Go with the flow

>>>>>>>>>>>>>

Viscosity of glass melts

V i s c o s i t y o f g l a s s m e l t s

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Outline

- Overview of fundamentals
- The non-Newtonian flow
- New approach to the $\eta \sim T$ relation
- New way to determine the cooling rate of glass fibers

About flow

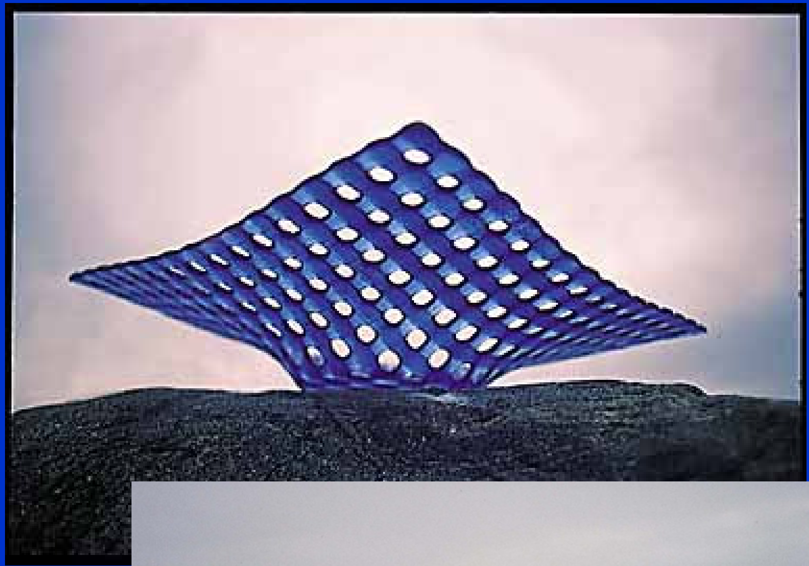
Haraclitus:
"*everything is in a state of flux*".

Confucius (孔夫子) stood by a river:
"*Everyting flows like this, without ceasing, day and night*".

Deborah:
"*Everything flows if you wait long enough, even the mountains*".

Flow is everywhere!

Flow is beautiful!



Flow is remarkable, but sometimes dangerous!

In philipin

In Hawaii

How to judge whether a substance is liquid or solid?

A fundamental number of rheology:

Deborah number (D_e)

$$D_e = \frac{\tau}{t}$$

Time of relaxation

Time of observation

If $\tau < t$, a substance is a liquid, otherwise, a solid!

Some liquids flow easily, some not.

How to quantify this?

Viscosity and

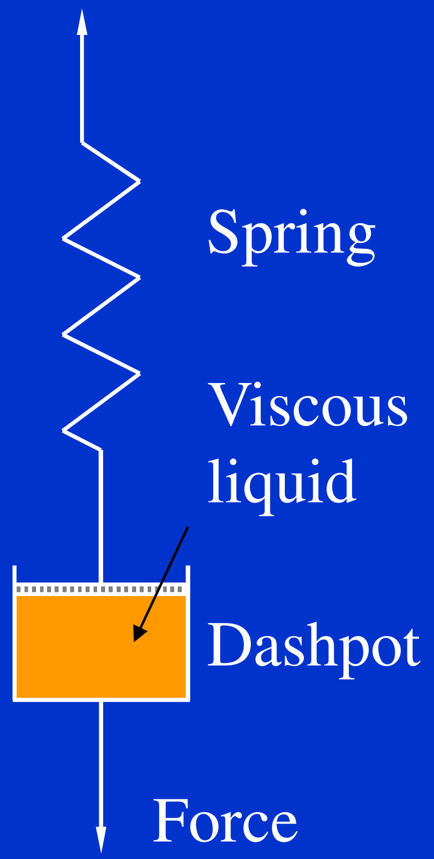
Viscoelasticity!

How to describe viscoelasticity?

The behavior including both viscous and elastic response is known as ***Viscoelasticity, or viscoelastic behaviour***.

Maxwell Model!

- The most common basic model
- Useful for calculation of order of magnitude of relaxation times, but does not represent the behaviour of actual melts.



- **Maxwell model:**

$$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta}$$

where $\dot{\gamma}$ is shear rate, τ is the shear stress, $\dot{\sigma}$ is the shear stress rate, G is the shear modulus, and η is the shear viscosity.

- Resolving this equation leads to the well-known expression:

$$\sigma(t) = \sigma_0 \exp(-t/\tau)$$

where $\sigma(t)$ is the stress at t, σ_0 is the stress at $t = 0$, and τ is the ***relaxation time*** ($\tau = \eta/G$).

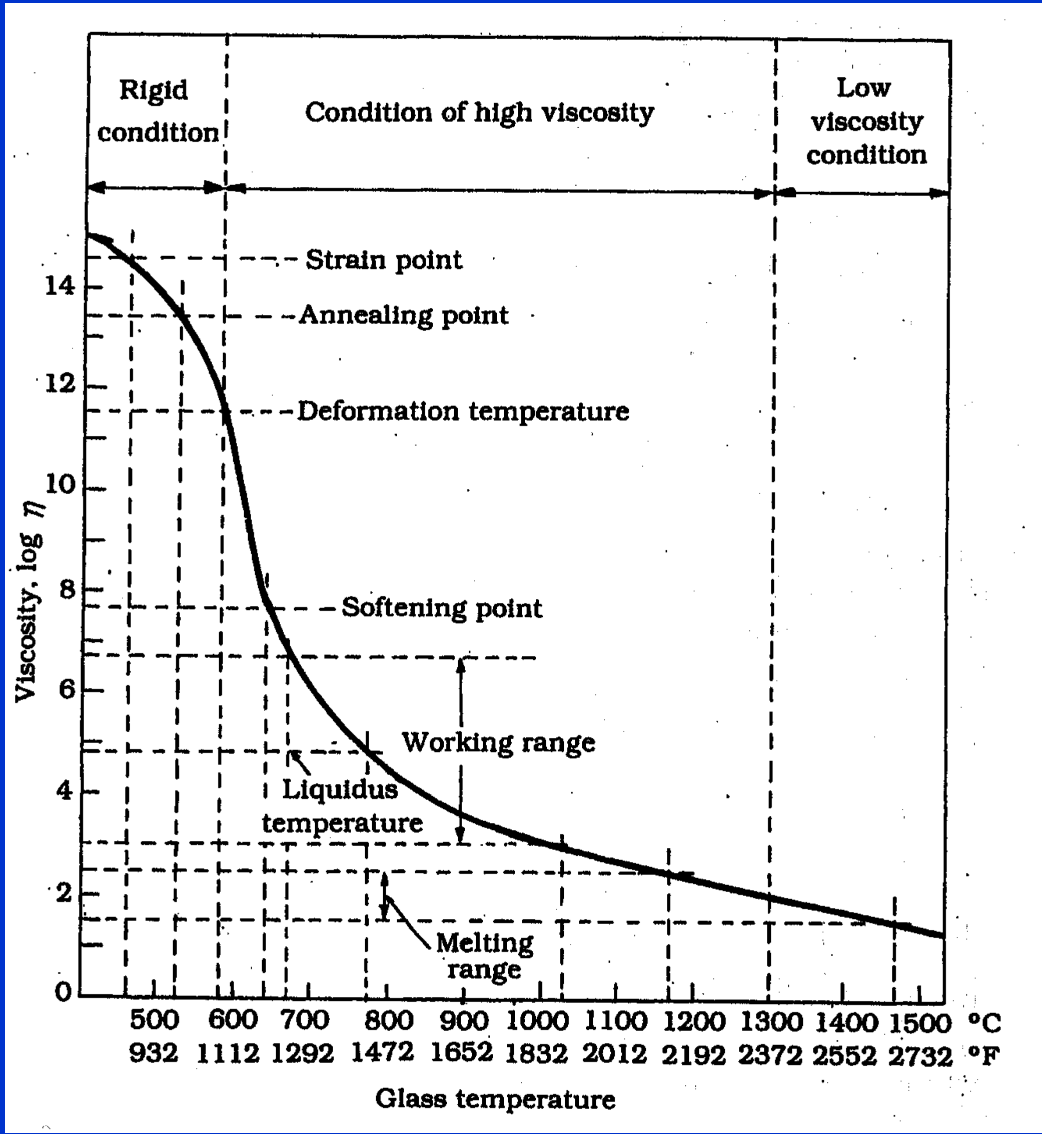
In reality, we need generalized Models.

- By multiple Maxwell and Voigt-Kelvin model, so that a spectrum of relaxation occurs.
- By groups of Maxwell elements in terms of the shear modulus:

  $G(t) = \Sigma G_i \cdot \exp(-t/\tau_i)$.
- By groups of Voigt-Kelvin elements in terms of the inverse of the shear modulus which is the shear compliance:

  $J(t) = \Sigma(1/G_i) \cdot [1-\exp(-t/\tau_{r,i})]$.

Viscosity is an important value for glass technologists.



Viscosity is one of the most important technological properties. It determines:

- Melting conditions
- Working and annealing ranges
- Finning behaviour
- Upper temperature of use
- Devitrification rate
- Glass forming
- Workability
- …….

Viscosity is also an important value for glass scientists.

It provides information on

- Glass dynamics
- Transport properties
- Glass structure
- Liquid fragility
- Thermodynamics
- Geology
- Crystallization
- ……..

A liquid above Tg can be regarded as a pure viscous system for proper observation time, and in this case, the flow behaviour may be described solely by viscosity.

Viscosity: shear and extensional viscosity
Here we focus on Shear Viscosity:

- A measure of the resistance of a liquid to shear deformation
- A measure of the ratio between the shearing force and rate of shear.

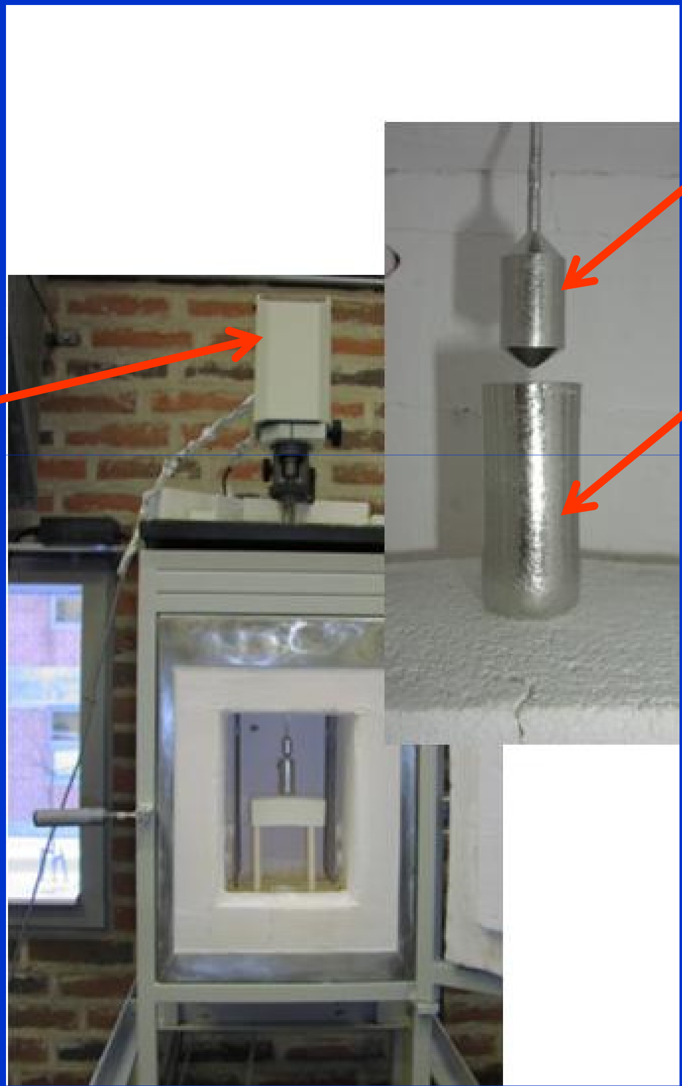
How to measure shear viscosity?

Common techniques:

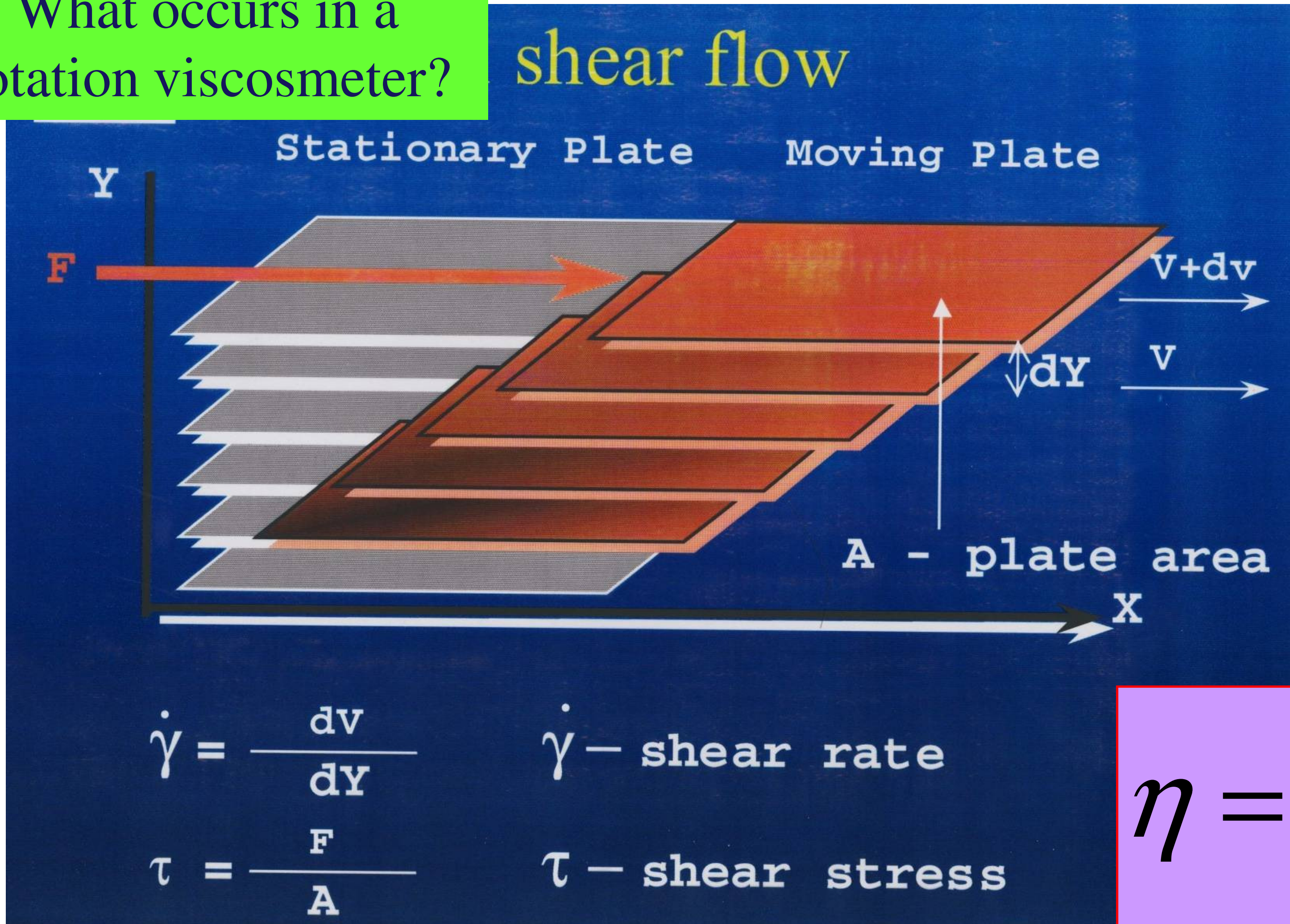
1. Concentric Cylinder (or Rotation)
2. Parallel-Plate Compression
3. Capillary
4. Beam Bending
5. Fiber Elongation
6. Penetration

…….

A rotation Viscometer

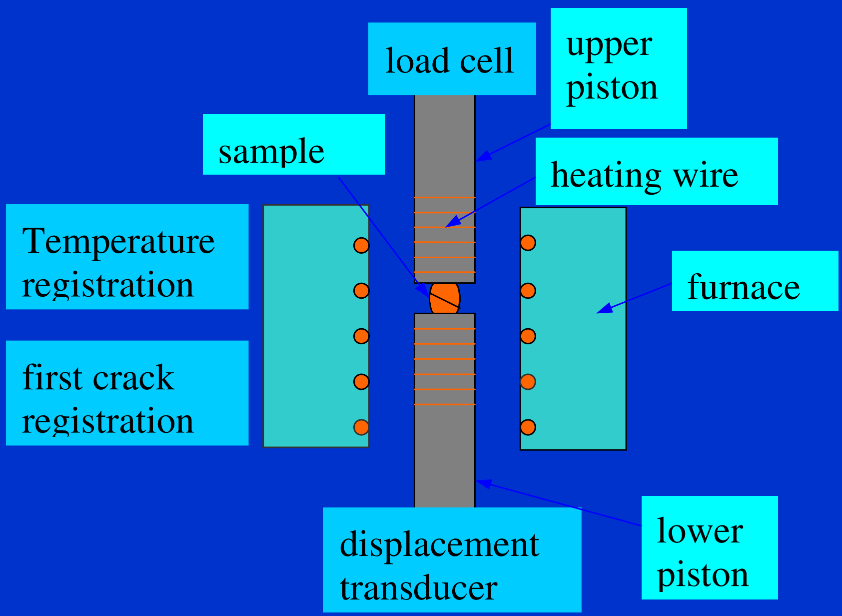


What occurs in a rotation viscosmeter?

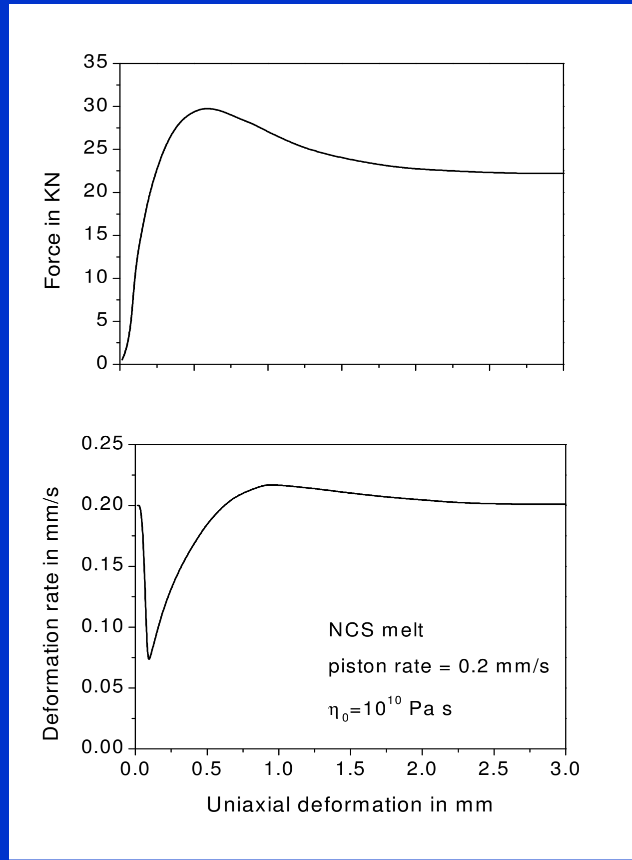


$$\eta = \frac{\tau}{\dot{\gamma}}$$

Parallel Plate Compression

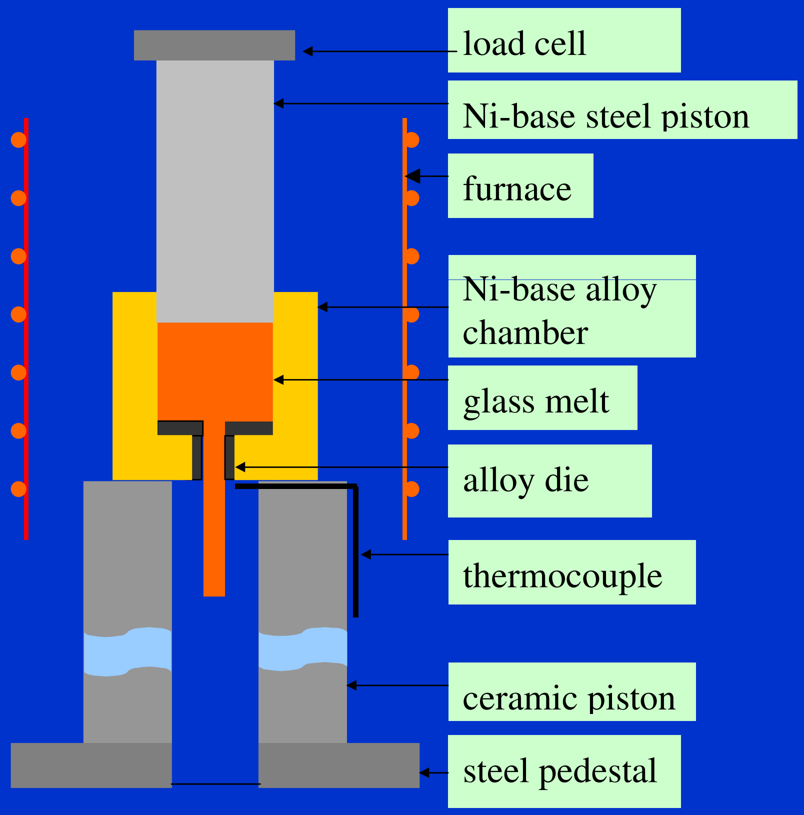


Schematic description of the MTS apparatus

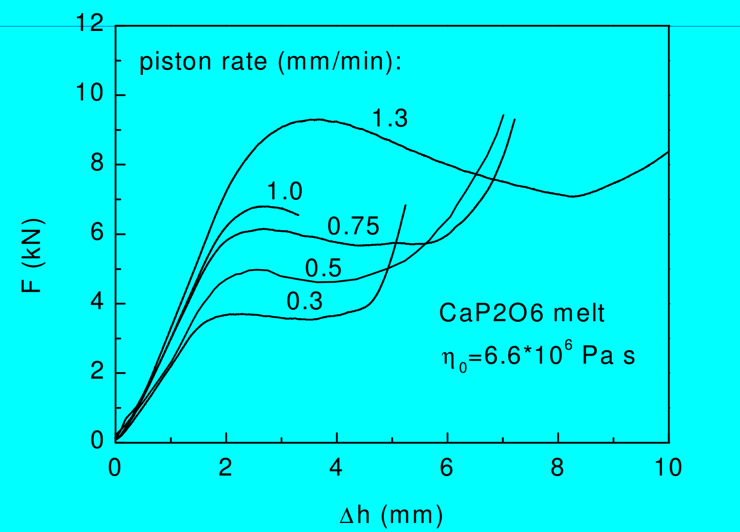


$$\eta = F / \left[3\dot{h}V \left(\frac{V}{2\pi h(t)^5} + \frac{1}{h(t)^2} \right) \right]$$

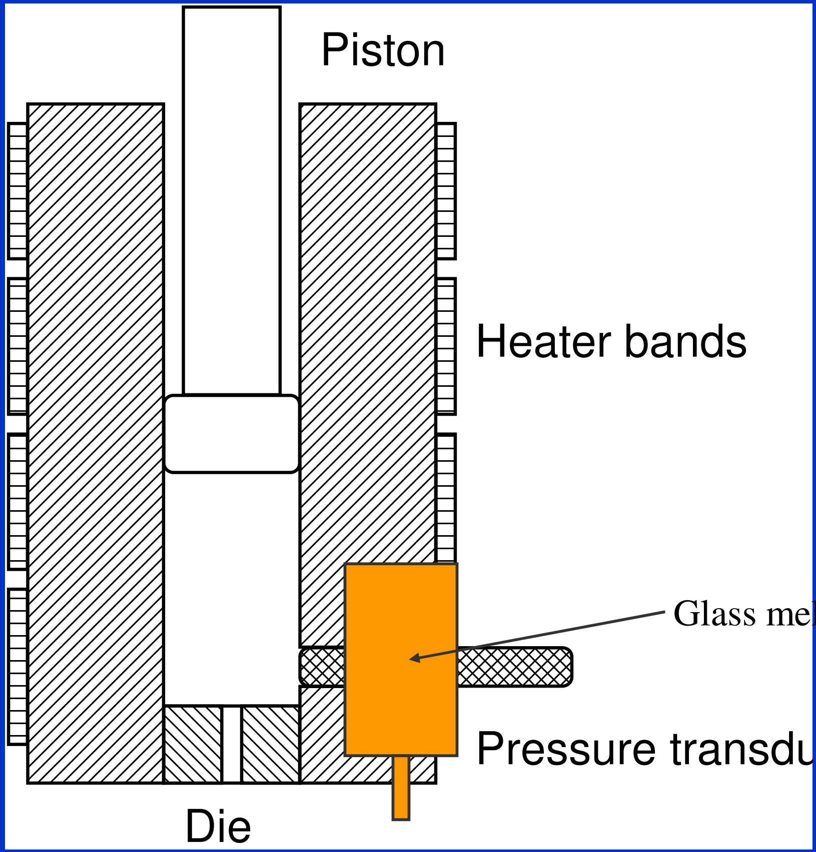
Capillary Viscometer (1)

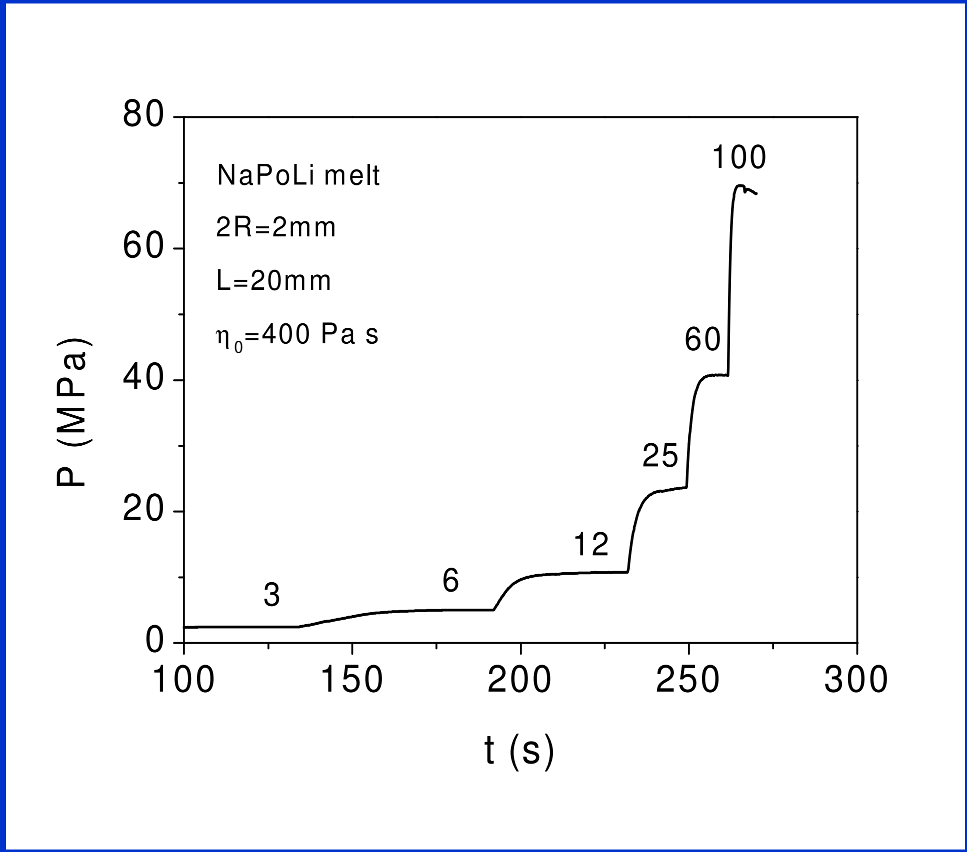


Directly measured force versus piston displacement

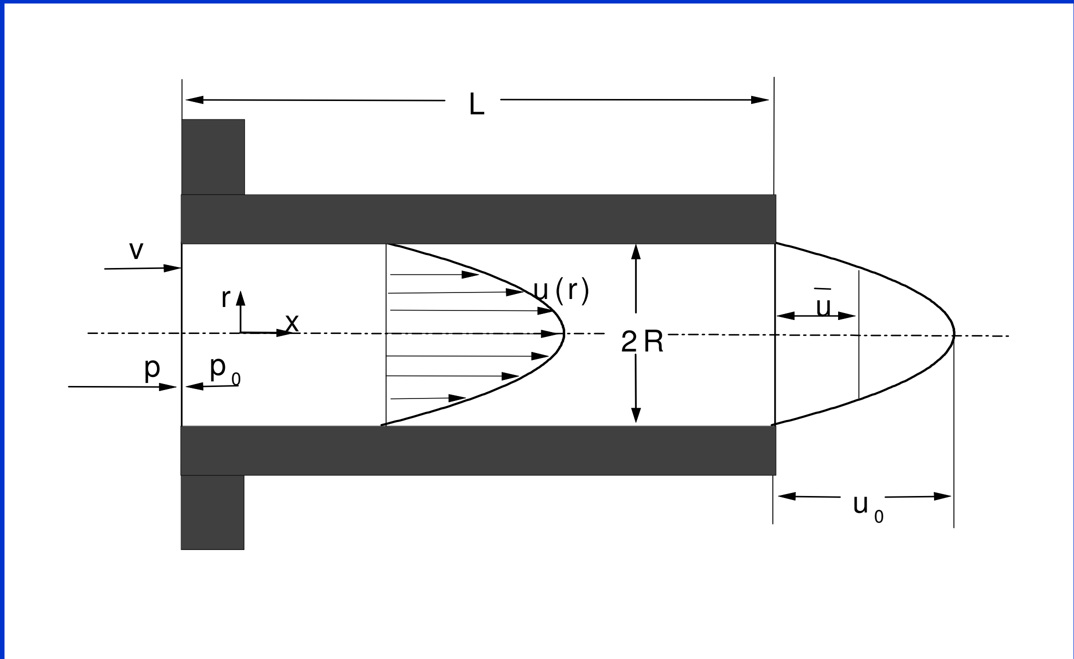


Capillary Viscometer (2)





Distribution of the flow rate of a glass melt extruded through the orifice, and calculation of shear viscosity



$$\eta = \frac{(P - P_0)R^4}{8LvR_0^2}$$

Viscosity of a melt varies with

- **Temperature**
- Time
- **Deformation rate**
- Pressure
- Composition
- Hydroxyl
- **Crystallization**
- Phase seperation
- Inclusions
- …….

“5 Nons” related to viscosity and to glass Relaxation

- Non-Arrhenian
- Non-Newtonian
- Non-linearity
- Non-exponentiality
- Non-Kohlrausch

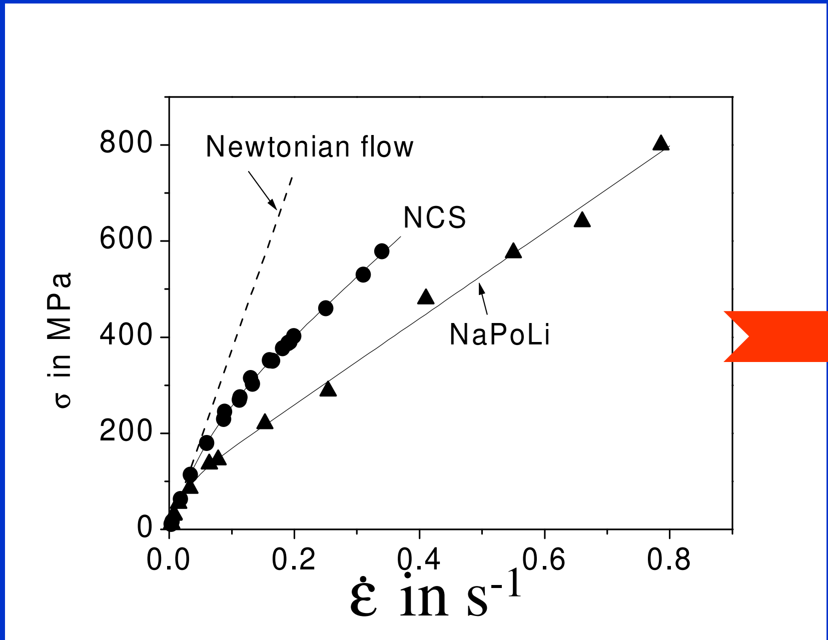
Dependence of η on deformation rate
(three phenomena)

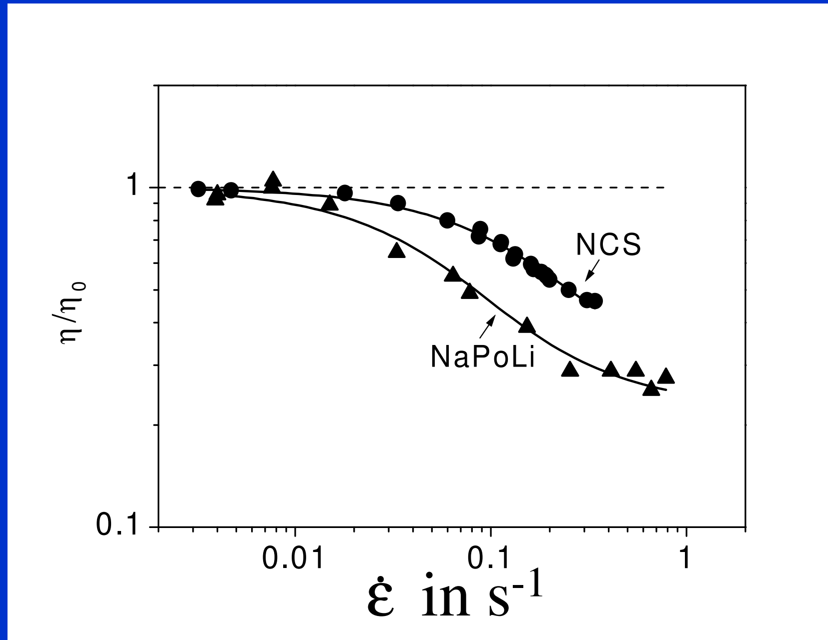
1. Non-Netwonian shear flow

2. Non-Newtonian dilatant flow

3. Non-Newtonian suspension effect

Non-Newtonian shear flow caused by Structural orientation



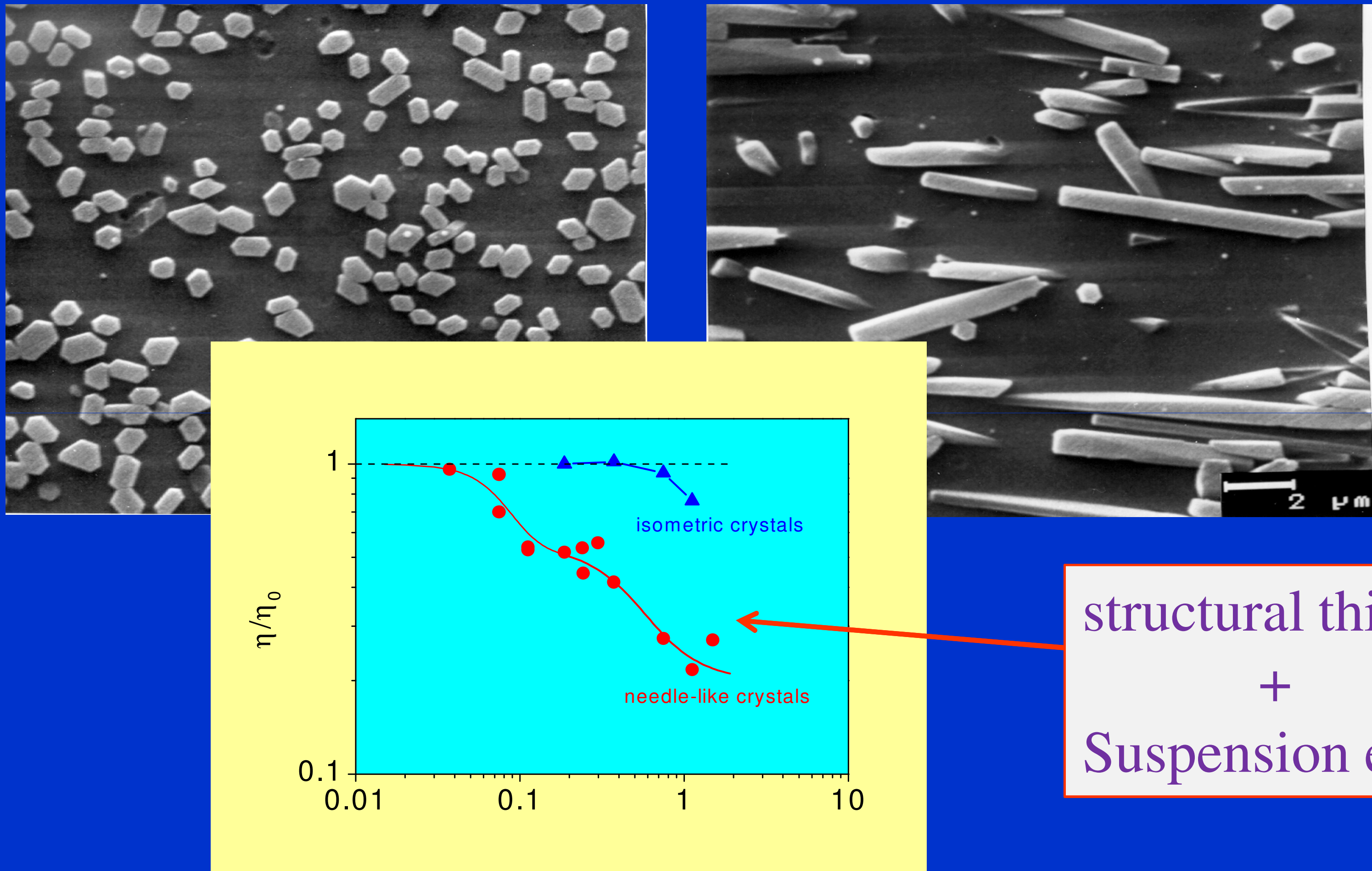


$$\sigma = \eta_\infty + (\eta_0 - \eta_\infty)\dot{\varepsilon}_g(1 - \exp(-\frac{\dot{\varepsilon}}{\varepsilon_g}))$$

$$\frac{\eta}{\eta_0} = \frac{\eta_\infty}{\eta_0} + (1 - \frac{\eta_\infty}{\eta_0})\frac{\dot{\varepsilon}_g}{\dot{\varepsilon}}[1 - \exp(-\frac{\dot{\varepsilon}}{\dot{\varepsilon}_g})]$$

Y. Z. Yue and R Brückner, J. Non-Cryst. Solids (1994)

Suspension effect caused by alignment of fluoroapatite crystals in a extruded melt

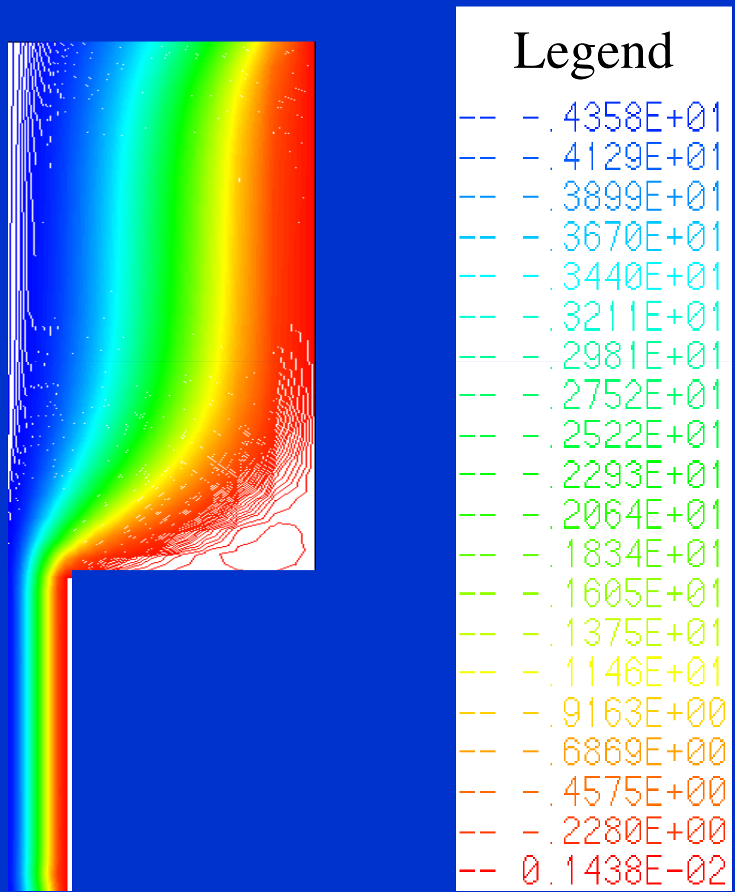


structural thinning
+
Suspension effect

Y. Z. Yue, C. Moisescu, G. Carl and C. Rüssel, Phys. Chem. Glasses (1999)

J. Deubener and R. Brückner, J. Non-Cryst. Solids (1997)

FEM Simulation of Stream Lines



Stream line of fluoroapatite glass-ceramic melt during extrusion under the following conditions: diameter of chamber = 21.6 mm, diameter of die = 5 mm, length of die = 14.3 mm, viscosity $\eta_0 = 1.8 \times 10^7$ Pa s and piston rate = 1 mm/min, obtained by means of a FEM program called Fidap 762.

Deborah number (D_e) as a creterien for judging whether non-Newtonian flow is involved or not

$$D_e = \frac{\dot{\gamma}}{\dot{\tau}}$$

Rate of deformation, e.g. shear

Rate of relaxation

If $\dot{\gamma} > \dot{\tau}$, the non-Newtonian flow is involved, otherwise, a Newtonian flow!

Temperature Dependence of Viscosity

1. Arrhenian Equation

$$\eta = \eta_0 \exp(\Delta H_\eta / RT)$$

2. Vogel-Fulcher-Tamman (VFT) equation:

$$\log \eta = A + B/(T-T_0)$$

3. Free Volume Model for Viscous Flow

$$\eta = \eta_0 \exp[B_1/(V-V_0)]$$

4. Entropy Model for Viscous Flow

This model is expressed by the equation:

$\eta = \eta_0 \exp[B_2/(TS_c)]$

where B_2 is a constant and S_c is the configurational entropy. If we replace S_c by the expression

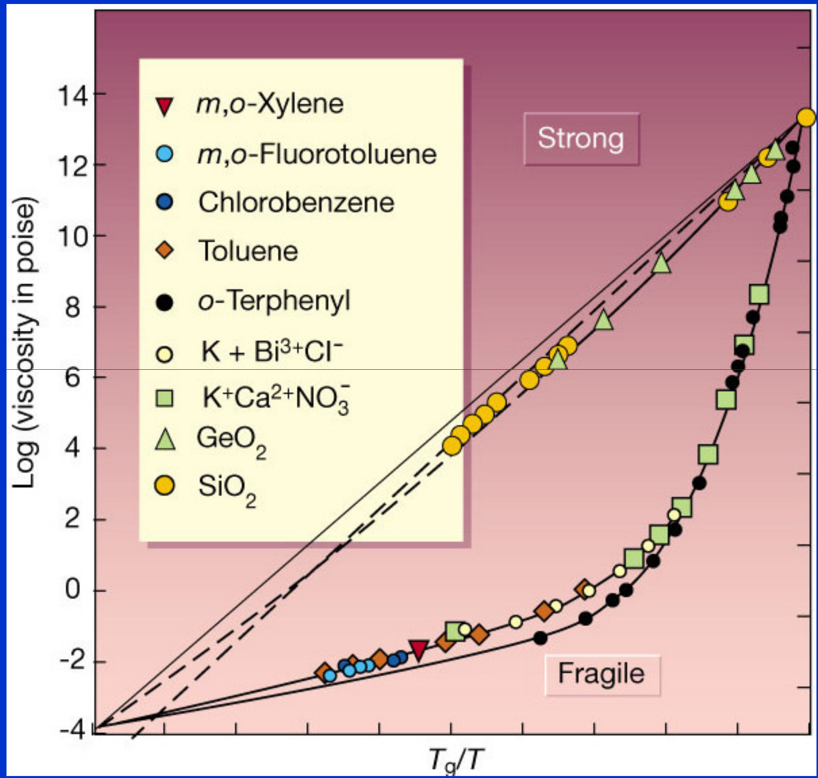
$S_c = \Delta C_p(T\text{-}T_0)/T$

where ΔC_p is constant with temperature, we get the VFT-equation.

A nice concept – Fragility!

Angell plot

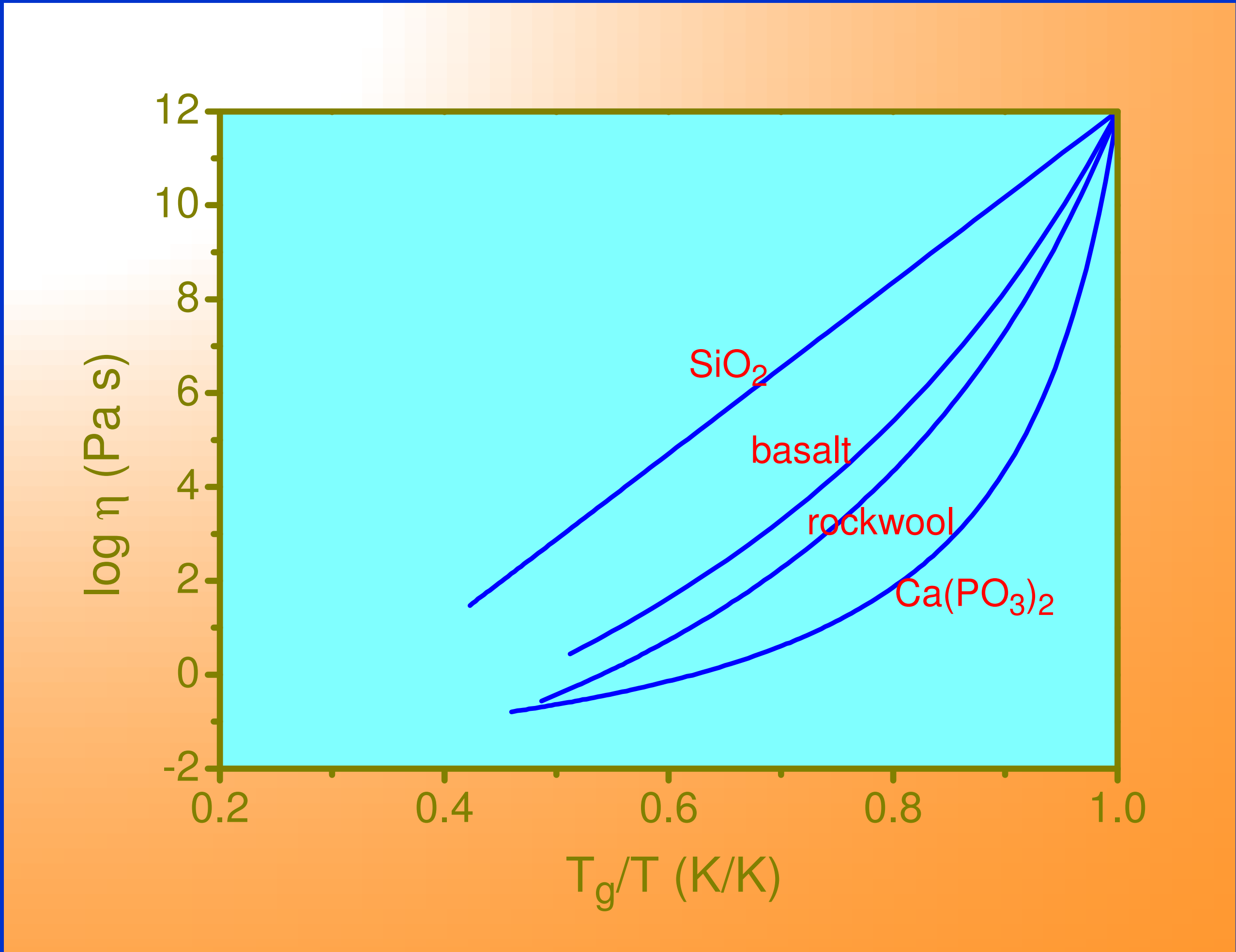
- **Strong melts**: showing small curvature, i.e. more Arrhenian behaviour
- **Fragile melts**: large curvature, i.e. less Arrhenian behaviour



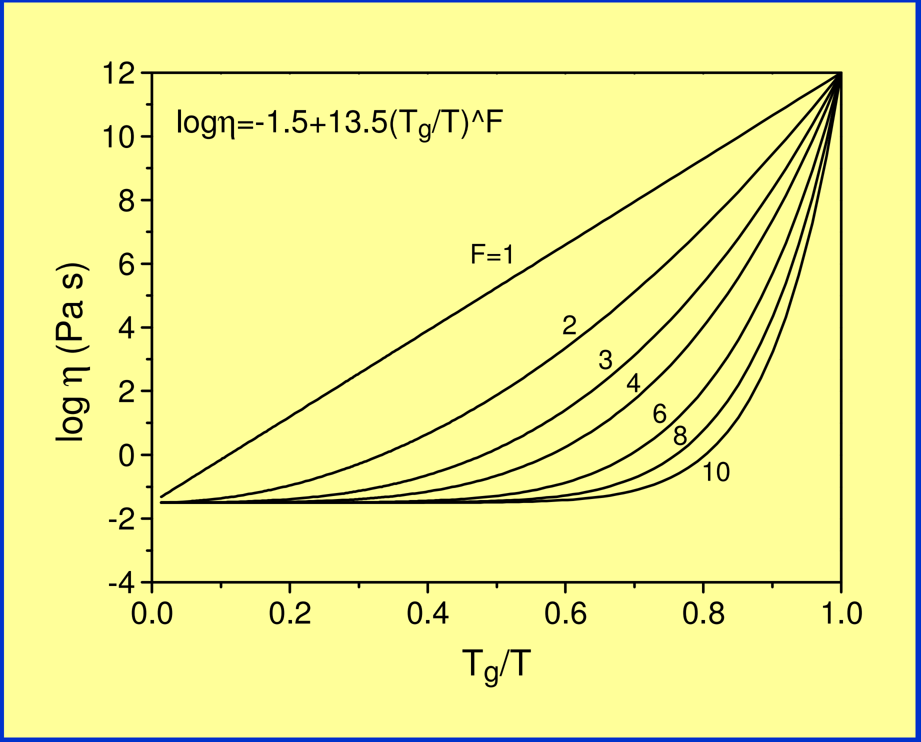
The fragility index is m = $\Delta H_\eta/(2.303R)$ at Tg

**C.A. Angell. Science (1995)*

Fragility of some oxide liquids



5. Milchev-Avramov (MA) model



$$\log \eta = A + B\left(\frac{T_g}{T}\right)^F$$

When T=Tg,

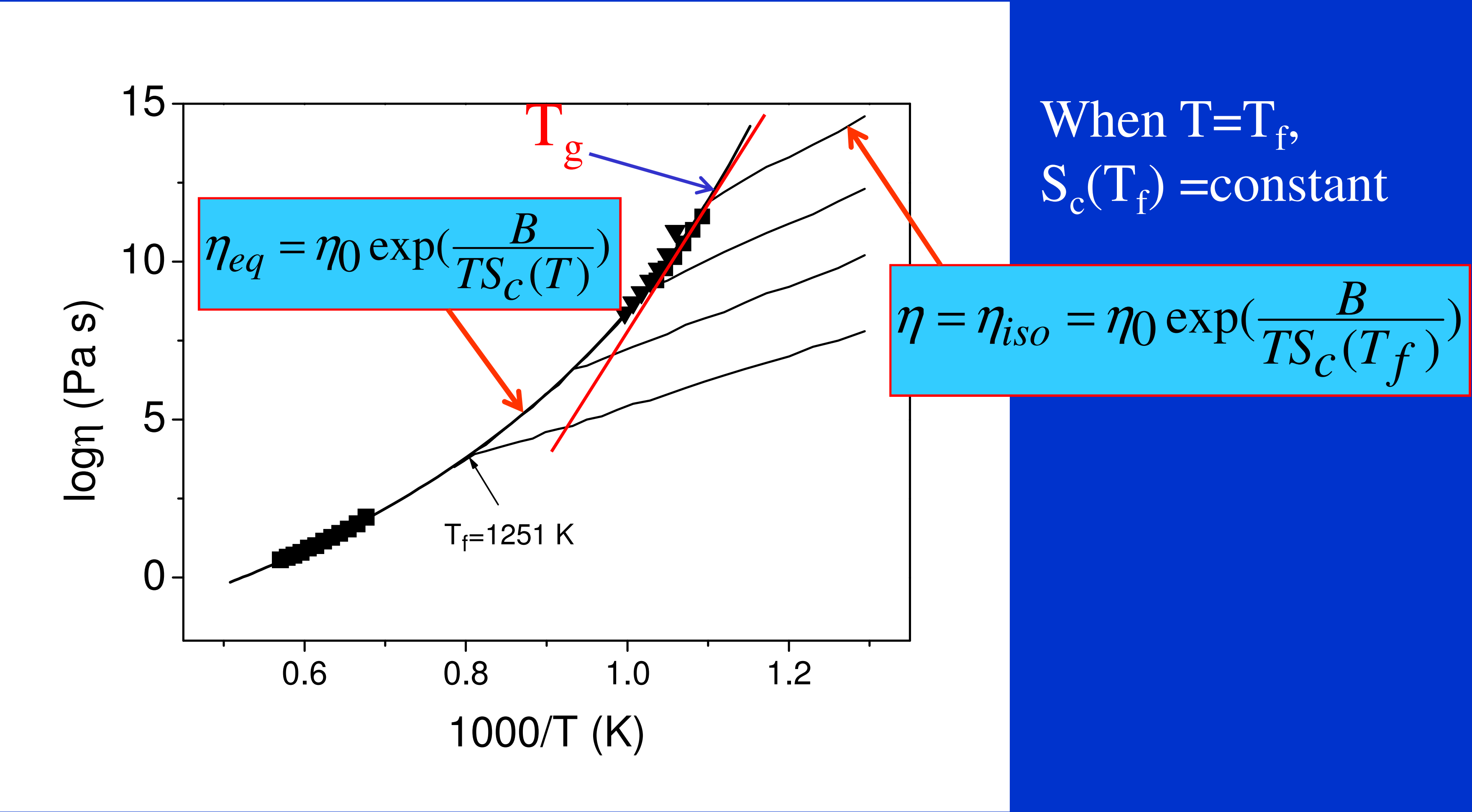
logη=A+B=12

This is a straightforward model describing the liquid fragility!

Now
We try to determine the $\eta \sim T$ relation
without use of a viscometer

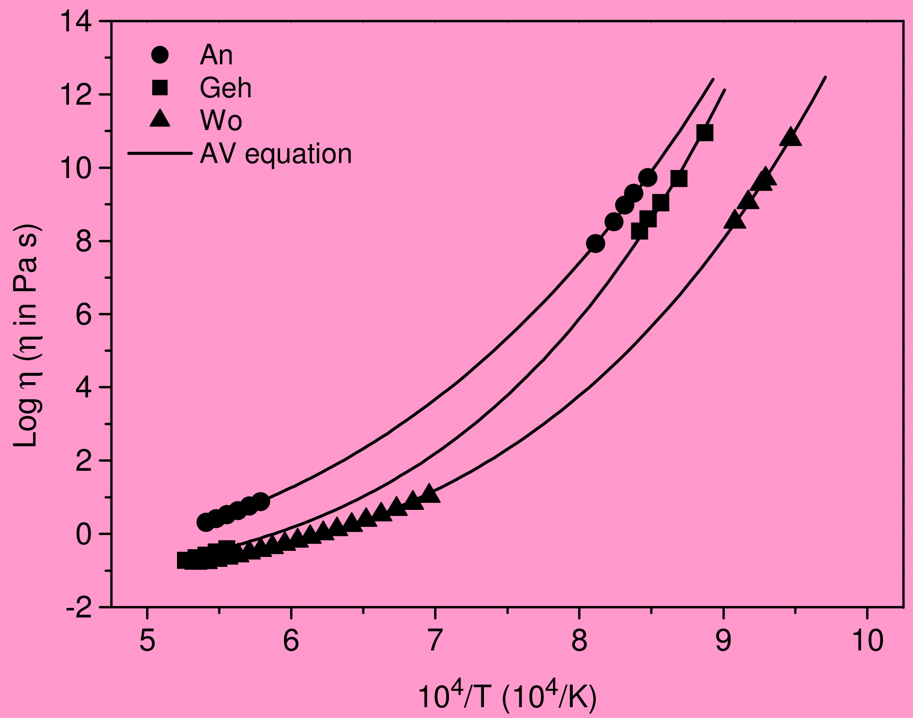
Differential Scanning Calorimeter (DSC)
Approach

Equilibrium viscosity (η_{eq}) and Iso-structure viscosity (η_{iso})



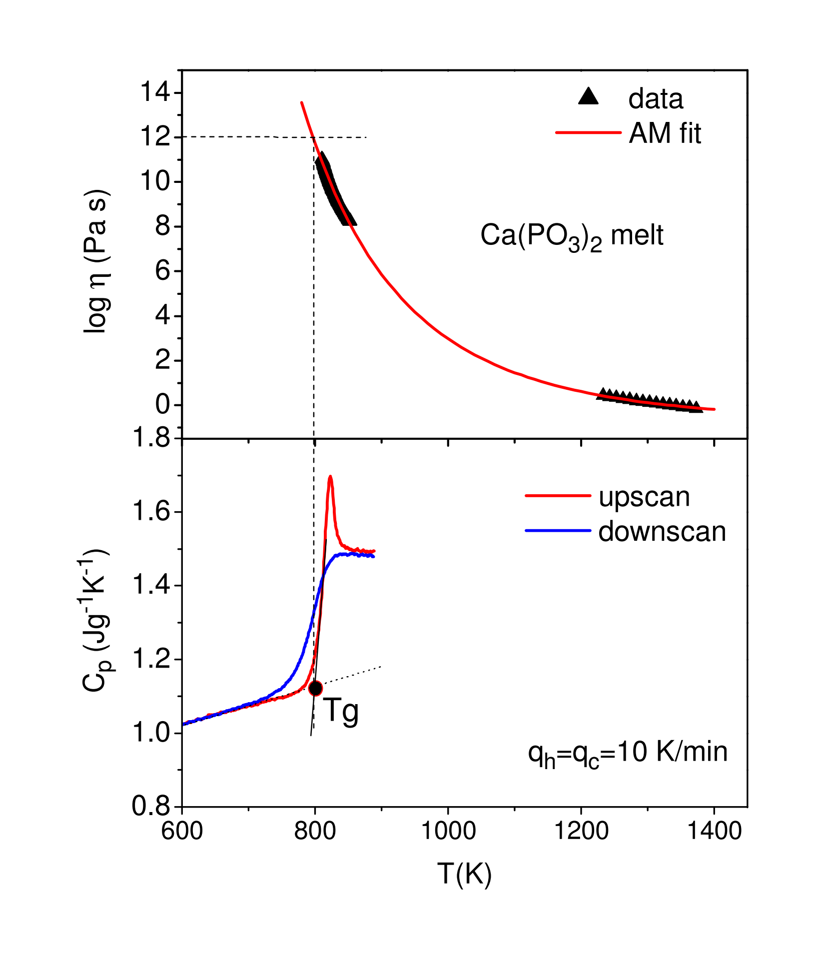
When $T=T_f$,
$S_c(T_f)$ =constant

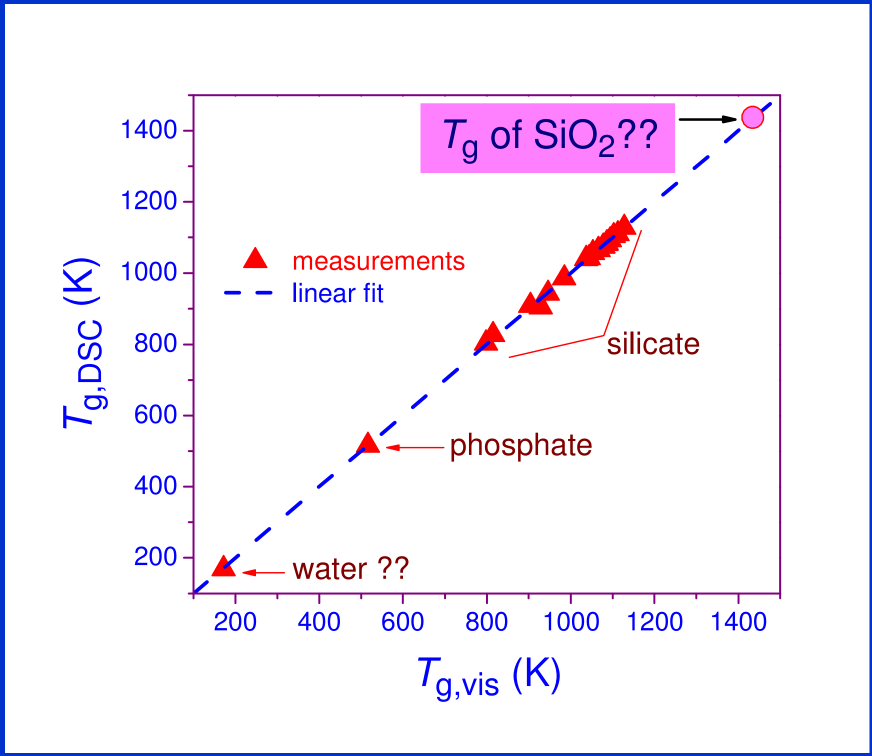
Fitting with $\log \eta = -1.5 + 13.5(\frac{T_g}{T})^F$



glass	Tg (Visco) (K)	Tg (DSC) (K)
CAS1	1044	1043
CAS2	1053	1057
CAS3	1067	1065
CAS4	1078	1075
CAS5	1087	1084
CAS6	1066	1066
CAS7	1078	1075
CAS8	1085	1082
CAS9	1094	1093
CAS10	1103	1104
Anorthite	1128	1128
Wollastonite	1037	1040
Gehlenite	1112	1110
$Na_2O{\cdot}Li_2O{\cdot}2P_2O_5$	516	516
$Ca(PO_3)_2$	798	803
Basalt Obersheld	904	908
ST wool	941	943
NIST	815	827
Diopside	985	986

Comparison between $T_{g,visco}$ and $T_{g,DSC}$

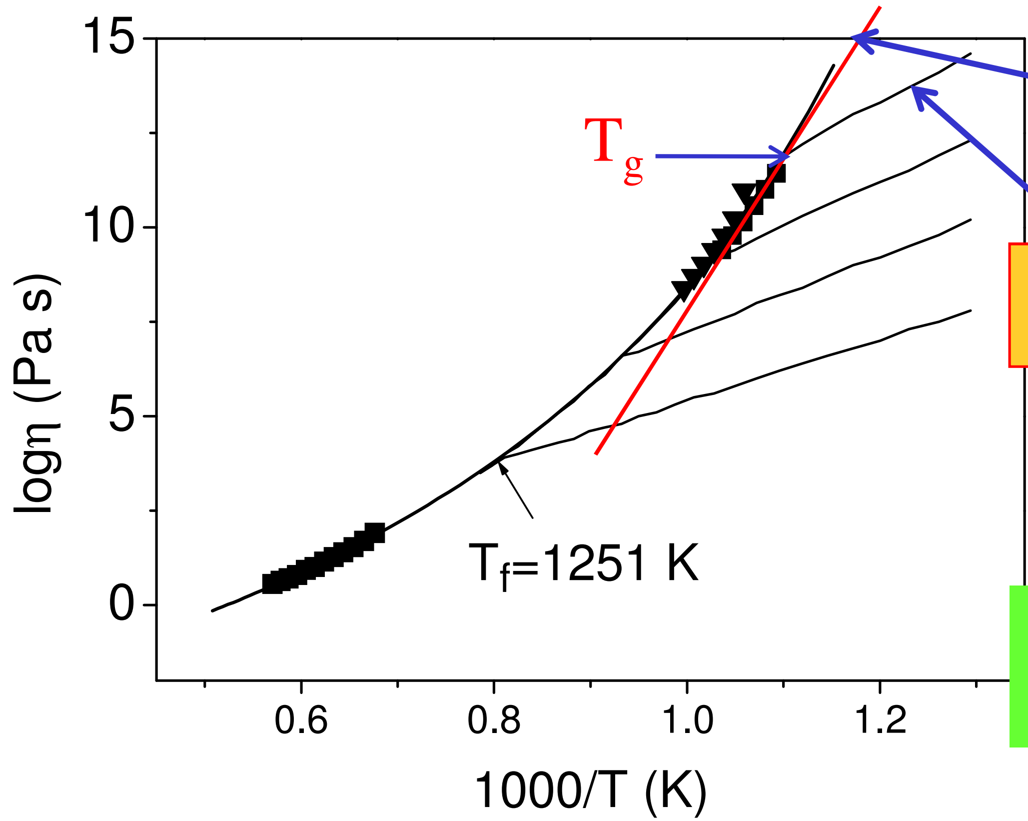




Reasonableness of fixing parameters A and B of the MA equation.

$$T_{g,10K/min} = T_{\log\eta=12}$$

Activation energy for equilibrium viscosity (E_{eq})
Activation energy for iso-structure viscosity (E_{iso})



Slope is $R \times E_{eq}$

Slope is $R \times E_{iso}$

Basalt glass

What is the relation between activation energies and fragility index *F*?

$$\log \eta = -A + B\left(\frac{T_g}{T}\right)^F$$

Determine E_{eq}, E_{iso} and F:

$$E_{eq} = R\frac{d \ln \eta}{d(1/T)} = 2.303B \cdot F \cdot R \cdot T_g \cdot \left(\frac{T_g}{T}\right)^{F-1}$$

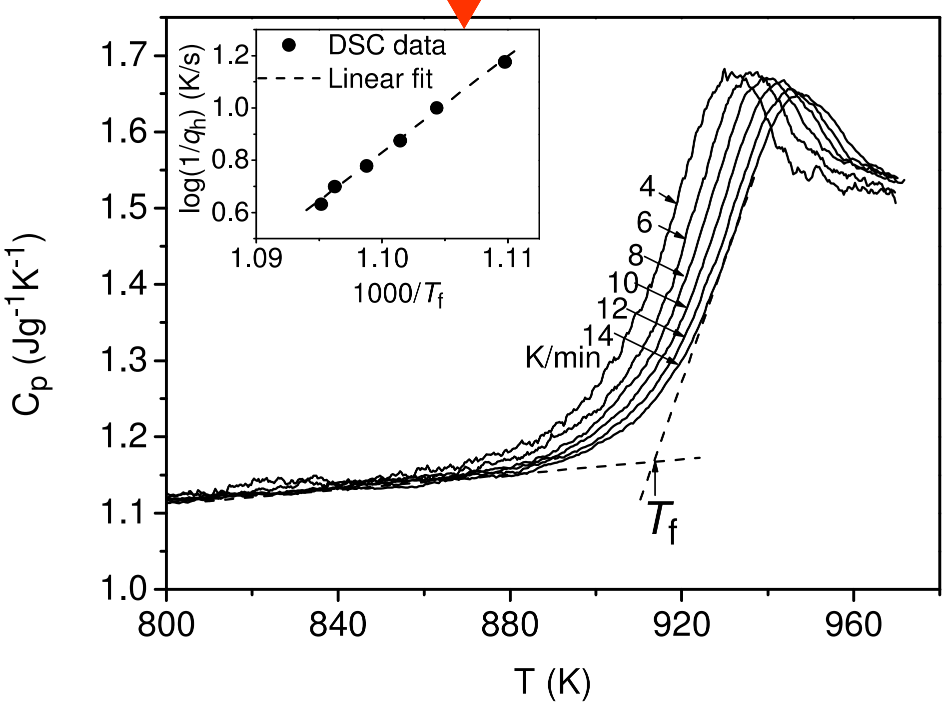
$$E_{iso} = 2.303B \cdot R \cdot T_g \cdot \left(\frac{T_g}{T}\right)^{F-1}$$

Foundation of my method

$$\frac{E_{eq}}{E_{iso}} = F$$

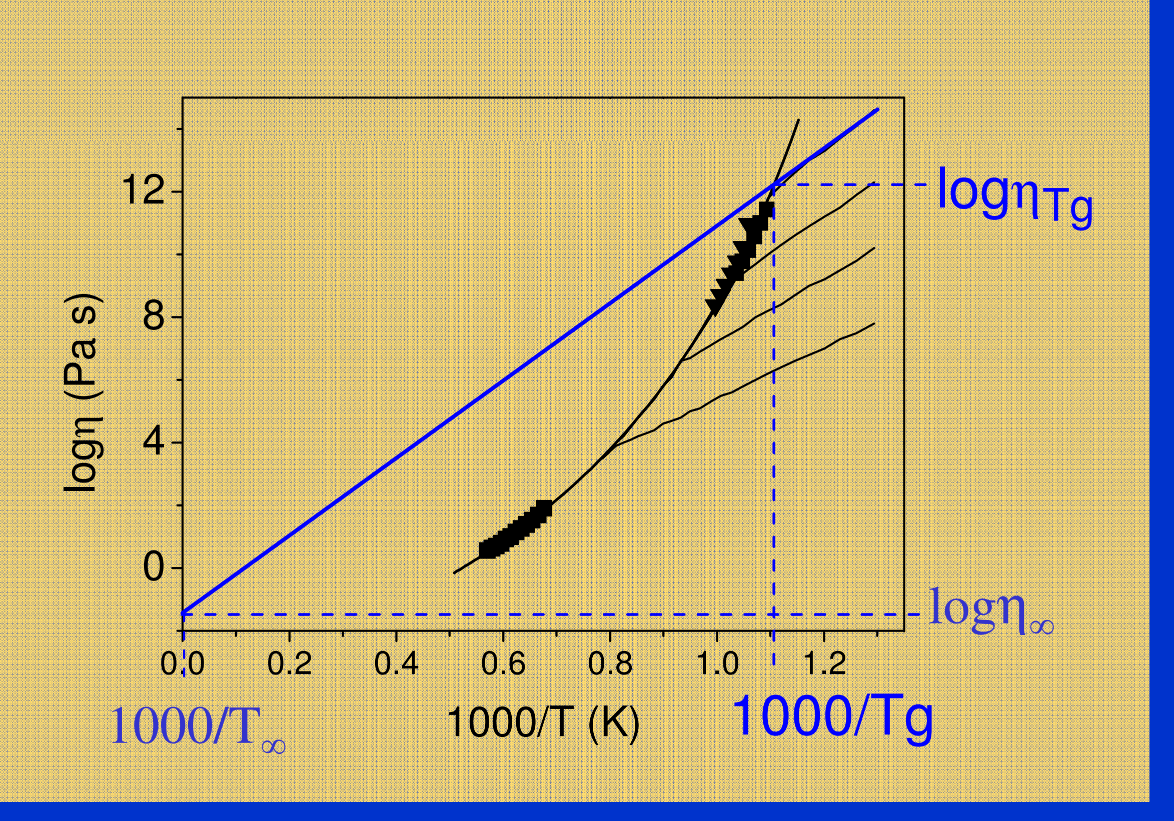
Determination of E_{eq}

$$\frac{d\ln\eta}{d(1/T)} = \frac{E\eta(T)}{R} = \frac{d\ln(1/q_c)}{d(1/T_f)} = \frac{Eq_c(T)}{R} = \frac{Eq_c(T)}{R}$$

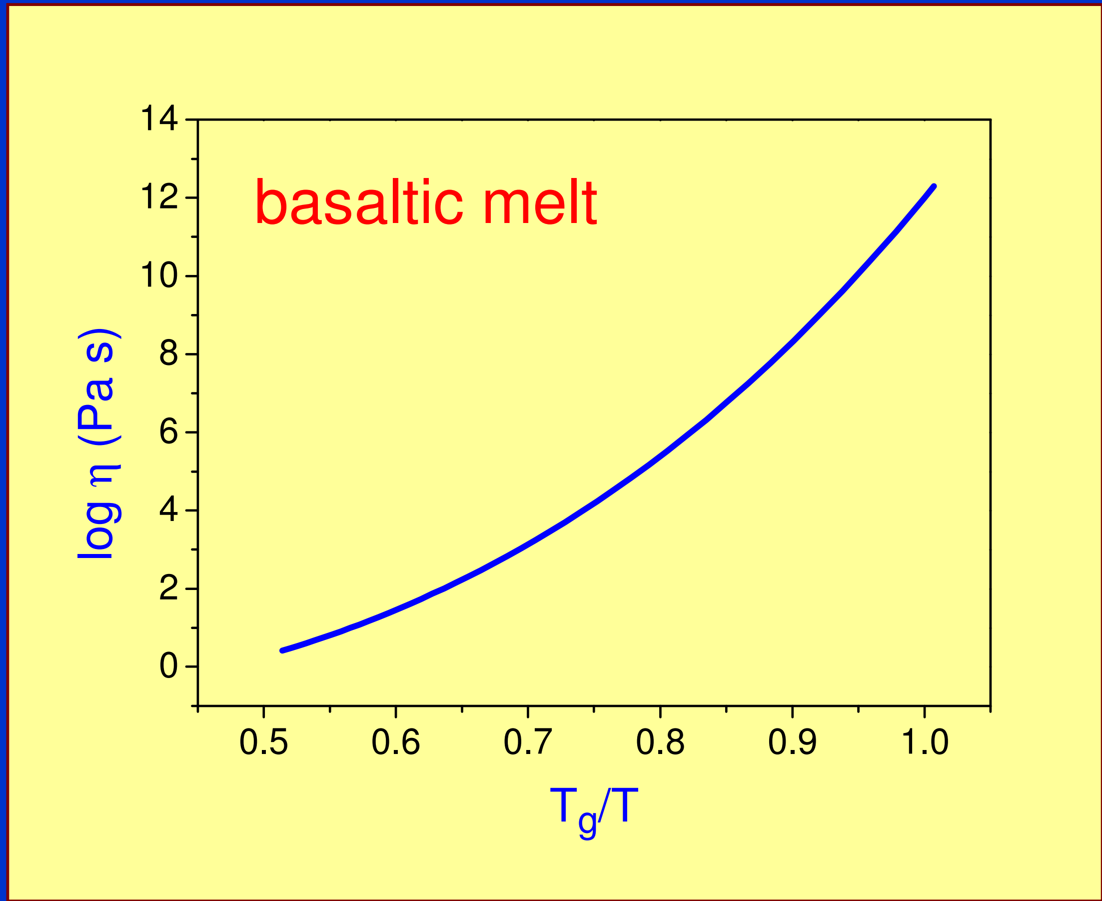


Determination of E_{iso}

$$E_{iso} = \frac{2.303(\lg \eta_{Tg} - \lg \eta_{\infty})}{\frac{1}{Tg} - \frac{1}{T\infty}} \times R = 31RT_g$$

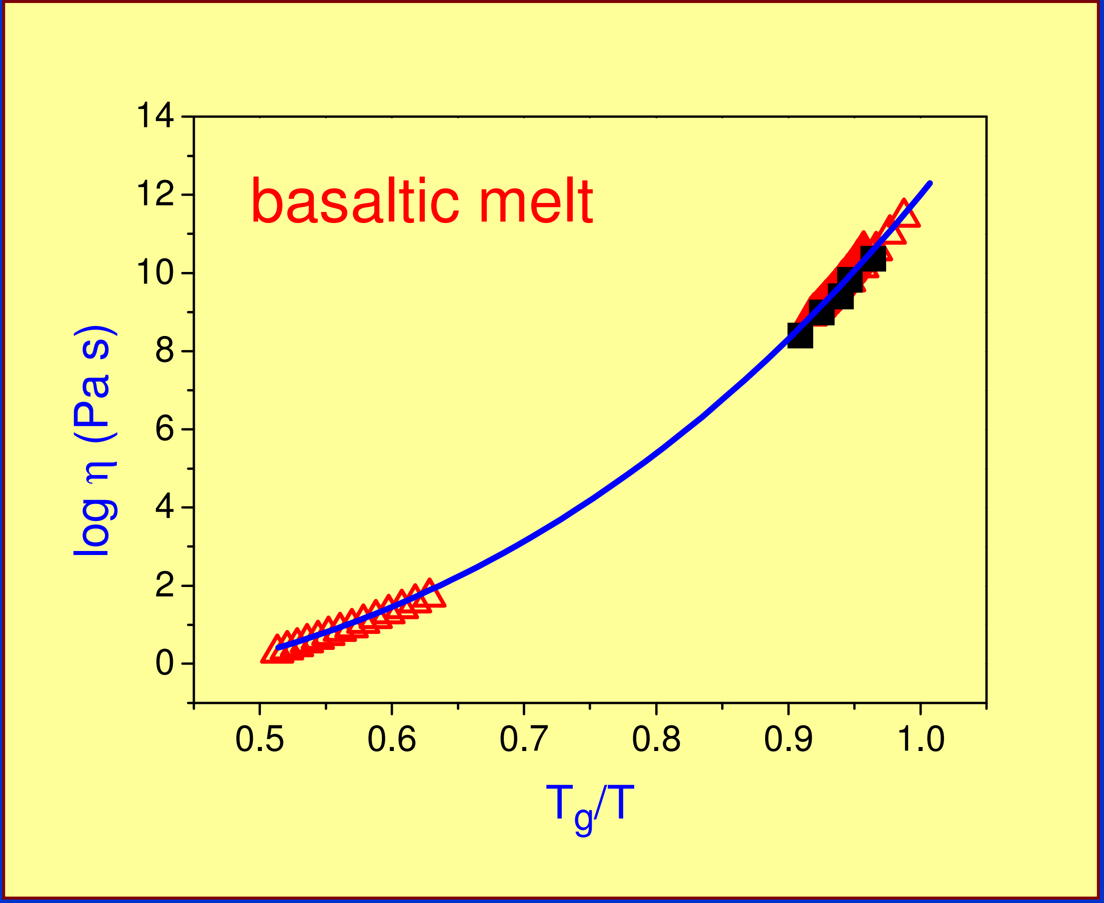


Viscosities by DSC



$$\log \eta = -1.5 + 13.5\left(\frac{910}{T}\right)^{3.1}$$

Comparison with viscometric data



$m = 13.5F$

$$\log\eta = -1.5 + 13.5\left(\frac{910}{T}\right)^{3.1}$$

Now
let's determine the cooling rate of
hyperquenched glasses

Determination of the cooling rate of glass fibers

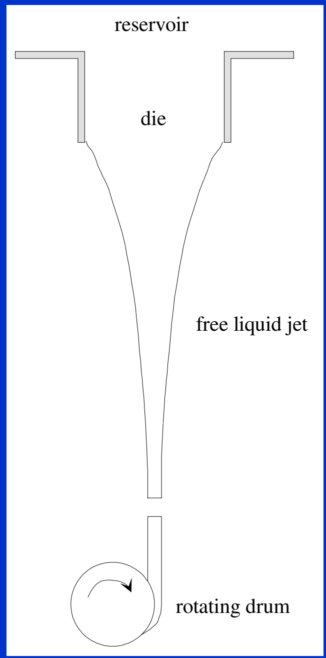
To do so, we need:

1. Fiber drawing
2. The $\eta \sim T$ relation
3. The $C_p \sim T$ relation from DSC
4. The relation between the cooling rate (q_c) and the fictive temperature (T_f)

Fiber drawing is a typical flow and hyperquenching process

Fast cooling
(> 10^5 K/s)

Low density
Large $C_{p,exc}$
Large ΔS_{excess}
High T_f

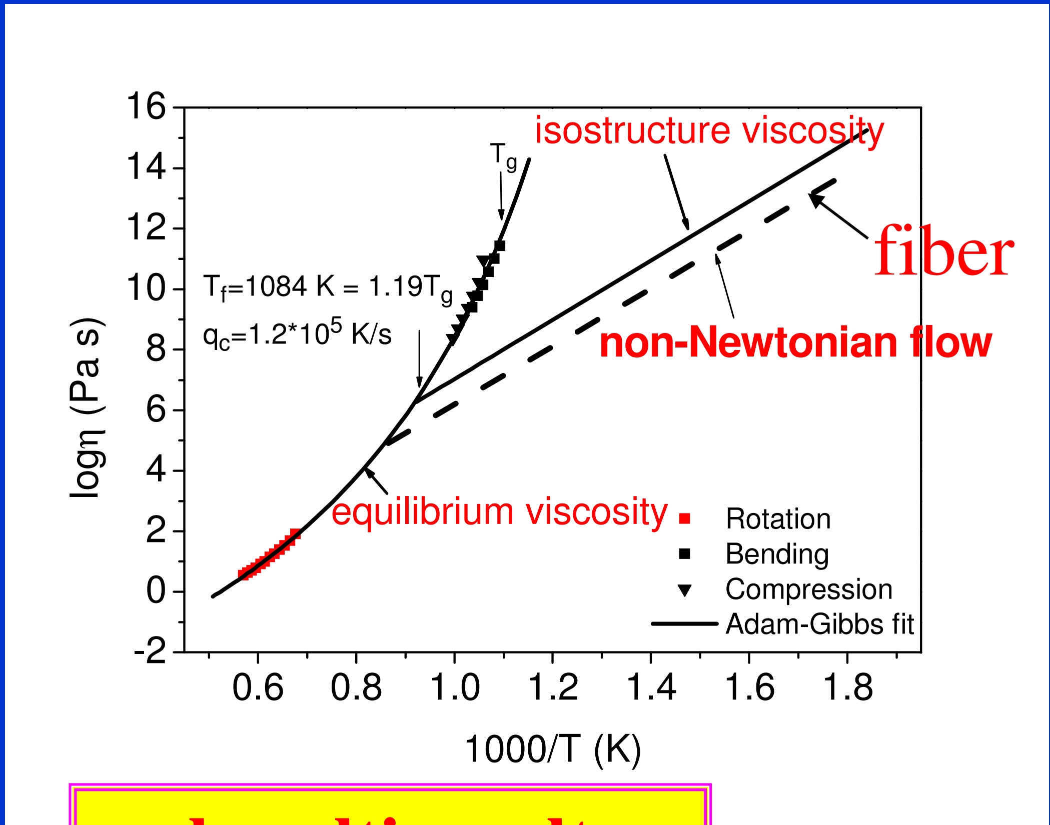


Large axial stress
(> 60~70 MPa)

Non-Newtonian flow
Oriented structure
Large ΔS_{excess}
Oriented defects

very different properties than bulk glass!

Influence of hyperquenching and drawing on the viscosity-temperature relationship



basaltic melt

Adam-Gibbs equation:

$$\eta = \eta_0 \exp\left(\frac{B}{TS_c(T)}\right)$$

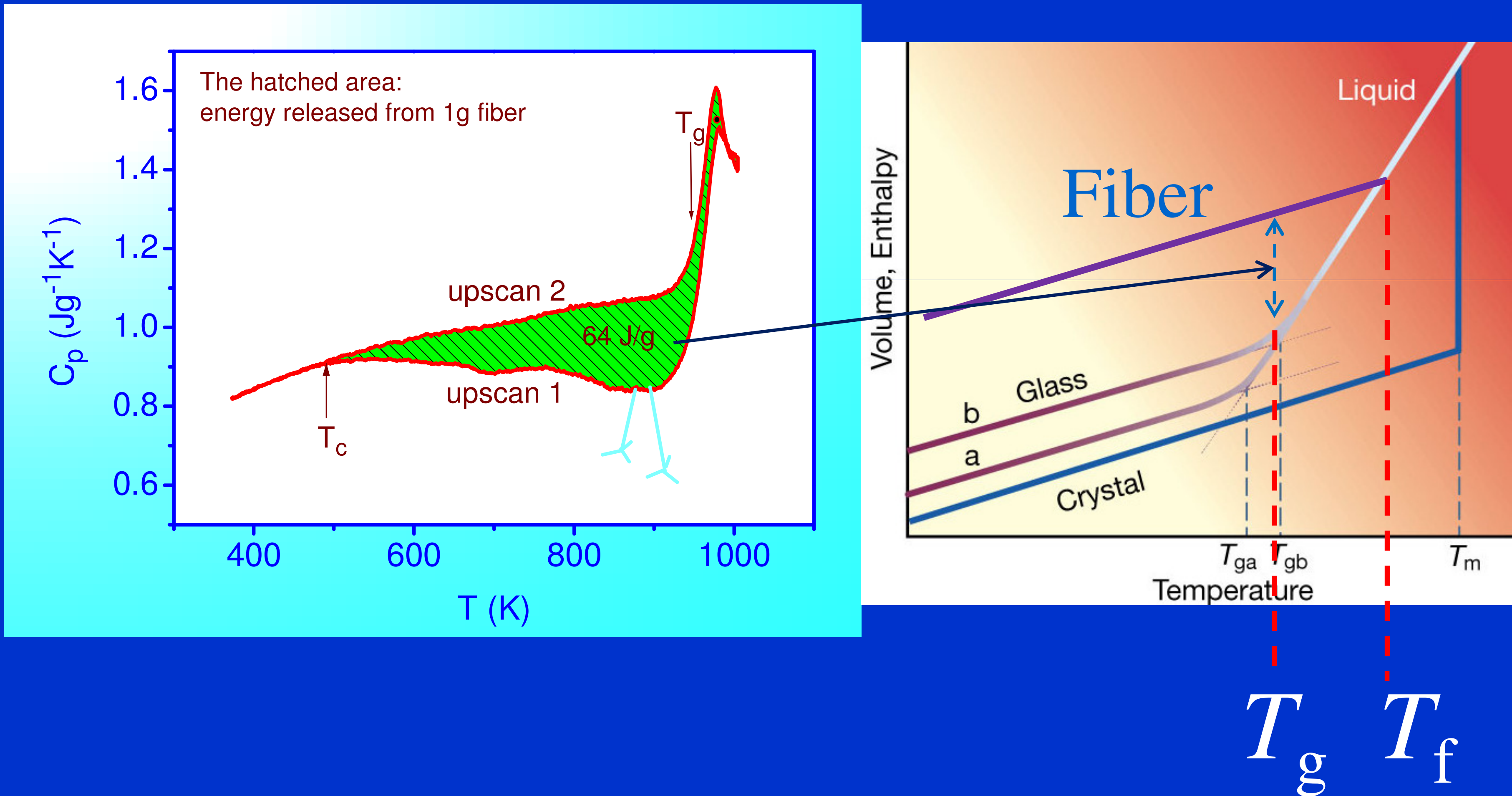
For the frozen structure, S_c is constant, only a function of T_f :

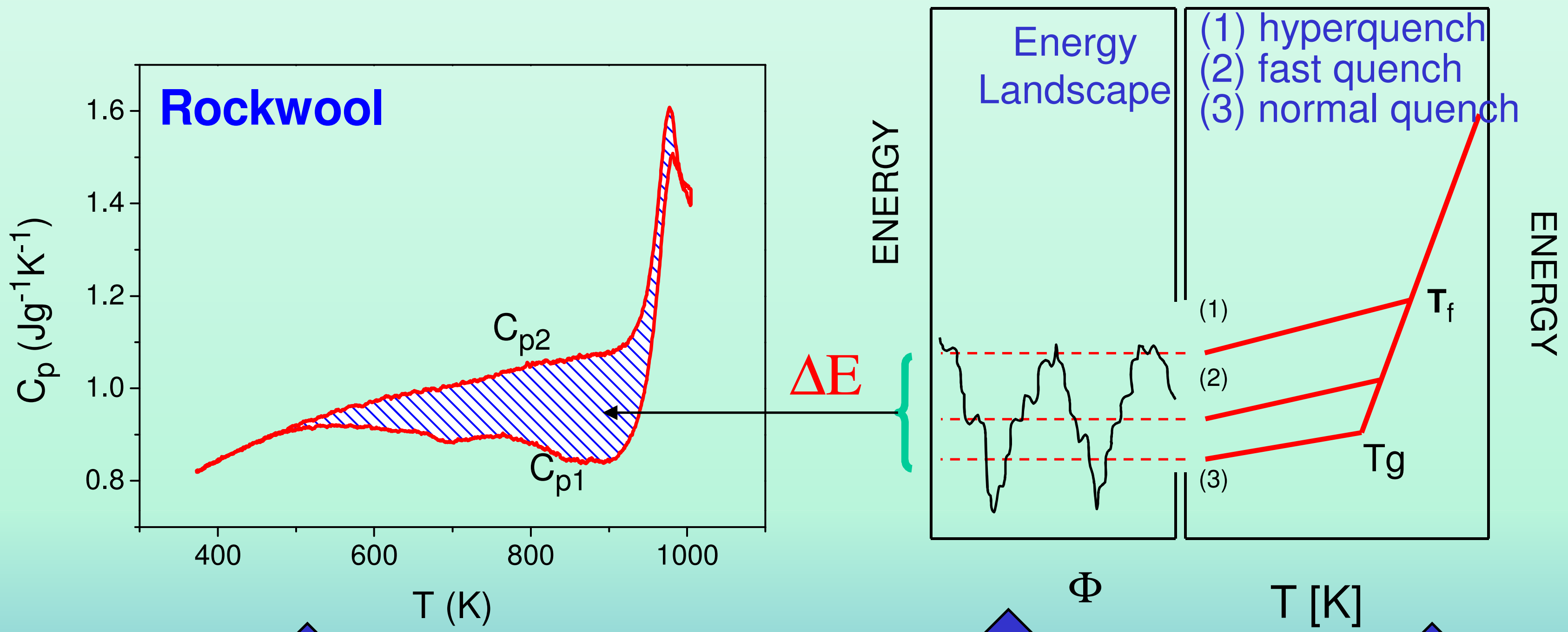
$$\eta = \eta_0 \exp\left(\frac{B}{TS_c(T_f)}\right)$$

Y. Z. Yue, et al., Chem. Phys. Lett. (2002)
Y.Z. Yue, et al., J. Chem. Phys. (2004)

Relaxation of glass fibers
("*Enthalpy bird*")

T dependence of liquid's *V* and *H* at constant *P*





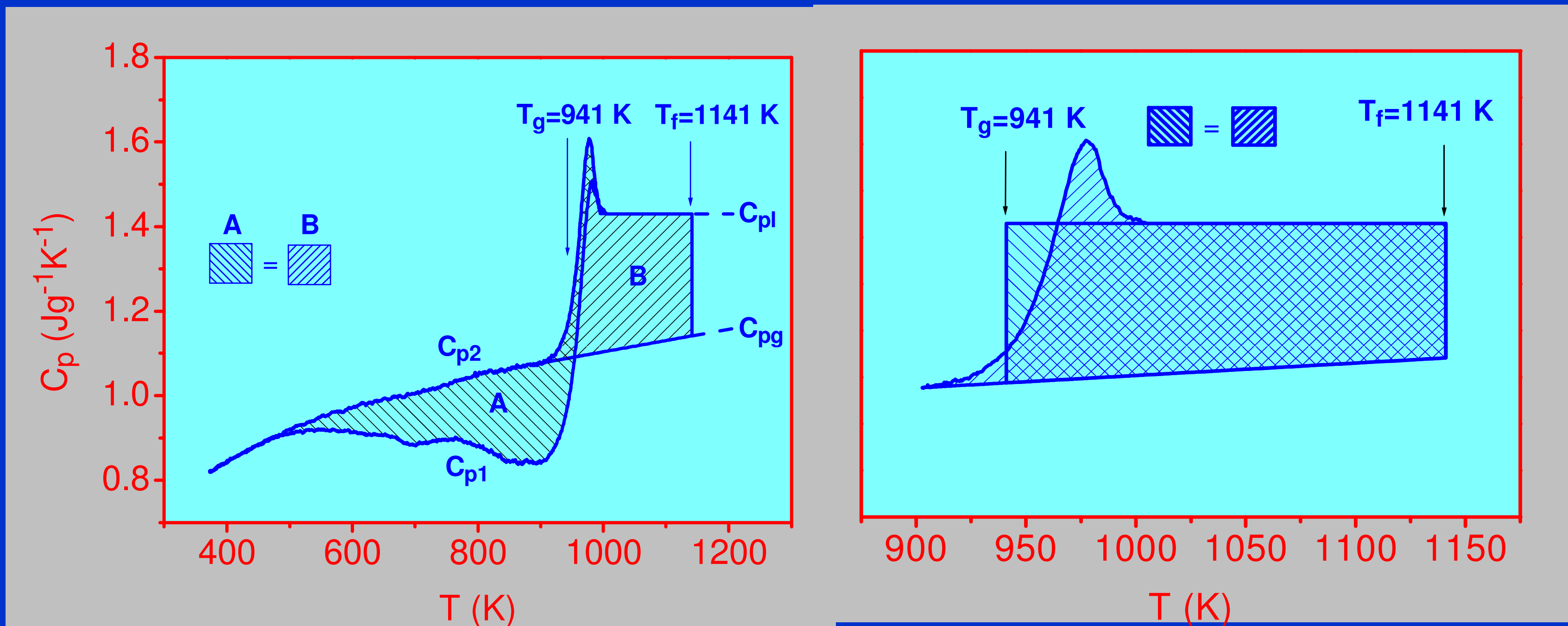
Enthalpy recovery ↔ Potential energy lanscape ↔ Enthalpy trap

Y. Z. Yue, S. L. Jensen, J. Christiansen, Appl. Phys. Lett. (2002)

C. A. Angell, Y.Z. Yue, et al. J. Phys: Cond. Mat. (2003)

A. Monaco, et al. Phys. Rev. Lett. (2006)

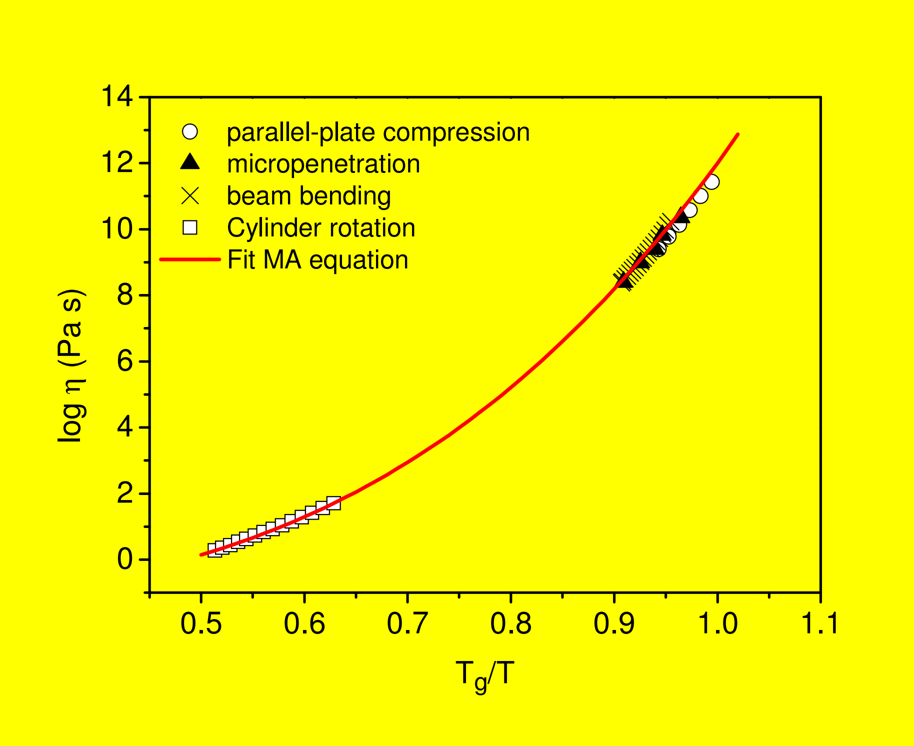
Determination of the glass transition (T_g) and the fictive temperatures (T_f)

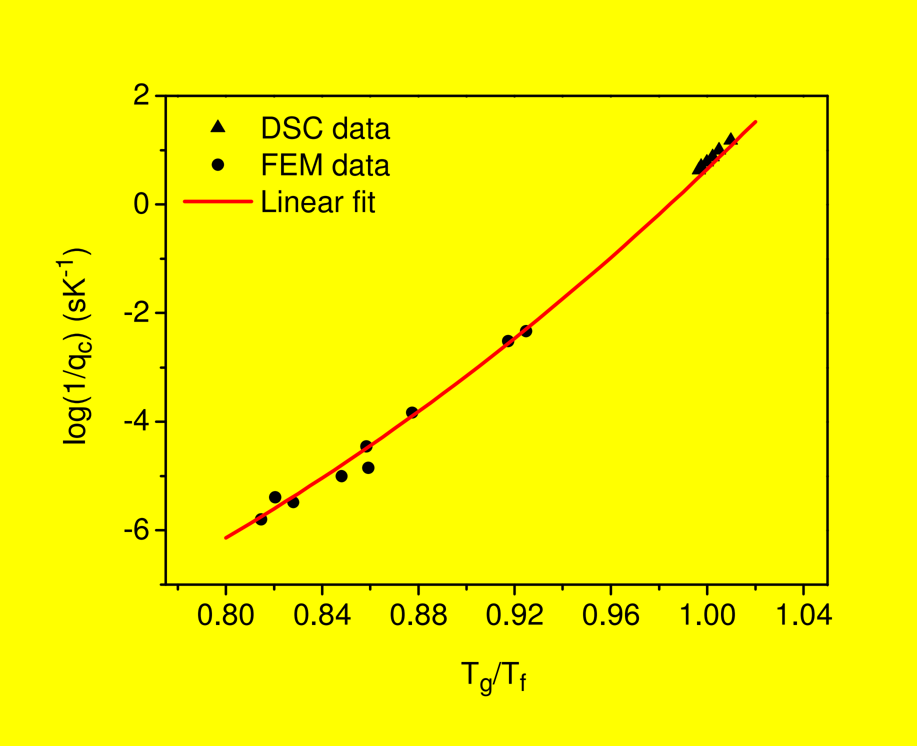


Basic equation: $$\int_{T_c}^{T_{eq}} (C_{p2} - C_{p1})dT = \int_{T_g}^{T_f} (C_{pl} - C_{pg})dT$$

Y. Z. Yue, J. Christiansen, and S.L. Jensen, Chem. Phys. Lett. (2002)

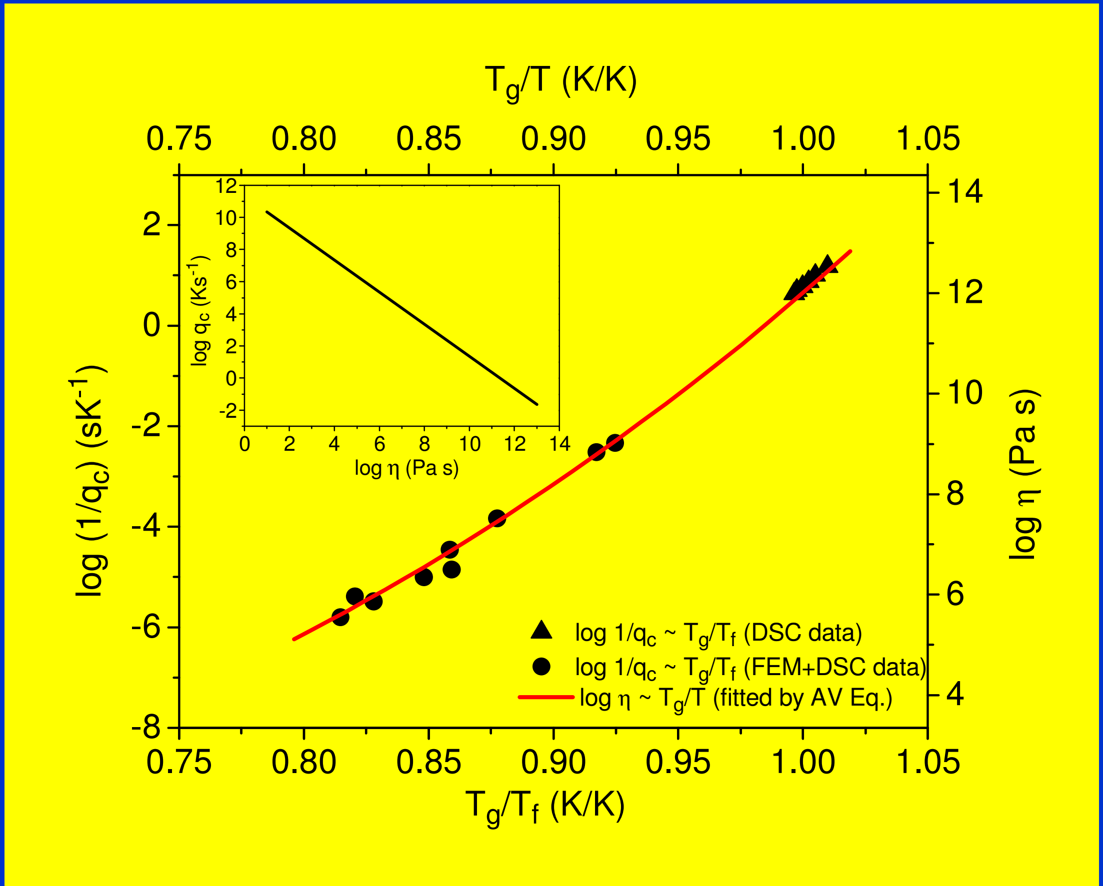
Viscosity and Cooling rate





Principle for determination of cooling rate

$$\log q_c + \log \eta = \log K_c = 11.35$$

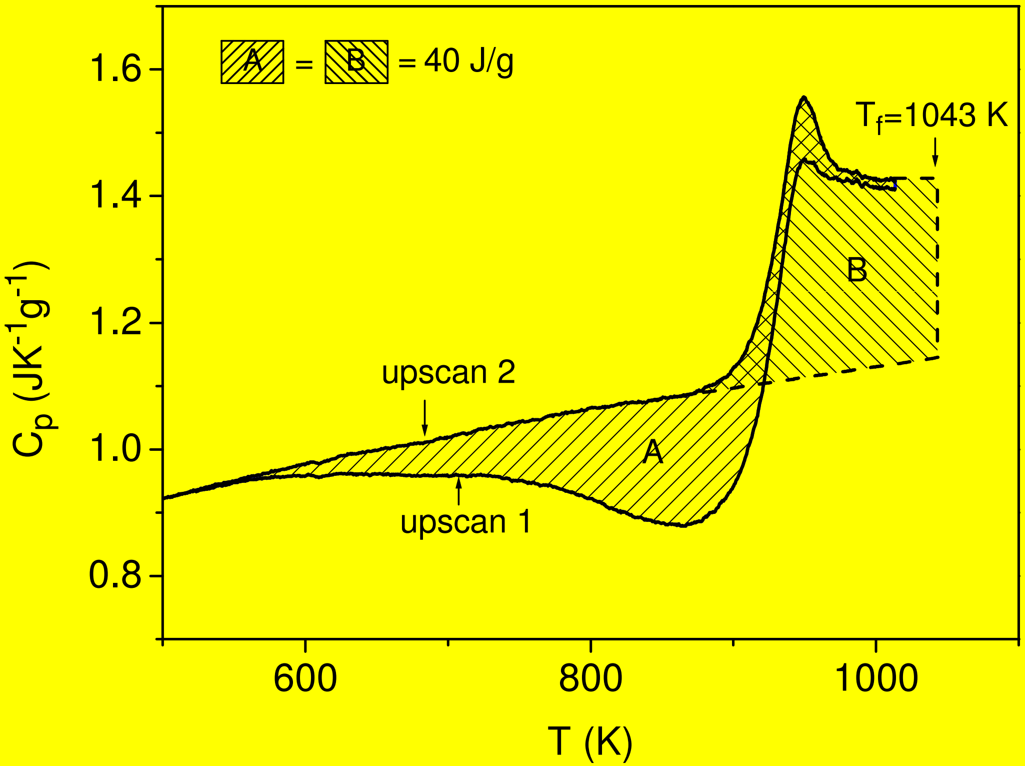


Y.Z. Yue, et al. J. Chem. Phys. (2004)

Pele's Hair

Here we found Pere's hair.

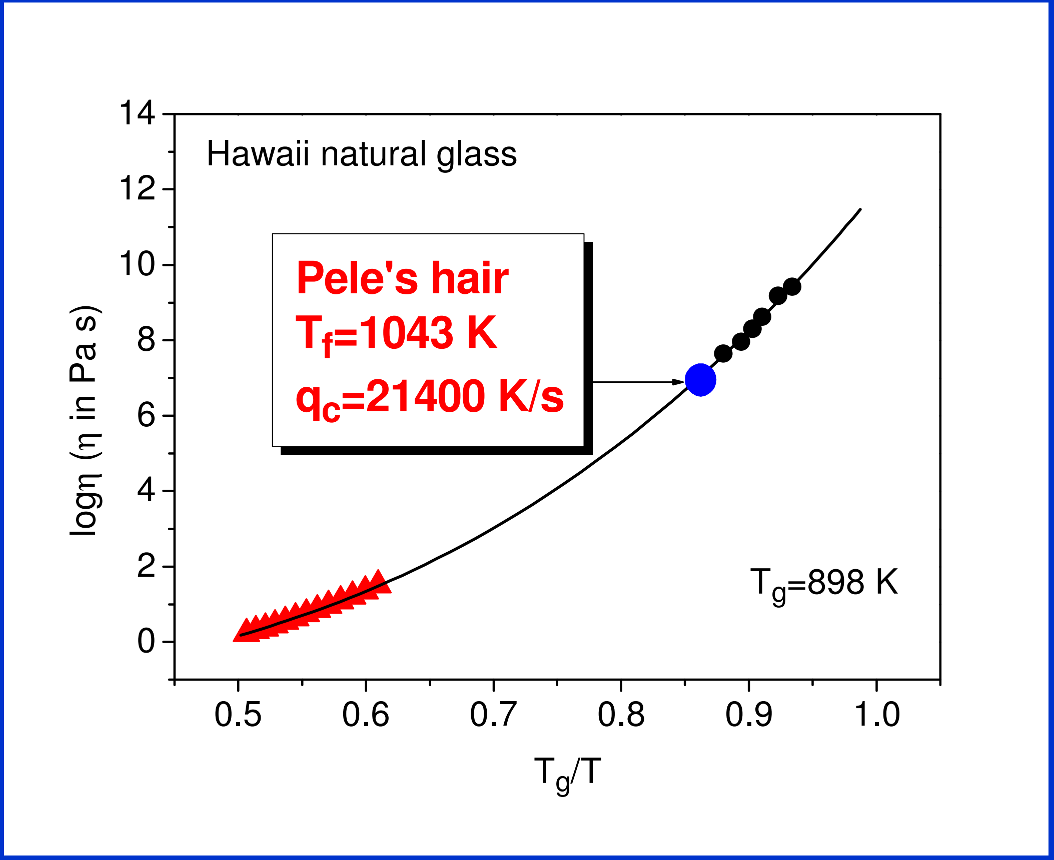
Determination of the fictive temperature of Pele's hair



Viscosity of Hawaii glass melts and cooling rate of Pele's hair

$$\log(\eta) = -1.5 + 13.5\left(\frac{T_g}{T_f}\right)^{3.22}$$

$$\log q_c + \log \eta = 11.35$$



Vielen Dank!