2010 Spring

"Amorphous Materials"

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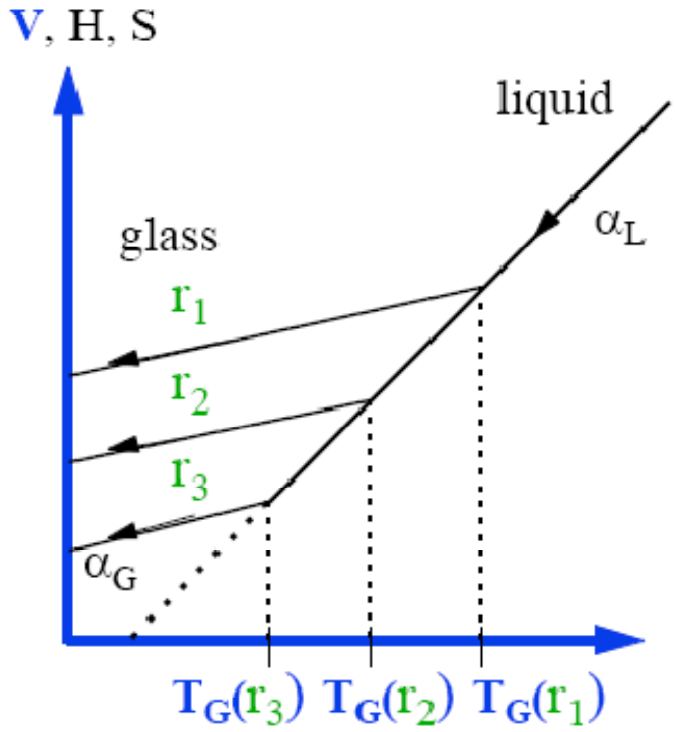
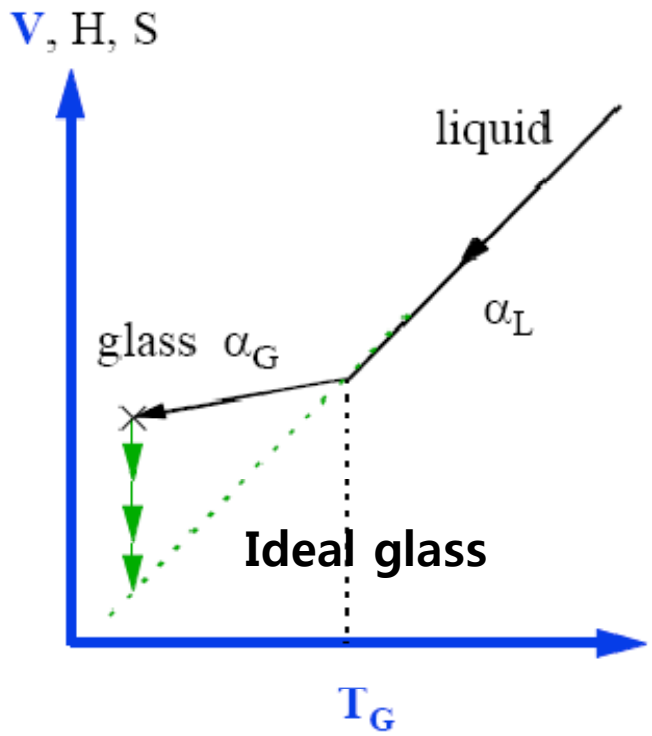
Contents for previous class

1) ***Glass transition is not thermodynamic nature,***
which is close to second order phase transition.

2) ***T_g depends on thermal history.***





Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$

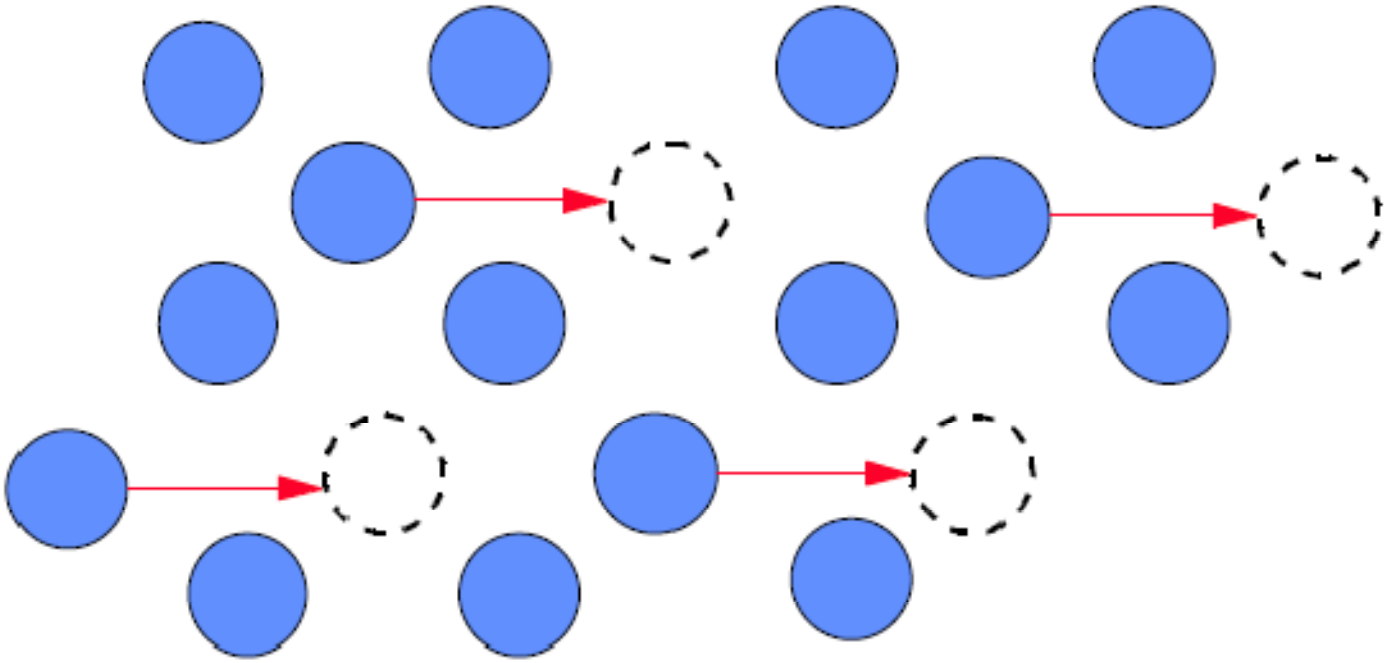
Specific Volume (density) of the glass depends on the time at a given $T < T_g$

Definition of a glass ?

$$\tau_{micro} \ll \tau_{exp} \ll \tau_{relax}$$

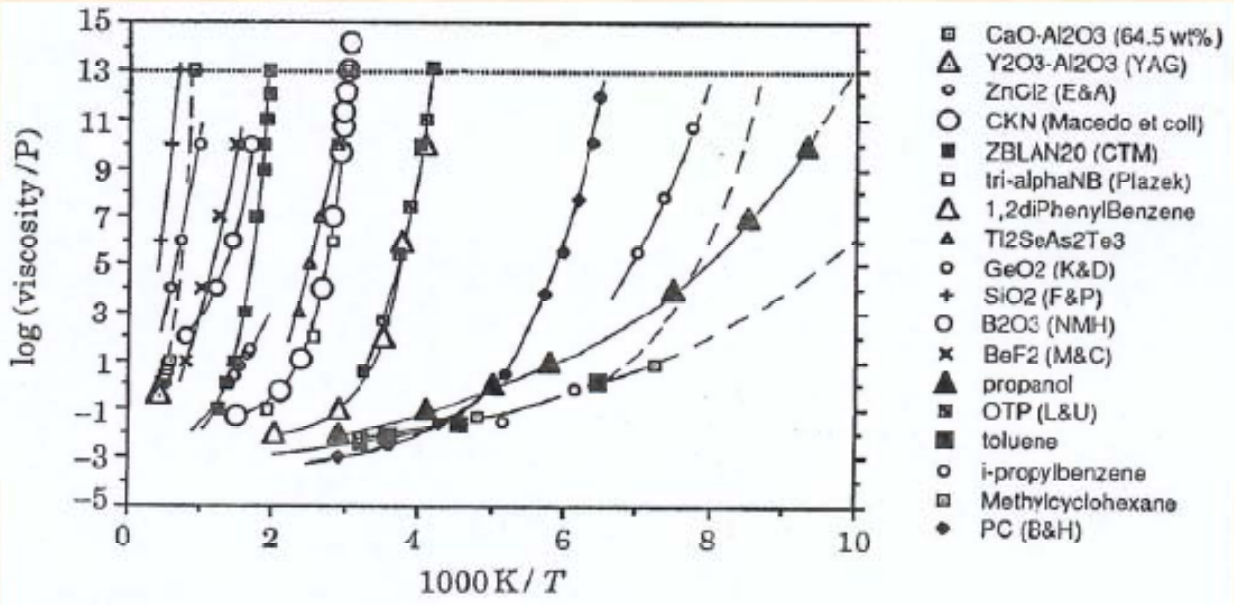
Time scale separation between microscopic, experimental, relaxation; the system is out of equilibrium on the experimental time scale.
(cf. S.K. Ma, Statistical Physics)

Temperature Dependence of Liquid Viscosity



Viscosity is a measure of the resistance to flow. The higher T, the larger the average size of the holes and the larger the energy of the molecules, the easier the molecule move past oneanother, the lower the resistance to flow.

Glass transition defined by typical viscosity η. Arbitrary but convenient



Arrhenius plot: log(time) or log(viscosity) versus 1/T.

Similar behaviour for relaxation times obtained using different methods (dielectric relaxation, NMR) . α relaxation time τ_α

Fragility

- **Fragility** ~ ability of the liquid to withstand changes in medium range order with temp.
  ~ extensively use to figure out liquid dynamics and glass properties corresponding to "frozen" liquid state

< Classification of glass >

Strong network glass **: Arrhenius behavior**

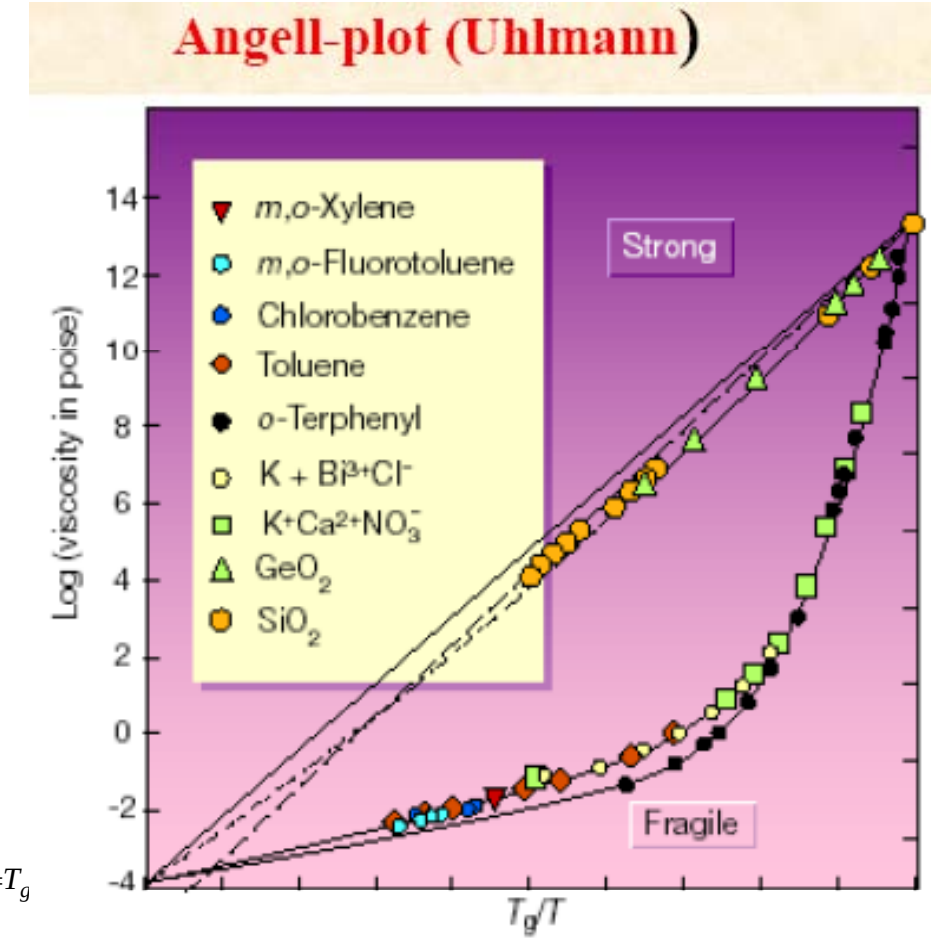
$$\eta = \eta_0 \exp[\frac{E_a}{RT}]$$

Fragile network glass **: Vogel-Fulcher relation**

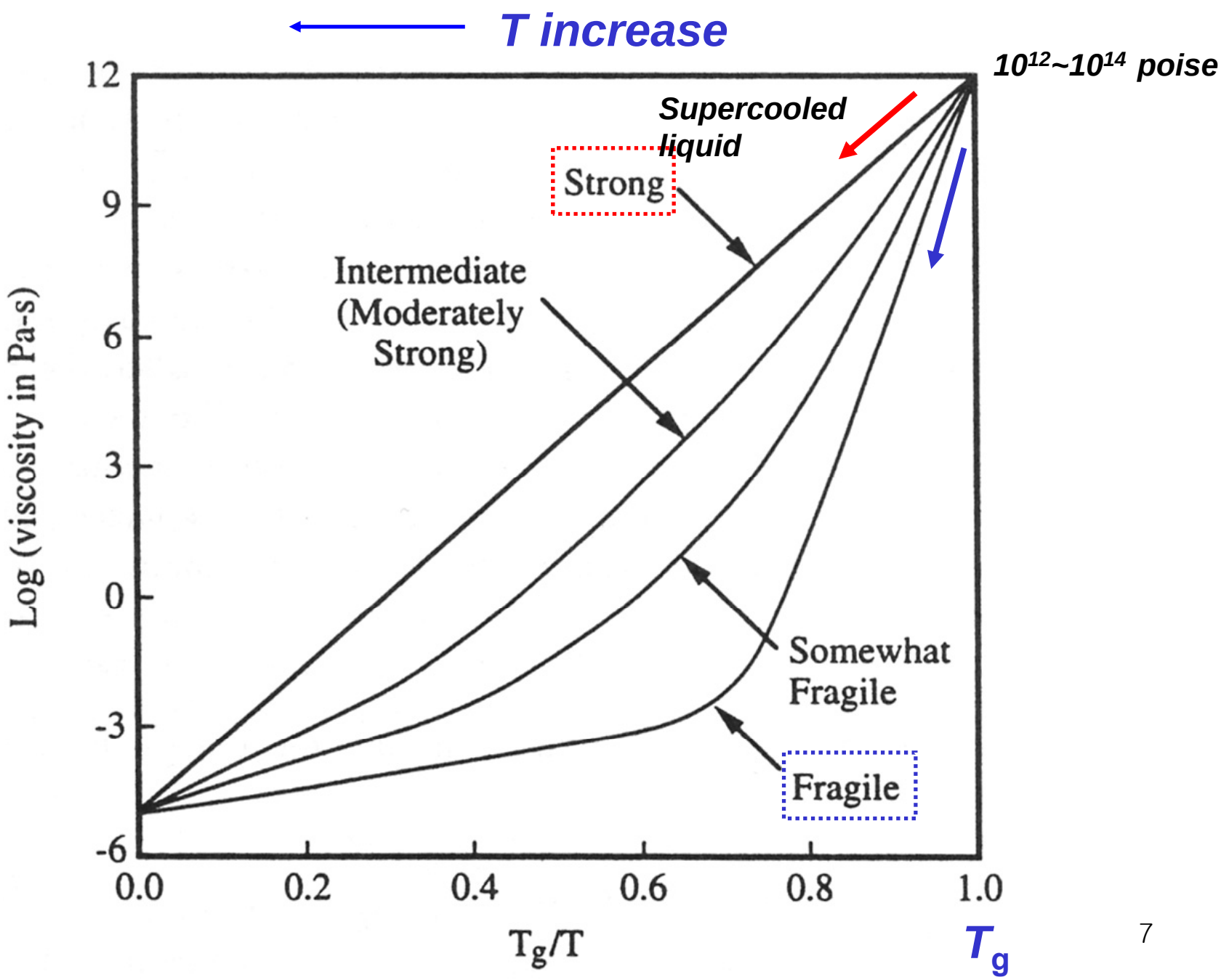
$$\eta = \eta_0 \exp[\frac{B}{T - T_0}]$$

< Quantification of Fragility >

$$m = \left.\frac{d \log \eta(T)}{d(T_{g,n}/T)}\right|_{T=T_{g,n}} = \left.\frac{d \log \tau(T)}{d(T_g/T)}\right|_{T=T_g}$$



Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g


T increase
10^12~10^14 poise
Supercooled liquid
Strong
Intermediate (Moderately Strong)
Somewhat Fragile
Fragile
Log (viscosity in Pa-s)
12
9
6
3
0
-3
-6
0.0
0.2
0.4
0.6
0.8
1.0
Tg/T
Tg

Fragility

Strong liquid vs. Fragile liquid

- ***Strong glass-forming liquid***

  → **covalent bond of SiO_2**

  → **small difference of C_p between SCL and glass at T_g**
  (small difference of structure)

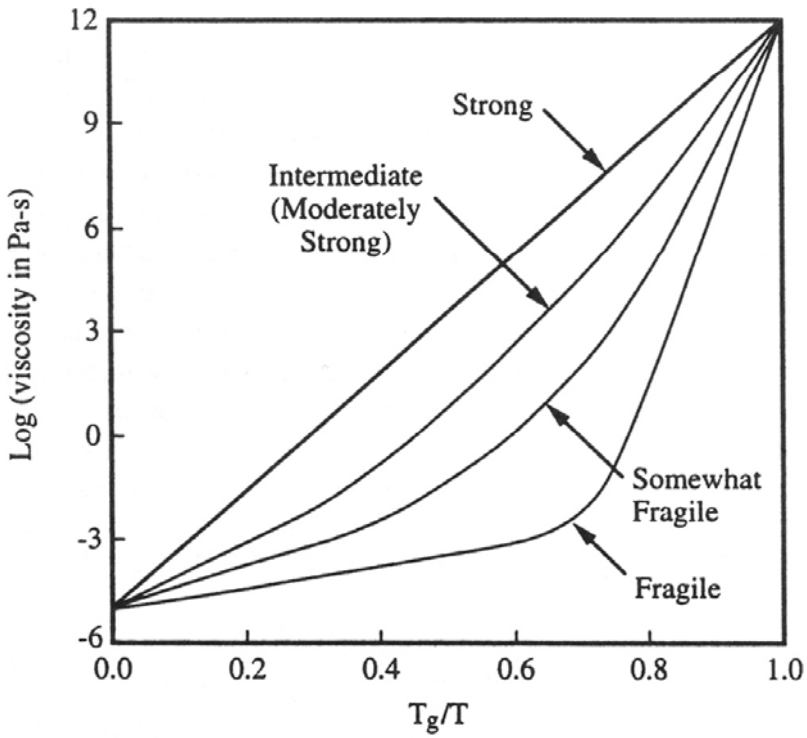
  → **SCL: relatively low entropy**

- ***fragile glass-forming liquid***

  → **non-directional bonding**
  (Van der waals bonding)

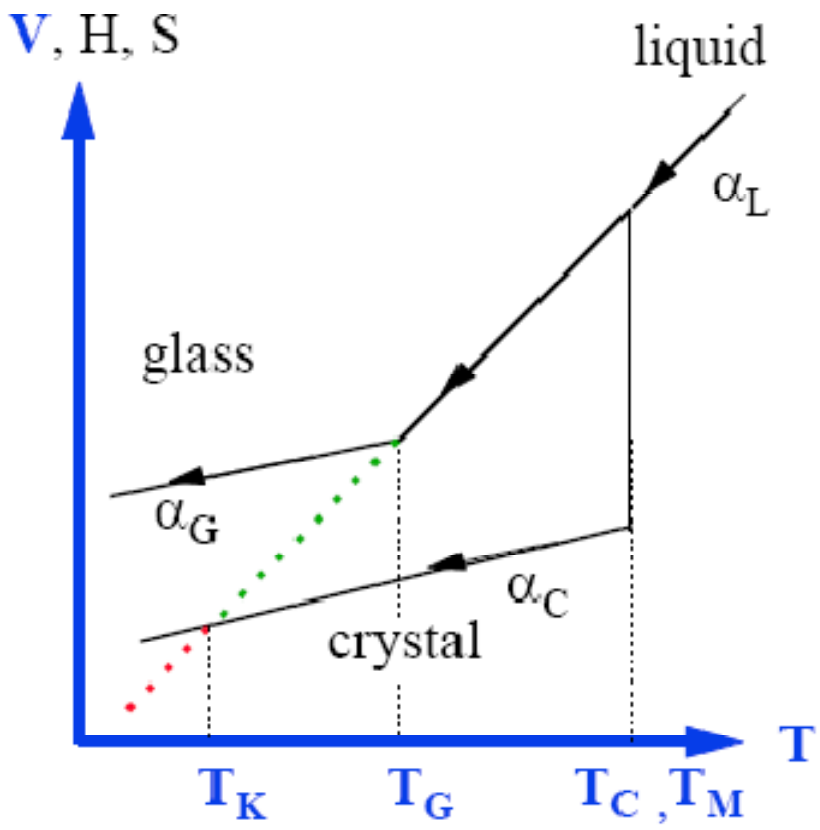
  → **large difference of C_p at T_g**
  (relatively large free volume)

  → **SCL: relatively high entropy**



Controversies in Amorphous Solids: The Kauzmann Paradox

If we extrapolate the specific volume of the liquid from above T_M to temperatures much below T_G, one must accept that at some temperature T_K well above 0 K, the specific volume, the enthalpy and the entropy of the equilibrium liquid would become lower than that of the crystal... Since the above statement is not possible (Kauzmann paradox) , two solutions are possible:



1) at some temperature (T_K), there is a true 2nd order phase tansition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!

Measuring Glass Transition Temperature

Differential scanning calorimetric (DSC)

Differential scanning calorimetry or **DSC** is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature.

1. Both the sample and reference are maintained at nearly the same temperature throughout the experiment.
2. the sample holder temperature increases linearly as a function of time.
3. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.
4. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transition, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic.

Heat Capacity

- dq_p/dt = heat flow
- dT/dt = heating rate
- $(dq_p/dt) / (dT/dt) = dq_p/dT = c_p$

<u>Specific heat capacity (a.k.a. Specific heat)</u>

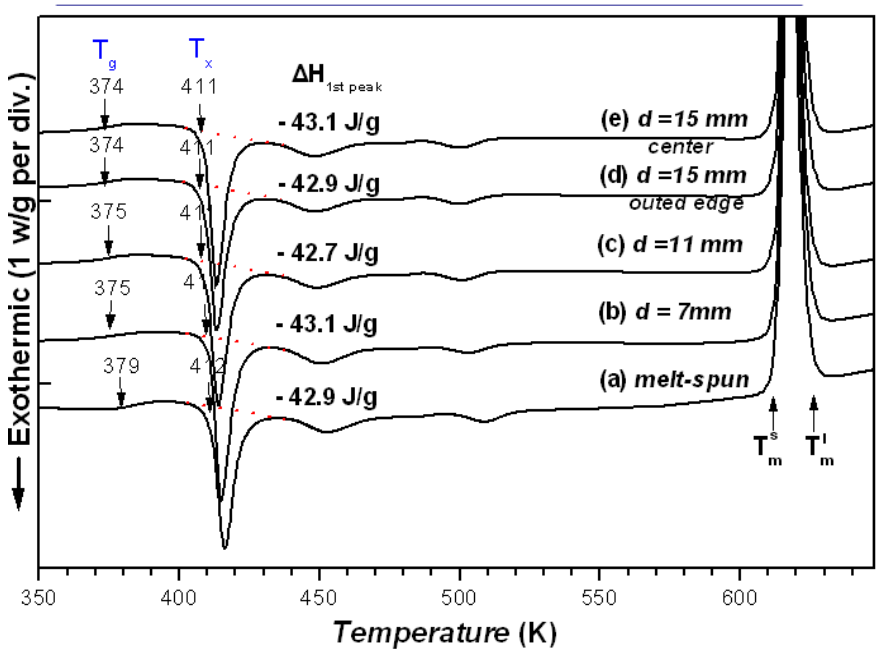
- **symbolized as c, units in J/g°C**
- **It's the heat required to raise *1 gram* of a substance by 1 °C**

<u>Heat capacity</u>

- **calculated by c x m, units in J/°C**
- **It's the heat required to raise the temperature of *an object* by 1 °C.**

<u>Molar heat capacity</u>: units in J/mol °C.

DSC curves



A schematic DSC curve demonstrating the appearance of several common features

(mw)

1. a curve of heat flux versus temperature or versus time.
2. two different conventions: exothermic reactions in the sample shown with a positive or negative peak; it depends by the different kind of technology used by the instrumentation to make the experiment.
3. This curve can be used to calculate enthalpies of transitions This is done by integrating the peak corresponding to a given transition.

   the enthalpy of transition ΔH :

   $\Delta H = KA$

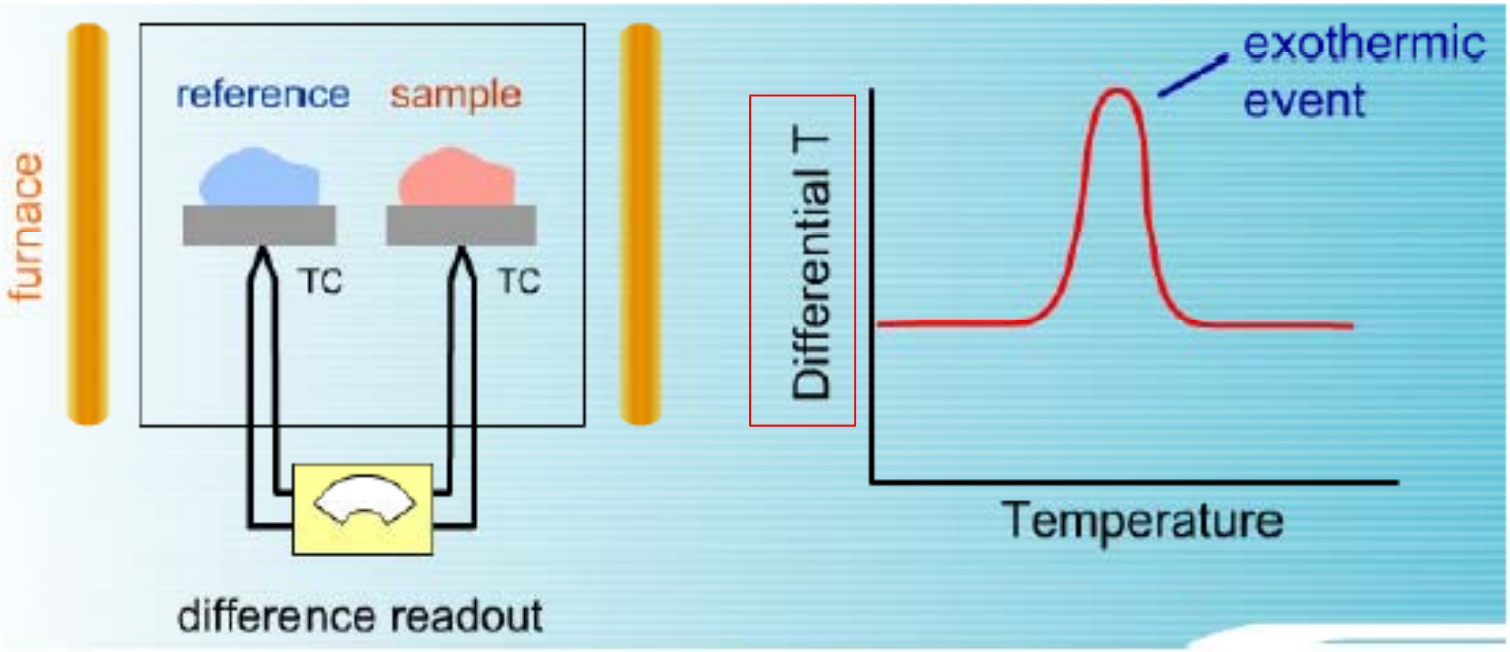
   K is the calorimetric constant,

   A is the area under the curve.
4. The calometric constant K will vary from instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition.

Differential Thermal Analysis

1. **DTA** involves heating or cooling a test sample and an inert reference *under identical conditions,* while recording *any temperature difference* between the sample and reference.
2. This differential temperature is then plotted against time, or against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference.
3. DTA can therefore be used to study thermal properties and phase changes which do not lead to a change in enthalpy.
4. The baseline of the DTA curve should then exhibit discontinuities at the transition temperatures and the slope of the curve at any point will depend on the microstructural constitution at that temperature.
5. A DTA curve can be used as a finger print for identification purposes.
6. The area under a DTA peak can be to the enthalpy change and is not affected by the heat capacity of the sample.

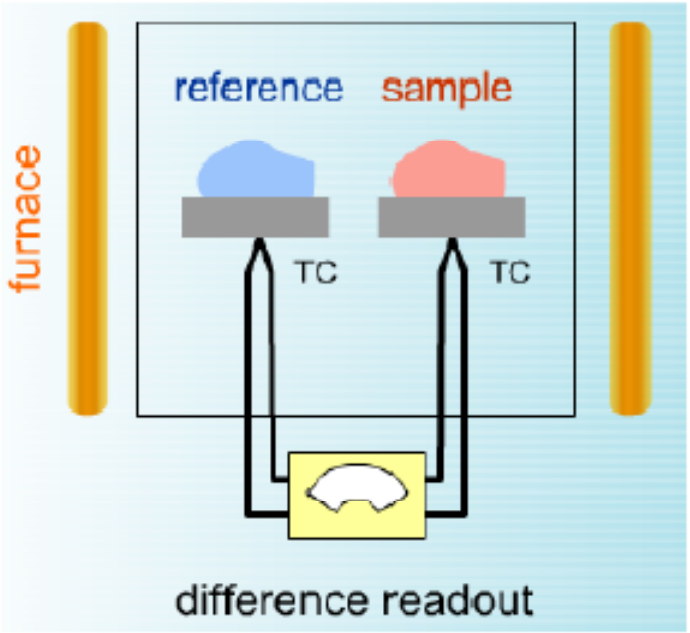
Measure sample temperature relative to a reference, for the same heat transferred

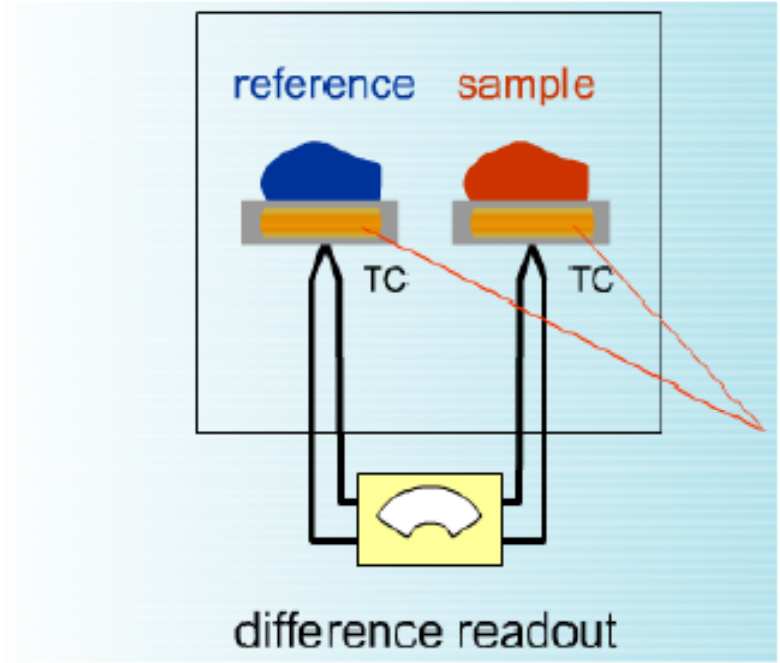


Thermal evants: Exothermic event and endothermic event

Reaction/decomposition
Melting
Crystallization
Change in crystal structure
Glass transition

DTA

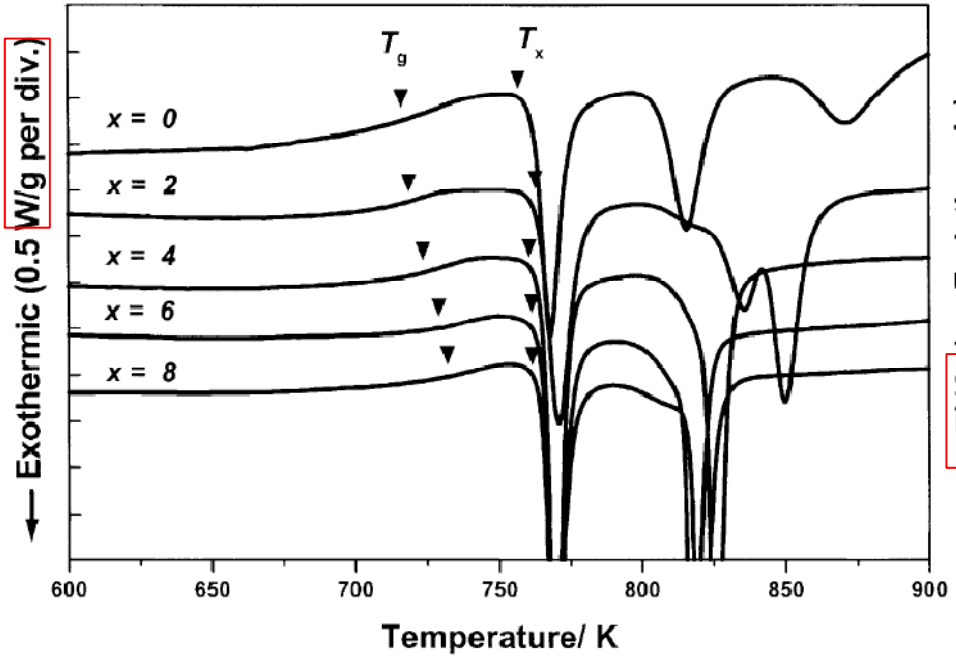




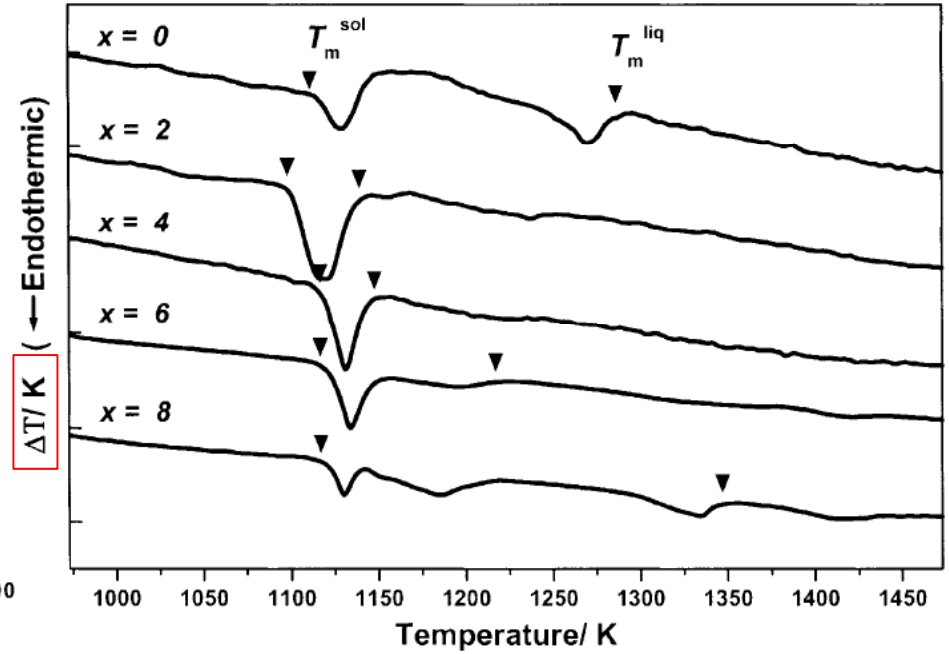
DSC

- similar concept as DTA (compare sample & reference)
- measure "heat flow" required to keep both specimens same temperature

DSC Scan



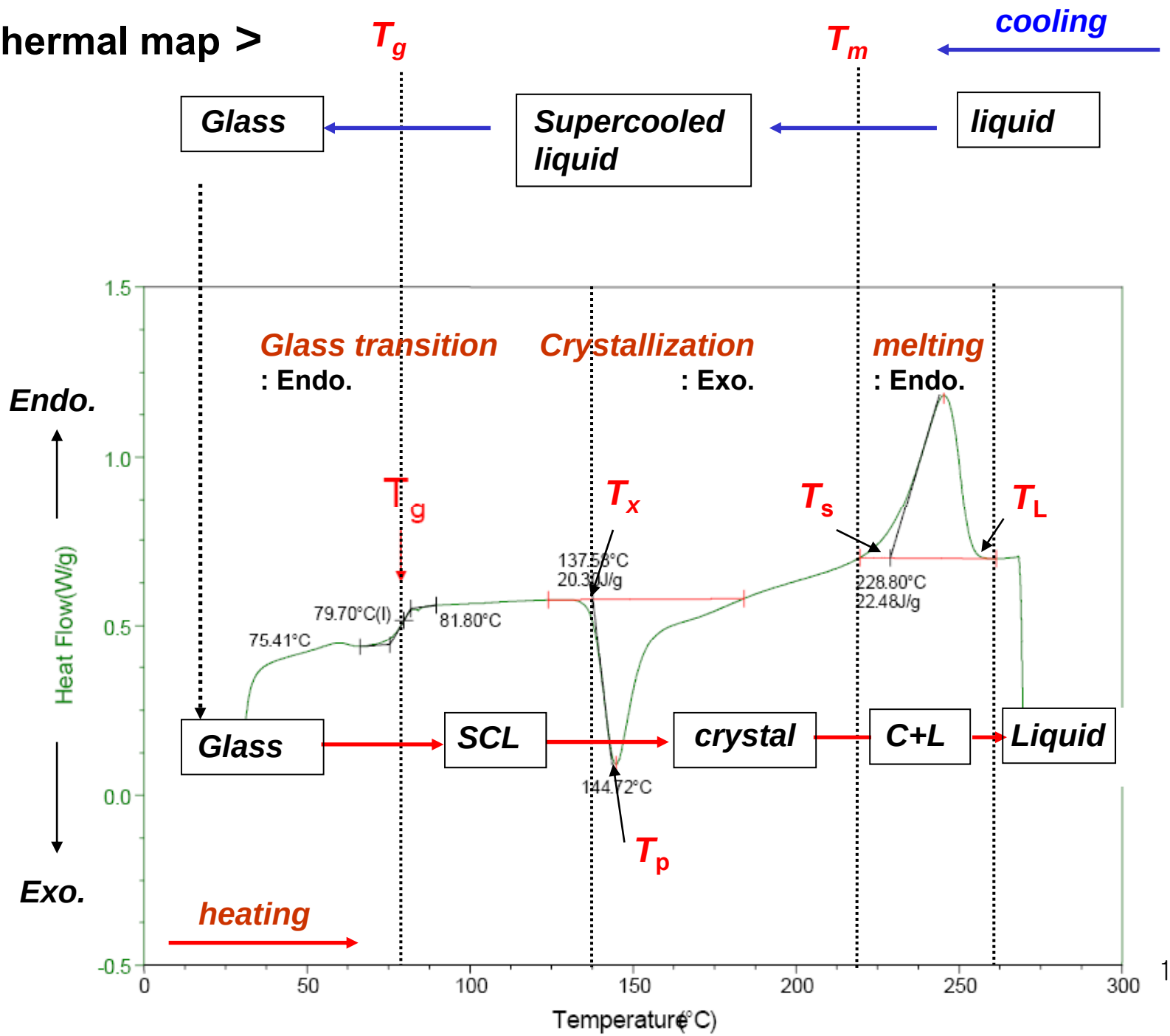
DTA Scan



Low temp. 253 K ~ 973 K

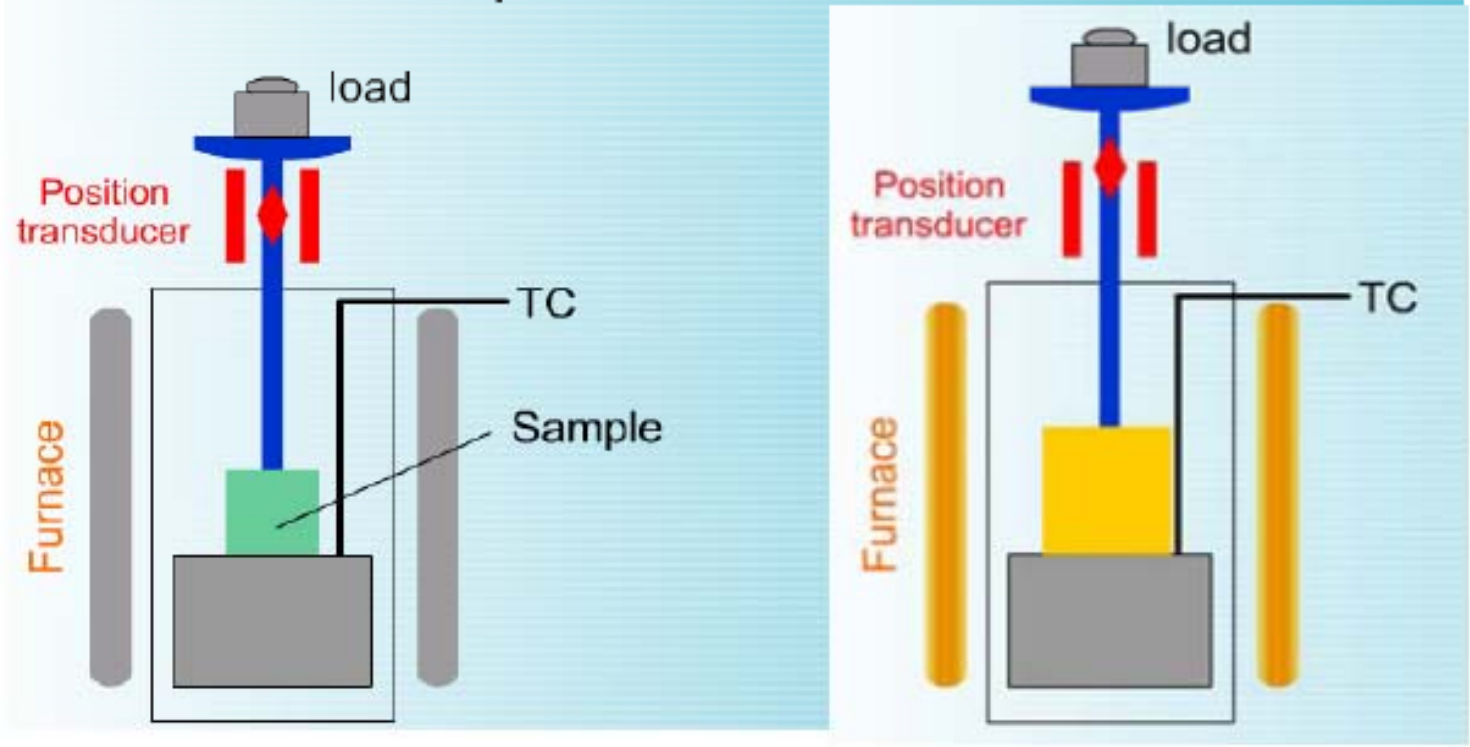
High temp. 373K ~ 1573 K

< Thermal map >


T_g
T_m
cooling
Glass
Supercooled liquid
liquid
Glass transition
: Endo.
Crystallization
: Exo.
melting
: Endo.
Endo.
Exo.
T_g
T_x
T_s
T_L
137.58°C
20.37J/g
228.80°C
22.48J/g
79.70°C(I)
81.80°C
75.41°C
144.72°C
T_p
Glass
SCL
crystal
C+L
Liquid
heating
Heat Flow(W/g)
Temperature(°C)
1.5
1.0
0.5
0.0
-0.5
0
50
100
150
200
250
300

Thermomechanical analysis (TMA):

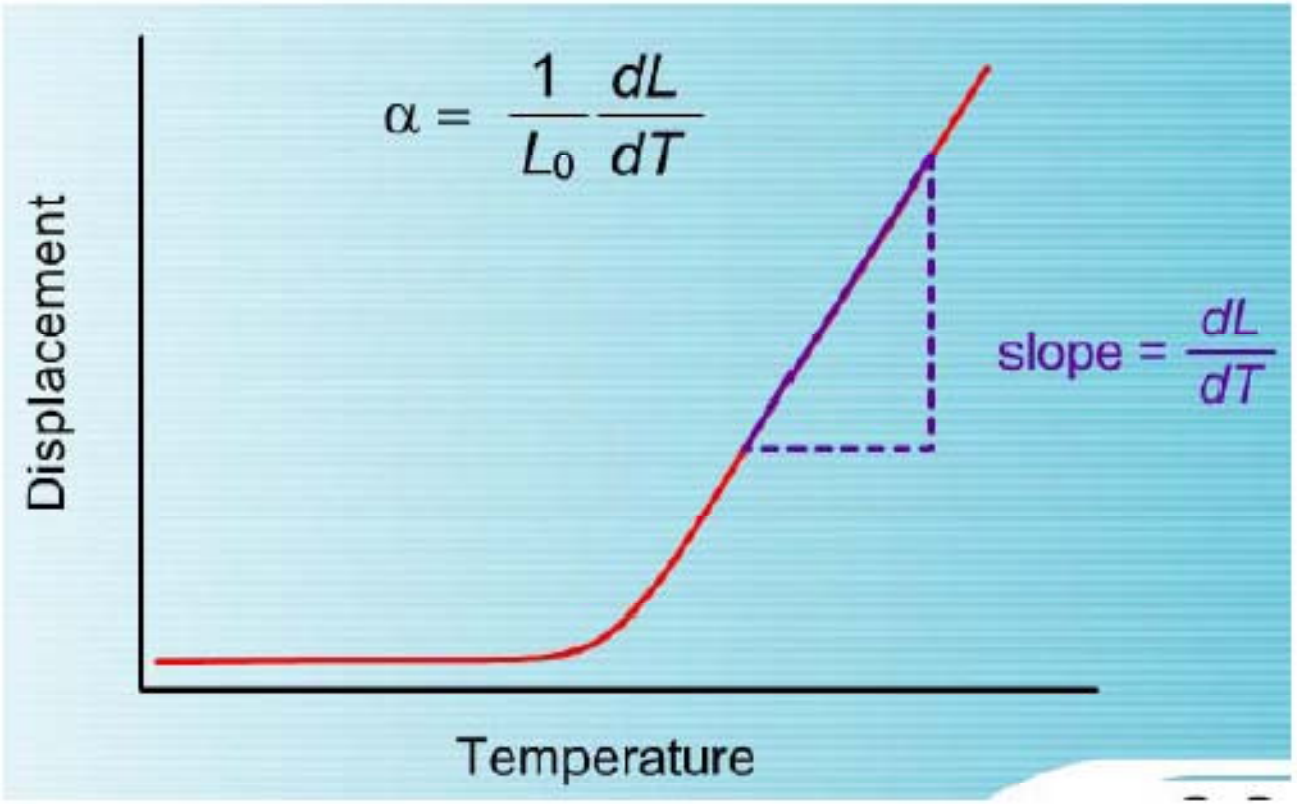
- measure dimension changes under constant load, as function of temperature



Measure d probe displacement → expansion /shrinkeage of sample

→ **dilatometry**

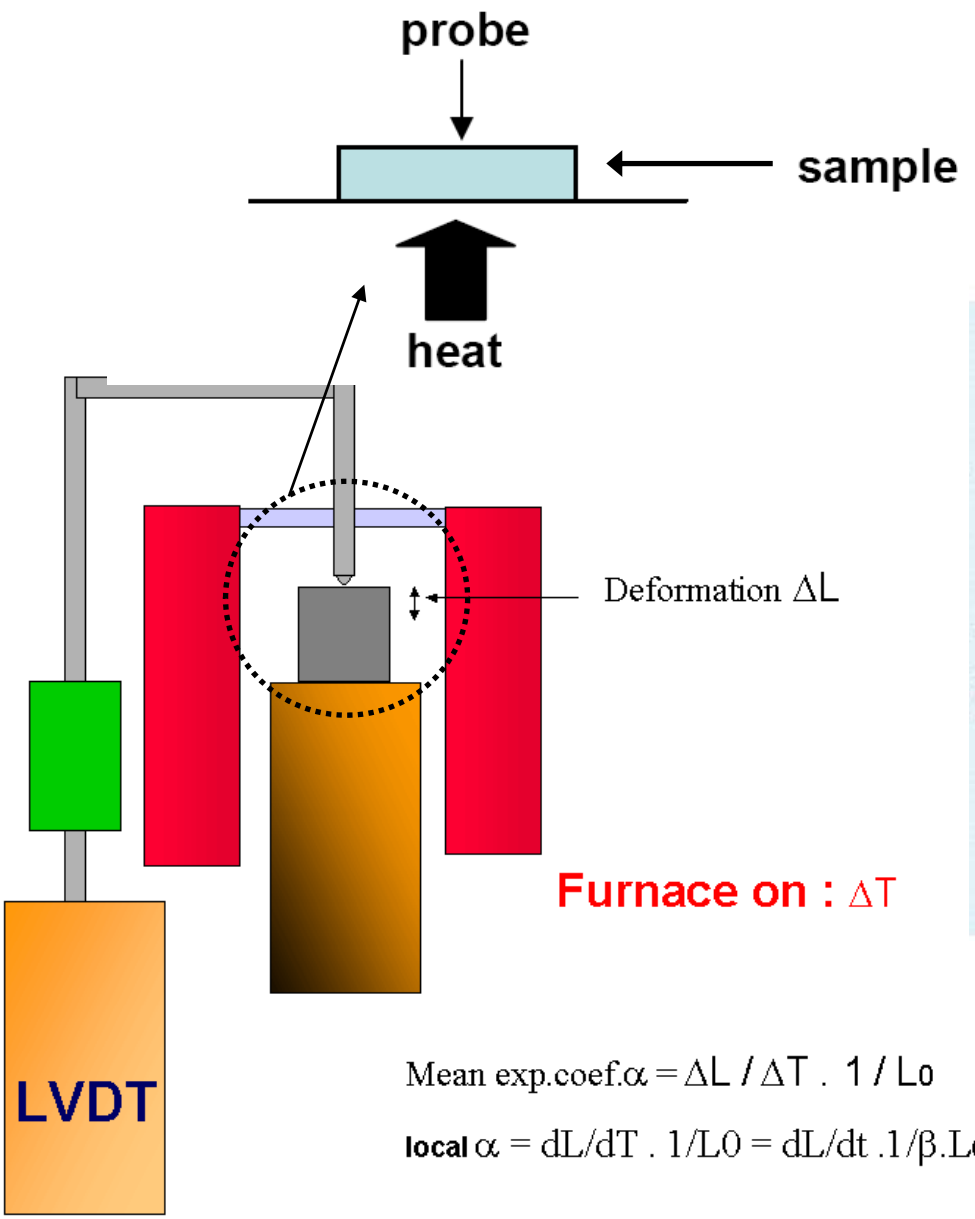
Measure dimension changes under constant load, as function of temperature



L_0: original length of the sample,

α: linear thermal expansion coefficient

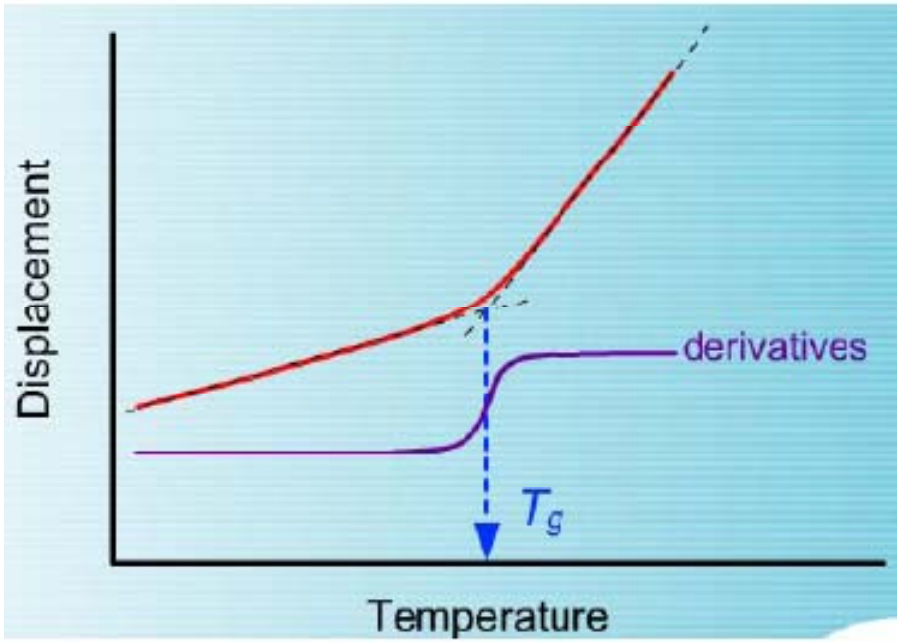
Thermomechanical analysis (TMA):

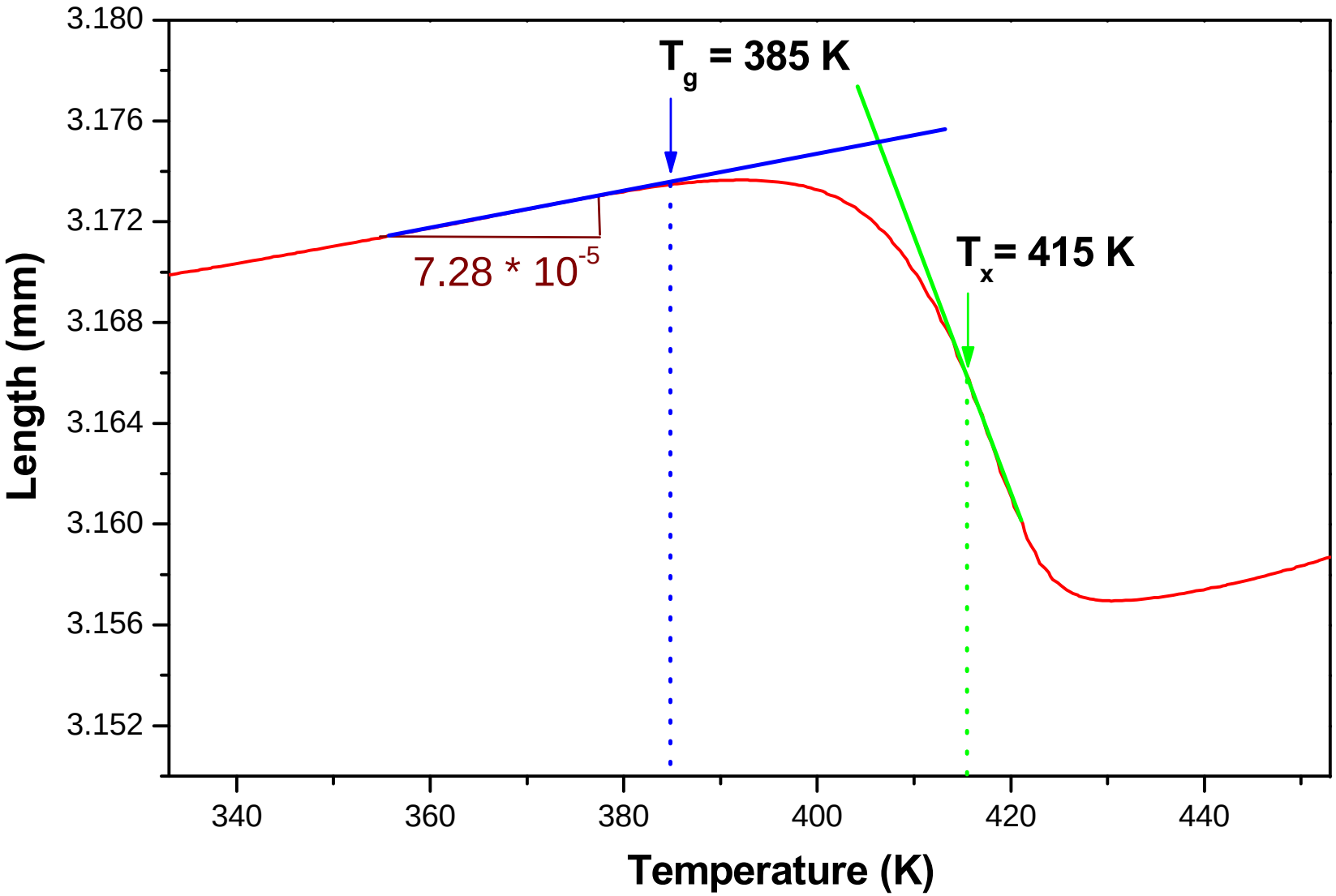


Mean exp.coef.$\alpha = \Delta L / \Delta T \cdot 1 / L_0$

local $\alpha = dL/dT \cdot 1/L0 = dL/dt \cdot 1/\beta . L_0$

Determination of T_g



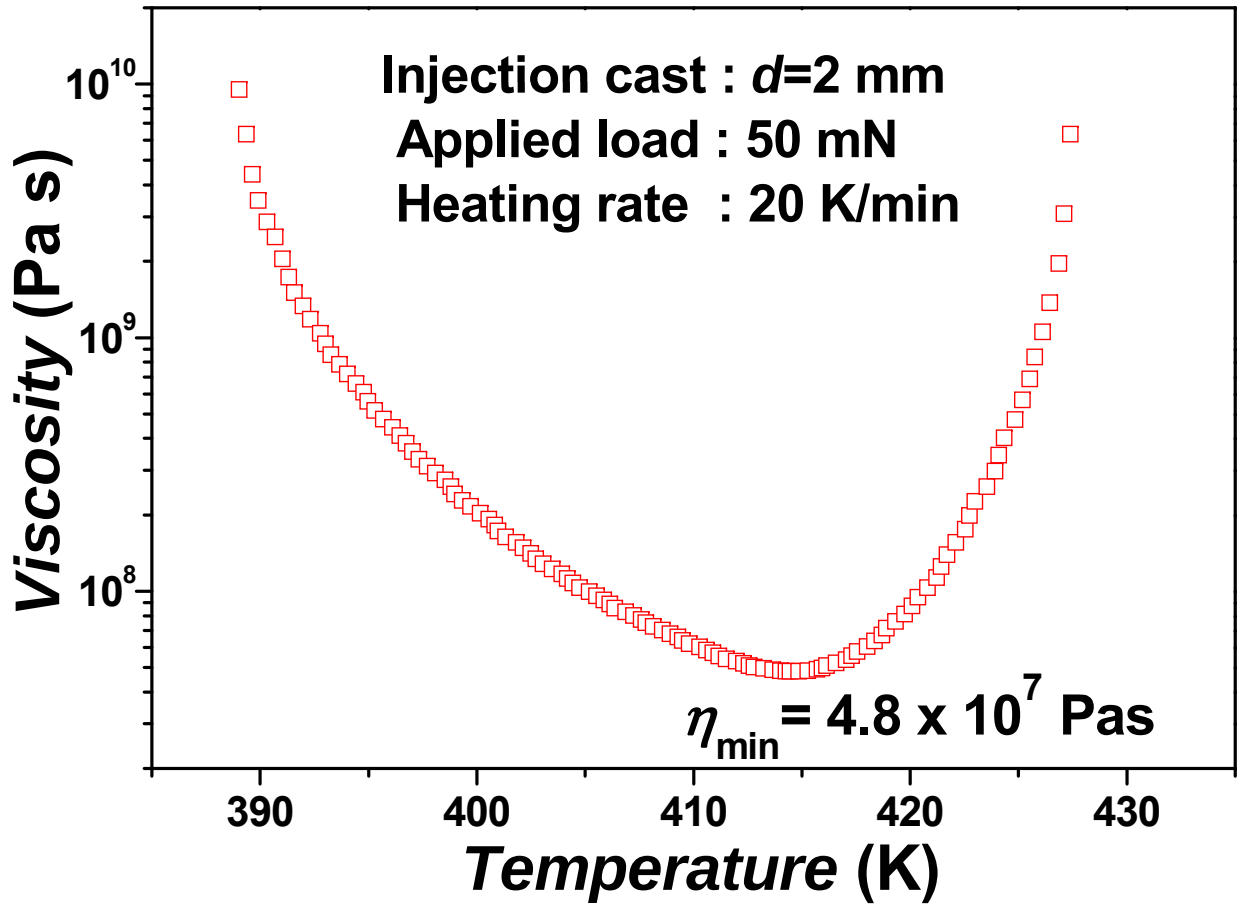


Thermal expansion curve obtained from the rod of $Ca_{65}Mg_{15}Zn_{20}$ (3 mm in height and 2 mm in diameter).

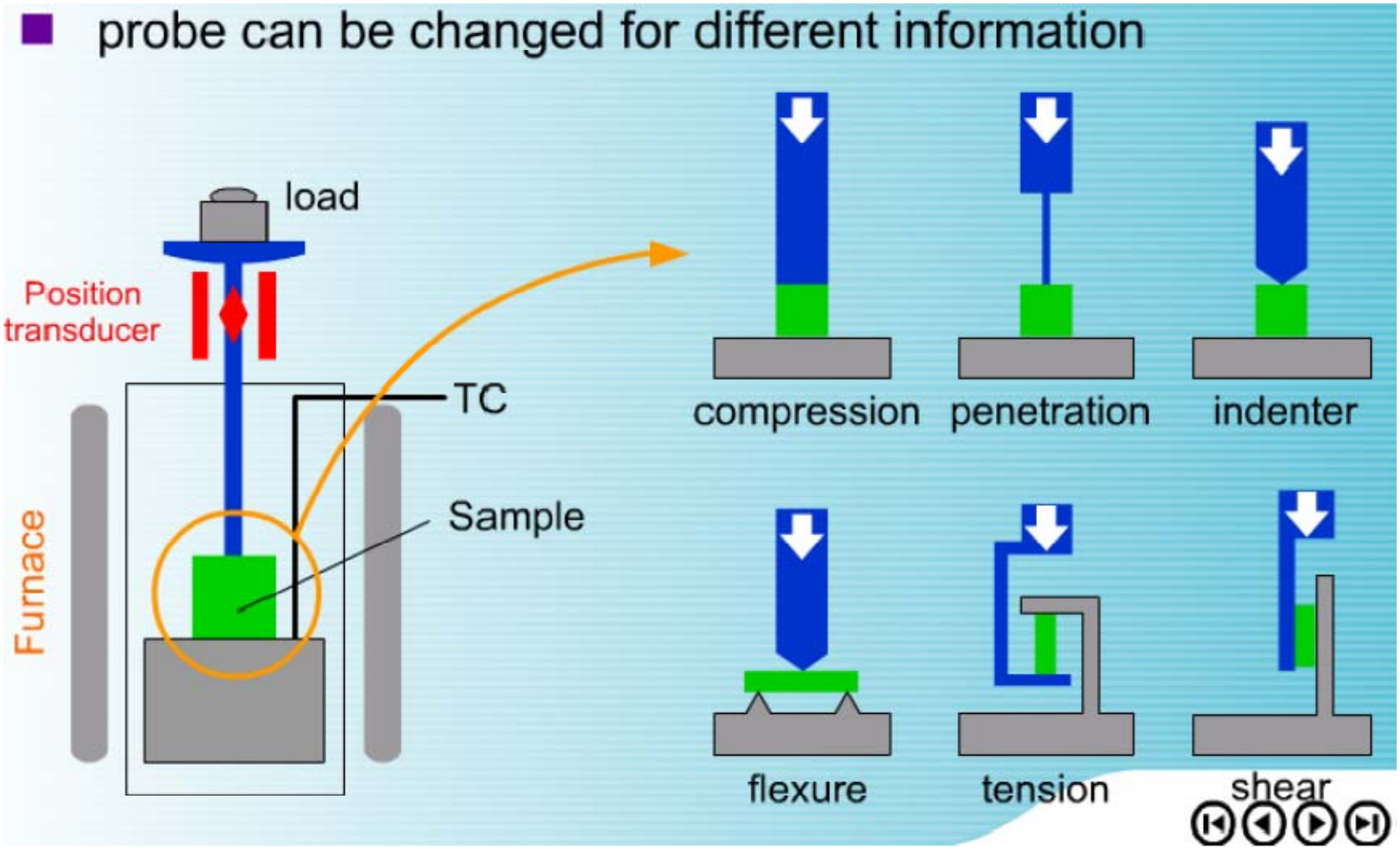
By measuring the height of the sample versus time, the viscosity at any temperature is given by the Stefan equation

$$\eta = -\frac{2Fh^3}{3\pi a^4 (dh/dt)},$$

where *F* is the applied load, *a* is the radius of the samples (1.5 mm), and *h* is the height of the sample.



Thermomechanical analysis (TMA):



Thermomechanical analysis (TMA):

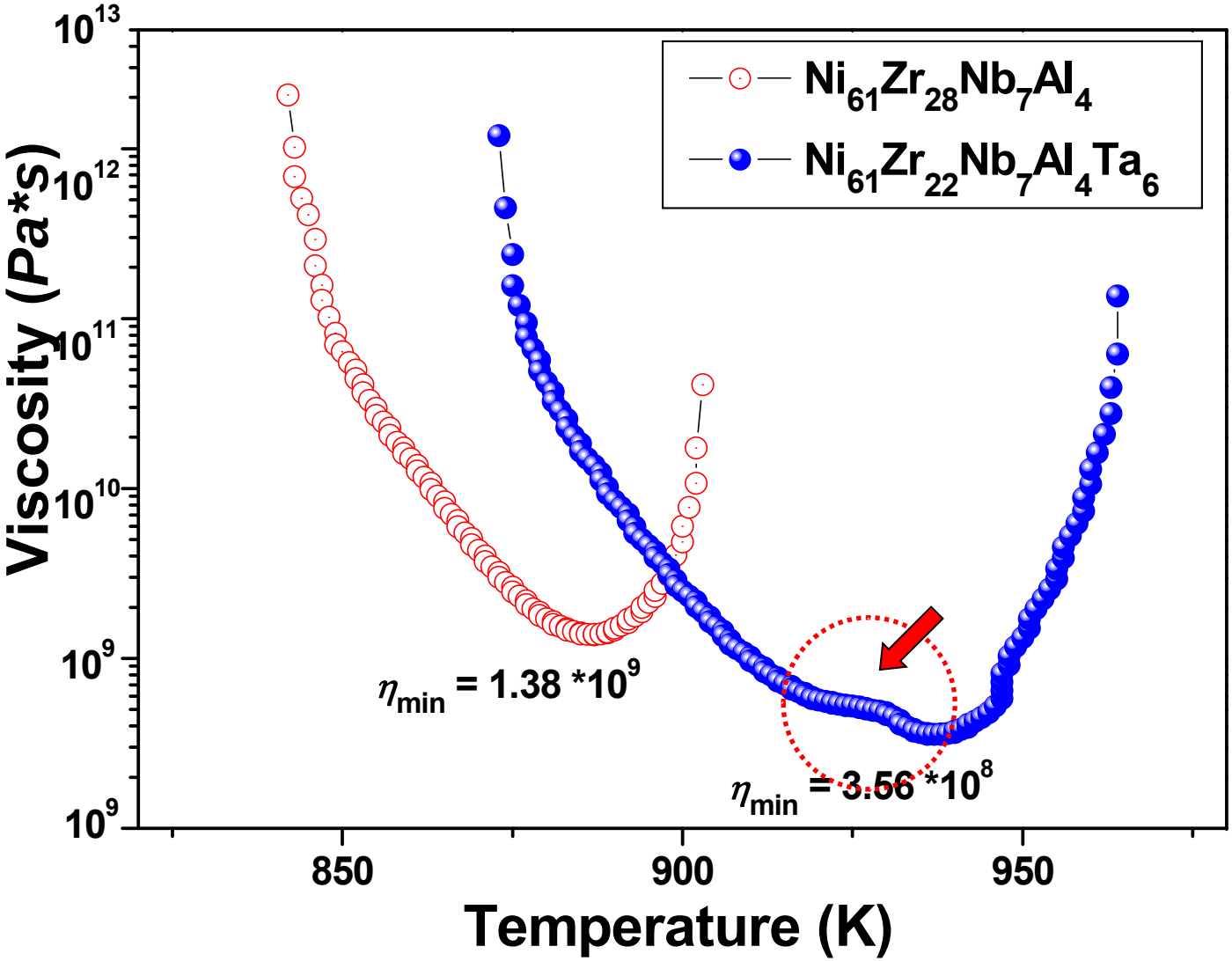
Advantages:

Not limited to bulk specimen (can apply to thin films and fibers)

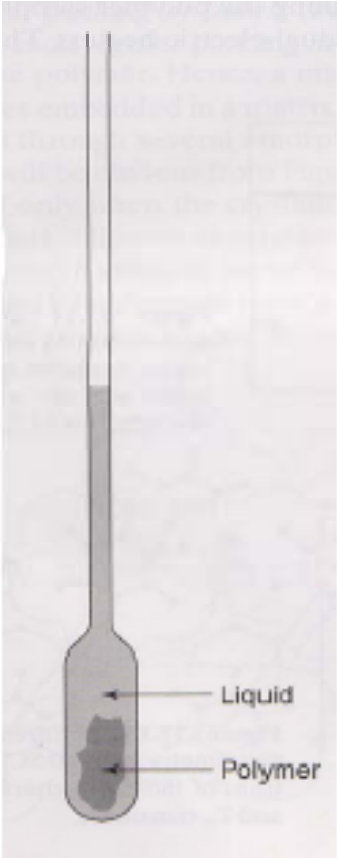
sensitive method to detect T_g

Can detect other properties besides thermal properties

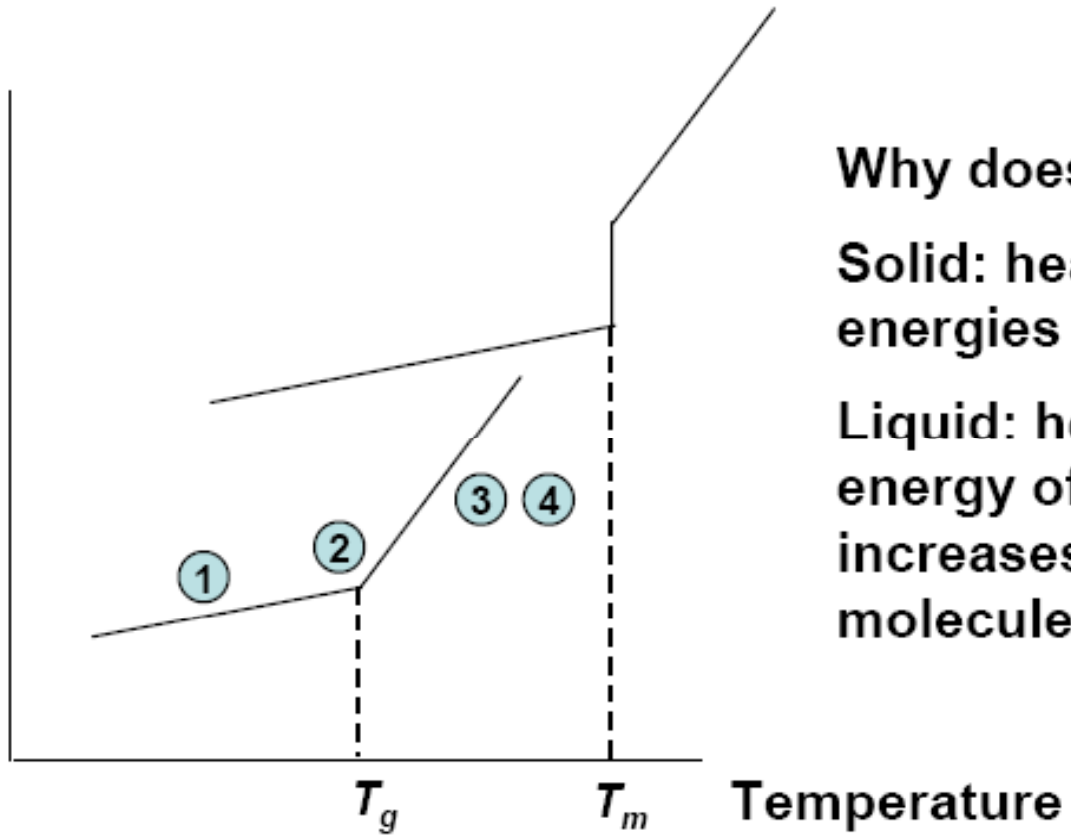
e.g. creep behavior, softening, modulus, viscosity


Viscosity (Pa*s)
Temperature (K)
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{9}
850
900
950
$Ni_{61}Zr_{28}Nb_7Al_4$
$Ni_{61}Zr_{22}Nb_7Al_4Ta_6$
η_{min} = 1.38 *10^9
η_{min} = 3.56 *10^8

Dilatometry



- Used to monitor change in volume of polymer plus surrounding liquid as a function of temperature by changes in height of liquid level in capillary tube.
- The liquid does not undergo sharp transitions when heated, but the polymer does.
  - Therefore, an abrupt increase in the slope of a volume versus temperature graph is attributed to a T_g transition.



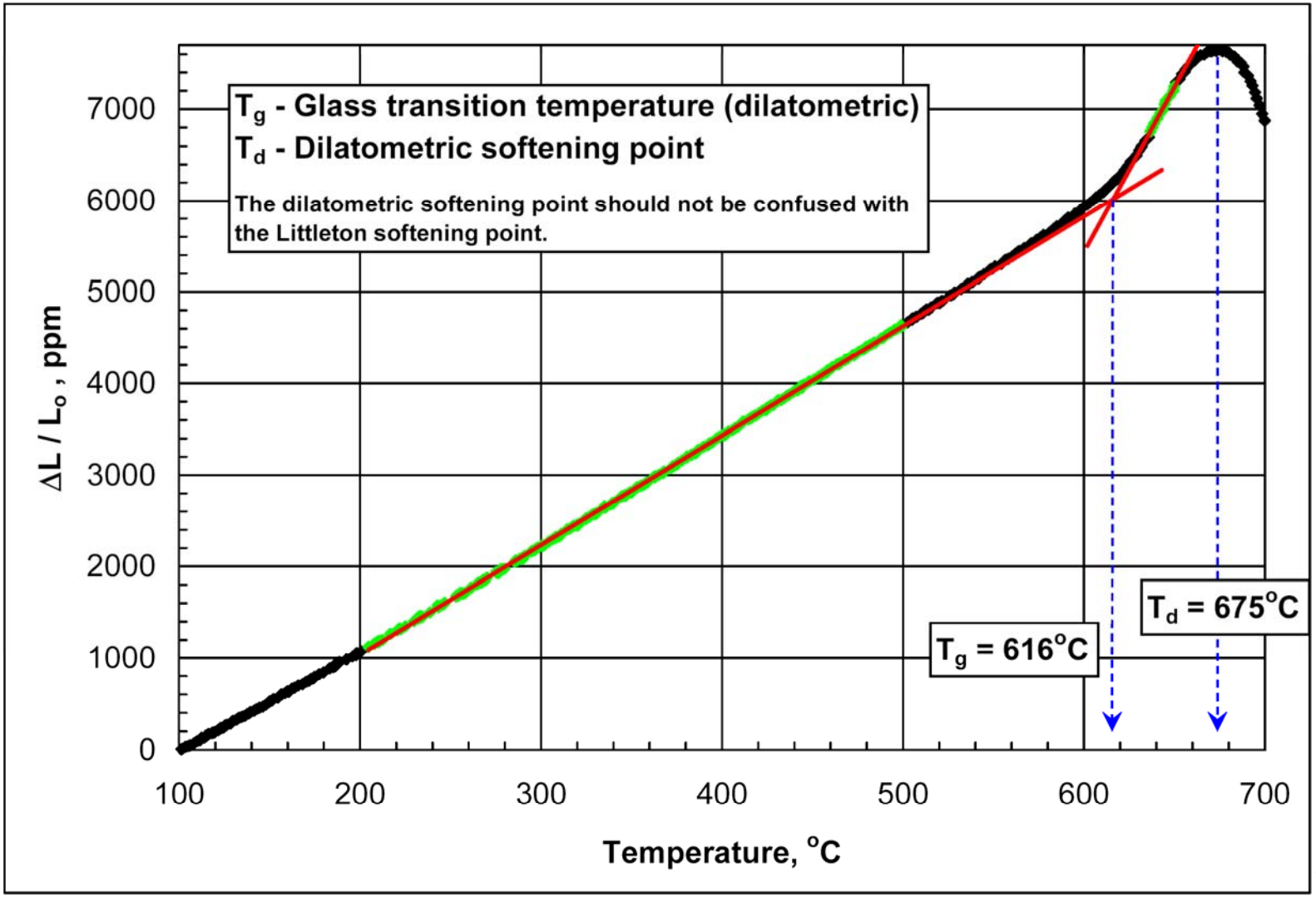
Why does slope change?

Solid: heating increases vibrational energies of atoms

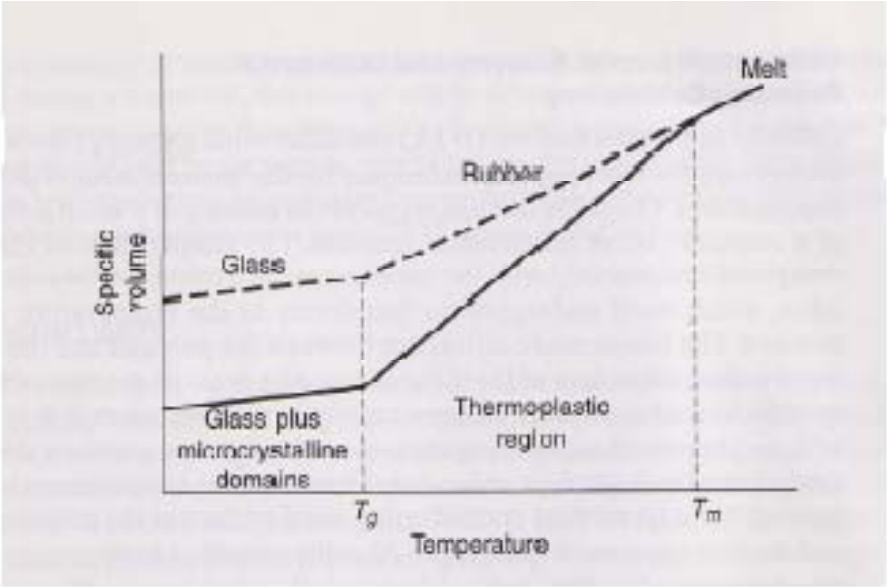
Liquid: heating increases thermal energy of system; effectively increases average spacing between molecules

Determination of Tg for glasses by dilatometry.

The linear sections below and above *T*g are marked green;
***T*g is the temperature at the point of intersection of the corresponding red regression lines.**

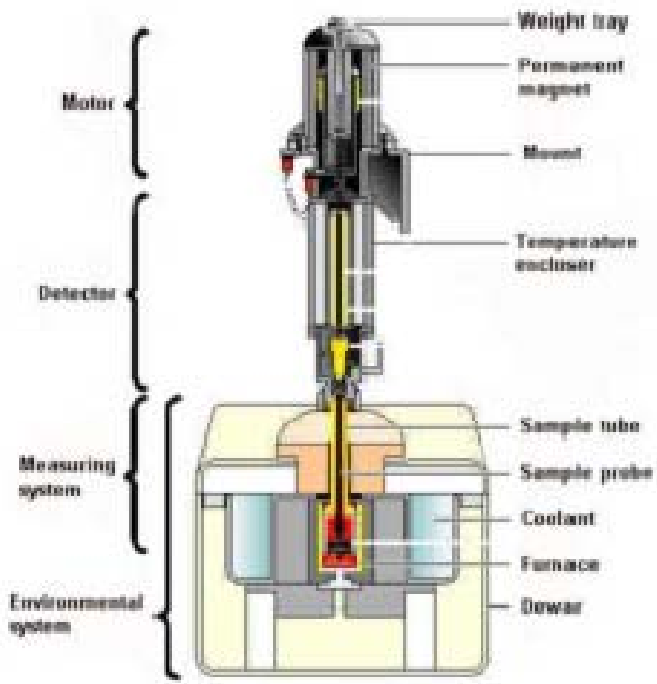


Dilatometry Graph



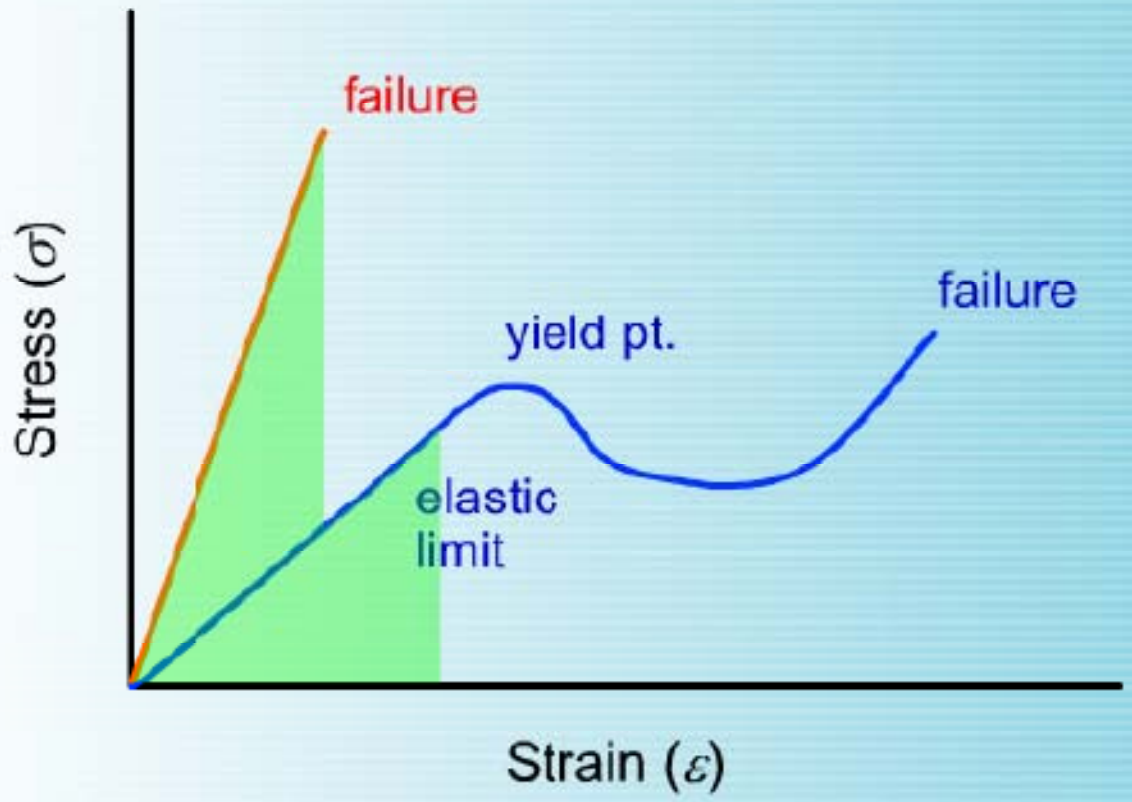
- The coefficient of volume expansion is the ratio of the change of volume per degree to the volume at 0°C.
- The coefficient of volume expansion varies with temperature, depending on whether the polymer occupies the glassy, rubbery, thermoplastic, or liquid state.
  - Therefore the change in slope of a volume versus temperature graph can be used to identify the glass transition temperature.

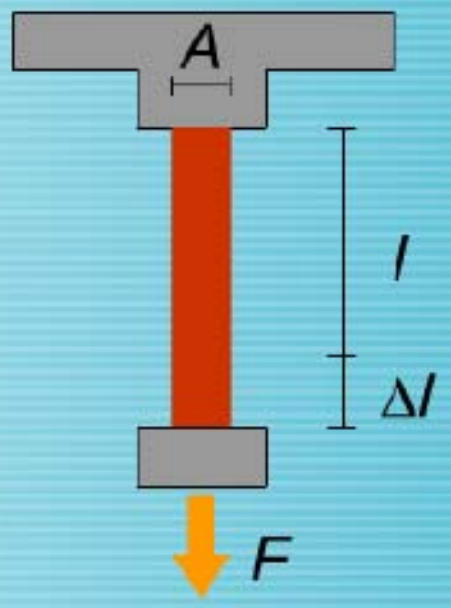
Dynamic Mechanical Analysis (DMA)



- Measures the stiffness and damping properties of a material.
- Stiffness depends on mechanical properties and is often converted to a modulus to enable sample inter-comparisons.
- Damping is expressed in terms of Tanδ and is related to the amount of energy a material can store.
- DMA is most sensitive for monitoring relaxation events, such as T_g, because mechanical properties change dramatically when relaxation behavior is observed.

DMA

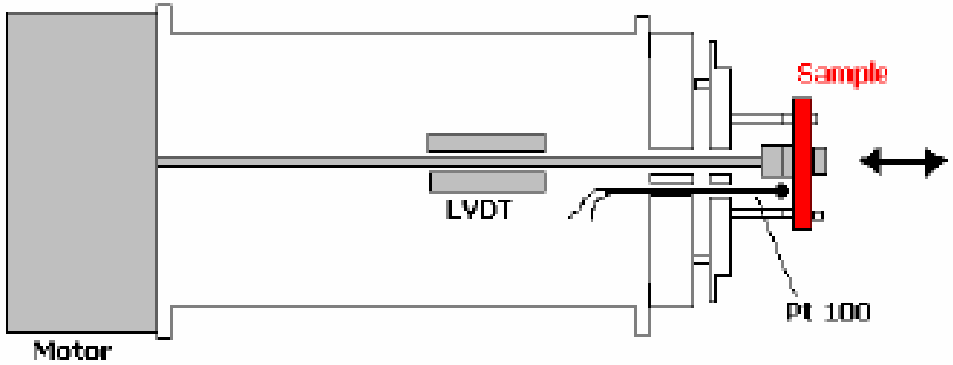




$$\sigma = \frac{F}{A} \quad , \quad \varepsilon = \frac{\Delta l}{l}$$

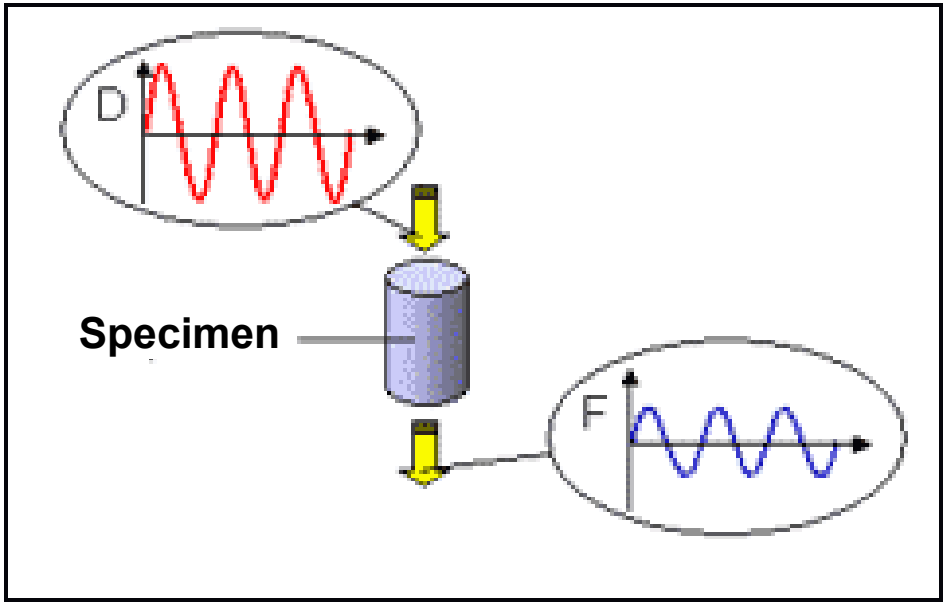
- For DMA, consider only within elastic region

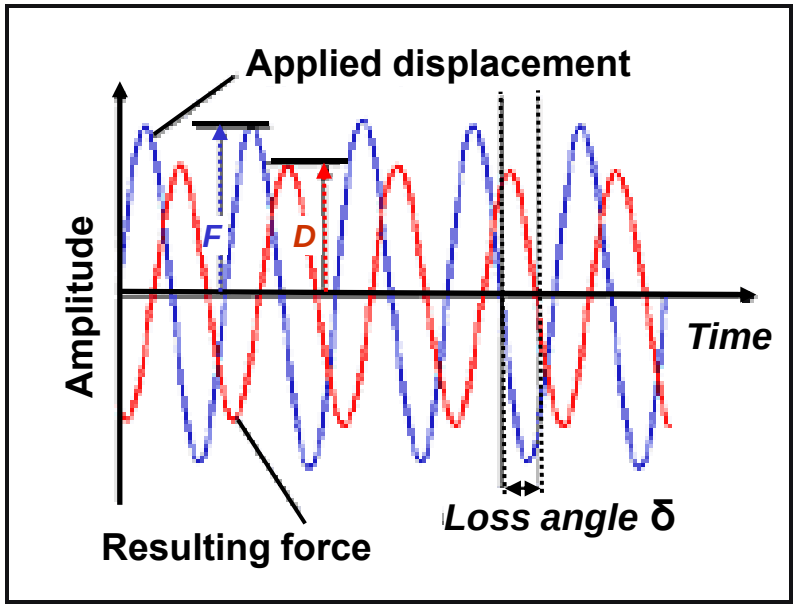
DMA



- Force (stress) is applied to the sample through a motor.
- The stress is transmitted through the drive shaft onto the sample which is mounted in a clamping mechanism.
- As the sample deforms, the amount of displacement is measured by a sensor.
- The strain can be calculated from the displacement.
- During the measurement the temperature of the sample is defined and can be changed.

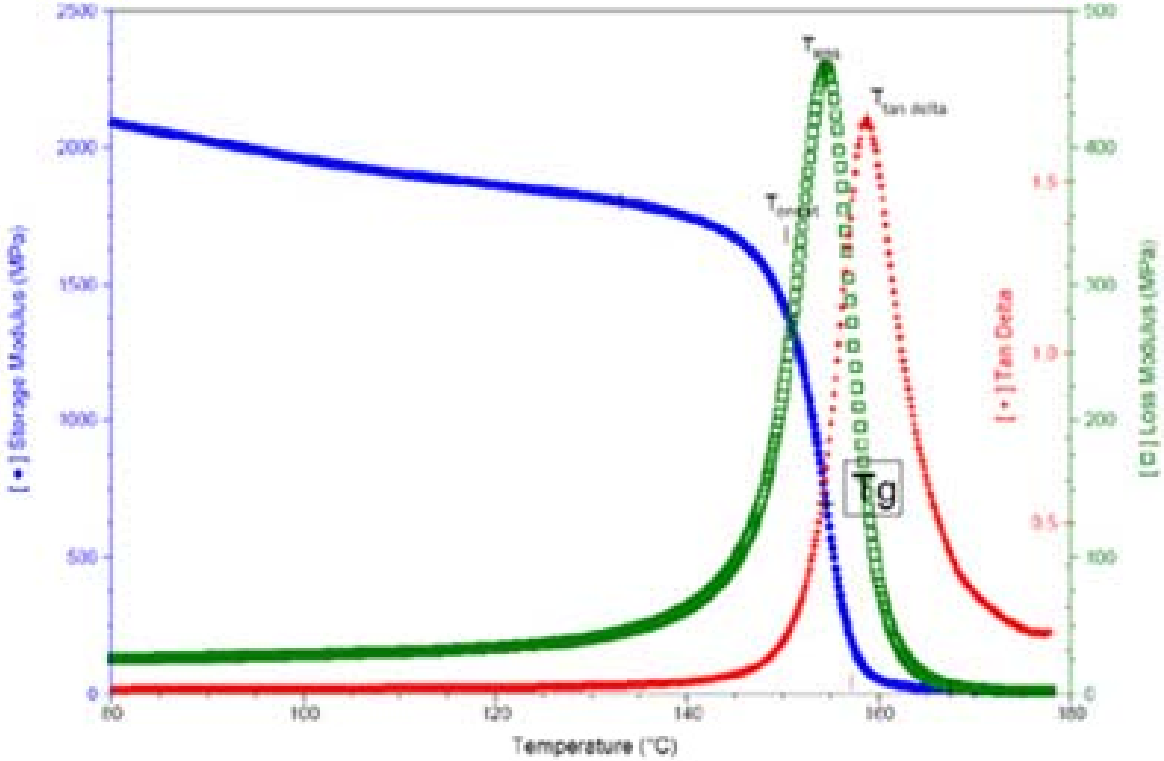
The Dynamic Mechanical Analysis is a high precision technique for measuring the viscoelastic properties of materials. It consists in applying a sinusoidal deformation to a specimen of material and measuring the resulting force transmitted through the specimen.





- The magnitude of the applied stress and the resultant strain are used to calculate the stiffness of the material under stress.
- The phase lag between the two (or δ) is used to determine Tanδ, the damping factor.

DMA



- A typical response from a DMA shows both modulus and Tanδ.
- As the material goes through its glass transition, the modulus reduces and the Tanδ goes through a peak.