Optical and Photonic Glasses

Lecture 10:
Viscosity of Glasses

Professor Rui Almeida

International Materials Institute
For New Functionality in Glass
Lehigh University

Viscosity (η)

Viscosity is the property which more directly controls glass-forming ability from the melt.

As previously discussed:

rate of homogeneous nucleation: $I_v \propto \exp(-\Delta G_m/RT) \sim \propto 1/\eta$ (with $\Delta G_m \sim E_\eta$)

rate of crystal growth: $u \propto \Delta T/\eta$

Also, the time needed for *fining* of the melt (removal of gas bubbles), is a function of the rate of rise of bubbles to the surface of the molten glass, given, for spherical bubbles of radius r in a melt of density ρ, by Stokes law:

$$v = 2/9 \ g \ r^2 \ \rho/\eta$$

For a *newtonian* fluid, the viscosity is constant at a given temperature and it is defined by Newton's law as:

$$\eta = \tau / (d\varepsilon/dt) \qquad \text{(in units of Pa.s)}$$

when a shear stress τ causes a rate of shear $d\varepsilon/dt$ (ε being the deformation).

When the viscosity of a fluid is not constant at a given temperature, but rather depends on the rate of shear, the fluid is said to be *non-newtonian*.

If the viscosity at a given temperature increases with the shear rate, the fluid is said to be *dilatant* (which is the case of mayonnaise, for example). If the viscosity decreases with the shear rate, rather, the fluid is said to be *pseudoplastic* (which is the case of ketchup, as another well known example).

Newtonian and non-newtonian behaviors

Glass-forming melts at high shear stresses may approach a pseudoplastic (also called *shear thinning*) behavior. This may become important during high speed pressing and blowing operations, as typically carried out in IS machines.

T = const.

Classes of non-Newtonian behavior.
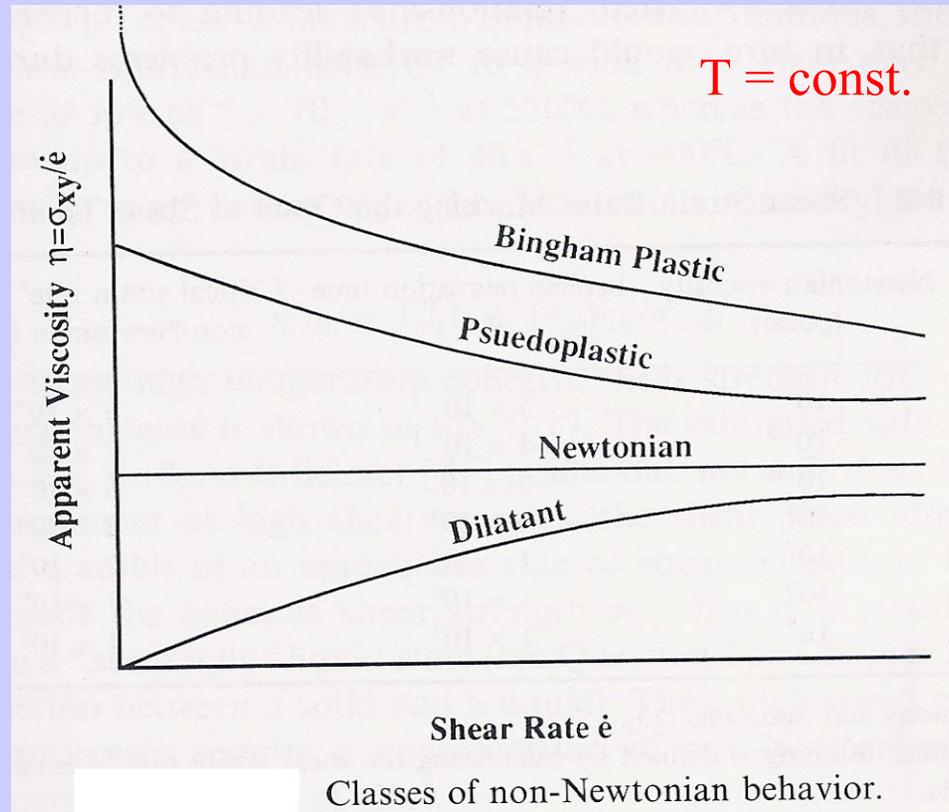
(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

The viscosity of molten glass is a strong function of **temperature**, rapidly decreasing when the temperature increases.

Variation of the viscosity of a common soda lime silica glass with temperature.
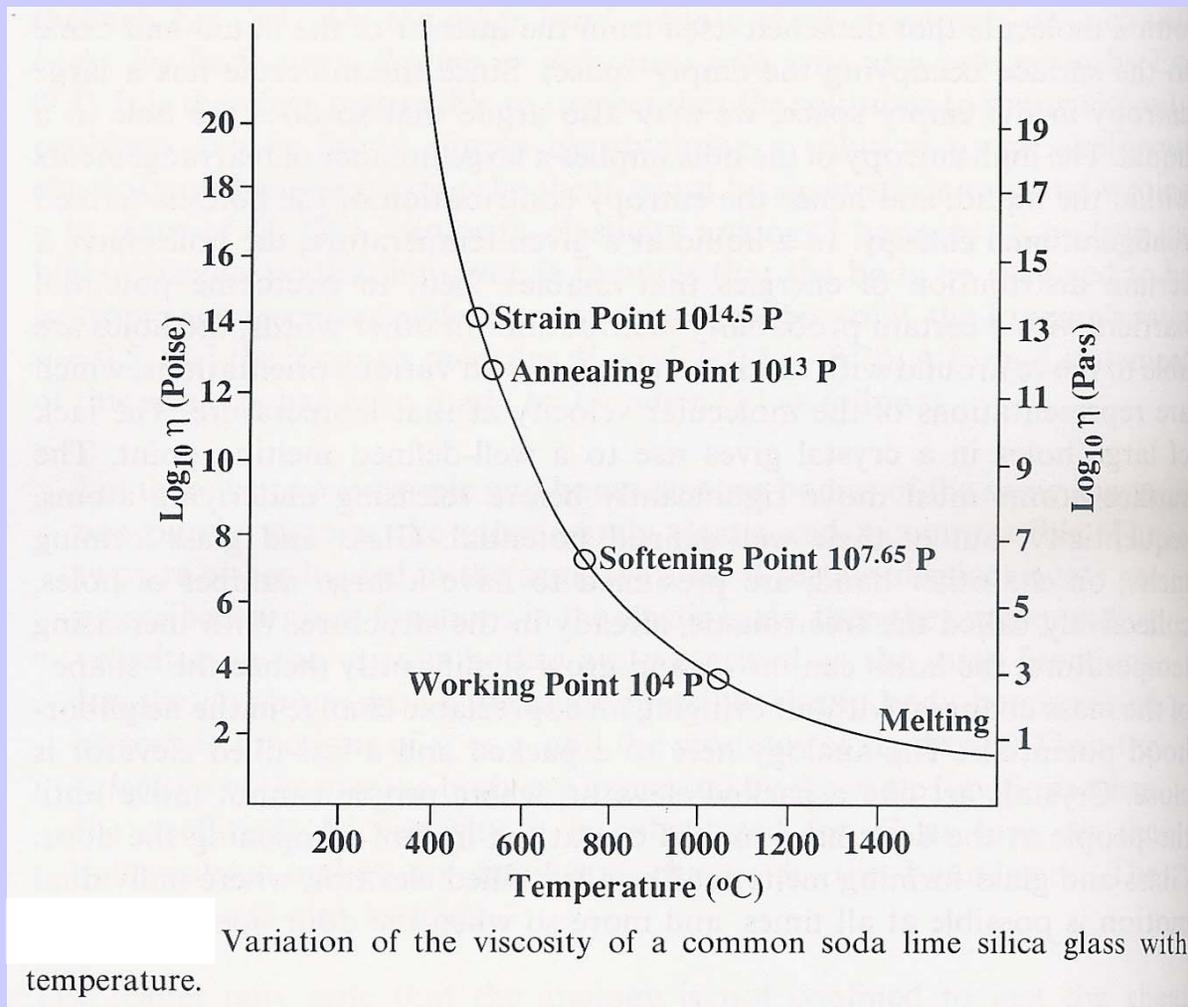
(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

Given the importance of viscosity in glass technology, there are five standard viscosity reference *points* (or temperature *ranges*):

- melting (fining)   *point* $\rightarrow$ T @ $\eta = 10$ Pa.s

- working (forming)   " $\rightarrow$ T @ $\eta = 10^3$ "

- softening (Littleton)   " $\rightarrow$ T @ $\eta = 10^{6.65}$ "

- annealing (T_g)   " $\rightarrow$ T @ $\eta = 10^{12}$ "

- strain   " $\rightarrow$ T @ $\eta = 10^{13.5}$ "

Stress release from the glass occurs in a matter of minutes at the annealing temperature and in a matter of hours at the strain point.

Viscosity standard reference points (°C)

Glass	Softening	Annealing (T_g)	Strain
v–SiO_2	1600	1100	1000
Borosilicate	820	565	520
Soda–lime	700	510	470

Effect of temperature and composition on glass viscosity
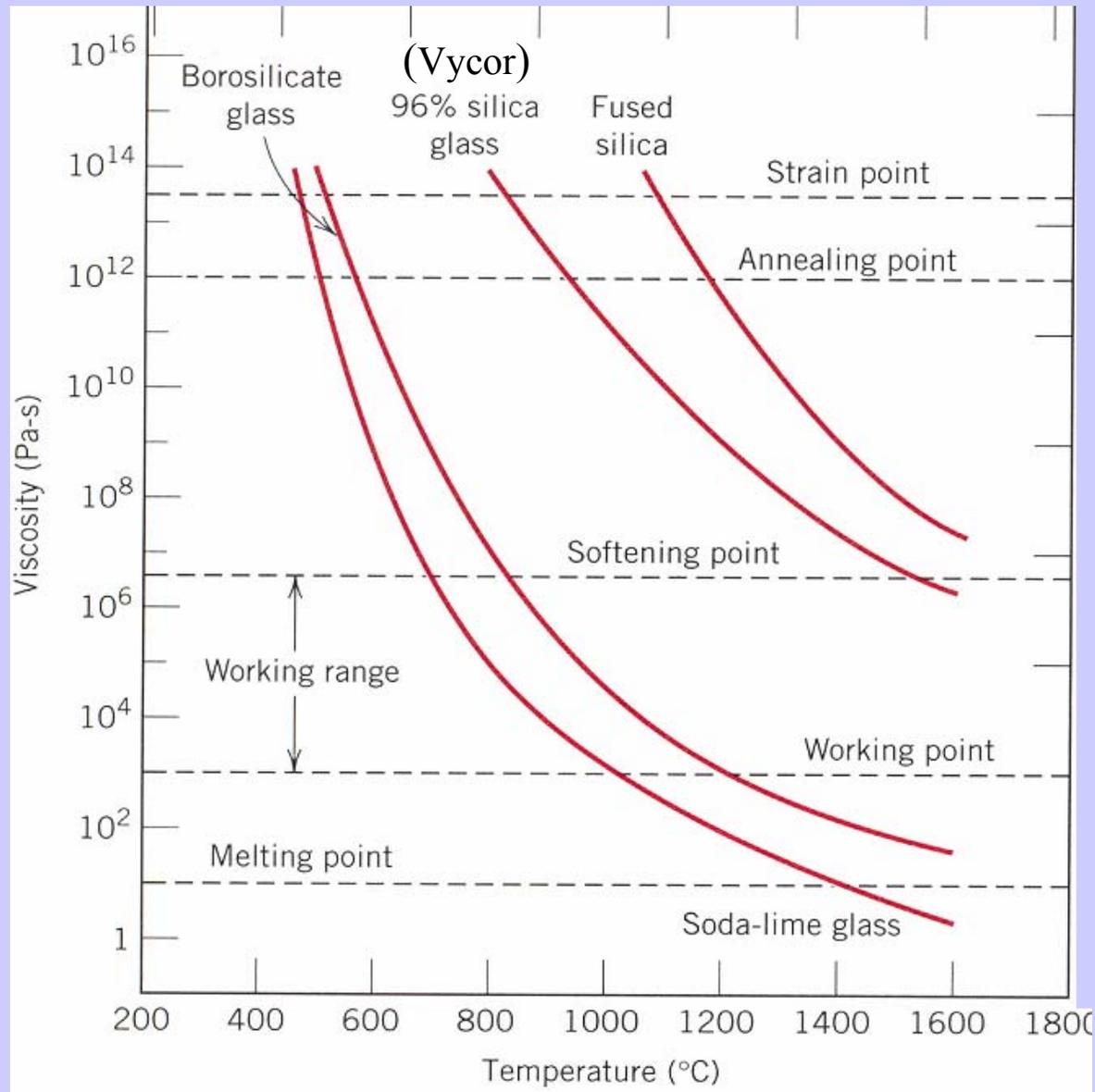
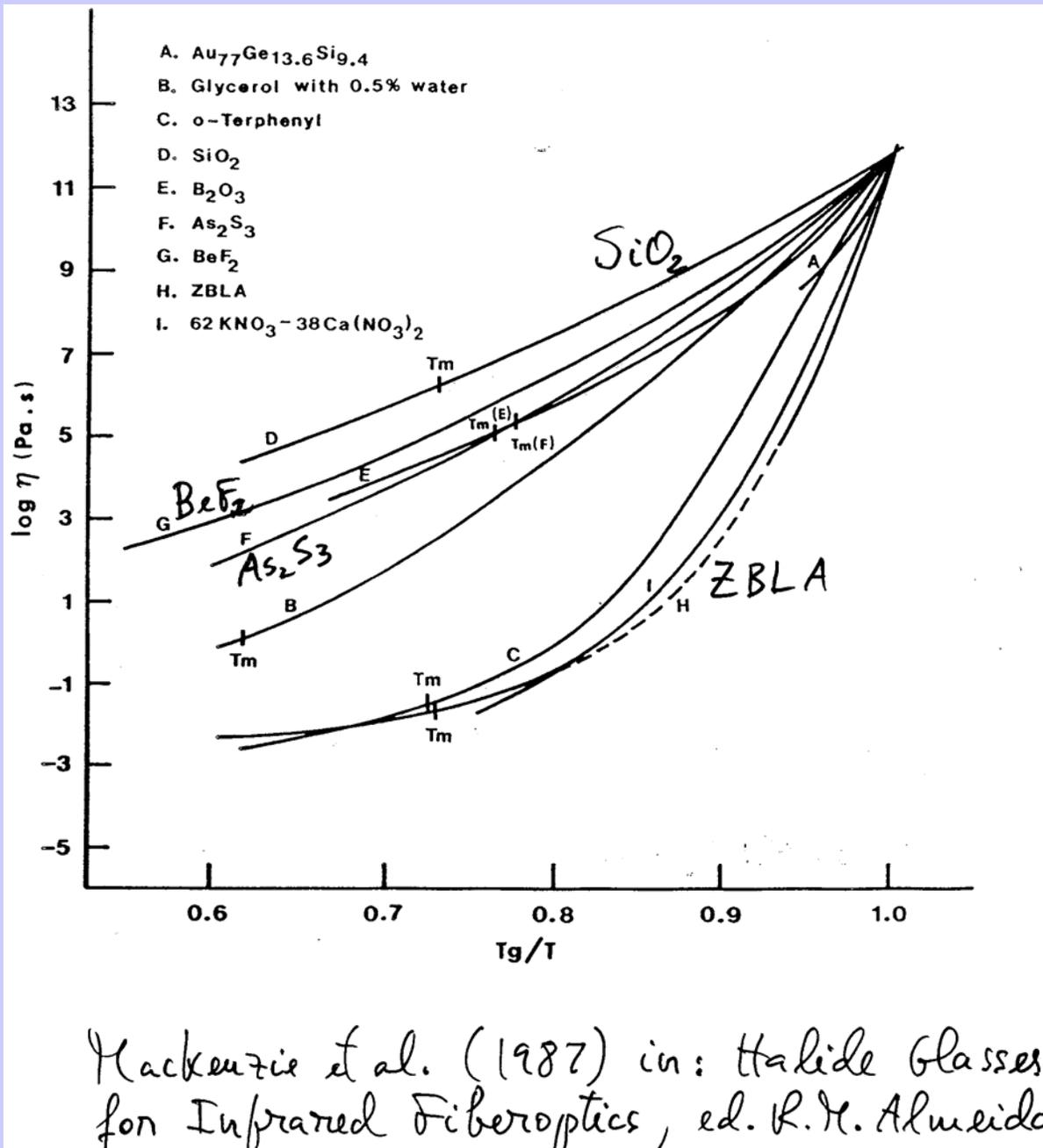(Adapted from: *Materials Science and Engineering*, W.D. Callister, John Wiley, 1994)

The variation of molten glass viscosity with temperature often follows the Arrhenius law:

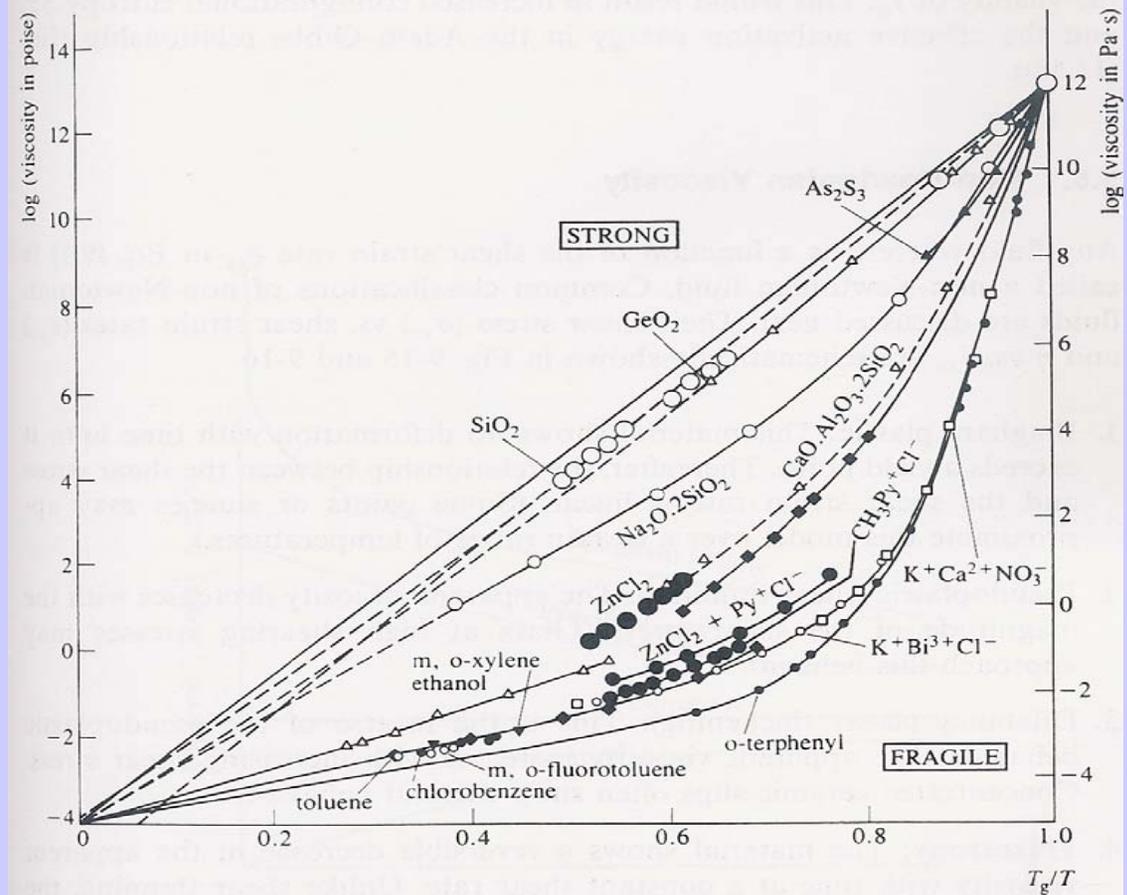$$\eta = \eta_o \exp(E_\eta/RT) \qquad (T \to \infty \; => \; \eta \to \eta_o)$$

where E_η is the activation energy for viscous flow (in kJ/mol), independent of temperature and of the order of the activation energy for diffusion across the liquid matrix/nucleous interface, ΔG_m, in the expression of homogeneous nucleation rate, I_v.

Arrhenius behavior is the case especially with melts with **strong glass-forming ability** (SiO_2, GeO_2, BeF_2, ...), sometimes referred as *strong* liquids.

On the other hand, strongly modified melts, or melts with **weak glass-forming ability**, like most glass-forming halides (ZrF_4–based compositions, $ZnCl_2$, ...), usually exhibit an activation energy for viscous flow which strongly decreases with increasing temperature, due to an accelerated depolymerization of the melt structure. Such melts are sometimes referred as *fragile* liquids, in a terminology due to C.A. Angell (1986).

A. $Au_{77}Ge_{13.6}Si_{9.4}$
B. Glycerol with 0.5% water
C. o-Terphenyl
D. SiO_2
E. B_2O_3
F. As_2S_3
G. BeF_2
H. ZBLA
I. $62 KNO_3 - 38 Ca(NO_3)_2$

Mackenzie et al. (1987) in: Halide Glasses for Infrared Fiberoptics, ed. R.M. Almeida

Variation of log(viscosity) versus T_g/T for "strong" and "fragile" liquids. (After Angell [19]. Reproduced with permission of Elsevier Science Publishers.)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

The temperature dependence of the viscosity of *fragile* liquids cannot be described by the Arrhenius equation and more complex expressions become necessary, such as the Vogel-Fulcher-Tammann equation, valid for $T > T_o$ (T_o, adjustable parameter $\sim T_g$):

$$\eta = \eta_o \exp[Q/(T-T_o)] \qquad \text{(Q independent of T)}$$

Fictive temperature (T_f)

This is the temperature at which the actual atomic scale structure of a quenched glass would be the *metastable equilibrium* structure (relative to the crystalline state) of the corresponding supercooled liquid (scl). One always has:

$$T_f \geq T_g$$

T_f can also be defined as the temperature at which the structure of the scl was *instantaneously frozen* into the glassy state, which has therefore kept the original structure of the scl and it can be estimated by the intersection between the supercooled liquid line and the extrapolated glass line, in a specific volume vs. temperature diagram of the type previously shown. For slow enough cooling rates, $T_f \rightarrow T_g$. For fast cooling, T_f may become considerably larger than the value of T_g measured at typical heating rates of $\sim$ 10-20 Ks^{-1}.