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

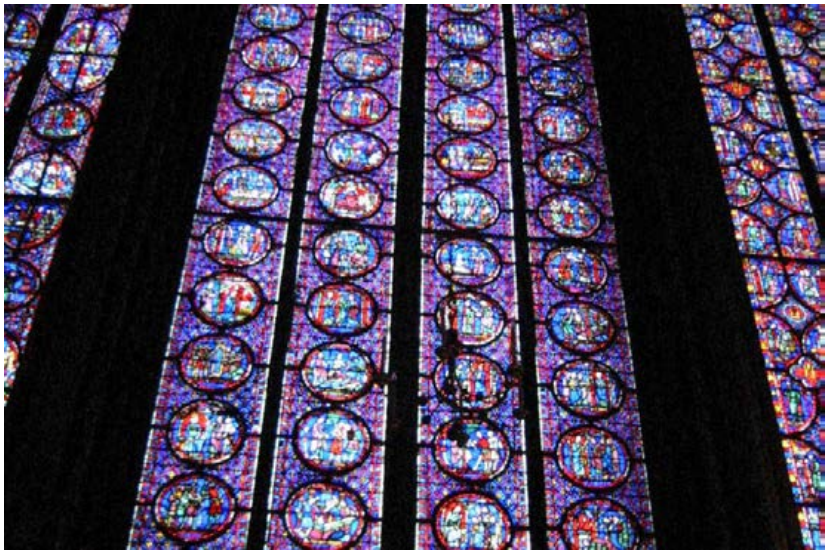
- The pitch drop experiment is a long-term experiment which measures the flow of a piece of pitch (asphalt)
- The most famous version of the experiment was started in 1927 by Professor Thomas Parnell of the University of Queensland in Brisbane, Australia. The ninth drop fell on 24 April 2014, allowing the experimenters to calculate that pitch has a viscosity approximately 230 billion times that of water.



Ig Nobel Prize in Physics, 2005

Courtesy the University of Queensland on Wikemedia Commons.
https://en.wikipedia.org/wiki/Pitch_drop_experiment#/media/File:University_of_Queensland_Pitch_drop_experiment-white_bg.jpg
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Is glass a solid or a viscous liquid?

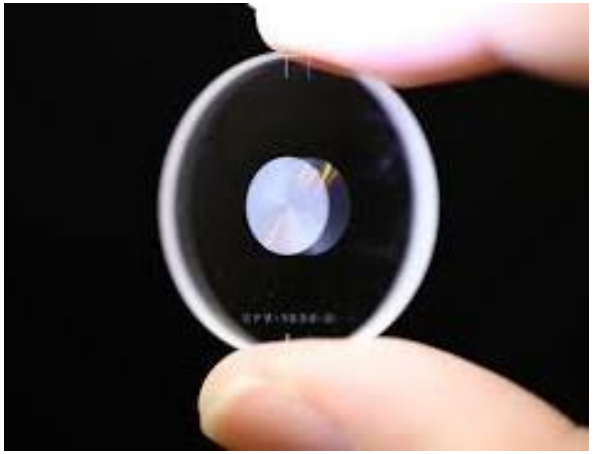


"It is well known that panes of stained glass in old European churches are thicker at the bottom because glass is a slow-moving liquid that flows downward over centuries."

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"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



Silica data storage disc © unknown. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/

Is glass a solid or a viscous liquid?

Solid

Elasticity

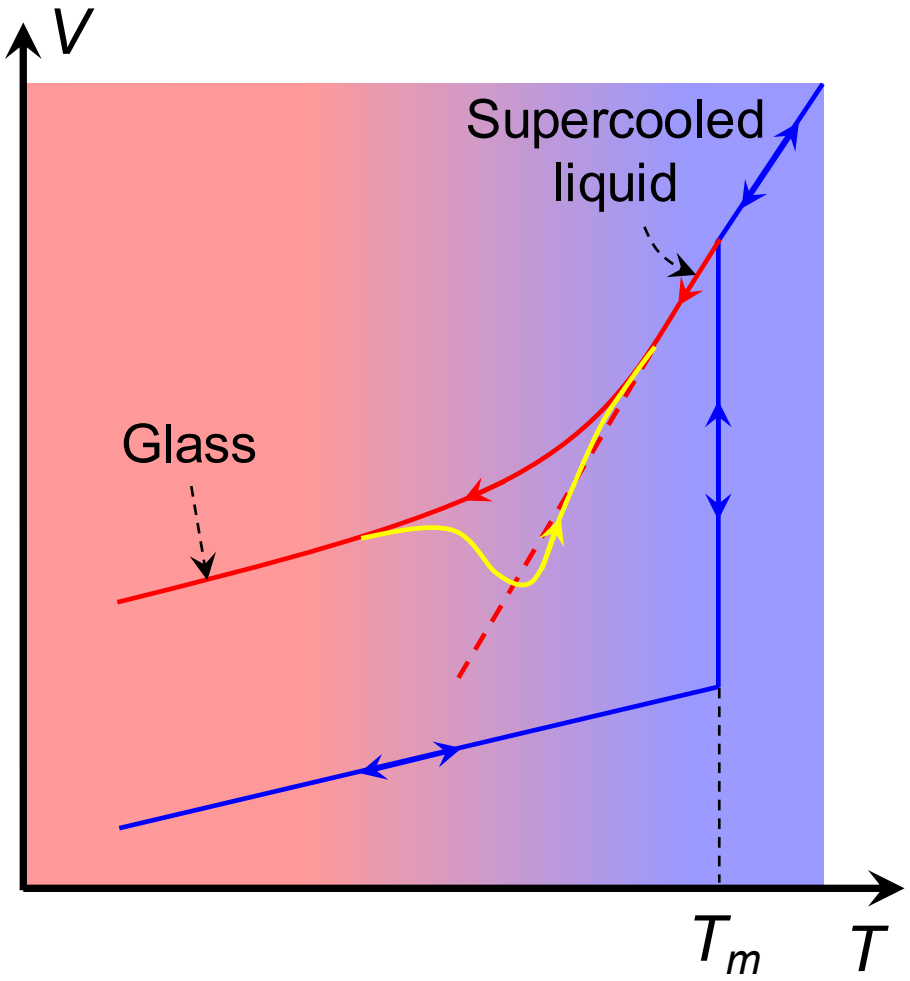
instantaneous, transient

$\sigma_x = E\varepsilon_x$

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

E : Young's modulus

G : shear modulus



Liquid

Viscosity

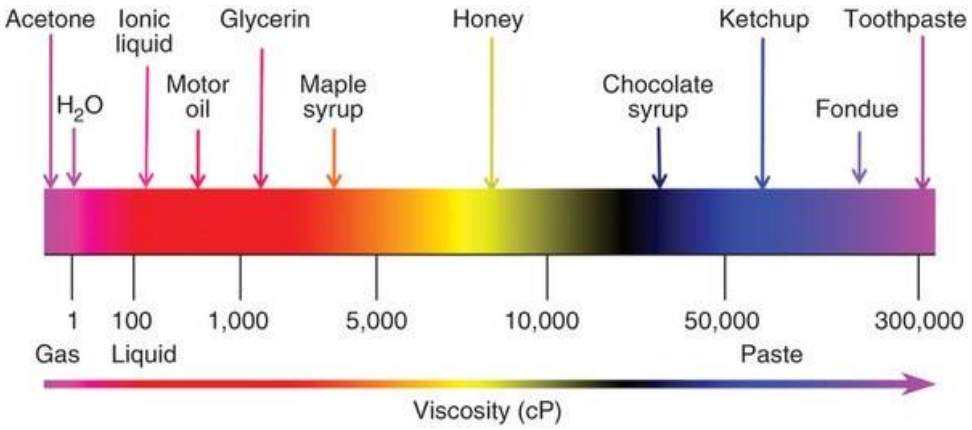
time-dependent, permanent

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

η : viscosity (unit: Pa·s or Poise)

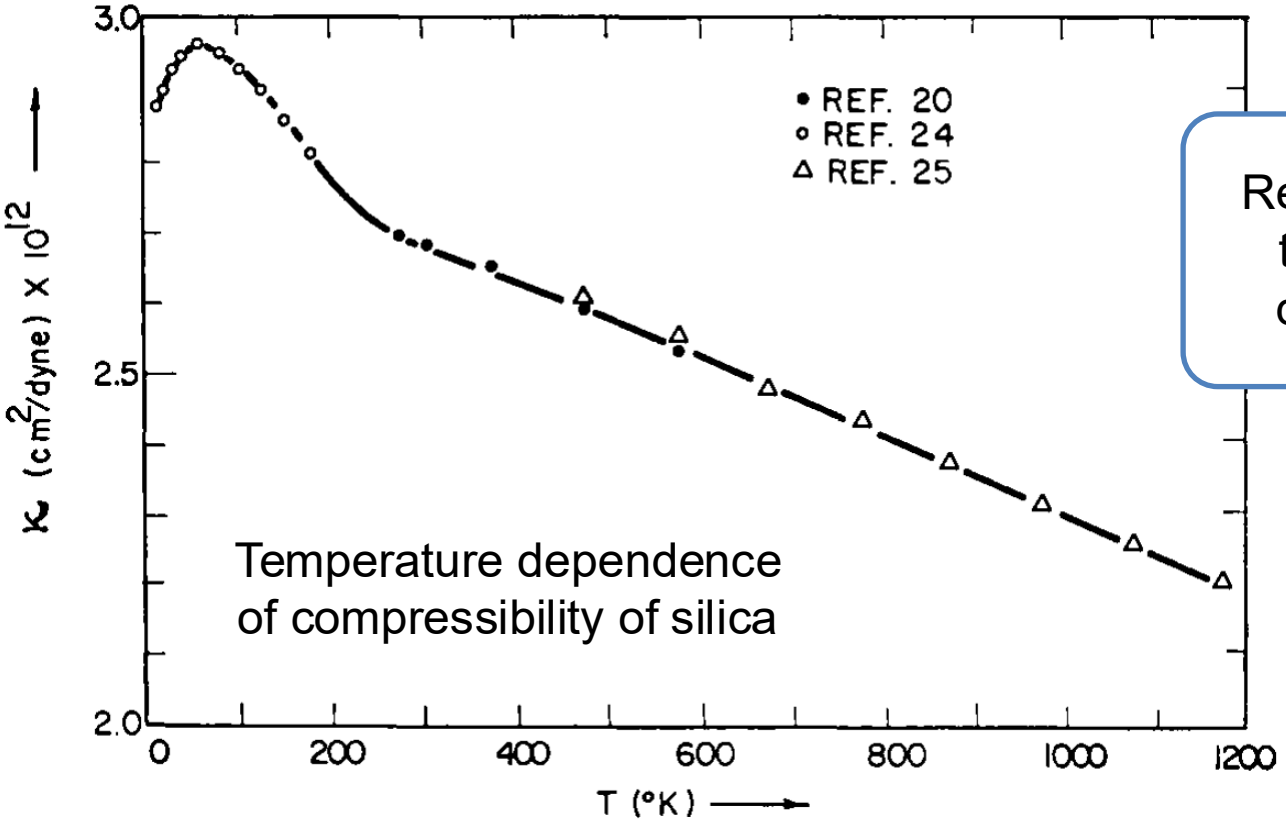
Microscopic origin of elasticity and viscosity

- 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

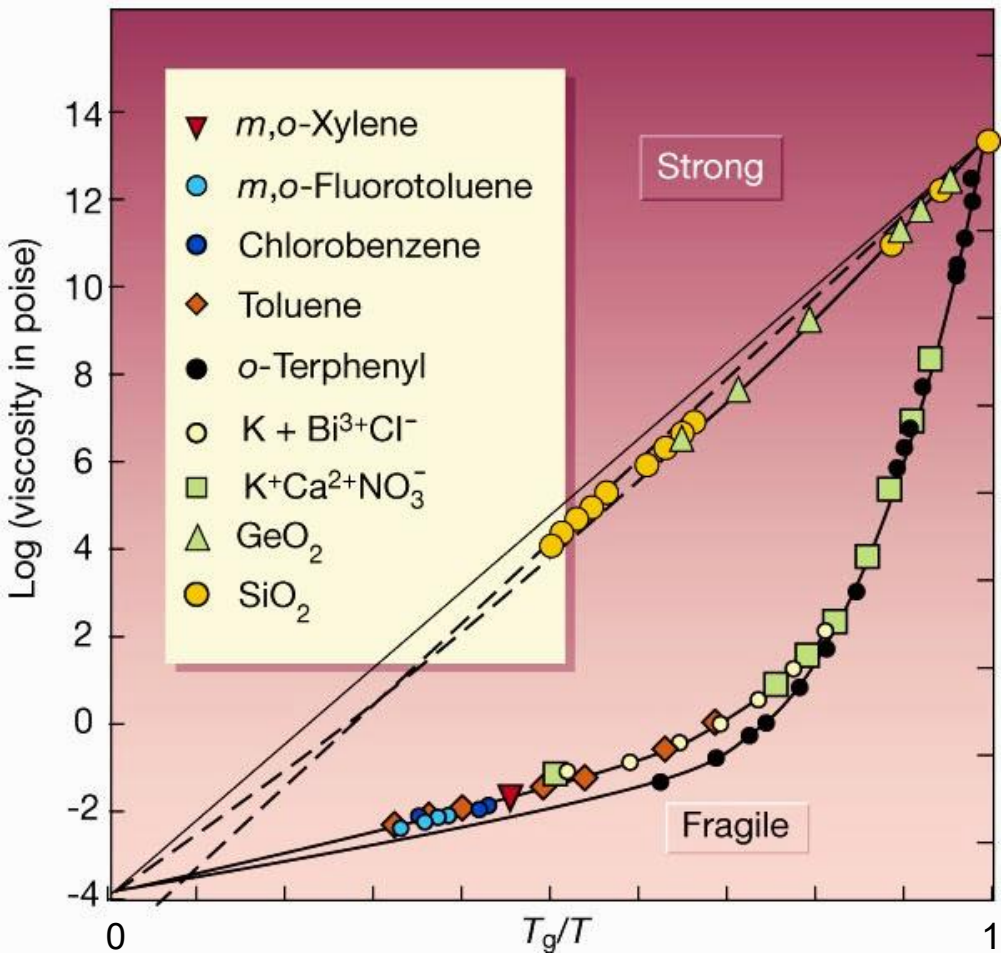
- Viscous flow is a thermally activated process

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

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 (Williams-Landel-Ferry equation)

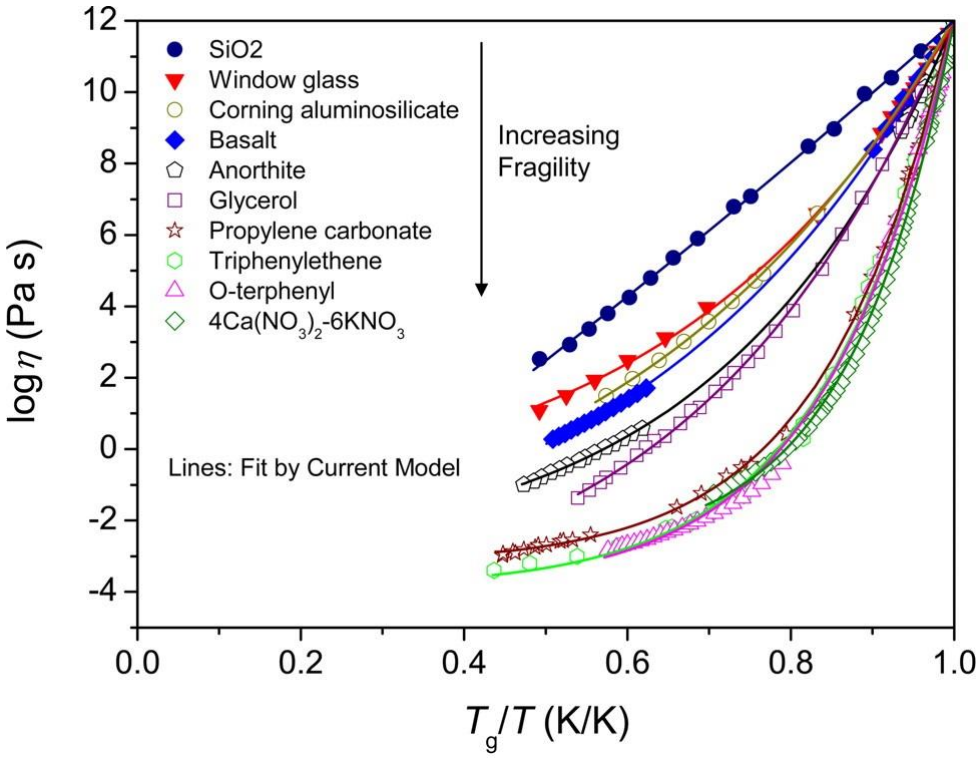
$$\eta = \eta_0 \exp\left(-\frac{A}{T - T_{VFT}}\right)$$

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

The MYEGA equation of viscosity

- The VFT equation diverges at low temperature
- The Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation:

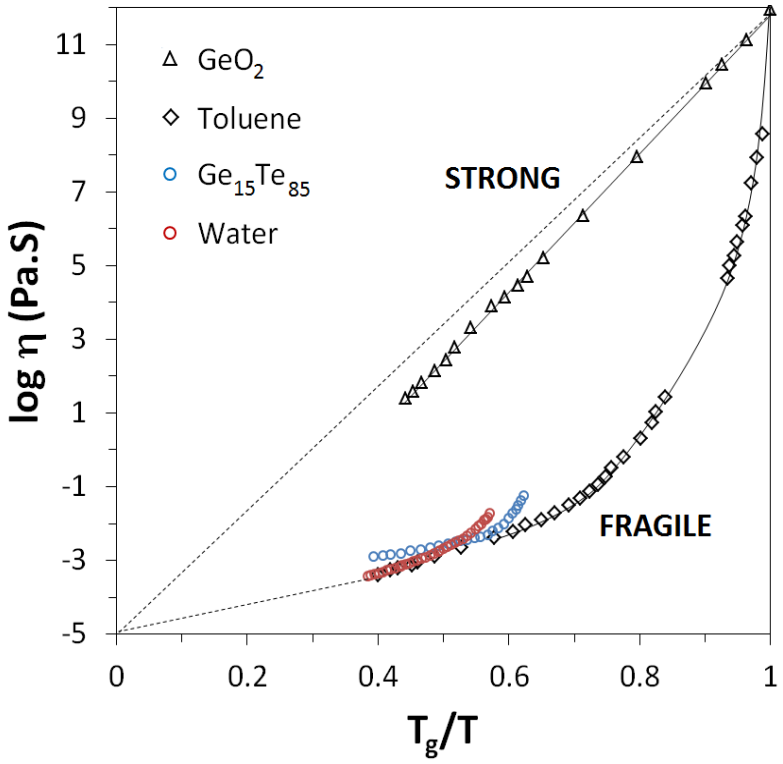
$$\log_{10}\eta(T) = \log_{10}\eta_0 + \frac{K}{T}\cdot\exp\left(\frac{C}{T}\right)$$



Proc. Nat. Acad. Sci. U.S.A. **106**, 19780-19784 (2009)

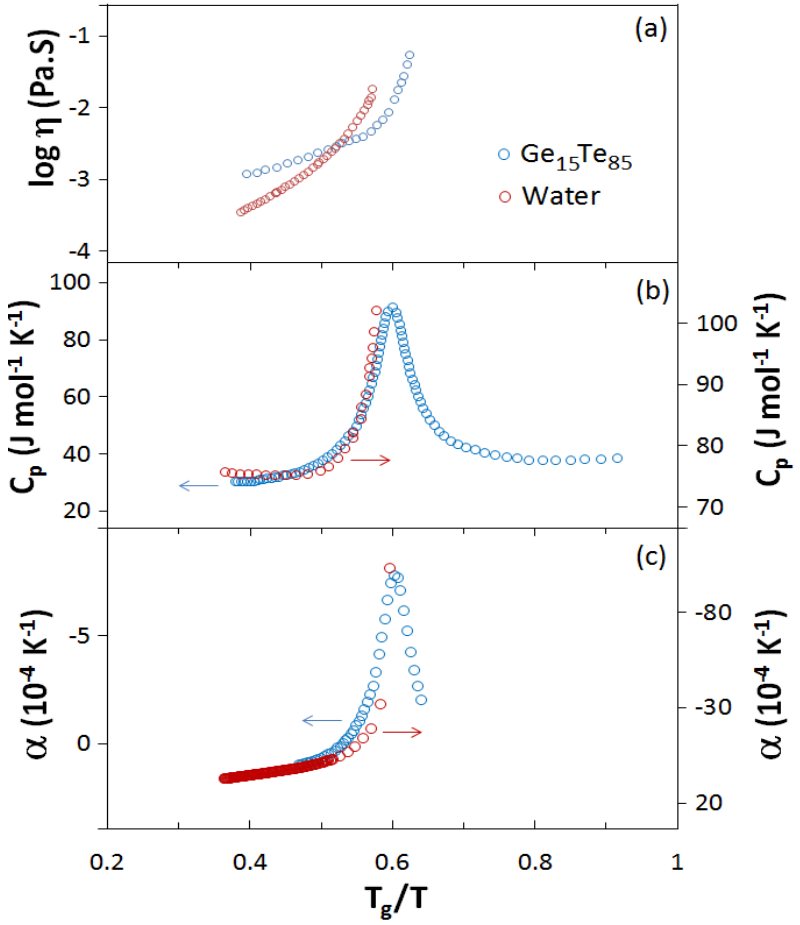
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Viscosity anomaly: fragile-to-strong transition



Underlying liquid-liquid phase transition

J. Non-Cryst. Solids X **4**, 100034 (2019)

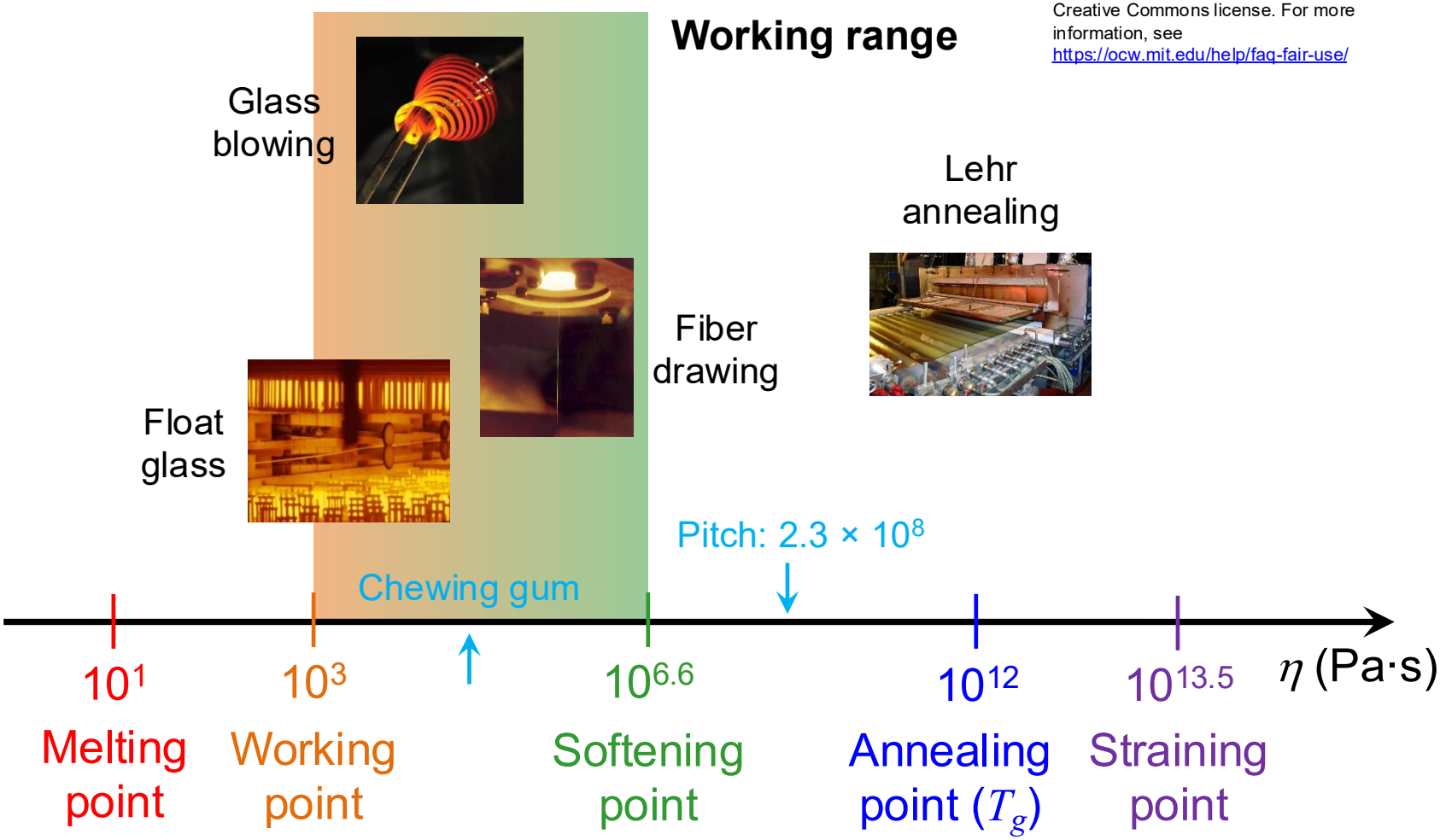


Figures 1 and 3 in Pierre Lucas, Fragile-to-strong transitions in glass forming liquids, Journal of Non-Crystalline Solids: X, Volume 4, 2019, 100034, ISSN 2590-1591, https://doi.org/10.1016/j.nocx.2019.100034. License: CC-BY

Viscosity reference points

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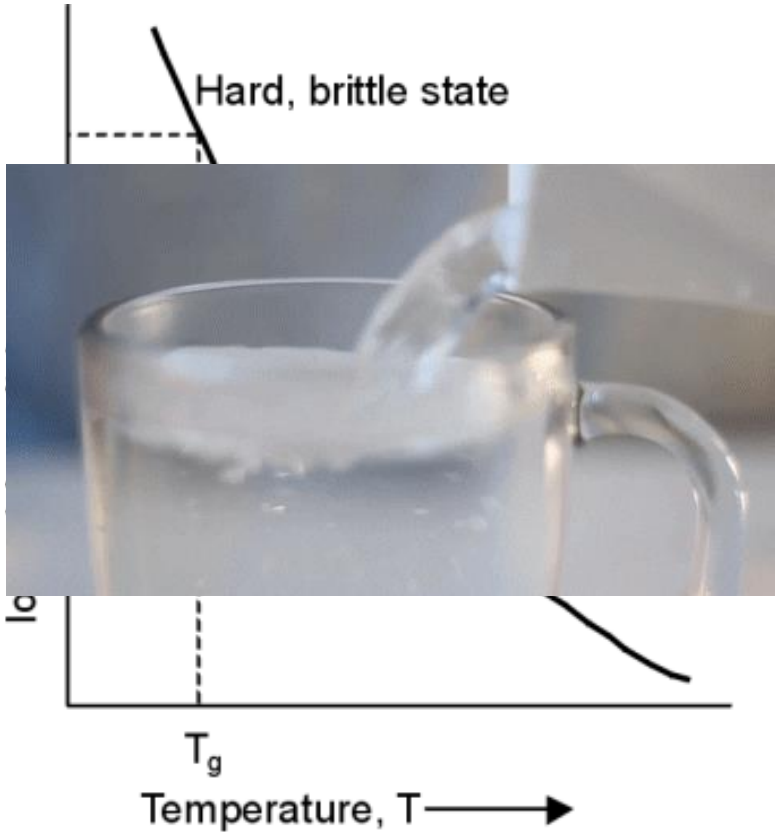
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Temperature-dependent viscosity of polymers

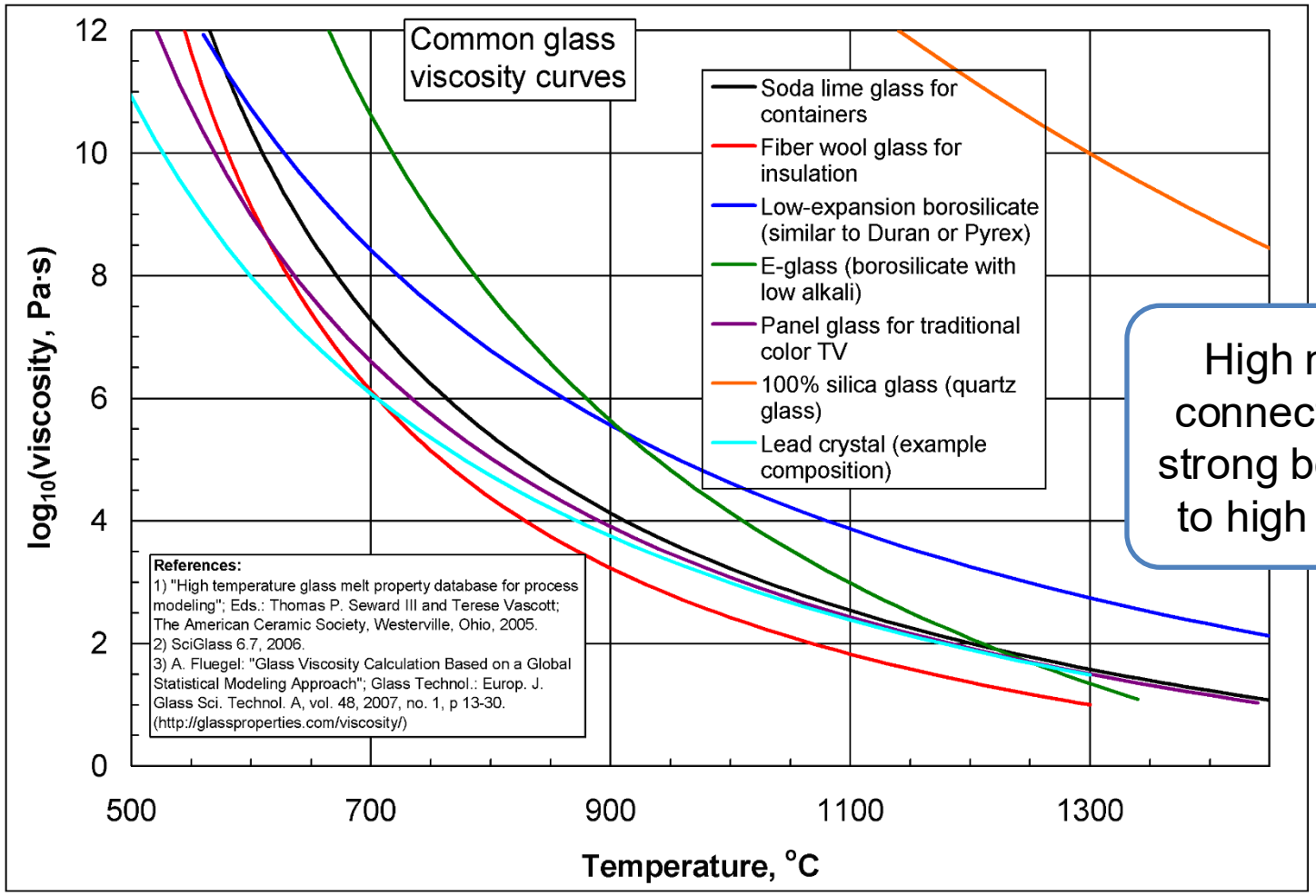


- All polymers with some level of an amorphous phase exhibit glass transition
- Above T_g, there is a large-scale cooperative movement of polymer chain segments
- Engineering T_g in polymers
  - Adding stiff chemical groups (e.g. benzene) increases T_g
  - Adding plasticizers decreases T_g

K. Budinski, *Engineering Materials: Properties and Selection*

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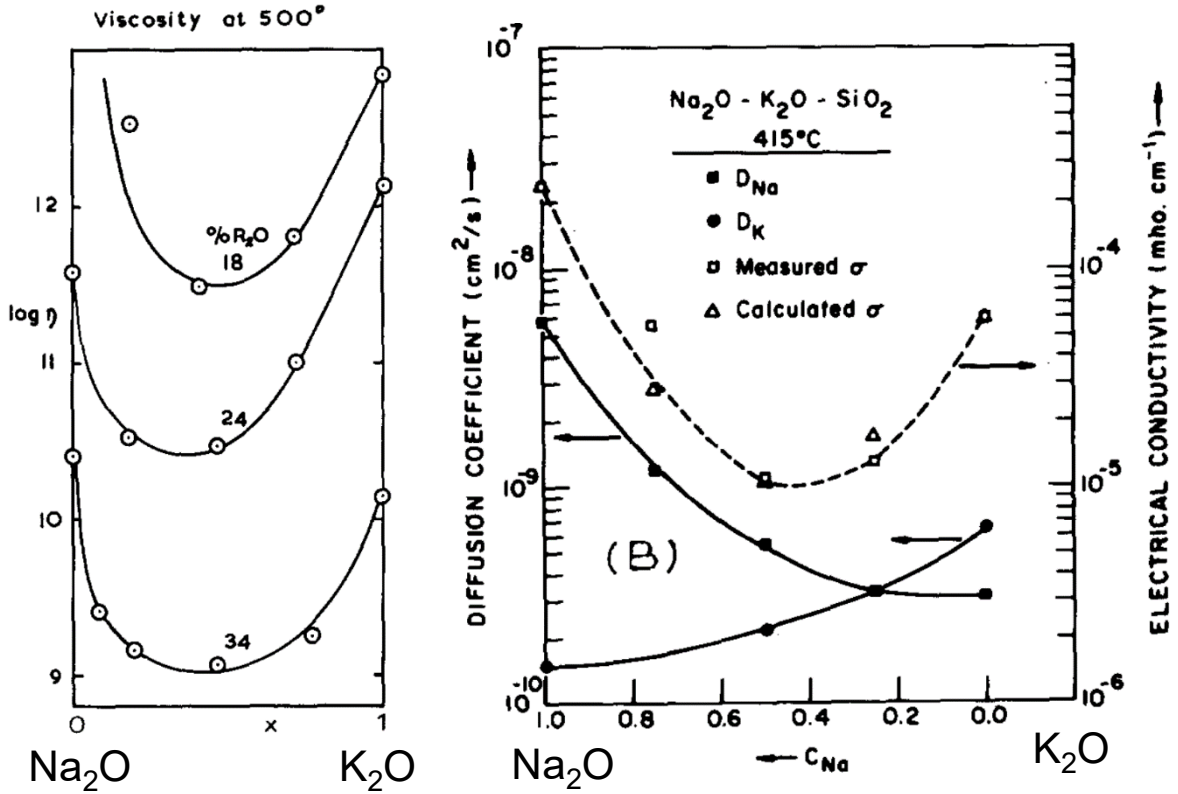
Composition dependence of viscosity



High network connectivity and strong bonds lead to high viscosity

Mixed alkali effect (MAE)

- 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).

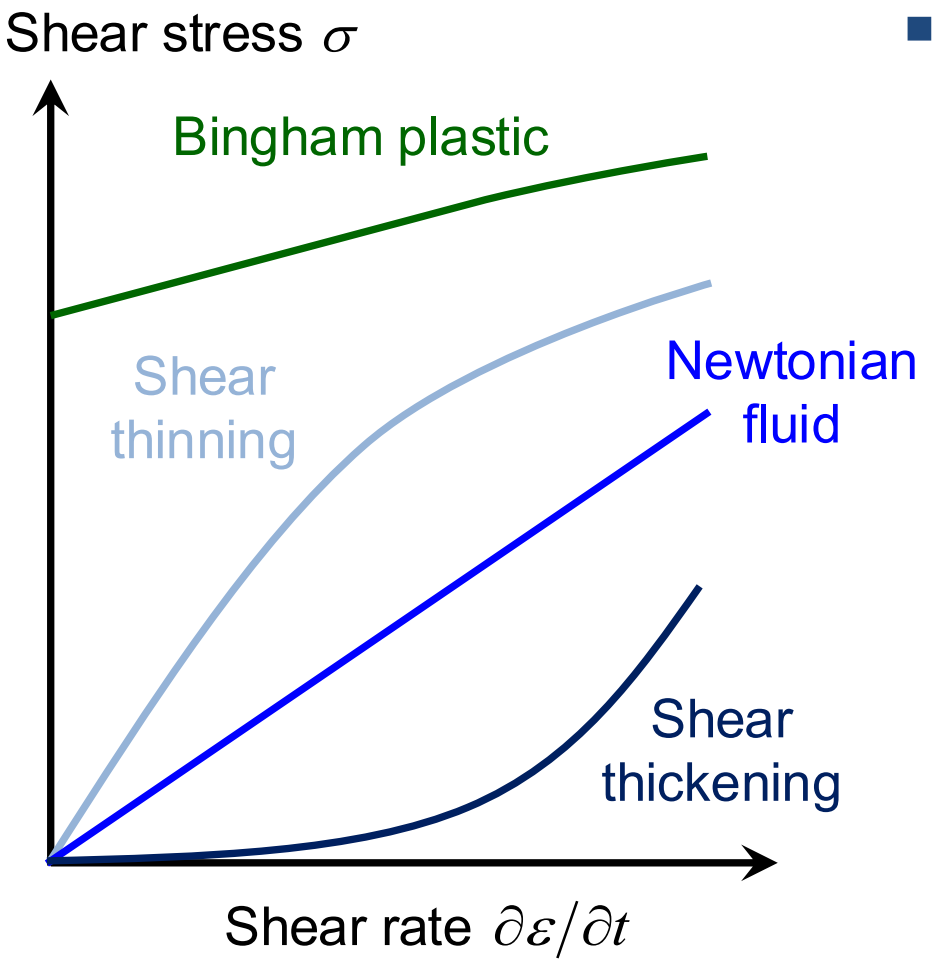
Figure 12 from J.O. Isard, "The mixed alkali effect in glass." Journal of Non-Crystalline Solids, Volume 1, Issue 3. Courtesy of Elsevier, Inc., https://www.sciencedirect.com. Used with permission.

The thermometer effect

"*In the last century and before, most thermometers were made of 'Thüringer Glas' which contains silica, lime and, more importantly, equal portions of (mobile) sodium and potassium ions. The problem with these thermometers was that they were rather inaccurate. If a calibrated thermometer was put into boiling water and later into ice of 0 °C, the thermometer did not show 0.0 °C, but about −0.5 °C. This so-called zero point depression took several months to vanish, if the thermometer was stored at room temperature. If it was heated up and cooled down, the effect occurred again. Weber found out in 1883 that this unwished relaxation effect could be diminished by a factor of 10 if only one type of alkali ion (sodium or potassium) was present in the glass, and little later Schott developed the first accurate Li-based thermometer.*"

From *Solid State Ion.* **105**, 1-13 (1998)

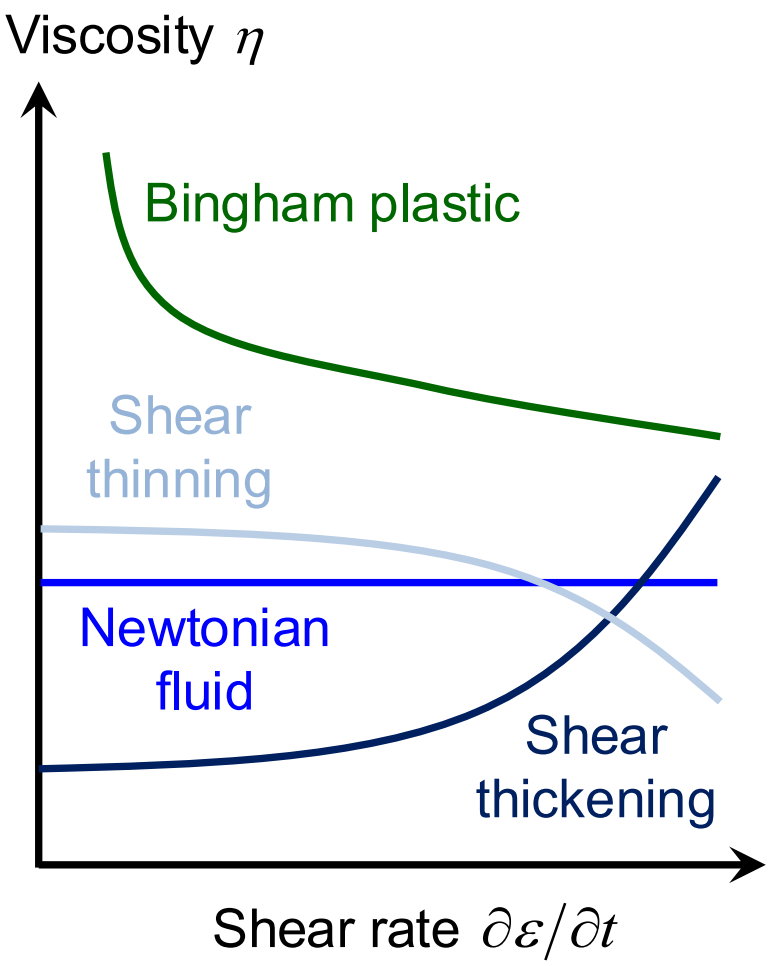
Non-Newtonian behavior



- Rate dependent viscosity

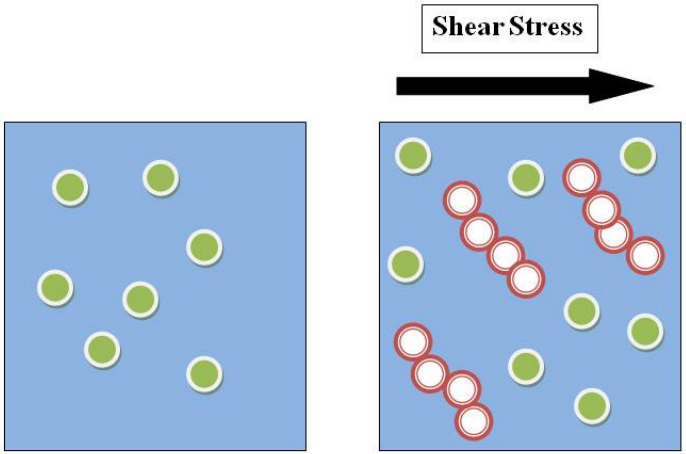
$$\sigma_{xy} = \eta\left(\frac{\partial \varepsilon_{xy}}{\partial t}\right)\cdot\frac{\partial \varepsilon_{xy}}{\partial t}$$

Non-Newtonian behavior



- Rate dependent viscosity

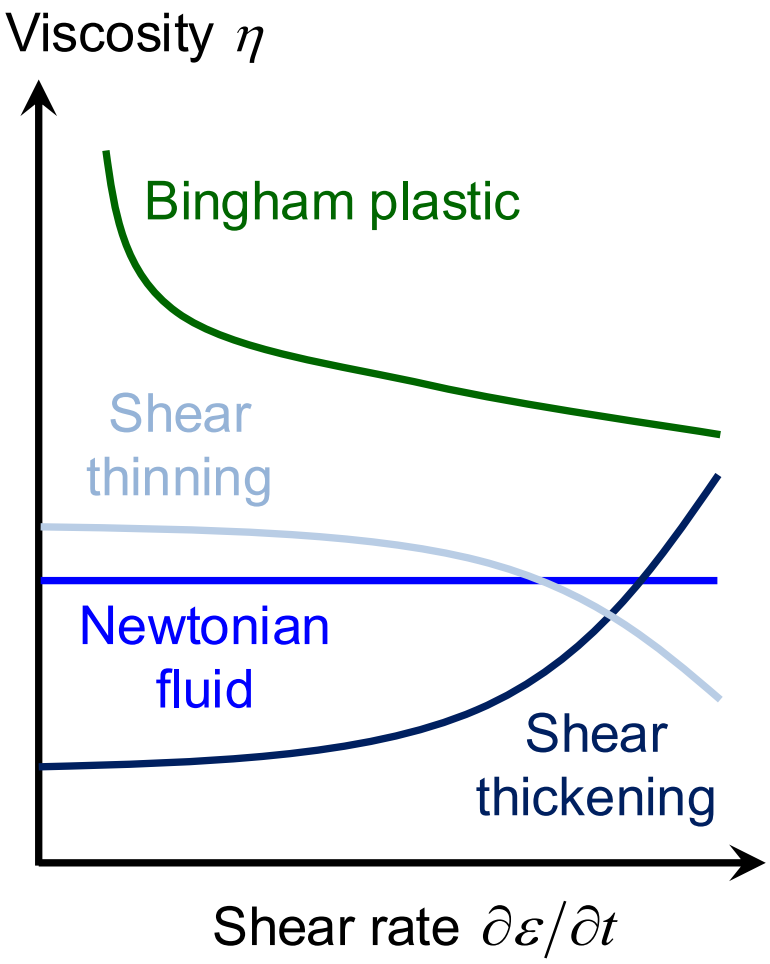
$$\sigma_{xy} = \eta\left(\frac{\partial \varepsilon_{xy}}{\partial t}\right)\cdot\frac{\partial \varepsilon_{xy}}{\partial t}$$



Hydroclustering (Image from Wiki)

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Non-Newtonian behavior



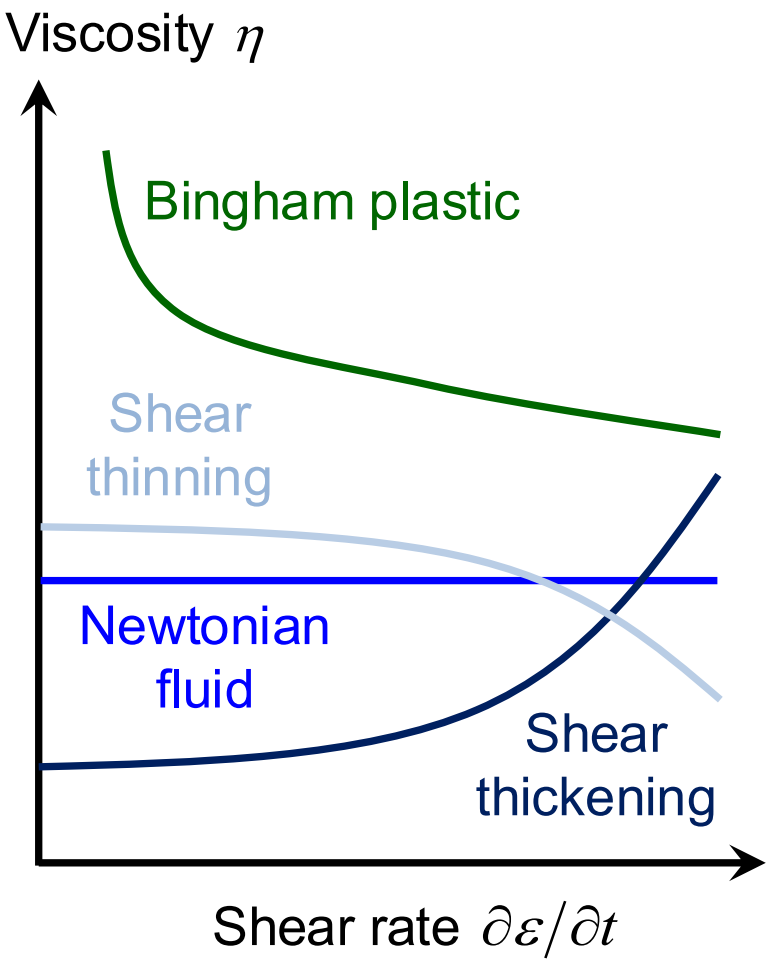
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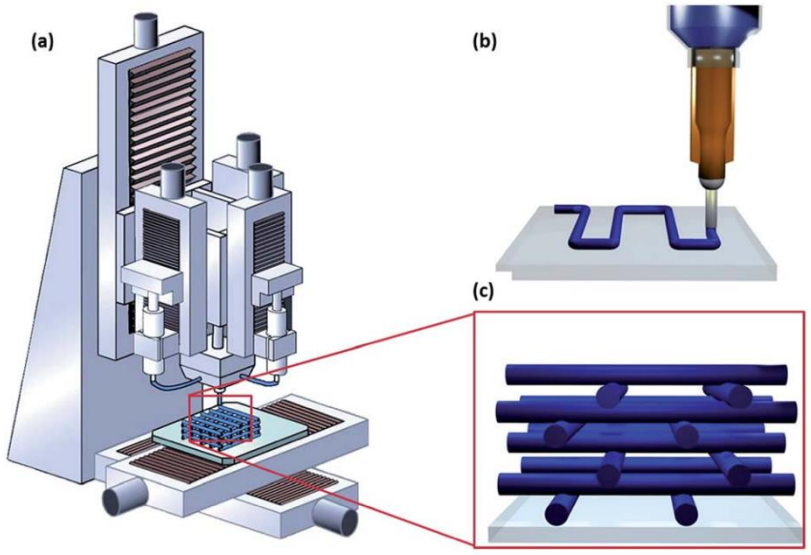
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Non-Newtonian behavior



- Rate dependent viscosity

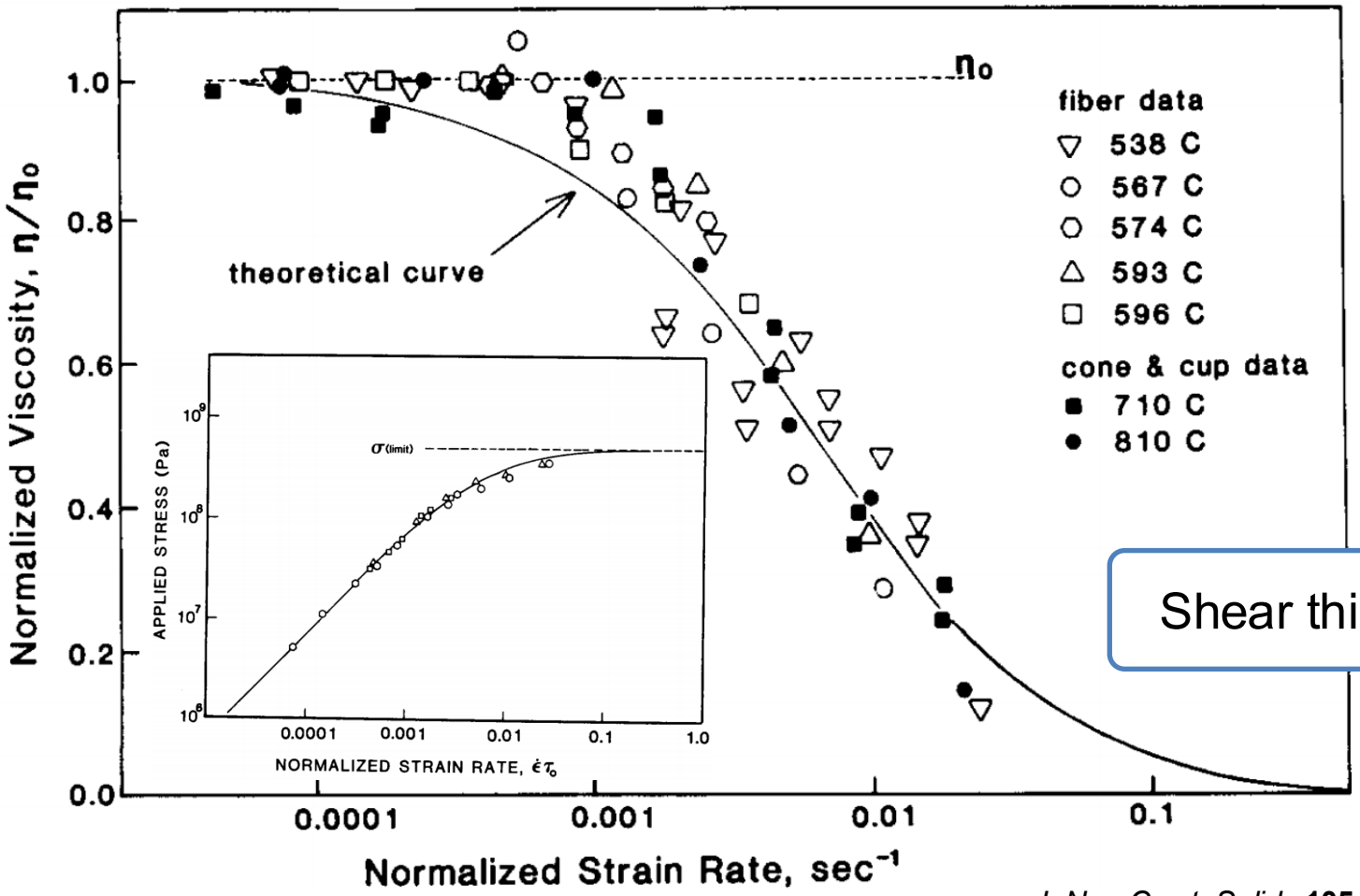
$$\sigma_{xy} = \eta\left(\frac{\partial \varepsilon_{xy}}{\partial t}\right)\cdot\frac{\partial \varepsilon_{xy}}{\partial t}$$



Nanoscale **6**, 10470 (2014)

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Non-Newtonian behavior of soda-lime glass

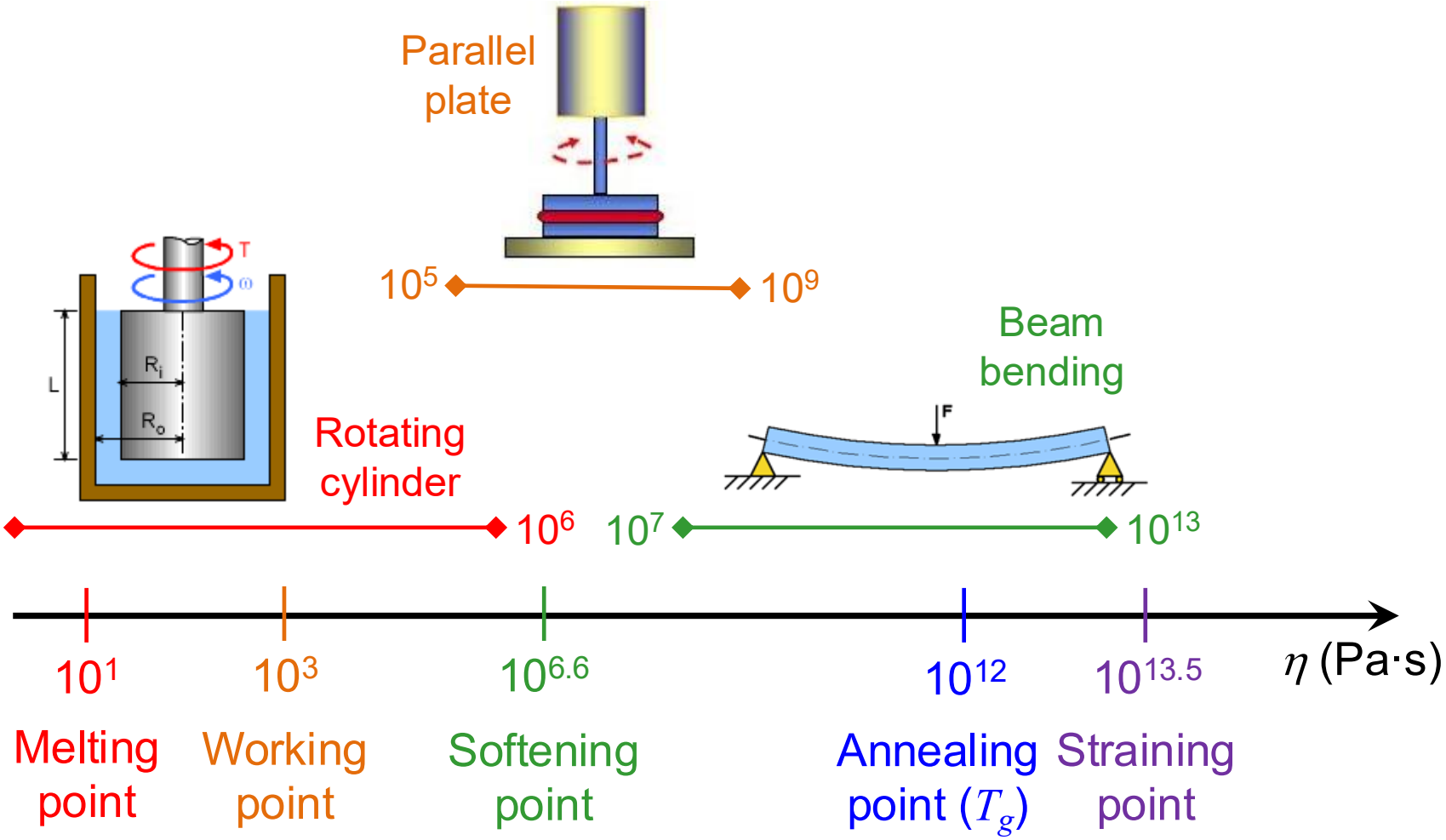


Shear thinning

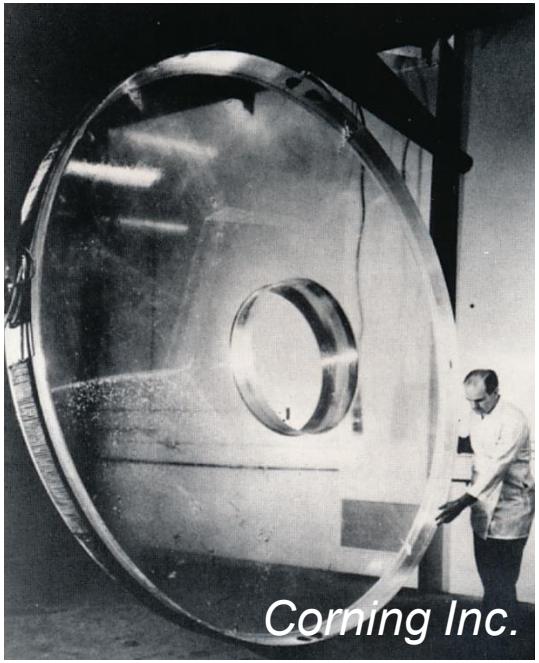
J. Non-Cryst. Solids **105**, 313-322 (1988)

Figure 8 in J. Non-Cryst. Solids 105, 313-322 (1988). Courtesy of Elsevier, Inc., https://www.sciencedirect.com. Used with permission.

Viscosity measurement: viscometry



Precision viscometry based on optical interferometry



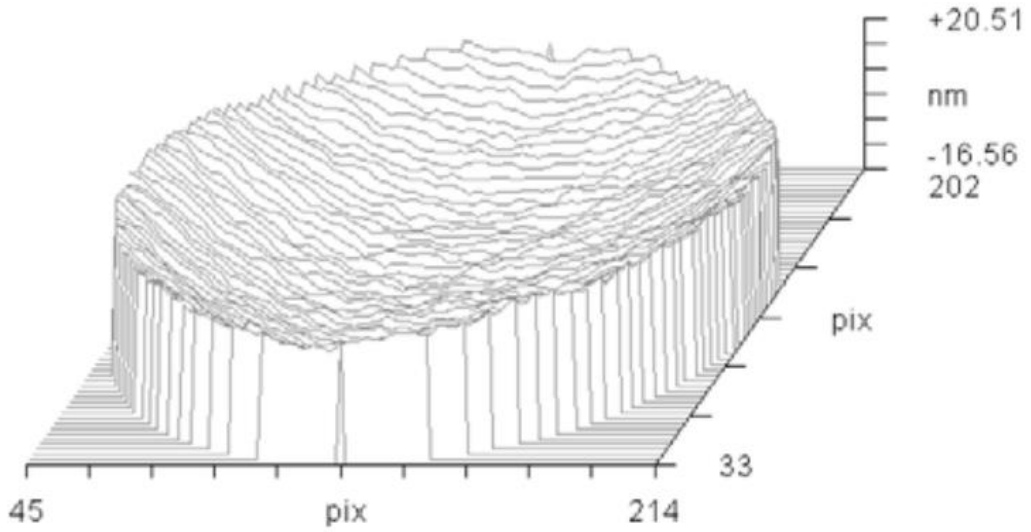


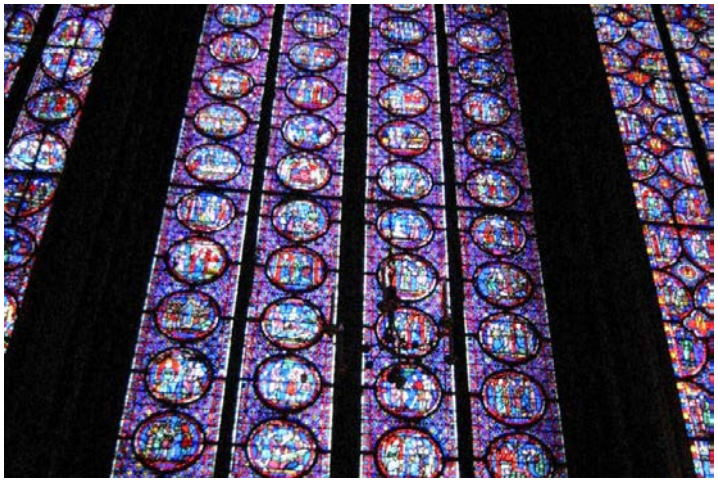
Fig. 1. Surface map of plate TF81 in 2008.

"… 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…"*

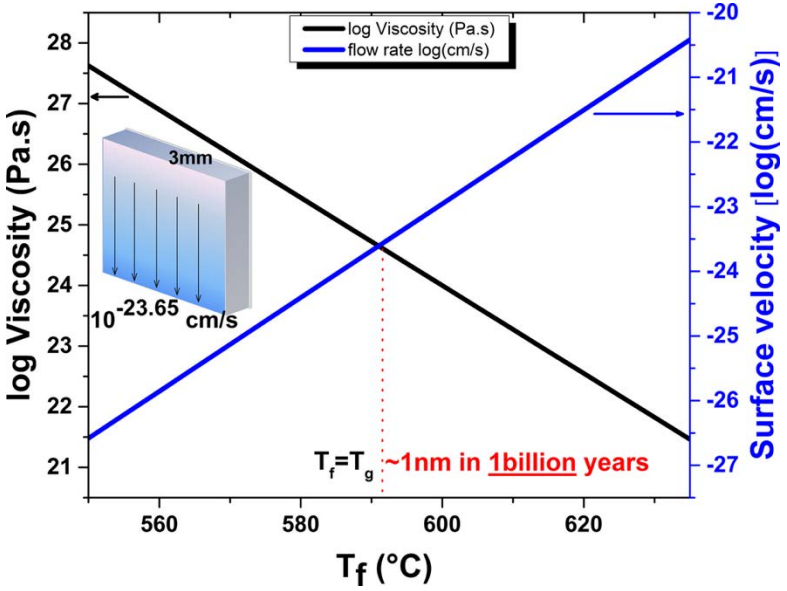
M. Vannoni *et al.*, *Eur. Phys. J. E* **34**, 92 (2011)

Figure 1 in Vannoni, M., A. Sordini, G. Molesini. "Relaxation time and viscocity of fused silica glass at room temperature." Eur. Phys. J. E 34 (2011): 92. © Springer Nature. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use/

Is glass a solid or a viscous liquid?



"Chocolate Melts,
Flowers Wilt,
~~Diamonds~~ are Forever"
Glasses



"Depending on the thermal history of the glass, the room temperature viscosity is on the order of 10^{24} to 10^{25} Pa·s... Using analytical expressions to describe the glass flow over a wall, we calculate ***a maximum flow of ~1 nm over a billion years****."*

DOI: 10.1111/jace.15092

Figure 4 in Gulbiten O, Mauro JC, Guo X, Boratav ON. Viscous flow of medieval cathedral glass. J Am Ceram Soc. 2018; 101: 5–11. © Wiley. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use/

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

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