

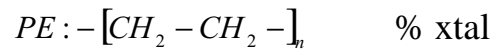
## Section 6. Polymers


In previous section; Random Coils . Disorder was the key.

### Polymer Crystallisation

The ordered bit of polymer science!

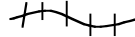
Many polymers are semi crystalline & % crystallinity can have a significant effect on properties.



96      HDPE   
Zeigler:- linear

80      LDPE   
High Pressure

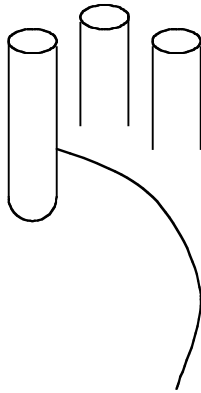
0      Some metallocene catalyst polyethylenes



The molecular packing of polymer chains.

Information from x-ray data. (Dr Moggridge's interest)

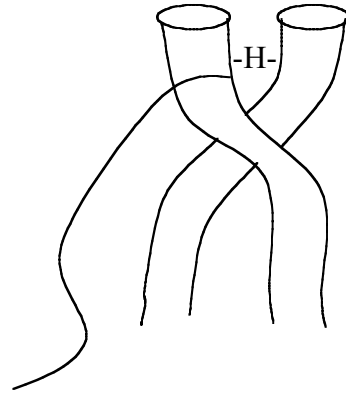
Straight chain



Helix



Intertwined Helix

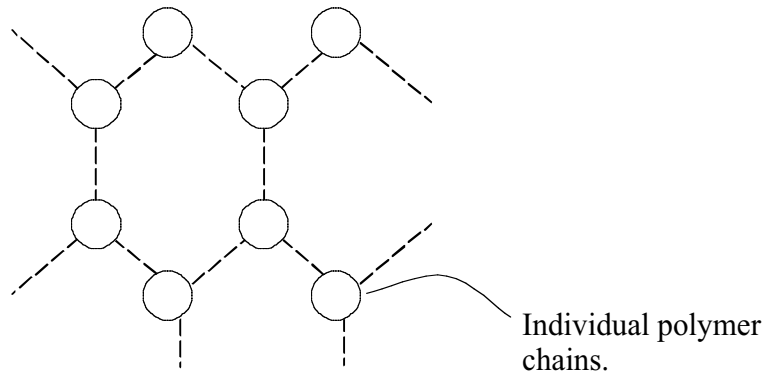


Bonding between chains. Interchain. Van de Waals bonding  $-5\text{kJ/mol}$   
Hydrogen – Nylon/DNA.

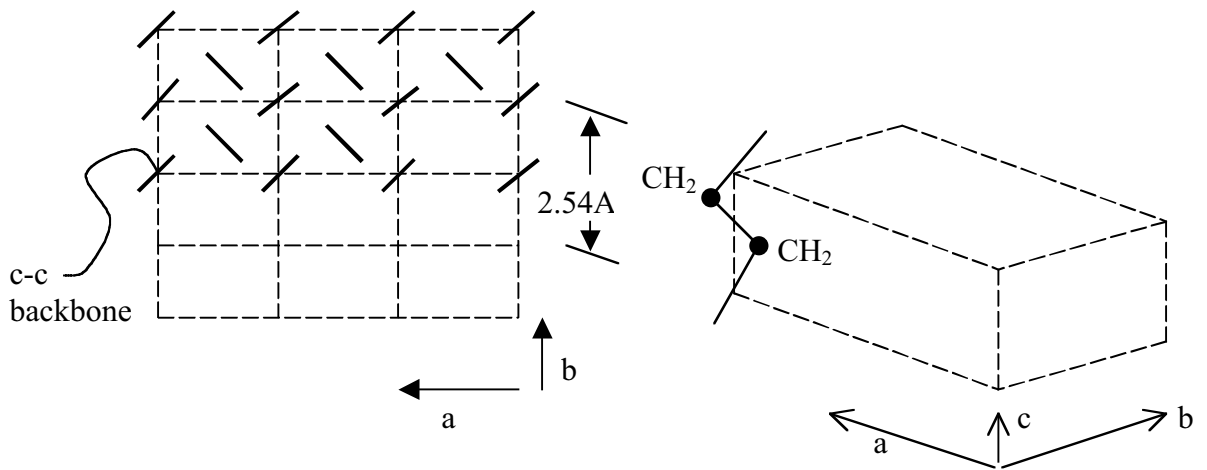
All weak terms compared with intra chain bonding  $\text{c} - \text{c}$  say  $\sim 348\text{kJ/mol}$ .

# Crystal Packing

Often pseudo hexagonal.



PE . Orthorhombic



For PE lattice:-

There are two chains/unit cell

$$= 1 + 4 \times \frac{1}{4} = 2$$

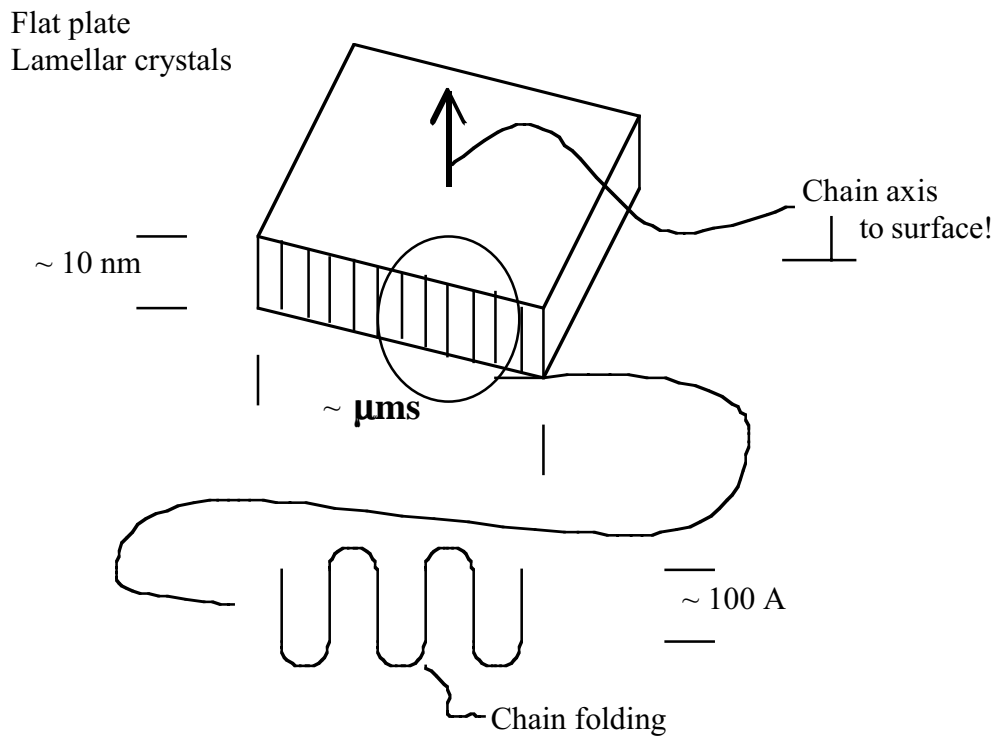
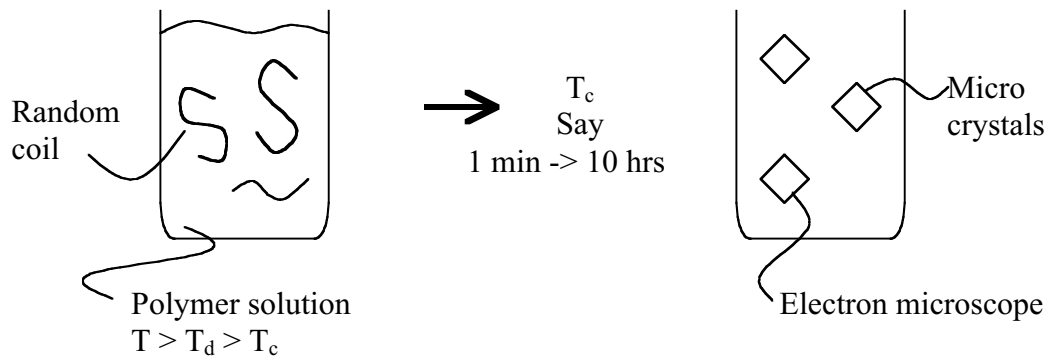
Central

Corners

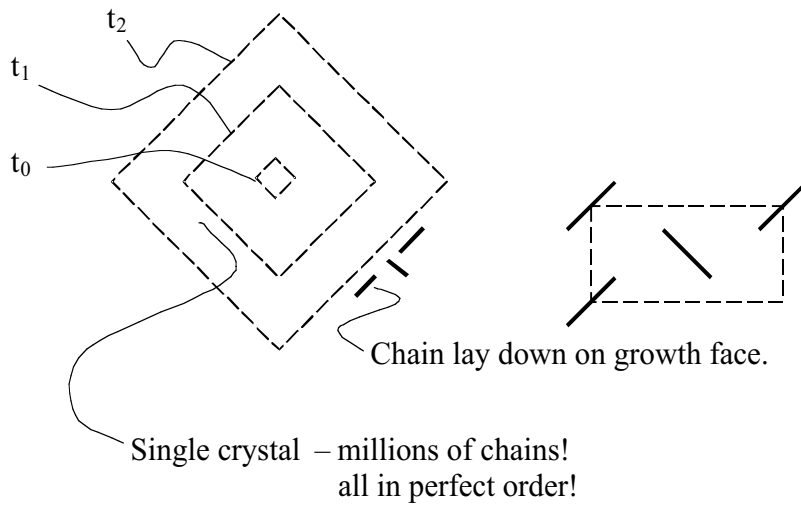
∴ There are four CH<sub>2</sub> groups/unit cell.

## How are the crystals organised? Crystal morphology

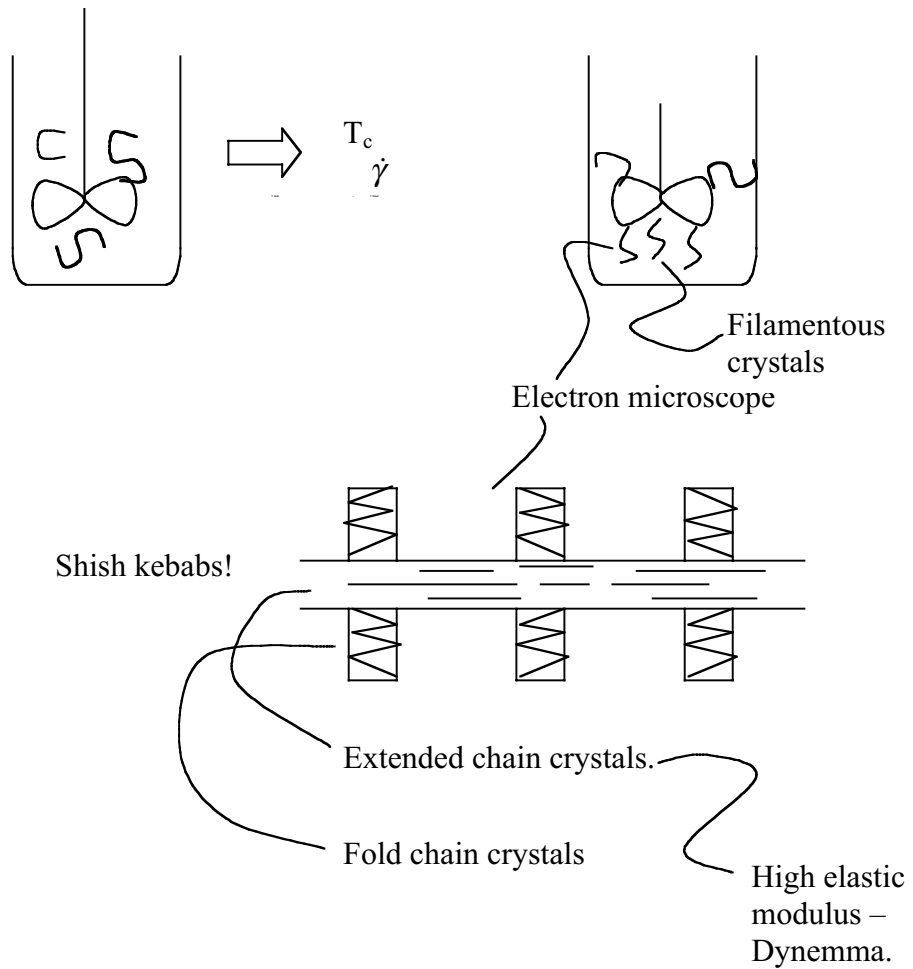
Best seen first from solution crystallisation.



Single crystals form from nuclei – grow as chain folded lamellae crystals.



### Solution crystallisation with flow

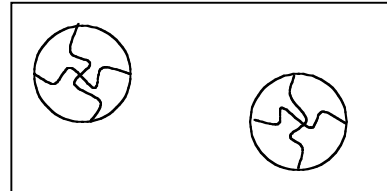
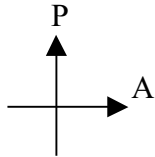


## Melt crystallisation

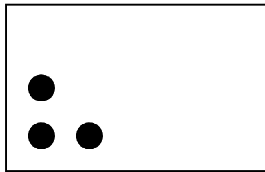
More complex than  
solution x'tal.

Use optical microscope ( $> 1\mu\text{m}$  resolution) & watch spherulites grow!

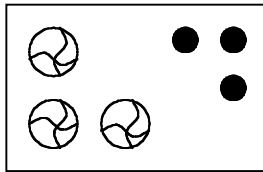
Observe **birefringence**  
between crossed polaroids.



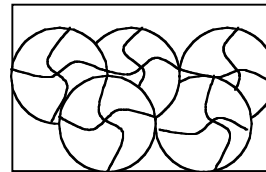
## Development with time



Nucleation



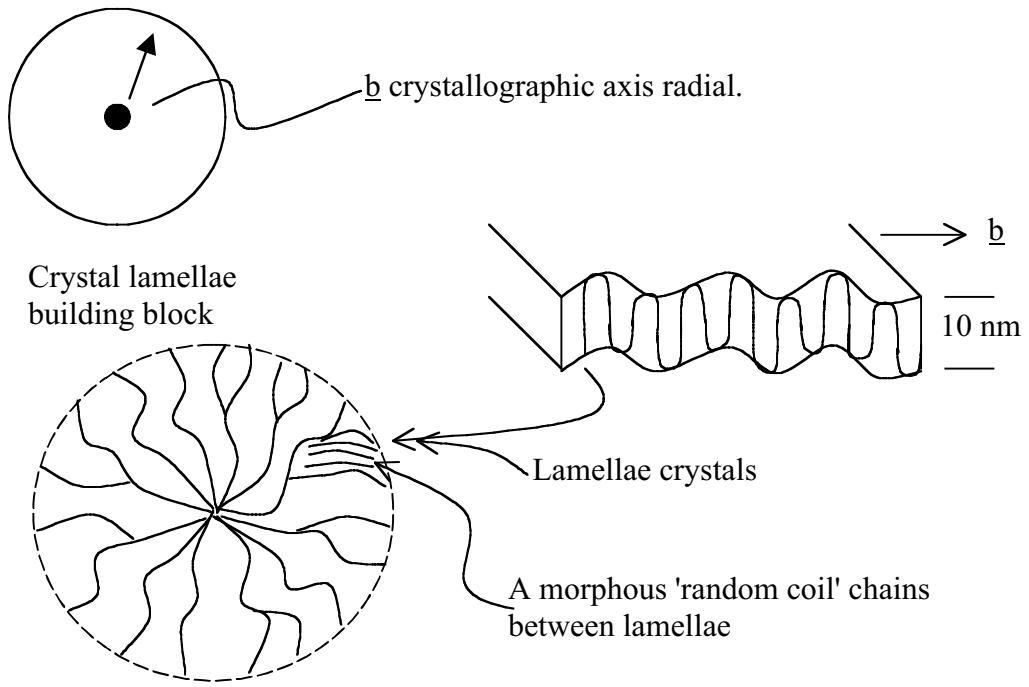
Growth



Impingement

## Structure of spherulite

From optic & EM microscopy.



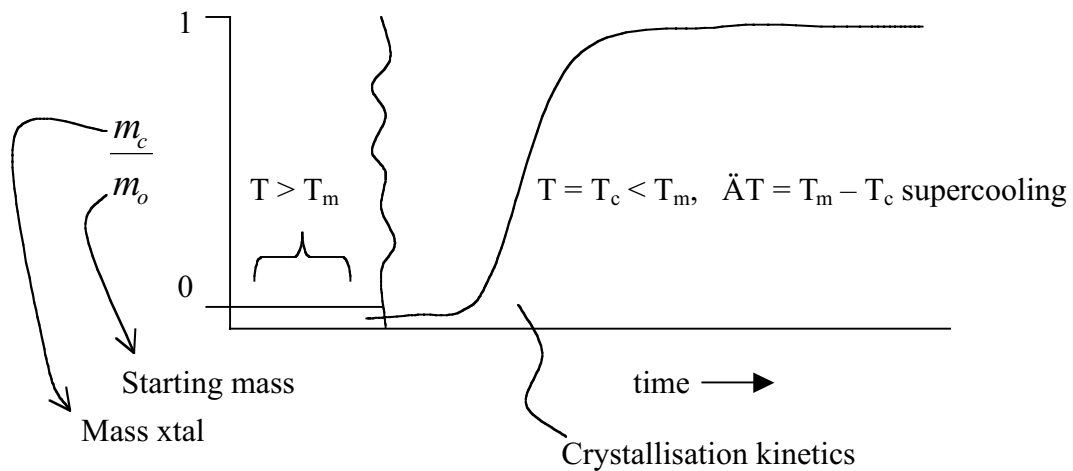


## Hierarchy of organisation

	Amorphous	Crystal
Atomic scale ( $\text{\AA}$ )	random packing	crystal structure
Mesoscopic scale ( $100 \text{ s\AA} - \mu\text{m}$ )	random coil	crystal lamellae
Microscopic scale ( $\sim \mu\text{m}$ )		spherulites
Macroscopic scale $> \sim 1\text{mm}$	bulk material	bulk material

## Kinetics of crystallisation

Important in terms of liquid to solid transition, extrusion, blow moulding, injection moulding, fibre spinning.



How long do polymers take to crystallise?

It depends on  $\Delta T$  the supercooling.

ms days

∠ large  $\Delta T$ .    small  $\Delta T$ .

## Avrami Kinetics

origins 1940's

See Sharples – Polymer crystallisation.

Develop simple model based on:

1. Nucleation.
2. Growth.

Can be applied to crystallisation of polymers, metals, salts \_.  
'Engineering Description' works at microscopic not molecular or mesophase length scale.

### 1. Nucleation

Let  $J$  = number of nuclei/unit vol ( $\text{m}^{-3}$ )

If melt is seeded with nuclei, (say talc crystals) then,

$$\frac{dJ}{dt} = 0 \quad \& \quad J = I_0 \quad (\text{a const})$$

If nuclei progressively appear with 1<sup>st</sup> order kinetics, then

$$\frac{dJ}{dt} = I \quad \Rightarrow \quad J = It$$

numbers of nuclei increases linearly with time.

In general

$$\frac{dJ}{dt} = I^n \quad \Rightarrow \quad J = \frac{1}{(n+1)} I t^{n+1}$$

$I$  is the **nucleation const** and is a strong function of  $T$  ( $\Delta T$ ).

## 2. Growth

Usually  $\frac{dr}{dt} = G \quad \Rightarrow r = Gt$

Where  $r$  is a linear dimension, such as radius of sphere

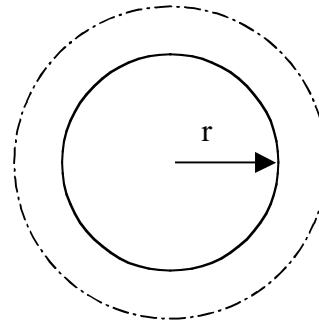
$G$  is **growth constant** ( $\text{m s}^{-1}$ )

$G$  is also a strong function of  $T$  ( $\Delta T$ ).

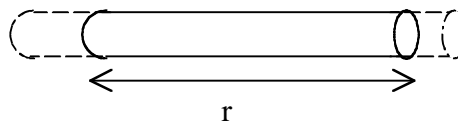
### What sort of crystals?

Analysis can be applied to polymers of different morphologies, metals, oxides and other inorganic or organic crystals.

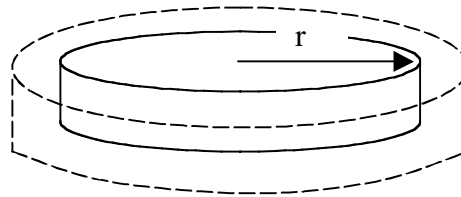
Spherulites = spheres  
(3D) growth  
 $r$  = radius



Rods  
(1D) growth  
 $r$  = length



Discs  
(2D) growth  
 $r$  = radius



## Base equations

## Early stages of crystallisation

Assume

Spherulite

Spheres

$$J = It$$

(say)

Nucleation

$$r = Gt$$

Growth

Isothermol x'tal. I & G const.

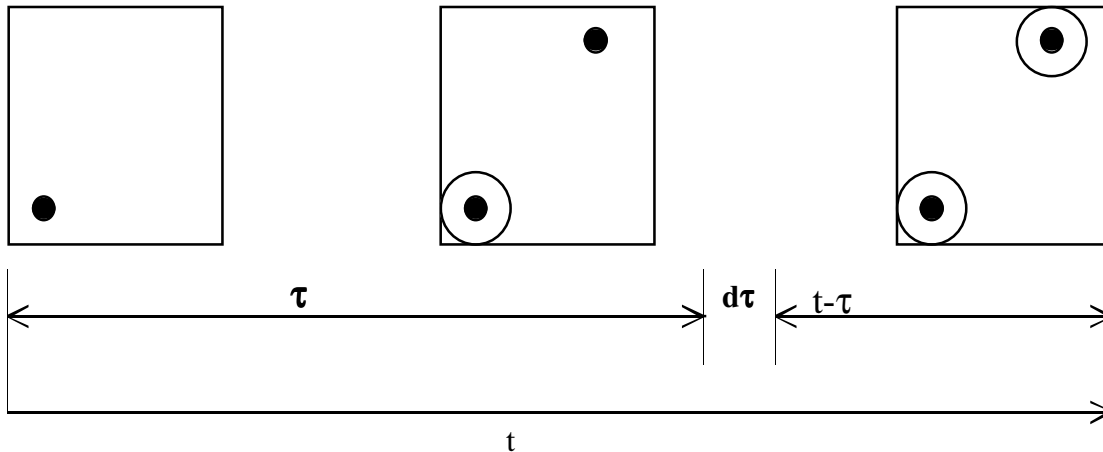
Let  $\rho_L$  = density of liquid phase (PE ~ 800 kg/m<sup>3</sup>).

$\rho_c$  = density of crystal phase (PE ~ 960 kg/m<sup>3</sup>).

$m_o$  = mass of starting liquid phase.

$m_c$  = mass of x'tal phase at t.

$m_L$  = mass of liquid phase at t.



Total number of nuclei formed between  $\tau$  &  $\tau + d\tau$ .

$$dJ = I d\tau \frac{m_o}{\rho_L}$$

|
|
|

nos/unit
|
|

vol
—
vol

Mass that these nuclei will have grown to at time t.

$$dm_c = \left( \underset{\substack{\text{nuclei} \\ \text{---}}}{I \frac{m_o}{\rho_L} d\tau} \right) \left( \underbrace{\frac{4}{3} \pi (G(t-\tau))^3 \rho_c}_{\substack{\text{sphere mass} \\ r = \overline{G}(t-\tau)}} \right)$$

Total mass crystallised.

The time from nucleation to t.

$$\int_0^{m_c} dm_c = \int_0^{\tau=t} m_o \frac{4}{3} \pi I G^3 \frac{\rho_c}{\rho_L} (t-\tau)^3 d\tau$$

$$\frac{m_c}{m_o} = \frac{\pi}{3} I G^3 \frac{\rho_c}{\rho_L} t^4$$

$$\frac{m_c}{m_o} = Z t^4$$

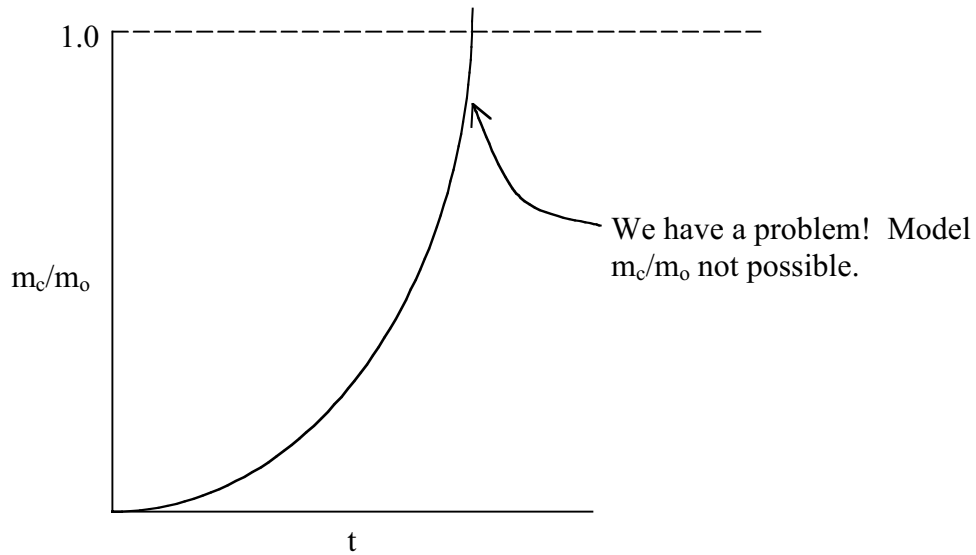
where

$$Z = \frac{\pi}{3} I G^3 \frac{\rho_c}{\rho_a}$$

Plot  $\ln \frac{m_c}{m_o} = \ln Z + 4 \ln t$

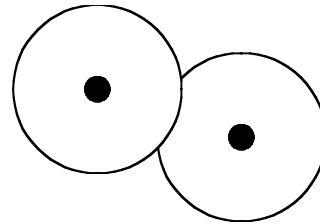
If model true st line intercept  $\ln Z$

slope 4 \_ Avrami exponent \_ different value for



### The impingement problem

Spherulites collide



Mass of uncrystallised material decreases with time thus if  $J = I t$  rate of nucleation decreases.

$$dJ = I d\tau \left( \frac{m_o - m_c}{\rho_l} \right)$$

decreasing mass available for crystallisation.

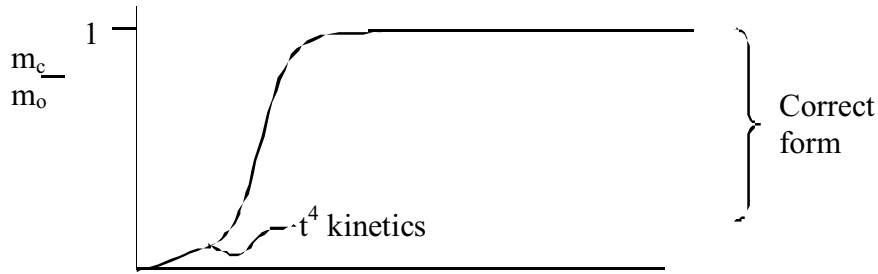
So mass crystallised now becomes

$$\int_0^{m_c} \frac{dm_c}{(m_o - m_c)} = \frac{4}{3} \pi I G^3 \frac{\rho_c}{\rho_L} \int_0^t (t - \tau)^3 J \tau$$



yields

$$\frac{m_c}{m_o} = [1 - \exp(-Zt^4)]$$



$$-\ln\left(1 - \frac{m_c}{m_o}\right) = Zt^4$$

$$\text{Plot } \ln\left(-\ln\left(1 - \frac{m_c}{m_o}\right)\right) = \ln Z + 4 \ln t$$

Intercept gives 2.

Slope = 4 ?

## The temperature dependence of crystal growth

### Nucleation

$$I = I_o \exp\left\{-\frac{\Delta F_1}{kT}\right\} \exp\left\{-\frac{\Delta \phi_1}{kT}\right\}$$

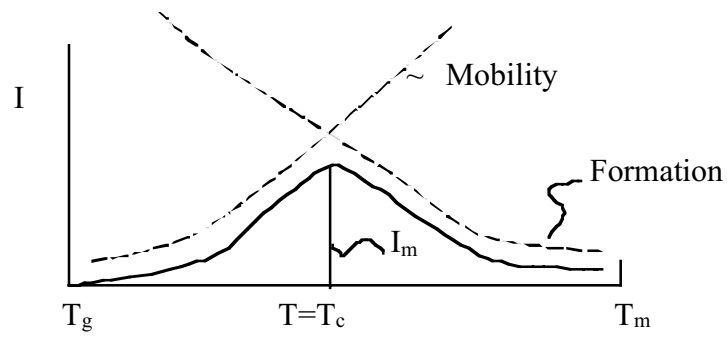
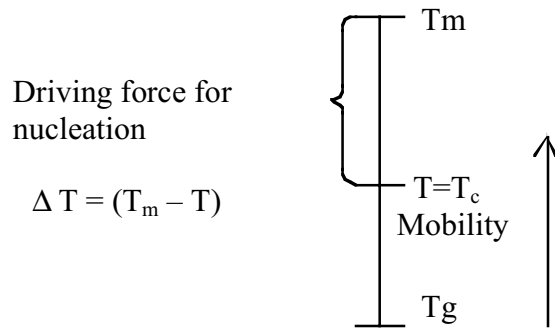
$\Delta F_1$  activation from transport.

$\Delta \phi$  activation for formation of nucleus.

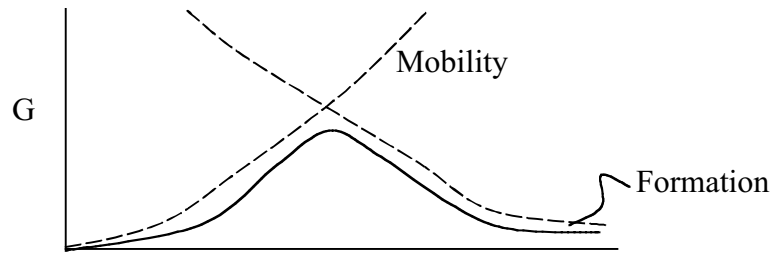
$$\text{Plausibly } I = I_o \exp\left\{\frac{-A}{T(T - T_g)}\right\} \exp\left\{\frac{-B}{T(T_m - T)^2}\right\}$$

Transport

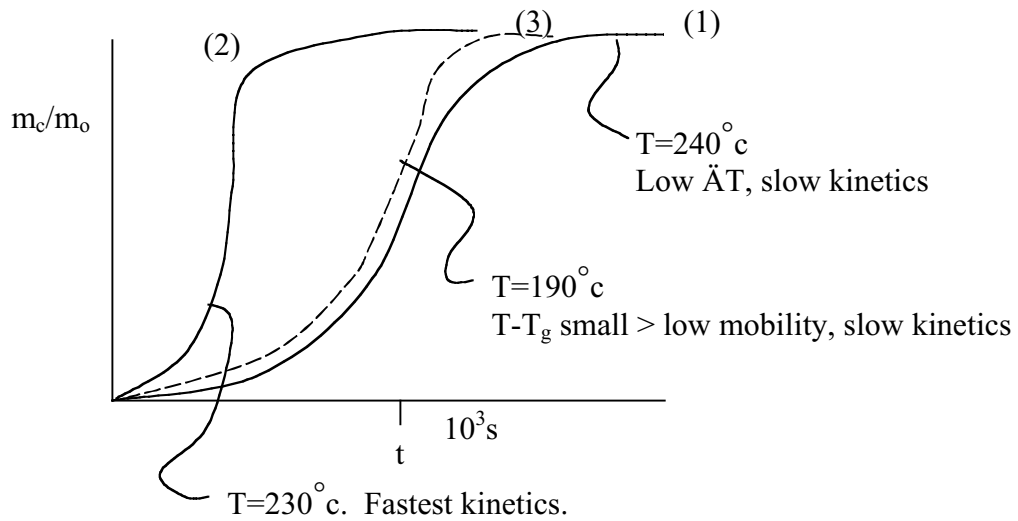
Nucleation



Similar story for Growth.



So Ex PET  $T_m=273^\circ\text{c}$   $T_g \sim 100^\circ\text{c}$



1. Lots of chain movement, no drive.
2. Lots of chain movement with drive
3. Little chain movement no drive.

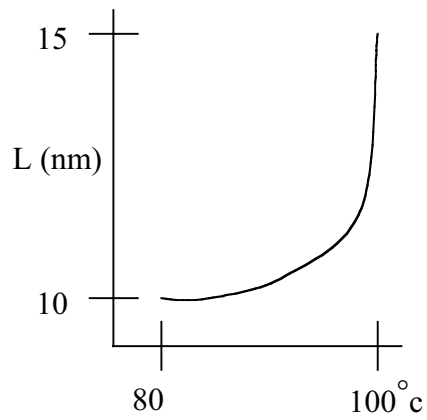
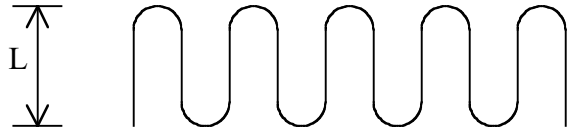
Intermediate temp gives fastest kinetics.

## Summary for crystal growth

Large crystals	Ease of handling, big diamonds	Low $T$ , few nuclei
Small crystals	Surface area, optical scatter control	High $T$ , many nuclei
Uniform size	Control	Seed, isothermal xtal
Max yield	Productivity	Intermediate temp
Flow & pressure	Can alter morphology!	

## Mechanism for Lamellar polymer crystal growth

Polymer crystals chain fold



Lamellar thickness  $L$ .  
Value of  $L$  depends on  
supercooling  $\Delta T$ .

$$L \propto \frac{1}{\Delta T}$$

Crystallisation  
temperature  $T_c$

Change in Free energy with crystallisation.

$$\Delta G = \Delta H - T_c \Delta S$$

Enthalpy  $\Delta H$       Entropy  $\Delta S$

At melting (dissolution) temperature  $T_m$

$$\Delta G = 0 \quad \Delta H = T_m \Delta S$$

So at  $T_c$

$$\Delta G = \left[ \Delta H - \frac{T_c}{T_m} \Delta H \right] \quad \Delta G = \frac{\Delta H \Delta T}{T_m} \dots \dots \dots \text{(I)}$$

Where supercooling

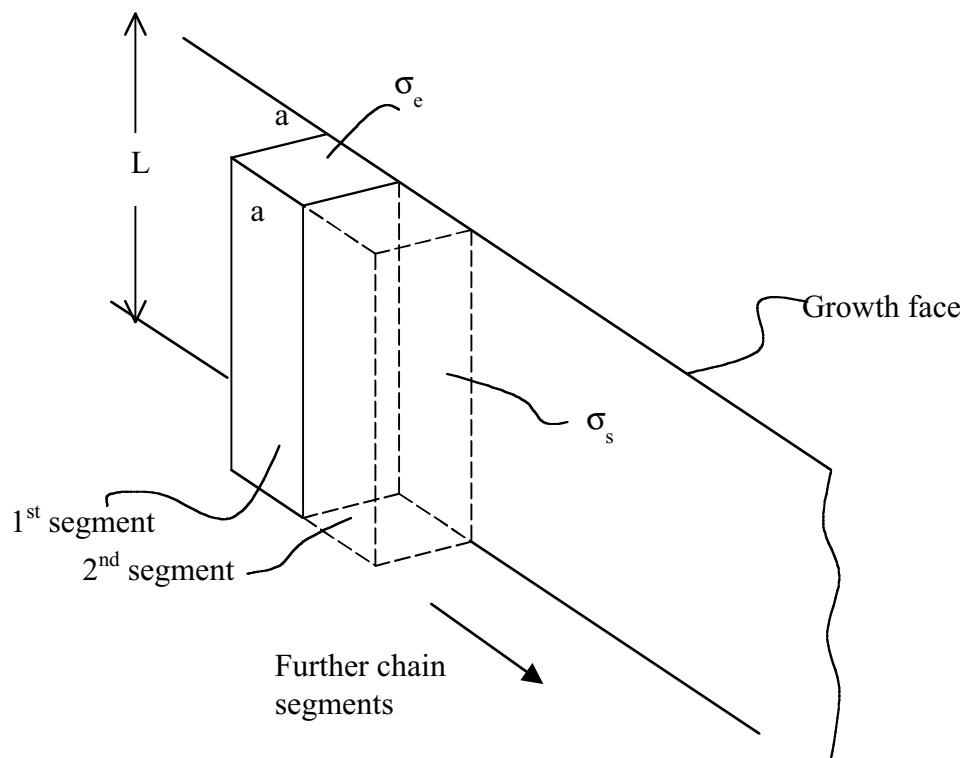
$$\Delta T = T_m - T_c$$

## The Mechanism

Assume that a crystal growth face exists.

Lay down 1<sup>st</sup> chain segment. In doing this we create two new side surfaces with surface energy  $\sigma_s$  and two new end surfaces with surface energy  $\sigma_e$ . The front faces covers up a part of growth face and so does not produce an extra term.

The creation of surfaces costs energy; however, the creation of a bulk volume of crystal  $a^2L$  yields free energy  $-G$ .



Chain segment = sequence of crystalline c-c bonds. Length  $L$ . Cross section  $a^2$ .

Energy change laying down 1<sup>st</sup> segment.

$$\Delta G_1 = \underbrace{2aL\sigma_s + 2a^2\sigma_e}_{\text{Surface energy penalty}} - \underbrace{a^2L\Delta G}_{\text{Bulk energy gain}}$$

Surface energy penalty.      Bulk energy gain.

Now if 2<sup>nd</sup> segment lays down next to first, only two new end surfaces are created; as side surfaces cover up existing ones.

Energy change laying down 2<sup>nd</sup> segment.

$$2a^2\sigma_e - a^2\Delta G$$

Similarly third & successive segments

$$\Delta G_v = 2a^2\sigma_e - 2a^2\Delta G$$

If

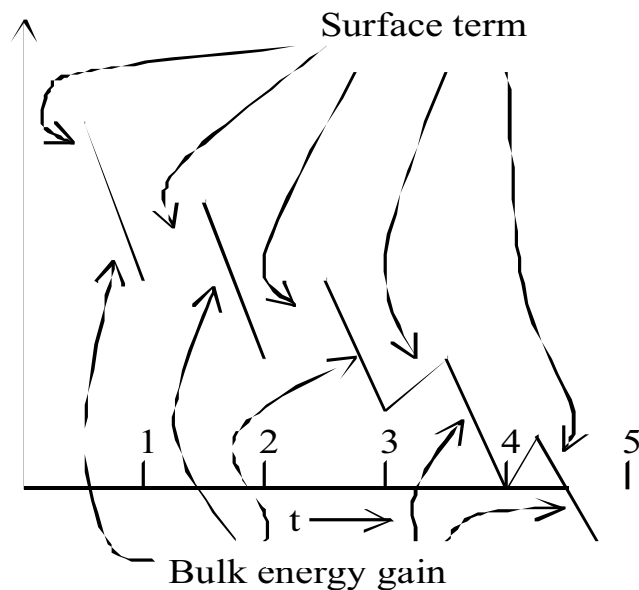
$$a^2\Delta G > 2a^2\sigma_e$$

Then it is possible that crystal can grow.

Consider limiting case then

$$L \Delta G = 2\sigma_e$$

$$L = \frac{2\sigma_e}{\Delta G}, \text{ combine with eqn (I)}$$



t = time to lay down segment  
1 → 5

So

$$L = \frac{2\sigma_e}{\Delta H} T_m \frac{1}{\Delta T} \quad \text{as experimentally observed.}$$

$\mathbf{L} \propto \frac{1}{\Delta T}$ , as experimentally observed.