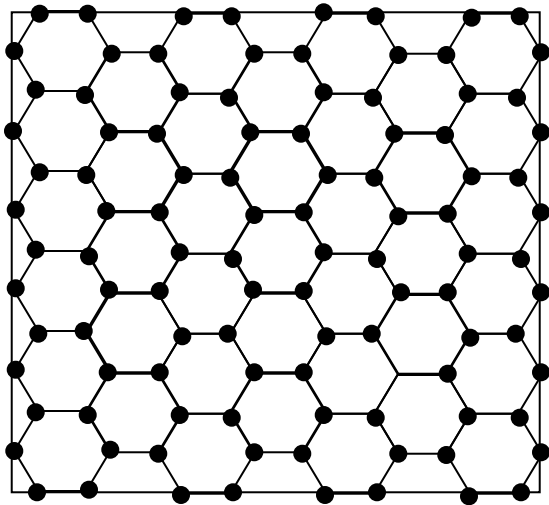


Glass and Glass Transition

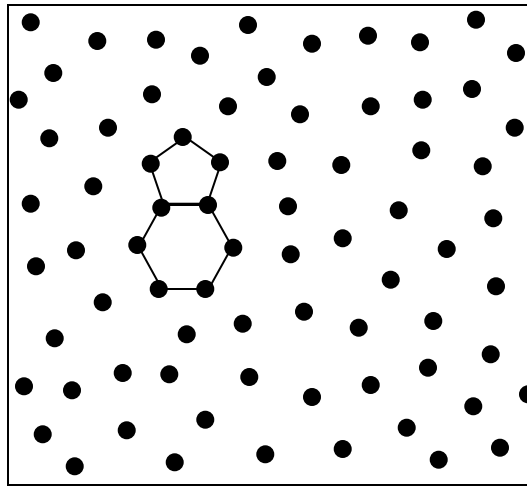
What is glass?

Glass: Structure characterized by the absence of the long-range order.
(May still possess short-range liquid-like order.)

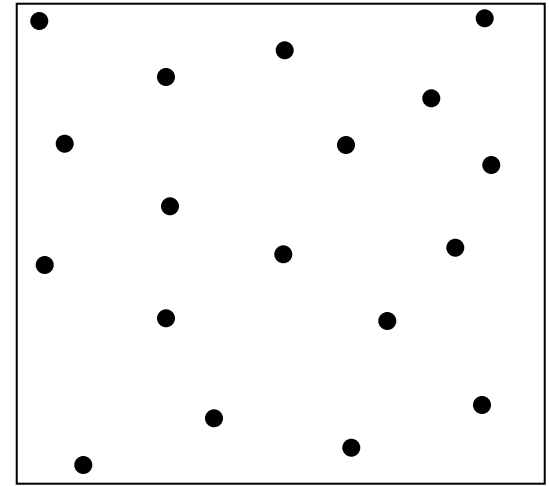
Atomic arrangement



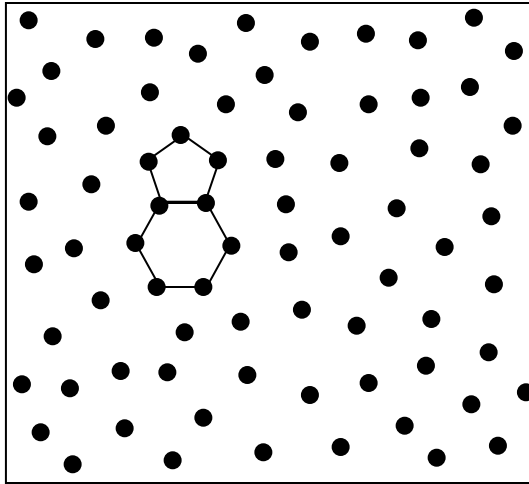
Crystal



Glass



Gas



Amorphous Solid or Glass:

Absence of the *long-range order*
(translational periodicity)

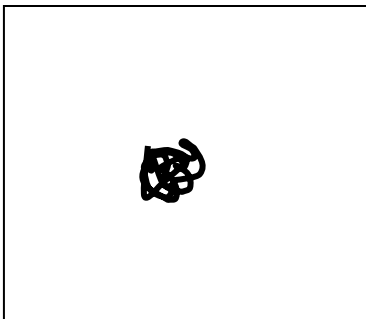
High degree of *short-range order*
(high degree of local correlations)

Effect of time on structure

Gas or Liquid: No enduring arrangement of molecules (fluidity);
Vibrational and translational motion.

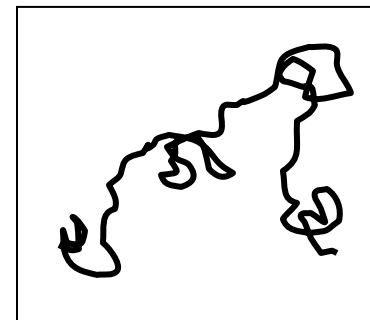
Solid: No drastic effect on structure;
Atoms stay close to well-defined equilibrium positions;
Only vibrational motion

Solid



Atom Trajectories

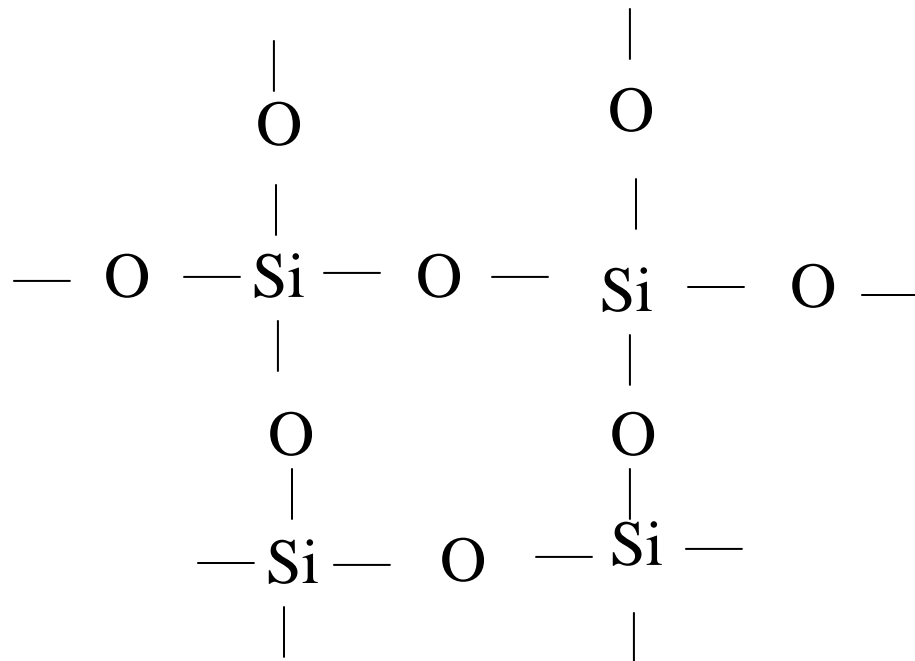
Liquid



Materials Exhibiting Glass Transition

1. Inorganic networks (SiO_2 , B_2P_3 , P_2O_5 etc..)

(Network glasses are three-dimensional polymers in which the repeat units are tri or tetrafunctional moieties like those in P_2O_5 or SiO_2 .)

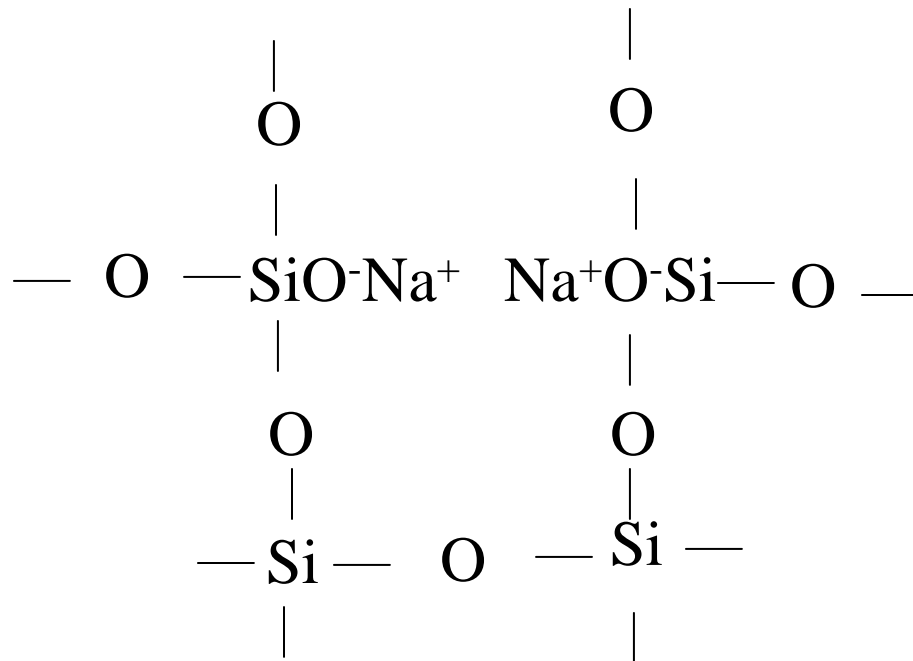


$T_g \sim 1200^\circ\text{C}$

Materials Exhibiting Glass Transition

2. Modified Networks ($\text{SiO}_2 + \text{Na}_2\text{O}$).

If network modifiers such as Na_2O or K_2O are introduced into the network, some network points are ruptured, and O-Si-O bridge is converted into two $-\text{SiO}-\text{Na}^+$ groups.



$T_g \sim 500^\circ\text{C}$

Materials Exhibiting Glass Transition

3 Polymers: Linear or Branched

$T_g \ll T_R$, elastomers

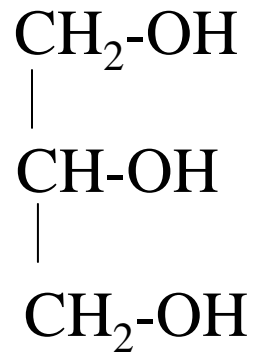
$T_g \sim T_R$, synthetic leather

$T_g \gg T_R$, plastic

Materials Exhibiting Glass Transition

4. Hydrogen-bonded compounds (relatively low T_g)

Glycerol T_g ~ -80°C



Materials Exhibiting Glass Transition

5. Salts or Salt mixtures (ZnCl_2 , BeF_2 , and K_2CO_3 MgCO_3)

$T_g \sim 200\text{--}500^\circ\text{C}$

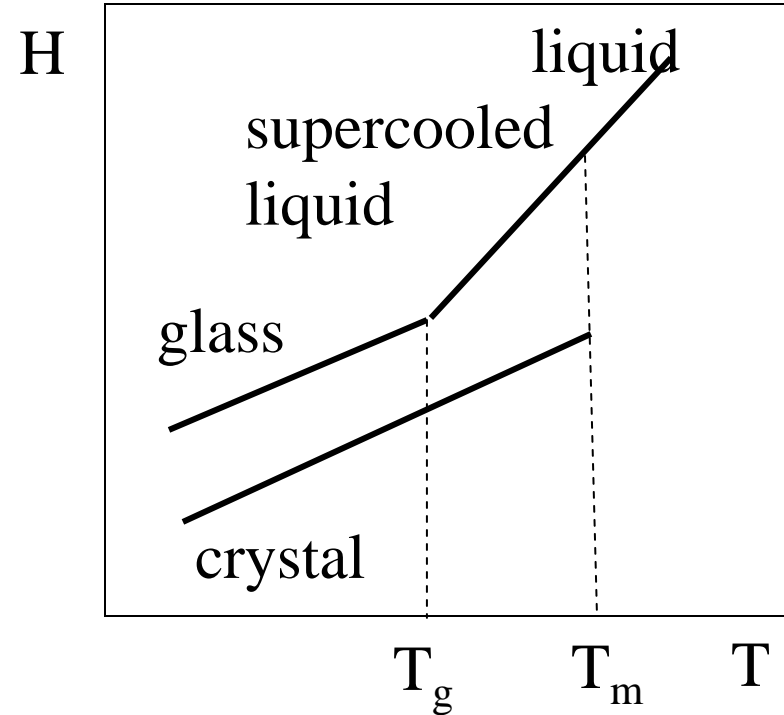
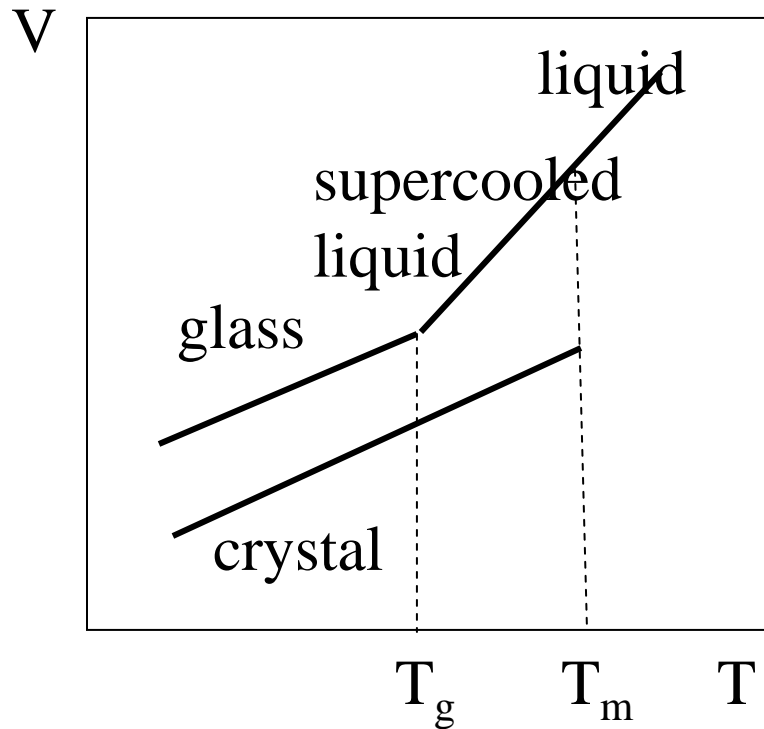
6. Amorphous Metals (quenched at 10^5 $^\circ\text{C}/\text{sec}$, $T_g \sim 0\text{--}200^\circ\text{C}$)

Examples: $\text{Pd}_{80}\text{Si}_{20}$ and $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$.

7. Low molecular weight organics ($T_g < -150^\circ\text{C}$)

Example: 2-Methylpentane.

Volume and Enthalpy Changes



First-order transition: First derivatives of the *Free energy* exhibit discontinuity.

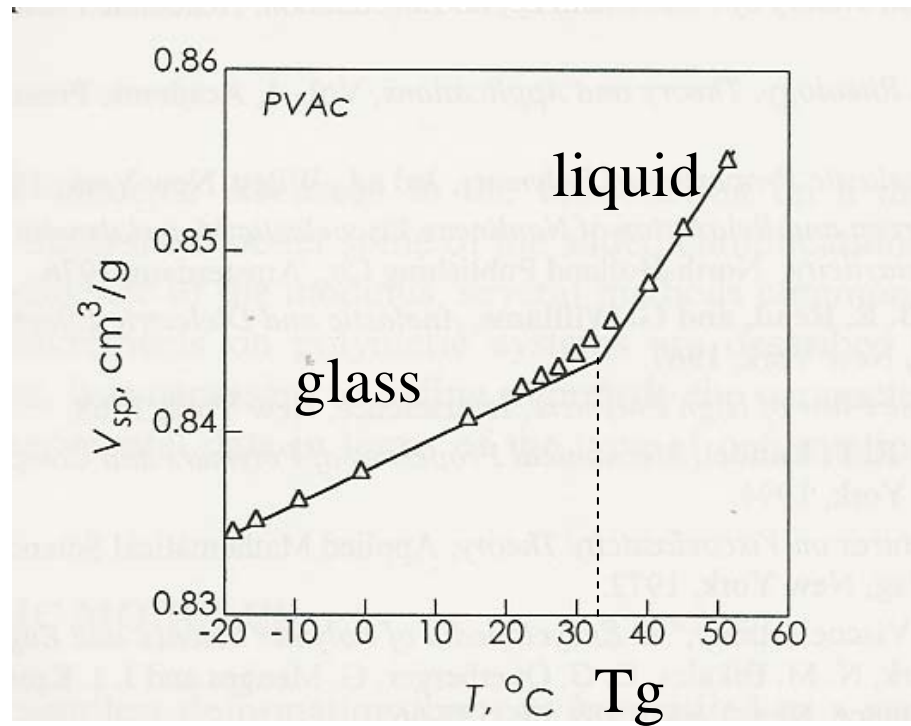
$$V \equiv \left(\frac{\partial G}{\partial P} \right)_T \quad S \equiv - \left(\frac{\partial G}{\partial T} \right)_P$$

(Gibbs' Free Energy)

$$dG = -SdT + Vdp$$

Volume and Enthalpy show discontinuities at T_m .

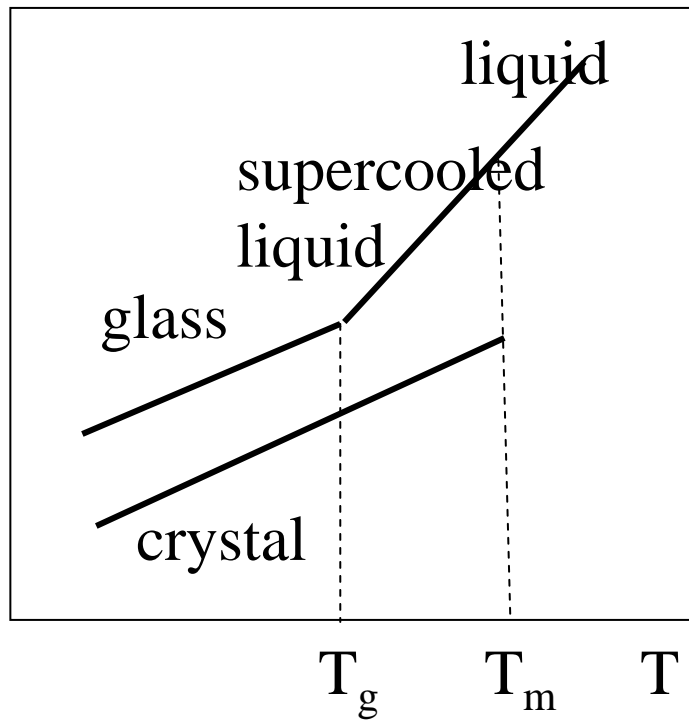
Specific Volume Change



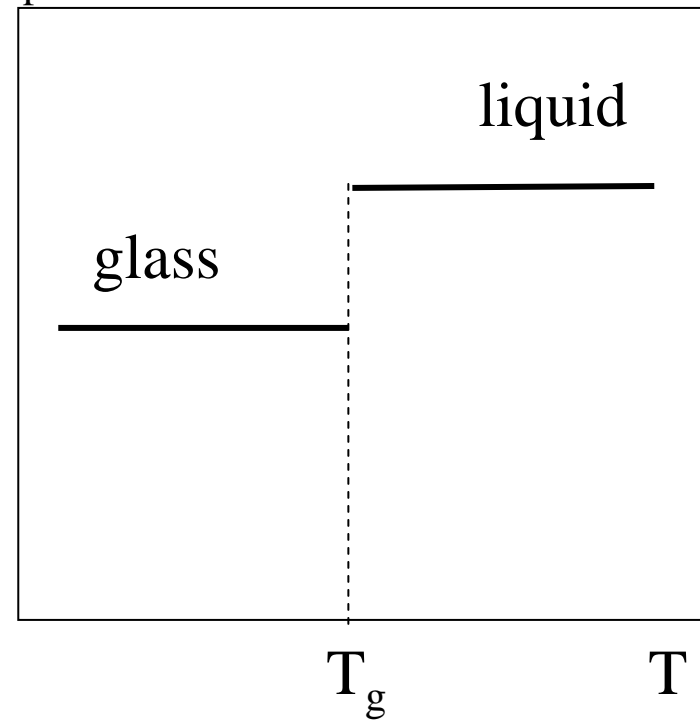
Second-order transition: Second derivative of the **Free Energy** exhibit discontinuity.

Coefficient of thermal expansion $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ Specific heat $c_P \equiv T \left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P$

V,H

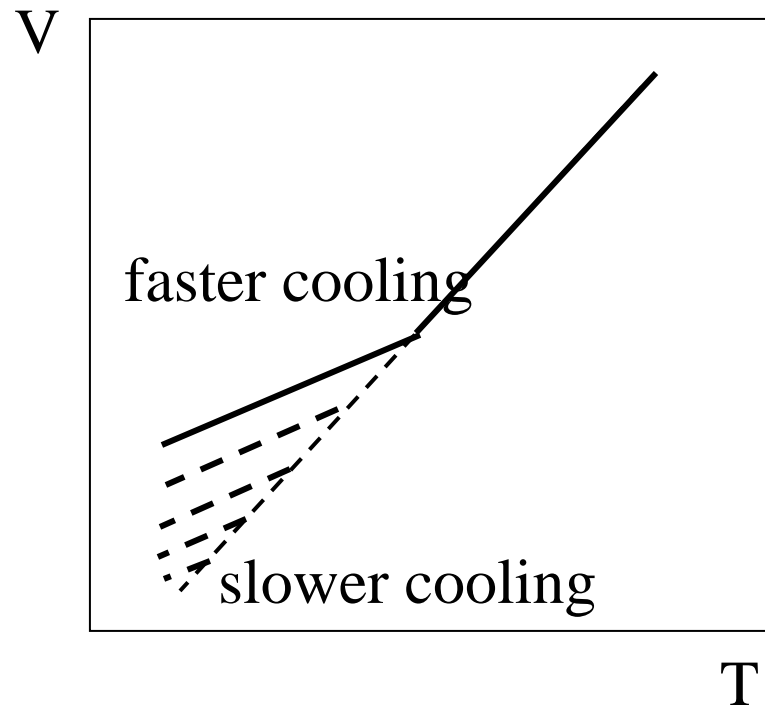


α, c_p



Kinetics of Glass Transition

Glass transition temperature depends on the rate of cooling

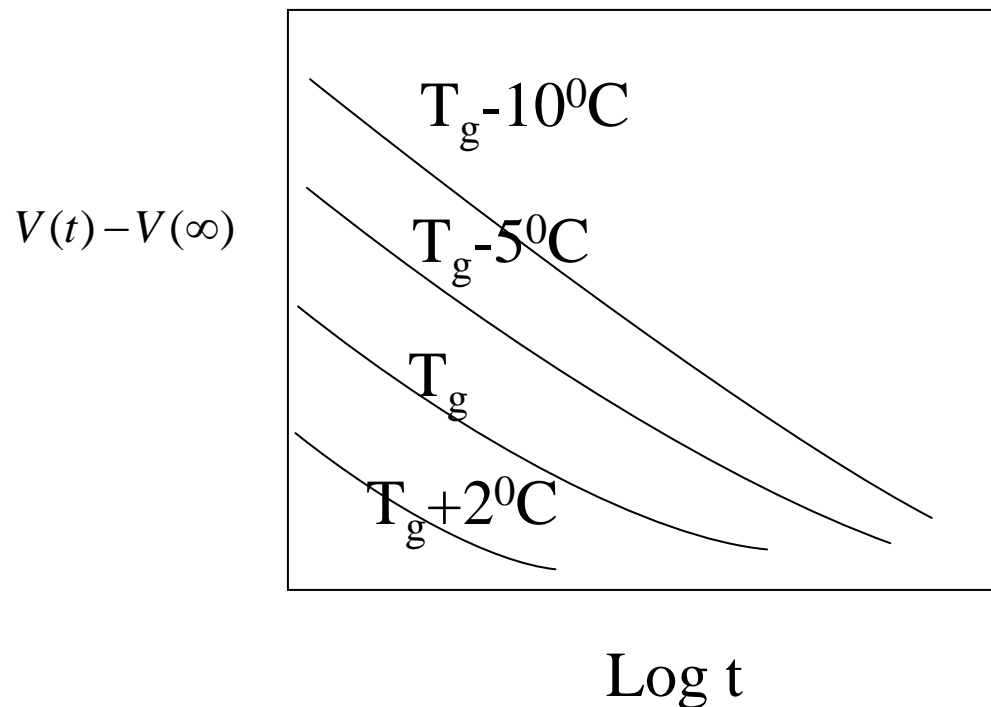


$T_g = f(\text{cooling rate})$ – T_g changes by 3% per order of magnitude change in cooling rate.

Glassy state is not in equilibrium!!!

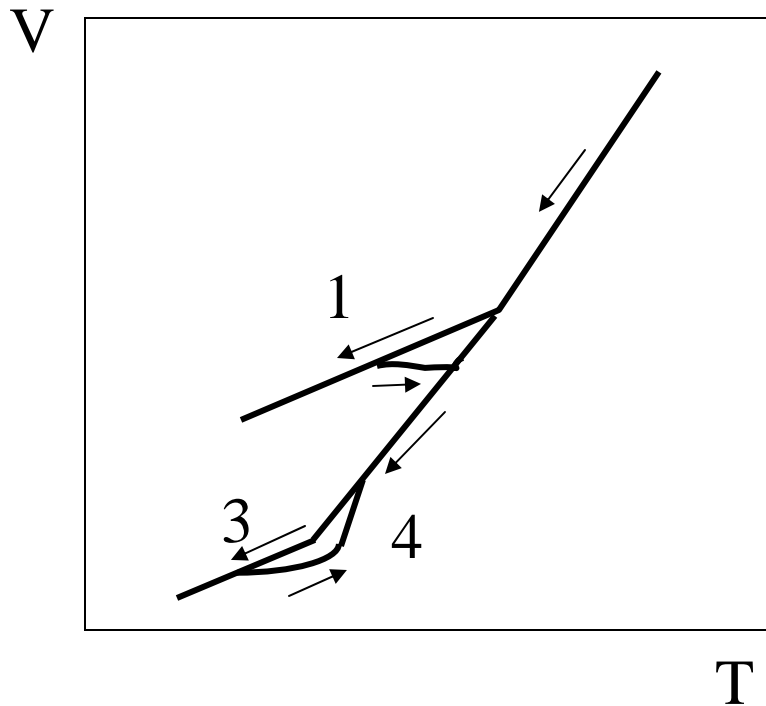
Aging effect

Isothermal volume contraction near the glass transition



Commercial importance: Volume keep changing with time. This can be significant if sample is cooled very quickly.

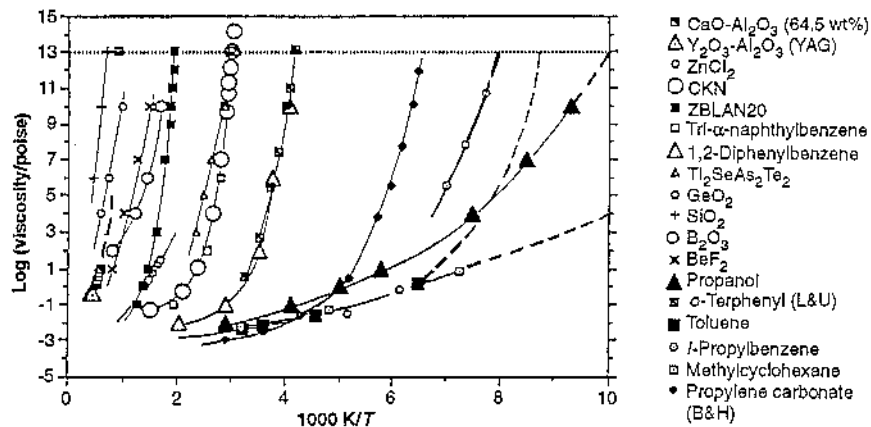
Hysteresis Effect



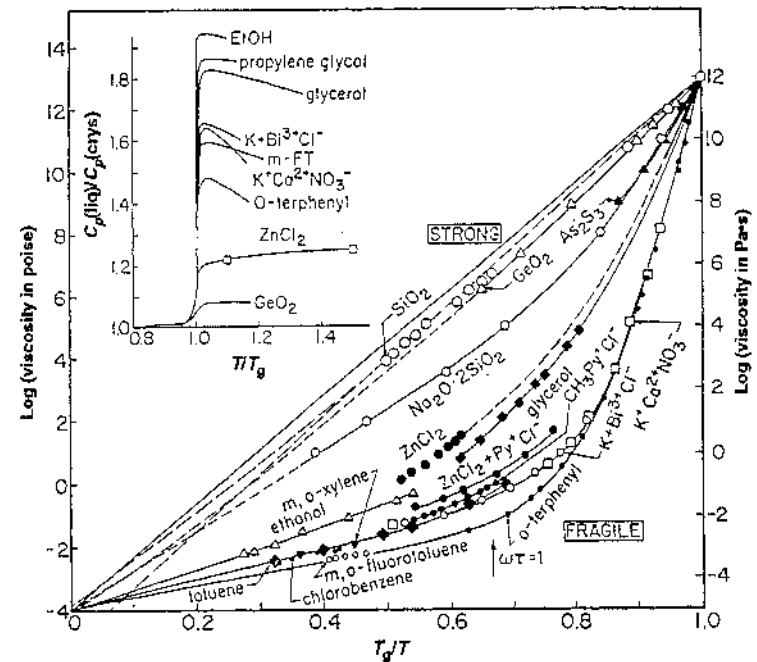
1. Fast cooling
2. Slow heating allows volume relaxation as T increases resulting in volume shrinkage below T_g .
3. Slow cooling – low apparent T_g .
4. Fast heating – overshoots original T_g and results in rapid expansion above T_g .

Changes in Mechanical Properties at Glass Transition

Viscosity

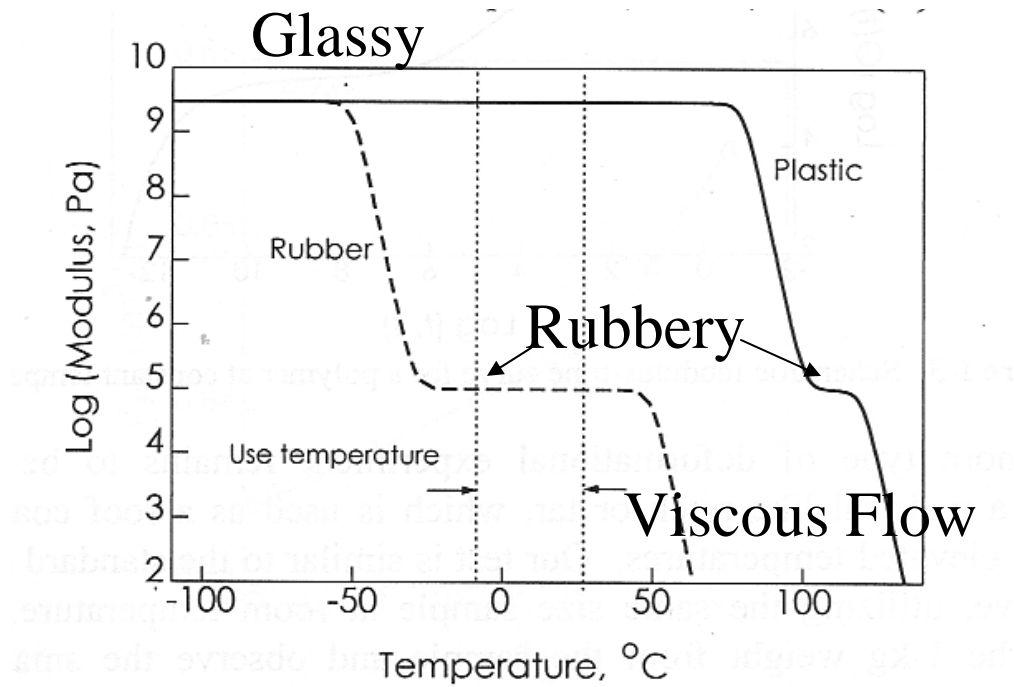


Different Classes of Glasses

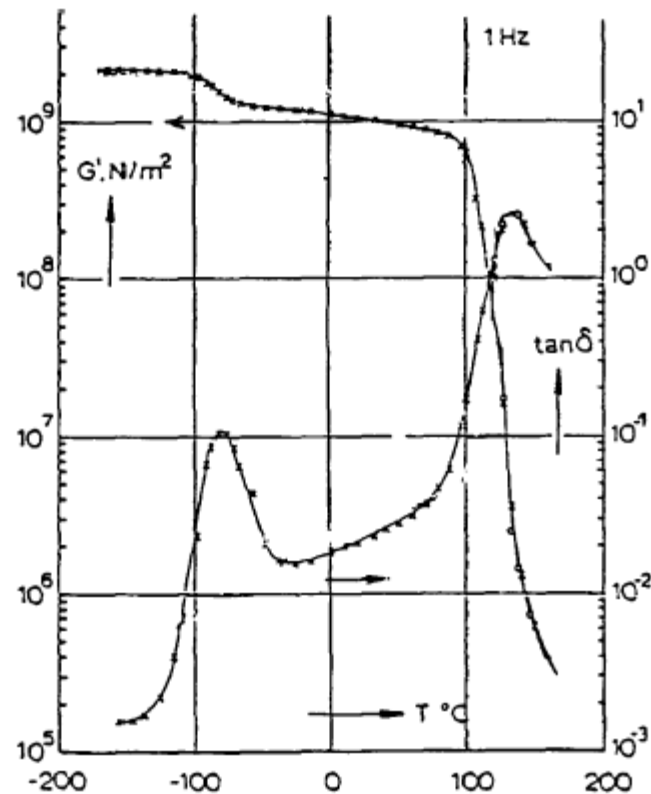


Modulus

Dependence of the shear modulus on temperature



Temperature Dependence of Storage and Loss Tangent



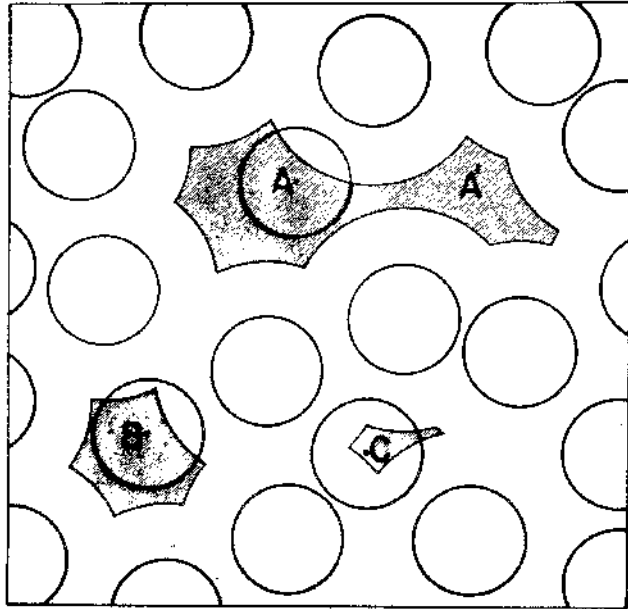
poly(cyclohexyl methacrylate)

Theories of the Glass Transition

Free Volume Theory

Free Volume Theory I

Motions of Molecules



B and C: oscillatory motion (vibration) within cage formed by nearest neighbors – **solid-like motion**.

A: vibrational and translational motion.
A \rightarrow A' – **liquid-like motion**.

Shaded area = free volume accessible to center of molecules A, B, and C.

Sufficient free volume is needed for translational motion!!!

Free Volume Theory II

1. Liquid-glass transition is a macroscopic manifestation of changes occurring in the microscopic distribution of molecular free volume.
2. Approaching transition from the liquid state: as temperature decreases, specific volume decreases and v_f decreases as well.
3. At some point, v_f is reduced to a critical value where there is insufficient room for the diffusive steps

T_g = temperature at which v_f reaches critical value.

Free Volume Theory III

Theory of molecular glasses (Cohen et al 1959-1962)

Relation between fluidity and distribution of the free volume

$$\eta^{-1} = \text{const} \int_{v_f^*}^{\infty} p(v) dv = \alpha \exp\left(-\beta \frac{v_f^*}{v_f}\right)$$

where the distribution of the molecular free volume is given by

$$p(v) = \frac{\beta}{v_f} \exp\left(-\beta \frac{v}{v_f}\right)$$

This distribution is obtained by maximizing the entropy of the free volume redistribution at constant number of particles and net free volume.

Free Volume Theory IV

Doolittle equation (*A. K. Doolittle, J. Appl. Phys., 22 (1951) 1471*)

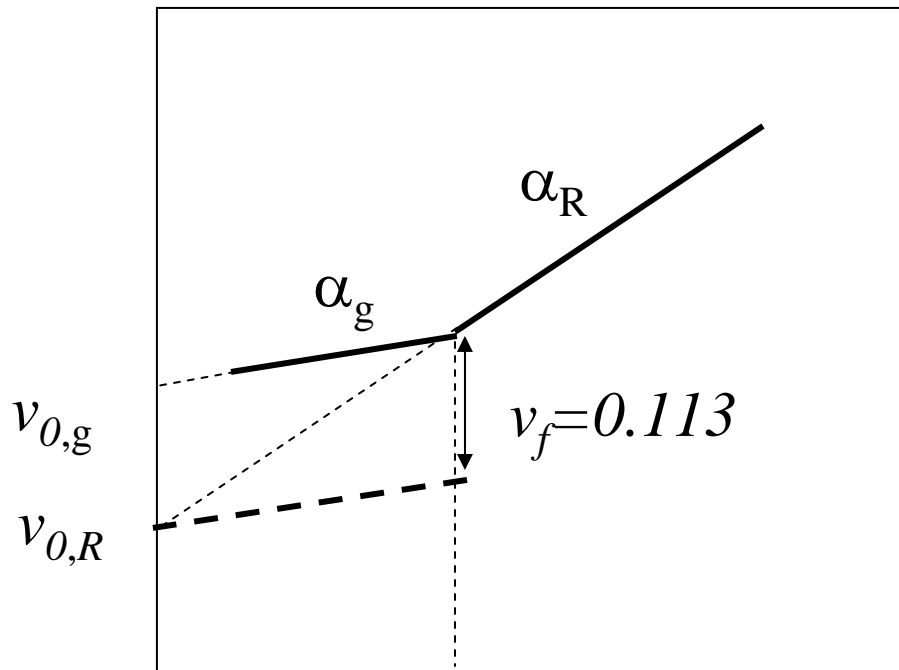
Semi-empirical equation for viscosity of liquids

$$\eta = A \exp \left(B \frac{v_0}{v_f} \right)$$

where v_0 and v_f are occupied and free volumes, respectively. A and B are numerical constants.

Free Volume Theory IV

T_g as an Iso-Free-Volume state.



Flory and Fox (1950) have established that above glass transition the specific free volume can be expressed as

$$v_f = K + (\alpha_R - \alpha_g)T$$

where K is the free volume at 0K

The free volume at T_g is defined as

$$v - (v_{0,R} + \alpha_R T) = v_f \quad \text{where the specific volume } v \text{ is } v = v_{0,R} + \alpha_R T$$

This leads to
$$K_1 = (\alpha_R - \alpha_G)T_g = 0.113$$

Test of the Glass Transition as an Iso-Free-Volume State

| Polymer | $T_g, ^\circ\text{K}$ | $\alpha_R \times 10^4$ $^\circ\text{K}^{-1}$ | $\alpha_R T_g$ (K_2) | $(\alpha_R - \alpha_G)$ $\times 10^4 ^\circ\text{K}^{-1}$ | $(\alpha_R - \alpha_G) T_g$ (K_1) |
|---------------------------|-----------------------|---|------------------------------------|--|---|
| Polyethylene | 143 | 13.5 | 0.192 | 6.8–8.0 | 0.097–0.113 |
| Poly(dimethyl siloxane) | 150 | 12 | 0.180 | 9.3 | 0.140 |
| | | 8.12 | 0.122 | 5.4 | 0.081 |
| Polytetrafluoroethylene | 160 | 8.3 | 0.133 | 7.0 | 0.112 |
| Polybutadiene | 188 | 7.8 | 0.147 | 5.8 | 0.109 |
| Polyisobutylene | 199.4 | 6.18 | 0.123 | 4.70 | 0.094 |
| Hevea rubber | 201 | 6.16 | 0.124 | 4.1 | 0.082 |
| Polyurethane | 213 | 8.02 | 0.171 | 6.04 | 0.129 |
| Poly(vinylidene chloride) | 256 | 5.7 | 0.146 | 4.5 | 0.115 |
| Poly(methyl acrylate) | 282 | 5.6 | 0.158 | 2.9 | 0.082 |
| Poly(vinyl acetate) | 302 | 5.98 | 0.18 | 3.9 | 0.118 |
| Poly(4-methyl pentene-1) | 302 | 7.61 | 0.23 | 3.78 | 0.114 |
| Poly(vinyl chloride) | 355 | 5.2 | 0.185 | 3.1 | 0.110 |
| Polystyrene | 373 | 5.5 | 0.205 | 3.0 | 0.112 |
| Poly(methyl methacrylate) | 378 | 5.0 | 0.189 | 3.05 | 0.115 |
| | 378 | 4.60 | 0.174 | 2.45 | 0.093 |

WLF Equation

M. L. Williams, R. F Landel, J. D Ferry, *J. Am. Chem. Soc.*, 77 (1955), 3701

Doolittle equation:
$$\eta = A \exp \left(B \frac{v_0}{v_f} \right)$$

Replace v_f/v_0 with fraction f : $\ln \eta = \ln A + B / f$

Use linear relation for the fraction of free volume near T_g

$$f = f_g + \alpha_f (T - T_g)$$

The ratio of viscosities at temperatures T and T_g is

$$\ln \frac{\eta}{\eta_g} = \ln a_T = B \left(\frac{1}{f} - \frac{1}{f_g} \right) \Rightarrow \ln a_T = - \frac{B}{f_g} \left[\frac{(T - T_g)}{(f_g / \alpha_f + T - T_g)} \right]$$

WLF Equation

$$\log a_T = -\frac{c_1(T - T_g)}{c_2 + T - T_g}$$

where universal constants $c_1 = \frac{1}{2.3 f_g} = 17.4$ and $c_2 = \frac{f_g}{\alpha_f} = 51.6$
 ($f_g=0.025$ and $\alpha_f=4.8 \cdot 10^{-4} \text{ K}^{-1}$)

In reality,

| Polymer | c_1 | c_2 (°K) | T_g (°K) | α ($10^{-4}/^\circ\text{K}$) |
|--------------------------|-------|------------|------------|---------------------------------------|
| polyisobutylene | 16.6 | 104 | 202 | 4.9 |
| natural rubber | 16.7 | 53.6 | 200 | |
| polyurethane | 15.6 | 32.6 | 238 | |
| polystyrene | 14.5 | 50.4 | 373 | 3.7 |
| poly(ethyl methacrylate) | 17.6 | 65.5 | 335 | 3.0 |

➡ $c_1 \approx$ universal value, but c_2 varies quite a bit $\Rightarrow \alpha$ also varies

Time-temperature Superposition

The stress relaxation modulus data at any given temperature T can be superimposed on the data at a reference temperature T_r using a time scale multiplicative shift factor a_T and a much smaller modulus scale factor b_T :

$$G(t, T) = b_T G\left(\frac{t}{a_T}, T_r\right)$$

The vertical shift factor $b_T = \rho_r T_r / (\rho T)$ is usually close to unity and is often neglected.

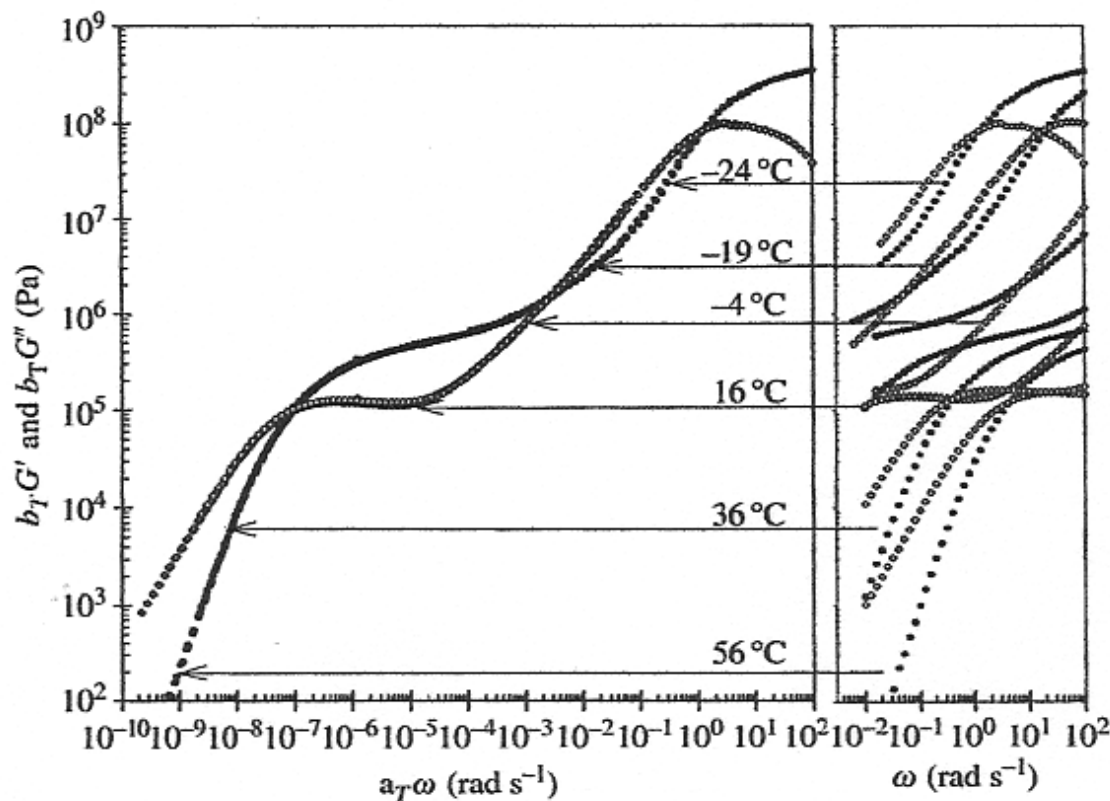
The time shift factor is determined from the WLF equation

$$a_T = \exp\left(\frac{B(T_r - T)}{v_r(T - T_0)}\right)$$

The reference temperature T_r is usually set to T_g for which $v_g = 0.025$

Time-temperature Superposition

Example of the time-temperature superposition of poly(vinyl methyl ether) (PVME) melt with $M_w = 120\,000\text{ g mol}^{-1}$ at a reference temperature $T_g = -24^\circ\text{C}$.



G' –filled circles
 G'' –open circles

Thermodynamic Theories of Glass Transition

Arguments for a Thermodynamic 2-nd Order Transition

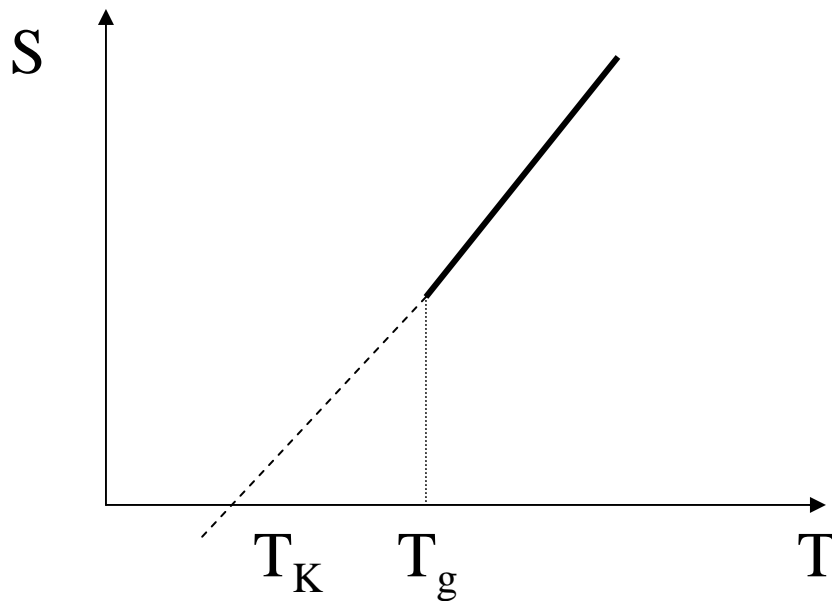
1. The kinetic nature of the observed T_g does not preclude the existence of a true second-order thermodynamic transition.
2. When polymer is cooled from liquid, volume contraction occurs that involves conformational rearrangements.
3. Above T_g thermal equilibrium is maintained.
4. At some point, the rate of conformational rearrangement becomes comparable with cooling rate.
5. Below this temperature, the volume relaxation can not occur during the time scale of experiment.
6. Discontinuity in c_p , α and β are observed.

An infinitely slow cooling rate is necessary to observe the true thermodynamic transition!!!!

The Kauzmann Paradox

W. Kauzmann, *Chem. Rev.* **43**, (1948) 219

Kauzmann Paradox: If the conformational entropy is extrapolated to low temperatures, it goes through zero at finite temperature (Entropy Crisis).



Kauzmann resolved paradox by claiming that the glassy state is not an equilibrium state and that before $S=0$ material will crystallize. This explanation denies the existence of the true 2nd order transition.

Gibbs-DiMarzio Theory

J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.* **28** (1958) 373.

Observations:

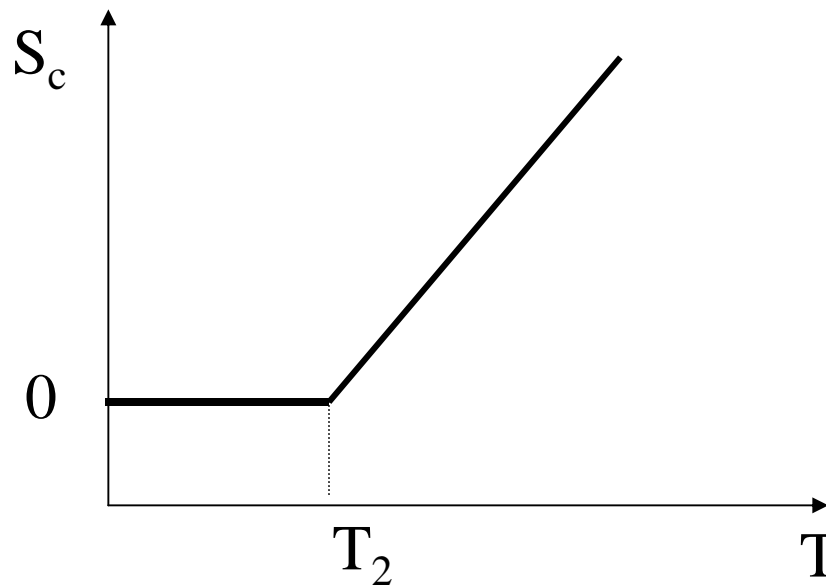
- The crystal state is not ubiquitous... there exist molecules that are inherently are not crystallizable.
- Certain collection of molecules have equilibrium amorphous properties in all temperature range.

Resolution of the **Kauzmann Paradox**: Glass formation is associated with condition of $S_{\text{conf}}=0!!!!$

Above transition, $T > T_g$, total entropy is vibrational and conformational
Below transition, $T < T_g$, entropy is only vibrational.

Gibbs-DiMarzio Theory

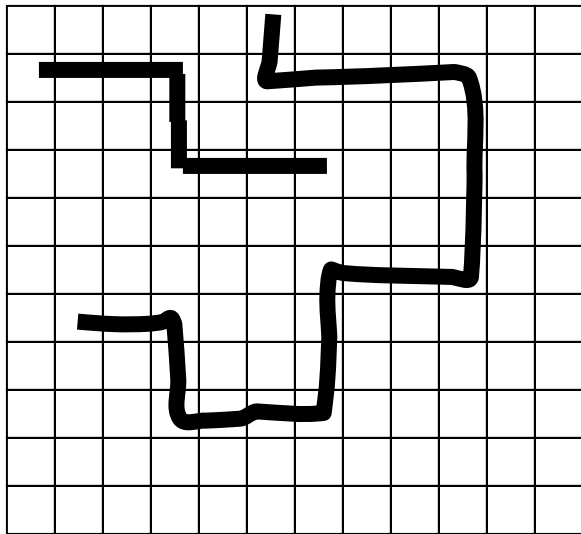
“ the [conformational] entropy equals zero condition [is] the Rosetta Stone for the hieroglyphics of glass formation.”



If cooling can be done infinitely slowly, a thermodynamic second order liquid to glass transition will occur at $T_2 < (T_g)_{\text{exp}}$.

Gibbs-DiMarzio Theory

Thermodynamic properties of amorphous , linear chains are obtained from statistical mechanics using a lattice theory that allows for chain stiffness and the variation of volume with temperature.



System free energy is calculated as function of:

Intermolecular hole energy
(concentration of holes corresponds to
a free volume)

Intramolecular bond rotational energy
(assumes trans and gauche conformations)

Transition is determined from: $S_{\text{conf}}(T_2)=0!!!$

Kinetic Theories of Glass Transition

Kinetic Theories

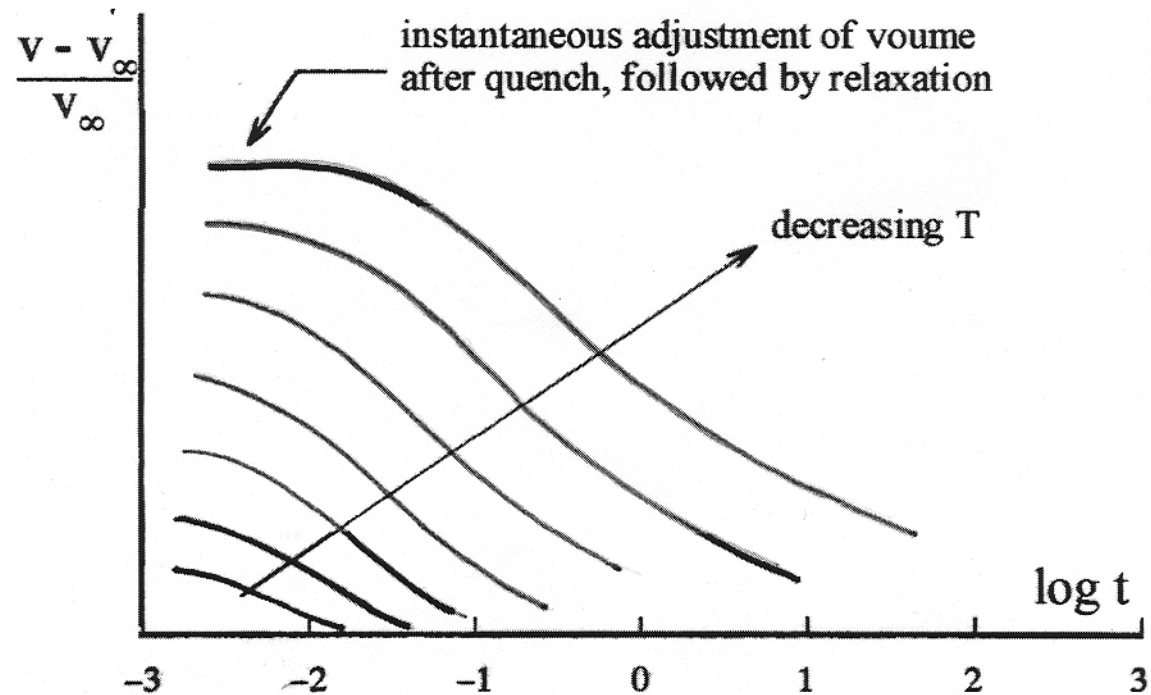
T_g is not a thermodynamic variable.

T_g is the temperature at which the relaxation time for the segmental motion in the main chain is of the same order of magnitude as the time scale of experiment.

Theory is concerned with describing the rate at which system approaches the equilibrium.

Kinetic Approach to T_g

Volume Contraction Isotherms (Volume relaxation after quench from $T > T_g$)



Kinetic Approach to T_g

For gases and liquids: $V=V(T,P)$

For glasses: $V=V(T,P,\xi)$

where ξ is the ordering parameter which measures how far the material is from its equilibrium volume.

Let $\delta = \frac{v - v_\infty}{v_\infty}$ normalized departure of volume from equilibrium.

Assumes that the rate of volume relaxation is a first order process

$$\frac{d\delta}{dt} = -\frac{\delta}{\tau(\delta)}$$

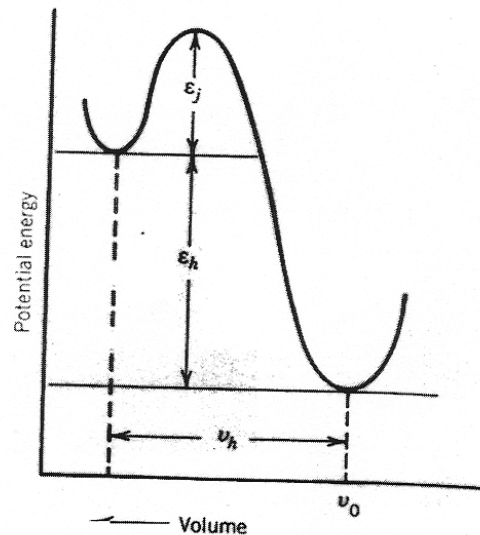
where $\tau(\delta)$ is the retardation time.

Hole Theory

Consider T_g as an activated process and determines the rate of disappearance of molecular size holes.

Parameters

- v_h = "molar volume" of a hole
- ϵ_h = molar excess of energy over the "no hole" situation
- ϵ_j = activation energy for the disappearance of a hole
- Q^h = partition function of holes
- Q^{\ddagger} = partition function of the activated state



Glass Transition Theories

Summary

| Theory | Advantages | Disadvantages |
|----------------------|---|---|
| Free-Volume Theory | <ol style="list-style-type: none"> 1. Time + temperature of Viscoelastic Events Related at T_g. 2. Relationship between coefficients of expansion above and below T_g. | <ol style="list-style-type: none"> 1. Actual molecular motions + nature of "free volume" are poorly defined. |
| Kinetic Theory | <ol style="list-style-type: none"> 1. Provides quantitative information about heat capacities above and below T_g. 2. Explains shifts of T_g with experimental time frame | <ol style="list-style-type: none"> 1. No T_g predicted at infinite time scales. |
| Thermodynamic Theory | <ol style="list-style-type: none"> 1. Predicts variation of T_g with MW, diluent, crosslink density, etc... 2. Predicts a true second order transition | <ol style="list-style-type: none"> 1. Infinite time scale required for measuring T_g. 2. True second-order transition is poorly defined. |

Molecular Parameters Affecting Glass Transition Temperature

1. Effect of pressure on T_g

Free volume near T_g at constant pressure: $f = 0.025 + \alpha_f (T - T_g)$

If the free-volume compressibility is κ_f , then

$$f = 0.025 + \alpha_f (T - T_g) - \kappa_f P$$

At glass transition $f=0.025$

$$\alpha_f (T_g (P) - T_g (0)) = \kappa_f P \Rightarrow \left(\frac{\partial T_g}{\partial P} \right)_f = \frac{\Delta \kappa_f}{\Delta \alpha_f} \Rightarrow \frac{dT_g}{dP} = \frac{TV \Delta \alpha}{\Delta C_p}$$

Effect of Pressure on T_g

| Material | T_g (°C) | dT_g/dP (°K/atm) |
|---------------------------|------------|--------------------------|
| Natural rubber | -72 | 0.024 |
| Polyisobutylene | -70 | 0.024 |
| Poly(vinyl acetate) | 25 | 0.022 |
| Rosin | 30 | 0.019 |
| Selenium | 30 | 0.015-0.004 ^a |
| Salicin | 46 | 0.005 |
| Phenolphthalein | 78 | 0.019 |
| Poly(vinyl chloride) | 87 | 0.016 |
| Polystyrene | 100 | 0.031 |
| Poly(methyl methacrylate) | 105 | 0.020-0.023 |
| Boron trioxide | 260 | 0.020 |

^aThe variation is probably due to the different compressibilities of ring and chain material.

Pressure leads to decrease in the free volume – increase in T_g.

Effect of Plasticizers on T_g

Various plasticizers have different effect on T_g; mostly they depress T_g, although some additives rise glass transition temperature.

Free volume approach:

In the presence of diluent the expression for the free volume is

$$f = 0.025 + \alpha_{f,p}(T - T_{g,p})V_p + \alpha_{f,d}(T - T_{g,d})V_d$$

where V_p and V_d are volume fractions of polymer and diluent.

Substituting $f=0.025$ and $T=T_g$ one has

$$T_g = \frac{\alpha_{f,p}V_pT_{g,p} + \alpha_{f,d}(1-V_p)T_{g,d}}{\alpha_{f,p}V_p + \alpha_{f,d}(1-V_p)}$$

Molecular Weight

Chain ends create excess free volume and low T_g.

$$T_g(M) = T_g(\infty) - \frac{K}{M}$$

Cross-Linking

With increasing the cross-link density the free volume in the sample decreases resulting in increase of the T_g.

$$T_g(M) = T_g(\infty) - \frac{K}{M} + K_x \rho$$

Flexible side chains

Flexible side chains increase free volume and lower T_g.

Effect of Side Chains

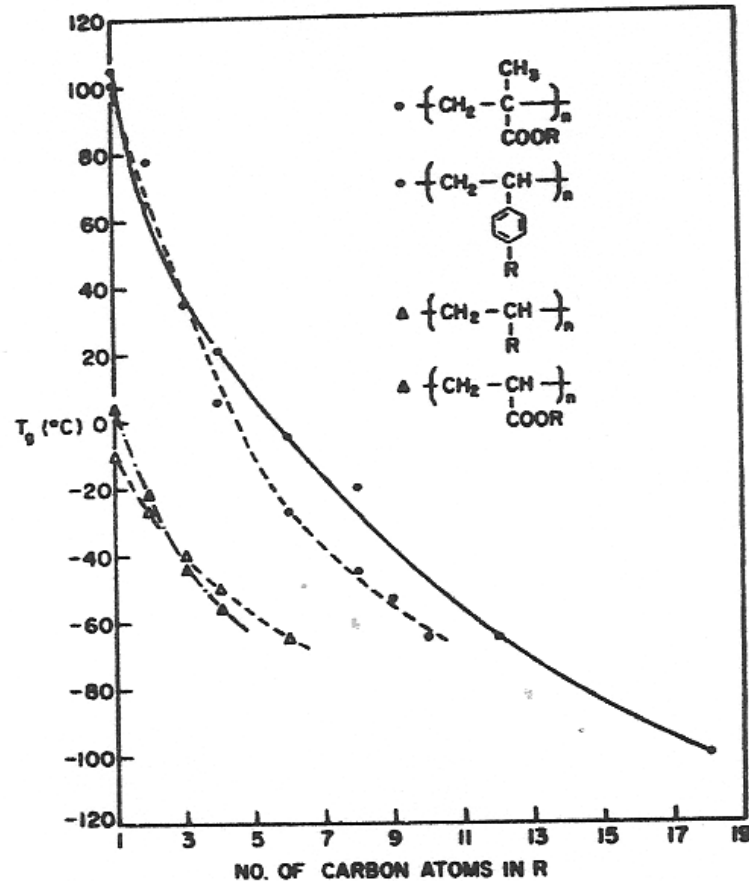


FIGURE 6.33 Effect of side-chain lengths on the glass transition temperatures of polymethacrylates (open circles [S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985, 1957]); poly-p-alkyl styrenes (solid circles [W. G. Barb, *J. Polym. Sci.*, **37**, 515, 1959]); poly-α-olefins (open triangles [M. L. Dannis, *J. Appl. Polym. Sci.*, **1**, 121, 1959; K. R. Dunham, J. Vandenberg, J. W. H. Farber, and L. E. Contois, *J. Polym. Sci.*, **1A**, 751, 1963]); and polyacrylates (solid triangles [J. A. Shetter, *Polym. Lett.*, **1**, 209, 1963]) (26).

Effect of Composition of Copolymers on Tg

Gibbs-DiMarzio Prediction: $T_g = x_A T_{g,A} + x_B T_{g,B}$

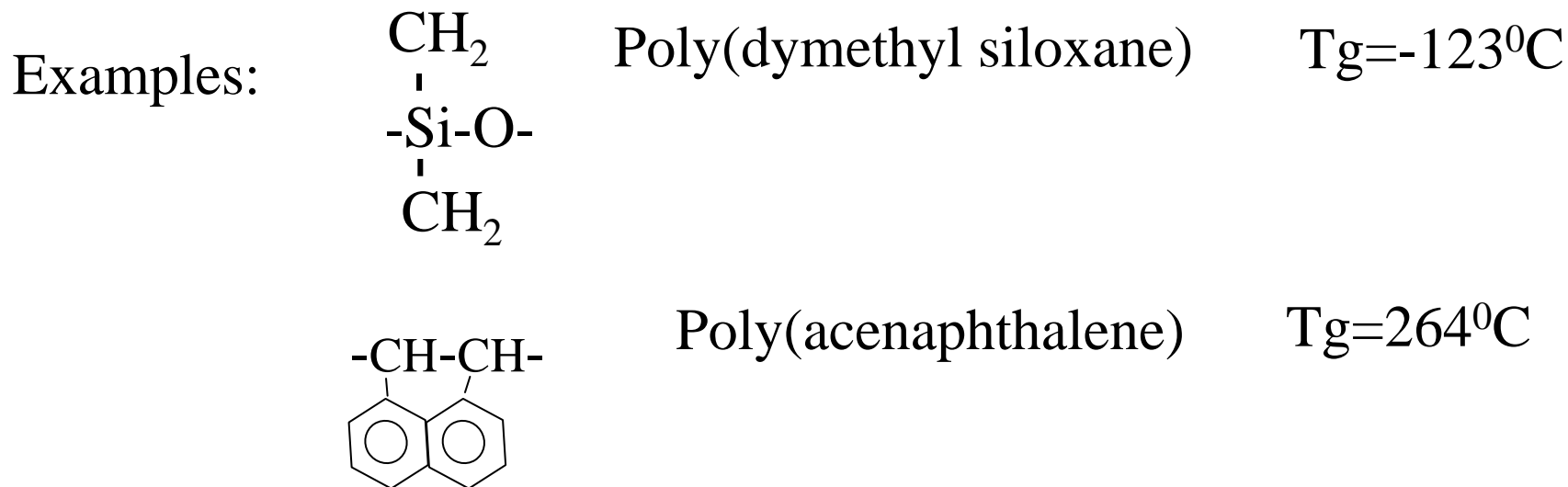
x-volume fraction

Fox equation: $\frac{1}{T_g} = \frac{w_A}{T_{g,A}} + \frac{w_B}{T_{g,B}}$

w- mass fraction

Effect of Chain Stiffness on T_g

Mobility of polymers is directly affected by the barriers of rotation around the backbone bonds. Steric barriers to rotate raises T_g;



Methods of Measuring Transitions in Polymers

Dilatometry Studies

In the most common volume-temperature measurements the polymer is confined by a liquid and the change in the volume is recorded as the temperature is changed. The usual confining liquid is mercury, since it does not swell polymers and does not have its own transition through the temperature range of interest.

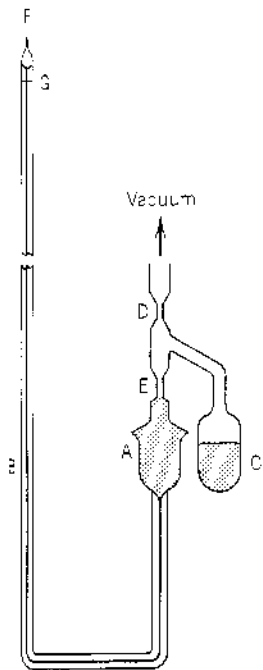


FIGURE 6.7 A mercury-based dilatometer (17). Bulb *A* contains the polymer (about 1 g), capillary *B* is for recording volume changes (Hg – polymer), *G* is a capillary for calibration, sealed at point *F*. After packing bulb *A*, the inlet is constricted at *E*. *C* contains weighed mercury to fill all dead space, and *D* is a second constriction.

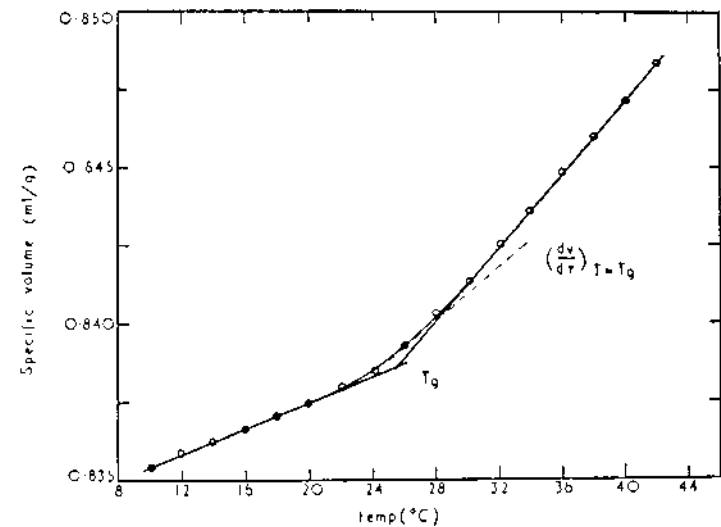


FIGURE 6.8 Dilatometric studies on branched poly(vinyl acetate) (17).

Thermal Methods

DTA – differential thermal analysis, and DSC- differential scanning calorimetry. These methods yield peaks related to endothermic and exothermic transitions, and show changes in heat capacity.

DTA-method:

The sample temperature is compared with the temperature of a reference material. (A typical heating rate 10-20°C per minute.)

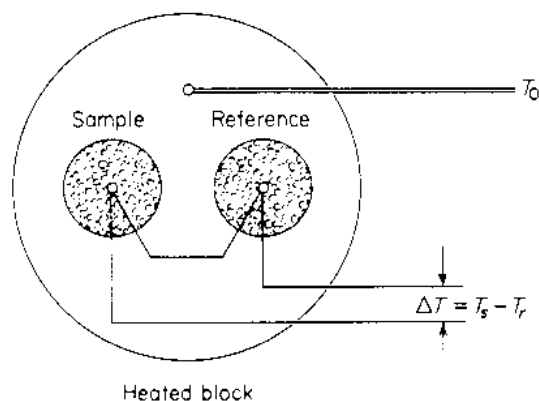


FIGURE 6.9 Schematic of differential thermal analysis (DTA) apparatus (1). Heated block programmed so that T_0 increases linearly with time. The difference between the sample temperature, T_s , and the reference temperature, T_r , ΔT , is recorded as a function of T_0 .

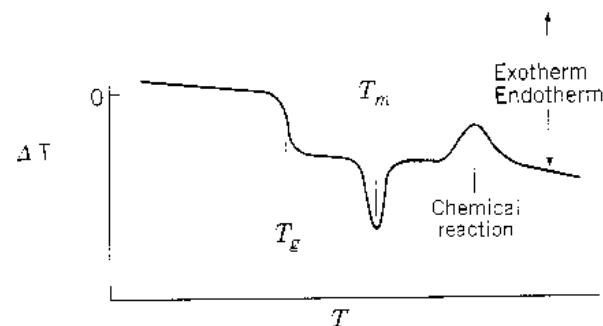


FIGURE 6.10 Schematic differential thermal analysis plot, showing (with increasing T) T_g by an increase in the specific heat, T_m , by an endotherm, and a chemical reaction, by an exotherm (1).

DSC-Method

The **DSC** method uses a servo system to supply energy at varying rate to the sample and reference material, so that the temperature of two stays constant. The **DSC** output plots energy supplied vs average temperature. The area under the peaks can be directly related to the enthalpic changes.

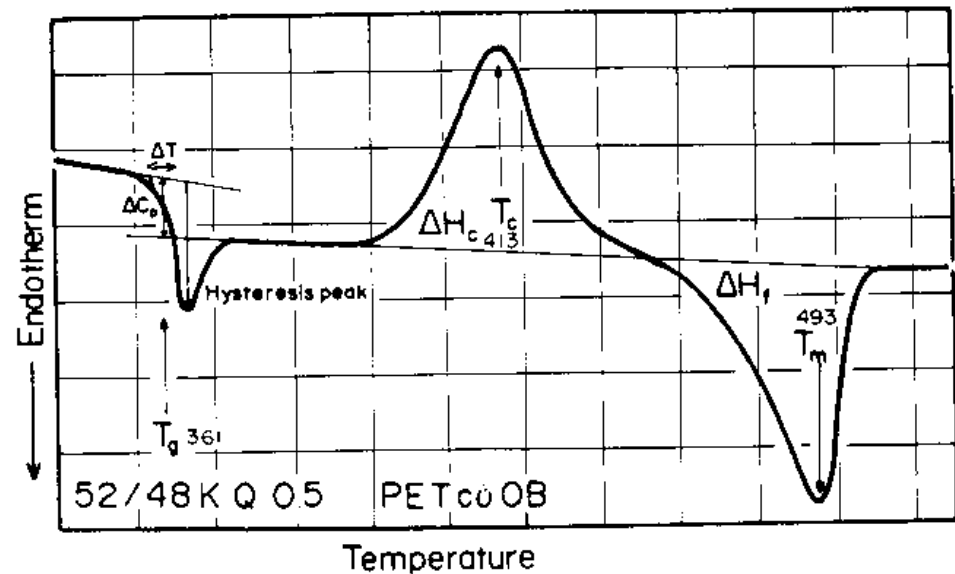
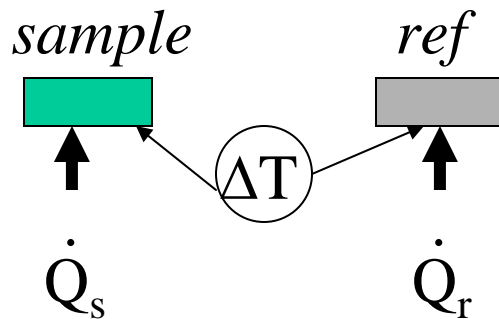


FIGURE 6.11 Example of a differential scanning calorimetry trace of poly(ethylene terephthalate-co-p-oxbenzoate), quenched, reheated, cooled at $0.5^\circ\text{K}/\text{min}$ through the glass transition, and reheated for measurement at $10^\circ\text{K}/\text{min}$ (27a). T_g is taken at the temperature at which half the increase in heat capacity has occurred. The width of the transition is indicated by ΔT .

Mechanical Methods

DMTA (dynamic mechanical thermal analysis) methods measure stress and strain in a periodically deformed sample at different loading frequencies and temperatures.



Torsion pendulum

Reversed uniaxial
tension

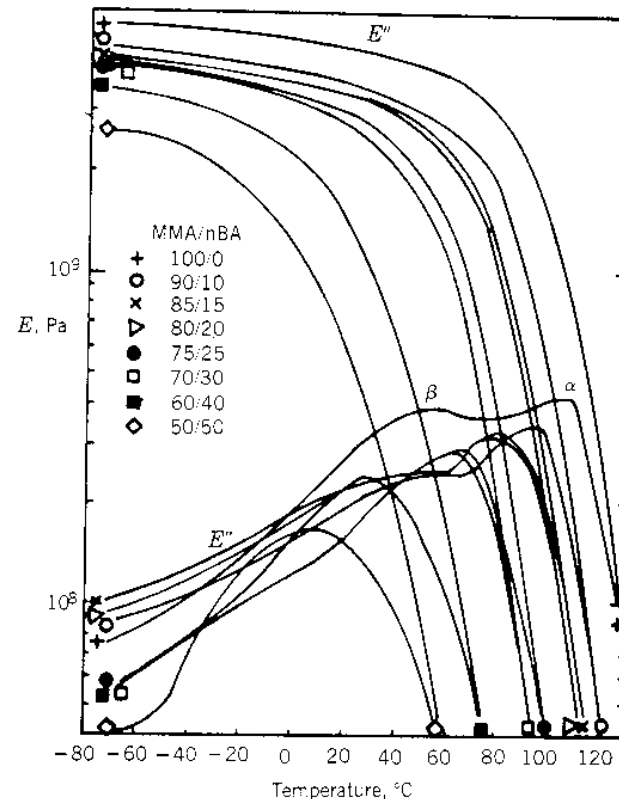


FIGURE 6.12 Dynamic mechanical spectroscopy on random copolymers of methyl methacrylate (MMA) and *n*-butyl acrylate (nBA) (23). The α -maximum in E' provides a reproducible measure of T_g . As the *n*BA mer content increases (T_g [PnBA] is $\sim 55^{\circ}\text{C}$), T_g decreases.

Dielectric and Magnetic Methods

1. The dielectric loss constant, ε'' , or its associated $\tan \delta$ are measured by placing a sample between parallel plate capacitor and alternating the electric field. Polar groups on the polymer respond to the alternating electric field. If the dielectric measurements are carried out at the same frequency range as DMTA measurements, the transitions will occur at the same temperature.
2. NMR measurements are sensitive to the mobility of the chain segments.