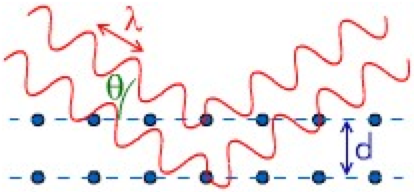
LEARNING PREREQUISITES – SOLID STATE OF POLYMERS

An X-ray which reflects from the surface of a substance has travelled less distance than an X-ray which reflects from a plane of atoms inside the crystal. The penetrating X-ray travels down to the internal layer, reflects, and travels back over the same distance before being back at the surface. The distance travelled depends on the separation of the layers and the angle at which the X-ray entered the material. For this wave to be in phase with the wave which reflected from the surface it needs to have travelled a *whole number* of wavelengths while inside the material. Bragg expressed this in an equation now known as Bragg's Law:

Bragg's Law:

$$n\lambda = 2d\sin(\theta)$$



where

λ is the wavelength of the rays

θ is the angle between the incident rays and the surface of the crystal

d is the spacing between layers of atoms

and constructive interference occurs when n is an integer (whole number)

When **n** is an integer (1, 2, 3 etc.) the reflected waves from different layers are perfectly in phase with each other and produce a bright point on a piece of photographic film. Otherwise the waves are not in phase, and will either be missing or feint.

Basic Mechanical Relationships

Term	**Definition**
σ	Normal stress
ε	Normal strain
γ	Shear strain
τ	Shear stress
E	Young's modulus
G	Shear modulus
B	Bulk modulus
D	Tensile compliance
J	Shear compliance
ν	Possion's ratio
η	Shear viscosity
λ	Elongational viscosity
β	Compressibilty

Perfect Viscosity

Newton's Law

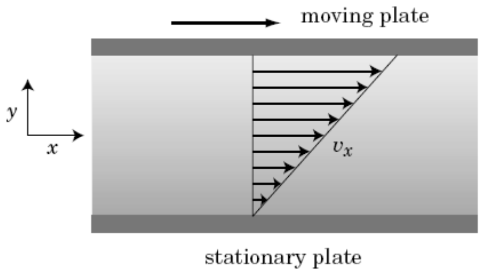


Figure 3.28. Fluid between a stationary bottom plate and a moving top plate. The velocity of the fluid is parallel to the plates and is proportional to the distance from the bottom plate, thereby generating a uniform velocity gradient.

Shear viscosity η for a perfect liquid:

$$\boxed{\eta = \tau / (d\gamma / dt)}$$

t: time
τ: shear stress
γ: shear strain

But for polymers the law represents an important limiting case

Perfect Elasticity: Application of Hooke's Law to Different Types of Deformation

1. Stretching along a single axis

$$\sigma = \frac{F}{A} = \frac{\text{force}}{\text{cross-section}}$$

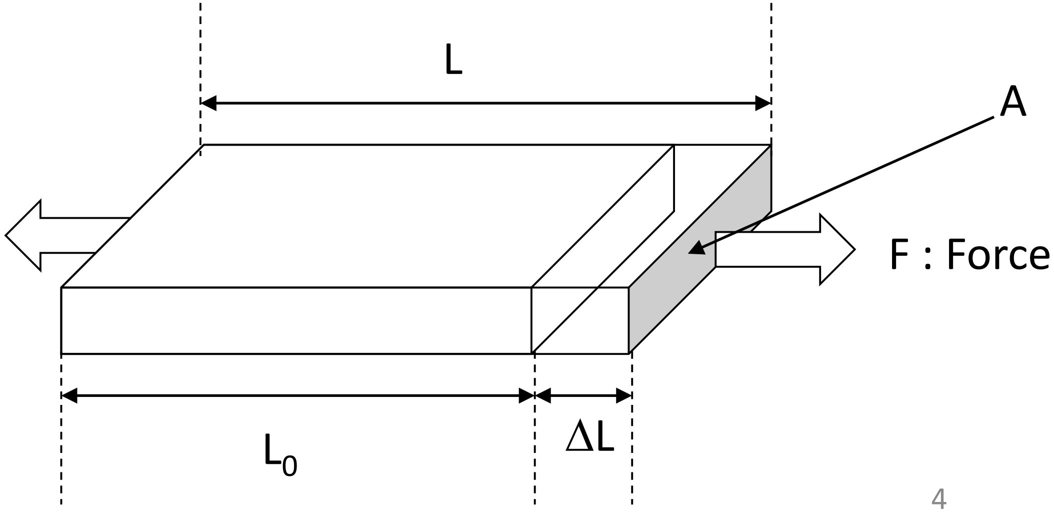
The "stress" applied to the sample

$$\varepsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} = \alpha - 1$$

The "strain" applied to the sample

$$\boxed{\sigma = E\varepsilon}$$

The proportionality factor between stress and strain is the **Young modulus E**. This equation is only valid in the elastic region, that is when $\Delta L \ll L_0$ (seen later)



2. Shearing

A force is applied on the upper part of a cube

$$\sigma = \frac{F}{A} = \frac{\text{force}}{\text{section}}$$

The "stress" applied to the sample

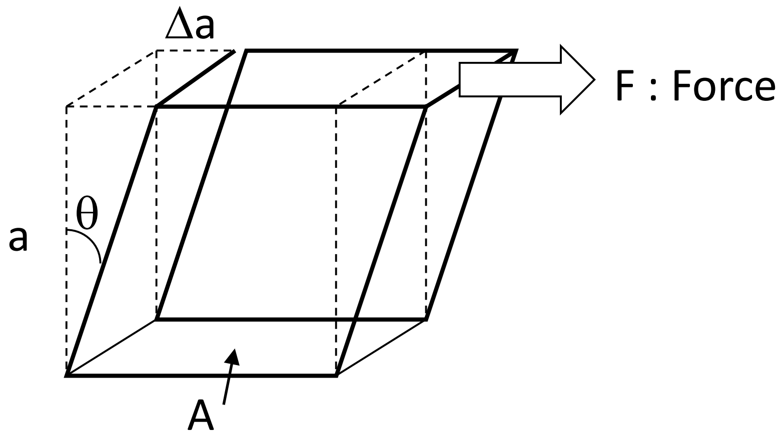
$$\gamma = \frac{\Delta a}{a} = \tan\theta$$

The "strain" applied to the sample

$$\Delta a = \frac{Fa}{AG}$$

$$\boxed{\sigma = G\gamma}$$

The proportionality factor between stress and strain is the **shear modulus G**. This equation is only valid in the elastic region, that is when Δa << a (seen later)



3. Compression

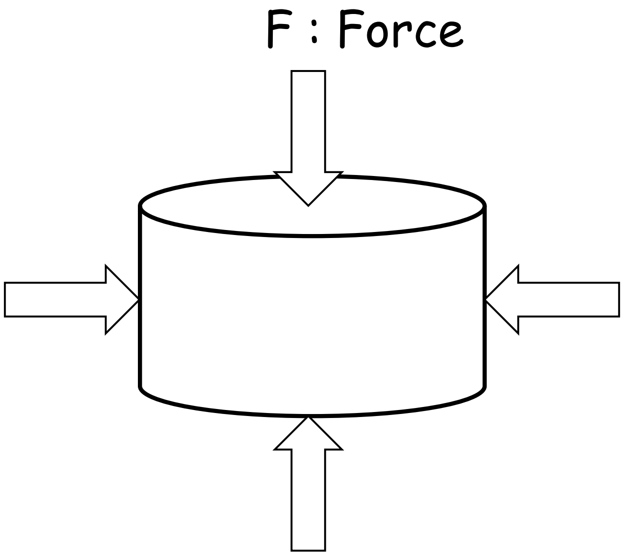
The **bulk modulus B** represents the resistance of a material to compression by an external pressure.

$$B = -V\left(\frac{dp}{dV}\right)_T \quad \text{or} \quad V = -B\left(\frac{dV}{dp}\right)_T$$

Where p is pressure and V is volume

The inverse of the bulk modulus is referred to as a material's compressibility

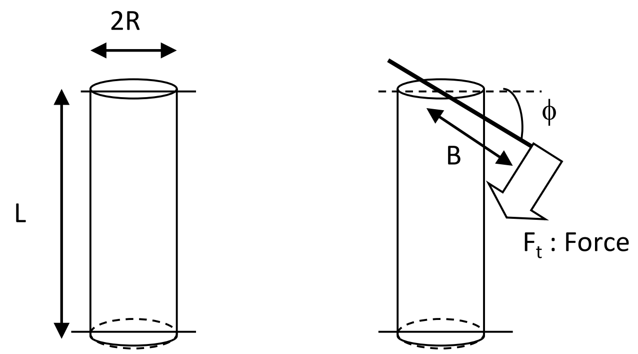
$$\beta = \frac{1}{B}$$



4. Other types of deformations

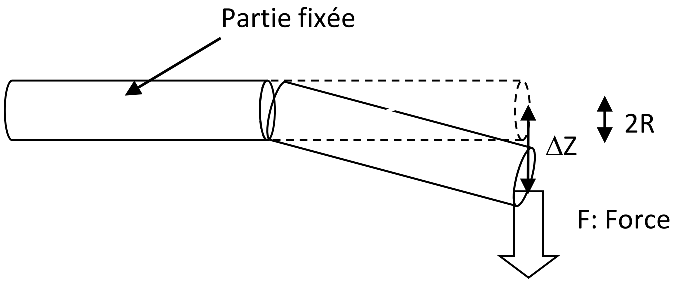
Other types of deformations exist, though these can be simplified into the three preceding deformations

For example: Torsion of a rod



$$M_t = F_t B = G\frac{\pi R^4}{2L}\phi$$

M_t: Torque applied to the rod
F_t: Force
B: Distance between center axis of rod and applied force
G: Torsion modulus = shear modulus
ϕ: Angle



$$F = E\frac{3\pi R^4}{4L^3}\Delta Z$$

F: Force
E: Young’s modulus
Δ: Distance by which the rod is deformed

Classification of Phase Transitions

Discontinuous phase transitions are characterized by a discontinuous change in entropy at a fixed temperature. The change in entropy corresponds to latent heat L=TΔS. Examples are solid–liquid and liquid–gas transitions at temperatures below the critical temperature. Continuous phase transitions involve a continuous change in entropy, which means there is no latent heat. Examples are liquid–gas transitions at temperatures above the critical temperature, metal–superconductor transitions and many magnetic ordering transitions.

Ehrenfest's classification scheme: the order of a transition is the order of the lowest differential of G which shows a discontinuity.

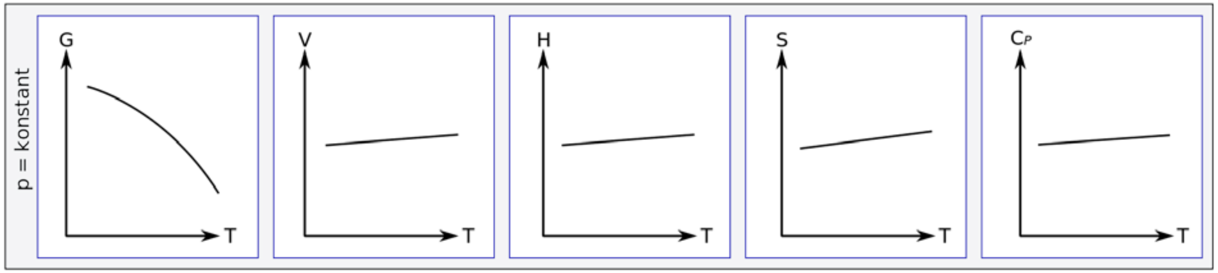
First order transitions have discontinuities in the first derivatives of G:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \qquad \left(\frac{\partial G}{\partial p}\right)_T = V.$$

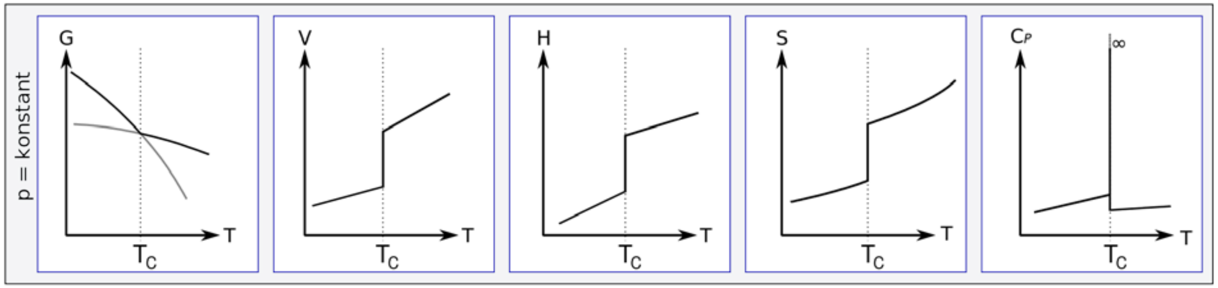
Second order transitions have discontinuities in the second derivatives of G:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\frac{c_p}{T}, \qquad \left(\frac{\partial^2 G}{\partial p^2}\right)_T = -V\kappa_T, \qquad \left(\frac{\partial^2 G}{\partial T \partial p}\right) = V\beta_p$$

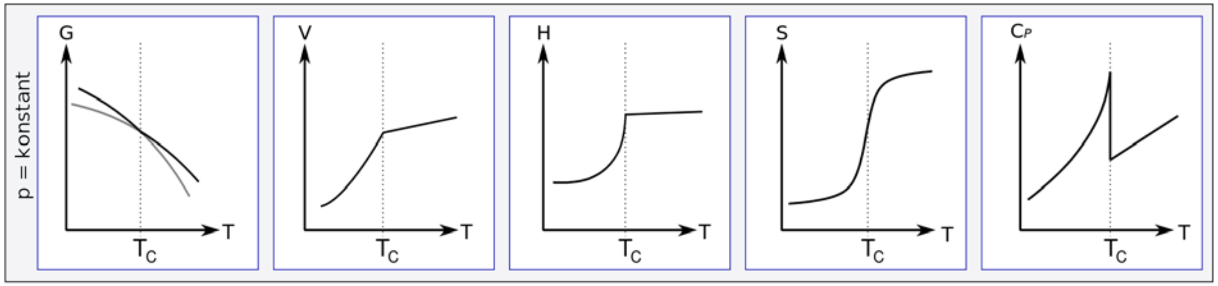
no phase transition



Phase transition of first order



Phase transition of second order



Effect of Temperature on Enthalpy

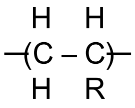
When the temperature increases, the amount of molecular interactions also increases. When the number of interactions increase, then the internal energy of the system rises. According to the equation $\Delta H=\Delta U+p\Delta V$, if the internal energy (U) increases then the ΔH increases as temperature rises. If there is no non-expansion work on the system and the pressure is still constant we can use the equation for heat capacity $C=q/\Delta T$ and $\Delta H = q$ to derive this relationship:

$$Cp=(\Delta H/\Delta T)_P$$

where the subscript p indicates the derivative is done under constant pressure.

Tacticity of Polymers

Generally, tacticity applies to addition polymers with one non-hydrogen substitute attached to the carbon chain for each monomer unit:



$$\left(\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}\right)$$

Tacticity has to do with which side of the chain the R group is placed (this contrasts with head-tail placement which has to with which carbon the R group is placed on.) Fischer projections can be used to show the three different types of tacticity:

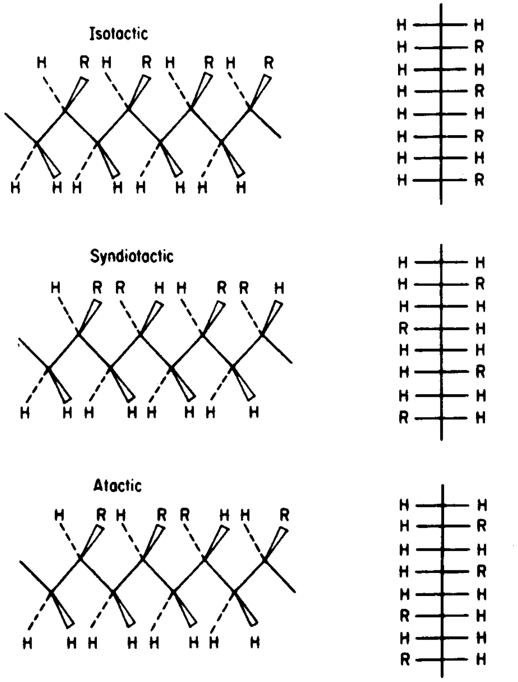


FIGURE 2.3 Three different configurations of a monosubstituted ethylene, $\left(CH_2-CHR\right)_n$. The dotted and triangular lines represent bonds to substituents below and above the plane of the carbon–carbon backbone chain, respectively (11).