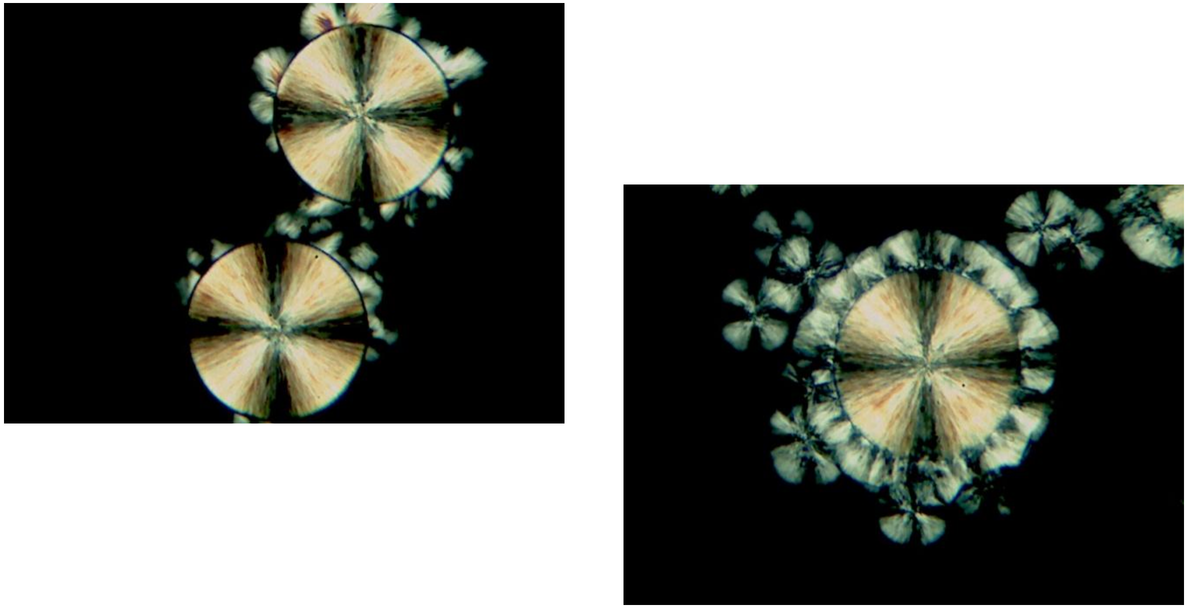
Polarized optical microscopy of semicrystalline polymers



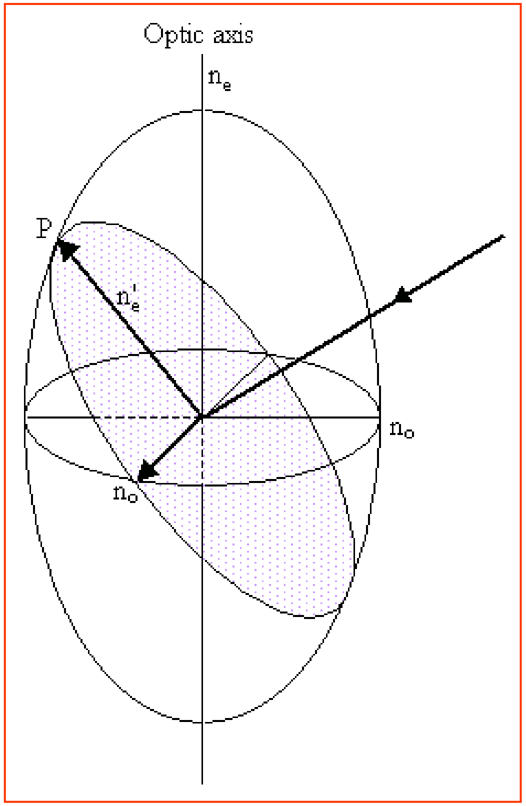
Dario Cavallo

Outline

- optical anisotropy and crystal birefringence
- polarized light optical microscopy
- semicrystalline polymer morphology
- nucleation and growth of polymer spherulites

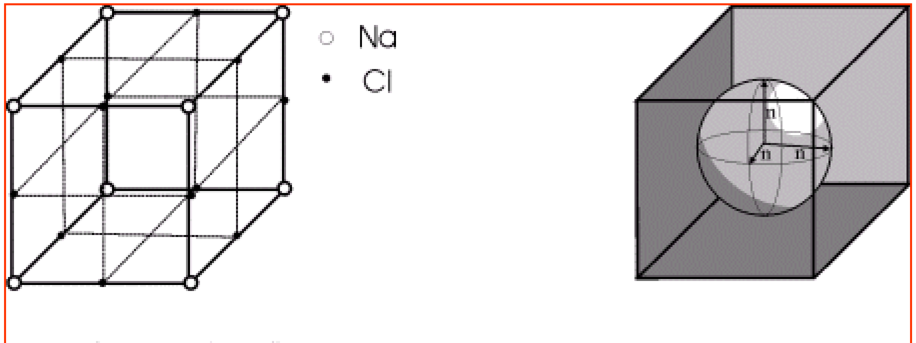
Optical anisotropy

Optical indicatrix:
Surface which represents the refractive indexes



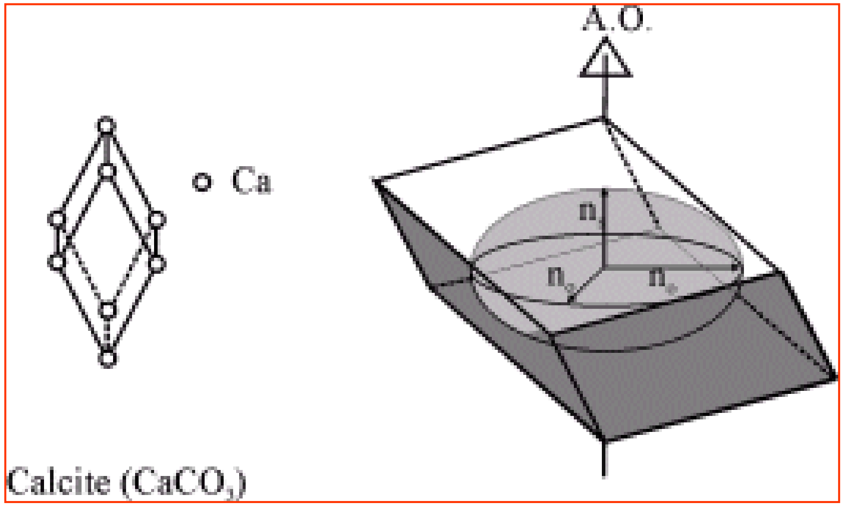
Two indeces of refraction for a generic orientation of the wavefront = BIREFRINGENCE

Optical anisotropy



Salgemma (NaCl)

Optically isotropic materials possess a single index of refraction, with a spherical indicatrix

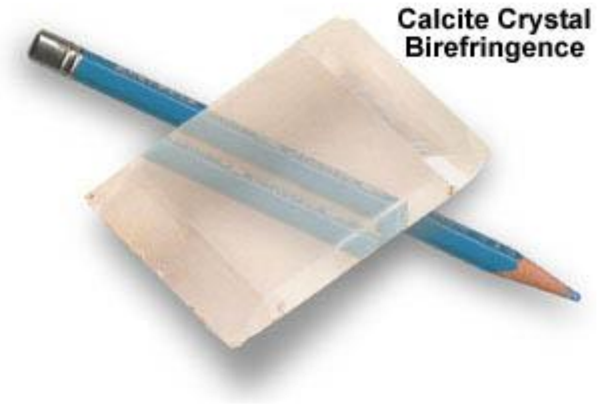


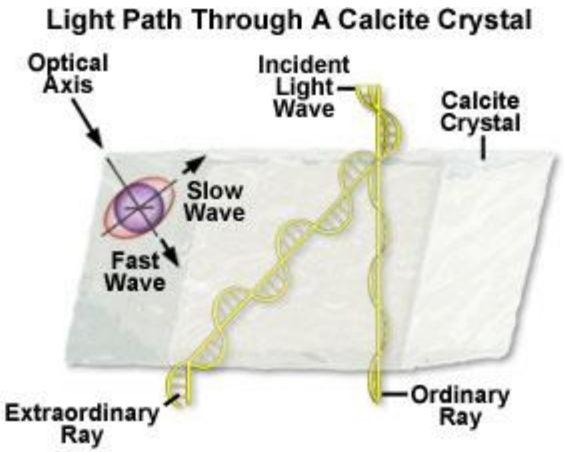
Calcite ($CaCO_3$)

Uniaxial crystals possess an indicatrix which is elipsoidal. They show two principal refractive indeces and an optical axis (parallel to the simmetry axis).

Birefringence

Double refraction

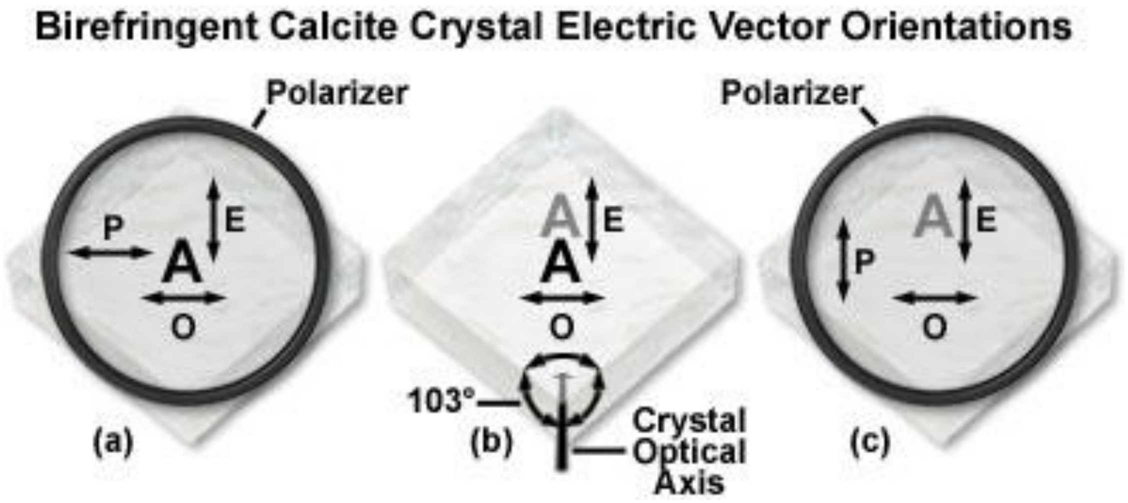




Obeys Snell's law

$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$

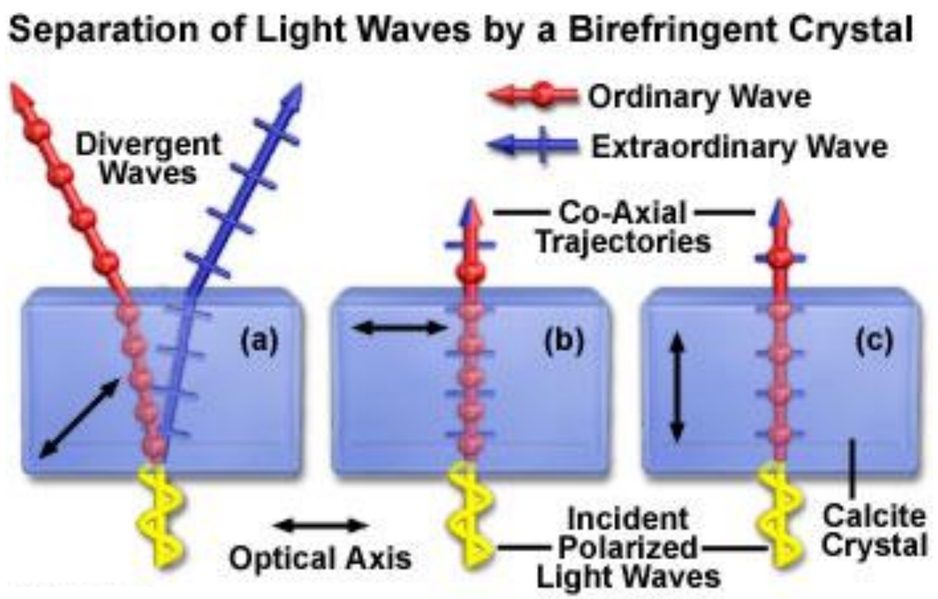
Birefringence



Ordinary and Extraordinary rays

<u>are linearly polarized at right angle</u>

Birefringence

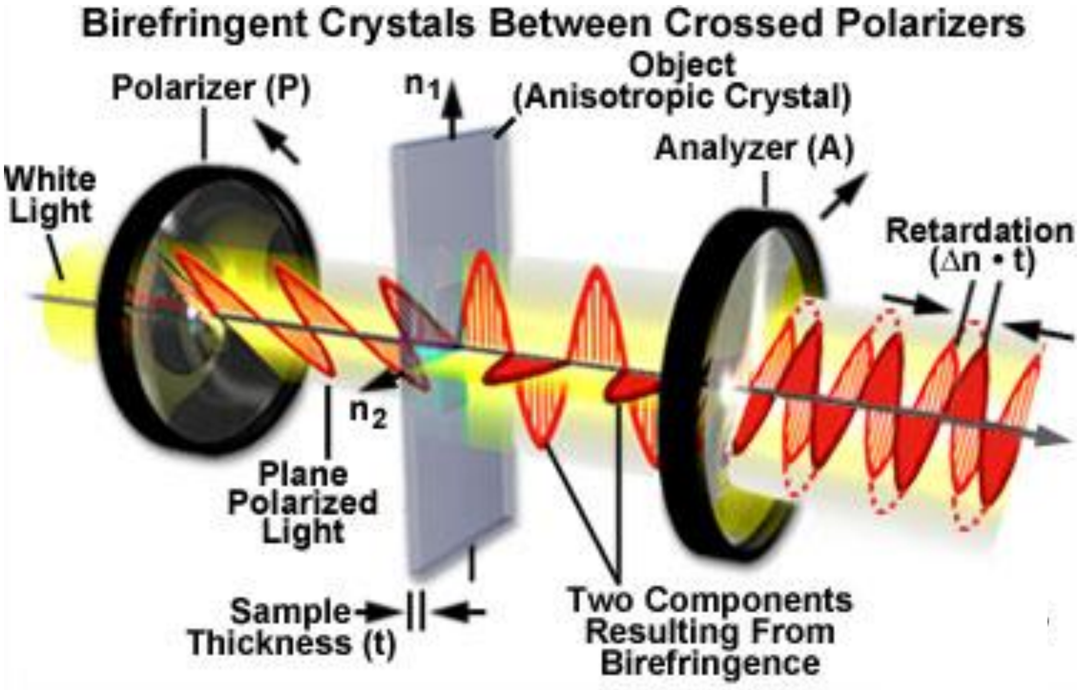


Ordinary and Extrordinary rays are
out of phase due to the different optical path
$\Lambda = \Delta t\,|n(o) - n(e)|$

$n(o) - n(e) =$ **birefringence**

Birefringence

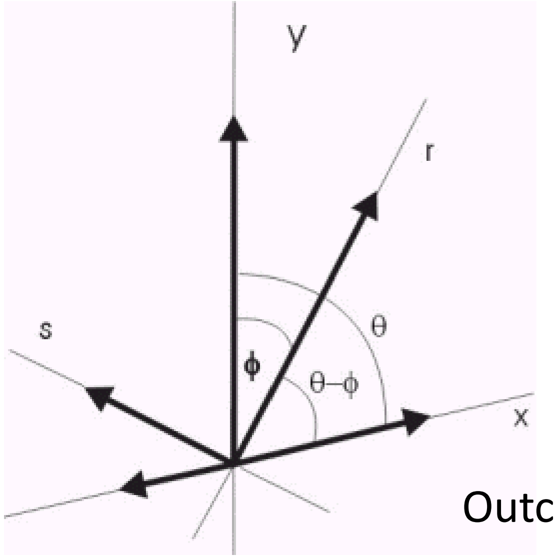
Light propagation in a birefringent crystal



The polarization state of the outcome light is correlated to the phase difference of the two waves linearly polarized in perpendicular directions.

It depends on birefringence, specimen thickness and wavelenght.

Birefringence



Extinction conditions

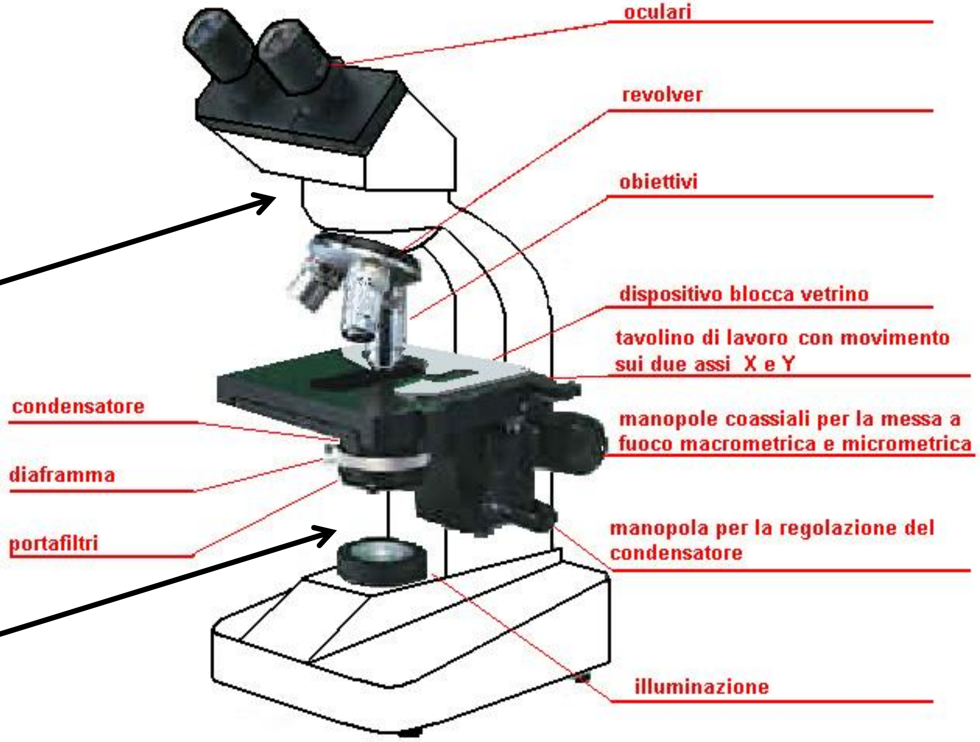
y = polarizer
x = analyzer
r , s = light vibrations direction in the birefringent sample

Outcoming light= $x = \mathbf{a\ sen\ (2\ \Phi)\ sen\ ((\pi d/\lambda)(n_e - n_o))}$

$x = 0$ for:

1. $\Phi = n\ 90°$ (the directions of the birefringent crystal coincides with those of the polarizer or analyzer; max intensity for $\Phi = n45°$)
2. $n_e = n_o$ (for isotropic materials)
3. $\mathrm{sen}\ ((\pi d/\lambda)(n_e - n_o)) = 0$ (destructive interference for the two outcoming waves)

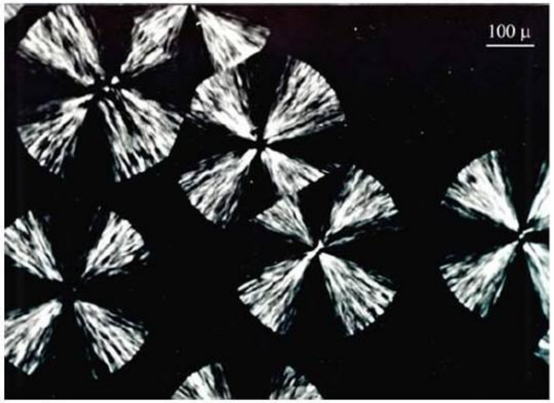
Polarized optical microscopy



analyzer

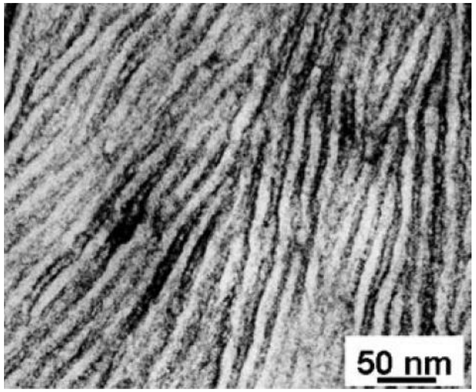
polarizer

Semicrystalline polymers



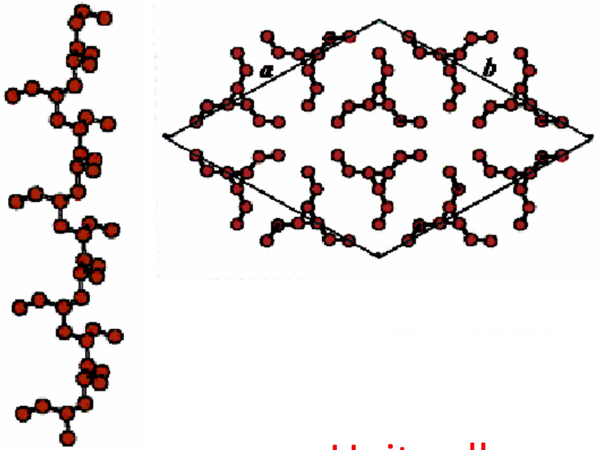
Spherulites
~10-100 μm

POM



Chain folded lamellae
~10 nm

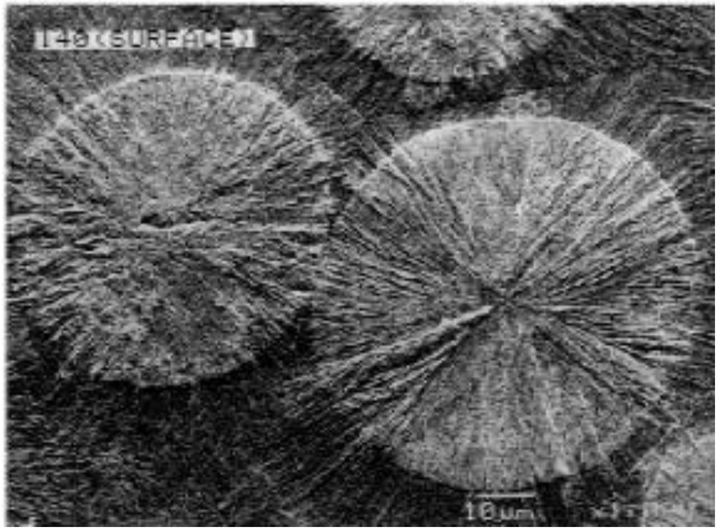
SAXS

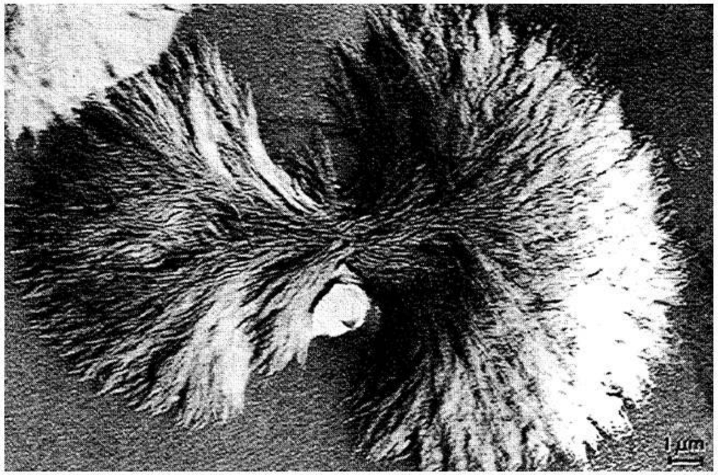


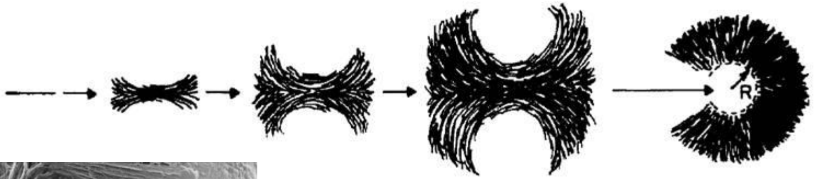
Unit cell
~1-10 Å

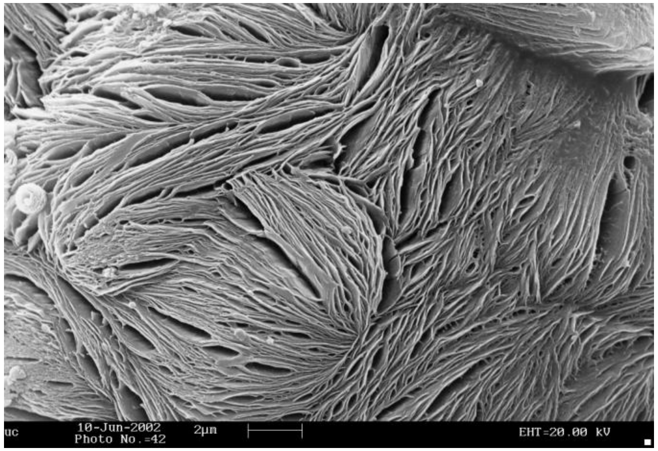
WAXD

Spherulites



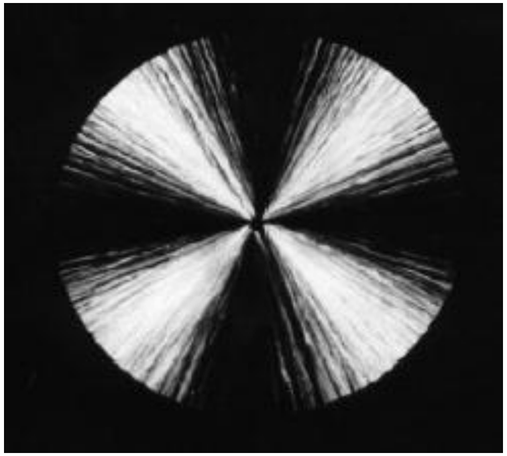


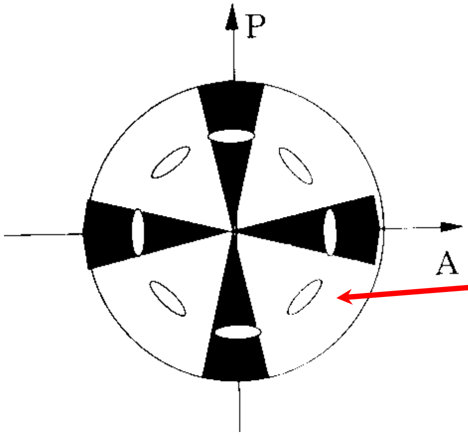




Optical properties of the spherulites

“Maltese Cross”



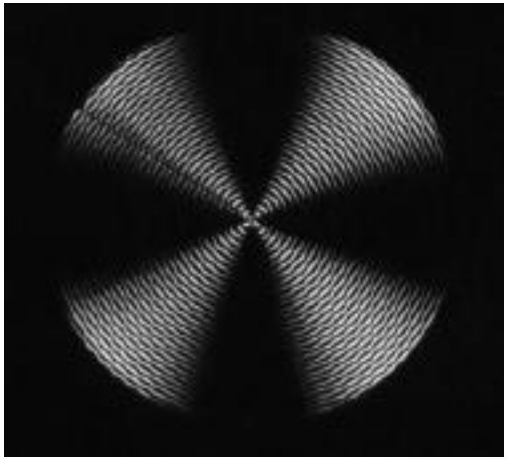


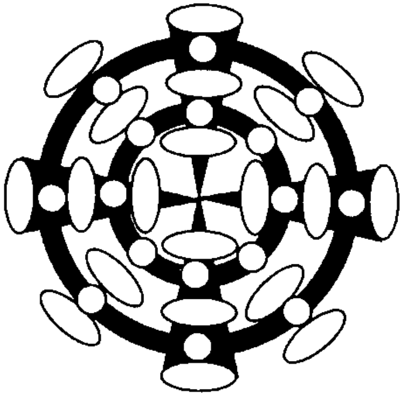
Optical indicatrix

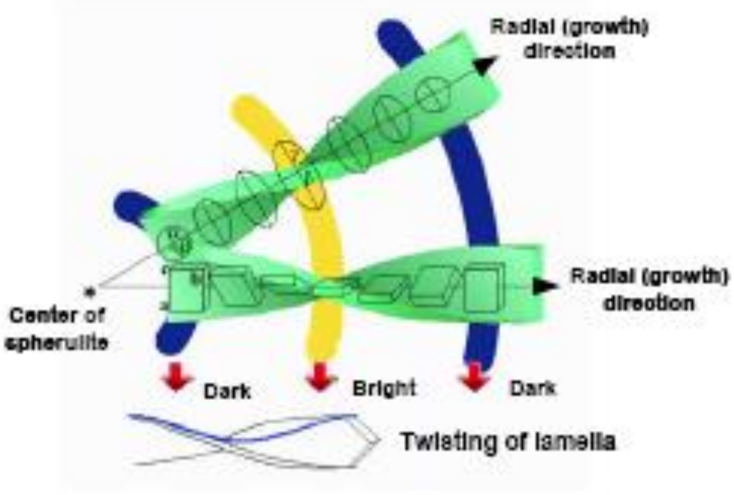
(refractive indexes elipsoid)

Optical properties of the spherulites

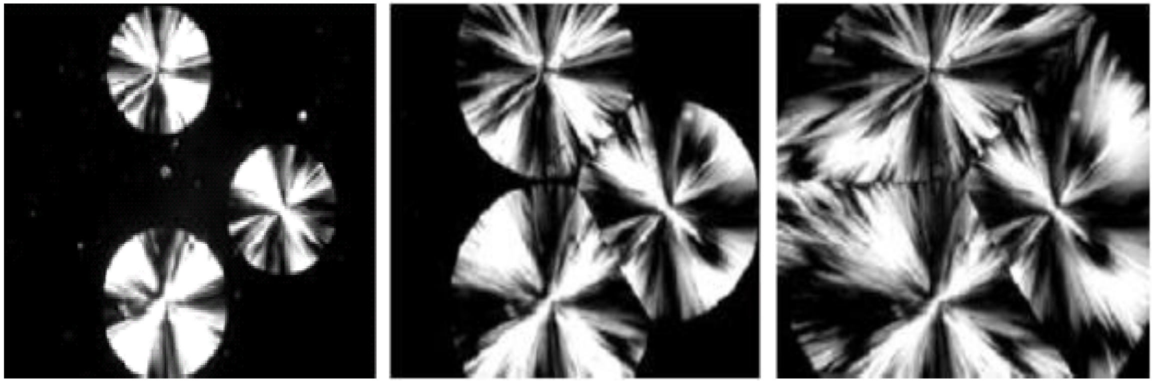
Banded spherulites



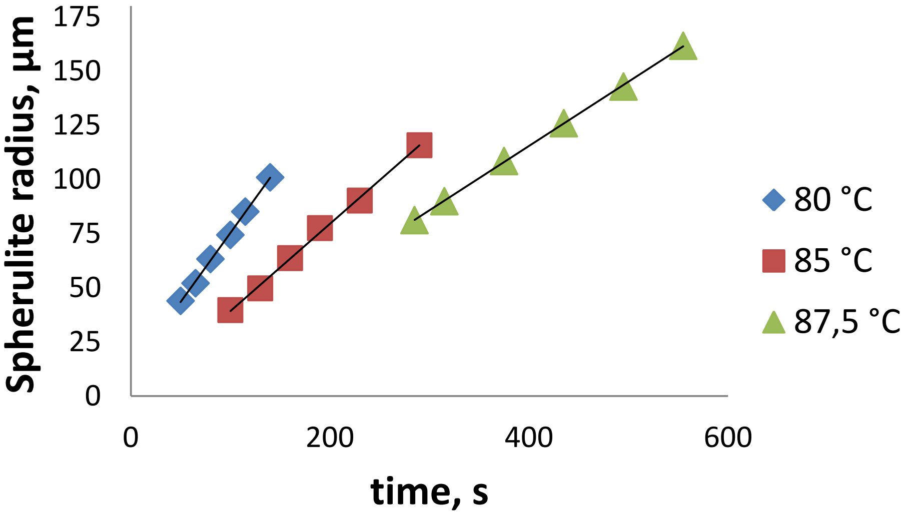




Sphrulitic growth rate

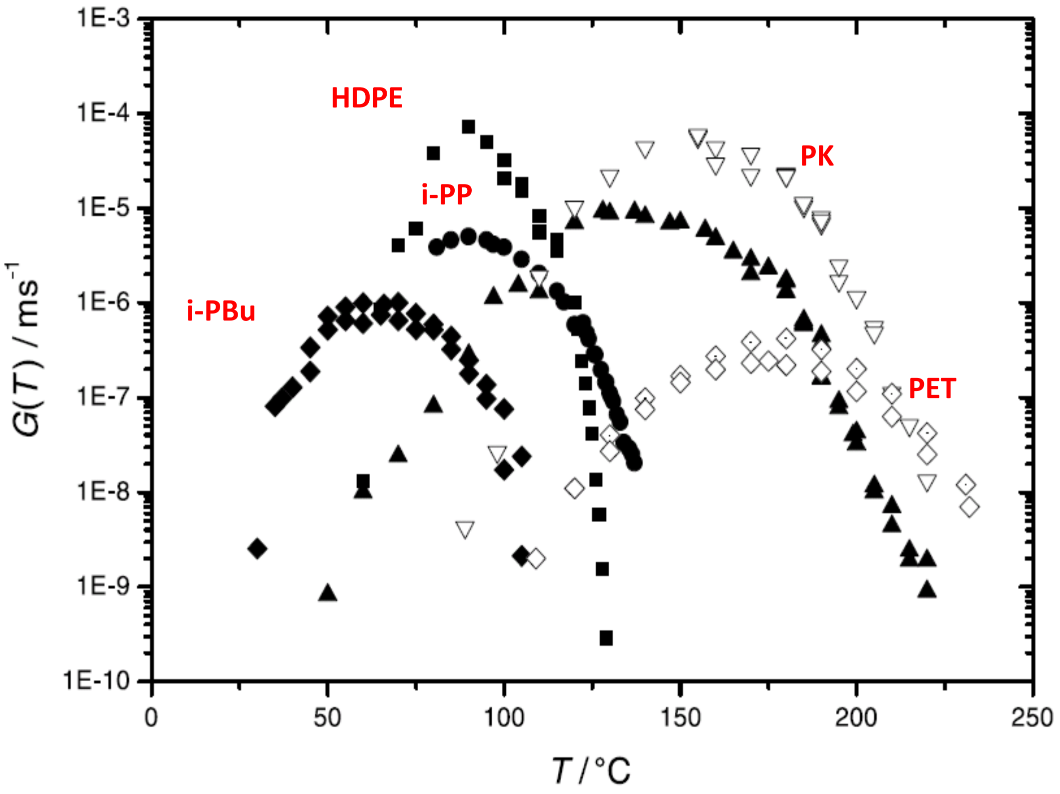


tempo



Spherulitic growth rate

Effect of crystallization temperature



T → Tm

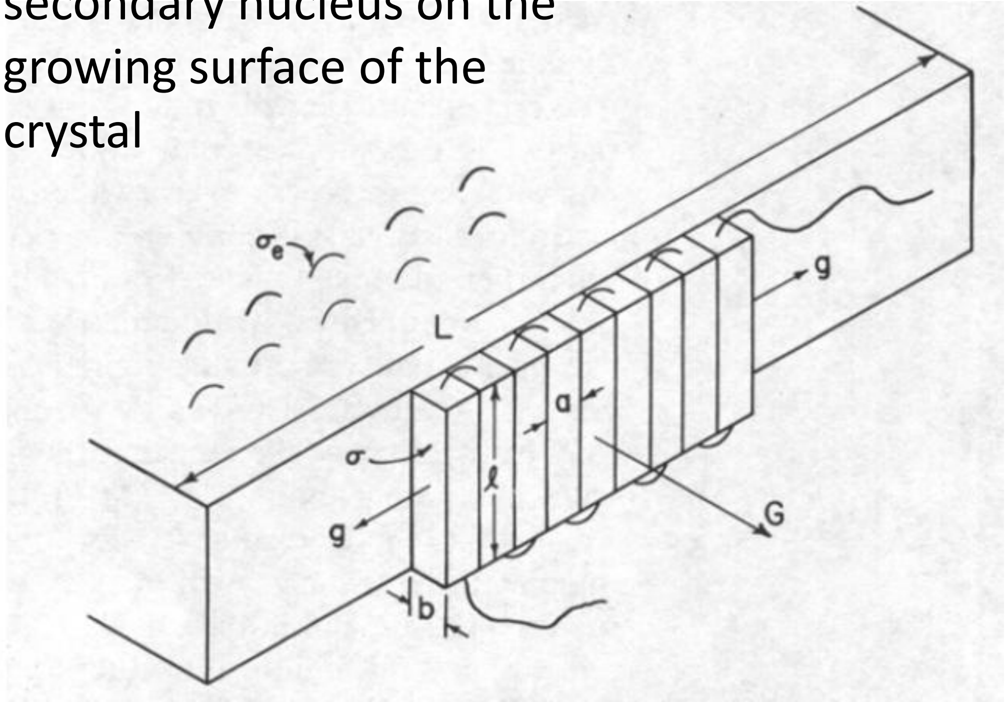
Rate limited by secondary nucleation

T → Tg

Rate limited by diffusion (mobility)

Hoffman-Lauritzen growth theory (secondary nucleation)

Formation of a stable secondary nucleus on the growing surface of the crystal



Variation of free energy for the attachemnt of a first stem

$$\Delta G = 2bl\sigma - abl\Delta g$$

Lateral surfaces

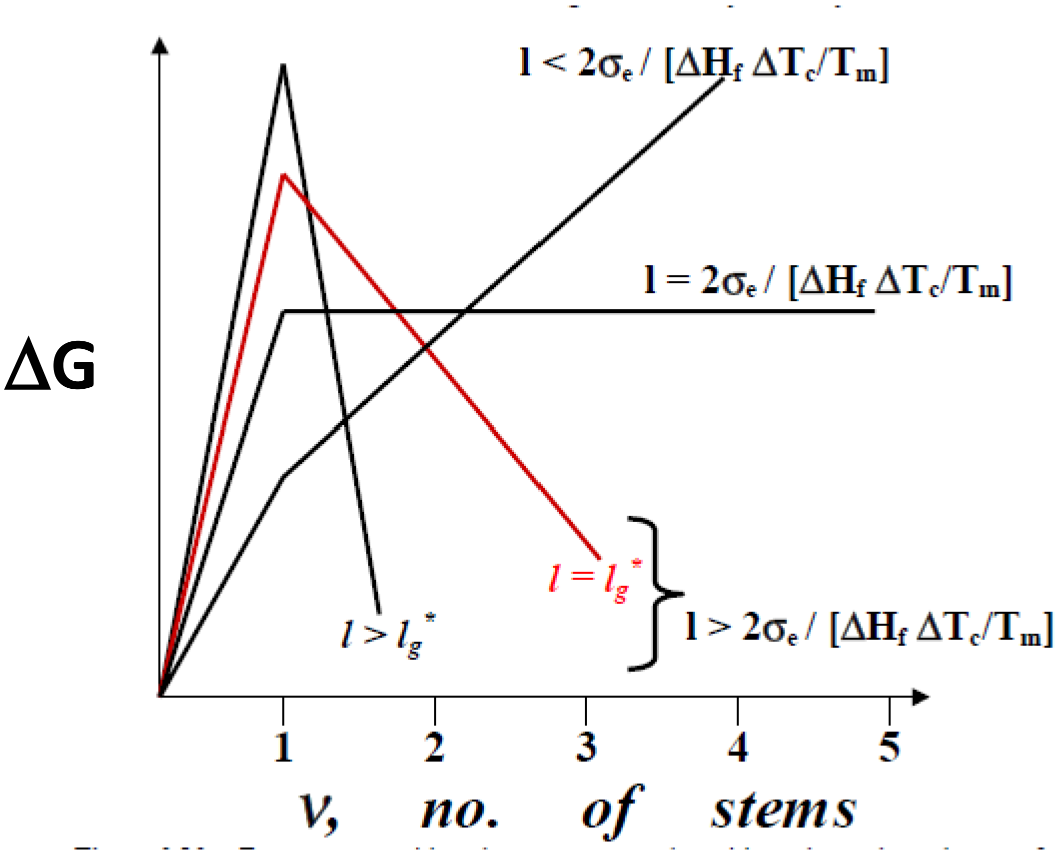
Volume

After the first attachment

$$\Delta G = 2ab\sigma_e - abl\Delta g$$

Folding surface

Hoffman-Lauritzen growth theory (secondary nucleation)



Setting $\Delta G = 2ab\sigma_e - abl\Delta g$

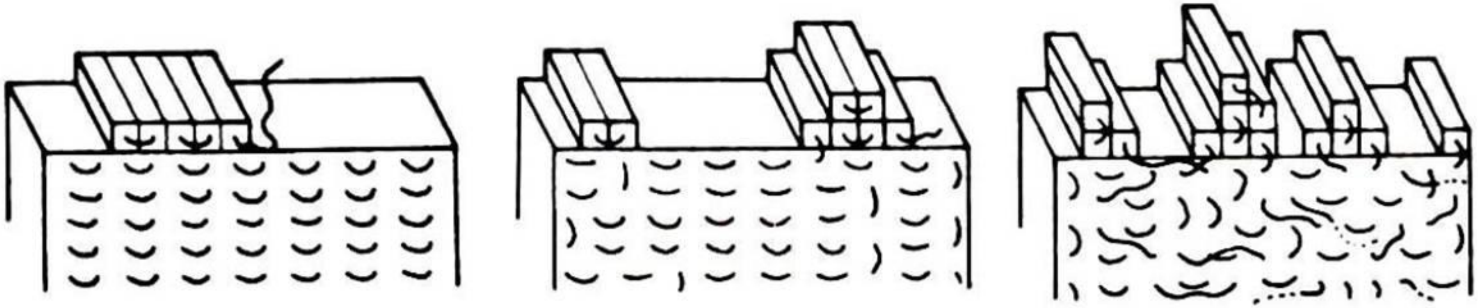
equal to zero

$$l^* = \frac{2\sigma_e}{\Delta g} = \frac{2\sigma_e T_m^0}{\Delta h \Delta T}$$

Hoffman-Lauritzen growth theory (secondary nucleation)

i = nucleation rate (nuclei per unit lenght per second)

g = lateral growth rate



Regime I:
$g >> i$

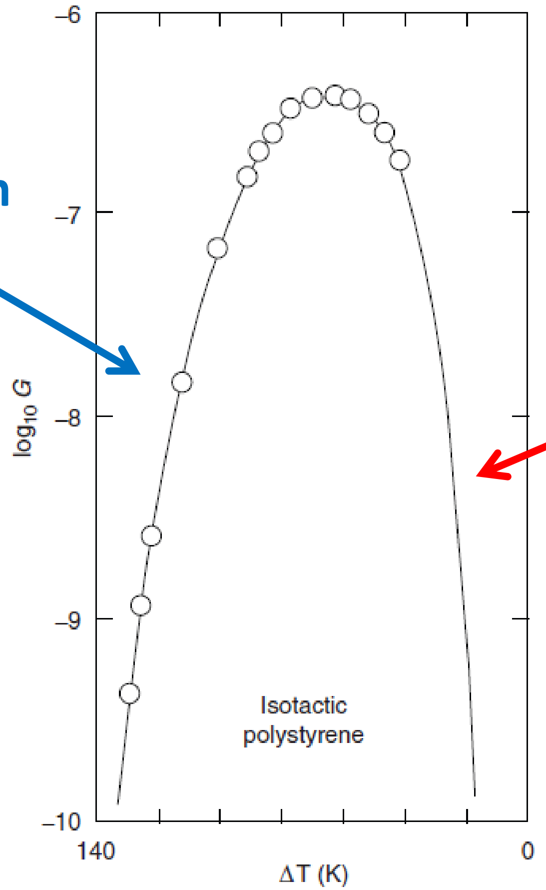
Regime II:
$g \approx i$

Regime III:
$g << i$

Low undercoolings ⟶ **High undercoolings**

Hoffman-Lauritzen growth theory

$$G(T) = G_0 exp\left[-\frac{U^*}{R(T - T_\infty)}\right] exp\left[-\frac{K_g}{T\Delta T}\right]$$



Transport term dominates

Nucleation term dominates

Hoffman-Lauritzen growth theory

$$G(T) = G_0 exp\left[-\frac{U^*}{R(T-T_\infty)}\right] exp\left[-\frac{K_g}{T\Delta T}\right]$$

G_0,= pre-exponential factor, temperature independent constant

U* = activation energy for transport of molecular segments (identical for all polymers, 1500 cal/mol)

T_∞ = limiting temperature at which chain segments are “frozen”, corresponds to T_g-30 °C

Hoffman-Lauritzen growth theory

$$G(T) = G_0 exp\left[-\frac{U^*}{R(T-T_\infty)}\right] exp\left[-\frac{K_g}{T\Delta T}\right]$$

$$K_g = \frac{Y b_0 \sigma \sigma_e T_m^0}{k \Delta H_f}$$

$\sigma\sigma_e$ = product of lateral and surface free energy of the developing lamellar crystals

$T°_m$ = equilibrium melting temperature of the specific polymer crystals

ΔH_f = melting hentalpy

b_0 = size of the molecular segment in the direction perpendicular to the growth plane

ΔT = undercooling

T = crystallization temperature

Y = constant: 4 in Regime I and III and 2 in Regime II

k = Boltzmann constant

Hoffman-Lauritzen growth theory

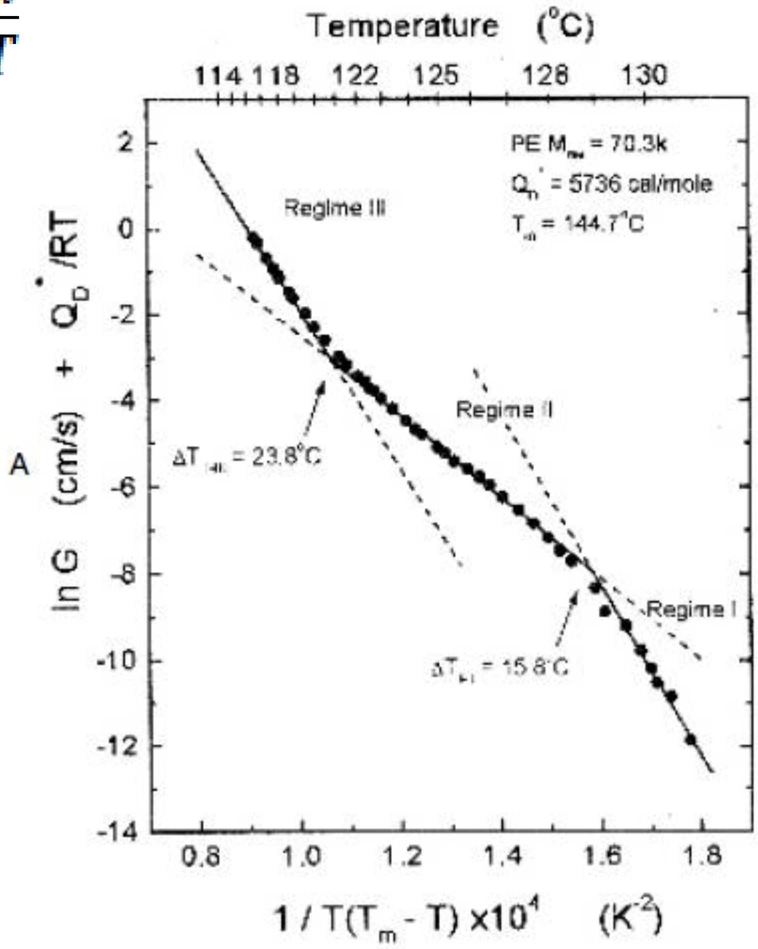
$$G(T) = G_0 exp\left[-\frac{U^*}{R(T-T_\infty)}\right] exp\left[-\frac{K_g}{T\Delta T}\right]$$

Can be linearized as:

$$\ln G + \frac{U^*}{R(T-T_\infty)} = \ln G_0 - \frac{4b_0\sigma\sigma_e T_m^0}{k\Delta H_f T\Delta T}$$

Hoffman-Lauritzen growth theory

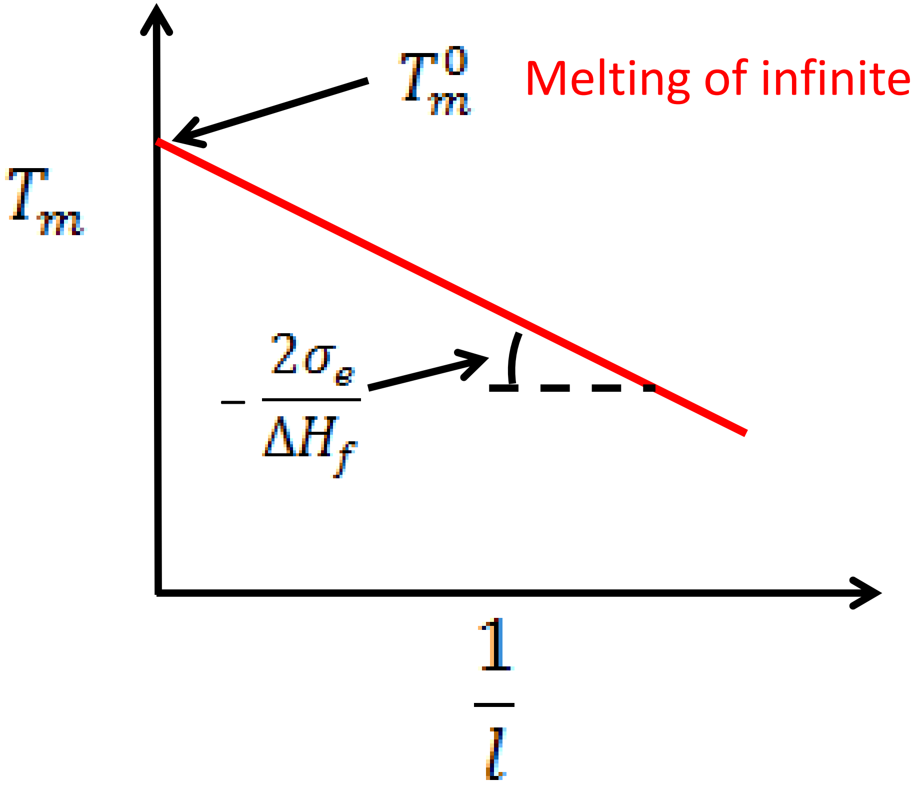
$$\ln G + \frac{U^*}{R(T - T_\infty)} = \ln G_0 - \frac{4 b_0 \sigma \sigma_e T_m^0}{k \Delta H_f T \Delta T}$$



Gibbs-Thomson equation

$$T_m = T_m^0 \left[1 - \frac{2\sigma_e}{l\,\Delta H_f} \right]$$

Depression of the melting point due to the nanometric thickness of the lamellae (contribution of the large folding surfaces)



Hoffmann-Weeks extrapolation

$$T_m = T_m^0 \left[1 - \frac{2\sigma_e}{l\,\Delta H_f}\right]$$

Gibbs-Thomson equation

$$l = l^* + \delta l = \frac{2\sigma_e}{\Delta H_f (T_m^0 - T_c)} + \delta l$$

Initial lamellar thickness from secondary nucleation theory

But T_m always > T_c due to thickening, considering a constant thickening factor β:
$l = \beta\ l^*$ and substituting in the Gibbs-Thomson equation :

$$T_m = T_m^0 \left(1 - \frac{1}{\beta}\right) + \frac{T_c}{\beta}$$

Hoffmann-Weeks extrapolation