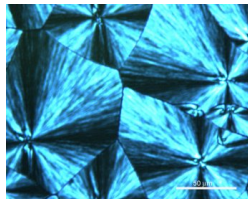


# Crystallinity in Polymers

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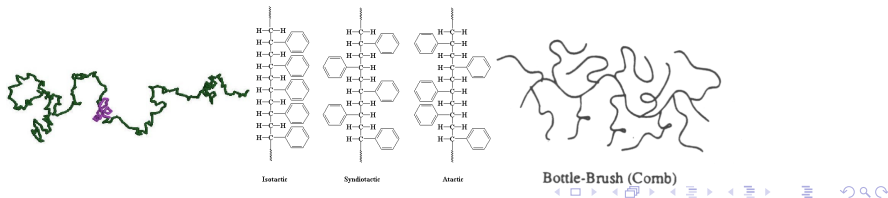
# Semicrystalline

Polymers are big, and can't easily form crystalline states. If cooled fast they turn glassy, otherwise partially crystallise with 20-60% crystallites surrounded by amorphous domains.

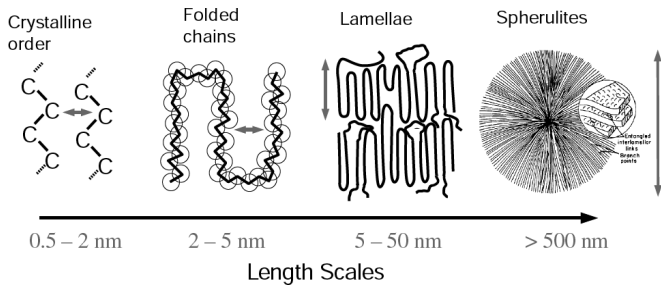
**Slow kinetics** Knots and entanglements in a melt takes ages to straighten out

**Quenched disorder 1** Random tacticity, random sequence of monomers in proteines/random copolymers

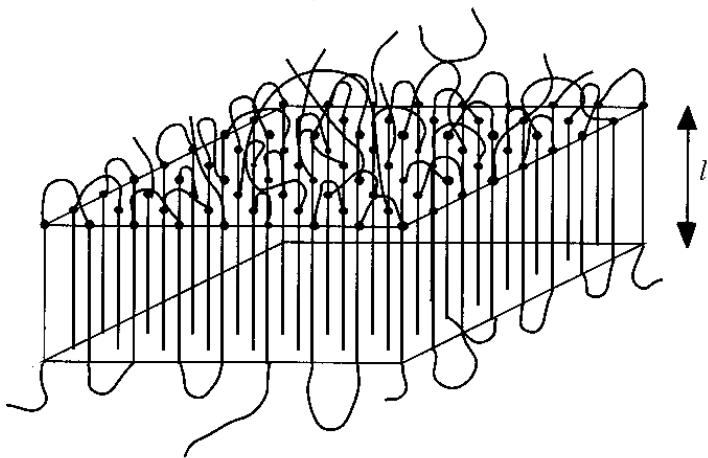
**Quenched disorder 2** Chain polydispersity, random side branches



# Spherulites



# Lamella



## Thermodynamic considerations

Assume one polymer stem of length  $l$  and crosssectional area  $a^2$  joins the lamella. Change in free energy is

$$\Delta g = \text{surface+volume} = 2a^2\sigma_f - \frac{\Delta H_m[T_m(\infty) - T]}{T_m(\infty)}la^2$$

Temperature  $T$ .  $T_m(\infty)$  ideal thermodynamic melting temperature.  $\Delta H_m$  latent heat of melting per unit volume. Depression of melting point due to finite size:

$$\Delta g = 0 \Rightarrow T_m(l) = T_m(\infty) \left(1 - \frac{2\sigma_f}{\Delta H_m l}\right)$$

Thermodynamic equilibrium for large  $l$ .

# Growth rates

Problems:

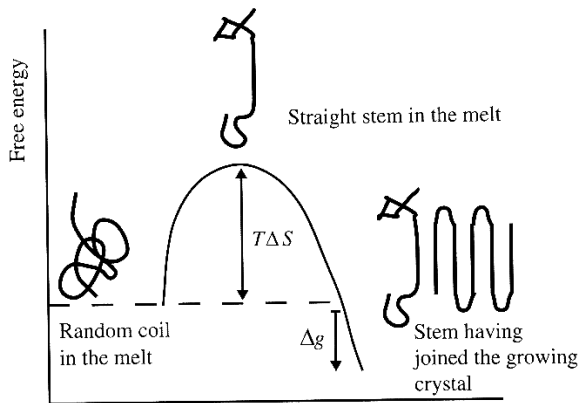
- Too thin** Too high surface to volume contribution to the free energy ( $\Delta g = \alpha - \beta l$ )
- Too thick** Grows slowly because it takes exponentially long time to straighten out a polymer, hence we are not in thermodynamic equilibrium.

Entropic cost of stretching a polymer:

$$\Delta S/k_B = \mu l/a \quad (1)$$

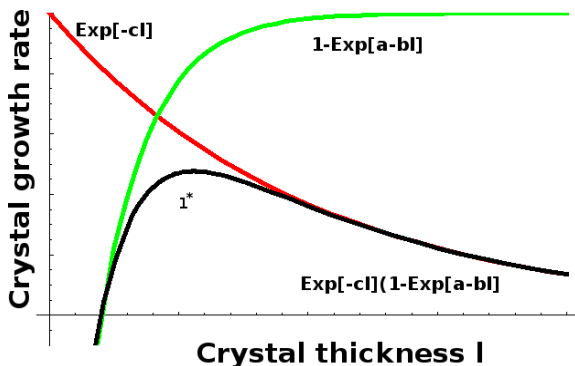
# Kinetics of crystallisation

$$r_{\rightarrow} = \tau^{-1} \exp\left(-\frac{T\Delta S}{k_B T}\right) \quad \text{and} \quad r_{\leftarrow} = \tau^{-1} \exp\left(-\frac{(T\Delta S - \Delta g)}{k_B T}\right)$$



# Net growth rate

$$u = r_{\rightarrow} - r_{\leftarrow} = \tau^{-1} \exp\left(-\frac{T\Delta S}{k_B T}\right) \left[1 - \exp\left(\frac{\Delta g}{k_B T}\right)\right]$$



## Net growth rate

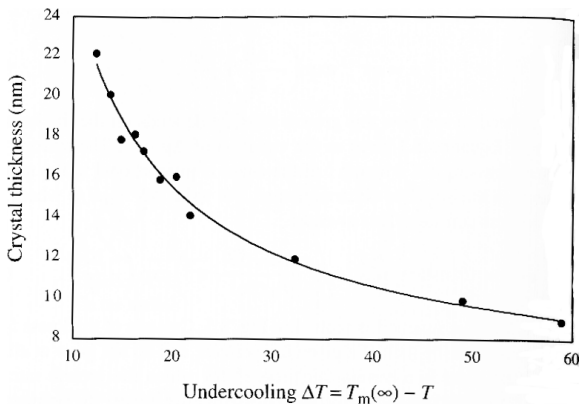
$$v(l) = au \approx a\tau^{-1} \exp\left(-\frac{T\Delta S}{k_B T}\right) \frac{\Delta g}{k_B T}$$
$$\propto \left(2a^2\sigma_f - \frac{\Delta H_m [T_m(\infty) - T]}{T_m(\infty)}\right) \exp\left(-\frac{\mu l}{a}\right)$$

Maximal growth rate at  $dv(l)/dl = 0 \Rightarrow$  optimal thickness

$$l^* = \frac{a}{\mu} + \frac{2\sigma_f T_m(\infty)}{\Delta H_m (T_m(\infty) - T)}$$

# Polyethylene

$$l^* = \frac{a}{\mu} + \frac{2\sigma_f T_m(\infty)}{\Delta H_m(T_m(\infty) - T)}$$



# Equilibrium?

Equilibrium would be a single crystal of long straight polymers. However, the time required to cross the kinetic barrier to find this state is too large, implying that polymers in practice are non-equilibrium structures in the semi-crystalline state.