- **Polymer-polymer interaction energetically favourable. Then**

$$<r^2>^{1/2} = N^{\nu} a \qquad \text{with } \nu < 1/2.$$

The chain shrinks compared with the ideal case. This applies for poor solvents, where polymer-polymer interactions preferred to polymer-solvent.

Both these situations apply when plenty of solvent molecules around ie dilute solutions.

- **Do ideal $<r^2>^{1/2} = N^{1/2} a$ statistics every apply?**

ie when no advantage or disadvantage to segments of the same chain coming into contact with each other? Yes!

a) In a 'θ solvent' the solvent-polymer and polymer-polymer interactions are energetically the same. The chain obeys Gaussian statistics.

b) In a melt. An individual segment may interact with segments from the same or different one, but energetically the same, so Gaussian statistics obeyed again.

Distribution of Chain Lengths

In general there will be a distribution of chain lengths present (due to most synthesis methods).

The molecular weight distribution can be characterised in various ways.

Suppose there are n_i molecules with DP N_i molecular weight M_i (where molecular weight is the number of monomers x the weight of one monomer).

$$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i} =$$ **number average molecular weight**

$$\overline{M_w} = \sum w_i M_i = \frac{\sum n_i M_i^2}{\sum n_i M_i} =$$ **wt average molecular weight**

i.e these are different moments of the molecular weight distribution.

For a monodisperse system $M_w/M_n=1$, but very hard to achieve. Best in practice ~ 1.03, and this can only be achieved for certain polymers and polymerisation routes. In practice M_w/M_n~2 for many polymerisation routes, but for PE typically much broader.

Polymer Crystallisation

See eg DC Bassett Principles of Polymer Morphology, CUP.

Not all polymers can crystallise.

- **Only polymers which are chemically and sterically regular can crystallise**

ie isotactic and syndiotactic can, atactic cannot.

For copolymers (polymers containing more than one unit):
AABABBABABBAB – random copolymer – cannot.
ABABABABABABA - alternating - can.
$(A)_n(B)_m$ - block - can.

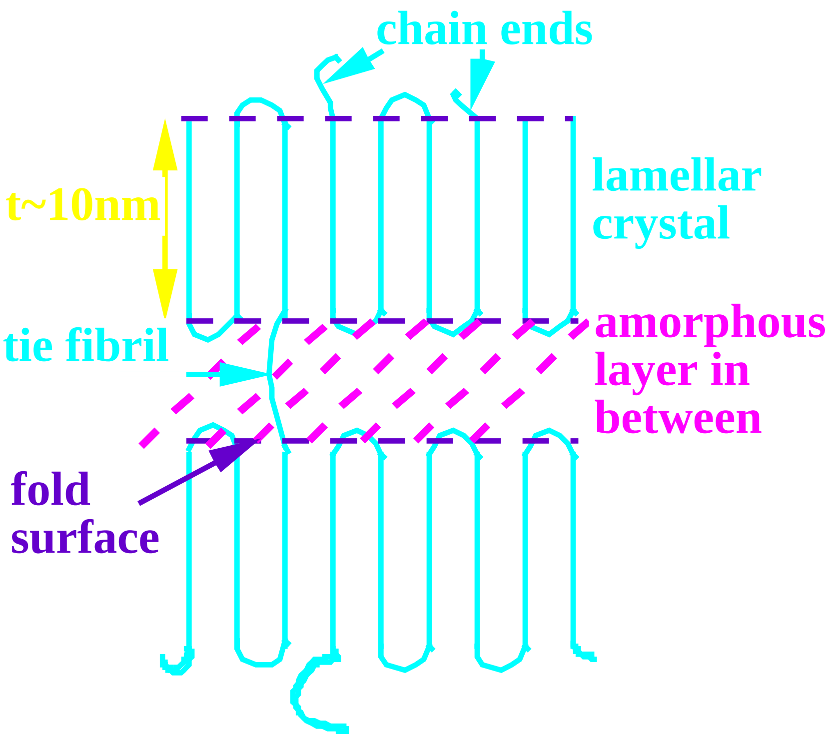
- **If a polymer molecule is branched, this impedes crystallinity. PE often has short chain branches. The length and frequency of these affect the ability to crystallise.**

- **Molecular weight also important.**

Crystallisation temperature depends on chainlength. For isothermal crystallisations, only chains of a certain length can crystallise – get fractionation by molecular weight.

- **No polymer is ever fully crystalline when prepared from solution or melt.**
- **Only examples of 100% crystalline polymer have been produced from epitaxially deposited monomer then polymerised in-situ.**

How do long, flexible chains crystallise?



Chain folded crystal

What is the evidence for a folded chain structure?

Comes from transmission electron microscopy (TEM) images of single crystals which have been 'shadowed' by heavy metal atoms at an inclined angle.

Size of shadow can be related to thickness of crystal, ~10 nm – much less than total chain length.

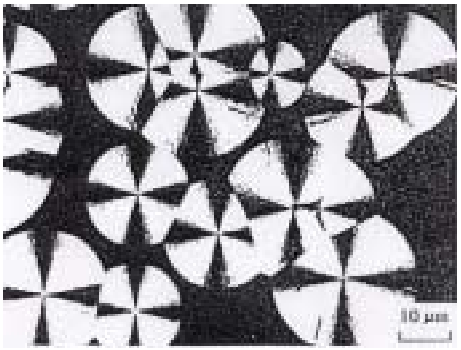
However it is still not clearly understood <u>why</u> chains fold as they do.

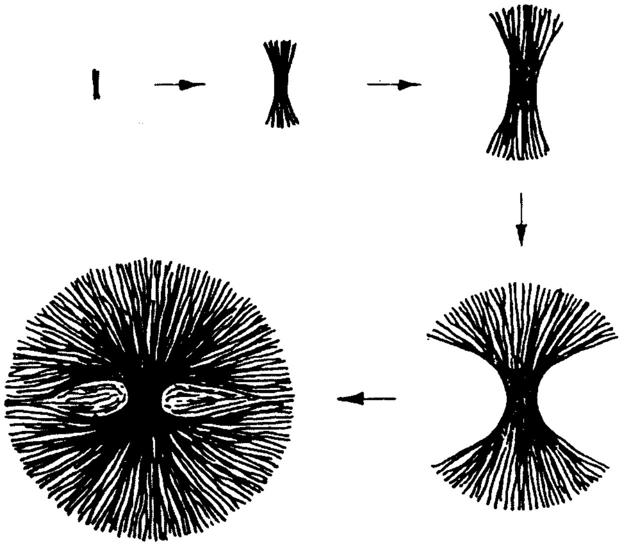
Single crystals of type seen in TEM are atypical, since they can only be prepared from dilute solution.

However such crystals do permit electron diffraction to provide information on the crystal structure (usually orthorhombic for PE).

More typical structures are spherulites.

Spherulites





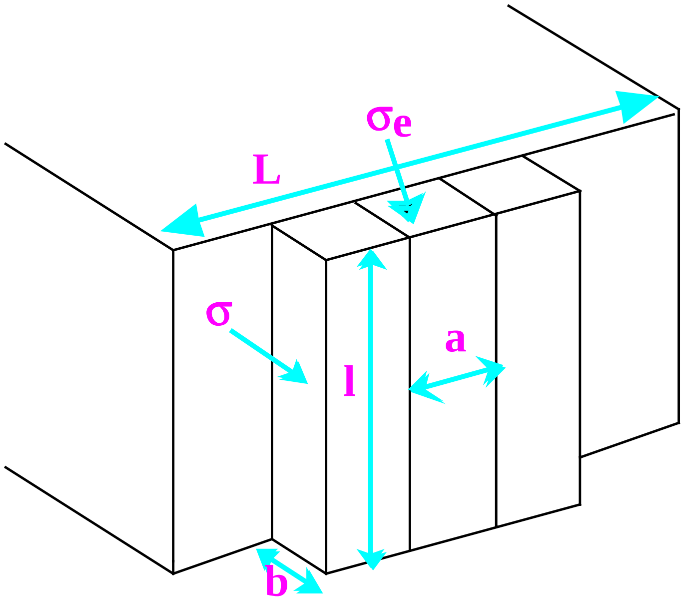
These have a Maltese Cross structure visible under crossed polars.

(Crossed polars show positions of extinction, where optic axis is parallel or perpendicular to polariser or analyser.)

Rotate polarisers and Maltese cross rotates too, implying radial symmetry.

Each unit in structure is a chain folded lamella with amorphous material in between.

Hoffman Model for Surface Nucleation and Growth of Crystal



n adjacent strands at surface; each with cross section ab and length l

Surface energy cost of this secondary nucleus is

$$2bl\sigma + 2nab\sigma_e$$

If there is free energy change/unit vol on crystallisation

$$= \Delta G_v$$

Then total free energy change when n strands crystallise

$$\Delta G_n = 2bl\sigma + 2nab\sigma_e - nabl\Delta G_v \qquad [1]$$

If T_o^m is the equilibrium melting temperature i.e the temperature at which an infinitely large crystal would melt, then, since $\Delta G_v = 0$ at T_o^m

$$\Delta G_v = \Delta H_v - T_o^m \Delta S_v = 0$$

$\Rightarrow \qquad \Delta S_v = \Delta H_v / T_o^m$

However crystal is not infinite, and crystallisation occurs at lower temperature T

Assuming ΔS_v is not strongly temperature dependent then

$$\Delta G_v(T) = \Delta H_v - T\Delta H_v / T_o^m$$

$\Rightarrow \qquad \Delta G_v(T) = \Delta H_v \Delta T / T_o^m$ **(where ΔT is supercooling)**

This equation can be inserted into equation [1], noting that since n is usually quite large, first term in equation [1] is usually negligible.

$$\Delta G_n \approx 2nab\sigma_e - nabl\Delta H_v\Delta T/ T_o^m$$

Thus there is a relationship between strand length and supercooling ΔT.

Critical strand length l^o when $\Delta G_n = 0$

$$\Rightarrow \qquad \boxed{l^o \sim \frac{2\sigma_e T_m{}^o}{\Delta H_v \Delta T}}$$

i.e crystal thickness less as supercooling increases.

Conversely thin crystals have the lowest melting point.

As you cool down high MW chains initially form thick crystals – fractionation by MW.

Different populations of crystals form.

Amorphous material tends to be low MW and/or branched chains.