaxation time and viscocity of fused silica glass at room temperature." *Eur. Phys. J. E* 34 (2011): 92.

Room temperature viscosity:
> 10^{19} Pa·s (fused silica, after stabilization)

"… the data reported are related to a single fused silica plate whose absolute shape was monitored over a period of ***6 years*** *during which the plate maintained the same posture; … The deformations that have to be detected are at* ***the scale of the nanometre****, over a lateral size of 100-150 mm…"*

M. Vannoni *et al.*, *Eur. Phys. J. E* **34**, 92 (2011).

Is glass a solid or a viscous liquid?

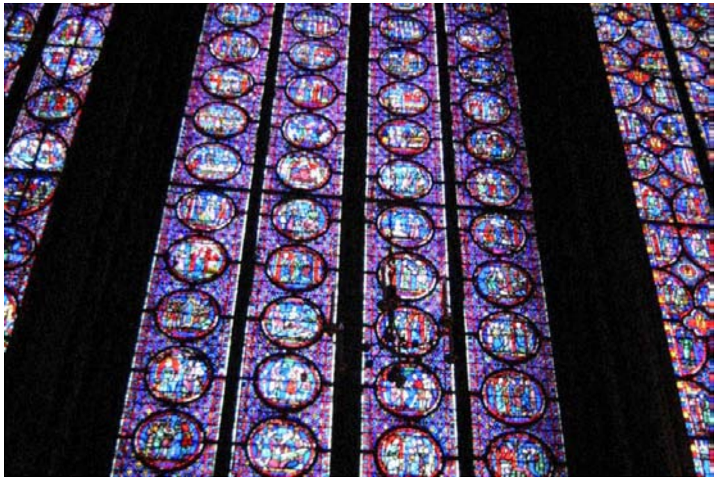


Image is in the public domain. Source: Wikimedia Commons.

"Chocolate Melts,

Flowers Wilt,

~~Diamonds~~ are Forever"

Glasses

- Time scale of viscous deformation due to self weight:

$$\tau \sim \frac{\eta\varepsilon}{\rho g H}$$

η : viscosity; ρ : density

H : component height

g : gravitational acceleration

- For fused silica glass:

$$\tau \sim \frac{10^{19} \cdot 10\%}{2.2\times10^{3} \cdot 9.8 \cdot 1}\,\mathrm{s} \sim 5\times10^{13}\,\mathrm{s}$$

~ 1.5 million years

Summary

- Constitutive relations for linear elasticity and Newtonian viscosity
  - Elastic deformation: instantaneous, transient
  - Viscous flow: time-dependent, permanent
- Temperature dependence of elasticity and viscosity
  - Elasticity: results from interatomic forces with minimal temperature dependence
  - Viscosity: motion of atoms/molecules with respect to neighbors, thermally activated process

Summary (cont'd)

- Fragility of glass forming liquids: temperature dependence of activation energy in viscous flow
  - Strong liquid: Arrhenius equation
  - Fragile liquid: VFT equation, size of collective motion units (molecular clusters) increases as temperature decreases
- Composition dependence of viscosity
  - Mixed alkali effect
- Non-Newtonian viscous flow
- Viscometry techniques