TXL211

Structure and Properties of Fibres

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- **The evaluation conducted will cover 50 points towards final grading**
- **2 Quizzes (20 + 30)**

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Polymer Crystallization

Following topics will be covered (9 – 10 Lectures):

- **Crystallization**
- **Why polymer crystallizes**
- **Molecular morphology of crystalline polymers**
- **Superstructural morphology of polymer crystals**
- **Thermodynamics of polymer crystallization**
- **Kinetics of polymer crystallization**
- **Factors influencing polymer crystallization and melting**
- **Degree of crystallinity and how to measure it**
- **Techniques for analyzing crystalline and/or oriented polymer structures**

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Essentials of Polymer Science and Engineering
by Paul C. Painter and Michael M. Coleman
(Chapter 8 and 10)

Introduction to Polymers
By Young and Lowell
(Chapter 17)

Polymer Physics
U12 Gedde

<u>Pre-requisites</u>: Knowledge of polymer chain configuration and conformation, crystal structures

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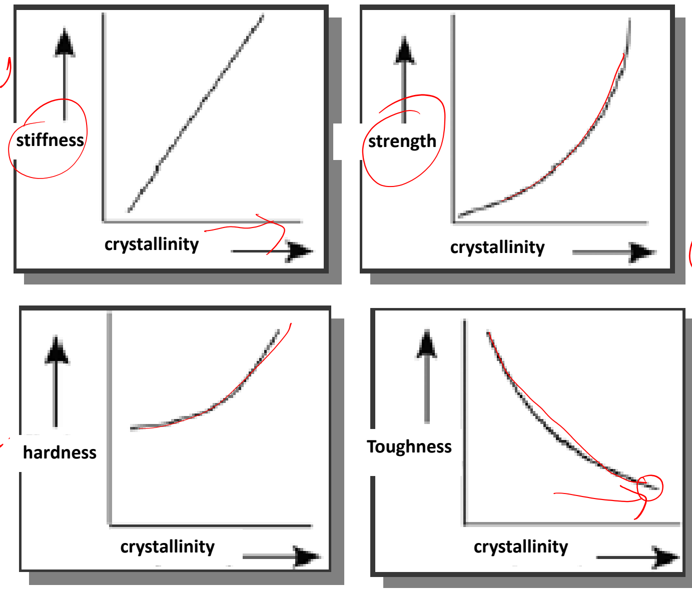
Importance of crystallization

Dimensional Stability

Fineness

orientation



→ amorphous orientation

→ crystalline orientation

Entropy Law

Orientation

Crystallization

Plasticizer

How do you think crystallization influences the properties of Textile Fibers??

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What is crystallization???

FCC

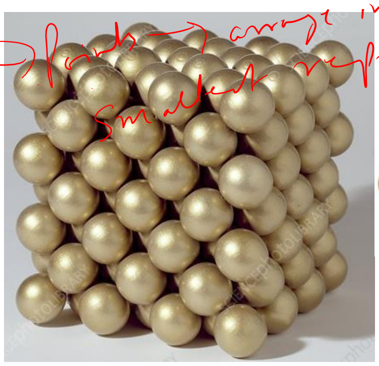
❖ *Process of crystal formation.*

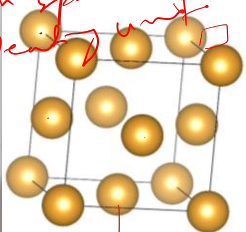
❖ *A crystal is defined as a portion of matter within which atoms are arranged in a regular, repeated, and three-dimensionally periodic pattern.*

Points → arrange in space

Smallest repeating unit

❖ *Lattices and unit cell*





Unit cell

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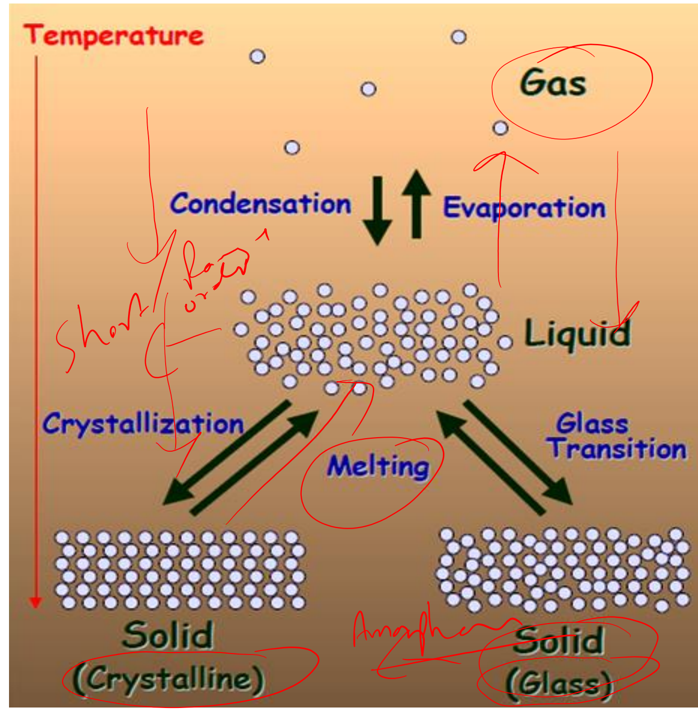
States of Matter

✓Solid

✓Liquid

✓Gas



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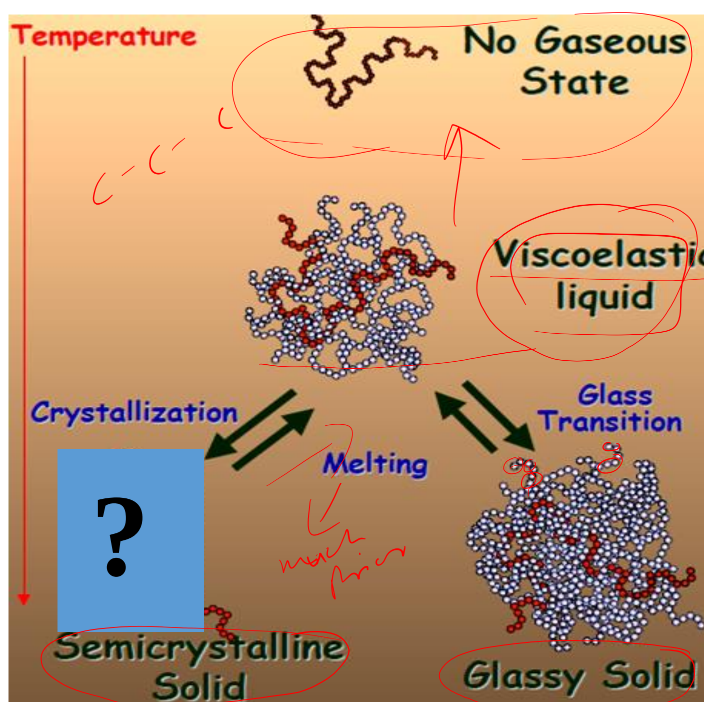
Polymers show complex phase transition behavior

States of Matter

✓Solid

✓Liquid

~~Gas~~



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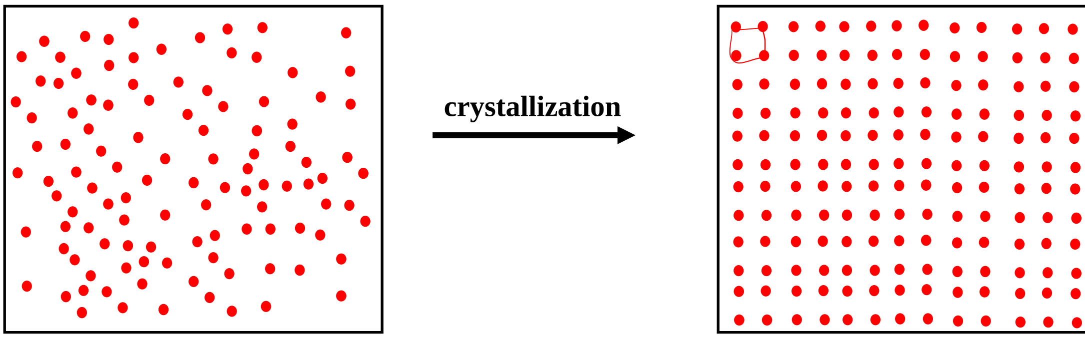
How crystallization in polymers is different than that in small molecules??



Small molecules

- Low molecular weight
- Monodisperse molecular weight
- No overlaps
- Size smaller than that of crystal unit cells

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crystallization

??????????

try to imagine

Polymers

- High molecular weight
- Polydispersity in molecular weight
- Entanglements
- Size much larger than that of crystal unit cells

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Crystalline Vs Polymer Materials

Simple Crystalline Materials

✓ ***Either crystalline (~100 %, neglecting defects) or amorphous at a particular temperature.***

✓ ***Melt at a sharp, well-defined temperature.***

Crystallizable Polymers

✓ ***Never 100% Crystalline.***

✓ ***Melt over a Range of Temperatures.***

Questions we want to discuss and answer:

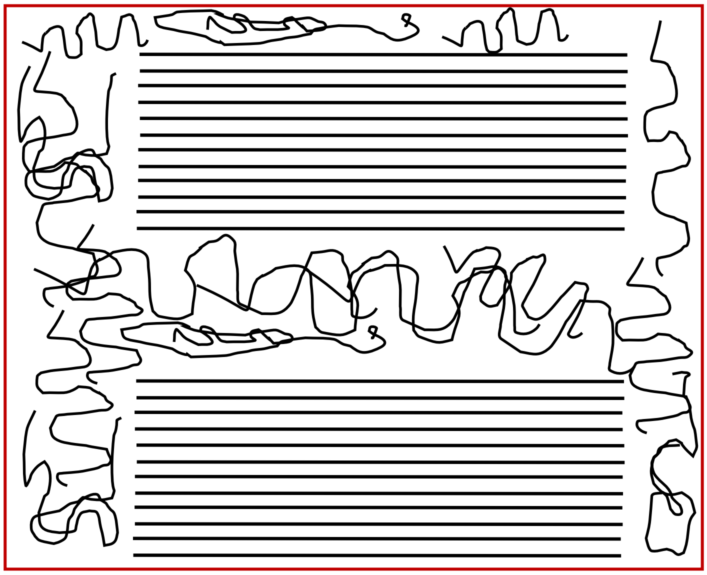
✓ ***What is the conformation of the chains in the crystalline domains and how are they stacked relative to one another?***

✓ ***What is the overall shape and form of the crystals?***

✓ ***Does polymer crystallizes fully? If not than what are the relative arrangements of the crystalline and amorphous parts?***

✓ ***How we can measure the crystallinity in polymers?***

Is this how the polymer crystallizes??



Or do a single polymer chain pass through both crystalline and amorphous regions!

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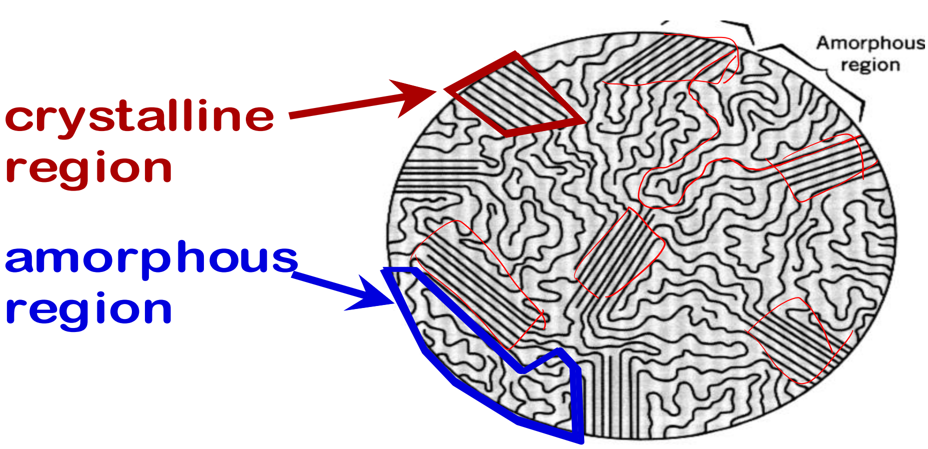
The first model for polymer crystallization: Fringed Micelle Model



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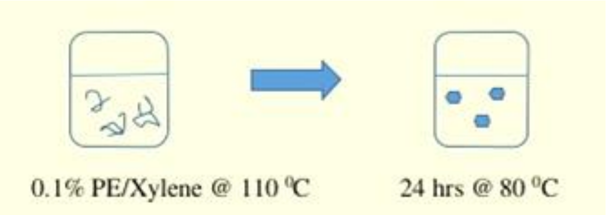
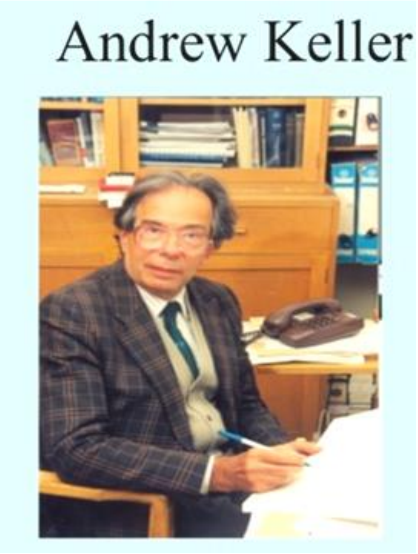
Polymer crystallization occurs by chain folding!!!





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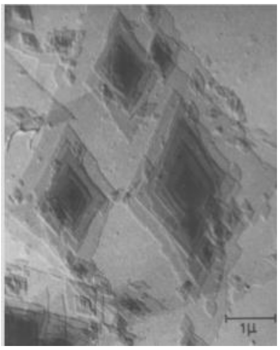

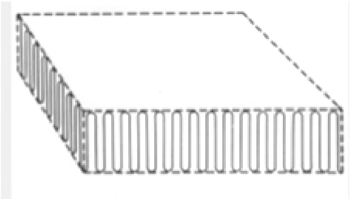

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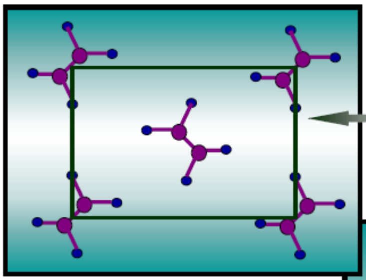
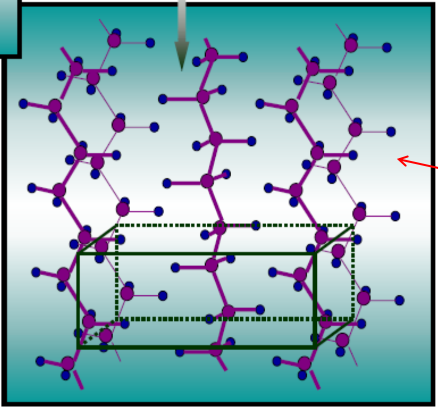
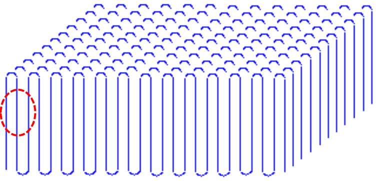
Polyethylene



Top view of Unit Cell

Side view





The unit cell contains segments of different chains.

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Not all polymers can crystallize!!

What are essential requirements for a polymer to crystallize?

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Why some polymer crystallizes at all??

- ✓ **Random coiled conformation of polymer chains in amorphous state have high entropy!**
- ✓ **Fully extended conformation and closed packed structures of polymer chains in crystalline state have low entropy!**
- ✓ **For crystallization to occur, $G_c < G_a$**
- ✓ **Intrachain energy in amorphous state higher because of many Gauche bond conformation.**
- ✓ **Interchain interaction energy in amorphous state is higher since distance between different atoms may be larger or smaller than the Van der Waals radii**

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Molecular Requirements for Crystallization *(Polymer Configuration)*

- ✓ **The configuration is fixed by the chemical synthesis.**
- ✓ **There should be no defects (branches, crosslinks, and excessive end groups), which will lead to disturbances within the crystal or rejection from the crystal.**
- ✓ **The size and disposition of a side group is important.**
- ✓ **If the structure is irregular, the side groups must be small, e.g., poly(vinyl alcohol) and poly(vinyl fluoride).**
- ✓ **Side groups may be of significant size if they are disposed regularly and symmetrically, e.g., isotactic and syndiotactic vinyl polymers and regularly repeating condensation polymers.**

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Molecular Requirements for Crystallization *(Polymer Conformation)*

- **Extended chain conformations (planar zigzag) are possible if the substituent's are small, e.g., polyethylene, poly(vinyl alcohol), most polyamides etc**
- **Helical conformations result for bulky substituent's, e.g., most isotactic and 1,1-disubstituted polymers.**

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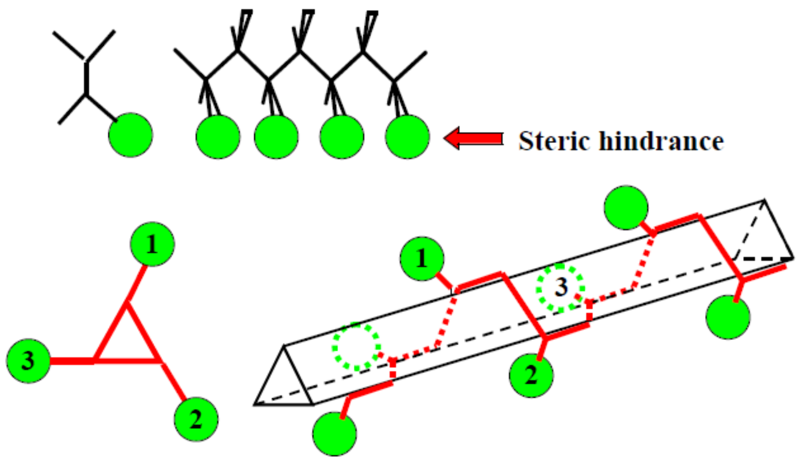
Helical conformation



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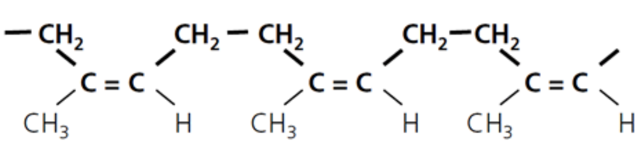
Natural rubber: has a very linear, regular structure but as such does not crystallize. Why??

Cis 1,4 - POLYISOPRENE



However, if you stretch and try to crystallize, it could crystallize!!

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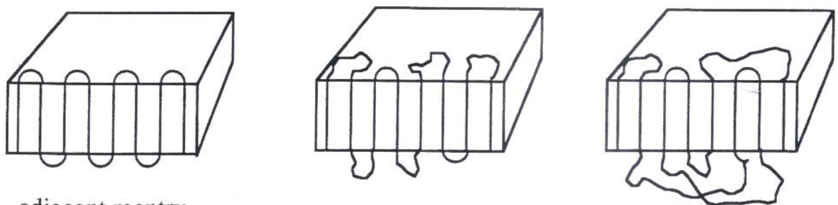
Molecular Morphology of a Polymer Single Crystal

(arrangement of polymer molecules in a isolated single crystal)



- **At low degree of supercooling or in solution, the crystallization is very slow, so the polymer chains probably will have sufficient time to fold tightly.**
- **At high degree of supercooling, the crystallization proceeds very fast, so the chains probably do not have time to reorganize themselves to form tight folds.**

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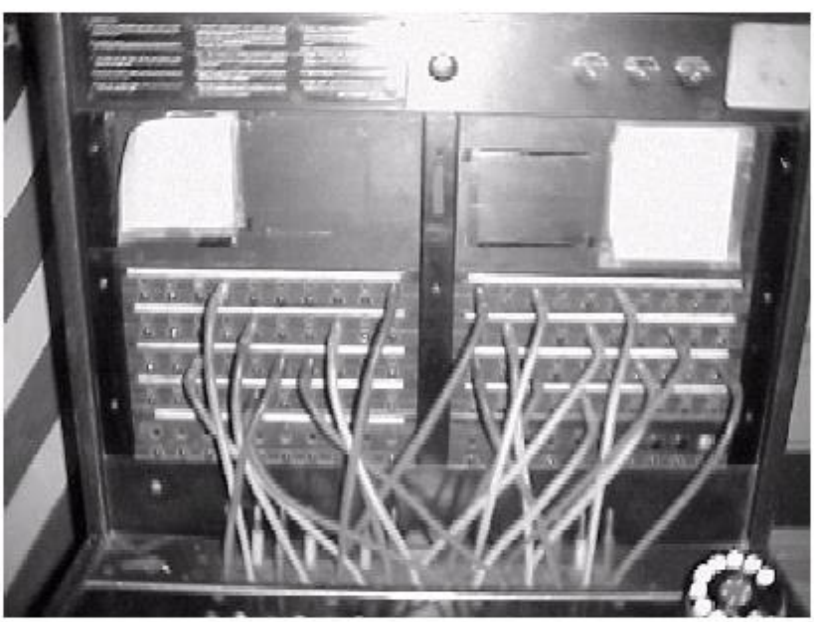
Switch-board Model



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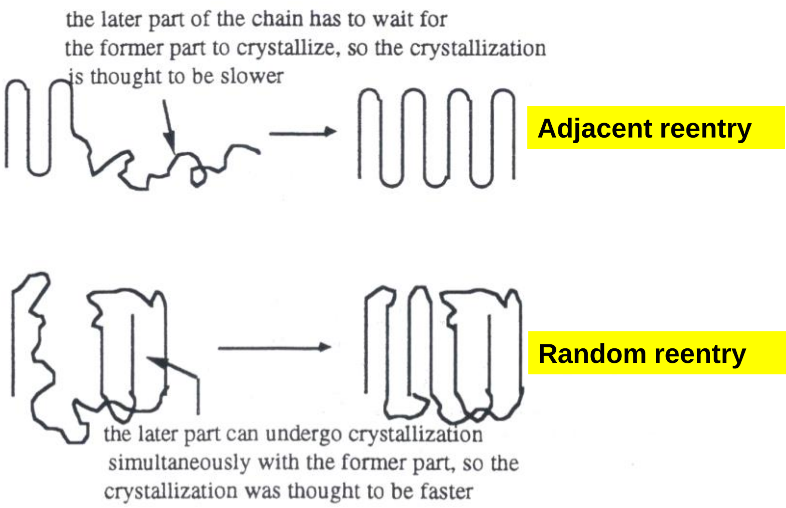
Adjacent re-entry *vs* Random re-entry



Still the biggest unresolved problem in polymer science!!!

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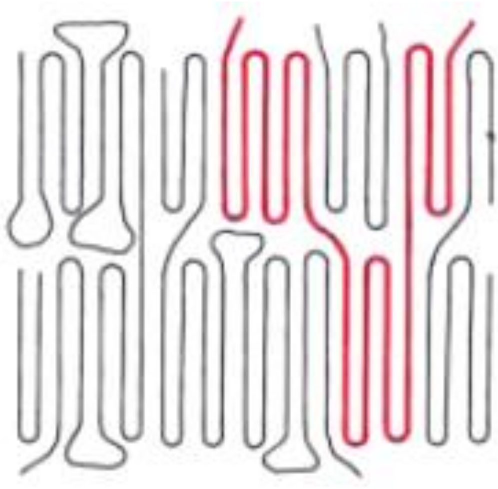
Presently accepted compromise model!

2/3 adjacent folding and 1/3 random re-entry



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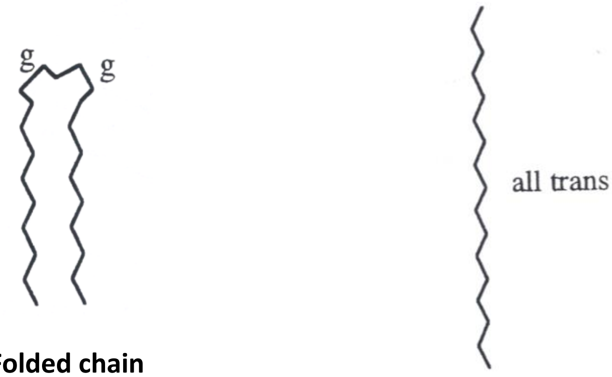
Why chain folding occurs?



Folded chain

Fully extended chain

$$E_f > E_e$$

Why does polymer choose a high energy state?

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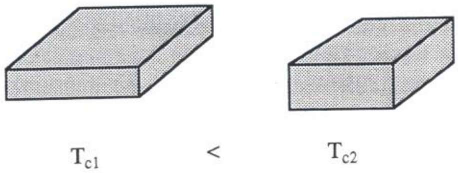
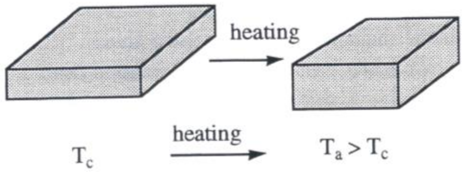
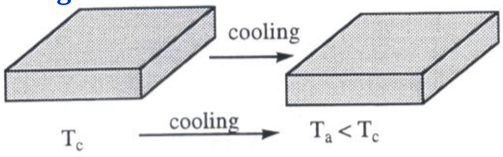
1. Thicker crystals are formed at higher crystallization temperature



2. Crystal formed at T_c when heated at higher temperature, thickening occurs



3. Crystal formed at T_c when cooled to lower temperature, thickness did not change



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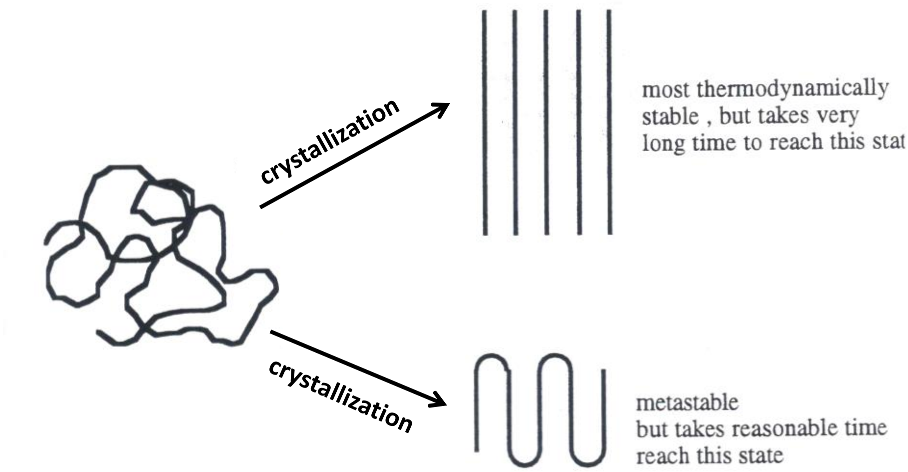

Chain folding is a compromise between the thermodynamics and kinetics of crystallization !!

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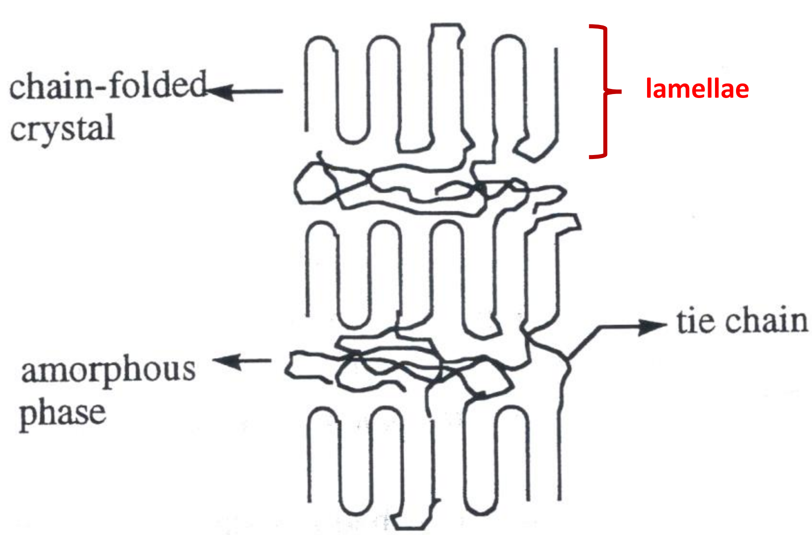
Molecular Morphology of Bulk Crystallized Polymer



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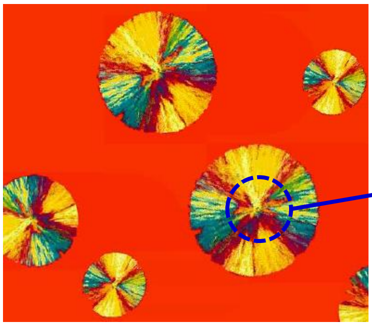
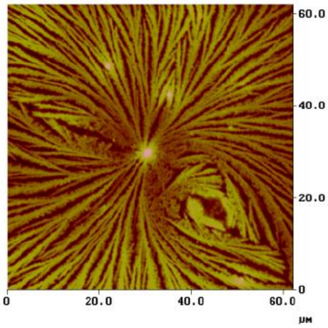
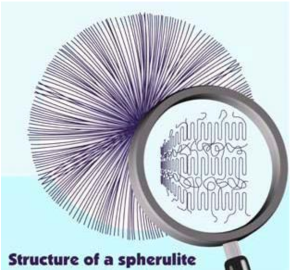
Superstructural Morphology of Polymer Crystals







Chain axis in lamellae is perpendicular to the radius of the spherulite.

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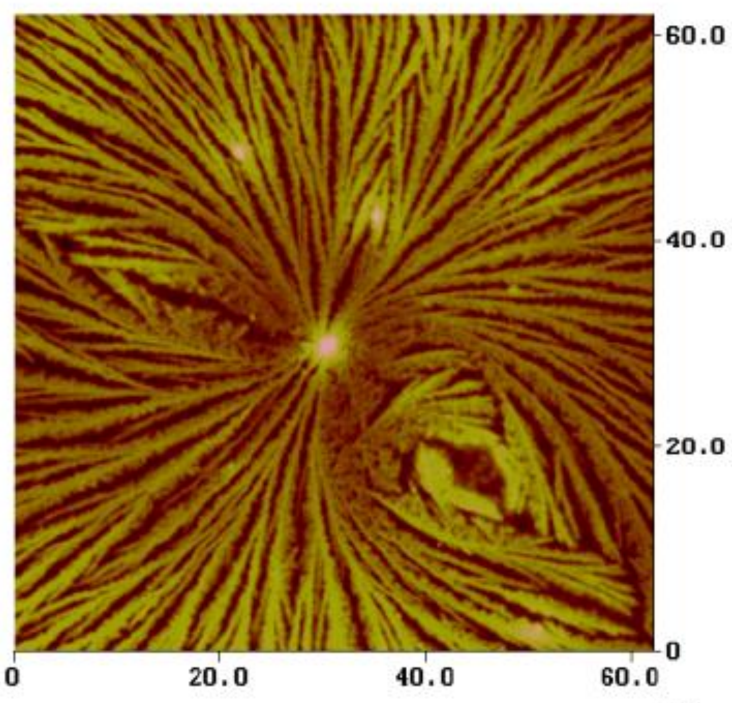

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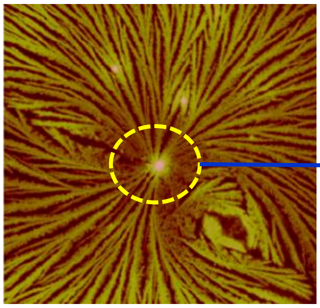

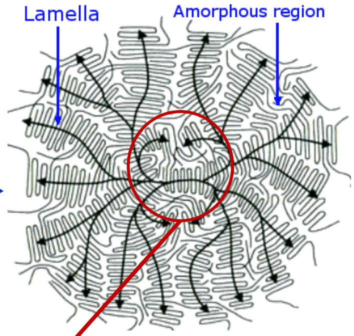

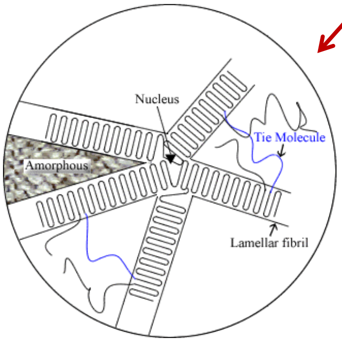

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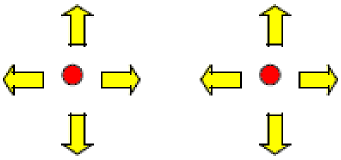
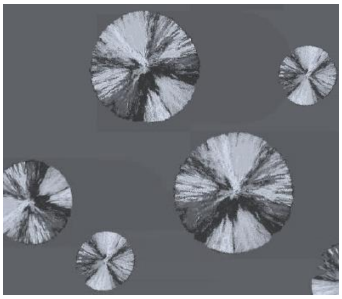
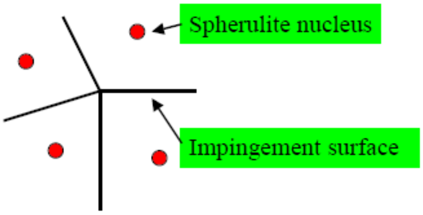
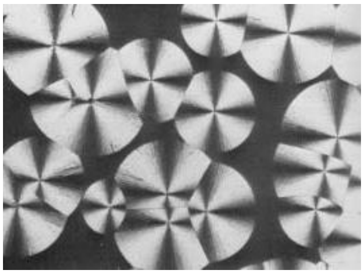
If crystallization is halted due to quenching, the bulk morphology consists of crystalline spherulites embedded in an amorphous matrix.





Normal spherulite growth in the bulk proceeds until impingement with another spherulite occurs.





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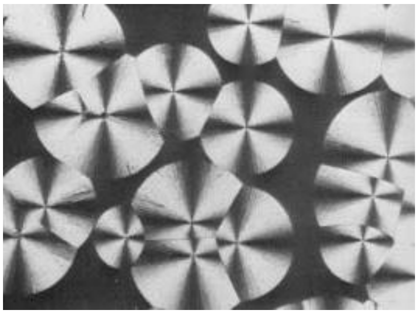

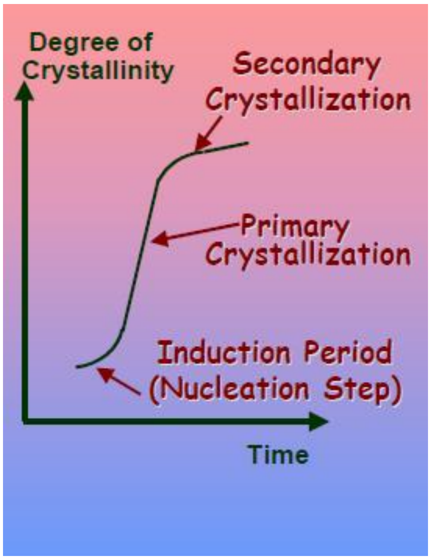

- **Induction period - formation of primary nuclei**
- **Primary crystallization - a period of fast spherulitic growth**
- **Secondary crystallization - a period of slower crystallization that occurs once the spherulites have impinged on one another**

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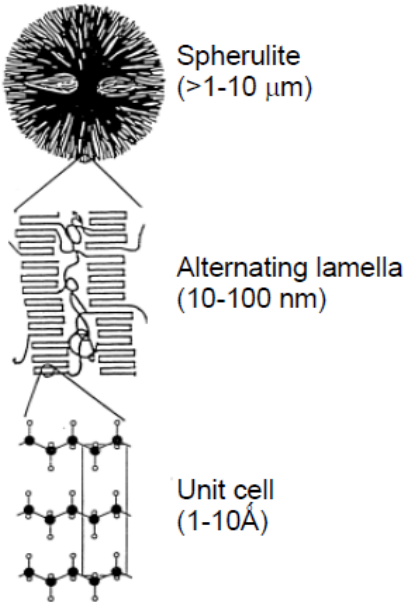
Summary of the Morphology Levels



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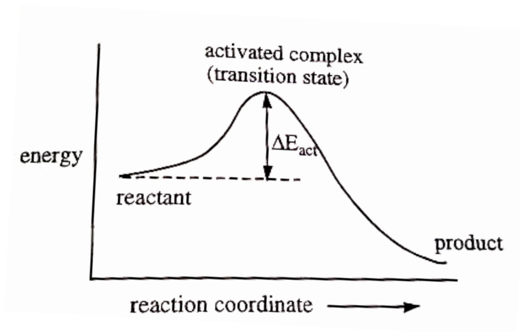
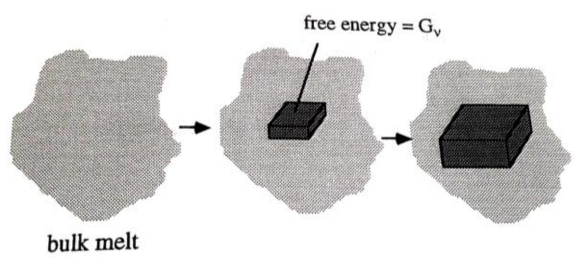
Nucleation Mechanism in Polymer Crystallization





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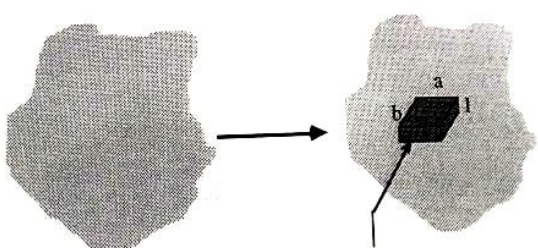
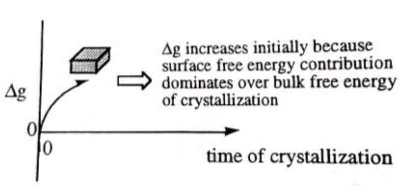
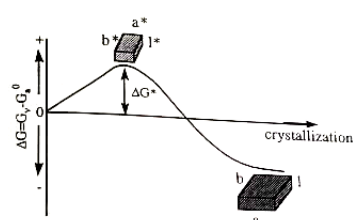


Bulk melt (no surface free energy contribution)

The crystal has 6 extra surfaces compared to bulk melt





The nucleation barrier can be overcome by local random fluctuation of order

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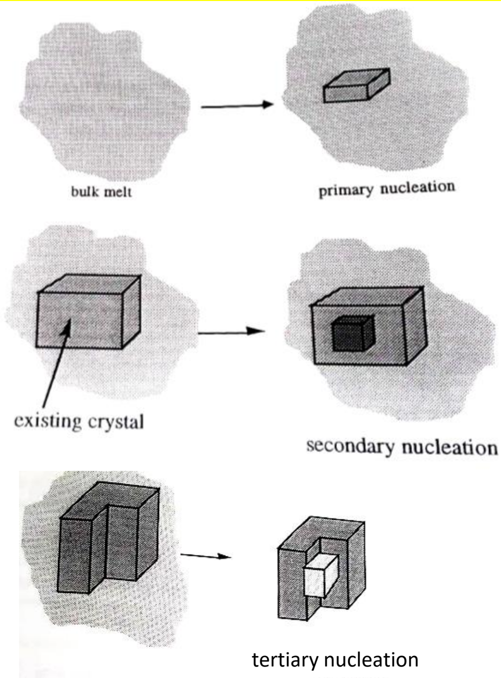
Primary, secondary and tertiary nucleation



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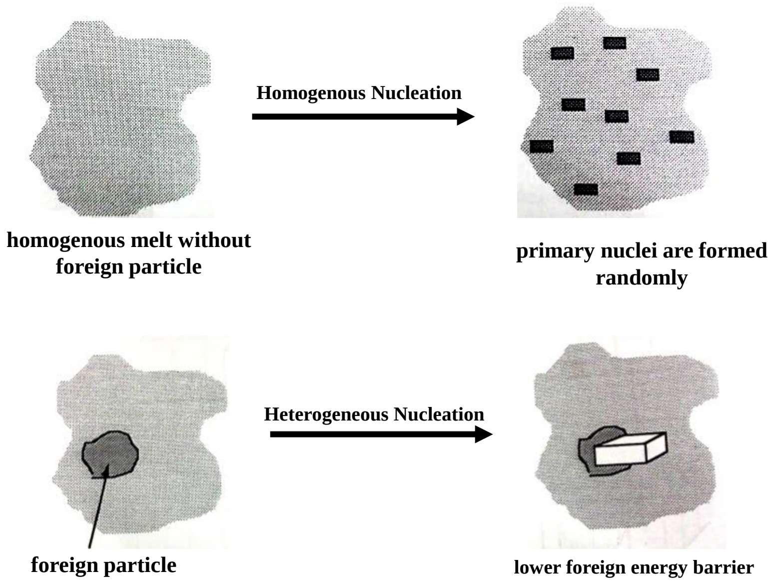
Types of Primary Nucleation



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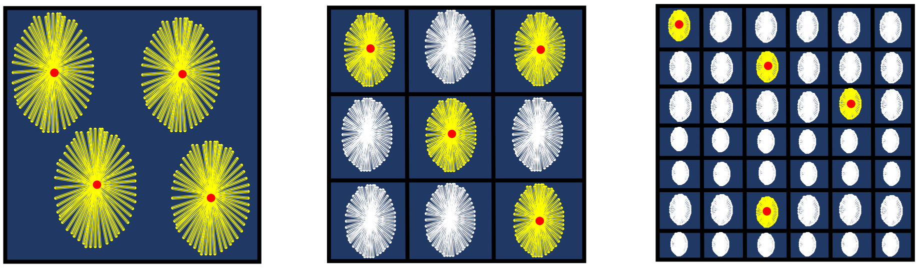
Homogenous *vs* heterogeneous nucleation



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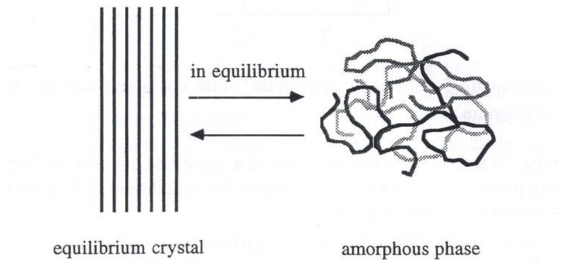
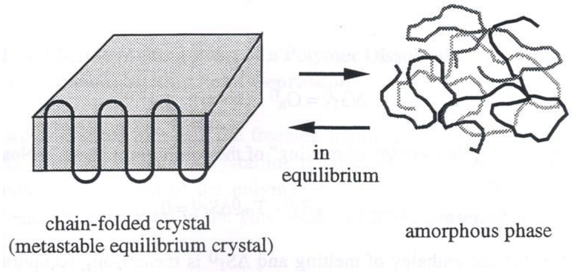
Equilibrium Crystallization Thermodynamics



Metastable Crystallization Thermodynamics



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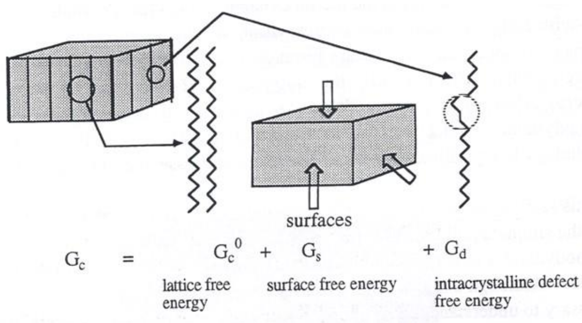
Equilibrium Thermodynamics

What is an "equilibrium crystal"??



Equilibrium crystal is that whose free energy is given only by the free energy of the perfect crystal lattice.

$G_c = G_c^o = G_{lattice} = H_{lattice} - Ts_{lattice}$

So, an equilibrium crystal also will be an infinitely thick crystal.

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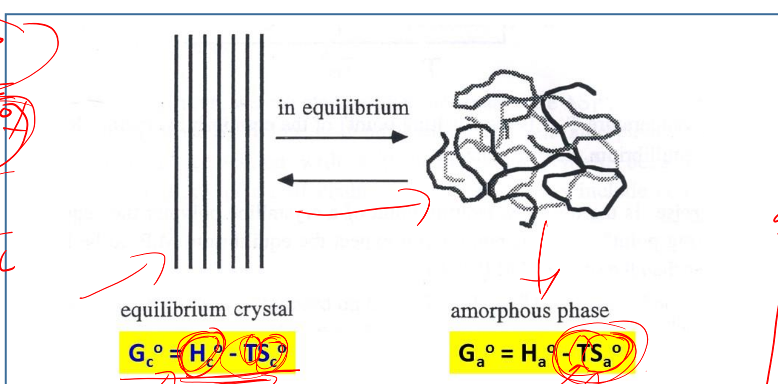
$T_m^o = \dfrac{H_a^o - H_c^o}{S_a^o - S_c^o}$

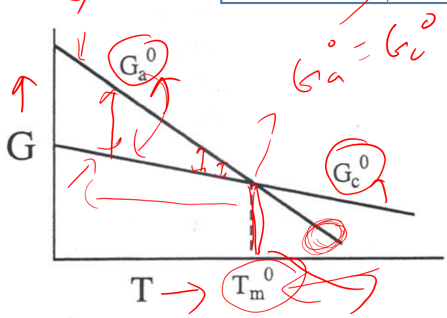
PE, 110°C

nylon-6 240°C

fusion/melting



$T_m^o = \dfrac{\Delta H_f^o}{\Delta S_f^o} = \dfrac{H_a^o - H_c^o}{S_a^o - S_c^o}$



$G_a^o = G_c^o$

T_m^o is the melting point of equilibrium crystal and is called the equilibrium melting point.

$G_c^o = G_a^o$

$\Delta G_f^o = G_a^o - G_c^o = 0$

$c \rightarrow a$

$\Delta G_f^o = G_a^o - G_c^o = 0$

$\Delta G_f^o = \Delta H_f^o - T_m^o \Delta S_f^o = 0$

$\Delta h_f - \Delta H_f^o - T_m^o \Delta S_f^o = 0$

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Melting point will increase if,

- ***Enthalpy of polymer crystal is decreased: Increase in the intermolecular strength***

and/or

- ***Entropy of amorphous phase is decreased: Increase in the rigidity of polymer backbone***

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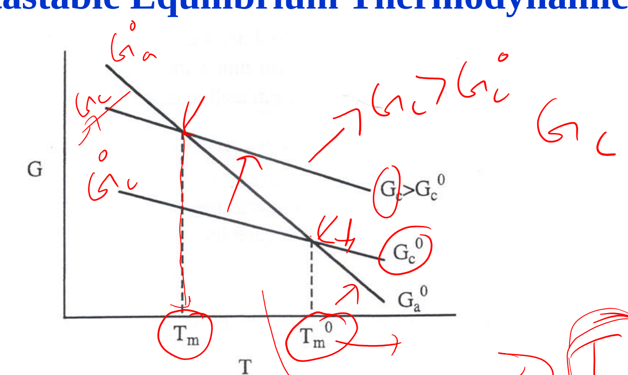
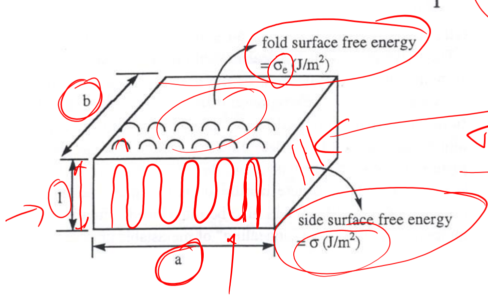
Metastable Equilibrium Thermodynamics





What will be the melting point of this metastable crystal??

Question to find T_m?

Is T_m related to T_m^0

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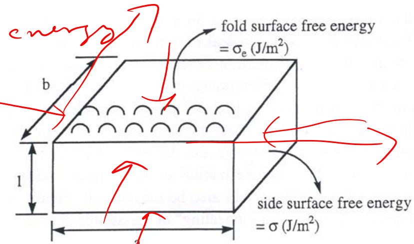
G_c = Lattice free energy + Surface free energy

$$= \underline{g_c^\circ abl} + 2\sigma_e ab + 2\sigma al + 2\sigma bl$$



g_c° = free energy of eq. crystal per unit volume

$$\Delta G_f = G_a - G_c$$

$$= g_a^\circ abl - (g_c^\circ abl + 2\sigma_e ab + 2\sigma al + 2\sigma bl)$$

$$= (g_a^\circ - g_c^\circ) abl - 2\sigma_e ab - 2\sigma al - 2\sigma bl$$

$$= \Delta g_f^\circ abl - 2\sigma_e ab - 2\sigma al - 2\sigma bl \quad (1)$$

now,

$\Delta g_f^\circ = \Delta h_f^\circ - T\Delta s_f^\circ$, at $T = T_m^\circ$, $\Delta g_f^\circ = 0$

so $\Delta h_f^\circ - T_m^\circ \Delta s_f^\circ = 0 \longrightarrow T_m^\circ = \frac{\Delta h_f^\circ}{\Delta s_f^\circ}$

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$\Delta g_f^\circ = \Delta h_f^\circ - T\Delta s_f^\circ$ and $T_m^\circ = \frac{\Delta h_f^\circ}{\Delta s_f^\circ}$

$$\Rightarrow \Delta g_f^\circ = \Delta h_f^\circ \left(1 - T\frac{\Delta s_f^\circ}{\Delta h_f^\circ}\right) \Rightarrow \Delta g_f^\circ = \Delta h_f^\circ \left(1 - \frac{T}{T_m^\circ}\right) \quad (2)$$

Put (2) in (1)

$$\Delta G_f = \Delta h_f^\circ \left(1 - \frac{T}{T_m^\circ}\right) abl - 2\sigma_e ab - 2\sigma al - 2\sigma bl$$

at $T = T_m$, $\Delta G_f = 0$

$$\Delta h_f^\circ \left(1 - \frac{T_m}{T_m^\circ}\right) abl - \underline{2\sigma_e ab} - \underline{2\sigma al} - \underline{2\sigma bl} = 0$$

a and b much larger compared to l and also $\sigma_e > \sigma$, Hence, $ab >> al$

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$$2\sigma_e ab >> 2\sigma al + 2\sigma bl$$

so,

$$\Delta h_f^\circ \left(1 - \frac{T_m}{T_m^\circ}\right) abl - 2\sigma_e ab = 0$$

$$\Rightarrow \Delta h_f^\circ \left(1 - \frac{T_m}{T_m^\circ}\right) l = 2\sigma_e \Rightarrow l = \frac{2\sigma_e}{\Delta h_f^\circ \left(1 - \frac{T_m}{T_m^\circ}\right)} \quad (3)$$

Rearrange eq. (3) in terms of T_m

$$\Rightarrow T_m = T_m^\circ \left(1 - \frac{2\sigma_e}{\Delta h_f^\circ l}\right)$$

Thompson-Gibbs eq.

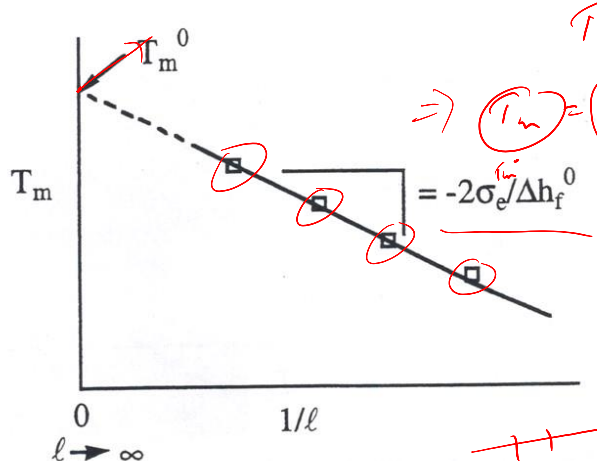
if $l \to \infty \Rightarrow T \to T_m^\circ$

How to find the equilibrium melting point??

$$T_m = T_m^\circ \left(1 - \frac{2\sigma_e}{\Delta h_f^\circ l}\right)$$

$$\Rightarrow T_m = T_m^\circ - \frac{2\sigma_e T_m^\circ}{\Delta h_f^\circ l}$$

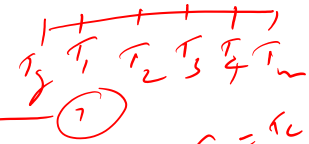
$y = mx + c$



$T_1 \; T_2 \; T_3 \; T_4 \quad T_m$

SAXS $l_4 > l_3 > l_2 > l_1 \rightarrow$ DSC $\rightarrow T_m$

Hoffman-Weeks plot



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

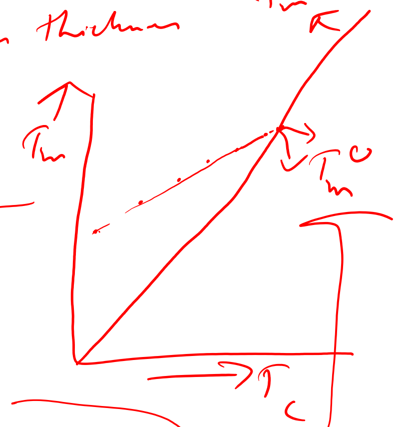
$\gamma = \frac{l}{l^*}$, l^* = crystalline nucleus thickness

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

⇒ when, $T_m = T_c$, $T_m = T_m^0$

$$T_m - \frac{T_m}{\gamma} = T_m^0\left(1-\frac{1}{\gamma}\right)$$

$$T_m\left(1-\frac{1}{\gamma}\right) = T_m^0\left(1-\frac{1}{\gamma}\right) \Rightarrow T_m = T_m^0$$



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$$T_m = T_m^0\left(1 - \frac{2\sigma_e}{\Delta h_f^0\, l}\right)$$

σ_e → Fold surface free energy

l → crystal thickness

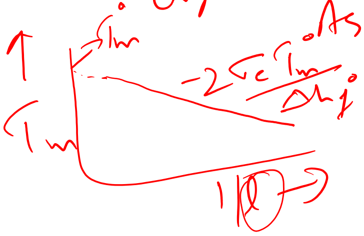
Δh_f^0 → Enthalpy change per unit volume during fusion/melting

$y = mx + c$

Thompson-Gibbs eq.

melting point of a given polymer only depends on crystal thickness

As $l \uparrow$, $T_m \uparrow$



Hoffman-weeks plot $\gamma = \frac{l}{l^*}$

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

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

when $T_m \to T_c$ ⇒ $T_m \to T_m^0$

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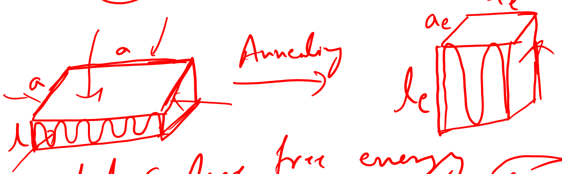


σ = side surface free energy

σ_e = Fold surface free energy

Total surface free energy

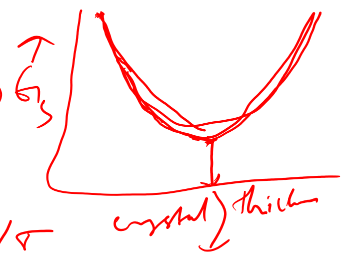
$$G_s = 4al\sigma + 2a^2\sigma_e \quad (1)$$

$$V = a^2 l = a_e^2 l_e$$

$$l = \frac{V}{a^2}$$

$$\left.\frac{\partial G_s}{\partial a}\right|_{a=a_e} = 0$$

$$G_s = \frac{4V\sigma}{a} + 2a^2\sigma_e$$



$$G_s = \frac{4V\sigma}{a} + 2a^2\sigma_e$$

$$\left.\frac{\partial G_s}{\partial a}\right|_{a=a_e} = 0 \Rightarrow \boxed{-\frac{4V\sigma}{a_e^2} + 4a_e\sigma_e = 0}$$

$$\Rightarrow a_e^3\sigma_e = \cancel{4\sigma}\, V\sigma$$

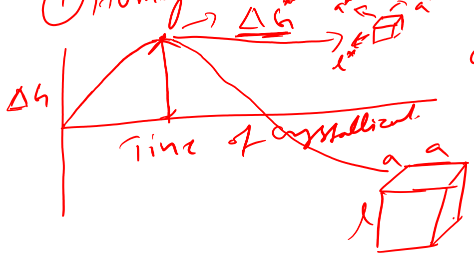
$$a_e = \left(\frac{V\sigma}{\sigma_e}\right)^{1/3} \quad (2)$$

$$\Rightarrow a_e^3\sigma_e = a_e^2 l_e \sigma$$

$$\Rightarrow \boxed{\frac{\sigma}{\sigma_e} = \frac{a_e}{l_e}} \quad (1)$$

$$l_e = \left(\frac{\sigma_e^2 V}{\sigma^2}\right)^{1/3} \quad (3)$$

① Homogeneous nucleation ② Heterogeneous nucleation



a^* ?

l^* ? ΔG^*

$$\Delta G = \Delta g_c^o a^2 l + 2a^2\sigma_e + 4al\sigma$$

$$= -\Delta g_f^o a^2 l + 2a^2\sigma_e + 4al\sigma \quad \text{— (1)}$$

(2) $\left.\dfrac{\partial \Delta G}{\partial l}\right|_{l^*,a^*} = 0$ (3) $\left.\dfrac{\partial \Delta G}{\partial a}\right|_{l^*,a^*} = 0$

$$\Delta G = -\Delta g_f^o a^2 l + 2a^2\sigma_e + 4al\sigma \quad \text{— (1)}$$

Now, for $\dfrac{\partial \Delta G}{\partial l} = 0 \Rightarrow -a^{*2}\Delta g_f^o + 4a^*\sigma = 0$

$$\Rightarrow a^* = \frac{4\sigma}{\Delta g_f^o} \quad \text{— (4)}$$

Also, for $\dfrac{\partial \Delta G}{\partial a} = 0$

$$\Rightarrow -2a^*l^*\Delta g_f^o + 4l^*\sigma + 4a^*\sigma_e = 0$$

$$\Rightarrow l^* = \frac{4\sigma_e}{\Delta g_f^o} \longrightarrow (5)$$

$$\Delta g_f^o = \Delta h_f^o - T\Delta S_f^o \Rightarrow \Delta g_f^o = \Delta h_f^o\left(1 - \frac{T\Delta S_f^o}{\Delta h_f^o}\right)$$

$$\Rightarrow \Delta g_f^o = \Delta h_f^o\left(1 - \frac{T_c}{T_m^o}\right) \quad \text{at } T = T_c$$

$$a^* = \frac{4\sigma}{\Delta h_f^\circ \left(1 - \frac{T_c}{T_m^\circ}\right)} = \frac{4\sigma T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)} \quad \text{— (6)}$$

$$l^* = \frac{4\sigma_e}{\Delta h_f^\circ \left(1 - \frac{T_c}{T_m^\circ}\right)} = \frac{4\sigma_e T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)} \quad \text{— (7)}$$

As $T_c \uparrow$ so, $l^* \uparrow$

As $T_c \to T_m^\circ$

$l^* \to \infty$

$$\Delta G = -\Delta g_f^\circ a^2 l + 2a^2\sigma_e + 4al\sigma$$

$$\Delta G^* = -\Delta g_f^\circ a^{*2} l^* + 2a^{*2}\sigma_e + 4a^* l^* \sigma \quad \text{— (8)}$$

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$$\Delta G^* = \frac{32\sigma^2\sigma_e T_m^{\circ 2}}{\Delta h_f^\circ (T_m^\circ - T_c)^2} \quad \text{— (9)}$$

$$\Delta G^* \propto \frac{1}{(T_m^\circ - T_c)^2}$$

as $T_c \uparrow$, $T_c \to T_m^\circ$ and, hence $\Delta G^* \uparrow$

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Homogeneous Nucleation

$$a^* = \frac{4\sigma T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)} \quad \text{as } T_c \uparrow,\ l^* \uparrow,\ a^* \uparrow$$

$$l^* = \frac{4\sigma_e T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)}$$

$$\Delta G^* = \frac{32\sigma^2 \sigma_e T_m^{\circ 2}}{\Delta h_f^\circ (T_m^\circ - T_c)^2} \Rightarrow \Delta G^* \propto \frac{1}{(T_m^\circ - T_c)^2}$$

$$\Delta G^* \uparrow \text{ as } T_c \uparrow$$

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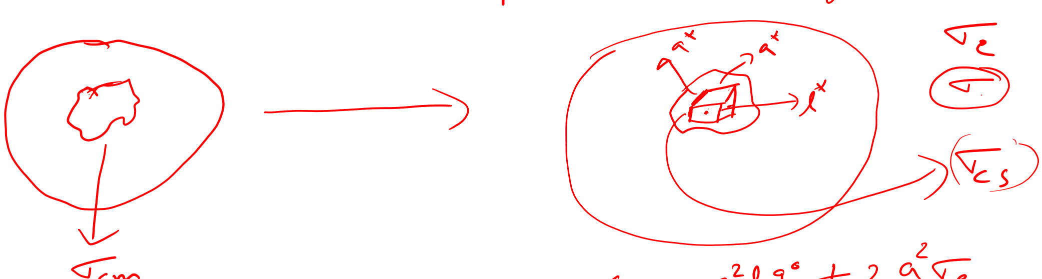
Nucleation process for Heterogeneous nucleation



$$G_a = a^2 l g_a^\circ + a l \sigma_{sm} \qquad G_c = a^2 l g_c^\circ + 2a^2 \sigma_e + 3al\sigma + al\sigma_{cs}$$

$$\Delta G = G_c - G_a = a^2 l g_c^\circ + 2a^2\sigma_e + 3al\sigma + al\sigma_{cs} - (a^2 l g_a^\circ + al\sigma_{sm})$$

$$\underline{\Delta\sigma = \sigma_{cs} + \sigma - \sigma_{sm}}$$

$$\Delta G = \underline{-a^2 l \Delta g_f^\circ} + 2a^2\sigma_e + 2al\sigma + \underline{al\Delta\sigma}$$

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$$\Delta G = -a^2 l \Delta g_f^\circ + 2a^2\sigma_e + 2al\sigma + al\Delta\sigma$$

$$\left.\frac{\partial \Delta G}{\partial l}\right|_{l^*, a^*} = 0 \Rightarrow -a^{*2}\Delta g_f^\circ + 2a^*\sigma + a^*\Delta\sigma = 0 \quad \text{①}$$

$$\left.\frac{\partial \Delta G}{\partial a}\right|_{l^*, a^*} = 0 \Rightarrow -2a^* l^* \Delta g_f^\circ + 4a^*\sigma_e + 2l^*\sigma + l^*\Delta\sigma = 0 \quad \text{②}$$

From ① and ②, solve for a^* and l^*

as $T_c \uparrow$

$$a^* = \frac{2\sigma + \Delta\sigma}{\Delta g_f^\circ} = \frac{(2\sigma + \Delta\sigma)T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)} \quad \text{③}$$

$$l^* = \frac{4\sigma_e}{\Delta g_f^\circ} = \frac{4\sigma_e T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)} \quad \text{④}$$

$$\Delta G^* = -a^{*2} l^* \Delta g_f^\circ + 2a^{*2}\sigma_e + 2a^* l^* \sigma + a^* l^* \Delta\sigma \quad \text{⑤}$$

Put ③ and ④ in ⑤, solve for ΔG^*

$$\Delta G^* = \frac{2(2\sigma + \Delta\sigma)^2 \sigma_e T_m^{\circ 2}}{\Delta h_f^\circ (T_m^\circ - T_c)^2} \quad \text{⑥}$$

as $T_c \uparrow$, $\Delta G^* \uparrow$

$$a^*_{hetero} < a^*_{homo}$$

$$a^*_{homo} = \frac{4\sigma T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)} = \frac{(2\sigma + 2\sigma) T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)}$$

$$a^*_{hetero} = \frac{(2\sigma + \Delta\sigma) T_m^\circ}{\Delta h_f^\circ (T_m^\circ - T_c)}$$

Hence,

$$\Delta\sigma < 2\sigma$$

$$\boxed{\Delta\sigma = \sigma_{cs} + \sigma - \sigma_{sm}}$$

$$\Delta G^*_{homo} = \frac{32\,\sigma^2 \sigma_e T_m^{\circ 2}}{\Delta h_f^\circ (T_m^\circ - T_c)^2} = \frac{2(2\sigma + 2\sigma)^2 \sigma_e T_m^{\circ 2}}{\Delta h_f^\circ (T_m^\circ - T_c)^2}$$

$$\Delta G^*_{hetero} = \frac{2(2\sigma + \Delta\sigma)^2 \sigma_e T_m^{\circ 2}}{\Delta h_f^\circ (T_m^\circ - T_c)^2}$$

$$\Delta G^*_{hetero} < \Delta G^*_{homo} \quad \text{if} \quad \Delta\sigma < 2\sigma$$

$$\boxed{\sigma_{cs} + \sigma - \sigma_{sm} < 2\sigma}$$

σ_{cs}

$$\sigma_{cs} < \sigma$$

$$\sigma_{sm} > \sigma_{cs}$$

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Degree of crystallinity

Two phase model

$$W_a + W_c = 1$$

$$W_a = 1 - W_c$$

$$\rho = W_c \times \rho_c^\circ + (1 - W_c)\rho_a^\circ$$

$$\text{So,} \quad W_c = \frac{(\rho_a^\circ - \rho)}{(\rho_a^\circ - \rho_c^\circ)}$$

W_c = Mass fraction crystallinity

Specific volume $= \frac{V}{m}$ $\left(\frac{m^3}{kg} \text{ or } cm^3/g\right)$

$$W_c = \frac{(V_a^\circ - V)}{(V_a^\circ - V_c^\circ)} = \frac{\frac{1}{\rho_a^\circ} - \frac{1}{\rho}}{\frac{1}{\rho_a^\circ} - \frac{1}{\rho_c^\circ}}$$

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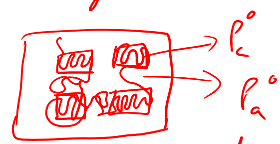
Degree of crystallinity

Two phase model



$$\rho = w_c \rho_c^\circ + w_a \rho_a^\circ$$

$$\Rightarrow \rho = w_c \rho_c^\circ + (1-w_c)\rho_a^\circ$$

specific volume (v) = $\frac{\text{vol}}{\text{mass}}$ m^3/kg, cm^3/g

$$\Rightarrow w_c = \frac{(\rho_a^\circ - \rho)}{(\rho_a^\circ - \rho_c^\circ)} = \frac{V_a^\circ - V}{V_a^\circ - V_c^\circ}$$

(Mass fraction crystallinity)

$$= \frac{\frac{1}{\rho_a^\circ} - \frac{1}{\rho}}{\frac{1}{\rho_a^\circ} - \frac{1}{\rho_c^\circ}}$$

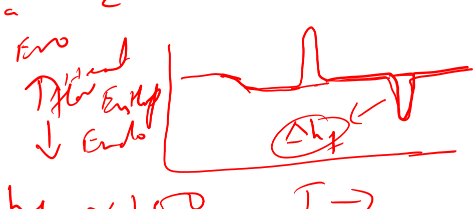
Volume fraction crystallinity

$$\rho = v_c \rho_c^\circ + (1 - v_c)\rho_a^\circ$$

$$v_c = \frac{\rho_a^\circ - \rho}{\rho_a^\circ - \rho_c^\circ} = \frac{\rho_a^\circ - \rho}{\rho_a^\circ - \rho_c^\circ}$$

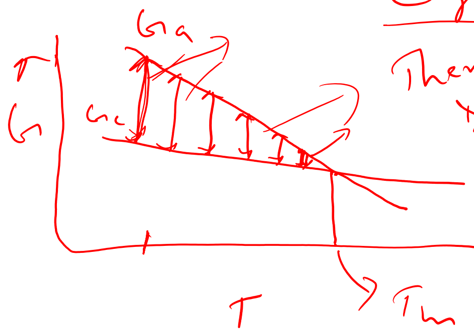
$\rho = \frac{m}{\text{vol.}}$ (g/cm^3)

Enthalpy (J/g)



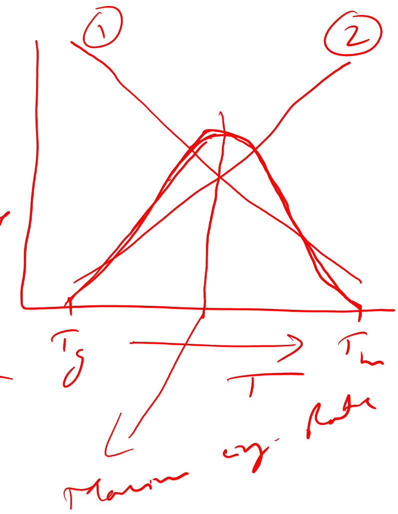
$$w_c = \frac{h_a^\circ - h}{h_a^\circ - h_c^\circ} = \frac{\Delta h_f}{\Delta h_f^\circ} \times 100$$

Crystallization kinetics



Thermodynamic driving force of crystallization

Chain mobility



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Overall crystallization kinetics (Avrami Eq.)

$$1 - X(t) = \exp(-kt^n)$$

$X(t)$ = degree of crystallinity at time, t

k = Rate constant

n = Avrami exponent (Dimensionality of crystal growth)

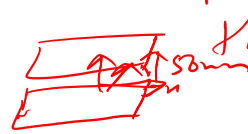
$n = 3$ (No boundary) (Three dimension)

$n = 2$ (one dimensional confinement)

$n = 1$ (Two dimensional confinement)

$n < 1$

1. All nuclei are randomly distributed
2. Spherulites do not interact
3. Rate of radial expansion unit.
4. Density of spherulite is independent of the radius



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$$1 - X(t) = \exp(-kt^n)$$

$$\ln[-\ln(1-X(t))] = \ln k + n\ln t$$

$$y = c + mx$$

Isothermal crystallization kinetics

$$X(t_1) = \frac{x(t_1)}{x(t_\infty)}, \quad X(t_2) = \frac{x(t_2)}{x(t_\infty)}$$ (at Constant T_c)

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